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NUCLEAR WASTE FIXATION

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Introduction

The current Federal Regulations for the management of high-level liquid waste (HLW) from nuclear fuel reprocessing plants require that the liquid waste be converted to a dry stable solid within 5 years after reprocessing the fuel, and that the dry stable solid be shipped to a federal repository within 10 years after reprocessing. ~~The conversion of the liquid HLW to a dry solid or calcine will be termed solidification.~~

Currently, it is intended that at the federal repository, the calcined waste will be incorporated in a silicate glass* or ceramic waste form for storage and ultimate disposal of the waste. The combined federal repository facility is to be called the Retrievable Surface Storage Facility (RSSF) and the Calcine ~~Vitrification? Conversion~~ Facility ~~(CVF)~~ CCF

For the purposes of the paper, the conversion of the liquid HLW to a solid will be termed solidification and the incorporation of the calcine into a glass* matrix will be termed fixation. A broader definition of the term fixation, as used here, is the incorporation of nuclear waste into an essentially nondispersible form, with both air and liquid media considered as dispersal mechanisms. Thus, two important variables are solubility and particle size.

Background

Glass or glass-like forms are being emphasized internationally in development programs for the near-term immobilization of power reactor wastes because they have the best proven durability of man-made materials. The earliest known man-made glass dates from the 23rd century B.C.[1] However, much older glass occurs

* The word glass will be used to refer to any silicate form, be it glass, glass-ceramic, or ceramic; the difference being the type and degree of crystallization present in the material.

DISCLAIMER

naturally. The survival of this glass, plus the studies that have been made on weathered glass surfaces, lend confidence to our ability to predict the future integrity of glass. For instance, by microscopic examination it has been possible to correlate the age of man-made glass and naturally-occurring obsidian with the depth of surface alteration. This has been done for glass over 1500 years old[2] and for obsidian surfaces up to 200,000 years old.[3]

Glass has the further advantage of being a very congenial material. Although only a few of the oxides, SiO_2, P_2O_5, B_2O_3, GeO_2, As_2O_3 are glass formers by themselves, much of the periodic table can be incorporated in oxide glass either as network formers or modifiers. This broad acceptance is of great benefit in the immobilization of high-level wastes, which are complex mixtures of about 35 fission product elements and 18 actinide and daughter elements.

The AEC currently has underway at Battelle Pacific Northwest Laboratory (BPNL) the Waste Fixation Program (WFP) which is directed toward providing technology for the solidification and fixation of commercial high-level waste.

The mainline emphasis of the WFP program is to develop the technology of incorporate commercial HLW into silicate glass or glass-like materials that will meet strict specifications concerning physical stability and resistance to leaching. In order to meet the requirements of remote operation, the basic process being demonstrated in the WFP is simple. It consists of melting dried waste after the addition of glass forming chemicals and casting the molten glass into stainless steel canisters. Several options for each processing step are possible, as shown in Figure 1.

Glass compositions for the WFP processes are currently under study and operation of the processing steps is being perfected in the nonradioactive pilot plant. Fully radioactive engineering scale demonstrations of the process are scheduled to begin in mid-1975. The radioactive demonstrations will 1) prove

the operability of the fixation process, including off-gas control, and 2) provide full-scale radioactive glasses for long-term characterization during typical handling and storage conditions. It is currently planned that radioactive waste calcine from General Electric's Midwest Fuels Reprocessing Plant (MFRP) will be used in the demonstrations at PNL.

Waste Compositions

The major source of high-level wastes is the raffinate or aqueous waste stream from the first cycle of the Purex solvent extraction process. This stream can be well characterized. It is a nitric acid solution, containing: over 99.9% of the fission products present in the irradiated fuel elements, iron in some instances, traces of uranium and plutonium, and all of the other actinide elements which are produced in nuclear power reactors. It will also contain iron, chromium and nickel from the corrosion of stainless steel and a small amount of phosphate from the phosphate-containing extractant used in the solvent extraction process. The high-level waste stream coming from the reprocessing plant is not made up exclusively of the first-cycle raffinate, however. It can also contain complements from subsequent solvent extraction cycles, and various scrubber and decontamination wastes, which are much less well characterized as to quantity and composition.

In order to demonstrate that the various potential high-level waste compositions are all amenable to immobilization, two standard waste compositions are being used in the WFP program. These are a "clean" waste, designated PW-4b, which is essentially first-cycle raffinate, and a "dirty" waste, designated PW-6, which contains large amounts of sodium and iron (see Table 1). It should be noted that there are other possible constituents of high-level wastes, such as fluoride, mercury and soluble poisons which will also have to be considered.

Constituents may be added during waste treatment also which will affect subsequent fixation processes. An example is the Al_2O_3 seed particles which will be used in the fluidized bed calcination of high-level wastes. The Al_2O_3, which will comprise about two-thirds by weight of the final calcine, will have large impact upon the flowsheet used for subsequent conversion of this waste to glass. Because of its large perturbation on glass-making, studies involving the MFRP calcine are being included in the WFP program.

Fixation in Silicate Melt Formulations

The silicate melt formulations being used for the fixation of radioactive wastes are quite different from industrial glass formulations. Thus, although the principles developed through the millenniums that man has produced glass are being used as guidelines, the glass formulations being used for waste fixation are, in essence being developed empirically.

Examples of the candidate glass formulations are shown in Table 2. These glass formulations are being developed for the reprocessing of PW-4b, PW-6 and calcine of the MFRP-type in the WFP equipment. As shown in Figure 1, two melter concepts are being developed in the WFP program, one operating at 1150°C and one operating at approximately 1400°C. The latter permits use of a higher-melting higher-silica content glass formulation which more closely approximates industrial glass compositions. The properties of these glass formulations are being determined in detail. Although the continued testing will undoubtedly reveal some desirable modifications, present indications are that glass formulations of the types in Table 2 can serve as satisfactory fixation media for high-level wastes.

Properties of the Silicate Melt Formulations

The glass formulations are being optimized to provide low leachability and high integrity when solidified, and yet are to have properites which will

permit trouble free processing as a melt in remotely operated equipment. The properties of most importance are:

Processing

- viscosity
- homogeneity
- corrosivity
- volatility

Storage and Disposal

- chemical inertness
  - -leachability
  - -canister corrosion
- physical stability
  - -long-term thermal effects
  - -thermal shock
  - -physical shock
  - -radiation effects
- homogeneity

Properties Required During Processing

The processing equipment places specific requirements upon the properties of the molten waste product. For instance, in the present WFP equipment the molten glass is drained out of the melter periodically and a melt viscosity of about 200 poises or less is required to do the melt discharging in a controlled and timely manner.

It has been found that a few of the many constituents of the waste glass are not completely dissolved in the current flowsheets using a metallic melter and a 1150°C melt temperature. Microcrystallites of the fission products CeO_2 and RuO_2 can settle gradually in the melter, resulting in a higher viscosity melt at the drain point which makes draining of the melter more difficult. For this reason, agitation of the metallic melter is required.

