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WASTE FORM DEVELOPMENT*

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ABSTRACT

In this program, contemporary solidification agents are being investigated relative to their applications to major fuel cycle and non-fuel cycle low-level waste (LLW) streams. Work is being conducted to determine the range of conditions under which these solidification agents can be applied to specific LLW streams. These studies are directed primarily towards defining operating parameters for both improved solidification of "problem" wastes and solidification of "new" LLW streams generated from advanced volume reduction technologies. Work is being conducted to measure relevant waste form properties. These data will be compiled and evaluated to demonstrate compliance with waste form performance and shallow land burial acceptance criteria and transportation requirements (both as they exist and as they are modified with time).

The work conducted under this program in FY 1982 and planned FY 1983 efforts are discussed.

PROGRAM SCOPE AND OBJECTIVES

The objective of the Department of Energy's National Low-Level Waste Management Program (NLLWMP) is to "provide an acceptable Low-Level Waste Management System by 1988" which will enable disposal "of materials that have been declared as low-level waste (LLW) in a manner which will protect public health and safety in the short and long terms." The Waste Form Development program is an integral part of the NLLWMP's plan to develop technology applicable to the aggregate of LLW streams from generation to disposal as expressed in Milestone B, "Develop Technology for Waste Treatment, Handling and Packaging for Shallow Land Burial Site Disposal." Data from this program also provide input into other NLLWMP Milestones.

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Low-level wastes at nuclear facilities have traditionally been solidified using portland cement. Urea-formaldehyde has also been used for LLW solidification while bitumen (asphalt) and thermosetting polymers will be applied to domestic wastes in the near future. However, operational difficulties have been observed with each of these solidification agents. Such difficulties include incompatibility with waste constituents inhibiting solidification, free standing water, premature setting and fires. Some specific wastes, so-called "problem" wastes, have proven difficult to solidify with one or more of the contemporary agents or are solidified at low efficiencies. Existing technologies may not be directly applicable to the solidification of "new" wastes which are beginning to be generated using advanced volume reduction technologies in an effort to reduce waste disposal costs. In addition, consideration must be given to the application of any additional agents which may be introduced in the near future for the solidification of low-level wastes. The scope of this work includes both major fuel cycle and non-fuel cycle LLW streams.

This program will identify and evaluate potential agents and processes for the improved solidification of low-level wastes and the solidification of "new" LLW streams generated from advanced volume reduction technologies. The data developed will provide input into DOE efforts to develop a handbook for LLW treatment and disposal by shallow land burial. It will also provide the basis to demonstrate compliance with waste form performance and shallow land burial acceptance criteria and transportation requirements (both current and as they change with time).

SELECTION OF SOLIDIFICATION AGENTS FOR FURTHER STUDY

A survey was conducted in FY 1981 to identify and review those agents and processes tht could be used for the solidification of LLW. A report entitled A Survey of Agents and Techniques Applicable to the Solidification of Low-Level Radioactive Wastes was issued at the end of FY 1981. Potential LLW solidification agents reviewed fell into several generic classes including hydraulic cements, thermoplastics, thermosetting polymers, glasses, ceramics, mineralization processes and composite processes. The information compiled in this effort was used to select agents and processes for further study. Such agents should potentially be capable of solidifying (either with or without modification) a wide variety of LLW streams, with particular emphasis on "problem" wastes and "new" wastes as previously described. Also, it is desirable if a particular agent chosen is compatible with existing installed waste solidification equipment so as to minimize the need for major capital expenditures. For these reasons, work in FY 1982 concentrated on the use of various hydraulic cements and thermosetting polymers for improved solidification of LLW.

WASTE COMPOSITION CHARACTERIZATION

In support of waste form development studies, efforts have been made to identify specific LLW streams and determine their compositions. Table 1 lists generic types and sources of LLW. The specific wastes produced within a given class vary considerably in regards to composition, activity content and concentration. While wet wastes obviously require solidification, some dry wastes, particularly incinerator ash and dry salts, must also be solidified because they are easily dispersible. In addition, some wet wastes, ion exchange resins in particular, have been disposed in a dewatered form. However, regulations and burial site operating licenses are moving to require solidification of these wastes.

The emphasis of FY 1982 waste form development studies was the solidification of "problem" wastes and "new" wastes. The "problem" wastes studied included ion exchange resins, oils and organic liquids and specific aqueous concentrates. Studies of "new" wastes included incinerator ash and dry nitrate salt waste.

