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CONVERSION OF HANFORD SALT CAKE TO GLASS: LABORATORY STUDIES

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ABSTRACT

Approximately 140 million liters of solid salt cake (mainly $NaNO_3$*), produced by evaporation of aged, alkaline high-level wastes, will be stored in underground tanks when the present Hanford Waste Management Program is completed in the early 1980's. These solid wastes can be converted to silicate-based glasses by melting them either at 1200° to 1300° C with appropriate amounts of sand and lime (soda-lime formulation) or at 1000° to 1100° C with appropriate amounts of Columbia River basalt and* B_2O_3 *(basalt formulation). Both formulations yield dense, immobile glasses of low water leachability (*10^{-7} *to* 10^{-6} *g* cm^{-2} day^{-1}*) suitable for terminal storage. The soda-lime formulation is presently preferred over the basalt formulation because it can accommodate more salt cake (50 wt% versus 30 to 40 wt%) while yielding a glass whose volume is 10 to 20% less than the volume of the salt cake in the melt charge.*

CONVERSION OF HANFORD SALT CAKE TO GLASS: LABORATORY STUDIES

INTRODUCTION

A significant part of the current Hanford Waste Management Program[1-4] involves vacuum evaporation of aged, alkaline waste liquors to solid salt cake. Salt cake is essentially a mixture of $NaNO_3$, $NaNO_2$, Na_2CO_3, $NaAlO_2$, NaOH, and Na_3PO_4 containing small amounts of ^{137}Cs, ^{90}Sr, actinides, and various relatively short-lived radioisotopes such as ^{106}Rh, ^{60}Co, and ^{125}Sb. [A metric ton of salt cake contains, typically, only about 200 milligrams of long-lived ($t_{1/2} \geq 25$ years) radionuclides.] By the early 1980's some 140 million liters of salt cake will be stored in the present Hanford underground tanks.

Present anticipations are that the salt cake wastes will be stored in the underground tanks for an interim period only. Eventually they will be retrieved and converted to a nonleachable immobile form suitable for terminal storage. Earlier laboratory studies[2,5,6] have shown that the salt cake can be transformed easily and smoothly into dense, silicate-based glass. Much additional laboratory work on the conversion of salt cake to glass has now been done; results of these latter investigations are summarized in this report.

Conversion of Hanford salt cake to glass would generate a very large amount of immobilized radioactive waste requiring expensive, high-integrity storage containers and facilities. To overcome this disadvantage, laboratory studies are now in progress to devise, if possible, radionuclide removal processes for partitioning salt cake wastes into a small volume of highly active waste requiring further immobilization for long-term storage and a large volume of chemical or very low-level radioactive wastes that can be stored safely or disposed of by inexpensive means. Development of satisfactory radionuclide removal procedures would obviate the need to convert salt cake to glass.

SUMMARY AND CONCLUSIONS

Extensive batch tests of the glassification of Hanford salt cake have been made with both synthetic and actual wastes. This work has established two satisfactory formulations for converting salt cake to dense, homogeneous, silicate-based glasses of low water leachability:

Soda-lime formulation: 40-50 wt% salt cake
40-55 wt% sand
5-10 wt% lime
Melt at 1250°-1350° C

Basalt formulation: 30-40 wt% salt cake
50-70 wt% basalt
0-10 wt% B_2O_3
Melt at 1050°-1100° C.

Although both formulations yield glasses considered suitable for long-term storage of Hanford salt cake, the soda-lime formulation is preferred over the basalt formulation because:

- It can accommodate a greater percentage of salt cake.
- It yields a smaller volume of glass.
- It is considered more suitable for use in large-scale, all-electric, continuous glass melters.
- Soda-lime salt cake glasses to not devitrify as readily as those made with the basalt formulation.

The volume of glass obtained with the basalt formulation is about equal to the volume of the salt cake in the melt charge while that produced from the soda-lime formulation is 10 to 20% less than that of the salt cake. Soda-lime salt cake glasses do not devitrify when heated two months at 500° C; under these conditions basalt glasses transform to crystalline materials substantially less (∿100-fold) resistant to water leaching. Glasses made with the soda-lime formulation have suitably low viscosities (50 to 200 poises) for use in continuous melters at temperatures above about 1250° C. Basalt-type glasses incorporating 30 to 40 wt% salt cake are pourable (50 to 200 poises) at temperatures as low as 1000° C. The presence of FeO, which strongly absorbs energy in the infrared spectral region, in the basalt formulation could complicate operations of large-scale melters through lowered melt thermal conductivity and undesirable thermal gradients.

Principal components of the off-gas resulting from conversion of Hanford salt cake to glass are NO_x, H_2O, and CO_2. Only small (2 to 8%) amounts of the ^{137}Cs in the waste volatilize during melting, at suitably slow rates, of either the soda-lime or the basalt formulations. This amount of volatilized radiocesium is considered well within the manageable range for large-scale continuous melter operation.

SALT CAKE GLASS - CONCEPTUAL PROCESS FLOWSHEET AND DESCRIPTION

Our batch-scale experiments with both synthetic and actual salt cakes have culminated in the conceptual glass-making scheme depicted in Figure 1. This process envisions