Corrosion of the glass-making melters must be maintained at an absolute minimum to promote long lifetimes for the melters. Laboratory-measured corrosion rates indicate melter lifetimes of from several months for metallic melters to several years may be achievable. for ceramic melters

Volatility from the high temperature melts can complicate the off-gas treatment; the policy is to recycle volatiles back to the process. For some elements, such as cesium and tellurium, this is a simple procedure. However, volatilized ruthenium, for instance, tends to plate out on stainless steel surfaces as difficult-to-remove RuO_2, therefore, in general the goal is to minimize volatility. Cesium, tellurium, ruthenium and molybdenum account for 95 wt% of the volatility at 1200°C[4] and the relative quantity volatilized is very dependent on melt geometry. As the melt gets deeper, as it will be in the engineering-scale equipment, the relative quantity volatilized decreases.

Properties Required During Storage and Disposal

The purpose of waste fixation processing is to provide the safest, most trouble-free containment of the radioactive wastes that can be devised. It is planned that the radioactive waste glasses will be cast in stainless steel canisters. It is customary to consider the solidified waste "package" (i.e., the stainless steel canister and its contents) as the integral product of the waste solidification or fixation process. Since the stainless steel canister is an integral part of the product, it is important that its integrity not be affected by interaction with the glass, either during the casting operation, when the glass in the canister is temporarily molten, or during storage. Measurements indicate the corrosion of stainless steel in waste borosilicate glasses is less than 1 mil/month at 900°C and rapidly becomes immeasurable as the temperature decreases below 900°C. It is generally agreed that external factors will govern the lifetime of the stainless steel canister.

If anything should happen to the stainless steel canisters, the properties of the waste glass become the ultimate control on the rate of release of radioactivity to the environment. The most probable mechanism for release to the environment is by dissolution in water. Thus, determination of water leaching

behavior is one of the principal factors considered in the evaluation of candidate solidified waste forms. The leaching of constituents from glass is a complex phenomenon. One obvious approach is to make comparisons with glass of known stability. This is done in Figure 2 where the leach rates of candidate waste glass are compared with a standard soda lime glass and with Pyrex glass. Waste glass can be made in metallic melters which compare quite well with soda lime glasses. If a high-temperature refractory melter is used, the leach rates of waste glass can approximate those of Pyrex. Incorporation of calcined waste into these glasses should reduce their leach rate by a factor of approximately 10^5 to 10^6. The leach rates shown in Figure 2 are for nondevitrified glass. As will be discussed later, devitrification of at least portions of the waste glass probably cannot be avoided. Indications are that devitrification increases the leachability of borosilicate waste glass, but not by more than a factor of about ten.

The quantity of radioactivity released in the event the glass product contacts water is a function of not only leachability, but also of surface area exposed. Thus, it is desirable to maintain the glass in large pieces to minimize the surface-to-volume (s/v) ratio. This is also important when considering the possibility of air dispersibility of small particles. Since glass is brittle, management procedures will be designed to minimize thermal and physical shocks to the glass canisters. Figure 3 puts into perspective the overall effect of s/v ratio. The difference in s/v ratio between particles of 100 μ calcine and a 1 ft x 10 ft monolith is approximately 6000. Thus, for a constant leach rate, the initial dissolution rate for the 100 μ particles is 6000 times greater. Combining the leach rate and s/v ratio effects, there can be a system improvement of approximately 10^8. It can also be seen from Figure 3, that when a glass or ceramic fractures, the s/v ratio is still significantly less than for 100 μ calcine.

Although for simplicity the word glass in this paper has been used to characterize the silicate waste fixation media, in reality they will be undoubtedly complicated mixtures of crystalline and glassy phases. This is due to the already mentioned fact that a few constituents may be somewhat insoluble in the glassy matrix used. However, a more important reason is because the glass will be self-heating. The amount of self-heating is a function of the radioisotopic content of the glass and may vary over a wide range in the canisters of solidified commercial HLW, depending on such factors as fuel exposure and cooling time. The thermal conductivity of the waste glass is typically 1 to 1.2 W/m°C. This relatively low thermal conductivity causes the centerline temperature of the typical waste glass canister to approach 500°C initially and to remain above 100°C up to about 100 years storage. Although these temperatures are below what is normally considered the devitrification temperature range (600 to 900°C for representative silicate waste glasses), some devitrification may still occur because of the extremely long times involved. Devitrification refers to the spontaneous crystallization of certain constituents in the initially amorphous glass structure.

Consideration is being given to purposely devitrifying each of the waste glass canisters, since the devitrified form is thermodynamically more stable. Controlled devitrification is the technological basis of glass-ceramics, which have seen rapidly spreading commercial application in the last 20 years. Properties of glass-ceramics, which would be desirable in a HLW media vis-a-vis true glass, include:

- stability at higher temperatures
- greater thermal and mechanical shock resistance
- greater assurance of long-term stability.

The composition and thermal treatment of commercial glass-ceramics is carefully controlled to achieve almost 100% conversion of the initial glass form to

to crystals of an essentially uniform size, a high proportion of which are less than 1 micron in size. Such careful control of composition and temperature will probably not be possible in HLW solidification, but the formation of quasi glass-ceramics with much of the advantages of true glass-ceramics may be possible. Investigations in this area are part of the PNL waste fixation program.

The high-level of self-induced radiation in the waste glass causes not only elevated temperatures; it may also produce other effects. Preliminary analyses indicate none of those other effects will have an important effect on solidified waste management. Investigations now underway as part of the PNL waste fixation program will verify the preliminary analyses experimentally. Some of the possible radiation effects to be studied are helium buildup, mechanical damage and stored energy. Most radiation effects have some common characteristics: 1) they are mainly due to the actinide content of the glass, and 2) they tend to be annealed out at elevated temperatures. Thus, it is only after the waste canisters have cooled (i.e., after most of the fission products have decayed out) that radiation effects of this type may become important.

Stored energy refers to energy which can be secreted in solid materials due to radiation-induced lattice displacements. The energy can be released as thermal energy if the temperature of the material is raised above a certain temperature which is unique for each material. It has been estimated that the stored energy in waste glass will not exceed 200 cal/g and analyses have indicated the release of this amount of energy would not have serious effects on a waste storage or handling facility.[5,6]

The PNL program to study stored energy, and other potential radiation effects, is utilizing curium-244, with a half-life of 18.1 years. Use of this short-lived actinide permits accelerated radiation effects studies to be made. We are in the process of preparing a series of glass specimens containing

approximately 1 wt% curium. The number of alpha particles emitted in these specimens in 1 year will be equal to the number of alpha particles emitted in a typical HLW glass in its first 100 years. Measurements of stored energy, density changes, helium diffusivity, friability and leach rate will be obtained on these specimens as a function of dose rate; however, no date are available as yet. An additional stored energy program, in which simulated solidified wastes are being neutron irradiated, is being carried out in conjunction with ORNL.

The WFEP Borosilicate Glasses

Good evidence already exists for the general thermal and radiation stability of borosilicate waste glass. Samples of WSEP borosilicate products were obtained by core-drilling the canisters after 2-to 3-year's storage. Leach rates of representative core-drilled samples from the canisters are compared with the leach rates of nonradioactive specimens in Figure 4. Note that two types of borosilicate glass were made in the WSEP program and that the leach rates of both types of borosilicate glass are considerably higher than those of the borosilicate glass being investigated for the new WFP program. This is because the earlier glass was formed in situ in its stainless steel canisters. Therefore, the temperature was maintained at 950°C or below to minimize corrosion of the canisters. The wall sections obtained during core drilling showed that no significant corrosion occurred.

