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WASTE FORM DEVELOPMENT PROGRAM ANNUAL REPORT

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ABSTRACT

This report provides a summary of the work conducted for the Waste Form Development/Test Program at Brookhaven National Laboratory in FY 1983 under the sponsorship of the U.S. Department of Energy's Low-Level Waste Management Program. The primary focus of this work is the investigation of new solidification agents which will provide improved immobilization of low-level radioactive wastes in an efficient, cost-effective manner.

A working set of preliminary waste form evaluation criteria which could impact upon the movement of radionuclides in the disposal environment was developed. The selection of potential solidification agents for further investigation is described. Two thermoplastic materials, low-density polyethylene and a modified sulfur cement were chosen as primary candidates for further study. Three waste types were selected for solidification process development and waste form property evaluation studies which represent both "new" volume reduction wastes (dried evaporator concentrates and incinerator ash) and current "problem" wastes (ion exchange resins).

Preliminary process development scoping studies were conducted to verify the compatibility of selected solidification agents and waste types and the potential for improved solidification. Waste loadings of 50 wt% Na_2SO_4 , 25 wt% H_3BO_3 , 25 wt% incinerator ash and 50 wt% dry ion exchange resin were achieved using low density polyethylene as a matrix material. Samples incorporating 65 wt% Na_2SO_4 , 40 wt% H_3BO_3 , 20 wt% incinerator ash and 40 wt% dry ion exchange resin were successfully solidified in modified sulfur cement. Additional improvements are expected for both matrix materials as process parameters are optimized. Several preliminary property evaluation studies were performed to provide the basis for an initial assessment of waste form acceptability. These included a two week water immersion test and compressive load testing.

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1. 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 [1.1]. 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 1.2-1.4.

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. The properties of solidified waste forms formulated from these new potential agents will be investigated.

This report covers the work performed for the Waste Form Development/Test program in FY 1983 and includes information in the following areas:

- The Development of Preliminary Waste Form Evaluation Criteria for Shallow Land Burial of LLW: These criteria, along with applicable standards and test methods, will be employed for the evaluation of waste form properties and performance in a burial environment.

- The Selection of Improved Solidification Agents for Further Investigation: A number of potential agents are surveyed and evaluated, with two primary candidates chosen for further study.

- The Selection of Waste Types to be Solidified With Improved Agents: Major contemporary waste streams, as well as advanced volume reduction wastes which are becoming increasingly important are discussed. Three waste types are selected for solidification process development and waste form property evaluation studies which represent both "new" volume reduction wastes and current "problem" wastes.

- Process Development Scoping Studies: Preliminary studies were conducted to provide verification of waste type-solidification agent compatibility and the potential for improved solidification.
- Preliminary Waste Form Property Evaluation Studies: Several preliminary property evaluation tests for waste type-solidification agent combinations formulated in process development scoping studies were conducted to provide a first order assessment of waste form acceptability.

In FY 1984 process development studies will be conducted to 1) ascertain the effects of processing parameters and methodology on waste solidification using improved agents, and 2) to optimize these parameters for maximum waste form volumetric efficiency. Property evaluation studies to fully characterize the physiochemical properties of waste forms solidified using improved matrix materials will be initiated.

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2. PRELIMINARY WASTE FORM EVALUATION CRITERIA FOR SHALLOW-LAND DISPOSAL OF LOW-LEVEL RADIOACTIVE WASTE

A primary objective of nuclear management programs is the disposal and isolation of radioactive waste in such a way as to minimize exposure to operational personnel, assure the safety and health of the public, and generally protect the environment from potentially hazardous releases of radionuclides. With regard to the disposal of low-level waste (LLW), current emphasis is placed on shallow-land burial which is the planned deposition of radioactive waste in a manner which is considered permanent and which provides the necessary isolation to preclude adverse environmental effects during the time required for the activity to decay to safe levels.

Historically, waste form characteristics were 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 cap or cover which, in turn, increases the potential for radionuclide migration by water infiltration, i.e., leaching, and other mechanisms. 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.

A working set of waste form evaluation criteria which could impact upon the movement of radionuclides in disposal was developed [2.1]. These criteria will identify specific chemical and physical properties of waste forms for subsequent evaluation studies. Consequently, it precludes criteria directly associated with the performance of the waste form or the waste package.

Implementation of waste form evaluation criteria, in association with specified test procedures, will develop a numerical waste form property data base suitable for:

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

2.1 Preliminary Waste Form Evaluation Criteria and Standards

Specific evaluation criteria are suggested for the waste form. Standard testing procedures will be used, where possible, for determining the pertinent properties of solidified waste forms. New testing procedures will be developed as needed and their reliability and effectiveness confirmed.

Assumptions:

It was necessary to make certain assumptions in developing the following waste form evaluation criteria. These assumptions are:

- the solidified waste form shall be a free standing monolithic solid.
- radioactive materials shall be homogeneously distributed throughout the waste form.

Waste Form Evaluation Criteria:

Criterion: The leachability of radionuclides from a waste form shall be measured.

Standard: "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes," American Nuclear Society Standards Committee, Working Group ANS 16.1 [2.2].

Discussion: Leachability refers to the release of radionuclides from the waste form by fluids. Mechanisms such as dissolution, diffusion and chemical reactions may contribute to this release. In shallow land burial, waste forms may be contacted by groundwater, percolate rainwater, or any other liquids present in the trenches which can transport radionuclides from the waste form into the environment. Knowledge of the release rates of radionuclides from different waste forms is important for site monitoring and modeling purposes.

Criterion: The compression strength of a waste form shall be determined.

Standard: "Test for the Compression Strength of Cylindrical Concrete Specimens," ASTM method C 39 [2.3].

Discussion: Waste disposal by shallow-land burial generally consists of placing waste forms into excavated trenches which are then backfilled with soil, capped, and mounded to facilitate rainwater run-off. Thus, a buried waste form must be of sufficient mechanical strength to maintain its integrity under loading pressures arising from land overburden. The degradation of a waste form under compression can lead to the settlement of trench contents followed by the subsidence or slumping of the trench walls and/or cover. This, in turn, increases percolation of water into the disposal trench which accelerates the rate of trench collapse and increases the potential of radionuclide migration by leaching.

Criterion: The impact strength of a waste form shall be determined.

Standard: The unnotched Izod Impact strength test, ASTM procedure D 256 [2.4].

Discussion: Prior to disposal, a waste form may be subjected to impact stresses resulting from normal transportation, handling and disposal operations. Sudden impact stresses can produce cracks and fractures which increase the effective surface area of the waste form while decreasing its overall structural stability. This enhances the potential for the

migration of radionuclides by leaching or dispersion, and increases the possibility of trench cap deterioration and/or subsidence.

Criterion: The effects of radiation on the physical and chemical properties of the waste form shall be determined.

Standard: To be determined.

Discussion: It is anticipated that the use of advanced volume reduction technologies will result in volume reduction factors ranging from 2 to over 100. This will substantially increase the activity levels of solidified waste forms. Self-irradiation by contained radionuclides may result in the degradation of the properties of the waste forms and the generation of gases from radiolysis which may lead to overpressurization of the waste form or container and the possible formation of a combustible atmosphere.

Criterion: The biological stability of a waste form containing organic materials shall be determined.

Standard: To be determined.

Discussion: A wide variety of organic substrates are present in low-level radioactive wastes. Considerable information has been collected demonstrating that these materials are metabolized by microbial processes to form radioactive gases such as tritiated and carbon-14 tagged methane and carbon-14 tagged CO₂. Trench cap deterioration and trench subsidence can be attributed to diminished volume of the waste material due to microbial conversion of the waste to gaseous and water soluble products.

Criterion: The effects of aqueous media on the stability of the waste form shall be determined.

Standard: To be determined.

Discussion: A low-level radioactive waste form must maintain its integrity under conditions encountered in land burial. One of the conditions is exposure to ground water which, depending on the type of waste, may cause swelling, dissolution, cracking and exfoliation of the waste form with time. These effects compromise the ability of the waste forms to adequately retain radionuclides. Swelling of the waste form may breach the container resulting in premature release of radionuclides. Disintegration of the waste form will reduce its integrity and/or volume resulting in trench cap deterioration or trench subsidence.

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3. SELECTION OF IMPROVED SOLIDIFICATION AGENTS FOR FURTHER INVESTIGATION

While a number of agents have been employed for the solidification of low-level radioactive waste, processing and/or performance difficulties have been encountered with each system under certain conditions. Such difficulties include incompatibility with waste constituents inhibiting the formation of a monolithic solid, poor solidification efficiency, the presence of free standing liquids, premature setting and processing/product flammability. Certain waste types in particular, e.g. boric acid evaporator concentrates and ion exchange resin wastes, have proven difficult to solidify with one or more of the contemporary agents. Similar problems are anticipated for the solidification of wastes generated by advanced high volume reduction technologies. These "new" waste streams include incinerator ash and dry evaporator concentrates.

A major objective of this task is 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 modified sulfur cement, low density polyethylene, polymer impregnated concrete, polymer concretes, and silicate glass. None of these materials are currently employed commercially for the solidification of low-level radioactive waste. Solidification agents including portland cements, vinyl ester-styrene, and bitumen have been previously developed for commercial applications to low-level waste solidification and, therefore have not been considered in this study.

3.1 SELECTION CRITERIA

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:

- waste-solidification agent compatibility
- solidification efficiency
- ease of processibility and quality control
- material costs and availability
- physical properties
- chemical properties

3.1.1 Waste-Solidification Agent Compatibility

Waste-solidification agent compatibility considers the ability of solidification agents to incorporate wastes without adverse consequences resulting in a failure to solidify, severe exothermic reactions or poor quality control.

3.1.2 Solidification Efficiency

Solidification efficiency defines the upper limits of waste loadings in a solidification agent. It is a function of factors such as physical and chemical forms of the waste and solidification agent. Solidification efficiency is expressed in terms of the waste to binder ratio or as the weight percent of the total.

3.1.3 Ease of Processibility and Quality Control

Ease of processibility and the ability to maintain quality control are criteria which reflect the inherent complexity of treating waste with a particular solidification agent. Such factors as complexity of system components, personnel training/operating requirements, maintenance and reliability must all be considered when evaluating potential solidification systems.

3.1.4 Material Costs and Availability

Materials for use as solidification agents should be economical and be commonly available in industrial bulk quantities.

3.1.5 Physical Properties

Physical properties of solidification agents refer to characteristics such as compressive strength, resistance to degradation during freeze-thaw cycling and resistance to degradation during water immersion.

3.1.6 Chemical Properties

Chemical properties of solidification agents refer to the ability of solidification agents to resist radionuclide leaching, biological degradation, and waste form dissolution.

3.2 Reviews of Potential Solidification Agents

The solidification agents which were reviewed for evaluation excluded those which are currently employed for low-level radioactive waste solidification in the United States. Although a large number of potential candidates was screened, many were eliminated from consideration based on such factors as limited waste application, system complexity, excessive cost or poor physico-chemical properties. Those materials judged to have reasonable potential as improved agents are reviewed in this section. Many of the agents surveyed represent unproven technologies for which limited information exists.

3.2.1 Glass

A system which utilizes a joule heated glass furnace to simultaneously incinerate or dry LLW while incorporating the residue in glass is under development at Monsanto Mound Laboratory [3.1]. The solidification matrix is a soda-lime silica which is molten at an operating temperature of approximately 1300°C.

As shown in Figure 3.1 solid waste is introduced into the furnace where it is incinerated in a zone of excess oxygen above the glass melt. After combustion, the residual ash mixes with the melt and then is drained to cool and solidify. Loadings of ash in the glass are very high (70-80%) and the resulting waste forms have excellent leaching qualities. As much as 50,000 lbs of combustible waste can be incorporated into a 2000 lb waste form [3.1].

