PROCESSES FOR PRODUCTION OF ALTERNATIVE WASTE FORMS

by

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INTRODUCTION

During the past 20 years, numerous waste forms and processes have been proposed for solidification of high-level radioactive wastes (HLW). The number has increased significantly during the past 3 to 4 yrs, and as this number of options increases, so does the difficulty in differentiating the options and making realistic comparisons.

At least five factors must be considered in selecting the waste form and process method. These include: 1) processing flexibility, 2) waste loading, 3) canister size and stability, 4) waste form inertness and stability, and 5) processing complexity. Because of the need for remote operations and maintenance, process complexity is one of the major factors. This paper describes various waste form processes and operations, and a simple system is proposed for making comparisons. This system suggests that one goal for processes would be to reduce the number of process steps, thereby providing less complex processing systems.

The objective of HLW management is to contain radionuclides until their activity has decreased to acceptable levels. The level of containment is determined in part by the waste form and its properties. Waste form properties are not considered in depth here, but it can be generally stated that improved waste form performance will normally require increased process complexity.

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PROCESS COMPARISON PARAMETERS

A detailed evaluation of processes should include consideration of process cell size and remote mechanical operations, as each involves major cost impacts. The latter are particularly important, since remote operations must be carried out behind five feet of concrete. Lead glass viewing windows are costly, and mirrors or television cameras are frequently required to see the equipment. This remote design requirement makes it essential that the equipment be reliable, have a long life expectancy, and be maintainable by remote means. Clearly, the more complex the equipment, the more difficult it is to meet design operation and maintenance requirements. The ideal process would utilize low temperatures and pressures, would have no moving parts, would have ready access for maintenance, would be dust-free to facilitate easy decontamination, and would require no material transfers. It must also have a reasonable production rate; otherwise, several parallel units would be required. While hot cells provide the ultimate containment of radioactivity, process equipment that can provide primary containment of the gross radioactivity is also highly desirable. The handling of flammable or explosive material within hot cells is generally very limited for safety considerations.

To date, no process can meet all of the desirable requirements. Compromises are necessary, and they complicate the process evaluations. We have not attempted to quantify each of the above parameters, because detailed process designs have not been prepared. After reviewing alternative waste forms and process methods, we will discuss our approach to a rating method.

ALTERNATIVE WASTE FORMS

For our review we have selected 15 processes and 14 current waste forms from among the hundreds of possible forms.[1] The waste forms are grouped by type, as shown in Table I. Crystalline forms are characterized by well-ordered structures that usually contain the waste elements in several stable, mineral-like phases. Glasses consist of a single phase, which is a solid solution of waste atoms in a random structure. The molecular stuffed product[2] contains a thin, protective high-SiO_2 glass layer over the glass containing the waste. Fusion-ceramics are characterized as a matrix containing glass and crystalline material. They are formed by use of a liquid or glass phase, but are

TABLE I. Grouping of Waste Forms by Generic Type

Crystalline or Mineral Ceramic	Glass	Fusion-Ceramics	Cermets	Cement
Supercaline	Borosilicate	Glass-Ceramics	Cermets	Portland
Spent Fuel	Phosphate	"SYNROC A"		High-Alumina
"SYNROC-B"	Molecular Stuffed	Sintered Glass-Ceramic		
Titanates				
Inert Coated				

processed to promote a crystalline structure. Cermets are a combination of metal and ceramic phases on a micron scale. Cements are formed with combinations of waste solution and cement that set up into solids. The waste forms can be formed in large "monolithics" or as smaller shapes and incorporated into a matrix.

PROCESS DESCRIPTIONS

Glass Forms

Four processes are considered for forming glass, and three of these are combined and shown schematically in Fig. 1. The spray calciner dries the liquid waste in all three cases. Waste solutions are sprayed into an 800°C chamber, where the majority of the nitrates and water are removed. The fine, dry powdered waste calcine falls from the bottom of the calciner into either an in-can melter (ICM) or a ceramic melter (CM). Glass frits are added below the calciner and pass on to either melter. For ICM, a canister is loaded into the furnace and waste and frit are melted into a glass.[3,4] For the CM option, the waste calcine and frit fall into a refractory oxide chamber, where they are melted by heat generated by the passage of an electric current through the molten glass. Glass frit and waste are continuously added and melted in this process. Periodic or nearly continuous drains of molten glass are made into the storage canister.[5]