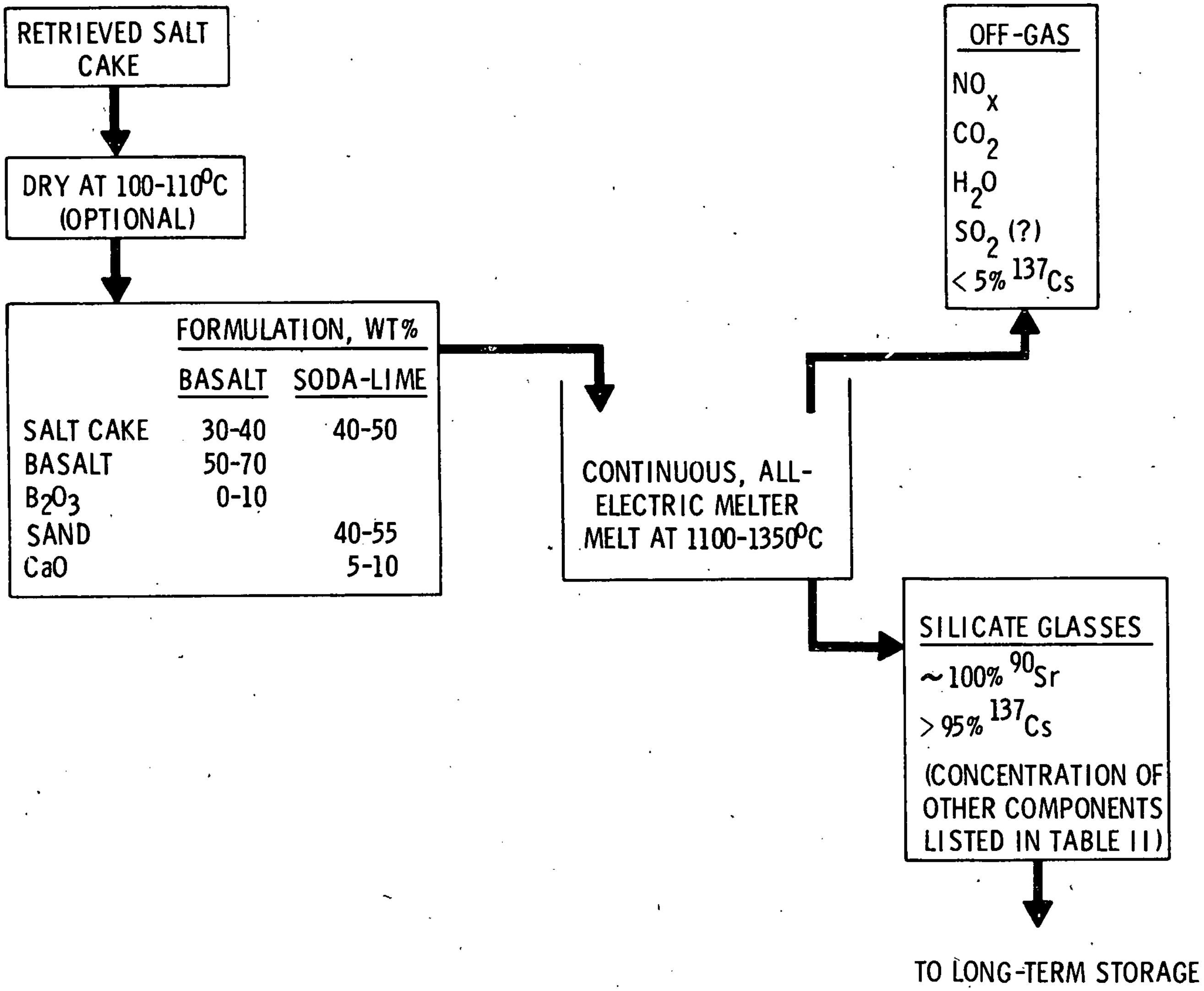

FIGURE 1

CONCEPTUAL PROCESS FOR CONVERSION OF SALT CAKE TO GLASS retrieval of the salt cake by dry-mining techniques.* Following preliminary drying, if necessary, the retrieved salt cake is converted to glass using either a soda-lime or a basalt formulation.

In the soda-lime formulation, the sodium-containing salt cake is mixed with sand and lime. The basalt formulation employs Columbia River-type basalt as a source of silica. Extensive deposits of this basalt underlie the Hanford Reservation so that it is readily available as a raw material for large-scale glass making. The chemical composition of typical Columbia River basalt is shown in Table I; physical properties of this type of basalt have been determined by Krupka[7] and Leibowitz, Williams, and Chasanov.[8] Addition of B_2O_3 to the basalt-salt cake mixture is beneficial, not only to lower the melting range from about 1100°-1150° C to 1000°-1050° C but also to reduce volatilization of radiocesium.

TABLE I

HANFORD BASALT - TYPICAL COMPOSITION

Component	wt%
SiO_2	52
$FeO \cdot Fe_2O_3$	14
Al_2O_3	13
CaO	8
MgO	4
Na_2O	3
TiO_2	2.5
K_2O	1.5

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*Hydraulic mining techniques are also being considered for salt cake retrieval. Very likely, extensive drying operations would be required to convert salt cake solutions to satisfactory feed for continuous glass-making equipment.

Using the soda-lime formulation (Figure 1), charges containing as much as 50 wt% salt cake can be successfully converted to what are judged acceptable glasses for long-term storage. The volume of such glass is 10 to 20% less than the volume of salt cake in the original charge. With basalt formulations, however, satisfactorily immobile glasses are obtained only when the process charge contains 40 wt% or less salt cake; leach rates of glasses made from basalt formulations containing more than about 40 wt% salt cake are inordinately high.[5] The volume of the glass obtained according to the basalt formulation flowsheet conditions of Figure 1 is about equal to the volume of the salt cake in the original charge.

The off-gas from melting of mixtures of salt cake with either basalt and B_2O_3 or sand and lime consists mainly of NO_x and CO_2 from decomposition of nitrate, nitrite, and carbonate salts. Some water vapor and, possibly, trace amounts of SO_2 and P_2O_5 will also be present in the off-gas. Not unexpectedly, some radiocesium also volatilizes when salt cake is converted to glass at 1100°-1200° C. Our batch melting tests, results of which are described in detail subsequently (p. 34) suggest, however, that on the order of only 2-8% of the radiocesium will volatilize when salt cake is converted to glass in a conventional tank-type continuous glass melter.

The average compositions of glasses produced from Hanford salt cake by the soda-lime and basalt formulations are listed in Table II. The composition of the soda-lime-type glass made from salt cake is quite similar to that of the commercial soda-lime glass; the radioactive glass contains slightly more Na_2O and slightly less SiO_2 than currently produced commercial soda-lime glass. Salt cake

TABLE II

SALT CAKE GLASS COMPOSITIONS

	Salt Cake Glasses[a]		
Component	Basalt Formulation[b]	Soda-Lime Formulation[c]	Commercial Soda-Lime Glass[d]
SiO_2	37	60	70-75
Na_2O	22	26	12-18
B_2O_3	13		
Al_2O_3	10	1	0.5-2.5
$FeO \cdot Fe_2O_3$	10		
CaO	6	13	0-4
MgO	2		

[a] Composition of minor components (*e.g.*, PO_4, SO_4, TiO_2, trace metal oxides, etc.) not shown.
[b] 35 wt% salt cake-55 wt% basalt-10 wt% B_2O_3.
[c] 45 wt% salt cake-45 wt% sand-10 wt% CaO.
[d] Composition range listed in Reference 9.

glasses made using the basalt formulation contain nearly the same amount of Na_2O as does the soda-lime-type but only about half as much SiO_2. The decreased silica content is compensated for by increased amounts of the network formers Al_2O_3 and Fe_2O_3. At least part of the iron in Columbia River basalt is present as FeO, and at least some of the FeO will likely persist even in the molten state at 1000°-1100° C.

Both the basalt and soda-lime formulations yield dense, immobile glasses of low water leachability and both can probably be used satisfactorily in a large-scale continuous, all-electric glass melter. There are, however, several reasons for preferring the soda-lime over the basalt formulation for glassification of Hanford salt cake. For example, large quantities of commercial soda-lime glass are made and marketed each year throughout the world; properties of commercial soda-lime glass and technology for its large-scale manufacture have been well-documented. No similar kind of knowledge about basalt formulation glasses exists. Furthermore, because of glass volume considerations already cited, costs of facilities and containers for safe, terminal storage of salt cake soda-lime glass would be less than those for glass made with the basalt formultion. Substitution of cheap CaO for the more expensive B_2O_3 also provides additional cost savings. Use of the soda-lime formulation would also avoid possible difficulties in operation of a continuous glass melter which might arise from the presence of some FeO in the basalt formulation. Iron(II) oxide strongly absorbs energy in the infrared spectral region, and this property could manifest itself in lowered melt thermal conductivity and undesirable thermal gradients. The principal disadvantage of the soda-lime formulation is that its use requires melter equipment capable of operation in the 1200°-1300° C range rather than in the lower 1000°-1100° C range required with the basalt-B_2O_3 formulation.

Thus far, conversion of salt cake to either basalt-type or soda-lime-type glass has been done only on batch- (30-200 g) scale. We are presently constructing a small (20-40 kg/day), all-electric, continuous glass melter; depending on the outcome of our Radionuclide Removal studies (*cf*. p. 1), this melter may be used eventually to demonstrate conversion of synthetic and actual salt cake to glass. A larger (one ton per day) all-electric, continuous glass melter is also being constructed by Battelle, Pacific Northwest Laboratories workers at Hanford;[10] this melter may also be used to demonstrate glassification of synthetic salt cake waste.

Finally, although not emphasized before, each of the underground tanks containing salt cake will also have a 30- to 60-cm thick layer of sludge on its bottom. [Sludge represents the heavy metals such as iron which precipitated when the original acid wastes were made alkaline; sludge is enriched in ^{90}Sr and the actinides.] Also, because of mixing which occurs in pumping and vacuum crystallization operations, all the salt cake itself will likely be contaminated to some extent, at least, with sludge. Both the soda-lime and the basalt formulations shown in Figure 1 will suitably accomodate salt cake containing small amounts of sludge. These formulations are not, however, particularly well suited for immobilizing undiluted sludge; laboratory studies to find satisfactory formulations for converting sludge to glass are now under way.

