# Fusion cast refractories: Roles of containment

**By Kevin Selkregg**

*Refractory linings in glass furnaces are a critical component of glass-based applications, including encapsulation of nuclear waste through vitrification. Careful design of these lining materials can ensure safe and long-lasting methods of nuclear waste storage.*

Credit: Monofrax

The role of glass in modern society is evident everywhere—from windows and wine bottles to car windshields and durable device touchscreens.

Industrial glass manufacturers require highly engineered high-temperature furnaces to contain glass in its molten state (3,000°F–3,200°F, or 1,600°C–1,800°C) so that convections in the melter allow proper mixing as well as melting of incoming raw batch materials. After the refining process, in which dissolved gases are allowed to escape, the glass has a chemical homogeneity ready for formation of the final article. This molten glass must be contained by a refractory lining in the furnace to allow safe operation over an extended time period to economically and efficiently manufacture high-quality glass products.

### Evolution of glass furnace refractory linings

Toward the end of the 19th century, fireclay, a bonded alumina refractory, was the glass furnace refractory lining of choice. This progressed to a better quality of fireclay, and later, the refractory lining package included bonded silica brick, which easily dissolved but did not affect glass quality. However, the furnace life of glass-contact silica refractory was only 8–12 months.

In the early 20th century, sillimanite ($Al_2O_3 \cdot SiO_2$) and then mullite ($3Al_2O_3 \cdot 2SiO_2$) found their way into use as bonded refractory materials that performed better than fireclay and silica bricks.[1,2] Typically, these refractory materials are pressed with binders to maintain geometry and fired at high temperatures to create a bonding phase for strength. These refractory bonded shapes typically have a porosity (~10–15%) that will severely reduce corrosion resistance in contact with a slag or glass at high temperatures, not to mention high solubility of their components.

Enter the advent of a refractory manufactured by fusing molten oxide powders at high temperatures (~3,800°–4,000°F). The process of fusion casting bypasses conventional bonding of refractory bodies mentioned earlier by developing crystalline intergrowths capable of exceptional corrosion resistance due to high density of the body. The batch, after dry blending, is fed to an electric arc furnace for fusion by energy released in arc-resistance paths. The furnace melting the material tilts to pour this liquid into molds designed for final applications.[3] Monofrax LLC pioneered this technology in the late 1930s with high-alumina fused cast refractory materials and, later, many compositional evolutions.

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Credit: Monofrax

Figure 1. (A) New AZS furnace lining during inspection before delivery and installation. (B) Corroded AZS furnace lining after 6.5 years of service in a soda-lime glass furnace. (C) Close-up of a corroded AZS furnace lining panel after 6.5 years of service in a soda-lime glass furnace.

After the Second World War, the refractory of choice for lining glass furnaces soon became a material called AZS, an acronym for a composition consisting of alumina, zirconia, and silica. Manufacture of fusion-cast AZS resulted in a refractory material with low porosity (~1%), high density, and good corrosion resistance—critical factors to extend life of the glass furnace. The material increased furnace life from ~18 months to 3–5 years, allowing furnaces to operate at higher temperatures and at greater throughput.[1,2]

Corrosion resistance of AZS results from its low porosity and high density, as well as the presence of zirconia, a highly insoluble phase. Even though the AZS refractory lining in contact with glass extends high-temperature glass furnace life dramatically over bonded refractory materials, furnace life cannot continue indefinitely. Corrosion and erosion of the lining will occur, eventually curtailing furnace operation until the lining is repaired or replaced. Figure 1A shows a new AZS furnace lining before delivery and installation, contrasted with a corroded AZS furnace lining after 6.5 years of service in a soda-lime glass furnace in Figures 1B and 1C.

Glass quality in soda-lime, borosilicate, and high alumina–silica glass compositions is critical to achieve clarity and strength because, without these properties, the items of interest will fail in their designed applications. This places high demand for quality refractories in contact with glass to not alter critical properties of the glass by refractory defects and dissolved refractory components. The images in Figure 1 of corroded AZS fused cast refractory lining are a revealing testament to the erosion of refractory linings during a glass furnace campaign.

The final glass article, be it a bottle or window, will actually have some trace of the refractory components (e.g., ~0.07% $ZrO_2$) dissolved in its structure, although at a level that does not affect required glass clarity and strength. Refractory lining in a typical glass furnace is designed to account for the types of corrosion encountered at molten glass contact or by corrosive vapor species in non-glass contact regions at temperatures of ≥2,700°F (1,500°C).

The philosophy in glass furnace refractory design is to ensure corrosion equivalency of differing refractory materials in the whole furnace, so the term of the campaign is not prematurely interrupted due to a single refractory region failure.

There are many compositional varieties of fusion-cast refractories available beyond AZS, such as high zirconia, high alumina, magnesium spinel, and chrome–magnesium–aluminate castings. Monofrax LLC supplies several compositional groups (~12 currently) to diverse glass manufacturing industries, including flat glass, containers, fiberglass, and, more recently, tough, thin glass touchscreen surfaces for electronic devices.

