

The Future of Fiberglass Superstructure Refractories

Low creep crowns and no toxic Cr⁶⁺

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Industry Changes

Traditionally fiberglass has either been a boron containing E-glass for structural filaments or a high alkali and boron C-glass for insulation wool

In recent years fibers have diversified in composition resulting in both higher and lower temperature melters.

Most melters are now oxy-fired which is spreading into oxy-fired forehearths.

The use of chromic oxide in superstructure has been standard in C-glass but the formation of carcinogenic Cr^{6+} during use has long been a problem waiting for a solution.

What about the refractories?

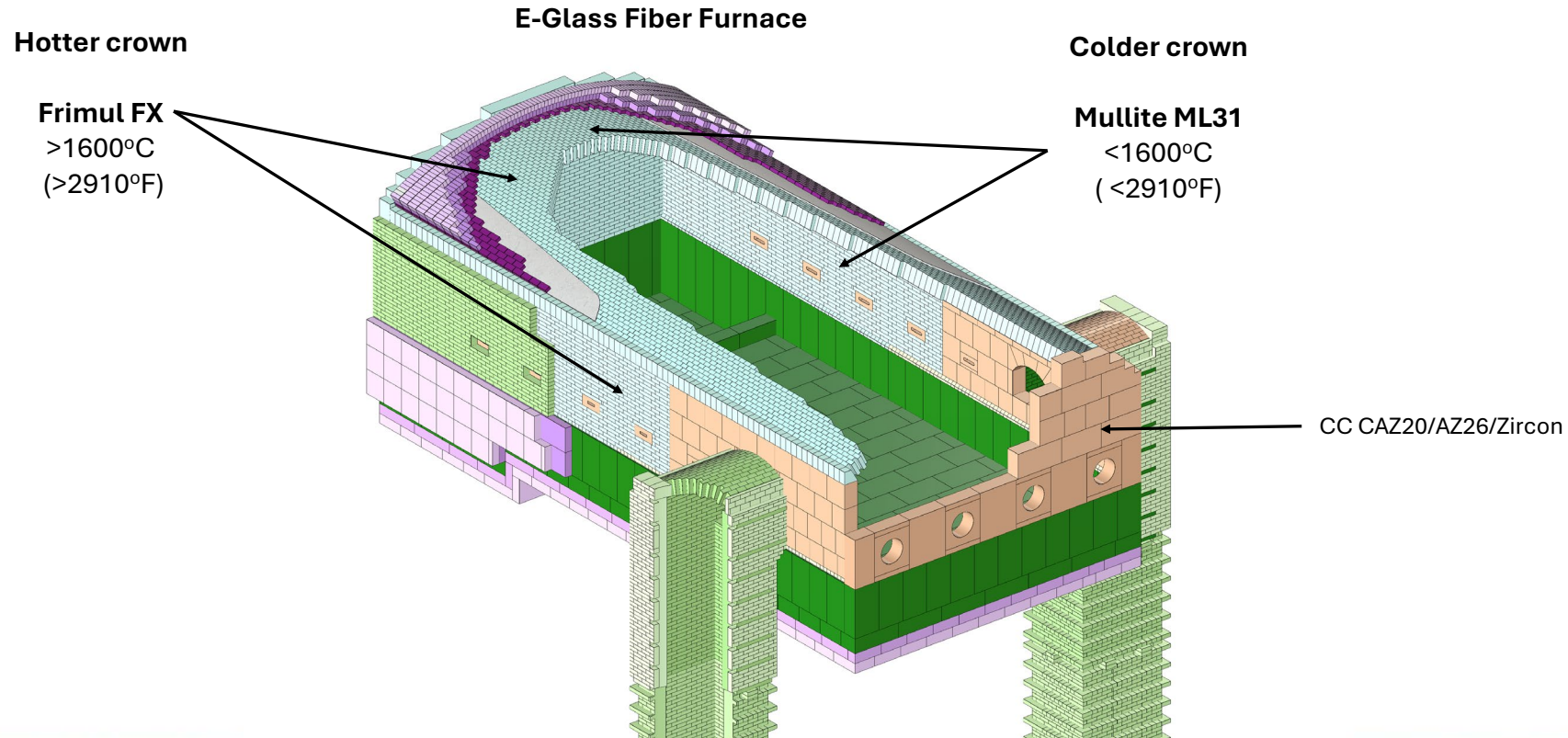
High and low temperature Mullite Crown Refractories

Typical Fused Mullite Crown



Structural Fiber Crown Refractories

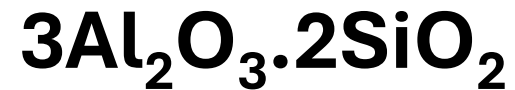
The choice of optimal crown mullite refractory depends on temperature of operation and high temperature creep resistance, separating into $>1600^{\circ}\text{C}$ operation and $<1600^{\circ}\text{C}$ operation



Mullite

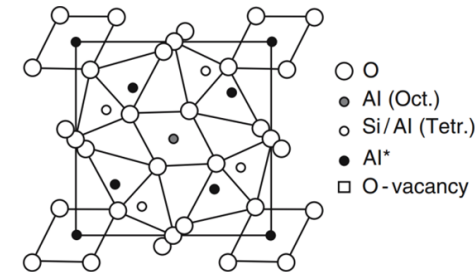
Mullite is the crystalline phase of choice for superstructure in filament fiber tanks because it has both resistance to boron vapour, a reasonable resistance to alkali vapour and has a **very good high temperature creep resistance**.

Mullite is the only stable intermediate phase in the alumina–silica system at atmospheric pressure.