EXPERIMENTAL

CHARGE PREPARATION AND MELTING

Process charges containing appropriate amounts of synthetic or actual salt cake, sea sand (or basalt), and B_2O_3 or CaO were melted using equipment and procedures described previously.[5] Lime was obtained from the Mississippi Lime Company while B_2O_3 was procured from Research Organic/Inorganic Chemical Corporation. Sea sand sold by Matheson, Coleman, and Bell Corp. was used; composition of this raw material was (all wt%) 99.7 SiO_2, 0.08 FeO, 0.08 Al_2O_3, 0.02 CaO, 0.01 MgO, 0.02 Na_2O, 0.09 TiO_2, and 0.01 K_2O. Crushed basalt (<35 mesh) was obtained from the extensive local Hanford deposits; composition of Hanford basalt is listed in Table I.

Glasses were made from both synthetic salt cake and from actual salt cake from the 105-S and 106-S Tanks. Compositions of the synthetic and actual salt cake are listed in Table III. The composition of the synthetic salt cake was selected on the basis of early (and erroneous)

TABLE III
COMPOSITION OF SALT CAKE WASTES

Synthetic Salt Cake		
Component	wt%	Added As
NO_3	29.9	$NaNO_3$
Na	29.2	
NO_2	13.3	$NaNO_2$
AlO_2	10.5	$NaAlO_2$
CO_3	8.54	Na_2CO_3
Cs	2.48	$CsNO_3$
Sr	1.82	$Sr(NO_3)_2$ $SrCO_3$
SO_4	1.08	Na_2SO_4
PO_4	1.03	NaH_2PO_4
OH	0.77	NaOH
Cl	0.55	NaCl

Actual Salt Cake		
	wt%	
Component	Tank 105-S	Tank 106-S
NO_3	61.4	73.1
Na	28.4	19.6
CO_3	5.76	2.32
AlO_2	1.42	0.43
NO_2	1.29	0.20
OH	0.85	0.43
PO_4	0.57	
CrO_4	0.35	
SO_4	~0.1	
^{137}Cs, μCi/g	8.9	17.2
^{90}Sr, μCi/g	0.055	
Pu, μCi/g	0.014	

thoughts about the nature of salt cake. In particular, the synthetic salt cake contained significantly less nitrate and considerably more nitrite and aluminum than do actual salt cakes. As pointed out subsequently, chemical durability of glasses made from the synthetic salt cake was considerably enhanced by the large amount of aluminum in the salt cake. Inert $CsNO_3$, $Sr(NO_3)_2$, and $SrCO_3$ were added to the synthetic salt cake to facilitate determination of water leachability of glasses made from it.

The sulfate content of actual Hanford salt cake is still not known exactly but is now believed to be substantially less than the 1.0 wt% present in the synthetic cake. [Current indications are that sulfate ion tends to concentrate in the highly alkaline terminal liquor produced during vacuum evaporation of the dilute waste solutions.] Recent analyses also demonstrate that at least some of the salt cake contains small amounts (0.2 to 0.5 wt%) of chromate. [This chromate represents dichromate ion added in Redox process operations.] Chromate was not added to the synthetic salt cake.

CESIUM VOLATILIZATION

A limited number of batch melting experiments with actual salt cake were performed to determine the amount of ^{137}Cs volatilized when the salt cake was converted to soda-lime- or basalt-type glasses. Equipment and procedures used in these experiments generally followed closely those described in Reference 5.

In experiments designed to determine effects of charge composition on ^{137}Cs volatility the charge contained in a platinum crucible of known dimensions was heated from 25° C to 1200° C over a 3.5-hr period. The resulting molten glass was then maintained at 1200° C for an additional 24-hr period. Separate off-gas systems were used to collect the ^{137}Cs volatilized during the first 3.5-hr and last 24-hr periods. Leach procedures mentioned in Reference 5 were used to determine the ^{137}Cs collected on walls of the off-gas tubing. The rate of ^{137}Cs evolution from the molten glass was calculated from the known surface area of the glass and the ^{137}Cs collected in the last 24-hr heating period.

Other experiments were performed to estimate the amount of ^{137}Cs volatilized when charges were heated to 1200° C at various rates. In one set of such experiments the platinum crucible containing the glass formulation was placed in a furnace at 25° C and heated to 1200° C over a 3.5-hr period; ^{137}Cs volatilized during this heating period was determined. In another set of experiments the crucible was placed in a furnace previously heated to 1200° C. The charge melted in 0.5 hr, and the molten glass was maintained at 1200° C for 3 hr. In a final set of experiments the charge was inductively heated to 1200° C in 0.5 min; ^{137}Cs given off during this rapid heating period was collected.

VISCOSITY MEASUREMENTS

Viscosities of representative melts in the temperature range 900° to 1400° C were determined with a Brookfield Synchro-Lectric^{R} (Brookfield Engineering Laboratories, Inc.) viscometer (Model RVT) mounted over the crucible furnace. The charge was heated to the desired temperature in a platinum crucible and allowed to reach thermal equilibrium. A #6 platinum-20% rhodium spindle was then attached to the viscometer and immersed in the melt to measure the viscosity.

PRODUCT QUALITY TESTS

Microstructural characterization and electrical conductivity measurements of representative products are described in References 11 and 12, respectively.

Several other physical and chemical properties of each product were measured to provide a basis for evaluating effects of changes in melt composition and temperature.

1. Appearance and State

Color and porosity were determined by visual inspection. X-ray diffraction techniques were used to differentiate between crystalline and glassy (amorphous) products.

2. Density

Product densities were calculated from the volume of water displaced by a weighed sample.

3. Leach Rates in Water

Products were leached using procedures and equipment described previously.[5] Atomic absorption spectrophotometric methods were used to analyze leach solutions of nonradioactive products for cesium and strontium. The concentration of ^{137}Cs in leach solutions of radioactive products was determined by gamma energy pulse height methods using a lithium drifted germanium [Ge(Li)] detector.

Leach rates based on Cs or Sr for products made with synthetic salt cake were calculated from the formula

$$\text{Leach rate based on A, g/cm}^2\text{-day} = \frac{\text{g of A leached}}{(\text{g of A/g of sample})(\text{sample area, cm}^2)(\text{time, days})}$$

where "A" = Cs or Sr. The same formula, using μCi of A in place of grams of A, was used to determine leach rates of radioactive products.

4. Devitrification Behavior

Representative glasses, made by melting inert ingredients at 1200° C, were stored at 500° and 700° C, respectively, for three months. At one-month intervals samples of the heat-treated products were cooled to room temperature and analyzed for crystallinity by visual and X-ray diffraction techniques. Leach rates in water of these products were also measured.

5. Volume Changes upon Melting

For several representative formulations the volume of the entire melt product was determined by water displacement. This value was compared with the volume of dry salt cake in the mixture to estimate volume changes which occurred during the melting process.

RESULTS AND DISCUSSION

GLASSES FROM SYNTHETIC SALT CAKE

Formulations used to prepare glasses from charges containing synthetic salt cake are listed in Tables IV-VI. Leach rates of these salt cake glasses in water are also listed in Tables IV-VI. Important features of these results are discussed in the following sections. Reference is also made to the report by Kupfer and Schulz[5] which presents detailed properties of glasses made from charges containing both synthetic and actual salt cake, basalt, and B_2O_3.

Product Appearance and State

Clear, colorless glass or crystalline products resulted when charges containing synthetic salt cake, sand, and, in some cases, B_2O_3 or CaO, were melted in platinum crucibles. When such charges were melted in clay-graphite crucibles, however, the resulting products were amber-colored. Basalt-based glasses made in either platinum or clay-graphite crucibles were colored black to green-black.

Glasses resulted from melting, at 1200° C, charges containing 30 to 60 wt% salt cake and 40 to 70 wt% sand (Table IV). Charges containing less than 30 wt% waste failed to melt completely at 1200° C and yielded crystalline products. X-ray diffraction patterns of these crystalline compounds were not indexed to any specific mineral or compound.

