CONF-8308106--14 BNL-33675

WASTE FORM DEVELOPMENT/TEST

BNL--33675

DE84 001158

by

P. D. Kalb and P. Colombo

Department of Nuclear Energy
Brookhaven National Laboratory
Upton, New York 11973

Paper presented at the Fifth Annual DOE LLWMP Participants Information Meeting. August 30 - Sept. 1, 1983, Denver, Colorado.

WASTE-FORM DEVELOPMENT/TEST

P. D. Kalb and P. Colombo
Department of Nuclear Energy
Brookhaven National Laboratory
Upton, New York 11973

ABSTRACT

The main objective of this study is to investigate new solidification agents relative to their potential application to wastes generated by advanced high volume reduction technologies, e.g., incinerator ash, dry solids, and ion exchange resins. Candidate materials selected for the solidification of these wastes include a modified sulfur cement and low-density polyethylene, neither of which are currently employed commercially for the solidification of low-level waste (LLW). As both the modified sulfur cement and the polyethylene are thermoplastic materials, a heated screw type extruder is utilized in the production of waste form samples for testing and evaluation. In this regard, work is being conducted to determine the range of conditions under which these solidification agents can be satisfactorily applied to the specific LLW streams and to provide information relevant to operating parameters and process control.

PROGRAM SCOPE AND OBJECTIVES

One of the overall objectives of the U.S. Department of Energy's Low-Level Waste Management Program (LLWMP) is to provide support for the disposal of low-level waste (LLW) in a manner which reduces the risk to public health and safety over both the short and long term, while improving efficiency and cost effectiveness [1]. In keeping with these LLWMP objectives, the work performed at Brookhaven National Laboratory under the Waste Form Development/Test program, provides information aimed at developing technology for the improved immobilization of LLW streams.

Program goals through FY 1982 concentrated on the characterization and optimization of solidification technologies which are currently being utilized in the commercial sector. Solidification matrices investigated under this completed phase of the program included hydraulic cement, modified gypsum cement and thermosetting polymers. Formulation development studies were conducted for the solidification of "problem" wastes including ion exchange resins, oil and organic liquids, and nitrate salt wastes which defined compositional envelopes that lead to successful solidification. Waste form performance testing and evaluation for these waste type-solidification agent combinations was performed. Details and results of this work are described in References 2, 3 and 4.

Beginning in FY 1983 the objectives of the Waste Form Development/Test program were modified in favor of the investigation of new solidification agents which are not currently employed for the immobilization of LLW streams. Particular emphasis is placed upon the solidification of wastes generated by advanced high volume reduction technologies e.g., incinerator ash and dry solid evaporator concentrates as well as those contemporary waste streams which continue to be troublesome e.g., ion exchange resins. This program will identify and evaluate new potential agents and processes and determine the range of conditions under which these materials can be successfully applied to the LLW streams indicated. Process control information and relevant operational parameters will be developed. Program objectives will be accomplished through the following subtasks.

SELECTION OF IMPROVED SOLIDIFICATION AGENTS FOR FURTHER STUDY

Work has been conducted to identify and evaluate improved solidification agents for further study. A list of potential candidates was developed based on experimental scoping data and a survey of available literature. The materials under consideration included sulfur cement, a cementitious combination of anhydrous lime and ash, low density polyethylene, polymer impregnated concrete, polymer concretes, low temperature silicate glass, polymer modified gypsum cement, an epoxy/inert carrier system, a modified hydraulic cement system, and various mineralization (clay reaction) processes. None of these materials are currently employed commercially for the solidification of low-level radioactive waste.

Candidate materials were screened based upon their potential for the improved solidification of low-level wastes, with an emphasis on the solidification of waste types resulting from advanced volume reduction techniques. The preliminary criteria upon which potential waste form solidification agents were judged consisted of:

- The ability to increase the amounts and/or types of waste incorporated.
- The simplicity of process operation and maintenance.
- Quality control requirements.
- Process economics
- Waste form properties which are relevant to the immobilization of radionuclides contained in the waste.