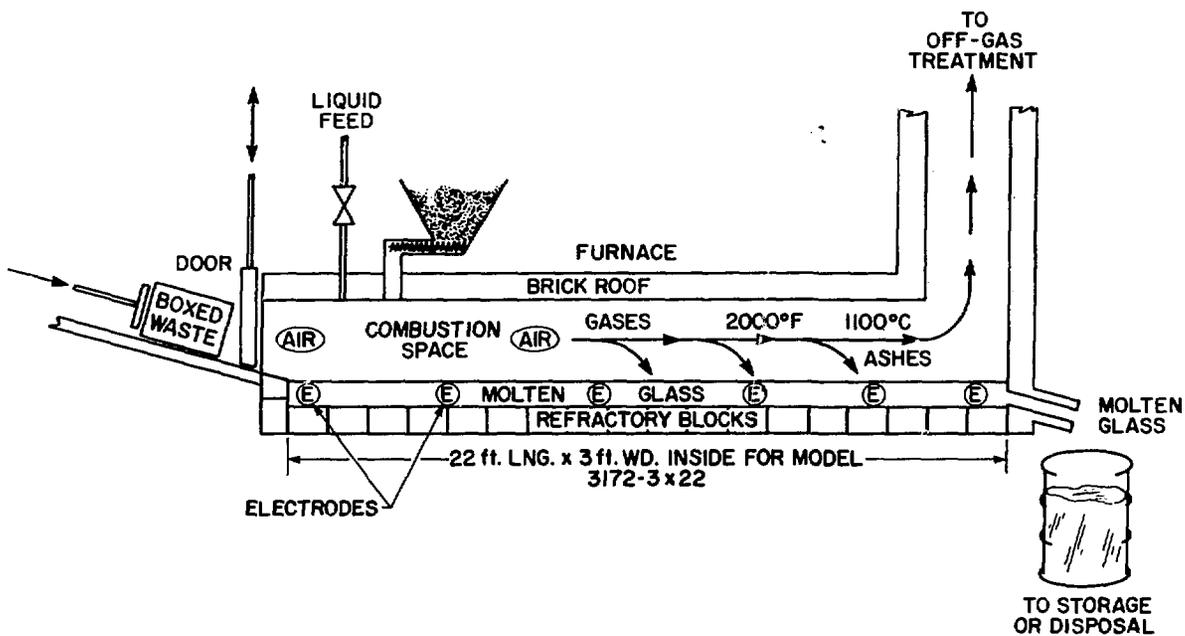


Figure 3.1 A glass furnace which simultaneously incinerates waste and incorporates the residue in glass. Redrawn from [3.2].

Some of the advantages and disadvantages for the use of glass as a low-level radioactive waste solidification matrix are given below [3.1,3.2].

ADVANTAGES:

- High volume reduction factors for solid wastes
- High loading efficiency of the waste form
- Excellent waste form characteristics

DISADVANTAGES:

- High process temperatures volatilize some isotopes found in LLW requiring complex offgas treatment. The large volume of excess air blown through the system to promote incineration carries ash out of the furnace along with non-volatilized radionuclides.
- Operating costs are expected to be high because of the energy usage to maintain the temperature within the furnace. It should be noted that temperatures of approximately 1000°C must be maintained in the furnace, even when no processing is in progress, in order to extend the lifetime of the refractory materials lining the furnace.

3.2.2 Polymer Concretes

Polymer concretes are composite materials originally developed at BNL, which result from the mixing of dry solids with monomers which are subsequently polymerized by chemical initiators. The monomers typically employed are those which have low viscosities and are easily polymerized by conventional methods. The monomer concentration in the waste form is dependent on the

void volume and can vary from 5 to 35 % by weight. In this process the waste is mixed with the monomer containing specific initiator systems. Alternatively, pre-mixed monomers can be used to flood a container of dry powdered or aggregate waste.

Some of the advantages and disadvantages of the use of polymer concrete materials are listed below [3.4,3.5].

ADVANTAGES:

- Good waste form properties, especially leaching and compressive strength.
- High loading efficiency

DISADVANTAGES:

- Problems associated with storage and handling of monomers and other necessary chemicals.
- Chemical incompatibility with some types of wastes.

3.2.3 Polymer Impregnated Concrete

Polymer Impregnated Concrete (PIC) is a material which utilizes polymers to seal the porosity of hardened hydraulic cement waste forms. This process first incorporates the waste into a hydraulic cement matrix and then impregnates the waste form with a polymerizable material to seal the porosity [3.7]. Impregnation can be achieved through either a soaking technique or an evacuation technique.

Leachability has been reported for polymer impregnated concrete as being at least two orders of magnitude less than that of comparable cement samples [3.8]. Figure 3.2 is a schematic of one PIC process.

Some of the advantages and disadvantages of polymer impregnated concrete are given below [3.6,3.7,3.8].

ADVANTAGES:

- Good waste form properties, particularly leachability, mechanical strength and resistance to chemical attack.

DISADVANTAGES:

- Problems associated with handling and storing monomers and other required chemicals.
- A multistep process is required.

3.2.4 Polyethylene

Polyethylene is a relatively inert thermoplastic material of the formula $(-CH_2-)_n$ with a relatively wide range of characteristics depending on chain length and specific gravity. Typically, polyethylenes are specified by their specific gravity and melt index. The latter is an indicator of viscosity at 190°C as determined by ASTM test D 1238. In the United States the only application of polyethylene to low-level wastes has been the experiments at Oak Ridge National Laboratory using a wiped film evaporator [3.10].

Some of the advantages and disadvantages of polyethylene as a rad-waste solidification agent are outlined below [3.11].

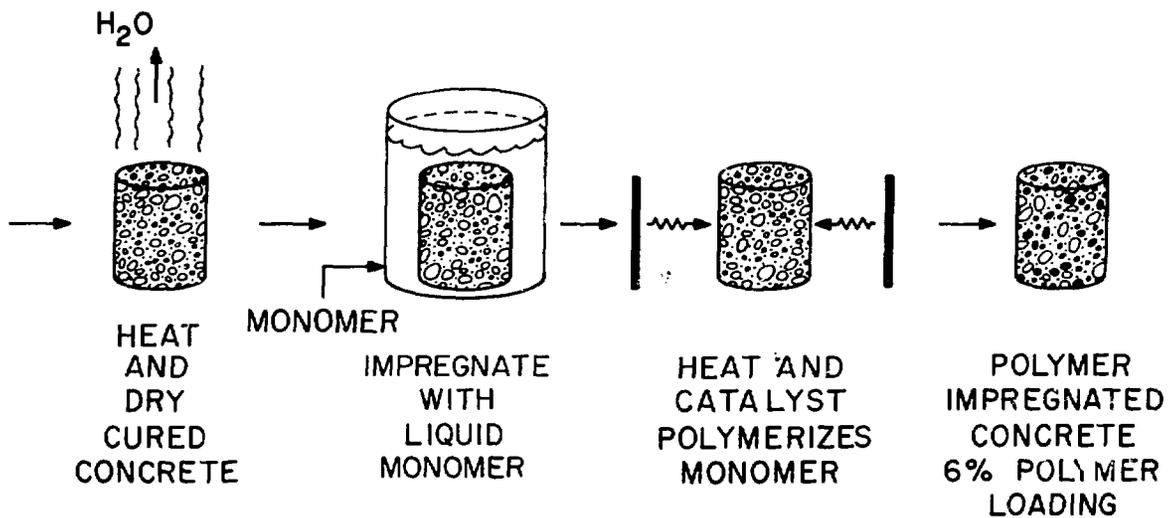


Figure 3.2 A schematic of one method of producing polymer impregnated cement [3.9].

ADVANTAGES:

- Inert material which is resistant to chemical attack.
- Does not require chemical reaction to solidify.

DISADVANTAGES:

- Requires elevated temperatures (approximately 130°C) for processing.

3.2.5 Modified Sulfur Cement

Modified sulfur cement is a compound which was developed by the United States Bureau of Mines as part of a program to develop uses for by-product sulfur. This material is composed primarily of elemental sulfur which has been reacted with organic oligomers to provide a material which is more stable than elemental sulfur. Modified sulfur cement is a thermoplastic material which melts at 119°C. The solid that forms when the sulfur has cooled appears to have good physical and chemical properties.

No work is evident from the literature regarding the use of modified sulfur cement for solidification of low-level radioactive waste. The U.S. Bureau of Mines has run tests which indicate that the material is very durable in hostile chemical environments such as electrolysis acid vats [3.12].

Some of the advantages and disadvantages for the use of modified sulfur cement are given below [3.12].

ADVANTAGES:

- High resistance to chemical attack.
- Does not require chemical reaction to solidify.

DISADVANTAGES:

- Requires elevated temperatures (120°C) for processing.

3.3 Solidification Agents Selected for Further Study

Due to budgetary constraints the selection of solidification agents for further investigation was necessarily restricted to two systems. It should be noted that in selecting a limited number of potential materials for further study, the relative merits of each agent were considered based on the criteria outlined previously. No solidification material, either among those currently in use or those 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 properties. As waste stream and solidification technology improve, this evaluation of potential agents may need to be revised.

The two materials which have been selected as radioactive waste binders for further investigation as improved solidification agents are: [3.13]

- Low Density Polyethylene
- Modified Sulfur Cement

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4. WASTE TYPE SELECTION

In this section three waste types will be identified that have been selected for use with the two solidification agents selected for further study (Section 3). Although low-level radioactive waste encompasses a large number of waste streams as currently being generated, budgetary and time restraints impose a limit to the number of waste types that can be considered for incorporation into selected solidification agents.

Selection of waste types was based on two concepts:

- 1) Wastes resulting from improved volume reduction techniques will become increasingly important. The need to minimize shipping and disposal volumes and costs may result in greater use of advanced volume reduction processes. In addition, the greater chemical stability of wastes resulting from advanced volume reduction, is an advantage in disposal.
- 2) Certain currently generated wastes cannot be satisfactorily solidified by available processes.

A review of the major contemporary low-level waste types as well as some of the advanced volume reduction techniques that are beginning to be applied to them is presented. From this review, the waste types selected will be identified.

4.1 Contemporary Wastes

There are two major categories of low-level radioactive waste:

- Reactor Wastes
- Institutional Wastes

Each category is composed of several specific waste types having different characteristics. These wastes are currently generated in significant quantities and can generally be treated in several ways. Table 4.1 provides an overview of contemporary low-level waste streams.

4.1.1 Reactor Wastes

A variety of waste types are generated by process streams used by reactors during routine operation. In general these wastes result from systems which are used to either cleanse coolant water or to control the quantity of boric acid in coolant which is used to control reactor power levels. These wastes are:

- Filter sludges
- Liquid concentrates
- Ion exchange resins

These waste types accounted for 20% of waste sent to commercial shallow land burial in 1979 and comprised 40% of wastes from power reactors. The volume of reactor process wastes was 15,790 m³ for that year and it contained over 40,000 Ci of activity [4.1]. In addition to process wastes nuclear power stations produce substantial volumes of contaminated trash.

● Filter Sludges

Filter sludges are wet wastes which are primarily comprised of filter precoat materials such as diatomaceous earth, powdex ion exchange resin or special cellulose fiber materials which are used to remove particulates from coolant. Other components of filter sludges include filtered particulates such as corrosion product particles and flocculating agents.