TABLE IV

SALT CAKE GLASSES: SAND-WASTE FORMULATIONS

Charge Composition,[a] wt%		Product Density g/cm^3	Product State	Leach Rate Based on Cs g/cm^2-day		Leach Rate Based on Sr g/cm^2-day	
Salt Cake	Sand			24 hr	96 hr	24 hr	96 hr
30	70	2.6	Glassy	7.8×10^{-5}	3.1×10^{-5}	3.3×10^{-5}	2.0×10^{-5}
40	60	*b*	Glassy	8.9×10^{-6}	1.9×10^{-6}	4.4×10^{-6}	1.1×10^{-6}
50	50	2.0	Glassy	1.7×10^{-5}	3.7×10^{-6}	2.0×10^{-6}	2.0×10^{-7}
60	40	2.4	Glassy	2.2×10^{-5}	7.7×10^{-6}	3.6×10^{-6}	1.6×10^{-6}

[a] All charges melted 1 hr at 1200° C.
[b] Not determined.

TABLE V

SALT CAKE GLASSES: SAND-WASTE-B_2O_3 FORMULATIONS

Charge Composition,[a] wt%			Product Density	Product	Leach Rate Based on Cs g/cm^2-day		Leach Rate Based on Sr g/cm^2-day	
Salt Cake	Sand	B_2O_3	g/cm^3	State	24 hr	96 hr	24 hr	96 hr
20	70	10	2.0	Crystalline	2.2×10^{-4}	9.5×10^{-5}	1.2×10^{-4}	2.7×10^{-5}
30	65	5	*b*	Crystalline	2.9×10^{-5}	9.4×10^{-6}	1.5×10^{-5}	5.7×10^{-6}
30	60	10	2.5	Glassy	2.3×10^{-5}	3.8×10^{-6}	2.5×10^{-5}	2.6×10^{-6}
30	55	15	2.0	Glassy	2.9×10^{-6}	7.3×10^{-7}	1.8×10^{-5}	1.0×10^{-6}
40	55	5	1.9	Glassy	1.8×10^{-5}	2.9×10^{-6}	7.2×10^{-6}	6.0×10^{-7}
40	50	10	2.4	Glassy	1.0×10^{-5}	9.0×10^{-7}	3.2×10^{-5}	1.5×10^{-6}
40	45	15	2.6	Glassy	2.1×10^{-5}	2.5×10^{-6}	6.5×10^{-6}	3.0×10^{-7}
50	45	5	2.7	Glassy	1.1×10^{-5}	1.7×10^{-6}	7.4×10^{-6}	2.0×10^{-7}
50	40	10	2.5	Glassy	1.2×10^{-5}	5.4×10^{-6}	5.2×10^{-6}	2.0×10^{-7}
50	35	15	2.5	Glassy	9.4×10^{-6}	2.0×10^{-6}	1.7×10^{-6}	2.0×10^{-7}
60	35	5	2.7	Glassy	1.8×10^{-5}	2.8×10^{-6}	5.0×10^{-6}	5.0×10^{-7}
60	30	10	2.5	Glassy	5.3×10^{-5}	2.3×10^{-5}	3.2×10^{-6}	2.2×10^{-6}
60	25	15	*b*	Glassy	2.1×10^{-4}	4.3×10^{-5}	3.8×10^{-6}	1.3×10^{-6}

[a] All charges melted 1 hr at 1200° C.

[b] Not determined.

TABLE VI

SALT CAKE GLASSES: SAND-WASTE-CaO (SODA-LIME) FORMULATIONS

Charge Composition,[a] wt%			Product Density g/cm^3	Product State	Leach Rate Based on Cs g/cm^2-day		Leach Rate Based on Sr g/cm^2-day	
Salt Cake	Sand	CaO			24 hr	96 hr	24 hr	96 hr
20	70	10	1.9	Crystalline	4.2×10^{-5}	9.4×10^{-6}	1.8×10^{-4}	5.5×10^{-5}
30	65	5	*b*	Crystalline	2.3×10^{-5}	2.4×10^{-6}	6.1×10^{-5}	1.7×10^{-5}
30	60	10	2.2	Glassy	2.2×10^{-5}	4.7×10^{-6}	2.3×10^{-5}	4.1×10^{-6}
30	55	15	*b*	Glassy	2.1×10^{-5}	3.0×10^{-6}	6.4×10^{-5}	2.8×10^{-5}
40	55	5	*b*	Glassy	2.0×10^{-5}	4.0×10^{-6}	1.2×10^{-5}	2.3×10^{-6}
40	50	10	2.4	Glassy	2.2×10^{-6}	4.6×10^{-6}	9.2×10^{-6}	7.2×10^{-6}
40	45	15	2.4	Glassy	1.1×10^{-5}	2.0×10^{-6}	8.2×10^{-5}	6.0×10^{-6}
50	45	5	2.6	Glassy	2.5×10^{-5}	3.6×10^{-6}	1.1×10^{-5}	2.0×10^{-6}
50	40	10	2.5	Glassy	8.7×10^{-6}	3.8×10^{-6}	2.2×10^{-5}	1.4×10^{-5}
50	35	15	2.7	Crystalline	1.9×10^{-5}	3.3×10^{-6}	7.1×10^{-5}	4.4×10^{-5}
60	35	5	2.5	Glassy	1.0×10^{-5}	4.1×10^{-6}	2.9×10^{-6}	2.7×10^{-6}
60	30	10	2.6	Glassy	2.9×10^{-5}	1.5×10^{-5}	7.9×10^{-5}	6.1×10^{-5}
60	25	15	2.7	Glassy	8.9×10^{-5}	4.1×10^{-5}	2.1×10^{-4}	6.4×10^{-5}

[a] All charges melted 1 hr at 1200° C.
[b] Not determined.

The density of the glassy products resulting from melting mixtures of salt cake, sand, and, in some cases, B_2O_3 or CaO, ranged from 2.2 to 2.6 g/cm^3. Although minor variations were noted, product densities were relatively insensitive to changes in reactant proportions.

Investigators at the Savannah River Laboratory[13] and elsewhere[14,15] have observed that sulfates are not compatible with all borosilicate glasses. In some cases a cesium-rich, water-soluble sulfate phase segregates during melting. No such second phase was observed in four special experiments in which charges containing (a) 40 wt% synthetic salt cake-50 wt% basalt-10 wt% B_2O_3; (b) 60 wt% salt cake-40 wt% sand, (c) 50 wt% salt cake-40 wt% sand-10 wt% lime, and (d) 50 wt% salt cake-40 wt% sand-10 wt% B_2O_3 contained in platinum crucibles were heated two hr at either 1100° C (B_2O_3 formulation) or 1200° C. All of the resulting glasses contained less than 0.8 wt% sulfate, the solubility of sulfate in borosilicate glasses as determined by Savannah River workers.[13]

Microstructure

Microstructural characteristics of two glasses made from salt cake were determined.[11] These glasses were made by melting at 1200° C for ∿4 hr charges containing, respectively, 30 wt% synthetic salt cake-60 wt% basalt-10 wt% B_2O_3 and 50 wt% synthetic salt cake-50 wt% sand.

The basalt glass was black in color and uniformly glassy throughout. Thin sections of the glass were gray-green by transmitted light. Pores, scattered randomly across all sections, ranged in diameter from about 20 μm to 1 mm. The highest pore concentration occurred near the top of the casting. The elemental composition of the basalt glass was very uniform throughout with the exception of small variations in silicon content and the presence of metallic iron inclusions.

The sand glass casting was amber in color and uniformly glassy throughout. Pores were somewhat smaller in size and fewer in number than those in the basalt glass. No metallic deposits or inclusions were found in the sand glass, consistent with the absence of iron in the starting materials. No detectable variation in composition was observed from one location to another in this glass.

