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CHARACTERIZING CONTAINERIZED MIXED LOW-LEVEL WASTE FOR TREATMENT

A Workshop Proceedings

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EXECUTIVE SUMMARY

This report is the product of a technical workshop held in May 1993 in Las Vegas, Nevada. The workshop was conducted by the Environmental Protection Agency (EPA) and the Department of Energy (DOE). Its purpose was to define the waste characterization that would be required to operate a mixed low-level waste treatment facility applying robust treatment methods to broad categories of waste. Evaluation of these characterization needs, and comparison with the needs defined under current programs, may allow DOE to realize savings in both its waste characterization and treatment efforts.

Mixed waste contains both hazardous components regulated under the Resource Conservation and Recovery Act (RCRA) and radioactive components regulated by DOE Orders. There are conflicts between the two sets of requirements. Moreover, the RCRA delisting of mixed wastes following treatment has not been generally approved by regulatory agencies, and treatment of mixed waste under the RCRA Debris Rule has not been demonstrated. Wastes generated and disposed on National Priorities List (NPL) sites are subject to further regulation under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). In formulating plans to treat its mixed waste, DOE is now on a schedule imposed by the Federal Facility Compliance Act of 1992. This Act requires that site treatment plans be in place by October 1995, and grants states approval authority over the plans.

This report concerns DOE's mixed low-level waste (MLLW). Within the DOE complex, MLLW is generated by defense-related activities, research programs, facility decontamination and decommissioning activities, and environmental restoration. Uranium, plutonium, fission products, and other radionuclides may be present. The wastes may contain up to 100 nCi/g of transuranic alpha activity. Lead, mercury, or other hazardous contaminants are present. DOE currently has custody of roughly 250,000 cubic meters of MLLW, and it is estimated that 3-4 times this amount will be added to the inventory over the next 5 years.

To address handing of its MLLW stockpile, DOE has initiated the Mixed Waste Treatment Project (MWTP). Its purpose is to identify promising technologies and strategies for MLLW characterization and treatment that can be applied to containerized waste throughout the DOE complex. The approach of the MWTP is to classify all MLLW waste streams into several very broad treatability groups, and treat these groups in an integrated facility relying on very robust (mostly thermal) treatment technologies (a minimum waste characterization/maximum treatment approach). The MWTP has generated a conceptual design for such an integrated facility. That facility may never be constructed; its value is as a model, a general framework for the definition of efficient waste characterization/treatment strategies.

The Las Vegas workshop attendees addressed what waste characterization would be required to operate the MWTP facility. The 75 workshop attendees, consisting predominantly of DOE contractors (see Acknowledgements), divided into three groups and considered the characterization needs in three stages: evaluating containerized wastes to route them to the proper treatment train; monitoring the pretreatment and treatment processes and their effluents; and characterizing final waste forms for disposal. For each stage, they identified the properties to be measured, data quality objectives, applicable methods, and associated research needs.

In an integrated MLLW treatment facility, the three purposes of up-front waste characterization are: to identify containers of transuranic waste mistakenly sent to the facility; to identify containers with mercury, lead, compressed gases, or other materials that will require special treatment; and to characterize the physical and chemical properties of the waste so that each container can be routed to the proper treatment line. The six waste properties that must be evaluated are:

- specific alpha activity
- physical properties, including debris content
- solids content, or pumpability
- organic constituents (qualitative and quantitative)
- hazardous elements or special materials
- radionuclides

An enormous number of waste containers must be evaluated, and the container contents are often heterogeneous. Consequently, measurement methods that assess the bulk properties of a container of waste are strongly preferred over those that require characterization at several points within the container. In practical terms, non-intrusive methods are given priority over intrusive methods, which in turn are favored over methods requiring full sampling. This hierarchy will enhance the safety, representativeness, and efficiency of initial waste characterization.

Several dozen methods were identified for evaluating the six properties in incoming wastes. Most are in some stage of research or development, but multiple "existing" methods were cited as potentially applicable for each property. Few of these can be considered "off-the-shelf;" nearly all would require some degree of testing and adaptation to this application. No existing non-intrusive methods were identified for organics or special hazardous materials. In a facility accepting varied waste streams, most of the six properties would have to be evaluated using a suite of techniques rather than one single method. The extent to which full sampling would be required cannot be specified at this time. That will depend on quantitative data quality objectives. Full sampling and analysis are most likely to be required for organic constituents and special hazardous materials, should their acceptable thresholds be low.

The workshop attendees identified a need for the documentation, verification, and use of process knowledge in formulating a waste characterization strategy. Methods research is particularly needed for assessing organics and special hazardous materials in a non- or minimally-intrusive way. Gamma neutron activation analysis and pulsed fast neutron analysis were identified as long-term research possibilities. In the near term, advances in intrusive methods utilizing fiber optic systems appear most promising.

Within the treatment facility, material streams will be monitored at a great many points in the pretreatment and treatment lines, as well as the offgas systems. The workshop group handling process monitoring noted that a careful scheme to batch and process like wastes together would lessen the need for in-plant characterization. The group identified existing methods for all of the in-plant monitoring needs, although some methods may require considerable development for this application. Offgas monitoring methods should receive the highest research priority. Real-time techniques for monitoring metals and radionuclides in offgases would be a major attribute for any treatment facility. Mercury detectors for solid matrices and improved in-plant radiation detectors also warrant research, as do screening methods for chemically heterogeneous matrices and

contaminant-specific detectors. The development of national performance standards for the non-standard (particularly radiation) methods is desirable. There is a need for a thorough evaluation by a multidisciplinary team on the relative benefits of up-front characterization versus versatile process design versus extensive process monitoring and control.

This report contains a discussion of the plasma arc vitrification process for waste treatment and the associated characterization needs. Plasma arc is not universally applicable to DOE's MLLW streams, and it is not one of the treatment technologies in the MWTP conceptual design. It is employed here as an example: if the minimum characterization/maximum treatment concept is taken to the extreme, what are the characterization needs? Feed drums with containerized liquids or compressed gases must be identified, so that they can be routed away from the plasma arc unit. Significant amounts of lead in the feed must also be detected, since lead will not be recoverable from the glass. Organics in the feed should not require identification or quantitation, since they will be completely destroyed (as demonstrated by trial burns). Some degree of confirmatory offgas monitoring for organics may be required. Mercury is a serious problem for plasma arc units, as for all thermal treatment techniques. Identification and re-routing of mercury-laden wastes is desirable. Furthermore, public acceptance of the plasma arc would be greatly facilitated by continuous, real-time monitoring for mercury (as well as radionuclides and other metals) in the stack gases. In sum, it appears that characterization needs are somewhat lessened in a plasma arc system. However, plasma arc shares with other thermal technologies the major characterization difficulties: identifying mercury in the feed containers and monitoring offgases in real time.

The MWTP facility will produce nine solid waste forms and materials for recycle:

- cement grouts (cement and organic-cement conglomerate)
- crystalline ceramic
- glass
- polymers (sulfur polymer and macroencapsulation)
- elemental lead
- elemental mercury
- ferrous metal alloys

Testing of these materials will be driven chiefly by regulation, although shipping requirements, treatment unit process control, and health and safety considerations will also apply. Twenty properties or parameters were identified for assessment in these materials (not all tests will be required for all materials). Additional waste acceptance criteria specific to the disposal site would apply, but these cannot be anticipated at present. In general, measurement methods for the final waste forms are well established. Many of the test protocols are established by regulation (the RCRA Characteristic Tests, for example). Most of the questions regarding final waste form testing relate to the interpretation of test results and regulatory uncertainty.

Appropriate sampling designs, and the statistical characteristics of individual batches of waste forms, must be established. This will be straightforward with the more uniform waste forms, but some, like polymer-encapsulated forms, will present a challenge. Polymer forms will require methods development to assay radionuclides and alpha activity, and to quantify gas generation. Whether neutron and gamma methods are sensitive enough to assess radionuclides in any of the waste forms is in question. There is an effective lack of methods for evaluating long-term physical

integrity and leaching properties of waste forms, in that prescribed methods are of questionable applicability. The creation of sulfur polymer waste forms needs further thought; it may be impossible to make these so they are not "reactive" — and hence hazardous — under RCRA.

A number of non-technical concerns related to waste characterization were voiced during the workshop. Waste characterization and treatment strategies must be developed in concert. The facility design team cannot first specify the treatment scheme and then plug in off-the-shelf measurement methods, since method shortcomings may constrain treatment design. They may also dictate operating mode: batch instead of continuous, uniform instead of varied batches. On the other hand, a careful batching scheme may obviate the need for sophisticated measuring devices at some points. Because of the complexity of the treatment facility, a state-of-the-art expert system integrating process monitors and controllers is called for. Some methods development for characterization may be driven by the need for public acceptance of the treatment facility. This appears to be especially true for characterizing process offgas streams.

The possibility exists that regulators may require full RCRA testing of all waste forms exiting an integrated treatment facility, regardless of the treatment technology. This would require an enormous characterization program, and would render moot the concept of 'minimum characterization followed by maximum treatment.' On the other hand, the 1992 RCRA Debris Rule and its amendments may substantially diminish the characterization requirements for large portions of the stored MLLW.

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ABBREVIATIONS AND ACRONYMS

AAS	atomic absorption spectrophotometry
ACS	American Chemical Society Act
AE	atomic emission
AEA	Atomic Energy Agency
AED	atomic emission detection
ALARA	as low as reasonably achievable
AMU	atomic mass unit
ANS	American Nuclear Society
ANSI	American National Standards Institute
APCD	air pollution control device
ARAR	Applicable or Relevant and Appropriate Requirement
ASTM	American Society for Testing and Materials
BACT	Best Available Control Technology
BAT	Best Available Technology (Economically Achievable)
BDAT	Best Demonstated Available Technology
BG	background
bm	benchmark glass
BPT	Best Practicable (Control) Technology or Treatment
BTU	British Thermal Unit
CAA	Clean Air Act
CAM	continuous air monitor
CEM	continuous emission monitoring
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFC	chlorofluorocarbon
cfm	cubic feet per minute
CFR	Code of Federal Regulations
cfs	cubic feet per second
CHCs	chlorinated hydrocarbons
CN	cyanide
COLIWASA	colorimetric liquid waste sampler
CPAC	Center for Process Analytical Chemistry (University of Washington)
cpm	counts per minute
CTEN	combined thermal - epithermal neutron
CWA	Clean Water Act
D & D	decommissioning and decontamination
D-T	deuterium-tritium
DDT	differential die-away technique
DEA	Drug Enforcement Agency
DMCP	DOE Methods Compendium Program
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
DQO	data quality objective
DRE	destruction removal efficiency
DTA	differential thermal analysis

EDX	electron diffractive x-ray
eH	redox potential
EM	Office of Environmental Management within DOE
EMSL-LV	Environmental Monitoring Systems Laboratory-Las Vegas
EP	Extraction Procedure
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
eV	electron volts
F&OR	functional and operational requirements
FA	flow injection analysis
FBI	fluidized bed incinerator
FFCA-92	Federal Facilities Compliance Act of 1992
FPXRF	field-portable X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
g	grams
GC	gas chromatography
GC/MS	gas chromatograph/mass spectrometry
H&S	health and safety
HAP	hazardous air pollutant
HEPA	high-efficiency particulate air
HPGe	high-purity germanium detector
HLW	high-level waste
HMTA	Hazardous Materials Transportation Act
HOC	halogenated organic carbon
HP	Health Physics
HPLC	high performance liquid chromatography
HQ	headquarters
HSWA	Hazardous and Solid Waste Amendment of 1984/RCRA
HVAC	heating, ventilation, and air conditioning (system)
IC	ion chromatography
ICP	inductively coupled plasma
ICP/MS	inductively coupled plasma/mass spectrometry
INEL	Idaho National Engineering Laboratory
IR	infrared spectroscopy
kw	kilowatt
kwh	kilowatt hour
LAER	lowest achievable emissions rate
LANL	Los Alamos National Laboratory
LDR	land disposal restrictions (of RCRA)
LIBS	laser-induced breakdown spectroscopy
LIPS	laser-induced plasma spectroscopy
LLNL	Lawrence Livermore National Laboratory
LLW	low-level waste
LOQ	level of quantitation

ABBREVIATIONS AND ACRONYMS (*Continued*)

LSC	liquid scintillation counting
MACT	maximum achievable control technology
MAER	maximum allowable emission rate
MATC	maximum allowable toxicant concentration
mCi	milliCuries
meV	millielectron volts
MLLW	Mixed low-level waste
MSDS	Material Safety Data Sheet
MWIP	Mixed Waste Integrated Program
MWTP	Mixed Waste Treatment Project
NACE	National Association of Corrosion Engineers
nCi	nanoCuries
NDE	non-destructive evaluation
NFPA	National Fire Protection Association
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
NRC	Nuclear Regulatory Commission
ORIA-LV	Office of Radiation and Indoor Air (EPA), Las Vegas
ORNL	Oak Ridge National Laboratory
OSWER	Office of Solid Waste & Emergency Response (EPA)
OTD	Office of Technology Development of DOE
P&T	purge and trap
PAH	polyaromatic hydrocarbon
PARCC	precision, accuracy, representativeness, completeness, and comparability
PCB	polychlorinated biphenyl
pCi	picoCuries
PCT	product consistency test
PFA	polyfluoroacetate
PFD	process flow diagram
PFNA	pulsed fast neutron analysis
PGNAA	prompt gamma neutron activation analysis
PIC	products of incomplete combustion
PNA	polynuclear aromatics
PNL	Pacific Northwest Laboratory
POHC	principal organic hazardous constituents
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PQM	piezoelectric quartz microbalance
QA/QC	quality assurance/quality control
RadCon	radiological control
RCRA	Resource Conservation and Recovery Act of 1976
Rem	Roentgen equivalent man
RTR	real-time radiography

SAW	surface acoustic wave (sensor)
SCFE	supercritical fluid extraction
scfm	standard cubic feet per minute
SEM	scanning electron microscopy
SERS	surface-enhanced Raman spectroscopy
SGS	segmented gamma scanner
SIMS	secondary ion mass spectrometry
SOA	state-of-the-art
SVOC	semivolatile organic compounds
TAP	toxic air pollutant
TBD	to be determined
TBP	tributylphosphate
TC	Toxicity Characteristic
TCLP	Toxicity Characteristic Leaching Procedure
TLD	thermoluminescent dosimeter
TOC	total organic carbon
TOX	total organic halogens
TRU	transuranic
TSCA	Toxic Substances Control Act
TSD	treatment, storage or disposal
TSDF	treatment, storage, and disposal facility
TSG	Technology Support Group
UHV	ultrahigh vacuum
UV/Vis	ultraviolet/visible (spectrum)
VOA	volatile organics analysis
VOCs	volatile organic compounds
W.C.	water column

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3. Final Waste Forms -Co-Chairs, Peter Lindahl, and Srini Venkatesh.

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Characterization for Treatment of Containerized Mixed Low-Level Wastes
Workshop
May 25-27, 1993

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Chapter 1

Introduction

Gretchen Rupp

Radioactive wastes that are generated in the nation's nuclear weapons program are stored at a number of facilities that are under the jurisdiction of the Department of Energy (DOE). These include substantial volumes of mixed low-level waste (i.e., low-level radioactive waste that is also hazardous under the Resource Conservation and Recovery Act (RCRA)). Over 1300 types of mixed low-level waste (MLLW) have been identified. There are more than a million containers of MLLW in storage at DOE sites.

Characterization of these wastes for treatment, storage and disposal currently requires enormous resources. Under the aegis of its Mixed Waste Treatment Project (MWTP), DOE is exploring a strategy to expedite treatment and minimize characterization requirements. In this approach, wastes would be classed into broad treatability groups and processed and treated by robust methods. Because of the robustness of the treatment, the need for initial waste characterization would be lessened.

DOE's Office of Technology Development (EM-50) has called on EPA's Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV) to support the characterize-to-treat portion of this strategy. This report is the product of a technical workshop conducted by EMSL-LV in May, 1993, co-sponsored by DOE and EPA. Its purpose is to define the characterization that would be required at each stage for operation of a MLLW treatment facility applying robust treatment methods to broad categories of MLLW. Evaluation of these characterization needs, and comparison with current needs, may allow DOE to realize savings in both its waste characterization and treatment efforts.

The Regulatory Situation

The following discussion is adapted from reference 1.

Mixed waste contains hazardous contaminants that are governed by RCRA and radioactive contaminants that are governed by DOE Orders. Requirements specified under these regulations conflict, in some instances. Generally, RCRA regulations are designed to cover both general and site-specific situations, while DOE orders require interpretation in specific situations.

Disposal criteria have not been established for mixed waste. There are several difficulties with finalizing such criteria. First, the selection of disposal sites and waste disposal criteria will be based on performance assessments. However, performance assessments for radioactive waste disposal do not account for the form of the waste.

Furthermore, the RCRA delisting of mixed waste after treatment has not been generally accepted or approved by the regulatory agencies. The treatment of mixed waste under the "Debris Rule" has not been demonstrated or approved, and development of the RCRA Rules for soil and debris is ongoing. The RCRA Hazardous Waste Identification Rule, that will address the "mixture" and "derived from" rules, is also still in development. The risk to the public and workers due to storage of legacy waste is not well defined; therefore, priorities cannot be established on a risk-based cleanup strategy. Finally, many treated DOE wastes will be disposed on NPL sites, where CERCLA cleanup standards, potentially very stringent, will apply.

Congress recognized the problems associated with mixed waste management and enacted the Federal Facility Compliance Act of 1992 (FFCA-1992). The Act waives sovereign immunity for Federal facilities, thereby allowing DOE to be subject to fines and penalties for failure to manage mixed waste according to RCRA. This congressional mandate for DOE to treat its mixed waste establishes a 3-year timetable (ending in October 1995) for development of site treatment plans, during which time the waiver is delayed. The Act gives states approval authority over the site treatment plans. Differing state requirements for the treatment plans are anticipated. After plans have been reviewed, it is further anticipated that equity brokering between states will occur regarding treatment, storage and disposal facility location.

Status of Waste Characterization and Treatment

Low-level waste is defined by DOE Order 5820.2A as all radioactive waste not classified as high level waste, transuranic waste, spent fuel, or by-product materials (uranium mill tailings, for example). Within the DOE complex, mixed low-level waste is generated by defense-related activities, research programs, facility decontamination and decommissioning activities (D&D), and environmental restoration. The principal radioactive components are uranium and plutonium, but many other radionuclides, including other transuranic elements, can be present. The wastes can contain up to 100 nCi/gram of transuranic alpha activity. Both contact- and remote-handled wastes are included. Mercury, lead, or other hazardous materials are present in all MLLW. MLLW takes many forms. Wastewaters, salts and sludges contribute a great deal to the waste volume, but cleaning materials, miscellaneous laboratory wastes, building and demolition debris, soil, spent filters, tools and discarded equipment are also included.

The most comprehensive survey of DOE mixed wastes is the April 1993 Draft Mixed Waste Inventory Report prepared by DOE to comply with FFCA-92 (2). According to the inventory report, MLLW comprises 42% of DOE's mixed wastes, and currently totals 247,000 cubic meters. The report estimates that an additional 280,000 m^3 of MLLW will be generated in the next five years of operations across the DOE complex. A rough estimate of the 5-year volume of MLLW that will be created by environmental restoration activities

is 620,000 m^3. In addition, a considerable - and unknown - portion of the currently stored TRU wastes are expected to be examined and reclassified as MLLW. More than four fifths of the MLLW is generated at five sites: the Hanford Reservation, the Idaho National Engineering Laboratory, Oak Ridge K-25 Plant, Oak Ridge Y-12 Plant, and Rocky Flats Plant. However, almost all DOE sites generate some MLLW. There are wastes stored at 48 sites in 22 states.

The Draft Mixed Waste Inventory Report includes a tabulation of approximately 1300 individual waste streams of mixed low-level waste. Of these, roughly 60% have been characterized using process knowledge, while the remaining 40% have been sampled. There are a number of existing and planned facilities for treatment of specific waste streams, but these facilities are generally not adaptable to treat a broader array of wastes (2). In addition, the Draft Inventory Report identifies "...an acute shortage of treatment capacity for treating alpha MLLW," that is, MLLW with transuranic alpha levels greater than 10 nCi/g, such that containment is of special concern.

Under the current approach to waste characterization and treatment, each DOE facility is involved in rigorous efforts to identify and describe mixed low-level wastes generated or stored at that facility. Characterization is needed to safeguard the environment and worker health and safety; to design, protect and optimize the treatment processes; to meet environmental regulations and to satisfy the waste acceptance criteria of the disposal sites. Many types of characterization technologies are needed, including some technologies that are now in development. The projected characterization costs for extensive, site-by-site waste analysis are 30-45 billion dollars over the next 30 years (3). Each DOE site that generates or stores MLLW would require waste characterization laboratories, waste handling facilities, and other resources. This approach embodies considerable potential for duplication of effort across the DOE complex.

The Mixed Waste Treatment Project

As a more efficacious alternative, DOE is exploring a strategy in which characterization would be performed just prior to and during waste treatment, to support the treatment needs. In its Mixed Waste Treatment Project (MWTP), DOE's Office of Waste Management (EM-30) has divided MLLW into 5 broad treatability groups (hereinafter called "the five waste streams"):

- aqueous liquids
- organic liquids
- wet solids
- homogeneous dry solids
- heterogeneous dry solids (also called debris).

Pre-conceptual waste segregation and treatment trains have been devised for each of these waste streams, and the functional and operational requirements (F&ORs) of a prototype treatment facility have been specified (4). The baseline treatment technologies are Best Demonstrated Available Technologies (BDATs) derived from RCRA treatment requirements, but alternative technologies have also been identified. It should be noted that design of the MWTP facility is an ongoing process. The design used as a baseline herein, the corresponding F&ORs, and the waste stream classifications are those of late 1992. They do not take into acccount the RCRA "Debris Rule" promulgated at that time. This will influence both facility design and characterization strategy (see concluding chapter for further discussion).

The MWTP is highly conceptual in nature and will not likely ever be constructed. Its purpose is to guide the selection of waste treatment and characterization methods that may be needed at actual facilities.

The Five Waste Streams

The five waste streams are defined on the basis of their physical and chemical properties, which dictate pre-treatment processing requirements and appropriate treatment technologies. The properties of the waste streams are described in detail in Appendix A. They are summarized below. All of the waste streams include both incoming wastes and internal transfer streams from within the treatment facility. Note that these waste streams include only MLLW that is contained in drums or boxes. The Hanford tank wastes (and those at other sites) will be treated by other processes.

Aqueous liquids These liquids contain less than 1 percent organic carbon. They may contain up to 35 or 40 percent solids, as long as they are pumpable. The average density of this waste stream (including drums) is 1049 kg/m^3.

Organic liquids These liquids may have as low as 1 percent organic content. They include miscellaneous organic liquids, scintillation cocktails, solvents, sludges, PCBs and mercury-contaminated organics. Their average density is 882 kg/m^3.

Wet solids These are wet wastes that are not pumpable. The solids may be mixed with either water or organic liquids. Components of this stream include sludges, absorbed liquids, resins and cemented sludges. The average density, including drums, is 1276 kg/m^3.

Homogeneous dry solids These solids have a particle size of less than 2 inches. The major component of this waste stream is soil from site remediation activities. The average density is 1181 kg/m^3.

Heterogeneous Dry Solids Demolition debris and lead forms are major components of this waste stream. The average density is 1234 kg/m^3.

Waste Handling and Treatment

In the preconceptual design of the MWTP prototype treatment facility, handling and treatment of the wastes have been specified according to the applicable DOE orders and guidelines (5,6,7), as well as the requirements of RCRA. The facility operates in batch mode, and is able to handle PCB-containing wastes under a Toxic Substances Control Act (TSCA) permit. Appendix B is a complete collection of the flow diagrams for the facility. The overall scheme is depicted in Figure 1.1. Each of the five waste treatment paths, herein referred to as "lines," begins with several waste handling and preparation operations, such as organics removal, suspended solids removal, size segregation, or removal of ferrous metals. Several internal transfer streams are generated at this pretreatment stage. In some cases, a waste stream is split into components of different density or particle size. The concentrated waste streams are then treated. Organics are destroyed by wet air oxidation or one of several thermal methods. Inorganic contaminants are stabilized within solid waste forms. Reusable materials are recovered in pure form. The final products of the facility are:

- clean water
- treated offgas
- ferrous metals
- elemental lead
- elemental mercury
- reusable containers
- compacted waste forms
- glass, ceramic, polymer or grout waste forms.

For planning and design purposes, it is assumed by DOE that roughly ten such treatment plants would be required across the DOE complex. Since each would accept only a limited number of the 1300 waste streams, there would probably be differences in the waste characterization and handling protocols among the plants. At least some of the plants would handle wastes about which very little *a priori* knowledge exists.

Related Programs and Initiatives

The Mixed Waste Integrated Program within the Office of Technology Development supports the MWTP by developing and demonstrating innovative and emerging technologies for the treatment and management of the DOE MLLW (8). As the treatment flowsheets evolve due to technology development, the characterization needs will be re-examined and updated.

A related activity within the Office of Environmental Management is the development of the Programmatic Environmental Impact Statement (PEIS) for management of DOE's waste streams. This document will evaluate options for treatment facility config-

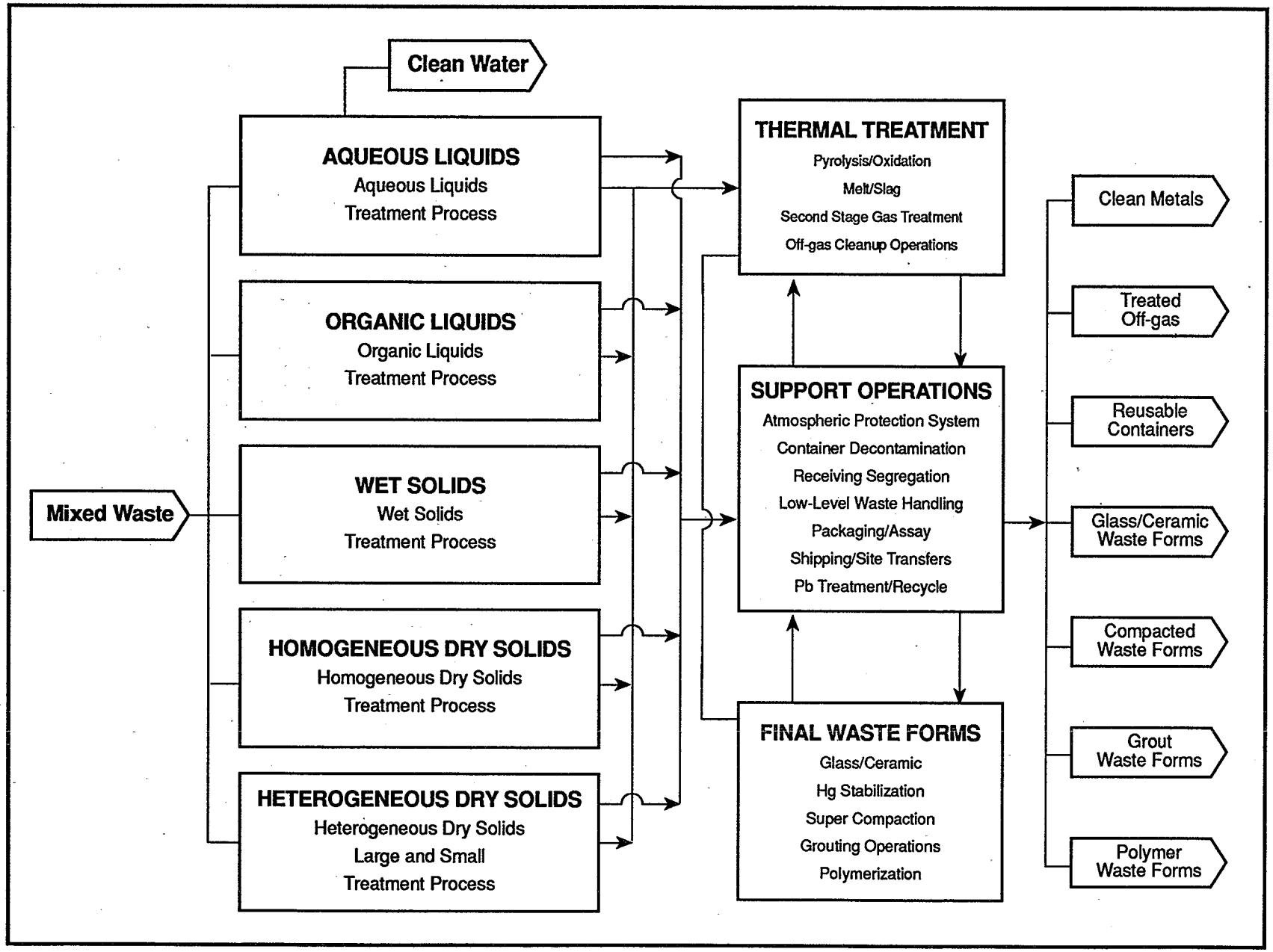

Figure 1-1 Schematic diagram of the MWTP facility. Adapted from (4).

uration, discuss risk-based decision making, and provide stakeholders with a forum for participating in the discussions. The draft PEIS will be released in the spring of 1994.

The National Governors' Association is providing a forum for states, EPA and DOE to discuss FFCA-92 implementation. The Western Governors' Association is actively seeking industry involvement in technology development. It has formed the Development of On-site Innovative Technologies Committee to foster technology development for mixed waste management (9).

Report Purpose and Scope

This report may serve as an accessory to the F&OR document and flow diagrams describing the treatment processes of the integrated MWTP facility. Its purpose is to identify and describe the characterization needed at each stage for the operation of an integrated MLLW treatment facility. As Site Treatment Plans are developed in compliance with FFCA-92, the report can be consulted as a description of a "baseline" characterization-for-treatment scenario.

Three general topical areas are covered:

- characterizing containerized MLLW prior to treatment, including characterization to direct the waste to the appropriate treatment train and to distinguish between LLW and transuranic waste - Chapter 2
- treatment process monitoring, and evaluation of sidestreams, including offgases - Chapter 3
- characterization of the final solid waste forms - Chapter 4.

The report is based on two technical workshops held in 1993. In January 1993, a preliminary characterization needs assessment was carried out by a working group in Albuquerque. That assessment showed the locations in the generalized treatment trains where measurements are needed, and compiled a preliminary list of the parameters to be measured. On that basis, a larger workshop of technical experts was convened in Las Vegas in May 1993. This workshop was sponsored by EMSL-LV and the DOE. On the basis of their areas of expertise, the participants were divided into three workgroups. Each group developed a rough sampling/analysis plan for its respective portion of the treatment facility. The emphasis of the workshop discussions was on the potentially applicable measurement methods: their strengths and drawbacks for the proposed uses, and any associated research or development needs.

The scope of this report is limited to those activities that take place within the treatment facility. Characterization needs for excavated wastes are not included, nor are the needs associated with waste transportation. The report covers process monitoring needs that

are special to these treatment trains; testing that is standard in process engineering (flow meters, level monitors, etc.) is covered only insofar as special requirements have been identified. Likewise, characterization for worker safety in such a facility is not dealt with explicitly, although special issues, such as waste criticality, are covered. There is a discussion of all effluent streams as they exit the facility, but out-of-plant, ambient environmental monitoring is not discussed. The five principal waste treatment trains are addressed, and the measurement needs for each of the baseline treatment technologies are defined.

Only characterization needs are dealt with in this report. Review and discussion of the generalized treatment trains for the five waste streams was not within the scope of the workshop. Workshop discussions did, however, identify several duplicative measurements that could be consolidated, and some instances where additional measurement points were needed. Points where the lack of satisfactory characterization technology could constrain the treatment design were identified.

Regulatory requirements can be expected to change over time, regardless of what characterization strategy is adopted by DOE. This report does not attempt to define characterization needs to meet a speculated future regulatory scenario. Instead, pertinent current regulations are assumed as the baseline operating environment.

Quality assurance and quality control are not discussed at length in this report. In the workshop discussions, QA/QC principally arose in the context of specific measurement technologies. The report reflects these discussions, with QA discussions centering on the data quality objectives for particular measurements, and the level of QA achievable with the recommended characterization methods. In some cases, particularly characterization of the final waste forms, the level of effort for quality assurance will be specified by regulatory requirements. In other cases, the work group leaders agreed that QA/QC activities should be assumed for planning purposes to represent 10-20% of total sampling and analysis efforts.

The workshop participants felt that the preconceptual design represented by the F&ORs was not specific enough to allow actual characterization sampling plans to be devised. For example, for many of the waste pre-treatment and treatment operations, it is not yet settled what constitutes a batch. Consequently, numbers of required samples per volume of waste handled cannot be specified. Where they could, the work groups specified numbers of measurements per sample or per batch.

Because a complete sampling plan cannot be devised for the treatment facility, comprehensive characterization costs cannot be estimated. In this report, the only cost figures given are the costs of the principal instruments needed for the onsite laboratory, and for on-line process monitoring.

Organization of the Report

Within this report, the technical discussion of characterization needs is concentrated in Chapters 2, 3, and 4. These correspond to the topical areas covered by the three workgroups at the Las Vegas workshop. Each of these chapters is centered on an analysis table, and each includes discussion of the characterization technologies recommended for each measurement. The chapters differ considerably in format, as befits their different topics. For example, characterization for process monitoring and control occurs at dozens of points in the facility, while characterization of final waste forms occurs at one point: a solid waste form about to exit the plant.

Chapter 2: Preliminary Waste Characterization

The domain of this chapter begins 'when the drums get to the dock' at the front end of the facility. It includes the waste pre-screening and screening stages, and any other operations preparatory to assigning the wastes to a treatment train and beginning pre-treatment.

The major activities covered by this chapter are:

- identifying any containerized TRU wastes mistakenly routed to the MLLW treatment facility
- physical/chemical characterization of containerized wastes to route them to the appropriate treatment train
- identifying hazardous or special materials within the containers so that they can be handled separately
- performing a radionuclide inventory on a container of waste.

The chapter's emphasis is on real-time or near-real-time, non-intrusive or minimally intrusive measurement methods. Measurements requiring complete sampling are also discussed.

Chapter 3: Process Monitoring and Control

This chapter covers characterization techniques for the treatment trains themselves, including any solids, gases or liquids that are recirculated within the facility. Both the pre-treatment and treatment operations are covered.

As a background, the chapter first gives a brief summary of the five treatment lines of the MWTP. This is followed with a listing of the points where measurements are needed, specification of those measurements, and recommended methods. Next, there is a discussion of the generic monitoring and controls needed for thermal treatment of MLLW; this section applies to several of the treatment units specified for the MWTP. As a detailed example, there is a description of the measurement needs for operation of a plasma hearth furnace.

The example is followed by a discussion of the tradeoff between rigor of characterization and robustness of treatment technology, with reflections on how this balance affects facility design. Finally, the observations and research recommendations of the process monitoring workgroup are summarized.

Chapter 4: Final Waste Forms

This chapter discusses the characterization of the solid wastes that exit the facility: glass, ceramic and grout waste forms; plus ferrous metals and elemental lead and mercury that are destined for re-use. It is focused on the properties of the solid waste forms requiring measurement, and the associated measurement parameters. The text concentrates on the test methods, which are usually established by regulatory requirements.

Concluding Chapter

The final chapter contains a comprehensive list of the research, development and demonstration priorities identified during the workshop. This is followed by a discussion of waste treatment strategy as influenced by characterization needs and shortfalls. Pertinent regulatory and institutional issues are summarized, and further work to define characterization needs is discussed.

Appendices

The text is augmented by six appendices:

- Appendix A - detailed waste stream descriptions showing the points where measurements are made.
- Appendix B - the 41 flow diagrams for the MWTP integrated facility.
- Appendix C - descriptions of the principal measurement methods identified for up-front waste characterization. Many of these methods are also cited in the chapters concerning process monitoring and final waste forms characterization.
- Appendix D - brief discussions of developing methods that may be of great utility in process monitoring.
- Appendix E - technology summary sheets for the analytical methods used on the final waste form samples.
- Appendix F - a bibliography of LLW characterization references.

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Chapter 2

Characterization Before Treatment

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Introduction

Prescreening, characterization and sorting of wastes for assignment to treatment trains will be accomplished as containers are received at the treatment facility. This chapter identifies measurement methods and instrumentation appropriate to screening and characterization of wastes contained in drums or boxes.

The number of containers and the range of wastes to be received at the facility suggest that a building separate from the treatment plant should be considered to receive containers where they can be characterized and accumulated into batches of similar wastes prior to sending to treatment trains. This building would house the characterization instrumentation, calibration standards, and the chemical laboratory. It would include areas to hold received containers prior to characterization, and to store batches of characterized containers with similar waste components that are awaiting treatment. A special storage area would also be needed to properly store containers that were mistakenly shipped to the MWTP facility and are awaiting return to the sender. A separate storage area may be needed for difficult-to-characterize containers that will require special handling and intrusive sampling. Some sampled containers may need to be set aside awaiting results from chemical analysis.

Containers should be visually checked for damage when received at the loading dock. Leaking containers should be set aside and must be repackaged before being moved into the characterization building, otherwise contamination of characterization instrumentation could occur.

The characterization strategy for waste containers consists of:

- identifying drums containing TRU wastes; these cannot be handled at the facility
- determining the radionuclides contained in drums, by quantity and isotope
- identifying hazardous and special materials that require separate handling of containers and processing outside the five primary treatment trains

- determining the physical and chemical properties of the wastes to enable assignment of the container to one of the five treatment trains.

Measurement Points and Techniques

Sample Points

The characterization requirements are expressed as "sample points." These are defined in the F&OR document for the treatment facility (1) and the points of measurement are shown on the flowsheets (Appendix B). For pretreatment characterization, all of the sample points are shown on flow diagram PFD 010. Each "sample point" requires the determination of a specific waste component in a container. For example, Sample Point 010.1 calls for the determination of the specific alpha activity to assure that containers with TRU wastes are identified and not sent to the treatment trains.

Although the F&ORs and the sample points establish a framework for evaluating the measurement technology, some specifics are lacking. For example, the accuracy, bias, or precision necessary for a successful measurement have not been specified in the highly conceptual MWTP design. In many instances, several measurement technologies address a sample point requirement. Choosing the optimum method balances cost, effort, measurement time, and whatever accuracy is necessary. The workgroup chose to address each sample point with a range of possible measurement methods rather than to specify an optimum measurement technique.

Another issue that is not settled is the waste processing mode. For example, it is possible that the characterization prior to treatment and container segregation would be done continuously and concurrently with processing of the waste drums. Conversely, it is possible that waste drums would be segregated into the different categories and then processed as batches. The processing mode also affects the selection of an optimum measurement technique.

Sample points appropriate to preliminary waste characterization consist of:

Point	Sample Parameter to be Characterized
010.1	**Specific alpha activity (< >100 nCi/gram).** This sample point rejects containers having alpha activity that exceeds 100 nCi/g to assure that TRU wastes are not sent to the treatment trains.

010.2 **Physical Properties**
This sample point determines whether the container contents are liquid, wet or dry solids, homogeneous solids, or heterogeneous solids.

010.3 **Particulate content, or Pumpability**
For containers of liquids or wet solids, determine whether the contents are pumpable or contain large particles (assumed to be particles with a diameter of eight inches or greater).

010.4 **Qualitative and Quantitative Organics**
This sample point determines the types and amounts of organic compounds in the container, to enable proper assignment to a treatment train.

010.5 **Hazardous Elements or Special Materials**
This measurement is made for safety and to determine unique processing requirements. For example, both lead and mercury require special processing, as do high-clorine wastes. Other materials might present a hazard either to personnel in the plant or to equipment.

010.6 **Radionuclides**
Both for safety and to assure land disposal requirements are met, the radionuclide content of containers must be determined.

100.12 **Total organic carbon**
This sample point applies to a treatment train and is equivalent to sample point 010.4. Sample point 100.12 can be satisfied during characterization before treatment and should not need to be repeated within the treatment train.

100.15 **Particulate content**
This measurement applies to liquids and wet solids, and determines whether the material is pumpable. It is equivalent to sample points 010.2 and 010.3. Sample point 100.15 can be satisfied during characterization before treatment and should not need to be repeated at the treatment train.

200.22 **Mercury content**
Mercury is a hazardous material and must be treated in a unique manner, outside the primary treatment trains.