Table 4.1

Contemporary Types of Low-Level Radioactive Wastes

Light Water Reactor Wastes

Ion exchange resins

Filter sludges

Filter cartridges

Liquid concentrates

Contaminated Trash

Institutional Wastes

Scintillation liquids

Biological wastes

Liquid wastes

Contaminated Trash

● Liquid Concentrates

Concentrated liquids comprise 28 volume percent of BWR wastes and 26 volume percent of EWR wastes [4.2]. They result from an evaporation process which allows the waste to be concentrated but still easily pumpable at process temperatures. Liquid concentrates may have a large variety of compositions although typically they are dominated by one of two chemistries.

One form of liquid concentrate, generated at BWRs is dominated by sodium sulfate. This waste type is produced as a by-product of ion exchange resin regeneration which is achieved by treating mixed bed resins with strong concentrations of sulfuric acid and sodium hydroxide. As hydrogen and hydroxyl ions are taken up by the resins, liberated sulfate and sodium ions combine to form sodium sulfate. Current evaporators concentrate this liquid waste to about 25% sodium sulfate with a pH range from 4.5 to 9 and a density of approximately 1.2 g/cm^3 [4.3].

The major chemical constituent of liquid concentrates generated at PWRs is boric acid which is added and removed from the primary coolant, as needed, to control reactor power levels. The waste is evaporated to a maximum boric acid concentration of 12 wt%, although it more typically is about 9 wt%. Liquid concentrates may contain a broad range of materials other than those discussed above. Antifoaming agents, decontamination solutions, laboratory wastes, floor drain waste and hot laundry waste may also be included. As a result, these evaporator bottoms also have a pH range of 4 to 9 [4.3].

- Ion Exchange Resins

Ion exchange resins are typically beads, approximately 0.5 to 1 mm in diameter, which are composed of polystyrene cross-linked with divinylbenzene. These resins have great capacity to sorb ionic species from solution and are therefore utilized to remove impurities from reactor coolant water. Ion exchange resins take up either anions or cations and therefore are regenerated generally with sodium hydroxide or sulfuric acid respectively. This regeneration process leads to the liquid concentrate wastes discussed previously. However, after a number of regenerations the resin is no longer as

effective as required and is replaced. In some cases resins are not regenerated at all and are replaced when they no longer are able to adequately sorb more ions. For disposal, ion exchange resins are dewatered to a moisture content of approximately 42 to 55 wt% [4.2]. Spent resins have been reported to produce carbon dioxide and oxides of both sulfur and nitrogen due to radiolytic and chemical decomposition [4.2].

Ion exchange resins typically have high activities per unit volume. For example, FWR resins have an average of 22.2 Ci per m³ [4.2] and higher activities are possible in special cases.

- Contaminated Trash

A broad spectrum of contaminated materials are generated at virtually all facilities using radionuclides. Typically contaminated trash will be low in activity and can be classified into sub-categories such as: compactible, combustible and non-combustible.

Compacted wastes do not require solidification and will not be considered here. Many compactible wastes such as clothing, rags, paper, filters, wood and plastics are also combustible and can be treated by incineration to achieve high volume reduction. Incineration of wastes will be discussed later in this section. Other materials are both non-combustible and non-compactible. These items such as contaminated tools, equipment and piping are usually packaged with or without prior solidification for disposal.

4.1.2 Institutional Wastes

Institutional wastes are a special classification of waste which is generated at institutions such as universities, private laboratories and hospitals. The wastes are often related to biological and medical research and nuclear medicine. These wastes consist primarily of: [4.2]

- Scintillation liquids and vials
- Laboratory liquids and glassware
- Animal carcasses, tissue, bedding and excreta
- Contaminated trash

Much of this waste is combustible and can be incinerated. In 1981 institutional waste accounted for 15% of low-level waste sent to commercial shallow land burial [4.4]. Activity levels of this waste, typically comprise about 1% of that sent to shallow land burial [4.1].

4.2 Advanced Volume Reduction

Advanced volume reduction techniques applicable to the waste types identified above are of two types:

- Evaporators
- Incinerators

These processes provide very high volume reduction factors and convert many wastes to forms which improve their chemical stability. A recent survey has indicated that a number of nuclear facilities are considering implementation of advanced volume reduction options [4.5]. A brief review of some of these processes is given below.

4.2.1 Fluidized Bed Dryer/Calciner/Incinerator

Fluidized bed processes are used to bring liquid waste to a dry powder or granular state and may also be used to incinerate combustible waste. This technique utilizes a flow of heated air to fluidize a bed of particles which then acts as a heating surface and nucleation site where fine droplets of liquid waste are rapidly evaporated to a dry solid state. By proper adjustment of process parameters, the size of the waste particulates and in part, their chemical form, can be controlled. In this way, many of the dissolved salts are converted to oxides [4.6].

In some processes the fluidized bed actually consists of particles of the material being dried. This is an "active" system. Other systems utilize "inert" beds of a relatively non-reactive material such as alumina or silica. A fluidized bed system at Rocky Flats used for incineration utilized a bed of sodium carbonate granules which helped control acid generation due to combustion of polyvinylchloride plastics and halogenated hydrocarbons [4.7].

Temperatures within fluidized bed systems vary significantly. One system utilizes a temperature of 400°C [4.2], another 600°C [4.7] and others, when used as combination calciners and incinerators, may have portions of the

chamber in excess of 1000°C. At these temperatures there may be volatilization of some elements of concern, such as iodine and ruthenium. Particles of dried waste are carried by the off-gas to a cyclone separator. Typical particle size is approximately 0.35 mm [4.7]. A schematic of a fluidized bed waste treatment system which includes incineration is shown in Figure 4.1.

4.2.2 Forced Circulation Evaporator/Crystallizer

Another means of bringing wet waste to a dry state is through forced circulation evaporation. This technique involves passing the liquid waste through a heat exchanger. It then flows to a vapor body where the steam induced by the previous heating is flashed off. Under optimum conditions waste can be brought to a crystalline slurry by this method. Pilot plant operations have indicated that neutralized sodium sulfate and boric acid solutions can be concentrated to 50 wt% [4.2]. Additional drying of these waste would then be required.

4.2.3 Thin Film Evaporators

Thin film evaporation, which employs a type of forced circulation evaporator, is a commonly used industrial process. It has recently been applied for the processing of LLW. Thin film evaporators consist of a heated drum within which a rotating blade scrapes the inner wall. Liquid waste is forced against this heated wall and spread to a thin film with proper characteristics for efficient evaporation with minimal entrainment in the vapor. In some cases waste may be brought to approximately 98 wt% concentration but more typically 50 to 60 wt% is achieved. This too would require additional drying.

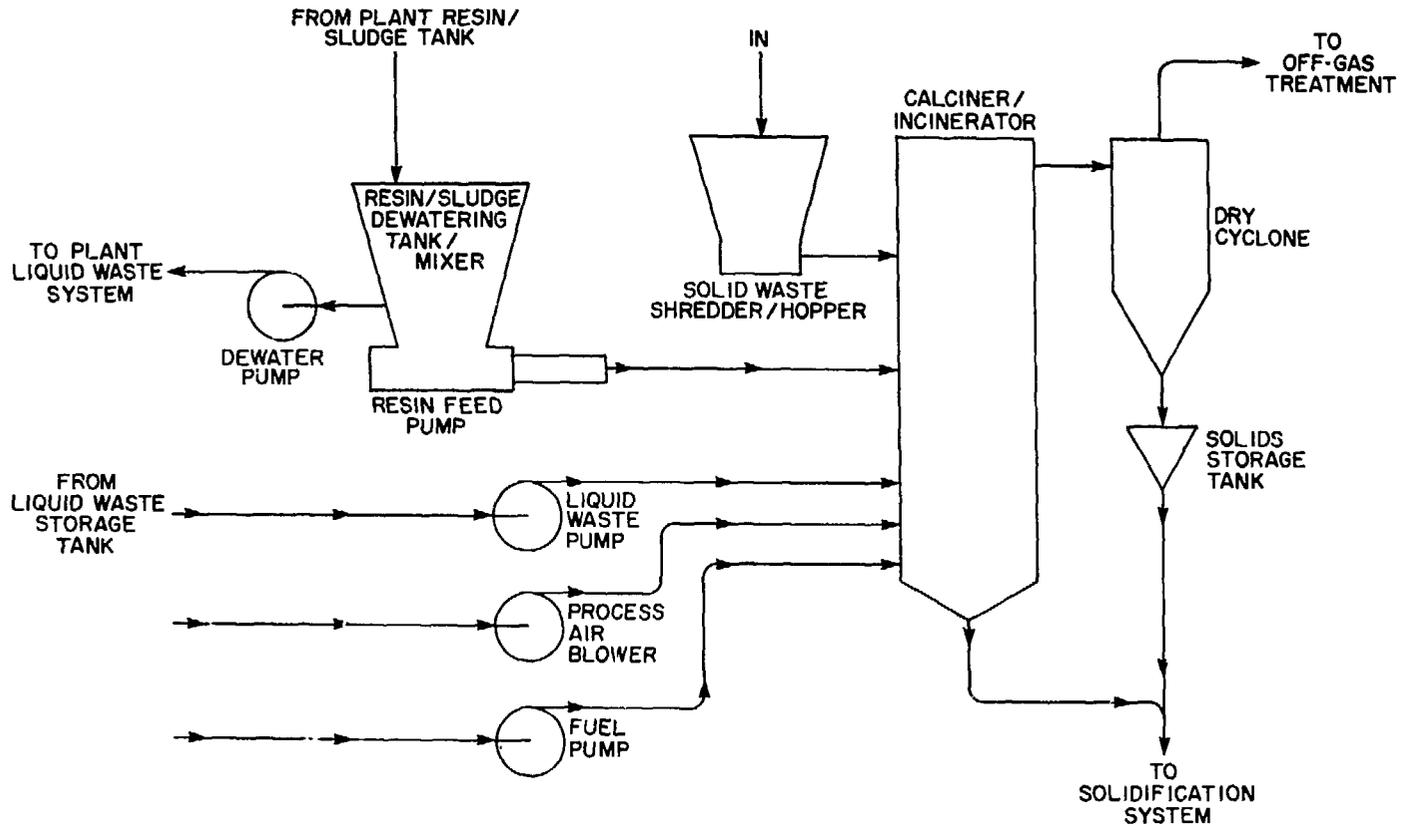


Figure 4.1 A schematic of a fluidized bed incinerator/calciner. Redrawn from [4.2].

4.2.4 Incinerators

Incineration is a technology which has had limited application to LLW. However, stringent burial site requirements, higher shipping costs, and regulatory changes could increase the use of this technology for treatment of radioactive waste.

Many processes involving combustion as a means of treating waste have been considered [4.2,4.7]. Among these processes are:

- Controlled Air Incineration
- Fluidized Bed Incineration
- Rotary Kiln Incineration
- Glass Furnace Incineration
- Cyclone Incineration
- Slagging Pyrolysis Incineration
- Single Hearth Incineration

Incinerator ash must be solidified in order to minimize possible dispersion in transportation and disposal. Some processes such as the glass furnace and slagging pyrolysis produce a glassy solid residue which would not need additional solidification.

Ash resulting from a controlled air incinerator has been characterized by workers at PNL [4.8]. The waste feed was typical of combustible waste generated by a light water reactor facility. Volume reductions of 13:1 and 22:1 were observed for ion exchange resin waste and general combustible trash respectively.

