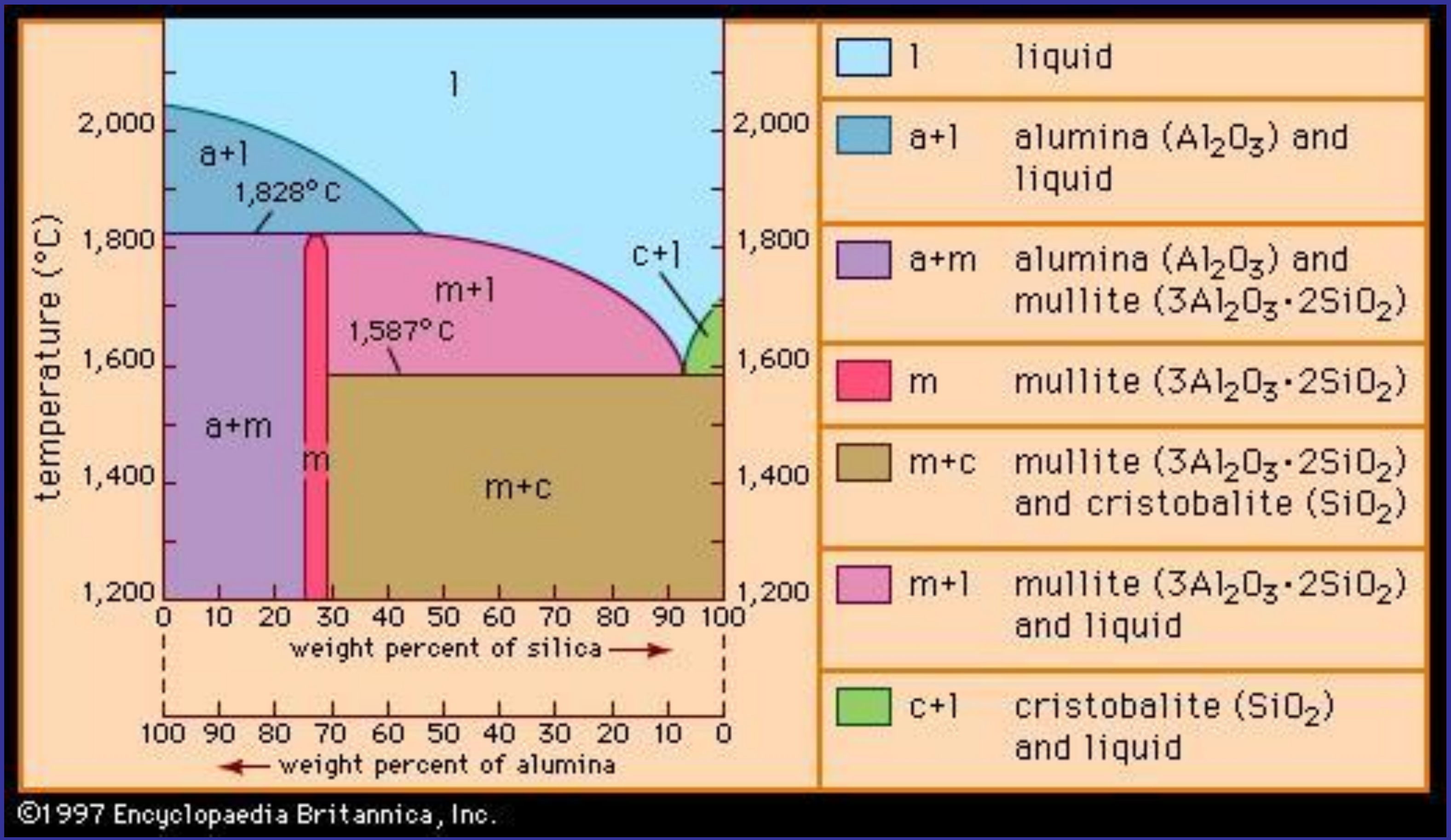
Institute of Refractories Engineers

Aumino-Silicate Refractories

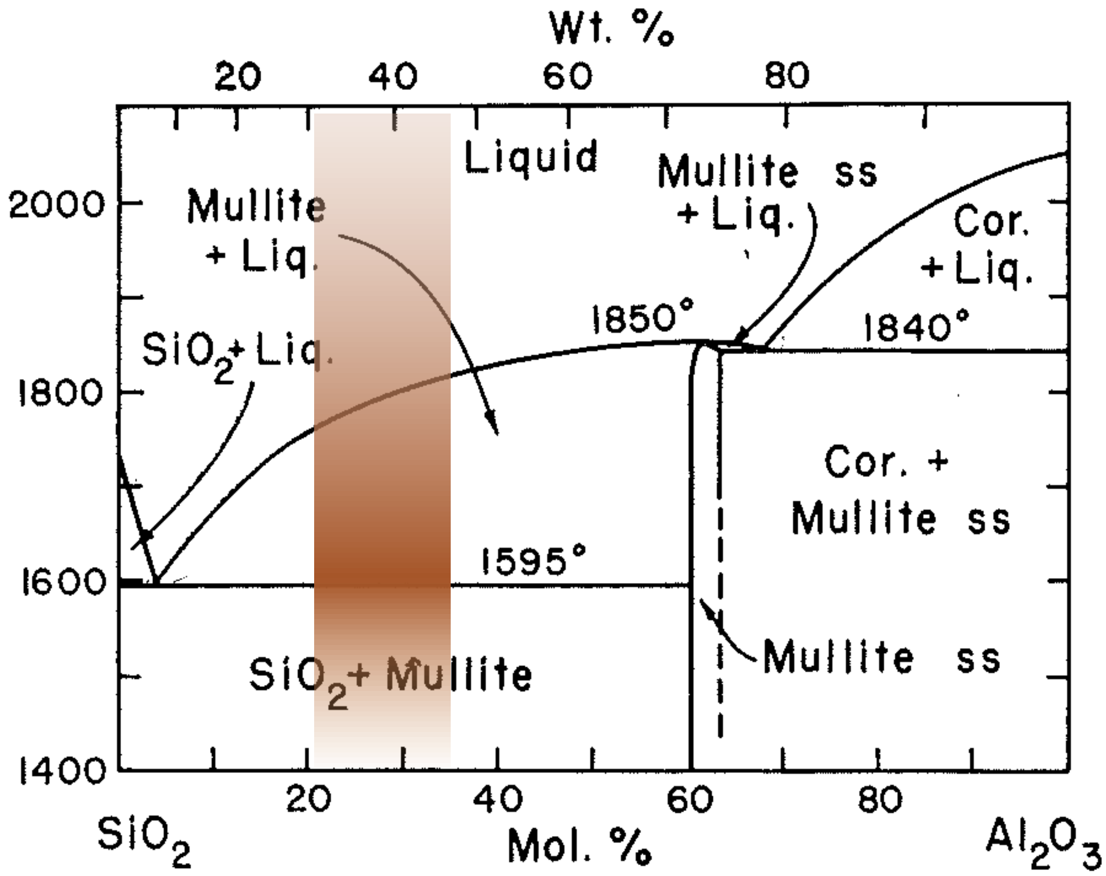
Kenwood Hall
31/10/13

Chris Windle

Alumio-silicate Compositions



Fireclay, 30 – 45% Al_2O_3

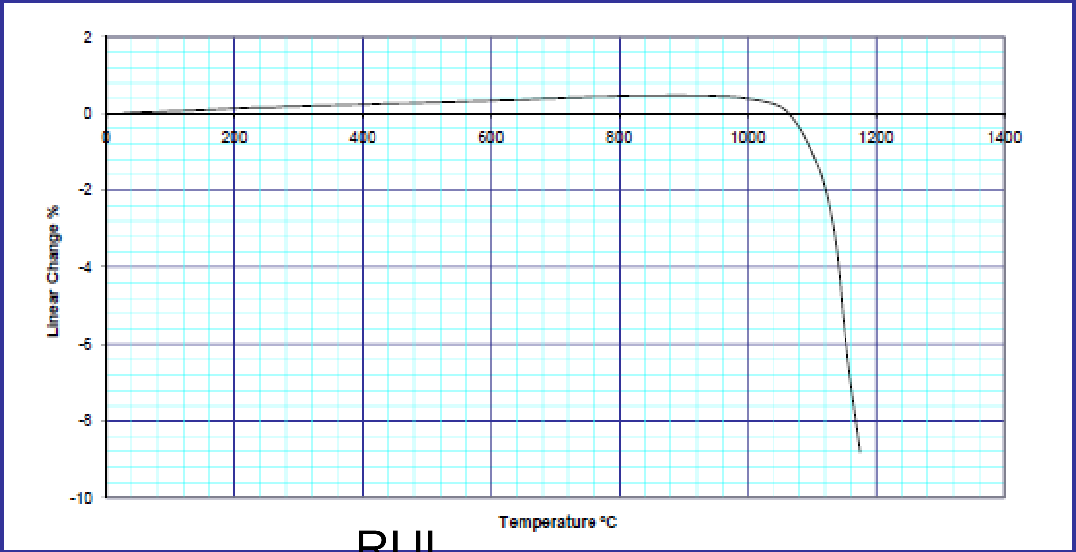


Fireclay

- Refractory manufactured from calcined densified clay aggregates mixed with plastic clays, dry pressed and fired to a range of temperatures
- Application defined by the amount and composition of the inherent glassy phase
- Classified by alumina content, softening behaviour (PCE), density/porosity, Refractoriness Under Load (RUL), and occasionally creep resistance (deformation of a refractory over time placed under a defined load at a defined temperature)

t 0.5% 1066°C
t 0.5% 1430°C

PCE



RUL

Fireclay, Classification

	Group	Al_2O_3	PCE	Density (g/cc)
BSi/ISO	FC30	≥30, <35		
	FC35	≥35, <40		
	FC40	≥40, <45		
	Medium Duty		29	
ASTM	High Duty		$31^{1/2}$	2.19
	Super Duty		33	2.24
Other	AO	≥ 42	34 (SK)	
	AI Special	40 - 42	33/34 (SK)	
	AI	37 - 40	33 (SK)	
	AII	33 - 37	32 (SK)	
	AIII	30 - 33	30 (SK)	

Fireclay, CO Resistance

Determination of Resistance to Carbon Monoxide
(BS EN ISO 12676: 2003)

1. Samples

The samples consisted of two prisms of dimensions 50mm x 50mm x 75mm

2. Results

Sample Mark	Observations	Classification in Accordance with Clause 9
KS/0306 1	Unaffected	1
KS/0306 2	Unaffected	1