300.11 **Size of large solids (>8 inches)**
This measurement also applies to liquids and wet solids and determines whether the material is pumpable. It is identical to sample point 010.3, and need not be repeated within the treatment train.

Measurement Techniques

Table 2.1 is a listing of measurement methods that are potentially applicable to characterizing the incoming wastes. The table entries are organized according to sample point. For each point, a number of techniques are listed. Those denoted by an asterisk were discussed in the workshop. Non-starred entries were added later, and should be considered less favorable choices. No specific "preferred method" is indicated for each measurement; instead, a full suite of potentially applicable methods is listed.

In the table, measurement methods are classified by their physical nature: non-intrusive (N), intrusive (I) such as headspace analysis, or full sampling (S). For reasons of safety, representativeness, and efficacy of container processing, non-intrusive methods are preferable to intrusive methods or sampling. For each sample point, they are listed first.

Method sensitivity, precision and accuracy are also noted, where the information is readily available. Many of these methods have been developed and applied in very different operating environments than the MWTP integrated facility. Sensitivity, precision and accuracy achievable within that facility may be very different than published values. The entry "TBD" in these columns denotes "to be determined," meaning information on these parameters was not readily available. Parameters clearly not applicable to the measurement are so noted.

The listed methods are also classified as to whether they are established techniques (E) or will require development (D) for this application. Where methods were recognized to need research, development or demonstration, an estimate of the number of months required is given. This estimate is very rough; it simply represents the "best judgement" of the workgroup members. It must be stressed that most of the "established" methods would also require adaptation and demonstration for this application.

Further details on the principal recommended methods are found in Appendix C. In the appendix, each individual technique is described and its capabilities and limitations are defined. Specific research that is necessary to bring the method to its full potential is also discussed.

In assembling information on the listed methods, a number of technical references were consulted. The primary references, many method-specific, are 2 through 7. Secondary references of a more general nature, including textbooks of analytical chemistry, are 8 through 16.

The charge made to the workshop attendees was to determine applicable technologies for waste characterization; however, quantitative data quality objectives have not been established. Although the techniques listed provide the type of information required by the F&OR guidelines, they may not provide these measurements at the required precision and accuracy. The facility designer has several alternatives for resolving this problem.

TABLE 2-1. MEASUREMENT METHODS FOR CONTAINERIZED WASTE

POINT: 10.1
PARAMETER: alpha (gross)
PURPOSE: Waste acceptance

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
(N) Passive Neutron Coincidence Counter	20nCi/gm	A: 5%-50% Depending on Matrix (DOM)	15 min.	The passive neutron coincidence counter is a passive counter that uses time correlations between neutron events to specifically measure fission events. It measures Pu content with high accuracy, from which the specific alpha activity is deduced.	E
(N) Passive Neutron Multiplicity Counter	20nCi/gm	A: 5%-100% DOM	15 min.	The passive multiplicity counter is an extension of the coincidence counter. Higher order coincidences are also measured to provide more assay knowledge.	D (6)
(N) Passive Neutron Add-A-Source	20nCi/gm	A: 5%	15 min.	The add-a-source system is an active matrix correction technique for passive neutron measurements. At present, it is coupled with passive neutron coincidence counting, but it could be extended to multiplicity counting for improved results.	D (6)
(N) Californium Shuffler Passive-Active Neutron	5mg Pu 1 gm U	A: 15%	15 min.	The californium shuffler is both a passive and active neutron measurement. In the passive mode it is equivalent to the passive multiplicity measurement above. In the active mode it measures delayed fission neutrons to assay U-235.	E
(N) Differential Die-Away Passive-Active Neutron	1nCi/gm	A: 15%	15 min.	The differential die-away system is also passive and active. However, the passive measurement has yet to use coincidence or multiplicity neutron counting. In the active mode it measures prompt fission neutrons, primarily for plutonium.	E

TABLE 2-1, GROSS ALPHA (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
(N) Secondary Ion Mass Spectrometry (SIMS)	TBD	TBD	TBD	Used for direct analysis on basalt contaminated with tributyl phosphate (TBP). TBP was widely used across DOE complex to recover U, Pu, Th, Np and Am and can be an indicator of the presence of these radionuclides.	D (12)
(N) segmented gamma scanner (SGS)	1 g U-235	A:1%-100% depending on sample	20 min	SGS is a passive, high-energy resolution gamma- ray spectroscopic measurement with an additional active correction for matrix attenuation. The SGS is an axial scanner that can resolve the axial distribution of emitting material within a 55 gallon drum. It assumes a homogeneous distribution within each axial segment.	E
(N) Tomographic Gamma Scanner (TGS)	1 g U-235	A:1%-8% depending on sample	30-50 min.	TGS is an extension of the existing SGS technology that allows for a non-uniform distribution of material in axial segments. A complete spatial distribution of emitting and attenuating material is determined. Measurement accuracy is improved significantly for heterogeneous and medium density samples because the matrix and position effects are fully compensated.	D (6)
*(I) Large-area Ionization Chamber Alpha Spec.	50 pCi/g	Instrument not designed to obtain precise, accurate measurements.	15 min.	Direct screening tool. Sample preparation consists of grinding a sample of soil. Process provides spectrometry without chemical preparation. Has been designed to screen for plutonium. Designed for health physics purposes. Installed in the rapid TRU monitoring laboratory developed at the INEL. Quality assurance developed for soil and water, application development needed.	D (6)

TABLE 2-1, GROSS ALPHA (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
*(I) gas proportional alpha/beta counter	0.5 meV	5% of cpm	immediate	Well established technology. Can be partitioned to read alpha only. Unable to distinguish between isotopes. Only applies to specific samples.	E
*(I) Electret dosimeter	0.1 mRem	10%	long-term monitoring	Capacitor that holds its charge without going under electric potential. Charge is bled off relative to the activity of radiation exposure. Used for detecting radon. Acts as a passive ionization chamber. Cost-effective passive monitor; sensitivities of a few pCi/g of Pu in soils over 24 hours possible.	E
*(I) GC/MS	ppm-ppb	TBD	minutes	Measures helium, which is an indicator of the presence of plutonium. Helium tends to leak from drum quickly. Method is probably not sensitive enough. Other methods currently developed are more appropriate.	E
*(S) Total Spectrometric Alpha (TSA)	.05 pCi/g, based on .5 gram sample	P: 5% A: As good as the precision of the measurement	4-6 hours	Perform total dissolution to obtain qualitative and quantitative information. Not all separations are performed on each sample. A very small amount of mixed waste is produced (approximately 10 milliliters).	E
*(S) Isotopic Alpha	Same as TSA	Same as TSA	8 hours	This is the same analytical method as TSA, however, all separations are automatically performed. May not be necessary depending on the isotopes found in the initial screening. A very small amount of mixed waste is generated (approximately 10 milliliters).	E
(S) Isotope Dilution Mass Spectrometry	TBD	TBD	6 hours	Able to measure natural levels of long-lived fission products and neutron-capture products as low as 10-7 atoms. Studies needed to enable quick analysis. Only applies to specific samples.	D (6)

TABLE 2-1, GROSS ALPHA (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
(S) Photon Analysis Spectrometry	Pu-239: 50 pCi/g, 15 min. count, 10 gram soil sample.	A: 10% P: 5%	45 minutes	Installed in the rapid TRU monitoring laboratory at the INEL. Measures alpha and gamma simultaneously using a germanium detector. Meets or exceeds the sensitivity required to detect most activities where a dose of 100 mRem/year is highest risk level to public. Can also be used to count stacked CAM filters and smears. Application development is needed for high concentration samples and various matrices.	D (24-36)

POINT: 10.2
PARAMETER: Solid/Liquid/Heterogeneous/Homogeneous
PURPOSE: Separation/ Classification

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
Radiographic Methods					
*(N) Real Time Radiography (RTR) *(N) Digital Radiography	Not Applicable	Not applicable	real - minutes	Does phase boundary between liquids and solids. A slurry may move and resettle slower. Disadvantage - will not differentiate between org/aq phases or liq/liq phases. Advantage - will see chunks of Pb and Hg. Can distinguish liquid/solid and homo/ heter. Can give some information on pumpability and viscosity. Will not recognize liquid in any container filled to top.	E
(N) Neutron Radiography	Not Applicable	Not Applicable	real - minutes	Similar to RTR and Digital radiography. Method may be able to differentiate between organic/aqueous or liquid/liquid phases. Further development for this capability needed.	D (6)
*(N) Computed tomography (CT), Active and Passive	Not Applicable	Not Applicable	minutes - hour	CT provides quantitative 3-dimensional stationary views compared to qualitative 2-dimensional movies for real time radiography. CT provides stationary views of boundaries between waste with differing densities. CT can measure density and boundary dimensions within a drum. CT can measure volumes of like densities (i.e., liquid) and container wall thickness (i.e., drum walls). CT identifies Pb and Hg. CT contrast resolution is capable of imaging dense waste matrices (i.e., cement). CT has similar or lower spatial resolution compared to real time radiography. CT can determine movement of materials (i.e., liquids) with view sequencing over time.	E

TABLE 2-1, PHYSICAL STATE (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
*(N) ultrasound	TBD	TBD	real	Liquids only. Cannot see through inner liner or inner barrel. Can differentiate between some liquid phases. Can determine how full barrel is. May be able to see if solids are wet (e.g., wet mop).	E
(N) Weight	35 pounds	± 5 pounds	real	The weight of a drum can indicate the presence of dense materials (lead), or very light materials (protective clothing, plastic sheeting, etc.). Technique must be coupled with other measurements, but can be used to batch.	E
*(I) visual (TV camera)	TBD	TBD	real	Will see phases. Uses fiber optics for image transmission. Small size, flexible, manueverable. Development needed to harden camera for hazardous environment.	D (12)
(I) Laser Induced Fluorescence	TBD	TBD	TBD	Good sensitivity. Relatively extensive research and development required. Less expensive methods available.	D (24-36)
*(S) COLIWASA	TBD	TBD	real	Used to visually inspect liquids or non-viscous solids. Will not penetrate viscous materials. Messy. Not a preferred method, but has been used in past characterization activities.	E
(S) X-ray Diffraction	1%	TBD	minutes - hours	Limited to analysis of powders and metals. Non-destructive, non-altering; identifies crystalline phases in solid samples.	E

POINT: 10.3.
PARAMETER: Pumpability
PURPOSE: Processing/Classification

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
*(N) acoustic monitoring	can be pumped (percent solids in solution; on the order of 30% solids)	10%	minutes	An acoustic receiver and transmitter have been installed on a mixer pump in tank 101-SY at Hanford. The power of this monitor is 1/10 of a watt. Phase shift in signal received indicates particulate concentration.	D (9)
Radiographic Methods					
*(N) Real Time Radiography (RTR) *(N) Digital Radiography	sufficient 10%	sufficient 10%	real - minutes	Can measure size of chunks. Locates phase boundary between liquids and solids. A slurry may move and resettle more slowly. Advantage - will see chunks of Pb and Hg. Will tell liquid/solid. Will tell homo/heter. Can give some information on pumpability and viscosity. Will not recognize liquid in any container filled to top.	E
(N) Neutron Radiography	unknown	unknown	real - minutes	Similar to RTR and Digital Radiography. Method may be able to differentiate between organic/aqueous or liquid/liquid phases. Further development for this capability needed.	D (24)

TABLE 2-1, PUMPABILITY (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
*(N) Computed tomography (CT), Active and Passive	TBD	TBD	minutes - hour	CT provides quantitative 3-dimensional stationary views compared to qualitative 2-dimensional movies for real time radiography. CT provides stationary views of boundaries between waste with differing densities. CT can measure density and boundary dimensions within a drum. CT can measure volumes of like densities (i.e., liquid) and container wall thickness (i.e., drum walls). CT identifies Pb and Hg. CT contrast resolution is capable of imaging dense waste matrices (i.e., cement). CT has similar or lower spatial resolution compared to real time radiography. CT can determine movement of materials (i.e., liquids) with view sequencing over time.	E
*(S) viscometer	can be pumped		real	Use with laboratory cone penetrometer to measure resistance. Option would be to just try to pump.	E
(S) Particle Size Analyzer				Use for powders and slurries	E

POINT: 10.4
PARAMETER: Qualitative and Quantitative Organic Content
PURPOSE: Classification

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
*(N) Prompt Gamma-Neutron Activation Analysis (PGNAA)	Reference 17 $\geq$ 5%	poor	real time	This method does not actually measure organics, it measures elemental composition. It may be possible to determine organic content from this. Separate calibration standards are needed for each matrix. Has been applied commercially to look at concrete, sulphur in coal, and BTU content using thermal neutron scattering. Can assay very large amounts at a time. These applications are indicative of the possibility of applying this technique to waste. Works best with elements that have high thermal neutron cross-sections.	D (12)
(N) Pulsed fast neutron analysis (PFNA)	TBD	TBD	real	Can detect Hg, Cl, PCBs, heavy metals, explosives, and pyrophorics. 3D elemental distribution maps of container contents are formed.	D (24)
*(I) Total Volatiles Analyzer (e.g., photoionization detector, flame ionization detector)	1 ppm	± 40%	real	Measurement only for volatile organic chemicals in the vapor phase. Measures headspace only. No qualitative capabilities.	E
*(I) Laser-induced plasma spectrometry	1 ppm	TBD	real	Can see organometallics, aromatics, PCBs. Can be done by headspace or fiber optics w/cone penetrometer. Will not see methanol or several hydrocarbons.	E

TABLE 2-1, ORGANICS (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
*(I) Raman spectroscopy	.1%	TBD	minutes	IR spectral scattering. Disadvantages - expensive, art, high skill level needed. Would see low level of organics in water. Extensive development to determine scattering effects in various matrices.	D (12)
(I) fiber optic chemical sensor (FOCS)	TBD	TBD	real	Inexpensive, but good for one use only. Remote sensing possible, sensor occupies low volume, inert to most chemical environments, readily adapts to most conventional optical spectroscopy. May be used to measure inorganic and organic chemicals and make physical (temperature, moisture, etc.) measurements. Development needed to enable sensor to withstand harsh chemical environments.	D (6)
(I) Fiber- optic/Fourier Transform Infrared probe	50 ppb - 1%	TBD	minutes	FTIR measurements have been demonstrated by several labs and industries. Results show the device can accurately predict mixtures of solvents in various matrices within 55 gallon drums (e.g., benzene, toluene, napthalene, methane, CO_2.	D (12)
*(I) direct sampling ion trap mass spectrometer (DSITMS)	ppb-ppm	TBD	minutes	Use with cone penetrometer. Developmental stage at Oak Ridge and Hanford. Not known how SVOCs would be reduced.	D (6)
*(I) near IR	TBD	TBD	minutes	Produces weaker and broader bands than IR. Questionable for this application. Applied in process control of known concentrated materials. Relatively inexpensive, small.	D (24 - 36)
*(I) ion mobility spectrometer	10-50 ppb (linear range)	± 5%	minutes	Used in military to detect nerve agents, mustard gas, pesticides. Cannot separate combination compounds, however, a GC can be attached. Also used by DEA for drug enforcement. Very portable.	D (12)

TABLE 2-1, ORGANICS (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
* (I) Draeger tubes, Sn-oxide	Not Applicable	Not Applicable	seconds to minutes	All commercially available. Inexpensive, relatively simple. Not designed to provide precise, accurate results.	E
(I) Fluorescence	TBD	TBD	TBD	Somewhat established, but specific compounds to be detected must be tested with another method before deployment. Used for explosives, pesticides, and aromatic hydrocarbons.	D (12)
(I) Piezoelectric quartz microbalance (PQM) and surface acoustic wave (SAW) sensor	ppb	Matrix dependent	real time	Methods quantify solvent vapors. Quartz crystal microbalances (both bulk and surface acoustic wave type) are molecular-size selective detectors. They oscillate at a precise frequency which is altered by deposit of vapor. SAW sensor is the more sensitive of the two.	D
*(S) Total Organic Carbon analyzer	ppm	P: 10% A: 5%	15 min.	Carbonate and bicarbonate can interfere. Procedure developed for homogeneous samples only.	D (3)
(S) Supercritical Fluid Chromatography	TBD	TBD	20 min.	Quantitatively measures non-volatile compounds in liquids, solids, and sludges.	E
(S) Immunoassay	10 ppm	P: 25% A: 25%	10 minutes	Provides semi-quantitative determination of PCBs and petroleum products. Suitable for radioactive contaminated materials. Not yet tested on various waste forms.	D (6)
(S) Nuclear Magnetic Resonance	TBD	TBD	TBD	An imaging technique; used as secondary method.	E

TABLE 2-1, ORGANICS (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
* (S) Gas Chromatograph/Mass Spectrometer (GC/MS) with Supercritical fluid extraction, purge and trap (SCFE, P&T)	ppb	Matrix dependent	20 min. minimum	Measures most organics. Commercially available, some development for application required. Complex instrumentation may not be appropriate for a rugged environment. Portable, rugged model developed, demonstration needed.	D (3)
* (S) portable gas chromatograph (GC) with thermal desorber, purge and trap (TD, P&T)	ppb-ppm	TBD	30 - 40 minutes	Can be set up quickly. Must be dedicated to specific organic types. Low cost, relatively low training. May be used for headspace analysis or a sample may be collected and extracted or digested. Instruments with several detectors to allow for wide application are available.	E
* (S) Derivitization followed by gas chromatography (GC)	ppb	TBD	1 hour	Measures chelating agents (e.g., herbicides). High resolution, very sensitive. Disadvantage: Needs high skill level, extra safety precautions for reactive, explosive gases. Advantage: GC/MS will provide additional analysis.	E
* (S) High Performance Liquid Chromatography (HPLC)	ppb-ppm	TBD	30 minutes	Direct analysis of chelators. Disadvantage - skilled operator needed. Will do a variety of complexing agents. Measures less volatile chemicals in liquid. Limited to liquid phase.	E
* (S) Ultraviolet Fluorescence	1 ppm	± 40% (A) ± 15% (P)	30 minutes	Simple and rapid determination of total polynuclear aromatics (PNA). Does not identifiy individual PNA compounds. Potential for significant matrix interference.	E

POINT: 10.5
PARAMETER: Special (Hg, Pb, Cl, noble metals, etc.)
PURPOSE: Separation/Classification

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
(N) Prompt Gamma Neutron Activation Analysis (PGNAA)	.1%	TBD	real	Commercially available, need to demonstrate usefulness for this application. Refer to Sampling Point 10.4 for further detail.	D (3)
(N) Pulsed fast neutron analysis (PFNA)	TBD	TBD	real time	Good for elemental analysis of metals.	D (24)
* (I) Mercury Vapor Analyzer	ppm (application 1) ppb (application 2)	TBD	minutes (application 1) hours (application 2)	Low cost, small (hand-held). Very sensitive (.2 ppb in solution). Two versions: 1. microprocessor: minimum sample prep., small samples 2. AA: generates small volumes of waste. Does Hg only, needs rigourous sample prep. Can be used for head space.	E
(I) Conductivity meter	1%	Not applicable	minutes	Measures ionic strength. Salt content may affect treatment. Best with dilute solutions.	E
* (S) Mass spectrometry (MS)	ppb	±1-5%	minutes	Measures liquids, solids (Cl, Pb, Hg). Cheaper methods available.	E
* (S) Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS)	ppb	TBD	minutes	Can perform isotopic analysis of elements. High cost for instrumentation, high level of operator training required. May not be rugged enough to survive process conditions. Requires sample preparation. Simultaneous measurement of many elements.	E

TABLE 2-1, SPECIAL MATERIALS (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
(S) Scanning Electron Microscope/Electron Diffractive X-ray (SEM/EDX)	ppt	TBD	<1 hour	Sub-micron surface resolution; broad elemental detection; useful for solids.	E
* (S) Field Portable X-ray Fluorescence (FPXRF)	matrix/count time dependent, ppm	P: 10% A: 25%	30 minutes	Elemental (> aluminium on periodic table). Advantages: non-chemically altering. Wide calibration range. Disadvantages: Subject to matrix effects, sampling effects, usually requires sample preparation.	E
* (S) Inductively-Coupled Plasma (ICP)/ Atomic Emission	ppb	TBD	hours	Will do most metals. Minimum detection limit dependent upon metal. Multi-element analysis. Rigorous sample preparation for some elements. Primarily a delivery technique.	E
* (S) Ion chromatography (IC)	ppm	Matrix dependent	1-2 hours	Does all anions, some cations: nitrates, nitrites, sulfates, chlorides, fluorides, cyanide, iodine, bromide, chelators, decon. solutions. Disadvantage - must be an ionic species. Advantage - very low detection limit. Not optimal for metals in complex matrices.	E
(S) Immunoassay	5 ppm-80 ppm (linear range)	TBD	minutes	Developed for analysis of mercury in soil. Development needed for application. It is not known how the assay will react in various media. Very low cost alternative to other methods. Available in portable kit form.	D (12)
(S) Distillation for Total CN	low ppm-0.1%	TBD	TBD	Useful in radioactive ferrocyanide wastes. Digestion prior to distillation required.	E
(S) Electron Spectroscopy for chemical analysis	ppm	P: 10% A: 10%	minutes	Technique dependent upon specified treatment process.	E

TABLE 2-1, SPECIAL MATERIALS (Continued)

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
(S) Wavelength Dispersive X-ray Spectroscopy	1%	TBD	TBD	Quantitative analysis of solid samples. Used in conjunction with electron microscopy. Laboratory instrument - more sensitive than energy dispersive fluorescence (XRF).	E
* (S) Atomic Absorption/Atomic Emission (AA/AE) Spectroscopy	0.1 ppm	P: ± 10% A: not available	30-40 minutes	Elemental, rapid, selective. High sensitivity for alkalies. Disadvantages - must be in a lab for safety. Not rapid if analyte change required. Cannot do chlorine. Can do Hg with a cold-vapor attachment and longer analysis time.	E
* (S) Ion Specific Electrodes (voltammetry)	ppm	TBD	minutes	Does anoins and cations in solutions only. Advantages: low cost, no waste generated, accurate. Technique has good selectivity for some hard to measure elements. Disadvantages: easily interfered with or poisoned. Not robust.	E
* (S) pH probe	Not Applicable	Matrix dependent	minutes	Used to measure the acidity or alkalinity of a liquid.	E
* (S) Chemical Classifier kits	Not applicable	Not applicable	minutes	Identifies material by chemical class (acid/base, oxidizers, fluoride, organic solvents/petroleum distillates and iodine/bromine/chlorine).	E
(S) Capillary Zone Electrophoresis (CZE)	ppt	TBD	TBD	Measures ionic and some neutral compounds. Used in the biomedical industry. Advantages - high resolution, ideal for ionic compounds, low cost, small sample required, low waste generation. Disadvantage - limited sensitivity	E
* (S) Total Organic Halides (TOX)	5 ppm	P: 5% A: 15%	30 minutes	Measures halogens in halogenated organics. Will not measure fluorine. Technique is very rugged.	E

POINT: 10.6
PARAMETER: Miscellaneous Radiological
PURPOSE: Radiological Control

METHOD[a]	SENSITIVITY ATTAINABLE[b]	PRECISION/ ACCURACY ATTAINABLE[c]	TIME TO MEASURE[d]	APPLICATION NOTES	METHOD STATUS[e]
(N) Tomographic gamma scanner	TBD	TBD	50 minutes	Simultaneous specific assay of multiple isotopes. Can perform as a normal SGS. Application is under development at Los Alamos National Laboratory. See sampling point 10.1 for details.	D (3)
*(N) gamma spectrometer	Limited by background, self-absorption, half-lives of measured isotopes	calculated	minutes to hours	May be used to screen for gross gamma activity only or for qualitative and quantitative analysis.	E
(N) segmented gamma scanner (SGS)	TBD	TBD	20 min	Nondestructive and particularly appropriate for radionuclide concentrations. See sampling point 10.1 for details.	E
*(I) cone penetrometer	TBD	TBD	minutes	Gamma capabilities in demonstration phase. No alpha or beta capability. Used for subsurface measurements in the field: Site Characterization and Analysis Penetrometer System (SCAPS).	D
*(S) ICP/MS with laser ablation	ppt	P: 20 % A: 10 %	minutes to hours	It has a multi-element capability. Isotopic analyses can be performed. Ions (ionized atoms) quadropole, measures all isotopes, calibrate hourly, needs to be ruggedized. Good for long-lived isotopes.	D (24)
*(S) gamma spectrometer	cpm; isotope dependent	TBD	minutes	Well established technology.	E

TABLE 2-1 CONCLUDED

a * = Techniques identified at May, 1993 workshop in Las Vegas
N = Non-intrusive assay
I = Intrusive Assay
S = Physical sample required

b. Sensitivity is evaluated from the standard deviation at the concentration level of interest, and is equal to the minimum difference in two samples of a given concentration that can be distinguished with 95% confidence. The sensitivities provided are for instruments operated under ideal conditions with optimum sample species and/or sample preparation. Actual analyses may show less sensitivity due to the varying nature of the waste and operational conditions.

The units provided are specific to the instrument and may be converted for program reporting purposes as required.

c. Precision is the standard deviation at any concentration point. Accuracy is the degree of agreement of a measured value with the true or expected value of the quantity of concern. Precision and accuracy are provided for instruments operated under ideal conditions with optimum sample species and/or sample preparation. Actual analyses may be less accurate and precise due to the varying nature of the waste and operational conditions.

A = Accuracy
P = Precision

d. Time to measure = estimated analysis time. Does not include sampling and sample preparation time. Real time refers to a measurement in which the result appears simultaneously with the measurement.

e. D (n) = Developmental (months to develop)
E = existing technology

Note: A technique may be fully capable in its current application, but may need development in the following scenario:

1. widely varying matrix from one measurement to the next
2. broad concentration range
3. complex combinations of contaminants
4. radioactivity up to 100 milliREM/hour on contact with sample container

Limitations in the specific characterization techniques can be accommodated by additional and more complete waste treatment; multiple instruments with complementary capabilities can be used in concert to achieve improved data quality; and additional research and development can be done to augment the existing instrumentation capabilities.

Several factors account for the limitations of characterization technologies. In some cases the available technologies were developed for other applications. These applications probably have different data quality objectives and different operating conditions. Although the underlying principals are similar, the specific application engineering may be quite different. Some measurement techniques may require only modest re-engineering to adapt them to this specific application. Other techniques may have been developed for less demanding applications and may require significant scientific development to sufficiently raise their capabilities.

Different instruments have different, and sometimes complementary capabilities. Few instruments can accurately measure a quantity under all circumstances. For example, gamma-ray spectroscopy is limited by the attenuation from high-Z (high atomic number) materials (e.g., metals). Drums with large amounts of metals cannot be effectively measured using gamma rays. Conversely, neutron-based measurements are largely unaffected by high-Z materials, but are strongly affected by low-Z materials (e.g., the hydrogen in plastics). These complementary limitations can be somewhat offset by properly combining individual instruments.

There is a significant problem with discrete sampling of heterogeneous waste. It is effectively impossible to sample drums of heterogeneous waste in a manner that assures the samples are representative of the entire container (18). Indeed, the need to circumvent this problem is one of the principal forces driving the development of a MLLW treatment facility based on very robust techniques. Discrete samples measure only a small portion of the containerized waste. It is possible to develop sophisticated sampling plans to assure that the ensemble of sample locations within the container is representative of the entire container. However, these strategies require significant knowledge of the material distribution in advance, which largely defeats the minimum-characterization approach. If the drum contents are initially unknown, it is not possible to sample a drum and assure that the samples are representative. Therefore, bulk measurements that measure the drum in its entirety should be used whenever possible, even if these methods have significantly higher bias errors. The important distinction is that the bias errors of bulk methods, such as radiation-based methods, are well known. Without knowing the material distribution in advance, the uncertainties from sampling are completely unknown. Therefore, it is essentially impossible to assign specific data quality objectives for sampling methods because the uncertainties cannot be quantified.

When a final measurement strategy is constructed from the required data quality objectives, these limitations must be considered. An optimum measurement strategy may use suites of measurement instruments for a single sample point in order to balance the

strengths and weaknesses of the individual techniques. Additional, perhaps significant, development may be necessary to improve some techniques to the required level of performance. In some cases insufficient measurement capability may compel yet more robust waste treatment methods. The measurement strategy designer must balance the costs and benefits of these various options.

Conclusions and Recommendations

At the receiving area of the treatment facility, some real-time and near-real-time measurements will be made on-line. However, for some containers, full sampling, with sample submittal to an analytical laboratory at the MWTP, will be necessary. This lab will measure both qualitative and quantitative attributes. A specific example of this need is the quantification of organics in drums whose contents are heterogeneous or are not well known *a priori*. The work group concluded that if organic content must be known to 1% it will be necessary to open many drums and conduct physical sampling.

A corollary of this is that a large storage area will be needed to stage containers while awaiting test results from the laboratory, for those containers requiring full sampling. The size of the staging area depends on the plant throughput and the analysis turnaround time. On-line, near-real-time (or better) measurements are not subject to this limitation.

The work group favored *in situ* measurements of the waste containers, even if those could not be made in real time. Improvements in field-portable instrumentation far outpace improvements in laboratory technologies. It is expected that the next ten years will see growing regulatory acceptance of *in situ* methods, continued refinement of existing methods, innovative application of new methods, and the need for fewer confirmatory analyses by traditional methods. As an example, the X-ray fluorescence instrument (XRF) can determine heavy metals in a soil matrix in minutes as compared to nearly a day for analysis by the atomic absorption spectrophotometer (AAS). Cost savings for field-portable XRF over traditional AAS are approximately a factor of ten. The more samples analyzed in the field, the greater the savings. Similar savings can be realized when "sniffers" are used for volatile organic compounds (VOCs). In the case of VOCs, an additional benefit is seen in the integrity of samples that, when shipped or handled, are destined to lose (preferentially) highly volatile compounds.

There were considerable differences of opinion within the work group on the proper role of process knowledge, and several experiences with seriously inaccurate container manifests were related by group members. There was agreement that the treatment facility should definitely use process knowledge and container manifests to the extent that they could be trusted. The current practice is to place little or no trust in process knowledge, particularly for wastes generated before the land disposal restrictions were put in place. One strategy that has been used is to verify process knowledge and identify sub-populations

within a waste stream using a screening technique such as real-time radiography. The group felt strongly that workers within the DOE complex need more guidance from DOE on the use of process knowledge.

One way to get around insufficient process knowledge is to encourage or require waste characterization at the shipping site if containers came from off-site. Many of the techniques cited are applicable at the point of waste generation. Unfortunately, this doesn't really diminish the characterization requirements - it just moves them to another location and time.

The next round of design for the MWTP integrated facility should include characterization experts as well as facility engineers. This goes for design of any treatment facility that is at this stage. The treatment design and the measurement design are intimately related. Field sampling experts should also attend.

No one technique can acquire all the needed information for diverse waste streams, especially for radiation measurements. A facility accepting a wide range of waste streams will need pairs or suites of methods, to cover the different waste types and configurations. These may be able to be narrowed down for each specific facility, where there is a limited range of incoming waste streams.

The group identified several indirect (non-intrusive) methods to assess pumpability of containerized materials. For each of these, some method has to be worked out to infer from an image - usually a radiographic image - whether the materials will pass through a pump.

Almost all the existing methods for evaluating the organic content of a closed container require sampling or intrusive sensing. PGNAA warrants continued development as a potential non-intrusive method. A related method, PFNA, also shows promise for non-intrusive characterization. Also important will be development of intrusive methods combined with fiber-optic systems for headspace sensing or submersion in containerized liquids. Sensing methods include immunoassay, FTIR, UV fluorescence, and others. These systems would likely require hardening for this application.

A very similar situation exists with respect to assessing special materials in containers. Many of the parameters of concern are currently difficult or impossible to sense or quantify non-intrusively. Here too, development of PGNAA, PFNA, and minimally intrusive sensing techniques hold the most promise for avoiding the need to sample.

Several of the measurement technologies which could be used in the characterization of containerized MLLW were developed for very different applications. In some cases all that is needed is to adapt the technology for the MLLW application, which should require only a modest development effort. In other instances the existing technology is insufficient

for this application and must be extended, which might require significant research and development.

In this work group, there was some difficulty in selecting methods because needed data accuracy and precision (or DQOs more generally) are not well defined at this point. When the group tried to address this matter, they found it thoroughly tangled with the issue of representative sampling - not easy in many of the waste streams, which may be very complicated matrices. In some of these waste streams it seems unlikely that rigorous quantitative DQOs can ever be met. Designers of the up-front characterization program need more information from the facility design engineers on how much uncertainty the initial waste processing operations can tolerate.

A significant technological issue is whether to use discrete sampling or bulk measurement. Discrete sampling suffers from the limitation that it may not represent heterogeneous matrices properly. There is no *a priori* method for insuring that discrete sampling completely characterizes a container. Bulk measurements are not subject to this limitation, and are thus favored, where they can meet requirements of the measurement.

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Chapter 3

Process Monitoring and Control

Ray Geimer, Gary Leatherman and Ellen Stallings

Introduction

This chapter discusses waste processing characterization/sensor needs for the treatment of mixed low-level waste. The MWTP flow diagrams and F&ORs have been used as the framework within which to discuss the nature of characterization and sensor needs and the availability and status of characterization/sensor technology to meet those needs.

This chapter is divided into several parts: a brief description of the MWTP flowsheet; a description of measurement points in the MWTP flowsheet where characterization is required with the suggested measurement techniques listed with information about each technique; an examination of the generic monitoring and controls required for operation of thermal treatment units for the treatment of low-level mixed waste (since the MWTP flowsheet relies heavily upon thermal treatment); as a detailed example, a description of the characterization/sensor requirements for the plasma hearth process (a technology which has the potential to be omnivorous thereby minimizing characterization and sorting requirements); and recommendations for technology development to meet the characterization needs identified by the workshop. The use of existing automation hardware and software for monitoring the processing of the mixed low-level waste is discussed in Appendix D. "Smart sensor" process monitoring control applications have been introduced by industry recently and will be used for the characterization of MLLW; see Appendix D for further details.

The Mixed Waste Treatment Project Integrated Treatment Facility

The MWTP facility (see Appendix B for flow diagrams) consists of five processing lines for treatment of incoming waste: aqueous liquids, organic liquids, wet solids, homogeneous dry solids, and heterogeneous solids. The types of wastes encompassed by these categories are described in detail in Appendix A. Incoming waste is sorted and assigned to one of these process lines. The basic working assumptions of this discussion are that incoming waste will be assigned to the correct treatment process line during initial characterization (as discussed in Chapter 2), and that characterization of the final waste

forms will take place after treatment is complete (see Chapter 4). Monitoring of process offgases is discussed in this chapter.

The aqueous treatment line is basically a standard waste water treatment process line. It contains unit operations for neutralization of acidic or caustic liquids, removal of suspended solids, separation of large quantities of organic compounds, destruction of residual organics by wet air oxidation, and final polishing of effluent water.

The organic liquids process line is more complicated, but primarily involves separating the incoming organic waste into dilute organics, concentrated organics, and heavy organics. After appropriate pretreatment such as solids removal, the dilute organics are treated in a controlled air incinerator, the concentrated organics in a rotary kiln incinerator, and the heavy organics in a car-bottom furnace.

The wet solids line consists primarily of a size reduction unit operation to insure pumpability of the incoming wet solids and a low temperature drying unit to dewater the sludges. The resulting dry solids are then assigned to the appropriate portion of the homogeneous solids processing line.

The homogeneous dry solids line sorts the incoming waste into organics, inorganics, nonferrous metals, and ferrous metals. Bakeout of liquids and mercury occurs if necessary. The organics are incinerated in a controlled-air furnace. The inorganics are vitrified in a joule melter and the metals melted in an electrically heated batch melter. The slag from the metal melters is tapped off separately and may with the addition of appropriate additives be processed in a joule melter to produce the final waste form.

The heterogeneous solids line includes size sorting and size reduction, then separates the waste into the above-listed categories of organics, inorganic solids, ferrous metals, and nonferrous metals. (It should be noted that, with the promulgation of the RCRA Debris Rule, most MLLW treatment facilities will have complete, separate treatment trains for wastes that can be classified as "debris" under that rule.)

The flowsheet also includes appropriate offgas systems for the thermal units, holding tanks, and transfer lines/valves etc. to enable the integrated operation of the facility.

Measurement Requirements for Process Control

The characterization requirements for the five treatment lines (flow diagrams 100-500) are listed below according to measurement numbers that match measurement points on the flow diagrams. The suggested measurement techniques are listed with limited information about each technique. Potential offgas monitoring instrumentation and radiometric research or development needs are also included.

Aqueous Liquids Treatment (flow diagrams MWTP-PFD-100)

The purpose of this process is to treat aqueous streams from both external newly generated and stored aqueous liquid waste and internal transfers from within the facility to produce a clean effluent water. The process has a feed preparation area, filtration units, pretreatment tanks, a primary carbon bed treatment unit, special feed treatment units, and a unit for feed containing organics. The feed must have < 1% organic content and must be pumpable (defined as <40% particulate).

The waste containers will be opened and the contents screened before the waste is introduced into the processing lines to prevent mixing of incompatible materials, and to verify that the feed is appropriate for the treatment line.

Preliminary Measurement Requirements (MWTP-PFD-100-1)

100.11 pH

Purpose: safety: ensure that highly acidic or caustic solutions are not mixed; to prevent a violent reaction in the tanks.

Matrix: solutions containing <1% organic content, <40% particulate (may contain heavy metals, radionuclides, salts, etc.)

Accuracy required: 1 pH unit

Precision: 10-20%

Time Frame: 5-15 minutes

Suggested Measurement Technique: pH probe, automated titration - Existing Technology

100.12 Total Organic Carbon

Purpose: protection of process line from out-of-specification feeds; verify solutions are < 1% total organic content

Matrix: same

Detection Limit: percent

Range: <1% or >1%

Accuracy: 50%

Precision: 10-20%

Time Frame: 5-15 minutes

Potential Measurement Technique: Total Organic Carbon Analyzer - Existing Technology

100.13 Compatibility

Purpose: safety; verify that a violent reaction will not occur as a result of mixing incompatible feeds

Matrix: same

Time Frame: < 15 minutes

Potential Measurement Technique: Differential Thermal Analysis (DTA) with offgas sampling. Existing technology.

Other: DTA generally requires one to several hours.

<u>Assign Treatment (MWTP-PFD-100-1)</u>

A processing decision must be made to assign the feed to the special feed tank, main feed tank, or to the organics feed tank.

100.14 Quantitative Total Organics

Purpose: If organics are present, the solution will be routed to the wet air oxidation feed tank for organic destruction.

Matrix: Large particulates (>3mm) are removed from the aqueous stream.

Detection Limit: 10 ppm

Range: 10-10,000 ppm

Accuracy: 10 ppm

Precision: 10-20%

Time Frame: <15 minutes

Potential Measurement Technique: Total Organic Carbon Analyzer - Existing Technology

100.15 Particulates

Purpose: If gross levels of particulates are present, the feed will be routed to the Special Treatment Line.

Matrix: same

Range: Determine if particulate content is > 1% or < 1%

Time frame: minutes

Potential Measurement Techniques: Conductivity, Acoustical Sensor - Existing Technology

100.16 Heavy Metals

Purpose: Gross amounts of heavy metals that would foul the carbon adsorption beds in the Primary Treatment Line will be removed in the Special Treatment Line.

