

**Refractories for Changing Conditions in Hydrogen and Hybrid Melters**

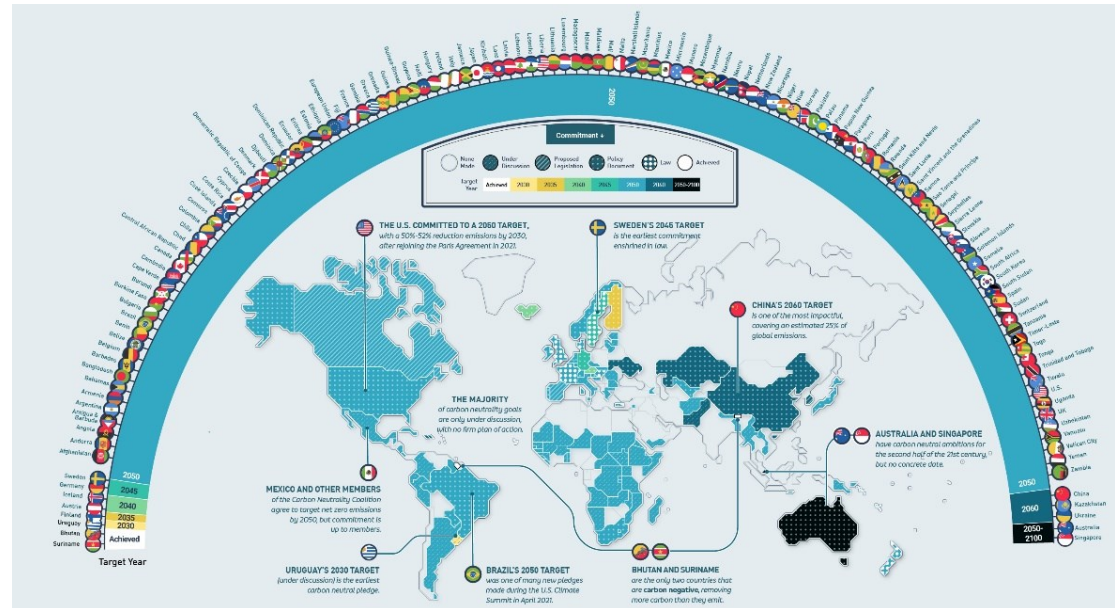
**TC11**



All industry will go carbon neutral to stop global warming

Most countries have committed to **2050**

This includes the entire supply chain so bottles, windows, furnaces and refractories.



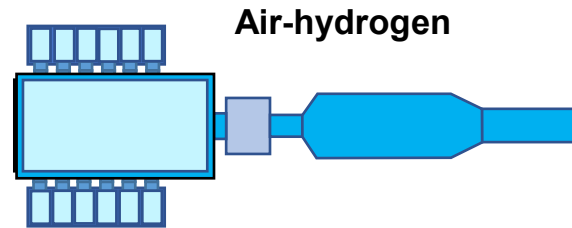
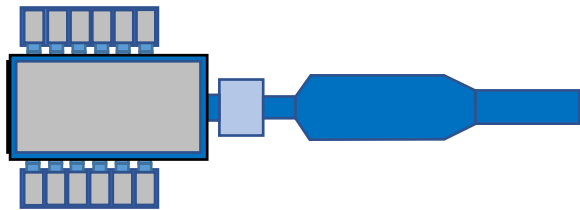
How will Glass furnaces change to go carbon neutral?

