dsf refractories

"Stuck in the 90's (alumina) or A New Hybrid Approach"

21st Century Mullite Refractories for Optimum SRU Lining Stability

Christopher J.Windle
Technical Director
DSF Refractories & Minerals Ltd

Introduction

Increasing consumption of fossil fuel based energy emits SO_2 into the atmosphere. This pollutant can harm the human respiratory system creating breathing difficulties and epidemiological studies have shown heightened sensitivity to SO_2 in asthma sufferers particularly children [1]

High concentrations of SO_2 in the air can lead to SOx based compounds which manifest as particulate matter. These small particles may penetrate deep into the lungs and in sufficient amounts to cause health problems.

In addition to the human interaction; SOx effects the wider environment contributing to acid deposition, affecting soil and water quality which in turn has adverse effects on aquatic ecosystems and damage to forests, crops and other vegetation.

In refining processes it is therefore vital that elemental sulphur is reduced and therefore recovered from fuels and associated acid gas streams.

The Claus process (patented 1883 Carl Friedrich Claus) has been the workhorse of the recovery of elemental sulphur from H_2S containing gas streams for over 50 years and the reaction furnace (sulphur recovery unit) lies at the heart of the process.

In the reaction furnace acid gas (H_2S bearing) is oxidised (burned) with sufficient air to convert ~1/3rd of the H_2S to SO_2; the unburned H_2S reacts with the SO_2 formed to yield elemental sulphur. This reaction is referred to as the Claus Reaction [2]:-

$$2H_2S + SO_2 \leftrightarrow SO_2 + H_2O$$

The refractory lining of the reaction vessel has to endure a severe thermo-mechanical and thermo-chemical environment.

Background

The traditional materials for SRU linings are based on 90's alumina and whilst these operate well; there has been a step change in recovery technology and therefore there should be a step change in the refractories available.

Although DSF has supplied generic mullite bonded Corundum (Fricor) materials for the hot face lining of the SRU since 2006, the adoption of oxygen enrichment for lean acid gas streams, additional capacity and capacity redundancy has created a more demanding environment for the hot face refractory.

DSF Refractories & Minerals are acknowledged as suppliers of premium grade re-bonded Fused Mullite refractories for long campaign (7 to 9 years) E glass and speciality glass melters.

Forming sprung self- supporting crown structures; DSF Fused Mullites are subjected to temperatures up to 3000°F (1650°C) and therefore must have intrinsic thermo-mechanical stability, that is, creep deformation resistance.

In reaction furnaces with 40% O_2 enrichment steady temperatures of 2700°F(1490°C) can be achieved and it is predicted that a system running at 60% O_2 enrichment will increase the operating temperature to ~2750°F (1510°C).

These temperatures per se, pose no significant threat to the lining stability, however it is abnormal process temperatures (temperature excursions) which although sporadic and short term can lead to lining deformation and subsequently campaign limiting.

Following anecdotal reports of linings failing prematurely and taking into consideration the views of industry experts; DSF developed a creep resilient mullite specifically for SRU linings; DSF Frimul FX.

The remit for this product was to exhibit minimal to zero creep deformation at 3000°F (1650°C).

Frimul FX is fired to 3100°F (1700°C) in batch intermittent kilns which ensures extensive solid state bonding throughout the brick matrix, this in turn imparts structural integrity at high temperatures and loads.

Whilst Frimul FX is a derivative of the predecessor product DSF Frimul F, the latter with proven thermo-mechanical stability over many years, it is never the less a significant step forward in materials design.

Following extensive research the binary phase diagram (Al_2O_3:SiO_2,Fig.1) has been reassessed and shows that the mullite stable phase field veers toward Al_2O_3 enrichment at elevated temperatures.

Frimul FX composition mitigates for this phenomenon which in conjunction with ultra pure fused and reactive insitu bonding materials contribute to negligible creep rates at 3000°F (1650°C).