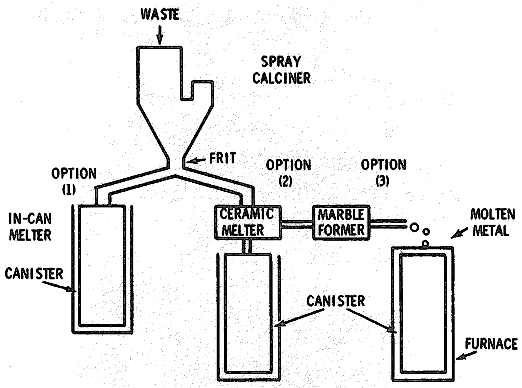

Fig. 1. Schematic of Alternative Glass Processes

To produce marbles, the molten glass stream from the CM is fed to a marble machine, which can be either a vibrating cup system[6] or a glass drop method like that used in the Pamela process.[7] The marbles are then loaded into a canister with molten metal to produce a massive waste form with high thermal conductivity. The fourth glass process, shown schematically in Fig. 2, is called molecular stuffing.[2] In this process, pre-forms of phase-separated glass are pre-leached to remove an interconnected sodium borate phase from the glass--leaving an open porous structure of high-silica glass. The pre-forms are introduced into the waste solution to fill the pores and are then removed and dried. It may be possible to recycle the pre-forms back into the waste solution to obtain higher waste loadings. Once fully loaded, the surfaces of the pre-forms are rinsed to remove the majority of activity from the near surface, then sintered to collapse the porous structure around the waste. The cleaned surface acts as a lower-activity protective barrier for the waste. We believe it would be necessary to incorporate the sintered pre-forms into a metal matrix similar to glass marbles.

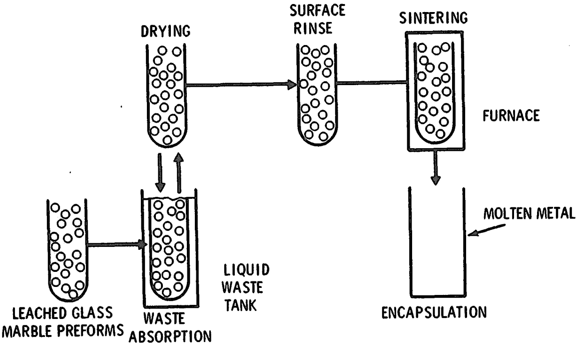

Fig. 2. Schematic of the Molecular Stuffing Process

Crystalline Waste Forms

There are five basic processes for production of crystalline waste forms. The first four options are shown in Fig. 3, and all four processes can be used for supercalcines. Hot isostatic pressing (option 4) is also being considered for SYNROC-B. The process begins with the addition of selected chemicals to the HLW solution. A major difference between supercalcines and SYNROC products involves the amount and type of chemical additions. The waste solutions and additives are calcined in the spray calciner, producing a well-mixed powder. In option 1 (sintered pellets in metal matrix) the powder is fed to a disc pelletizer with a binder, where the powder forms into spherical pellets. These pellets are tranferred to a sintering furnance for consolidation and crystallization. Sintered pellets and molten metal are then added to the canister to form the final waste form.[6]

The second option involves coating the option 1 sintered pellets with pyrolytic carbon and Al_2O_3 by fluid-bed or drum coating before incorporating them into a metal matrix.[6] Such coatings provide additional inertness and protection to the waste.[6]

The simplest crystalline product (option 3) lets the supercalcine powder fall from the calciner into a canister similar to