The assessment of potential solidification agents, based upon the selection criteria outlined above, is summarized in Table 1. Many of the agents surveyed represent unproven technologies for which limited data bases exist. In such cases judgements were made based upon the best available information. Where sufficient data to make a reasonable determination was lacking, information gaps are indicated. More extensive waste form testing for those

TABLE 1. ASSESSMENT OF POTENTIAL IMPROVED SOLIDIFICATION AGENTS

AGENT	Waste Compatibility	Solidification Efficiency	Processibility/ Quality Control	Material Cost/ Availability	Process Economics	Mechanical Properties	Chemical Properties	COMMENTS
MODIFIED SULFUR CEMENT	3	3	?	3	?	3	?	Wide range of waste type compatibility and solidification efficiency. Good mechanical properties. Low materials cost. Unproven technology.
LIME/ASH	1	2	3	3	2	?	?	Limited waste stream application.
LOW DENSITY POLYETHYLENE	3	3	3	3	2	?	?	Wide range of waste type compatibility and solidification efficiency. Favorable mechanical and chemical properties. Unproven technology.
POLYMER IMPREGNATED CONCRETE	2	2	1	2	1	3	3	Same range of waste type compatibility and solidification efficiency as current cement systems. Good mechanical and chemical properties. Complex and costly processing requirements. Unproven technology.
POLYMER CONCRETE	3	3	2	2	1	3	3	Wide range of waste type compatibility and solidification efficiency. Good mechanical and chemical properties. Processibility is waste sensitive.
SILICATE GLASS	3	3	1	3	1	3	3	Good volume reduction. High temperatures, high processing & maintenance costs. Presently under investigation at Mound Laboratory.
POLYMER MODIFIED GYPSUM CEMENT	3	2	3	3	2	1	1	Wide range of waste type compatibility (including oils and organic liquids). Poor waste form performance, e.g., susceptible to erosion in water and high leachability.
MINERALIZATION (CLAY REACTION PROCESSES)	1	2	1	3	?	?	3	Low leachability. Results in large waste volume increase. Unproven technology.
MODIFIED HYDRAULIC CEMENT	3	2	3	3	3	?	?	Proven technology.
EPOXY/INERT CARRIER SYSTEM	?	3	?	2	1	?	?	A complex volume reduction/solidification process. Unproven technology.

KEY: 3 = good
2 = fair
1 = poor
? = insufficient information available to date

solidification agents selected will be carried out in future property evaluation studies. These studies will be based upon the preliminary waste form evaluation criteria described later in this report.

Due to budgetary constraints the selection of solidification agents for further investigation was necessarily restricted to three systems. These include: 1) modified sulfur cement, 2) low-density polyethylene and 3) an improved hydraulic cement system. It should be noted that in selecting a limited number of potential materials for further study, the relative merits of each agent were considered for the criteria outlined previously. No solidification material, either among those currently in use or these proposed for further investigation, have proven to meet all of the stated requirements under all conditions. Based upon available information, the materials which have been selected represent those judged most likely to provide an overall improvement in waste solidification processing and waste form performance without imposing unreasonable economic penalty. As waste stream and solidification technology improve, this evaluation of potential agents may need to be revised.

Modified Sulfur Cement

In efforts directed towards creating a useful construction material from abundant byproduct sulfur, the United States Department of the Interior Bureau of Mines has developed a new, modified sulfur cement [5]. Sulfur cement is a thermoplastic material which flows when heated above its melting point (116°C) and forms a monolithic solid upon cooling. The material developed by the Bureau of Mines is formulated by reacting elemental sulfur with several chemical additives to form linear polymeric polysulfides. This polymer modification inhibits the allotropic transformation from the monoclinic sulfur ($S\alpha$) to the orthorhombic form ($S\beta$). If not eliminated, this phase transformation present in un-modified elemental sulfur, creates internal stresses due to variations in the densities associated with each phase, leading to degradation of product integrity. Thus modified sulfur cement can be expected to maintain durability over extended periods of time. In addition, this material has been shown to be extremely corrosion resistant in both acid and alkaline environments. Laboratory scale modified sulfur cement waste form specimens are being processed utilizing a screw extruder. This technique involves the simultaneous heating and mixing of the raw materials and transformation into a formed solid product by forcing it through a die and cooling.