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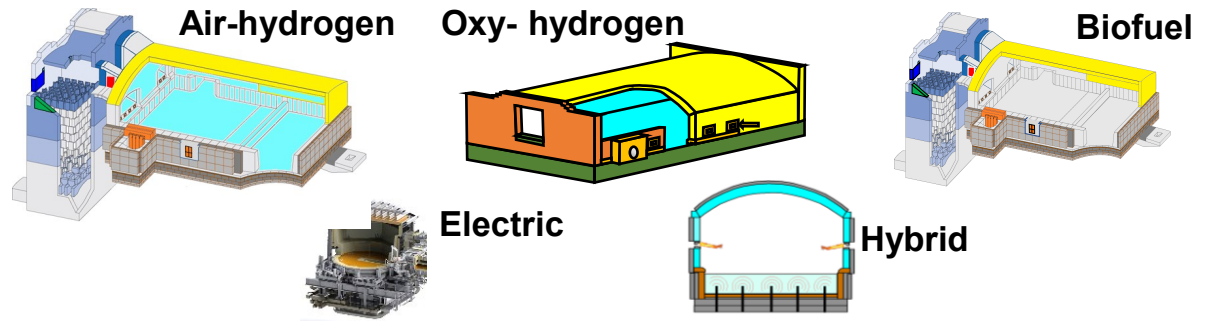
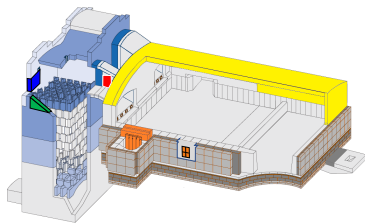
Now – 98% natural gas or oil fired

De-carbonised

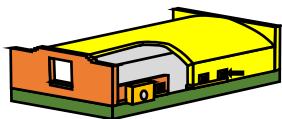
Float - cross fired regenerative



Container – end fired regenerative



Fibre & Special glass - Oxy fired



Oxy- hydrogen



Electric



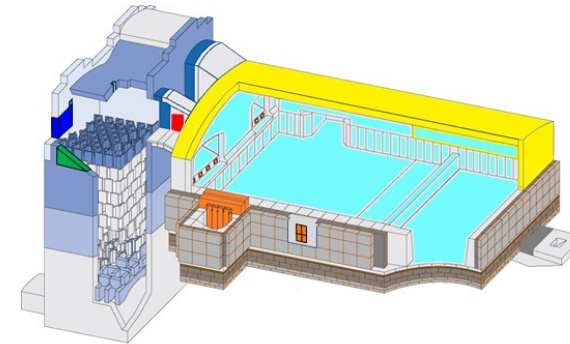
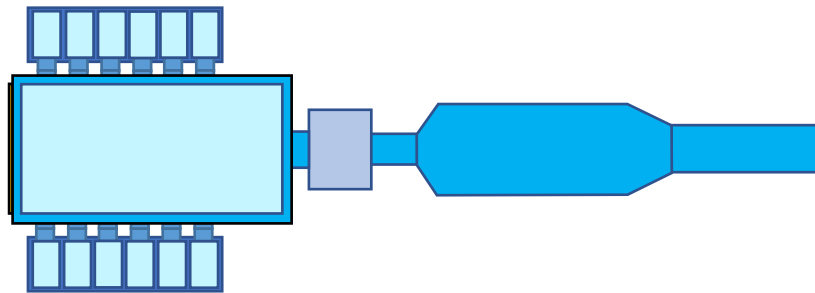
How do these Changes Effect the Refractories?

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- |                 |  |
|-----------------|--|
| Hydrogen Firing | <ul style="list-style-type: none"><li>- High water vapour concentrations</li><li>- Higher water pulls more NaOH into atmosphere</li><li>- Possible increase in crown temperatures</li><li>- Increased foam on sidewall</li></ul> |
| Hybrid Furnaces | <ul style="list-style-type: none"><li>- Hot and cold superstructure temperatures</li><li>- Temperature changes over lifetime</li></ul>   |

Hydrogen – Air fired Furnaces

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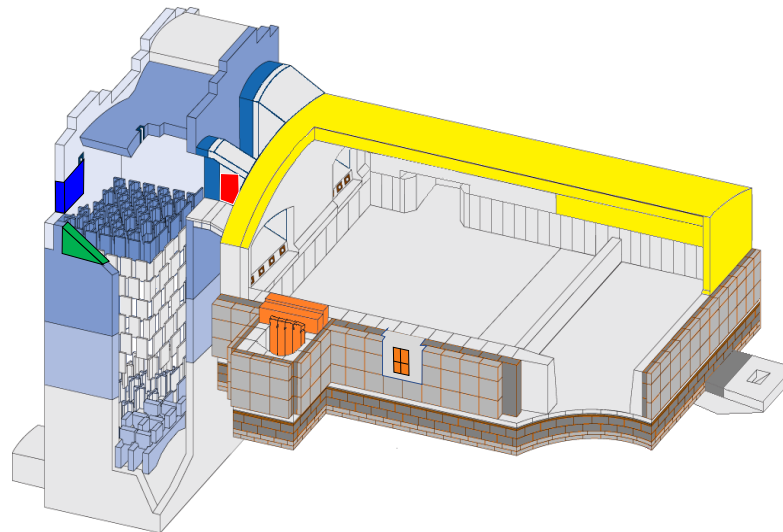


