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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 1981 and planned FY 1982 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.

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 evalute 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).

SURVEY OF POTENTIAL SOLIDIFICATION AGENTS

A survey was conducted in FY 1981 to identify and review those agents and processes that could be employed for the solidification of LLW. This survey included not only those agents and processes currently used for LLW solidification, but also those either under development or proposed. In addition, agents and processes utilized for the solidification of other types of wastes, such as chemical toxic wastes and high-level radioactive wastes, were also considered. Available information concerning the characteristics of solidification agents, solidification agent chemistry and applicability to specific waste streams, processing techniques and waste form properties was collected. 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. Agents and processes described in this report must be capable of meeting existing waste form performance requirements and also not be so complex and/or expensive as to preclude reasonable applicability to LLW. Potential LLW solidification agents reviewed fall into several generic classes including hydraulic cements, thermoplastics, thermosetting polymers, glasses, ceramics, mineralization processes and composite processes. A partial listing of

these agents is found in Table 1. The information compiled in this effort will be 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.

WASTE COMPOSITION CHARACTERIZATION

In support of waste form development studies, efforts are directed at identifying specific LLW streams and determining their compositions. Table 2 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 typically been disposed in a dewatered form. However, regulations and burial site operating licenses are moving to require solidification of these wastes.

The emphasis of initial waste form development studies is the solidification of "problem" wastes and "new" wastes. The "problem" wastes currently under study include ion exchange resins, oils and organic liquids, specific aqueous concentrates and decontamination solutions. Studies of "new" wastes include incinerator ash, dry solids, such as those generated by thin film evaporators and calciners, and high solids content evaporator concentrates.

FORMULATION DEVELOPMENT STUDIES

Work is being 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 1981 formulational development work included the waste-solidification agent combinations listed in Table 3. Work has been initiated to investigate the solidification of ion exchange resins, incinerator ash, oil wastes, scintillation liquids and nitrate salt and concentrate wastes. Solidification agents applied include hydraulic cements (portland type I

and III cements and high alumina cement), polymer modified gypsum cement (Envirostone) and thermosetting polymers (primarily vinyl ester-styrene). Both the polymer modified gypsum cement and vinyl ester-styrene are recently developed agents that appear applicable to the initial wastes studied. Work with hydraulic cements includes a variety of cement types and additives with a view towards applying existing facilities to improved solidification of current wastes and investigating their potential for the solidification of "new" wastes. Formulational development information is typically expressed in the form of a ternary phase diagram such as those shown in Figures 1-4 for the solidification of ion exchange resin wastes in portland type III cement. Acceptable formulations must be capable of meeting existing waste form criteria (free standing monolithic solid with "no" free standing water) and also pass a water immersion test which is indicative of long-term waste form integrity. The development of acceptable formulations requires study of a variety of parameters. For example, formulations for the solidification of ion exchange resin wastes were found to be dependent upon cement type, resin type, resin loading and water content, and water/cement ratio. Information related to mechanical operating parameters, such as mixing method and order of addition of constituents is also being developed.

Work has been conducted to identify well characterized, readily available commercial additives that could be used to reduce leachability (particularly cesium leachability from cement waste forms). Such an additive(s) could be readily applied to a wide range of fuel cycle and non-fuel cycle operations. A number of potential additives have been identified and subjected to screening sorption tests using solutions indicative of actual conditions. Leaching tests of concrete waste forms containing additives have been initiated to investigate improvements in activity retention.

WASTE FORM PROPERTY EVALUATION STUDIES

The waste form formulations developed in this program for the solidification of various wastes are being tested to determine their characteristics relative to desired waste form properties. Property studies include leachability, mechanical properties (compressive strength, impact strength), radiation stability, thermal properties (flammability, thermal conductivity), chemical stability, corrosivity towards the waste form container and biodegradability. Property evaluation studies were begun in FY 1981 for ion exchange resin and organic liquid waste forms. This effort has progressed furthest with ion exchange resin waste forms for which leachability, mechanical properties, radiation stability and biodegradability testing have begun. For example, leach studies of portland type III cement-mixed bed