This equates by weight to 72% Al_2O_3 , 28% SiO_2

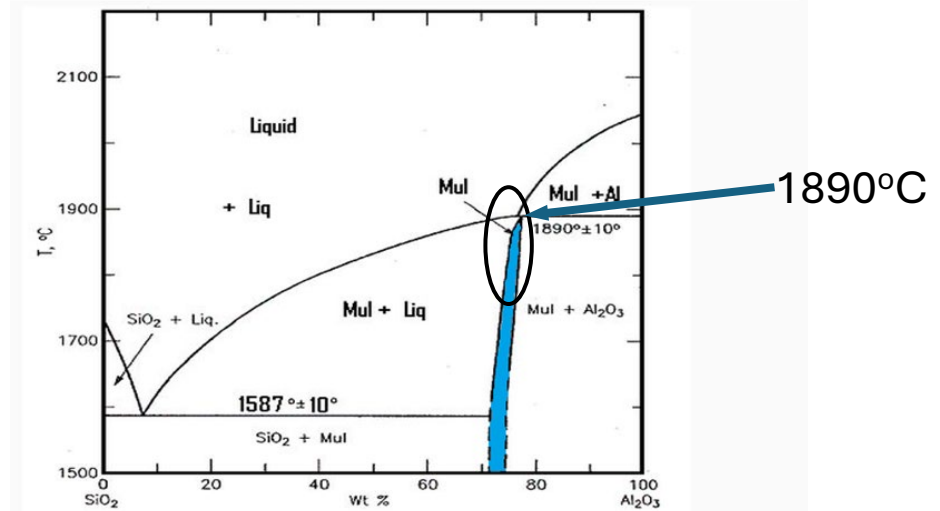
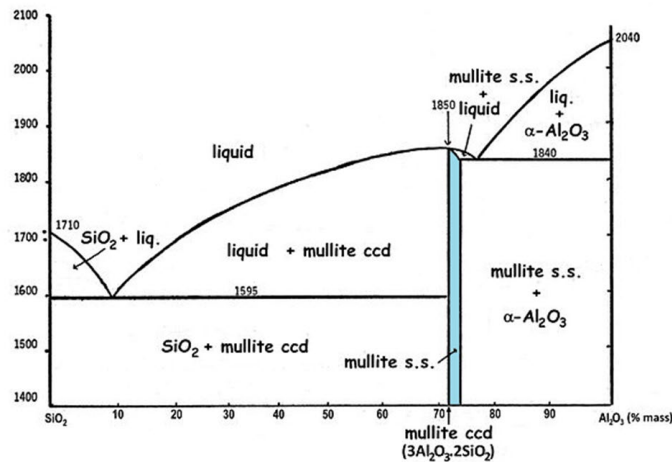
The solid solution can however go all the way over to $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$



Orthorhombic crystal structure

High Temperature Crowns >1600°C

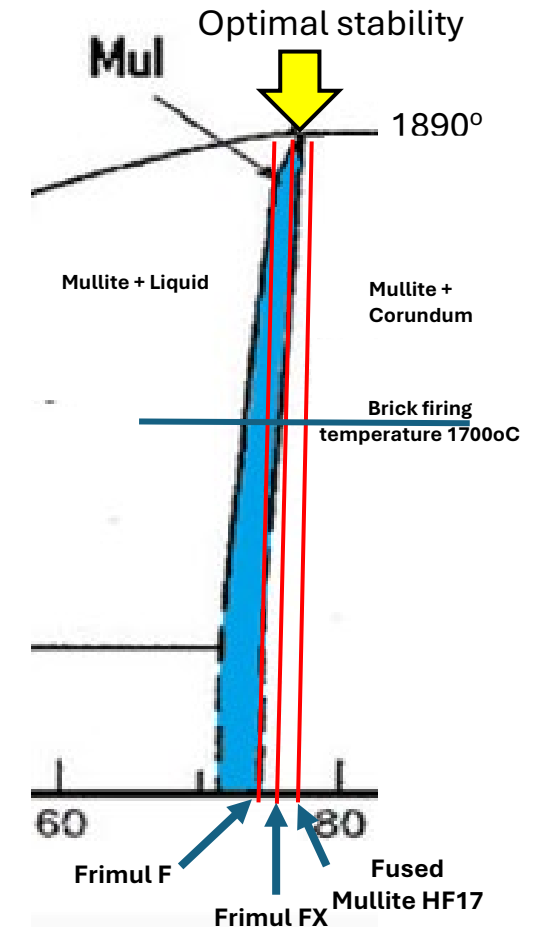
Older phase diagrams showed simply a stable mullite phase field with an 1850°C melting point but more recent measurements show Mullite has a higher temperature stability to 1890°C (3434°F) with a slightly higher alumina content



High Temperature Crowns >1600°C

DSF have specialised in getting the lowest creeps possible in fused mullite brick moving from Fused Mullite with a large excess of corundum to the proven standard 100% crystalline mullite Frimul F and now a new optimised stability composition Frimul FX.

	Al ₂ O ₃ (wt/%)	Mullite (%)	Corundum (%)	Theoretical phases at 1890°C
Fused Mullite HF17	77.6	85	15	Mullite + corundum
Frimul F	74.6	100	0	Mullite + liquid
Frimul FX	75.6	95	5	Mullite