The water vapour concentrations are increased but slightly less than oxy-methane firing so treat melter as oxy-fired tank, keeping regenerators unchanged\*

\* Slightly higher wear and increased blocking of regenerators likely.

Biofuel fired Furnaces

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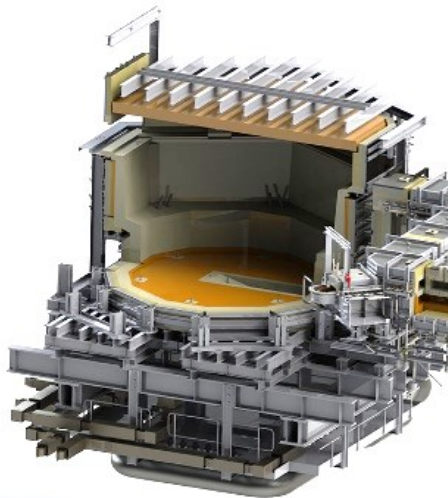


Current biofuels give near identical conditions to oil fired tanks – **no refractory change**

Any new biofuel needs to be considered before use as some natural materials have concentrated fluxes that can damage refractories.

Cold top Electric Furnaces

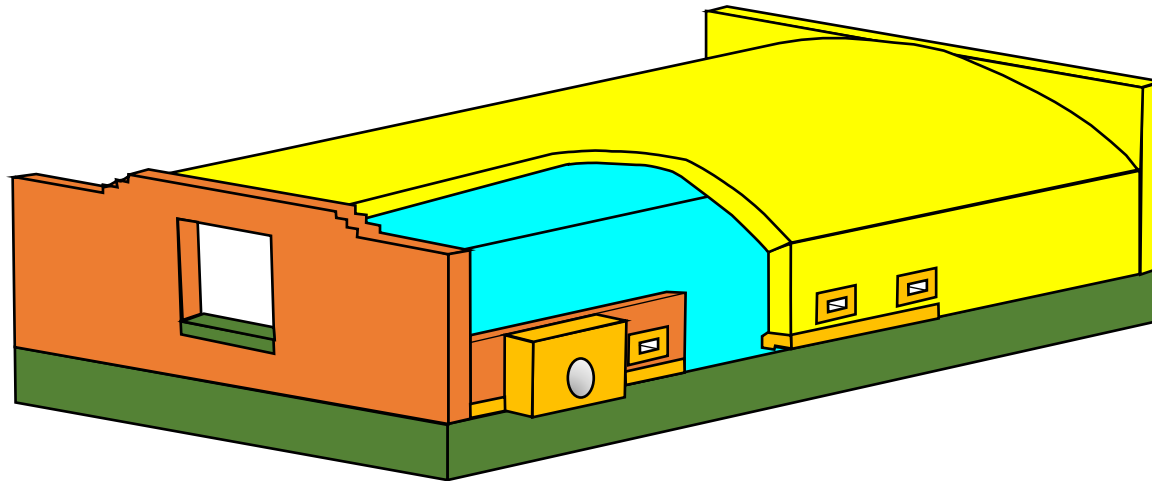
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Known technology – **no refractory change**