The WSEP canister of rising-level borosilicate glass in particular was subjected to extreme storage conditions. As formed, the canister was generating 310 W/liter of radioactive decay energy. The canister was then held 1.8 years in controlled storage with an average wall temperature of 425°C; during this period the centerline temperature of the 6-in. diameter canister varied from 740 to 480C. The initial leach rate was somewhat higher than obtained on non-radioactive simulated waste glass of the same composition, but the leach rate

dropped within 4 weeks to be very comparable with the nonradioactive comparison samples.

Two canisters of in-pot melting borosilicate glass were made in the WSEP program. The in-pot melting borosilicate was a more leach-resistant glass composition than the rising-level glass, since it contained more silica and less B_2O_3. (It should be noted however that the rising-level glass contained almost 50 wt% fission products, illustrative of the very high-waste loading that can be achieved in borosilicate glass, albeit with some sacrifice in chemical durability.)

Core-drilled samples were taken from the 8-in. diameter in-pot melting glass canisters after the canisters had been stored almost 3 years and had received 1×10^{11} Rad or more of radiation. Leach data from the core-drilled samples are shown to bracket the nonradioactive control data in Figure 4. Experience has shown that differences in leach rate of the magnitudes shown are within experimental deviation, which are believed to be associated mainly with inability to determine surface areas accurately. The shape of the radioactive and nonradioactive leach rate curves for the in-pot melting glass are similar and it may be concluded that no significant deterioration in the quality of this radioactive glass has occurred.

Metallic Melters

Continuous metallic melters are being developed in France, Germany and the USA for use in the fixation of HLW. Most of these melters are constructed of Inconel alloys (600, 601, and 690) and will have a useful life of one to six months. A platinum continuous melter was used in the WSEP program at BPNL, so experience with these types of metallic melters dates back to the early 1960s. In England and France and in the WSEP program, batch type metallic melters have also undergone considerable development. In France, production operation with actual

nuclear wastes is underway in the case of the PIVER process. Table 3 summarizes the plans of several countries for the fixation of HLW.

The metallic melter being used in the WFP program, shown in Figure 5, is constructed of Inconel 690, which is the most corrosion resistant, nonprecious metal that has been tested to date with simulated HLW silicate melt formulations. The laboratory measured corrosion rates (Table 4) and an extended 13-day run with the Inconel 690 melter indicate a melter lifetime of several months is probably achievable.

The metallic melter used in the WFP program is designed to operate at 1150 to 1200°C with an 1150°C zinc borosilicate melt formulation. It is operated with continuous input of approximately one part waste (based on wt% of final glass) and two parts of additive as a glass frit. The discharge of the melt is on a batch basis by means of freeze drain valve which during melter filling contains a frozen plug of glass.

An agitator has recently been placed in the WFP melter, primarily to facilitate making a homogeneous glass as was described above. However, the added agitation enables a melter throughput that is approximately double that without agitation. The WFP melter (Figure 5) can process HLW in excess of that from a 1 MT/day reprocessing plant based on the PW-4b waste composition. This glass-making capacity of this size melter is approximately _____ liter of glass per day. Scale-up calculations for the stirred melter(~~10~~ 7) indicate that a melter approximately double the size of the WFP melter will handle the HLW from a 5 MT/day reprocessing plant. Dimensions of such a melter would be ( ) with a melt holdup of approximately _____ liters.

Volatilization of fission products from the melter at 1150°C should not be a significant problem, based on results from the WSEP program where platinum melters similar in size to the WFP Inconel melter were used.

Heating of the metallic melters can be by a resistance furnace or by induction coupling to the melter wall. Resistance furnaces at 1200°C may not be as reliable as induction heated furnaces; however, melter wall warpage evantually leads to hot spots when induction heating is used. This requires earlier changeout (ca. 1000 to 2000 operating hours) of the melter.

Refractory Melters

Refractory-type electrode heated melters for glass making have been utilized by the glass-making industry for several years. For this reason, various glass industries are providing design assistance for the WFP refractory melter. This type of melter is designed for operation at approximately 1400°C. In general, this temperature increase, above the 1150°C metallic melter temperature range, allows the production of a more durable glass. This is primarily because the glass composition can be made much higher in silica at the expense of leaving out more leachable species, such as boron, which is required in the lower temperature glass formulation.

Operation of the refractory melter (Figure 6) is quite similar to that described above for the metallic melter; with the major difference being the temperature increase, and the utilization of a "cold cap" or crown on top of the melt. This cold cap will help control volatility in engineering-scale equipment. Since this melter will be heated by passing an electric current through the molten melt, the area in the top of the melter will be relatively cool. The waste calcine and glass frit will be added at the top of the melter where it will float as a thick "cold cap" to trap the volatiles from the hotter melt below. This is a standard operating practice in the glass-making industry.

Refractory materials such as high chrome oxide or zircon may give melter lifetimes of several years, based on laboratory-measured corrosion rates (Table 4). It must be emphasized that this conclusion has been reached on the basis of extrapolation of laboratory and short-term engineering tests; long-term

tests, particularly with waste glasses in engineering scale continuous refractory melters, have not been made.

Heating of the melter is by joule heating; passing a current of electricity between electrodes submerged in the melt. Typical electrode operating parameters at a 1400°C melt temperature and at an anticipated melt resistivity of _____, are _____volts and _____amps. The melter must be designed to optimize the current flow paths between the electrodes for optimum melting conditions and to maintain a low electrode current density to prolong the electrode life. A potential design problem when using zircon or high-chrome ore refractories is that some current flow can take place through the refractory; shortening the life of the melter wall.

The principle electrode materials being considered for use in the refractory melter are molybdenum, molybdenum di-silicide, tin oxide, and electrodes sheathed in platinum. Thus far, the two types of molybdenum electrodes have been tested successfully in short-term tests. Since it is anticipated that the electrode lifetime may be shorter than the refractory wall, movable insertable electrodes may be desirable to attain maximum melter life. Potential disadvantages of the refractory type melters arise from the fact that refractory materials lifetime is shortened by thermal cycling, requiring that the melter be heated and cooled slowly (ca. 10-50°C/hr) and that the melter be maintained continuously at operating temperature for as long as possible to minimize the number of heating-cooling cycles. Use of electrodes presents some startup problems, since no current will flow until the melt becomes fluid. Startup techniques being investigated include use of infrared heaters above the melt and use of resistance heaters within the furnace walls or bottom.

The French are currently developing a novel refractory-type melter made out of zirconium alumium silicate. This melter utilizes direct induction coupling with the melt for heating. Startup is attained by dropping aluminum pellets on the unmelted material in the melter and then melting. The pellets ~~are melted~~ by

induction coupling. This forms a heated area which melts the frozen glass, leading to direct coupling with the glass. The melter has water-cooled walls to give longer refractory lifetimes by maintaining a frozen layer of glass between the refractory and the high-temperature corrosive melt.

Comparision of Melting Processes

The two types of refractory melters, the metallic melter, and in-pot melting are briefly compared in Table 5. In-pot melting is a batch process where calcined oxide and glass-forming additives are blended and melted in the final storage canister. This has been done on an engineering scale with radioactive waste in the WSEP program.(3) To achieve the 1150°C and 1400°C temperatures for the melt flowsheets described above requires the use of special high-temperature canisters such as Inconel for 1150°C and a coated graphite for 1400°C. These cans would probably be heated by direct induction coupling with the can wall.

