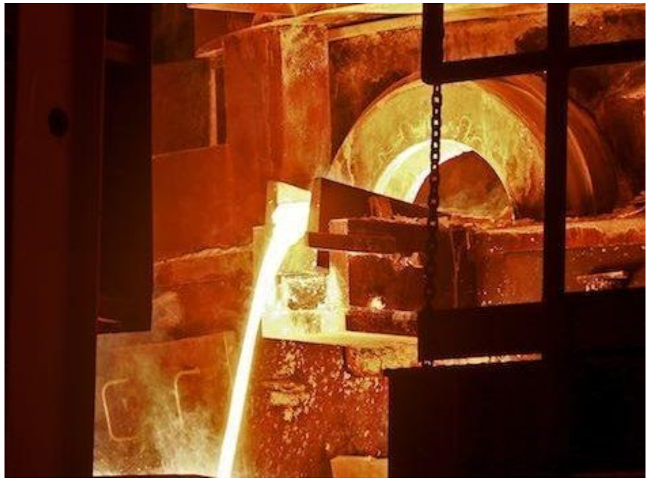


Monofrax

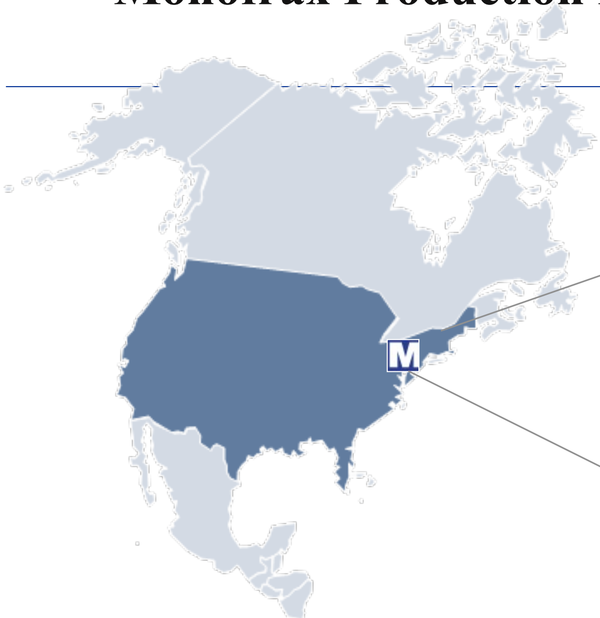
Joint ICTP-IAEA International School on Nuclear Waste Vitrification

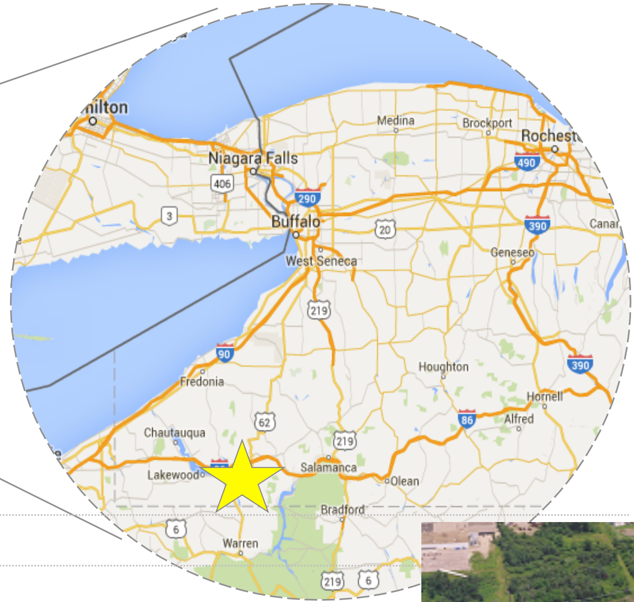
“Fusion Cast Refractories: Roles of Containment”

Kevin Selkregg

September 24, 2019

Monofrax Production Facility

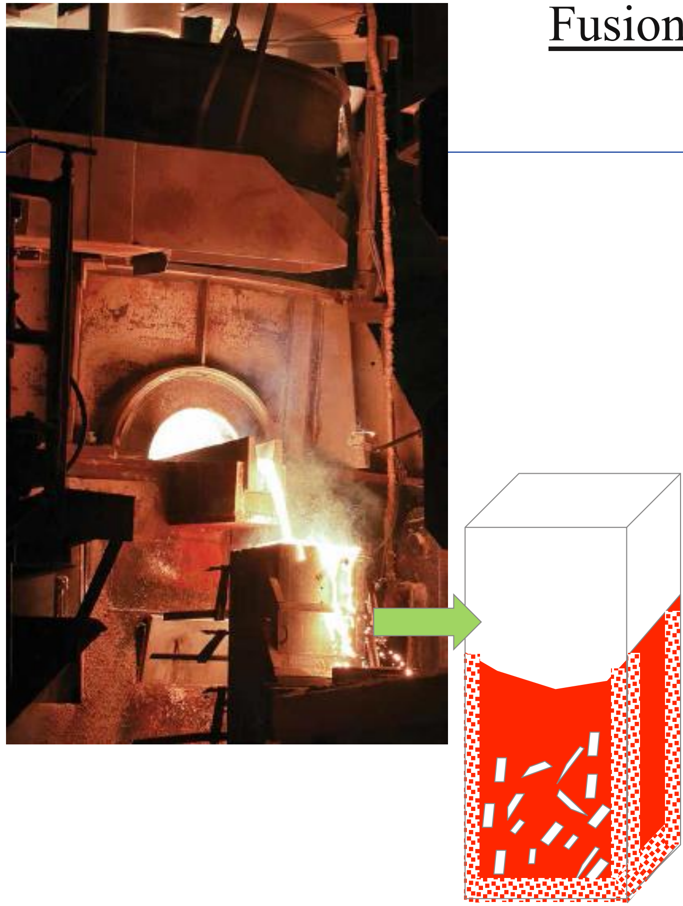




Total area	▪ 28,000 m^2
Manufacturing 14,000 m^2	▪ 4 electric arc furnaces ▪ Mold-making operations ▪ State-of-the-industry cutting & finishing equipment ▪ Proprietary grinding equipment
Laboratory & Office Space 2500 m^2	▪ 3 research labs for product development & testing with premises dedicated to chemistries testing, glass defect analysis and product testing ▪ Office space for mangement & sales, application & process engineers

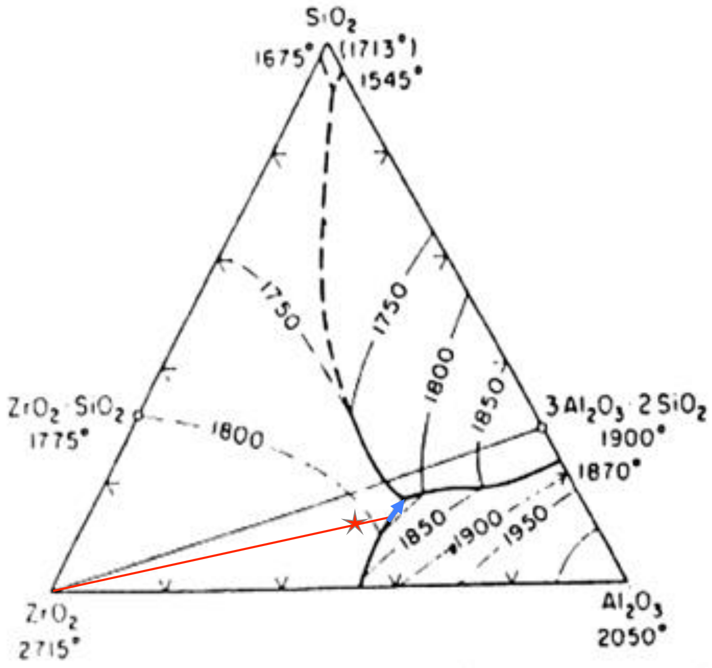
Scope

- Fusion Cast process and comparison with bonded refractories
- Industrial glass furnace corrosion mechanisms in contact with AZS fused cast refractory
  - Glass contact and Superstructure corrosion
  - Passivation layer
- Vitrification of Nuclear Waste
  - History perspective
- Corrosion Studies
  - SRL Pilot Reactor 1983-1984 (Monofrax K3)
  - PNNL RSM #7 (Monofrax K3)
  - Finger Corrosion Test Samples (Monofrax M, A2, CS3, K3, and E)
    - F 40 type glass
    - MS26AZ102F-2
- Summary

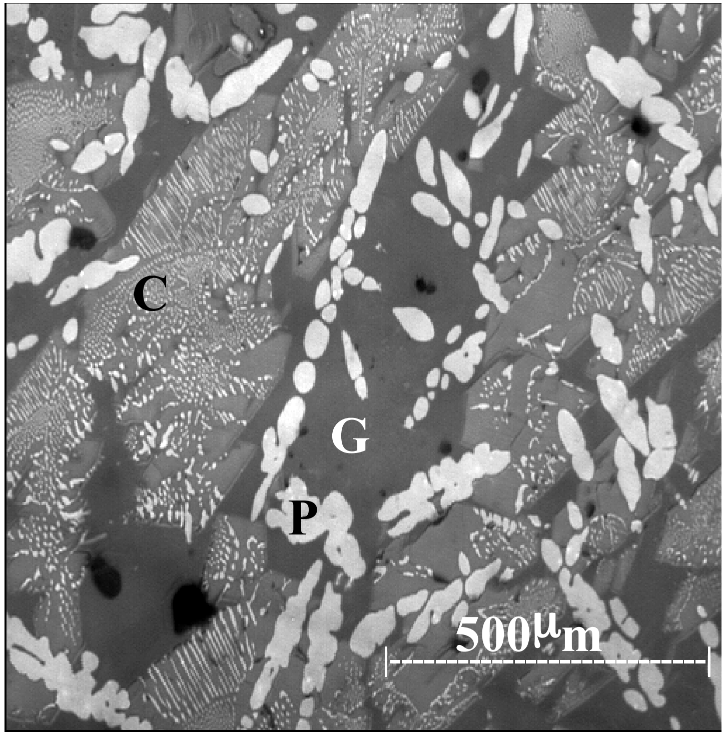


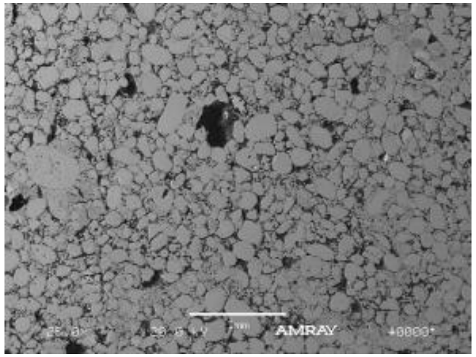
Fusion Cast Refractory Process

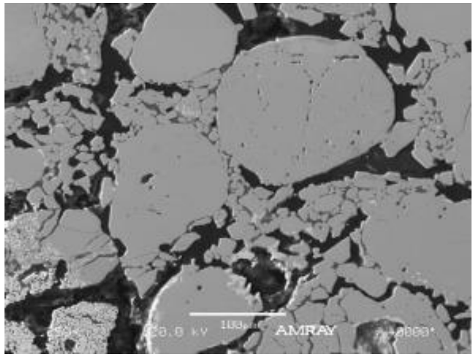
- Dry oxide powder batch blended to calculated mix portions
- Fused into a melt in electric arc furnace by energy released in arc resistant paths between three graphite electrodes
- After melting and homogenization, poured into molds of predetermined shape to solidify as it loses heat
- As melt loses heat, crystals form (precipitate) out of the melt based upon their melting point temperatures and phase equilibria.
- "Annealed" for slow cooling and later sawed and machined for final application
- The final result is a very dense refractory body with low porosity



- AZS: 40% ZrO2, 46.5 Al2O3, 13.5% SiO2
- ZrO2 Precipitates along red line.
- Al2O3 and ZrO2 co-precipitate
- Mullite should precipitate at eutectic with Al2O3 and ZrO2; but Na2O promotes glass





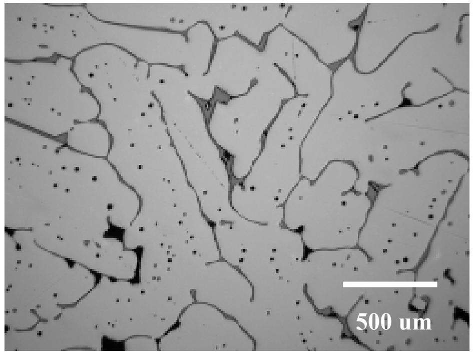


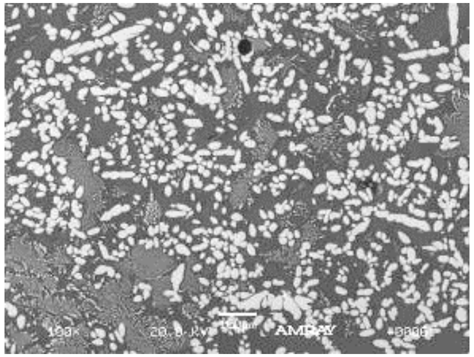
Bonded refractory structure

vs.

