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VITRIFICATION OPTIONS:
Further discussion of my previous oral statement

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ABSTRACT:

Unresolved vitrification problems are reviewed. In spite of these potential problems, vitrification is seen to be a better method of long-term radioactive-waste containment than either shale fracturing or in-tank solidification. It is proposed that calcination be done at West Valley, but that vitrification be done elsewhere, mainly in order to reduce the volume of wastes to be transported. At best, this volume would be reduced by a factor of about 22; at worst, by a factor of about 5, compared to the volume to be transported according to the DOE vitrification option. Shipment of canisters of calcined wastes is shown to be feasible in terms of heat dissipation and radiation attenuation. For several reasons, including heat dissipation, it is proposed that the particles of calcined waste be temporarily "glued" together to form a relatively non-porous solid in each canister. Preferably, a material such as boric oxide glass or sodium silicate glass would be used as the binder, since neither of these materials would need to be removed when the calcined wastes were vitrified.

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Vitrification: Pro and Con

Vitrification, or incorporating the wastes into a glass, is presented in the DOE Study Report (1) as the best method for converting the West Valley high-level liquid wastes into a stable form for long-term protected storage. In all three vitrification options that are considered in the report (2), the radioactive substances from tanks 8D2 and 8D4 (along with some non-radioactive substances from both tanks) would be calcined to produce a dry radioactive powder. This calcined powder would be mixed at a high temperature with silica, boric oxide (3), and other glass-forming additives to produce a molten glass mixture that would gradually solidify as it cooled. The result would be a radioactive vitrified solid, that is, a type of borosilicate glass in which the radioactive atoms are bound into the molecular structure of the glass. The glass would be sealed into stainless steel canisters for long-term storage at a site assumed to be several thousand kilometers away (4).

Vitrification probably is the best method for assuring long-term containment of the radioactive wastes. In my opinion, at least, vitrification is the best option that is presently available, and I assume in this paper that the wastes can be and should be vitrified, although not necessarily at West Valley. Nevertheless, in spite of my preference for vitrification, I believe that there are some unanswered questions about the long-term integrity of vitrified wastes. Before proceeding, I will review some of these potential problems.

Pyrex-type borosilicate glasses, consisting almost entirely of boric oxide (B_2O_3) and silica (SiO_2), and true binary borosilicate glasses, consisting entirely of B_2O_3 and SiO_2, are known to be very stable. These types of glasses are highly resistant to leaching and devitrification (5). Thus, in discussing the ternary Na_2O-B_2O_3-SiO_2 system, Morey (6) states that "no mixtures on the side B_2O_3-SiO_2 could be crystallized", and Rockett and Foster (7) report similar conclusions from their work on the binary B_2O_3-SiO_2 system. Resistance to leaching is well-known for borosilicate glasses which contain a fairly high ratio of SiO_2 to B_2O_3.(8).

However, there are three things that should be borne in mind. First, vitrified radioactive wastes are not as similar to Pyrex-type borosilicate glass as is sometimes implied (9). The borosilicate (B_2O_3 + SiO_2) content of the radioactive glasses proposed by DOE would be only about 55% (10) instead of the 94% borosilicate content of typical Pyrex glasses. Second, although borosilicate and other glasses are usually considered to be homogeneous, it has been shown that they frequently consist of fine-scale two-phase mixtures, as will be discussed below. Third, radiation may cause gradual degradation of the glass, as will be discussed below.

The first of these three considerations does not require much further discussion, except to say that the known stability of Pyrex-type borosilicate glasses does not imply anything about the stability of a glass with a borosilicate content of only 55%.

The second consideration is the fine-scale two-phase structure of many glasses which is described, for example, by Doremus in his book, Glass Science (11). Chapter 4 of this book, "Phase Separation", describes the phenomenon and provides some interesting electron micrographs of phase separation in various glasses. Regarding the fine-scale phase separation of Pyrex borosilicate glass, Doremus states that "the matrix phase is rich in silica, and the borosilicate phase is separated at such a fine scale that it cannot be leached out, so that the glass shows a chemical durability approaching that of vitreous silica" (12). He also suggests that "it seems likely that there is little solubility of borate in silicate, as would be expected from the different structures of these amorphous oxides... Therefore, the silica-rich phases in sodium borosilicate glasses are also probably close to 100% silica" (13). The potential problem with phase separation is that it may decrease the leach resistance of a glass. According to Doremus (14),

> "...weathering and devitrification are faster the lower the silica content of a phase. Thus a glass separated into a silica-rich phase and another containing less silica might weather or devitrify more rapidly than a homogeneous glass. The resultant properties depend on the scale of the separation, since in some borosilicate glasses, as mentioned before, the very fine scale of phase separation leads to a more chemically resistant glass."

In a Pyrex-type borosilicate glass there is enough silica to provide this fine-scale structure, wherein the silica-rich matrix surrounds and thus protects the tiny "islands" of the other, more soluble phase. It remains to be seen whether the vitrified wastes contain enough silica to afford this protection, if phase separation occurs.

The third consideration is possible degradation of the glass, mainly due to radiation emitted by the radioactive components of the glass. A report written by An Ad Hoc Panel of Earth Scientists for the U.S. Environmental Protection Agency (15) raises questions about leaching and devitrification in the presence of alpha radiation and other conditions expected during long-term storage, and suggests that

> "...there is no evidence that incorporation into a glass will ensure resistance to significant leaching over time scales of a decade. We wish to make clear that this is an area in which experiments can be done. If carefully controlled, such studies should be able to answer the question reasonably well."

The same report (16) contains an interesting observation on the manner in which devitrification may occur:

> "The consequences of devitrification are the formation of one or more crystalline phases. Such processes commonly result in the formation of materials with simpler chemical compositions than the glass. The new phase excludes impurities. If the impurities include the class of nuclides that are the fission products or TRU's, then these will end up in intergranular boundary areas. Leaching of these would then be relatively easy, and the bulk of the original glass need not even go into solution, but could remain as relatively non-radioactive crystals."

Doremus (17) suggests that, in some cases at least, crystallization may be more likely to occur in silica-poor phases than in silica-rich phases:

> "Often phase separation gives one phase that is more easily crystallized than the bulk glass. For example, in a sodium borosilicate glass phase separation leads to one silica-rich phase and another sodium borosilicate phase containing less silica than the glass as a whole. This sodium borosilicate phase crystallizes during heat-treatment at relatively low temperatures..."

Regardless of which phase crystallizes, it seems likely that the glass will become less resistent to leaching. Another possibility is suggested in the recently released Battelle-Columbus report on West Valley (18):

> "Helium production from actinides in vitrified wastes could cause some problem in disruption of the microstructure of the glass. This might increase the leach rate of the glass..."

