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GLASS MELTER OFF-GAS SYSTEM PLUGGAGES: CAUSE, SIGNIFICANCE, AND REMEDIATION (U)

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ABSTRACT

Liquid high-level nuclear waste will be immobilized at the Savannah River Site (SRS) by vitrification in borosilicate glass. Experimental glass melters, used to develop the vitrification process, have occasionally experienced problems with pluggage of the off-gas line with solid deposits. The deposits were determined to be mixtures of alkali rich chlorides, sulfates, borates, and fluorides with entrained insoluble particles of Fe_2O_3, spinel, and frit. The distribution and location of the alkali deposits throughout the off-gas system indicate that the deposits form by vapor-phase transport and condensation. Condensation of the alkali-rich phases cements the entrained particulates causing the off-gas system pluggages. The identification of vapor phase transport as the operational mechanism causing off-gas system pluggages indicates that deposition can be effectively eliminated by increasing the off-gas velocity. The cementitious alkali borates, halides, and sulfates comprising the off-gas line deposits were determined to be water soluble. Thus pluggages can be effectively removed with water and/or steam.

INTRODUCTION[1]

High-level liquid nuclear waste (HLLW) will be immobilized at the Savannah River Site (SRS) by vitrification in borosilicate glass. Glass will be poured into stainless steel canisters in the Defense Waste Processing Facility (DWPF) for eventual disposal in a geologic repository. Since the late 1970's, experimental glass melters have been used to develop the vitrification process for immobilization of the waste. Occasionally, these melters have experienced problems with pluggage of the off-gas line with solid deposits.

The 2/3 scale DWPF melter, designated the Scale Glass Melter (SGM), exhibited problems with off-gas line pluggages between the off-gas film cooler (OGFC) and the quencher. These pluggages were at greater distances from the off-gas line entrance than pluggages in previous research melters, e.g. the Large Slurry Fed Melter (LSFM). The SGM pluggages were not anticipated because the OGFC had been designed and tested during several LSFM campaigns and problems with off-gas line pluggages had been reported to have been alleviated.[1]

Use of the OGFC in SGM successfully minimized deposits at the off-gas system entrance but did not eliminate deposits farther along the off-gas system during Campaigns 7, 8, and 9. The design used in the 2/3 scale SGM is prototypic for the full scale DWPF melter. The 1/10th scale Integrated DWPF Melter System (IDMS) uses a similar system.

The current DWPF off-gas system design and operation are based on a hypothesis that pluggages near the off-gas line entrance are caused by adhesion of partially melted entrained particulates. Particulate adhesion was thought to be aggravated by insufficient cooling of the off-gas pipe. This hypothesis resulted in the use of air and/or steam to cool the off-gas. The 9th SGM campaign was run in a temperature-control mode for nine months and no deposits were observed to form in the off-gas line. The lack of deposition was attributed to temperature control at <350±25°C. Although off-gas velocities were not reported during SGM-9 operation in the temperature control mode, subsequent calculations indicated that the off-gas velocity had to be 70±5 fps in order to maintain the off-gas below 350±25°C.

Since initial startup, the IDMS was run in the recommended temperature control mode but at an off-gas velocity of only 40 fps. Off-gas deposits formed in the horizontal pipe near the OGFC during Campaigns 1 and 2 confirming that temperature control alone would not alleviate off-gas system pluggages.

The objectives of the current study were to determine the phase identification and chemistry of off-gas deposits taken from the 2/3 scale SGM, the 1/100th scale minimelter, and 1/10th scale IDMS. Once the phase chemistry and phase distribution as a function of distance along the off-gas line was determined, the mechanism responsible for deposit buildup was identified. When the depositional mechanism was understood, then the operating conditions necessary to eliminate deposition could be defined. Understanding the depositional mechanism and the phase chemistry also provided a remediation methodology for deposit removal.

EXPERIMENTAL

Off-gas pluggage samples were taken at known locations along the off-gas line after SGM-7. Samples from the off-gas line were also removed after the SGM-8 and SGM-9 Campaigns. Off-gas deposits from the 1/100th scale minimelter were examined for comparison as were samples from the IDMS melter Campaigns 1 and 2.