AZS fused cast materials such as Monofrax CS-3 and CS-5 are typical glass contact and non-glass contact mate-

## Capsule summary

### CONTAINMENT

Disposal of nuclear waste is a complex problem—one solution is vitrification, in which glass is used as a containment medium to stabilize radioactive waste.

### DESIGN

As with industrial glass furnaces, refractory designs for nuclear waste vitrification melters call for a variety of refractories that corrode equivalently. Refractory linings in the glass furnace are a critical component of molten glass containment for glass articles.

### LONGEVITY

Nuclear applications have already generated thousands of tons of nuclear waste, and that amount will continue to increase. Although operational challenges still exist in melters, vitrification provides a proven method of nuclear waste storage.

rials, while high-alumina materials such as Monofrax M and H are used in lower temperature glass contact refiner and distributor regions. Chrome/alumina/magnesia-bearing materials, such as Monofrax K-3 and E, are often used in weir walls and throat cover blocks, which require the highest level of corrosion resistance and can tolerate potential chrome coloration.

## Clarity to containment

On December 2, 1942, a team of 49 scientists, led by Enrico Fermi, proved that a self-sustaining nuclear chain reaction could be initiated. Conducted under Stagg Field of the University of Chicago, this experiment, called the Chicago Pile-1 reactor, became the integral first step of the Manhattan Project to develop the atomic bomb.[4]

In the midst of this dash to successfully create a controlled nuclear chain reaction, there is no known reference that any of these scientists foresaw the immensity of the amount of nuclear waste that harnessing such energy in weaponry and power generation would create.

However, as of January 2009, the amount of spent nuclear fuel from the 104 nuclear reactors operating within the United States alone reached 64,000 metric tons.[5] In the U.S., defense and weapon-related activities are another source of waste, with the largest quantities created in the early days of nuclear weapon development and testing.

The U.S. Department of Energy officially discontinued reprocessing spent nuclear fuel in 1992, although the U.S. has generated 347,300 $m^3$ of waste incidental to reprocessing.[6] Most of this liquid high-level waste (HLW) is stored in underground tanks at the Hanford site in Richland, Wash., and the Savannah River site in Aiken, S.C. Another portion of HLW was calcined to a dry powder and is stored at the Idaho National Laboratory in Idaho Falls, Idaho.

Weapons-grade plutonium production stopped in the 1980s. However, the consequence of this material lingers on in the form of waste. The current emphasis of nuclear fission is electricity generation in the U.S., but not to the extent of its role in other countries, such as Canada and China.

In the public sector, developing uranium fuel to produce power from nuclear plants generates different forms of waste (e.g., mine mill tailings, conversion, enrichment)—which all will need disposal. Rod Ewing[7] states that "...the complexity of the nuclear waste disposal problem has delayed final choices of waste disposal sites in most countries that have nuclear waste inventories. So much so that, there are, at present, no operating [geologic] nuclear waste repositories for spent nuclear fuel from commercial nuclear power plants or for HLW from the reprocessing of spent fuel."

Complexity in the disposal of nuclear waste is partially due to the variety of waste compositions that ultimately drive the need for different glass containment formulations. Waste containment plant designs are dictated by radioactive loads, which may require fully remote designs or permit a hands-on approach. At the Hanford and Savannah River sites, HLW is further separated into a smaller volume containing most of the radioactivity and a larger volume of contaminated liquid with much lower

radioactivity (low activity waste, or LAW), which has a different disposal strategy. However, each facility treats LAW differently—Savannah River grouts LAW, while Hanford vitrifies it. Regardless of the means, nuclear waste must be reduced to a solid form before disposal and must resist leaching.

## Vitrification

The term vitrification connotes involvement of glass, which serves as a host medium to stabilize radioactive waste. Durability is the top priority for containing radioactive waste for thousands of years. This contrasts with other applications, such as commercial glasses designed for optical clarity.