Disruption of the microstructure could be a major problem if the microstructure consists of a protective silica-rich matrix surrounding tiny "islands" of another, more soluble phase, which would presumably contain most of the radioactive components of the glass.

Nevertheless, it seems to me that these problems can be avoided if a suitable glass formulation is used. Vitrification technology appears to be fairly well developed at several glass-manufacturing companies and nuclear facilities, including Pacific Northwest Laboratories. The DOE report (19) states that, "since 1966, over 50 million curies of radioactive materials have been incorporated into glass at Pacific Northwest Laboratories (PNL) in a series of demonstrations." The glass formulation will depend, of course, on the types of wastes to be incorporated into the glass, and some further work will be required to develop a glass suited to the West Valley wastes (20).

In any case, it seems obvious that the leach resistance of vitrified wastes will be much better than the leach resistance of the radioactive cement mixes proposed by DOE for the other two major options in the report, Shale Fracturing and In-Tank Solidification (21). Thus, of the presently available options, vitrification seems to be the best choice. There are some indications that ceramic or glass-ceramic forms of radioactive waste solidification are better (i.e., more stable, in a thermodynamic sense) than vitrification, but these need much more development work before they can be relied on. In the meantime, clean-up work must be started at the West Valley site. The wastes cannot be left there indefinitely while the search continues for an "ideal" disposal method for nuclear wastes.

The Option of Calcining at West Valley, Vitrifying elsewhere

Unfortunately, the high price tag and the high radiation-exposure figure assigned to vitrification in the DOE report make it appear to be a prohibitively expensive and dangerous option. Note, however, that these high figures are based on a questionable assumption, namely, the assumption that the complete vitrification process will be carried out at the West Valley site. Not everyone makes this assumption. For example, it has been proposed that the calcination step might be done at West Valley and that the vitrification step might be done at Pacific Northwest Laboratories. The DOE report does not consider this possibility, even though it could make a significant reduction in costs and radiation exposure.

In DOE's breakdown of estimated vitrification costs (22) and estimated population exposure (23), the largest single items are associated with the transportation of the canisters of vitrified wastes. Transportation accounts for 40.7 million of the 130 million dollars estimated for the complete vitrification process (including removal of wastes from tanks, partial separation of wastes, calcination, vitrification, and transportation to storage site), and transportation accounts for 10 of the 14 man-rem estimated for the population exposure during this process. The costs and radiation doses are high because DOE is talking about transporting at least 224 canisters of vitrified wastes, each two feet in diameter and ten feet long (24).

For comparison, consider the fact that the calcined radioactive waste powder would fit into ten canisters of this size, if it were not mixed with the glass-forming additives and other non-radioactive substances that go into the glass. Thus, there could conceivably be a 22-fold reduction in the number of canisters that would be shipped. Transportation costs could conceivably be reduced from 40.7 million to perhaps 4 million dollars, and the radiation exposure to people living along the transportation route could conceivably be cut from 10 to 1 man-rem (25).

It may not be realistic to reduce the number of canisters from 224 down to ten. Nevertheless, it appears that the number can be brought down to somewhere between ten and forty canisters, if calcined powder is shipped out for vitrification elsewhere. Ten canisters is the approximate minimum, assuming that the calcined powder consists entirely of radioactive material, as shown in Table 1. If it is not

Table 1

APPROXIMATE INVENTORY OF RADIOACTIVE CALCINED POWDER DERIVED FROM BOTH TANKS (COMBINED)

Substance	Mass (kg)	Volume of solids only (ft^3)	Bulk volume of powder (ft^3)
ThO_2	17600	70	140
U_3O_8	6000	30	60
PuO_2	35	0.5	1
Fission products, actinides, etc.	5000	35	70
TOTALS	28635 kg	135.5 ft^3	271 ft^3

Thus, the total volume of radioactive calcined powder would be approximately 271 ft^3, assuming that the powder contains 50% voids, which is typical for a powdered material. Each DOE canister has a capacity of about 28 ft^3, so ten canisters would be needed to accommodate this powder. Quantities in the above table are based on the somewhat inconsistent data in <u>Companion Report</u>, pp. 3-24, 3-26, 3-28, 3-29, 4-23, C-1, C-2, C-3, and C-5.

Table 2

APPROXIMATE INVENTORY OF NON-RADIOACTIVE CALCINED POWDER DERIVED FROM TANKS 8D2 AND 8D4

Substance		Moles	Mass (kg)	Volume of solids only (ft^3)	Bulk volume of powder (ft^3)
Fe_2O_3	(in 8D2)	330000	52700	355	710
Cr_2O_3	" "	30000	4560	31	62
NiO	" "	25000	1870	9	18
Al_2O_3	" "	5500	560	5	10
AlF_3	" "	18000	1510	17	34
MnO_2 or MnO	" "	25000	1975	14	28
	TOTALS FOR 8D2		63175 kg	431 ft^3	862 ft^3
Fe_2O_3	(in 8D4)	20000	3190	22	44
Cr_2O_3	" "	5200	790	5	10
NiO	" "	5500	410	2	4
Al_2O_3	" "	8500	870	8	16
MnO_2 or MnO	" "	600	50	0.5	1
	TOTALS FOR 8D4		5310 kg	37.5 ft^3	75 ft^3
TOTALS FOR BOTH 8D2 AND 8D4			68485 kg	468.5 ft^3	937 ft^3

Quantities in the above table are based on the somewhat inconsistent data in <u>Companion Report</u>, pp. 3-20, 3-26, 3-28, and 3-29. The values in the table may be changed slightly if "residual nitrate and uncalcined materials" (p. 4-14) replace some of the fully-calcined oxides.

feasible to carry out a complete separation of the radioactive and non-radioactive compounds, then the number of canisters could be as high as 43. Table 2 lists the main non-radioactive substances that would be calcined, if they could not be separated from the radioactive substances. Even including all these non-radioactive wastes, the total volume of calcined powder would only be about 1200 ft^3, which is much less than the 6300 ft^3 of glass proposed in DOE's "best" vitrification option. Thus, at worst, shipping the calcined powder would require only 43 canisters, instead of the 224 required to ship the glass.

The extent of separation will depend on the amount of research and development that is done. According to the DOE report (26):

> "Ideally, in order to reduce subsequent storage and transportation costs, only the radioactive fractions would be vitrified; the inert salts that make up by far the greater bulk of the wastes would be solidified by a different process for less costly disposal. The sodium nitrate-nitrite in the tank 8D2 supernate is the chief inert constituent, and the supernate, which is a single-phase solution, is susceptible to separation into active and nonactive fractions; a considerable background of information is available on the separation procedure. The sludge, which is predominantly inert ferric hydroxide, presents a much more complex problem; the sludge could also be divided into inert and active fractions, but a considerable amount of research and development would be required to ensure a workable process."