Oxy-Hydrogen Furnaces

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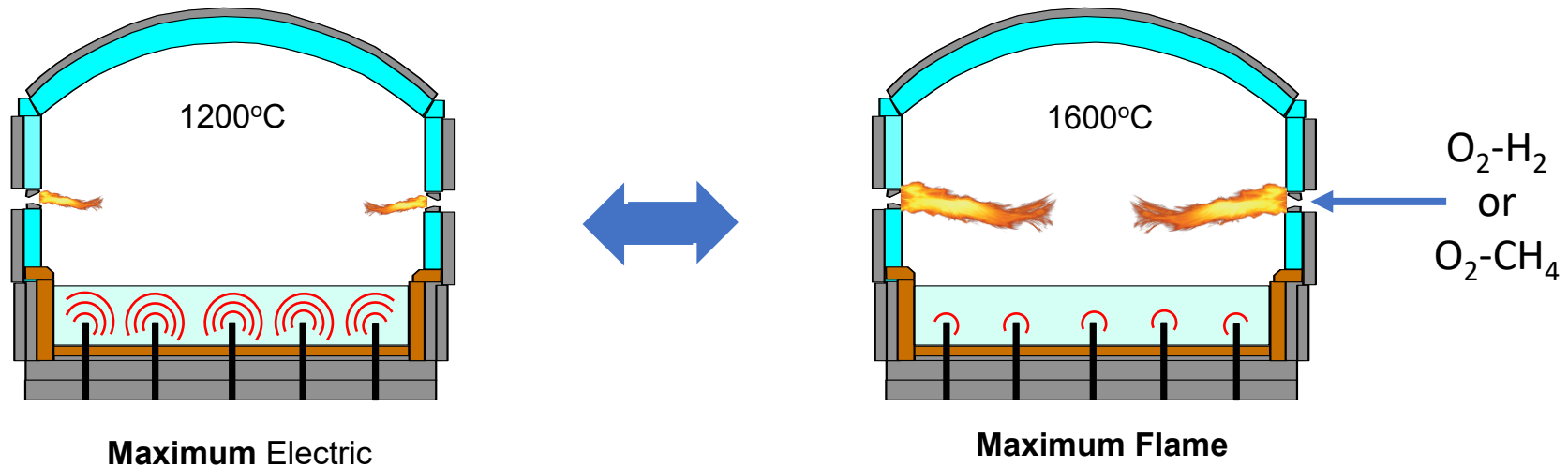
Without dilution air and higher NaOH pulled from the glass, silica crowns almost certainly will not survive

**A different crown material resistant to high NaOH concentrations is required.**

Higher foam levels above the fluxline means tuckstone materials will need to be glass resistant

Hybrid Furnaces

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Hybrid tanks with variable top firing and high electric boost are likely to be popular for low running costs, flexible cullet rates and ability to switch energy balance if price or availability changes

Most current refractories will fail at either high or low temperature

Crown temperature

1200°C maximum electric mode – Silica alkali corrosion & aluminosilicates nepheline spalling

1600°C in maximum firing mode – Creep deformation & AZS exudate

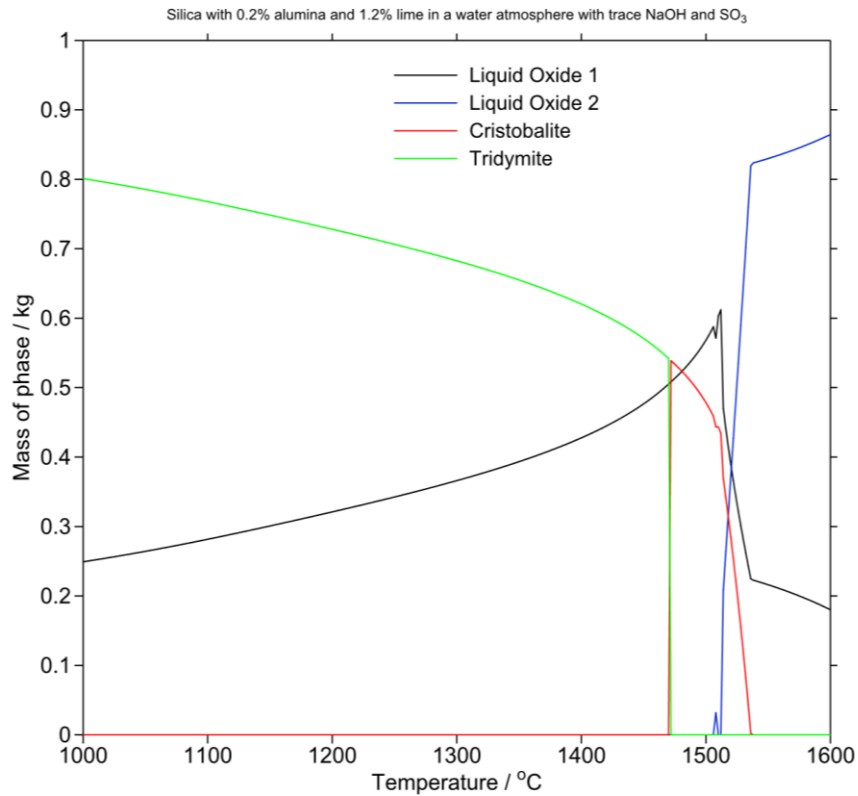
Practically Hybrid furnaces are likely to start top firing on oxy-methane then transfer to oxy-hydrogen when price and availability becomes viable, so linings should be designed H<sub>2</sub> ready