Matrix: same

Range: ppb-ppm, depending on metallic species

Time frame: minutes

Potential Measurement Techniques: LIBS, ICP/MS, XRF, IC, UV-Fluorescence, Voltammetric Measurements, FA/Flow Probe, Capillary Zone Electrophoresis

LIBS (Laser Induced Breakdown Spectroscopy)

Constituents Measured: Most of the periodic table

Detection Limits: ppm - percent

Time for Measurement: Real-time

Instrument Cost: 80-100K

Technology Status: R&D; 3-4 years for development

Other: Non-invasive measurements possible for most of the periodic table in any matrix

ICP/MS (Inductively Coupled Plasma/Mass Spectroscopy)

Constituents Measured: 80% of the periodic table

Detection Limits: ppt - ppm

Time for Measurement: Real-time

Instrument Cost: 250 - 300K

Technology Status: Commercially available, needs adaptation to application

Other: Provides isotopic information; cost is high; instrument may not be rugged enough to survive processing floor conditions

XRF (X-ray Fluorescence)

Constituents Measured: Elements higher than aluminum in the periodic table

Detection Limits: high ppm - percent

Time for Measurement: Real-time

Instrument Cost: 75-90K

Technology Status: Commercially available

Other: Provides a penetrating analysis (not just surface)

IC (Ion Chromatography)

Constituents Measured: metals, anions

Detection Limits: ppm

Time for Measurement: 10's of minutes

Instrument Cost: 50-70K

Technology Status: Commercially available

Other: Not optimal technology for metals in complex matrices

UV-Fluorescence

Constituents Measured: U, Actinides, specific metals

Detection Limits: ppm - percent

Time for Measurement: Real-time

Instrument Cost: 25-35K

Technology Status: R&D; 3-4 years to develop for this application (currently a laboratory technique)

Other: May be a low cost option

Voltammetric Measurements

Constituents Measured: U, Fe, Cu, V, heavy metals

Detection Limits: ppb

Time for Measurement: Minutes

Instrument Cost: 25-35K

Technology Status: Commercially available, needs adaptation to application

Other: May be a low cost option; technique has good selectivity for some hard-to-measure elements

FA (Flow Injection Analysis)/Flow Probe

Constituents Measured: heavy metals

Detection Limits: ppm - percent

Time for Measurement: Minutes

Instrument Cost: 5-25K

Technology Status: Some applications are developed, others would require R&D

Other: Inexpensive sensors for specific constituents may be practical for some applications

CZE (Capillary Zone Electrophoresis)

Constituents Measured: Heavy metals detection limits; ppt - ppm

Time for Measurement: Real-time

Instrument Cost: 50-70K

Technology Status: Commercially available, needs adaptation to application

Other: This multi-element technique uses small sample volumes

100.17 pH

Purpose: Feeds requiring neutralization will be routed to the Special Treatment Line.

Matrix: same

Accuracy: 1 pH unit

Precision: 10-20%

Time frame: minutes

Potential Measurement Techniques: pH Probe, Titration, Acid Sensor - Existing Technology

100.18 Other problematic compounds (cyanide, chelating agents, nitrates, etc.)

Purpose: Determine if other compounds are present that may interfere with down-line processes, or affect final waste form integrity.
Measurement parameters cannot be specified.

Potential Measurement Techniques: IC (see 100.16), ISE

ISE (Ion Specific Electrodes)

Constituents Measured: Anions, cations

Detection Limits: ppm

Time for Measurement: Minutes

Instrument Cost: 15-20K

Status of Technology: Commercially available

Other: Interferences are major problems in many cases; technique is rugged; some chemistry is required

Special Treatment (MWTP-PFD-100-2)

The special treatment unit of the aqueous line will remove gross concentrations of heavy metals, salts, radionuclides, etc., that may foul the main activated carbon beds in the primary treatment unit. The treatment may include manual addition of chemical additives for precipitation, neutralization, valence adjustment, etc., or may contain specialized ion exchange resins to remove specific contaminants.

Measurement Requirements

100.21 Contaminant Concentration (heavy metals, radionuclides, etc.)

Purpose: Determine when treatment is complete (for example, continuously monitor the effluent exiting ion exchange columns to determine effectiveness of treatment)

Matrix: Aqueous solutions with most particulate material removed, may range from dilute solutions to solutions that contain substantial dissolved solids

Detection Limit: ppm range

Range: ppm - percent

Accuracy: ppm

Precision: ppm

Time frame: Real-time or near real-time

Potential Measurement Techniques: Ion Specific Sensors or Electrodes, spectroscopy, alpha, beta, gamma detectors, etc.

- These measurements are highly dependent on the treatment technology

100.22 Oxidation State

Purpose: Some specialized treatments (such as ion exchange) may require oxidation state adjustment to feed.

Matrix: same as above

Detection Limit: ppm range

Range: ppm - percent

Accuracy: ppm range

Precision: 10-20%

Time frame: real-time or near real-time

Potential Measurement Technique: Spectroscopy

- Specialized treatment diagnostic instrumentation is highly dependent on the process; some measurement techniques may be required that measure process characteristics rather than specific constituents and some spectroscopic techniques (Near Infrared Spectroscopy) may be useful.

100.23 pH or Acid Concentration

Purpose: Determine when feed neutralization is complete

Matrix: same

Accuracy: 1 pH unit

Precision: 10-20%

Time frame: minutes

Potential Measurement Techniques: pH Probe, Titration - Existing Technology

100.24 Ionic Strength or Conductivity

Purpose: High salt content can affect treatment

Matrix: same

Detection Limit: percent range

Time frame: minutes

Potential Measurement Techniques: Conductivity Meter - Existing Technology

<u>Organic Separation and Wet Air Oxidation (MWTP-PFD-100-3)</u>

Organics are oxidized to carbon dioxide and water in the organics oxidation unit that is based on the wet air oxidation process. The oxidizing agent is high pressure plant air.

Measurement Requirements

100.31 Organic content

Purpose: verify effectiveness of treatment (determine if feed should be routed to primary treatment or final polishing)

Matrix: Aqueous solutions will still contain inorganic contaminants, but the organics should have been destroyed.

Detection Limit, Accuracy, and Precision: Regulatory levels (ppb-ppm) that will apply downstream. Must meet EPA standards for Quality Assurance.

Time frame: minutes

Potential Measurement Technique: GC/MS

GC/MS (Gas Chromatography/Mass Spectroscopy)

Constituents Measured: Volatile and Semi-volatile organics

Detection Limits: ppb - ppm

Time for Measurement: 10's of minutes

Instrument Cost: 100 - 120K

Status of Technology: Commercially available

Other: This measurement will probably be made in the facility's support laboratory rather than at the process line

Primary Treatment (MWTP-PFD-100-4)

Once all appropriate pretreatment is completed, the dissolved (and some suspended) inorganics are removed in the activated carbon beds in the Primary Treatment Unit.

Measurement Requirements

100.41 pH

Purpose: Neutralization of feed, if necessary, before introduction to the carbon beds.

Matrix: same

Accuracy: 1 pH unit

Precision: 10-20%

Time frame: minutes

Potential Measurement Techniques: pH Probe, Titration

Second Stage Polishing (MWTP-PFD-100-5)

This unit removes all remaining inorganic ions from the clean water stream. This is accomplished using ion specific technologies such as media beds or membranes.

Measurement Requirements

100.51 Condensate quality (NPDES requirements)

Purpose: Determine if condensate meets specifications for release to the environment, or recycle. These will be established under a facility-specific NPDES permit.

Matrix: evaporator condensate (clean water)

Detection Limit, Accuracy, Precision: As per NPDES requirements set forth by EPA or the State.

Potential Measurement Techniques: EPA-specified methods

- Existing Technologies

Solids Concentration/Dewatering Treatment (MWTP-PFD-100-6)

The purpose of the solids concentration/dewatering unit is to evaporate the water associated with the separated solids.

Measurement Requirements

100.61 Evaporator Bottoms Moisture Content

Purpose: Determine when dewatering is complete

Matrix: Sludge in evaporator

Detection Limit: percent

Accuracy: percent

Precision: 10-20%

Time frame: real-time, continuous

Potential Measurement Techniques: TBD

- Workshop participants did not think this measurement will be necessary

100.62 Radionuclide concentration potential

Purpose: Safety; verify that radionuclide concentration doesn't build up in the evaporator.

Matrix: Sludge in the evaporator

Time frame: real-time, continuous monitor

Potential Measurement Techniques: On-line Alpha, Gamma, Beta, Neutron Monitors

- Should meet DOE/NRC Quality Assurance standards for criticality control

- Workshop participants determined that radionuclide content in the evaporator would be controlled by measuring what goes in, so the evaporator itself will not need to be monitored.

Organic Liquids and Slurries Treatment (MWTP-PFD-200)

The function of this line is to process dilute organic liquids, concentrated organic liquids, and organic sludges to produce waste forms that can be further processed in other treatment lines.

Segregation (MWTP-PFD-200-1)

Organic waste is segregated into four categories: category 1 (concentrated organic liquids); category 2 (concentrated organic sludges and slurries), category 3 (concentrated organic liquids containing solids); and category 4 (dilute organics), according to the shipping manifest. Aqueous liquids may be present at up to 99% in category 4 wastes. The concentrated organic wastes have no discrete aqueous layer present.

Assign Treatment (MWTP-PFD-200-2)

The function of the assign treatment process is to verify drum content and route the waste to the proper downstream process.

Measurement Requirements

200.21 Pumpable or sludge?

Potential Measurement Techniques: Real-time-radiography

- Existing Technology

200.22 Mercury

Purpose: Organics contaminated with mercury will be treated separately

Matrix: Organic liquids and sludges

Detection Limit: low ppm range

Range: low ppm - low %

Accuracy: 50%

Precision: 10-20%

Time frame: minutes

Potential Measurement Techniques: PGNAA, Hg Vapor Analysis, Immunoassay, Jermone Mercury Analyzer

PGNAA (Prompt Gamma Neutron Activation Analysis)

Constituents Measured: Heavy metals, chlorides

Detection Limits: High ppm - percent

Time for Measurement: Real-time

Instrument Cost: 100 - 120K

Status of Technology: Commercially available, need to demonstrate usefulness to this application

Mercury Vapor Analysis

Constituents Measured: Mercury

Detection Limits: ppb-ppm

Time for Measurement: Real-time

Instrument Cost: 25-30K

Status of Technology: Commercially available, needs adaptation to application

Other: Very specific for elemental mercury

Immunoassay

Constituents Measured: Mercury

Detection Limits: ppb - ppm

Time Measurement: Real-time

Instrument Cost: information not available

Status of Technology: In demonstration by EPA Superfund Office

Other: Highly sensitive and specific, non-renewable (one-time use of sensor)

Jermone Mercury Analyzer

Constituents Measured: Mercury

Detection Limits: ppb - ppm

Instrument Cost: 10-15K

Status of Technology: Commercially available, some adaptation to application

Other: Non-reversible, accumulative

200.23 Dilute or concentrated organics? (How much water is present?)

Purpose: Routing decision

Range: <10% or >10%

Time frame: minutes

Potential Measurement Technique: Karl Fisher

Dilute and Concentrated Organics Separation (MWTP-PFD-200-4)

The dilute organic fraction from the continuous decanter is routed to the wet air oxidation treatment unit, and the heavy organics will be burned in the car bottom furnace.

Measurement Requirements

200.41 Organic content of dilute fraction

Purpose: Ensure the wet air oxidation unit can treat the level of organics present (same as measurement 100.14)

Wet Solids Treatment (MWTP-PFD-300)

Wet solids are size reduced, if necessary, and then dried in preparation for treatment in the Thermal Treatment Line.

Feed Preparation (MWTP-PFD-300-1)

Measurement Requirements

300.11 Does drum contain large aggregate solids (>8 inches in the largest dimension)?

Purpose: Drums that contain large aggregates are directly routed to size reduction.

Time frame: minutes

Potential Measurement Techniques: NDE, such as X-ray

Feed Tankage (MWTP-PFD-300-3)

Sludge coming from the grit screen is pumped either to special feed tank or main feed tanks, depending on the properties of the sludge. Main process feed is wet solid material that can be fed to the main feed dryer that operates at about 200 degrees centigrade without deleterious effects. The specialized feed may include nitrated wet solids, ion exchange resins, organics as cellulosic adsorbents, spent activated carbon, mercury contaminated wet solids, chlorine salts, etc. Each of these has unique properties that require a low temperature rotary vacuum type dryer. These materials can be thermally sensitive, have higher than normal radioactivity levels, or produce harmful vapors if subjected to the higher temperature in the primary dryer.

Measurement Requirements

300.31 Screening for high nitrate, mercury, lead, chloride

Purpose: Determine if sludge will be routed to the high temperature dryer or the low temperature dryer.

Detection Limit: low ppm

Range: low ppm - low %

Accuracy: 50%

Precision: 10-20%

Time frame: minutes

Potential Measurement Techniques: (see 100.16, 100.18, and 200.22)

300.32 pH or Acid Content

Purpose: Highly acidic or alkaline sludge will be neutralized.

Matrix: Sludge

Accuracy: 1 pH unit

Precision: 10-20%

Time frame: minutes

Potential Measurement Techniques: may require a combination of high acid sensors, high caustic sensors, and pH probes.

Homogeneous Dry Solids Treatment (MWTP-PFD-400)

This process consists of separating the homogeneous dry mixed waste into combustible, ferrous metal, non-ferrous metal and inert streams for further processing in the melt/slag and thermal treatment lines.

Preliminary Sorting (MWTP-PFD-400-2)

Measurement Requirements

400.21 Mercury

Purpose: Mercury contaminated dry solids will be processed separately.

Range: ppm - low %

Accuracy: <10 ppm or > 10 ppm

Time frame: Real-time continuous monitoring

Potential Measurement Techniques: (See 200.22)

400.22 Lead

Purpose: Lead contaminated dry solids will be processed separately.

Range: ppm - low%

Accuracy: <10 ppm or >10 ppm

Time frame: Real-time continuous monitoring

Potential Measurement Techniques: (See 100.16)

Magnetic Separation Treatment (MWTP-PFD-400-5)

Ferrous metals are removed from the homogeneous dry solids stream by a magnetic separator. The non-magnetic ferrous alloys and non-ferrous metals must be sorted for treatment in separate melters.

Measurement Requirements

400.51 Separation of non-magnetic ferrous alloys from non-ferrous metals

Purpose: Separation of incompatible metals for melting, as these materials will be processed to final waste forms in separate melters.

Potential Measurement Techniques: Alloy detectors

Heterogeneous Dry Solids (MWTP-PFD-500)

This process consists of separating, and size reducing if necessary, the heterogeneous dry mixed waste into combustible, ferrous metal, nonferrous metal and inert streams that are further processed separately.

The measurements are the same as those for homogeneous dry solids (see above). On the flowsheets they are numbered 500.21 through 500.51.

Radiometric Measurements for Process Control

The work group felt that measurement of radionuclides during waste treatment deserved special attention. The group's general observations on this topic are:

1. Tracking the radionuclides throughout the process is probably essential.

2. Neutron and photon (X-ray and gamma-ray) detection and pulse processing is an advanced technology. Its use on-line in DOE processing facilities has been demonstrated. These detectors should be employed often throughout the process streams.

3. Ash from thermal treatment is the best physical form for radionuclide assay. It should be batched into containers (within glovebox containment) and measured with segmented Gamma-Ray Scanner (SGS) and Passive/Active Neutron Counter (coincidence counting and active interrogation). This combined assay will provide the best data on Pu and U (and other radioisotopes) before final waste form processing.

4. A large component of the development of a system is assurance of data quality. This includes proper calibration technique, continuous measurement control, and on-line data analysis. Computer control employing real-time continuous, unattended operation has been demonstrated.

In addition, several research and development needs and priorities for tracking radionuclides were identified during the workshop. These are:

1. Room temperature, solid state detectors (photons) with resolution better than NaI, such as CdTe, HgI_2 (see EG & G, Santa Barbara work), pin diodes, photodiodes, and other silicon technologies are needed. These would be applicable to many harsh environments, especially where liquid nitrogen, refrigeration, and the presence of maintenance personnel are precluded. Operational saving are possible; however, continuing expensive development is required.

2. Radioactive tracer nuclei may be beneficial for sensitive determination of breakthrough in an ion exchange resin (for example, photon systems).

3. Development of real-time, continuous, unattended monitoring including measurement control for QA after initial calibration (neutron and photon systems) should be continued.

4. Neutron detector development (perhaps coated solid state) would be useful. Efficiency is important: polyethylene moderators with imbedded He^3 tubes are good, but expensive (approximately $800/tube and 1 tube/3 inches coverage is required).

5. Pulse-processing developments for neutron counting should continue to maximize the available information (e.g., multiplicity and, perhaps, crude imaging).

6. Development of radionuclide monitoring techniques for stack gases must continue.

Potential Offgas Monitoring Instrumentation (MWTP-PFD-1001)

GC/MS (Gas Chromatography/Mass Spectrometry)

Constituents Measured: Volatile and semi-volatile organics

Detection Limits: ppb - ppm

Time Measurement: 10's of minutes

Instrument Cost: 100 - 125K

Status of Technology: Commercially available; some adaptation for this application

Other: Complex instrumentation that may not be appropriate for stack gas monitoring

MS (Mass Spectrometry)

Constituents Measured: PICs (Products of Incomplete Combustion)

Detection Limits: ppb - ppm

Time for Measurement: Real-time

Instrument Cost: 100 - 125K

Status of Technology: R&D required for this application

Other: Limited selectivity, may not be appropriate for a stack gas monitor

FTIR (Fourier Transform Infra-Red Analysis)

Constituents Measured: Organics, nitrate

Detection Limits: ppm - percent

Time for Measurement: Real-time

Instrument Cost: 60 - 80K

Status of Technology: Commercially available

TOC (Total Organic Carbon Analyzer)

Constituents Measured: Organics

Detection Limits: ppm - percent

Time for Measurement: 10's of minutes

Instrument Cost: 40 - 60K

Status of Technology: Commercially available

Other: Rugged and process proven

CARS (Coherent Antistokes Raman Spectroscopy)

Constituents Measured: Organics and temperature

Detection Limits: percent

Time for Measurement: Real-time

Status of Technology: R&D

Other: Need more information on this technique

PGNAA (Prompt Gamma Neutron Activation Analysis)

Constituents Measured: Heavy metals, chloride

Detection Limits: High ppm - percent

Time for Measurement: Real-time

Instrumentation Cost: 100 - 125K

Status of Technology: Commercially available, needs demonstration for this application

Other: Matrix dependant

Laser Induced Fluorescence Spectroscopy (LIFS)

Constituent Measured: Heavy metals, volatile and semi-volatile organics

Detection Limits: ppb - ppm

Time for Measurement: Real-time

Status of Technology: R&D; 2 years needed to develop

Other: Good sensitivity

Specific compound sensors

Constituents Measured: Developed for specific constituents

Status of Technology: R&D; 3 years to develop

Generic Monitoring and Controls Required for Operation of Thermal Units for the Treatment of Mixed Low-level Waste

These requirements relate to the thermal treatment units shown in flow diagrams 801-808, and 1001 (see Appendix B). Most are measured in the offgas from the secondary combustion chamber (flowsheet 808) or at the stack (flowsheet 1001).

Major Species Requiring Characterization

Continuous monitoring of **oxygen** (O_2) is required by regulations to correct carbon monoxide concentrations in the unit to a standard basis of 7% oxygen by volume. Oxygen continuous monitoring is also necessary for control purposes and will be tied into the thermal treatment unit control system. Regulations allow the O_2 monitor to be located anywhere in the offgas system from the secondary combustion chamber (SCC) exit to the stack, though preferably as close as possible to the SCC exit. For combustion control purposes, the O_2 monitor should be located at the SCC exit. Monitoring conditions are as follows: O_2 range from 0 to 25% (air is 21% oxygen by volume but the expanded range covers oxygen enrichment processes); temperature range from ambient to 2200°F; depending on monitor location and offgas equipment, normal operating pressure could range from about -100 in. W.C. to atmospheric pressure (some positive pressure surges from upset conditions in the thermal treatment device are expected); offgas environment is generally oxidized with "puffs" of a reducing environment expected; offgas will contain acid gases such as HCl, HF, SO_2, SO_3, and nitrogen oxides (NO_x) at levels generally below a few hundred parts per million (ppm) but could be as high as 10% for certain wastes and certain thermal treatment devices; particulate in the form of inorganic oxides, inorganic salts, carbon (soot), and elemental species will be present at loadings that can exceed a concentration of 5 grains per dry standard cubic foot (5 gr/dscf). The current state-of-the-art for oxygen monitors is analysis of an extractive sample or the use of a probe for an *in situ* analysis. Because of the

harsh conditions in the offgas at the SCC exit, monitors at this location are subject to frequent maintenance and calibration.

Carbon monoxide (CO): continuous monitoring is required by regulations to determine the amount of CO emitted and as an indication of the combustion efficiency of hydrocarbons. Although the CO monitor is not normally tied into the thermal treatment unit control logic, it is frequently used by operators as an indicator of changes that need to be made or how well changes that have been made affect operations. As with the O_2 monitor, the CO monitor can be located anywhere in the offgas system but near the SCC exit is desirable from both a regulatory and an operational standpoint. Monitoring conditions are as follows: CO content ranges from essentially 0 CO to over 1000 ppm with normal operating range between 40 - 100 ppm. The EPA requires a dual range CO monitor with ranges from 0 - 200 ppm and 0 - 3000 ppm. All other conditions are the same as those for the O_2 monitor.

Carbon dioxide (CO_2) monitoring is required when burning polychlorinated biphenyl (PCB) liquids or waste contaminated with PCB liquids. The CO_2 monitoring is not required to be continuous but must provide a data point at least every 15 minutes. The CO_2 concentration is required to be determined so that a combustion efficiency can be calculated. As with the CO and O_2 monitor, the CO_2 monitor can be located anywhere in the offgas train. The conditions encountered in the offgas system would depend on the location of the monitor, ranging from the harsh conditions at the SCC exit to the significantly milder, but potentially wet, conditions at the stack. Normally when burning PCB waste, the CO_2 content can vary from essentially 0% to approximately 20%. If, however, the waste matrix is nearly pure carbon, such as contaminated charcoal or graphite, and the oxidant is pure oxygen rather than air, then the CO_2 content in the offgas would approach 100%.

Radionuclide monitoring at the stack is required for regulatory purposes. Current regulations do not require real-time monitoring, but the offgas must be continuously sampled. However, continuous real-time monitor would be desirable. One of the important improvements that could be made in radionuclide monitoring is the development of monitors that can detect radionuclides that are converted to gases when thermally treated (e.g., tritium or radioiodine). Current methods to detect these nuclides rely on absorption or adsorption with media that also collect other combustion products and are therefore rapidly saturated.

At a minimum, nuclide monitoring should include a beta/gamma scan down to picocurie levels. Depending on the type of waste and local/regional regulatory requirements, it may be necessary to monitor for alpha and difficult-to-control nuclides such as tritium, carbon-14, radioiodine, and noble gases. Since alpha-emitting radionuclides are usually attached to particulate matter, real-time continuous alpha monitoring would probably be performed between HEPA filters in series and serve essentially as an upset or filter breakthrough monitor. The downstream HEPA filter(s) would provide additional protection should an upstream filter fail. Conditions in the stack will be substantially milder than at the SCC exit: temperature will range from about 150 - 500°F; system pressure will be slightly below or above atmospheric; acid gases will be 100 ppm or less downstream of a

scrubber; particulate loadings will be below 0.015 gr/dscf (significantly lower than this figure downstream of HEPA filters); the offgas may be saturated with moisture depending on the type of air pollution control equipment used.

Hydrochloric acid (HCl): Continuous emissions monitoring at the stack is not usually required by regulatory agencies but is recommended for process control purposes, particularly in dry and semi- dry offgas treatment systems to control alkali reagent addition. Conditions will be the same as for radionuclide monitoring.

For SO_x and NO_x continuous monitoring at the stack may be required if Prevention of Significant Deterioration (PSD) concerns exist. Low sulfur levels in the waste will likely preclude the need for SO_x continuous emission monitoring (CEM). A NO_x CEM is likely due to the high levels of nitrogen in some waste feed streams and may also be needed due to the thermal NO_x generated by the thermal treatment device. Where waste with a high nitrogen content is being treated, a NO_x abatement technology is required and installed. Monitors should be able to monitor levels as high as 10,000 ppm in an abatement equipment failure situation. The conditions in the stack will be the same as listed above for radionuclides.

Particulate monitoring in real-time is not likely required because of the use of redundant HEPA filters. Stack particulate sampling, including that for radionuclides attached to particulate, should be conducted at isokinetic conditions. Under normal operation, strictly from a technical standpoint, isokinetic sampling downstream of HEPA filters would not be required. However, should the HEPA filters fail, allowing larger particulate to be emitted, then isokinetic sampling would be required to measure the actual particulate emission.

Heavy (toxic) metals monitoring is not currently a standard requirement, but some EPA regions have required it of certain facilities (such as when the waste stream is known to have a high quantity of heavy metals or if public pressure persuades the EPA). Ideally, heavy metals monitoring would be done on a continuous real-time (or near real-time) basis, but continuous extractive sampling, followed by analysis in a laboratory, is currently an accepted method. For a future mixed waste treatment facility, continuous real-time monitoring for mercury, because of its high volatility, may be desirable both for emissions performance and internal process control. Development of a continuous monitor for emissions of the toxic metals regulated by the EPA is considered a high priority. Monitoring for metal levels down to a mass emission rate of a few grams per hour will be necessary. Conditions at the stack will be the same as for radionuclide monitoring.

Organics monitoring is currently required by the Boiler and Industrial Furnace (BIF) Regulations for total hydrocarbons (THCs) depending on the demonstrated CO levels in the offgas. THC monitoring is usually performed in the high temperature zone of the thermal treatment unit, such as at the SCC exit. Real-time continuous monitoring for a variety of organics in the offgas such as principal organic hazardous constituents (POHCs) and products of incomplete combustion (PICs) is currently not required, but improvements and developments in CEMs for organics would be beneficial. As such monitoring instrumentation at the required detection limits becomes available, its use should be

encouraged to help future mixed waste treatment processes become more acceptable to the public.

Trial burn monitoring requires measurements of particulate and, in most cases, HCl and heavy metals emissions at the stack. A determination of the destruction and removal efficiency (DRE) of the POHCs will be required and measurement of the emissions levels of PICs may also be required. There are standard EPA methods for measurement of these species.

Temperature: The temperature of the offgas should be measured at various points throughout the offgas system starting at the thermal treatment unit. Conditions will vary from about 2200°F with high levels of primary pollutants (acid gas, NO_x, particulate, heavy metals, radionuclides) to nearly ambient conditions at the stack with the majority of the pollutants removed. Depending on the type of offgas system, the offgas at the stack could be near water saturation. The temperature of the gas at each combustion chamber exit must be measured to verify that the operating conditions stay within the operating envelope established during the trial burn in order to ensure that the required organics destruction is achieved. In general, the inlet temperature to air pollution control devices (APCDs) must be monitored if the APCD is required to meet permit conditions and if the APCD has a temperature limit for proper operation. For example, in offgas systems having a baghouse for particulate removal, the baghouse inlet temperature must be monitored to ensure that the bags are not damaged by high temperatures. In addition to monitoring temperatures for regulatory purposes, temperatures at various locations in the offgas system should also be monitored to ensure proper operation, which in turn can have a direct effect on meeting permit conditions. For example, the quencher exit temperature is a monitored variable in a wet offgas system to verify that the offgas is being adequately cooled to maintain the integrity of downstream process equipment including HEPA filters. Likewise, where offgas reheaters are required to raise the offgas above the dew point prior to HEPA filtration, temperature differential across the reheater unit is a necessary control variable to ensure the HEPA filters are not damaged by moisture.

Pressure and Differential Pressure: Absolute pressure and differential pressures must be monitored and controlled at various points throughout the offgas system. Process conditions will be the same as described for temperature measurements. Control of the thermal treatment unit's internal pressure, slightly below atmospheric, will be required for operational safety purposes. Differential pressures across specific APCDs must be controlled to stay within the operating envelope established during the trial burn and to maintain high particulate removal efficiencies. The pressure of the liquid flow to the scrubber must also be monitored. For other APCDs such as packed tower scrubbers, the differential pressure must be monitored to avoid upset conditions such as flooding. Baghouses typically require monitoring of differential pressure to monitor for bag filter failure. For HEPA filters, a measurable minimum pressure drop indicates the integrity of the filter; a maximum allowable particulate loading is indicated by high pressure drop and the subsequent need to change filters.

Gas Flowrates : Flowrate measurements for both input gas streams into the thermal treatment unit and for the offgas at selected points in the offgas train including the stack

are important. Input gas streams are essentially air but can contain contaminants, such as in chemical venting operations. The gas may be wet, contain relatively high concentrations of organics, and have a relatively high dust loading. Input gas flow pressures will be slightly negative with respect to atmospheric, and temperatures will be near ambient. The SCC exit offgas flowrate must either be monitored directly or readily determined through calculation to determine the average gas residence time in the SCC. Final stack offgas flowrate monitoring is useful for material balance purposes and required in order to calculate mass emission rates of monitored pollutant species as well as for isokinetic particulate sampling. Conditions at the stack are the same as those described above for radionuclide monitoring.

Liquid Flowrates: For wet or semi-wet offgas systems, the flowrate of circulating scrubber liquid at various points in the system is an important process control parameter. For example, the flowrate of scrubber liquid to many APCDs such as particulate and acid gas scrubbers, affects the removal efficiency of these pollutants and must be monitored to verify that flowrates are reflective of operating conditions used during the trial burn. The proper flowrate of liquid to an offgas quencher is the variable that controls the quencher exit temperature. Emergency water addition to a wet offgas system may also be controlled by scrubber liquid flowrate. For regulatory purposes, monitoring of the scrubber liquid blowdown flowrate is almost always required and is useful for overall process material balance closure. Scrubber liquid conditions are generally as follows: slightly caustic (pH of 8 - 9 optimally, but periodically higher or lower), slightly elevated temperature (80 - 180°F). The aqueous liquids normally contain dissolved solids (salts such as NaCl, NaF, and Na_2SO_4) and suspended solids (primarily flyash consisting of soot, metal oxides, and inorganics in elemental form).

pH of Scrubber Liquid: The pH of scrubber liquid is an important system control variable and also happens to be one of the most difficult process parameters to control satisfactorily. The pH must be controlled within a prescribed range, typically 8 to 9, to maintain acid gas removal efficiency, avoid precipitation of gelatinous metal hydroxides, and meet scrubber blowdown pH discharge requirements. The scrubber liquid pH is the measured variable that controls caustic addition. Conditions are the same as those described for flowrates.

Power and voltage monitoring is required for certain APCDs that rely on electrical input to create electrostatic forces for the collection of particulate. These monitors are used to ensure that the particulate removal equipment is operated under the same conditions as those used during the trial burn so that the particulate removal efficiency will be nearly the same as that obtained during the trial burn. The primary APCDs that will be required to monitor these variables are: electrostatic precipitators (ESPs), wet electrostatic precipitators (WESPs), and ionizing wet scrubbers (IWS). Obviously, these monitors will not be in contact with the offgas and will not be subjected to the extreme conditions associated with the offgas.

General Monitoring Needs for Control Purposes

Density and/or Conductivity of Scrubber Liquid: Continuous monitoring and control of density or electrical conductivity is a means of controlling dissolved solids concentration of the recirculating scrubber liquid. Blowdown of scrubber liquid is normally based on controlling either or both of these two parameters at a specified setpoint. The liquid blown down is replaced with fresh makeup water to maintain a constant inventory of liquid in the system. Conditions are the same as those described above for liquid flowrates.

Liquid Level: The level of scrubber liquid in APCD sumps and surge tanks must be controlled to avoid dry pump suction and the loss of flow of liquid to APCDs. Level control is also required to avoid overflow of process vessels.

Fissile Material Monitoring: For avoidance of criticality concerns, especially in wet offgas systems processing waste with fissile materials, a means of monitoring key process areas that could expect holdup of material should be provided. Such areas include APCD sumps and scrubber liquid recirculation tanks.

Vibration Monitoring of Rotating Equipment: Key rotating machinery in an offgas system includes induced draft blowers and liquid pumps. To maintain safe operating conditions, monitoring for vibration should be considered at a minimum for induced draft blower performance to anticipate maintenance requirements and avoid failure of equipment during operations.

Monitoring of Chemical Species in Selected Gas Streams

For various gas streams within the MWTP facility, additional monitoring may be indicated for control purposes. Following are species that would likely require monitoring for process control:

- Organics - Measurement of the organics content of input gas streams to the thermal treatment unit, though not critical, can provide information concerning heat input into the thermal treatment unit. Conditions will be similar to those described above for flowrate measurement of input gas streams.

- Acid Gas - Acid gas (primarily HCl and SO_x) content of stack gases may need to be measured if a dry or semi-dry offgas system is used. This measurement would be used for feed forward control of the addition of alkali reagent for acid gas scrubbing in such a system.

- Chlorine Gas - Chlorine (Cl_2) gas monitoring in the exhaust from chlorine gas scrubbing is needed for control purposes. Gas temperature will be slightly above ambient (120 - 160°F). The gas will be fairly clean but will be saturated with moisture.

- Mercury - Mercury monitoring in the offgas from a mercury cleanup scrubber and from the activated carbon bed absorber downstream of the mercury vacuum still is needed for control purposes and may be beneficial in demonstrating regulatory compliance. Such monitors would indicate proper operation of the scrubber and approach to breakthrough of the carbon bed.

The Minimum Characterization/Maximum Treatment Concept

Overview

The approach to mixed waste treatment embodied in the MWTP is more efficient than an exhaustive, waste stream-by-waste stream characterization and treatment effort. However, it still begins with an extensive characterization of the waste materials, followed by a rigorous screening, segregation and sorting step. Characterized, segregated waste streams then undergo treatment in a variety of treatment processes specifically designed for individual waste stream treatment applications. This approach satisfies treatment requirements, but may result in a significant cost in conducting the characterization needed, as well as in the multiple pre-treatment steps required. Some reduction in characterization needs may be gained through development and use of some of the analytical and process monitoring techniques discussed in previous sections of this chapter.

An alternative approach would be to employ a mixed waste treatment technology that is sufficiently robust to treat a very wide range of differing waste classifications and physical types. This approach combines three basic strategies in designing a waste treatment facility to attain the goal of minimizing the costs for characterization: robust primary treatment, complete gaseous products cleanup, and in-process monitoring. These three elements, when used in concert, should allow the design and operation of a mixed waste treatment facility that can be operated with a minimum need for precharacterization of current inventories of mixed waste, as well as future mixed waste volumes.

The basis of this strategy is that the primary treatment step must be sufficiently robust that a wide array of waste types can be effectively treated by the process, minimizing the need for waste segregation and multiple treatment technologies. Hazardous organic components of the waste must be fully destroyed in the primary treatment step. Treatment residuals must be sufficiently stabilized such that inorganic hazardous components will not leach from the solid matrix. Treatment residuals must be much more homogeneous than the untreated waste so that characterization of the residual solid product is simplified.

Secondly, a complete gaseous-phase cleanup system must be employed to treat gaseous discharge from the primary treatment process such that facility stack discharge will be fully compliant with regulatory discharge requirements. The gas cleanup system must take into account a wide range of contaminants that must be removed, and it must be flexible enough to operate over a wide range of operating conditions and pollutant concentrations.

Thirdly, in-process monitoring and characterization technologies can be employed to ensure proper operation of the treatment process, thus ensuring that treatment system performance is as required.

Plasma arc vitrification is an example of one developing technology that has the potential for application over a wide spectrum of wastes. Plasma arc vitrification processes have been demonstrated in the treatment of waste materials such as bulk combustible waste items (e.g., rubber gloves, clothing, paper, wood), high-metal-content wastes (steel, aluminum, copper), organic and inorganic sludges, soils and other remediation-derived wastes, construction and/or facility decontamination and decommissioning (D&D) wastes, and mixtures of these contained in a single matrix. Plasma arc vitrification technology may be able to replace the need for multiple waste-specific technologies in a waste treatment facility, potentially reducing the degree of characterization and pretreatment needed, and thereby significantly reducing facility operating costs. Plasma arc vitrification processes have demonstrated destruction of a range of organic contaminants. The technique produces a very stable, homogeneous, glassy treatment residual which inhibits leaching of elements in the matrix. This technology is also very amenable to the use of current state-of-the-art offgas control technologies for offgas cleanup. For these reasons, a plasma arc vitrification process may represent a good option as a primary treatment technology that would minimize pre-characterization requirements for many DOE wastes.

This section provides a preliminary evaluation of how a plasma arc vitrification process could be employed in a mixed waste treatment facility as a primary treatment process in the context of the alternative treatment process described above, and what in-process monitoring techniques may be useful or necessary in order to complete the strategy.[1]

Plasma Arc Vitrification Process Description

A plasma arc vitrification process converts electrical energy into intense heat within a primary waste treatment chamber. The plasma arc vitrification process uses a "plasma arc torch" to generate the plasma in the chamber. The plasma is created by initiating and maintaining a gaseous electrical current conductor, the plasma arc column, between the plasma arc torch and a molten pool of waste materials. Waste materials are fed into the primary chamber, where they are melted by the plasma torch, and are incorporated into the molten pool. The molten material is then removed from the chamber and cooled to form a very stable, glassy final product. Glass forming materials can be added to the molten slag, if needed, to optimize the properties of the slag. Some of the potential advantages of plasma treatment include:

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[1] This discussion should not be viewed as an endorsement of plasma arc vitrification for the treatment of MLLW. There are many waste streams for which it would not be suitable. But this technology can serve as a useful model when considering the characterization needs for a very robust waste treatment process and its effluents, in the same way that the (highly conceptual) MWTP serves as a model for defining the general needs of a treatment facility.

- efficient destruction of organics,
- a high-integrity, vitrified final waste form with encapsulation of heavy metals and radionuclides,
- maximum volume reduction,
- a one-step treatment process (no pre- or post-treatment required), and
- capability to process many waste types.

In the high temperature zone of the primary process chamber, essentially all organics in the waste are destroyed. A secondary combustion chamber is often used to ensure the complete destruction of organics, and thus to achieve the required destruction and removal efficiency (DRE) for hazardous organics in the waste. The remaining inert materials form a molten, vitreous slag which, when removed from the furnace, cools and solidifies into a stable final waste form. Most of the hazardous heavy metals in the waste remain in the molten slag and are sufficiently bound that the vitrified final product will consistently pass EPA Toxicity Characteristic Leaching Procedure (TCLP) tests for heavy metal leachability. Radionuclides will also be bound in the non-leaching slag.

Plasma arc vitrification systems have been developed that accept whole, unopened drums of waste material into the primary chamber for processing. This eliminates some of the concern raised in treatment scenarios that require mixing of potentially incompatible materials in pre-treatment operations. It also serves to reduce the potential for exposure of facility personnel.

A state-of-the-art offgas cleanup system is installed on the outlet of the plasma arc vitrification process to provide conditioning of the process offgas prior to release. Offgas conditioning requirements are dictated by EPA regulations governing release of hazardous components that may be part of the process offgas. Offgas conditioning will be required to remove particulate material entrained in the offgas, treat and remove acid gas components (e.g. HCl), remove volatile heavy metals from the offgas stream (e.g. lead, mercury), and possibly to reduce high concentrations of oxides of nitrogen generated in the process. A schematic representation of a complete plasma arc vitrification process, including offgas equipment, is provided in Figure 3-1.

Characterization Needs in a Plasma Arc Vitrification Facility

While the plasma arc vitrification concept provides many advantages in minimizing precharacterization requirements, there are still a number of limitations that must be considered in developing precharacterization and in-process monitoring requirements. In the end, there will remain some degree of characterization. With thoughtful use of existing techniques and technologies, combined with development of promising characterization concepts, the cost for characterization within the waste treatment facility can be minimized.