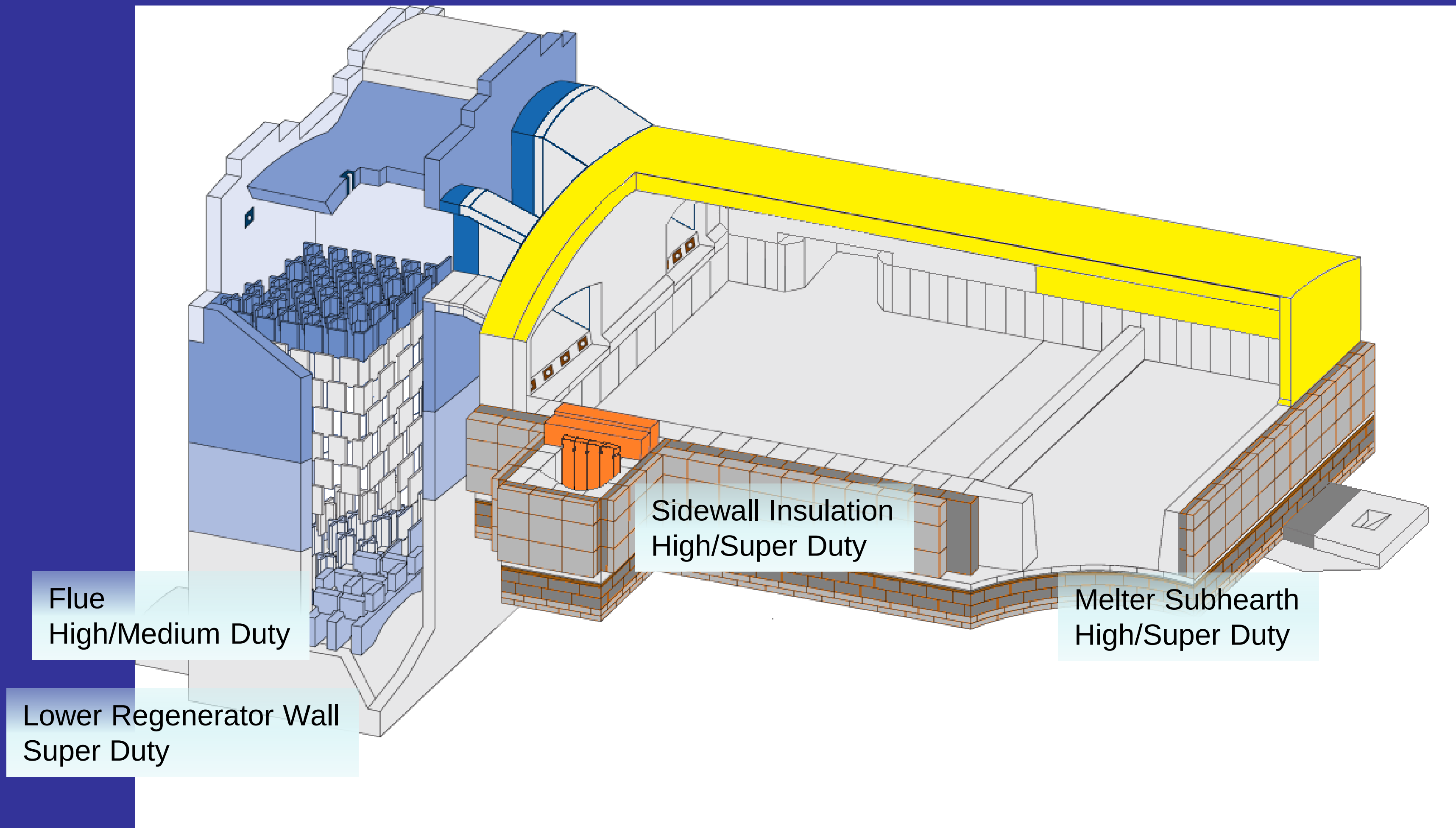
The test temperature was maintained at 500 +/- 10^{O}C

The CO gas flow rate was maintained at 30cc/min.

The planned duration of the test was 200 hours and the actual test duration was 200 hours.

Fireclay, CO Resistance

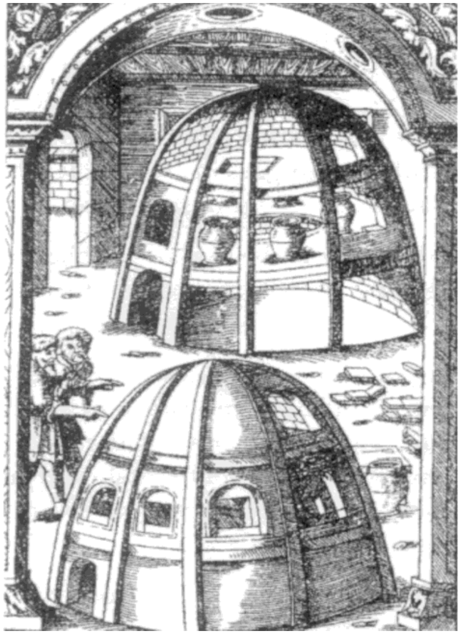
Fireclay Applications (Glass)



Fireclay

DSF

1400 to 1700 AD, Venetian Glass Dominates



A typical pot furnace in Venice

The bottom section contained the fire which spread up a central eye, in the middle section the glass was melted in pots, and the top section running at a much lower temperature was used for annealing or batch pre-heating.

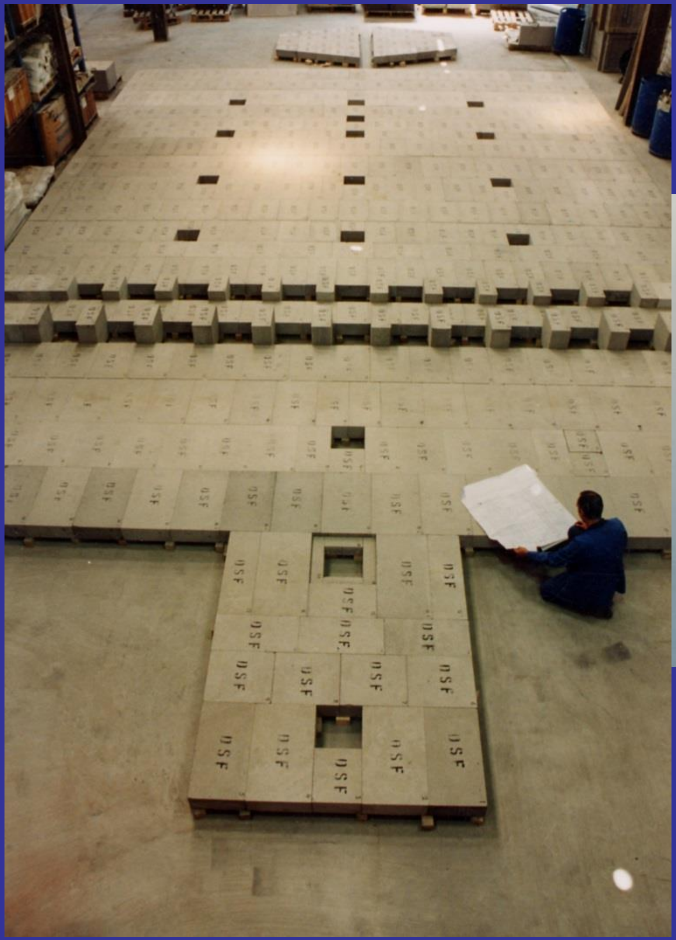
Wood was essential for heat and the supply of alkalis form the ash.

Dire penalties for glassmakers who took their skills abroad, even death!

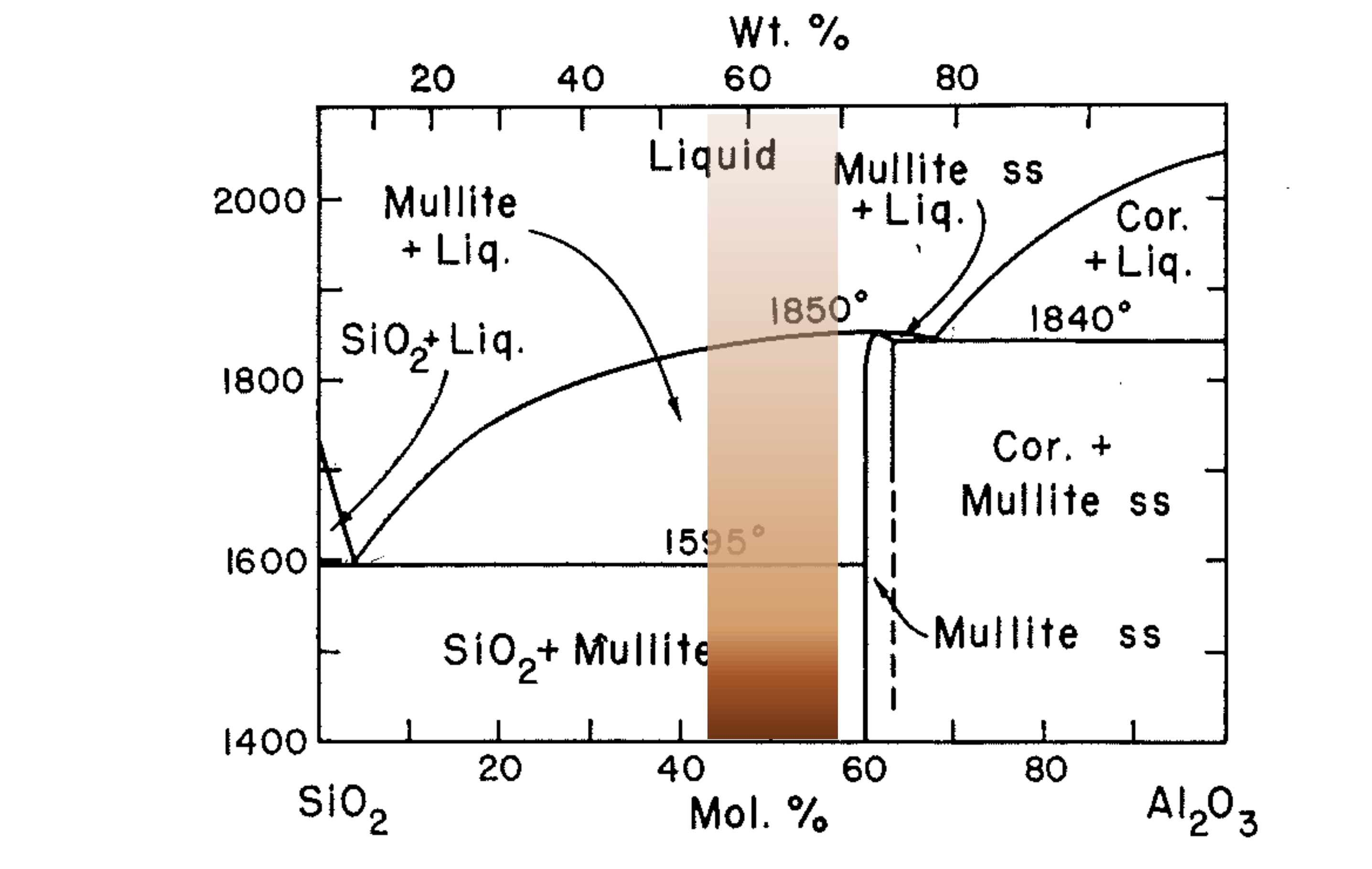
Developed cristallo glass from quartz pebbles, soda ash (marine plant) and manganese.