Last Generation Fused Mullite

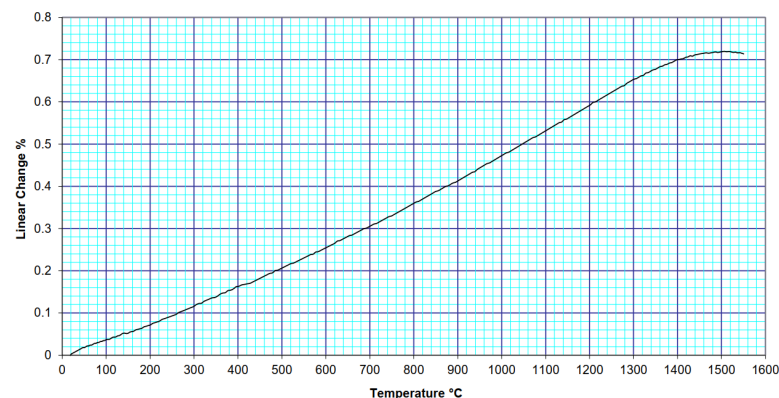
Original Fused Mullite HF17 1550°C Creep (0.2 MPa)

Fused Mullite HF17

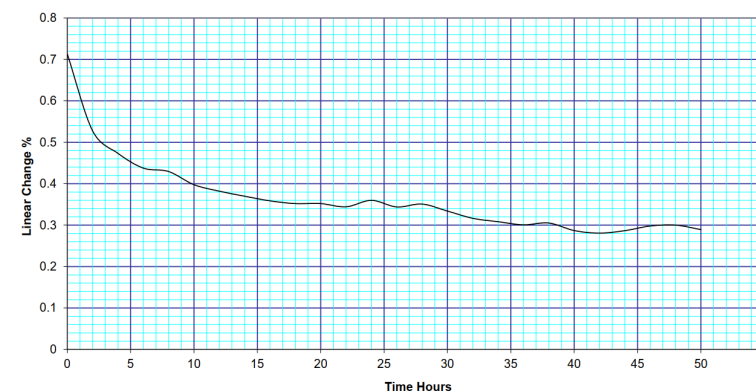
Typical Chemical Analysis (wt %)	
Al ₂ O ₃	77.6
Fe ₂ O ₃	0.05
SiO ₂	22.1

Typical Physical Properties	
Bulk Density (g/cm ³)	2.59
Apparent Porosity (%)	18.3
Cold Crushing Strength (MN/m ²)	55

85% Mullite
15% Corundum



Determination of Creep in Compression
(B.S EN 993-9 : 1997)



0.4% creep @ 1550°C (2822°F)

The large excess of corundum compromises the creep resistance

Current Generation Fused Mullite

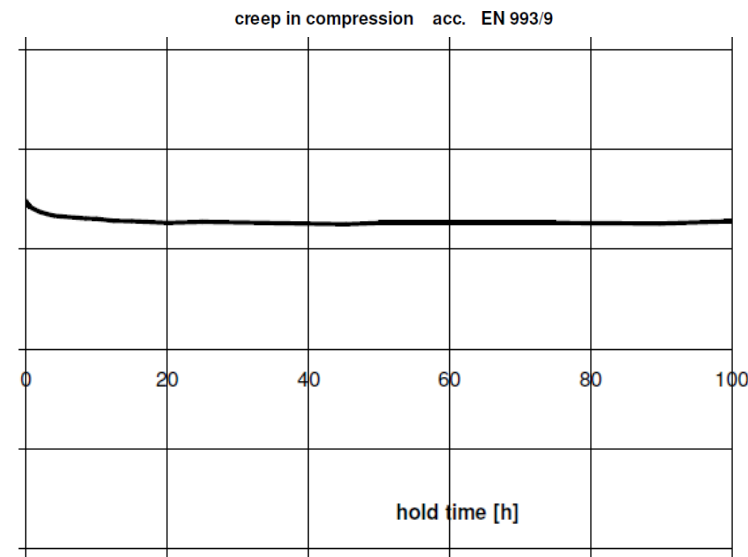
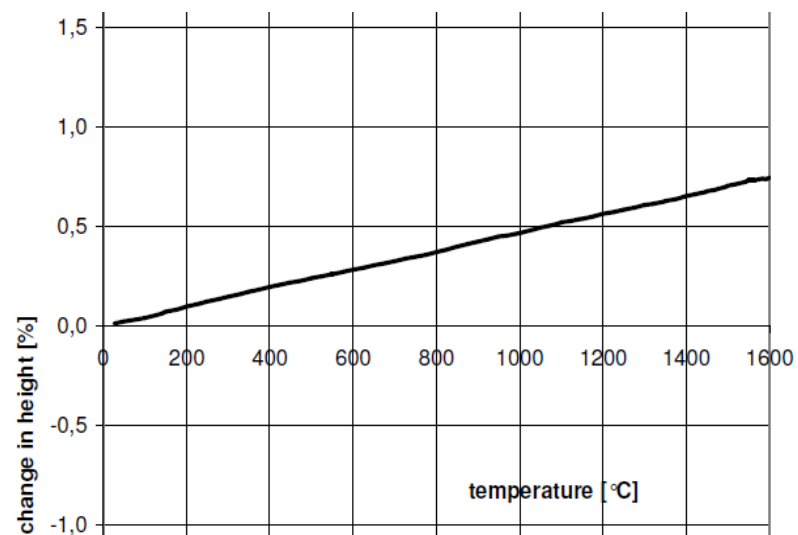
Frimul F 1600°C Creep (0.2 MPa)

Frimul F

Typical Chemical Analysis (wt %)	
Al ₂ O ₃	74.6
Fe ₂ O ₃	0.08
SiO ₂	24.6

Typical Physical Properties	
Bulk Density (g/cm ³)	2.60
Apparent Porosity (%)	16.2
Cold Crushing Strength (MN/m ²)	83

100% Mullite



0.2% creep @ 1600°C (2912°F)