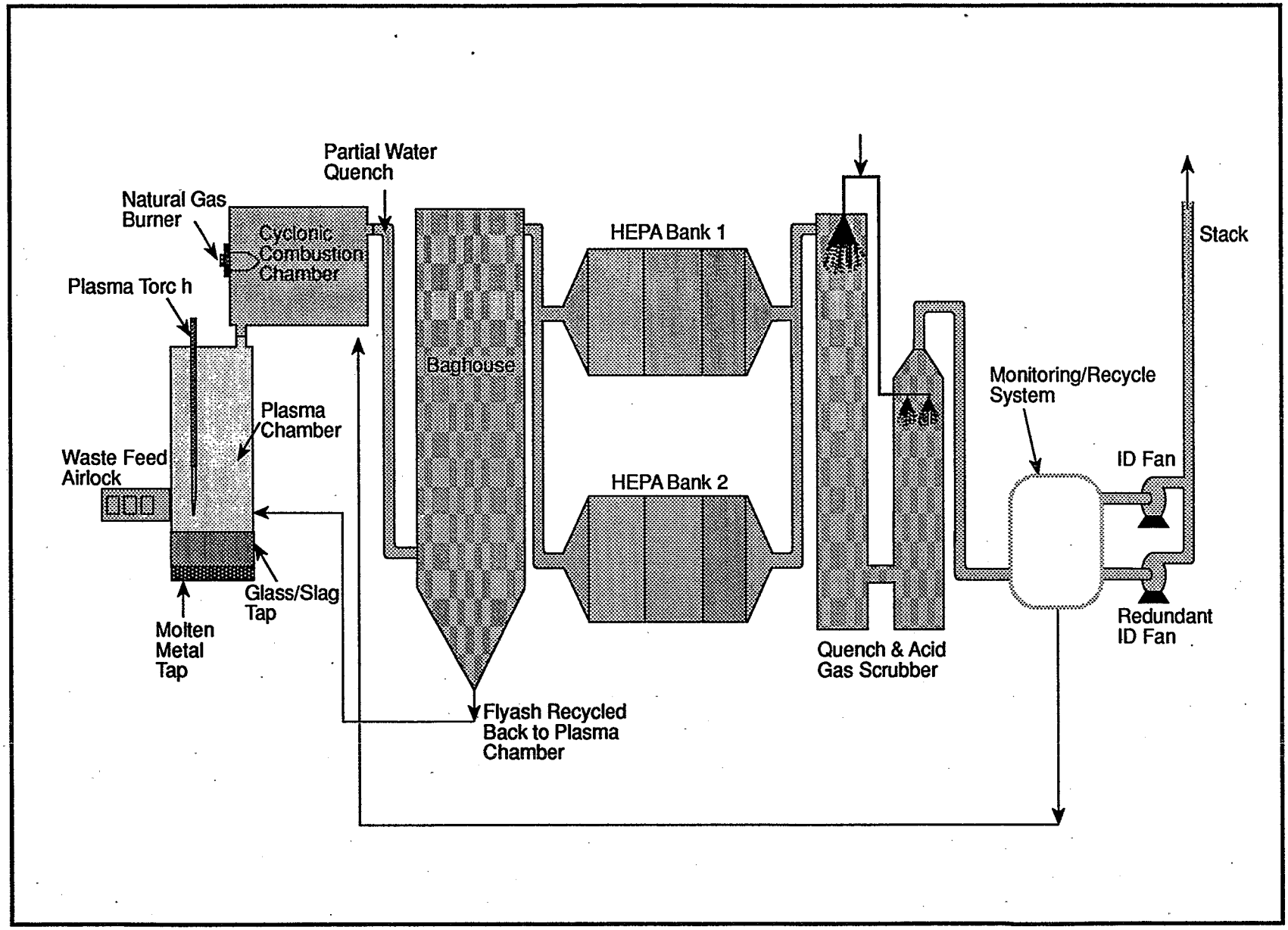

Figure 3-1. Plasma Furnace System Schematic.

Hazardous Heavy Metals

The EPA currently regulates the quantity of hazardous heavy metal constituents that can be released from a waste treatment process. The regulation is a risk-based approach that relies on a complex evaluation strategy that takes into account factors such as facility location relative to population, local geographical and climatological characteristics, and concentrations of specific heavy metals in the stack release. Compliance with the regulation requires a balance of control of the materials introduced into the treatment process and the use of offgas control technologies that remove volatile heavy metals from the offgas prior to release at the stack.

In any high-temperature process, certain heavy metal contaminants are volatilized into the offgas stream in varying percentages. This is particularly of concern for lead and mercury, two components present in a large quantity of DOE mixed waste. Thus, capture and control of these volatile heavy metals in the offgas cleanup system will be a high priority.

In this concept, the primary method that is used to address the volatile heavy metal issue is a robust offgas cleanup system that reliably removes the metals from the offgas (e.g., the suite of methods incorporated into the High-Level Defense Waste Processing Facility at Savannah River). The metal-laden particulate may then be collected and recycled to the primary chamber, where they can eventually be captured in the vitrified residual. However, there will most likely be a need to couple this primary approach with some degree of precharacterization and in-process monitoring.

It would be desirable to characterize the offgases after offgas cleanup to ensure heavy metal concentrations are below permit limitations. The current state-of-the-art to accomplish this is a complex sampling and analysis procedure adopted by the EPA, which requires significant operator involvement in collecting the sample and conducting the analysis using wet chemistry methods. This is a very labor intensive and costly process that only provides an "instant-in-time" assessment of the process performance. Some hazardous waste treatment facilities have been forced to adopt this concept, taking these samples on a daily basis.

An alternative would be to provide a real-time analysis of the offgas stream in the stack, which would give the facility operator a continuous assessment of the concentration of heavy metals in the offgas. However, current technology is not sufficiently developed for full-scale application in this area. Several technologies (as discussed in previous sections) are being developed, and if successful, would provide an optimum strategy when combined with the use of a robust offgas cleanup system.

The final, and least favorable way to address this issue is to provide for an analysis of the feed material to the process to ascertain where high concentrations of heavy metals may be encountered. This is least favorable because it would require a major allocation of resources for sampling and analysis of heterogeneous wastes. Perhaps the one area of development that could prove beneficial in this regard would be the development of a technology that could ascertain the presence of relatively large quantities of mercury and/or

lead in a drum. Thus, with minimal prescreening (e.g. a head space analysis for mercury, NDE examination for large lead objects), potential problem waste drums could be routed to areas for removal of the offending objects prior to feed to the plasma arc process, or to separate, specialized treatment lines (e.g. mercury recovery).

Hazardous Organics and Products of Incomplete Combustion

One of the primary purposes of the thermal treatment process is to provide an environment that will effect the complete destruction of hazardous organic materials in the waste by converting the organic molecules to principally carbon dioxide and water vapor. Some organic materials are relatively easy to destroy, while other compounds are much more difficult. In addition, especially for the more difficult to destroy constituents, it is possible that some organic materials may be converted through incomplete chemical reaction to form different organic compounds, some of which may be more hazardous than the original compound. These compounds are known as Products of Incomplete Combustion (PICs). Both the release of unaltered Principal Hazardous Organic Constituents (POHCs) and PICs are regulated by the EPA.

It would be helpful to know, prior to processing, which individual hazardous organics are present in a given waste container. Often the EPA requires a detailed listing of the organics in a particular waste stream. This would present a very difficult challenge to DOE, given that much of its waste has been in storage for long periods of time, and records that might identify contaminants present are incomplete. Sampling and analysis of these heterogeneous matrices will also be difficult and expensive, will lead to exposure of workers, and may not be accurate or representative in many cases.

In the minimum characterization scenario, the principal means of assuring proper destruction of organics and minimal formation of PICs is vested in the primary and secondary thermal treatment devices, or in this example, the plasma chamber and a close-coupled secondary combustion chamber. The approach relies on the fact that the plasma process has a very high efficacy of destruction of organic material, due to the intense heat and controlled reaction environment in the primary plasma chamber. The secondary destruction chamber is designed in accordance with EPA criteria, including sufficient temperature, adequate residence time in the chamber, and sufficient heat in the presence of copious quantities of oxygen (air) to ensure that any PIC or unconverted organic that did pass from the primary chamber would be destroyed in the secondary chamber. This is proven in a "trial burn" test conducted on the treatment process, where known amounts of materials are introduced to the process, and extensive sampling and analysis is conducted on the offgas to ensure proper destruction is being attained. The trial burn is conducted using the most difficult-to-destroy organic materials as feed compounds, permitting the inference that other compounds would be more readily destroyed. This is consistent with current EPA approaches to thermal treatment of organic wastes.

Having demonstrated that the primary process can treat essentially any organic in the waste, the second component is to provide some form of monitoring that will ensure destruction will be attained on a routine, continuing basis. The main way this is accomplished is by monitoring the operating parameters of the thermal treatment process

and maintaining them within the bounds of the operating parameters of the trial burn. This is commonly done on currently permitted thermal treatment devices and is augmented by some minimal form of monitoring of various constituents in the offgas. Carbon monoxide is monitored on a real-time basis as a measure of completion of the combustion reactions, and must be maintained below 100 ppm on average. Oxygen content is measured to assure a certain excess is available in the process to complete the conversion. Sometimes total hydrocarbon (THC) concentrations are measured to assure a very low concentration of both the original compound and PICs are contained in the stack gas.

Some thermal treatment facilities, mainly in Europe, have installed offgas equipment beyond the secondary chamber for the purpose of removing trace quantities of PICs and POHCs from the offgas stream, further ensuring a minimal release. One example is use of an activated carbon bed. Such a strategy should be considered under this scenario, especially since the residual material could be reintroduced to the feed to the plasma process to ultimately provide the complete destruction required.

These strategies have been allowed for operation of a permitted waste treatment facility in the past, and should continue to be allowed in the future. Thus, it should not be necessary to fully characterize organic concentration and type prior to treatment. No advanced characterization technology or process monitor should have to be developed in this case; the current state-of-the-art is sufficiently advanced to implement the strategy as outlined. It may be beneficial to develop a continuous, real-time monitor that can identify specific PIC or POHC concentrations as a means of further assurance; however, this is a lower priority development.

Feed containing containerized liquids or compressed gases

Several of the DOE waste streams are likely to include liquids inside of closed containers and/or compressed gas cylinders. These sealed vessels, when introduced into the high temperature plasma processing chamber, will heat up along with their contents, increase in pressure, and will cause small explosions within the chamber when the container is ultimately breached. This is of particular concern when the containerized fluid is flammable material. Therefore, containerized liquids and compressed gas cylinders are restricted from feed into a plasma process.

Some form of screening is needed to determine if liquid containers or gas cylinders are present within a given drum. This would be best accomplished using a non-destructive means of assay, where drums containing these materials could be routed aside for opening and removal of the restricted items in a controlled environment. The state-of-the-art is advancing in this area, with some real-time radiography techniques being able to detect this type of waste component. Further development to better automate such a process, which now relies on operator interpretation, may prove beneficial.

Feed of large quantities of lead

The DOE has used and disposed of copious quantities of lead in its operations over the years. Most often, the lead takes the form of drum liners or bricks of lead that have

become contaminated. Aside from the potential for lead emissions discussed above, it may be beneficial for the DOE to provide for the decontamination and recycle of these bulk quantities of lead for future use. In the plasma process, the majority of the lead will likely be unrecoverable as a resource if introduced into the primary chamber with the other waste materials, and will instead be incorporated into the residual for disposal. A prescreening step, using a technique such as real-time radiography, could allow for segregation of drums containing large lead items, so that those drums could be handled separately and the lead removed.

Radionuclides

Stack emissions of radionuclides are regulated by both the EPA through the Clean Air Act and the DOE through the DOE Orders. Radionuclide releases are evaluated using a procedure similar to that discussed for heavy metal emissions. A complex computer model is developed to simulate the anticipated transport of radionuclides after release. Releases are limited to a value that would result in less than a certain level of exposure to a theoretical maximally exposed individual living nearest the release site.

Some prescreening of radionuclide concentration is possible by a variety of gross and isotope-specific measurement techniques. However, since releases are often controlled on an isotope-by-isotope basis, it is often difficult to provide sufficiently accurate measurements for all radionuclides of concern. A gross radiation screening method will undoubtedly be used in the type of operation being considered here.

Radionuclides will not be destroyed at all in any treatment process. Most radionuclides will be retained within the primary chamber of the plasma process, and contained within the molten residual. However, some radionuclides will evolve from the process as gases, vapors or as small particulate entrained in the offgas stream. Thus, the primary strategy to be relied upon will be a carefully designed process for removal of radionuclides from the offgas stream prior to release.

Radionuclides evolved as vapors will be condensed into solid particulate material in the initial quenching section of the offgas treatment train. This condensed particulate, as well as particulate carried over as solid material, will be readily removed from the offgas by current state-of-the-art technologies for particulate removal. Removal efficiencies as high as 99.97% are possible using a baghouse/HEPA filter combination.

Radioactive isotopes evolved as gases in the process chamber will be more difficult to control. Fortunately, they represent a relatively small portion of the overall DOE radionuclide inventory. Two notable exceptions are carbon-14 and tritium, which are responsible for significant quantities of mixed waste. However, neither of these radionuclides is of great concern from an exposure standpoint, and very high release limits are allowed for these items. Some up-front screening will have to be done, as a minimum to identify drums that may contain significant quantities of gaseous radionuclides so that potential release problems can be identified and controlled processing initiated where necessary (e.g., blending with other waste drums to lower the release potential).

Current techniques for radioactive material measurements in the stack emission of thermal treatment processes are limited to sampling and laboratory analysis. The sampling involves a collection of particulate in a stream of the stack gas by use of a fine filter. This requires a sample drawn over a long period of time in order to provide a sufficient concentration for analytical detection. It can provide an indication of breakdown of efficiency in the offgas cleanup system, but several days may pass before routine analysis is conducted and the problem is discovered. It also provides no method to detect gaseous radionuclides, which would pass through the filter undetected.

An advance that would greatly enhance the operation of a plasma system, or any other thermal treatment device, would be the development of real-time monitoring capability for radionuclides in an offgas effluent stream. This would serve a number of useful functions. First and foremost, regulatory authorities would have the ability to ensure that stack releases were indeed within the bounds permitted. Facility operators would have a real-time indication of a potential problem in the offgas treatment equipment, and would be able to make immediate adjustments in the process to correct the problem. In addition, if gaseous radionuclides were discovered, drums from the rest of that particular batch could be more carefully screened to ensure annual release rates would not be exceeded.

Summary

The use of a plasma arc vitrification system, or other robust treatment technology, when combined with a comprehensive offgas cleanup system and a degree of in-process monitoring, should result in an approach that will allow DOE to conduct only minimum, and in most cases non-intrusive, characterization of waste inventories. This approach would be fostered by the development of a number of novel concepts for in-process monitoring, as well as some screening level pre-characterization techniques. Overall, this approach has the potential to significantly reduce the cost for waste characterization currently facing the DOE, as well as improve the safety of operations by minimizing exposure of workers to hazardous materials during sampling operations.

The approach is not without costs, however. It replaces the need for extensive waste characterization with a requirement for very rigorous offgas treatment and monitoring. A facility accepting a wide range of wastes would need a very elaborate system for offgas handling. Establishing the adequacy (and cost-effectiveness) of the system for monitoring and controlling a variety of potential problem species would require a great deal of work. DOE Idaho's current trial burn program, which is setting the standard for such work, has achieved promising results in offgas monitoring and cleanup.

Conclusions and Recommendations

The general consensus of the workshop group felt that the following research needs were of the highest priority:

1. Public acceptance of any thermal treatment technology for mixed waste demands the development of continuous emission monitors for metals and radionuclides in gaseous effluents. These monitors must be capable of operating in a hostile environment and should be simple to operate, reliable, and not cost-prohibitive. This is probably the most promising area for technology development relating to process monitoring or control.

2. Cost-effective sample extraction techniques for containerized heterogeneous waste need to be developed. In addition cost-effective, simple measurement calibration techniques are required.

3. Mercury is an extremely troublesome species with regard to thermal treatment. Detection technology for mercury in solid matrices is a real need.

4. The heterogeneous nature of much of the waste and the potential presence of multiple troublesome species requires the development of screening methods for heterogeneous matrices and specific detectors for specific constituents.

5. Improvement in radiation detection is also required, particularly for real-time gas-phase monitoring of process effluents. Two particularly promising areas are neutron detector development and room temperature solid state detectors with resolution superior to NaI-based detectors.

In the course of the discussions that produced the detailed information on process monitoring technologies, several overarching issues concerning the strategy for mixed waste treatment were identified:

1. A thorough evaluation by a multi-disciplinary team is required on the relative benefits of up-front characterization versus versatile process design versus in-process monitoring/control. The optimum solution to mixed waste treatment will most likely be some combination of all three strategies.

2. There may be an inappropriate tendency to "high tech" the approach to process monitoring/control of the treatment of mixed waste. For instance, real-time analysis technologies may not really be required when an on-site dedicated laboratory can provide quick turn-around. In addition, standard process control measurements can often be used to indirectly assess more difficult-to-measure properties.

3. It is almost impossible when bulking/staging dissimilar waste materials to ensure compatibility (i.e. the prevention of chemical reactions which may at best adversely affect treatment or at worst create potentially hazardous situations). Batching by waste stream or drum by drum processing may be more cost-effective approaches.

4. There is a need for the establishment of national performance standards for many of the cited measurement techniques.

Chapter 4

Final Waste Form Characterization

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Introduction

The principal force determining characterization requirements for final waste forms is regulation. The waste forms created by the MWTP facility will be regulated under the EPA's Land Disposal Restrictions and must be disposed in compliance with applicable state and federal requirements. In general, treatment requirements include elimination of organic hazardous constituents and stabilization of inorganic hazardous constituents. In addition, the long-term stability and safety of the waste forms must be assessed. Final waste forms must meet both EPA leach testing and DOE disposal acceptance criteria. In addition to the EPA and DOE criteria, final waste form characterization may be required by the Nuclear Regulatory Commission (NRC), Department of Transportation (DOT), disposal site waste acceptance criteria (WAC), accepting states, and for process control and health and safety.

Under RCRA, the EPA requires that owners/operators of treatment, storage, or disposal (TSD) facilities obtain a chemical and physical analysis of a representative sample[2] of the waste. The purpose of this analysis is to assure that owner/operators have sufficient information on the properties of the waste to ensure proper management.

In addition, the requirements and frequency of analysis for a given facility will be spelled out in the facility's waste analysis plan. The waste analysis plan specifies the parameters for which each hazardous waste will be analyzed, the rationale for selecting these parameters (i.e., how analysis for these parameters will provide sufficient information on the waste's properties), and the test methods that will be used to test for these parameters. The waste analysis plan also will specify the sampling method that will be used to obtain a representative sample of the waste to be analyzed; the frequency with which the initial analysis of the waste will be reviewed or repeated to ensure that the analysis is accurate and up to date; and, for off-site facilities, the waste analyses to be supplied by the hazardous waste generators. In this case, the generator is the MWTP facility, and the "hazardous waste" is the final waste form created in the facility. The appropriate

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2 A representative sample means a sample of a universe or whole (e.g., waste pile, lagoon, groundwater, final waste form) which can be expected to exhibit the average properties of the universe or whole (40 CFR § 260.10).

parameters for each waste analysis plan are determined on an individual basis as part of the permit application review process.

NRC regulations do not describe specific testing requirements for wastes to determine if a waste is radioactive. However, both NRC and Department of Transportation regulations contain requirements applicable to characterizing the radioactive content of the waste before shipment. For example, NRC's regulations in 10 CFR 20.311 (20.2006 of the Revised Part 20) require that the manifest include, as completely as practicable, the radionuclide identity and quantity, and the total radioactivity. NRC regulations also require that generators determine the disposal class of the radioactive waste and outline waste form requirements that must be met before the waste is suitable for land disposal. These regulations are referenced in 10 CFR 20.311 (20.2006 of the Revised Part 20) and are outlined in detail at 10 CFR Part 61.55 and 61.56. Mixed waste generators such as the MWTP must satisfy both RCRA and NRC waste testing and waste form requirements.

All of the RCRA strategies allowing hazardous waste to be land-disposed will be employed at the MWTP facility. Where LDR requirements must be met, it is planned that (a) specific treatment technologies (BDATs) will be used for some of the wastes, (b) final waste forms will not exceed the maximum concentration level designated for some regulated constituents, and (c) other waste forms will be created so as not to exceed the concentration limit established by a leach test procedure. In some cases, RCRA delisting of final waste forms will allow their on-site disposal. Key to satisfying disposal requirements is the implementation of appropriate treatment for individual hazardous wastes. The objective of treatment standards is either (a) the removal/destruction of the hazardous characteristic or constituent or (b) the stabilization/immobilization of toxic materials in a durable matrix. The assumption is that waste residue thus treated can be placed safely in a land disposal facility. Therefore, final waste forms must be produced that meet the requirements for control of inorganic and organic constituents and radionuclides. Process control requirements for each final waste form should be assessed and defined in a formal process control program.

Because of concern about the inherent safety and health hazards of sampling and analyzing mixed waste materials, and in particular, the potential risk to workers from exposure to radiation and hazardous chemicals posed by duplicative testing of mixed wastes, redundant testing should be avoided. In addition, waste analysis plans should include provisions to keep radiation exposures as low as reasonably achievable (ALARA) and incorporate relevant Atomic Energy Agency requirements and regulations. Further, testing should be conducted in laboratories licensed by NRC or the appropriate NRC Agreement State authority. In this case, it is assumed that the testing will be performed in a dedicated laboratory at the MWTP facility.

The final waste forms and recyclable materials expected to be products of the MWTP facility are listed below, along with the sample points at which they are characterized:

- cement grouts (cement and organic-cement conglomerate); sample point 1002.10
- crystalline ceramic; sp 803.10

- glass; sp 901.10
- polymers (sulfur polymer and polyethylene macroencapsulation); sp 902.2
- lead; sp 902.10
- mercury; sp 905.10
- ferrous alloys; sp 804.10.

The workgroup identified the general suite of final waste form properties or parameters that should be evaluated, and recommended their applicability to each of the final waste form types. Priority was given to glass and ceramic waste forms, and recyclable metals. The applicable tests were assessed as to when these tests were needed and the frequency at which they should be applied. Three levels of frequency were specified: one-time, at process start-up; once per batch of waste forms; and every waste form. Assigning testing frequency was difficult in some cases, because of uncertainty as to what would constitute a batch, i.e., whether it would have uniform feed or not. The process flow diagrams that correspond to the discussion of this chapter are 901, 902, 903, 904 and 905 (see Appendix B).

The chief sources drawn on for waste form testing were:

- RCRA requirements - 40 CFR 260 *et seq.*
- NRC requirements - 10 CFR 61 *et seq.* It should be noted that these requirements are not currently binding on DOE wastes.
- DOT regulations
- general process control practices for creation of waste forms
- customary health and safety guidelines for handling LLW, as set forth in DOE Orders and Guidelines
- The Waste Acceptance Criteria for the Waste Isolation Pilot Plant (WIPP) and the Nevada Test Site (NTS) waste repository.

Parameters and Tests

The workgroup identified 21 parameters/properties to be assessed for characterizing final waste forms. These are listed in Table 4-1, along with the regulation or purpose driving the measurement. Several additional properties require testing in materials to be recycled. Each final waste form does not require determination of the full suite of parameters/properties. Tables 4-2 through 4-10 list the properties to be measured, the recommended measurement frequency, some data quality objectives, and recommended test methods for each of the waste forms or materials for recycle. As many of the testing requirements are established by regulation, the tables often simply cite the pertinent regulation for test method or data quality objective. The properties and test methods are described below. Summaries of some of the most important analytical instruments used in final waste form characterization are given in Appendix E.

Table 4-1. Parameters Tested in Final Waste Forms.

Property/Parameter	Purpose or Regulatory Requirement
Leach Resistance	NRC regulations
Free Liquids	RCRA
Radionuclides	NRC, DOT, Risk/Performance Assessment
Transferable Contamination	DOT, DOE Rad Con
Specific Alpha Activity	TRU-LLW Distinction, gas gen.
Dose Rate	H&S, DOT
Weight/Size	process control
Labeling Requirements	DOT, DOE Orders
Hardness Test	process control
Drum Weight	WAC, DOT
Major Matrix Elements	process control, WAC
Toxicity Characteristic	RCRA (define hazardous waste)
Ignitability	RCRA (define hazardous waste)
Corrosivity	RCRA (define hazardous waste)
Reactivity	RCRA (define hazardous waste)
Waste Acceptance Criteria	site specific requirements
Land Disposal Restriction Tests	RCRA
Void Volume	minimize post-burial settling (WAC)
Gas Generation	risk to container integrity
Compressive Strength	process control, leachability
Set Time	process control

Table 4-2. Characterization of Glass Waste Forms

Property	Sampling Frequency	Requirements	Methods	Detection Limits
Leach Resistance	Every batch		PCT, ANS 16.1	95% conf. that better than blank
Free Liquids	Every Container	<0.5% by Vol. (RCRA)	Inspection EPA 9095	no visible moisture
Radionuclides	Every Container	For discussion assume 10 CFR 61	SGS for drum HPGe for pellet neutron method for α	10 CFR 61
Transferable Contamination	Every Container	220 dpm/dm^2 α 2200 dpm/dm^2 β, γ	α Chamber $\beta.\gamma$ counter	3σ/BG<limit
Specific α Activity	Every batch	≤100 nCi/g	neutron method for α	3σ/BG<limit
Dose Rate	Every Container	200 mrem/hr @ surface	Count rate meters	3σ/BG<limit
Weight/Size	Every batch		Balance optical comparator	± 0.2% wt.
Other Labeling Requirement	Every Container	Site specific DOT		
Hardness Test	Every batch			
Weight of Drum	Every Container	<1200 lb (on-site) 800 lb (DOT)	"truck" scale	± 10 lbs
Major Matrix Elements	Every Batch	elem present @ > 1 wt %	XRF; ICPMS; ICP; NAA	10 rel % at 1 abs wt % if possible
Toxicity	Every Batch	limits in RCRA 40 CFR 261	TCLP-Method 1311	SW-846
Ignitability	NR			
Corrosivity	NR			
Reactivity	NR			
LDR	Every Batch	banned by waste	TCLP - SW-846	
Void Volume	Every Container	< 10%	calculation	as specified in 40 CFR 265
Gas Generation	NR			
Compressive Strength	NR			
Set Time	NR			

Table 4-3. Characterization of Ceramic Waste Forms

Property	Sampling Frequency	Requirements	Methods	Detection Limits
Leach Resistance	Every batch		needed	
Free Liquids	Every Drum	<0.5% by Vol. (RCRA)	Inspection EPA 9095	no visible moisture
Radionuclides	Every Drum	For discussion assume 10 CFR 61	SGS for drum HPGe for pellet neutron method for α	10 CFR 61
Transferable Contamination	Every Drum	220 dpm/dm^2 α 2200 dpm/dm^2 β, γ	α Chamber $\beta.\gamma$ counter	3σ/BG<limit
Specific α Activity	Every Rep	≤100 nCi/g	neutron method for α	3σ/BG<limit
Dose Rate	Every Drum	200 mrem/hr @ surface	Count rate meters	3σ/BG<limit
Weight/Size	Every Batch		Balance, optical comparator	±0.2% of wt of pellet
Other Labeling Requirement	Every Drum	Site specific DOT		
Hardness Test	Every Batch		Rockwell hardness tester	Manufacturer's specification
Weight of Drum	Every Drum	<1200 lb (on-site) 800 lb (DOT)	"truck" scale	± 10 lbs
Major Matrix Elements	Every Batch	elem present @ >1 wt %	XRF; ICPMS; ICP; NAA	10 rel % at 1 abs wt % if possible
Toxicity	Every Batch	limits in RCRA 40 CFR 261	TCLP-Method 1311	SW-846
Ignitability	NR			
Corrosivity	NR			
Reactivity	NR			
LDR	Every Batch	banned by waste	TCLP SW-846	
Void Volume	Every drum	< 10%	calculation	40 CFR 265
Gas Generation	NR			
Compressive Strength	NR			
Set Time	NR			

Table 4-4. Characterization of Cement (organic) Waste Forms

Property	Sampling Frequency	Requirements	Methods	Detection Limits
Leach Resistance	Every Batch		ANSI 16.1	
Free Liquids	Every Drum	<0.5% by Vol.	Inspection EPA 9095	no visible moisture
Radionuclides	Every Batch	For discussion assume 10 CFR 61	Dissolve rep sample and HPGe	10 CFR 61
Transferable Contamination	Every Drum	220 dpm/dm^2 α 2200 dpm/dm^2 β, γ	α chamber ß, γ counter	3σ/BG<limit
Specific α Activity	Every Batch	≤ 100 nCi/g	neutron method	3σ/BG<limit
Dose Rate	Every Drum	200 mrem/hr @ surface	count rate meter	3σ/BG<limit
Weight/Size	NR			
Other Labeling Requirement	Every Drum	Site specific DOT		
Hardness Test	NR			
Weight of Drum	Every Drum	<1200 lb (on-site) 800 lb (DOT)		± 10 lbs
Major Matrix Elements	Every Batch	elem present @ > 1 wt %	XRF; ICPMS; ICP; NAA org - IR, Raman	10 rel % at 1 abs wt % if possible
Toxicity	Every Batch	limits in RCRA 40 CFR 261	TCLP-Method 1311	SW-846
Ignitability	NR			
Corrosivity	NR			
Reactivity	NR			
LDR	Every Batch	banned by waste	TCLP SW-846	
Void Volume	Every Drum	< 10%	calculation	40 CFR 265
Gas Generation	Every Batch		calculation	
Compressive Strength	Every Batch		ASTM C-39, D-1633	
Set Time	Every Batch		ASTM C-403	

Table 4-5. Characterization of Cement (inorganic) Waste Forms

Property	Sampling Frequency	Requirements	Methods	Detection Limits
Leach Resistance	Every Batch		ANSI 16.1	
Free Liquids	Every Drum	<0.5% by Vol.	EPA 9095	no visible moisture
Radionuclides	Every Batch	For discussion assume 10 CFR 61	Disolve rep. sample and HPGe	10 CFR 61
Transferable Contamination	Every Drum	220 dpm/dm^2 α 2200 dpm/dm^2 β, γ	α Chamber β. γ counter	3σ/BG<limit
Specific α Activity	Every Batch	≤ 100 nCi/g	neutron method	3σ/BG<limit
Dose Rate	Every Drum	200 mrem/hr @ surface	count rate meter	3σ/BG<limit
Weight/Size	NR			
Other Labeling Requirement	Every Drum	Site specific DOT		
Hardness Test	NR			
Weight of Drum	Every Drum	<1200 lb (on-site) 800 lb (DOT)	"truck" scale	± 10 lbs
Major Matrix Elements	Every Batch	elem present @ > 1 wt %	XRF; ICPMS; ICP; NAA	10 rel % at 1 abs wt % if possible
Toxicity	Every Batch	limits in RCRA 40 CFR 261	TCLP-Method 1311	SW-846
Ignitability	NR			
Corrosivity	Every Batch		9040; 9041; 1110	
Reactivity	If needed every batch		SW-846	
LDR	Every Batch	banned by waste	SW-846	
Void Volume	Every Drum			
Gas Generation	Every Batch		calculation	
Compressive strength	Every Batch		ASTM C-39, D-1633	
Set Time	Every Batch		ASTM C-403	

Table 4-6. Characterization of Inorganic/Sulfur Polymer Waste Forms

Property	Sampling Frequency	Requirements	Methods	Detection Limits
Leach Resistance	NR			
Free Liquids	Every Container	<0.5% by Vol.	Inspection after cooling	No visible moisture
Radionuclides	Every Container	For discussion assume 10 CFR 61	TBD	
Transferable Contamination	Every Container	220 dpm/dm^2 α 2200 dpm/dm^2 β, γ		3σ/BG <limit
Specific α Activity	Every Rep	≤ 100 nCi/g	TBD	
Dose Rate	Every Container	200 mrem/hr @ surface	count rate meter	3σ/BG <limit
Weight/Size	NR			
Other Labeling Requirement	Every Container			
Hardness Test	NR			
Weight of Drum	Every Container	<1200 lb (on-site) 800 lb (DOT)		± 10 lbs
Major Matrix Elements	Every Batch	elem present @ > 1 wt %	same as before	
Toxicity	Every Batch	limits in RCRA 40 CFR 261	TCLP - Method 1311	SW-846
Ignitability	NR			
Corrosivity	Every batch		EPA 9040, 9041; NACE 1110	
Reactivity	Every batch		For sulfide-Ch7, SW-846	
LDR	Every Batch	banned by waste		
Void Volume	Every Container		calculation	
Gas Generation	Every batch		calculation	
Compressive Strength	Every batch		TBD	
Set Time	Every batch		TBD	

Table 4-7. Characterization of Organic Polymer Waste Forms

Property	Sampling Frequency	Requirements	Methods	Detection Limits
Leach Resistance	NR			
Free Liquids	Every Container	<0.5% by Vol.	Inspection	No visible moisture
Radionuclides	Every Container	For discussion assume 10 CFR 61	Tomographic scan	
Transferable Contamination	Every Container	220 dpm/dm^2 α 2200 dpm/dm^2 β, γ	α Chamber $\beta.\gamma$ counter	3σ/BG <limit
Specific α Activity	Every Rep	≤ 100 nCi/g	Process knowledge	
Dose Rate	Every Container	200 mrem/hr @ surface	count rate meters	3σ/BG <limit
Weight/Size	NR			
Other Labeling Requirement	Every Container	Site specific DOT		
Hardness Test	NR			
Weight of Drum	Every Container	<1200 lb (on-site) 800 lb (DOT)	"truck" scale	± 10 lbs
Major Matrix Elements	Every Batch	elem present @ > 1 wt %	same as before	
TCLP	Every Batch	limits in RCRA 40 CFR 261	TCLP-Method 1311	SW-846
Ignitability	NR			
Corrosivity	NR			
Reactivity	NR			
LDR	Every Batch	banned by waste		
Void Volume	Every Container		calculation	
Gas Generation	Every batch		calculation	
Compressive Strength	Every batch		TBD	
Set Time	Every batch		TBD	

Table 4-8. Characterization of Ferrous Metal Waste Forms

Property	Sampling Frequency	Requirements	Methods	Detection Limits
Purity	Per item		Alloy analyzer	
Radionuclides	Every Batch	For discussion assume 10 CFR 61	TGS/SGS	10 CFR 61
Dose Rate	Every item	200 mrem/hr @ surface	dosimeters; count rate meters	3σ/background < limit
Specific α activity	Per item		Passive & active neutron counts	
Labeling	Per item	DOT, NFPA, WAC	MSDS	
Transferable Contamination	Every Batch	220/2200 dpm/dm^2	Smear, PAN	3σ/BG < limit

Table 4-9. Characterization of Elemental Lead Waste Forms

Property	Sampling Frequency	Requirements	Methods	Detection Limits
Purity	Per item	98%	Spectro-photometric	
Radionuclides	Every Batch	For discussion assume 10 CFR 61	HPGe on sample	
Dose Rate	Every item	200 mrem/hr @ surface	dosimeters; count rate meters	3σ/BG < limit
Specific α activity	Per item		Sampled long range	
Labeling	Every item	DOT, NFPA	MSDS	
Transferable Contamination	Every Batch	220/2200 dpm/dm^2	Smear, PAN	3σ/BG < limit

Table 4-10. Characterization of Elemental Mercury Waste Forms

Property	Sampling Frequency	Requirements	Methods	Detection Limits
Purity	Per item	100%	Process knowledge	
Radionuclides	Every Batch	For discussion assume 10 CFR 61	HPGe on sample	
Dose Rate	Every item	200 mrem/hr @ surface	dosimeters; count rate meters	$3\sigma/BG < limit$
Specific α activity	Per item		as before	
Labeling	Per item		49 CFR 172.101	
Transferable Contamination	Every Batch	220/2200 dpm/dm^2	Smear container	$3\sigma/BG < limit$

Leach Resistance

Several tests have been applied to evaluate the chemical durability of final waste forms. These tests are designed to determine the rates of release of various chemical species from a crushed final waste form sample to a test solution. Commonly applied tests include product consistency tests (PCTs), the Toxicity Characteristic Leaching Procedure (TCLP), and the ANSI/ANS 16.1 leachability test (1). The TCLP is described in a separate section below.

The PCT Methods These methods were developed within DOE's High-Level Waste Program. Test Methods A and B have been used to evaluate the chemical durability of homogeneous and devitrified glasses (2,3,4). The evaluation is performed by measuring the concentrations of the chemical species released from a crushed glass to a test solution and comparing them to the results for a "benchmark" glass.

Test Method A was developed specifically to test the durability of radioactive waste glasses during production. It can also be used to test simulated waste glasses. The method is easily reproducible, can be performed remotely on highly radioactive samples and can yield results rapidly. The glass does not need to be annealed prior to testing. In this method the glass is crushed and sieved to -100 to +200 mesh. The particles are cleaned of adhering fines, and an amount of sized and cleaned glass that is greater than or equal to 1 gram is placed in a 304L stainless steel vessel. An amount of ASTM Type 1 water equal to 10 times the sample mass is added and the vessel is sealed. The vessel is placed in a convection oven at 90°C. After 7 days the vessel is removed from the oven and cooled to room temperature. The pH is measured on an aliquot of the leachate and the temperature of the aliquot at the time of the pH measurement is recorded as well. The remaining leachate is filtered and sent for analysis.

Test Method B was developed to test the durability of radioactive, mixed, or simulated waste glasses. The method is similar to Test Method A except for the following differences: (a) In this method the glass is crushed and sieved to -100 to +200 mesh <u>or</u> to the size range of interest as long as the glass particles are <40 mesh. (b) The particles are cleaned of adhering fines (note: devitrified glasses containing soluble secondary phases require special handling procedures), and an amount of sized and cleaned glass greater than or equal to 1 gram is placed in either a 304L stainless steel vessel or a Teflon\ vessel. Sample mass-to-volume of solution (S/V) ratios other than 1:10 are allowed and other leachants than ASTM Type 1 water are allowed. (d) The vessel is placed in a convection oven, generally at 90°C but other test temperatures are allowed. After 7 days, or other optional test durations, the vessel is removed from the oven and cooled to room temperature. The pH is measured on an aliquot of the leachate and the temperature of the aliquot at the time of the pH measurement is recorded as well. The remaining leachate is filtered and sent for analysis.

The ANS 16.1 Test This is a sequential-batch test in which small coupons of cemented waste are extracted in distilled water. This test was developed for grouted waste forms containing radionuclides. From the concentrations that leach into the successive leaching solutions, an effective diffusivity and logarithmic leachability index are calculated for each nuclide of interest. If leaching can be assumed to be diffusion-controlled, these parameters have value in predicting cumulative leaching over time, and relative leachability of various waste/grout formulations.

Free Liquids

EPA Method 9095, "Paint Filter Liquids Test," is used to determine the presence of free liquids in a representative sample of waste and is specified as the method to be used to determine compliance with 40 CFR 264.314 and 265.314. In the test a predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within the 5-minute test period, the material is deemed to contain free liquids.

Radionuclide Content

A specific inventory for all radionuclides is a difficult measurement because of all the possible nuclides that must be measured independently. For the common isotopes of plutonium and uranium, the neutron measurements discussed in the section for specific alpha activity (below) are the most effective. Neutron multiplicity counting can also identify americium and curium in some samples, but not with high sensitivity.

The standard method for identifying elemental constituents in a sample is gamma-ray analysis. Passive gamma ray analysis will identify radioactive nuclides that decay by spontaneous gamma ray emission. Gamma ray spectroscopy is a standard nuclear chemistry technique. Passive gamma ray instruments for laboratory use are available from several commercial sources as standard laboratory instrumentation.

Another approach to passive gamma-ray spectroscopy is the segmented gamma scanner (SGS). The SGS instrument makes chordal measurements of the sample drum to determine qualitatively the nuclear material distribution. It also has the ability to do a transmission correction using a gamma ray source of known strength. Two measurements are made, one with the source to determine the chordal attenuation and one to make the isotopic determination. The passive measurement is corrected using the attenuation results.

Recently, the SGS system has been extended to a full tomographic system, modeled somewhat after the medical imaging technology. In this case, the spatial distribution of both attenuating medium and gamma-ray emission is determined by inverting chordal measurements at many different angles and heights of the sample drum. A complete matrix of linear attenuation is constructed from the data which is used to correct the passive

gamma ray measurement. Both the SGS and the tomographic scanner are designed to measure the more prominent gamma ray lines of spontaneously decaying radionuclides.

For those nuclides that decay by processes other than spontaneous gamma ray emission, or for fissile material which does not have a high decay rate, active gamma ray assay is necessary. The active techniques typically use a neutron source to induce the n-gamma or the n-prime-gamma reactions. (The n-gamma reaction is a thermal neutron capture process; the n-prime-gamma reaction is a neutron inelastic scattering process.) These instruments use either a neutron source such as californium or a neutron generator. Typical neutron generators electrostatically collide deuterium and tritium ions to excite the D-T fusion reaction. Several manufacturers produce commercially available neutron sources. Laboratory and industrial instruments for elemental identification are also commercially available.

Transferable Contamination

The NRC has established limits of removable external radioactive contamination, i.e., transferable contamination as part of the requirements described in 10 CFR 71 on Packaging and Transportation of Radioactive Material. The level of non-fixed (removable) radioactive contamination on the external surfaces of each package offered for shipment must be as low as reasonably achievable. The level of non-fixed radioactive contamination may be determined by wiping an area of 300 square centimeters of the surface concerned with an absorbent material, using moderate pressure, and measuring the activity on the wiping material. Sufficient measurements must be taken in the most appropriate locations to yield a representative assessment of the non-fixed contamination levels. Except as provided under the next paragraph of this section, the amount of radioactivity measured on any single wiping material when averaged over the surface wiped, must not exceed the limits given below at any time during transport. Other methods of assessment of equal or greater efficiency may be used. When other methods are used, the detection efficiency of the method used must be taken into account and in no case may the non-fixed contamination on the external surfaces of the package exceed ten times the limits listed in Table 4-11 below.