Also famed for filigree ornate glass

Fireclay



Sillimanite & the Polymorphs, 55 – 65% Al_2O_3



Sillimanite and the Polymorphs

Sillimanite; named after Dr Benjamin Silliman (1779-1864), Professor of Chemistry at Yale

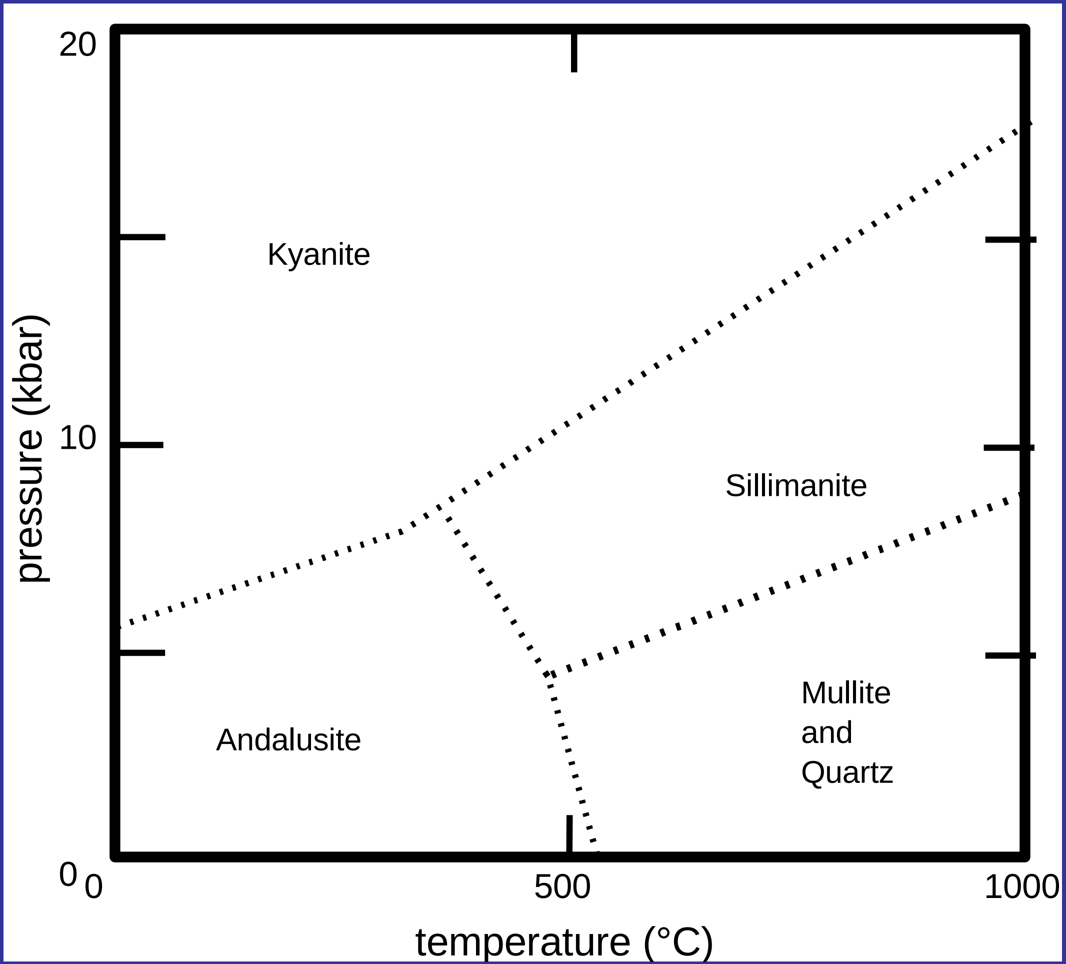
Sillimanite is an anhydrous alumino-silicate; formula $Al_20_3.SiO_2$

Sillimanite is the rarest of the trimorphs (andalusite & kyanite); formed at temperatures >500C under pressure

Sillimanite; now a generic refractory term encompassing all products suitable for the glass making environment with Al_2O_3 contents between 55 – 65 %

“Sillimanite blocks have given very satisfactory results and are in many **glassworks found to be much more durable than fireclay blocks (11 months against 6 weeks)”**
A.B.Searle 1940

Sillimanite and the Polymorphs

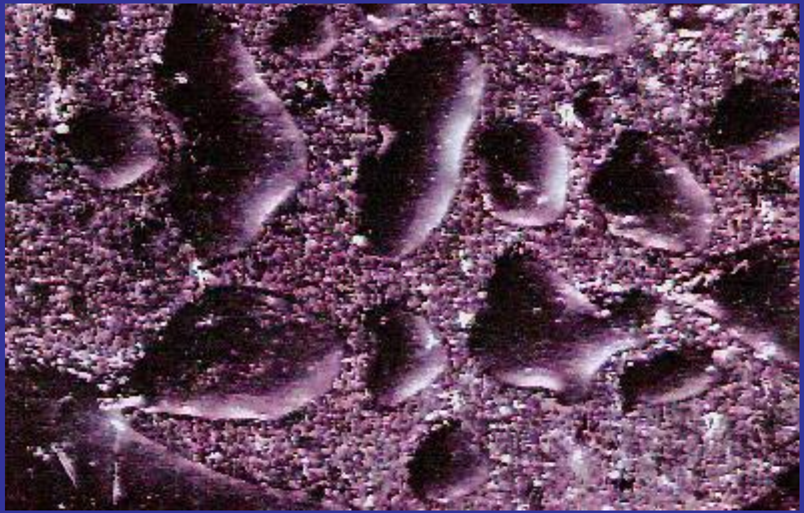


Sillimanite and the Polymophs; Andalusite

Name taken from location; Andalucia (Spain)

As with all the trimorphs; converts to the high performance refractory phase Mullite on firing + SiO_2 glass

$3(Al_2O_3.SiO_2)$ → $3Al_2O_3.2SiO_2$ + SiO_2 → + Al_2O_3; secondary mullite



Expelled glass droplets from mullitised Andalusite monocrystal

Sillimanite Group

Properties	Andalusite	Sillimanite	Kyanite	Bauxitic-Chamotte	Chamotte-Mullite
Mullitisation Temp/C	1380	1550	1350	Pre-calcined	Pre-calcined
Expansion (vol %)	+5	+7	+18	0	0
Associated Products (Al_2O_3)	55 - 63	Similar to Andalusite	Matrix only	58 – 68	55 – 60
Phase Analysis (Mullite %)	79 - 90	Similar to Andalusite	Mullite catalyst	77 - 87	60 - 65
Creep resistance (def @ temp)	Good to excellent	Similar to Andalusite		Poor	Good
TSR (cycles 950 C to water)	15 - 30	Similar to Andalusite	Not applicable	Poor	10 - 20

Sillimanite Group

All sillimanite group products resist alkali attack and the associated nepheline formation (shown below) through the formation of protective layers:-

$$3Al_2O_3.2SiO_2 + 2SiO_2 \xrightarrow{+ 2Na_2O} 2\,(Na_2O.Al_2O_3.2SiO_2) + Al_2O_3$$

+ 28% volume expansion

Andalusite; composite properties, mullite framework surrounding silica rich (SiO_2 80%) glass

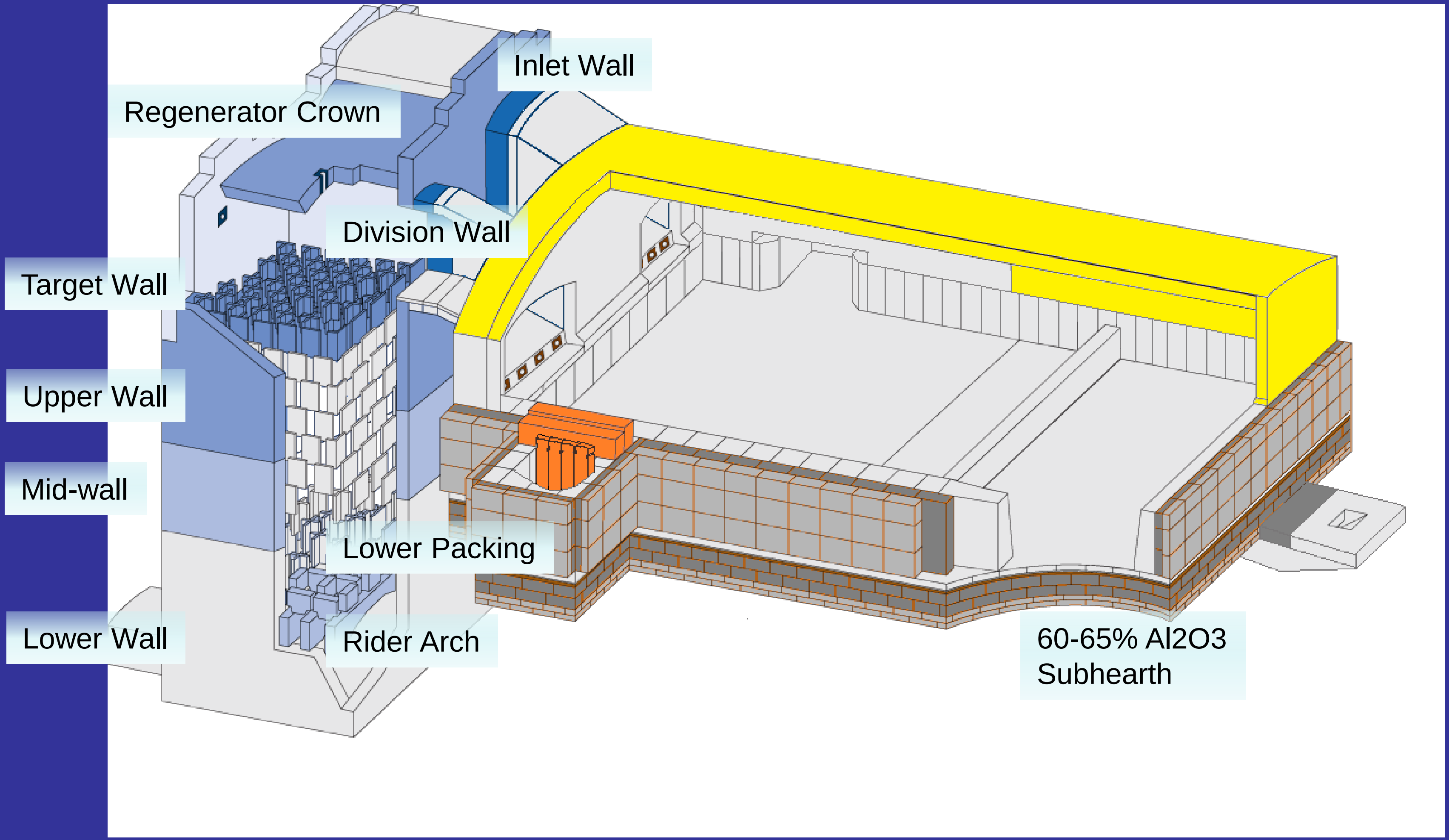
Dual nature; mullite provides deformation resistance; glass absorbs alkali

Sillimanite Group

All sillimanite group products can be considered as mullitic with varying amounts of glass phase. The mullite/glass balance is adjusted in accordance with the application temperature, induced load and alkali concentration.

Products can be formulated from single constituents or blended to promote the particular attributes of a mineral.