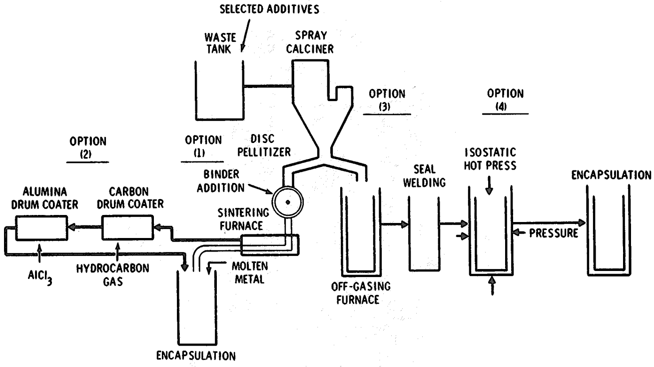

Fig. 3. Schematic of Alternative Crystalline Ceramic Process

the ICM. The calcine is heat-treated at 1000°C to complete the decomposition of residual nitrates and water and to crystallize the powder.[8]

For the fourth option in Fig. 3, large billets of crystalline material are produced by hot isostatic pressing. Here the spray calcine powder is fed into the thin-walled canister. The calcine is heated-treated at about 850°C to remove residual nitrates and water, after which the canister is evacuated and seal-welded. The sealed thin-walled canister is then isostatically hot-pressed at about 1000°C and 1000 psi to consolidate and crystallize the waste form[9], after which it is placed in a heavy-walled canister for subsequent handling. Another process option would be to hot press by uniaxial compression, as illustrated in the next process schematic. Both processes are about equally complex.

The titanate ion exchange process is shown in Fig. 4. Ion exchange negates the need for a spray- or fluid-bed calciner by separating the waste ions onto a sodium titanate and a zeolite bed. The beds are mixed as slurries and dried. The dried powder is loaded into a large hot-pressing die, and is then consolidated at 1000°C and 1000 psi. The solid ceramic is cooled, removed and loaded into a canister with other pressings and then sealed.[10,11] A high-temperature calcining step to remove nitrate and water before hot pressing may not be necessary, and

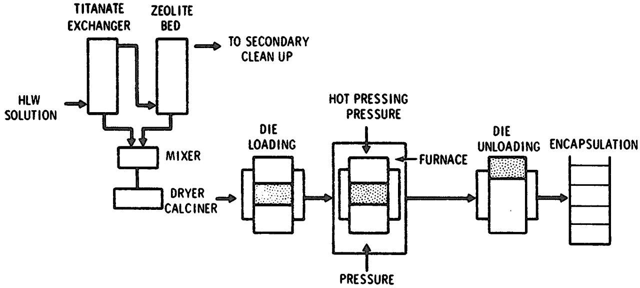

Fig. 4. Schematic of Ion Exchange/Hot Pressing Process

is not shown because the dies are not completely sealed and gasses are not trapped as they are in the isostatic system.

The final crystalline waste form considered is spent fuel. Preparation for disposal could simply involve loading spent fuel and stabilizer (possibly helium or sand) into a canister.[12] Little or no processing would be required, thus making this the nearly "ideal" form from a processing standpoint. However, the final requirements for disposal of spent fuel may make the process much more complex.

Fusion-Ceramic Processes

Fusion-ceramics, being a hybrid, can be formed by either glass or ceramic processes. Figure 5 shows the two conventional process options for fusion castings and glass-ceramics. Calcining, ceramic melting, bulk casting, and pellet forming and casting were discussed as glass processes. The process additions for glass-ceramics involve heat-treating either glass castings (option 1) or marbles in metal matrix (option 2) at moderate temperatures ($\sim$650°C) to nucleate many small crystals--then increasing the temperature to 750°C to 900°C and allowing the crystals to grow.[13] In the SYNROC-A process (option 1) the melting temperature may be increased to 1500°C for compositional purposes. The nucleation step is bypassed, and a single crystallization hold at about 1100°C is used.[11]

The third glass-ceramic option is sintered glass-ceramics. This term is used to describe processes such as the one noted in Fig. 6. In this process, the calcined waste is mixed with a