**Is there a refractory that can survive in both temperature extremes and is resistant to the High NaOH and water concentrations?**

Oxy-Hydrogen and Hybrid Furnace Superstructure

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Low lime Silica - Thermodynamic stability



Sodium Carbonate testing – 1600°C



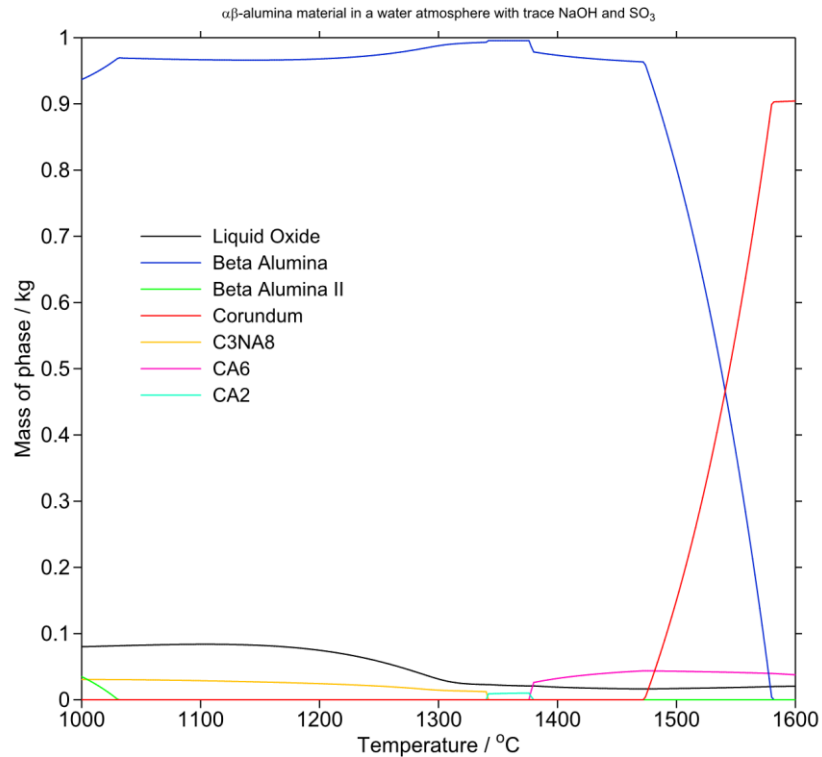
**Not stable** - all converted to liquid

Thermodynamic calculations used 1kg of solid material in a 10kg gas atmosphere containing 99% H<sub>2</sub>O, 0.7% NaOH, 0.3% SO<sub>3</sub> (by mass). The calculations were carried out using MTDATA version 7.2

Oxy-Hydrogen and Hybrid Furnace Superstructure

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$\alpha$ - $\beta$  Alumina – Thermodynamic stability



Refractory stays solid but transitions between  $\beta$  to  $\alpha$  stable between above  $\sim 1470^\circ\text{C}$  with slight shrinkage.