| Table 1. Soda-lime glass composition typical for flat glass and examples of vitrification melter glass chemistries | | | | | | |
|---|---|---|---|---|---|---|
| Wt% | Soda-lime[a] | HLW[b] | WDVREF6[c] | SRL-EA[d] | LAWA24[e] | AZ-101[f] |
| $SiO_2$ | 71.7 | 44.9 | 43.5 | 45.9 | 35.4 | 38.47 |
| $Al_2O_3$ | 1.85 | 5.1 | 5.4 | 3.4 | 12.4 | 7.84 |
| $CaO$ | 7.1 | 6.7 | 0.7 | 1.1 | 3.3 | 0.54 |
| $MgO$ | 3.9 | 4.4 | 1 | 1.6 | | 0.12 |
| $Na_2O$ | 14.1 | 11.6 | 8.3 | 16.9 | 20.0 | 17.81 |
| $K_2O$ | 0.7 | 0.1 | 5 | | 5.5 | 0.32 |
| $B_2O_3$ | | 12.3 | 14.5 | 11.3 | 6.1 | 7.63 |
| $Li_2O$ | | 2.2 | 4.1 | 4.3 | | 1.9 |
| $BaO$ | | 3.5 | | | | 0.09 |
| $MnO$ | | | 1.2 | 1.6 | | 0.33 |
| $V_2O_5$ | | 1.5 | | | | |
| $Fe_2O_3$ | 0.1 | 3.4 | 12.2 | 10.8 | 6.0 | 17.5 |
| $CeO_2$ | | 1.9 | | | | 0.19 |
| $Cr_2O_3$ | | 0.3 | 0.1 | 0.3 | 0.3 | 0.16 |
| $SO_3$ | 0.4 | 0.7 | | | 0.5 | 0.08 |
| $NiO$ | | 0.4 | 0.3 | 0.8 | 0.1 | 1.5 |
| $Sb_2O_5$ | | 0.5 | | | | |
| $P_2O_5$ | | | 1.3 | | 1.7 | 0.31 |
| $ZrO_2$ | | | 1.4 | 0.6 | 3.0 | 3.97 |
| $TiO_2$ | | | 0.9 | 0.8 | | 0.03 |
| $ZnO$ | | | | | 3.0 | 0.02 |
| $La_2O_3$ | | | | | | 0.22 |
| $Nd_2O_3$ | | | | | | 0.17 |
| $CdO$ | | | | | | 0.62 |
| $SnO_2$ | | | | | | 0.1 |
| $CuO$ | | | | | | 0.04 |
| Other | | | | | 2.3 | |
| | 99.85 | 99.5 | 99.9 | 99.4 | 99.6 | 100.0 |

[a] Flat glass industrial furnace, Glaverbel S.A. Belgium.
[b] China simulated HLW waste, Karlsruhe Nuclear Research Center, Germany.[18]
[c] West Valley, NY.[19]
[d] Savannah River, EA Glass.[19]
[e] Hanford Low Activity Waste Vitrification Project, 2002.[19]
[f] PNNL, glass for research scale melter test.

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Figure 2. (A) A melter box consisting of Monofrax K-3 during inspection before shipment to the Hanford site. (B) Low activity melter unit containing K-3 melter box being readied for use at Hanford.

At Savannah River and Hanford sites, radioactive waste is transitioned into a molten borosilicate glass through a variety of steps involving a liquid slurry with dry additives that form a blanket on the glass called a cold cap. The bottom portion of this cold cap melts into a foamy glass and ultimately melts into the pool, which is poured into a robust stainless steel canister (~1–3 m high) and allowed to cool, forming a solid matrix.

Containers are welded shut, ready for storage and final disposal. This encapsulation in molten glass and solidification in final storage containers is called vitrification and is a suitable and adequate process for management of ILW and HLW.

Figure 2A shows a K-3 melter box in the setup area at Monofrax with a similar layout to soda-lime industrial glass tanks. The melter box contains glass slurry as nuclear waste is encapsulated within the glass. This box is a portion of the larger unit at the Hanford site (Figure 2B).

Refractory design experience, philosophy, and technology for melting of industrial commercial glasses (e.g., soda-lime, borosilicate, and high-alumina cover glasses) has been transferred in a similar fashion when designing the nuclear waste vitrification melter. In this case, the design uses another property of glass.

Unlike the clarity and strength necessary in soda-lime and borosilicate glass,

the chemistry of encapsulating glass in nuclear waste treatments is unique in its ability to immobilize radionuclides. Specific oxides determine various properties in soda-lime glass, such as melting point, mechanical properties, or color. For example, iron is incorporated at low levels (0.1–2.0% iron oxide) in soda-lime glass to reduce the effect of harmful UV rays for construction glass.[8]

Design of the glass composition necessary for nuclear waste encapsulation involves a complicated selection process with non-radioactive glass-forming additives. These chemistries are tailored to create a favorable viscosity–temperature relation, meaning radionuclide volatilities are not in play.[9] In this case, boron has an important role in reducing glass viscosity at temperatures below radionuclide volatility temperatures of >1,200°C.

Vitrification is a particularly attractive immobilization route because the glassy product has high chemical durability.[10] Borosilicate glass contains waste material through direct chemical incorporation into the glass structure (i.e., dissolution), although some studies also have evaluated the feasibility of physically encapsulating solid wastes. The durability of borosilicate glass allows storage for thousands of years, even under conditions of irradiation by incorporated radioactive materials, which do not crystallize the oxide glass.

The temperatures encountered in vit-

rification melters (~1,050°C–1,200°C) are considerably lower than in commercial soda-lime glass tanks (~1,500°C–1,600°C). Table 1 lists soda-lime glass compositions typical for flat glass, alongside some examples of vitrification melter glass chemistries.

