EVALUATION OF TREATMENT TECHNOLOGIES FOR IMMOBILIZATION AND VOLUME REDUCTION OF MIXED WASTE*

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ABSTRACT

The Consolidated Incineration Facility (CIF) is a rotary kiln incinerator that processes low-level radioactive, hazardous, and mixed wastes generated at the Savannah River Site (SRS). The incinerator offgasses are cleaned by a wet offgas system that generates a secondary aqueous waste stream (blowdown). This waste stream is a mixed waste that requires treatment prior to disposal. The blowdown contains approximately 80 wt% water and 20 wt% chloride salts, ash, radioactive and hazardous contaminants.A SRS task team completed an evaluation of existing commercial and developmental technologies to treat aqueous mixed waste. Treatment technologies included both de-watering to reduce disposal costs and stabilization of the resultant residue to meet the regulatory disposal requirements. The team recommended evaporative drying and thermoplastic encapsulation (polyethylene, sulfur cement, and bitumen) as the technologies of choice for treating the CIF blowdown (1). Further bench-scale testing of evaporative technologies and thermoplastics is planned (FY-93) to determine the most effective drying process and thermoplastic binder for treating the CIF blowdown.

INTRODUCTION

There are two secondary mixed waste streams produced by the CIF. The first is kiln bottom ash, the heavy ash residue produced in the primary combustion chamber. This bottom ash will be solidified and stabilized in a cement-based waste form and disposed of in a hazardous waste/mixed waste disposal facility (HW/MWDF) at SRS. The other waste stream is the offgas aqueous blowdown waste contaminated with chloride salts (produced from the neutralization of acid gases) and fly ash entrained from the kiln. The blowdown will also contain radioactive and hazardous contaminants which are also entrained or volatilized during incineration. The liquid blowdown is more difficult to stabilize than the incinerator ash because it has a higher concentration of salts and soluble metals.

SELECTED WASTE TREATMENT TECHNOLOGIES

The evaluation was based on two types of waste treatments for the CIF blowdown: de-watering and solidification/stabilization (S/S) technologies. The de-watering technologies considered were waste water treatment (WWT) and evaporation. De-watering reduces the volume of blowdown, and hence, minimizes disposal costs. The blowdown residue remaining after de-watering will require stabilization to reduce contaminant leaching. Solidification is the process of tying up free water while stabilization encapsulates or binds the contaminants to decrease their mobility. The study evaluated S/S technologies in the following four major categories:

1. Thermoplastic Polymers (i.e., require increased temperature for solidification): Bitumen, Polyethylene, Sulfur Cement
2. Glass or Ceramic
3. Thermosetting Polymers (i.e., require chemical reactions for solidification): Vinyl Ester Resin, Epoxy
4. Hydraulic Cement

GENERAL APPROACH

Potential technologies to treat the CIF blowdown were identified and data collected from a variety of sources including vendors, developers, and technology experts. After reviewing existing technologies, the team concluded that a demonstrated technology was not available to treat the CIF blowdown. In fact, many Department of Energy (DOE) sites, which are the major producers of mixed waste, are all actively conducting research and development (R&D) to identify the "best available" technology to treat their waste streams. Table I lists a few DOE mixed wastes and the technologies that are being developed or used to treat the waste for final disposal. This report focuses on technologies that are already in commercial use and those that are in the advanced developmental stage.

The approach used in this evaluation was first to characterize the waste and then to develop the evaluation criteria before comparing the treatment technologies. Both of these

TABLE I
Status of Mixed Waste Treatment Technology

DOE Site	Waste Treatment		
	Waste Type	Existing	R&D Investigation
Oak Ridge	K-25 Kiln Ash	None	Alternatives Assessment
	K-25 Blowdown	WWT	Not Required
	WWT Precip. Sludge	None	Microwave
	Sodium Nitrate Waste	None	Bitumen, Ceramic
Rocky Flats	Sodium Nitrate Waste	Cement	Polyethylene

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objectives were major tasks without the benefit of an operating facility and a mixed waste disposal area with waste form requirements in place. These requirements are ultimately *important in* selecting suitable waste treatment technology.