Fused Cast refractory structure

→ Bonding matrix and porosity are points of weaknesses in bonded refractories





Bonded

Fused Cast

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- Mold shaped by graphite boards
- Pins released to free boards after few minutes delay
- Lifted by tongs at header base
- Casting moved to annealing bin

- Mold shaped by graphite boards
- Pins released to free boards after few minutes delay
- Lifted by tongs at casting bottom
- Casting moved to annealing bin

Anneal, clean, saw, grind, inspect

Assembl

Monofrax Products

Product Groups and Applications	Monofrax	
AZS: Most commonly used fused cast products (high corrosion resistance)	CS-3	34% ZrO_2
	CS-4	36% ZrO_2
	CS-5	40% ZrO_2
Alumina: Quality sensitive glass tank applications (float, crowns) (magnesium and aluminum reduction cells)	M	α/β
	H	β
	A1/A2	α
Chrome: Used by fiberglass producers, vitrification of nuclear waste,non-glass	K-3	Cr_2O_3 (27%)/Spinel
	E	Cr_2O_3 (74%)/Spinel
Zirconia: TFT, lead glass, aluminosilicate some non-glass applications	Z/ZHR	93% ZrO_2
	L	Al/Mg Spinel

Fusion Cast Refractory Containment Roles – Sodalime Glass

Monofrax

Total surface area in commercial glass furnaces for containment of molten glass and atmosphere components is significant

Container: ~3600 ft^2 (~334 m^2)
Float: ~ 14,000 ft^2 (~1300m^2)

Refractories for Sodalime Glass Furnace

Goal of containment of molten glass within a tank involves:

- **Good corrosion and erosion resistance (i.e. preventing leakage)**
- **Maintaining glass purity**
- **No defects (or at least below threshold limit)**
- **Tolerating dissolution into glass from refractory corrosion (~0.07% ZrO_2)**

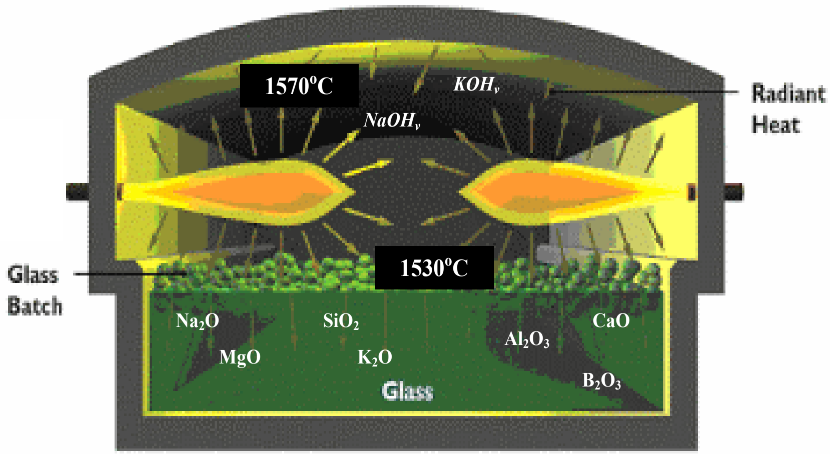
Refractory Corrosion

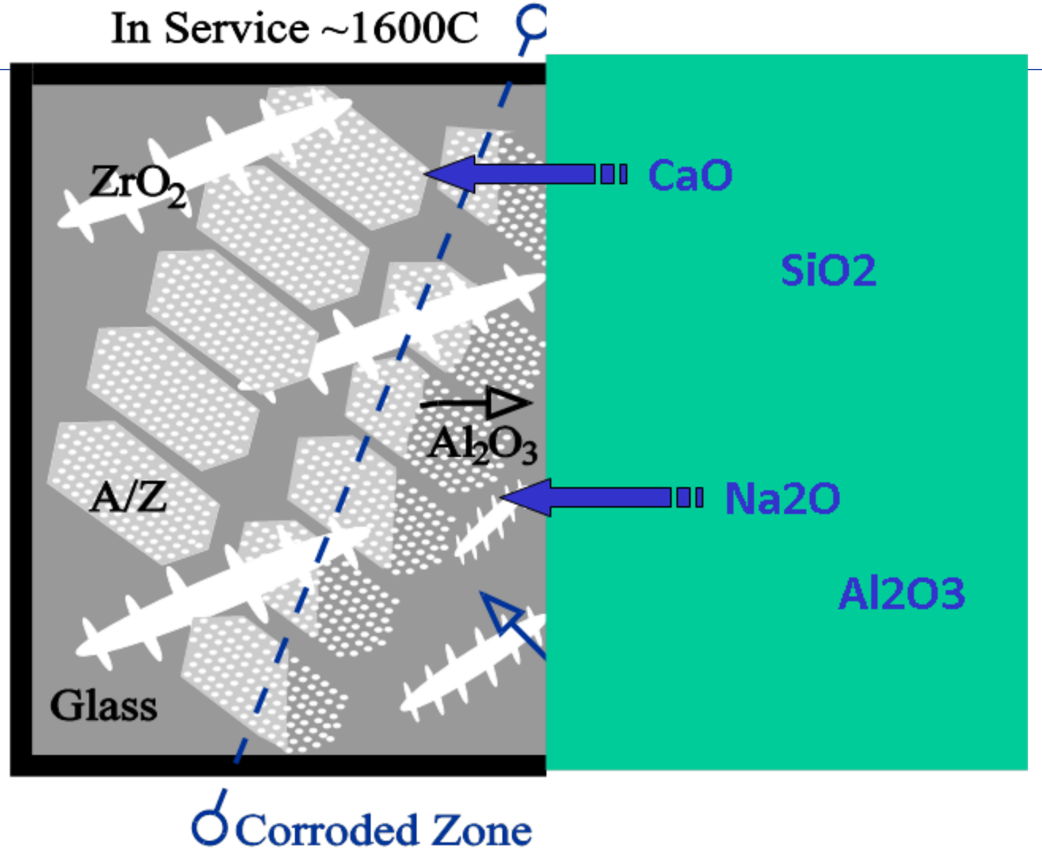
<u>Above-Melt</u>: Corrosion of refractory lining by 3 distinct modes of transport

- NaOH, KOH, and PbO vapors enter refractories by diffusion and atmospheric flow
- Condensed Phase Species may precipitate upon cooler refractory surfaces
- Batch components may be transported to the refractory surfaces. Allows access of species with low vapor pressure (SiO_2, BaO, CaO, etc.), which would not otherwise reach the superstructure refractory

<u>Below Melt Line (glass contact):</u>

- Dissolution of alumina from AZS to form passivation layer
- Convection currents removing surface layer in erosive manner
- Upset of zirconia-rich glass in dead zones of tank forming viscous knot defects

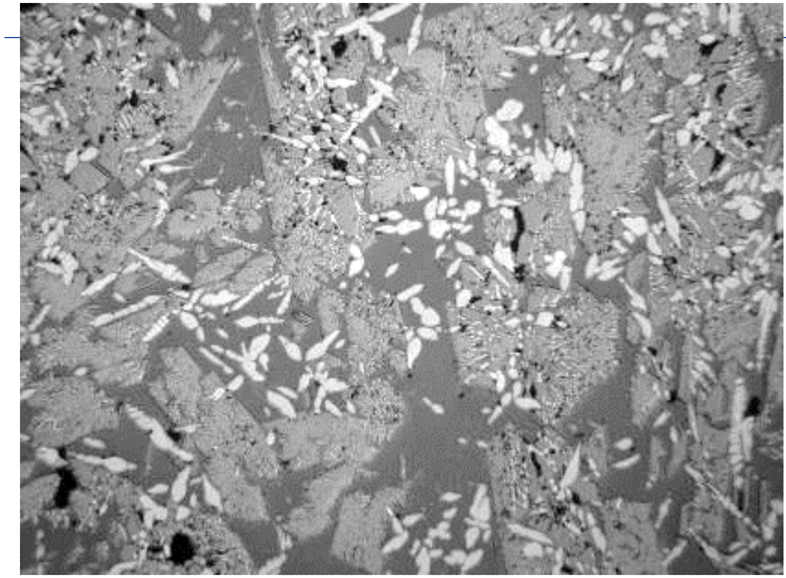




Dissolution Of Corundum In Co-Precipitate Phase Promoted By In-Diffusion Of Calcia And Soda

Zirconia From Co-Precipitate Remains In Passivation Layer In Original Co-Precipitate Array

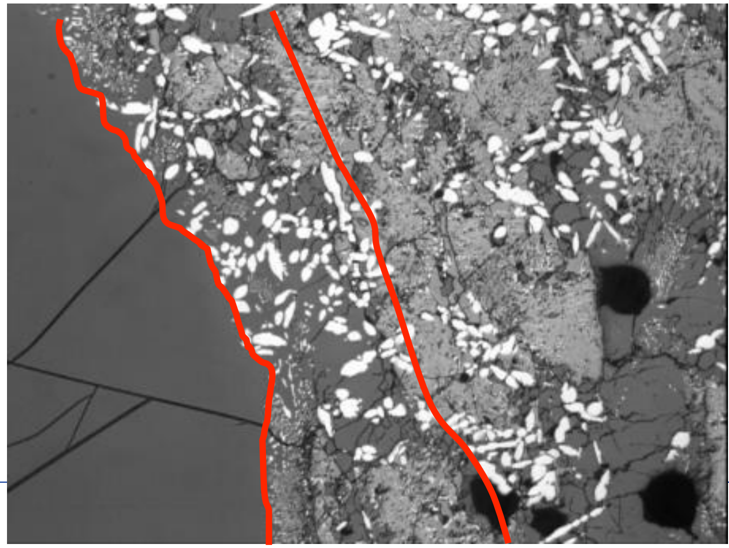
Corrosion of AZS at Glass Contact



Wt%	AZS Glass Phase	Passivation Layer	Sodalime Tank Glass
Al2O3	23.2	32.0	1.2
SiO2	68.0	46.0	74.0
CaO	0.2	3.3	10.0
Na2O	6.5	15.5	14.0
Fe2O3	0.3	0.1	0.0
K2O		0.3	0.0
MgO		1.0	0.2
ZrO2	1.8	1.9	
Total	100.0	100.0	99.5

Passivation Layer

- Dissolved alumina from AZS creates high alumina glass in layer
- Undissolved zirconia present
- Acts as inhibitor of further corrosion (i.e. passivates)



Post-campaign Glass Contact AZS Corrosion: Sodalime Container 10 Years

Comparison of the degree of alteration between glass contact (solid) and superstructure (open) CS3 refractory lining

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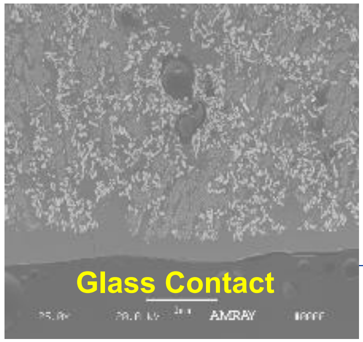
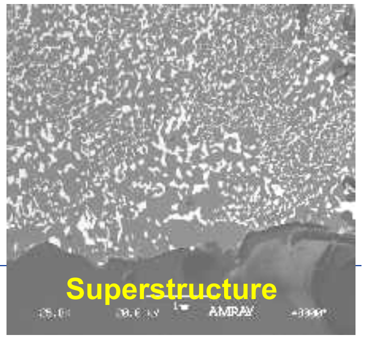
Tank Glass Chemistry:Wt%