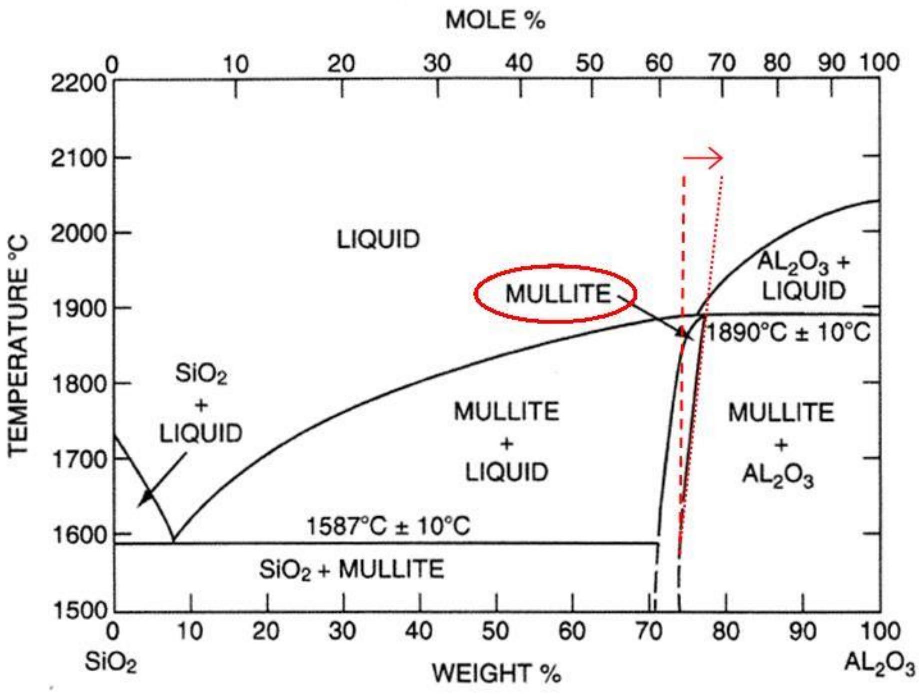


Fig. 1 Alumina-silica binary phase diagram showing mullite phase field veering towards alumina enrichment with increasing temperature (Klug et al 1987) [3]

Physical & Chemical Properties

A comparison of physical and chemical properties of Frimul FX and traditional mullite bonded corundum products is outlined in Table 1 overpage.

In addition to creep resistance, other intrinsic physical and thermal attributes positively influence lining and therefore unit stability:-

- Density; ~14% lower cf traditional lining materials
- Thermal conductivity; ~21% lower (@1832°F) cf 90s traditional lining materials
- Thermal Expansion; ~21% lower (@2732°F) cf 90s traditional lining materials

The above properties mean a Frimul FX SRU lining weighs less than that constructed with traditional material, the backing thickness can be reduced without detrimental increase in shell temperature and overall heat loss is reduced. This maintains an appropriate shell temperature (350-550°F) to avoid condensation of sulphuric acid at lower temperatures or sulfidation at higher temperatures. A potential decrease in backing lining thickness can increase the overall reactor capacity by 3.4% (see example for 12ft diameter reactor in Table 2 overpage).

Property	DSF Frimul FX	90's
Bulk Density, lb/ft3 (g/cc)	164 (2.62)	190-199 (3.05-3.18)
Apparent Porosity, %	16.2	16.0-16.8
Cold Crushing Strength, psi (MPa)	16099(111)	11313-14504 (78-100)
Chemical Composition		
Al_2O_3	75.6	90.0-96.0
SiO_2	24.2	3-9.28
K_2O	0.08	0.01
Na_2O	0.20	0.17
Phase Composition		
Mullite	96	7.0-16.6
Corundum	1	80.6-87.0
Thermal Properties		
Thermal Expansion 68-2732^oF/20-1500°C, %	0.91	1.15
Thermal Conductivity, Btu in/ft^{2}h^{o}F @ hot face 1832^{o}F	14.3	18.0

Table 1. DSF Frimul FX vs Typical 90's SRU Lining Materials

	3" backing	4"backing
Calculated hot face lining volume (m^3)	20.26	19.95
Traditional material weight (T)	61.597	60.642
Frimul FX weight (T)	53.087	52.263

Table 2. Refractory lining volume and associated tonnage

Creep Under Load

The objective was that Frimul FX should exceed the creep resistance of present materials and meet the future auspices of relevant API standards, to qualify this it was specified that maximum deformation should be 0.5% from the 50th to 100th hour hold ASTM C832 or DIN EN 993-9 creep under load at 3000^{o}F/1650^{o}C, 25psi.

Frimul FX has been through an extensive creep testing programme encompassing both ASTM and ISO/BSEN test methods. A summary of all tests performed at 3000^{o}F/1650^{o}C is shown in the following figures. There does seems to be an anomaly in the results when a cylinder specimen is tested to ASTM ; the deformation recorded during the test does not correlate closely to the before/after measurements which may be due to an idiosyncrasy with the measurement system.

Numerous tests have also been performed at 2900^{o}F/1600^{o}C; at this temperature virtually no creep is observed, the material is perceived as "zero" creep within the constraints of experimental error and the inherent stability of the creep apparatus.