FORMULATION DEVELOPMENT STUDIES

Work has been conducted to determine appropriate operating parameters for the solidification of specific LLW streams with various solidification agents. This includes verification of the compatibility of solidification agents with various waste types, identification of waste stream constituents which impede or impair solidification and determination of appropriate compositional limits. FY 1982 formulational development work included the waste-solidification agent combinations listed in Table 2. Work was conducted to investigate the solidification of ion exchange resins, incinerator ash, oil wastes, organic liquids and nitrate salt and concentrate wastes. Solidification agents applied included hydraulic cements (portland type I and III cements and high alumina cement), hydraulic cements with additives, polymer modified gypsum cement (Envirostone) and thermosetting polymers (primarily vinyl ester-styrene).

Formulation acceptability criteria employed for this work require waste forms which are monolithic free-standing solids, homogeneous (on a macroscopic scale) and contain no drainable free standing liquid. These criteria have been applied conservatively in order to provide reasonable assurance that satisfactory solidification will occur for full-scale waste forms using formulations that were initially developed in the laboratory. In addition, waste forms are also required to pass a two week water immersion test without loss of mechanical integrity.

Table 1. Sources and Types of Low-Level Radioactive Wastes

	TYPES OF WASTE GENERATED												
	DRY WASTES				WET WASTES								
	COMBUSTIBLE		NONCOMBUSTIBLE										
SOURCES	COMPACTIBLE	NONCOMPACTIBLE	COMPACTIBLE	NONCOMPACTIBLE	FILTER CARTRIDGES	SPENT RESINS	SLURRIES AND SLUDGES	AQUEOUS CONCENTRATES	SPECIAL AQUEOUS SOLUTIONS[a]	OILS	OTHER ORGANIC LIQUIDS	MEMBRANES[b]	BIOLOGICAL
GOVERNMENT DEFENSE	●	●	●	●	●	●	●	●	●	●	●	●	
D & D[c]	●	●	●	●		●			●				
RD & D[d]	●	●	●	●		●	●	●	●	●	●	●	●
COMMERCIAL FUEL CYCLE MINING	●	●	●	●			●	●					
MILLING	●	●	●	●			●	●					
UF_6 PRODUCTION	●	●	●	●			●						
ENRICHMENT	●	●	●	●			●			●	●		
FUEL FABRICATION	●	●	●	●			●			●			
POWER PLANTS	●	●	●	●	●	●	●	●	●	●		●	
SPENT FUEL STORAGE	●	●	●	●		●	●						
D & D	●	●	●	●		●			●				
NONFUEL CYCLE MEDICAL	●		●	●							●		●
PHARMACEUTICAL[e]	●			●							●		●
UNIVERSITIES	●		●	●		●					●		●
OTHER INDUSTRIES[e]	●			●		●							

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a Decontamination, pickling, etching, electropolishing, etc. solutions.
b Membranes from processes such as ultrafiltration (UF) and reverse osmosis (RO).
c Decontamination and decommissioning (D & D) operations.
d Research, development, and demonstration (RD & D) programs.
e Data on these wastes are incomplete and difficult to obtain.

Table 2. Formulation Development Studies in FY 1982

Waste Type	Hydraulic Cements (w, w/o additives)	Polymer Modified Gypsum Cement	Thermosetting Polymers
Ion exchange resins	X	X	X
Incinerator	X	X	X
Oils	X	X	
Organic Liquids	X	X	
Nitrate Concentrates	X		X
Nitrate Salt Waste	X		X

ION EXCHANGE RESIN WASTES

Formulations have been developed for the solidification of ion exchange resin wastes in portland cements, high alumina cement, polymer modified gypsum cement and vinyl ester-styrene. These studies employed cation, anion and mixed bed Nuclear Grade Amberlite[(a)] "gel" type synthetic ion exchange resins. Resins were employed in both loaded and unloaded conditions. Formulations are expressed as ternary phase diagrams in terms of wt% dry resin, water and solidification agent. Dry resin weight percentages are used in this work in order to provide formulation data in a consistent manner that is universally applicable. Handling practices for ion exchange resin wastes are diverse and as a result, the percentage of water in so-called dewatered and slurry resin wastes may vary considerably.