Small bright spots (∿1 μm in diameter) of unknown origin were uniformly distributed throughout both glasses. X-ray fluorescence analysis showed no difference between these spots and the surrounding matrix indicating that the spots were either fragments or a second phase of matrix material or contained only light elements not detectable by X-ray analysis.

Glass Volumes

Typical volume changes which occurred during melting at 1200° C of charges containing synthetic salt cake and glass-forming ingredients are summarized in Table VII. As already noted, the volume of soda-lime-type glasses made from charges containing 50 wt% salt cake was 10 to 20% less than the volume of the salt cake. Conversely, the volume of the basalt-type glass made from charges containing 40 wt% salt cake was about equal to the volume of the salt cake.

Leach Behavior

Sand-Waste Formulations. Simple melting at 1200° C of charges containing synthetic salt cake and sand yielded immobile glasses (Table IV). Leach rates, based on cesium,

TABLE VII

VOLUME CHANGES UPON GLASSIFICATION OF SALT CAKE

Charge Composition, wt%					Volume Ratio
Salt Cake	Sand	Basalt	B_2O_3	CaO	Salt Cake/Glass
40	50		10		1.1
40	50			10	1.1
50	45			5	0.9
50	40			10	0.8
40		50	10		1.0
40		60			0.9

of such glasses in water ranged from 3.7 x 10^{-6} to 3.1 x 10^{-5} g/cm^2-day; leach rates based on strontium were even lower, ranging from 2.0 x 10^{-7} to 2.0 x 10^{-5} g/cm^2-day. Leach rates of the sand-waste glasses appeared to vary periodically with the amount of salt cake in the melt formulation; the minimum leach rate was observed with a glass made from a charge containing 40-50 wt% waste and 50-60 wt% sand.

Water leachability of glasses made at 1200° C from sand-waste formulations containing $\geq$40 wt% synthetic salt cake were about 100-fold lower than those of glasses made from basalt-waste formulations (Table VIII). As pointed out previously, the high aluminum content of the synthetic salt cake undoubtedly contributed significantly to the low leachability of the sand-waste glasses.

Sand-Waste-B_2O_3 Formulations. Boron trioxide is often added to glass formulations as a melting agent and to enhance thermal endurance of glasses.[16] Excessive additions of B_2O_3 can, however, have a detrimental effect on the ability of the glass to resist chemical attack. In our tests (Table V) leach rates of glasses made from sand-waste

TABLE VIII

COMPARISON OF SALT AND BASALT AS SOURCES OF SILICA IN SALT CAKE GLASSES

Charge Composition, wt%			Leach Rate (96 hr), g/cm^2-day[a]	
Salt Cake	Basalt	Sand	Based on Cs	Based on Sr
30	70		1.1×10^{-6}	5.2×10^{-7}
30		70	3.1×10^{-5}	2.0×10^{-5}
40	60		1.1×10^{-6}	1.6×10^{-6}
40		60	1.9×10^{-6}	1.1×10^{-6}
50	50		2.7×10^{-4}	2.9×10^{-4}
50		50	3.7×10^{-6}	2.0×10^{-7}

[a] Data for basalt-based glasses taken from Reference 5.

formulations were not significantly affected by incorporation of 5 to 15 wt% B_2O_3 in the formulation.

Waste-Sand-CaO Formulations. Lime is commonly used in glass formulations to increase chemical durability.[17] Table VI, referred to earlier, lists formulations used to prepare several soda-lime-type glasses from synthetic salt cake. For these particular glasses, incorporation of 5-15 wt% lime in the sand-waste formulation certainly did not noticeably improve resistance to water leaching. Indeed, in some cases, addition of lime to the glass formulation actually decreased chemical durability. Some of the variations in leachability of these glasses are probably attributable to the changes in Na/Si atom ratios caused by substitution of CaO for SiO_2. However, the principal reason why addition of lime to sand-synthetic salt cake mixtures did not increase chemical durability of the glasses prepared from them is, we believe, because of the presence of large quantities of the network former Al_2O_3 in the synthetic waste. Alumina itself, of course, is highly effective in increasing chemical durability of glasses.

Actual Hanford salt cake, in contrast to the synthetic salt cake used in these studies, contains only minor amounts of alumina (*cf.* Table III). Incorporation of agents such as B_2O_3 or lime in the waste-sand formulation is thus essential to produce a glass with satisfactorily low water leachability.* [Lime is preferred to B_2O_3 primarily because of its lower cost.] As discussed in more detail later (*cf.* p. 30), soda-lime-type glasses made from actual salt cake are suitably resistant to attack by water.

Atom Ratios for Acceptable Glasses

Important atom ratios of glass components for formulation of acceptable glasses have been stated by several investigators[18,19] as follows:

Designation	Ratio
A	$\frac{Si}{Al + B}$
B	$\frac{\text{Oxygen}}{\text{network formers}}$
C	$\frac{\text{Network Formers}}{\text{network modifiers}}$
D	$\frac{\text{Network Modifiers}}{O-(2)(\text{network formers})}$

In these ratios silicon, boron, and aluminum are network formers while sodium, potassium, and calcium are network modifiers.

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*The vastly greater chemical durability of Na_2O-SiO_2-CaO glasses over Na_2O-SiO_2 glasses has been reemphasized in a recent paper, "Aqueous Corrosion of Soda-Silica and Soda-Lime-Silica Glass," by D. E. Clark, M. F. Dilmore, E. C. Ethridge, and L. L. Hench, published in the *J. Amer. Ceram. Soc.*, 59:62 (1976).

According to Savannah River Laboratory workers,[18] "When Ratio A is 1.5 leachability is low. The melting point of the glass increases as A increases. With Ratio B between 2.2 and 2.4 glass formation is best and leachability is low. Excess oxygen is needed to balance the electronic charge of network modifiers. Glass density increases as A decreases and B increases. Ratio C should be ∿2 for good glass formation. As C decreases, the polymeric network is disrupted and the tendency for glass formation decreases. Ratio D represents the ratio of network modifiers to excess oxygen not required for network formers to be four-coordinate. D should be as near as possible to 2."

Typical formulations for making glass from synthetic salt cake are listed in Table IX with their associated atom ratios. With one exception the atom ratio A was >1.5 for all these formulations implying low water leachability of the resulting glass. All of the other atom ratios deviated to some extent from the preferred values indicating that these glass formulations were not optimum.

TABLE IX

ATOM RATIOS FOR VARIOUS SALT CAKE GLASS FORMULATIONS

Charge Composition, wt%					Atom Ratios[a]			
Salt Cake	Basalt	Sand	B_2O_3	CaO	A	B	C	D
30	70				2.66	3.26	1.03	0.77
30	60		10		1.06	2.86	1.35	0.86
40	60				2.35	3.70	0.85	0.70
40	50		10		0.90	3.17	1.12	0.76
40		60			13.9	2.93	2.06	0.53
40		50	10		2.33	2.72	2.28	0.61
40		50		10	11.6	3.29	1.30	0.60
50		50			9.28	3.34	1.42	0.52
50		40	10		1.78	3.06	1.60	0.59
50		40		10	7.42	3.88	0.91	0.58

[a] Defined in text, page 22.

Devitrification

Glasses are, of course, thermodynamically unstable with respect to devitrification to crystalline materials. Significant increases in water leachability oftentimes accompany conversion of glasses to crystalline forms; this behavior has been observed, for example, for some of the devitrified glasses made from simulated commercial Purex process high-level waste.[20]

Because of their relatively low radionuclide content, the center-line temperature of glasses made from Hanford salt cake will be about 25° C. There will therefore be little or no driving force for devitrification of such glasses. Nevertheless, it was of interest to study effects of storing salt cake glasses at elevated temperature. Results of this study (Tables X and XI) showed that soda-lime-type glasses were much more resistant to devitrification at 500° to 700° C than were the basalt-type glasses. Thus none of the soda-lime-type glasses devitrified at 500° C and only one devitrified when heated two months at 700° C. Conversely, all three of the test basalt-type glasses crystallized after heating two months at either 500° or 700° C. Leach rates of the devitrified basalt-type glasses in water were about 100-fold higher than those of the original glasses. Heating soda-lime-type glasses for one to two months at 500° or 700° C did not significantly affect their leachability in water.