DEVELOPMENT OF EVALUATION CRITERIA

Evaluation criteria chosen were representative of DOE needs for final disposal of mixed waste in the HW/MWDF. Selection of the evaluation criteria was based upon the following:

- EPA Requirements regulating Hazardous Waste Disposal
- DOE Orders governing disposal of Low-Level Waste (LLW)
- NRC Guidelines for predicting waste form behavior over extended disposal conditions

Environmental Protection Agency (EPA) Requirements

The hazardous component of the CIF blowdown is subject to regulations under the Resource Conservation and Recovery Act (RCRA), administered at the Federal level by the EPA. Specific restrictions regarding hazardous waste land disposal were established in 1984 by the Hazardous and Solid Waste Amendments (HSWA) to RCRA. Included in this amendment are the Land Disposal Restrictions (LDR) which prohibit the land disposal of hazardous wastes that do not meet treatment standards established by the EPA. These regulations require stabilization of hazardous constituents through solidification with specified leachability limits for the toxic metals measured in the Toxicity Characteristic Leaching Procedure (TCLP) test. HSWA also requires "no free-liquid" in the final waste form. Evidence of free water may be indicative of improper waste form preparation or curing.

Department of Energy (DOE) Orders

The DOE has established the requirements for management of radioactive wastes in DOE Order 5820.2A. Pertinent requirements from this DOE order that will apply to the HW/MWDF are:

- Wastes with transuranic radionuclide concentration of 100 nCi/g or less shall be considered LLW.
- LLW shall not contain free liquids.
- Fine particulate wastes such as ashes shall be immobilized.

Nuclear Regulatory Commission (NRC) Guidelines

Disposal of LLW in the commercial sector is regulated in the U.S. under the provision of the NRC regulations. The NRC regulations regarding the waste form state, "stability is intended to ensure that the waste does not structurally degrade, and thereby, lead to water infiltration (through leaching of contaminants)." Guidance on how to meet the intent of he NRC requirements for structural stability are provided in a "Technical Position on Waste Forms," which recommends a series of tests to evaluate waste form stability (2). The tests involve subjecting the waste specimens to conditions of compression, thermal cycling, irradiation, biodegradation, immersion and leaching. Most of the tests are intended to provided confidence, by exposing specimens to relatively short-term conditions, that LLW forms will have the desired long-term (over 300 years) structural stability.

The results from extensive research based on NRC testing guidelines form a baseline to enable comparison of the structural stability of various waste forms. However, many "gaps or holes" remain in the research due to use of differing experimental parameters, i.e., waste type and waste concentration.

Evaluation Criteria

The following evaluation criteria were developed after considering all current requirements for hazardous and LLW disposal. These criteria are divided into two groups: the final waste form and the treatment process.

Criteria Relating to the Waste Form

The immobilized waste form should:

1. Minimize leaching of both radioactive and hazardous contaminants.
2. Be mechanically stable to ensure the waste form is resistant to long-term leaching. To evaluate the structural stability, the waste form should undergo applicable testing involving:
   a. Extreme temperatures
   b. Saturated disposal conditions
   c. Gamma irradiation
   d. Fungal, bacterial, and chemical attack
3. Have a low flammability rating.

High waste loadings are desired in order to minimize the final waste form volume, and hence, educe disposal costs.

Criteria Relating to the Treatment Process

1. The process should not produce secondary effluents which require additional treatment (i.e., low operational temperatures are preferred to reduce potential volatilization of contaminants).
2. The treatment must be a viable production process and meet all regulatory requirements.
3. The process should be simple with minimum maintenance requirements.
4. The process must be able to treat variable waste compositions.

SUMMARY OF DE-WATERING TECHNOLOGY EVALUATION

Evaluation of Waste Water Treatment

Selection of the S/S technology is dependent on the de-watering treatment selected for the CIF blowdown since the residue composition from waste water treatment (WWT) and evaporation is different. Table II shows the difference between the qualitative residue compositions from WWT and evaporation.

Immobilization of evaporation residue containing salts and soluble metals is difficult since these contaminants are more conducive to leaching. In addition, chloride salts can cause swelling in some plastic waste forms due to osmotic pressure differences. Therefore, de-watering by WWT would be preferred, if technically feasible, since the chloride salts could be released in the effluent and the metal salts would be converted to an insoluble form.

Testing of WWT techniques, including microfiltration and co-precipitation, using the CIF blowdown indicated that WWT would not meet regulatory effluent discharge limits

TABLE II
Wastewater Treatment and Evaporation Residues

Wastewater Treatment Residue	Evaporation Residue
Ash Insoluble Metals Additives (i.e., flocculates)	Ash Soluble Metals Sodium Chloride Salts

(DOE Order 5400.2) for some radioactive contaminants. Those contaminants that exceeded the discharge limits are listed in Table III (1).