Ref	Standard	Sample	Load (PSI)	Loading Orientation	Expansion (%)	Creep (%)		
						50-100h	Total	Before/After
D4314	DIN EN 993-9	Cylinder	29	Pressing	0.79	0	+0.02	
D4315	ASTM C832	Prism	25	Perpendicular	1.04	-0.09	-0.23	-0.19
D4316	ASTM C832	Prism	25	Perpendicular	0.96	-0.1	-0.19	-0.17
D4495A	ASTM C832	Prism	25	Perpendicular	0.92	-0.04	-0.12	-0.08
D4495D	DIN EN 993-9	Cylinder	29	Pressing	1.00	-0.08	-0.22	-0.05
D4496	ASTM C832	Cylinder	25	Pressing	1.07	-0.17	-0.56	-0.17
D5125	DIN EN 993-9	Cylinder	29	Pressing	0.78	0	-0.178	
API DIN	DIN EN 993-9	Cylinder	29	Pressing	1.00	-0.07	-0.2	

Table 3. Summary of Frimul FX Creep tests performed at 3000°F/1650°C

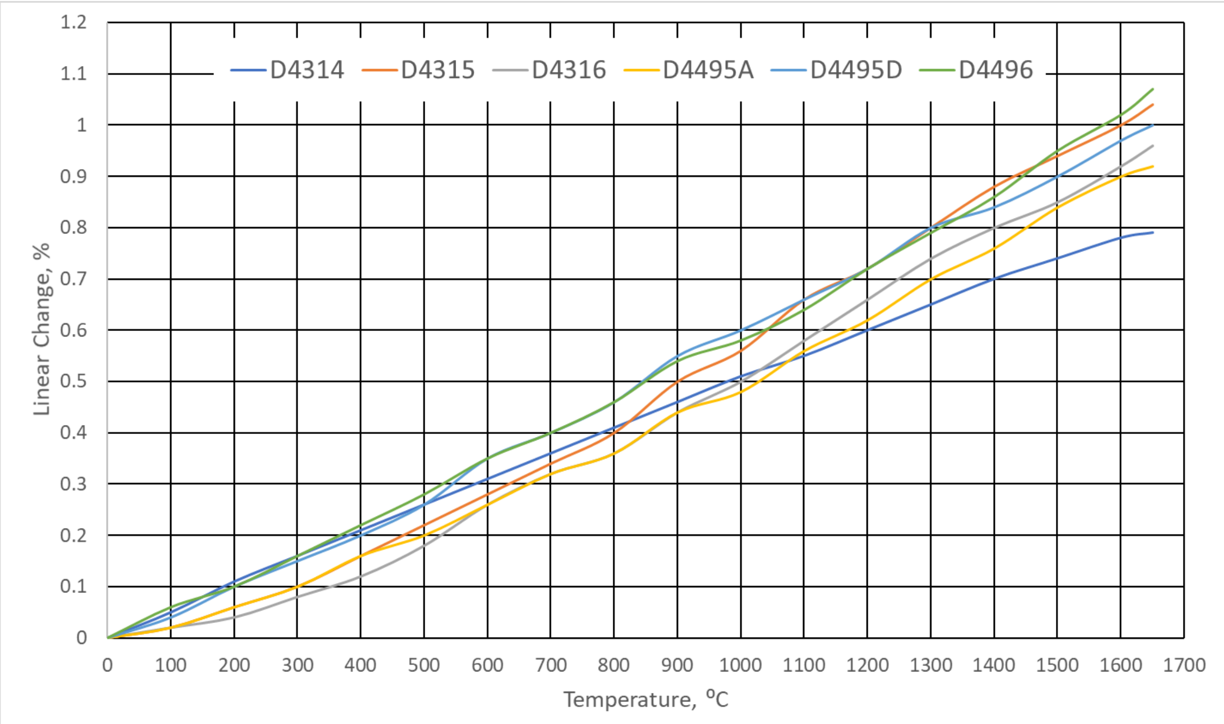