Most of the items compared in Table 5 were discussed above and are self-explanatory. In general, the ability to process the low-silicate (1150°C) and high-silicate (1400°C) flowsheets is dependent on the melter operating temperature. Similarly, the glass quality or lowest leach rate is indirectly dependent on the temperature available for making the glass.

Alternative Fixation Methods

Although glass or other melt-formed ceramic materials are considered to be very acceptable media for the permanent fixation of radioactive wastes, more advanced waste forms being investigated may offer added increments of safety or economy in the future. AEC-sponsored research is currently being carried out on such system on a laboratory scale with nonradioactive materials.

The current glass processes produce radioactive glass encased in stainless steel. It is obvious that the protection achieved can be augmented by the addition of more layers of inert material. Storage basins, shipping casks,

etc., are common examples of ~~type~~ the type of redundant protection, but the waste form itself can also be designed in layers to provide a multiple barrier of protection. This concept has been coined the "Russian Doll" after the multi-layered wooden toys of that name (see Figure 7). The goal of the multiple barrier approach is to first tie up the individual radioactive atoms in the most stable configuration achievable, then various layers and coatings of different inert materials, each perhaps chosen for a certain specific special property, can be added.

Work is being done at Pennsylvania State University, for the PSC under a subcontract with PNL. One goal of the Penn State work is the development of inert, thermodynamically stable chemical forms for the individual radioactive atoms. This is a long-term fundamental research program and will involve synthesizing tailor-made mineral-like compounds of the fission products and studying their properties. These compounds will then be formed by a scheme such as 1) chemical mixing of the waste with additives, 2) formation of the mineral-like compounds in a spray calciner or fluidized bed to form a "supercalcine", and 3) any of several final treatment steps, such as firing of the calcine, cold pressing and firing, or hot pressing. Hot pressing of either the tailor-made compounds or waste oxide calcine in inert matrix materials have produced promising results using quartz as the matrix material.[8]

Advanced waste form work is also being carried out at PNL and at the Idaho Falls Chemical Processing Plant. At PNL, high temperature gas cooled reactor fuel technology is being applied to waste solidification. Waste particles are being coated with pyrolytic carbon followed by a cover coat of silicon carbide. In keeping with the multiple barrier concept these coated particles would be placed in a matrix of inert material contained in a canister of yet another material. At Idaho Falls, various concepts are being evaluated that will lead

to fixation of fluidized bed calcine in a low solubility matrix. One system being studied involves the incorporation of either coated or uncoated calcine in a metal matrix.

Figure 10 reveals a systematic approach to the determination of what multiple barrier waste schemes are possible. The columns present the various layers of waste protection that can be considered, and the horizontal rows present possible options for each layer of protection. The example shown on the figure is for glass in a metal canister.

Summary

In conclusion, current waste management research and development is directed toward near-term technology for the fixation of commercially-produced high-level wastes in silicate glass or ceramic forms. Second, a comprehensive examination of potential advanced waste forms is being carried out which may offer further increments of safety or economy over the long term.

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TABLE 2
WASTE COMPOSITIONS SELECTED FOR WASTE FIXATION PROGRAM

	CONSTITUENTS [a]	CONCENTRATION, M AT 378 LITER/MTU PW-4b	PW-6
PROCESS INERTS	H	1.0	3.0
	Na	—	2.0
	Fe	0.05	0.5
	Cr	0.012	0.045
	Ni	0.005	0.020
	PO_4	0.025	0.025
FISSION PRODUCTS	Mo	0.095	0.095
	Tc (Mo)	0.022	0.022
	Sr	0.027	0.027
	Ba	0.027	0.027
	Cs (K)	0.054	0.054
	Rb (K)	0.010	0.010
	Y + RE (RE MIX)	0.208	0.208
	Zr	0.106	0.106
	Ru (Fe)	0.059	0.059
	Rh (Co)	0.010	0.010
	Pd (Ni)	0.032	0.032
	Te	0.012	0.012
	Ag	0.002	0.002
	Cd	0.002	0.002
ACTINIDES	Np (U)	0.0085	0.0085
	U + Pu (U)	0.011	0.054
	Am Cm	0.0022	0.0022

(a) CHEMICAL STAND-INS USED ARE SHOWN IN PARENTHESES

Table (2)

TYPICAL HLW GLASS COMPOSITIONS

	LOW TEMPERATURE GLASS (low silicate) (FOR METALLIC MELTER OPERATING @ 1150°C)	HIGH TEMPERATURE GLASS (high silicate) (FOR REFRACTORY CERAMIC MELTER OPERATING @ 1400°C)
SiO_2, WT%	27-34	50-53
B_2O_3	10-12	—
Na_2O, K_2O	8-9	5-6
ZnO	19-22	11-13
Fe_2O_3	2-6	7-9
CaO, MgO, SrO, BaO	5-6	—
FP OXIDES	12-23	11-14
MISCELLANEOUS, (ACTINIDE OXIDES, NiO, Cr_2O_3, P_2O_5, ETC.)	2-4	2-4
Typical Volume of Glass (ft^3/MTU)	1.7-3.4	3.5
Density (gm/cm^3)	3.0-3.4	2.9

Table 3

INTERNATIONAL PLANS FOR FIXATION OF POWER REACTOR HLW IN GLASS

COUNTRY	GLASS TYPE	PROCESS	SCHEDULE
ENGLAND	BOROSILICATE	RISING LEVEL GLASS	HOT SMALL SCALE, 1975 (WINDSCALE) FULL SCALE, 1985 (WINDSCALE)
FRANCE	BOROSILICATE	ROTARY CALCINER-CONTINUOUS MELTER	FULL SCALE, 1977 (MARCOULE) (a) FULL SCALE, 1981 (LA HAGUE)
GERMANY	BOROSILICATE	SPRAY CALCINER-CONTINUOUS MELTER	HOT PILOT PLANT, 1977 (KARLSRUHE) FULL SCALE, 1982 OR LATER (POSSIBLY WILL BE LOCATED OVER A SALT MINE)
RUSSIA	PHOSPHATE	FLUIDIZED BED CALCINER-BATCH MELTER	NOT KNOWN
USA	BOROSILICATE	VARIOUS CALCINERS-CONTINUOUS MELTER	HOT PILOT PLANT, 1966-70, 1975-, FULL SCALE, ?