resin waste forms showed that activity retention is relatively independent of leachant composition (demineralized water-seawater) and leachability is not affected by Co-60 gamma irradiation doses of up to 10^8 rads. Irradiation and leaching experiments using unsolidified mixed bed resin were also conducted to provide a baseline for solidification studies. Property evaluation studies will continue for these waste forms and progress to include other relevant waste form properties. Similar efforts with additional waste-solidification agent combinations will begin as their respective formulation development studies are completed. The results of the property evaluation studies can be used to optimize waste form formulations. The data developed will also be needed to demonstrate compliance with waste form performance criteria, disposal site criteria and transportation requirements. In addition, these data are useful in assessing and developing alternative disposal options and establishing shallow land burial site performance criteria which can be used to judge the acceptability of site locations, trench designs and operating practices for new and existing sites.

TECHNICAL ASSISTANCE

The Waste Form Development program has established a nucleus of competent individuals with a range of expertise that can be called upon by the NLLWMP to provide technical assistance as necessary. In FY 1981, technical assistance requests consisted of expert participation in ad hoc task groups on waste classification and on LLW treatment, packaging and handling system performance standards. In addition, system evaluation and leaching experiments were conducted in support of a demonstration at the Maxey Flats, KY shallow land burial site of a new polymer solidification system (ALAP waste form, Imperial Professional Coatings, Inc.).

FY 1982 EFFORTS

In FY 1982, formulational development work will be completed for ion exchange resins, oil and organic liquid wastes, incinerator ash and nitrate salt wastes. Waste form property testing will continue and progress to include measurements not initiated with these systems in FY 1981. Topical reports will be issued on ion exchange resin waste solidification and for the solidification of oil and organic liquid wastes. Studies to investigate the solidification of additional wastes will begin. Technical assistance will be performed as requested by the NLLWMP. FY 1982 efforts are summarized in Table 4.

Table 1. POTENTIAL LLW SOLIDIFICATION AGENTS

HYDRAULIC CEMENTS	GLASSES
Portland Cement	Soda-Lime Glass
High Alumina Cement	Phosphate Glass
Masonry Cement	Borosilicate Glass
Gypsum Cements	Nepheline-Syenite
Cement Grouts	Thermite
Pozzolanic Cements	Slag
Cement - Sodium Silicate	
Polymer Impregnated Cement	
Hot Pressed Cement	
THERMOPLASTICS	**OTHERS**
Bitumen	Ceramics
Polyethylene	Pelletized-Coated
Sulfur	Pelletized-Impregnated
THERMOSETTING POLYMERS	
Vinyl Ester-Styrene	
Water Extendable Polyester	
Epoxy	
Polyester-Styrene	

Table 2. TYPES AND SOURCES OF LLW

DRY WASTES	FUEL CYCLE	NON-FUEL CYCLE
Combustible (paper, clothing, plastics)		
Compactible	X	X
Non-Compactible	X	
Non-Combustible (metals, glass, incinerator		
Compactible ash, dry salts)	X	X
Non-Compactible	X	
WET WASTES		
Spent Resins	X	X
Slurries	X	
Sludges	X	
Aqueous Concentrates	X	
Special Aqueous Solutions	X	
Filter Cartridges	X	
Oil	X	
Other Organic Liquids	X	X
Membranes	X	
Biological	X	X

Table 3. FORMULATION DEVELOPMENT STUDIES INITIATED IN FY 1981

Waste Type	Hydraulic Cements (w, w/o additives)	Polymer Modified Gypsum Cement	Thermosetting Polymers
Ion exchange resins	X	X	X
Incinerator ash	X	X	X
Oils	X	X	
Scintillation liquids	X	X	
Nitrates	X		X

Table 4. FY 1982 EFFORTS

(1) Formulation development work will be completed for:

- ion exchange resins
- oils
- organic liquids
- incinerator ash
- nitrate wastes

(2) Waste form property measurements will continue and be expanded to include additional waste form types.

(3) Topical reports will be issued for the solidification of:

- ion exchange resin wastes
- oils and organic liquids

(4) Formulational studies for the solidification of additional waste streams will begin.

(5) Technical assistance will be performed as requested by NLLWMP.