Each off-gas pipe sample was analyzed for crystalline phase content by x-ray diffraction (XRD). Since the waste glass component of the pluggage material is amorphous and cannot be detected by XRD analysis, X-ray fluorescence (XRF) analysis was employed to determine if the heavier elemental components of the waste glass were present.

Each sample was also analyzed by Scanning Electron Microscopy (SEM) coupled with the qualitative elemental analytic capability of Energy Dispersive Analysis by X-ray (EDAX). The off-gas samples were dissolved and chemically analyzed. The details are given elsewhere.[1]

RESULTS AND DISSCUSION

Chemistry of Off-gas Line Deposits[1]

The chemical analyses of the nine SGM-7 off-gas deposits revealed that they were enriched in Na, K, and Cs compared to the relative amounts in the waste glasses melted in SGM from startup. The deposits were also highly enriched in anions, primarily SO_4 and Cl. Small amounts of F were present as well. Enrichment in Cr, Fe, and B was also observed.

The deposits from the off-gas pipe entrance contained more Fe and B than the deposits further along the line indicating that entrained glass and iron-rich spinels were probably present as observed at the off-gas system entrance during the LSFM campaigns. The x-ray fluorescence (XRF) analyses indicated the presence of the heavier minor constituents of the glass, e.g. Ti, Zr, and Sr confirming glass entrainment.

Deposits further from the off-gas pipe entrance contained more Cr, Cl, and SO_4. Sodium and F were distributed evenly in the off-gas pipe deposits regardless of location. The initial chemistry, therefore, suggested that salt deposits, entrained spinel, and glass were the major species present.

The SGM-8 deposits were found in the same section of the off-gas system as the SGM-7 deposits. This section of the pipe had been cleaned after SGM-7 and dry feed (165 black frit) had been melted during Campaign 8. The chemistry of the deposits were similar to those of SGM-7 but the Cl concentrations were significantly higher.

The SGM-9 off-gas deposits were found further along the off-gas line between the off-gas header and the isolation valve. These deposits had Cl and F concentrations equivalent to those found in SGM-7 but were highly enriched in SO_4.

Samples of off-gas deposits from the 1/100th scale minimelter and the 1/10th scale IDMS were also analyzed. Samples of IDMS off-gas pipe deposits removed from close to the exit of the off-gas film cooler after Campaign 1 were analyzed. Loose deposits as well as deposits which were stuck on the pipe were examined. In general, the off-gas deposit chemistry was similar to that of the SGM deposits.

Phase Composition of Off-gas Line Deposits

The x-ray diffraction analysis of nine SGM-7 off-gas line deposits revealed very complex crystalline phase chemistry. The samples contained from six to twelve individual crystalline phases. Many of the phases were solid solutions of halide salts such as (Na,K,Cs)Cl. Pure NaCl, pure KCl, and mixtures such as $(Na_{0.4}K_{0.6})Cl$ can all be present giving distinctly different but closely overlapping x-ray spectra.

The crystalline portion of the SGM-7 deposits are primarily mixtures of (Na,K,Cs)Cl, $(Na,K,Cs)_2SO_4$, spinel of the $NiFe_2O_4$ type, Fe_2O_3 (believed to be an unreacted sludge component), SiO_2 and $Na_2B_4O_7$. Traces of KBF_4 and $(Na,K)CrO_4$ were also detected. The major constituent of each deposit is NaCl and either Na_2SO_4 or mixed $(Na,K,Cs)_2SO_4$. The SEM and EDAX analyses confirmed that white and yellow colored deposits were rich in the salt components S, Cl, K, and Na. The black colored deposits were enriched in glass and spinel components (Fe, Ni, Mn, Ti).

One amorphous species identified in the SGM-7 off-gas deposits was entrained glass. However, based on the known Li/B ratio of the glasses run in SGM, boron is enriched in great excess over Li. This indicates that boron enrichment is coming from a secondary amorphous source and not merely from entrained glass. Since x-ray diffraction analysis detected some poorly crystalline $Na_2B_4O_7$ in almost all the samples, the excess boron was determined to be present as amorphous or poorly crystallized $Na_2B_4O_7$.

The major phases identified in the SGM-8 deposits were (Na,K)Cl and $(Na,K)_2SO_4$ in agreement with the results of the chemical analyses. Other phases present were

$(Na_{0.5}K_{0.5})B_4O_7$, spinel, and Fe_2O_3. Only minor traces of KBF_4 were present as noted in the SGM-7 deposits.