Regardless of whether the compounds of iron, chromium, nickel, etc., are separated from the radioactive constituents of the sludge, I assume in accordance with the DOE report that the separation of the radioactive constituents from the sodium salts in the 8D2 supernate will be carried out prior to calcination. This separation procedure, employing ion-exchange columns (27), makes it possible to exclude the sodium salts from the calcination step. The Battelle-Columbus report refers to this separation procedure as a sort of afterthought (28), but the calcination and vitrification options proposed in

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the Battelle-Columbus report assume that the sodium salts will <u>not</u> be removed prior to calcination (29). Thus, that report suggests some unnecessarily large final volumes of wastes: 30,000 ft^3 of calcined powder, or 40,000 ft^3 of glass (30).

In summary, I propose calcining the 8D2 and 8D4 wastes at West Valley, after separating the sodium compounds from the 8D2 wastes, in essentially the same manner proposed in the DOE report. This will not be an easy task. I think that the DOE report underestimates or understates the difficulty of some parts of it, particularly the removal of the sludge from tank 8D2. Nevertheless, the task must be done as a prerequisite for any option that converts the wastes into a stable, leach-resistant form.

Calcination will produce a quantity of radioactive powder, perhaps as little as 270 ft^3, or perhaps as much as 1200 ft^3, depending on whether the non-radioactive substances in Table 2 are eliminated or included. I propose shipping this calcined powder elsewhere for vitrification, either to an established nuclear facility such as Pacific Northwest Laboratories which is already equipped for vitrification, or to a possible vitrification facility adjacent to a repository site. The main reason for this proposal is to reduce the number of canisters that would be shipped. Another feature of the proposal is that vitrification could be carried out several years later than calcination. The calcination process could be done in the near future, perhaps within five years, so that the liquid wastes at West Valley would be converted into a semi-stable form. The vitrification process could be deferred for as much as a decade or two, until all doubts about vitrification are cleared up, or - possibly - until ceramic or glass-ceramic technology is shown to be superior to vitrification.

Heat Dissipation in Canisters of Calcined Powder

An important consideration is the amount of heat generated by radioactive decay in each canister of calcined powder. Since the total heat generation rate of the 8D2 and 8D4 wastes is in the neighborhood of 450,000 BTU/hr (31), the heat output per canister will range from about 10,000 to about 45,000 BTU/hr, depending on how many canisters are used. Thus, the heat output of each canister would be very roughly comparable to the winter heating requirements of a house in Western New York.

The powdered material in the canisters will not be a very good conductor of heat, due to the air spaces between the particles. Many powdered or granular materials consist of about 50% air (by volume), and I assume that this would also be the case with the calcined powder in the canisters. Consequently, the calcined powder in the canisters will be generating a lot of heat and, at the same time, it will be a good thermal insulator. This will cause the centers of the canisters to heat up to too high a temperature, unless the spaces between the particles are filled with something that is a better heat conductor than air is.

There are a number of materials that could be used for this purpose. Besides having good thermal conductivity, such a material should also act as a binder, to help hold the particles together in case the canister broke open in an accident; it should have a fairly low vapor pressure; it should be a material that can be combined fairly easily with the powder, at a fairly low temperature; and it should be removable prior to vitrification, unless it can actually be incorporated into the glass.

Two of the most likely candidates for this purpose are materials that would be incorporated into the glass: either boric oxide (B_2O_3) or a sodium silicate mixture ($Na_2O + SiO_2$). Both of these materials are glasses themselves, but since they melt or soften at lower temperatures than ordinary glasses, and since they will gradually dissolve in water, they would not be suitable for long-term containment of the wastes. However, as a temporary matrix for the calcined powder, either boric oxide glass or sodium silicate glass should work well. Each of these glasses is described in more detail in a following section of this paper.

Thermal conductivities of some of the calcined powders and of the proposed glass matrix materials are shown in Figure 1. Note that these will determine the overall conductivity of the powder-in-glass composite in the canisters. For the sake of illustration, I will assume 0.002 cal/(sec-cm-°C) for the overall thermal conductivity; this is a rather conservative estimate.

If the rate of heat generation and the thermal conductivity are both uniform throughout the canister, and if heat flow is strictly radial, then the temperature difference ΔT between the center and the wall of the canister can be expressed as

$$\Delta T = \frac{\dot{q} r^2}{4k} \qquad \text{(Eq. 1)}$$

where $\dot{q}$ is the heat generation rate per unit volume; r is the canister radius; and k is the thermal conductivity, here assumed to be about 0.002 cal/(sec-cm-°C). Alternatively, Equation 1 can be rewritten as

$$\Delta T = \frac{\dot{Q}}{4\pi h k} \qquad \text{(Eq. 2)}$$

where $\dot{Q}$ is the total heat generation rate within the canister and h is the length or height of the canister. 655 259

Equation 2 indicates that ΔT is proportional to $\dot{Q}/h$, the rate of heat generation per unit length of canister, but is independent of the canister radius r (32). This relationship is shown in Table 3, where the wastes are considered to be divided among ten, twenty, or forty canisters. The calculated values of ΔT are 418°C, 209°C, and 104°C, respectively. The first of these values seems unacceptably high, implying that either the thermal conductivity or the number of canisters must be increased. The second value (ΔT = 209°C) would probably be acceptable. The third value (ΔT = 104°C) seems quite satisfactory.

While the boric oxide glass or sodium silicate glass would be expected to fill most of the space between the particles of calcined powder, there still might be some porosity in the powder-in-glass

Table 3

DIVISION OF WASTES AMONG 10, 20, OR 40 CANISTERS, DEPENDING ON HOW MUCH NON-RADIOACTIVE MATERIAL IS CALCINED

Number of canisters used	$\dot{Q}$ (BTU/hr)	$\dot{Q}$ (cal/sec)	h (cm)	k (cal/(sec-cm-°C))	ΔT (°C)
10	45,000	3149	300	0.002	418
20	22,500	1575	300	0.002	209
40	11,250	787	300	0.002	104

$\dot{Q}$, the heat generation rate per canister, is equal to 450,000 BTU/hr divided by the number of canisters used. The canister length h is 3 meters or 300 cm, as specified by DOE. The thermal conductivity k is assumed, as explained in text. The temperature difference ΔT between canister center and canister wall is calculated from Equation 2.

mixture in the canisters. The reduction in thermal conductivity due to porosity has been investigated by Loeb (33) and Francl and Kingery (34) who find that, for isotropic porosity,

$$k_p = k_s(1 - P_v) \qquad \text{(Eq. 3)}$$

where k_s is the thermal conductivity of a solid or nonporous piece of a given material; k_p is the thermal conductivity of a porous piece of the same material; and P_v is the volume pore fraction of the porous piece. Since the porosity would probably not exceed 10% by volume ($P_v = 0.1$), the thermal conductivity should not be greatly affected.