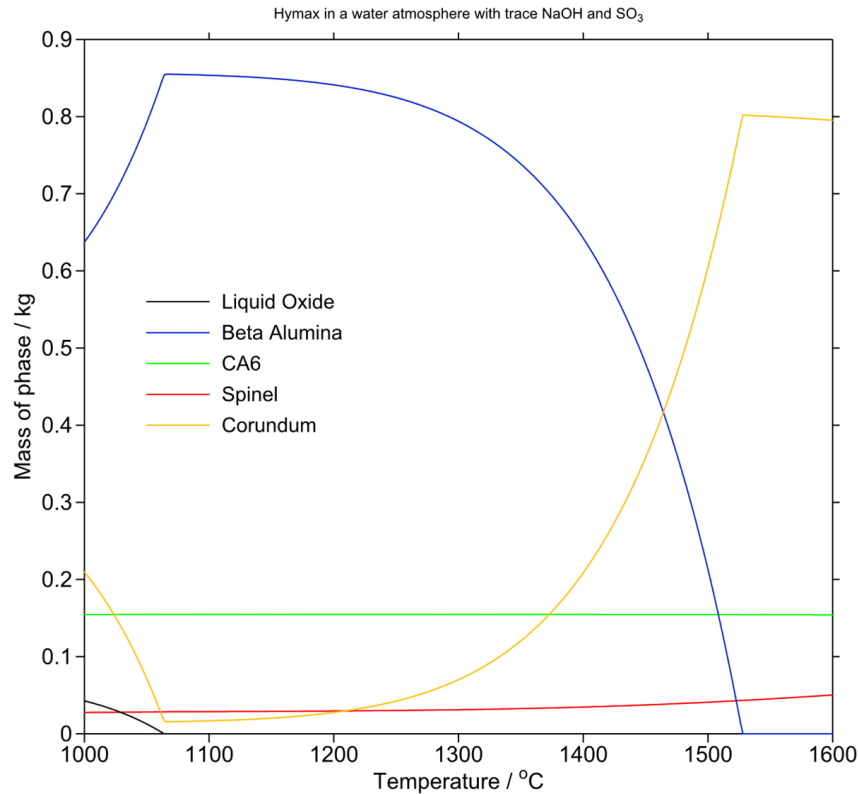
Possible problems over multiple transitions



Oxy-Hydrogen and Hybrid Furnace Superstructure

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CA6 bonded  $\alpha$ -alumina (Hymax) - Thermodynamic stability