The major phases identified in the SGM-9 deposits were $(Na,K)_2SO_4$ and (Na,K)Cl in agreement with the results of the chemical analysis. Entrained Fe_2O_3, spinel, and sulfur were also identified by x-ray diffraction. Entrained spheres of Si rich glass frit were observed by SEM and their composition identified by EDAX analysis.

Off-gas samples from the 1/100th scale minimelter and the 1/10th scale IDMS contained similar alkali and oxide species. X-ray diffraction analysis indicated that the major component of the "loose" deposits was entrained spinel. The major components in deposits stuck to the pipe were NaCl and Na_2SO_4. These deposits also contained significant amounts of $Na_2B_4O_7$, Na_2CrO_4, KBF_4, and sulfur. The SEM analysis confirmed that Na, K, Cs, Cl, and SO_4 were the major species present. A wide angle detector was used on the SEM-EDAX and the presence of B was confirmed in these deposits in the absence of other glass forming components such as Fe and Si. This data confirmed the presence of amorphous or poorly crystalline $Na_2B_4O_7$.

Phase Distribution for the SGM Off-gas Line Deposits

The x-ray diffraction and chemical analyses of the off-gas deposits indicate that the primary amorphous and crystalline phases are the following:

- Sodium/potassium/cesium salts
  $(Na,K,Cs)_2SO_4$, (Na,K,Cs)Cl, $(Na,K,Cs)BF_4$
- Sodium/potassium borate
  $(Na,K)_2B_4O_7$
- Sodium/potassium chromates
  $(Na,K)_2CrO_4$
- Oxides
  $NiFe_2O_4$ (spinel), Fe_2O_3, SiO_2, glass

A molar mass balance was calculated from the wet chemical analyses. The phases chosen were based on the five sodium/potassium rich phases and the residual oxides. The mass balance calculations provided a semi-quantitative measure of the phases in each off-gas deposit. The details of the mass balance calculations are given elsewhere.[1]

The relative abundances of the $(Na,K)_2SO_4$ and the (Na,K)Cl salts calculated from the mass balance were superimposed on a schematic of their relative positions along the SGM off-gas pipe (Figure 1). A similar schematic was made for the borate phases, the chromate phase, and the oxide phases (Figure 1).

From the schematics shown in Figure 1 it is readily apparent that the major salt deposits form further from the off-gas entrance while the major entrained oxides (glass, spinel, Fe_2O_3, SiO_2) are relatively constant regardless of position along the off-gas pipe. The chromate phase appears to be concentrated higher in the off-gas system line as well but the distribution is somewhat erratic. This may in part be due to contributions of Cr in the deposits from adhering Inconel 690 rather than due to vapor phase transport of Cr from the melt. This may also be due to redox effects since Cr^{6+} can be semi-volatile while Cr^{3+} can be transported as a particulate species.

The borate phases are concentrated at the off-gas system entrance and primarily along the top surfaces of the pipe. This is especially noticeable in the lack of borate phases in the portions of the off-gas line furthest from the entrance, e.g. in the vicinity of the SGM-9 deposits. Concomitantly, the chlorides and sulfates are at their maximum concentration along this portion of the line.

The phase distribution indicates that the alkali halides, chromates, and borates form by vapor phase transport and subsequent condensation. The borate phases, having a higher vapor pressure, condense lower in the off-gas line than the chlorides, fluorides, sulfates, and chromates. The oxide species are distributed evenly along the off-gas line and hence are deposited by entrainment and cemented in place by the condensing vapor species.