Radiation of thermal energy from the outside surface of each canister should be an adequate method of heat rejection, as long as each canister is kept away from other hot surfaces (including other canisters) that would radiate thermal energy back toward the canister. Assuming that each canister has a radius of 30 cm, a length of 300 cm, and an emissivity of 0.8, the rate of thermal radiation from the outside surface of each canister (excluding both ends) would be about 16,900 BTU/hr or 1185 cal/sec at a surface temperature of 100°C, or about 28,000 BTU/hr or 1960 cal/sec at 150°C, or about 43,800 BTU/hr or 3065 cal/sec at 200°C. These values, in combination with the values in Table 3, suggest that the number of canisters could be anywhere between twenty and forty. If twenty canisters were used, the surface of each canister could radiate enough heat to stay below 150°C, so that the temperature at the center of the canister could stay below 350°C. If forty canisters were used, the surface of each canister could radiate enough heat to stay below 100°C, so that the temperature at the center could remain below 200°C.

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Radioactivity of Canisters of Calcined Powder

While I have no background in radiological measurement and protection, I will attempt to show that the transportation of the twenty to forty canisters of calcined powder (in boric oxide or sodium silicate matrix) poses no unusual radiological hazard. It appears from the published literature that a comparison can be made with the transportation of spent fuel elements, and that the radioactivity of each of the proposed canisters of calcined powder is less than the radioactivity of 1 MTU spent fuel. Since 1 MTU is typical of the quantity of spent fuel shipped in a truck cask, it appears that a similar cask would provide adequate shielding for a canister of calcined powder.

According to Fitzgerald (35), each pressurized water reactor (PWR) fuel element contains approximately 0.5 MTU (metric tons of uranium), while each boiling water reactor (BWR) fuel element contains approximately 0.25 MTU. Until commercial reprocessing ceased in this country with the shut-down of the West Valley plant, the usual practice was to hold each fuel element at the reactor site for about 150 days after removal from the reactor, before shipping it to be reprocessed. The spent fuel elements, still highly radioactive, were shipped in casks designed to cut the radiation down to acceptable levels (e.g., no more than 10 mrem/hr at six feet from the vehicle surface, as is also assumed in the DOE report).

Fitzgerald (36) also states that

> "Casks containing spent fuel may be shipped in trucks, railroad cars, and on barges. A truck cask may be designed to carry 1 to 3 PWR fuel elements and from 2 to 7 BWR elements. A truck-cask will be cylindrical in shape, approximately 5 ft in diameter and 17 ft long. Such a cask may weigh up to 35 MT. A railroad-cask is similar in shape but bigger and may weigh from 70 to 100 MT. The railroad-cask may be designed to carry up to 7 PWR or up to 18 BWR elements."

The casks proposed in the DOE report for transporting the 224 canisters of vitrified wastes would weigh 27 MT loaded (37), and are thus apparently truck casks, even though shipment by rail was assumed by DOE for the vitrified wastes (38).

In any case, the information given above implies that a truck cask typically contains about 1 MTU of spent fuel, while a railroad cask would carry more. Table 4 shows the approximate levels of radioactivity for 1 MTU spent fuel after 150 days cooling, and also for one of the proposed canisters of calcined powder, assuming that the calcined powder is divided among either 20 or 40 canisters. The comparison should be regarded as approximate, since the distribution of radioactivity for the calcined powder would be similar but not identical to the distribution of radioactivity for the spent fuel elements. Even leaving some room for this uncertainty, it appears from Table 4 that each canister of calcined powder would be less radioactive than 1 MTU spent fuel and could thus be shipped in a typical truck cask. If more shielding were needed, a railroad cask could be used.

The rate at which heat is generated by radioactive decay in 1 MTU spent fuel after 150 days cooling is about 20 kw or about 68,500 BTU/hr (39). Since the heat generation rate in a canister of calcined powder would be less than this - i.e., about 10,000 to 45,000 BTU/hr, as described previously - there should be no unusual heat-dissipation problem during shipment in a truck cask.

Table 4

RADIOACTIVITY OF SPENT FUEL ELEMENTS COMPARED TO CANISTERS OF CALCINED POWDER

1 MTU of spent fuel after 150 days cooling:

Fission products	4.39×10^6 curies
Actinides	1.36×10^5 curies
TOTAL	4.53×10^6 curies

One canister of calcined powder, assuming that 20 canisters are used:

Fission products	2.1×10^6 curies
Actinides	4.3×10^3 curies
TOTAL	2.1×10^6 curies

One canister of calcined powder, assuming that 40 canisters are used:

Fission products	1.0×10^6 curies
Actinides	2.1×10^3 curies
TOTAL	1.0×10^6 curies

Figures for spent fuel after 150 days cooling are from Fitzgerald, op. cit., p. 222, Table 5B.11. A similar figure for total radioactivity per MTU after 150 days cooling is given in Companion Report, p. 5-4. Figures for calcined powder are based on the somewhat inconsistent data in Companion Report, pp. 3-22, 3-23, 3-24, 3-28, 3-29, and 3-62, and in the Battelle-Columbus report, op. cit., pp. 19 and 20. Total radioactivity of fission products from tanks 8D2 and 8D4 is taken to be 4.1×10^7 curies; this is divided by the number of canisters used. Total radioactivity of actinides from tanks 8D2 and 8D4 is taken to be 8.5×10^4 curies; this is divided by the number of canisters used.

Calcined Powder in Boric Oxide Matrix

Boric oxide (B_2O_3) glass is one of the matrix materials that I propose mixing with the calcined radioactive waste powder, in order to form a temporary solid mass in each canister. This glass melts or softens at a relatively low temperature and will gradually dissolve in water. Boric oxide has a high affinity for water, and a small amount of water will tend to remain as an essentially stable constituent of the glass, unless the glass is held at a high temperature for an extended period to drive off this residual water (40).

I propose mixing the calcined waste powder into the molten glass, at as low a temperature as possible, which would probably be about 600°C. The viscosity-temperature curve for boric oxide glass is shown in Figure 2. The proposed mixing or kneading process could be tested with a non-radioactive calcined powder to determine its feasibility. Such a mixing process will not be easy, but with proper design may be feasible. It would be roughly comparable to the problem of mixing a powdered material (such as talcum powder) into a fluid whose viscosity is like cold honey, but whose temperature is verging on visible red heat, without mixing in too many air bubbles. Higher temperatures would make mixing easier by reducing the viscosity of the boric oxide, but would increase the required operating temperature of the mixing equipment and might also increase the volatilization of some of the radioactive substances. For comparison, calcination temperatures are in the neighborhood of 500°C, while vitrification temperatures are in the neighborhood of 1100°C (41).

