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A Division of Southwest Research Institute™
6220 Culebra Road • San Antonio, Texas, U.S.A. 78228-5166
(210) 522-5160 • Fax (210) 522-5155

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U.S. Nuclear Regulatory Commission
ATTN: Mrs. Deborah A. DeMarco
Two White Flint North
11545 Rockville Pike
Mail Stop T8 A23
Washington, DC 20555

Subject: Programmatic Review of Paper Titled Nuclear Waste Glasses

Dear Mrs. DeMarco:

Enclosed is the subject paper that was prepared at the invitation of the Glass Researcher Magazine published bi-annually by the Center for Glass Research at Alfred University in Alfred, New York. The work cited in the paper is extracted from the reports published in the past under the TWRS program. Since the work is also of interest to the Repository program and contains information on the status of that program, it is submitted to you for programmatic review.

Please advise me of your programmatic review. Your cooperation in this matter is appreciated. If you have any questions regarding this paper, please feel free to contact Vijay Jain at (210) 522-5439.

Sincerely yours,

Budhi Sagar
Technical Director

VJ:jg
Enclosure

cc:
J. Linehan
B. Meehan
D. Riffle
W. Reamer
J. Greeves
K. Stablein
A. Campbell
B. Leslie
S. Wastler
D. Brooks
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L. Yang
D. Dunn
P. Maldonado
T. Nagy (contracts)

Washington Office • Twinbrook Metro Plaza #210
12300 Twinbrook Parkway • Rockville, Maryland 20852-1606

Nuclear Waste Glasses

On February 14, 2002, President George W. Bush recommended Yucca Mountain in Nevada for development as a geologic repository for the disposal of high-level nuclear wastes. This recommendation initiated a series of events including Nevada's Notice of Disapproval to the United States Congress on April 8, 2002, and the United States House of Representatives and Senate overrule of Nevada's disapproval on May 8, and July 9, 2002, respectively. If licensed by the U.S. Nuclear Regulatory Commission, the repository will receive 70,000 metric tons of heavy metal (MTHM) contained in approximately 11,750 waste packages with 65,333 MTHM coming from various types spent nuclear fuel and 4,667 MTHM from vitrified high-level radioactive wastes (HLW).[1] The 4,667 MTHM of vitrified HLW comprising approximately 40 million kg of glass will be contained in approximately 3,400 waste packages. In the United States, HLW vitrification is ongoing at the West Valley Demonstration Project (WVDP), West Valley, New York and the Defense Waste Processing Facility (DWPF), Aiken, South Carolina, while vitrification is currently planned for the HLW contained in 177 aging underground storage tanks at the Hanford site in the state of Washington. Similar wastes must also be processed at the Idaho National Engineering and Environmental Laboratory.

The joule-heated melter technology and induction melting technology are the two most widely accepted and mature technologies for vitrifying HLW.[2] Glass melting via joule-heating is used in the United States, Japan, Former Union of Soviet Socialist Republics, Germany, and Belgium, while glass melting via induction-type heating is used in France and England. HLW vitrification facilities are complex in design because components are maintained and operated remotely inside shielded walls to minimize radiation exposure to workers. Figure 1 shows a view of a HLW vitrification facility at the WVDP before the start of the radioactive operations.