In the case of packages transported as exclusive-use shipments by rail or highway only, the non-fixed radioactive contamination at any time during transport must not exceed ten times the levels prescribed in the first paragraph of this section. The levels at the beginning of transport must not exceed the levels prescribed in the first paragraph of this section.

Table 4-11. Removable External Radioactive Contamination Wipe Limits.

Nuclides	Maximum Permissible Limits	
	$\mu Ci/cm^2$	dpm/cm^2
Beta-gamma emitting radionuclides; with half-lives less than ten days.	10^{-5}	22
All other alpha emitting radionuclides.	10^{-6}	2.2

Specific Alpha Activity

Measurement methods for specific alpha activity are discussed in detail in Appendix C. The following paragraphs summarize that discussion.

Specific alpha activity is the rate of alpha particle emission per weight, measured in curies per gram. The present limit for distinguishing low-level waste (LLW) from transuranic waste (TRU) is 100 nanocuries per gram. Specific alpha activity is important for two reasons. First, it directly affects the generation of gas by radiolysis. Gas generation can affect the physical integrity of the container. Also, alpha activity is typically associated with a certain class of radionuclides which have a severe environmental impact. The most notable are the isotopes of plutonium. Leaching of these isotopes out of the waste form container could cause a significant environmental impact.

Because of the short mean free path of alpha particles, alpha activity is usually measured indirectly. The most common approach is to exploit the alpha-neutron reaction: an alpha interacts with a moderate atomic number (Z) material which then gives off a neutron. Inferring the alpha activity from the neutron emission is a common and effective technique. In the case of LLW waste assay, it is particularly reliable because the presumption is that small quantities of waste are involved, so that the plutonium (or other alpha emitting material) is naturally oxidized.

Passive Totals Counting Passive neutron totals counting is used to determine specific alpha activity from the induced neutron emission. Typical instruments are the passive counting aspect of the californium shuffler, and the passive add-a-source counter. The passive-active neutron differential die-away counter can also make this passive neutron measurement. This technique is typically used as a "screening" measurement; it determines the upper bound of the alpha activity rate rather than a precise measurement.

Passive Coincidence Counting A more accurate but somewhat less sensitive method is passive coincidence counting. Passive coincidence counting counts the number of

simultaneous neutron pairs. Neutron pairs are a specific signature of a nuclear fission, so this measurement determines the amount of fissionable material. Because the fissionable isotopes are also typically those that decay by alpha emission, the alpha activity can also be inferred. Passive coincidence counting systems for 55 gallon drums can operate down to the 10 nanocuries per gram level in well-shielded environments (the sensitivity depends on the background count rates).

The passive coincidence measurement can be extended to neutron multiplicity counting. Multiplicity counting counts simultaneous neutron events consisting of multiple neutrons, extending the coincidence concept of counting neutron pair events. This technique can reduce many of the uncertainties from matrix effects, additional isotopes such as curium, and detector efficiencies.

Another extension of the passive coincidence measurement is the add-a-source technique. The add-a-source technique provides a correction to a passive multiplicity or coincidence counting for matrix-induced errors. The passive measurement is significantly less sensitive to matrix effects than active measurements, but the induced bias error can be reduced further. The add-a-source method introduces a known source with a neutron spectrum similar to fission neutrons, and measures the effect of the waste drum matrix on the source neutrons.

Active Interrogation The third principle measurement of specific alpha activity is done by active neutron interrogation. The active measurement interrogates the sample with a neutron source. Typically, a neutron generator is used in the case of the passive active neutron, differential die-away (PAN/DDA) system and a californium source is used in the PAN/californium shuffler. In both cases fissions are induced in the sample material and the resulting fission neutrons are measured. The PAN/DDA system measures prompt fission neutrons and the shuffler measures delayed neutrons. The isotopes that are specific to this measurement are the odd isotopes of plutonium (^{239}Pu, ^{241}Pu predominantly) and ^{235}U.

An important variant of the PAN/DDA system is the combined thermal-epithermal neutron system (CTEN). The CTEN system now under development addresses one of the important limitations of the PAN/DDA system, namely that the interrogation is done with thermal neutrons. The penetration of thermal neutrons is very small, roughly a few hundred microns in metallic plutonium. If significant quantities of plutonium are present in a sample, it is possible that the active PAN/DDA system will significantly underestimate the quantity. The CTEN directly addresses this problem.

Because the active assay instruments can also make a passive measurement, occasionally the active interrogation is combined with a passive multiplicity or coincidence measurement. The most common instruments are the passive multiplicity counter with add-a-source matrix correction, the californium shuffler, and the differential die-away system.

Method Selection The choice of which system to use for final waste form certification depends somewhat on the anticipated application. If the waste drum must be characterized for low-level waste disposal only, then the passive multiplicity with add-a-source is the most robust measurement. If a highly sensitive measurement is required, such as for Department of Transportation regulations, then the PAN/DDA system has the required sensitivity. If uranium is anticipated in the waste form, then the PAN shuffler measurement is perhaps the most appropriate. Other active and passive neutron-based instruments are also under development which may alleviate some of the problems discussed here.

Dose Rate

The Department of Transportation (DOT) has established radiation level limitations, i.e., dose rate, for radioactive materials offered for transportation. Each package shall be designed and prepared for shipment so that under conditions normally incident to transportation the radiation level does not exceed 200 millirem per hour at any point on the external surface of the package, and the transport index does not exceed 10. If a package exceeds the radiation level limits specified in the first paragraph, it shall be transported by exclusive-use shipment only, and the radiation levels for such shipment must not exceed the following during transportation:

(1) 200 millirem per hour (2 millisievert per hour) on the external surface of the package unless the following conditions are met, in which case the limit is 1000 millirem per hour (10 millisievert per hour). The shipment is made in a closed transport vehicle; the package is secured within the vehicle so that its position remains fixed during transportation; and there are no loading or unloading operations between the beginning and end of the transportation.

(2) 200 millirem per hour (2 millisievert per hour) at any point on the outer surfaces of the vehicle, including the top and underside of the vehicle; or in the case of a flat-bed style vehicle, at any point on the vertical planes projected from the outer edges of the vehicle, on the upper surface of the load (enclosure is used), and on the lower external surface of the vehicle.

(3) 10 millirem per hour (0.1 millisievert per hour) at any point 2 meters (6.6 feet) from the outer lateral surfaces of the vehicle (excluding the top and underside of the vehicle); or in the case of a flat-bed style vehicle, at any point 2 meters (6.6 feet) from the vertical planes projected by the outer edges of the vehicle (excluding the top and underside of the vehicle.

(4) 2 millirem per hour (0.02 millisievert per hour) in any normally occupied space, except that this provision does not apply to private carriers if exposed personnel under their control wear radiation dosimetry devices and operate under provisions of a State or Federally regulated radiation protection program.

Various commercially-available dosimeters and scanners can be used to measure the dose rate. These include thermoluminescent dosimeters (TLDs), thermoluminescent neutron dosimeters and critical neutron dosimeters.

Weight/Size

The weight and size measurements are expected to be part of the process control scheme for those processes that produce pellets as the final waste forms, e.g., crystalline ceramic waste forms. Current thinking is to weigh and measure the size of the pellets occasionally during operation to determine density, as a quality control measure. The pellets will be weighed with an electronic balance and measured with calipers.

Labeling Requirements

General labeling and marking criteria include the following:

- Shall meet the labeling/marking requirements of DOT.
- Labels and markings shall be permanently applied with paint or other materials that have a predicted 20-year life expectancy in the expected storage environment and are compatible with the container and protective coating. Epoxy-polyamide paint or Electromark plastic stickers are examples of 20-year labeling and marking.
- All labels and markings shall be in clear, legible English in a color contrasting with the background. Stencils (for paint-applied markings) or adhesive labels shall be used for all markings.
- All labels and markings shall be nonfading and nonsmearing.
- Drums being banded to pallets shall be positioned to permit visual inspection of the labels and markings.

Hardness Test

Hardness testing is expected to be part of the process control scheme for those processes that produced pellets as a final waste form, e.g., crystalline ceramic waste forms. Currently, hardness testing is not being conducted.

Weight of Drum

For waste forms from the MWTP that are transported off that site for disposal, the DOT requires that individual drums not exceed 800 lbs. For on-site disposal, higher weights may be permitted (at the Nevada Test Site the limit is 1200 lbs). In either case, the measurement can be made using a truck scale.

Major Matrix Elements

Major matrix element components and chemical composition contained in the final waste form can be determined by a number of instrumental techniques, including atomic absorption spectrophotometry, inductively coupled plasma-atomic emission spectroscopy, and X-ray fluorescence spectrometry. Depending on the approach preferred by the facility or on the requirements in the WAC for these measurements, all of the aforementioned techniques can perform the necessary measurements, either individually or in some complementary combination. For example, XRF may be chosen for frequent measurements, backed up by periodic ICP/AES measurements. For those techniques requiring dissolution of the final waste form material prior to assay, solubilization techniques and methods are readily available.

Toxicity Characteristic

Each batch of waste forms produced by the treatment facility that was not created in a BDAT process will have to be tested for the Toxicity Characteristic. The TC will be shown if the TCLP extract from a subsample of the waste contains any of the contaminants listed in 40 CFR §261.24 at a concentration greater than or equal to the respective value given.

The Toxicity Characteristic Leaching Procedure is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A subsample of a waste is extracted with a buffered acetic acid solution for 18 ± 2 hours. The extract obtained from the TCLP (the "TCLP extract") is then analyzed to determine if any of the thresholds established for the 40 Toxicity Characteristic constituents have been exceeded. If the TCLP extract contains any one of the TC constituents in an amount equal to or exceeding the concentrations specified in 40 CFR §261.24, the waste possesses the characteristic of toxicity and is a hazardous waste. Both the leaching and extract analysis methods are specified by RCRA.

Ignitability

The objective of the ignitability characteristic is to identify wastes that either present fire hazards under routine storage, disposal, and transportation or are capable of severely exacerbating a fire once started. The following definitions that apply to solid final waste forms have been taken nearly verbatim from the RCRA regulations (40 CFR §261.21) and the DOT regulations (49 CFR §§ 173.300 and 173.151). They specify the required tests.

A solid waste exhibits the characteristic of ignitability if a representative sample of the waste has any of the following properties:

(1) It is a liquid, other than an aqueous solution, containing <24% alcohol by volume, and it has a flashpoint <60°C (140°F), as determined by a Pensky-Martens Closed Cup Tester, using the test method specified in ASTM Standard D-93-79 or D-93-80, or a Setaflash Closed Cup Tester, using the test method specified in ASTM standard D-3278-78, or as determined by an equivalent test method approved by the Administrator under the procedures set forth in Sections 260.20 and 260.21. (ASTM standards are available from ASTM, 1916 Race Street, Philadelphia, PA 19103.)

(2) It is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture, or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard.

(3) It is an oxidizer, as defined in 49 CRF §173.151.

For the purpose of the regulation, an oxidizer is any material that yields oxygen readily to stimulate the combustion of organic matter (e.g., chlorate, permanganate, inorganic peroxide, or a nitrate).

Corrosivity

The corrosivity characteristic, as defined in 40 CFR §261.22, is designed to identify wastes that might pose a hazard to human health or the environment due to their ability to:

(1) Mobilize toxic metals if discharged into a landfill environment.

(2) Corrode handling, storage, transportation, and management equipment.

(3) Destroy human or animal tissue in the event of inadvertent contact.

To identify such potentially hazardous materials, EPA has selected two properties upon which to base the definition of a corrosive waste. These properties are pH and corrosivity toward Type SAE 2020 steel.

The procedures for measuring pH of aqueous wastes are detailed in EPA Method 9040, Chapter Six. EPA Method 1110 describes how to determine whether a waste is corrosive to steel. Use EPA Method 9095, "Paint Liquids Test," to determine free liquid.

According to the RCRA regulations, a solid waste exhibits the characteristic of corrosivity if a representative sample of the waste has either of the following properties:

1. It is aqueous and has a pH ≤2 or ≥12.5, as determined by a pH meter using either the test method specified in this manual (Method 9040) or an

equivalent test method approved by the Administrator under the procedures set forth in Sections 260.20 and 260.21.

2. It is a liquid and corrodes steel (SAE 1020) at a rate >6.35 mm (0.250 in.) per year at a test temperature of 55°C (130°F), as determined by the test method specified the National Association of Corrosion Engineers (NACE), Standard TM-01-69, as standardized by EPA Method 1110 or an equivalent test method approved by the Administrator under the procedures set forth in Sections 260.20 and 260.21.

Reactivity

The regulation in 40 CFR §261.23 defines reactive wastes to include wastes that have any of the following properties.

(1) Readily undergo violent chemical change.

(2) React violently or form potentially explosive mixtures with water.

(3) Generate toxic fumes when mixed with water or, in the case of cyanide- or sulfur-bearing wastes, when exposed to mild acidic or basic conditions.

(4) Explode when subjected to a strong initiating force.

(5) Explode at normal temperatures and pressures.

(6) Fit within the Department of Transportation's forbidden explosives, Class A explosives, or Class B explosives classifications.

This definition is intended to identify wastes that, because of their extreme instability and tendency to react violently or explode, pose a problem at all stages of the waste management process. The definition is to a large extent a paraphrase of the narrative definition employed by the National Fire Protection Association.

A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:

(1) It is normally unstable and readily undergoes violent change without detonating.

(2) It reacts violently with water.

(3) It forms potentially explosive mixtures with water.

(4) When mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

(5) It is a cyanide- or sulfide-bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

(6) It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

(7) It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

(8) It is a forbidden explosive, as defined in 49 CFR §173.51, or a Class A explosive, as defined in 49 CFR §173.53, or a Class B explosive, as defined in 49 CFR §173.88.

Land Disposal Restrictions (LDR)

Most or all of the waste streams that enter the treatment facility will be subject to the RCRA Land Disposal Restrictions. Each waste stream may contain one or many RCRA-listed wastes. For many of these waste streams, the Land Disposal Restrictions will be satisfied by treatment that uses the Best Demonstrated Available Technology (BDAT). But for others, testing will be necessary to verify that the final waste forms can be disposed on land. The required test will be one of two types, as specified in 40 CFR 268: either an assay of total concentrations of the constituents of concern in the waste form, or measurement of these constituents in an extract of the waste form created using the TCLP.

As an example, consider a waste stream comprised of a hundred drums of contaminated soil, that was created in the course of site remediation. Attached to this waste stream is the waste code F039, defined as "leachate (liquids that have percolated through land disposed wastes) resulting from the disposal of more than one restricted waste classified as hazardous..." There is no BDAT defined for F039 wastes. In the facility, this waste stream is treated by drying it and stabilizing the dried soils into inorganic grout waste forms. To assure that these waste forms meet LDR limits, representative samples of each batch must be collected (perhaps in the form of small grouted coupons cast specifically for testing). They must be ground and extracted via the TCLP. The extract must be analyzed for a suite of ten metals using methods listed in SW-846 (5). If the extract does not exceed the limits listed in 40 CFR 268.41 for any of the ten metals, the waste forms satisfy this part of the RCRA requirements (RCRA characteristic testing, as for corrosivity, may also be required).

Because of the RCRA "mixing rule," it may be necessary to test every batch of waste forms for the constituents of concern from <u>every</u> listed waste that had previously passed

through the treatment facility, for which treatment was not by a BDAT. After many waste streams were processed, this could require very extensive testing of final waste forms to satisfy the Land Disposal Restrictions. Alternatively, the operator could demonstrate to the regulator that the treatment technologies used are equal in effectiveness to the BDATs (where those exist); this would obviate the need for RCRA testing of waste forms derived from that waste stream. Such a demonstration program would be worthwhile for larger waste streams, but for the many waste streams that are comprised of only a few containers, the need for RCRA testing of the final waste forms can be anticipated.

Void Volume

Void volume, internal void spaces in LLW packages intended for disposal, shall be minimized to the maximum extent practical; 10 percent is suggested as a maximum. This requirement is likely to be among the WACs at the disposal site. It is intended to prevent subsidence of the burial ground final cover after package deterioration.

The internal void space of any LLW package disposed at the TSD facilities shall not exceed 10% of the total internal volume of the waste package. This requirement is based on a similar requirement for hazardous waste disposal in 40 CFR §265.315. For the purposes of this requirement, the internal void space shall include any opening within the waste matrix that exceeds 5 cm (2 in.) in diameter. Spaces smaller than 5 cm (2 in.) such as small horizontal planar spaces (e.g., the space between a waste package and its overpack) need not be included in the void calculation. Spaces larger than 5 cm (2 in.) must be eliminated either by vacuum compression, compaction of the waste, or by filling with an approved void space filler.

Gas Generation

Packages of MLLW with the potential for gas generation or to reach explosive concentrations of hydrogen and oxygen or other explosive gases (e.g., methane, volatile organic compounds) may require vents or catalyst packs to deplete free oxygen and prevent explosive concentrations. Packages with potential of H_2 generation should be analyzed by standard calculation methods such as developed by C. P. Delkate of EPRI, or if required, the use of catalysts or vents will be applicable. Liners other than plastic bags shall be provided with positive gas communication to the outer container.

Compressive Strength

The 28-day compressive strength is a property often measured for quality control in creating grout waste forms. It is also widely used to assess the long-term physical integrity of the waste forms, although interpretation of the data in this context is not without ambiguity. The tests that are used are unconfined, triaxial tests such as those specified in ASTM standards C-39 and D-1633.

Set Time

Set time is a process control variable evaluated in the creation of grout waste forms. It should be tested at the beginning of each batch, using a penetration resistance procedure such as ASTM standard C-403.

Waste Acceptance Criteria

Any disposal site that accepts final waste forms from the MWTP facility for disposal will require that they satisfy a particular set of waste acceptance criteria. These WACs, specific to the disposal site, will include various measures of radioactivity, material integrity, chemical composition, labelling and physical properties. In all likelihood, they will include many of the tests discussed in this chapter, or similar tests.

Many waste forms will be disposed on NPL sites. In these cases, CERCLA requirements will be among the waste acceptance criteria. The site-specific Applicable or Relevant and Appropriate Requirements (ARARs) may be much more stringent than corresponding RCRA requirements.

Envirocare, Utah is now a permitted disposal site for MLLW from the DOE complex. That site's operating plan may be consulted for an example set of waste acceptance criteria.

Additional Properties

The MWTP facility will produce lead, mercury and ferrous metals as well as waste forms. Since these materials will be returned to use rather than disposed, they will be subject to a different testing regimen than the waste forms. It is not now known whether the distribution of these materials will be restricted in any way. If not, they will have to be tested to assure the standards of the General Services Administration (GSA) are met. If recycle is confined to the site itself, a more limited set of tests, shown in Tables 4-8 through 4-10, will suffice. Material purity and labelling requirements will differ from those already discussed.

Material Purity The needed purity will depend on the intended use of the material. It is assumed that all will be relatively pure upon exit of the plant. An alloy analyzer or XRF can be used to evaluate the ferrous metals; the lead can be assessed by spectrophotometry, and the mercury by process knowledge.

Labelling/DOT The materials for recycle are to be accompanied by Material Safety Data Sheets. They are to be handled according to DOT regulations and have NFPA labels.

Radionuclides In lead, these will have to be measured by creating special samples.

Conclusions and Recommendations

The insufficiency of analytical testing methods was judged by the workshop participants to be not nearly so pronounced for final waste forms as upstream in the process. There are several reasons for this. In general, the matrix tested is much more uniform, so representative sampling is not so difficult. The need for real-time or near-real-time testing is not so great as within the waste treatment trains. The testing environment is not harsh, compared to the environments monitored during processing. And finally, many of the tests are done by older, established methods or methods that are required by regulation. Several method development needs were identified at the workshop, but the principal problems and outstanding questions identified relate to interpretation of test results and regulatory impediments.

Further effort must be devoted to clarifying sampling issues for final waste forms. Questions to be addressed include:

- should destructive sampling use cores or separate coupons cast specifically for testing?

- What constitutes representative sampling in the different waste forms and materials for recycle? For the more uniform materials this will not be a difficult issue to resolve, but what is a representative sample of a polymer-encapsulated waste form?

- how uniform are individual batches of waste forms? This will profoundly influence the sampling/analysis design.

The work group noted several research needs specific to testing of the organic polymer waste forms. Methods development is needed here for assaying radionuclides, for monitoring specific alpha activity and for quantifying gas generation.

Within the work group, there was serious disagreement as to whether neutron and gamma methods can achieve the desired detection limit of 3 σ over background in quantifying radionuclides. One recent study (6) suggested that they cannot. More work, with actual waste forms, is needed.

There is insufficient guidance and consensus at present concerning waste form leach resistance. What are the appropriate attributes for a test of leach resistance, and how can test results be interpreted - and extrapolated - correctly? The work group identified a paucity of trustworthy tests for leaching behavior in LLW repositories. Performance assessment methods and the use of TCLP results in particular were noted as potentially inappropriate.

It was pointed out that a sulfur polymer waste form will probably itself qualify as reactive under RCRA. Without careful pilot testing, the treatment facility may itself create new hazardous waste. There are a number of outstanding questions concerning measuring the properties of this waste form, as well.

A major concern is the effect the RCRA "Mixing Rule" could have on characterizing final waste forms. The rule could be - and recently has been - interpreted by regulators to require testing for the full suite of RCRA characteristics in every waste form and recyclable material, once a listed waste has passed through the plant. Treatment that occurs by BDATs can be judged irrelevant. If such a requirement were imposed on an integrated MLLW treatment facility, waste form testing would call for an enormous resource allocation. The balance between maximum treatment and minimum characterization would be broken.

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Chapter 5

Conclusions and Recommendations

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Identified Research, Development, and Demonstration Needs

At the workshop, each of the three workgroups identified needed research, development, and demonstration efforts for characterization methods. The importance of technology development was viewed differently by the three groups. In the area of preliminary waste characterization, the conclusion reached was that efficient characterization for the parameters of concern will depend on improved technology. Technology advances are also needed for process monitoring and control, but basic facility design and public perception issues will be equally important in establishing the characterization protocol. Improvement of measurement methods is of less importance for final waste forms. The outstanding questions relating to waste forms are the degree of testing that will be required by regulators and what constitutes valid surrogate tests of long-term waste form properties.

Measurement-specific research, development and demonstration needs are listed below. Larger unresolved characterization issues are discussed in later sections of this chapter.

Pretreatment Waste Characterization

The baseline treatment scheme embodied in the MWTP will require a great deal of characterization, especially at the upstream end of the facility. The difficulty of representative characterization of heterogeneous waste is acute. This leads to two general recommendations for RD&D. First, development of methods for bulk measurement of waste properties should be emphasized over those for measurement of small samples. Second, where heterogeneous waste streams (that cannot be classified as debris) must be treated, very robust treatment technologies that can accommodate a variety of waste matrices (such as plasma furnace treatment units) should be considered. While treatment process selection is technically outside of waste characterization, the balance between treatment technique and characterization protocol cannot be avoided when considering either.

The general consensus of the work group felt that the following research needs were of the highest priority for pretreatment characterization:

1. Determine the reliability of process knowledge as an indicator of waste properties. A standardized guidance for preparation of shipping manifests and describing and verifying process knowledge should be developed.

2. Development of non-intrusive technologies to differentiate between organic/aqueous or liquid/liquid phases in the near real time is a very high priority. Some technologies such as neutron radiography are in the research stage and may have this capability.

3. Non-intrusive methods to pinpoint radiation hot spots within containers in a timely fashion require development for this application.

4. No known method for non-intrusively measuring the organic content of containerized wastes appears to be commercially available. The non-intrusive technique prompt gamma-neutron activation analysis (PGNAA) is being developed to help determine organic content through the measurement of elemental composition, but it is still in the research stage. Another promising method, still in development, is pulsed fast neutron analysis (PFNA). Consequently, minimally-intrusive technologies should be developed. These technologies would most likely utilize the fiber optic cable and sensor systems that are being developed for vadose-zone and groundwater measurements. The instrumentation would have to be hardened to overcome the harsh environment within the containers.

5. There are similar limitations in the available methods for measuring special materials in closed containers. At the workshop, only PGNAA was identified to make these measurements non-intrusively, and it is not certain how many of the contaminants of concern can be detected by this method. Here too, intrusive methods that test the headspace or contained liquids deserve development.

6. Many existing methods were identified as potentially useful for measurement of incoming wastes. However, very few of these can be considered "off-the-shelf" technologies. Almost all will require adaptation and demonstration for this application. In many cases, pilot- and full-scale evaluation using test bed facilities will be needed. The resource requirements for this adaptation will not be trivial.

Process Monitoring and Control

Increased public awareness of safety, health, and environmental concerns has generated a regulatory environment that places greater demands on the operation of chemical process facilities. The DOE complex waste clean-up efforts will require facilities that are operating chemical processes, which makes them a target for even more stringent regulations because of the nature of the waste materials requiring processing. Considering the present and future regulatory climate, the processes must be optimized to minimize generation of secondary waste streams, limit worker exposure to hazardous and radioactive

materials, and be capable of producing a final waste form for disposal that is both chemically inert and resistant to physical degradation. One method for achieving process optimization is to develop operating methods with process control based on near-real-time chemical analyses. Achieving better control requires increased knowledge of the chemical and radiological parameters that affect the process operations.

Characterization of waste during processing and treatment is needed to (1) identify chemical and physical components that interfere with the formation of a stable final waste form, (2) optimize/control reagent addition, (3) minimize secondary waste streams, and (4) provide process control based on real-time or near-real-time measurements. Instrumentation and sensors must be rugged enough to operate in a processing environment and must provide accurate quantitative determinations of contaminants at levels of interest in a usable time frame for process control purposes.

The general consensus of the work group felt that the following research needs were of the highest priority:

1. There is a lack of real-time instrumentation to monitor the releases of heavy metals, radionuclides, and various hydrocarbon species from offgas systems. Development of this instrumentation is vital for public acceptance of treatment facilities.

2. Cost-effective, simple measurement calibration techniques are needed to insure the reliability of in-line measurements. As instrumentation is placed into the process environment, innovative calibration techniques must be developed.

3. Detection technology for mercury in solid matrices needs improvement.

4. The heterogeneous nature of much of the waste and the potential presence of multiple troublesome species requires the development of screening methods for heterogeneous matrices and specific detectors for specific constituents. Examples are heavy metals and concentrated salts.

5. Improvement in radiation detection is also required, particularly for tracking alpha activity through the process. Two particularly promising areas are neutron detector development and room temperature solid state detectors with resolution superior to NaI-based detectors.

6. In the systems analysis area, there is a need to develop hardware and software systems that are capable of interfacing several treatment operations and continuously monitoring all aspects of a given treatment operation (air contaminants, temperature, pressure, feed rate, influent and effluent properties, etc.).

7. Because the MLLW treatment facilities across the DOE complex will be very complicated, DOE should consider developing a baseline simulation technique

(neural network, electrical analog, etc.) for modelling the facilities. This would be adapted to be site-specific. Its principal utility would be in facility design, testing, and troubleshooting a malfunction in the operating facility.

Thermal treatment is likely to be the cornerstone of MLLW treatment across the DOE complex. Many of the most difficult treatment issues, technical and otherwise, concern the offgases from thermal units. Those developing Site Treatment Plans would be greatly aided by a concise compendium of methods for the monitoring of process gases. Such a report should handle gases influent to the treatment unit, upstream of the offgas cleanup units, and at the stack. A document that includes a narrative description of each method (as in Appendix C herein) and summarize its capabilities and status (as in Table 2-1) should be developed. An expanded report could include case histories, descriptions of protocols for testing the methods, and discussion of the trade-off between up-front waste characterization and segregation, and extensive, costly off-gas controls and monitoring.

Final Waste Forms

Research and development projects should target the following:

1. Methods for reliably quantifying radionuclides in final waste forms need demonstration. In particular, the sensitivity, precision and accuracy of neutron and gamma methods for this application need to be established.

2. Appropriate methods for sampling final waste forms should be standardized. The protocols should specify where samples should be collected when destructive sampling is required. Sampling schemes that guarantee representativeness must be established.

3. Further background work is needed to develop these representative sampling protocols. The thermal treatment engineers need to establish the variation in the characteristics of waste forms derived from each treatment technology. These "population parameters" may have to be established in preliminary or pilot tests.

4. Methods for sampling organic polymer waste forms and measuring their properties should be standardized. Especially needed are methods to quantify gas generation, specific alpha activity and the radionuclide content of these waste forms.

Waste Treatment and Institutional Issues

Effective waste characterization for treatment cannot be assured simply by intensifying methods development. Many of the impediments to developing a characterization plan are institutional or regulatory in nature, or relate to the design and operation of the facility itself. These "larger issues," that were of considerable concern to workshop participants, are discussed briefly in this section.

Facility Design and Operation

Facility design cannot precede characterization plan development. Those who are experts in the various measurement methods are essential members of the design team. Process design engineers cannot assume there will be off-the-shelf measurement techniques available to equip a facility treating mixed wastes. The lack of adequate measurement methods may constrain process design; conversely, without explicit data quality objectives, measurement experts cannot select appropriate characterization techniques.

A vivid example of this treatment/characterization balance is the need to quantify organics in incoming waste containers. At the workshop, it was assumed that the plant operators must know whether any container's contents are more than one percent organic. In many cases this can be determined semi-intrusively using some type of headspace analysis. But for heterogeneous materials like lab packs, full sampling would be required. Based on the types of incoming waste streams, a choice must be made: should there be a set of processing and treatment operations that will require this high level of preliminary waste characterization, or should the facility incorporate more robust unit operations, avoiding the need to quantify organics in every container? If these unit operations are not BDATs, demonstrating them to the satisfaction of the regulatory agency may be a lengthy process, cancelling out the health benefits and savings realized by not measuring organics.

A similar balance exists between characterization and facility operation. Workshop participants warned that ensuring compatibility of wastes processed together is crucial, but the needed methods have not been assembled. DOE could develop a suite of methods to meet this need, and perform the tests at the head of each treatment train. Alternatively, careful consideration of waste container batching, staging and processing may avoid the need for such rigorous compatibility testing.

The characterization will employ a host of *in-situ* sensors to provide near-real-time data on the treatment process. It is recommended that waste characterization and process monitoring within the treatment facility incorporate a state-of-the-art expert system to assure optimal operation levels and to assist in the analysis of the sub-systems during down time. This would involve the development of an off-line model which would evolve into an on-line application that infers in real time. The analysis and modeling would involve the documentation of the problem-solving logic, symptoms, interactions, and patterns of plant operating behavior. Based on tendencies, pattern matching and measured data, the expert system would assure optimal operations and could forcast an operating deviation as much as hours in advance. Continuous use of the expert system would allow the operators to enhance their understanding of the treatment process.

An in-plant analytical laboratory will be needed at each facility. This laboratory will perform all the physical and chemical tests required for the final waste forms. It will be used to calibrate on-line instrumentation. Waste samples may also be analyzed there, depending on the final characterization strategy.

Regulatory and Institutional Issues

Workshop participants repeatedly expressed a need for explicit guidance from DOE on the use of process knowledge to characterize wastes. The effort devoted to up-front waste testing could be decreased greatly if many containers could be reliably characterized by process knowledge. The benefits would be especially pronounced for heterogeneous wastes.

Workshop participants also stressed the need to develop consensus on tests to evaluate the long-term properties of final waste forms. Tests of leaching and material integrity, in particular, need work. TCLP leachability is a property that will certainly be required in facility WACs, but it only has validity in the environment of a sanitary landfill. Long-term performance assessments of glass or ceramic waste forms are subject to considerable controversy among materials scientists. This issue has technical, regulatory, and public perception aspects. Reaching agreement on these tests is vital for the approval of site-specific waste treatment plans.

A similar type of issue is the need for national performance standards for many of the measurement methods. The well-established methods have agreed-upon performance standards. Examples are the codification of many chemical techniques in ASTM standards or EPA's SW-846 (1). But many nuclear methods discussed herein have no such standards; measurement results are subject to varying interpretation. This variation will impede public acceptance of facilities relying on these methods.

The issue of public acceptance arose throughout the workshop, but particularly in discussions of the thermal treatment units. Public concern over these processes must be accomodated by methods development for sensing/controlling system upsets and for monitoring offgases.

The RCRA Debris Rule may have a dramatic effect on the characterization and treatment requirements for many mixed waste streams. If the specified BDAT is used to treat the contaminated debris, the initial characterization requirements are significantly reduced. Also, the requirement to verify that the final waste form meets the LDRs is waived. To date, all work that has been conducted toward evaluation of debris technologies (extraction, destruction, and immobilization) has focused on hazardous waste. DOE's Mixed Waste Integrated Program is pursuing projects to demonstrate, test, and evaluate debris treatment technologies for mixed waste debris. As mixed waste streams are reclassified as debris, the flowsheets for treatment could change significantly. To be eligible for the LDR verification waiver for debris, treatment facilities will need a separate treatment line for mixed waste debris.

A final regulatory issue raises the concern that extensive characterization may be required, no matter how carefully the treatment facility is designed and operated. A regulatory agency could interpret the RCRA mixing rule to require exhaustive

characterization of every solid waste form, regardless of whether treatment was by a BDAT. There are no direct technical answers to this concern. However, reaching consensus on test protocols, developing national performance standards, and involving regulators in developing the waste characterization protocol may help diminish the likelihood of this outcome.

Continuing Work

This report describes a baseline characterize-to-treat strategy for mixed low-level waste. Further technical work will be of two kinds:

- technology research, development or demonstration to enhance characterization capabilities, and
- development of individual Site Treatment Plans.

The technology RD&D efforts will be led by DOE headquarters offices. At each site, the waste characterization strategy (really, the treatment-characterization strategy) will be tailored to that site, and will be based on a risk-benefit analysis. It is recommended that the strategy be developed by process design engineers and characterization technology experts working together, along with field sampling experts, if necessary. Insofar as possible, explicit data quality objectives should form the basis for technology selection. For some measurements, a suite of complementary technologies will be needed; this will be site-specific and will depend on the incoming waste streams. In general, the more varied the waste streams, the greater the range in needed measurement options. The process planners will need to allow for 10 - 20% added characterization costs for quality assurance and quality control measurements.

In addition, public stakeholders should be involved at each stage, to lower non-technical hurdles. Successful treatment of DOE's MLLW stockpile is a goal shared by all interested parties.

Reference

1. U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste. SW-846. 3rd edition and revisions. Office of Solid Waste and Emergency Response, Washington, D.C.

APPENDIX A

Appendix A

The Five Waste Streams

John Koutsandreas

The five general waste streams correspond to the five treatment trains of the Mixed Waste Treatment Project. The descriptions of their characteristics are drawn from References 1 through 4. This classification dates from late 1992; more recent treatability groupings differ somewhat from this. The word "debris" as used here is not equivalent to the "debris" described in the RCRA Debris Rule. The current (spring 1994) methodology for assigning waste streams to treatability groups is laid out in Reference 5.

Aqueous Liquids

Aqueous liquids consist of aqueous solutions and slurries. The total organic carbon (TOC) is less than 1%. Some aqueous liquids are waste waters but not all will meet the EPA definition of waste water under RCRA because they contain greater than 1% total suspended solids. Non-wastewaters may contain suspended solids up to the pumpable limit (30-40%) of the mass. Waste streams may exhibit multiple hazardous characteristics. Streams may contain some of the following: As, Cd, Cr, Pb, Hg, Ag, and organics. Ignitable and reactive characteristics could be exhibited by the following: benzene; solvents; electroplating sludges, cyanides, and tetrachloroethylene. Corrosive characteristics could be exhibited by sodium azide; chloroform; formaldehyde; formic acid; hydrofluoric acid; and pyridine. Many different waste streams could exhibit the toxicity characteristic.

Acidic aqueous liquids include liquids with a pH of less than 6.0. Neutral aqueous liquids include liquids with a pH between 6.0 and 8.0. Basic aqueous liquids include liquids with a pH in excess of 8.0.

Homogeneous Solids

1. Wastes with matrices that are at least 90% homogeneous solids, including particulate materials that do not meet the LDR criteria for classification as debris. The homogeneous solids are further classified as particulates or cemented solids. Liquids, if present, contain less than 1% TOC. The subcategory definitions follow.

   A. Inorganic Particulates
   Waste with matrices that are at least 90% inorganic particulates, including residual or minimal absorbed water.

A.1 Ash
Waste with matrices that are at least 90% ash including incinerator bottom and fly ash.

A.2 Sand Blasting Media
Waste with matrices that are at least 90% unused or spent surface cleaning or decontamination particulate material including coarse sand or glass beads.

A.3 Inorganic Bulk Chemicals
Waste with matrices that are at least 90% inorganic particulate absorbent materials such as clay, vermiculite or diatomaceous earth.

B. Inorganic Cemented Solids
Inorganic homogeneous solids that have been immobilized with cement, or other inorganic stabilization agents, and cured into a solidified form.

2. Waste with matrices that are at least 90% homogeneous solids may be mixtures of organic and inorganic materials. Liquids, if present, may contain at least 1% TOC or more. Included are particulates, cemented solids and hardened paint waste. The subcategory definitions follow.

A. Inorganic/Organic Particulates
Wastes with matrices that are at least 90% inorganic particulate absorbent materials with absorbed organic liquids such as clay, vermiculite, or diatomaceous earth with absorbed solvents.

A.1 Inorganic Particulate Absorbents w/Absorbed Organic Liquids
Waste with matrices that are at least 90% a mixture of inorganic and organic particulates such as organic liquids absorbed onto inorganic particulate absorbents.

3. This category includes waste with matrices that are immobilized solids containing both inorganic and organic homogeneous materials that have properly cured into a solidified form but do not meet disposal criteria. An example of waste that might be included in this category is organic liquids solidified with an inorganic stabilization agent. The subcategories follow.

A. Paint Chips/Solids
Waste with matrices that are at least 90% solid such as dried paint chips or containers filled with dried paint.

4. This category includes waste with matrices that are least 90% homogeneous solids. On a dry basis, the homogeneous solids are organic. Organic homogeneous solids are further classified as particulates.

A. Organic Particulates
Waste with matrices that are at least 90% organic particulates including residual or absorbed liquids.

A.1 Activated Carbon
Waste with matrices that are at least 90% spent or unused activated carbon used for removal of organic materials from off-gas streams or waste water operations.

A.2 Organic Resins
Waste with matrices that are at least 90% spent or unused organic based resins, other than activated carbon.

A.3 Organic Particulate Absorbents
Waste with matrices that are at least 90% organic particulate absorbent materials, including any absorbed aqueous liquids, such as sawdust or ground corn cobs.

A.4 Organic Bulk Chemicals
Waste with matrices that are at least 90% solid, unused organic chemicals packaged in bulk form that are either being excessed or have expired.

5. This category includes waste with matrices that are at least 90% a mixture of homogeneous solids and debris with the homogeneous solids fraction comprising at least 50%, but no more than 90%, of the matrix.

A. Inorganic Homogeneous Solids (50%-90%)/Debris
Waste with matrices that are at least 90% a mixture of homogeneous solids and debris with inorganic homogeneous solids comprising at least 50%, but no more than 90%, of the matrix such as scrap iron (35%) and incinerator ash (65%).

B. Inorganic/Organic Homogeneous Solids (50%-90%)/Debris
Waste with matrices that are at least 90% a mixture of homogeneous solids and debris with homogeneous solids comprising at least 50%, but no more than 90% of the matrix. The homogeneous solids are a mixture of inorganic and organic materials with neither fraction contributing 50%, or more, to the matrix.

C. Organic Homogeneous Solids (50%-90%)/Debris
Waste with matrices that are at least 90% a mixture of homogeneous solids and debris with organic homogenous solids comprising at least 50%, but no more than 90%, of the matrix such as 65% organic particulate absorbents and 35% rags.

6. This category includes waste with matrices that are greater than 50% soil. Following are the subcategory definitions.

A. Soil (>90%)
This category includes waste that is at least 90% soil.

B. Soil (50%-90)/Debris
This category includes waste with matrices that are at least 90% a mixture of soil and debris with soil comprising at least 50%, but no more than 90%, of the mixture.

7. This category includes debris (>50%) materials that meet the LDR criteria for classification as debris. The definitions for debris subcategories follow.