Fig. 2 Heat up of Frimul FX creep tests performed at 3000°F/1650°C

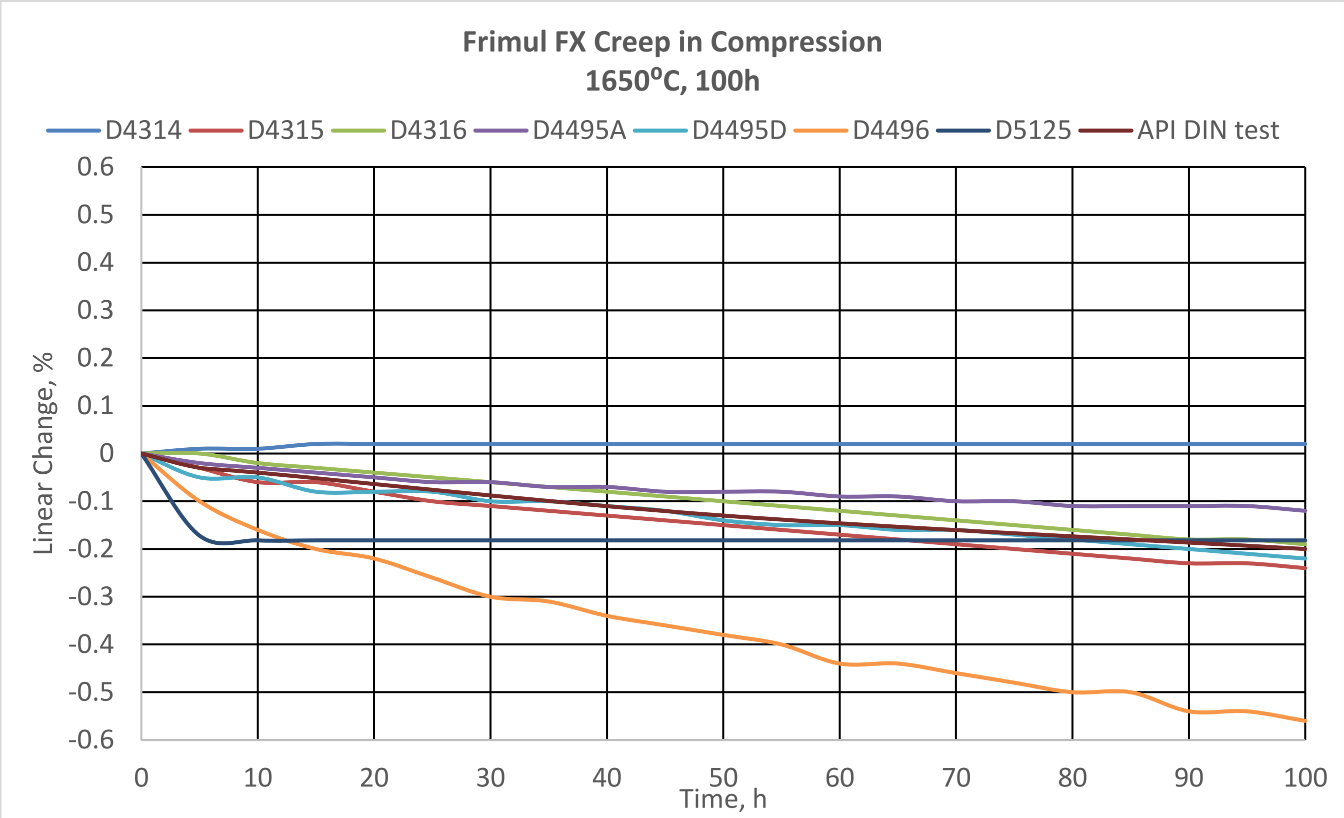


Fig. 3 100 hour hold period of Frimul FX creep tests performed at 3000⁰F/1650⁰C

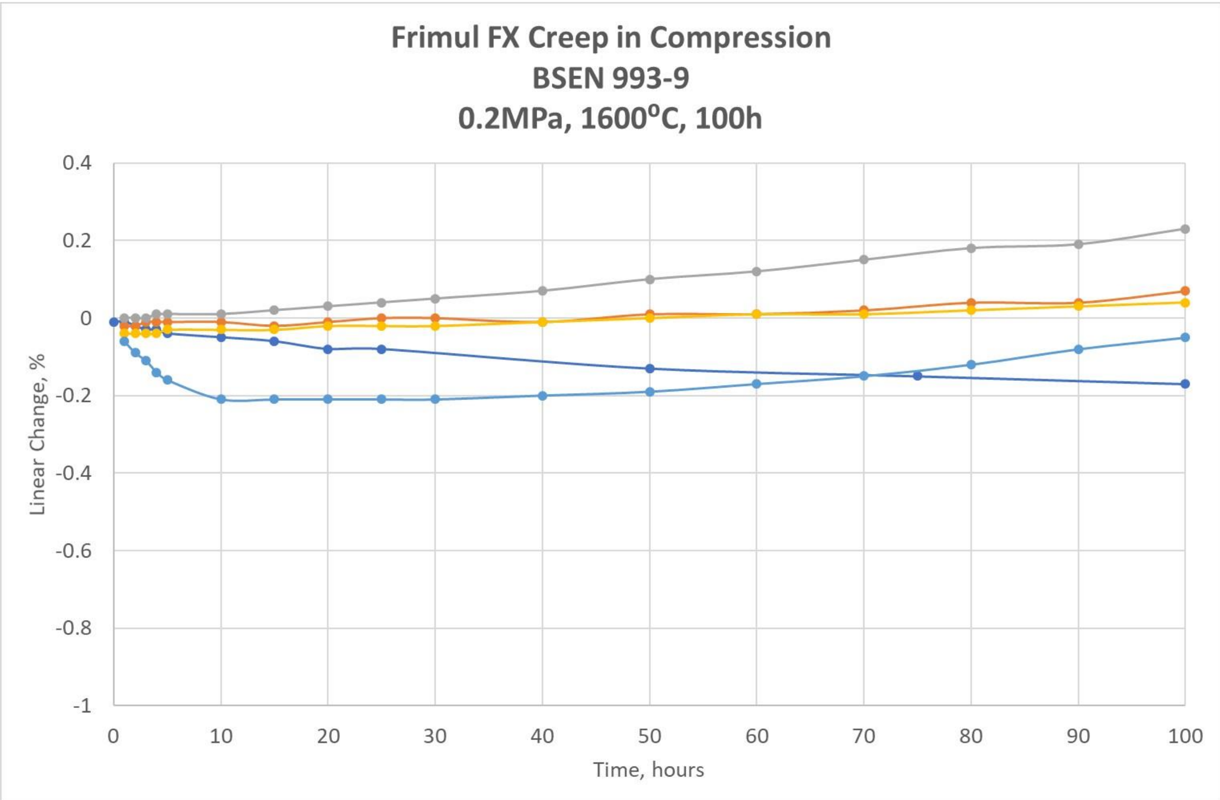
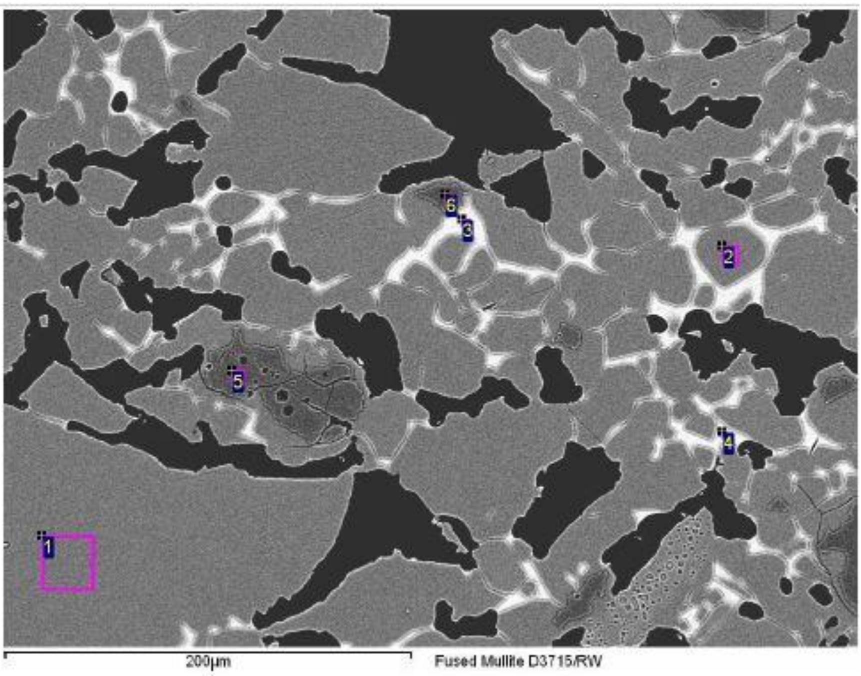


Fig. 4 100 hour hold period of Frimul FX creep tests performed at 2900⁰F/1600⁰C

Microstructure & SiO_2 Stability

A SEM back scattered image of Frimul FX is shown in Figure 5 below, high firing temperature (3100°F) ensures extensive mullite intragranular and intergranular bonding (light grey); there is no free silica, the silicate (bright) that remains is encapsulated in the mullite matrix. The residual corundum (dark grey) is mainly intragranular which under high loading imparts a small expansion to stabilise the material.



Wt% Oxide	1 - mullite	2 - mullite	3 – silicate bond	4 – silicate bond	5 - alumina	6 - alumina
Na_2O	0.3	nd	3.9	3.6	nd	nd
MgO	nd	nd	0.3	nd	nd	nd
Al_2O_3	77.9	75.3	15.0	16.0	100	100
SiO_2	21.8	24.4	76.1	75.3	nd	nd
K_2O	nd	nd	2.8	2.4	nd	nd
CaO	nd	nd	1.2	1.1	nd	nd
TiO_2	nd	0.3	nd	0.4	nd	nd
Fe_2O_3	nd	nd	nd	nd	nd	nd
ZrO_2	nd	nd	0.9	1.2	nd	nd

nd – not detected

Figure 5 Frimul FX Back-scattered image

Depletion of SiO_2 in H_2 Reducing Environments

H_2 can reduce SiO_2 containing components in refractory compositions to SiO(g) vapour phase from temperatures in excess of ~800°C; the reaction is as follows:-