(a) MARCOULE PLANT WILL OPERATE ON RELATIVELY LOW EXPOSURE PRODUCTION REACTOR WASTES

TABLE 5 #3

DEFINITIVE TESTING

MELTER CORROSION — A BASIC PROCESSING PARAMETER

REPRESENTATIVE CORROSION RATES:

1150°C GLASS (72-68) (DISSOLVING STAINLESS STEEL ACCELERATES RATES)	INCONEL-600	7.5 MILS/MO.
	INCONEL-690	1.4
	20-45-5	7.8
1400°C GLASS (73-109) (SHORT-TERM STATIC COMPATIBILITY TESTS @ 1450°C)	ZrO_2	<1
	ZrO_2-SiO_2 (ZIRCON)	<0.5
	CHROME ORE (80% Cr_2O_3)	<0.5

THERMAL STABILITY — ALL GLASS DEVITRIFIES IN SOME TEMPERATURE RANGE

DEVITRIFICATION TEMPERATURES:

1150°C GLASS (72-68)	650-800°C
1400°C GLASS (73-109)	750-900°C

Table 5 1150°C 1400°C

COMPARISON OF MELTING PROCESSES

MELTING	OPERATING TEMPERATURE, °C	FLOWSHEET PROCESSABILITY* LOW SILICATE	FLOWSHEET PROCESSABILITY* HIGH SILICATE	GLASS QUALITY, LEACH RATE g/cm²-DAY	POTENTIAL PROBLEMS	STATE OF DEVELOPMENT
ELECTRODE MELTER (refractory)	~1400	YES	YES	10^{-6}-10^{-7}	~~SMALL-SCALE.~~ VOLATILIZATION, BUT CAN HAVE COLD CAP. REMOTE STARTUP.	DEVELOPED FOR GLASS INDUSTRY ONLY
INDUCTION COUPLED MELTER (refractory)	1400	YES	YES	10^{-6}-10^{-7}	VOLATILIZATION, but might utilize cold cap.	NO RADIOACTIVE EXPERIENCE
METALLIC MELTER	1150 (INCONEL)	YES	NO	10^{-5}-10^{-6}	~~CAPACITY-LIMITED.~~ MAY REQUIRE AGITATION for capacity and homogeneous melt	NEARLY DEVELOPED
IN POT MELTING	1000 SST 1150 INCONEL 1400 SILICON CARBIDE COATED GRAPHITE	YES YES YES	NO NO YES	10^{-4} 10^{-5} 10^{-6}-10^{-7}	CAPACITY COULD BE LIMITED (1 TO 3 POT LINES) EXPENSIVE CANISTERS. SiC GRAPHITE CANS MAY REQUIRE RECANNING.	NEARLY DEVELOPED FOR METALLIC CANS COATING TECHNOLOGY NEEDED FOR LARGE CANS