Sodium Carbonate testing – 1600°C

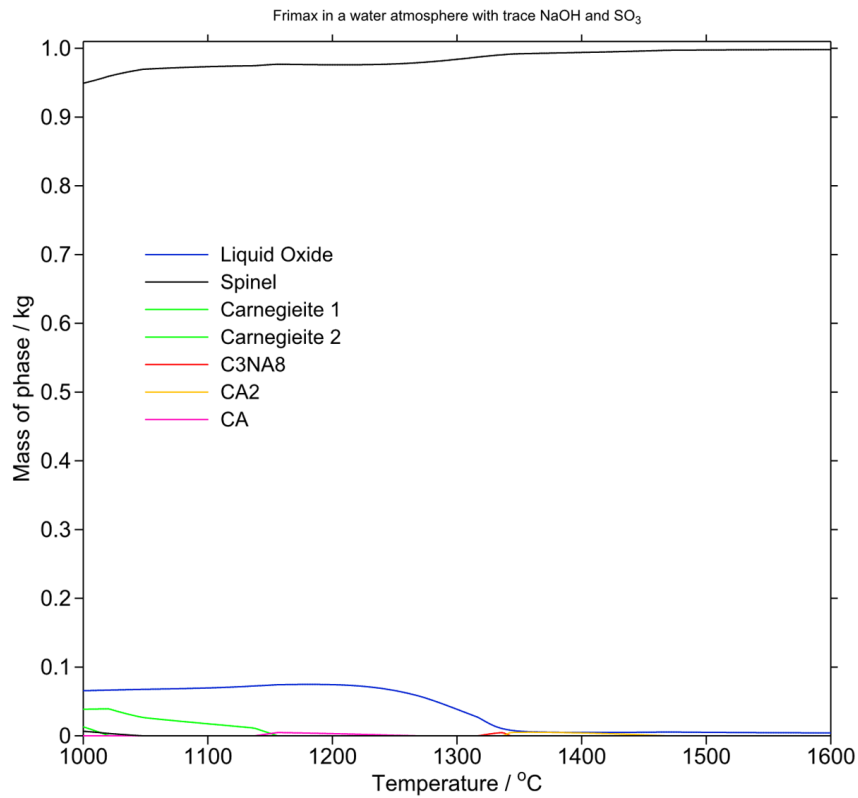


Alumina converts but calcium hexaluminate bonding & spinel stays unchanged

Oxy-Hydrogen and Hybrid Furnace Superstructure

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Mag-Alumina Spinel (Frimax)- Thermodynamic stability



Sodium Carbonate testing – 1600°C

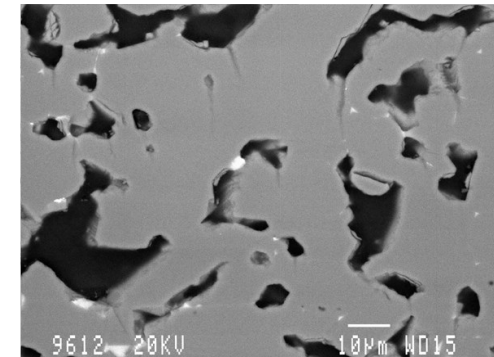
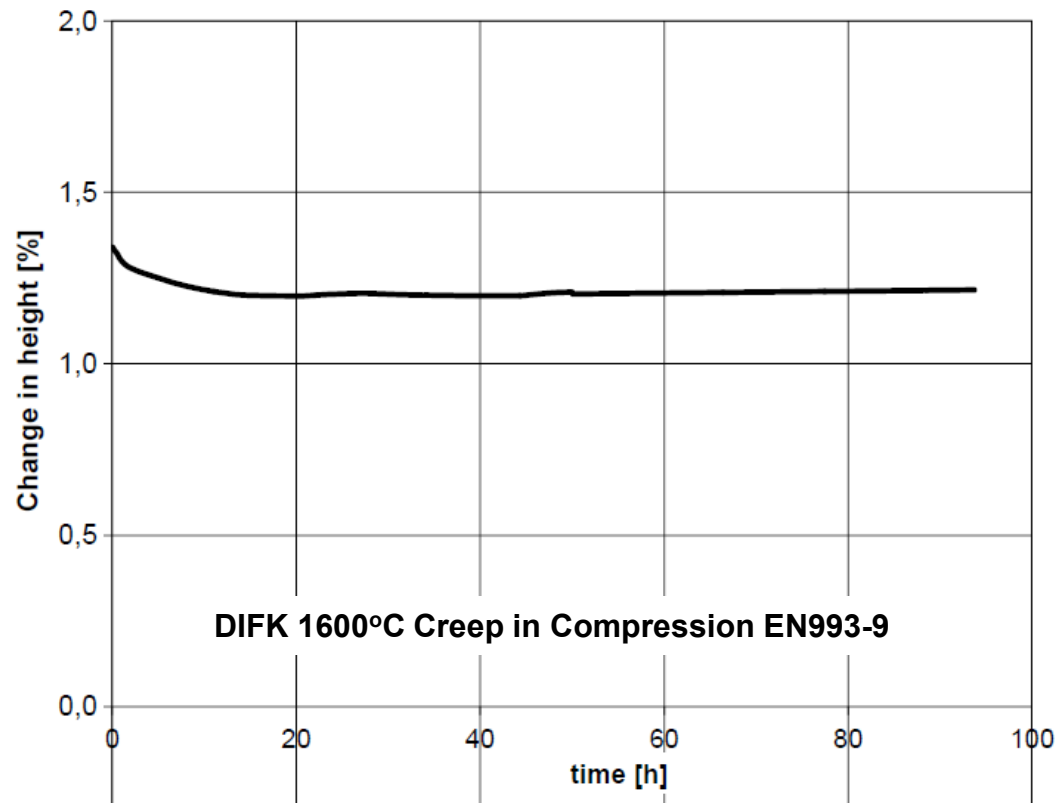