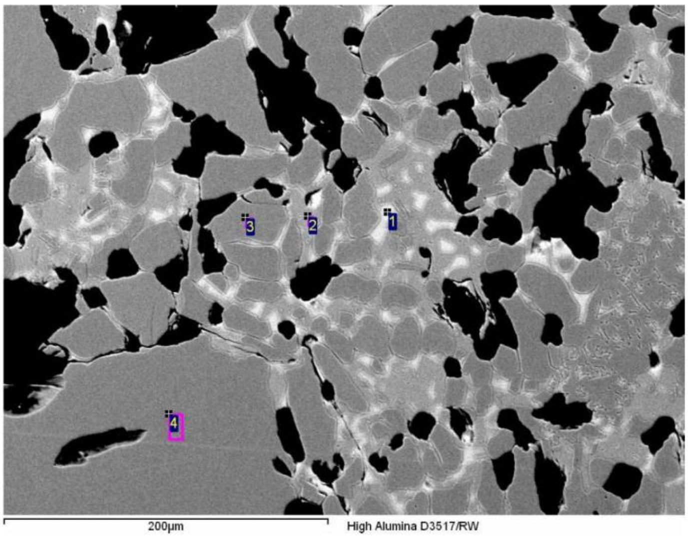
$$SiO_2 + H_2 \longrightarrow SiO(g) + H_2O$$

The reaction affects all SiO_2 containing materials and therefore in regard to SRU hot face lining materials whether mullite or mullite bonded the phenomenon has to be assessed.

For high H_2 concentrations (~13vol/%), it is acknowledged that all mullite/mullite bonded materials will suffer SiO2 depletion.

Whilst pure Al_2O_3 is chemically the most resilient composition for H_2 environments; in comparison with mullite it has poor thermo-mechanical stability and relatively high creep characteristics.

Samples of Frimul FX and a more traditional mullite bonded corundum material were placed on the working lining of an SRU (5 exposed faces) for a period of 2 years to investigate the interaction with H_2. The reaction surface was examined by SEM in back scattered and elemental mapping modes, (Figures 7 and 8).



Mullite Bonded Corundum Microstructure as supplied

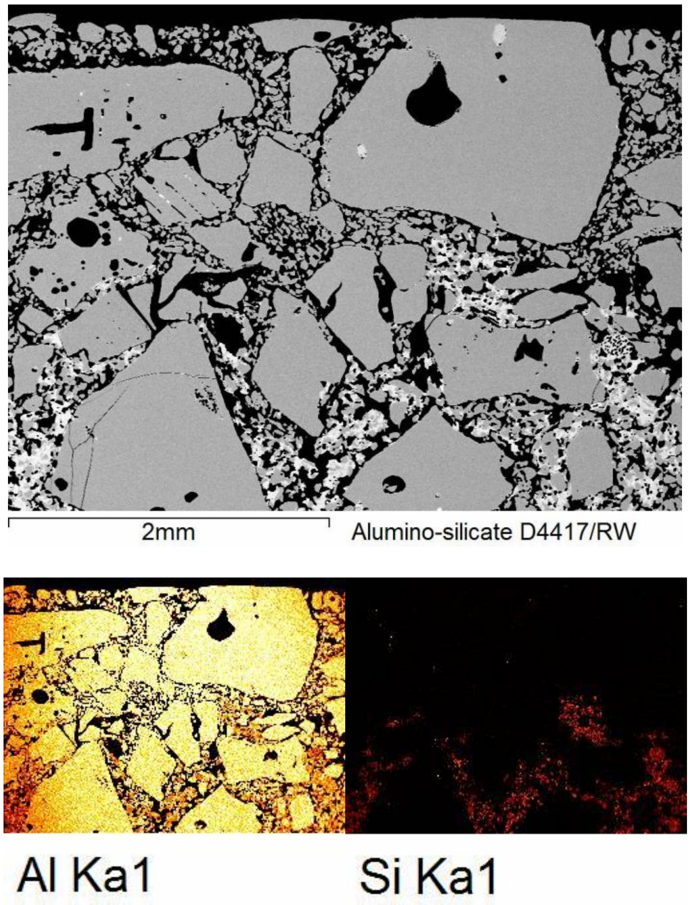
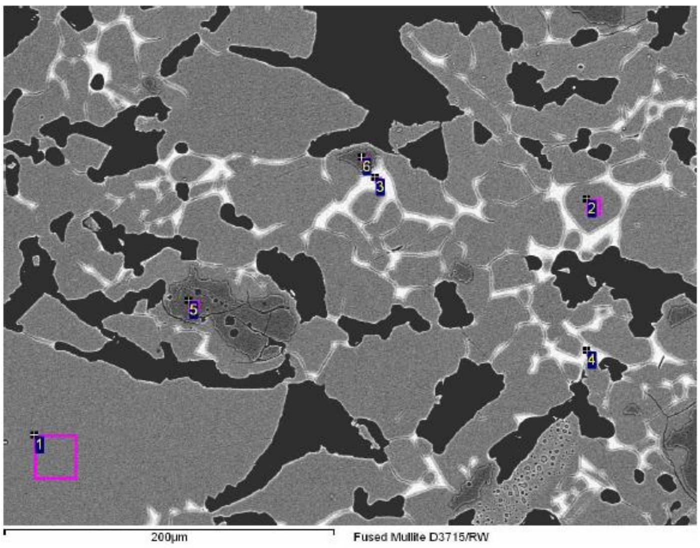