Hydraulic Cements

Previous work and experience with the use of hydraulic cements (portland cement) as a solidification agent for ion exchange resin wastes indicated instances of waste form expansion which resulted in low product integrity and/or waste form disintegration. This behavior has been shown to be a function of both resin type and resin content in the waste form. A large number of formulations were prepared and tested to determine acceptable formulations and to investigate the effects of cement type, resin type, resin loading and water content. Ternary compositional phase diagrams were developed for the solidification of ion exchange resin waste with portland cements and high alumina cement.

Anion, cation and mixed bed resins yielded unique regions of acceptable formulations. Anion resin formulations indicated a wide region of free standing water but initially acceptable formulations were not susceptible to degradation in the water immersion test.

Although less restricted by free standing water problems, the performance of cation resin formulations in portland cements was limited by excessive swelling and deterioration of mechanical integrity both after curing and in immersion testing. Based upon these results, the swelling and cracking of the ion exchange resin waste forms studied can be directly attributed to the cation form of the resin.

The compositional phase diagram for the solidification of mixed bed resin in portland type III cement shows a resultant envelope of acceptable formulations similar to that observed for cation resin. While the diagram does show some of the characteristics of anion resin solidification, the behavior of mixed bed resin is dominated by its cation resin component. However, waste form degradation in immersion was not observed for high alumina cement waste forms containing mixed bed resin.

(a) Rohm and Haas Co., Philadelphia, PA

A much larger range of acceptable formulations was observed for the solidification of loaded mixed bed resins in portland cement. Fewer of these formulations failed by the free standing water and immersion test criteria than with unloaded mixed bed resins.

Studies indicated that portland type III cement formulations were capable of incorporating larger quantities of water than portland type I cement and pass free standing water and immersion criteria. The minimum water requirements for workability (mixability limit) were similar for both cement types. Type III cement also appears capable of incorporating larger quantities of ion exchange resin in acceptable formulations. High alumina cement was observed to be capable of incorporating both larger quantities of water and high waste loading while meeting acceptance criteria.

Maximum resin loadings providing acceptable waste forms are listed in Table 3.

Limited work was also conducted to investigate resin pretreatment and the use of additives to cement systems to improve resin loading and product properties. These studies included use of water extendible polyester, sodium silicates, and furfuryl alcohol. Some improvements were noted.

Table 3. Maximum Resin Loadings for Cement/Resin Combinations Satisfying Acceptance Criteria

Cement Type	Resin Type[(a)]	Dry Resin Wt%	Cement Wt%	Water Wt%
portland III	loaded M.B.	25	22	53
high alumina	M.B.	23	35	42
portland III	M.B.	13	52	35
portland I	M.B.	11	58	31
portland III	cation	12	59	29
portland III	anion	20	31	49

(a) M.B. = mixed bed

Polymer Modified Gypsum Cement

Formulations were developed for the solidification of mixed bed ion exchange resin waste in polymer modified gypsum cement (Envirostone). This agent is capable of incorporating as much as 25 wt% dry unloaded mixed bed ion exchange resin. Waste form swelling did occur during immersion testing which was pronounced for those formulations containing greater than 10 wt% dry resin. It was also noted that surface hardness decreased as a result of immersion testing. Although remaining intact for the duration of the two week immersion test, those formulations with high resin contents (>20 wt%) tended to become brittle and have poor mechanical strength when removed from the water.

The ability of the matrix to swell, thus conforming to resin bead volume increases, may account for the absence of cracking and crumbling behavior in immersion.

Vinyl Ester-Styrene

Vinyl ester-styrene(a), a proprietary thermosetting polymer was studied for the solidification of unloaded mixed bed dewatered and slurry resin waste streams. In this work, the resin slurry waste consisted of 20 wt% dry resin and 80 wt% water. The maximum dry resin content obtained for the solidification of slurry waste was 18.4 wt%. As much as 28.6 wt% dry resin could be incorporated if excess and interstitial water was first removed from the waste to form "damp" resin (42 wt% dry resin, 58 wt% water). The limiting constraint in solidifying resin slurry wastes was the amount of water that could be incorporated in the water-monomer emulsion during mixing. Maximum loadings of damp resin were limited by the viscosity of the mixture and the volume of binder avaliable to provide mechanical integrity of the waste form.

INCINERATOR ASH WASTE

Solidification studies were conducted with portland type I cement, high alumina cement, polyester-styrene and vinyl ester-styrene. This work utilized an incinerator ash produced by the rotary kiln incinerator developed at the Rockwell International Rocky Flats plant. This incinerator was used to burn a non-radioactive waste feed whose composition is representative of the combustible low-level wastes generated at the plant. This waste feed composition is listed in Table 4.