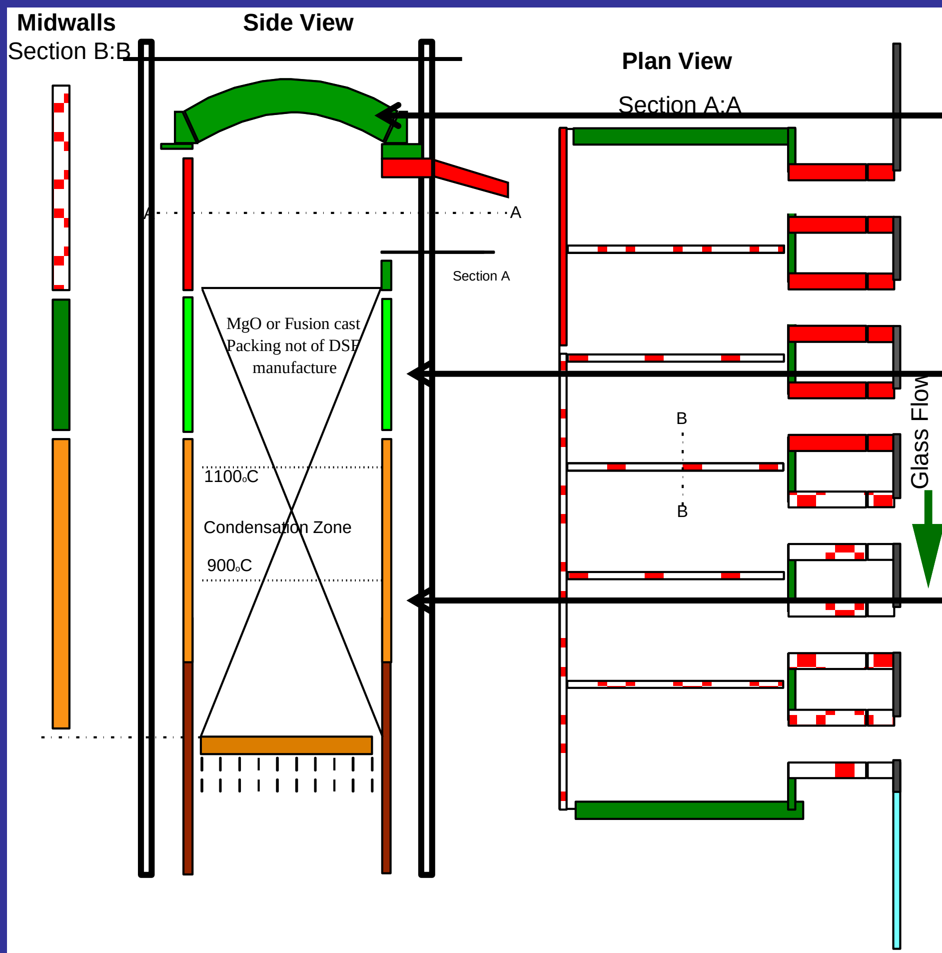
Sillimanite Group; Applications (Glass)



Mullite Regenerator

% Mullite	79	81	90	97	99
BD (g/cc)	2.48	2.50	2.55	2.52	2.56
AP (%)	13.8	13.4	14.1	18.5	17.0
CCS (MPa)	86	80	75	90	60
TSR (950 to water)	4	8	30	16	8
Creep, % @ 1550°C	N/A	1.45 (1500 C)	0.5	0.109	0.084
Thermal Expansion (% 20-1500°C)	0.72	0.54	0.64	0.72	0.80
Thermal Cond' (W/mk)	1.55	1.82	1.76	2.03	2.32

Mullite Regenerator



90% Mullite

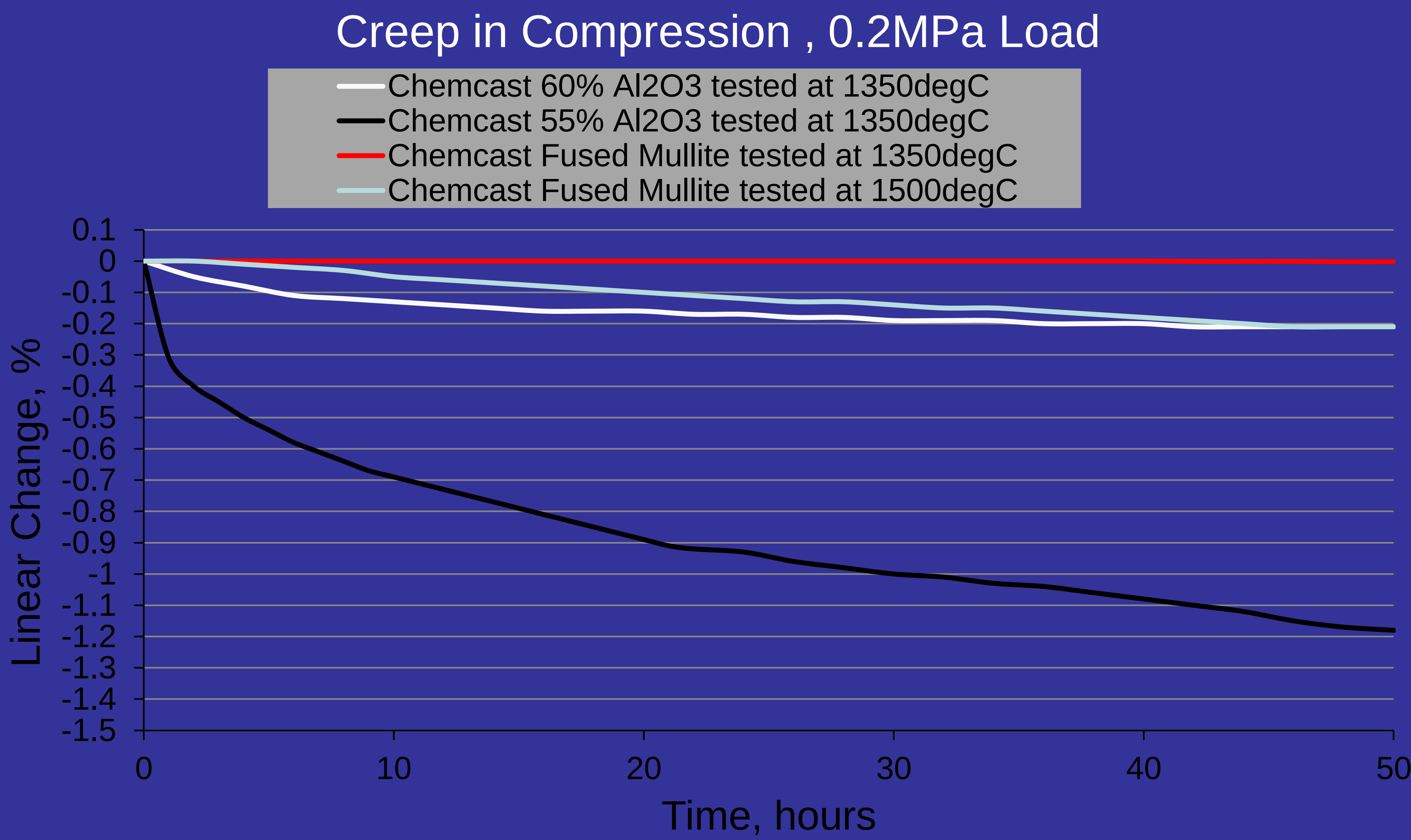
81% Mullite

79% Mullite

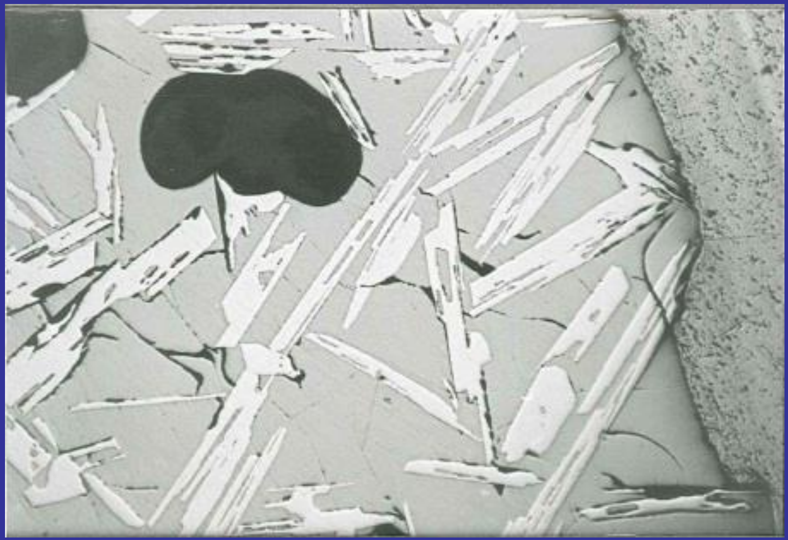
Sillimanite, Working End and Forehearth Superstructure

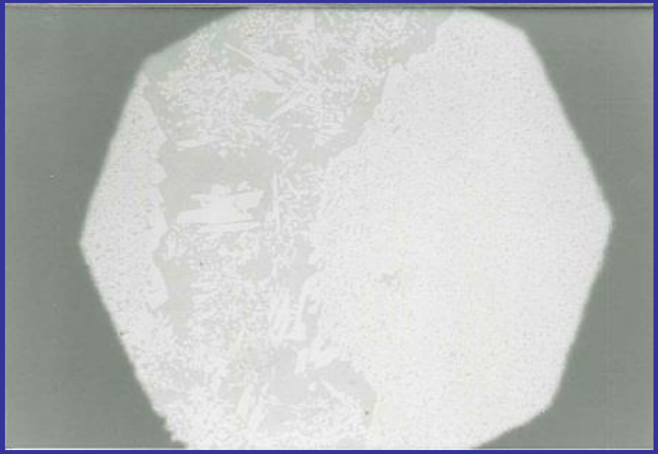
% Mullite (% glass)	61	82	83	100	Bauxitic- Chamotte
Al_2O_3	54.5	60.2	74.6	76.7	
Fe_2O_3	0.75	0.81	0.39	0.07	
BD (g/cc)	2.25	2.38	2.49	2.53	
TSR (950degC to water)	16	30	12	30	1
Creep @ mean temp (% after 50hrs, 0.2MPa)	1.18 1350 C	0.26 1350 C	0.46 1427 C	0.21 1500 C	2.64 1350 C
Glass types	SLS	SLS	SLS Borosilicate	SLS, Colour Borosilicate	
Span (mm)	1524 (60”)	1524 (60”)	1524 (60”)	1830 (72”)	Not utilised
Temperature of application	1400	1450	1500	+1500	

Sillimanite, Forehearths



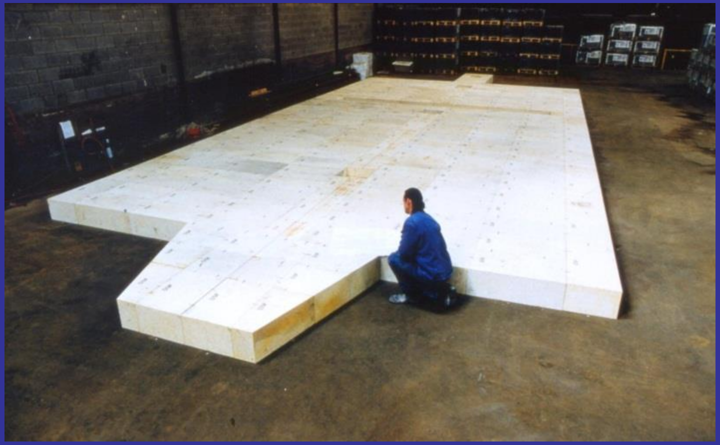
Sillimanite, Protection Layers at Forehearth Temperatures