4.3 Selection of Waste Types

Three waste types have been chosen for use with the improved solidification agents selected earlier. These choices represent either 1) wastes which will be increasingly significant in the next decade as more advanced volume reduction processes are applied to low-level wastes or 2) those which are currently problem wastes. The wastes selected for this program are: [4.9]

- Dried Evaporator Concentrates (boric acid wastes and sodium sulfate wastes)
- Incinerator Ash
- Ion Exchange Resin

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5. PROCESS DEVELOPMENT SCOPING STUDIES

A number of processing techniques were surveyed for use with low density polyethylene and modified sulfur cement, including batch heating vessels, wiped film evaporators and screw extruders. Based on such considerations as ease of processibility, quality control, and the use of a proven and available technology, the extrusion method was selected. This process, which employs a simultaneous mixing and heating of the waste-binder mixture, is described in detail in Section 5.1. Both polyethylene and sulfur cement are thermoplastic materials with properties which make them well suited for processing via this technique.

In order to assess the feasibility of each waste-solidification agent combination, process development scoping studies were conducted. These scoping studies were intended to provide verification of process applicability prior to the more extensive process development studies scheduled for FY 1984. Specifically the objectives of preliminary scoping studies included the investigation of:

- waste-binder compatibility
- waste form volumetric efficiency
- sensitivity of process parameters

Physical and chemical compatibility of the solidification matrix material with each of the waste types is of primary concern. Differences in physical form, i.e., particle size, density, hardness etc., between the waste

and solidification agent may present processing difficulties. Chemical interactions are a potential problem, especially under the conditions of elevated temperatures and pressures which are inherent in the processing of thermoplastic materials.

The volumetric efficiency, or quantity of waste which can successfully be incorporated in each solidification matrix material is an important economic consideration. This scoping work is not intended to define compositional limits, but rather estimate the potential of each agent. Through additional process development work (FY 1984), relevant parameters will be optimized leading to improved waste loading potential.

The effective application of thermoplastic materials is dependent upon the control of processing parameters within a finite operating range. The effect of adding materials such as radwaste serves to narrow this range and thus place further emphasis on the precise control and monitoring of the system. Preliminary process development work was designed to provide information on system sensitivity toward the following parameters:

- melt temperature
- melt pressure
- screw speed
- feed method
- feed rate
- machine strain (amperage draw)

Each of these parameters and their relative importance will be discussed in more detail in Sections 5.2.3 and 5.3.3.

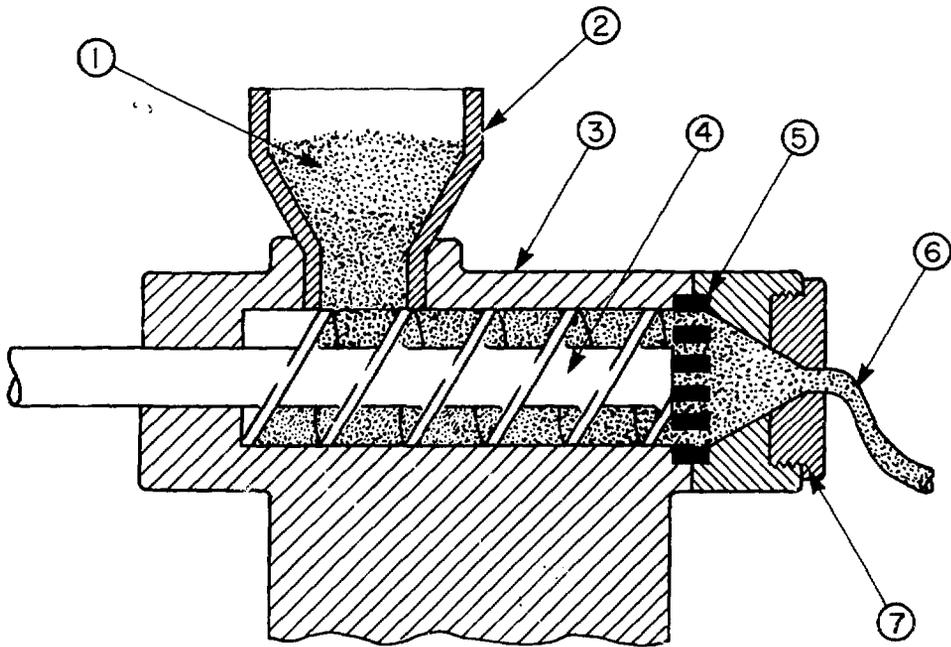
5.1 Thermoplastic Processing System

The BNL processing system for the incorporation of radioactive waste in low density polyethylene (LDPE) and modified sulfur cement employs a single screw extruder which mixes, heats and extrudes the material in one operation. Screw-type extruders were first employed in the United States in the rubber industry and were adapted for the extrusion of thermoplastics in 1938 [5.1]. The use of extruders for the processing of various thermoplastic materials is commonplace in industry today. Experience in the incorporation of dry solids such as graphite powders or fiberglass for increased mechanical strength of plastics, is prevalent as well. Although the feasibility of LDPE as a rad-waste matrix material has been demonstrated using wiped film evaporator technology [5.2] no experience is available in this country and little on a world-wide basis for the use of an extrusion system in this application. As modified sulfur cement is a relatively new product, no precedence exists either for its use as a solidification agent or for the processing of this material using a screw extruder.

An extruder consists of four basic components: 1) a feed hopper, 2) a rotating auger-like screw, 3) a heated cylinder and 4) an output die assembly. These components are depicted in the simplified schematic diagram of Figure 5.1.

The extrusion process for the solidification of radioactive waste involves the following steps:

- The solidification material, pre-mixed with dry waste in measured quantities, is loaded into the feed hopper.



KEY

- ① Feed Material
- ② Feed Hopper
- ③ Heating Unit
- ④ Mechanical Screw
- ⑤ Strainer
- ⑥ Extruded Product
- ⑦ Die

Figure 5.1 Sectional view of a simplified screw extruder. The sketch depicts the flow of material from the hopper to the output die, where it is extruded in a molten state. Redrawn from [5.1].

- The mixture is conveyed through a heated cylinder by the motion of the rotating screw.
- It is masticated under pressure due to the compressive effects of a gradual reduction in area between the screw and cylinder. The motion of the screw also mixes the material to a homogenous state.
- The gradual transfer of thermal energy by the combined effects of the screw and barrel heaters serves to melt the mixture.
- The melted thermoplastic-waste mixture is forced through an output die and is allowed to cool and solidify.

5.1.1 Bench Scale Extruder

Bench scale waste forms for process development scoping studies were produced using a Model KL-125 single screw extruder manufactured by Killion Extruders, Inc., Verona, NJ. A schematic view of the extruder is included as Figure 5.2.

This machine is equipped with a 1 1/4 inch diameter chrome plated screw with a length to diameter ratio (L/D) of 24/1 and compression ratio of 3/1 as shown in Figure 5.3. The 2 1/2 inch OD barrel is fabricated of 4140 steel and is Xalcy lined. This barrel is heated by three separately controlled heat zones consisting of 1250 watt electric resistance mica band heaters. A separate die zone heater is used. In order to provide more precise control of barrel temperatures, the unit is equipped with three zones of automatic air cooling fans. All heating and cooling functions are governed by four separate

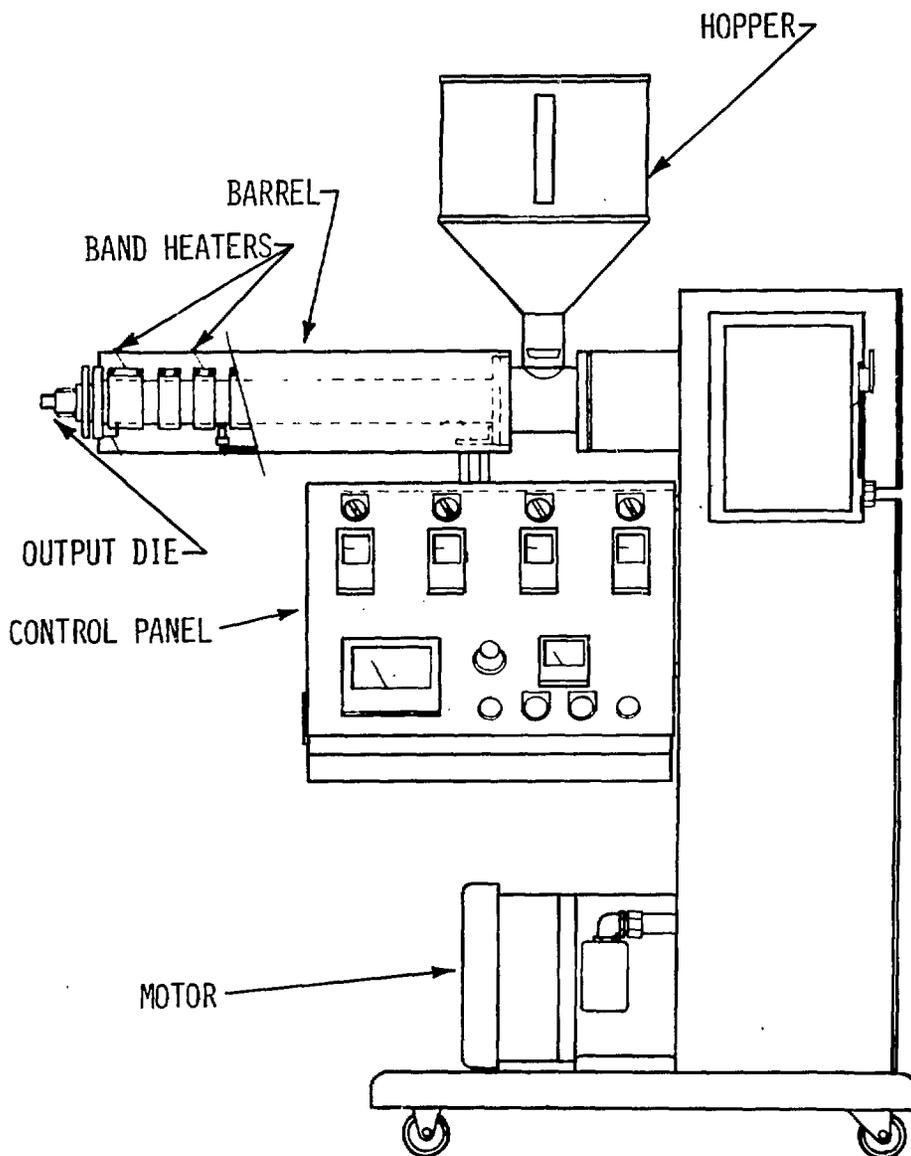


Figure 5.2 Single screw extruder used in the production of laboratory scale waste form specimens [5.10].

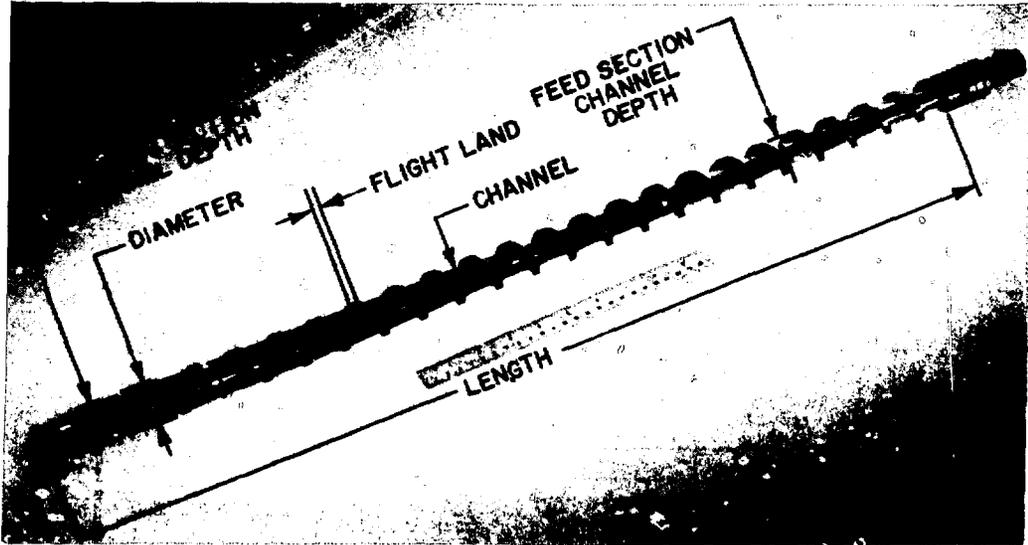


Figure 5.3 Photograph of the 1 1/4" diameter extruder screw. Material enters at the feed section which is located on the right hand side and is conveyed by the helical flights toward the metering section on the left. The decrease in the depth of the channels as the material is conveyed along the screw creates a compressive force.

solid state time proportioning controllers (Eurotherm Type 103, Eurotherm Corp., Reston, VA) In addition, the feed throat region is water jacketed for cooling.