It may be possible to add small amounts of some other material to the boric oxide to reduce its viscosity. Various "fluxes" are commonly added to silica for this purpose, in the manufacturing of

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silicate glasses, but it is not clear whether this technique can significantly reduce the viscosity of boric oxide in the vicinity of 600°C. Speaking of various simple oxide glasses such as silica, boric oxide, and germania, Doremus (42) states that:

> "The viscosities of the simple oxides decrease sharply with the addition of most impurity ions. Such impurities as water, in the form of -OH groups, and alkali oxides are particularly effective in lowering the viscosities.... The addition of 0.165 mole % Na_2O to germania lowers the viscosity about a factor of 46 at 1000°C... The addition of other oxides to silica invariably lowers its viscosity.... The viscosity of B_2O_3 also decreases when other oxides are added, but much less than for SiO_2. This result is expected because of the lower viscosity of B_2O_3, resulting from some weaker bonds already present in the pure oxide. A summary of viscosities and other properties of borate melts is given by Mackenzie."

Mackenzie (43) in turn indicates that, at 600°C, the addition of various other oxides will not reduce the viscosity of boric oxide by more than a factor of about 2. At higher temperatures, the viscosity reduction is somewhat greater. Residual water in boric oxide glass may reduce the viscosity by a factor of two or more, perhaps up to a factor of about six, according to Boow (44) and others (45). It does not appear, however, that the viscosity can be reduced much more than this. A ten-fold or hundred-fold reduction, if it could be achieved, would greatly facilitate mixing.

It is possible that mixing could be done, albeit rather slowly, by simple gravitational settling of the relatively dense calcined powder into the less dense molten boric oxide. This could easily be determined with non-radioactive powders.

Up to now, it has been assumed that the calcined radioactive waste powder and the boric oxide glass would each occupy 50% of the volume of each canister, with the glass filling the spaces between the particles of powder. It may be more practical to increase the ratio of glass to calcined powder, especially if gravitational settling is used for mixing. Thus, each canister might be enlarged slightly, from 2 feet to 2.5 feet diameter, so that it could accommodate 30% calcined powder and 70% boric oxide glass, by volume. By weight, each of these canisters would contain roughly 2280 kg (57%) calcined powder and roughly 1720 kg (43%) boric oxide glass, for a total net weight of about 4000 kg. This enlargement of the canister diameter should not have any significant effect on heat dissipation (see Table 3 and Equation 2) except insofar as the greater proportion of boric oxide glass reduces the overall thermal conductivity. The DOE vitrification formula (46) calls for roughly equal weights of calcined powder and boric oxide in the final glass; thus, the proposed amount of boric oxide glass in each canister would not be too much for the vitrification process.

Some of the radioactive and non-radioactive materials in the calcined powder may dissolve to some extent in molten boric oxide, which might affect the viscosity. At 1200°C, Foëx (47) reports that Cs_2O is soluble in all proportions with B_2O_3, and that some of the other oxides present in the calcined powder have the following solubilities <u>per 100 moles of boric oxide</u>: 1.80 moles SrO, 1.60 moles CoO, 1.58 moles MnO, 1.55 moles NiO, 0.80 mole Cr_2O_3, 0.72 mole Al_2O_3, and 0.15 mole ThO_2. At the temperature of about 600°C under consideration here, the solubilities may be lower. In any case, most of the calcined powder would not be dissolved, but would remain as individual particles.

The powder-in-glass mixture would either be mixed directly in a stainless-steel canister or be put into the canister while still molten; it would then be cooled and sealed into the canister. For vitrification, the canister would be reopened and the powder-in-glass mixture remelted. The remelted mixture would be mixed with SiO_2, Na_2O, and perhaps some extra B_2O_3, in order to form the final glass.

Calcined Powder in Sodium Silicate Matrix

A sodium silicate glass (sometimes known as "water glass") could be used instead of boric oxide glass as a matrix material for the calcined powder. Sodium silicate glasses, consisting of Na_2O and SiO_2 in various proportions, resemble boric oxide glass in their low melting or softening point, their gradual solubility in water, and their high affinity for water.

Anhydrous sodium silicate glasses typically consist of 50% to 90% SiO_2, with the remainder being Na_2O. Viscosity-temperature curves for representative sodium silicate glasses are shown in Figure 2. The composition of the glass is frequently expressed as the ratio of SiO_2 to Na_2O by weight (48), so that a 2.0:1 ratio anhydrous glass consists of 66.7% SiO_2 and 33.3% Na_2O.

Sodium silicates are used in industry as water-based adhesives, and they are sold on a commercial scale as aqueous solutions containing various proportions of SiO_2, Na_2O, and H_2O. Viscosities of these solutions range from about 1 poise to 700 poises and upward. These and other properties of sodium silicates are reviewed in two papers by Wills (49,50) that deal both with the aqueous adhesive solutions and with the partially or fully dried sodium silicate glasses obtained as the solutions dry and harden. Wills (51) describes the transition from sodium silicate solution to anhydrous glass in this manner:

> "A soluble silicate film having a viscosity as low as 50 centipoises initially, dries to a hard vitreous film which does not readily dissolve but will continue to hold some moisture until heated to about 1000°F (550°C), which means that the adhesive bond will have some resiliency and be less brittle than the anhydrous glass. Figure 1 shows that at ordinary humidities the silicate bond may contain as much as 40% water; in fact, even at only 10% relative humidity it will have approximately 20% water.... The most nearly insoluble silicate bonds are obtained by drying at temperatures sufficiently high to remove all of the water. They have the characteristics of glasses.... In drying a sodium

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silicate film in air, about 15 to 20% of water will ordinarily remain. Baking at 100°C will leave approximately 1 to 10% water. Complete dehydration requires heating to 550°C."

I propose mixing the calcined waste powder into an aqueous solution of sodium silicate, then drying to remove most or all of the water (§2). The process might have to be done gradually, in layers, to avoid problems due to the shrinking of the silicate as it dries. Thus, a slurry of calcined powder in sodium silicate solution might be made up, and thin layers of the slurry might be added and dried, added and dried, etc., in each canister. Alternatively, if a canister were made to rotate on a horizontal axis (more or less like a ball-mill jar), and if small quantities of slurry were added periodically, it might be found that the slurry would dry and harden in a gradually increasing layer on the inside of the canister. The outside of the canister might be insulated in order to utilize the self-heating properties of the radioactive calcined powder during this accumulation process. Alternatively, a gradually increasing layer might be built up on the inside of the canister if the slurry were sprayed into the canister.

It would probably be feasible to obtain 50% calcined powder and 50% sodium silicate (by volume) in the canisters, after drying and hardening of the slurry. Thus, if a 2.0:1 ratio sodium silicate were used, and if a two-foot-diameter canister were used, the canister would contain approximately 2275 kg (70% by weight) calcined powder, 650 kg (20%) SiO_2, and 325 kg (10%) Na_2O, for a total net weight of about 3250 kg.