Fig.6 H_2 Depletion of silica at front face (2 years exposure)



Frimul FX Microstructure as supplied

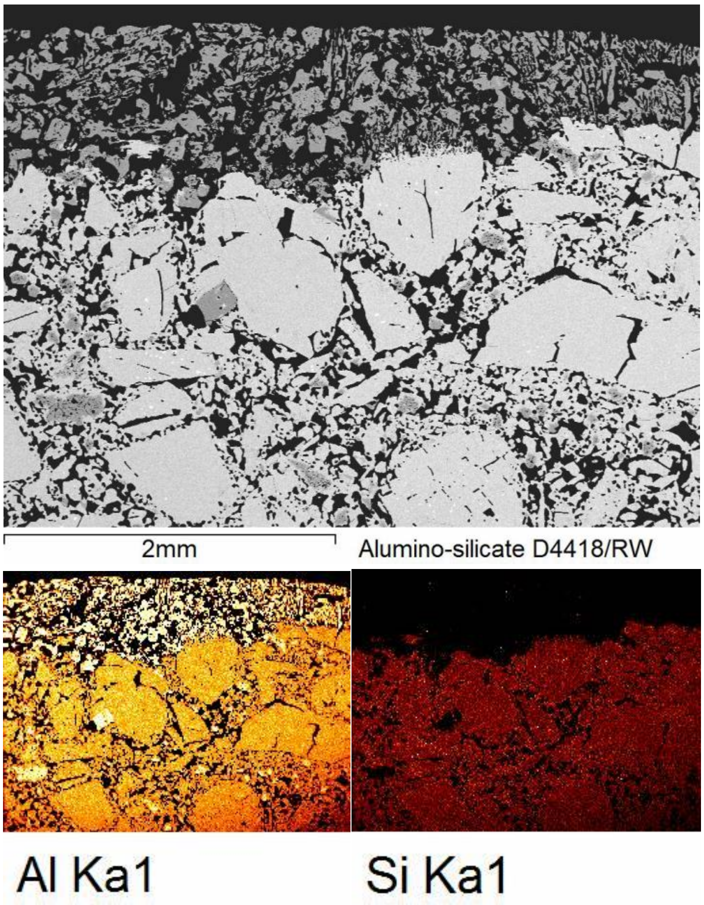


Fig. 7 H_2 Depletion of silica leaving corundum layer at front face (2 years exposure)

From Figures 6 and 7, the removal of SiO_2 from the structure is clearly evidenced from the elemental mapping Si Ka1 images.

The process could be isokinetic, that is the depletion of SiO_2 continues at a constant rate without any barriers to the “speed” of the process.

If this is the case then Frimul FX is affected to a depth of ~1mm per annum which is similar to the traditional mullite bonded corundum compositions.

Following consideration by industry experts this affect is noted but not considered as significant due to acknowledgment that a 25 year campaign would potentially affect only 25mm of refractory; even in this hypothesis the load bearing stability portion of the refractory would not be compromised.

Mitigating SiO_2 Depletion Phenomenon

Whilst as stated above, the rate of SiO_2 depletion of the refractory is not considered detrimental to the thermomechanical performance over the thermal reactor campaign, in due acknowledgment of this phenomenon however, a solution to mitigate if not eliminate the process has been sought.

The driving force to minimise this perceived adverse process is to avoid SiO_2 rich condensate fouling the tubesheet, although it is likely that other vapour species are the root cause.

In contrast, the capacity increases by running the reactor at high temperatures circa 2900^{o}F (1580^{o}C) with a thermo-mechanically stable refractory are compelling; so a thermo-chemical equilibrium or near equilibrium scenario is sought.

This has led to two approaches:-

i) Pure corundum coating on the hot face of the refractory with inherent H_2 resistance of low permeability to create chemical energetic hurdle to SiO_2 depletion (Fig.8)
ii) Hybrid thermal reactor design (Fig.9), pure corundum refractory lining (DSF 99 & DSF 99C) utilised in zones of low thermal stress, hence overall SiO_2 volume exposed to potential H_2 reduction is lowered to conventional lining levels. It is suggested that all Checker Wall and some Choke Rings are constructed from pure corundum refractories (pressed or cast) as these structures are particularly vulnerable to SiO_2 depletion due to an increased surface area exposure to reaction vapour species