Good but significantly higher creep at increased load

New Generation Fused Mullite

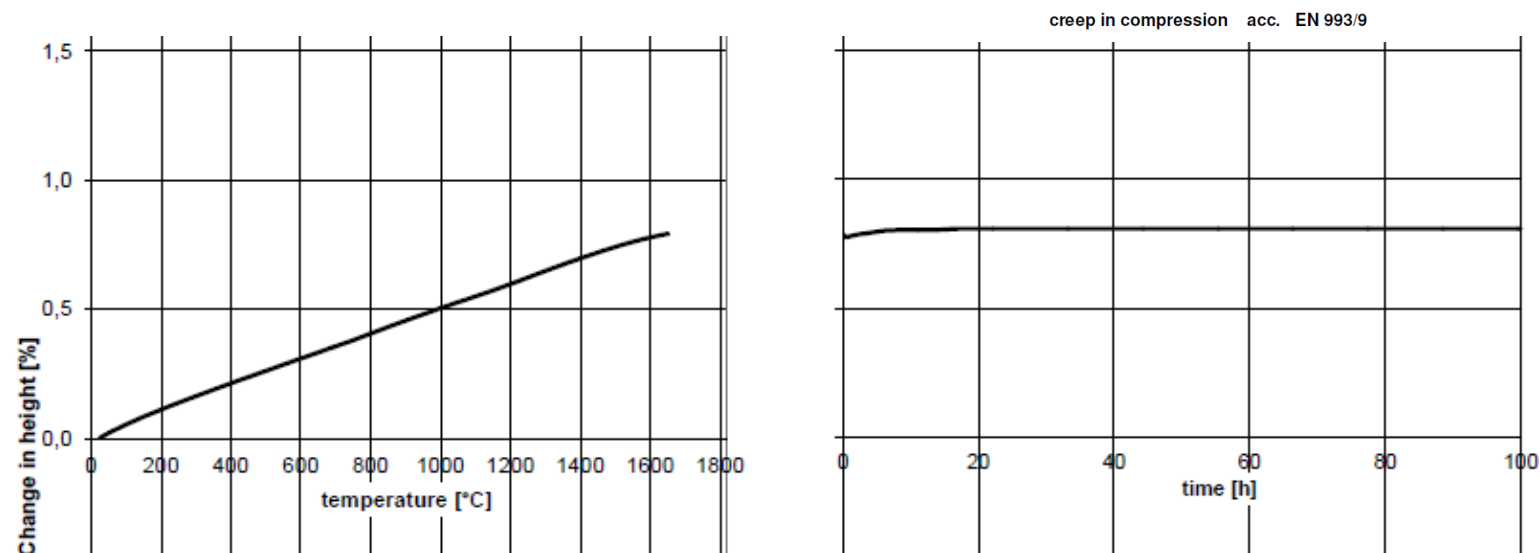
Frimul FX 1650°C Creep (0.2 Mpa) – Higher Temperature

Frimul FX

Typical Chemical Analysis (wt %)	
Al ₂ O ₃	75.6
Fe ₂ O ₃	0.05
SiO ₂	24.2

Typical Physical Properties	
Bulk Density (g/cm ³)	2.62
Apparent Porosity (%)	16.2
Cold Crushing Strength (MN/m ²)	111

95% Mullite
5% Corundum



ZERO creep @ 1650°C (3002°F)

High Temperature Crowns >1600°C

Frimul FX 1600°C Creep (0.5 Mpa) – Higher Load

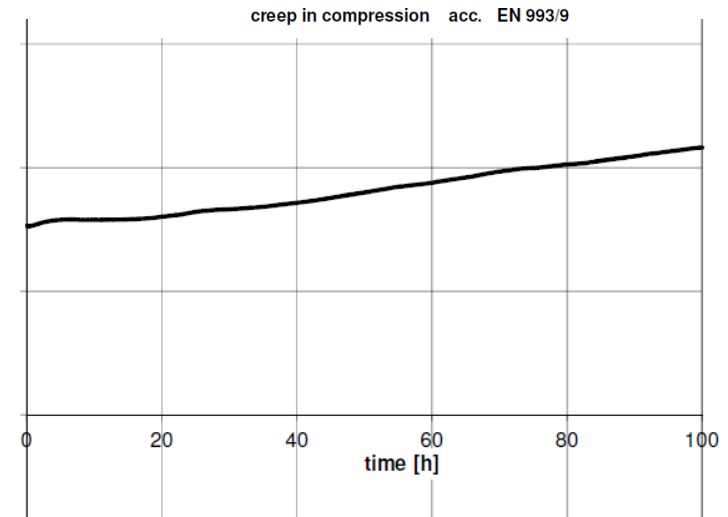
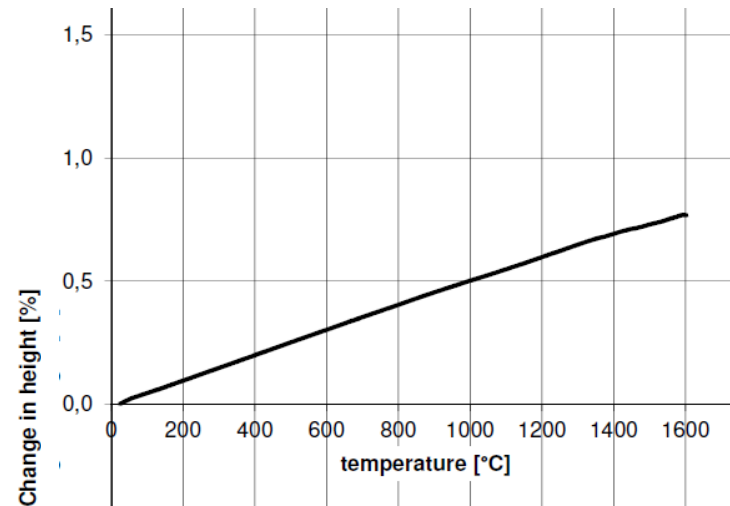
Under higher load the Frimul FX structure pushes back against the creep