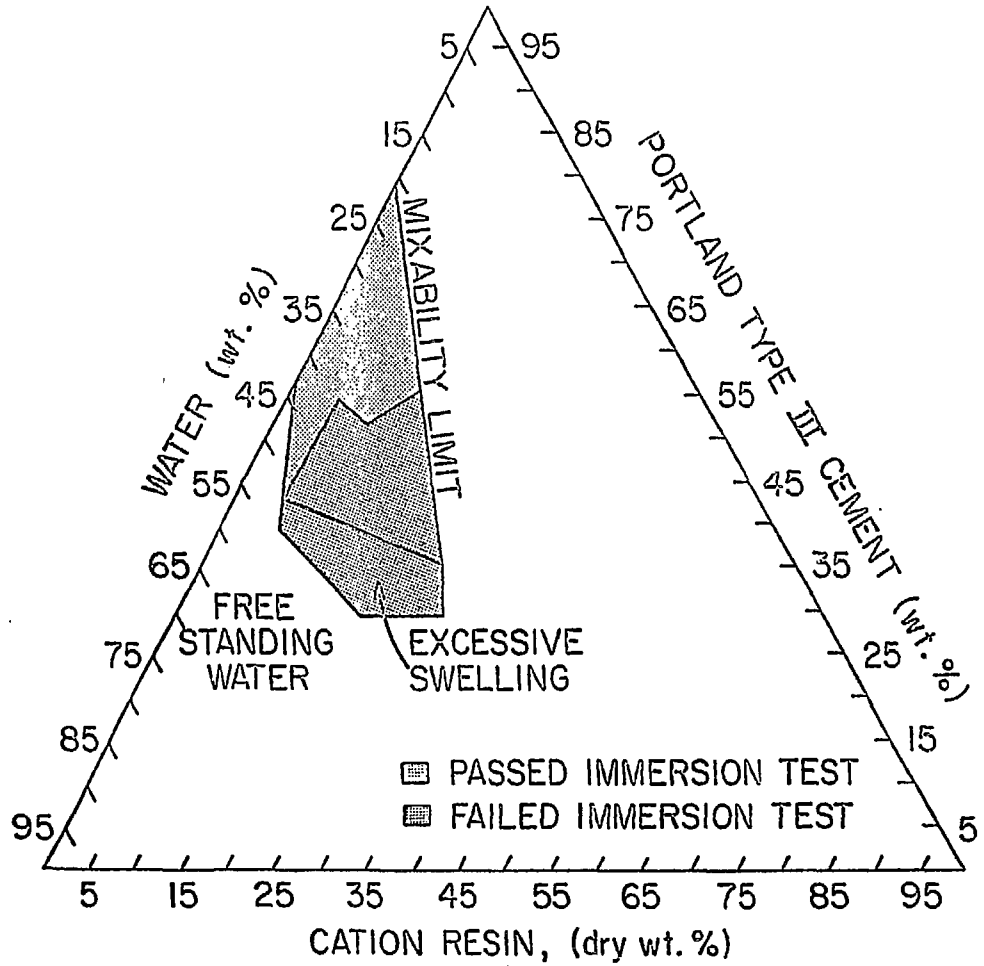

Figure 1. Ternary composition diagram for the solidification of unloaded cation resin in portland type III cement.