Deposition Mechanisms

Sodium borate, sodium sulfate, sodium chloride, and sodium fluoride deposits have been observed to form in commercial melters by condensation.[2-5] During melting of sodium borosilicate glass in commercial melters, sodium borate deposits occur in the middle sections of glass regenerators while the sodium sulfate and sodium chloride deposits form in the higher sections.[3-4] Potassium[2] and rubidium[5] behave similarly to sodium but condense at somewhat lower temperatures. This is in agreement with the identification of $Na_2B_4O_7$ and mixed $(Na,K)_2SO_4$-$(Na,K)Cl$ as the immiscible low melting (~700°C) phase found in the SGM off-gas deposits.[1]

The mode of formation of borate and sulfate deposits in commercial melters has been extensively studied.[2-6] Gaseous $NaBO_2$, $Na_2(BO_2)_2$, and $Na,Rb(BO_2)_2$ have been observed by mass spectrometric techniques over sodium borosilicate glass melts at temperatures between 533-880°C.[5] Condensation of salt components or metal oxides on the cold channel surfaces or on regenerator bricks has been defined as the operative mechanism of deposit formation at >627°C during commercial borosilicate glass melting.[3-4] Sodium, sulfur, and chloride-containing molecules are vapor phase transported toward the deposition surface. At the cold surface chemical reactions and condensation occur, causing a growing deposition layer of Na_2SO_4 and/or NaCl, NaF, and $Na_2B_4O_7$. Deposition of fine particles entrained from earlier condensation reactions is the operative mechanism of deposit formation at <527°C during commercial borosilicate glass melting.[3-4]

Alkali metaborates have also been observed in the off-gas systems of melters at the Pacific Northwest