The rotary kiln ash has a bulk density of approximately 0.23 g/cm^3, has a visual appearance similar to cigarette ash and is gray-white in color but exhibits color gradations and has carbon present as a distinct particulate. In the presence of water the ash exhibits a pH of approximately 6.

(a) Dow Chemical Company, Midland, MI

Table 4. Rotary Kiln Feed Compositions

Constitutent	Weight %
Paper	40.0
Polyethylene	22.8
Neoprene	18.8
Kerosene	9.5
Polyvinyl Chloride	7.9
Tributyl Phosphate	1.0

Hydraulic Cements

Portland type I cement and high alumina cement were used to solidify the rotary kiln incinerator ash. Since the ash itself is dry, water must be added to this system for cement hydration. The amount of water added is important since sufficient water must be present to form a workable and pourable cement mix. However, the addition of an excessive amount of water can result in the presence of free standing water after solidification. While it is also desirable to incorporate as much incinerator ash as possible into the final waste form, sufficient cement must be included in the formulation to hold the waste form together producing a monolithic mass. Also, the cement-waste mixture must have a sufficiently long set time to allow complete mixing and transfer from the mixing equipment to the container in which the mixture is cast.

It was determined that the ash has considerable water absorption capacity. The ash was difficult to mix directly with a cement-water mixture, unless sufficient water was first added to satisfy the ash's absorptive requirements. Conversely, adequate workability was only achieved when cement powder was added to wetted ash with sufficient water present to satisfy both ash absorption and cement workability requirements. However, the water required to saturate the ash is weakly held since when sufficient water is added, a minimum of mixing typically results in an excessively wet mixture in which some water separates to the top.

Prior ball milling of the ash was found to minimize these tendencies. Ball milling decreases the ash particle size and changes its geometry, lowers ash water absorption requirements and results in a more homogeneous ash waste with a bulk density of approximately 0.37 g/cm^3.

The increased ash bulk density also facilitates fabrication of the waste form and appears to permit an increase in the amount of ash waste that can be incorporated.

A ternary compositional phase diagram was developed for the solidifiction of rotary kiln incinerator ash in portland type I cement. Portland type I cement can incorporate as much as 50 wt% ash in the solidified waste form. This formulation contains relatively little cement, but is sufficient to form a waste form of reasonable mechanical integrity. High alumina cement was also capable to incorporating up to 50 wt% rotary kiln ash.

Polyester-Styrene

Polyester-styrene resin (LB-183-13[(a)]) containing 50 wt% styrene was used to solidify the rotary kiln ash. Methylethyl ketone peroxide (1.2 wt% resin) was used as a catalyst and cobalt napthenate (0.5 wt% resin) as a promoter in order to provide a room temperature polymerization. Ball-milled rotary kiln ash could be incorporated in the polyester-styrene matrix at up to 55 wt%. A maximum ash loading of 45 wt% was achieved with the as-received ash.

Work was conducted with a polyester-styrene resin containing 20 wt% styrene. This resin was considerably more viscous and difficult to mix. However, a maximum loading of ∿50 wt% was achieved with the ball-milled ash.

Vinyl Ester-Styrene

Difficulties were encountered during solidification of the rotary kiln incinerator ash with the proprietary vinyl ester-styrene[(b)] resin. An incomplete polymerization producing a "rubbery" solid was often observed. This is believed to result from an interaction of the catalyst and/or promoter used with components in the ash. Increases in the catalyst and promoter addition and changes in the order in which they were used improved the degree of polymerization. However, completely polymerized products were not reliably produced.

OIL AND ORGANIC LIQUID WASTES

Work was conducted to investigate the applicability of selected solidification media for oil and organic liquid wastes. The solidification studied included various cement and cement with additive(s) systems.

(a) U.S.S. Chemical Co., Linden, NJ

(b) Dow Chemical Co., Midland, MI

Oil waste was simulated by use of a hydrocarbon vacuum pump oil. Solidification of a liquid organic waste mixture ("NEN") generated by a radiopharmaceutical manufacturer was also investigated. The composition of the "NEN" simulated organic liquid waste is given in Table 5. The individual solidification agents applied to the solidification of oil waste and "NEN" organic liquid waste are listed in Table 6.