* See Table 2

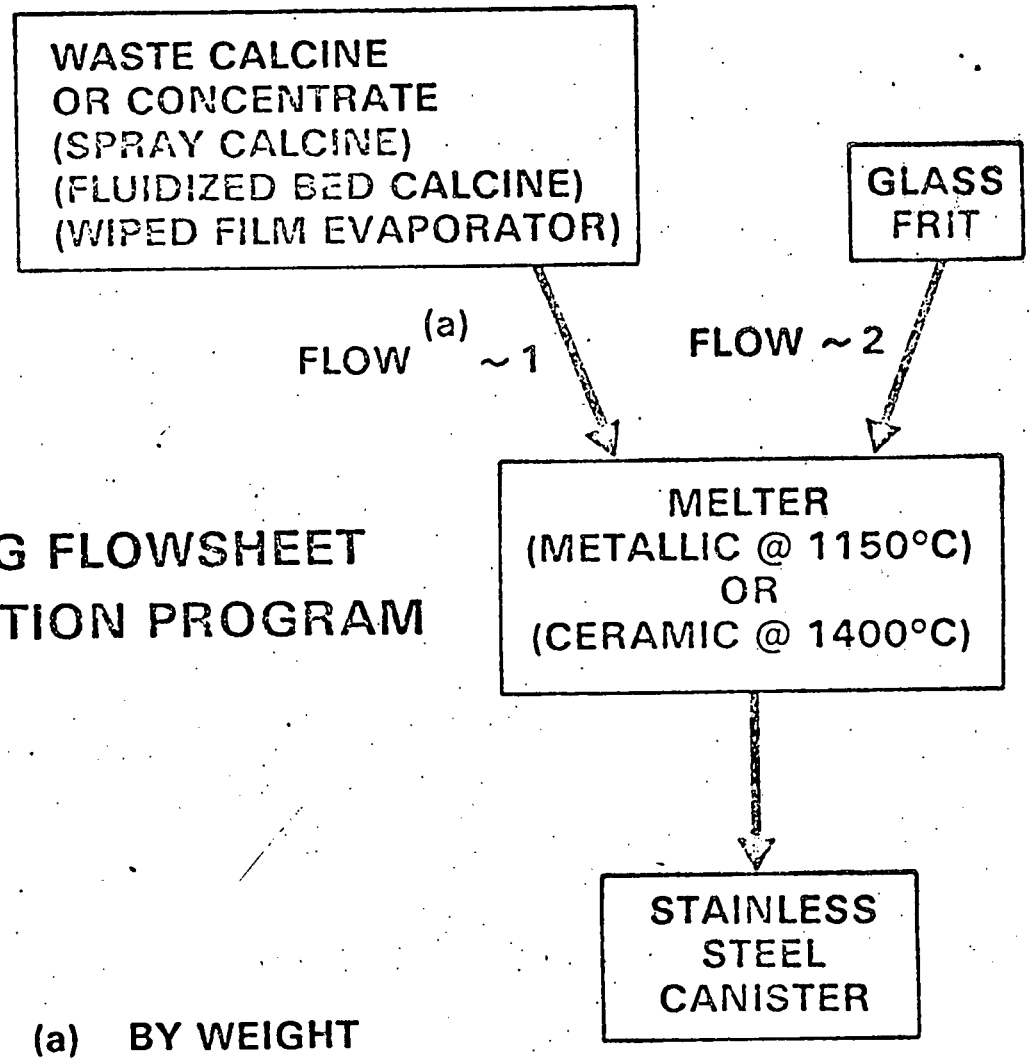


FIGURE 1

BASIC GLASSMAKING FLOWSHEET
UTILIZED IN WASTE FIXATION PROGRAM

(a) BY WEIGHT

DEFINITIVE TESTING