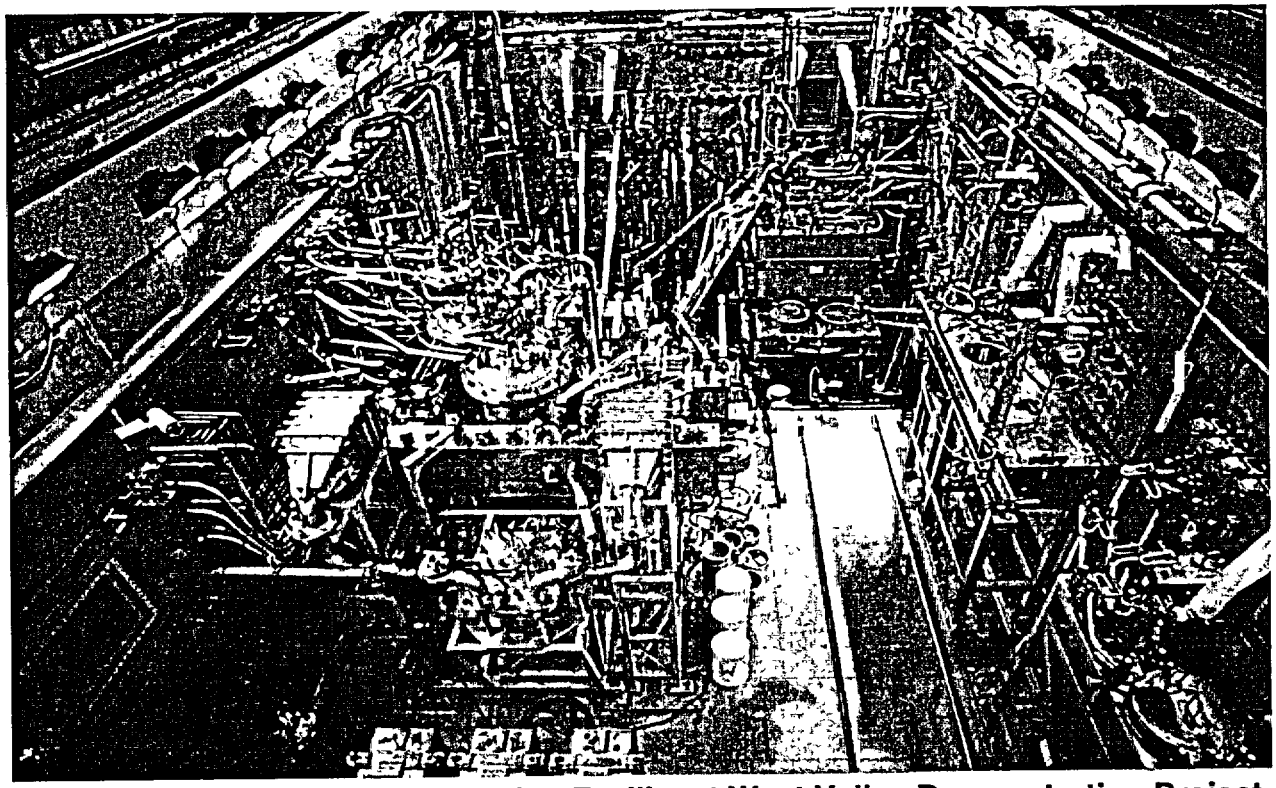

Figure 1. A View of the Vitrification Facility at West Valley Demonstration Project Before the Start of Radioactive Operations.

Research and development of waste forms for immobilization of liquid radioactive wastes began in the mid-1950s. Initial investigations included evaluation of waste forms such as borosilicate glass, phosphate glass, nepheline-syenite glass, a variety of polyphase ceramics, and bituminous and concrete materials. A systematic evaluation by the United States Department of Energy in 1977 selected borosilicate glass-based waste form as a reference waste form for immobilization of 9.16×10^8 Ci contained in 3.73×10^5 m^3 of HLW stored at four locations in the United States.[3] Presently, vitrified waste forms produced by melting HLW with glass forming oxides are being used in the United States, France, England, Germany, Belgium, Japan, the Former Union of Soviet Socialist Republics, and India as the preferred technology for the disposal of HLW. Except for the phosphate-based HLW glass used by the Former Union of Soviet Socialist Republics, borosilicate-based HLW glass is the preferred waste form for HLW around the world.

Both the vitrification technology and the guidelines for disposal at a proposed geological repository impose stringent requirements for producing an acceptable product, as shown in Table 1. The glass composition designed for vitrification should meet (i) processing constraints, such as viscosity, melting and liquidus temperatures, electrical conductivity, redox condition of the melt, solubility of noble metals, and sulfur and phosphate concentration; and (ii) product constraints, such as chemical durability, crystallinity, and glass transition temperature. Failure to meet these constraints on the design of glass composition and aspects of the glass melting process can potentially compromise radiological safety during operations and long-term performance of the repository. While borosilicate glass is widely accepted as a waste form of choice, the target compositions developed by waste producers are unique for each waste type and component concentrations vary significantly. Table 2 summarizes the range in which the target borosilicate glass compositions have been developed by various HLW glass producers.

Even though HLW glass production is underway at WVDP and DWPF, research and development is continuing to enhance melter designs and develop new glass compositions that can accommodate high concentrations of sulphur and a wider range of waste compositions, or increase production rates without impacting the quality of HLW glass or deteriorating melter life.

Table 1. Constraints in Developing Glass Compositions for High-Level Radioactive Waste

Constraint	Range	Technical Basis
Electrical conductivity (S/m)	10–100	The lower limit of 10 S/m for electrical conductivity is imposed on the glass melts at melting temperature to ensure the electrical conductivity of the glass melt is significantly higher than the electrical conductivity of the refractories surrounding the glass melt. The upper limit of 100 S/m for electrical conductivity is imposed to ensure the glass melt provides enough joule heating for melting without exceeding the maximum operating current density for Alloy 690 electrodes.