A. Metal Debris (> =90%)
This category includes inorganic debris that is at least 90% metal. Metal debris are further subdivided below according to lead or cadmium content.

A.1 Metal Debris (w/o Pb or Cd)
Waste that is at least 90% metal debris and does not contain any bulk lead or cadmium.

A.2 Lead-Containing Metal Debris
Waste that is at least 90% metal debris and contains separable or bonded lead as part of the matrix such as glovebox parts containing lead clad in stainless steel.

A.3 Cadmium-Containing Metal Debris
This category includes waste for which the entire matrix (e.g., > =90%) is essentially elemental cadmium. An example of waste in this category is cadmium sheets.

A.4 Uranium Chips/Turnings
This category includes waste that is at least 90% uranium metal components. An example of waste that might by included in this category is uranium lathe turnings. The waste can be contained in particulate materials to reduce their reactivity.

A.5 Reactive Metals/Equipment Containing Reactive Metals
This category includes waste with matrices that are essentially bulk reactive metals. Retired equipment containing reactive metals such as pumps and pipe sections from handling reactive metals are included. Typically these waste are sodium metal or sodium metal alloys, but they can also include particulate fines of aluminum, magnesium zirconium, or other pyrophoric materials. These are defined as waste meeting the criteria for classification as water reactive or ignitable reactive per the Third LDR rule.

B. Metal/Nonmetal Debris
Inorganic debris that is a mixture of metal and inorganic, nonmetal debris with each fraction comprising less than 90% of the matrix including bulk, separable or bonded, lead.

B.1 Metal (> =50%)/Nonmetal Inorganic Debris
Inorganic debris that is a mixture of metal and inorganic nonmetal debris with the metal fraction comprising at least 50% of the matrix such as a drum contain 65% scrap iron and 35% concrete.

B.2 Metal/Nonmetal (> =50%) Inorganic Debris
Inorganic debris that is a mixture of metal and inorganic, nonmetal debris with the nonmetal fraction comprising at least 50% of the matrix such as 65% concrete and 35% scrap iron.

C. Inorganic Nonmetal Debris
Inorganic debris that is at least 90% inorganic, nonmetal materials

C.1 Concrete
Inorganic, nonmetal debris that is at least 90% concrete such as concrete chunks and blocks.

C.2 Glass
Inorganic, nonmetal debris that is at least 90% glass such as leaded glass windows, bottles, or light bulbs. Crushed glass is included if it meets the LDR particle size criteria for classification as debris.

C.3 Ceramic/Brick
Inorganic, nonmetal debris that is at least 90% ceramic or brick materials such as bricks, ceramic crucibles, or ceramic refractories.

C.4 Rock

C.5 Asbestos

Waste that is at least 90% asbestos or asbestos based materials requiring special handling based on content such as gloves, fire hoses, aprons, flooring tiles, pipe insulation, boiler jackets, laboratory table tops, and concrete.

D. Organic Debris

This category includes organic debris that is at least 90% plastic and/or rubber materials including plastic or rubber sheeting, containers, gloves, gaskets, and components of benelex or plexiglass. Also included are wood, paper/cloth and graphite based solid materials of at least 90%, and animal carcasses.

D.1 Leaded Gloves/Aprons

This category includes plastic rubber organic debris that is at least 90% leaded glovebox gloves or aprons.

D.2 Halogenated Plastic/Rubber

This category includes plastic/rubber organic debris with halogenated plastic, such as PVC.

D.3 Nonhalogenated Plastic/Rubber

This category includes plastic/rubber debris excluding leaded gloves and aprons, which do not include halogenated plastics, such as PVC.

D.4 Wood

Includes organic debris that is at least 90% wood or wood products other than paper such as structural timbers, boxes, or pallets.

D.5 Paper/Cloth

Includes organic debris that is at least 90% paper or cloth such as protective clothing, rags or wipes.

D.6 Graphite

Includes organic debris that is at least 90% graphite based solid materials such as crucibles, graphite components, or pure graphite.

D.7 Biological

Includes organic debris that is at least 90% biological material such as biological samples and animal carcasses.

8. Hazardous Materials (> =90%)
This category includes waste in which the entire matrix is hazardous such as elemental lead, reactive metals and liquid mercury, or wastes for which the waste form is regulated. The subcategories follow.

A. Nonactivated Elemental Lead (> =90%)
This category includes waste consisting of elemental lead that is surface contaminated with radionuclides.

B. Activated Elemental Lead (> =90%)
This category includes waste consisting of elemental lead that has bulk radioactive contamination or has been contaminated through induction.

C. Beryllium Dust (> =90%)
This category includes waste that is essentially beryllium dust or chips and fines that may contain beryllium dust. This category does not include debris waste that is contaminated with beryllium dust.

D. Explosives
Includes wastes consisting of substances which undergo rapid chemical transformations which produce large amounts of gases and heat and explosions such as liquid nitroglycerine and TNT.

E. Compressed Gases/Aerosols
Includes waste meeting the criteria for classification as ignitable compressed gases for the Third LDR rule such as pressurized gas cylinders or potent aerosol cans.

F. Reactive metals
Typically these wastes are sodium metal or sodium metal alloys, but they can also include particulate fines of aluminum, magnesium, zirconium, or other pyrophoric materials. These are defined as waste meeting the criteria for classification as water reactive or ignitable reactive per the Third LDR rule.

F.1 Bulk Reactive Metals
Includes waste with matrices that are essentially bulk reactive metals.

F.2 Equipment Containing Reactive Metals
Includes retired equipment waste that contains reactive metals such as pumps and pipe section for handling reactive metals.

G. Liquid Mercury
This category includes waste containing bulk quantities of pourable liquid mercury. The liquid mercury may be also packaged in small containers within a larger container holding other materials (e.g., labpack configuration).

Organic Liquids

1. Non-Halogenated Organics
These are solvents free of F, Cl, Br, e.g., oils, hexane, methanol. Streams may contain Cd, Cr, Pb, Hg, and Se as trace contaminants. Ignitable characteristics and corrosive characteristics could be exhibited by Cd, Cr, Pb, Hg, Se, benzene, carbon tetrachloride, 1-2-dichloroethane, 1-1-dichloroethylene, tetrachloroethylene, trichloroethylene, degreasing solvents, methanol, toluene, xylene, and benzene.

2. Halogenated Organics
These are solvents containing F, Cl, Br, etc. They include all PCB contaminated organic streams. Streams may contain Cd, Cr, Pb, Hg, and Ag as trace contamination. Ignitable characteristics, corrosive characteristics and reactive characteristics may be exhibited by Cd, Cr, Pb, Hg, Ag, benzene, carbon tetrachloride, chlorobenzene, chloroform, 1-2-dichloroethane, 1-2-dichloroethylene, tetrachloroethylene, trichloroethylene, and solvents.

3. Scintillation Cocktails
These are solutions used for scintillation counting. Solutions are most often in the original glass or plastic analysis bottles. Streams may contain Cd, Cr, and Pb as trace contamination. Ignitable characteristics and corrosive characteristics may be exhibited by Cd, Cr, Pb, chloroform, degreasing solvents and other solvents.

4. Low TOC Organic Liquids contain at least 1%, but less than 10% TOC. This includes:

   A. Halogenated low TOC organic liquids containing at least 1% (10,000 ppm) halogenated organic compounds (HOC).

   B. Non-halogenated low TOC organic liquids containing less than 1% (10,000 ppm) HOC.

5. Moderate TOC Organic Liquids contain at least 10%, but less than 90% TOC. This includes:

   A. Halogenated moderate TOC organic liquids containing at least 1% (10,000 ppm) HOC.

B. Non-Halogenated moderate TOC organic liquids containing less than 1% (10,000 ppm) HOC.

6. High TOC Organic Liquids includes liquids for which the TOC is at least 90%. This includes:

A. Halogenated high TOC organic liquids containing at least 1% (10,000 ppm) HOC.

B. Non-halogenated high TOC organic liquids containing less than 1% (10,000 ppm) HOC.

Heterogeneous Solids

1. Heterogeneous Debris (Inorganic > =50%)
This category includes heterogeneous debris that is at least 50% inorganic debris material including a mixture of 65% scrap metal with 35% rags, or a mixture of 75% concrete with 25% plastic.

A. Heterogeneous Debris (Metal> =50%)
Includes heterogeneous debris that is at least 50% metal debris material such as 65% scrap metal with 10% concrete and 25% rags, or a mixture of 75% glove box sections with 15% empty glass bottles and 10% paper wipes.

B. Heterogeneous Debris (Nonmetal> =50%)
Includes heterogeneous debris that is at least 50% inorganic, nonmetal debris material such as a mixture of 65% brick with 35% rags, or a mixture of 75% concrete with 25% plastic.

2. Heterogeneous Debris (Organic > =50%)
This category includes heterogeneous debris that is at least 50% organic debris material such as a mixture of 65% rags with 35% scrap metal, or a mixture of 75% plastic with 25% concrete.

3. Asphalt
This category includes waste that is at least 90% asphalt or other bituminous materials such as roadways, shingles, bituminous cement or other materials containing both tar and gravel.

4. Debris (50-90%)
This category includes waste with matrices that are at least 90% a mixture of homogeneous solids and debris, with the debris fraction comprising at least 50%, but no more than 90%, of the matrix. Also included are mixtures of soils and debris with

the debris fraction comprising at least 50%, but no more than 90%, of the matrix. The subcategories follow.

A. Inorganic Debris (50%-90%)/Homogeneous Solids
Includes waste with matrices that are at least 90% a mixture of homogeneous solids and debris, with inorganic debris comprising at least 50%, but no more than 90%, of the matrix such as a combination of 65% scrap iron and 35% incinerator ash.

B. Heterogeneous Debris (50%-90%)/Homogeneous Solids
Includes waste with matrices that are at least 90% a mixture of homogeneous solids and debris, with debris comprising at least 50% but not more than 90% of the matrix. The debris is a mixture of inorganic and organic materials with neither fraction contributing 50% or more to the matrix. An example is a combination of 35% concrete, 30% rags, and 35% sludge.

C. Organic Debris (50%-90%)/Homogeneous Solids
Includes waste with matrices that are at least 90% a mixture of homogeneous solids and debris, with organic debris comprising at least 50%, but no more than 90% of the matrix. An example might be a combination of 65% rags and 35% sludge.

D. Inorganic Debris (50%-90%)/Soil
Includes waste with matrices that are at least 90% a mixture of soil and debris, with inorganic debris comprising at least 50%, but no more than 90%, of the matrix. An example is a combination of 65% concrete and 35 % soil.

E. Heterogeneous Debris (50%-90%)/Soil
Includes waste with matrices that are at least 90% a mixture of soil and debris, with debris comprising at least 50%, but no more than 90% of the matrix. The debris is a mixture of inorganic and organic materials with neither fraction contributing 50% or more. An example is a combination of 35% scrap iron, 30% rags, and 35% soil.

F. Organic Debris (50%-90%)/Soil
Includes waste with matrices that are at least 90% a mixture of soil and debris, with organic debris comprising at least 50%, but no more than 90% of the matrix. An example is a combination of 65% rags and 35% soil.

G. Batteries (> =90%)
This category includes waste consisting of batteries. The batteries may be packaged with absorbent materials (e.g., particulates, rags, etc.)

G.1 Lead Acid Batteries
This category includes drained or undrained lead acid batteries that have been excessed or retired.

G.2 Cadmium Batteries
This category includes cadmium batteries that have been excessed or retired.

G.3 Mercury Batteries
This category includes mercury batteries that have been excessed or retired.

Wet Solids

1. Wastes with matrices that are at least 90% homogeneous wet solids include sludges and salts. Liquids, if present, contain less than 1% TOC. The subcategory definitions are listed below.

A. Inorganic Sludge

A.1 Waste Water Treatment Sludge
Waste with matrices that are at least 90% inorganic secondary sludge or filter cakes.

A.2 Plating Waste Sludge
Waste with matrices that are at least 90% inorganic secondary sludge or filter cakes.

A.3 Pond Sludge
Waste with matrices that are at least 90% inorganic sludge from remediation of surface impoundments, such as evaporation or sedimentation basins.

A.4 Scrubber Sludge
Waste with matrices that are at least 90% inorganic sludge from wet off-gas treatment systems.

A.5 Halogenated Inorganic Sludge
Waste with matrices that are at least 90% inorganic sludge containing at least 1% HOC.

A.6 Non-Halogenated Inorganic Sludge
Waste with matrices that are at least 90% inorganic sludge containing less than 1% HOC.

B. Organic Sludge

B.1 Halogenated Organic Sludge
Waste with matrices that are at least 90% organic sludge containing greater than 1% HOC.

B.2 Non-Halogenated Organic Sludge
Waste with matrices that are at least 90% organic sludge containing less than 1% HOC.

C. Salt Waste

C.1 Chloride/Sulfate Salt Waste
Waste with matrices that are at least 90% chloride and/or sulfate salts.

C.2 Nitrate Salt Waste
Waste with matrices that are at least 90% nitrate salts.

D. Paint Waste
This category includes waste with matrices that are at least 90% new, used or removed paint.

D.1 Paint Liquids/Sludge
Waste with matrices that are at least 90% pourable paint and includes paint that has partially dried to a sludge but can still be poured or easily removed.

E. Inorganic Particulates
This category includes waste with matrices that are at least 90% inorganic particulates including residual or absorbed water. There is lower water content in the sludge with particulates.

E.1 Inorganic Ion Exchange Resins
This category includes waste with matrices that are at least 90% unused or spent inorganic exchange resins.

F. Labpacked Organic Liquids
This category includes labpacked organic liquids.

F.1 Labpacked Discarded Organic Liquid Chemicals.
This category includes labpacked organic liquid chemicals which are either being excessed or have expired.

F.2 Labpacked Organic Scintillation Fluids
This category includes organic scintillation fluids contained in vials that are packaged in a labpack configuration.

G. Labpacked Aqueous Liquids

This category includes labpacked aqueous liquids.

G.1 Labpacked Discarded Aqueous Liquid Chemicals
This category includes labpacked aqueous chemicals which are either being excessed or have expired.

G.2 Labpacked Aqueous Liquid Scintillation Fluids
This category includes aqueous scintillation fluids contained in vials that are packaged in a labpack configuration.

References

1. U.S. Department of Energy. 1993. Draft Waste Treatability Group Guidance. Matrix parameter categories. Office of Waste Management (EM-30). 7/14/93.

2. U.S. Department of Energy. 1993. Interim Mixed Waste Inventory Report: Waste Streams, Treatment Capacities, and Technologies. Vol. 5.

3. W. Ross. 1993. Mixed Waste Matrix - Contaminant Treatment Matrix. Personal communication (facsimile) to Stanley Wolf (EM-55). Pacific Northwest Laboratory. 6/22/93.

4. W. Ross. 1993. Waste Stream Characteristics - DOE's MLLW. Presentation to MLLW Steering Committee, Albuquerque, NM, Jan. 1993. Pacific Northwest Laboratory.

5. Kirkpatrick, T. and W. Ross. 1993. DOE Waste Treatability Groups Guidance. Final Draft. Office of Waste Management, Office of Environmental Restoration and Waste Management, U.S. Dept. Energy. September 1993.

APPENDIX B

Appendix B

MWTP Process Flow Diagrams

Drawing Title	No.'s
Receiving and Segregation	MWTP-PFD-010
Aqueous Liquids Treatment	MWTP-PFD-100 (6 sheets)
Organic Liquids Treatment	MWTP-PFD-200 (5 sheets)
Wet Solids Treatment	MWTP-PFD-300 (3 sheets)
Homogeneous Dry Solids Treatment	MWTP-PFD-400 (5 sheets)
Heterogeneous Dry Solids Treatment	MWTP-PFD-500 (6 sheets)
Thermal Treatment-Heavy Organic	MWTP-PFD-801
Thermal Treatment-Low Residue	MWTP-PFD-802
Thermal Treatment-Non-Metallics	MWTP-PFD-803
Thermal Treatment-Ferrous Metal	MWTP-PFD-804
Thermal Treatment-Non-Ferrous Metal	MWTP-PFD-805
Thermal Treatment-Hg Bakeout	MWTP-PFD-806
Thermal Treatment-Hg Condensation	MWTP-PFD-807
Thermal Treatment-Secondary Condensation and Off-Gas	MWTP-PFD-808
Final Forms Treatment-Glass Melter	MWTP-PFD-901
Final Forms Treatment-Lead Treatment	MWTP-PFD-902
Final Forms Treatment-Grouting	MWTP-PFD-903
Final Forms Treatment-Super Compaction	MWTP-PFD-904
Final Forms Treatment-Hg Distillation and Polymer Solidification	MWTP-PFD-905
Support Operations-Off-Gas Cleanup	MWTP-PFD-1001
Support Operations-Container Decon	MWTP-PFD-1002

The sample points referred to in the text are shown on the diagrams by number. These points may designate actual locations where on-line measurements are made, or they may be points where material samples are collected for analysis elsewhere. Locations of some of the points are not settled. For example, monitoring of the thermal treatment trains may be done by measuring gaseous species at any of several points in the treatment train.

Source: Bechtel Environmental, Inc., September 1992. Mixed Waste Treatment Project Process Systems and Facilities. Design Study and Cost Estimates. Prepared for Lawrence Livermore National Laboratory.

APPENDIX C

Appendix C

Method Descriptions for Characterization of Incoming Waste

This appendix is a compendium of descriptions for a number of the measurement techniques cited in Chapter 2. The descriptions were submitted after the workshop by members of the Characterization before Treatment workgroup. There is no attempt to offer a comprehensive discussion of all the methods identified by this group. Many of these methods may also be useful in process monitoring and final waste forms characterization. Several of these techniques are undergoing development or demonstration in projects funded by DOE.

High-Performance Liquid Chromatography (HPLC)

High-performance liquid chromatography (HPLC) is a chromatographic method in which pumps capable of producing pressures in excess of 300 atmospheres are used to push a liquid mobile phase through a column packed with stationary particles having an average diameter of 20 μm or less. An organic component injected prior to the column is partitioned between the mobile phase and the stationary phase, resulting in retention. The most common type of detection is by ultraviolet/visible (UV/Vis) absorption. In UV/Vis detection, the wavelength and quantity of light absorbed is characteristic of the type of molecule (or ion) and its concentration. Other types of detectors used in HPLC include fluorescence, electrochemical, and mass spectrometry.

HPLC has the ability to separate and detect a wide variety of organic compounds. These include neutral, polar, and ionic organic species. Many species not amenable to gas chromatography because they are thermally labile or non-volatile can be successfully analyzed by HPLC. The chromatographer has a wide selection of mobile phases and column types among which to choose for optimal results.

Gas Chromatography - Mass Spectrometry (GC/MS)

Gas chromatography/mass spectrometry (GC/MS) is a technique which provides separation of volatile organic molecules by gas chromatography and detection by mass spectrometry. In gas chromatography, a "carrier gas" (typically hydrogen or helium) flows through a heated column which contains a stationary phase. Organic analytes injected into the gas stream prior the column are vaporized and carried through the column. The organic molecule's affinity for the stationary phase dictates the extent of retention. In electron impact mass spectrometry, molecules are introduced into the ion source where they are bombarded by 70 eV electrons. The interaction of the molecules with the electrons

produces ions which are characteristic of the molecular weight of the analyte. After formation the ions exit the ion source and are filtered (focused) into a detector such as an electron multiplier. A computer then interprets the signal and produces a mass spectrum that relates ionic abundance to the mass-to-charge ratio of the ion. The mass spectrum is often considered a "fingerprint" of the molecule and is very useful for compound identification.

The mass spectrometer is maintained at a high vacuum (10^{-6} Torr) and cannot withstand much gas flow into the ion source. When GC/MS first emerged, the packed columns used for GC had flow volumes too great for the mass spectrometer to handle and, therefore, the sample had to be "split" resulting in less analyte reaching the mass spectrometer's ion source. Modern GC/MS methods of analysis use small diameter (0.25 mm) fused silica capillary columns which can be introduced directly into the ion source of the mass spectrometer with no splitting necessary. Not only does the capillary column simplify the operation, it has greater resolution than the old packed columns.

X-ray Fluorescence (XRF)

X-ray fluorescence spectrometry uses x-ray photons produced from an x-ray tube or radioactive source to bombard a sample to produce secondary fluorescent x-ray photons which are characteristic of the elements and their quantities present in the sample. The primary advantage of this method is that minimal sample preparation is required, making the method suitable for field applications.

XRF is based on the principle that a percentage of the incident photons that impinge on the electron shells in atoms of the sample are absorbed and their kinetic energy transferred to inner shell electrons of the sample atoms. This process results in ejection of an inner shell electron from the sample atoms and leaves the atom's electron configuration in an excited state. The sample atom returns to a ground state electron configuration when the vacant inner electron shell is filled with an electron from the outer shell. The outer shell electron loses energy as an x-ray photon during the transfer in the process called x-ray fluorescence.

There are two types of XRF spectrometers, energy dispersive (EXRF) and wavelength dispersive (WXRF). The EXRF detects the quantity and number of x-ray photons as a function of photon energies. The EXRF can simultaneously measure x-ray photons from all elements heavier than fluorine in concentration ranges from a few parts per million to 100%. WXRF uses diffraction to measure x-ray photons at each wavelength but requires a specific detector at each wavelength. WXRF, while more sensitive than EXRF, cannot easily perform different arrays of multi-element analyses. Both spectrometers are more sensitive as the analytes of interest increase in atomic number.

Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)

Inductively coupled plasma (ICP) spectrometry uses an argon plasma which has been excited by an inductively coupled radiofrequency field. This plasma is used to induce emission from ions and atoms which have been injected into the plasma. At room temperature, almost all of the atoms in a sample are in the ground state. Excitation of electrons to higher orbitals is accomplished by the heat of the plasma. This excited state lasts briefly and then the electron returns to the ground state. As the electron relaxes, a characteristic quantum of radiation is emitted. This radiation can be used to identify and quantify the inorganic analyte of interest.

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

ICP-MS uses an argon plasma which has been produced by an inductively coupled radiofrequency field as an ion source with a quadrupole mass spectrometer for the detection and quantitation of ions of differing mass-to-charge ratios. The mass spectrometer is capable of differentiating between masses which nominally differ by 1 atomic mass unit. Detection of ions is performed by a channel electron multiplier, a faraday cup, or an active film multiplier.

The ICP-MS is more sensitive than ICP-AES for many elements. More importantly, ICP-MS allows for discrimination of isotopes of an element within a specified sample. If the isotope ratios of an element found within a sample differ significantly from the naturally occurring isotope ratios, the isotope ratio data can be used as a means of source identification of a sample. The capability of ICP-MS to distinguish between isotopes of an element makes it an extremely valuable tool for analysis of radioactive wastes. Radioactive samples which are analyzed using counting techniques require extensive wet chemistry preparation prior to analysis due to the non-specificity of the detectors. The mass spectrometer is a specific detector and ICP-MS, therefore, requires minimal sample preparation prior to analysis. Consequently, turnaround times are greatly reduced.

Laser Ablation Inductively Coupled Plasma - Mass Spectrometry (LA ICP-MS)

Laser ablation ICP-MS uses a high energy Nd:YAG (Neodymium YAG) laser to ablate or vaporize a solid sample prior to analysis. The laser is focused onto a small (tens of microns) area of the sample of interest using a binocular microscope, and a series of laser pulses is triggered to ablate the sample. The number of pulses fired can be varied and is dependent on the concentration of analyte in the sample. Lower concentrations require more pulses to provide sufficient vaporized sample for analysis. The ablated, or vaporized, sample is then transported into the ICP plasma by means of an argon gas flow.

Data acquisition using the ICP-MS is rapid: scans taking in all elements can be obtained in as little as 100 milliseconds, although scan times of 60 to 90 seconds are necessary to obtain accurate concentration measurements. The capability of directly

sampling a solid eliminates the need for sample dissolution which is necessary for analysis using ICP-AES, ICP-MS and GFAAS. LA ICP-MS has been shown to be applicable to a variety of solid matrices, including ceramics, glasses, whole rock and mineral samples, semiconductor materials, metals and powders.

Atomic Absorption Spectrometry (AAS) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

Atomic absorption spectrometry (AAS) is useful in the determination of metal atoms. For absorption of radiation by a metal atom to occur, the energy of the source radiation must exactly match the energy difference between the ground state and one of the excited states of the absorbing species. The decrease in the intensity of the source radiation due to absorption by the analyte atoms can be related to the concentration of absorbing atoms in the sample.

Graphite furnace atomic absorption spectrometry (GFAAS) utilizes an electrical current for vaporization of the sample prior to analysis. This is generally accomplished in 3 stages: 1) a drying stage during which the solvent is vaporized; 2) an ashing stage during which any organic components present in the sample are burned off; and 3) an atomization stage during which the analyte is atomized into a vapor. This vapor is subsequently analyzed for the element(s) of interest. The method requires much smaller sample volumes (μL as opposed to mL) and allows for lower absolute detection limits than conventional flame AAS.

Gamma Ray Spectroscopy

The primary purpose of the measurement is to apply appropriate radiological safety in processing drums. Here, a simple dose-rate measurement is sufficient. However, much more qualitative and quantitative information can be obtained in reasonable times with a variety of commercially available instruments. All rely on gamma-ray spectroscopy using low or high-resolution detectors. Either of two different methods may be used: whole-drum counts (WCD) or segmented gamma scanning (SGS).

Whole-Drum Counter

In the WDC method, the drum is usually placed in a shielded enclosure viewed by typically one to three detectors. Detector selection depends on the complexity of the measurement task. For waste containing only a few radionuclides, low resolution sodium iodide, NaI(Tl), detectors may suffice. But for more variable or unknown wastes, high-resolution high purity germanium (HPGe) detectors are a better choice.

The drum is rotated inside the enclosure as it is viewed by the detector(s). A spectrum is required, stored in computer memory, and analyzed for the energies and intensities of the detected gamma rays. If the drum contents are reasonably homogeneous

and of low density, good corrections for attenuation of the gamma rays, as they pass through the waste matrix, can be made. Most gamma-emitting nuclides can be measured at levels of 1-10 pCi/g under ideal conditions with assays of 5-10%. As the waste becomes more dense and/or heterogeneous, quantification accuracy decreases significantly. However, qualitative information, as to the identity of nuclides present, is often still obtainable and useful.

Segmented Gamma Scanner

The SGS represents a refinement of gamma counting which can overcome some of the limitations of the WDC. It uses a single HPGe, since the method is aimed primarily at high resolution measurements of enriched uranium or plutonium in waste. Here, the detector is shielded and collimated so as to view only a narrow vertical segment of the drum. As before, the drum is rotated, but in addition, a beam of gamma rays from a transmission source can be shone through the drum as a measure of the waste's attenuation of the nuclide of interest. Each segment is scanned sequentially and summed to provide an assay of the entire drum.

SGS, under optimum conditions, can provide assays of a few percent for plutonium at 100 nCi/g or more. This requires longer count times (30-60 min.) and more complex hardware than for WDC. Also, SGS is generally set up to optimize measurement of a single radionuclide like Pu-239 or U-235. While fission/activation products will also be detected, their quantification is not as good, and they may interfere with the uranium or plutonium determination.

Acoustic Monitoring

Acoustic monitoring probes have been installed on a mixer pump within tank 101-SY on the Hanford site. There are two types of probes installed; one of them is applicable to monitoring containerized wastes. These are "density monitors" which are 1/10 of a watt in power and consist of a transmitter and a receiver. Currently particulate concentration data obtained from these probes is converted to density information. The density information tells operators the "degree of mobilization" of the waste. This information will aid during the retrieval of double-shell tank waste by indicating when the sludge within a tank is homogeneously mixed with the supernatant liquid inside it. Other possibilities include in-line determination of particulate concentration. In-line particulate monitoring could be utilized during single shell tank retrieval. Wastes are recirculated during sluicing operations. This type of monitor would provide operators with information which would allow them to switch from recirculation mode to transfer mode. Particulate concentrations of 30% are the target for pumping the material out from the single shell tanks during sluicing operations. Time to develop an acoustic probe system for in-drum application is approximately nine months and $200K. The point of contact for this DOE demonstration project is Al Tardiff, DOE-HQ, EM-542, (301) 903-7670.

Laser-induced Plasma Spectroscopy

Laser-induced plasma spectroscopy (LIPS, also known as laser-induced breakdown spectroscopy, LIBS) is an atomic spectroscopy technique for the determination of elements directly in solids, liquids, and gases. Radiation from a laser is tightly focused to achieve an energy density sufficient to form an atmospheric plasma. The portion of a sample brought in contact with this plasma is vaporized and the resultant sample atoms emit spectra characteristic of the consistent elements. The spectral emission is quantified using a conventional grating spectrometer and detector.

Because the laser plasma generated by a LIPS system has a temperature of 25,000°C, it is capable of vaporizing any solid, liquid, or gas. It is most readily usable for solids and gases, but several methods are available for the direct analysis of aqueous and organic liquids. It has seen application to bulk metals, soil, rubber, atmospheric particulates, process solutions, and numerous other sample types.

Since the laser beam can be transmitted by fiber optics or by telescopic lenses, and the resulting atomic emission can be returned to the spectrometer by the same means, LIPS is applicable to samples in remote or hostile environments. Using relatively small laser and spectrographic components, the system can be sufficiently reduced in size and weight to be portable.

Detection limits for solids are in the 0.1 to 10 $\mu g/g$ range for many elements. LIPS has been shown to be sensitive to chlorine, bromine and several other elements that are difficult to analyze by ICP-atomic emission methods. Its sensitivity for mercury is substantially poorer than the cold vapor atomic absorption and atomic fluorescence methods often used for this element.

LIPS is not commercially available at this time. However, development programs at several of the national laboratories may result in the transfer of LIPS technology to the commercial sector within the next several years. Los Alamos National Laboratory has developed several real-time LIPS monitors for beryllium and lead in air, and is currently configuring a portable system for several elements in soil. Sandia Laboratory at Livermore is developing a multi-element LIPS system for the real-time determination of toxic metals in the effluent of hazardous waste incinerators. A multi-element system is expected to cost in the same range as current ICP-atomic emission systems.

Fiber Optic Chemical Sensors

The fiber optic chemical sensor includes a fiber optic core surrounded by a protective cladding. Additional protection around the cladding for strengthening the cable is often employed. The principle behind the fiber optic sensor is an alteration of the light being transmitted in the core of the fiber optic cable. This is done either through an alteration of the cladding around the core or else through an interaction of a medium that either

replaces or is included in the cladding, which in either case produces a change in the light parameter in the core. This change conveys the information from the sensor. A reagent can be included in place of the cladding and upon interaction with the analyte (e.g., contaminant) changes in the optical properties of the core produce the information or signal. The signal travels at light speeds, but information acquisition is usually near-real-time due to the fact that additional processing of the information is required. The major advantages of the fiber optic sensors are:

- remote sensing is possible
- no sampling is required
- the sensor occupies a low volume
- it is inert to most chemical environments
- FOCS readily adapt to conventional optical spectroscopy.

For purposes of measuring chemical contaminants, fiber optic sensors can be classified according to whether they exhibit intrinsic or extrinsic properties. In the intrinsic sensor, the chemical contaminant interacts directly with the light in the fiber. The fiber itself responds to the chemical parameter, and modulation of the optical signal occurs while light is guided within the fiber. Intrinsic sensors with a modified fiber cladding can perform immunoassays and are very promising as a way to measure very low concentrations of chemicals in complex solutions. The modified cladding-to-fiber interface acts as the sensing element by trapping specific chemicals in complex solutions.

With the extrinsic sensor, the fiber primarily acts as a conduit to and from an external medium that alters the properties of the transmitted or reflected light. The combination of electrochemistry with surface-enhanced Raman spectroscopy (SERS) and fluorescence spectroscopy make extrinsic sensors which provide a sensitive means to monitor chlorinated hydrocarbon solvents, light aromatics, and other common contaminants in vapor and liquid phases. Modular fiber-optic spectroelectrochemical probes serve several important functions, including: generating reagents that react with select analytes to produce fluorescent or Raman-active products with a laser diode excitation source; absorbing and concentrating reaction products from solution for greater sensitivity; and providing a surface that enhances Raman spectroscopic signals up to a million-fold. The narrow Raman bands hold promise for simplifying the identification of individual components in complex mixtures. Data analysis methods for real-time processing of Raman signals of contaminants are forthcoming in the near future.

Fiber optic chemical sensors (FOCS), when used for process monitoring, can present a great savings in money and time for making measurements. For process monitoring and control in the pulp/paper, oil and gas, and chemical processing industries, fiber optic sensors tend to be applied in difficult niches employing remote spectroscopy or Raman spectroscopy. Though other types of conventional transducers are available, adopting optical multiplexing in the process plant enables a single control device to monitor multiple stations in fiber optic networks.

Fiber Optic/Fourier-Transform Infrared Probe

A fiber optic/Fourier Transform Infrared probe has been tested for the identification of organics in containerized waste. This is a Small Business Innovative Research Project at Brooks Air Force Base. This project has successfully completed the phase I portion of the development work. Phase I of the project designed probes and demonstrated that mixtures of organics could be accurately identified. Phase II of the program will be to design, fabricate, test, and deliver to the Air Force an IR fiber optic sensor/FTIR measurement system for the field screening of liquid hazardous wastes. This first system will be a benchtop unit that can be readily transported and that will be suitable for use in sheltered field environments. It will enable a trained technician to perform rapid on-site screening/analysis of liquid wastes stored in drums or tanks. The proposed phase II system will include a full-function FTIR spectrometer, personal computer, complete IR spectral analysis software package (including calibration data for waste identification), color printer/plotter and a supply of probes with connecting fiber optic cables (Figure C-1).

Computed Tomography

Computed tomography (CT) provides quantitative, nondestructive, and noninvasive stationary views of liquids, solids, homogeneous, and heterogenous waste drums and provides cross-sectional and full drum volume views of contents that include density and three dimensional information. Cross-sections are stacked to present computer generated 3-D volume views of drum content. A CT image is a computer generated density map of waste that is approximately proportional to the CT grey or color scale. With CT, dimensional and volume measurements are provided based on known boundary locations. CT is useful for measuring a reduced drum wall thickness due to corrosion, the volume of liquids or solids, and the density of a heavy metal such as Pb or Hg. In addition, CT has a wide dynamic range and thus has contrast resolution which is useful in imaging dense waste matrices (i.e., cements or soils) or differentiating substances with similar densities both of which are difficult for real-time radiography (RTR). As an example, CT can distinguish cement from sand or wet sand from dry sand in a drum. CT can measure the volume or the difference in volume between cured Portland cement and water in a drum. In addition, CT can measure the volume of liquid surrounding cement as well as the amount of liquid inside cement pores, cavities and inside a can within a drum. CT can identify water vs. oil volumes from density differences. CT images are available in seconds to minutes per image depending on the scanner model and imaging techniques used as compared to real-time acquisition with RTR. As a result, CT drum throughput can be minutes to hours per drum. CT can determine liquid motion with time sequenced views between drum movements. Ranges of measurement limits for typical CT systems that can image 55 to 110 gallon waste drums are defined below. All capabilities may not be available on a single CT system simultaneously:

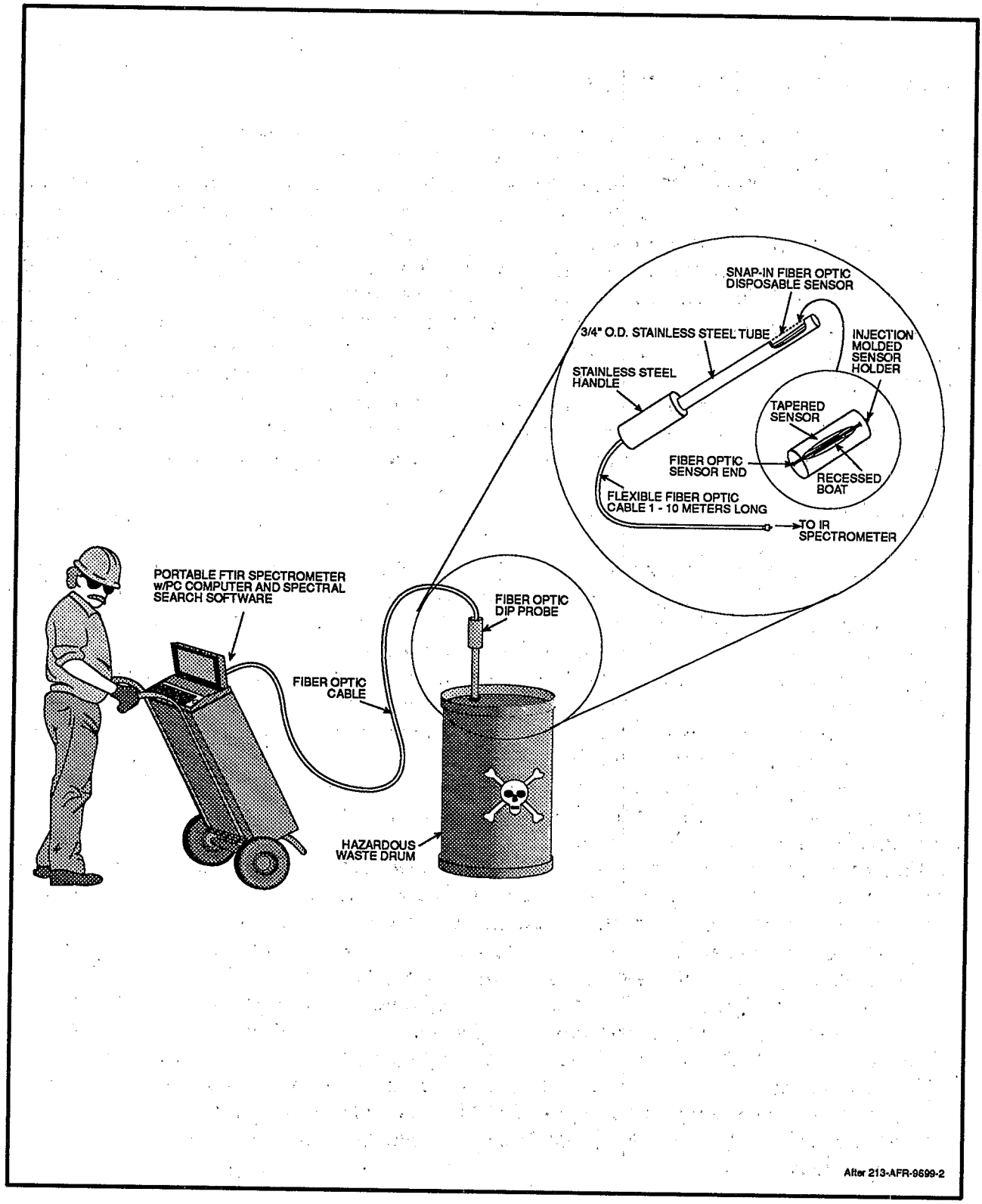


Figure C-1. Fiber Optic System for Drum Examination.