There are numerous critical components of the vitrification melter used to heat glass to 1,050°C–1,150°C, not the least of which is the refractory lining. Monofrax has manufactured a chrome-bearing fused cast refractory designed for this lining for over 30 years, since the beginning of the process of encapsulating nuclear wastes. In one instance at Savannah River National Laboratory, the designed life of this lining was estimated to be 2–6 years.[11] However, in actual practice at SRNL, the life of Melter #1 was 8.5 years and Melter #2 was >14 years, eventually shutting down due to mechanical failures that were not refractory related.[12]

## Corrosion in soda-lime glass tanks

Corrosion kinetics and byproducts of fused cast refractories in contact with soda-lime glasses of the container and flat glass industries are well known. AZS refractories have three microstructural components: zirconia dendrites, a coprecipitate component of zirconia and corundum, and a high-alumina glass.

When the AZS lining interacts with molten glass, there is typically a corrosion reaction layer at glass contact that remains attached to the lining. Continued corrosion takes place by erosion of this layer and, in some cases, may "peel" off, creating some glass quality problems.

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**Types of nuclear waste**

HLW = High level waste—highly radioactive due to reprocessed nuclear fuel
ILW = Intermediate level waste—requires shielding when handling
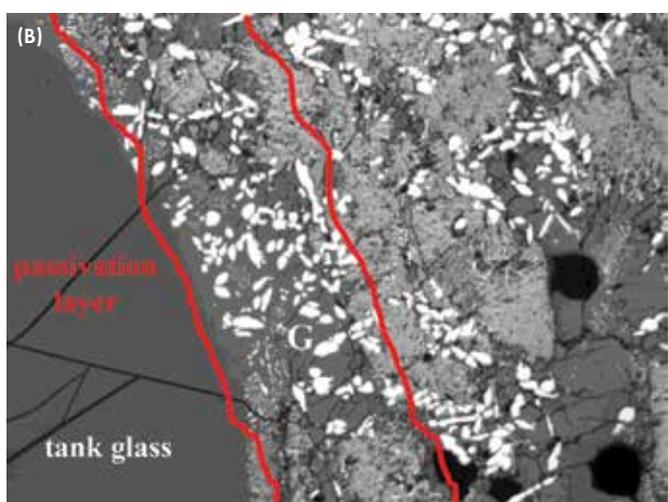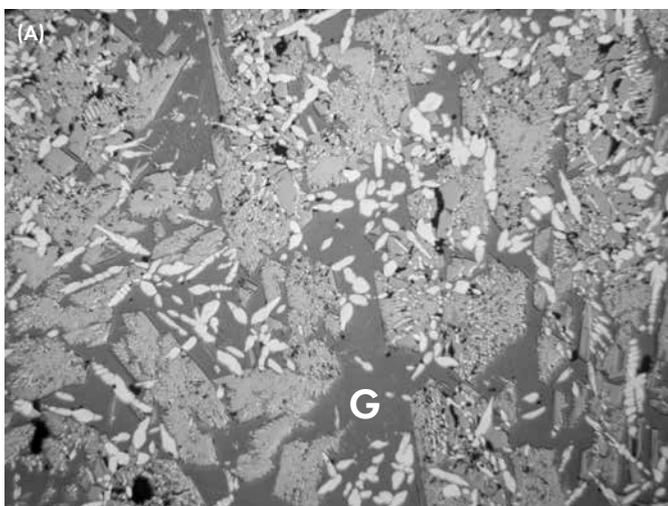LLW = Low level waste—contaminated by radioactive materials, but not inherently radioactive

Figure 3. Electron micrographs of (A) virgin AZS and (B) corroded AZS.

Table 2. Chemistry of glass in the AZS glass phase, soda-lime tank glass, and passivation layer

| Wt% | AZS glass phase | Passivation layer | Sodalime tank glass |
|---|---|---|---|
| $Al_2O_3$ | 23.2 | 32.0 | 1.2 |
| $SiO_2$ | 68.0 | 46.0 | 74.0 |
| CaO | 0.2 | 3.3 | 10.0 |
| $Na_2O$ | 6.5 | 15.5 | 14.0 |
| $Fe_2O_3$ | 0.3 | 0.1 | 0.0 |
| $K_2O$ | | 0.3 | 0.0 |
| MgO | | 1.0 | 0.2 |
| $ZrO_2$ | 1.8 | 1.9 | |
| Total | 100.0 | 100.0 | 99.5 |

This thin reaction layer, often called the passivation layer ("G" in Figures 3A and 3B) because it serves to "passivate" further corrosion, is a byproduct of incongruent dissolution into the tank glass. Alumina in the coprecipitate alumina–zirconia component of AZS goes into solution at the glass–refractory interface, creating a layer of highly aluminous glass with undissolved zirconia (Figure 3 and Table 2).