TABLE 5. COMPOSITION OF "NEN" SIMULATED ORGANIC LIQUID WASTE STREAM

Simulated Organic Liquid Waste Stream Composition		Component Formula
Component	Vol%	
Methanol	22	CH_3OH
Ethanol	22	C_2H_5OH
Acetone	9	CH_3COCH_3
Isopropanol	5	$CH_3CHOHCH_3$
Diethyl ether	9	$C_2H_5OC_2H_5$
Ethyl acetate	4	$C_2H_5COOCH_3$
n-Hexane	9	$CH_3(CH_2)_4CH_3$
Benzene	4	C_6H_6
Toluene	4	$C_6H_5CH_3$
Acetonitrile	4	CH_3CN
1,2-Ethylene dichloride	4	$C_2H_4Cl_2$
Chloroform	4	$CHCl_3$
	100	

Table 6. SOLIDIFICATION MEDIA INVESTIGATED

	Immobilization of Oil	Immobilization of "NEN"
Portland Type I Cement	X	
Vermiculite and Portland Type I Cement	X	
Nutek 380-Cement	X	X
Emulsifier, Portland Type I Cement, and Silicate	X	
DCM Cement	X	
Environstone Cement	X	X

The results obtained in this study indicate that there are several options available for the solidification of oil or organic liquid LLWs at low waste loadings ($\leq$ 10 volume-%). For higher waste loadings, the choices are more limited and there is greater probability of obtaining unsatisfactory solids. This study concentrated on high waste loading formulations which are assumed to be more representative of actual LLW generators' practices. Based on the criteria applied in this study, acceptable solids were obtained (i.e., selected formulations yielded free-standing monolithic solids with < 1 vol-% free liquid, which passed a water immersion test). However, there are indications that these formulations may not be completely satisfactory on the basis of other or evolving LLW acceptance criteria.

In the case of oil, volumetric waste loadings of the order of 30-40 volume-% may be realized with specimens of reasonable physical integrity. For "NEN", however, acceptable formulations are generally below about 10 volume-%. Especially for organic liquid wastes, alternative treatments such as incineration may be preferable to direct immobilization.

A topical report on the solidification of oil and organic liquid wastes was issued in July 1982.

NITRATE SALT WASTES

The solidification of nitrate salt concentrate wastes (containing up to 85 wt% sodium nitrate) and dry sodium nitrate wastes in portland type I cement, high alumina cement and vinyl ester-styrene was studied.

Ternary compositional phase diagrams were developed for each of these solidification agents. Portland type I cement was able to incorporate up to 68 wt% sodium nitrate in solidified waste forms, while the maximum quantity of sodium nitrate was 64 wt% for high alumina cement waste forms. In addition, the portland cement forms were capable of incorporating a larger quantity of water in the waste. Vinyl ester-styrene waste forms were limited to a maximum of approximately 57 wt% sodium nitrate for nitrate concentrate wastes. However, this matrix could accommodate a much larger range of water from nitrate concentrate wastes. Up to 80 wt% dry sodium nitrate could be incorporated into vinyl ester-styrene waste forms.

WASTE FORM PROPERTY EVALUATION STUDIES

The waste form formulations developed in this program for the solidification of various wastes were tested to determine their characteristics relative to desired waste form properties. Properties studied include leachability, mechanical properties (compressive strength, impact strength), radiation stability, and thermal properties. This data will be described in detail in the Waste Form Development Program annual report.

TECHNICAL ASSISTANCE

This subtask has provided assistance to the LLWMP lead contractor and/or lead laboratory as appropriate. Technical assistance efforts in FY 1982 included participation in working committees for the development of low-level waste acceptance criteria and environmental release criteria development.

FY 1983 EFFORTS

In FY 1983, the emphasis of this program will be the development of waste forms produced using improved agents and processes not commercially employed for low-level wastes. Such agents may include polymer concretes, low melting glasses, specially processed cements, sulfur compounds, and mineralization processes. Process development studies will be made with selected agents to ascertain the effects of processing parameters. Waste form property evaluation studies will be conducted to develop physiochemical data for improved waste forms. One or more of the improved solidification processes will be demonstrated on a scale approximate to that required in actual operation and the properties of the process demonstration product will be evaluated and compared to data obtained in previous studies for laboratory scale specimens. Technical assistance will be performed as required by the LLWMP.