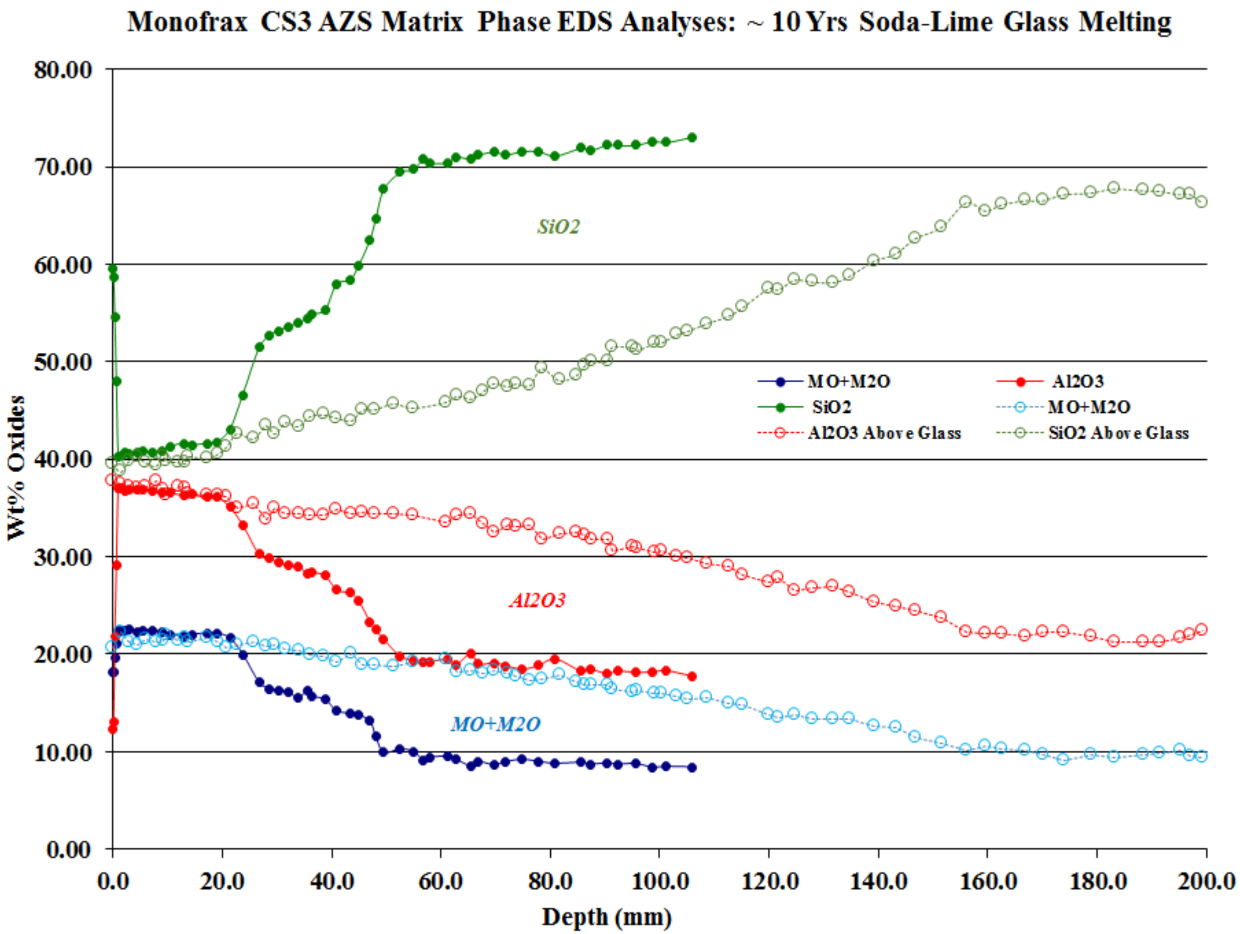
Na2O	13.0
MgO	1.5
Al2O3	1.5
SiO2	70.0
ZrO2	
K2O	0.25
CaO	10.5

Maximum Corrosion depth at the glass contact (solid circles) is less (`~ 55mm) than observed above glass contact (~150mm)

Higher Degree of Alteration In Superstructure Than At Glass Contact







Fusion Cast Refractory Containment Roles – Nuclear Waste

Monofrax

Chicago Pile 1 Reactor Under University of Chicago Stagg Field. December, 1942

First major technical achievement for the Manhattan Project

A "pile" of graphite bricks with holes containing uranium and other bricks with holes for the cadmium "control rods".

- **49 scientists led by Enrico Fermi, proved that a self-sustaining chain reaction could be initiated**

…"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." K Selkregg, American Ceramic Society Bulletin, March 2018

Melter Vitrification Technologies and Timeline

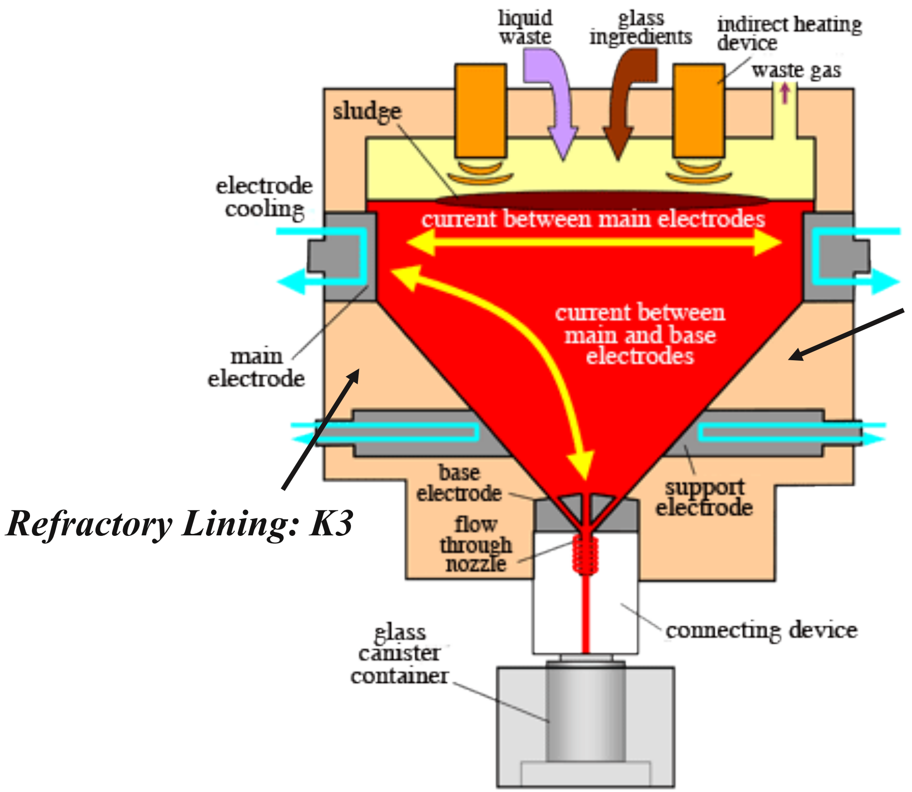
❖ Joule-heated Ceramic-lined melter (JHCM)

- PAMELA facility; Belgium 1985-1991. Surface area 0.72m^2
- West Valley, NY ; 1988-2003 Surface area 2.2m^2
- Savannah River Site; 1995- 2014(?) Surface area 2.6m^2 and 5m^2
- Tokai Plant, Tokai Japan; 1994 - ?
- Rokkasho, Japan
- Mayak Chemical Combine (MCC), Russia 1987 - ?
- German Vitrification Plant (VEK) 2009 - ?
- Next generation JHCM; Hanford (WTP) 2022? Surface area 10m^2 and 3.75m^2
- China

❖ Hot-walled induction melter (HWIM)

- Marcoule 1978-2009;
- LaHague 1989 – present;
- Sellafield 1991-present
- Kalpakkam, India
- Tarapur, India
- Trombay, India

Fusion Cast Refractory Containment Roles – Nuclear Waste

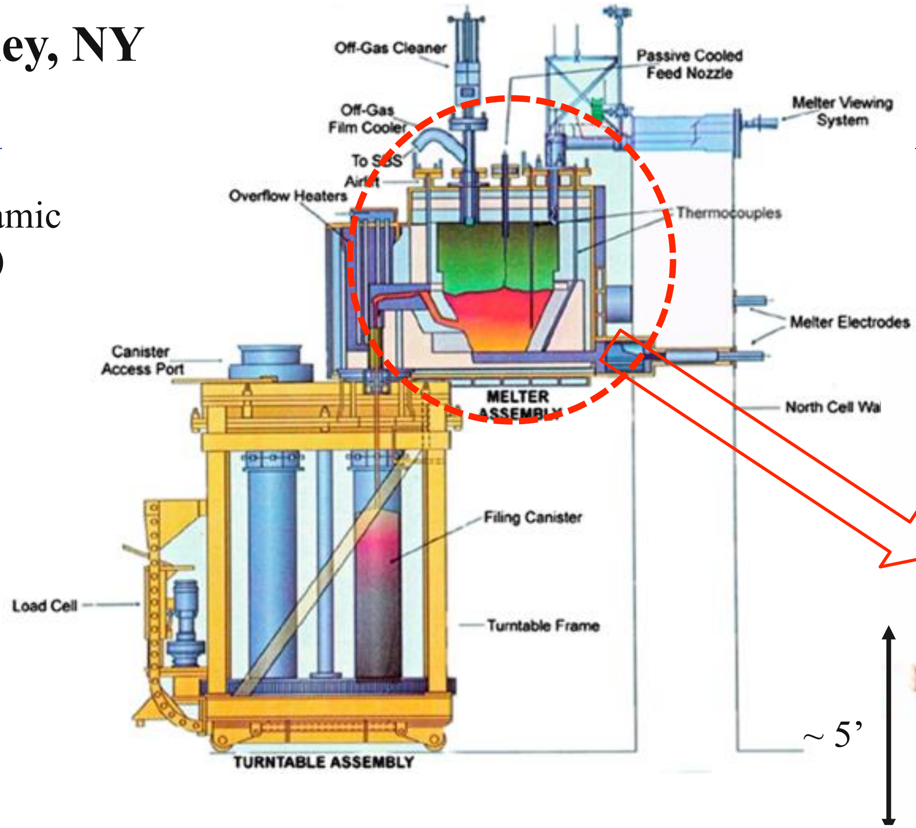


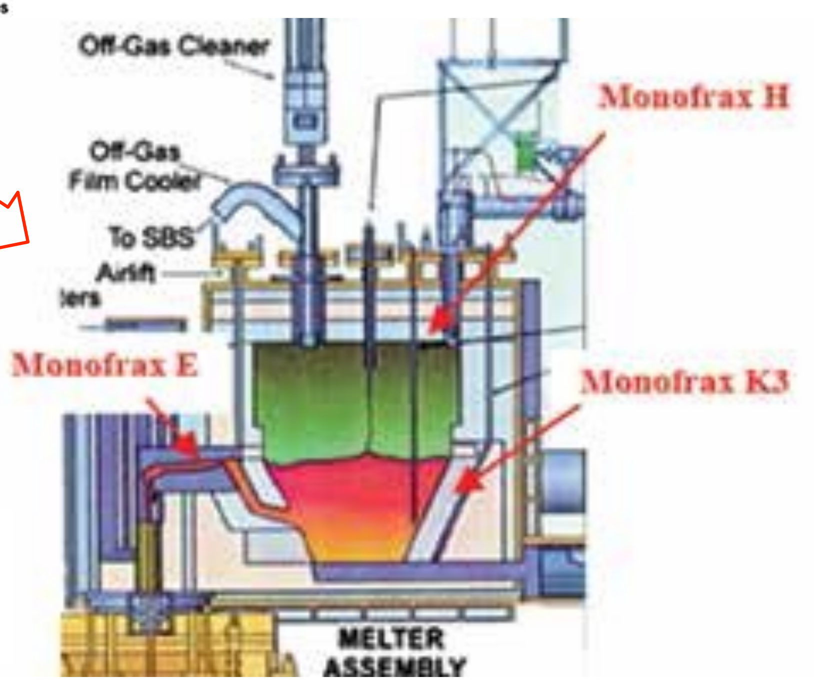
High Active Liquid Waste Vitrification Equipment Outline (Glass Melting Furnace)

- **Schematic of Rokkasho, Japan melter**
- **Monofrax K3 used as the refractory directly in contact with the glass**
- **Post mortem analyses common with refractories from industrial glass furnaces (e.g. sodalime).**
  - **Observe corrosion rate**
  - **Observe erosion patterns such as “drilling”, convection flow wear and aggressive attacks at joints and cracks**
  - **Key in understanding of effectiveness of refractory performance**
- **Post mortem analyses not an option with vitrification melters.**
- **Reliance on understanding corrosion behavior at glass/ refractory interface in test melters**

West Valley, NY

Slurry-fed Ceramic Melter (SFCM)





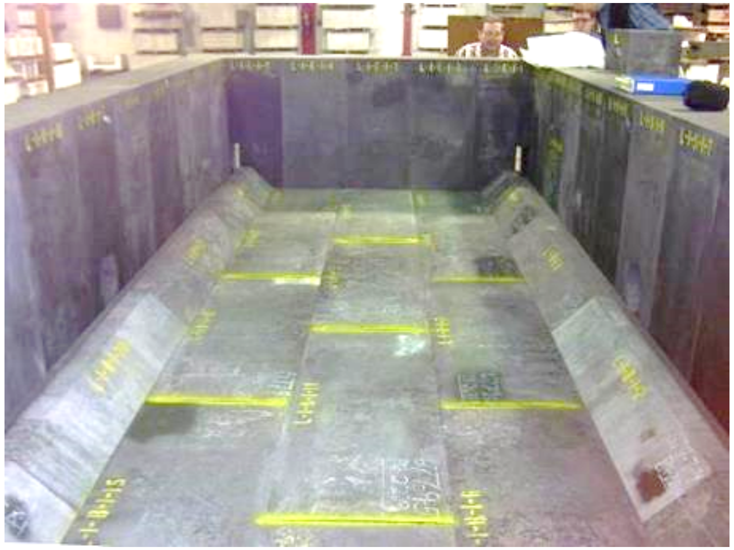
- 660,000 US gallons (2500 m^3) of HLW was created from the reprocessing effort. From 1988 – 2002, this waste was vitrified into borosilicate glass and stored in 275 stainless steel canisters.