The screw is powered by a 3 horsepower DC drive electric motor with electronic speed control through a 15:1 gear reduction. Screw speed can thus be varied between 12 and 120 RPM. An output die and related equipment were custom fabricated at BNL to enable the production of laboratory scale (approximately 5.1 cm diameter x 10.2 cm in height) simulated waste forms. The die assembly can be seen in Figure 5.4.

Instrumentation and monitoring of process parameters are essential in the control of the system. Melt temperature and pressure are monitored through transducers in conjunction with digital readout indicators and/or a chart recorder. An adjustable over-pressure alarm provides an audible signal when a potentially damaging pressure level is reached. Motor load is displayed by an ammeter which contains an automatic overload shutoff. Screw speed is displayed by an analog tachometer.

5.2 Polyethylene Process Development Scoping Studies

5.2.1 Characterization of Polyethylenes

Polyethylene was first developed by Imperial Chemical Industries, Ltd., in 1933. Their first industrial process was started in 1939. Current U.S. production capacity is approximately 4×10^6 metric tons [5.3].



Figure 5.4 Photograph of single screw extruder and output die assembly for the production of laboratory scale waste form specimens.

Polyethylene has a wide range of characteristics depending on the density of the material. Density in turn is dependent upon the manufacturing process. Two processes are used to produce polyethylene. Both result in the production of long chains of polymerized ethylene. Low density polyethylene (LDPE) is produced by a process which utilizes high reaction pressures (15,000 to 45,000 psi) which result in the formation of large numbers of polymer branches, giving the material an open structure. Typically LDPE's have densities ranging from 0.910 to 0.925 g/cm³. High density polyethylene (HDPE) is manufactured by a low pressure (<1500 psi) process in the presence of special catalysts which produce long linear polymer chains. As there is relatively little side branching of HDPE molecules the chains tend to be more closely packed. Densities of HDPE range between 0.941 to 0.965 g/cm³. By manipulating process parameters during polymerization, or by combining LDPE and HDPE, materials of medium density (0.925 - 0.941 g/cm³) can be formulated.

The properties of low, medium, and high density polyethylenes are compared in Table 5.1. These data indicate that the properties of high density polyethylene, e.g., mechanical strength and resistance to harsh chemical environments might provide a slight advantage vis-a-vis the solidification of low level radioactive waste. Processing of high density polyethylene is more difficult, however, as it requires greater temperatures and pressures. The properties of low density polyethylene are none-the-less favorable, and thus it was selected for use in these studies based upon the relative ease of processibility.

Low density polyethylene is commercially available in a number of forms depending primarily upon density, molecular weight, and melt index. The molecular weight is the average of all sizes of polymer chains produced during

Table 5.1
Properties of Polyethylenes^a

Property	Low Density	Medium Density	High Density
Compression Molding Temp, °C	135 - 177	150 - 190	150 - 230
Density, g/cc	0.910 - 0.925	0.926 - 0.940	0.941 - 0.965
Tensile Strength, MPa	4.14 - 15.86	8.27 - 24.13	21.37 - 37.92
(psi)	600 - 2300	1200 - 3500	3100 - 5500
Compressive Strength, MPa	---	---	18.61 - 24.82
(psi)	---	---	2700 - 3600
Water Absorbance, (24 hr, 1/8" thick, %)	<0.01	<0.01	<0.01
Flammability (Burn Rate, in/min)	1.04	1.00 - 1.04	1.00 - 10.4
Average Extent of Burning, in.	0.8	0.6	---
Average Time of Burning, sec.	<5 - 25	10 - 60	---
Effect of Weak Acid	Resistant	Very Resistant	Very Resistant
Effect of Strong Acid	Attacked by	Attacked Slowly	Attacked Slowly
	Oxidizing Acids		
Effect of Weak Alkalies	Resistant	Very Resistant	Very Resistant
Effect of Strong Alkalies	Resistant	Very Resistant	Very Resistant
Effect of Organic Solvents	Resistant Below 60°C Except to Chlorinated Solvents	Resistant Below 60°C Except to Chlorinated Solvents	Resistant Below 80°C

^a
Data drawn from [3].

polymerization. LDPE's are available in a wide range of molecular weights. As polymers are made up of molecules of varying chain length, the molecular weight distribution describes the range of chain sizes present. A narrow molecular weight distribution provides an optimal balance between mechanical properties and ease of fabrication. Typically the molecular weight distribution for LDPE's ranges between 2.5:1 to 18:1 [5.3]. The melt index is a measure of the material's flow rate at 190°C in units of g/10 minutes and is inversely proportional to molecular weight. Melt index values can range from <1 to >4000 g/10 minutes for some low molecular weight polyolefins. For most applications however, the melt index varies between 1-60 g/10 minutes.

- Types of Low Density Polyethylene Considered

A number of commercially available materials were selected from several manufacturers for potential application. They represent a range in density, molecular weight, and melt index, and are listed along with their properties in Table 5.2. These materials are employed commercially in the production of coatings and films and for extrusion and injection molding of plastic components. The dramatic effects of thermoplastic material properties, e.g. melt index, upon relevant processing parameters can be seen in Figures 5.5-5.8, which are presented in Section 5.2.3.

Initial work has been aimed at determining which products in general appear to be most applicable. As the physicochemical properties of waste streams are quite variable, future work will involve the selection of LDPE which is best suited for each individual waste type application.

Table 5.2

Average Properties of LDPE Materials Selected for Investigation^(a)

LDPE Type	End Use	Density ^(b) g/cm ³	Melt Index ^(c) g/10 min	Molecular Weight ^(d)	Molecular Weight Distribution ^(e)
A	Extruded Film	0.924	2.0	NA ^(f)	NA
B	Injection Molding	0.924	8.0	70,000	3.0
C	Injection Molding	0.924	27.0	60,000	2.5
D	Injection Molding	0.924	35.0	55,000	2.5
E	Injection Molding	0.924	55.0	40,000	2.5
F	Non-Emulsifiable Wax	0.918	1.6	23,000	3.8
G	Non-Emulsifiable Wax	0.917	20.0	19,000	3.6

a) Data as supplied by manufacturers

b) Determined by ASTM Test Method D1505

c) Determined by ASTM Test Method D1238

d) Determined by Gel Permeation Chromatography (GPC)

e) Ratio of weight average molecular weight to number average molecular weight.

f) Not available

5.2.2 Processing Procedure

Sample waste forms were processed with LDPE for each waste type discussed in Section 4. Simulated, non-radioactive waste was used for this work. Anhydrous sodium sulfate reagent (Na_2SO_4) was employed to simulate BWR regenerative waste which has been brought to dryness by means of a fluidized bed evaporator or equivalent volume reduction technique. Boric acid waste from a FWR which has been processed to dryness in a similar fashion was

simulated by using orthoboric acid reagent (H_3BO_3). The actual form of boric acid may vary depending upon the type of waste treatment process employed. At temperatures greater than $170^{\circ}C$ a transition to metaboric acid (HBO_2) occurs. For solidification in LDPE either form of boric acid may be used as long as the melt temperature is maintained below $170^{\circ}C$.

Actual incinerator ash produced by the rotary kiln incinerator developed at the Rockwell International Rocky Flats Plant was utilized. The ash was produced by burning non-radioactive waste, the composition of which was representative of the combustible low-level wastes generated at this facility [5.4]. The constituents of this waste feed are given in Table 5.3. An analysis of the elemental composition of the ash can be found in Reference 5.4.

Unloaded mixed-bed ion exchange bead resins in a ratio of 2 parts cation to 1 part anion, manufactured by Rohm and Haas, Philadelphia, PA, were used in this investigation. Resins were oven dried at $110^{\circ}C$ overnight prior to solidification. This step was necessitated by design constraints of the bench scale extruder, which preclude the presence of moisture.

Table 5.3

Rotary Kiln Incinerator Feed Composition

<u>Constituent</u>	<u>Weight %</u>
Paper	40.0
Polyethylene	22.8
Neoprene	18.8
Kerosene	9.5
Polyvinyl Chloride	7.9
Tributyl Phosphate	1.0

Initial scoping studies employed an extrusion grade polyethylene with a density of 0.924 and a melt index of 2.0. Waste and binder material were pre-weighed and mixed prior to placing in the feed hopper for extrusion.

5.2.3 Preliminary Process Development Results

The quantity of each waste type incorporated in LDPE as a result of process development scoping studies is presented in Table 5.4

Table 5.4

Waste Loadings Obtained in Process Development Scoping Studies for LDPE^(a)

<u>Waste Type</u>	<u>Waste Loading for Dry Waste, wt%</u>	<u>Equivalent Waste Loading for Comparable Aqueous Waste, wt%</u>
Sodium Sulfate	60	240 ^(b)
Boric Acid	25	208 ^(c)
Incinerator Ash	25	Not Applicable
Ion Exchange Resin	50	250 ^(d)

(a) Formulated using LDPE Type A, as specified in Table 5.2

(b) Based on 25 wt% Na₂SO₄ aqueous waste

(c) Based on 12 wt% H₃BO₃ aqueous waste

(d) Based on 20 wt% ion exchange resin slurry waste

These preliminary results appear favorable especially relative to the incorporation of sodium sulfate, boric acid and ion exchange resin wastes. In each case the major constraints limiting the incorporation of additional waste were a combination of: 1) poor output due to the high viscosity of the waste-binder mixture, 2) excessive pressure surges and 3) excessive strain on

the processing equipment. As a basis of comparison the equivalent quantity of each waste type from a typical aqueous waste stream is included in Table 5.4. These comparisons were derived assuming waste concentrations of 25 wt% for Na_2SO_4 , 12 wt% for H_3BO_3 , and 20 wt% for ion exchange resin wastes. The latter value represents the dry wt% of ion exchange bead resins typically contained in a resin slurry [5.5].

The extruder parameters which are most important for the processing of low-level radioactive waste in LDPE include melt temperature, melt pressure, feed rate and mechanism, and electrical load (amperage draw). Each of these parameters is discussed below:

- Temperature: The melt temperature is dependent upon the type of LDPE and waste to be processed. Temperature has an inverse effect upon melt pressure. This phenomenon is illustrated in Figures 5.5 and 5.6 which plot temperature vs. pressure at a constant screw speed for two types of LDPE's.

From the standpoint of processing, the greater the melt temperature (within a given range) the lower the pressure and thus the easier it is to extrude. For radwaste, however, minimum temperatures are preferable to reduce volatilization and possible decomposition reactions. For some waste types a compromise in optimal melt temperature is necessary.