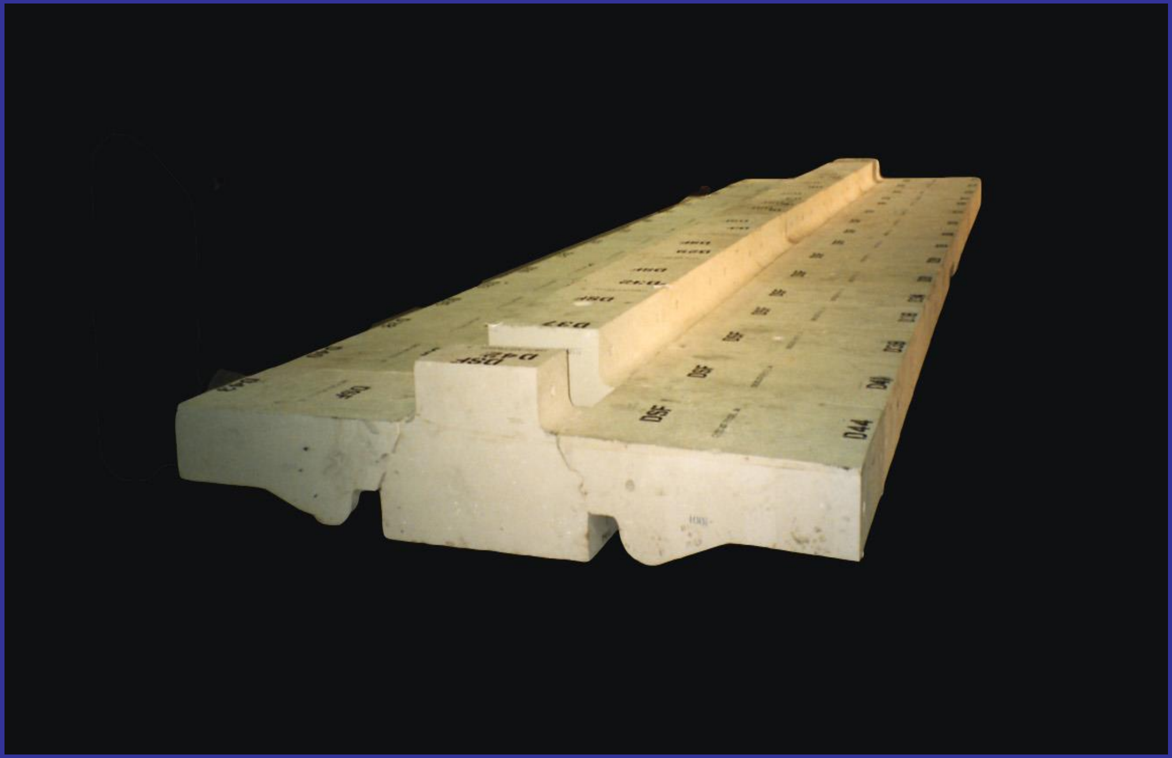


Sillimanite, Sidewall & Subhearth Insulation

Al_2O_3	55	59.6
BD (g/cc)	2.48	2.45
AP (%)	13.2	16.6
Max size	800 x 600 x 150	1150 x 700 x 300
Tolerance for layout 6 face ground	overall dimensions < 0.2%	overall dimensions < 0.2%



Sillimanite, Working End & Forehearth Superstructure

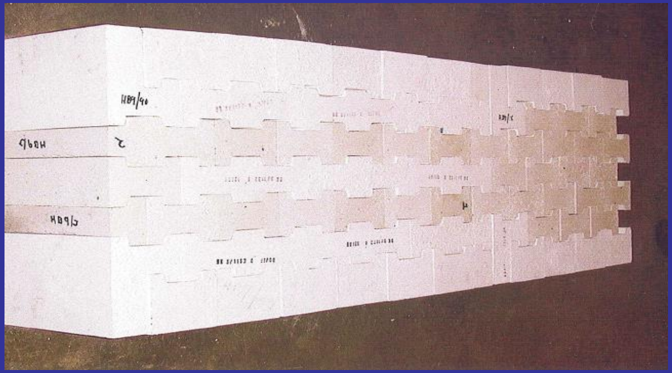


Sillimanite, Other Items

Mullite Cover Blocks for E-glass Fibre

Mullite Channel Blocks

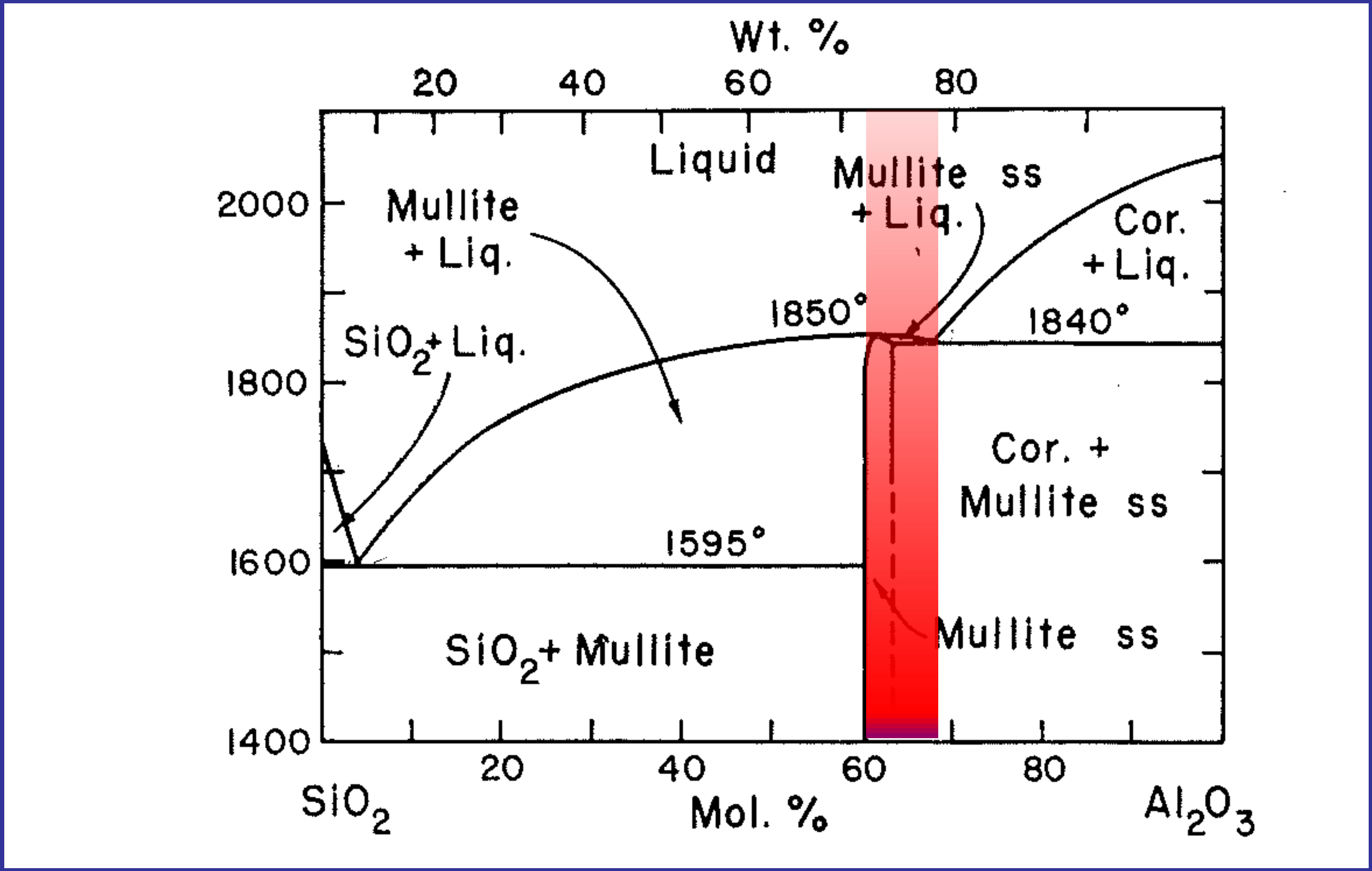
Interlocking Mullite Shapes



Sillimanite Tin Bath Roof

Mullite, 70-78% Al_2O_3

Congruently Melting Compound

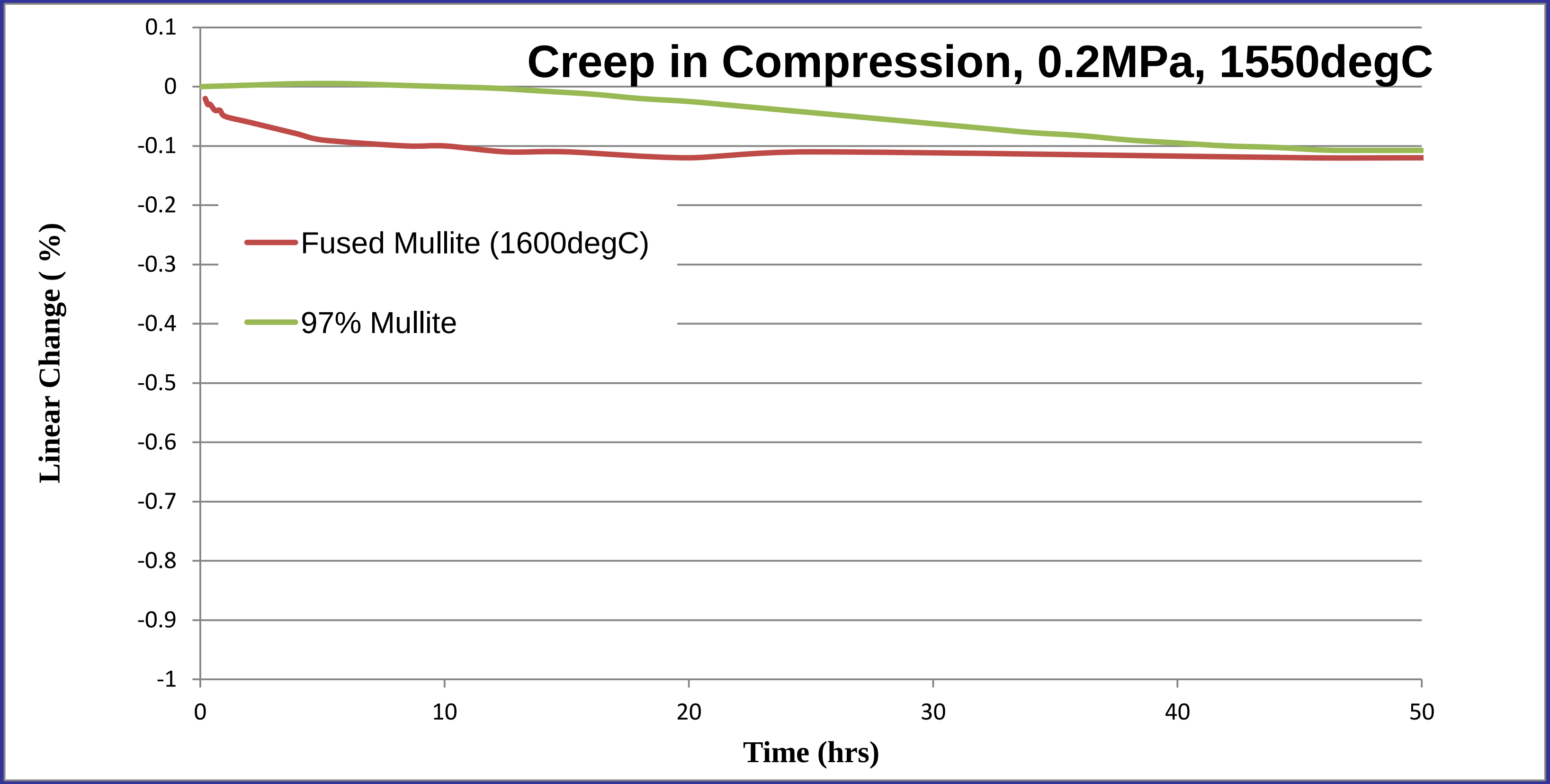


Mullite, The Refractory “Workhorse”

Mullite; extremely rare in nature; can be manufactured synthetically by fusion or sintering of kaolin, alumina and silica in defined proportions.