Corrosion with soda-lime glass is not restricted to the immediate glass contact, however, as the glass phase component of AZS provides a pathway for diffusing alkali and alkaline earth species, such as potassium, sodium, magnesium, and calcium. Alkalis are more rapid diffusers than alkaline earths, as observed by Kasselouri et al.[13] as well as others—potassium and sodium species migrate to deeper depths than magnesium and calcium. Consequently, alkalis such as potassium and sodium promote corrosion of the corundum primary phase at depths into the AZS body beyond the immediate glass–refractory contact.

## Corrosion in vitrification melters

Facilities active in vitrification of nuclear waste cannot afford failure of the melter due to refractory lining failure either by excessive corrosion or spalling. During the life of the melter, different glasses formulated due to differing waste compositions can have a variable impact on the refractory corrosion rate. Care must be taken to not formulate glasses that will be highly aggressive to the refractory.

Some of the most corrosion-resistant refractory materials available contain chromium oxide as a major component (e.g., Monofrax K-3 and E). Since the beginning of vitrification of nuclear waste, Monofrax K-3 chrome refractory has been a refractory of choice for lining melters in the U.S. and, in later years, Japan.

Chromium oxide is more insoluble than even zirconia in most glasses, making it a desirable component of refractory lining. Potential coloration of the glass by chrome refractories is a concern in soda-lime container and flatglass industries, but is not an issue for nuclear waste glass.

***What are the chemical and microstructural factors that make a chrome refractory, such as Monofrax K-3, perform so well as the glass contact refractory liner in vitrification reactors?***

As aforementioned, fused cast materials such as K-3 have low porosity and an interlocking, tight microstructure. The typical microstructure of Monofrax K-3 is a binary phase assemblage primarily of an $(Mg,Fe)O \cdot (AlCr)_2O_3$ spinel, and an $R_2O_3$ ($Cr_2O_3$-$Al_2O_3$ solid solution) phase, with minor glassy phase and low level reduced iron as free metal at grain boundaries. Further, the $R_2O_3$ phase is present as chemically inhomogeneous cored grains, with relatively $Cr_2O_3$-rich centers and relatively $Cr_2O_3$-poor rims (Figure 4).

When in contact with melter glass, Monofrax fused cast chrome materials (K-3 and E) react with glass in an incongruent fashion (as in AZS in contact with soda-lime glass), leaving a byproduct at the glass–refractory interface. Magnesium and aluminum are the most soluble components of K-3, generally leaving the most insoluble component, $Cr_2O_3$, behind at the corrosion interface.

Monofrax K-3 in contact with waste glass simulant at the SRNL melter was characterized after service in 1984.[14] Nickel and iron in the glass chemically behaved as a spinel former at the interface to create a nickel–iron–chrome spinel layer, somewhat metastable in the melter environment. This layer also inhibits further reaction at the interface by "passivating" corrosion rate at the glass contact. This chromium-rich spinel "skin" containing nickel is thermodynamically more stable

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## West Valley, NY case study

West Valley Demonstration Project in western New York was a site for private reprocessing of spent nuclear fuel as part of a program to make this a commercialized enterprise in the 1960s.[A]

This business venture was set up under a private company called Nuclear Fuel Services Inc., with construction beginning in 1963 and completed in 1966. From 1966–1971, 640 metric tons of fuel from defense and commercial power reactors were reprocessed, more than half of which came from the Hanford nuclear reactor.

When operations at this facility halted in 1972 for modifications to increase reprocessing capacity and efficiency, the Atomic Energy Commission at the same time established new regulations for reprocessing spent nuclear fuel. These new regulations affected the West Valley facility by dramatically increasing operational costs, making it too costly to continue under its design.

Nuclear Fuel Services withdrew from this business in 1977 and turned it over to the state of New York to deal with the site. Eventually it took an "act of Congress" in 1980 to create the West Valley Demonstration Project (WVDP) Act to deal with what now became a "clean-up," rather than a business venture of reprocessing spent nuclear fuels.

A key requirement and high priority of the WVDP Act was solidification of HLW, because LLW could be dealt with by incorporation into grout and disposal at the Nevada Test Site, which contains 20,000 71-gallon drums.[B] The consequence of reprocessing 640 metric tons of fuel during its short business operation was to create 600,000 gallons of liquid HLW. Higher-activity waste was mixed with a borosilicate glass frit, melted, poured into 275 stainless steel canisters, and solidified—i.e., vitrified—which continued during 1996–2002.



Schematic of West Valley Demonstration Project melter. Reprinted from: J.D. Vienna, "Nuclear waste vitrification in the United States: Recent developments and future options," *Int. J. Appl. Glass Sci.*, **1** (3), 309–321 (2010).