Table 1. Constraints in Developing Glass Compositions for High-Level Radioactive Waste (continued)		
Constraint	**Range**	**Technical Basis**
Viscosity (Pa-s)	2–10	The limits are imposed on glass melts at melting temperature to ensure the glass melt is fluid enough to homogenize and pour. If the viscosity of the melt is below 2 Pa-s (20 P), the glass melt could increase erosion of the refractory; volatilization of alkalis, boron, and radionuclides; penetration of melt along the refractory joints; or settling of noble metals. If the viscosity is greater than 10 Pa-s (100 P), glass melt could plug the pour spout during pour, have undissolved components in the melt, or crystallize at cold spots in the melter.
Glass transition temperature (T_g°C)	>400	At the time of shipment to a repository, the HLW producer certifies that, after the initial cool-down, the waste form temperature has not exceeded 400 °C. This product specification was established to ensure the waste form is in a solid form at the time of shipment.
Liquidus temperature (T_L°C)	1,050	In joule-heated melters operating at an average temperature of 1,150 °C, the T_L limit is set at 1,050 °C. If the lowest temperature in the melter is lower than the T_L of the melt, crystalline phases can precipitate and cause processing problems. If the crystalline phases are electrically conductive, electrical shorting could occur in the melter.
Redox	0.01–0.5 Fe^{2+}/Fe^{3+}	A glass melt is defined as extremely reducing if the Fe^{2+}/Fe^{3+} ratio is greater than one. Under such conditions, sufficient accumulation of conductive metals and metal sulfides could occur and short-circuit the melter. If the Fe^{2+}/Fe^{3+} ratio is less than 0.01, a glass melt is defined as extremely oxidizing. Under extremely oxidizing conditions, foaming is observed in the melter. Foam creates an insulating layer of gas bubbles between the cold cap and the melt, disrupting the thermal gradients in the melter.
Noble metal concentration		Noble metals such as Ru, Rd, and Pd in the HLW originate from the fission of U-235. Noble metals in the borosilicate glass melts have been a major concern in the HLW vitrification process because of their low solubility, high volatilization rate, and high electrical conductivity. In 1985, the accumulation of the noble metals on the floor of the Pamela melter, in Mol, Belgium, resulted in electrical shorting of a joule-heated melter.

Table 1. Constraints in Developing Glass Compositions for High-Level Radioactive Waste (continued)		
Constraint	**Range**	**Technical Basis**
Sulfur solubility	< 0.25 wt%	Borosilicate glass-based waste forms have limited sulfur solubility. The SO_3 solubility limit is established based on the operating redox range of 0.01 to 0.5. In the WVDP and DWPF waste forms, SO_3 levels are maintained below 0.25 wt% to avoid formation of an immiscible sodium sulfate phase in the melt.
Chemical durability		Producers of HLW glass ensure product quality by conducting durability test per ASTM C1285 and comparing results to a standard EA glass.[4] Durability of the HLW is important to meeting the dose limits specified in 10 CFR Part 63.
Phase stability		Glass compositions are designed to ensure that liquid-liquid phase separation or crystallization do not occur on cooling the melt. The phase stability requirements include development of a temperature-time-transformation (TTT) diagram for each projected waste type. Phase separation and crystallization processes can result in the development of an inhomogeneous microstructure that may affect the reliability of the waste glass process and product performance including the durability.

Table 2. Borosilicate Glass Composition Range in Which Target Compositions Were Produced			
Component	**Minimum (mol %)**	**Average (mol %)**	**Maximum (mol %)**
SiO_2	37.8	52.6	58.7
B_2O_3	4.8	12.8	21.0
Na_2O	4.3	11.8	25.3
Li_2O	0	6.9	10.8
Al_2O_3	0.1	3.2	11.4
Fe_2O_3	0	2.6	6.1
CaO	0	2.3	6.2
MgO	0	1.8	10.0
TiO_2	0	1.0	4.6
ZrO_2	0	0.9	2.7

Table 2. Borosilicate Glass Composition Range in Which Target Compositions Were Produced (continued)			
Component	Minimum (mol %)	Average (mol %)	Maximum (mol %)
MnO_2	0	0.7	3.0
K_2O	0	0.5	3.8
P_2O_5	0	0.2	1.3
U_3O_8	0	0.1	0.4

References

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Acknowledgment

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