Definition; $3Al_2O_3.2SiO_2$, min 70% Al_2O_3, +80% mullite phase, <5% glass phase

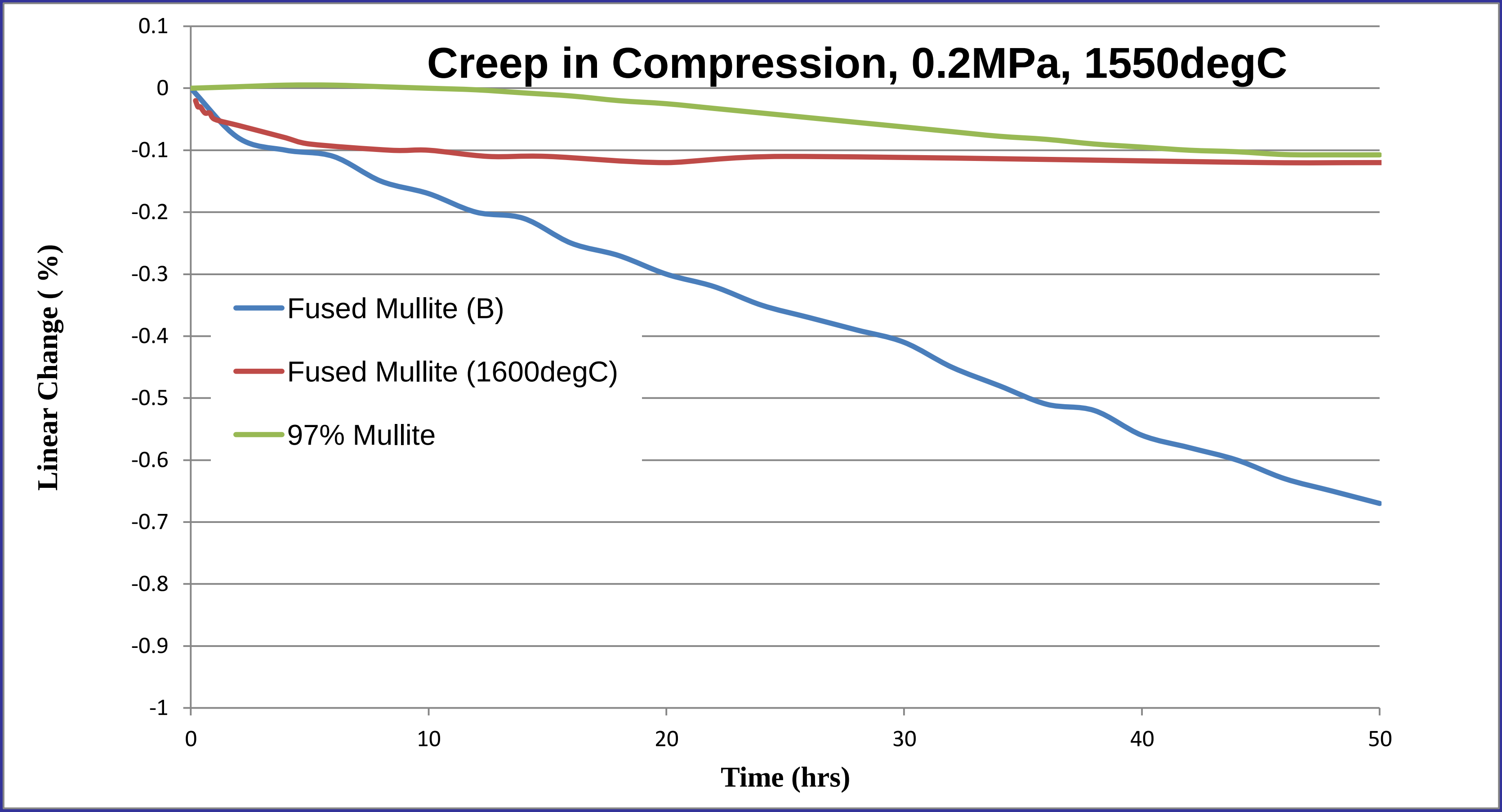
Structural Stability



Stability

% Mullite	97%	Fused Mullite 99+ %	Fused Mullite (B)
Bulk density (g/cc)	2.52	2.60	2.68
Apparent Porosity (%)	18.5	16.2	16
Cold Crushing Strength (MPa)	90	83	57
Al2O3	70.4	74.6	76.9
SiO2	27.7	24.6	21.7
TiO2	0.27	0.05	0.2
CaO + MgO	0.28	0.13	0.19
Na2O + K2O	0.48	0.23	0.44
	Mullite Amorphous	Mullite (~100%)	Mullite (48%) Corundum(47%) Andalusite

Structural Stability (mullite?)



Carry-over:- Mullite

Mullite is very resistant to silica carry-over.
No expansile phases are formed between silica and mullite.

Normal conditions (end fired container tank)
All walls stable corundum & glass layer.

Fused Mullite after 14 years

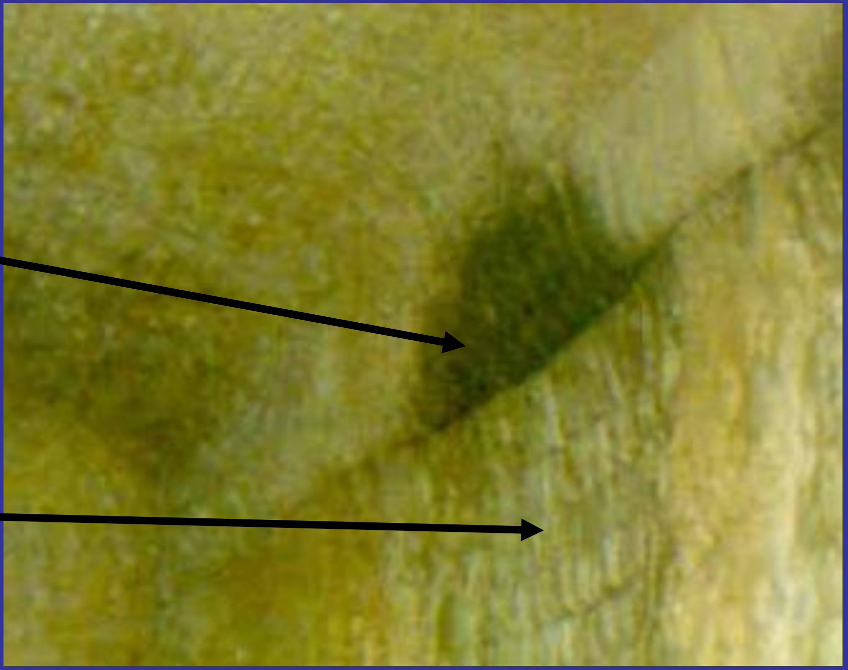
Extreme conditions (narrow cross fired tank target wall)
slow corrosion by glass formation on the surface.

Carry-over:- Protective Layers vs Performance

Mullites formed reactively during manufacturing firing process have proved better at carry over resistance than traditional re-bonded mullites