- Pressure: The melt pressure is a function of LDPE and waste type, melt temperature and process rate (screw speed). The relationship between screw speed and melt pressure at a constant temperature can be seen in Figures 5.7 and 5.8. Pressures exceeding design limitations can lead to

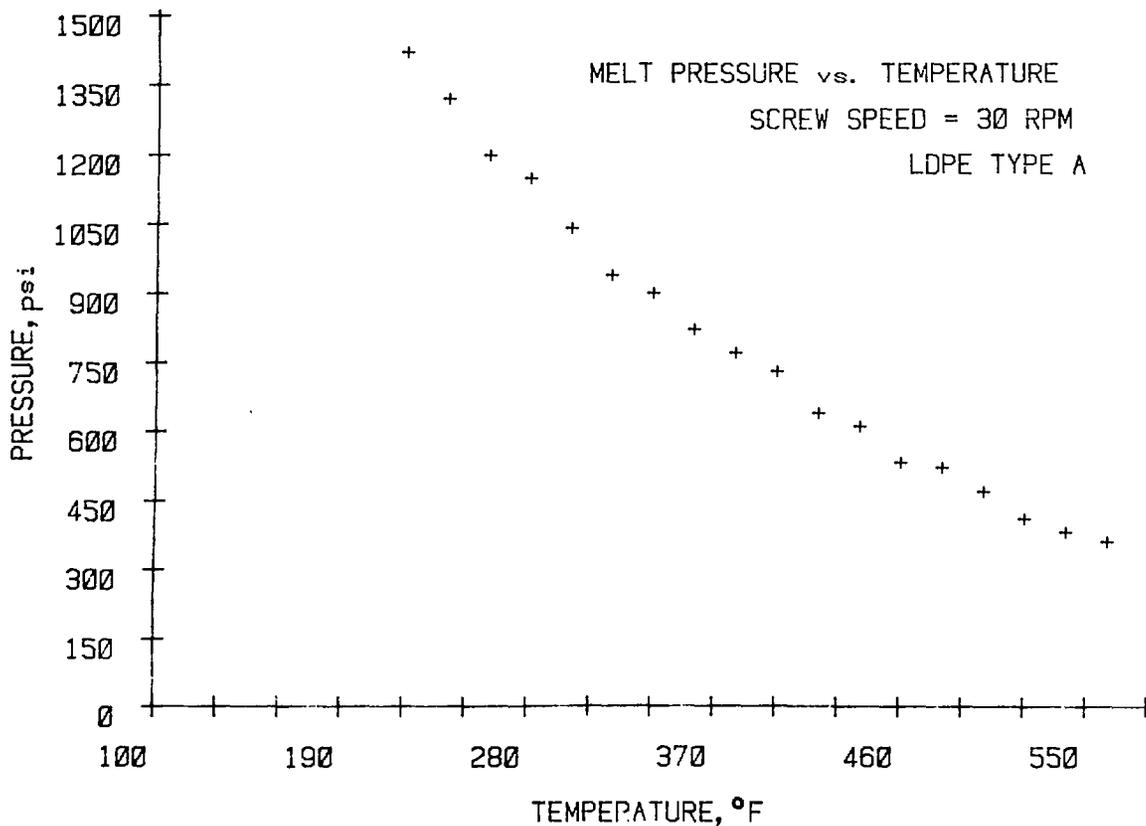


Figure 5.5 Extruder melt temperature and pressure data taken at a constant screw speed of 30 RPM for an LDPE with a melt index of 2.0.

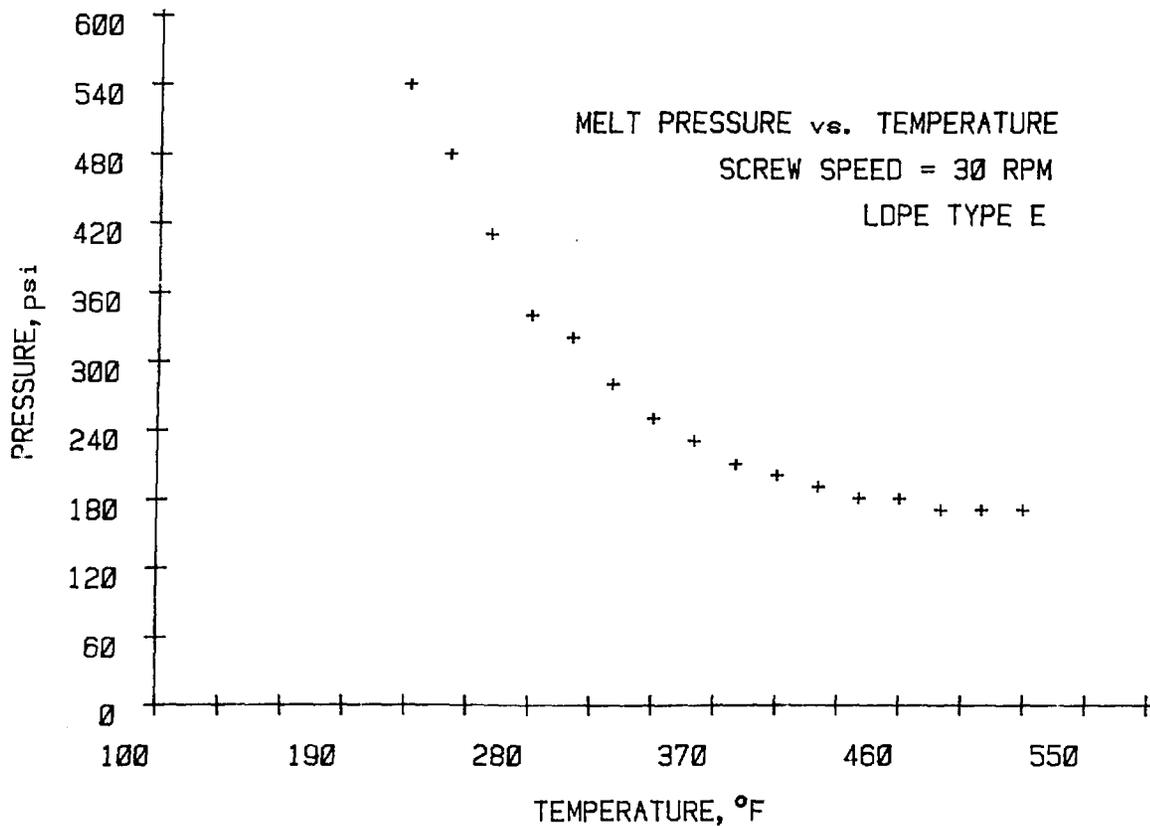


Figure 5.6 Extruder melt temperature and pressure data taken at a constant screw speed of 30 RPM for an LDPE with a melt index of 55.0.

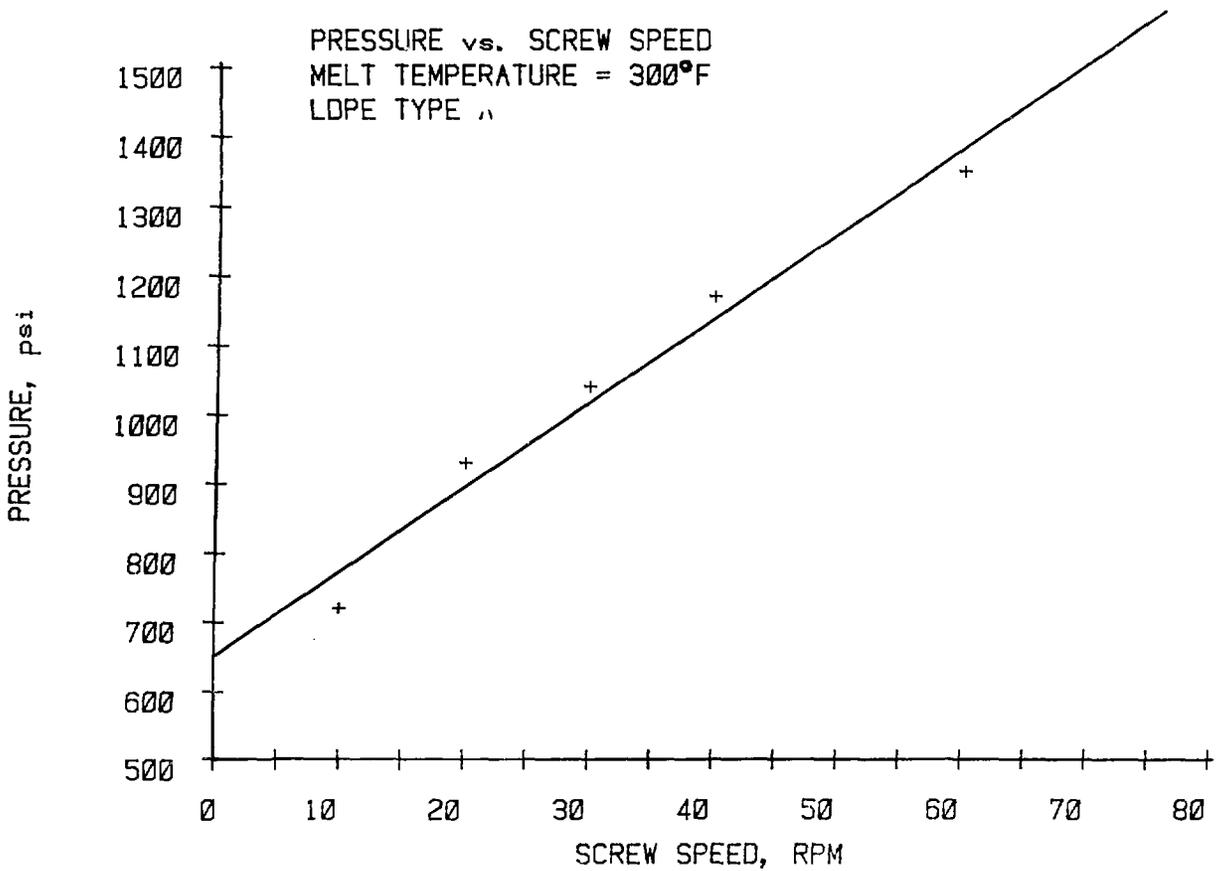


Figure 5.7 Extruder melt pressure as a function of screw speed taken at a constant melt temperature of 300°F (149°C) for an LDPE with a melt index of 2.0. The straight line represents a linear regression fit with an $R^2 = 0.971$.