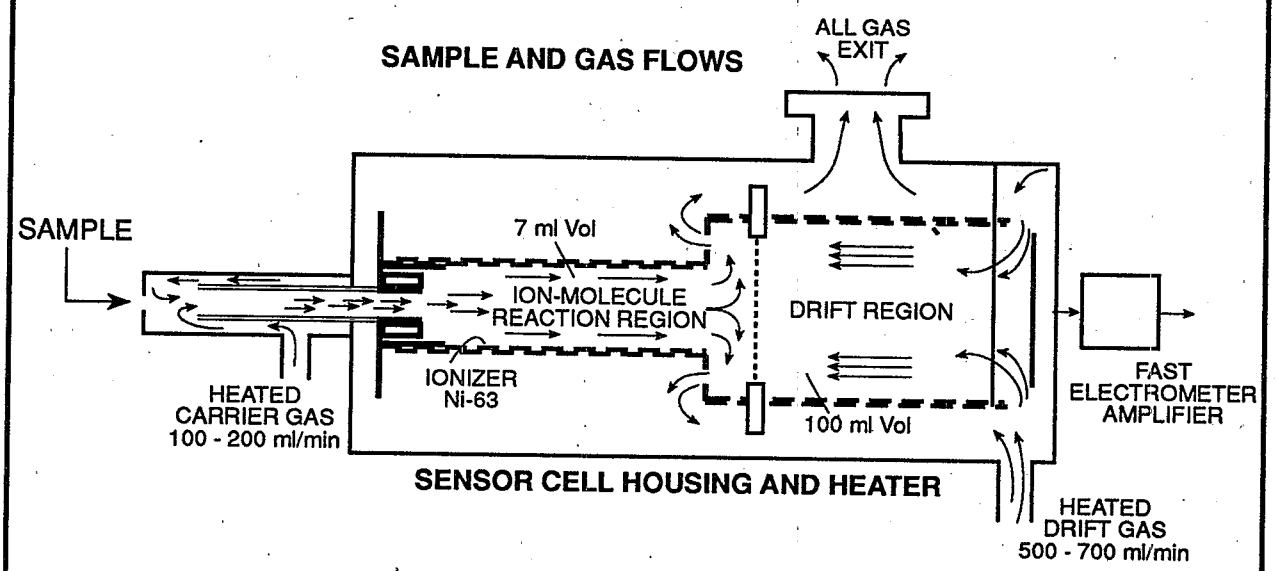
CT Parameters	Typical CT Sensitivity
Fields of view	up to 1.5 meters diameter by 1.5 meters tall
Radiation voltages	320 kV to 9 MV
Density differences measured	0.1% to 10.0%
Dimensional accuracy	50 microns to 125 microns
Volumes measured	1 ml to over 100 ml
Spatial resolutions	0.5 to 1.5 line pairs per mm at 10% contrast
Resolvability range	50 to 100 microns at high contrast
Dynamic range	16-bits (65,000 data values) to 20-bits (1 million data values)

CT cannot image moving liquid surfaces in real-time or the boundaries of phases with the same densities. CT spatial resolution can be equal to or less than RTR.

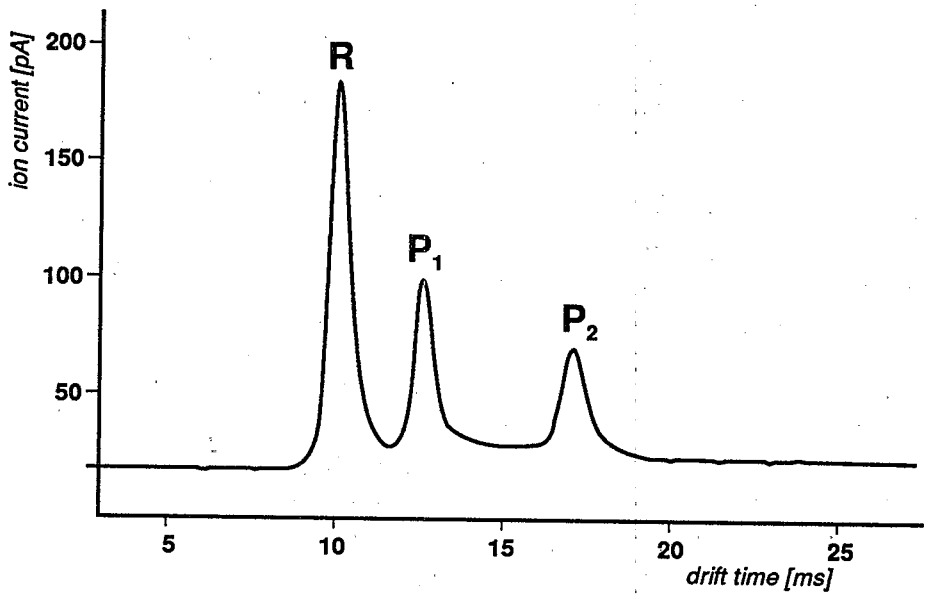
Ion Mobility Spectrometry

The ion mobility spectrometer (IMS) is not a chemical sensor as are piezoelectrical devices or fiber optic sensors. However, it comprises a chemical sensor system, much as the gas chromatograph (GC) and mass spectrometer (MS). Due to its portability, it has the potential to be a useful device for quick looks at contaminated containers. In addition, it has excellent sensitivity, in particular when paired with a GC. Most IMS systems can only analyze vapors. However, particles can be analyzed using a sniffing technique, by collecting contaminants of interest on a filter. The filter is then placed at the input to the IMS, where it is heated with ranges up to 300 degrees centigrade. The resulting vapor is then analyzed by the IMS. For explosives, heating to a temperature of 100 degrees centigrade or less is satisfactory for the detection of 50 to 600 picograms of explosives.

A schematic diagram of the IMS is shown below, in Figure C-2. The instrument is basically an electric-field drift tube comprising an ionizer and reactor coupled via an electronic shutter grid to an ion drift region. The drift tube consists of a series of stacked cylindrical guard rings which produce a uniform electric field along the axis of the cylinder. The entire cell is at atmospheric pressure. The sample vapors enter the ion molecule reaction region through a short quartz tube. Ionization of the carrier gas results in the formation of certain reactant ions. These efficiently ionize a large fraction of the trace sample molecules in the carrier gas stream, accounting for the great sensitivity of the IMS. All the ions thus formed move down the reaction region under the influence of the voltage gradient until the shutter grid is encountered. This grid is repeatedly opened at brief intervals, admitting pulses of mixed ions into the drift region. As they drift, the ions in any particular pulse (i.e., due to grid opening and closing) separate into their individual chemical species based upon their differing intrinsic mobilities. The arrival of the individual ion pulses at the collector electrode produces a characteristic ion arrival time spectrum. Typical drift times range from 10 to 20 milliseconds which provides the real-time monitoring capa-



a. Schematic of the unit.



b. A typical IMS spectrum with a reactant ion peak R and two product ion peaks P_1 and P_2 (e.g., contaminants).

Figure C-2. Ion mobility Spectrometer.

bility of the IMS. Since the shutter grid is repeatedly pulsed, a continuous spectrum can be directly viewed or summed for enhanced signal-to-noise ratio.

Ultrahigh Vacuum Analytical Techniques

While there are a number of ultrahigh vacuum (UHV) instrumental techniques that have ben adapted for analytical applications, perhaps the best known ones are x-ray photoelectron (XPS) (sometimes also called electron spectroscopy for chemical analysis, or ESCA) and Auger electron spectroscopy (AES).[1,2,3] These techniques work under vacuums of 10^{-9} to 10^{-11} torr and are applicable to all solid samples involving toxic chemical elements and species that are commonly encountered at DOE sites. The samples may be powders, wafers, chips, films, or any other solid form that is amenable to the UHV conditions. With instrumental modifications and low-temperature cells, liquid and wet samples can also be analyzed; however, analyses of this kind are best performed using a dedicated instrument. Both techniques mirror approximately the top 10-30 Angstroms of the surface of the sample being studied.

X-ray photoelectron and Auger spectroscopy have a number of advantages as analytical techniques. First, both techniques can be used in the survey scan mode to give a quick compilation of the elements that are present in a particular sample. Toxic heavy metal samples such as copper, lead, and chromium are easily detected using the two techniques. Equally spectroscopically visible are anionic polyatomic waste species such as phosphates and nitrates, along with other waste non-metallic species such as iodides.

The second advantage of the two techniques is that they can be used not only to detect the presence of an element but also to study its chemistry in detail when the spectra are obtained in the high resolution mode, giving such information as the oxidation state of the central element as well as the functional group that might contain it. There are several examples of this, including the ability to distinguish cobalt(II) from cobalt(III), chromium(III) from chromium(VI), and sulfur(-II) from sulfur(VI). In this last case, a researcher can thus easily differentiate between a sulfide and a sulfate. Additionally, the chemical and electronic state of other elements associated with the sulfur species can most likely be determined.

The third advantage of the two techniques is that, using the appropriate instrumental setup, they can complement one another to a very great degree. Specifically, using a standard x-ray anode radiation source for soft x-rays that are typically used to perform the normal x-ray photoelectron experiment, a researcher can also observe the Auger electron spectrum that is concomitantly generated by the x-radiation; as a result, both the x-ray photoelectron and Auger spectra are contained in the form of a combined spectrum. This allows a direct comparison of the two spectra of a sample without worrying about experimental aspects that might normally cause difficulty in the interpretation of the data, one possibility being the problem of "charging." By being able to look at the x-ray

photoelectron and Auger spectra in the same printout, this problem can be eliminated and combined spectral parameters can be generated for a particular element of interest.

The fourth advantage of the two techniques is that they can be used to study samples that are not homogeneous on the surface. As mentioned above, the techniques reflect the near-surface of a sample that is being studied, thus allowing a researcher to study contaminants that may have attached themselves to the original species. Both x-ray photoelectron and Auger spectroscopy can be used to perform point analysis on samples, meaning that locations of a few microns in area on a sample can be studied. This is most easily accomplished using Auger spectroscopy under the conditions in which an electron beam is used to generate the Auger spectrum; it is not so easily effected using x-ray photoelectron spectroscopy, since the throughput of samples is reduced dramatically.

Finally, several drawbacks do exist for using UHV techniques for analysis. First, there is the fact that samples are, practically speaking, restricted to solids. Second, the establishment and breaking of vacuum is costly in time, restricting the number of samples one can quickly run. Third, one must check to see if any radiation damage occurs as a function of time; this can alter the interpretation of the data as they relate to chemical state information such as oxidation state. Still, the UHV techniques provide a wealth of knowledge about a wide variety of toxic elemental species.

Neutron Techniques for Specific Alpha Measurement

Specific alpha activity is the rate of alpha particle emission per weight, measured in curies per gram. The present limit for distinguishing low-level waste (LLW) from transuranic waste (TRU) is 100 nanocuries per gram. The difficulty with measuring the specific alpha activity is that the mean free path of an alpha particle in almost any medium is very short. In air, the mean free path is only a few centimeters. For drum-sized containerized waste, essentially none of the emitted alpha particles would reach an alpha detector.

Specific alpha activity is important for two reasons. First, it directly affects the generation of gas by radiolysis. Gas generation is important because it can affect the physical integrity of the container. Also, alpha activity is typically associated with a certain class of radionuclides which have a severe environmental impact. The most notable are the isotopes of plutonium. Leaching of these isotopes out of the waste container could cause a significant environmental impact.

Because of the short mean free path of alpha particles, alpha activity is usually measured indirectly. The most common approach is to exploit the alpha-neutron reaction: an alpha interacts with a moderate atomic number (Z) material which then gives off a neutron (4). This nuclear reaction is common for many oxidizing materials, such as oxygen or fluorine. In most waste cases the nuclear material, such as plutonium, is in its oxidized rather than metallic form (plutonium is a strong reducing agent). Therefore, inferring the

alpha activity from the neutron emission is a common and effective technique. In the case of LLW waste assay, it is particularly reliable because the presumption is that small quantities of waste are involved, so that the plutonium (or other alpha emitting material) is naturally oxidized.

The technique that is used to determine specific alpha activity from the induced neutron emission is passive neutron totals counting (4,5,6). Typical instruments are the passive counting aspect of the californium shuffler, and the passive add-a-source counter. The passive-active neutron differential die-away counter can also make this passive neutron measurement. Because there are other sources of neutrons besides the alpha-n reaction, the total neutron counting technique generally provides only an upper bound to the alpha activity rate. In addition, the reaction cross sections for alpha-n reactions vary for different oxidizing materials. This technique is typically used as a "screening" measurement; it determines the upper bound of the alpha activity rate rather than a precise measurement (4,6).

A more accurate but somewhat less sensitive method is passive coincidence counting (5,6). Passive coincidence counting counts the number of simultaneous neutron pairs. Neutron pairs are a specific signature of a nuclear fission, so this measurement determines the amount of fissionable material. Because the fissionable isotopes are also typically those that decay by alpha emission, the alpha activity can also be inferred. For example, one of the most common alpha emitters found in nuclear waste is plutonium, which also has a significant spontaneous and induced fission component. By counting the neutron coincidences, the fission rate can be determined. Knowing that plutonium is the dominant source of alpha emission, the alpha rate can be inferred directly from the nuclear decay properties of plutonium. Passive coincidence counting systems for 55 gallon drums can operate down to the 10 nanocuries per gram level in well-shielded environments (the sensitivity depends on the background count rates). This sensitivity is well below the 100 nanocurie per gram regulatory limit for distinguishing low level and TRU waste.

The passive coincidence measurement can be extended to neutron multiplicity counting (6). Multiplicity counting counts simultaneous neutron events consisting of multiple neutrons, extending the coincidence concept of counting neutron pair events. This technique can reduce many of the uncertainties from matrix effects, additional isotopes such as curium, and detector efficiencies.

Another extension of the passive coincidence measurement is the add-a-source technique (5). The add-a-source technique provides a correction to a passive multiplicity or coincidence counting for matrix induced errors. The passive measurement is significantly less sensitive to matrix effects than active measurements, but the induced bias error can be reduced further. The add-a-source method introduces a known source with a neutron spectrum similar to fission neutrons, and measures the effect of the waste drum matrix on the source neutrons. The effect on the source is assumed to be the same as the matrix

effect on the sample. The passive measurement of the sample is corrected using the measured effect on the added source.

The third principle measurement of specific alpha activity is done by active neutron interrogation (7,8,9,10,11). The active measurement interrogates the sample with a neutron source. Typically, a neutron generator is used in the case of the passive active neutron, differential die-away (PAN/DDA) system and a californium source is used in the PAN/californium shuffler. In both cases fissions are induced in the sample material and the resulting fission neutrons are measured. The PAN/DDA system measures prompt fission neutrons and the shuffler measures delayed neutrons. In both instances the measured neutrons are proportional to the amount of fissionable material in the sample. The isotopes that are specific to this measurement are the odd isotopes of plutonium (^{239}Pu, ^{241}Pu predominantly) and ^{235}U.

For the active neutron measurement two assumptions are made: the first is that the alpha-emitting material is essentially all plutonium. For example, the measurement will be in error if there are significant quantities of americium present, which decays by alpha emission but does not have a significant induced fission cross section. Americium is common to the plutonium production cycle. The second assumption is that the isotopic distribution of the plutonium is known. (Typically, the isotopic distribution is assumed to be weapons-grade material for DOE complex waste.) For certain samples with noninterfering matrices, the isotopic distribution of plutonium can also be measured using gamma-ray techniques, such as the segmented gamma scanner. Although active techniques are more dependent on the underlying assumptions about the material distribution, they are also the most sensitive. However, active techniques are considerably more sensitive to the matrix material than passive techniques.

An important variant of the PAN/DDA system is the combined thermal-epithermal neutron system (CTEN) (11). The CTEN system now under development addresses one of the important limitations of the PAN/DDA system, namely that the interrogation is done with thermal neutrons. The penetration of thermal neutrons is very small, roughly a few hundred microns in metallic plutonium. If significant quantities of plutonium are present in a sample, it is possible that the active PAN/DDA system will significantly underestimate the quantity. The CTEN directly addresses this problem.

Because the active assay instruments can also make a passive measurement, occasionally the active interrogation is combined with a passive multiplicity or coincidence measurement. The total neutron counts are also included in the coincidence or multiplicity counting. The most common instruments are the passive multiplicity counter with add-a-source matrix correction, the californium shuffler, and the differential die-away system.

The choice of which system to use depends somewhat on the anticipated application. If the waste drum must be characterized for the TRU/LLW distinction only, passive multiplicity with add-a-source is the most robust measurement. If a highly sensitive

measurement is required, then the PAN/DDA system has the required sensitivity. If uranium is anticipated in the source stream, then the PAN shuffler measurement is perhaps the most appropriate. Other active and passive neutron-based instruments are also under development which may alleviate some of the problems discussed here.

Immunochemistry

Immunochemistry includes the techniques immunoaffinity, chromatography, and immunoassay. Sample preparations based on immunoaffinity take advantage of the attraction between an antibody and a specific analyte. The procedure has potential for cleanup of complex samples like soils and sludges. By rinsing a sample over an antibody-treated surface, chemists can isolate particular compounds that adhere to the antibody. The isolated compound is then eluted from the immobilized antibody and is ready for analysis by chromatography or by immunoassay. One common immunoassay is the enzyme-linked immunosorbent assay (ELISA). In this technique, the selectivity of the antibody for the analyte and the resultant antibody-analyte complex is the basis for the specificity of immunoassays.

Immunoassay techniques can be incorporated within fiber optic systems to facilitate analysis of organic contaminants. Antibodies that specifically bind to the substance to be detected are trapped on an optical fiber. The fiber is placed in a small column, where the polluted sample is poured, and the pollutant binds to the trapper antibody. A second antibody, tagged with a fluorescent compound, is put into the chamber to bind to the pollutant, and light pulses measure the amount of reaction. The color intensity is related to the sample analyte concentration. This technology has been developed to test for contaminants in food, water, and soil, and on contaminated surfaces. Fiber optic immunosensors have been developed to detect drugs and explosives at the ppb threshold.

Raman Spectroscopy

Raman spectroscopy detects the vibrational characteristics of molecules of a contaminant after intense monochromatic excitation, typically provided by an ultraviolet (UV), visible, or near-infrared (NIR) laser. The inelastic scattering caused by the irradiation is representative of the induced polarization of bonding electrons due to vibrational motion of the molecule (i.e. Raman effect). It has been used to detect VOCs in soil and in the vadose zone. Raman spectroscopy, combined with fiber optic techniques, has been found to be particularly useful for detecting and monitoring VOCs in groundwater or remote locations. Fiber optic probes are used to perform surface-enhanced Raman Spectroscopy (SERS) of analyte molecules absorbed on the surface of an electrode at the end of the probe assembly. Real time monitoring of carbon tetrachloride and TCE have been demonstrated.

Piezoelectric Sensors

Piezoelectricity is produced by applying pressure to a crystal of dielectric material. The applied pressure deforms the crystal lattice causing a separation of charges which results in an electrical potential. Application of an electrical potential (voltage) to the crystal produces physical distortions and the crystal vibrates mechanically for short periods until physical equilibrium is attained. Several types of piezoelectric sensors are available including the surface acoustic wave (SAW) sensor. The SAW sensor is a mass sensitive device and uses a shift in resonant frequencies as the indicating signal, through coatings that chemically sorb analytes. The SAW is a microsensor and occupies a volume smaller than one millionth of a liter. SAW sensors have found wide application because of their small size, ruggedness, low cost, electronic output, sensitivity, and adaptability to a wide variety of vapor phase analytical problems (e.g. VOCs).

Prompt Gamma Neutron Activation Analysis

This is a non-invasive method whereby interrogation of containerized waste is possible through the interaction of neutrons directed at the sample (e.g. contaminant) being analyzed. The PGNAA performs an elemental analysis of the sample. The neutron initiates a nuclear reaction and there is an instantaneous gamma emission from the sample. The high-energy gamma ray is the contaminant elemental signature. The energy levels give a better signal-to-background ratio than conventional instrumental neutron activation analysis. The per sample costs are lower than conventional laboratory analysis and the analysis results are available in minutes. There is no sample collected for shipping and disposal. The PGNAA is also configurable for a field survey vehicle. PGNAA is reported to be effective throughout the periodic table. Elements such as U, Th, Cd, Cu, Pb, Hg, As, Ba, Cl and Cr have been detected with PGNAA at sensitivities below the limiting regulatory requirement.

Electrochemical Sensors

Electrochemical sensors have been developed to measure ions and gases. They are classified as potentiometric, amperometric, or conductimetric according to the influence of the analyte in the electrochemical cell. To be detected, a gas must elicit an electrochemical response. Most VOCs are electrochemically inactive and must be converted to electroactive reaction products (e.g. CO, Cl_2, HCl, HF) using pyrolysis techniques prior to detection. The electrochemical sensors are fast, sensitive, miniature, and inexpensive. Response and recovery times are most often less than one minute and the interaction of the analyte and surface is usually completely reversible. Detection levels range from 500 ppb to 1000 ppm and are dependent on pre-detection operations.

Pulsed Fast Neutron Analysis (PFNA)

PFNA is a non-intrusive system that uses a rapidly-pulsed beam of high-energy neutrons to induce element-specific gamma-ray signatures of materials inside a sample. This method will detect hazardous elements such as mercury and chlorine, and hazardous compounds such as PCBs. Elemental maps are formed for nitrogen, oxygen, chlorine, silicon, aluminum, iron, and other elements of interest. By combining these maps, it is possible to screen for particular hazardous materials. PFNA has very broad applicability in waste treatment and disposal where elemental composition and spatial distribution influence operational decisions.

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10. P.M. Rinard. 1991. Shuffler instruments for the nondestructive assay of fissile materials. LA-12105. Los Alamos National Laboratory, Los Alamos, NM.

11. K.L. Coop. 1989. A combined thermal-epithermal neutron interrogation device to assay fissile materials in large waste containers. in Proceedings of the 11th Annual ESARDA Symposium on Safeguards and Nuclear Material Management. Commission of the European Communities Report EUR 12193 EN, Luxembourg.

APPENDIX D

Appendix D

Advanced Technologies for Process Monitoring and Control

Gary Leatherman

Automating the Monitoring of the Waste Treatment Process

Adaptation of existing automation hardware and software for monitoring the processing of the mixed low-level waste (MLLW) should be investigated. Waste water treatment systems have been automated and some of this technology may be appropriate for MLLW characterization for treatment. Typically, new sensors and controller hardware are added to an existing distribution control system (DCS) of the waste treatment area (1). An existing DCS could be modified to handle MLLW treatment requirements. In this automation, operator display terminals can be placed where needed. A flexible system that uses standard hardware and software components can be installed and maintained by in-house personnel.

Personal computers (PC) could be the ideal engine for distributed control. Connected to generic input and output devices wired directly to sensors and actuators, the PC could provide a graphical display of process monitoring information, execute control algorithms, and provide data logging and reporting. PCs can be linked together through low cost networking technology enabling the transfer of information to each other.

The majority of PC-based automation software include the ability to acquire and display real time data in a variety of formats: trend charts, bar charts, numerically, etc. The monitoring instruments should use an interface standard so that linkage to the automated system is easily accomplished.

Data reporting and archiving requirements in treatment of MLLW will require specific information mainly because the format and contents of the reports are mandated by regulatory agencies (e.g., EPA and state regulators). Monitoring data acquired from the process needs to be sent directly to spreadsheets in real time, so that calculations are up to the minute and reports show an instantaneous snapshot of the operating process. Modular software is best because new features and functions can be purchased separately as needed.

Laptop computers have become commonplace for the engineers called on to diagnose and solve a variety of manufacturing or process related problems. Usually an external device is needed that can digitize signals from sensors and store the data directly in the

laptop's file. The use of these devices would help expedite the characterization for processing of the MLLW and be more cost effective than a mainframe computer.

Smart Sensors

Smart sensors/transducers are defined as sensing devices with built-in intelligence. This intelligence usually results in some form of digital signal processing. Smart sensor design is evolving in several directions. These devices show promise for the monitoring of MLLW treatment processes.

The initial focus was on digital processing of the sensor output signal to improve the accuracy of temperature compensation and normalization. Later designs incorporated enhanced digital features such as remote communication and addressability. The most recent developments include the integration of a manufacturing test system interface that allows batch mode fabrication of transducers. This advance significantly reduces manufacturing cost and significantly improves the price/performance ratio (2).

Smart sensor process monitoring control applications have been introduced by industry recently. In one application the process control transmitter used three monitoring sensor input signals: differential pressure, temperature and static pressure. In addition to basic signal conditioning functions, the software included the static pressure compensation necessary for process control applications. The process control transmitter design incorporated several key advanced digital features such as remote calibration over a 400:1 range, addressability and diagnostics.

The evolution of smart sensor and transducer design is bringing outstanding products to market. While they represent a small market segment at present, it is expected that their share will grow quite rapidly as they gradually replace classical analog designs. Several factors confirm this trend. The growing demand for communication and networking capabilities cannot be satisfied with analog transducer designs. Industrial applications of single chip smart transducers can be expected in the current decade, with further price/performance improvements; single chip smart sensor developments have already been reported by research and academic centers. As a result of increasing volumes and levels of integration for smart transducers, the conversion of a major sector of the existing low cost sensor market can be expected.

References

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2. N. Najafi. March 1993. A Multi-element Gas Analyzer utilized in a Smart Sensing System. Proc. Sensors Expo West, San Jose, Ca.

APPENDIX E

Appendix E

Instrumentation for Waste Form Characterization

MLLW Workshop - Final Waste Forms

Sampling Point: Final Waste Forms

Technique Name: Sampling and Sample Preparation

Description: Punch Cores

Application - Sampling technique for solid materials.

Summary - Solid materials such as final waste forms including sludges, concretes can be sampled by collecting cores from core punching equipment.

Costs:

Instrument/Equipment _____

Per Sample _____ or Operating Costs/yr _____

Capability and Limitations:

Advantages -

Commercial equipment is available.

Limitations -

May not be applicable to metallic final waste forms.

Accuracy routinely achieved/expected under these conditions -

N/A

Status: Accepted technology

Sampling Point: Final Waste Forms

Technique Name: Sampling and Sample Preparation

Description: Microwave Assisted Acid Digestion

Application - Solid matrix materials can rapidly digested for the determination of inorganic elements.

Summary - A representative sample of a solid matrix material including final waste forms such as sludge and concrete is digested with concentrated acid in a closed teflon vessel using microwave heating with a suitable microwave unit.

Costs:

Instrument/Equipment $25-50K

Per Sample $25 or Operating Costs/yr _____

Capability and Limitations:

Advantages -

Effective in digesting and extracting trace elements from soils and complex matrices prior to analysis. This is an emerging technology that shows much promise in reducing the amount of work produced in sample analysis as well as increasing the quality of the data obtained.

Limitations -

May not be applicable to the digestion of metallic final waste form samples.

Accuracy routinely achieved/expected under these conditions -

N/A

Status: Accepted technology

Sampling Point: Final Waste Forms

Technique Name: Laboratory Characterization and Analysis

Description: Flame Atomic Absorption (FAA) Spectrophotometry

Application - A technique for the determination of metals and metalloids. Samples must be subjected to an appropriate dissolution step prior to analysis.

Summary - Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. Atomic absorption spectrophotometry is based on the absorption of radiation from a line spectral source of the analyte being determined by ground state analyte atoms. In FAA either a nitrous-oxide/acetylene or air acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state making analyte atoms available for absorption of light. Absorbance is measured as a function of analyte concentration.

Costs:

Instrument/Equipment $60K

Per Sample $25-50/determination or Operating Costs/yr

Capability and Limitations:

Advantages -

It is a standard, well-accepted methodology for sensitive and selective determination of single elements, metals and some metalloids.

Limitations -

Samples must be solubilized. If proper flame and analytical conditions are not used, chemical and conization interference can occur.

Accuracy routinely achieved/expected under these conditions -

3-5%

Status: Accepted technology

MLLW Workshop - Final Waste Forms

Sampling Point: Final Waste Forms

Technique Name: Sampling and Sample Preparation

Description: Sample Mixing and Homogenization

Application - Mixing and homogenization of final waste form samples.

Summary - Samples of the final waste materials are collected for characterization and assessment of product material. Samples will need to be prepared for analysis.

Costs:

Instrument/Equipment $300K

Per Sample _____ or Operating Costs/yr _____

Capability and Limitations:

Advantages -

Equipment for mixing and homogenizing solid materials is available.

Limitations -

Equipment has not been specifically designed for use with radioactive samples.

Accuracy routinely achieved/expected under these conditions -

N/A

Status: Accepted technology

Sampling Point: Final Waste Forms

Technique Name: Sampling and Sample Preparation

Description: Toxicity Characterization Leaching Procedure (TCLP)

Application - The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

Summary - The particle size of the solid waste form is reduced, if necessary. The solid is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter. The extraction fluid is analyzed.

Costs:

Instrument/Equipment $2-3K

Per Sample _____ or Operating Costs/yr _____

Capability and Limitations:

Advantages -

"Satisfactory" test if this procedure is meaningful for the prescribed disposal conditions.
Limitations -

The test may not be meaningful for the prescribed disposal conditions. Potential interferences may be encountered during analysis.

Accuracy routinely achieved/expected under these conditions -

N/A

Status: Accepted technology

Sampling Point: Final Waste Forms

Technique Name: Laboratory Characterization and Analysis

Description: Cold Vapor Atomic Absorption (CVAA) Spectrophotometry

Application - A technique for the determination of mercury. Samples must be subjected to an appropriate dissolution step prior to analysis.

Summary - Prior to analysis, solid or semi-solid samples must be prepared according to the appropriate dissolution procedures. The CVAA technique is based on the absorption of radiation at the 253.7-nm wavelength by the mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

Costs:

Instrument/Equipment $25-30K

Per Sample $50 or Operating Costs/yr

Capability and Limitations:

Advantages -

Highly sensitive and selective for mercury. In widespread routine use.

Limitations -

Limited to the determination of mercury. High concentrations of sulfide, copper, chloride and certain volatile organic compounds may cause interferences.

Accuracy routinely achieved/expected under these conditions -

5-10%

Status: Accepted technology

Sampling Point: Final Waste Forms

Technique Name: Laboratory Characterization and Analysis

Description: Graphite Furnace Atomic Absorption (GFAA) Spectrophotometry

Application - A technique for the determination of metals and metalloids. Samples must be subjected to an appropriate dissolution step prior to analysis.

Summary - Prior to analysis, samples must be solubilized or digested using appropriate. Sample Preparation Methods. Atomic absorption spectrophotometry is based on the absorption of radiation from a line spectral source of the analyte being determined by ground state analyte atoms. In GFAA an electrically heated graphite furnace is used as an energy source to dissociate the sample into the free atomic state making atoms available for absorption of light. Absorption, either peak height or peak area, is measured as a function of the analyte concentration.

Costs:

Instrument/Equipment $75K

Per Sample $50-100/determination or Operating Costs/yr _____

Capability and Limitations:

Advantages -

It is a standard, well-accepted methodology for sensitive and selective determination of single elements, metals and some metalloids.

Limitations -

Samples must be solubilized. Because the technique is so sensitive, interferences can be a problem.

Accuracy routinely achieved/expected under these conditions -

5-10%

Status: Accepted technology

Sampling Point: Final Waste Forms

Technique Name: Laboratory Characterization and Analysis

Description: Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)

Application - A technique for the determination of metals and metalloids. Samples must be subjected to an appropriate digestion prior to analysis.

Summary - Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. The technique measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line are monitored by photomultiplier tubes. Depending on the instrument analytes can be determined simultaneously or sequentially.

Costs:

Instrument/Equipment $150-200K

Per Sample $100-150 or Operating Costs/yr _____

Capability and Limitations:

Advantages -

It is a standard, well-accepted methodology. It allows multielement determinations.

Limitations -

Samples must be in solution. Background and spectral interferences can occur; appropriate corrections must be made.

Accuracy routinely achieved/expected under these conditions -

3-5%

Status: Accepted technology

Sampling Point: Final Waste Forms

Technique Name: Laboratory Characterization and Analysis

Description: Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS)

Application - Inductively coupled plasma-mass spectrometry (ICP-MS) is a technique which is applicable to μg/L concentrations of a large number of elements in water and wastes after appropriate sample preparation steps are taken.

Summary - Prior to analysis, samples which require total values must be digested using appropriate sample preparation methods. The technique measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of a water-cooled interface, into a quadrupole mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier.

Costs:

Instrument/Equipment $250-300K

Per Sample $100-200 or Operating Costs/yr

Capability and Limitations:

Advantages -

It has multielement capability. Isotopic analyses can be performed.

Limitations -

Solution samples should have low dissolved solids. Interferences for background ions from the plasma gas, reagents, and sample matrix constituents must be corrected.

Accuracy routinely achieved/expected under these conditions -

0.2-0.5%

Status: Evolving technology

APPENDIX F

Appendix F

Bibliography for Characterization of Low-Level Waste

Clare Gerlach

Introduction to Bibliography

A series of institutions were searched via INTERNET on-line computer catalogs to establish this appendix. References listed here are from the libraries of the University of Nevada, Las Vegas, the University of Texas, Austin, the University of Waterloo, Ontario, the Massachusetts Institute of Technology, and the Dialog Database.

Each system has its own individual search software. Some can only search one word at a time, others can use combinations of multiple one-word searches, and others can search multiword phrases. For the present search tens of search combinations were employed using allowable combinations of the one-word search terms: low-level, waste, radioactive, containerized, characterization, disposal, treatment, mixed, nuclear, medium-level, dumping, and sludge. Thus, the references are not limited to mixed waste or low-level waste. Nonetheless, the techniques described may be useful for MLLW.

This is by no means a comprehensive bibliography, but it should provide the interested reader with a broad background in the topic and lead to identification of additional references.

Information Available Through the Government Documents Repositories at the University of Nevada System

Current Sudoc = Library Call Number for the University of Nevada System
GPO Item No. = U.S. Government Printing Office Item Acquisition Number
MF = Microfiche

Current SuDoc: Y 3.N 88:25/4162
GPO Item No.: 1051-H-11 (MF)
Title: Survey of statistical and sampling needs for environmental monitoring of commercial low-level radioactive waste disposal facilities / prepared by L.L. Eberhardt, J.M. Thomas.
Description: 1 v. (various pagings) : ill. ; 28 cm.
Author: Eberhardt, L. L. (Lester Lee)
Date: 1986

Current SuDoc: E 1.28:ICP-1187
GPO Item No.: 429-T-4 (MF)
Title: Methods evaluation for the continuous monitoring of carbon-14, krypton-85, and iodine-129 in nuclear fuel reprocessing and waste solidification facility off-gas / S.J. Fernandez et al.
Author: Idaho National Engineering Laboratory.
Description: v, 28 p. : ill. ; 28 cm.
Date: 1979
Location: UNR Government Publications

Current SuDoc: E 1.28:ICP-1174
GPO Item No.: 429-T-4 (MF)
Title: Methods evaluation and development for the monitoring of technetium-99 and selenium-79 in nuclear fuel reprocessing and waste solidification facility off-gas / by S. J. Fernandez, R. C. Girth; prepared for the Department of Energy, Idaho Operations Office
Author: Fernandez, S. J. (Steven Joseph)
Description: iii, 27 p. : ill., graphs ; 28 cm.
Date: 1978

Current SuDoc: EP 1.89/2:W 28/12
GPO Item No.: 431-L-12
Title: Securing containerized hazardous wastes with welded polyethylene encapsulates
Author: H.R. Lubowitz et al.
Description: 3, [1] p. : ill. ; 28 cm.
Date: 1981

Current SuDoc: EP 6.10/7:77-3
GPO Item No.: 431-I-61
Title: Characterization of selected low-level radioactive waste generated by four commercial light-water reactors.
Author: Dames & Moore.
Description: 77 p. in various pagings : ill. ; 28 cm.
Series: United States. Environmental Protection Agency. Office of Radiation Programs. Technical note - Office of Radiation Programs; ORP/TAD-77-3.
Date: 1977

Current SuDoc: Y 3.N 88:25/5343
GPO Item No.: 1051-H-11 (MF)
Title: Radionuclide characterization of reactor decommissioning waste and spent fuel assembly hardware: progress report
Author: D.E. Robertson et al.
Description: 1 v. (various pagings) : ill. ; 28 cm.
Date: 1991

Current SuDoc: GA 1.13:RCED-87-103 FS
GPO Item No.: 546-D (MF)
Title: Nuclear waste : status of DOE's nuclear waste site characterization activities : fact sheet for the chairman, Subcommittee on Energy and Power, Committee on Energy and Commerce, House of Representatives / United States General Accounting Office.
Description: 41 p. : ill. ; 28 cm.
Date: 1987

Current SuDoc: E 1.28:DP-1483
GPO Item No.: 429-T-4 (MF)
Title: Chemical characterization of SRP waste tank sludges and supernates
Author: Gray, L. W. (Lucinda Wentworth), M. Y. Donnan, B. Y. Okamoto
Description: 140 p. : ill., graphs ; 27 cm.
Date: 1979

Current SuDoc: Y 3.N 88:25/5343
GPO Item No.: 1051-H-11 (MF)
Title: Radionuclide characterization of reactor decommissioning waste and spent fuel assembly hardware: progress report
Author: D.E. Robertson et al.
Description: 1 v. (various pagings) : ill. ; 28 cm.
Date: 1991

Current SuDoc: E 1.28/15:
GPO Item No.: 474-B-8
Title: Annual water quality data report for the Waste Isolation Pilot Plant.
Description: v. : ill., maps ; 28 cm.
Date: 1986

Current SuDoc: Y 3.N 88:25/4938
GPO Item No.: 1051-H-11 (MF)
Title: Occupational radiation exposures associated with alternative methods of low-level waste disposal **Author:** Herrington, W. N., R. Harty, S.E. Merwin.
Description: 1 v. (various pagings) : ill. ; 28 cm.
Date: 1987

Current SuDoc: C 13.58:81-2409
GPO Item No.: 247-D (MF)
Title: Bibliography of literature on underground corrosion of metals and alloys considered for use in the construction of containers for nuclear waste
Author: Sanderson, B. T., J. Kruger; prepared for U.S. Department of Energy.
Description: 43 p. ; 28 cm.
Series: NBSIR ; 81-2409
Date: 1982

Current SuDoc: Y 4.En 2:S.hrg.100-293
GPO Item No.: 1040-A, 1040-B (MF)
Title: Civilian radioactive waste disposal : hearings before the Committee on Energy and Natural Resources, United States Senate, One hundredth Congress, first session, on S. 1007 ... S. 1141 ... S. 1211 ... S. 1266 ... S. 1428, July 16 and 17, 1987.
Author: United States. Congress. Senate. Committee on Energy and Natural Resources.
Description: iii, 618 p. : ill., maps ; 24 cm.
Series: United States. Congress. Senate. S. hrg. ; 100-293.
Date: 1987

Current SuDoc: Y 3.N 88:25/4519
GPO Item No.: 1051-H-11 (MF)
Title: Technology, safety, and costs of decommissioning reference nuclear fuel cycle facilities : classification of decommissioning wastes
Author: Elder, H. K.
Description: 32 p. in various pagings : ill. ; 28 cm.
Date: 1986

Current SuDoc: E 1.28:PNL-2690
GPO Item No.: 429-T-4 (MF)
Title: Conceptual design of a nuclear waste vitrification facility
Author: D. E. Larson et al. Pacific Northwest Laboratory.
Description: viii, 57 p. : ill. ; 28 cm.
Date: 1978

Current SuDoc: E 1.28:PNL-3129
GPO Item No.: 429-T-4 (MF)
Title: Environmental control aspects for fabrication, reprocessing, and waste disposal of alternative LER and LMBR fuels
Author: Nolan, A. M., M. A. Lewallen, G. W. McNair.
Description: ca 100 p. in various pagings : ill. ; 28 cm.
Date: 1979

Current SuDoc: E 1.28:PNL-3038
GPO Item No.: 429-T-4 (MF)
Title: Technical summary, Nuclear waste vitrification project
Author: E. J. Wheelwright et al. Pacific Northwest Laboratory.
Description: viii, 67 p. : ill. (some col.) ; 28 cm.
Date: 1979

Current SuDoc: E 1.28:DP-1535
GPO Item No.: 429-T-4 (MF)
Title: Small-scale, joule-heated melting of Savannah River Plant waste glass
Author: Plodinec, M. J., P. H. Chismar.
Description: 30 p. : ill. ; 28 cm.
Date: 1979

Current SuDoc: E 1.28:DP-1498
GPO Item No.: 429-T-4 (MF)
Title: Evaluation of glass as a matrix for solidifying Savannah River Plant waste : properties of glasses containing Li40
Author: Plodinec, M. J., J. R. Wiley.
Description: 40 p. : ill., graphs ; 28 cm.
Date: 1979

Current SuDoc: E 1.28:DP-1488
GPO Item No.: 429-T-4 (MF)
Title: Electrical resistivities of glass melts containing simulated SRP waste sludges
Author: Wiley, J. R. (John Robert), prepared for the U.S. Department of Energy
Description: 23 p. : ill., graphs ; 28 cm.
Date: 1978

Current SuDoc: E 1.28:DP-1483
GPO Item No.: 429-T-4 (MF)
Title: Chemical characterization of SRP waste tank sludges and supernates
Author: Gray, L. W. (Lucinda Wentworth), M. Y. Donnan, B. Y. Okamoto; prepared for the U.S. Department of Energy
Description: 140 p. : ill., graphs ; 27 cm.
Date: 1979

Current SuDoc: E 1.28:ORNL/TM:6350
GPO Item No.: 429-T-4 (MF)
Title: A literature survey : methods for the removal of iodine species from off-gases and liquid waste streams of nuclear power and nuclear fuel reprocessing plants, with emphasis on solid sorbents
Author: Holladay, D. W.
Description: vi, 165 p. : ill. ; 28 cm.
Date: 1979

Current SuDoc: E 1.18:0028/v.1-5
GPO Item No.: 429-P
Title: Technology for commercial radioactive waste management.
Author: United States. Dept. of Energy. Office of Nuclear Waste Management.
Description: 5 v. : ill. ; 28 cm.
Date: 1979

Current SuDoc: ER 1.11:CONF-770102
GPO Item No.: 1051-C
Title: Ceramic & glass radioactive waste forms
Author: Compiled & edited by D. W. Readey, C. R. Cooley
Description: 282 p. in various pagings : ill. ; 27 cm.
Date: 1977

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Title: Activities related to low - level radioactive waste management at AECL
Author: Atomic Energy of Canada Limited.
Imprint: Pinawa, Man. : Whiteshell Nuclear Research Establishment, 1987.
Call Number: CA1 AE 685T360 v. 2

Title: Activities related to low - level radioactive waste management at AECL
Imprint: Chalk River, Ont. : Chalk River Nuclear Laboratories, 1987.
Author: Atomic Energy of Canada Limited.
Call Number: CA1 AE 685T360 v. 3

Title: Activities related to low-level radioactive waste management at AECL
Author: Atomic Energy of Canada Limited.
Imprint: Chalk River, Ont. : Chalk River Nuclear Laboratories, 1988.
Call Number: CA1 AE 685T360 v. 4

Title: Activities related to low-level radioactive waste management at AECL
Author: Atomic Energy of Canada Limited.
Imprint: Chalk River, Ont. : Chalk River Nuclear Laboratories, 1988.
Call Number: CA1 AE 685T360 v. 5

Title: Analytical source term for a low-level radioactive waste repository.
Author: Atomic Energy of Canada Limited.
Imprint: Chalk River, Ont. : Chalk River Laboratories, 1991.
Call Number: CA1 AE 690T510

Title: Stability of candidate buffer materials for a low-level radioactive waste repository.
Imprint: Pinawa, Man. : Whiteshell Nuclear Research Establishment, 1991.
Physical Description: 33 p.
Series: Atomic Energy of Canada Limited. Technical record TR ; 513
Associated Name(s): Torok, J.
Issuing Body: Atomic Energy of Canada Limited.