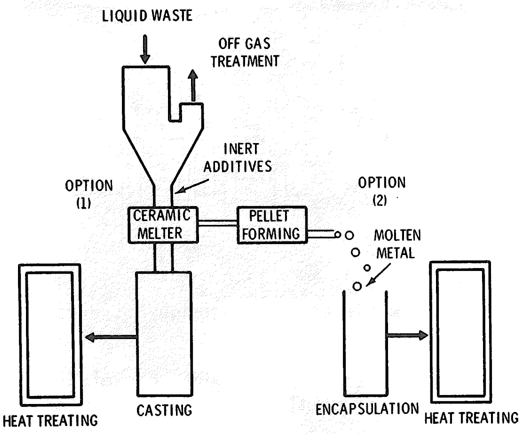

Fig. 5. Schematic of Fusion Casting and Glass Ceramic Processes

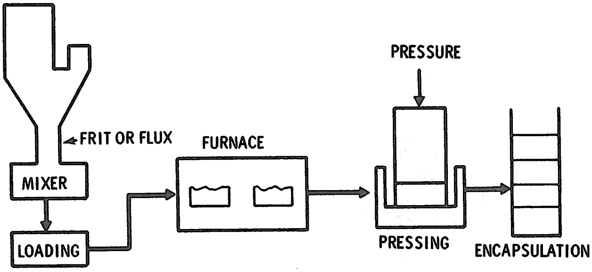

Fig. 6. Schematic of Sintered Glass-Ceramic Process

glass frit or flux and loaded into shallow, thin-walled containers. The containers are heated to about 900°C to react and sinter the flux and waste. Both crystalline phases and a glass phase are present after reacting--hence, the name "sintered glass-ceramics." The heated mass is removed from the furnace and uniaxially compressed. After cooling, the containers are loaded into canisters.[14]

Cermets

The cermet process schematic is shown in Fig. 7. Additives are introduced to the waste and then precipitated with the waste in molten urea. The precipitate is calcined in air at 800°C, then reduced by H_2 gas. The cermet powder is mixed with wax and extruded to form rods. These rods are densified by sintering at 1200°C in a reducing atmosphere, and are then encapsulated.[15]

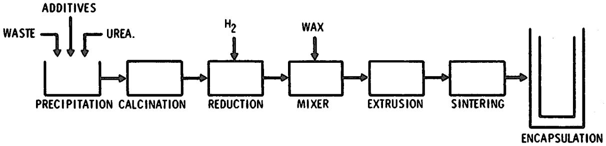

Fig. 7. Schematic of Cermet Process

Cements

Cements have generally not been considered to be viable for high-heat, high-level waste, but they have been considered (along with grouts) for solidification of intermediate wastes and existing defense wastes.[16] The process is conceptually simple: waste and cement are mixed together and cast either in drums or canisters. It is also conceptually possible to mix and solidify the cement waste form in the canister itself.

RANKING OF PROCESS COMPLEXITY

So far we have simply described the processes; some of these processes will operate effectively in a remote-radioactive environment, but others may not. A complete process evaluation and ranking would ideally consider each unit operation with respect to the items discussed in the Process Comparison Parameters section. However, many of the concepts are new, and detailed process studies are not available. A previous process review was subjective and did not include some of the current concepts.[17] To allow a quantitative comparison we propose a simple method for assessment of process complexity. The processes would be ranked according to the following:

- 10 points for each process step (i.e., calcination, pelletizing, encapsulation, etc.)
- 1 point for each 100°C required for each process step
- 1 point for each 100 psi of pressure used in each process step
- 5 points for each process additive or auxilliary operation (feed addition, frit addition, gas addition, off-gas treatment, etc.).

The total score represents a complexity level. We recognize that all process steps are not equally complex, and that complexity does not increase linearly with temperature and pressure. Nor do we consider capacity or reliability in the scoring. Nevertheless, we feel the rankings do represent relative levels of complexity.

This ranking system has been applied to the processes described in the Process Descriptions section, with the results shown in Table II in order of decreasing complexity. These results are based on the previously described reference processes. These systems could either become simpler or more complex as they are further developed. For example, in the cermet process considerable simplification might be possible through: 1) the use of spray calcination instead of urea precipitation and calcination, 2) the ability to simultaneously mix and extrude, and 3) combination of the reduction and sintering steps. With these changes the process would have a complexity score of 103--a simplification/reduction of 32 points.

Due to the simplifying assumptions made in the analysis, small differences are probably not meaningful. However, the results show that there are potentially major differences in process complexities. It is likely that the relationship between process complexity and process cost and reliability would resemble that shown in Fig. 8, with increasing complexity producing rapidly rising costs and rapidly decreasing reliability. For example, if a typical process operates at 80% reliability and is then complexed by a factor of three, the reliability may be reduced to 51% [(.8)(.8)(.8)]. This could necessitate addition of a second, equal-sized process, which would mean that the costs for the complex processes could be up to six times the cost of the initial process. This type of cost pattern, coupled with the limited increase in waste form inertness discussed initially, emphasizes the importance of keeping processes as simple as possible.