Evaluation of Evaporation

The evaluation team recommended evaporation as the de-watering treatment for the CIF blowdown, since WWT could not meet the regulatory discharge limits. The recommended evaporative method is dependent on the type of stabilization binder chosen. The selection criteria required the evaporative process to: control formation of particle size and density, withstand highly abrasive liquids, operate at temperatures less than the volatility of metals, and operate at low air flows to minimize entrainment of waste contaminants. Based on these criteria, the team recommended forced-circulation evaporation for pre-concentration of the blowdown for glass or cement stabilization, if required (1). Thermoplastics and thermosetting polymers require additional drying to prevent formation of steam pathways during the stabilization phase.

The particle size and density are crucial parameters in encapsulation of polyethylene and other viscous binders that require extrusion. Rocky Flats conducted unsuccessful tests when utilizing spray drying in conjunction with polyethylene extrusion. The reason for the waste form failure was that spray drying produced small size, low density particles that did not mix well during excursion. Brookhaven National Laboratory (BNL) indicated successful polyethylene extrusion in conjunction with particle sizes generated by a stirred-dryer system.

The recommended evaporator and stirred-dryer system could be successfully used with thermoplastics and thermosetting polymers. However, low-viscosity binders, such as some types of bitumen, are used commercially and are producing acceptable waste forms via a combined drying and stabilization stage, i.e., a wiped-film evaporator.

SUMMARY OF SOLIDIFICATION AND STABILIZATION EVALUATION

A SRS task team after completing an evaluation of existing commercial and developmental S/S technologies recommended thermoplastic encapsulation (i.e., bitumen, polyethylene, sulfur cement) for stabilization of the CIF blowdown. The results of the technology evaluation based upon the waste form and process criteria are shown in Table IV. The basis for selecting thermoplastic encapsulation over glass, cement, or thermosetting polymers is explained below.

TABLE III
Predicted Decontamination of the CIF Blowdown by WWT

		CIF Blowdown (pCi/ml)		
Nuclide	DF	Influent	Effluent	DOE Order 5400.2 Limits
Co-60	153	1,749	11	5
Zr-95	57	6,397	112	40
Ru-106	6.3	2,635	418	6.0
Cs-137	1.0	3,085	3,085	3.0

Thermoplastic Polymers

Previous Test Work: Bitumen is currently used commercially for immobilization of radioactive contaminants while polyethylene and sulfur cement immobilization are in the advance developmental stage. The commercially available bitumen process commonly uses evaporation and solidification in a single vessel, i.e., a wiped-film evaporator. The offgas system requires a condenser, an oil separator, pre-filter, a high efficiency carbon absorber, and high efficiency particulate air (HEPA) filters (3). The offgas process required for bitumen processing is more elaborate than that required for polyethylene or sulfur cement since these processes operate at lower temperatures (120°C) (4,5).

Data from BNL and Oak Ridge National Laboratory indicted that waste forms composed of thermoplastic polymers had very good to excellent mechanical properties and passed the RCRA and NRC leaching requirements (4,5,6,7). BNL demonstrated that adding sulfide compounds reduced hazardous metal solubility, and therefore, increased the leaching performance of sulfur cement (8). Sulfide addition is also expected to reduce leaching from bitumen and polyethylene waste forms.

Minor concerns over thermoplastic stabilization of residue containing fly ash and chloride salts include waste form swelling and flammability. Waste form swelling can be resolved by improving the mechanical integrity of the plastic by glass fiber addition (4) and by reducing the salt concentration in the waste form to below 40 wt% (3). The flammability rating of organic binders is higher than that of glass or cement. However, final waste form fire hazards are not a concern as long as the disposal area temperature remains below the binder flash point. The thermoplastic flashpoint ranges between 260-350°C which is higher than that of paper, wood, and cotton (3,4,5).

Future Test Work: A baseline data comparison is needed to evaluate the leachability and mechanical integrity of thermoplastic waste forms to determine the most suitable binder (i.e., polyethylene, sulfur cement, bitumen) for encapsulation of the CIF blowdown. This experimental work, planned for FY93, will be used to select the most effective thermoplastic encapsulant. Test plans consist of a 4 phased approach as shown below:

Phase I — Evaporation/drying and characterization of the resultant residue and determination of viable encapsulation formulations,

Phase II — Thermoplastic waste form NRC/EPA performance tests: compressive strength, TCLP leaching test, water immersion, and flammability,

Phase III — Comparison of thermoplastic, glass, and cement waste forms using leachability and waste loading data,

Phase IV — Thermoplastic final waste form and operation optimization.