Fig. 2

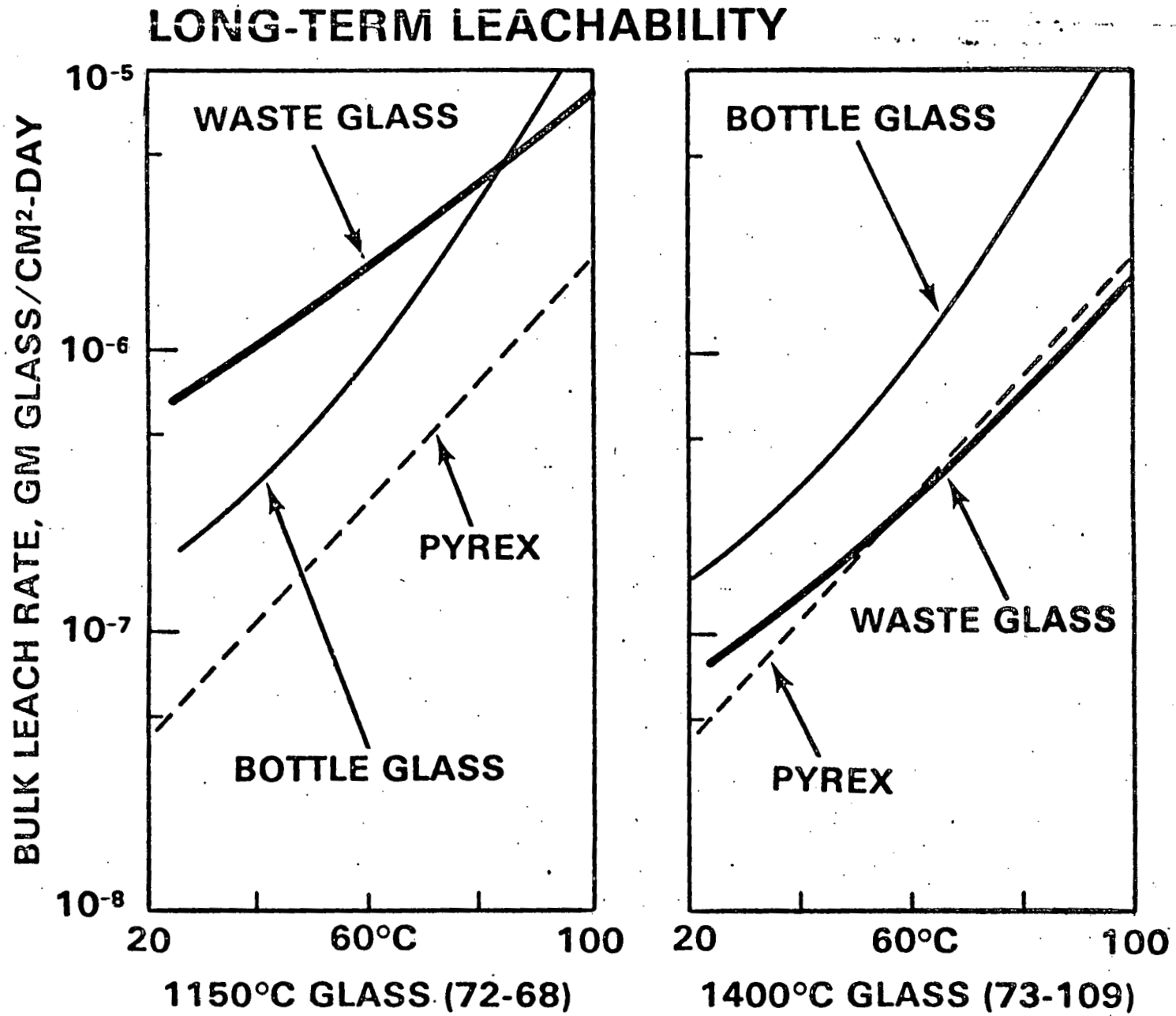


Fig. 3

SURFACE TO VOLUME RATIOS

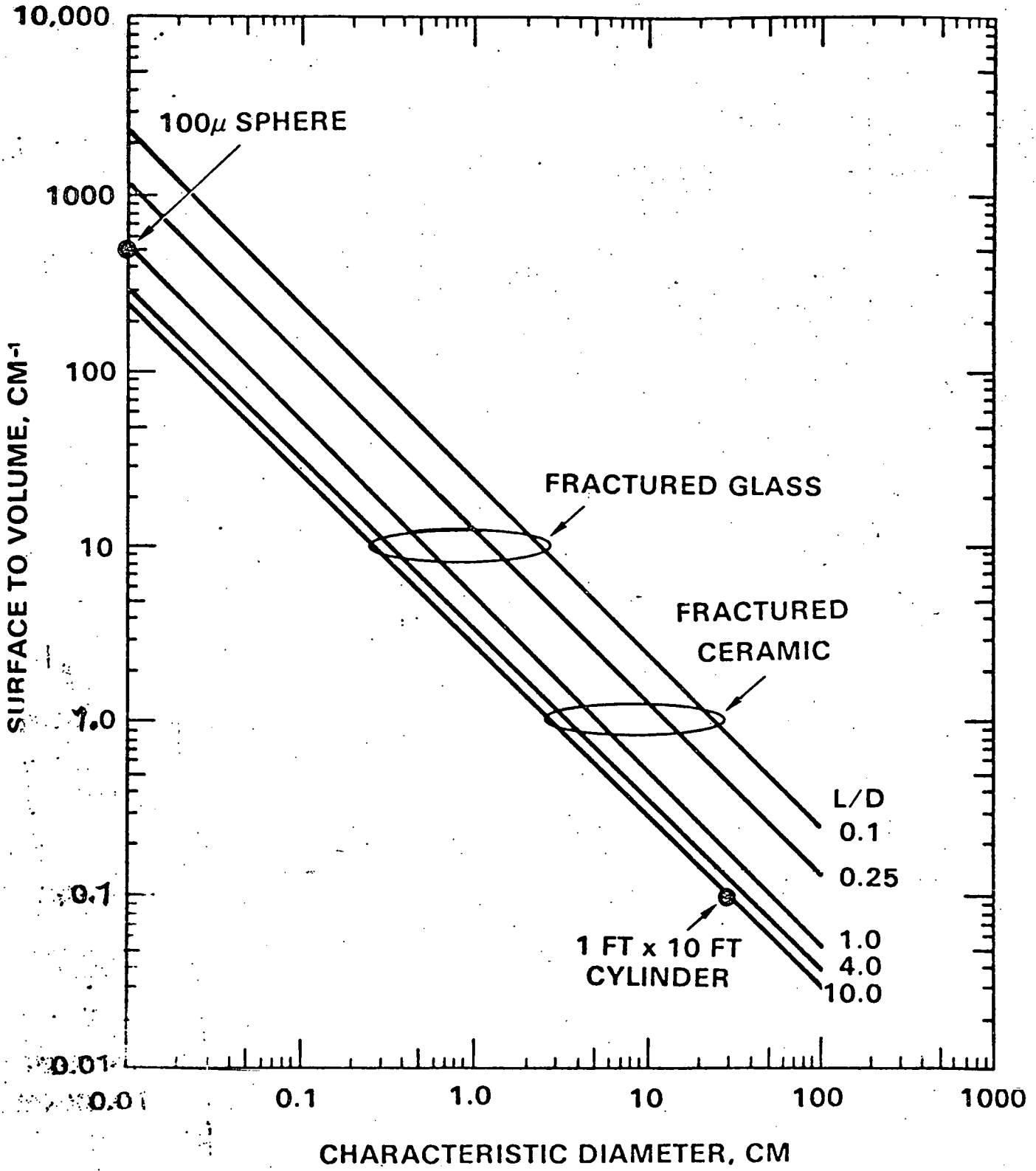
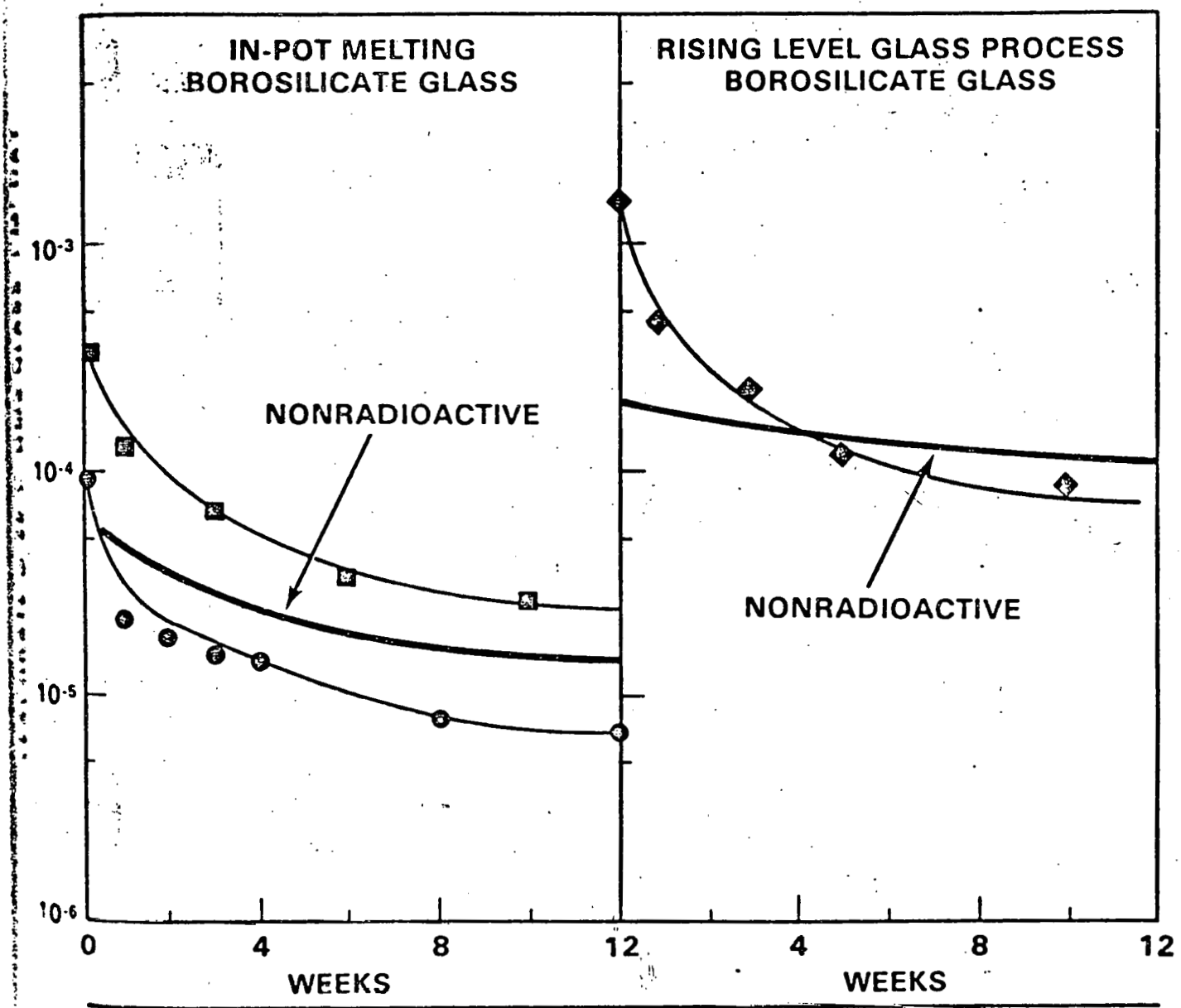