The melter, shaped like an inverted prism, was 6 feet deep and continuously received a water-saturated feed slurry at a rate of 20 gallons/hour. Wastes and glass formers melted into the glass pool, where they mixed by natural convection at 1,050°C–1,150°C, with a 2–3 day residence time before being transferred to stainless steel canisters. The melt was slowly poured into these ten-foot canisters over a period of 63 hours.

The lining in that melter cavity consisted of Monofrax K-3 fused cast chrome refractory—the first of many applications of Monofrax K-3 in vessels vitrifying radioactive HLW. However, even though most of the lining consisted of K-3, other portions contained other Monofrax fused cast material. Monofrax E (78% $Cr_2O_3$) composed two riser blocks of the overflow chambers because of its higher thermal conductivity to maintain a high glass temperature in the externally heated riser. Non-glass contact regions of the plenum area of the melter cavity consisted of high-alumina Monofrax H fused cast material because of its resistance to vapor corrosion and thermal shock.
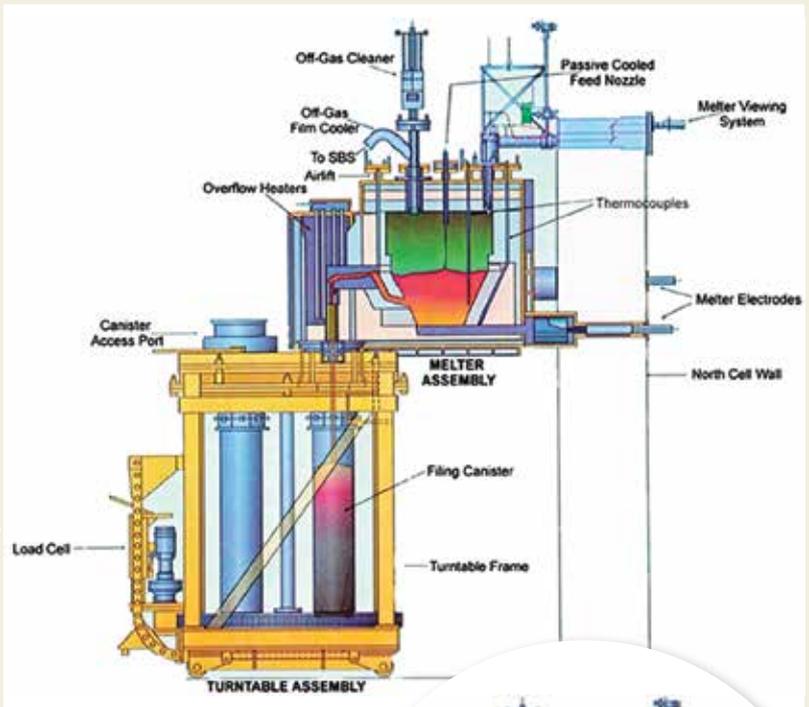
Therefore Monofrax's involvement in vitrification of ILW and HLW began in the mid-1980s—currently reflecting more than 30 years of refractory experience in this application. During this period, additional facilities have adopted Monofrax K-3 in melters, including the following, some of which are not yet operational.[C]

- Savannah River Site's Defense Waste Processing Facility and the Duratek Duramelter 5000 unit M-Area facility in South Carolina
- HLW and LAW treatment melters in Hanford, Wash.
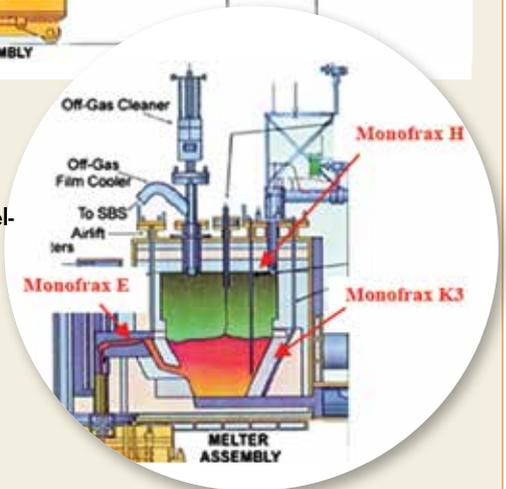- Japan Nuclear Fuels Limited HLW melters in Rokkasho, Japan

[A]D.E. Carl, J. Paul, J.M. Foran, R. Brooks, "West Valley Demonstration Project Vitrification Process Equipment Functional and Checkout Testing of Systems (FACTS)," West Valley Nuclear Services Co., Contract No. DE-AC07-81NE 44139. September 30, 1990.