If the powder-in-glass mixture is built up in layers, it might be annealed before the canister is sealed. The canister would later be reopened for vitrification, and the powder-in-glass mixture would be melted. Boric oxide would be added, along with additional SiO_2 and Na_2O, in order to form the final glass.

Sintering of Calcined Powder

Sintering of the calcined powder would probably be easier than creating a glass matrix from either molten boric oxide or a sodium silicate solution. The main question is whether the calcined powder can be sintered to form a solid mass of low enough porosity. If the porosity is too high, heat dissipation will be a problem.

I propose using either anhydrous boric oxide glass or anhydrous sodium silicate glass as a binder, so that the sintering could be done at or near the softening temperature of the glass - i.e., roughly 500°C. By volume, the resulting sintered mass in each canister might consist of something like 30% glass, 60% calcined powder, and 10% voids.

The first step in the sintering process would be to prepare a mixture of properly-sized particles of anhydrous glass and calcined powder. The importance of the particle size distribution and its effect on porosity of the sintered mass are reviewed by Ryshkewitch (53). It might be advantageous to add a small amount (perhaps 1% by weight) of a fumed silica product such as "Cab-O-Sil" to the mixture of glass particles and calcined powder particles.

This mixture of particles would be put into the canisters, where it would be heated and pressed to sinter it. While heat could be supplied from some external source, it would probably be even easier to insulate the outside of the canister in order to use the internally-generated heat from radioactive decay. The powder mixture should be pressed or tamped before sintering; it might or might not need to be pressed during the heating cycle.

It might be advisable to monitor the thermal conductivity of each canister for a short period before sealing it, using thermocouples positioned at the center and against the wall of the canister. After it was sealed, the canister would be ready for shipment. Each canister would subsequently be reopened for the vitrification process, and its contents would be removed by heating it to soften the boric oxide or sodium silicate glass binder holding the calcined powder particles together. The remaining quantities of glass-forming additives would be mixed in then, in order to form the final glass.

Figure 1

THERMAL CONDUCTIVITIES

References: (54)

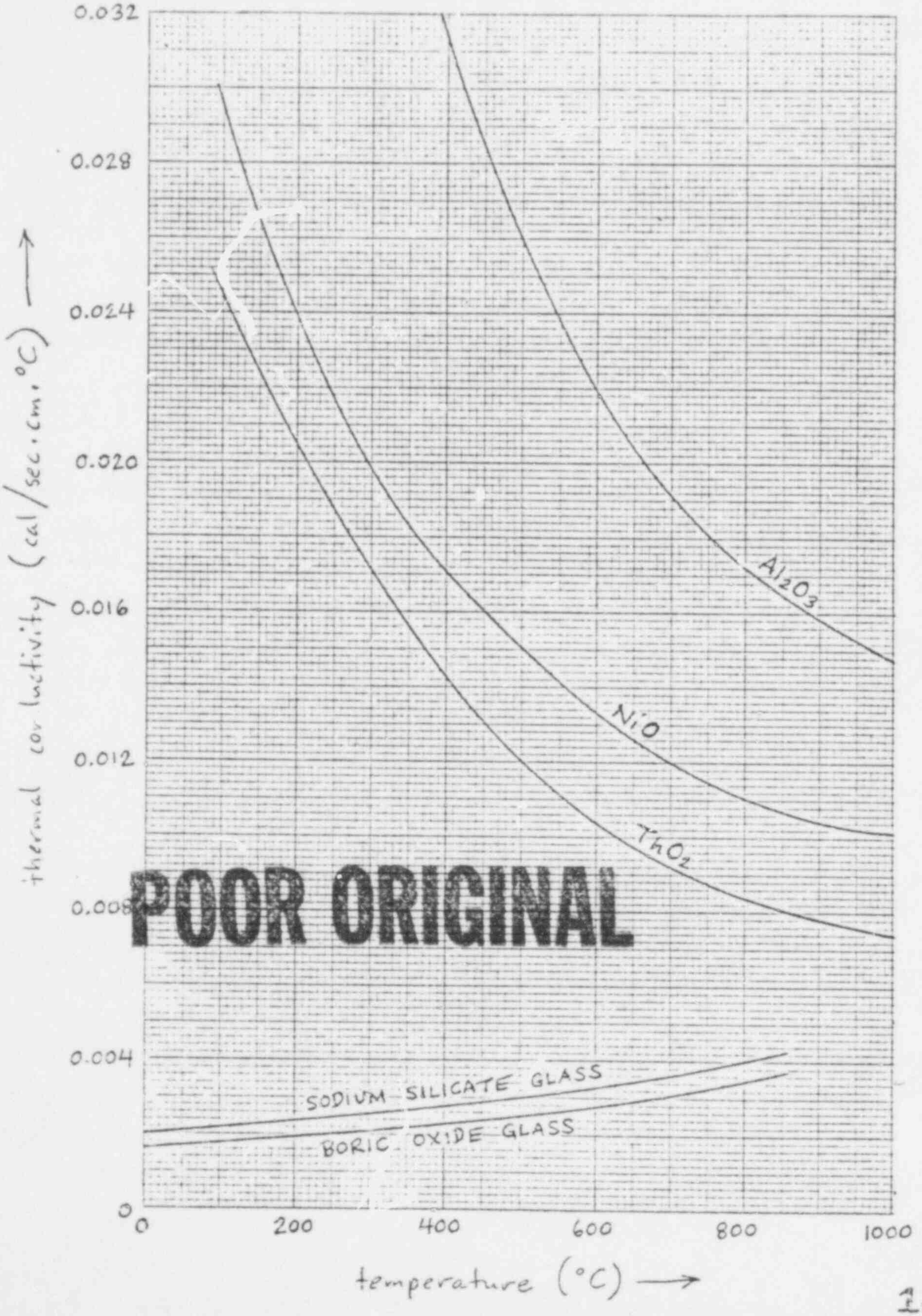
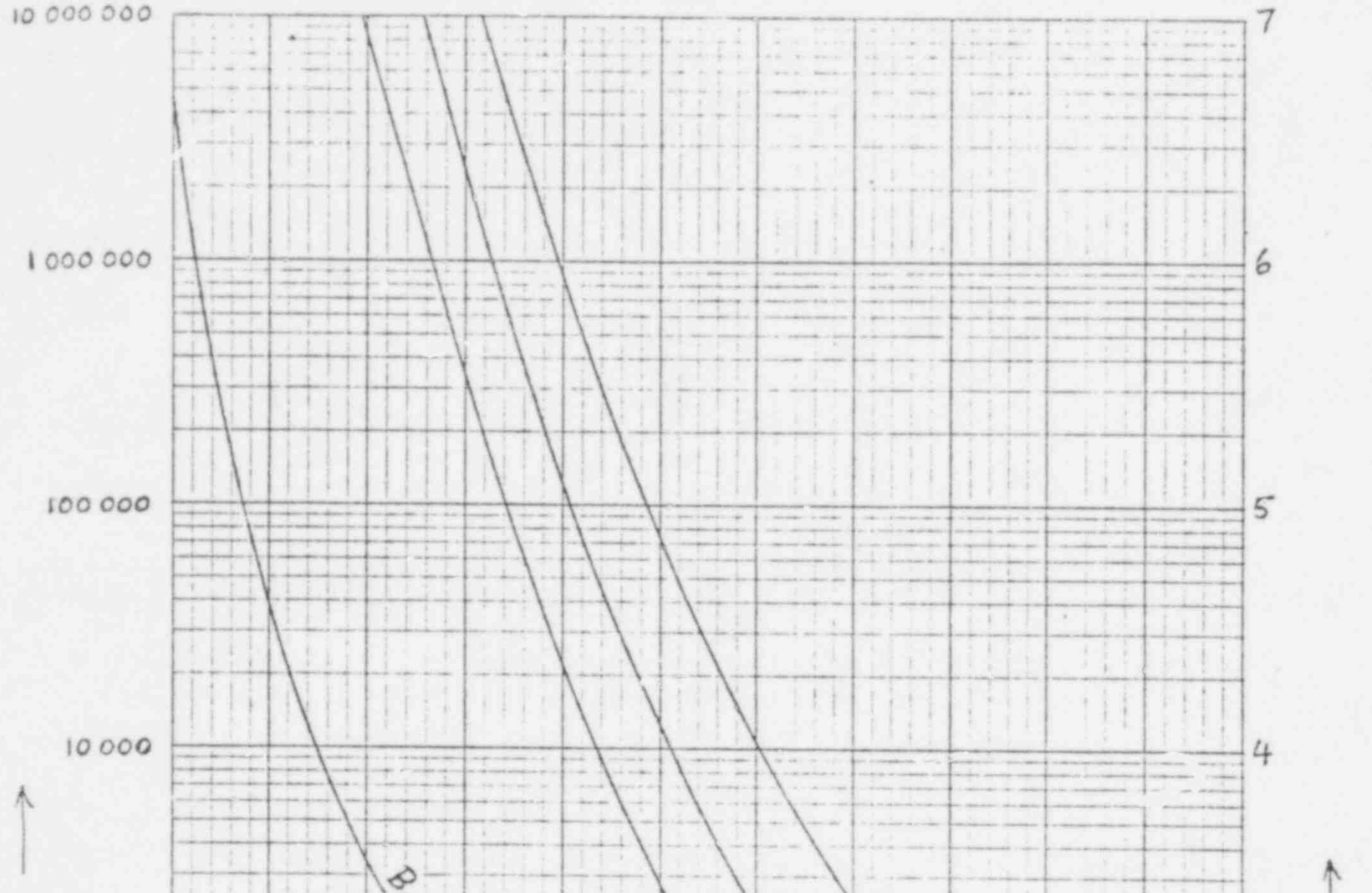