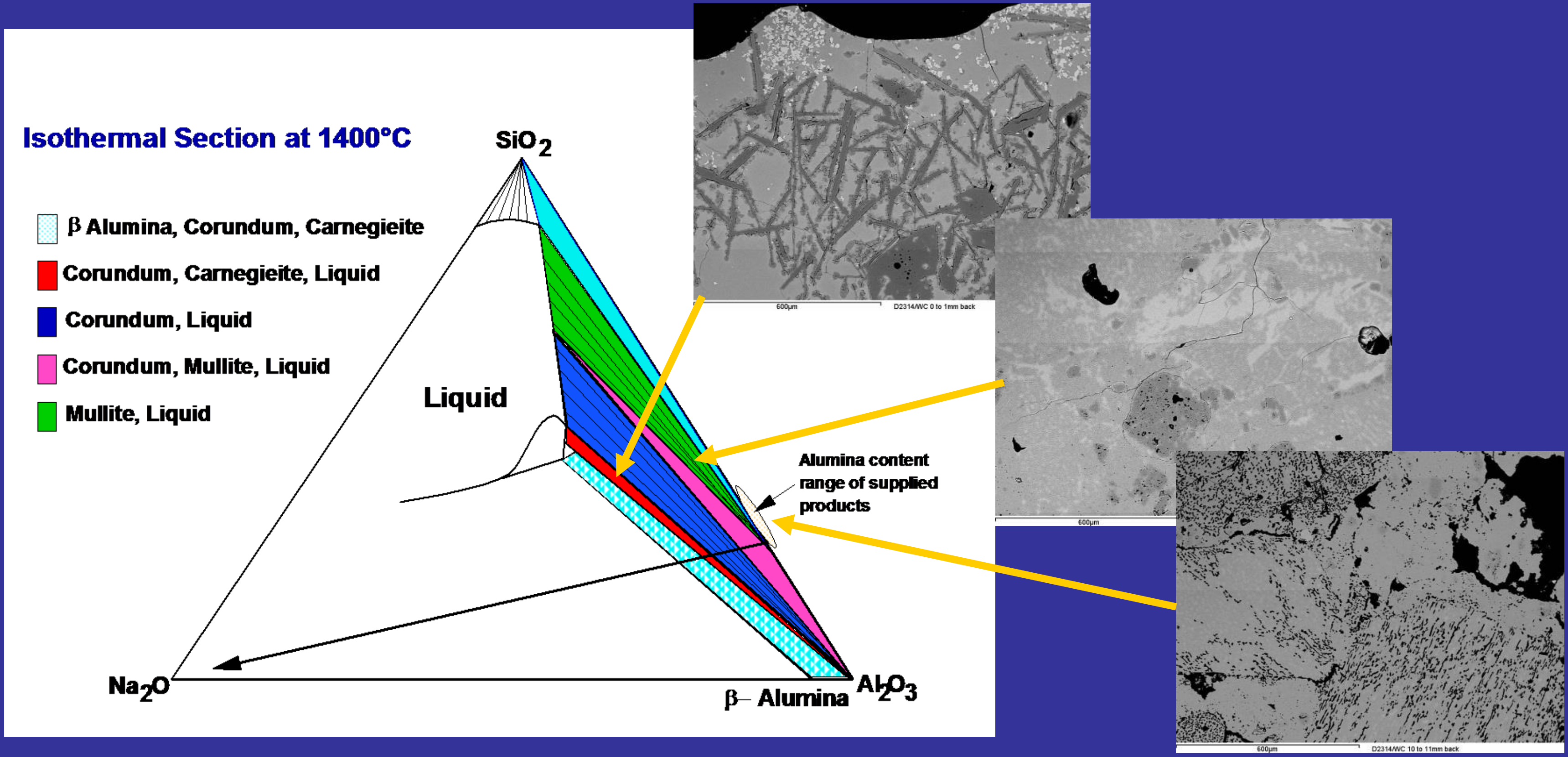
Mullite formed insitu

Heterogeneous mullite + amorphous phase



Narrow regenerator target wall after 9 years

Carry-over:- Protective Layers



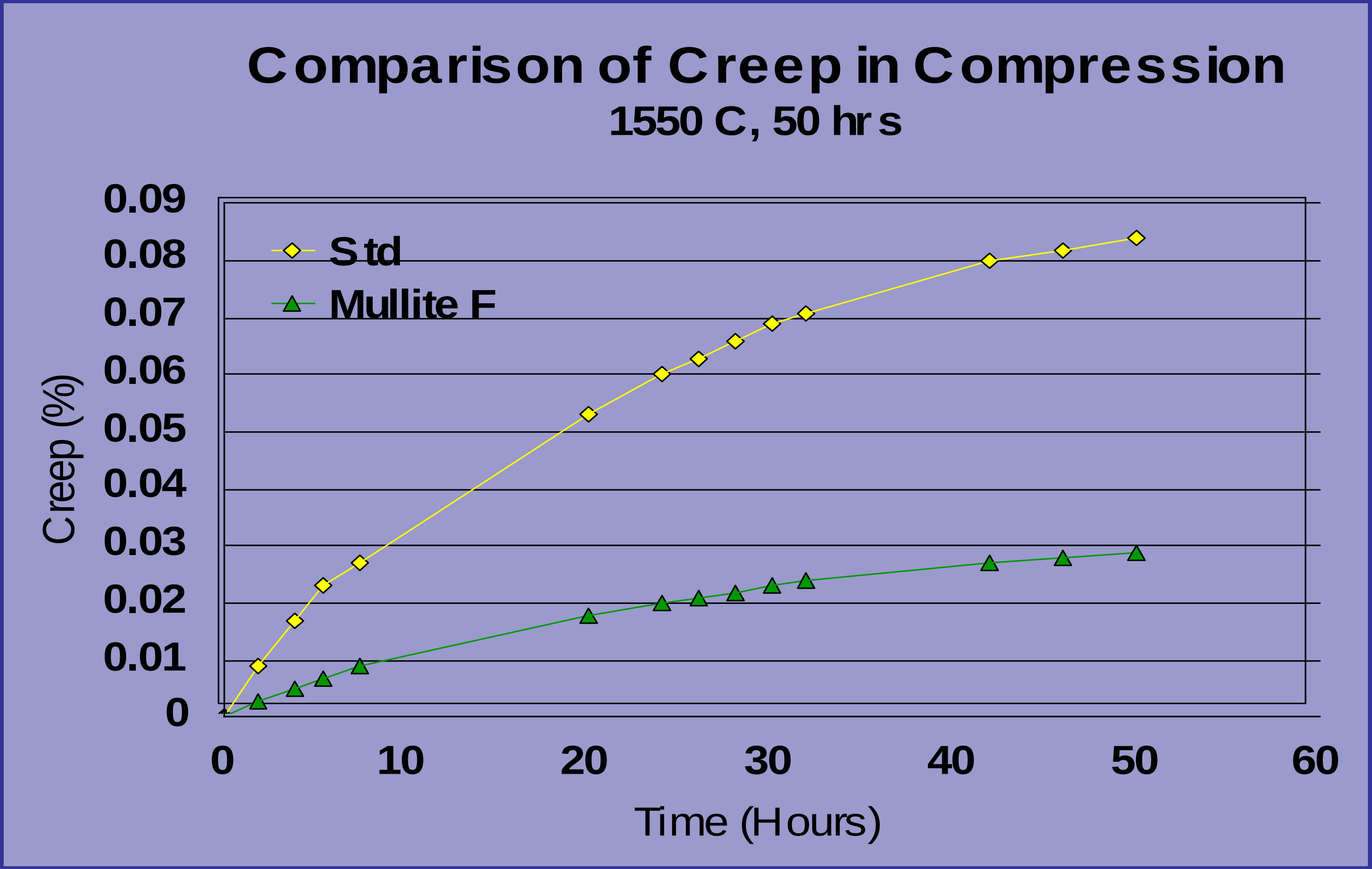
Dense reaction layers to unaltered composition; Na_2O reduces from 10-15% to < 0.8% in 11mm

Regenerator:- Mullite Solution

- Stability, carry over resistance (critical due to batch pre-heating) & improved thermal efficiency are all provided by mullite superstructure
- Not all mullites are the same! Check mineralogy; creep resistance; how was it formed?
- 16 year campaigns are feasible provided the mullite lining is zoned correctly

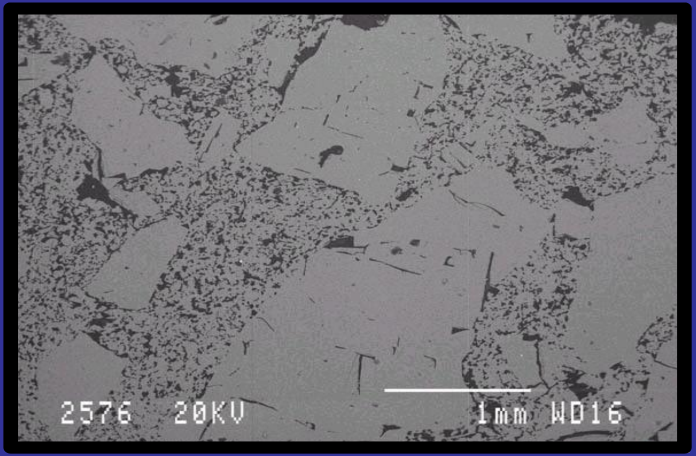


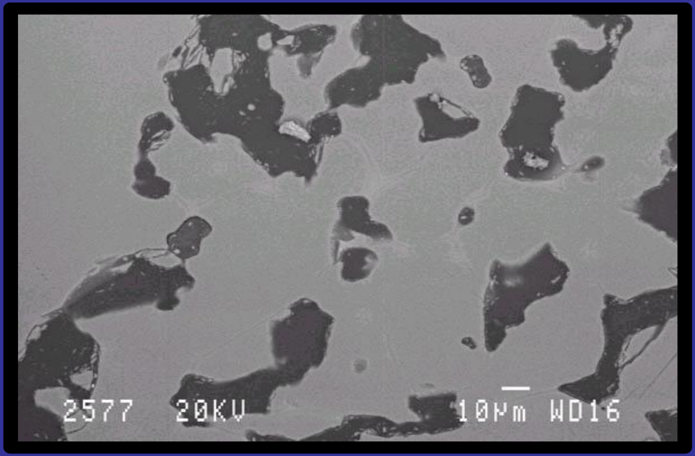
Mullite for Furnace Crowns, E and Special Glasses



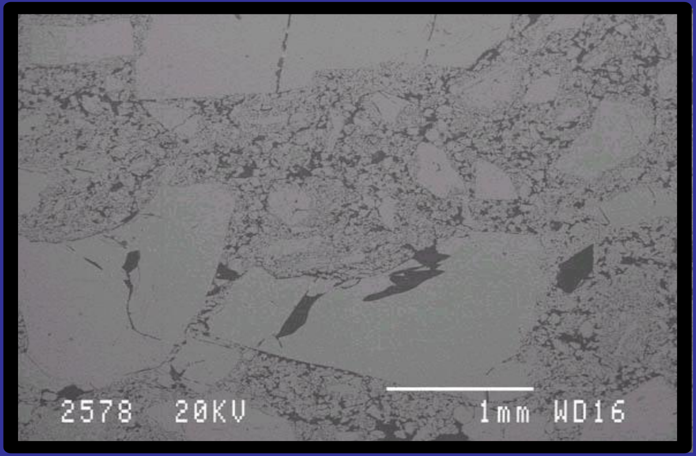
Mullites for Furnace Crowns, E & Special Glasses