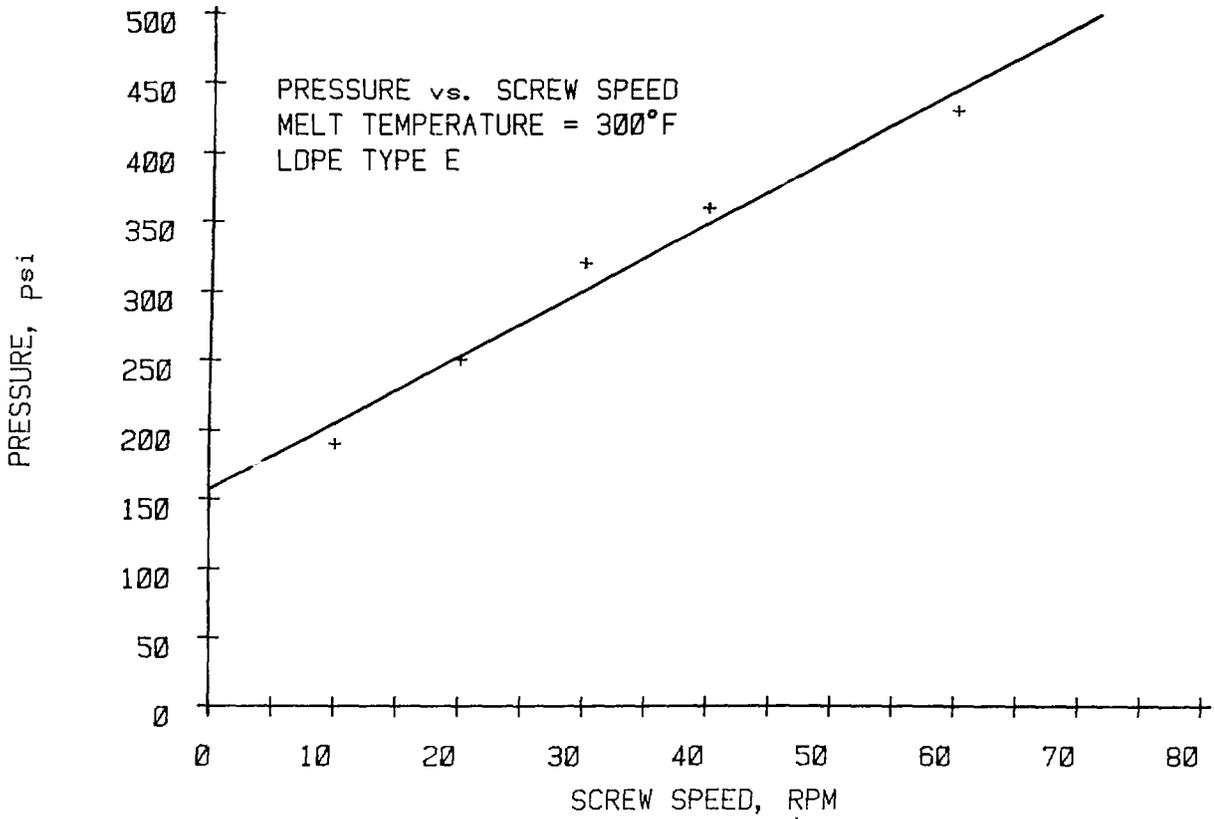


Figure 5.8 Extruder melt pressure as a function of screw speed taken at a constant melt temperature of 300°F (149°C) for an LDPE with a melt index of 55.0. The straight line represents a linear regression fit with an $R^2 = 0.973$.

failure of the rupture disk and/or screw. Melt pressure can be controlled by proper selection of LDPE and waste/binder ratio, as well as adjustment of the process temperature and feed rate.

- Feed Rate and Mechanism: The feed rate is an operator controlled parameter which, as seen in Figures 5.7 and 5.8 directly affects the melt pressure. From the standpoint of process efficiency and ultimate operational costs, maximum feed rates are preferable. However, adverse pressures may result, dictating the use of slower feed rates. The feed mechanism may affect process continuity and homogeneity of the solidified product.

- Electrical Load: The electrical load required for processing varies, and is directly proportional to the ease of processibility. A highly viscous or dry waste-binder mixture will result in a large amperage draw which is a direct indication of the strain on the machine. Operation under large electrical load reduces the process rate, and adversely influences operating and maintenance costs.

Table 5.5 summarizes the relevant extruder parameters for formulations corresponding to those reported in Table 5.4, obtained during LDPE process development scoping studies. This data is system specific and parameters may vary when applied for use with other processing equipment.

As in the development of any new process application, a number of potential problem areas were uncovered during the course of this scoping work.

Table 5.5

Extruder Parameters for Selected Formulations Obtained in Process Development Scoping Studies
for LDPE^(a)

Run #	Waste Type	Dry Waste Wt%	Temperature Control Settings °C, (°F)				Instrumentation Readings			
			Zone 1	Zone 2	Zone 3	Die Zone	Melt Temp., °C (°F)	Melt Press., MPa, (psi)	Load, Amps	Screw Speed, RPM
6-21-3	Na ₂ SO ₄	60	121 (250)	160 (320)	204 (400)	209 (408)	195 (383)	7.72 (1120)	5	30
7-22-2	H ₃ BO ₃	25	93 (200)	135 (275)	135 (275)	149 (300)	132 (270)	10.34 (1500)	5	20
6-22-7	Incinerator Ash	25	121 (250)	160 (320)	190 (375)	218 (425)	179 (354)	6.20 (900)	4	10
7-21-1	Ion Exchange Resin	50	93 (200)	135 (275)	135 (275)	177 (300)	132 (270)	17.24 (2500)	5	15

(a) All reported data was formulated using LDPE Type A, as specified in Table 5.2, and corresponds to formulations presented in Table 5.4.

Optimization of waste loadings was limited, in general, by a number of factors, many of which are interrelated. These factors are described below, along with a discussion on how they have been or plan to be overcome.

- Separation: Differences in density and particle size between dry waste and the binder material, at times caused separation in the feed hopper. This, in turn, affected uniform flow through the extruder as well as homogeneity of solidified specimens. Plans are being developed to incorporate a modified feed system to ameliorate this separation.

- Viscosity: 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 high pressure, machine strain, and/or screw seizure. Viscosity of the waste-binder mixture may be reduced by the use of higher melt index LDPE's, enabling the incorporation of more waste and thus, improving overall waste loading efficiency.

- Foaming: Moisture contained in the waste resulted in entrapped vapors and foaming of the waste-binder mixture. This phenomenon led to solidified products which were low in density and contained reduced quantities of waste. By insuring that wastes were completely pre-dried, foaming was eliminated.

- Uniform Flow: Contained moisture was also found to create pressure surges as the vapors accumulated. Difficulties controlling the uniform product flow in the extruder were the result, but were mitigated by the complete pre-drying of the waste.

- Waste Decomposition: Decomposition of some waste streams, e.g., dry solid boric acid, 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, i.e., pressure surging and foaming. Decomposition can be avoided by carefully maintaining the process melt temperature below the critical decomposition temperature.

5.3 Modified Sulfur Cement Process Development Scoping Studies

5.3.1 Characterization of Modified Sulfur Cement

Modified sulfur cement is composed principally of elemental sulfur with additions of plasticizing agents to inhibit crystal growth and to control polymerization and viscosity [5.6]. The components are reacted at elevated temperatures to form the final modified sulfur cement. This material is then cooled, crushed and packaged for distribution. In use, the granular modified sulfur cement is heated to a working temperature of about 120°C prior to mixing with aggregate (or dry waste) and poured into a form.

- Elemental Sulfur: The basic raw material of modified sulfur cement is elemental sulfur. Sulfur, with an atomic weight of 32.06, has a multitude of allotropic forms in both the liquid and solid states. The two crystalline solid forms of sulfur which are important to the long term stability of sulfur material as a solidification agent are an orthorhombic form

(α -sulfur) and a monoclinic form (β -sulfur). The orthorhombic form has a melting point of 112.8°C and a specific gravity of 2.07 at 20°C [5.7]. The monoclinic form has a melting point of 119°C and a specific gravity of 1.957 [5.7]. The α -sulfur form is that which is typically found in nature and which results from chemical separation as it is stable below 95.6°C . The β -sulfur form is rare in nature but can be found in association with volcanic exhalative processes and with burning coal dumps [5.8]. With the allotropic transformation of β -sulfur to α -sulfur, which occurs at temperatures below 95.6°C , an increase in density results, creating residual stresses in the material. Fracturing will subsequently occur if the solid is shocked, for instance by impact or by thermal changes. Thus it is desirable to retain the sulfur material in the β -form in order to optimize structural characteristics.

The mixed modifier system developed by the U.S. Bureau of Mines (USBM) appears to maintain sulfur concrete in the β -form. It should be noted that additional phases of non-crystalline sulfur may also be present between crystal grains in this material [5.9].

- Organic Modifiers: The organic materials which are reacted with elemental sulfur to form modified sulfur cement are a mixture of technical grade dicyclopentadiene (DCPD) and an oligomer of cyclopentadiene (CPD), consisting of trimers through pentamers.

The reaction of these two materials with sulfur, at elevated temperatures, yields a product which maintains the β -form even after repeated thermal cycling.

The USBM has done extensive research to determine the effects of varying the percentages of total modifier added, the relative proportions of modifier constituents, i.e. DCPD and CPD oligomer, and reaction methodologies. From the point of view of developing a useful construction material, the USBM selected a formulation containing 5 wt% modifiers consisting of equal parts of DCPD and an oligomer of CPD. This formulation yields a product of low viscosity upon melting, an advantage for mixability and handling considerations. Varying compositional parameters results in modified sulfur cements with a wide range of properties. Formulations developed with an increased proportion of modifiers (from 10-40 wt%) and varying ratios of DCPD/oligomer produced higher viscosity end products which were more elastic in nature than those containing 5 wt% modifiers [5.9].

● Commercial Production of Modified Sulfur Cement: The modified sulfur cement utilized in this investigation was manufactured by Chemical Enterprises, Inc., Houston, Texas and is marketed under the tradename Cement 2000. Chemical Enterprises, Inc. is licensed to produce the USBM formulation of 5 wt% modifier concentration with DCPD/oligomer ratio = 1.0. Although other licenses have been issued, they are currently the sole commercial producer.

Dual steam heated reactor vessels with a combined capacity of 18 tons of molten sulfur are used for the processing of Cement 2000. Molten elemental sulfur is reacted with the modifier mixture at $140\pm 5^{\circ}\text{C}$ under constant stirring for a total of four hours. The material is then fed to a water cooled belt where it solidifies, is chopped into 1/8 inch thick diameter particles and is packed in 50 pound bags for shipment. As the commercial

production of modified sulfur cement is accomplished by batch processing, the end-product properties can be expected to vary slightly from batch to batch.

5.3.2 Processing Procedure

Processing of modified sulfur-cement waste mixtures can be accomplished by several methods. Initially a batch-type heated mixing vessel was employed. This technique, although feasible, was limited by the rapid setting of the waste-binder mixture upon removal of the heat, due to the relatively low specific heat capacity of the material (approximately 0.17 cal/(g)(°C)). Use of the single screw extruder for processing of modified sulfur-waste mixtures provided several advantages. As the extruder releases a molten mixture directly into the mold, no premature setting was encountered. In addition, because the extruder is a dynamic process rather than a batch method, considerable time and cost efficiencies can be realized.

Sample waste forms were thus processed incorporating each waste type described earlier with modified sulfur cement. The extruder system employed was the same as that described in Section 5.1.1. Simulated dry waste was combined with modified sulfur cement, heated, mixed and extruded in a molten state, and allowed to cool forming a monolithic solid.

5.3.3 Preliminary Process Development Results

The quantity of each waste type solidified in modified sulfur cement as a result of process development scoping studies is reported in Table 5.6.

Table 5.6

Waste Loadings Obtained in Process Development Scoping Studies for
Modified Sulfur Cement

<u>Waste Type</u>	<u>Waste Loading for Dry Waste, Wt%</u>	<u>Equivalent Waste Loading for Comparable Aqueous Waste, Wt%</u>
Sodium Sulfate	65	260 ^(a)
Boric Acid	40	333 ^(b)
Incinerator Ash	20	Not Applicable
Ion Exchange Resin	40	200 ^(c)

(a) Based on 25 wt% Na_2SO_4 aqueous waste

(b) Based on 12 wt% H_3BO_3 aqueous waste

(c) Based on 20 wt% ion exchange resin slurry waste

The waste loadings obtained in process development scoping studies given in Table 5.6 indicate that a significant amount of dry radwaste can be incorporated in modified sulfur cement. The solidification of incinerator ash was limited to 20 wt%. When included in quantities greater than 20 wt%, the ash tended to sorb the molten sulfur forming a thick, dry paste which was difficult to extrude. In some cases where the waste-binder mixture was extremely dry, excessive electrical loads were recorded. For ion exchange resin, quantities greater than 40 wt% lacked sufficient fluidity to be conveyed by the screw. Pressure surging which was experienced in extruding LDPE was not seen for modified sulfur cement, probably due to the material's lower viscosity when molten.