Savannah River Sites HLW Defense Waste Processing Facility (DWPF)

	Melter # 1	Melter # 2	Total*
Years Operated	8.5 y (6.5 yrs rad op) (05/94 to 11/02) (03/96 to 11/02 rad)	>14 y (03/03 to Present)	>18.5 yrs (rad)
Canisters Produced	1,339 rad. + 80 non-rad.	2903 rad	4242 (rad)
Glass Produced (kgs)	2.83E+05	6.92E+06	7.20E+06
Curies Processed	1.03E+06	5.584E+07	5.95E+07

- Two melters lined with K3 processed HLW glass from 1994 – 2002 and from 2003 – 2017
- Refractory corrosion test programs of K3 gave an estimated life of 2 years in this application. In both cases the melter unit was stopped after 8.5 and 14 years due to failure of the heaters.
- Over 8000 metric tons of HLW glass was processed filling a total of 4158 stainless steel canisters

Monofrax K3 at Hanford



- Monofrax K3, 10 m^2 melter box (left photo) during inspection at Monofrax plant before shipment to Hanford site
- Melter unit at Hanford containing melter box being readied for use (right photo)

Containment

- The **containment role in industrial glass furnaces** emphasizes containing glass in a furnace volume at high temperatures allowing the glass to be refined to a high quality for its assigned purpose (e.g. sodalime bottles, plate glass, and even cover glass)

- The **containment role in the vitrification of nuclear waste** has a dual role; involves containing a variety of glass compositions (e.g. borosilicate and iron phosphate groups) in a melter designed to also contain nuclear waste in a stable form; all safely within a melter to be solidified in SS cylinders

Sodalime Glass and Examples of Vitrification Melter Glass Chemistries

Wt%	sodalime[0]	HLW[1]	WDVREF6[2]	SRL-EA[3]	LAWA24[4]	AZ-101[5]
SiO2	71.7	44.9	43.5	45.9	35.4	38.47
Al2O3	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
Na2O	14.1	11.6	8.3	16.9	20.0	17.81
K2O	0.7	0.1	5		5.5	0.32
B2O3		12.3	14.5	11.3	6.1	7.63
Li2O		2.2	4.1	4.3		1.9
BaO		3.5				0.09
MnO			1.2	1.6		0.33
V2O5		1.5				
Fe2O3	0.1	3.4	12.2	10.8	6.0	17.5
CeO2		1.9				0.19
Cr2O3		0.3	0.1	0.3	0.3	0.16
SO3	0.4	0.7			0.5	0.08
NiO		0.4	0.3	0.8	0.1	1.5
Sb2O5		0.5				
P2O5			1.3		1.7	0.31
ZrO2			1.4	0.6	3.0	3.97
TiO2			0.9	0.8		0.03
ZnO					3.0	0.02
La2O3						0.22
Nd2O3						0.17
CdO						0.62
SnO2						0.1
CuO						0.04
"other"					2.3	
	99.85	99.5	99.9	99.4	99.6	100.0

0 Flat glass industrial furnace. Glaverbel S.A. Belgium
1 China simulated HLW waste
Karlsruhe Nuclear Research Center, Germany [16]
2 West Valley, NY [19]
3 Savannah River, EA Glass [19]
4 Hanford Low Activity Waste Vitrification Project. 2002 [19]
5 PNNL, glass fo Research Scale Melter test

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❖ Compared to Sodalime glass:

- Melter glass borosilicate type
- Larger number of species in melter glass
- SiO2 much lower
- Melter glass higher in Al2O3 and Fe2O3
- Many transition metal oxides are present in melter glass; even though it is low it plays a major role in spinel formation

Sodalime and Vitrification Melter Glass Types For Corrosion Studies

	Industrial Glass	Nuclear Waste Vitrification Glass			
corrosion environment	Container Tank 10 years	SRL Pilot Melter	PNNL - RSM #7	Monofrax Finger Corrosion Test	
glass type	Sodalime	1983-1984 "vintage"	AZ-101	MS26AZ102F-2	F40
SiO2	71.7	54.4	38.45	5.58	
Al2O3	1.85	4.7	7.84	13.28	
P2O5				38.06	57.1
CaO	7.1	1.3	0.54	1.06	
MgO	3.9	0.7	0.12		
Na2O	14.1	10.6	17.81	20.03	
B2O3		7.4	7.63	0.03	
Li2O		5.1	1.9		
MnO		2.8	0.33		
Fe2O3	0.1	12.3	17.5	7.1	42.9
CeO2		0.3	0.19		
NiO		1	1.5		
ZrO2		0.6	3.97	0.71	
CeO2		0.3	0.19		
Cs2O		0.1		0.13	
SO3	0.4		0.1	4.37	
K2O			0.32	0.78	
Cr2O3			0.16	2.7	
CdO			0.62		
Bi2O3				1.77	
ZnO				3.55	
La2O3				0.71	

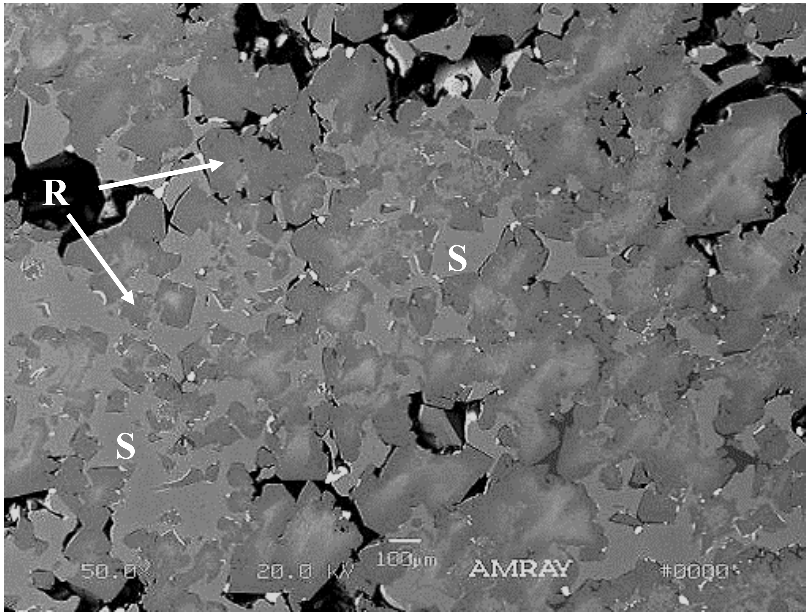
❖ Compared to Sodalime glass:

- Borosilicate and iron phosphate types in vitrification melter glass
- SiO2 much lower or not present, as in F40 glass
- Vitrification melter glass higher in Al2O3 and Fe2O3
- Spinel forming oxides common in vitrification melter glass:

e.g. Al2O3, Fe2O3, MnO, NiO, Cr2O3, ZnO

As Produced Monofrax K3 Refractory

Monofrax



	Bulk Chemistry	Spinel	R2O3
Al2O3	57.7	42.67	73.92
Cr2O3	27.6	28.54	26.08
FeO	5.8	9.25	
MgO	6.1	19.55	
Na2O	0.3		
SiO2	1.8		
TiO2	0.1		

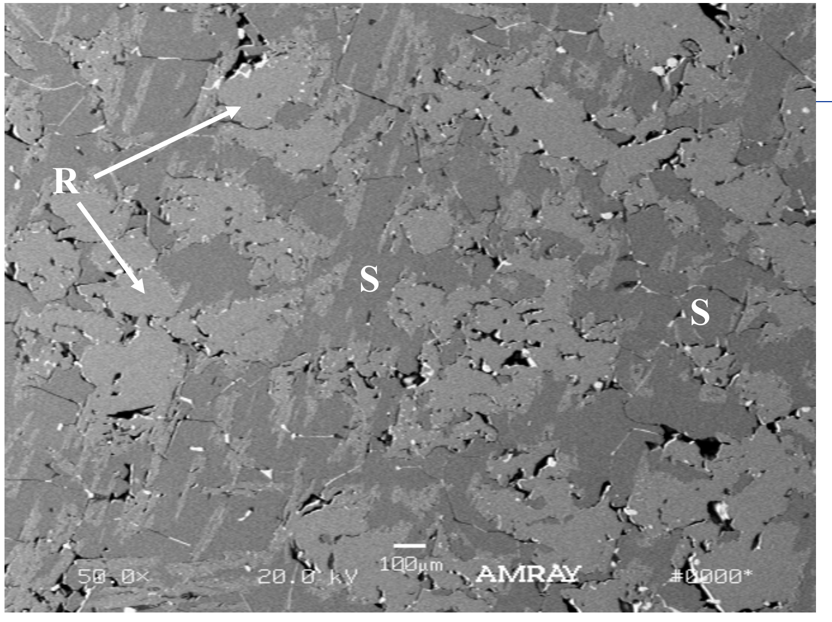
Bi-Phasic Refractory

Solid Solution Phases of MgO-FeO-Al2O3-Cr2O3 Spinel ("S") and R2O3 ("R")with Cr and Al

Spinel: $(Mg_{0.8}\ Fe_{0.2})\ (Al_{1.4}\ Cr_{0.6})\ O_4$

R2O3 (corundum $_{ss}$): $Al_{1.6}\ Cr_{0.4}\ O_3$

As Produced Monofrax E Refractory



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Bi-Phasic Refractory

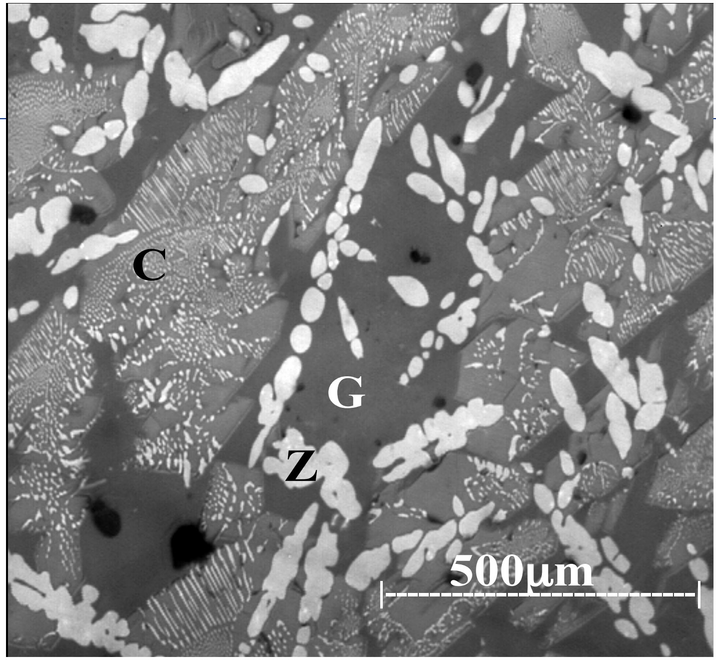
Solid Solution Phases of MgO-FeO-Al2O3-Cr2O3 Spinel ("S") and R2O3 ("R")with Cr and Al

	Bulk Chemistry	Spinel	R2O3
Al2O3	8.1	7.98	7.76
Cr2O3	75.7	68.38	92.10
FeO	5.3	4.55	
MgO	8.2	19.09	
Na2O	0.3		
SiO2	1.9		
TiO2	0.2		

Spinel: $(Mg_{0.9}\ Fe_{0.1})\ (Al_{0.3}\ Cr_{1.7})\ O_4$

R2O3 (corundum $_{ss}$): $Al_{0.2}\ Cr_{1.8}\ O_3$

As Produced AZS Refractory (CS3)



	Bulk Chemistry	Glass
Al2O3	**48.2**	**23.8**
SiO2	**15.1**	**67.1**
ZrO2	**34.4**	**2.1**
Na2O	**1.7**	**6.4**
CaO		**0.3**
TiO2	**0.1**	**0.2**
Fe2O3	**0.1**	**0.3**