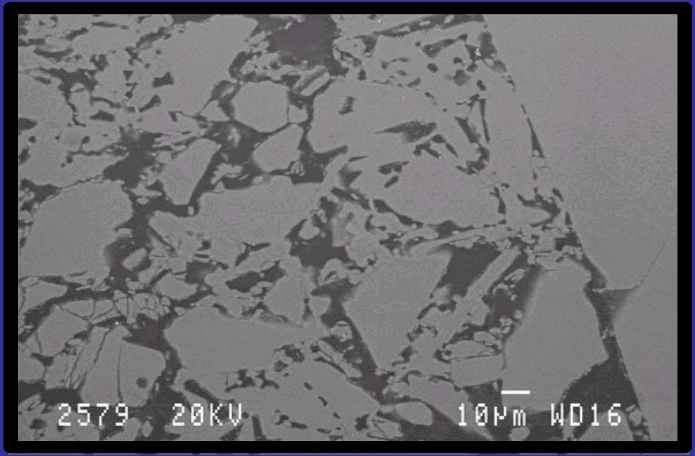
Mullite F



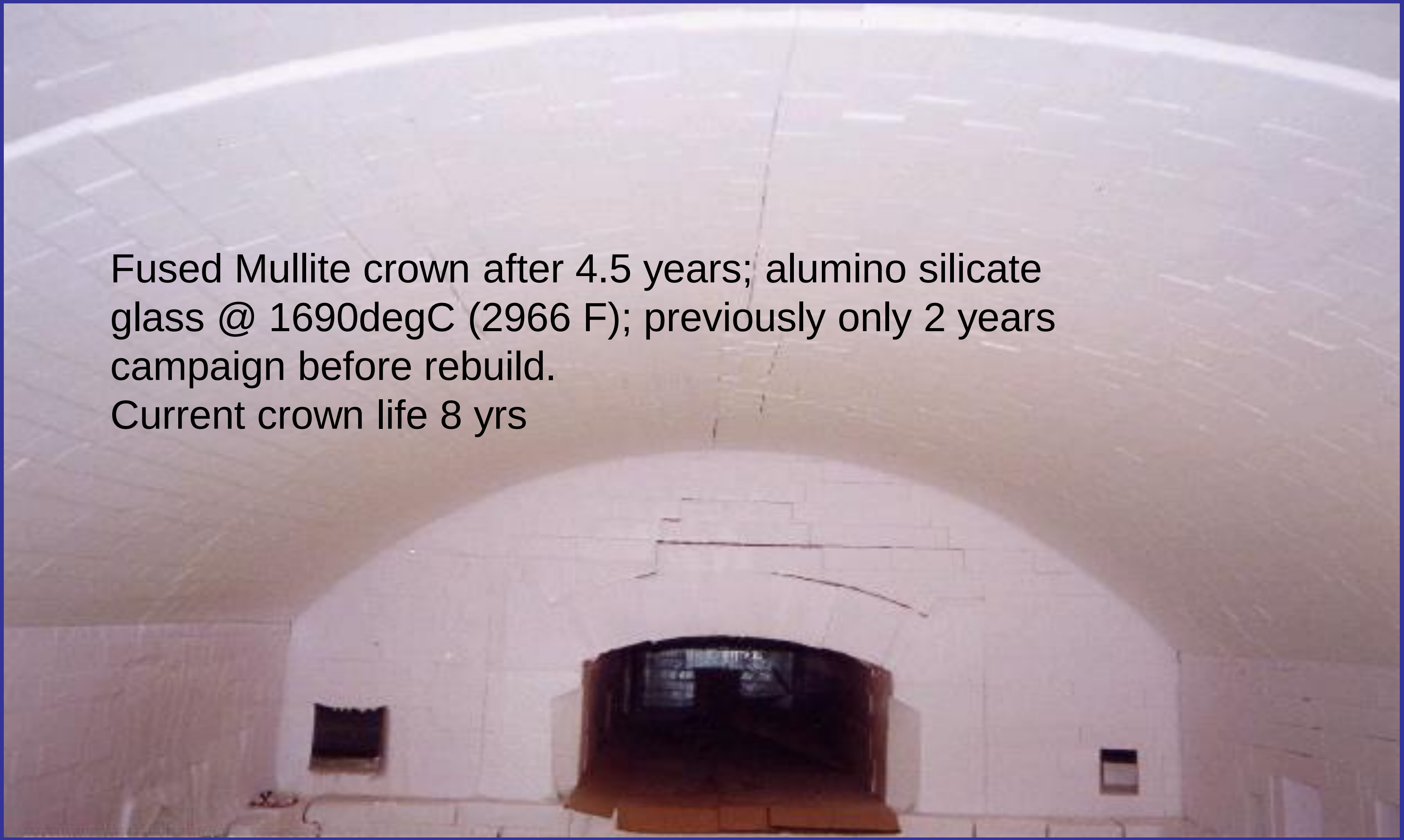


Standard Mullite





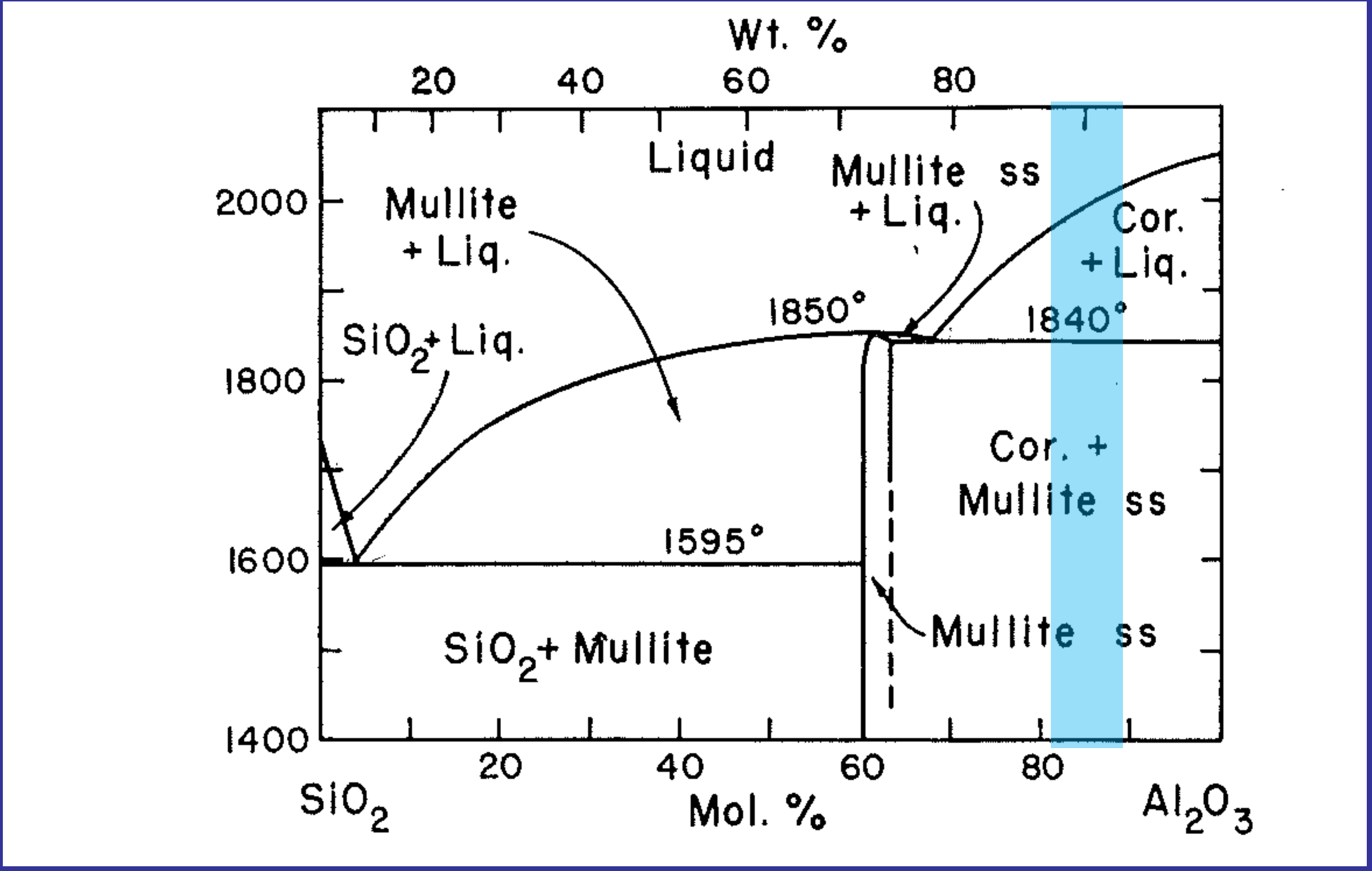
Mullite for Furnace Crowns, E & Special Glasses



Fused Mullite crown after 4.5 years; alumino silicate glass @ 1690degC (2966 F); previously only 2 years campaign before rebuild.

Current crown life 8 yrs

Bauxite, +80% Al_2O_3



Bauxite Bricks

Steel teeming ladles; phosphate bonded, fired and phosphate bonded and fired. Fused alumina added for slag and abrasion resistance.

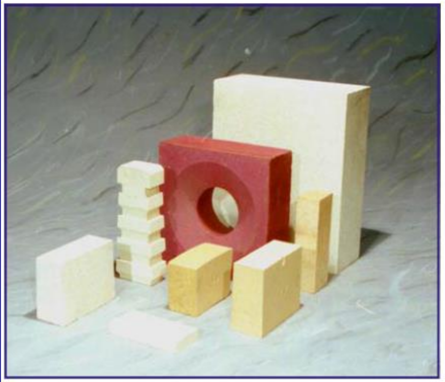
Bauxite Bricks (Steel)

Typical Chemical Analysis (wt %)	
Al_2O_3	84.4
Fe_2O_3	1.23
SiO_2	8.24
TiO_2	3.11
CaO	0.03
MgO	0.05
K_2O	0.06
Na_2O	0.05
P_2O_5	2.18

A bauxite based refractory with low iron and alkali content. Its good shape, dimensional accuracy and excellent high temperature properties make it ideally suited for use in electric arc furnace roofs, steel ladles and high duty concast tundish nozzles. Also widely used in transition zone and high wear areas of rotary cement kilns - particularly cooler cam sections and nose rings.

Typical Physical Properties		
Bulk Density	(g/cm^3)	2.90
Apparent Porosity	(%)	17.0
Cold Crushing Strength	(MN/m^2)	55
Permanent Linear Change	(%) 2 hrs @ 1700°C	+0.61
Thermal Expansion	(%) 20-1500°C	1.24
Thermal Conductivity at Hot Face Temp.		
	(W/mK) 800°C	3.19
	1000°C	2.97
	1200°C	2.21

Bauxite Bricks (Steel)

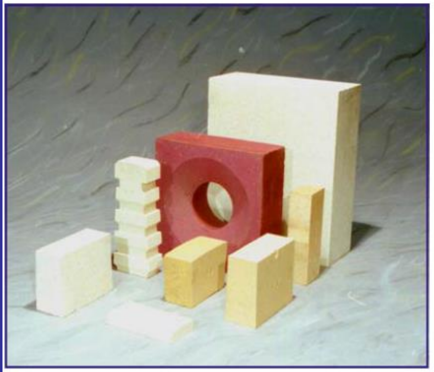


Typical Chemical Analysis (wt %)	
Al_2O_3	88.0
Fe_2O_3	0.76
SiO_2	8.59
TiO_2	2.30
CaO	0.13
MgO	0.03
K_2O	0.07
Na_2O	0.06

DSF 88 is a high alumina product with a mullitised bond for superior hot strength and resistance to hermal shock. Additions of fused grades provide excellent high temperature stability combined vith abrasion and slag resistance. A supreme steel ladle sidewall product capable of withstanding he severe slag attack and temperature conditions present in ultra low carbon and low sulphur steel manufacture.

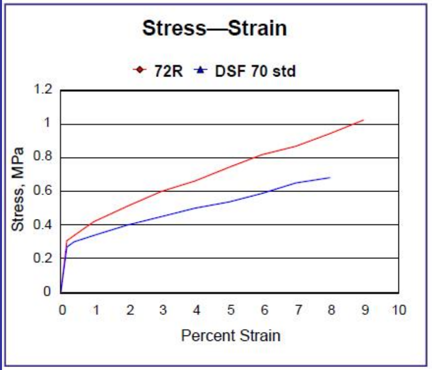
Typical Physical Properties		
Bulk Density	(g/cm^3)	2.86
Apparent Porosity	(%)	20.5
Cold Crushing Strength	(MN/m^2)	70
Permanent Linear Change	(%) 2 hrs @ 1700°C	-0.60
Thermal Expansion	(%) 20-1500°C	1.25
Thermal Conductivity at Hot Face Temp.		
	(W/mK) 1000°C	2.60

Bauxite (Rotary Kilns)



Typical Chemical Analysis (wt %)	
Al_2O_3	69.5
Fe_2O_3	1.01
SiO_2	26.5
TiO_2	2.53
CaO	0.11
MgO	0.06
K_2O	0.14
Na_2O	0.05

DSF 72R is a mixed mineral based product, specifically designed to provide a tight lining in rotary kilns, without excessive expansion that would lead to spalling. DSF 72R has been developed to operate in strongly reducing atmospheres and is unaffected by carbon monoxide. Ideally suited to rotary coke and direct reduction kilns.



Typical Physical Properties		
Bulk Density	(g/cm^3)	2.62
Apparent Porosity	(%)	17.5
Cold Crushing Strength	(MN/m^2)	65
Permanent Linear Change	(%) 5 hrs @ 1500°C	+1.9
Thermal Conductivity at Hot Face Temp.		
	(W/mK) 1000°C	2.04
CO Resistance	200 hrs @ 500°C	Unaffected

Thank-You for Listening

Chris Windle

DSF Refractories & Minerals

cwindle@dsf.co.uk