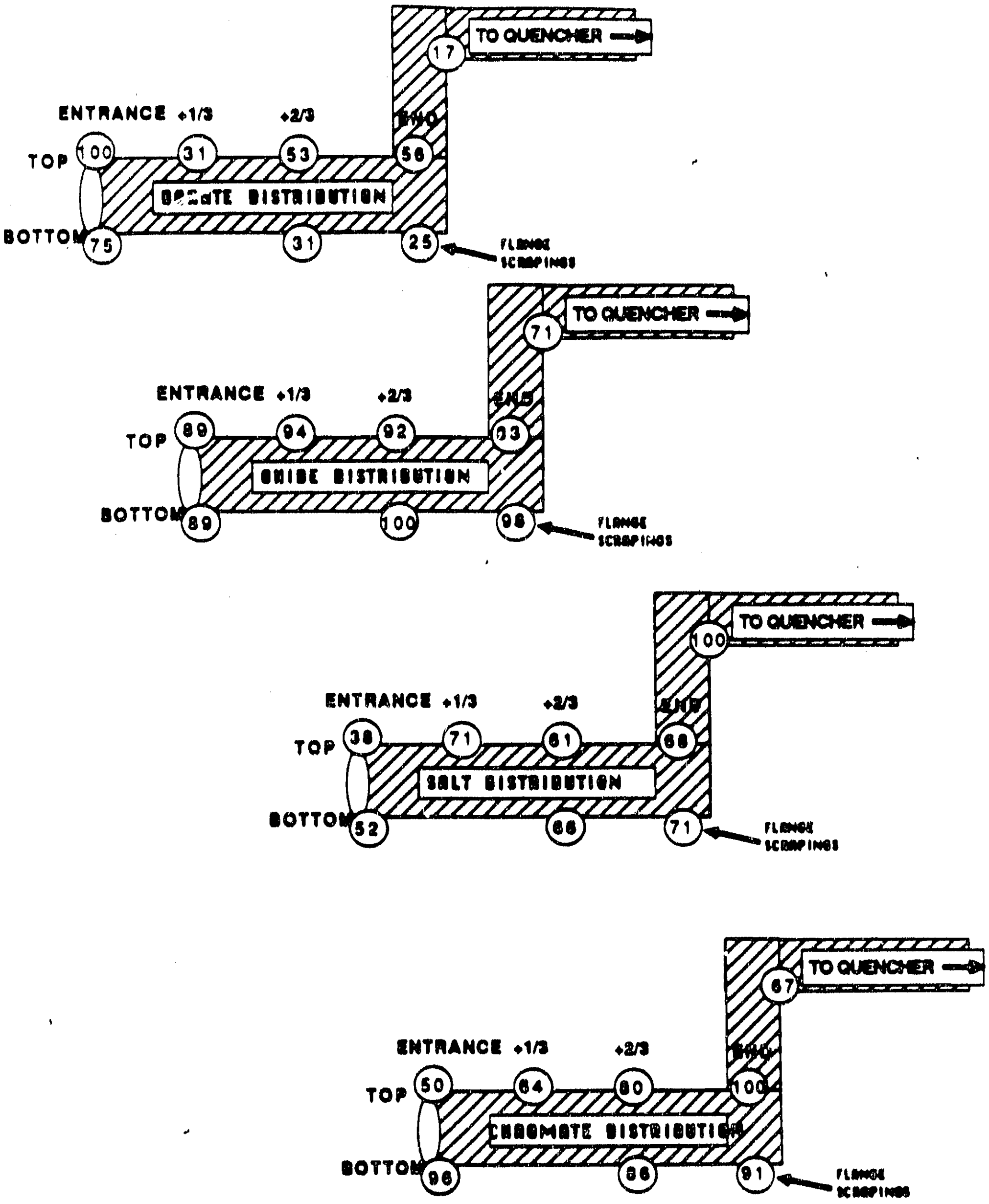

Figure 1. Schematic distribution of the relative % salt, oxide, chromate and borate phases from Scale Glass Melter off-gas Pluggages.

Laboratory.[7] The mechanism of formation has been attributed to feed entrainment and volatilization/ condensation.[8] Studies with High-Level Waste Glass (J-10) at the Japan Atomic Energy Research Institute demonstrated that cesium was found to vaporize as $CsBO_2$ and to condense and react with the steel chamber used to carry out the experiments.[9]

Vaporization of the alkali species (Na, Cs, and Li) from SRS glasses was extensively studied by Wilds in 1978.[10] This study demonstrated that the primary vapor species was $Li_2O \bullet B_2O_3$ and $Na_2O \bullet B_2O_3$. Increased vaporization of these alkali metaborates was observed with increased melt temperature, increased Na and Li concentrations in the glass, and increased time at temperature. No $Cs_2O \bullet B_2O_3$ was observed to vaporize and it was hypothesized that the Cs species vaporizing was gaseous Cs and CsO.

Mass spectrometric analyses of simulated SRS waste glasses in 1983 indicated that gaseous Na, Li, Cs, O_2, $NaBO_2$, and $LiBO_2$ were present above the melt at temperatures between 800-1150°C.[11-12] The glass studied did not contain K_2O and so KBO_2 was not observed but is predicted to form similarly to $NaBO_2$ and $LiBO_2$. In the presence of water vapor, which would be present in steam from the OGFC and/or from slurry feeding in DWPF, HBO_2 was the principal gaseous species detected.

Conditions of Deposition Versus Non-Deposition

Experience with waste glass melters has suggested that the minimum velocity of 50 fps[1] is more important than temperature in controlling off-gas deposition.[7] West Valley Nuclear Fuel Services (WVNFS) have never experienced off-gas line pluggages in the jumper section of their off-gas line. They attribute the lack of pluggage to never allowing their off-gas line velocity to fall below the 50 fps recommended by SRL[1] in the early 1980's (Table 1).

In summary, the critical off-gas line operating parameter appears to be velocity (Table 1). Although the temperaturos of the LSFM, SGM, PNL, and WVNFS melters varied, all have remained free of off-gas line deposition when the off-gas line velocity was >50 fps (Table 1).

Table 1. Summary of Conditions of Off-gas System Deposition and Non-Deposition.

Melter/ Campaign	**Velocity (fps)**	**Steam**	**Temp. (°C)**	**Off-gas Deposits**
LSFM-7	60	Yes	350-450	No
LSFM-9	60	Yes	350-450	No
SGM 6,7,8	nct reported	No	450	Yes
SGM-9	70±5	Yes	325 ± 25	No
IDMS	40	No	325 ± 25	Yes
PNL	>50	?	?	No
WVNFS	>50	?	?	Never

Remediation of Off-gas Deposits[1]

A hard piece of the SGM off-gas material was put in deionized water in an ultrasonic bath at room temperature for ~5 minutes. The cementitious portion of the material was water soluble and rapidly left a residue of dispersed black solid particles. The water was decanted and found to be highly enriched in SO_4, Na, K, Cl, Cs, Li, Ca, B and Cr. The SO_4 was the most abundant species. The dispersed black solid particles were dried and sent for x-ray analysis. Spinel of the $NiFe_2O_4$ type, Fe_2O_3, and pure SiO_2 were the main components of the insoluble particles.