Title: A waste characterization monitor for low - level radioactive waste management.
Imprint: Chalk River, Ont. : Chalk River Nuclear Laboratories, 1985.
Physical Description: 6 p.
Series: Atomic Energy of Canada Limited. AECL, 0067-0367 ; 8851
Associated Name(s): Davey, E. C. Csullog, G. W. Kupca, S.
Issuing Body: Atomic Energy of Canada Limited.

Title: Low - Level Radioactive Waste Management - Consultant Report.
Author: California. Energy Resources Conservation and Development Commission
Call Number: US2CAER 78L54

Title: Low-level radioactive waste : from cradle to grave
Author: Edward L. Gershey
Subject(s): Radioactive wastes. Low-level radiation - Environmental aspects.
Imprint: New York : Van Nostrand Reinhold, c1990.
Notes: Bibliography: p. 177-180. Includes index.
ISBN: 0442239580

Title: The management and disposal of intermediate and low level radioactive waste. -
Subject(s): Radioactive waste disposal - Management.
Imprint: London : Mechanical Engineering Publications for the Institution of Mechanical Engineers, 1987.
Notes: "Papers presented at a seminar organized by the Nuclear Energy Committee of the Power Industries Division of the Institution of Mechanical Engineers and held at the Institution of Mechanical Engineers on 19 March, 1987." Includes bibliographies.
ISBN: 0852986238 (pbk.)
Physical Description: 51 p. : ill. ; 30 cm.
Associated Name(s): Institution of Mechanical Engineers (Great Britain). Nuclear Energy Committee.

Title: Safe disposal of radionuclides in low-level radioactive-waste repository sites : Low-Level Radioactive-Waste Disposal Workshop, U.S. Geological Survey, July 11-16, 1987, Big Bear Lake, Calif., proceedings.
Imprint: [United States : s.n.], 1990.
Physical Description: ix, 125 p. : ill., maps.
Series: United States. Geological Survey. Circular ; 1036
Associated Name(s): Bedinger, M. S. Stevens, Peter R. (Peter Ryan), United States. Geological Survey.
Government Document Number: I19.4/2:1036

Title: A planner's guide to low-level radioactive waste disposal
Author: Smith, Thomas P.
Subject(s): Radioactive waste disposal - United States. Radioactive waste disposal - Law and legislation - United States. Radioactive wastes - Transportation.
Imprint: Washington, D.C. : American Planning Association, 1982.
Notes: Cover title. Bibliography: p. 48-53.
Physical Description: 53 p. : ill. ; 28 cm.
Series: Report / American Planning Association. Planning Advisory Service ; no. 369

Title: Radioactive dating and methods of low-level counting : proceedings Monaco, 2-10 March 1967.
Imprint: Vienna, Austria : International Atomic Energy Agency, c1967.
Physical Description: 744 p. : ill.
Series: Proceedings series (International Atomic Energy Agency), 0074-1884
Associated Name(s): International Atomic Energy Agency. Joint Commission on Applied Radioactivity.
Government Document Number: STI/PUB/152

Title: Low-level radioactive waste : joint hearing [microform].
Imprint: Washington, D.C. : USGPO, 1989.
Notes: Microfiche : [Bethesda, Md.] : Congressional Information Service, 1990 - 1 microfiche.
Physical Description: iv, 11 p.
Associated Name(s): United States. Congress. House. Committee on Interior and Insular Affairs. Subcommittee on Energy and the Environment.
Issuing Body: United States. Congress. House. Committee on Energy and Commerce. Subcommittee on Energy and Power.

Title: Specification and performance of on-site instrumentation for continuously monitoring radioactivity in effluents.
Subject(s): Radioactive waste disposal. Radioactivity - Instruments - Standards - United States. Nuclear facilities - Equipment and supplies - Standards - United States.
Imprint: New York, N.Y. : Institute of Electrical and Electronics Engineers, 1980, c1974.
Notes: Sponsors, Atomic Industrial Forum and Institute of Electrical and Electronics Engineers. Approved September 19, 1974, reaffirmed August 15, 1980, American National Standards Institute. "Formerly designated as ANSI N13.10-1974." Original designation covered by label. Includes bibliographical references.
Issuing Body: American National Standards Institute.

Title: Geochemical aspects of radioactive waste disposal
Author: Brookins, Douglas G.
Subject(s): Radioactive waste disposal. Geochemistry.
Imprint: New York : Springer-Verlag, c1984.
Notes: Bibliography: p. [307]-328. Includes index.
ISBN: 0387909168 3540909168
Physical Description: xiii, 347 p. : ill. ; 25 cm.

Title: Denitration of radioactive liquid waste / edited by L. Cecille and S. Halaszovich.
Subject(s): Radioactive waste disposal. Nitrification.
Imprint: London : Graham and Trotman for the Commission of the European Communities, 1986.
Notes: Conference proceedings. Includes bibliography.
ISBN: 0860108546 (pbk.)
Physical Description: viii, 180 p. : ill. ; 24 cm.
Related Work(s): Cecille, L. Halaszovich, S. Commission of the European Communities.

Title: Research and development on radioactive waste management and storage : second annual progress report of the European Community Programme, 1980-1984.
Subject(s): Radioactive waste disposal.
Imprints: New York : Harwood Academic Publishers ; Brussels : For Commission of the European Communities, c1982.
ISBN: 3718601486 (The Commission)
Physical Description: 310 p. : ill. ; 23 cm.
Series: Radioactive waste management (New York, N.Y.) ; v. 8.
Associated Name(s): Commission of the European Communities.

Title: Disposal of radioactive wastes / Zdenek Dlouhy ; contributions, Frantisek Cejnav et al.
Author: Dlouhy, Zdenek
Subject(s): Radioactive waste disposal.
Imprint: Amsterdam : Elsevier Scientific Pub. Co., 1982.
Notes: Translated from the Czech. Includes bibliographical references and index.
ISBN: 0444997245
Physical Description: 264 p. : ill. ; 25 cm.
Series: Studies in environmental science ; 15

Title: Treatment, recovery, and disposal processes for radioactive wastes : recent advances / edited by J.I. Duffy.
Subject(s): Radioactive waste disposal.
Imprint: Park Ridge, N.J. : Noyes Data Corp., 1983.
Notes: Includes indexes.
ISBN: 0815509227
Physical Description: xii, 287 p. : ill. ; 25 cm.
Series: Pollution technology review, 0090-516X ; no. 95 Chemical technology review ; no. 216.

Title: Testing and evaluation of solidified high level radioactive waste / edited by A.R. Hall.
Subject(s): Radioactive waste disposal.
Imprint: London : Graham & Trotman for the Commission of the European Communities, 1987.
Notes: Includes bibliographies.
ISBN: 0860108937 0860109291 (Series)
Physical Description: 354 p. : ill. ; 24 cm.
Series: Radioactive waste management series

Title: Radioactive waste forms for the future / edited by Werner Lutze, Rodney C. Ewing.
Subject(s): Radioactive waste disposal.
Imprint: Amsterdam : North-Holland, 1988.
Notes: Includes bibliographies and indexes.
ISBN: 0444871047
Physical Description: xiii, 778 p. : ill. ; 25 cm.

Title: Radioactive waste technology / sponsored by the American Society of Mechanical Engineers and American Nuclear Society ; edited by A. Alan Moghissi, Herschel W. Godbee, Sue A. Hobart.
Subject(s): Radioactive waste disposal.
Imprint: New York, N.Y. : American Society of Mechanical Engineers, c1986.
Notes: Includes bibliographies.
Physical Description: x, 705 p. : ill. ; 27 cm.

Title: Understanding radioactive waste
Author: Murray, Raymond LeRoy
Subject(s): Radioactive wastes. Radioactive waste disposal.
Edition: 2nd ed.
Imprint: Columbus : Battelle Press, c1983.
ISBN: 0935470190 (pbk.)
Physical Description: ix, 117 p. : ill. ; 28 cm.

Title: Radioactive waste disposal.
Author: Roy, Rustum.
Subject(s): Radioactive waste disposal.
Imprint: New York : Pergamon Press, 1982
Notes: Includes bibliographical references.
Contents: v. 1. The waste package
ISBN: 0080275419 (v. 1)
Physical Description: v. : ill. ; 25 cm.

Title: Die Reinigung radioaktiv kontaminierter Abwasser durch Kontaktenthartung und Ionenaustausch. Mit 91 Abb., davon 60 Abb. auf 23 Taf., u. 67 Tab.
Author: Sachse, Gunter.
Subject(s): Radioactive waste disposal. Sewage - Purification - Ion exchange process. Water - Softening.
Imprint: Berlin, Akademie-Verl., 1971.
Notes: Bibliography: p. [130]-131.
Physical Description: 131 p. illus. 30 cm.
Series: Abhandlungen der Sachsischen Akademie der Wissenschaften zu Leipzig. Mathematisch-naturwissenschaftliche Klasse, Bd. 50, Heft 4

Title: Radioactive waste : issues and answers / American Institute of Professional Geologists ; [Fred Schroyer, compiler].
Subject(s): Radioactive waste disposal
Imprint: Arvada, Colo. : The Institute, 1985.
Notes: Cover title. Bibliography: p. 27.
Physical Description: 27 p. : col. ill. ; 28 cm.

Title: Radioactive waste management
Author: Tang, Y. S. (Yu S.), James H. Saling.
Subject(s): Radioactive waste disposal. Uranium mill tailings.
Imprint: New York : Hemisphere Pub. Corp., c1990.
Notes: Includes bibliographies and index.
ISBN: 0891166661
Physical Description: xi, 460 p. : ill. ; 24 cm.
Associated Name(s): Saling, James H.

References Available from Massachusetts Institute of Technology Library

Title: Conditioning of low- and intermediate-level radioactive wastes.
Edition: 1983.
Imprint: Vienna : International Atomic Energy Agency ; [New York : Exclusive sales agent in the United States of America, UNIPUB],
Call Number: HD9698.A1.I61 no.222

Title: Geochemical behavior of disposed radioactive waste
Author: Barney, G.S., J.D. Navratil, W.W. Schultz
Imprint: Washington, D.C. : American Chemical Society, 1984.
Physical Features: ix, 413 p. : ill ; 24 cm.
Series: ACS symposium series, 0097-6156 ; 246
Notes: Includes bibliographical references and indexes. "Based on a symposium jointly sponsored by the Divisions of Nuclear Chemistry and Technology, Industrial and Engineering Chemistry, and Geochemistry at the 185th Meeting of the American Chemical Society, Seattle, Washington, March 20-25, 1983".

Title: Geological disposal of radioactive waste : research in the OECD area : national and international research activities related to geological disposal of radioactive waste / Coordinating Group on Geological Disposal of Radioactive Waste, Nuclear Energy Agency, Organization for Economic Co-operation and Development.
Imprint: Paris : Nuclear Energy Agency, OECD, 1982.
Physical Features: 54 p. : ill., maps ; 24 cm.
Notes: Bibliography: p. 50-51.
Other Authors, etc: OECD Nuclear Energy Agency. Coordinating Group on Geological Disposal of Radioactive Waste.
Subjects: Radioactive waste disposal in the ground.

Title: Proceedings of the Workshop on Geological Disposal of Radioactive Waste: In Situ Experiments in Granite. Stockholm, Sweden 25th-27th October 1982
Author: Workshop on Geological Disposal of Radioactive Waste: In Situ Experi...
Edition: 1983.
Imprint: Paris : Nuclear Energy Agency, Organization for Economic Cooperation and Development
Call Number: TD898.W595 1982

Title: Design and instrumentation of in situ experiments in underground laboratories for radioactive waste disposal : proceedings of a workshop jointly organized by the Commission of the European Communities & OECD Nuclear Energy Agency, Brussels, 15-17 May 1984
Edition: 1985.
Imprint: Rotterdam ; Boston : Published for the Commission of the European Communities by A.A. Balkema,
Call Number: TD898.D47 1985

Title: A study of the lime-soda softening process as a method for decontaminating radioactive waters / by Robert F. McCauley,
Author: McCauley, Robert F., Robert A. Lauderdale and Rolf Eliassen.
Imprint: Cambridge, Mass. : Sedgwick Laboratories of Sanitary Science, Massachusetts Institute of Technology, 1953.
Physical Features: vi, 88 p. : ill. ; 28 cm.
Notes: Includes bibliographical references (p. 87-88). "NYO 4439."
Subjects: Radioactive pollution of water. Radioisotopes. Water -- Purification -- Lime-soda ash process.

Title: Management of low-level radioactive waste / edited by Melvin W. Carter, A. Alan Moghissi, Bernd Kahn.
Imprint: New York : Pergamon Press, c1979.
Physical Features: 2 v. (1214 p.) : ill. ; 24 cm.
Notes: Includes bibliographies and index. Based on papers presented at a symposium sponsored by Georgia Institute of Technology, and others, held May 23-27, 1977, in Atlanta.
Subjects: Radioactive waste disposal -- Congresses. Nuclear facilities -- Waste disposal -- Congresses. **LC Card:** 78-27550
ISBN: 0080239072

Title: Partnerships under pressure : managing commercial low-level radioactive waste.
Imprint: Washington, DC : Congress of the U.S., Office of Technology Assessment : For sale by the Supt. of Docs., U.S. G.P.O., 1989
Physical Features: vii, 153 p. : ill. ; 26 cm.
Notes: Include bibliographical references. Shipping list no.: 90-011-P. November 1989--P. [4] of cover. "OTA-O-426"--P. [4] of cover.
Other Authors, etc: United States. Congress. Office of Technology Assessment.
Other Titles: Managing commercial low level radioactive waste.
Subjects: Radioactive waste disposal -- United States -- Management. Radioactive waste disposal -- Research -- United States. Hazardous waste management industry -- United States.
LC Card: 89-600772
Government Document Number: Y 3.T 22/2: 2 P 25
Publisher's Number: Tech.Report no.: OTA-O-426

Title: Proceedings of the Meeting on Low Level Radioactive Waste held at Incline Village, Nevada, February 20-21, 1980 / Office of State Programs, U.S. Nuclear Regulatory Commission [and] Department of Human Resources, State of Nevada.
Author: Meeting on Low Level Radioactive Waste (1980 : Incline Village, NV)
Imprint: Washington, D.C. : The Commission : Available from GPO Sales Program, Division of Technical Information and Document Control, U.S. Nuclear Regulatory Commission ; Springfield, Va. : National Technical Information Service, 1980.
Physical Features: vi, 96 p. : ill. : 28 cm.
Notes: Date published: July 1980.
Other Authors, etc: Nevada. Dept. of Human Resources. U.S. Nuclear Regulatory Commission. Office of State Programs.

Title: Monitoring of radioactive contamination on surfaces; a manual prepared by R.F. Clayton. **Author:** Clayton, R.F.
Imprint: Vienna, International Atomic Energy Agency, 1970.
Physical Features: 33 p. illus. 24 cm.
Series: Technical reports series, no. 120 International Atomic Energy Agency. Technical reports series, no. 120 cn
Notes: Bibliography: p. 30-33. "STI/DOC/120."
Subjects: Contamination (Technology). Radioactivity -- Safety measures.
LC Card: 71-524940

Title: Proceedings of the Seminar on the Monitoring of Radioactive Effluents seminar organized by the OECD Nuclear Energy Agency, in collaboration with the German Ministry for Research and Technology and the Karlsruhe Nuclear Research Centre.
Author: Seminar on the Monitoring of Radioactive Effluents, Karlsruhe, 1974.
Imprint: Paris : OECD, 1974.
Physical Features: 446 p. : ill. ; 24 cm.
Notes: Includes bibliographical references. On cover: Monitoring of radioactive effluents. English or French; summaries in English and French.
Other Authors, etc: Organization for Economic Cooperation and Development. Nuclear Energy Agency.
Other Titles: Monitoring of radioactive effluents.

Title: A planner's guide to low-level radioactive waste disposal.
Author: Smith, Thomas P.
Imprint: Chicago, IL (1313 E. 60th St., Chicago 60637) : American Planning Association, 1982. **Physical Features:** 53 p. : ill. ; 28 cm.
Series: Report / American Planning Association, Planning Advisory Service ; no. 369.
Notes: Bibliography: p. 48-53. Cover title.
Other Authors, etc: American Planning Association.
Subjects: Radioactive waste disposal in the ground, Handbooks, manuals, etc., Factory and trade waste, Handbooks, manuals, etc.
LC Card: 83-105921//r83

Title: Radiation protection principles for the disposal of solid radioactive waste : a report / of Committee 4 of the International Commission on Radiological Protection.
Author: International Commission on Radiological Protection. Committee 4.
Edition: 1st ed.
Imprint: Oxford ; New York : published for the Commission by Pergamon Press, 1985.
Physical Features: v, 23 p. : ill. ; 25 cm.
Series: ICRP publication, 0146-6453 ; 46 Annals of the ICRP ; v. 15, no. 4
Notes: Bibliography: p. 23. At head of title: Radiation protection. "Adopted by the Commission in July 1985."
Subjects: Radioactive waste disposal -- Management. Radiation -- Safety measures.
ISBN: 0080336663

Title: Principles of monitoring for the radiation protection of the population : a report
Author: International Commission on Radiological Protection. Committee 4.
Edition: 1st ed.
Imprint: Oxford ; New York : published for the Commission by Pergamon,
Call Number: RA1231.R2.I614 no.43

Title: Management of radioactive waste : the issues for local authorities : proceedings of the conference organized by the National Steering Committee, Nuclear Free Local Authorities, and held in Manchester on 12 February 1991 / edited by Stewart Kemp.
Imprint: London : Thomas Telford, 1991.
Physical Features: 177 p. : ill. ; 24 cm.
Notes: Includes bibliographical references.
Other Authors, etc: Kemp, Stewart. Nuclear Free Local Authorities (Great Britain). National Steering Committee.
Subjects: Radioactive waste disposal -- Great Britain -- Congresses.
ISBN: 0727716441

Title: Radioactive waste management.
Author: Berlin, Robert E., Catherine C. Stanton.
Imprint: New York : Wiley, c1989.
Physical Features: xvi, 444 p. : ill. ; 25 cm.
Notes: Includes bibliographies and index. "A Wiley-Interscience publication."
Other Authors, etc: Stanton, Catherine C.
Subjects: Radioactive waste disposal -- United States. Radioactive waste sites -- United States.
LC Card: 88-17359
ISBN: 0471857920

Title: Denitration of radioactive liquid waste / edited by L. Cecille and S. Halaszovich.
Imprint: London ; Norwell, Mass. : Graham and Trotman for the Commission of the European Communities, 1986.
Physical Features: viii, 180 p. : ill. ; 24 cm.
Series: Radioactive waste management series
Notes: Includes bibliographies. "EUR 10650" Conference proceedings.
Other Authors, etc: Cecille, L. Halaszovich, S. Commission of the European Communities.
Subjects: Radioactive waste disposal. Nitrification.
LC Card: G.B. 86-27362
ISBN: 0860108546 (pbk) :
Publisher's Number: Tech.Report no.: EUR 10650

Title: Radioactive waste technology / sponsored by the American Society of Mechanical Engineers and American Nuclear Society ; edited by A. Alan Moghissi, Herschel W. Godbee, Sue A. Hobart.
Imprint: New York, N.Y. (345 E. 47th St., New York 10017) : American Society of Mechanical Engineers, c1986.
Physical Features: x, 705 p. : ill. ; 27 cm.
Notes: Includes bibliographies.
Other Authors, etc: Moghissi, A. Alan. Godbee, H. W. Hobart, Sue A. American Society of Mechanical Engineers. American Nuclear Society.
Subjects: Radioactive waste disposal.
LC Card: 86-151343

Title: Radioactive waste management.
Author: Radioactive waste management (Chur, Switzerland : 1980)
Imprint: Chur [Switzerland] ; New York : Harwood Academic Publishers, c1980-c1982.
Physical Features: 2 v. : ill. ; 23 cm.
Notes: Quarterly (irregular) Indexed by Biological abstracts 0006-3169 Computer & control abstracts 0036-8113 Sept. 1980-June 1982 Electrical & electronics abstracts 0036-8105 Sept. 1980-June 1982 Physics abstracts. Science abstracts. Series A 0036-8091 Sept. 1980-June 1982 GeoRef 0197-7482 Title from cover. Continued by: Radioactive waste management and the nuclear fuel cycle 0739-5876 (DLC) 83648101 (OCoLC)9052909
Other Titles: Abbreviated title: Radioact. waste manage. (Chur, Switz. 1980)
LC Card: 83-648100
ISBN: ISSN: 0142-2405

Title: Radioactive waste management.
Imprint: Oak Ridge, Tenn. : Technical Information Center, U.S. Dept. of Energy, 1981.
Physical Features: v.; 28 cm.
Notes: Semimonthly "A current awareness bulletin." Caption title. PB81-902914.
Other Authors, etc: United States. Dept. of Energy. Technical Information Center.
Other Titles: Abbreviated title: Radioact. waste manage. (Oak Ridge, Tenn.)
Subjects: Radioactive wastes -- Abstracts -- Periodicals. Radioactive waste disposal -- Abstracts -- Periodicals.
LC Card: sn 81-476
ISBN: ISSN: 0275-3707

Title: The management of radioactive waste : a report by an international group of experts.
Imprint: London : Uranium Institute, 1991.
Physical Features: 70 p. : ill. ; 30 cm.
Notes: August 1991.
Other Authors, etc: Uranium Institute.
Subjects: Radioactive wastes -- Management. Radioactive wastes -- Management -- Case studies. Radioactive waste disposal. Radioactive waste disposal -- Case studies.
LC Card: 91-217337
ISBN: 0946777217

Title: Radioactive waste processing and disposal; an annotated bibliography of selected literature.
Imprint: Oak Ridge, Tenn. : United States Atomic Energy Commission, Technical Information Service etc.; Washington, D.C. : available from the Office of Technical Services, Dept. of Commerce etc.
Series: 1958, 1964-80: TID; 3311 1960-62: TID; 3555 1980: NUREG 643-644 1981 : DOE/TIC 3311
Other Authors, etc: Voress, Hugh E., Davis, Theodore F. United States. Atomic Energy Commission.
Subjects: Radioactive wastes -- Abstracts. Radioactive waste disposal -- Abstracts. Reactor fuel reprocessing -- Abstracts.

Title: Radioactive waste management at the Savannah River Plant : a technical review / Panel on Savannah River Waste, Board on Radioactive Waste Management, Commission on Natural Resources, National Research Council.
Imprint: Washington, D.C. : National Academy Press, 1981.
Physical Features: xii, 68 p. : ill. ; 28 cm.
Notes: Bibliography: p. 58-68.
Other Authors, etc: National Research Council. (U.S.) Panel on Savannah River Wastes.
Subjects: Atomic power-plants -- South Carolina -- Aiken -- Waste disposal. Radioactive waste disposal -- South Carolina -- Aiken.
LC Card: 81-85742
ISBN: 030903227X

Title: Management of radioactive waste from U.S. light-water reactor operation.
Author: Losk, Richard Bryan.
Imprint: c1978.
Physical Features: 50 [i.e. 49] leaves : ill., charts ; 28 cm.
Series: Massachusetts Institute of Technology. Dept. of Nuclear Engineering. Thesis. 1978. B.S. cn
Notes: Thesis (B.S.)--M.I.T., Dept. of Nuclear Engineering, 1978. Includes bibliographical references. Microfiche copy available in archives and science. Supervised by Irving Kaplan.
Subjects: Radioactive waste disposal. Reactor fuel reprocessing.

Title: Testing, evaluation, and shallow land burial of low and medium radioactive waste forms : proceedings of a seminar organized under the R & D Programme of the Commission of the European Communities on Radioactive Waste Management and Disposal, held at the Central Bureau for Nuclear Measurements, Geel, Belgium, 28-29 September 1983 / edited by W. Krischer and R. Simon.
Imprint: Chur, Switzerland ; New York, NY, U.S.A. : Hardwood Academic Publishers for the Commission of the European Communities, c1984.
Physical Features: xi, 227 p. : ill. ; 23 cm.
Series: Radioactive waste management, 0275-7573 ; v. 13
Notes: Includes bibliographies.
Other Authors, etc: Krischer, W., Simon, R., R & D Programme of the Commission of the European Communities on Radioactive Waste Management and Disposal.
Subjects: Radioactive waste disposal in the ground -- Congresses.

Title: Radioactive wastes at the Hanford Reservation : a technical review / Panel on Hanford Wastes, Committee on Radioactive Waste Management, Commission on Natural Resources, National Research Council.
Author: National Research Council. Panel on Hanford Wastes.
Imprint: Washington : National Academy of Sciences, 1978.
Physical Features: xvi, 269 p. : ill. ; 28 cm.
Notes: Bibliography: p. 253-269.
Subjects: Hanford Engineer Works. Nuclear facilities -- Washington (State) -- Hanford -- Waste Disposal. Radioactive waste disposal.
LC Card: 78-52310
ISBN: 0309027454

Title: Radioactive wastes from the nuclear fuel cycle / R. E. Tomlinson, editor ; [3 contributors] P. Auchapt et al.
Imprint: New York : American Institute of Chemical Engineers, 1976.
Physical Features: vi, 178 p. : ill. ; 28 cm.
Series: AIChE symposium series ; no. 154, v. 72 American Institute of Chemical Engineers. AIChE symposium series ; no. 154.
Notes: Includes bibliographical references. Papers from several symposia sponsored by the Nuclear Engineering Division of the American Institute of Chemical Engineers in 1975.
Other Authors, etc: Tomlinson, R. E., Auchapt, P. American Institute of Chemical Engineers. Nuclear Engineering Division.
Subjects: Atomic power-plants -- Waste disposal -- Addresses, essays, lectures. Reactor fuel reprocessing -- Waste disposal -- Addresses, essays, lectures.
LC Card: 76-23229

Title: Management of radioactive wastes from the nuclear fuel cycle : proceedings of a symposium on the management of radioactive wastes from the nuclear fuel cycle / jointly organized by the International Atomic Energy Agency and the OECD Nuclear Energy Agency and held in Vienna, 22-26 March 1976.
Imprint: Vienna : International Atomic Energy Agency ; New York : sold by UNIPUB, 1976.
Physical Features: 2 v. : ill. ; 24 cm.
Series: Proceedings series - International Atomic Energy Agency
Notes: Includes bibliographical references. "STI/PUB/433." English, French, Russian, or Spanish.

Title: Guide to the safe handling of radioactive wastes at nuclear power plants.
Imprint: Vienna : International Atomic Energy Agency, 1980.
Physical Features: 84 p. : ill. ; 24 cm.
Series: Technical reports series - International Atomic Energy Agency ; no. 198 Technical reports series (International Atomic Energy Agency) ; no. 198.
Notes: Bibliography: p. 48. "STI/DOC/10/198." Supplements much of no. 28 in the IAEA safety series, which was published under title: Management of radioactive wastes at nuclear power plants.
Other Authors, etc: International Atomic Energy Agency.
Other Titles: Management of radioactive wastes at nuclear power plants.
Subjects: Atomic power-plants -- Waste disposal. Radioactive waste disposal. Radioactivity -- Safety measures.
ISBN: 9201250800 :

Title: American National Standard N542 : sealed radioactive sources, classification.
Author: American National Standards Institute. Subcommittee N43-3.3.
Imprint: Washington : Dept. of Commerce, National Bureau of Standards : for sale by the Supt. of Docs., U.S. Govt. Print. Off., 1978.
Physical Features: vii, 20 p. ; 26 cm.
Series: NBS handbook ; 126 United States. National Bureau of Standards. Handbook ; 126.
Other Titles: Sealed radioactive sources, classification.
Subjects: Radioactive substances -- Safety measures -- Standards.
LC Card: 83-601612
Government Document Number: C 13.11: 126

Title: Table of radioactive isotopes / Edgardo Browne.
Author: Browne, Edgardo., Richard B. Firestone ; Virginia S. Shirley, editor.
Imprint: New York : Wiley, c1986.
Physical Features: xxiii, 29, [900] p. ; 29 cm.
Notes: Bibliography: p. xxii-xxiii. "A Wiley-Interscience publication."
Subjects: Radioisotopes -- Tables.
LC Card: 86-9069
ISBN: 047184909X

Title: Table of radioactive isotopes and of their main decay characteristics.
Author: J. Blachot, C. Fiche.
Imprint: Paris ; New York : Masson, 1981.
Physical Features: 218 p. : ill. ; 26 cm.
Series: Annales de physique, 0003-4169 ; v. 6, (suppl.)
Notes: Bibliography: p.4. Cover title: Tableau des isotopes radioactifs et des principaux rayonnements emis. "Numero special supplementaire." Chiefly tables. Includes indexes.
Other Titles: Tableau des isotopes radioactifs et des principaux rayonnements emis.
Subjects: Radioisotopes -- Decay -- Tables.

Title: The treatment and handling of radioactive wastes / edited by A.G. Blasewitz, J.M. Davis, M.R. Smith.
Imprint: Columbus, [Ohio] : Battelle Press ; New York : Springer Verlag, c1982.
Physical Features: xiii, 658 p. : ill. ; 29 cm.
Notes: Includes bibliographical references and indexes. Selected papers presented at the American Nuclear Society Topical Meeting on "The Treatment and Handling of Radioactive Wastes" held Apr. 19-22, 1982, in Richland, Wash.
Subjects: Radioactive waste disposal -- Congresses.
LC Card: 82-22695

Title: Treatment, recovery, and disposal processes for radioactive wastes : recent advances / edited by J.I. Duffy.
Imprint: Park Ridge, N.J. : Noyes Data Corp., 1983.
Physical Features: xii, 287 p. : ill. ; 25 cm.
Series: Pollution technology review, 0090-516X ; no. 95 Chemical technology review, no. 216 Chemical technology review ; no. 216.
Notes: Includes indexes.
Subjects: Radioactive waste disposal.
LC Card: 82-22260
ISBN: 0815509227 :

References from the University of Texas at Austin Libraries

Title: Design validation final report/ U.S. Department of Energy. Waste Isolation Pilot Plant.
Author: Waste Isolation Pilot Plant (N.M.)
Published: San Francisco, Calif. : Bechtel National, 1986.
Description: 2 v. (various pagings) : ill., maps ; 30 cm.
Notes: October 1986. Job 12484.

Title: Nuclear waste handling and storage : proceedings of a session / sponsored by the Structural Division of the American Society of Civil Engineers in conjunction with the ASCE National Convention, Boston, Massachusetts, October 31, 1986; edited by Ralph A. Kohl.
Published: New York, N.Y. : ASCE, c1986.
Description: v, 70 p. : ill. ; 22 cm.
Notes: Includes bibliographies and indexes.
Subjects: Radioactive waste sites, design and construction, Congresses. Radioactive wastes--Congresses.
ISBN: 0872625621 (pbk.)
OCLC Number: 14271182

Title: Use of the GENII computer code in a low-level radioactive waste disposal facility performance assessment methodology /by Arnold Blaine Preece.
Author: Preece, Arnold Blaine
Published: 1993.
Description: x, 80 leaves : ill. ; 28 cm.
Notes: Vita.Thesis (M.S. in Engin.)--University of Texas at Austin, 1993. Includes bibliographical references (leaves 76-80).
Subjects: Radioactive waste sites--Environmental aspects--Texas--Evaluation.Dept.: Engineering, Mechanical.
OCLC Number: 28833960

Title: Radwaste '86 : proceedings volume, Conference on the Treatment and Containment of Radioactive Waste, and Its Disposal in Arid Environments, 7-12 September 1986, Cape Town, Republic of South Africa / sponsors, the Atomic Energy Corporation of South Africa Limited, ESCOM ; compiled and edited by L.C. Ainslie.
Author: Conference on the Treatment and Containment of Radioactive Waste and Its Disposal in Arid Environments (1986 : CapeTown, South Africa)
Published: Pretoria, Republic of South Africa : Atomic Energy Corporation of South Africa Ltd., 1986.
Description: 1043 p. : ill. ; 30 cm.
Notes: Accompanied by map entitled: Geological map of the Vaalputs National Radioactive Waste Disposal Facility, Northwestern Cape, South Africa. Includes bibliographies. Radioactive waste disposal in the ground--Congresses. Arid regions--Congresses. Radioactive waste sites--South Africa--Congresses.
ISBN: 0869608320
OCLC Number: 18342181

Title: Nuclear waste : quarterly report on DOE's nuclear waste program as of June 30, 1989 : report to Congressional requesters / United States General Accounting Office.
Published: Washington, D.C. : The Office, 1989.
Description: 27 p. ; 28 cm.
Notes: Cover title."December 1989"--Cover. "RCED-90-59""B-202377"--P. 1.
Subjects: United States. Dept. of Energy.Radioactive waste disposal--United States. Radioactive waste disposal--Law and legislation--United States. Radioactive pollution--United States. Radioactive pollution--Law and legislation--United States. Hazardous waste sites--United States. Radioactive waste sites--United States.
Document Number: GA 1.13: RCED-90-59
OCLC Number: 21257756

Title: Quality assurance guidance for low-level radioactive waste disposal facility : final report / C.L. Pittiglio, Jr.
Author: Pittiglio, C. L.
Published: Washington, DC : Division of Low-Level Waste Management and Decommissioning, Office of Nuclear Material Safety and Safeguards, U.S. Nuclear Regulatory Commission, 1989.
Description: 1 v. (various pagings) ; 28 cm.
Subjects: Radioactive waste sites--United States--Design and construction. Radioactive waste disposal--United States.
U.S. Document Number: Y 3.N 88: 10/1293/989
OCLC Number: 23086340

Title: Treatment of alpha bearing wastes.
Published: Vienna : International Atomic Energy Agency, 1988.
Description: 69 p. : ill. ; 24 cm.
Subjects: Radioactive wastes
Other Author(s): International Atomic Energy Agency
Series: Technical reports series (International Atomic Energy Agency)no. 287.
ISBN: 9201253885
OCLC Number: 18808633

Title: Treatment of low- and intermediate-level solid radioactive wastes.
Published: Vienna : International Atomic Energy Agency, 1983.
Description: 93 p. : ill. ; 24 cm.
Notes: "STI/DOC/10/223" "... replaces the 1970 IAEA technical reports series no. 106,The Volume reduction of low-activity solid wastes."--Foreword. Bibliography: p. 83-90.
Subjects: Radioactive wastes Radioactive waste disposal
Series: Technical reports series (International Atomic Energy Agency)no. 223.
ISBN: 9201251831 :
OCLC Number: 9614148

Title: : Treatment of off-gas from radioactive waste incinerators.
Published: Vienna : International Atomic Energy Agency ; (Lanham, MD : UNIPUB, distributor), 1989.
Description: 229 p. : ill. ; 24 cm.
Notes: "STI/DOC/10/302"-- T.p. verso. "October 1989."Bibliography: p. 219-225.
Subjects: Radioactive wastes Incinerators
Other Author(s): International Atomic Energy Agency
Series: Technical reports series (International Atomic Energy Agency)no. 302.
ISBN: 9201253893
OCLC Number: 20796480

Title: Data for radioactive waste management and nuclear applications.
Author: Stewart, Donald Charles
Published: New York : Wiley, c1985.
Description: x, 297 p. : ill. ; 24 cm.
Notes: A Wiley-Interscience publication. Includes index. Bibliography: p. 281-292.
Subjects: Radioactive wastes Ionizing radiation
ISBN: 0471886270 :
OCLC Number: 11289332

Title: Stabilization and solidification of hazardous, radioactive, and mixed wastes. 2nd volume / T. Michael Gilliam and Carlton C. Wiles, (editors).
Published: Philadelphia, PA : ASTM, c1992.
Description: xii, 501 p. : ill. ; 24 cm.
Notes: "Contains papers presented at the Second International Symposium on Stabilization/Solidification of Hazardous,Radioactive, and Mixed Wastes, which was held in Williamsburg, Virginia, 29 May to 1 June 1990."--Foreword. Includes index. Includes bibliographical references.
Subjects: Hazardous wastes--Congresses. Radioactive wastes--Congresses.Sewage sludges digestion--Congresses.**Other Author(s):** Gilliam, T. M.Wiles, Carlton C.
Author(s): International Symposium on Stabilization/Solidification of hazardous, Radioactive, and Mixed Wastes (2nd : 1990 : Williamsburg, Va.)
Series: ASTM special technical publication. 1123.
ISBN: 0803114435
OCLC Number: 25276639

Title: Management of gaseous wastes from nuclear facilities : proceedings of an International Symposium on Management of Gaseous Wastes from Nuclear Facilities / jointly organized by the International Atomic Energy Agency and the Nuclear Energy Agency of the OECD, and held in Vienna, 18-22 February 1980.
Author: International Symposium on Management of Gaseous Wastes from Nuclear Facilities (1980 : Vienna, Austria)
Published: Vienna : International Atomic Energy Agency ; (New York : exclusive sales agent in United States of America, UNIPUB),1980.
Description: 699 p. : ill.; 24 cm.
Notes: "STI/PUB/561"English, French, or Russian with abstracts in the language of the paper and English. Earlier work see under variant name: Symposium on Operating and Developmental Experience in the Treatment of Airborne Radioactive Wastes.
Notes: Includes bibliographies and indexes.
Subjects: Radioactive wastes--Congresses. Radioactive pollution--Congresses. Nuclear power plants--Waste disposal--Congresses. Air--Pollution--Congresses.
Series: Proceedings series (International Atomic Energy Agency) 1980
ISBN: 9200203809
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Title: Monitoring of radioactive effluents from nuclear facilities : proceedings of the International Symposium on the Monitoring of Radioactive Airborne and Liquid Releases from Nuclear Facilities, held by the International Atomic Energy Agency in Portoroz, Yugoslavia, 5-9 September 1977.
Author: International Symposium on the Monitoring of Radioactive Airborne and Liquid Releases from Nuclear Facilities, Portoroz, 1977.
Published: Vienna : International Atomic Energy Agency, 1978.
Description: 610 p. : ill. ; 24 cm.
Notes: "STI/PUB/466" In English, French or Russian. Includes bibliographical references and index.
Subjects: Radioactivity--Measurement--Congresses. Radioactive wastes--Congresses.
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Description: xii, 239 p. : ill. ; 25 cm.
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Author: Mann, W. B., S.B. Garfinkel.
Published: Princeton, N.J., Published for the Commission on College Physics (by) Van Nostrand (1966)
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Notes: Includes bibliographical references.
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