Frimul FX

Typical Chemical Analysis (wt %)	
Al ₂ O ₃	75.6
Fe ₂ O ₃	0.05
SiO ₂	24.2

Typical Physical Properties	
Bulk Density (g/cm ³)	2.62
Apparent Porosity (%)	16.2
Cold Crushing Strength (MN/m ²)	111

95% Mullite
5% Corundum



0.3% expansion @ 1600°C (2912°F)

Ideal for hot E-glass melters and other hot special glass crowns

Lower Temperature Crowns <1600°C

Mullite ML31 1600°C Creep (0.2 Mpa)

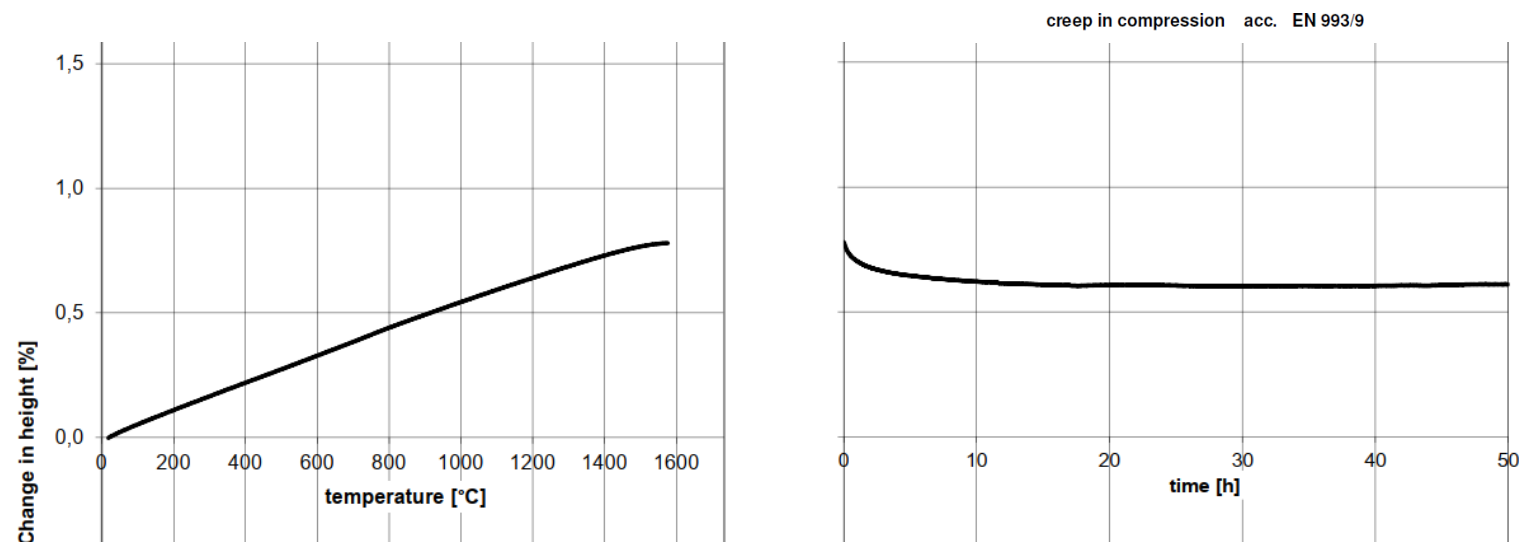
For furnaces with crowns below 1600°C **Mullite ML31**, use a low creep sintered mullite

Mullite ML31

Typical Chemical Analysis (wt %)	
Al ₂ O ₃	70.4
Fe ₂ O ₃	0.74
SiO ₂	27.7

Typical Physical Properties	
Bulk Density (g/cm ³)	2.51
Apparent Porosity (%)	18.8
Cold Crushing Strength (MN/m ²)	65