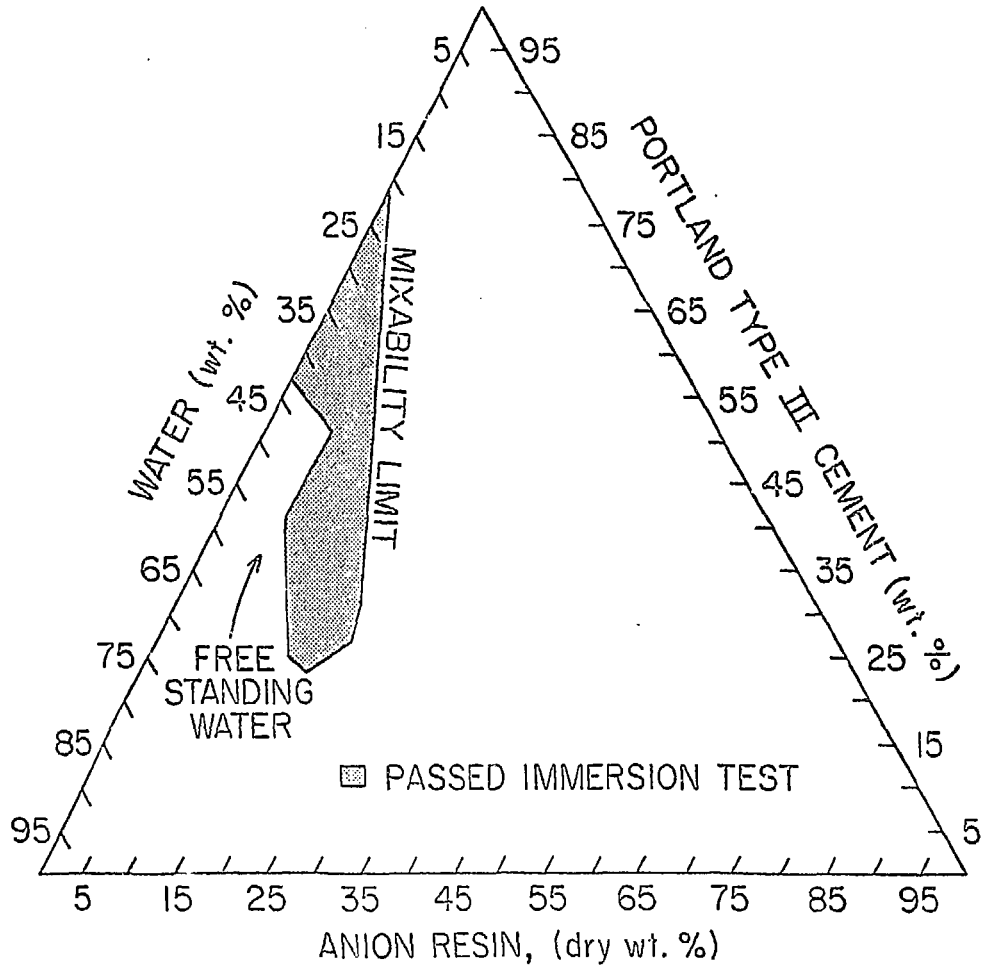

Figure 2. Ternary composition diagram for the solidification of unloaded anion resin in portland type III cement.