Low Density Polyethylene

Although the use of polyethylene as a potential radwaste solidification agent was first suggested a number of years ago [6], several new developments warrant a more thorough examination of its applicability and properties, vis-a-vis the incorporation of low-level waste. These developments include improvements in waste processing and solidification technologies (which provide improved waste-binder compatibility and cost effectiveness), as well as conforming to the more stringent waste form acceptance criteria imposed for shallow land burial. Due to its high viscosity upon melting and a tendency to entrain air, polyethylene is also processed using a screw extruder. Low density polyethylene is available in a wide range of melt indexes (a measure of the materials's viscosity and flow characteristics upon melting).

Proper selection of the polyethylene type best suited for each waste stream enhances the compositional (loading) efficiency and waste form performance characteristics.

Improved Hydraulic Cement

Solidification experience using hydraulic cement is well documented. Previous studies at BNL have provided information which suggest that modifications to contemporary cement systems may provide significant improvement in waste form performance [2]. These modifications include the use of sorption additives for improved radionuclide retention, and compositional additives for greater waste stream compatibility and improved mechanical integrity. Development of an improved hydraulic cement system is planned for FY 85.

In summary, as both sulfur cement and polyethylene are thermoplastic materials which form a monolithic solid upon cooling, they are not dependent upon complex chemical interactions and solidification of the waste is assured. These materials are especially well suited for the incorporation of dry wastes resulting from advanced volume reduction systems. A key advantage of employing a modified hydraulic cement system is its compatibility with existing contemporary solidification systems.

SELECTION OF WASTE TYPES

The selection of low-level waste types, for use in the studies for advanced solidification agents, was based on the following factors:

- wastes with relatively high generation rates
- wastes resulting from improved volume reduction techniques
- wastes which cannot be satisfactorily solidified by available processes

Although the above considerations encompass a large number of waste streams, as presently being generated, budgetary and time restraints impose a limit to the number of waste types which can be considered for incorporation into selected solidification agents. The waste types selected for this study include:

1. Incinerator Ash

Incineration of combustible waste is a viable technology which can provide volume reduction factors as high as 100:1. Extensive volume reduction in combination with the fact that incinerated residue ash is chemically inert and therefore not susceptable to biodegradation, makes this technique a favorable option for the processing of combustible LLW. Although current generation rates are relatively low, it is anticipated that incinerator ash will represent a major waste type in the future. In order to reduce dispersability in both transportation and the shallow land burial environment the solidification of ash is desirable.

2. Evaporator Concentrates

Typically, evaporator concentrates comprise 28 volume percent of boiling water reactor (BWR) low-level waste and 26 volume percent of pressurized water reactor (PWR) low-level waste. BWR evaporator concentrates result from the use of sulfuric acid and sodium hydroxide in the regeneration of ion exchange resins. The neutralized liquid contains sodium sulfate as its principal chemical constituent. The major chemical constituent of PWR evaporator concentrates is boric acid which is added to primary cooling water to control reactor power levels. Although the majority of this waste is currently solidified from an aqueous state, further volume reduction of up to 9:1 can be achieved by evaporating to dryness. Furthermore, increased waste form loading can be achieved by evaporation to a dry solid condition.

3. Ion Exchange Resins

Ion exchange resins are a contemporary waste which continue to present solidification problems. The swelling and cracking of waste forms incorporating ion exchange resins in hydraulic cement is well documented [3]. Current generation rates for ion exchange resin wastes are approximately 0.08 m^3/MW(e)-yr for BWR's and 0.02 m^3/MW(e)-yr for PWR's. While this represents only 10 volume percent and 4 volume percent of total low-level waste volumes, respectively, these wastes contain 35 percent and 57 percent of the activity generated as low-level waste from light water reactors [7]. Due to the importance of resin wastes and the difficulties associated with their solidification this waste type has been included in the study.

PRELIMINARY WASTE FORM DEVELOPMENT SCOPING STUDIES

Some preliminary waste form development scoping work has begun in order to better assess the potential of those solidification agents selected. Sample waste forms were processed for each waste type-solidification agent combination to confirm process compatibility and determine approximate quantities of waste which can be successfully incorporated in each matrix. Further formulational development studies are scheduled for FY 1984 to better define the compositional and operational parameters relevant to each system.