Figure 2

VISCOSITIES OF BORIC OXIDE
AND SODIUM SILICATE GLASSES

References: (55)



Notes and References

1. Actually two reports: Western New York Nuclear Service Center Study: Final Report for Public Comment, U.S. Department of Energy, November 1978, TID-28905-1, and Western New York Nuclear Service Center Study: Companion Report, U.S. Department of Energy, n.d., TID-28905-2.

2. See Final Report for Public Comment, p. 19, and Companion Report, pp. 4-15 through 4-29 and Appendix C.

3. May be added as boric acid or as borax.

4. Presumably, the long-term storage site or repository will be in an area that has a very low population density and a very dry climate. For the purpose of estimating costs and radiological doses associated with transportation, DOE assumed that the distance to the repository would be 4800 km (Companion Report, p. 4-27) or 3000 miles (Final Report for Public Comment, p. 19).

5. Devitrification refers to the tendency of glasses to change, under certain circumstances, from their normal state (glassy, vitreous, amorphous) to a crystalline state. A crude analogy can be made to the tendency of honey to crystallize.

6. G.W. Morey, The Properties of Glass, 2nd edition, ACS Monograph Series/Reinhold Publishing, New York, 1954, p. 56.

7. T.J. Rockett and W.R. Foster, "Phase Relations in the System Boric Oxide-Silica", Journal of the American Ceramic Society, vol. 48 (1965), pp. 75-80.

8. The molar ratio of SiO_2 to B_2O_3 must be approximately 4:1, or greater, to assure leach-resistance, according to L.G. Van Uitert, D.A. Pinnow, et al., "Borosilicate Glasses for Fiber Optical Waveguides", Materials Research Bulletin, vol. 8 (1973), pp. 473-74.

9. For example, in Final Report for Public Comment, p. 19.

10. Companion Report, pp. 4-23, C-2, C-3, and C-5, where Tables 4.3. and C.1. both indicate 57.3% borosilicate content, Table C.2. shows 35% to 55% borosilicate, and Table C.3. shows either 52.1% or 50.0%.

11. R.H. Doremus, Glass Science, Wiley, New York, 1973, pp. 44-73.

12. Ibid., p. 44.

13. Ibid., p. 51.

14. Ibid., p. 49.

15. Ad Hoc Panel of Earth Scientists (B. Giletti, R. Siever, J. Handin, J. Lyons, and G. Pinder), State of Geological Knowledge Regarding Potential Transport of High-Level Radioactive Waste From Deep Continental Repositories, U.S. Environmental Protection Agency, EPA/520/4-78-004, pp. 6-8.

16. Ibid., p. 7.

17. Doremus, op. cit., p. 78.

18. Battelle-Columbus report, p. 132. This report was written by several authors headed by F.A. O'Hara and is entitled Preliminary Environmental Implications of Alternatives for Decommissioning and Future Use of the Western New York Nuclear Services Center, Battelle Columbus Laboratories, December 1978, BMI-X698.

19. Final Report for Public Comment, p. 19.

20. The glass must be compatible with the radioactive substances summarized in Table 1. The substances in Table 2 may or may not be included in the glass, depending on how much separation is done. The sodium salts from tank 8D2 would not be included in the glass; they would be removed prior to calcination.

21. In-Tank Solidification is described in Final Report for Public Comment, p. 18, and Companion Report, pp. 4-29 through 4-35. By contrast, twenty pages are devoted to Shale Fracturing in Companion Report (pp. 4-35 through 4-55), but no description of this option is given in Final Report for Public Comment. Isn't the public supposed to comment on Shale Fracturing?

22. Companion Report, p. 4-28.

23. Ibid., p. 4-27.

24. Final Report for Public Comment, p. 19. Metric dimensions for the canisters are given as 0.6 meter diameter and 3 meters length or height, in Companion Report, pp. 4-18 and 4-24.