Electrical Conductivity

Plant-scale conversion of the large volume of Hanford salt cake to glass would most likely be done in continuous, all-electric melters. Knowledge of the electrical conductivity of salt cake glasses is essential to permit design of

TABLE X

DEVITRIFICATION BEHAVIOR OF SALT CAKE GLASSES: SODA-LIME TYPE

Glass	Storage Conditions			Leach Rate,[a] g cm^{-2}-day^{-1}			
	Temperature	Time		Based on Cs		Based on Sr	
No.[b]	°C	Months	Final State	Initial	Final	Initial	Final
1	500	2	Glass	5.7×10^{-7}	1.7×10^{-5}	9.1×10^{-7}	5.9×10^{-6}
	700	2	Glass	5.7×10^{-7}	1.4×10^{-5}	9.1×10^{-7}	2.5×10^{-6}
2	500	2	Glass	8.7×10^{-7}	9.2×10^{-6}	1.4×10^{-6}	1.5×10^{-6}
	700	2	Glass	8.7×10^{-7}	5.6×10^{-6}	1.4×10^{-6}	9.2×10^{-7}
3	500	2	Glass	1.7×10^{-6}	3.0×10^{-6}	3.9×10^{-6}	4.0×10^{-7}
	700	2	Glass	1.7×10^{-6}	1.1×10^{-5}	3.9×10^{-6}	6.5×10^{-6}
4	500	2	Glass	4.5×10^{-6}	1.7×10^{-5}	6.8×10^{-6}	2.1×10^{-6}
	700	2	Crystalline	4.5×10^{-6}	1.4×10^{-5}	6.8×10^{-6}	1.1×10^{-5}

[a] 96 hr in deionized water.

[b] Charge compositions used to prepare these glasses were as follows:

Glass No.	wt% Salt Cake	wt% Sand	wt% CaO
1	40	55	5
2	40	50	10
3	50	45	5
4	50	40	10

TABLE XI

DEVITRIFICATION BEHAVIOR OF SALT CAKE GLASSES: BASALT-TYPE

	Storage Conditions				Leach Rate,[a] g cm^{-2}-day^{-1}					
					Based on Cs			Based on Sr		
Glass No.[b]	Temperature °C	Time Months	State 1 Month	State 2 Months	Initial	1 Month	2 Months	Initial	1 Month	2 Months
1	500	2	Glass	Crystalline	1.2×10^{-6}	4.4×10^{-5}	5.7×10^{-6}	2.2×10^{-6}	1.1×10^{-5}	5.9×10^{-7}
	700	2	Crystalline	Crystalline	1.2×10^{-6}	4.9×10^{-3}	7.3×10^{-4}	2.2×10^{-6}	1.9×10^{-4}	1.3×10^{-5}
2	500	2	Glass	Crystalline	8.3×10^{-6}	8.6×10^{-6}	1.1×10^{-5}	2.4×10^{-6}	5.5×10^{-6}	4.1×10^{-6}
	700	2	Crystalline	Crystalline	8.3×10^{-6}	1.8×10^{-4}	6.2×10^{-5}	2.4×10^{-6}	2.4×10^{-4}	4.6×10^{-6}
3	500	2	Crystalline	Crystalline	1.2×10^{-6}	9.2×10^{-5}	4.8×10^{-5}	2.9×10^{-6}	4.5×10^{-5}	9.0×10^{-6}
	700	2	Crystalline	Crystalline	1.2×10^{-6}	9.1×10^{-5}	4.2×10^{-4}	2.9×10^{-6}	3.8×10^{-5}	3.3×10^{-5}

[a] 96 hr in deionized water.

[b] Charge compositions used to prepare these glasses were as follows:

Glass No.	wt% Salt Cake	wt% Basalt	wt% B_2O_3
1	30	60	10
2	40	50	10
3	40	60	0

satisfactory melters and electrode systems. To this end, J. L. Bates of Battelle, Pacific Northwest Laboratories, measured the electrical conductivity of three nonradioactive salt cake glasses as a function of temperature.[12] Unfortunately, composition (Table XII) of these glasses was chosen early in the program before sufficient leach and other data were available to specify the soda-lime and basalt glass formulations (Table II) for immobilizing salt cake. With the notable exception, however, that it contained no iron, the composition of the glass denoted 2A in Table XII was approximately the same as that of a basalt-type salt cake glass (Table II).

TABLE XII

COMPOSITION OF SALT CAKE GLASSES USED IN ELECTRICAL CONDUCTIVITY MEASUREMENTS

Component	Concentration, wt%		
	Glass 1	Glass 2	Glass 2A
SiO_2	68.9	68.6	44.2
Na_2O	15.5	13.6	34.9
B_2O_3	13.0	12.9	8.3
Al_2O_3	0.7	3.1	8.0
Cs_2O	1.0	0.9	2.3
SrO	0.7	0.6	1.6
P_2O_5	0.2	0.3	0.7

For the glasses studied by Bates logarithmic plots (Figures 2 and 3) of electrical conductivity versus 1/T were approximately linear at temperatures below 800° C; electrical conductivity of these glasses was increasingly less temperature-dependent at temperatures above 800° C. Also at temperatures above 800° C electrical conductivity was higher when measured with 1000 Hz current than with 40 Hz current; according to Bates such behavior is often observed in ionic conducting systems where polarization can take place near