The relevant extruder parameters for formulations given in Table 5.6 are presented in Table 5.7.

Table 5.7

Extruder Parameters for Selected Formulations Obtained in Process Development Scoping Studies for Modified Sulfur Cement

Run #	Waste Type	Dry Waste Wt%	Temperature Control Settings °C, (°F)				Instrumentation Readings			
			Zone 1	Zone 2	Zone 3	Die Zone	Melt Temp °C (°F)	Melt Press., MPa, (psi)	Load, Amps	Screw Speed RPM
6-7-3	Na ₂ SO ₄	65	107 (225)	135 (275)	149 (300)	149 (300)	139 (283)	0.28 (40)	1	30
6-8-2	H ₃ BO ₃	40	79 (175)	121 (250)	121 (250)	135 (275)	127 (261)	0	3	40
6-14-8	Incinerator Ash	20	79 (175)	121 (250)	121 (250)	149 (300)	137 (279)	0	2	30
6-14-6	Ion Exchange Resin	40	79 (175)	121 (250)	121 (250)	149 (300)	140 (284)	0	2	30

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6. PRELIMINARY WASTE FORM PROPERTY EVALUATION STUDIES

In order to better assess the feasibility of the selected waste type-solidification agent combinations investigated in process development scoping studies, several preliminary waste form property evaluation tests were conducted. Although specific waste form tests have yet to be identified, these property evaluations were performed in accordance with the preliminary waste form evaluation criteria as outlined in Section 2. Specifically, the criteria of interest for this study include:

- determination of the effects of aqueous media
- determination of compressive strength

These criteria were selected to provide the basis for an initial assessment of waste form acceptability.

6.1 Stability in an Aqueous Environment

For the purposes of a first order examination of the effects of an aqueous environment on waste form stability, a water immersion test was conducted for a period of two weeks. Laboratory scale specimens with nominal dimensions of 5.1 cm (2.0 in.) in diameter by 10.2 cm (4.0 in.) in height were immersed in demineralized water. At the end of the two week test period the specimens were observed for gross failures in mechanical integrity. Results of preliminary immersion testing for LDPE and modified sulfur cement specimens are given in Tables 6.1 and 6.2, respectively. None of the LDPE waste form test specimens were found to deteriorate under these conditions. Figure 6.1 is a



Figure 6.1 Low density polyethylene waste forms incorporating (from left to right) 30, 40 and 50 wt% dry ion exchange resin having undergone a two week water immersion test.

photograph of LDPE waste forms incorporating 30, 40 and 50 wt% dry ion exchange resins at the conclusion of a two week water immersion test. Modified sulfur cement specimens incorporating between 5 and 40 wt% ion exchange resins failed in immersion. The dramatic effects of water immersion on this waste-binder combination can be seen in Figure 6.2 which depicts the deterioration of a modified sulfur cement specimen containing 10 wt% dry ion exchange resins over a period of 5 minutes. This phenomenon is due to the exertion of tensile forces by the resin beads (which expand in the presence of moisture) greater than the tensile yield strength of the matrix material. It is concluded, therefore, that modified sulfur cement as currently formulated is not suitable for the solidification of ion exchange resin wastes.

Table 6.1

Results of Preliminary Immersion Test for LDPE Waste Forms

<u>Waste Loading</u> (a)	<u>Immersion Results</u>
60% Na ₂ SO ₄	Passed (b)
25% H ₃ BO ₃	Passed
25% Incinerator Ash	Passed
50% Ion Exchange Resin	Passed

a) Expressed as dry wt%.

b) No sample failures (gross loss in mechanical integrity) within two weeks.

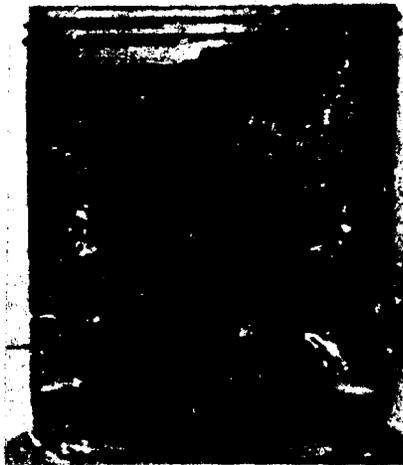


Figure 6.2 Modified sulfur cement waste form incorporating 10 wt% dry ion exchange resin while undergoing a water immersion test. All three photographs are of the same sample, taken within five minutes of the initiation of the test. Complete structural failure of the sample was observed in less than one day.

Table 6.2

Results of Preliminary Immersion Test for Modified Sulfur Cement Waste Forms

<u>Waste Loading</u> ^(a)	<u>Immersion Results</u>
65% Na ₂ SO ₄	Passed ^(b)
40% H ₃ BO ₃	Passed
20% Incinerator Ash	Passed
40% Ion Exchange Resin	Failed ^(c)

a) Expressed as dry wt%.

b) No sample failures (gross loss in mechanical integrity) within two weeks.

c) Sample failure within two weeks.

6.2 Waste Form Compressive Strength

LDPE specimens do not fail in compression by a rigid fracture. Plotting stress (load per unit area) versus strain (ratio of the change in length to the original length) for this material as seen in Figure 6.3, yields an infinitely increasing slope with no discernable failure point. Therefore, standard compression strength tests such as ASTM C 39 or D 695 [6.1,6.2] are not applicable for LDPE waste form testing. In order to provide a preliminary measure of the response of LDPE waste forms under a compressive load pending the development of an appropriate standard method, the following approach was employed.

Standard laboratory scale specimens measuring 5.1 cm (2.0 in.) in diameter by 10.2 cm (4.0 in.) in height were subjected to a constant compressive load of 0.69 MPa (100 psi) for a period of 5 minutes while change in sample

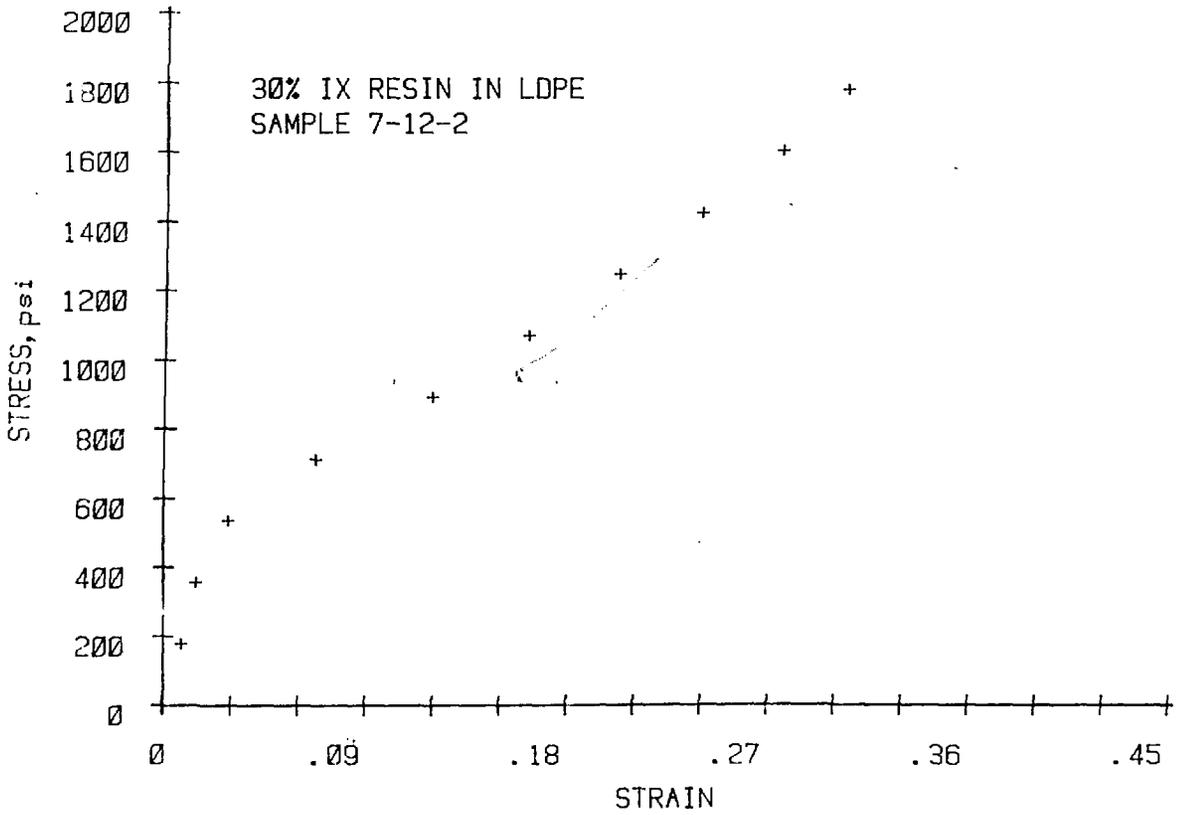


Figure 6.3 Stress strain curve for LDPE waste form incorporating 30 wt% ion exchange resin. Note that no discernable yield point is evident.

length was recorded. The specified load was selected to represent twice the maximum expected load that a waste form may experience due to overburden in a burial environment. Strain data for specimens tested in this way are given in Table 6.3. The observed sample deformation in each case occurred within the initial few seconds of the applied load and remained stable for the duration of the test. The maximum deformation as indicated in Table 6.3 was found to be less than 0.4%. The data for all samples are in close agreement indicating no clear dependence on waste type. Although the results of this test should be viewed as preliminary, they indicate that LDPE waste forms will provide adequate structural integrity for transportation and disposal operations.

Table 6.3

Results of Constant Load Compressive Testing for Representative LDPE Specimens ^(a)

<u>Waste Loading</u> ^(b)	<u>Strain</u>
65% Na ₂ SO ₄	0.0029
40% H ₃ BO ₃	0.0037
20% Incinerator Ash	0.0033
40% Ion Exchange Resin	0.0030

a) Measured at a constant load of 0.69 MPa (100 psi) for a period of 5 minutes.

b) Expressed as dry wt%.

Compressive strength testing of modified sulfur cement waste forms was conducted in accordance with ASTM C 39, "Standard Method of Test for Compressive Strength of Cylindrical Concrete Specimens [6.2]. Cylindrical specimens were prepared by a batch heating method, rather than by extrusion, and measured 5.1 cm (2.0 in.) in diameter by 10.2 cm (4.0 in.) in height. Modified

sulfur cement specimens failed by plastic deformation with a clearly discernable yield point where the compressive load began to decrease. Data are therefore given in Table 6.4 as compressive yield strength. As unmodified sulfur cement fails by rigid fracture, the difference in behavior under compressive load between these materials can be attributed to the addition of the polymer modifiers. As indicated, the incorporation of waste in modified sulfur cement acts as aggregate and increases the compressive strength above that of neat modified sulfur cement. Compressive yield strength for modified sulfur cement waste forms is waste dependent, but all samples tested demonstrated the ability to withstand forces far greater than those which they may be expected to encounter. In light of their failure in immersion testing, ion exchange resins solidified in modified sulfur cement were not tested in compression.

Table 6.4

Compression Test Results for Representative Modified Sulfur Cement Specimens^(a)

Waste Loading ^(b)	Compressive Yield Strength, MPa (psi)
Neat Modified Sulfur Cement	9.51 (1380)
65% Na ₂ SO ₄	21.79 (3160)
40% H ₃ BO ₃	10.76 (1560)
20% Incinerator Ash	36.54 (5300)

a) Conducted in accordance with ASTM C 39 [6.1].

b) Expressed as dry wt%.

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