Multi-Phasic Refractory

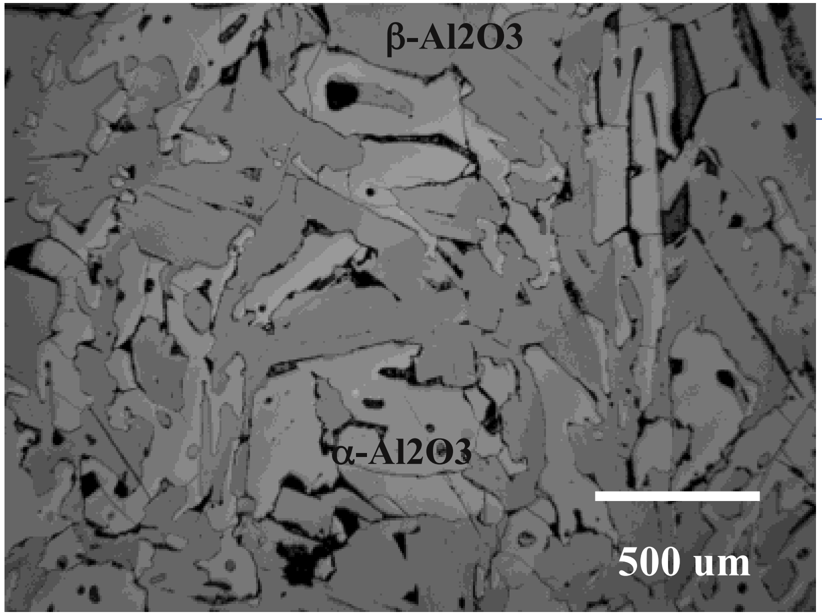
Crystalline Alumina Plates Containing Coprecipitated Zirconia Crystals ("C")

Glass Phase ("G")

Independent Dendritic Zirconia ("Z")

- *At refractory/glass interaction; AZS glass phase is one-third the volume of the structure influencing the degree of alteration during corrosion.*

As Produced Monofrax M Refractory



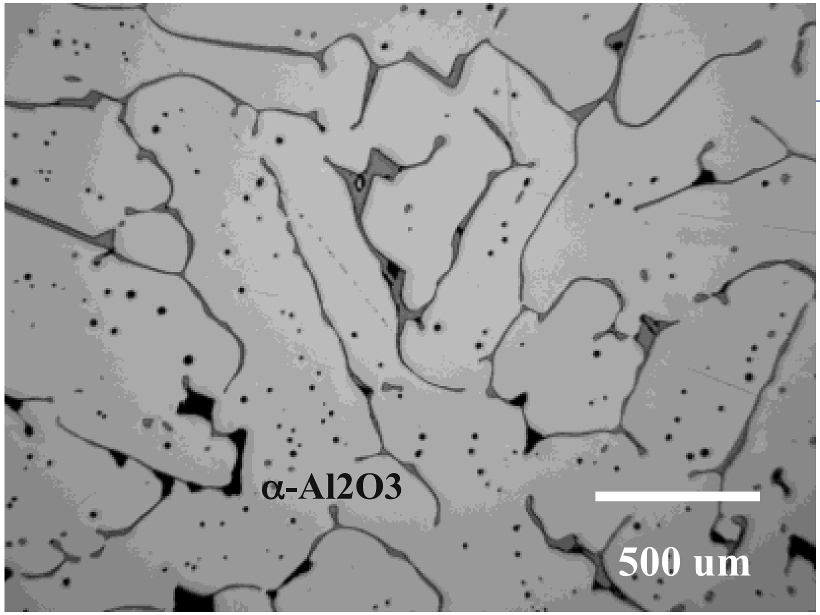
	Bulk Chemistry	β-Al2O3	Corundum
Al2O3	94.7	94	100
SiO2	1.05		
Na2O	4.24	6	
CaO	0.23		
ZrO2	0.02		

Bi-Phasic Refractory

β-Al2O3 and corundum phases in ~ 55 % and 45% (volume) respectively

Calcium - nephelitic grain boundary

As Produced Monofrax A2 Refractory



		Grain Boundary	
	Bulk Chemistry	Glass	Corundum
Al_2O_3	98.8	25.4	100
SiO_2	0.56	34.6	
B_2O_3	0.34	27.7	
Na_2O	0.2	9.2	
CaO	0.1	2.1	
ZrO_2	0.02	0.4	

Single Phase Refractory

Interlocking corundum grains with borosilicate grain boundary glass

Corrosion of Monofrax K3 at Glass Contact
SRL 1983-1984

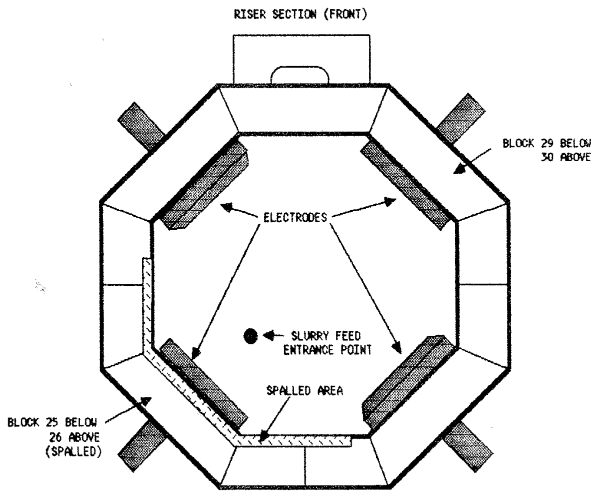


Figure 1

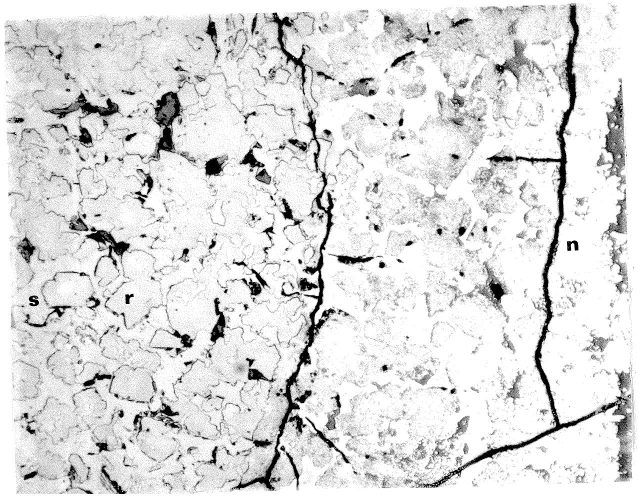
- Large Slurry Fed Pilot Melter at SRL, 1983-1984
- ~ 2 meters ID and ~ 1.5 meters deep
- Operated at 1150°C for 2 years
- Slurry fed for 193 days producing 234 tons of glass

Melter Glass Chemistry

Wt%	
SiO_2	54.0
Al_2O_3	4.7
CaO	1.3
MgO	0.7
Na_2O	10.6
B_2O_3	7.4
Li_2O	5.1
MnO	2.8
Fe_2O_3	12.3
CeO_2	0.3
NiO	1.0
ZrO_2	0.6
CeO_2	0.3
Cs_2O	0.1
	101.2

Corrosion of Monofrax K3 at Glass Contact
SRL 1983-1984

Monofrax



- Large Slurry Fed Pilot Melter at SRL, 1983-1984
- Primary K3 microstructure on left (“s” = spinel and “r” = R2O3)
- Reaction layer on right (“n”)
- Protective spinel skin formation reflects loss of MgO and Al2O3 in structure and addition of NiO

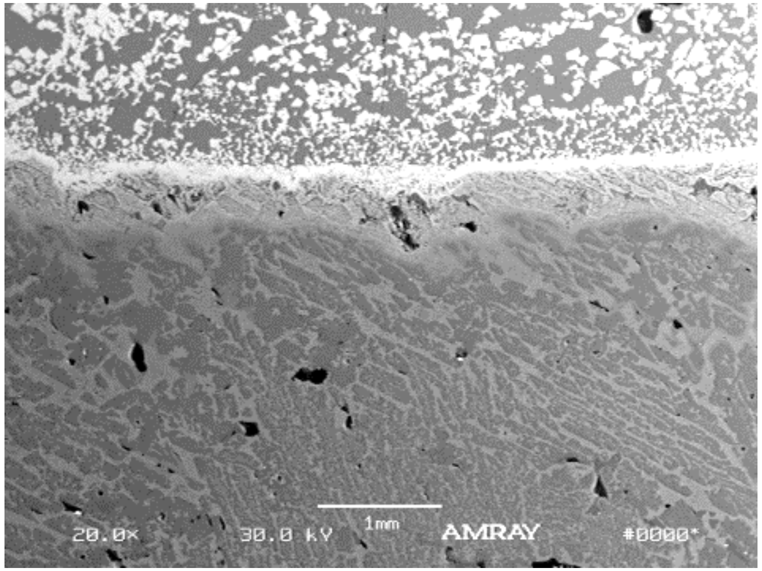
	K3			spinel layer	
	Spinel	R2O3			
				1	2
MgO	10.6			3.0	3.1
Al2O3	49.6	80.6		7.4	1.6
Cr2O3	32.1	19.4		45.8	27.5
FeO	7.7			31.6	51.8
NiO				12.1	16

$$(Mg_{0.8}\ Fe_{0.2})\ (Al_{0.95}\ Cr_{1.04})\ O_4$$

Spinel alteration at glass contact

$$(Mg_{0.2}\ Ni_{0.4}\ Fe_{0.4})\ (Al_{0.3}\ Cr_{0.7-1.3}\ Fe_{0.5-1.2})\ O_4$$

Corrosion of Monofrax K3 at Glass Contact
PNNL 2016 (RSM #7)



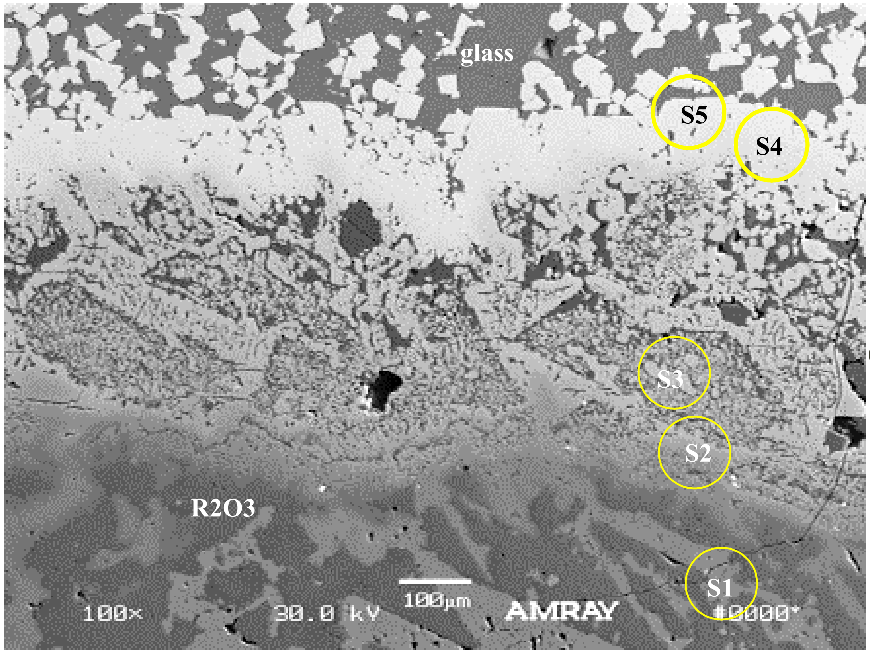
- Research Scale Melter at PNNL
- AZ-101 glass at 1050°C-1150°C for 11 weeks
- Primary K3 spinel takes on Fe2O3 and NiO as it loses MgO and Al2O3 closer to glass contact
- R2O3 solid solution phase dissociates closer to glass contact

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

Corrosion of Monofrax K3 at Glass Contact
PNNL 2016 (RSM #7)

- S1-S5: <u>Spinel</u> compositional trend approaching glass refractory contact

Spinel: A B_2 O_4



$(Ni_{0.8}\ Fe_{0.1})\ (Fe_{1.9}\ Cr_{0.2}\ Al_{0.1})\ O_4$

$(Ni_{0.7}\ Fe_{0.2})\ (Fe_{1.4}\ Cr_{0.5}\ Al_{0.1})\ O_4$

$(Mg_{0.2}\ Ni_{0.3}\ Fe_{0.6})\ (Al_{0.8}\ Cr_{0.7}\ Fe_{0.5})\ O_4$

$(Mg_{0.3}\ Fe_{0.5})\ (Al_{1.5}Cr_{0.6})\ O_4$

$(Mg_{0.4}\ Fe_{0.3})\ (Al_{1.6}Cr_{0.6})\ O_4$

- Approaching the glass refractory contact
  - MgO became depleted
  - Al2O3 became depleted
  - NiO replaced MgO and iron oxidized and replaced Al2O3

Phosphate Glass

Monofrax

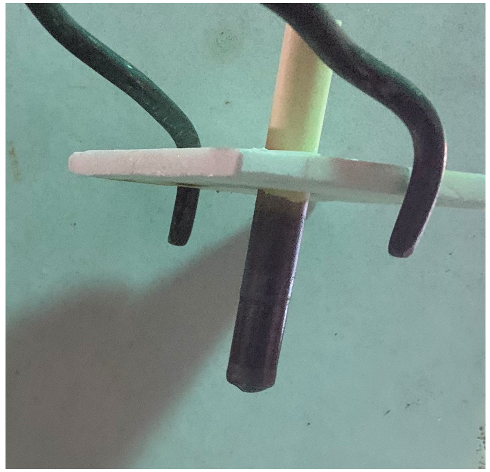
- Two types evaluated:
  - F40 and MS26AZ102F-2
  - More corrosive glasses than borosilicate type