Fig. 4

INTERIM STORAGE HAS LITTLE EFFECT ON BOROSILICATES



SS-12	SS-13	PC-9
90W/LITER 2.8 YRS AIR STORAGE 1.0 x 10'' RAD	200 W/LITER 2.8 YRS WATER STORAGE 3.9 x 10'' RAD	300 W/LITER 1.8 YRS 425°C AIR STORAGE 4.6 x 10'' RAD

Fig. 5

Melissa Miller

Maybe put all melbs on 1 sheet

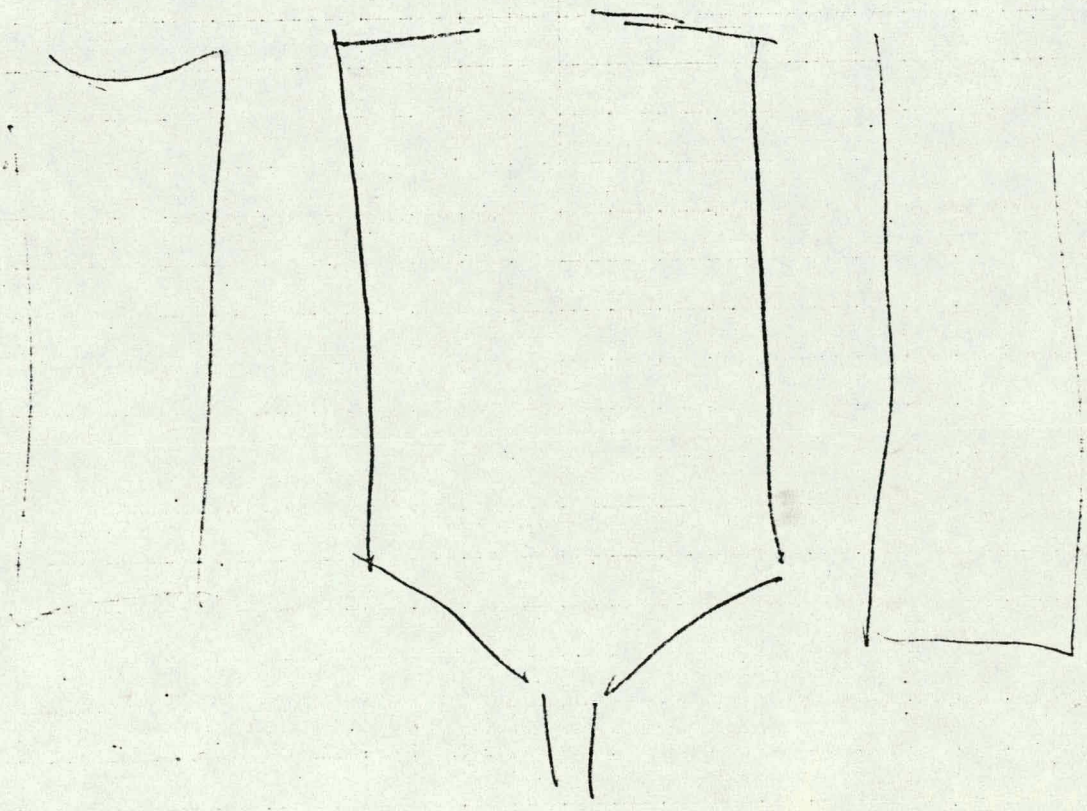


Fig 6

SCHEMATIC VIEW OF ELECTRODE-TYPE CERAMIC MELTER

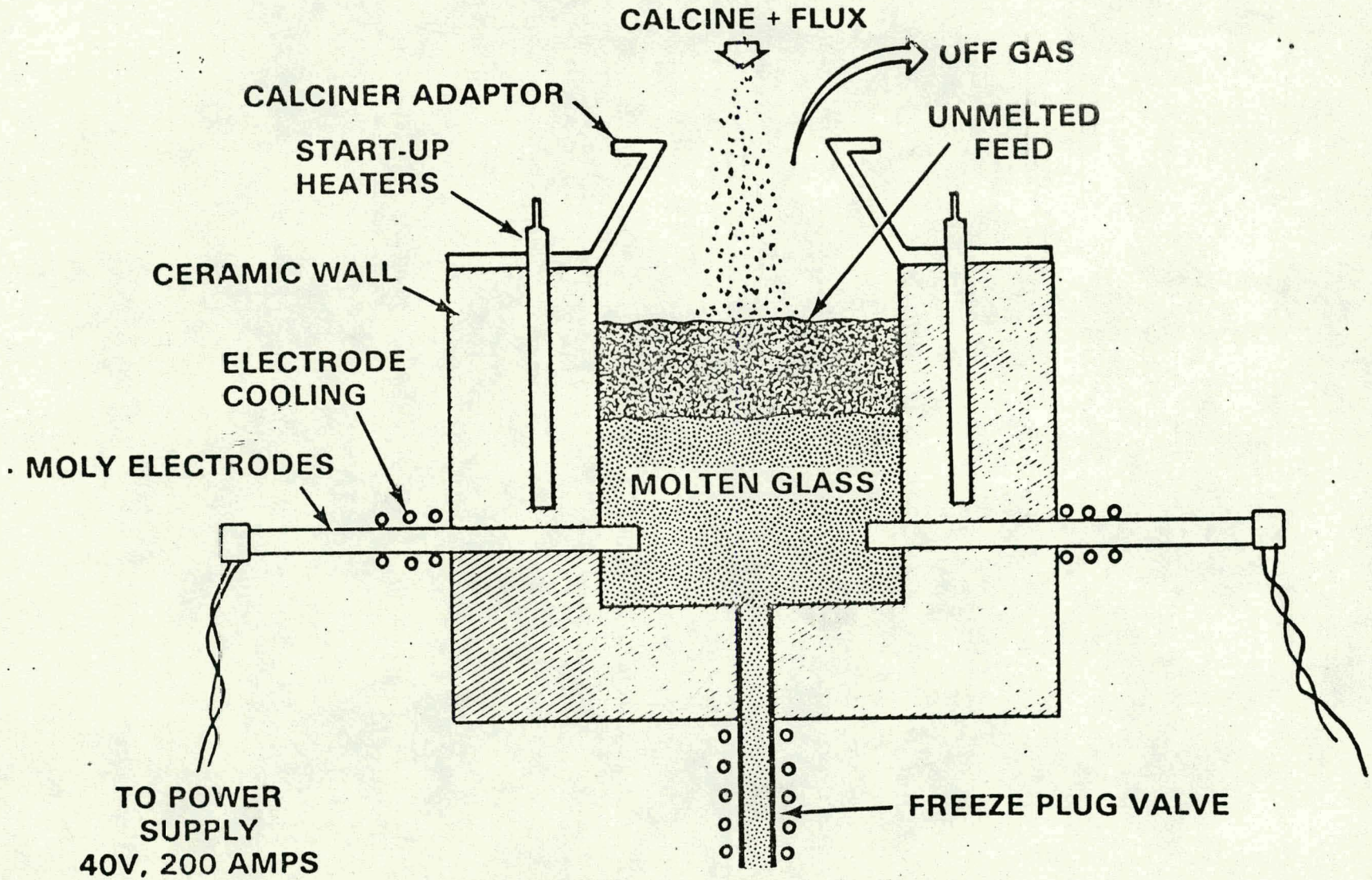


FIGURE 7

THE "RUSSIAN DOLL" CONCEPT

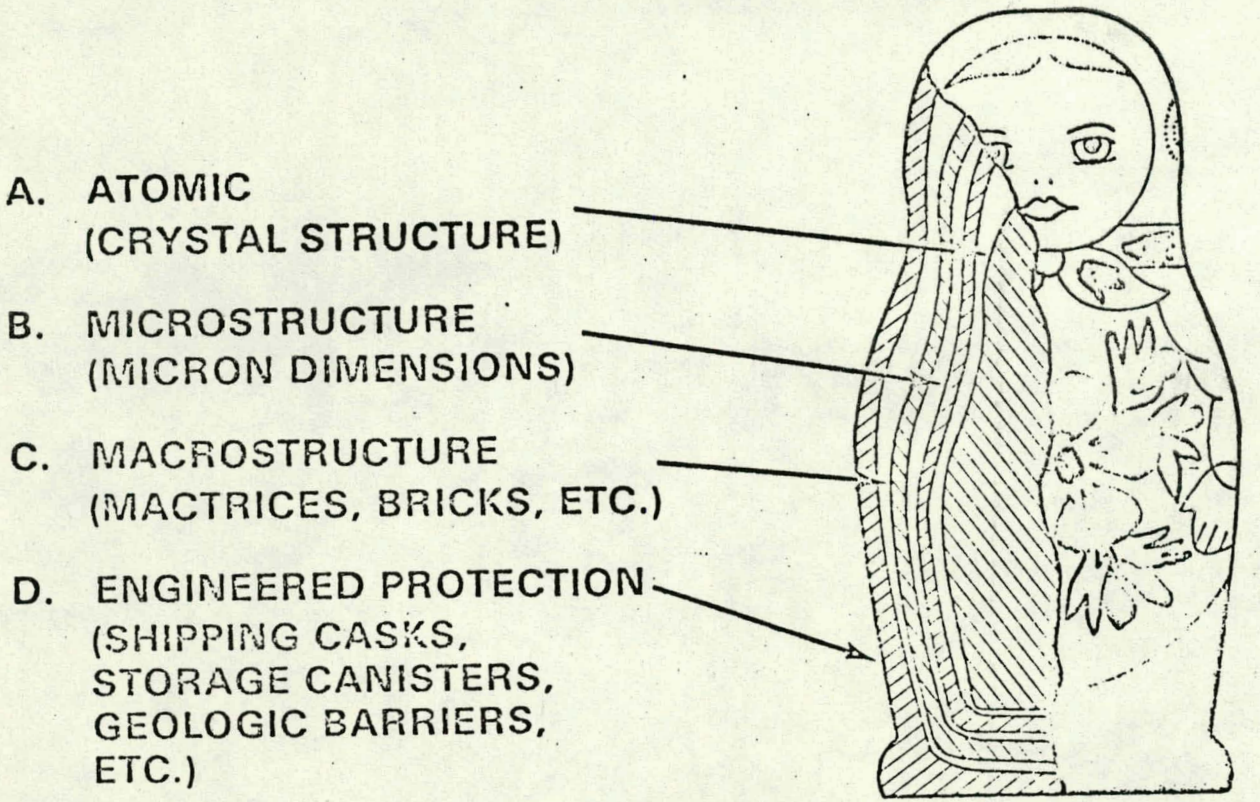


Figure 8

SURVEY OF POTENTIAL WASTE FORMS:
MORPHOLOGICAL BOX APPROACH

OPTIONS for each layer. / (layer) PARAMETERS	1	2	3	4	5	6
PRIMARY	GLASS	OXIDE CALCINE	CRYSTALLINE, MINERAL-LIKE	SORBED OR PHYSICALLY BOUND	CERMET	METAL
COATINGS AND FILMS	NONE	CARBON, SILICON CARBIDE	SURFACE TREATMENTS (LEACHING OR CATION EXCHANGE)	GLASS	METAL	OXIDE
MATRIX	NONE	CRYSTALLINE, MINERAL-LIKE	METAL	GLASS	GRAPHITE	CONCRETE
CANISTER	NONE	METAL	COATED METAL	CERAMIC	CONCRETE	GRAPHITE

☐ current concept - glass in a metal canister.