92% Mullite
6% Corundum

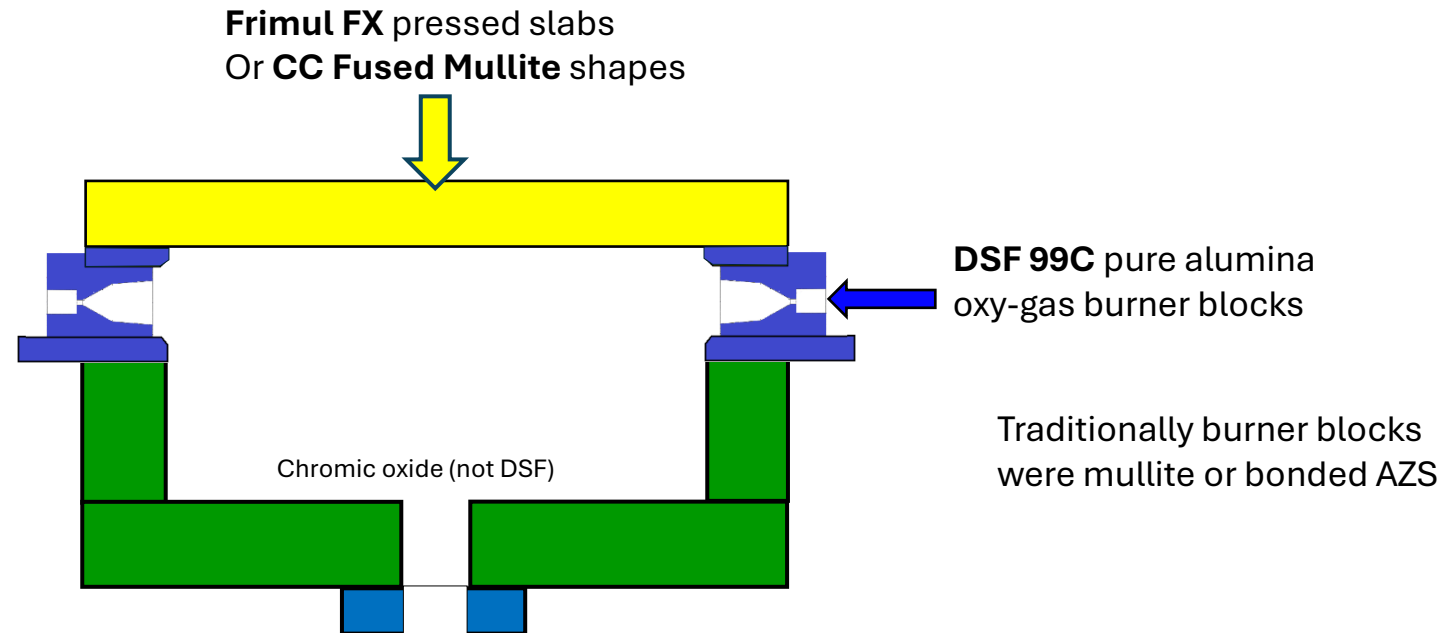


The mullite in ML31 is formed during high firing above 1650°C to give a lower cost mullite crown for operating below 1600°C, suitable for some fiberglass compositions and sodium silicate.

Pure Thermally Shock Resistant Burner Blocks for Oxy-fired Forehearths

Oxy-fired Forehearth Burners

Better new materials have been developed for E-glass forehearth burners with a new thermal shock resistant pure alumina outperforming traditional materials



DSF 99C at 99.8% Al_2O_3 has a higher melting point than mullite or bonded AZS materials close to 2050°C

Thermally Shock Resistant Alumina

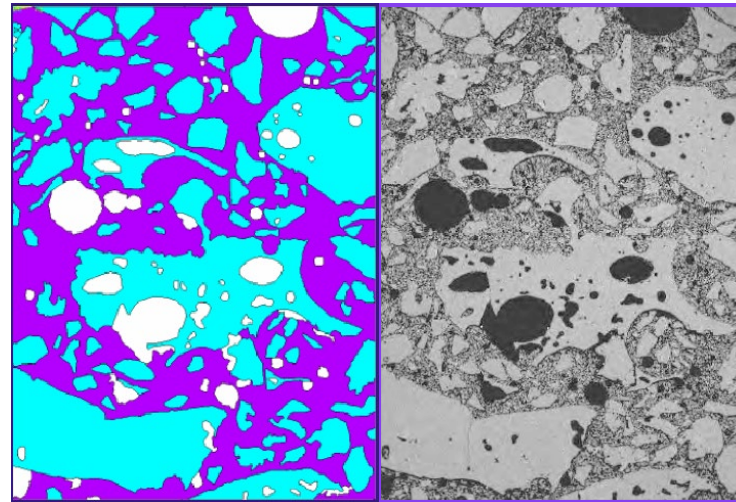
DSF 99C

Typical Chemical Analysis (wt %)	
Al ₂ O ₃	99.8
Fe ₂ O ₃	0.01
SiO ₂	0.09

Typical Physical Properties		
Bulk Density	(g/cm ³)	3.18
Apparent Porosity	(%)	19.6
Cold Crushing Strength	(MN/m ²)	90
Thermal Shock Resistance	(cycles survived) 950°C to water	>30

DSF 99C at 99.8% Al₂O₃ uses a pure alumina casting method resulting in a microstructure that gives >30 cycles (950°C to water) thermal shock resistance

DSF 99C oxy-fired forehearth burner blocks first installed 2015 and now proven performance



Low Permeability **AZS** replacement for **Chrome** C-Glass Superstructures

The Problem with Alumina-chrome

C-glass insulation fiber melters typically use refractories based on alumina and chromia in their superstructures to resist the high level from sodium and boron vapour.

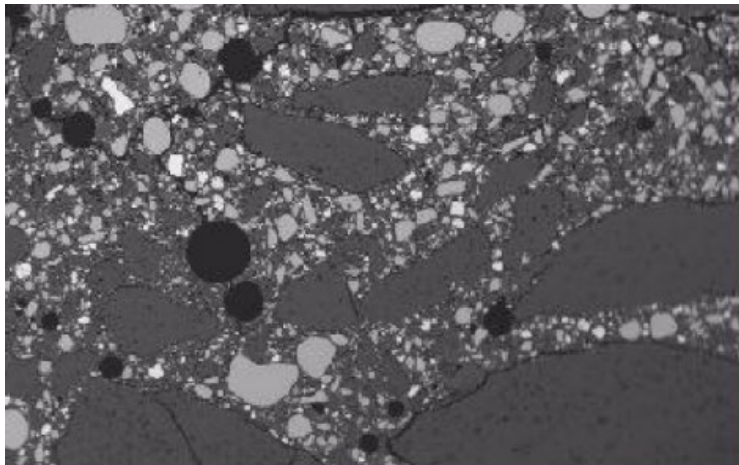
However, the chromium in alumina-chrome formed **toxic** carcinogenic Cr^{+6} with the alkali vapour during the campaign.

This means a complicated demolition procedure and expensive disposal of used furnace superstructure refractories.

Is there a refractory that will work that is non-toxic after use?