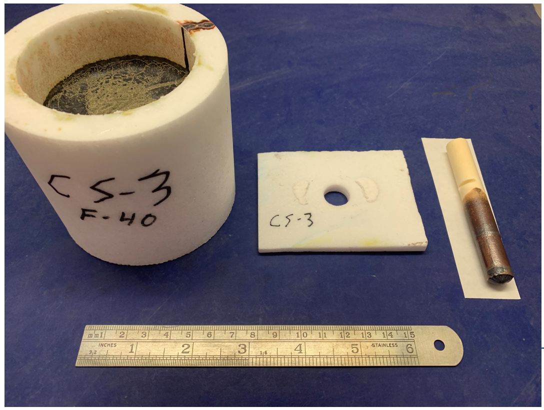
- Finger corrosion comparing chrome fused cast (K3 and E), high alumina (A2 and M), and AZS (CS3 – 36% zirconia)
  - F40 glass corrosion test – 1150°C/288 hrs
  - MS26AZ102F-2 glass corrosion test – 1050°C/306 hrs

F40	
P2O5	57.1
Fe2O3	42.9

MS26AZ102F-2	
Al2O3	13.28 ←
B2O3	0.03
Cr2O3	2.7 ←
Cs2O	0.13
F	0.16
K2O	0.78
Na2O	20.03 ←
P2O5	38.06 ←
Re2O7	0.03
SiO2	5.58 ←
SO3	4.37 ←
Bi2O3	1.77
CaO	1.06
Fe2O3	7.1 ←
La2O3	0.71
ZnO	3.55 ←
ZrO2	0.71

Finger Corrosion





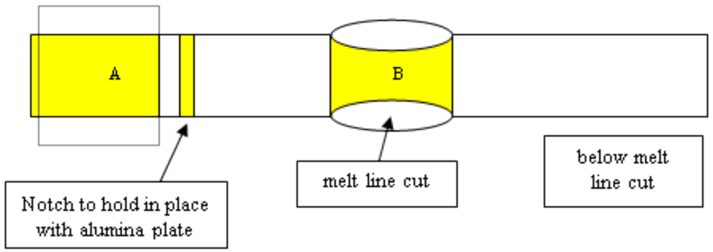
- Monofrax M crucibles in lieu of platinum crucibles

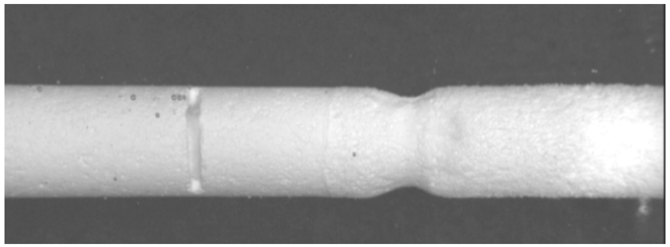
Phosphate Glass Finger Corrosion

Modified Version of ASTM C621 Corrosion Test

Monofrax

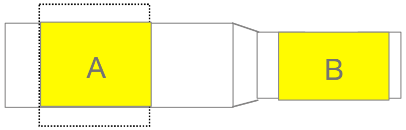
Image Analyses





Sodalime: 1450°C/68.5 hrs

	% Corrosion Cut
CS5	13
Z	15.6
K3	6.4



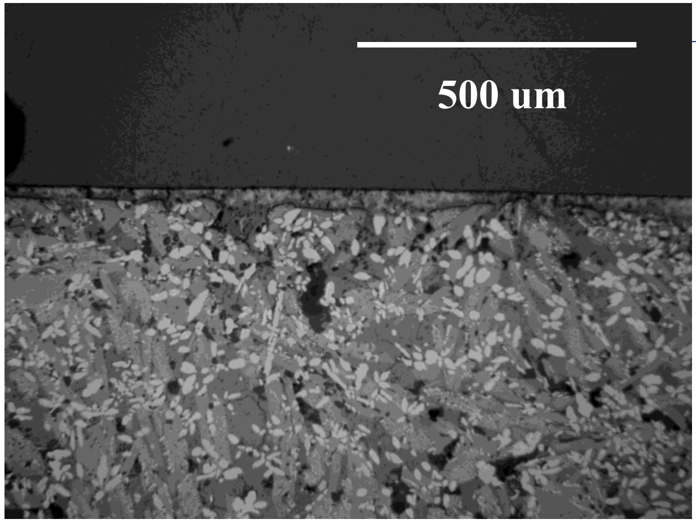
F40: 1150°C/288 hrs
MS26AZ102-F: 1050°C/306 hrs

F40

MS26AZ102F-2

	% Corrosion Cut	
	F40	MS26AZ102F
CS3	5	4.4
A2	4	4.4
K3	0	0
E	2.7	0

Phosphate Glass Corrosion Analyses
F40 Type

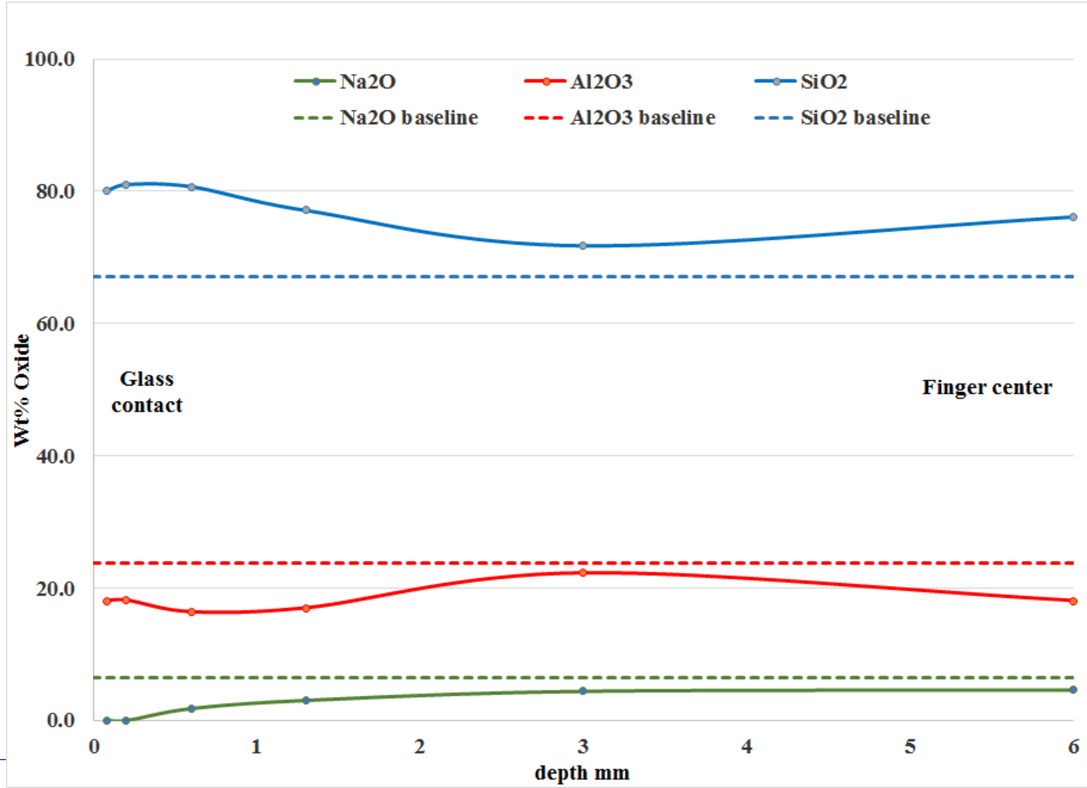


AZS – Monofrax CS3

No in-diffusion of Fe or P through glass

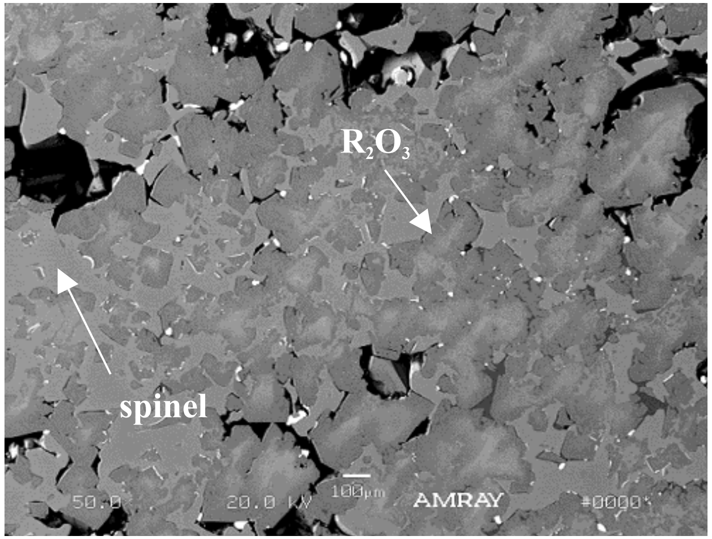
Al2O3 becomes soluble in Iron phosphate at contact

Glass Phase Chemistry



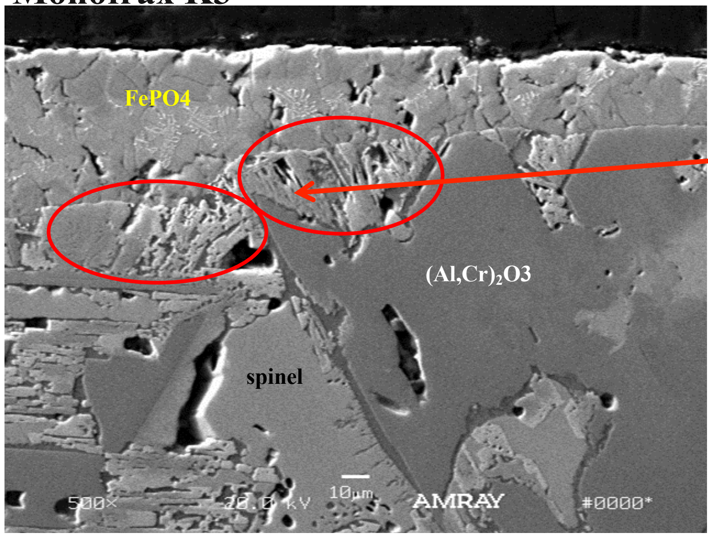
Phosphate Glass Corrosion Analyses
F40 Type

Virgin K3



	R2O3	R2O3 core	Spinel
Al2O3	73.9	33.9	42.7
Cr2O3	26.1	66.1	28.5
Fe2O3	0.0		
FeO			9.2
MgO			19.5
Total	100.0	100.0	100.0

Chrome – Monofrax K3



$(Al_{1.2}\ Cr_{1.0}\ Fe_{0.1})\ O_3$

Spinel dissociates to R2O3 (red circles)

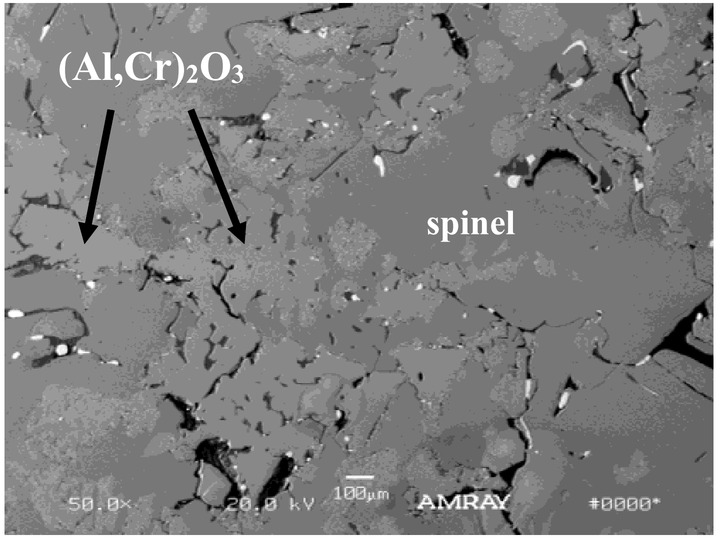
Al2O3	47.9
Cr2O3	46.4
Fe2O3	5.7
Total	100.0