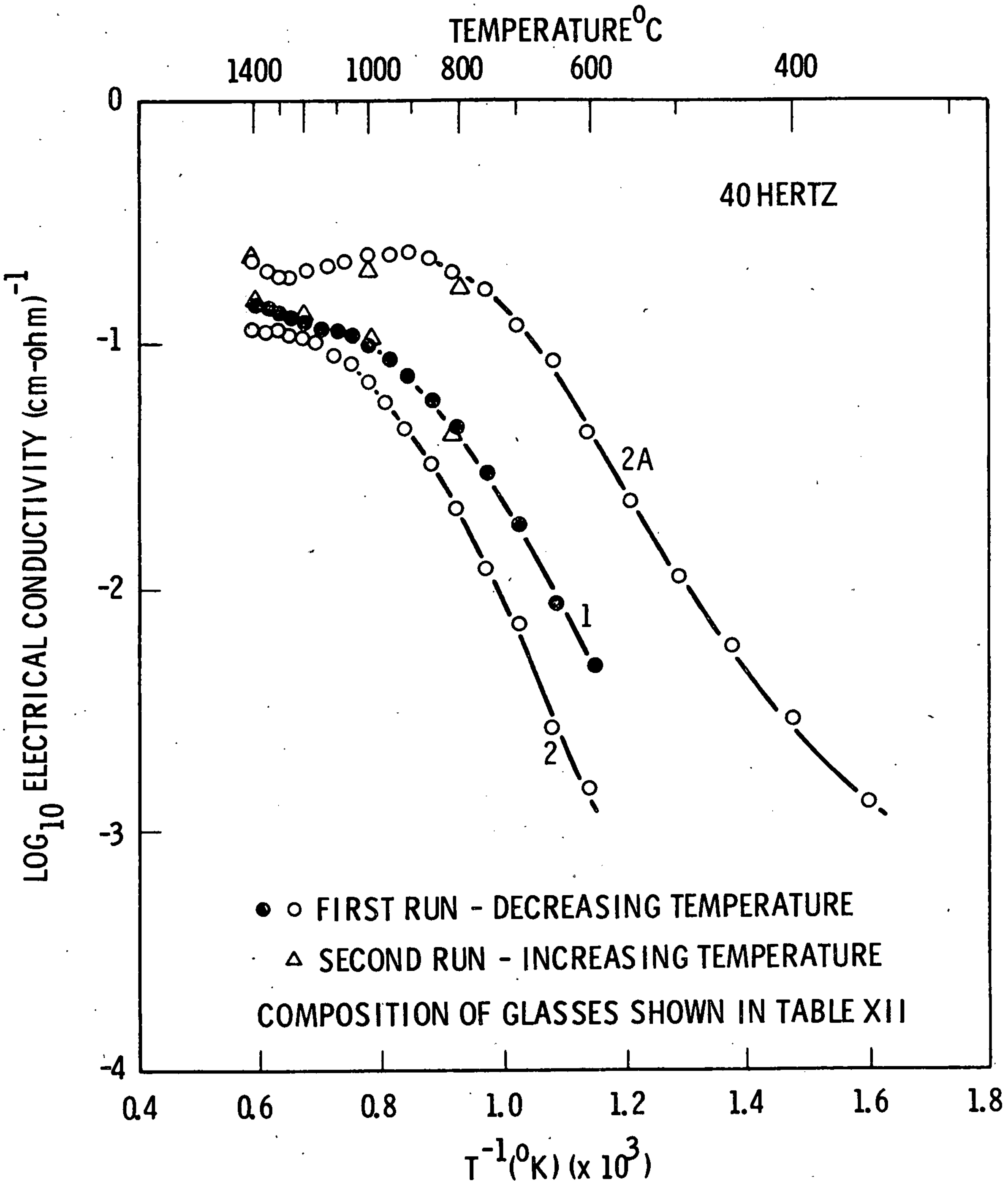

FIGURE 2

ELECTRICAL CONDUCTIVITY OF SOME SALT CAKE GLASSES

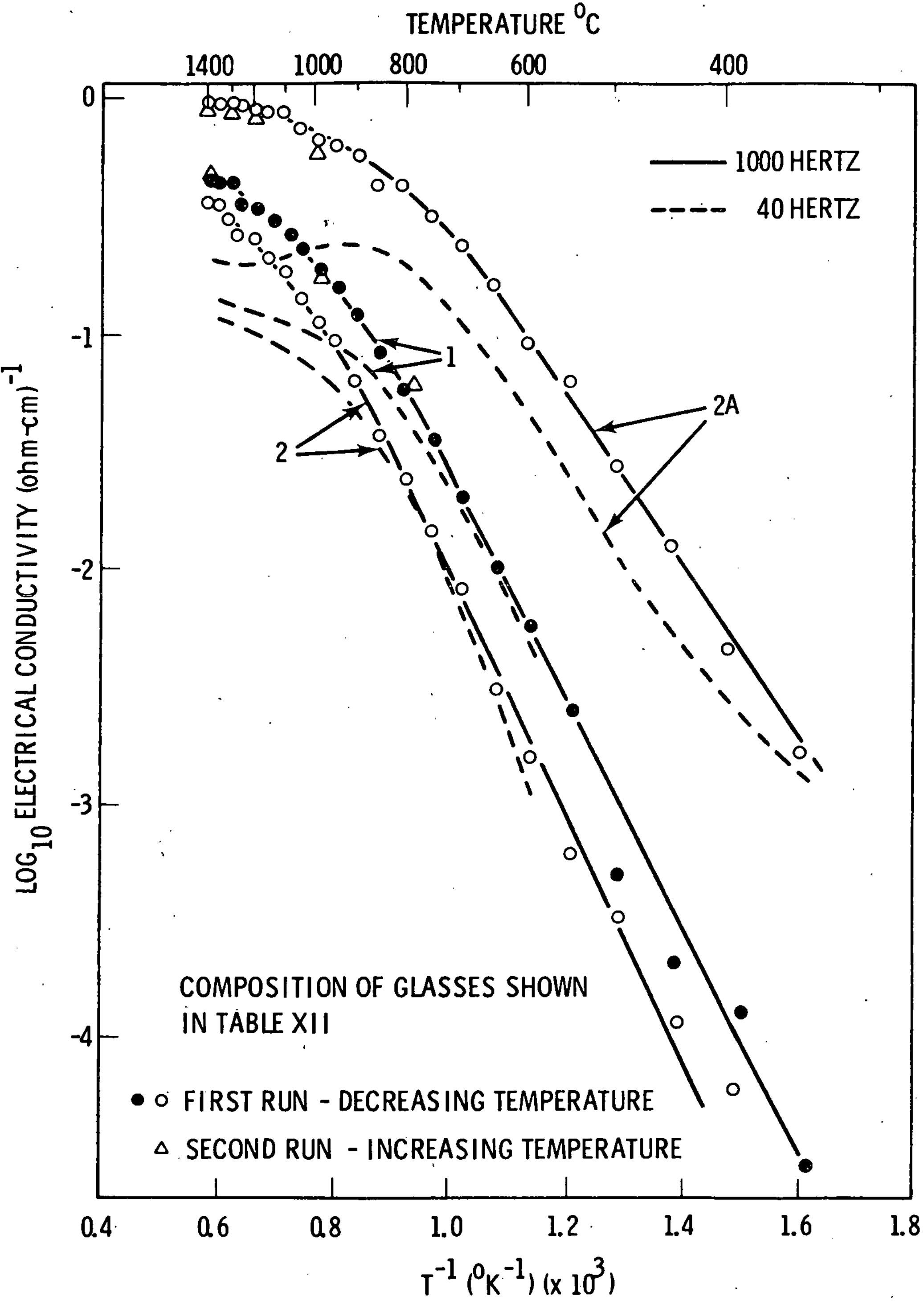

FIGURE 3

VARIATIONS OF ELECTRICAL CONDUCTIVITY OF SOME SALT CAKE WITH CURRENT FREQUENCY the electrodes. Bates suggests that higher frequency currents might be used in a continuous melter to take advantage of the increased electrical conductivity.

Viscosity

Viscosities of both basalt-type and soda-lime-type salt cake glasses are tabulated in Table XIII. Typically, molten glasses with viscosities in the range 50-200 poises can be satisfactorily poured from continuous glass melters. On this basis, basalt-type glasses incorporating 30 to 40 wt% salt cake are pourable at temperatures as low as 1000° C. Conversely, furnace temperatures greater than about 1200° C are required to obtain suitably fluid soda-lime-type salt cake glasses. Generally, the viscosity of both the basalt-type and soda-lime-type glasses at a particular temperature decreases with increased amount of salt cake in the glass.

GLASSES FROM ACTUAL SALT CAKE

Conditions used to prepare a basalt-type and a soda-lime-type glass from actual salt cake are listed in Table XIV. Properties of these glasses, especially their low leachability, provide convincing proof that Hanford salt cake can indeed be satisfactorily immobilized by conversion to silicate-based glasses. Significantly, the water leachability of the soda-lime glass made from a charge containing 50 wt% salt cake was about the same as that of the basalt glass made from a charge containing only 30 wt% salt cake.