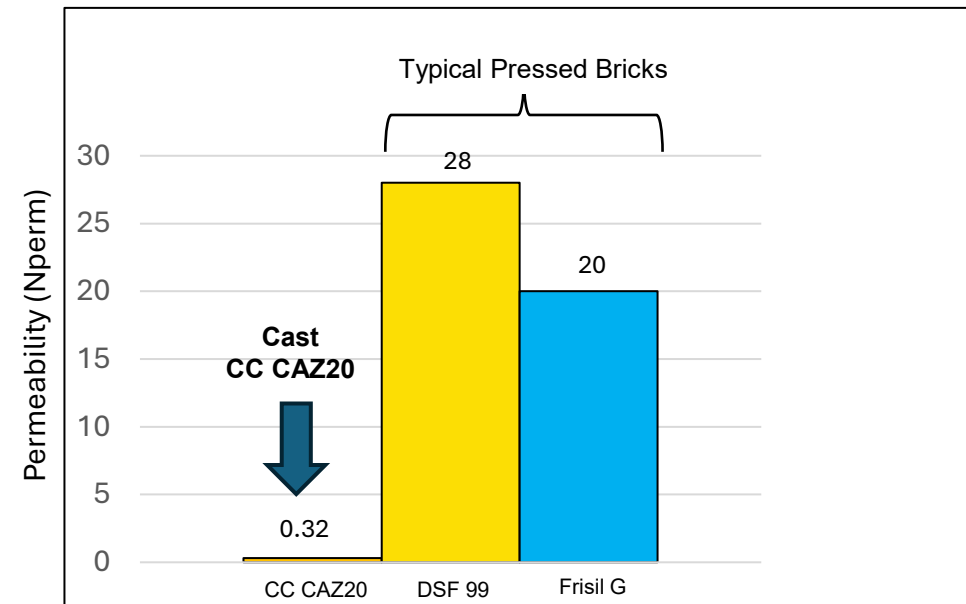
Yes – Low Permeability Bonded AZS

CC CAZ20 is an alumina-zircon-zirconia material with a low permeability structure to stop penetration into the surface and a high purity matrix to stop zircon dissociation



CC CAZ20 Microstructure

Typical Chemical Analysis (wt %)	
Al ₂ O ₃	70.7
ZrO ₂	17.9
SiO ₂	9.7



Determination of permeability to Gases

BS 1902:Section 3.9: EN993-4: 1995

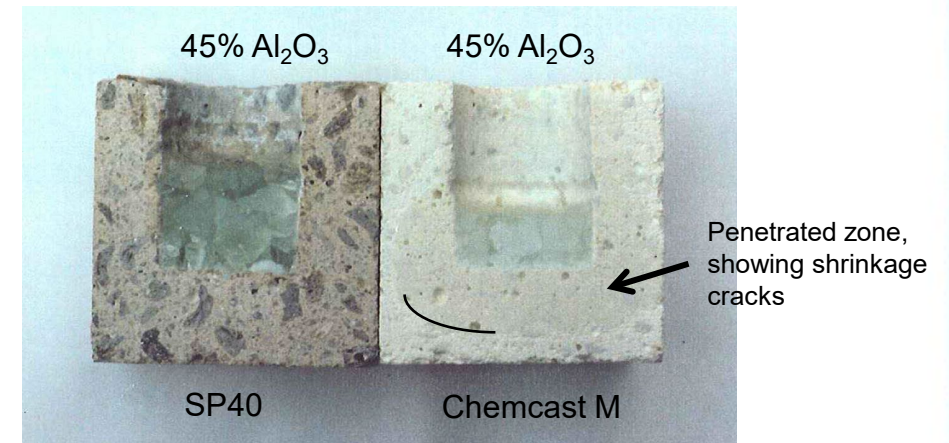
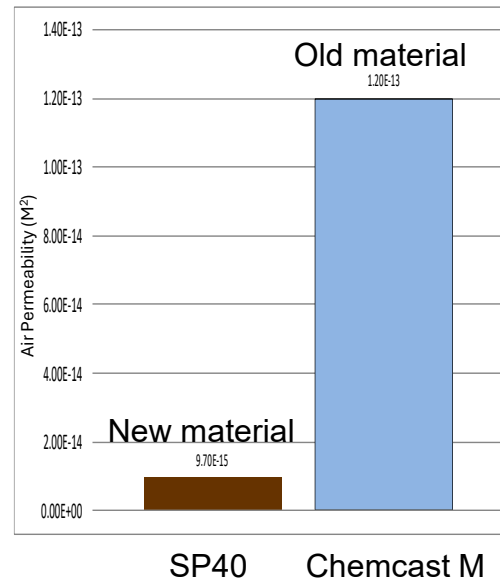
How Much Can Permeability Affect a lifetime?

Case Study on a Sodium Phosphate Tank Melter Superstructure

This is a case study on another glass where we have already increased melter wall life by changing only the permeability NOT the chemistry of the lining