[B]J.P. Curcio, C. Dayton, D. Garber, G. Gorsuch, "Process improvements result in schedule and cost savings for waste shipping campaign – 8456," WM2008 Conference, Phoenix, Ariz., February 24–28, 2008

[C]C.M. Jantzen, K.J. Imrich, J.B. Pickett, K.G. Brown, "High chrome refractory characterization: Part II. Accumulation of spinel corrosion deposits in radioactive waste glass melters," *Int. J. Appl. Glass Sci.*, **6** (2), 158–171 (2015). ∎
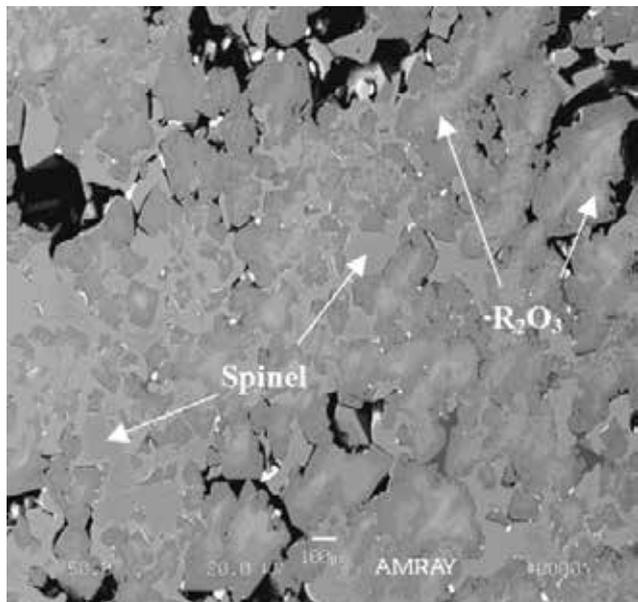
**Figure 4. Electron micrograph of Monofrax K-3 showing (Mg,Fe)O•(AlCr)₂O₃ spinel phase and the R₂O₃ (Cr₂O₃-Al₂O₃ solid solution) phase. The R₂O₃ phase is present as chemically inhomogeneous cored grains.**
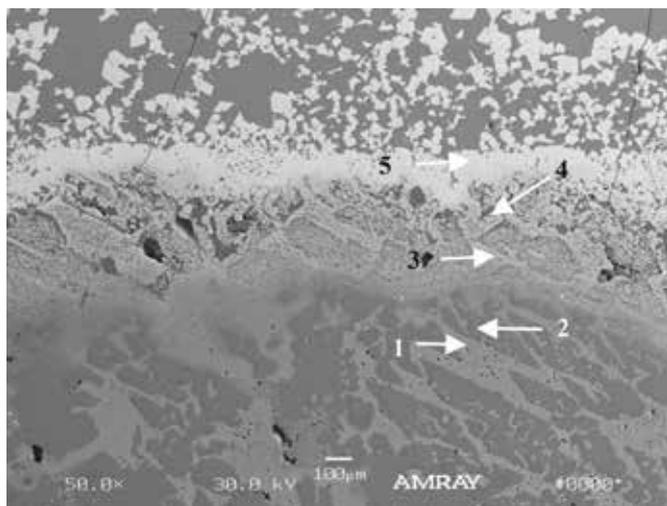
Figure 4. Electron micrograph of Monofrax K-3 showing $(Mg,Fe)O \cdot (AlCr)_2O_3$ spinel phase and the $R_2O_3$ ($Cr_2O_3$-$Al_2O_3$ solid solution) phase. The $R_2O_3$ phase is present as chemically inhomogeneous cored grains.
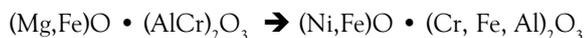


Figure 5. Scanning electron micrograph of the glass–K-3 interface at the bottom of the melter, revealing secondary phase formation at the reaction layer. Phases 1 and 2 are spinel and $R_2O_3$ solid solution, respectively. Phases 3, 4 and 5 are spinels with increasing nickel content and oxidized iron closer to the glass.

| Table 3. Phase compositions present in the glass–K-3 interface at the bottom of the melter | | | | | |
|---|---|---|---|---|---|
| Wt% | 1 | 2 | 3 | 4 | 5 |
| MgO | 10.3 | | 6.4 | 2.5 | |
| FeO | 18.2 | | 19.3 | | |
| Fe₂O₃ | | | | 39.6 | 65.7 |
| Al₂O₃ | 44.1 | 81.5 | 41.4 | 15.1 | 1.0 |
| Cr₂O₃ | 27.4 | 18.5 | 26.5 | 25.0 | 4.1 |
| NiO | | | 6.4 | 16.9 | 28.7 |
| MnO | | | | 1.0 | 0.5 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

with this melter consisted of eleven weeks at temperatures of 1,050°C–1,150°C to observe the behavior of crystals precipitating out of the melt, which potentially can clog the outlet feeder to the holding cylinder.

Glass used in the test was a high nickel–iron–borosilicate glass (see Table 1) that resulted from a feed of the simulant liquid slurry mixed with glass formers (referred to as AZ-101 simulant). The scanning electron image in Figure 5 is from the glass–K-3 interface bottom of the melter, revealing secondary phase formation at the reaction layer. Phases 1 and 2 are spinel and $R_2O_3$ solid solution, respectively, with chemistries slightly altered from typical K-3 (Table 3).