TABLE IV
Comparison of Solidification/Stabilization & Encapsulation Treatments

			Thermosetting Polymers		Thermoplastic Polymers		
Criteria	Glass	Cement	Vinyl Ester	Epoxy	Bitumen	Polyethylene	Sulfur Cement
Leach Resistance	Excellent	Poor-Good: Highly Porous	Good-Excellent: Further testing	Good-Excellent: Pretreat additives may increase leaching	Good-Excellent: Needs further test work	Good-Excellent: Needs further test work	Good-Excellent: Some Pre-treatment required; Needs further test work
Mechanical Integrity	Excellent	Good: All NRC tests not required	Excellent	Excellent	Good-Excellent: Water Immersion causes swelling	Excellent: Water Immersion reduces compressive strength	Excellent: Glass fibers required to minimize swelling
% Waste in Binder	50 wt% (96 wt% vol. reduction from Cl removal)	18-25 wt%	40-50 wt%	35-40 wt%	40 wt%	40 wt%	43 wt%
Process Produces Secondary Waste	Yes	No	No	No	No	No	No
Treats Variable Waste Compositions	No: Carbon and Chlorides increase metals volatility	No: Chem. Rxns. required; Contaminants can interfere	No: Chem. Rxns. between binder and catalyst; Waste can interfere	No: Chem. Rxns. required	Yes	Yes	Yes
Process Commercially Available	Yes	Yes	Yes	Yes	Yes	No	No
Relatively simple & Min. Maintenance	No: Requires elaborate off-gas & frequent replacement of equipment due to high chlorides	Yes	No: Difficult to store resin; Highly flammable	Yes: Requires water removal	Yes: Requires some offgas equipment and fire protection	Yes: Requires water removal; Developmental stage	Yes: Requires water and S gas removal; Developmental stage

The most crucial parameter affecting thermoplastic waste form leachability is the particle size distribution and fly ash/salt residue density. Evaporative drying is crucial in determining the particle size and density distribution. Previous test work conducted on Rocky Flats Plant nitrate salts indicated that spray drying generated particles of small size and low density that did not mix well in the polyethylene extrusion process. Further test work is required to determine if other evaporative drying techniques will generate particle sizes amenable to polyethylene encapsulation. BNL has indicated successful polyethylene extrusion using particle sizes generated by a stirred-dryer system.

Glass/Ceramic

Previous Test Work: Data in Table IV indicates that glass and ceramic waste forms are superior to other waste forms when considering leach resistance, mechanical stability, flammability, and volume reduction. Glass processing can result in a large volume reduction since chloride salts in the CIF blowdown would be volatilized during the melting process.

Despite the superiority of glass waste forms, the high temperature melting process required for glass is not recommended for immobilizing incinerator aqueous waste with high concentrations of soluble salts, metal salts, and carbon. High temperatures ($>1000°C$) and chlorides will increase the volatility of contaminants at temperatures as low as 500°C (9). Furthermore, carbon in the ash will reduce metal oxides (which would normally remain in the glass) to the elemental state which is volatile at melting temperatures (10). These volatilized contaminants would be captured in the melter offgas system, and hence, generate a waste stream requiring additional treatment. The high-temperature melting processes also generate chlorine gas and acids that accelerate corrosion of the melter and offgas equipment (11). Frequent equipment replacement should be factored into the life-cycle cost analysis for high temperature melting processes. Unless these corrosive salts can be separated from the remaining contaminants or until glass developmental work can reduce contaminant volatility, glass immobilization of the aqueous residue is not recommended.

Future Test Work: Glass crucible studies using CIF blowdown simulant containing chloride salts produced excessive embrittlement and cracking in the waste forms. To prevent generation of poor waste forms, Savannah River Technology Center recommends a stirred-melter to generate CIF blowdown-glass waste forms. The stirred-melter should facilitate volatilization of the chloride gases to prevent entrapment in the glass to reproduce higher integrity waste forms. However, volatilization of a larger fraction of contaminants may also be facilitated by the stirring action of the melter. Therefore, the blowdown from the stirred-melter offgas system could contain higher quantities of contaminants than that of a non-stirred melter. Stirred-melter tests are planned for FY93 to quantify volatilization of chlorides and metals from the melter.

Hydraulic Cement and Thermosetting Polymers

Binding agents that require chemical reactions for solidification are not recommended for immobilizing contaminants in the incinerator blowdown. As shown in Table IV, these binders include hydraulic cement and thermosetting polymers, i.e., vinyl ester resin and epoxy. The two inherent problems with thermosetting polymers are potential interactions between the binding agent and contaminants, and high exotherms during the chemical reactions. These factors can retard solidification, decrease mechanical integrity, and increase the leaching rate in the final waste form (12,13,14). While these shortcomings do not preclude use of thermosetting or cement solidification process, they do retard the success rate of generating waste forms which meet all disposal regulatory requirements. Due to the variation in the blowdown composition, cement and thermosetting polymers are not recommended for stabilization of the CIF blowdown.

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