The cementitious alkali borates, halides, and sulfates comprising the off-gas line deposits were determined to be water soluble. If pluggages occur beyond the off-gas line entrance, then the deposits can be effectively removed with water and/or steam. Therefore, if deposits do occur in the off-gas line, removable sections of the off-gas system, e.g. the jumper, could be water or steam cleaned. In addition, engineering designs are being investigated to take advantage of the water soluble nature of the off-gas deposits for in-situ cleaning so that the need for mechanical disassembly and cleaning of the highly radioactive (^{137}Cs and ^{106}Ru) off-gas line could be eliminated in DWPF.For example, an auxiliary off-gas line could be used while cleaning the plugged line in-situ with hot water. The alkali rich hot water could be recycled to the melt pool in a manner similar to slurry feeding or recycled to on of the feed preparation tanks such as the Slurry Mix Evaporator.

CONCLUSIONS

The chemistry and distribution of the alkali phases found in the SGM and IDMS off-gas deposits is the same as that found in commercial borosilicate glass melters. Sodium borate phases deposit closer to the off-gas line entrance while the more volatile alkali sulfates, chlorides, and fluorides form at greater distances from the entrance. The mode of formation is vapor phase transport and condensation.

The identification of vapor phase transport as the operational mechanism causing off-gas system pluggages beyond the entrance, indicates that deposition can be effectively controlled by high velocity air and/or steam. Velocities higher than 50 fps are necessary to transport the volatile species to the quencher rather than having them condense in the off-gas line. Velocity is, therefore, considered a more important criterion for controlling off-gas pluggage than temperature control.

The cementitious alkali borates, halides, and sulfates comprising the off-gas line deposits were determined to be water soluble. Thus, deposits can be effectively removed with water and/or steam.

REFERENCES

1. C.M. Jantzen, "Glass Melter Off-gas System Pluggages: Cause, Significance, and Remediation," USDOE Report WSRC-TR-90-205, Westinghouse Savannah River Co., Aiken, SC (March, 1991).

2. R. O. Williams and A. E. Pasto, "High-Temperature Chemistry of Glass Furnace Atmospheres," J. Am. Ceramic Society, 65, 602-606 (1982).

3. R. C. G. Beerkens and H. de Waal, "Simulation of the Condensation and Deposition Processes in Regenerators of Glass Furnaces," Glastech. Ber., 61, 36-42 (1988).

4. R. C. G. Beerkens and H. de Waal, "Experimental and Thermodynamic Characterization of Deposition and Condensation Products from Exhaust Gases of Glass Furnaces," Glass Technology, 28, 246-251 (1987).

5. M. Asano and T. Kou, "Vaporization of Sodium-Rubidium Borosilicate Glasses," Physics and Chemistry of Glasses, 30, 39-45 (1989).

6. B. J. Kirkbride, "The Chemical Changes Occurring During the Cooling of Hot Gases From Flat Glass Furnaces," Glass Technology, 20[5], 174-180 (1979).

7. H. C. Burkholder and R. A. Brouns, "Nuclear Waste Treatment Program Annual Report for FY 1986," U.S. DOE Report PNL-6325, Battelle Pacific Northwest Laboratory, Richland, WA (September, 1987).

8. H. C. Burkholder and C. R. Allen, "LFCM Vitrification Technology Quarterly Progress Report July-September 1986," U.S. DOE Report PNL-5904-4, Battelle Pacific Northwest Laboratory, Richland, WA (June, 1987).

9. H. Kamizono, S. Kikkawa, Y. Togashi, and S.Tashiro, "Volatilization of 137Cs and 106Ru from Borosilicate Glass Containing Actual High-Level Waste," J. American Ceramic Society, 72[8], 1438-1441 (1989).

10. G. W. Wilds, "Vaporization of Semi-Volatile Components from Savannah River Plant Waste Glass," U.S. DOE Report DP-1504, Savannah RIver Laboratory, E.I.duPont deNemours & Co., Aiken, SC (August, 1978).

11. J. W. Hastie, E. R. Plante, and D. W. Bonnell, "Vaporization of Simulated Nuclear Waste Glass," NBSIR 83-2731, National Bureau of Standards, Washington, DC (June, 1983).

12. D. W. Bonnell, E. R. Plante, and J. W. Hastie, "Vaporization of Simulated Nuclear Waste Glass," J. Non-Crystalline Solids, 84, 268-275 (1986).

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