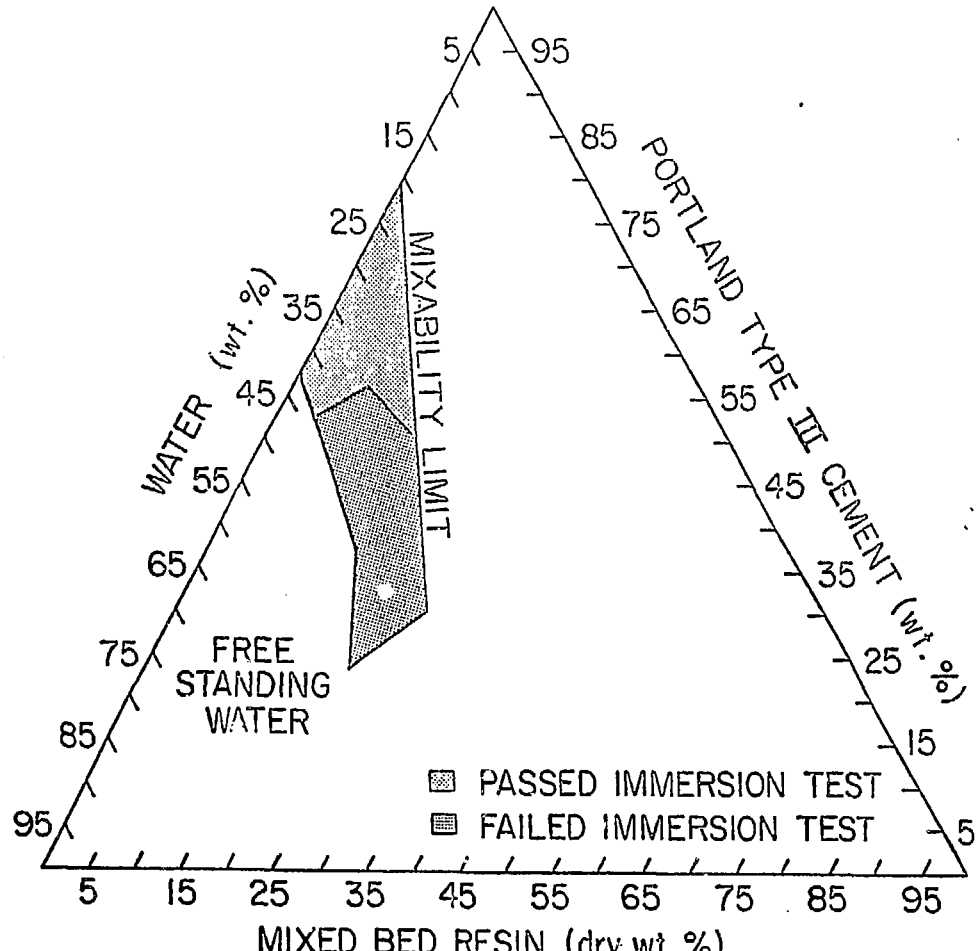

Figure 3. Ternary composition diagram for the solidification of unloaded mixed bed resin in portland type III cement.

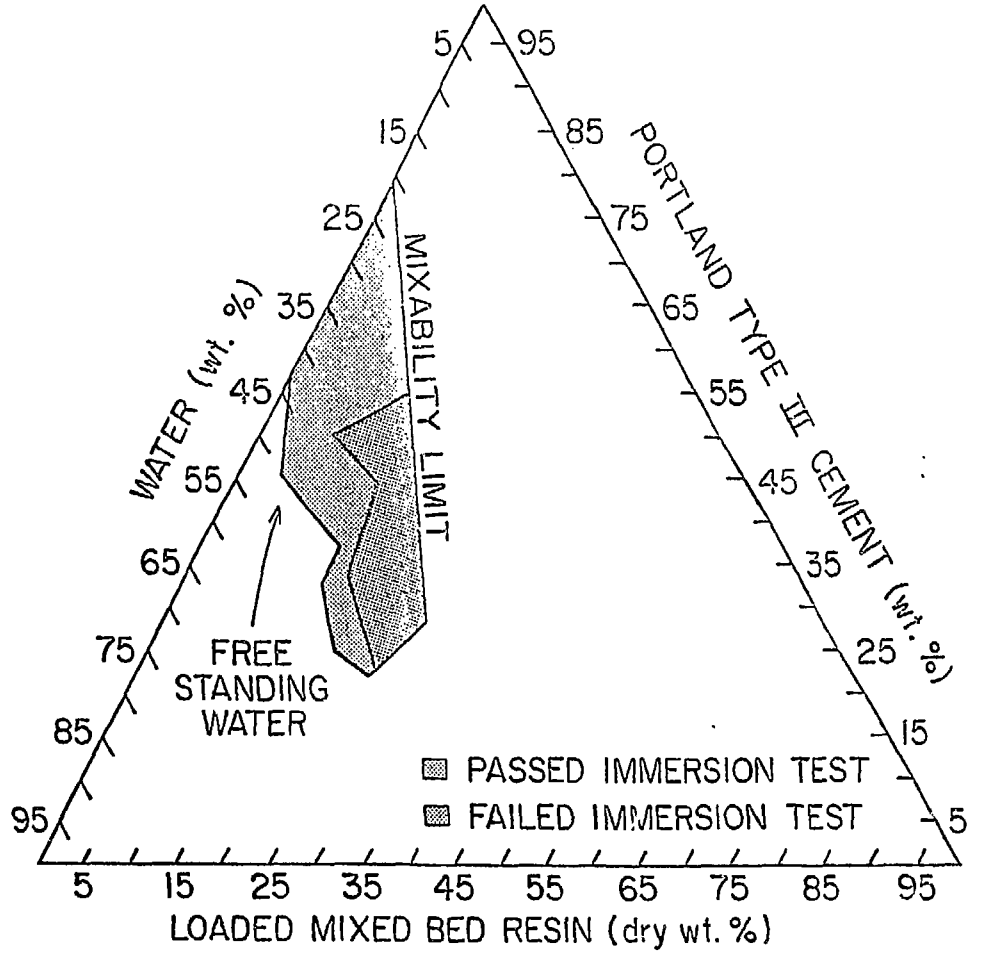

Figure 4. Ternary composition diagram for the solidification of loaded mixed bed resin in portland type III cement.