25. I am assuming that a 22-fold reduction in the number of canisters shipped could cut transportation costs and radiation exposure by a factor of about 10. This is generally consistent with DOE's estimating methods for costs and radiological doses (Companion Report, pp. 4-2 through 4-5; 4-27; 4-28). It may seem odd that radiation exposure to people living along the transportation route depends on the number of canisters shipped, not on the quantity of radioactive material shipped. Nevertheless, this is a built-in feature of the DOE estimating method,

as long as radiation from the vehicle surface does not climb above the regulatory limit of 10 mrem/hr at six feet. "The problem with this approach is that it is totally dependent on the number of shipments," according to the Battelle-Columbus report, op. cit., p. 155.

26. Companion Report, p. 4-15.

27. Ibid., pp. 4-15 through 4-21.

28. Battelle-Columbus report, op. cit., p. 140 ("...it is possible to vitrify only the sludge, or only the sludge and the eluate from the supernate stripping process...") and p. 192 ("...the feasibility of stripping the radionuclides from the supernatant.").

29. Ibid., pp. 138-141, 166-168, and 192-193.

30. Ibid., pp. 139 and 141. The quantity of glass is given as three thousand canisters of 100-gallon capacity, which is equivalent to 40,000 ft^3. One paragraph on p. 140 acknowledges that elimination of the sodium compounds could reduce the volume of glass to 7000 ft^3, which is close to the DOE estimate of 6300 ft^3. The quantity of calcined powder is given as "30,000 ft^{13}", which is apparently a misprint for 30,000 ft^3. No mention is made of the much smaller volume of calcined powder (about 1200 ft^3) that would be obtained if the sodium compounds were eliminated. See also Table 4-1 on p. 144.

31. Companion Report, p. 4-29.

32. Equation 2 is based on the assumptions that heat flow is strictly radial and that heat generation and thermal conductivity are both uniform throughout the canister. In reality, these assumptions may not quite be met, so that r may affect ΔT slightly.

33. A.L. Loeb, "Thermal Conductivity: VIII, A Theory of Thermal Conductivity of Porous Materials", *Journal of the American Ceramic Society*, vol. 37 (1954), pp. 96-99.

34. J. Francl and W.D. Kingery, "Thermal Conductivity: IX, Experimental Investigation of Effect of Porosity on Thermal Conductivity", *Journal of the American Ceramic Society*, vol. 37 (1954), pp. 99-107.

35. J.J. Fitzgerald, "Large Radiological Sourhes and Safeguards", in N.I. Sax et al., *Dangerous Properties of Industrial Materials*, 4th edition, Van Nostrand Reinhold, New York, 1975, pp. 221-22.

36. Ibid., p. 222.

37. *Companion Report*, p. 4-25.

38. Ibid., p. 4-2.

39. Fitzgerald, op. cit., p. 223, Table 53.13, and *Companion Report*, p. 5-4.

40. See, for example, J. Boow, "The Viscosity of Fused Boric Oxide", *Physics and Chemistry of Glasses*, vol. 8 (1967), pp. 45-55.

41. Battelle-Columbus report, op. cit., pp. 139 and 141, and *Final Report for Public Comment*, p. 19.

42. Doremus, op. cit., pp. 108-109.

43. J.D. Mackenzie, "Structure of Some Inorganic Glasses from High Temperature Studies", in *Modern Aspects of the Vitreous State*, edited by J.D. Mackenzie; Butterworths, London, 1960, pp. 210-11, including Figures 13 and 14.

44. Boow, op. cit.

45. See, for example, R.A. Eppler, "Viscosity of Molten B_2O_3", *Journal of the American Ceramic Society*, vol. 49 (1966), pp. 679-80.

46. *Companion Report*, p. 4-23.

47. M. Foëx, "Solubilité des oxydes dans l'anhydride borique fondu, à 1200°", *Comptes Rendus*, vol. 206 (1938), pp. 349-50.

48. Note that SiO_2 and Na_2O have rather similar molecular weights, so that weight % and mole % are almost identical in the SiO_2-Na_2O system.

49. J.H. Wills, "Inorganic Adhesives and Cements: Soluble Silicates", in *Adhesion and Adhesives*, edited by R. Houwink and G. Salomon, 2nd edition, Elsevier, Amsterdam, 1965, vol. 1, pp. 439-80.

50. J.H. Wills, "Inorganic Adhesives and Cements", in *Handbook of Adhesives*, edited by I. Skeist, 2nd edition, Van Nostrand Reinhold, New York, 1977, pp. 117-38.

51. Ibid., pp. 119-20 and 123.

52. Note that I am proposing mixing the calcined powder with either *molten* boric oxide or a sodium silicate *solution*. In theory, it would also be possible to use either a molten sodium silicate or a boric oxide (boric acid) solution. However, molten sodium silicates tend to be more viscous than molten boric oxide, as indicated in Figure 2, so that mixing would be difficult. Boric oxide has a limited solubility in water; hence, a solution does not tend to dry to a vitreous solid, but tends to become saturated as evaporation occurs, so that all the boric oxide eventually precipitates as boric acid crystals.

53. E. Ryshkewitch, Oxide Ceramics, Academic Press, New York, 1960, pp. 12-30 and 300-303.

54. Thermal-conductivity curves for boric oxide glass and sodium silicate glass are estimated on the basis of CRC Handbook of Chemistry and Physics, 59th edition, pp. E-7 and E-8; E.B. Shand, Glass Engineering Handbook, 2nd edition, McGraw-Hill, New York, 1958, pp. 26-30; and A. Andrews, Porcelain Enamels, 2nd edition, Garrard Press, Champaign, Illinois, 1961, p. 53. Morey, op. cit., may possibly give better thermal-conductivity data for these glasses. Thermal-conductivity curves for Al_2O_3, NiO, and ThO_2 are based on Kingery, Francl, et al., "Thermal Conductivity: X, Data for Several Pure Oxide Materials Corrected to Zero Porosity", Journal of the American Ceramic Society, vol. 37 (1954), pp. 107-10; Ceramic Data Book, Cahners Publishing Company, Chicago, 1974, p. 266; and Ryshkewitch, op. cit., pp. 129-30 and 411.

55. Viscosity curves are based on Bocw, op. cit., Table 3; Eppler, op. cit., Table 1; Bockris, Mackenzie, and Kitchener, "Viscous Flow in Silica and Binary Liquid Silicates", Transactions of the Faraday Society, vol. 51 (1955), p. 1736; Wills, in Adhesion and Adhesives, op. cit., p. 451, Fig. 8.11; and Wills, in Handbook of Adhesives, op. cit., pp. 123-24, Table 2 and Fig. 8.