Phosphate Glass Corrosion Analyses

F40 Type

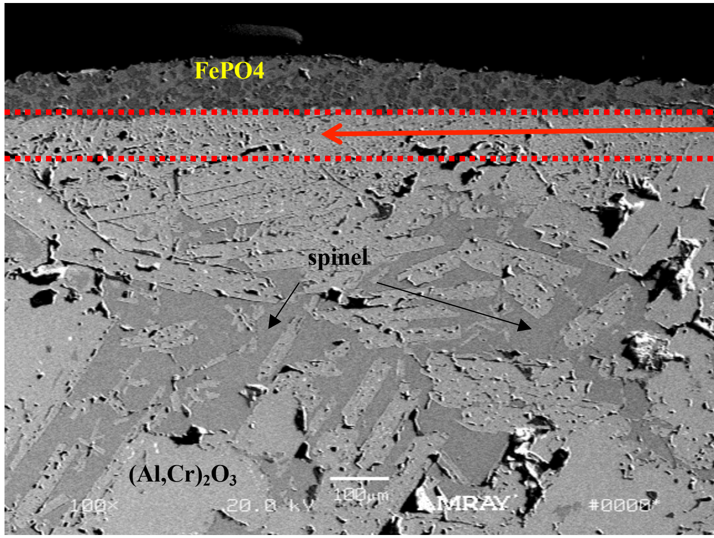
Monofrax

Virgin E)



	R2O3	Spinel
Al2O3	7.76	7.98
Cr2O3	92.10	68.38
FeO		4.55
MgO		19.09
Total	99.85	100.00

Chrome – Monofrax E



$(Al_{0.3}\ Cr_{1.4}\ Fe_{0.3})\ O_3$

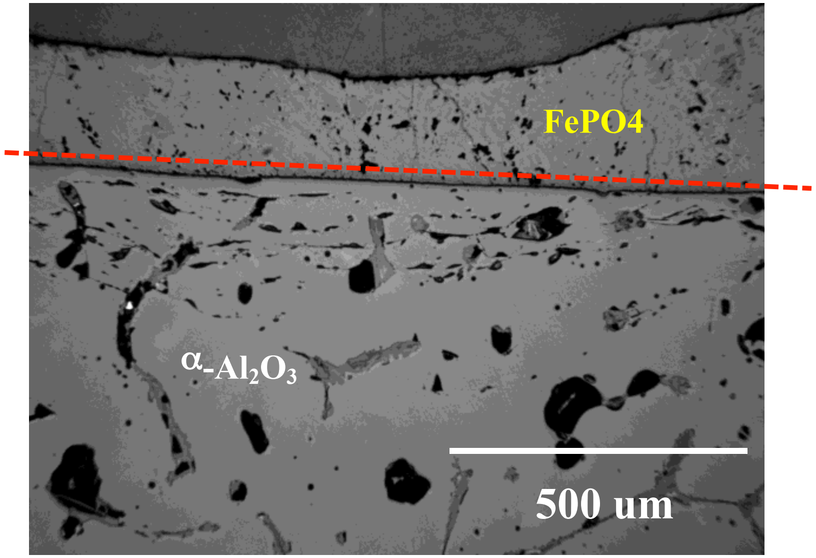
Spinel dissociates to R2O3 Layer (red borders)

	Secondary	
	R2O3 @ Skin	spinel @ layer
Al2O3	10.4	7.6
Cr2O3	72.0	63.9
Fe2O3	17.6	
FeO		5.6
MgO		22.9
Total	100.0	100

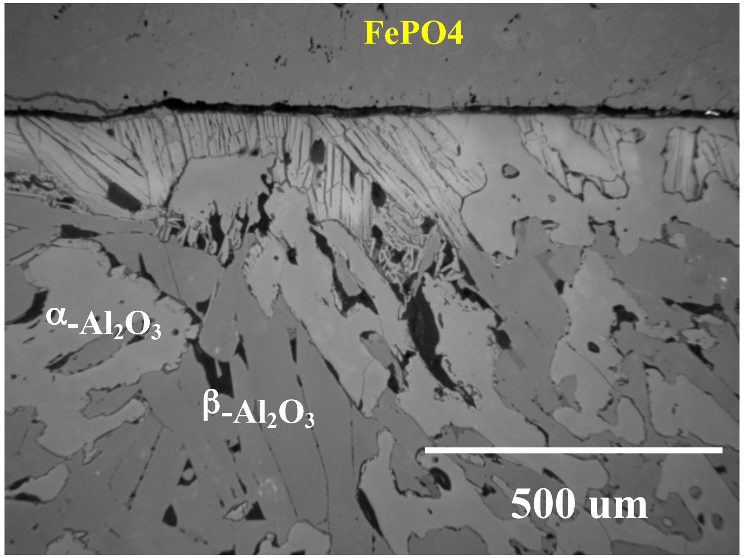
MgO not stable and readily migrates into the glass

Phosphate Glass Corrosion Analyses
F40 Type

High Alumina – Monofrax A2 and M



	Linescan
Al2O3	4.6
P2O5	52.4
Fe2O3	43.1
Total	100.0

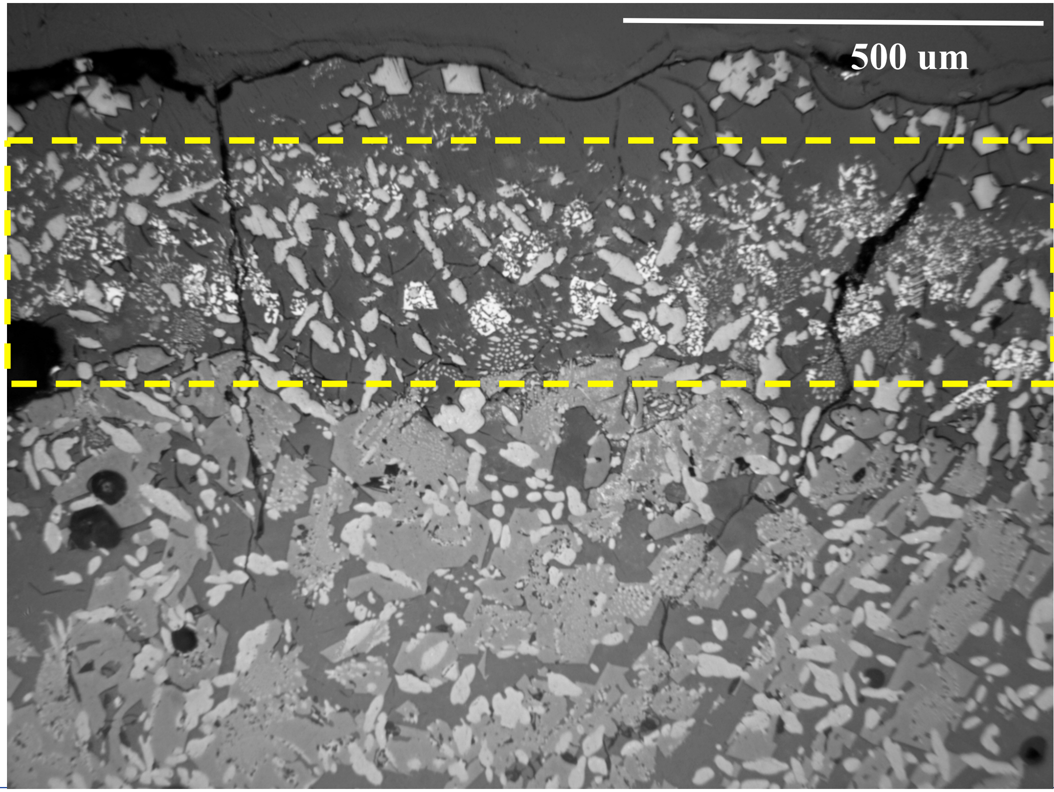


$\beta\text{-}Al_2O_3 \longrightarrow \alpha\text{-}Al_2O_3$

Evidence of Al2O3 going into solution within the iron phosphate layer

AZS – Monofrax CS3

Phosphate Glass Corrosion Analyses
MS26AZ102F-2 Type

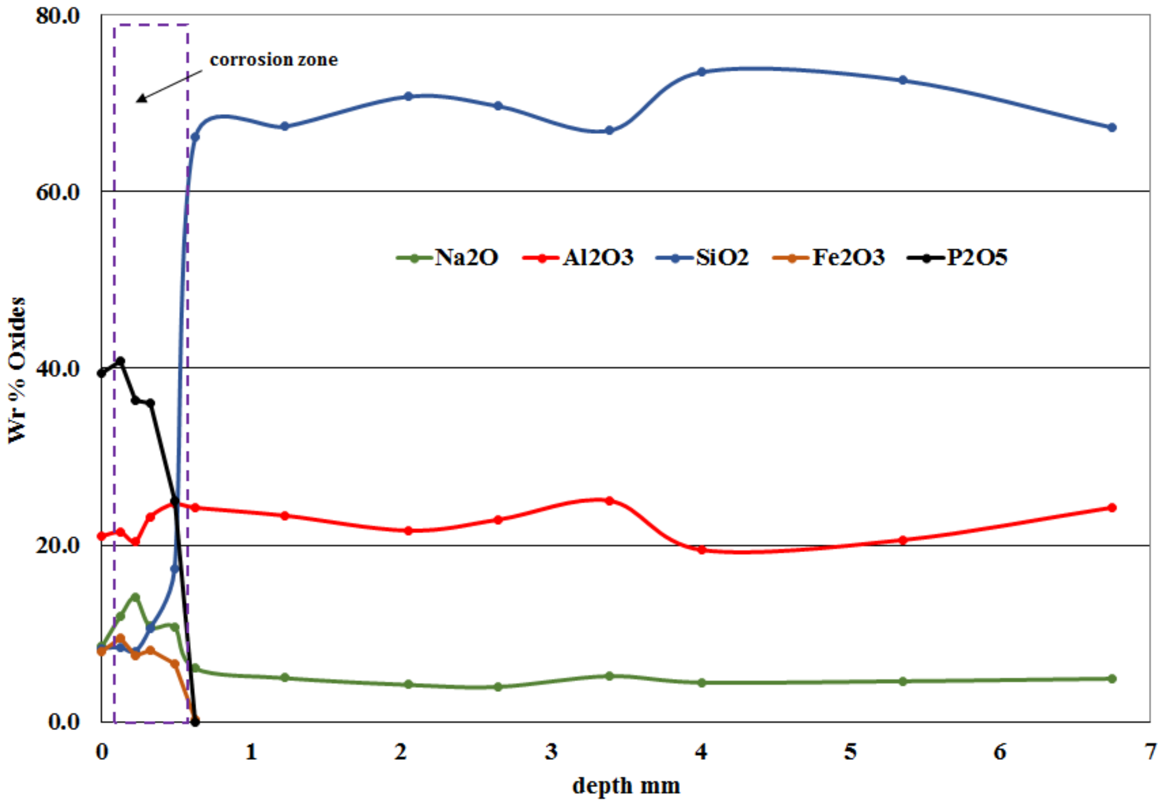


- Corrosion Zone
- Some similarities in passivation layer formation in AZS contact with sodalime glass

Phosphate Glass Corrosion Analyses
MS26AZ102F-2 Type

AZS – Monofrax CS3

Glass Phase Chemistry Trend

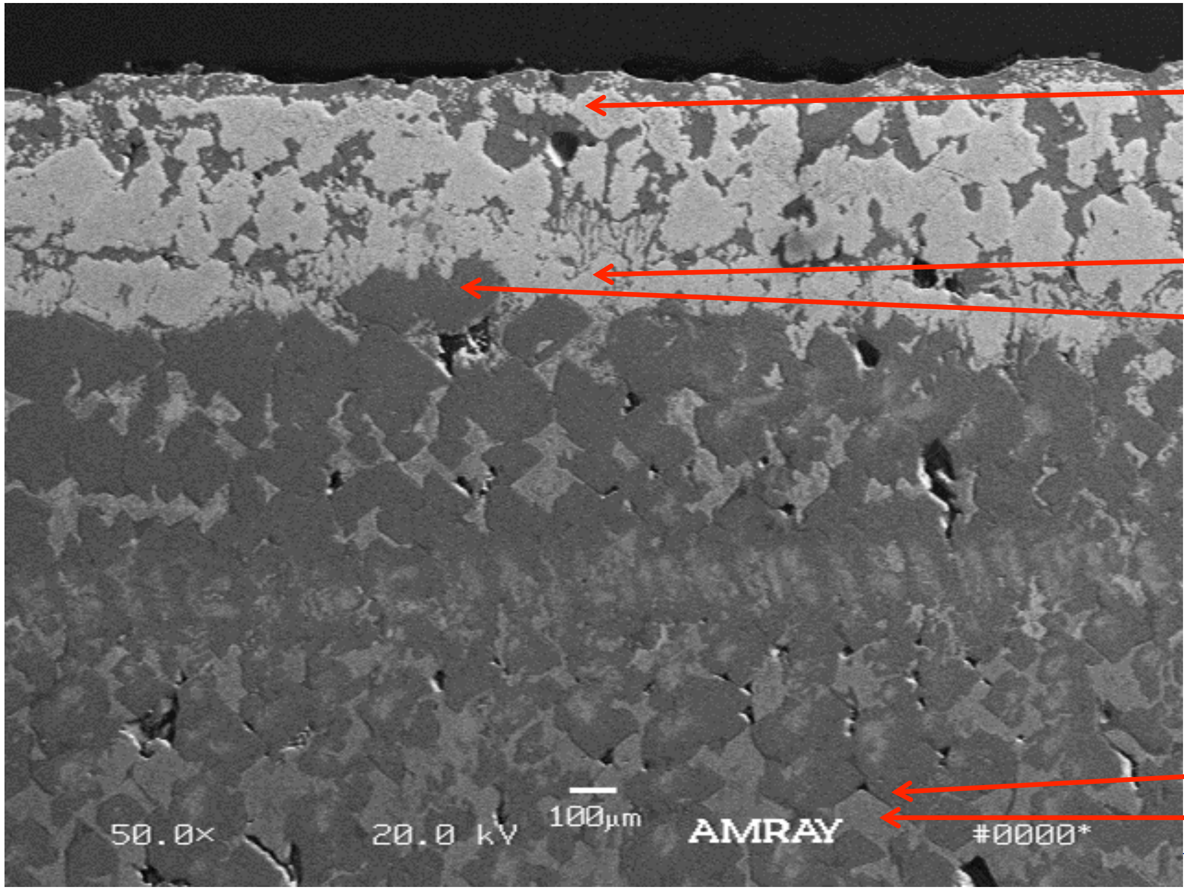


Primary AZS corundum goes into solution in corrosion zone. Promoted by Na2O increase and perhaps Fe2O3