In general, properties of the glasses made from the actual wastes were comparable to those made from synthetic salt cake. Atom ratios (*cf.* p. 23) for the formulation used to made soda lime glass from actual salt cake were A = 69.6, B = 4.28, C = 1.04, and D = 0.42; corresponding ratios for

TABLE XIII

VISCOSITY OF SALT CAKE GLASSES

Charge Composition, wt%					Viscosity, poise, at							
Salt Cake	Sand	Basalt	CaO	B_2O_3	900°C	1000°C	1050°C	1100°C	1150°C	1200°C	1300°C	1350°C
40	50			10		1640		445		162	82	
40	55		5							820	320	
40	50		10					1220		405	160	
50	45		5					960		350	150	
50	40		10				980		300			66
30		60		10	1600	245		75		32		
40		50		10	1300	102		37		17		
40		10						>20000		90	37	

TABLE XIV

GLASSES FROM ACTUAL SALT CAKE: PREPARATION-PROPERTIES

I. MELT CONDITIONS

Charge Formulation:	Melt 1	Melt 2
	30 wt% Tank 105-S waste[a] 60 wt% basalt 10 wt% B_2O_3	50 wt% Tank 106-S waste[b] 45 wt% sand 5 wt% CaO
Melt Temperature, Time	1200° C, 28 hours	1200° C, 30 hours

II. PRODUCT

	Melt 1	Melt 2
Color	Black	Amber
Density (g/cm^{+3})	2.74	
^{137}Cs content, $\mu Ci/g$	9.22	7.69

Leach rate,[c] based on ^{137}Cs

Total Time days	Rate g/cm^2-day	Total Time days	Rate g/cm^2-day
1	2.46×10^{-5}	1	3.26×10^{-5}
5	9.58×10^{-6}	8	2.57×10^{-6}
9	1.06×10^{-5}	15	3.42×10^{-6}
16	3.25×10^{-7}	29	3.38×10^{-6}
23	6.16×10^{-7}	43	4.98×10^{-6}
30	8.16×10^{-6}	50	4.14×10^{-6}
37	9.49×10^{-6}	57	3.87×10^{-6}
44	6.95×10^{-6}	64	3.74×10^{-6}
51	1.01×10^{-5}	71	3.65×10^{-6}
58	3.67×10^{-6}	85	3.54×10^{-6}
65	3.03×10^{-6}	92	4.78×10^{-6}
72	3.60×10^{-6}	99	4.22×10^{-6}
86	5.33×10^{-6}	106	4.03×10^{-6}
93	2.82×10^{-6}	113	4.91×10^{-6}
100	1.72×10^{-6}	120	5.04×10^{-6}
114	1.59×10^{-6}	134	4.51×10^{-6}
121	1.44×10^{-6}		
128	1.13×10^{-6}		
142	4.02×10^{-6}		
149	2.57×10^{-6}		
156	1.97×10^{-6}		
163	3.95×10^{-6}		

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[a] 26.9 g Tank 105-S waste.

[b] 56.2 g Tank 106-S waste.

[c] 9.3 g samples (187 cm^2) leached in 200 ml deionized water at 25° C.

approximately the same formulation (*cf.* Table IX) with synthetic salt cake were A = 7.42, B = 3.88, C = 0.91, and D = 0.58. No evidence for the presence of a sulfate-rich (*cf.* p. 18) second phase in either of the actual salt cake glasses was found.

CESIUM VOLATILIZATION

The off-gas from converting Hanford salt cake to glass in an all-electric, continuous melter will contain mainly NO_x, H_2O, and other nonradioactive components. Small amounts (2-8%) of ^{137}Cs will also be present in the off-gas. The exact amount of ^{137}Cs which will volatilize during large-scale glassification of salt cake depends on several factors including charge formulation, melter configuration, and melter operation (*i.e.*, time to melt charge, presence or absence of "cold cap", etc.). Limited batch melting experiments were performed with actual salt cake to provide at least some knowledge of factors affecting ^{137}Cs volatility; experimental techniques were discussed previously (*cf.* p. 11).

The radiocesium volatility studies reported here complement and supplement earlier[5] studies with synthetic salt cake. These previous tests showed that 1 to 5% of the cesium volatilized when charges containing 10-40 wt% synthetic salt cake and 60-90 wt% basalt were melted at 1050°-1200° C. Volatilization of cesium from such charges was reduced to 1% or less by incorporation of 2-16 wt% B_2O_3 in the formulation. Nukerji and Kanyal[21] state that a solid-state reaction between $CsNO_3$ and B_2O_3 occurs at temperatures as low as 130° to 150° C.

Effects of Melt Composition

Table XV lists the amounts of ^{137}Cs that volatilized when typical salt cake glass charges were heated slowly to 1200° C and maintained at that temperature for 24 hr. The most significant aspect of these data is that in all cases less than 8% of the ^{137}Cs in the salt cake volatilized. This amount of volatilized radiocesium is considered well within the manageable range for large-scale continuous melter operation. Even smaller amounts of ^{137}Cs might volatilize if "cold cap" (a cap of unmelted glass-forming ingredients maintained over the melt at all times) melting techniques were employed.

Unfortunately, the small amount of actual salt cake available to us when these experiments were done did not permit extensive duplicate runs to estimate experimental error associated with ^{137}Cs volatility measurements. From the limited data in Table XV it appears, however, that more ^{137}Cs volatilized during preparation of soda-lime-type glasses than from melting charges containing boron. Addition of TiO_2 to the soda-lime formulation also appeared to decrease volatilization of cesium. Other workers[13] have also noted a similar beneficial effect of titania addition in suppressing volatilization of radiocesium.

Of the total ^{137}Cs volatilized in the experiments listed in Table XV greater than 98% evolved at temperatures below 1200° C. Other experiments in which ^{137}Cs volatilization was briefly studied as a function of furnace temperature indicated more than 50% of the total ^{137}Cs volatilized was given off in the temperature range 450°-650° C. Less than 1% of the total ^{137}Cs volatilization occurs over the temperature range 25° to 450° C.

TABLE XV

VARIATION OF ^{137}Cs VOLATILIZATION WITH MELT COMPOSITION

Charge Formulation						^{137}Cs Volatilized %[b]	Rate of ^{137}Cs Volatilization at 1200° C, μCi/cm^2-hr[c]
Salt Cake[a]	Basalt	Sand	B_2O_3	CaO	TiO_2		
30	70					5.4	1.7×10^{-3}
30	65		5			3.9	2.1×10^{-3}
30	60		10			4.7	
50		40	10			1.5	
50		45		5		7.6	1.1×10^{-3}
50		40		5	5	4.4	

[a] Actual salt cake from Tanks 105-S and 106-S; see Table III.

[b] Percent of ^{137}Cs in salt cake volatilized when charge was heated 3.5 hr from 25° to 1200° C and 24 more hr at 1200° C.

[c] Calculated from amount of ^{137}Cs evolved over last 24 hr-heating period at 1200° C.

Finally, Table XV also lists approximate rates at which ^{137}Cs volatilizes at 1200° C from molten salt cake glasses. Because of various experimental uncertainties these data should be regarded only as indicative of how fast ^{137}Cs volatilizes under such conditions. In particular, the experiments from which the rate data shown in Table XV were calculated were not designed to insure that all of the ^{137}Cs evolved from the molten glass over a 24-hr period and only that cesium accumulated in the second off-gas assemblage.

Effect of Melt Time

Large (14 to 35%) amounts of ^{137}Cs volatilized when salt cake glass formulations were heated very rapidly (0.5 min) to 1200° C (Table XVI). However, when such formulations were heated to 1200° C sufficiently slowly ($\geq$0.5 hr) solid state reactions between cesium and B_2O_3 and/or silicates which fix ^{137}Cs and prevent its volatilization proceeded to completion. These results thus further emphasize the desirability of "cold cap" operation of large-scale continuous melters for glassification of Hanford salt cake.

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TABLE XVI

VOLATILIZATION OF ^{137}Cs AS A FUNCTION OF MELT TIME

Charge Formulation, wt%					Time to Heat to 1200° C, hr	^{137}Cs Volatilized %
Salt Cake[a]	Basalt	Sand	B_2O_3	CaO		
30	60		10		0.008	23.9[a]
					0.5	1.3[b]
					3.5	4.7[b]
50		40	10		0.008	13.6[a]
					0.5	1.8[b]
					3.5	1.5[b]
50		45		5	0.008	34.9[a]
					0.5	6.3[b]
					3.5	7.6[b]

[a] Over 0.008-hr heating period.
[b] Over 3.5-hr heating period.

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