As discussed previously, both modified sulfur cement and low-density polyethylene are thermoplastic materials which are combined with a given waste, mixed, heated and extruded by use of a single screw extruder. A 1 1/4" diameter screw, 3 horsepower DC drive floor model extruder manufactured by Killion Extruders, Inc., Verona, NJ, as shown in Figure 1, was employed to process laboratory scale waste form specimens. This machine is equipped with four separate solid state time proportioning controlled heat zones, automatic air cooling, 12 to 120 RPM speed range, and melt pressure and temperature instrumentation.

The results of preliminary formulational development scoping studies for modified sulfur cement and polyethylene are presented in Table 2. These data provide the approximate quantities of dry waste solids which have thusfar been successfully incorporated in each solidification matrix material.

TABLE 2. WASTE LOADINGS OBTAINED IN FORMULATIONAL DEVELOPMENT SCOPING STUDIES FOR THERMOPLASTICS

Agent	Waste Loading, dry wt%			
	Na_2SO_4	H_3BO_3	Ash	Ion Exchange Resin
Modified Sulfur Cement	65	40	20	40
Low Density Polyethylene	60	25	25	50

During the course of process development scoping studies a number of potential problem areas were uncovered. Optimization of waste loadings for both thermoplastic matrix materials was limited, in general, by a number of factors:

- Moisture contained in the waste created excessive vapor pressure upon heating, upsetting the uniform flow of material through the extruder. Product foaming also resulted from entrapped moisture, reducing the quantity of waste contained in the solified waste form.

- Decomposition of some waste streams, e.g., dry solid boric acid concentrates, occasionally occurred within the range of extruder operating temperatures, causing the subsequent release of water vapor and/or other volatile gases. The net effect on solidified waste products due to such decomposition reactions was similar to those outlined above for contained moisture.

- Differences in density and particle size between dry waste and binder material, at times caused separation and resultant homogeneity problems in solidified specimens.

- The viscosity of the waste-binder mixture which is a function of the properties of both the matrix material and waste stream as well as the waste/binder ratio, was a major limiting factor. Excessive mixture viscosity was found to cause machine strain and/or screw seizure.

Each of the problems outlined above was partially mitigated in the production of scoping study waste form specimens. To the extent that these limiting factors can be further overcome as a result of continuing process development studies, improvements in waste form volumetric efficiencies beyond those reported in Table 2 can be expected.

PRELIMINARY WASTE FORM EVALUATION CRITERIA

Historically, waste form characteristics have been considered to be of secondary importance to burial site selection; however, experience obtained in operating LLW disposal sites has made it apparent that waste form properties can play a significant role in the overall objective of environmental containment. Degradation of waste forms through chemical and mechanical instabilities can lead to slumping, collapse, or other failure of a burial trench or trench cap which, in turn, increases the potential for radionuclide migration by water infiltration (e.g., leaching) and other mechanisms (e.g., dispersion). Since complete isolation by land burial is difficult, the practicality of minimizing releases through improved waste forms is now recognized as both desirable and necessary.

Work was conducted during the first quarter of FY 83 to provide a working set of waste form evaluation criteria which encompasses the chemical and physical properties of waste forms that can potentially affect the migration of radionuclides in the burial environment. The growing awareness of the need for more extensive waste form evaluation criteria is evidenced by the fact that the U.S. Nuclear Regulatory Commission (NRC) has recently published a technical position paper which elaborates a number of tests to be performed in support of the general requirements established in 10 CFR Part 61 [8]. Implementation of waste form evaluation criteria, in association with specified test procedures, will develop a numerical waste form property data base suitable for:

- Providing a comparative ranking of waste form properties.
- Developing waste form and/or waste package performance criteria from which specifications for the safe disposal of radioactive wastes can be formulated.
- Determining container and/or package requirements for disposal under varying environmental conditions (humid, arid sites).

Specific evaluation criteria along with related testing procedures where established, are outlined in Table 3.