Moving closer to the glass–K-3 interface, the $R_2O_3$ phase dissociates by giving up its alumina portion. The spinel phase experiences oxidation with the FeO component going to $Fe_2O_3$, MgO, and FeO replaced by NiO, and alumina dissociating out to the glass as in the $R_2O_3$ phase (spinel phases 3, 4, and 5). The spinel stable phase at the glass–K-3 contact is a nickel spinel in the form: $Ni_{0.9}(Fe_{1.9}Cr_{0.1}Al_{0.5})_2O_4$. Well-formed crystals in the waste glass simulant above the reaction layer are nickel spinel precipitates, which form in the glass and accumulate on the bottom.

The chart in Figure 6 tracks the chemical trend of magnesium, aluminum, and nickel from the glass–K-3 interface region towards the interior. This shows nickel replacing magnesium in the spinel phase, with a concomitant decrease in alumina as it migrates to the glass. The "normal" spinel composition for K-3 is found ~1 mm deep, keeping alteration of K-3 within a restricted zone at the glass–K-3 contact.

The major phases of Monofrax K-3, spinel, and $R_2O_3$ are both solid solution phases and demonstrate the ability to adapt to transition metal levels in the waste glass. The consequence of this adaptability is formation of a secondary protective spinel layer reflecting the glass chemistry and oxidation state. In the PNNL melter, nickel replaces magnesium and reduced iron in the primary spinel of K-3, and ferric iron replaces alumina.

## Future challenges of nuclear waste containment in glass

Operational challenges still exist in melters, specifically involving phase separations in the melter feed. Precipitation of a neph-

than original phases containing higher alumina and magnesia. Spinel layer byproduct evolution path formation is as follows.

$$(Mg,Fe)O \cdot (AlCr)_2O_3 \rightarrow (Ni,Fe)O \cdot (Cr, Fe, Al)_2O_3$$

Work by Jantzen[15] at Savannah River Technology Center on the corrosion of K-3 by reducing and oxidizing feeds also found a highly insoluble protective layer of nickel spinel ($Ni(Cr_{0.8}Fe_{0.2})_2O_4$) at the K-3–glass interface.

Additional characterization of K-3 involved a research scale melter (RSM) from the Pacific Northwest National Laboratory (PNNL) that consisted of a small Monofrax K-3 cylindrical chamber with a 6-inch diameter melt pool. A test

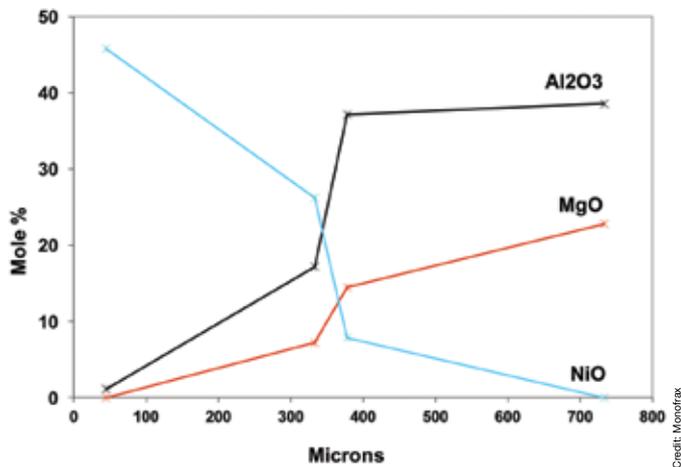# Fusion cast refractories: Roles of containment



**Figure 6.** Spinel chemistry as a function of depth for magnesium, aluminum, and nickel oxides from the glass–K-3 interface region toward the interior (data from spinels in Table 3).

eline phase limits waste form performance by reducing chemical durability in the glass. Crystallization of transition metal spinels $(Ni, Zn, Mn, Fe) (Fe,Cr)_2O_4$ that accumulate at melter bottoms do not affect glass durability, but can plug outlet tubes, restricting flow to the stainless steel canisters for final disposal. The presence of molybdenum in many oxidation states within borosilicates can decrease the glass's ability to prevent leaching in waste forms in longterm disposal sites.[16]

There is a surprising statistic concerning the number of nuclear reactors currently under construction in the world. The number under construction in Russia, India, the U.S., South Korea, United Arab Emirates, and Japan combined—approximately 30—matches the total under construction in China alone. China is the fastest-growing nuclear energy industry in the world with a 30% growth rate.[17,18]

Over the last forty years, nuclear applications have generated an estimated ~80,000 tons of spent nuclear fuel waste. As the number of operational plants increase, the amount of nuclear waste also will increase towards 2050. In particular, the amount of HLW is increasing because, while most of Europe and Asia reprocesses their spent fuel, the U.S. and Canada do not. Therefore, there is a growing need for acceptable and tested methods of nuclear waste storage, which vitrification can provide.

## About the author

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