Superstructure corroded by volatile soda and phosphate



**Sidewall life increase
from 9 months to 3 years.**

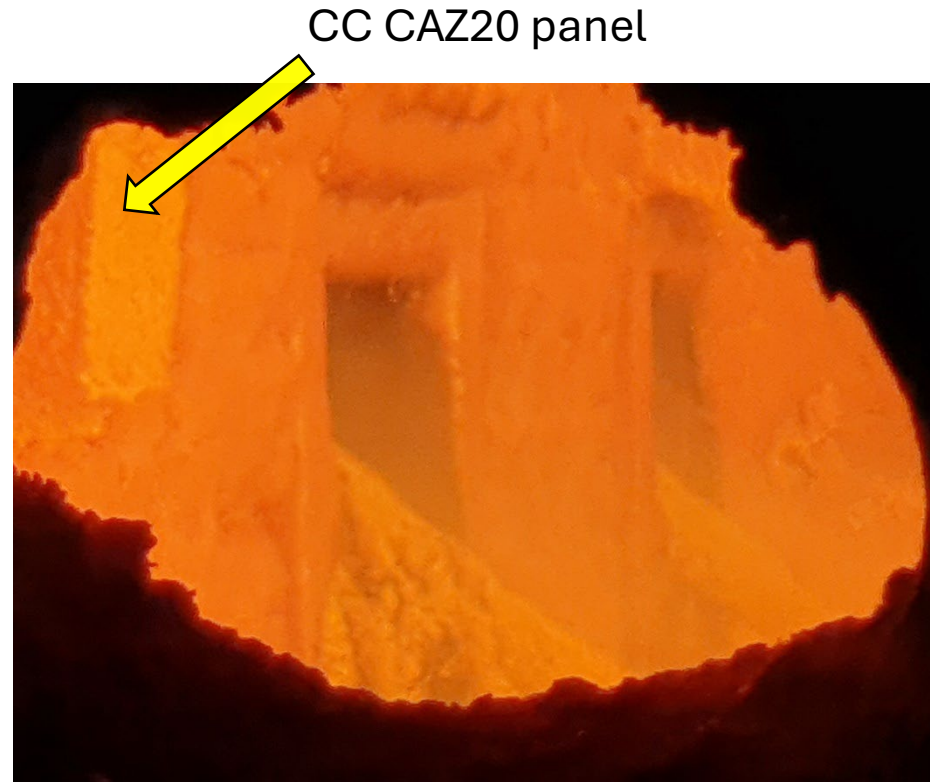
C-Glass Fiber Melter Wall Trial

The trial block of CC CAZ20 was put in a 30% Cr_2O_3 - Al_2O_3 wall between batch chargers in December 2017.

Na_2O ~14%
 B_2O_3 ~5%

Furnace came down after **5y10m** with the CC CAZ20 trial panel looking 'at least as good as the chrome'.

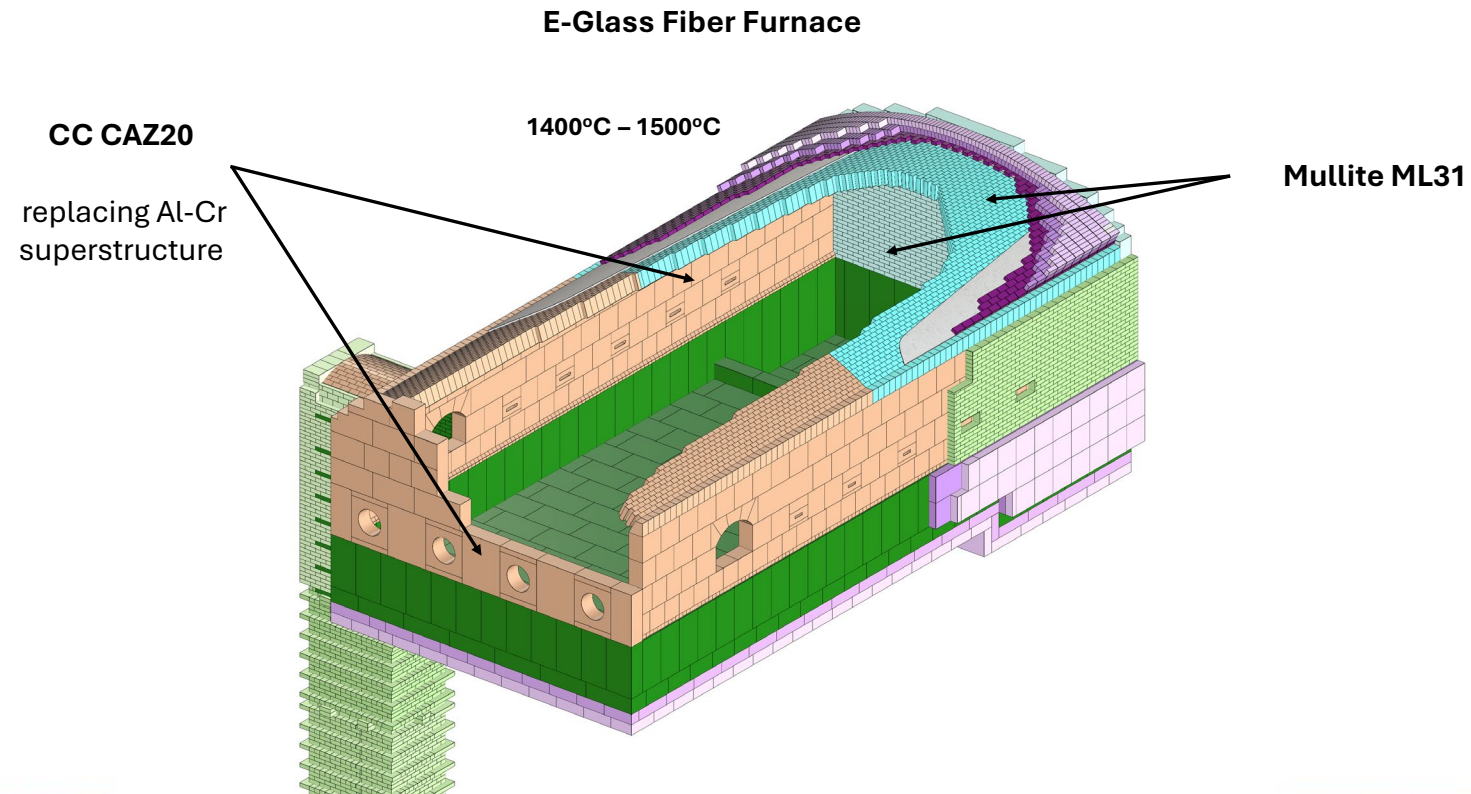
A second trial is still in a forehearth, currently on 6 years.



After 4 years 1 month
January 2022

C-Glass Fiber Melter Wall Trial

The low permeability CC CAZ20 can now replace the alumina-chrome in insulation fiber melter superstructures making them non-toxic after use



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Thank you to the glass makers that allowed photographs to be used in this presentation