Phosphate Glass Corrosion Analyses

MS26AZ102F-2 Type

Chrome – Monofrax K3



$Zn_{0.9}$ $(Al_{0.8}\ Cr_{0.8}\ Fe_{0.4})\ O_4$

$Zn_{0.9}$ $(Al_{1.2}\ Cr_{0.6}\ Fe_{0.3})\ O_4$

$(Al_{1.6}\ Cr_{0.4})\ O_3$

- MgO immediately decreases
- Zinc spinel forms at contact
- Al2O3 decreases

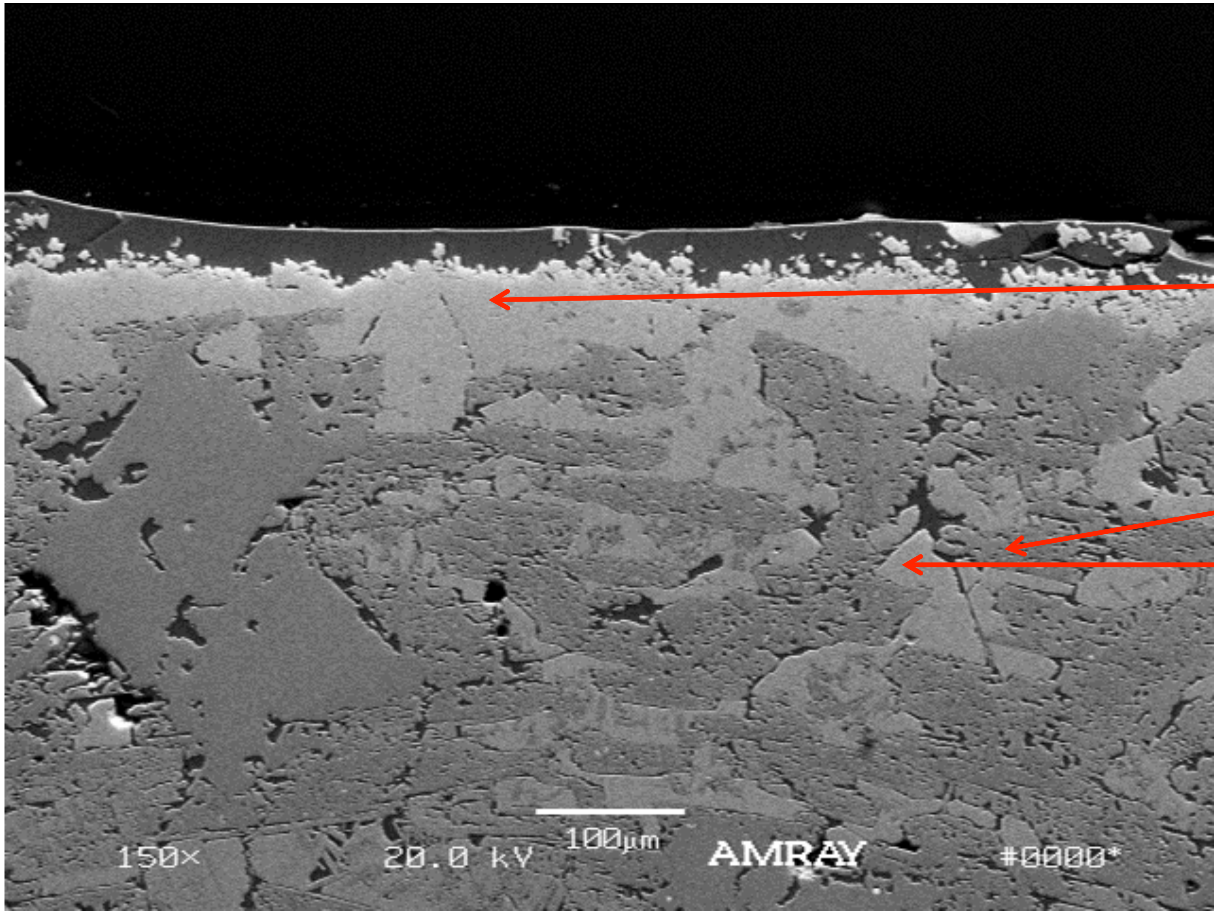
$(Al_{1.6}\ Cr_{0.4})\ O_3$

$Mg_{0.9}$ $(Al_{1.2}\ Cr_{0.7}\ Fe_{0.3})\ O_4$

Phosphate Glass Corrosion Analyses

MS26AZ102F-2 Type

Chrome – Monofrax E



$Zn_{0.9}$ $(Al_{0.1}\ Cr_{1.7}\ Fe_{0.2})\ O_4$

$(Al_{0.1}\ Cr_{1.5}\ Fe_{0.5})\ O_3$

$Zn_{0.9}$ $(Al_{0.2}\ Cr_{1.8}\ Fe_{0.2})\ O_4$

- Chrome-rich Zn-spinel skin formation
- Much less Al2O3 in spinel skin than seen in K3

Phosphate Glass Corrosion Analyses
MS26AZ102F-2 Type

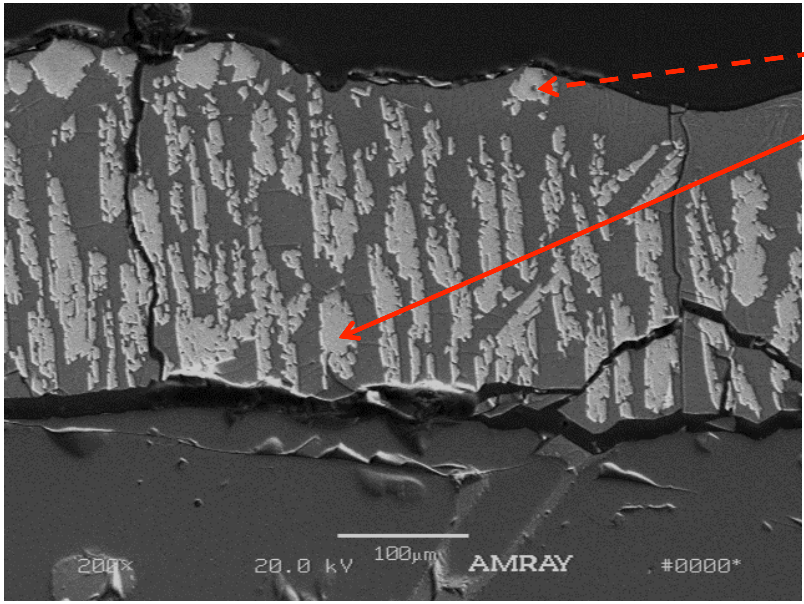
Monofrax

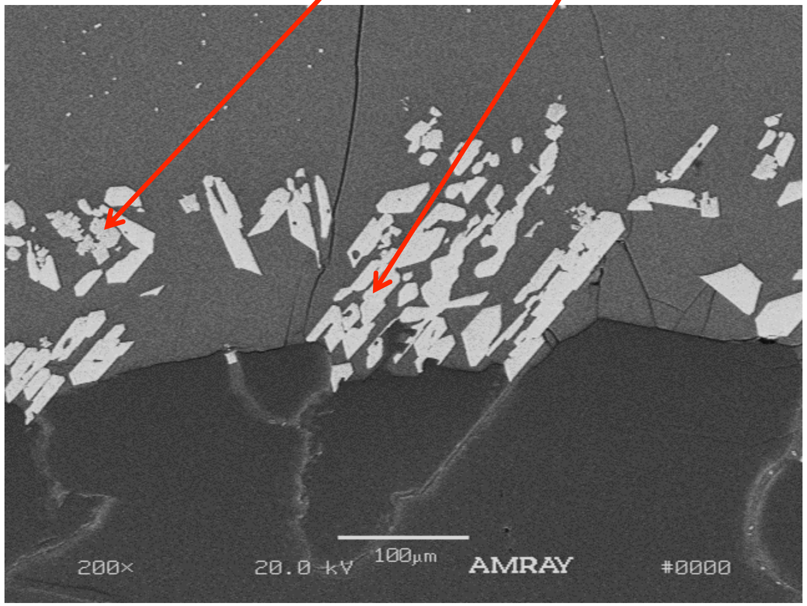
High Alumina – Monofrax A2 and M

$Zn_{1.0}$ $(Al_{1.3}\ Cr_{0.5}\ Fe_{0.3})\ O_4$?

$(Al_{0.2}\ Cr_{0.2}\ Fe_{1.6})\ O_3$

$(Al_{0.2}\ Cr_{0.1}\ Fe_{1.7})\ O_3$





- **Al2O3 goes into solution forming loose crystals of iron-rich R2O3 and a Zn-Spinel . No "protective layer"**

Summary

- Corrosion Behavior of **Chrome Fused Cast Refractory (Monofrax K3 and E)**
  - SRL 1983-1984: K3 → Ni, Fe, Cr spinel layer
  - PNNL: K3 → Ni, Fe, Cr spinel layer
  - $FePO_4$: K3 → R_2O_3 corundum solid solution layer

    E → R_2O_3 corundum solid solution layer
  - MS26AZ102F-2: K3 → Zn spinel layer

    E → Zn spinel layer

- Corrosion Behavior of **Fused Cast AZS (Monofrax CS3)**
  - $FePO_4$: No in-diffusion of Fe or P through glass phase. ZrO_2 → iron zirconate
  - MS26AZ102F-2: Corrosion zone (passivation layer?). Dissolution of primary corundum

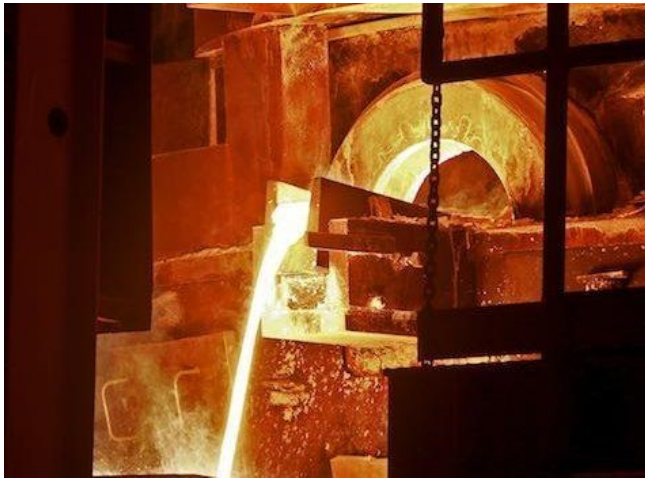
Summary

- Corrosion Behavior of **<u>High Alumina Fused Cast Refractory (Monofrax M and A2)</u>**
  - FePO4: A2 → Alumina dissolution into phosphate glass

    M → β-Al_2O_3 → α-Al_2O_3 alteration at glass contact
  - MS26AZ102F-2: A2 & M → High alumina phases dissociate to form Zn spinel and iron rich R2O3
- Finger corrosion results show Monofrax K3 and E perform the best over AZS and A2 for Iron Phosphate glasses
- Spinel forming oxides common in vitrification melter glass lead to forming protective spinel skin at glass contact (e.g. Al2O3, Fe2O3, MnO, NiO, Cr2O3, ZnO). Exception being the R2O3 layer in F40 corrosion of K3 and E
- Fusion cast chrome refractory materials well suited as refractory lining in contact with nuclear waste glass types.

Acknowledgments/Thanks

- Donna Guillen (INL), Albert Kruger (DOE), and Will Eaton (DOE) supplied K3 samples from Research Scale Melter #7
- CW Kim from MO-SCI Corporation supplied the F40 and MS26AZ102F-2 Iron Phosphate glasses for the finger corrosion tests
- Carol Jantzen of SRNL for comments and feedback
- Kai Xu of Wuhan University for comments and feedback



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QUESTIONS?

kevin.selkregg@monofrax.com