TABLE 3. PRELIMINARY WASTE FORM EVALUATION CRITERIA

Properties	Test Method
Leachability	ANS 16.1
Compressive strength	ASTM C 39
Impact strength	TBD[a]
Radiation stability	10^8 Rads, ASTM C 39
Biological stability	TBD
Freeze-thaw resistance	ASTM C 666/B 553, C 39
Water immersion	TBD

a. TBD = to be determined.

PRELIMINARY WASTE FORM PROPERTY EVALUATION STUDIES

In order to better assess the feasibility of the selected waste type-solidification agent combinations, several preliminary waste form performance tests were conducted i.e., two week water immersion and compressive strength tests. These two tests provide the basis for an initial assessment of waste form acceptability. The remaining evaluation criteria outlined previously are of little significance if either of these criteria are not met. For the purposes of this study waste form specimens were subjected to compressive loads of at least 50 psi in order to ascertain their ability to withstand the overburden pressure typically experienced in shallow land burial. None of the waste form test specimens listed in Table 2 failed to meet this criteria. The results of two week immersion testing for these same formulations is given in Table 4.

TABLE 4. RESULTS OF IMMERSION TEST FOR FORMULATIONS CONTAINING WASTE LOADINGS AS SPECIFIED IN TABLE 2[a]

	Waste Type			
Agent	Dry Na_2SO_4 Concentrate	Dry H_3BO_4 Concentrate	Dry Ash	Dry Ion Exchange Resin
Modified Sulfur Cement	●	●	●	X
Low Density Polyethylene	●	●	●	●

a. x = Sample failure (gross loss in mechanical integrity) observed within two weeks.

● = No sample failures observed within two weeks.

CONCLUSIONS

From analysis of the preliminary data generated thusfar, it has been demonstrated that each solidification process selected for further investigation has potential application for the solidification of one or more waste type. As discussed earlier, no single solidification agent appears superior for all waste types in question. For the solidification of dry evaporator concentrate salts, both thermoplastic materials appear promising, possibly with a slight edge in favor of modified sulfur cement. Solidification of ion exchange resin waste was accomplished most successfully by the use of low density polyethylene. Based upon overall waste stream compatibility and preliminary waste form performance test results the potential effectiveness of these solidification matrices can be ranked in the following order:

1) low density polyethylene

2) modified sulfur cement

3) improved hydraulic cement

Process development and waste form property evaluation studies for each of these materials is scheduled to continue in FY 1984 and into FY 1985, so that one system can be selected for scale-up demonstration which will commence in FY 1985.

REFERENCES

1. DOE LLWMP, Five Year Program Management Plan, Low-Level Waste Management Program, Volume II, Defense Program, US DOE, Idaho Operations Office, Idaho Falls, ID, March 1983.

2. Nielson, R.M. Jr. and P. Colombo, Waste Form Development Program Annual Progress Report, Oct. 1981-Sept. 1982, BNL-51614, Brookhaven National Laboratory, Upton, NY, September 1982.

3. Neilson, R.M., Jr. and P. Colombo, Solidification of Ion Exchange Resin Wastes, BNL-51615, Brookhaven National Laboratory, Upton, NY, August 1982.

4. Clark, D.E., P. Colombo and R.M. Neilson, Jr., Solidification of Oils and Organic Liquids, BNL-51612, Brookhaven National Laboratory, Upton, NY, July 1982.

5. Sullivan, T.A. and W.C. McBee, Development and Testing of Superior Sulfur Concretes, Report of Investigations 8160, United States Department of the Interior Bureau of Mines, Washington, DC, 1976.

6. Fitzgerald, C.L., H.W. Godbee, R.E. Blanco and W. Davis, Jr, "The Feasibility of Incorporating Radioactive Wastes in Asphalt or Polyethylene" Nuclear Applications and Technology, Vol. 9, December 1970.

7. Wild, R.E., O.I. Oztunali, J.J. Clancey, C.J. Pitt and E.D. Picazo, Data Base for Radioactive Waste Management, Waste Source Options Report, NUREG/CR-1759, Volume 2, 1981.

8. US NRC, "Technical Position Waste Forms," U.S. Nuclear Regulatory Commission, Washington, DC, May 1983.