Table II. Complexity Level Determinations of Alternative Waste Form Processes

PROCESS	SPENT FUEL PACKAGING	CEMENT CASTINGS	SUPERCALCINE POWDER IN CANISTER	GLASS CASTING-SPRAY CALCINER IN-CAN MELTER	GLASS CASTING-SPRAY CALCINER CERAMIC MELTER	MOLECULAR STUFFING OF GLASS	GLASS MARBLES-METAL MATRIX	GLASS-CERAMIC CASTINGS (SYNROCK A)	SUPERCALCINE PELLETS-METAL MATRIX	SINTERED GLASS-CERAMICS	HOT PRESSED BILLETS SUPERCALCINE-SYNROCK B	GLASS-CERAMIC PELLETS IN METAL MATRIX	HOT PRESSED BILLETS ION EXCHANGED TITANATES	CERMET RODS	COATED SUPERCALCINE PELLETS-METAL MATRIX
ION EXCHANGE													10		
WASTE ABSORPTION						10									
CALCINATION			10	10	10		10	10	10	10	10	10	10	10	10
TEMP. ÷100			8	8	8		8	8	8	8	8	8	3	8	8
PRECIPITATION DRYING						10								10	
TEMP. ÷100														2	
SURFACE RINSE						10									
HEAT TREATMENT			10					10			10	10			
TEMP. ÷100			10					11			9	8			
MIXING		10								10			10	10	
MELTING				10	10		10	10				10			
TEMP. ÷100				11	11		11	13				13			
MARBLE FORMING							10					10			
PELLETIZING									10						10
EXTRUSION														10	
PRESSING										10					
SINTERING						10			10	10				10	10
TEMP. ÷100						9			12	9				12	12
SEALING LINER											10				
DIE LOADING										10			10		
HOT PRESSING											10		10		
TEMP. ÷100											10		10		
PRESSURE											10		10		
DIE UNLOADING													10		
REDUCING														10	
TEMP. ÷100														8	
COATING															20*
TEMP. ÷100															22*
ENCAPSULATION	10	10			10	10	10	10	10	10	10	10	10	10	10
TEMP. ÷100					6	5	5		5			5			5
PROCESS ADDITIVES X5	5	10	10	10	10	10		10	20	10	10	15	10	25	25
SPECIAL OFF-GAS TREATMENT														5	5
OFF-GAS TREATMENT			5	5	5	5	5	5	5	5	5	5	5	5	5
TOTAL	15**	30	53	54	70	79	84	87	90	92	102	104	108	135	142

*TWO SEPARATE OPERATIONS REQUIRED

**COMPLEXITY LIKELY TO INCREASE

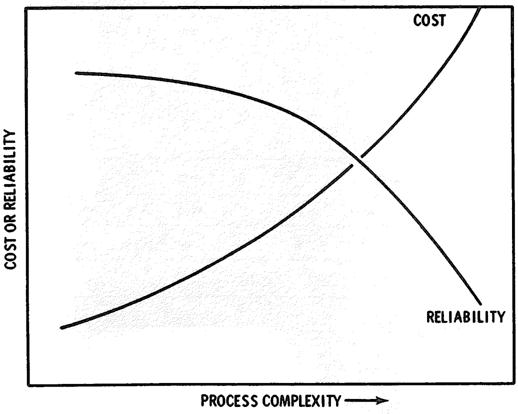

Fig. 8. Relationship Between Process Complexity and Reliability or Cost

CONCLUSIONS AND RECOMMENDATIONS

- Several processes exist for producing alternative waste forms.
- A simple technique has been illustrated for comparison of waste form process systems.
- There are major incentives for minimizing the number of waste processing steps, and this should be an objective of process development.
- Simplest processes are cement and spent fuel encapsulation.
- The most complex processes are cermets and coated pellets in a metal matrix.
- More detailed evaluations of process complexity and waste form inertness should be obtained before final selection is made.

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