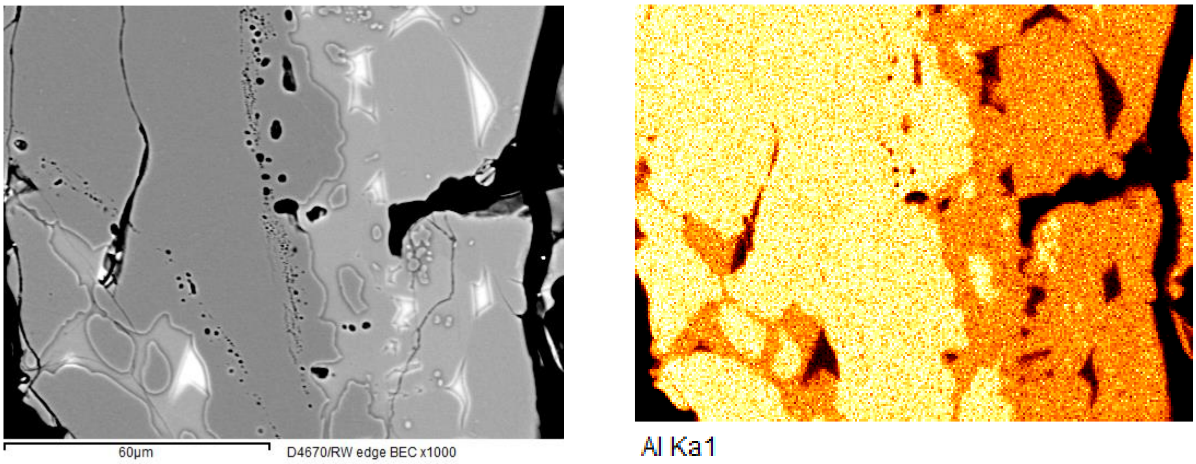


Fig.8 Backscattered SEM (left) and element mapping (right) of Corundum coating on DSF Frimul FX substrate

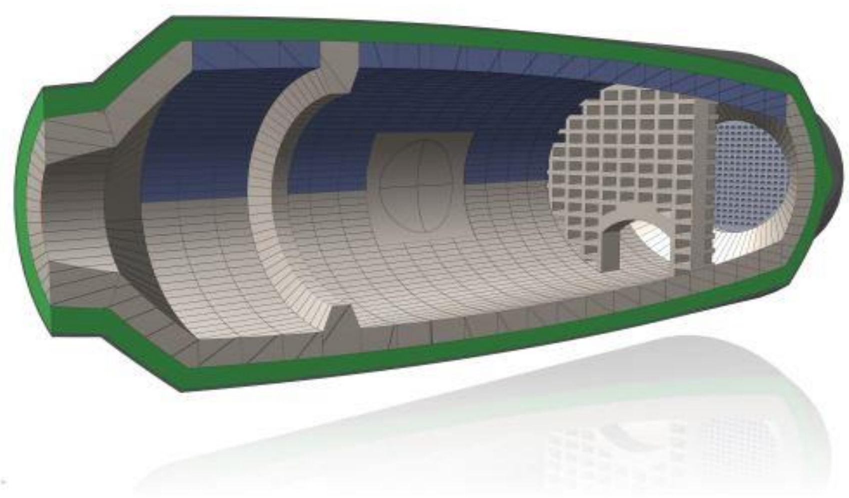


Fig.9 Hybrid Thermal Reactor; light grey DSF 99/C, blue Frimul FX and green IFB/fibre insulation

Summary

DSF Frimul FX represents a step change in SRU lining materials exhibiting (to our knowledge) unparalleled creep resistant characteristics which are intended to not only meet but exceed the auspices of API standards and more importantly define a material with capability to withstand both normal and abnormal operating temperatures.

DSF Frimul FX is in current use as the sprung crown of an E-glass melter operating continuously at ~2912°F. The melter is oxy-fuel fired; the span is 13ft with an aggressive boron containing environment. It is new to the SRU industry, however technical due diligence has been performed and to date there have been no significant parameters which would negate the use of this material.

Utilising a mullite material has other intrinsic benefits compared with traditional 90s materials:-

- Comparable maximum service temperature ie. pragmatic molten point to mullite bonded corundum
- Shell temperature is maintained in the range 350-550^{o}F
- Lower density which correlates with a reduced footprint weight
- Lower thermal conductivity, potential for thinner linings to increase reaction capacity and no significant change to shell temperature
- Lower and linear thermal expansion; there are no peaks or troughs in the expansion curve and therefore no heterogeneous reaction to temperature swings specifically during power outages
- Excellent resistance to creep at high loads and temperature providing stable lining construction
- Potential to increase design capacity by increasing reactor temperature

C.Windle
Technical Director
24/08/22

References

[1] US EPA Sulphur Dioxide the Basics

[2] Fundamentals of Sulphur Recovery by the Claus Process: B.Gene Goar; Steve Fenderson

[3] Ceramic and Glass Materials: Structure, Properties and Processing; D.J.Duval; S.H.Risbud; J.F.Shackleford