Stable at all temperatures

Oxy-Hydrogen and Hybrid Furnace Superstructure

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Thermo-mechanical stability for 1600°C crown use

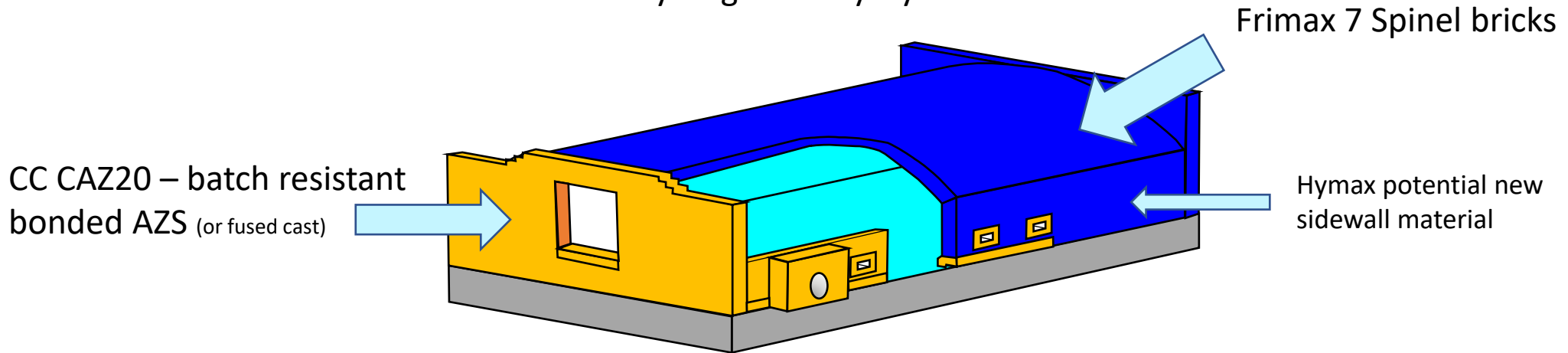


Frimax 7 - 1700°C fired fused spinel brick microstructure

Oxy-Hydrogen and Hybrid Furnace Superstructure

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Materials for hydrogen ready Hybrid Melter



**We have supplied >500 tonnes of spinel over 25 years to the glass industry**

Spinel has been used mainly for oxy-fired special glass melter and float melter superstructures

Oxy-Hydrogen and Hybrid Furnace Superstructure

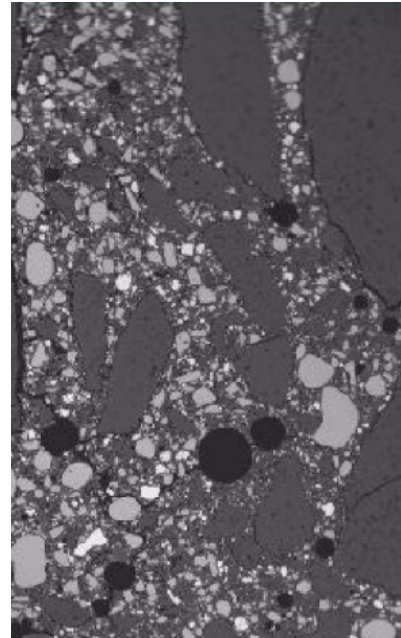
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**Batch End**

Low permeability stable bonded AZS – CC CAZ20



CC CAZ20 after 4 years oxy-methane  
C glass melter



CC CAZ20 Microstructure

**Or fused cast AZS**  
Any exudate defect should be  
digested before throat

### Case Studies

Silica crown after 5 years



Oxy-gas lighting glass tank operating with soda-lime and 1.2% boron at 1450°C



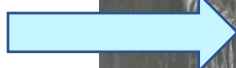
Silica patched after 1 year, sections replaced at 3.5 yrs

Spinel (Frimax 7) after 1 year (plant closure)

### Case Studies

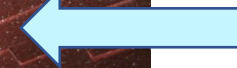
Low temperature 1350°C crown in soda-lime lighting glass tank

Rundown



Oxy-fired soda-lime crown showing Fused Cast AZS exudate after ~4 years

No Run-down

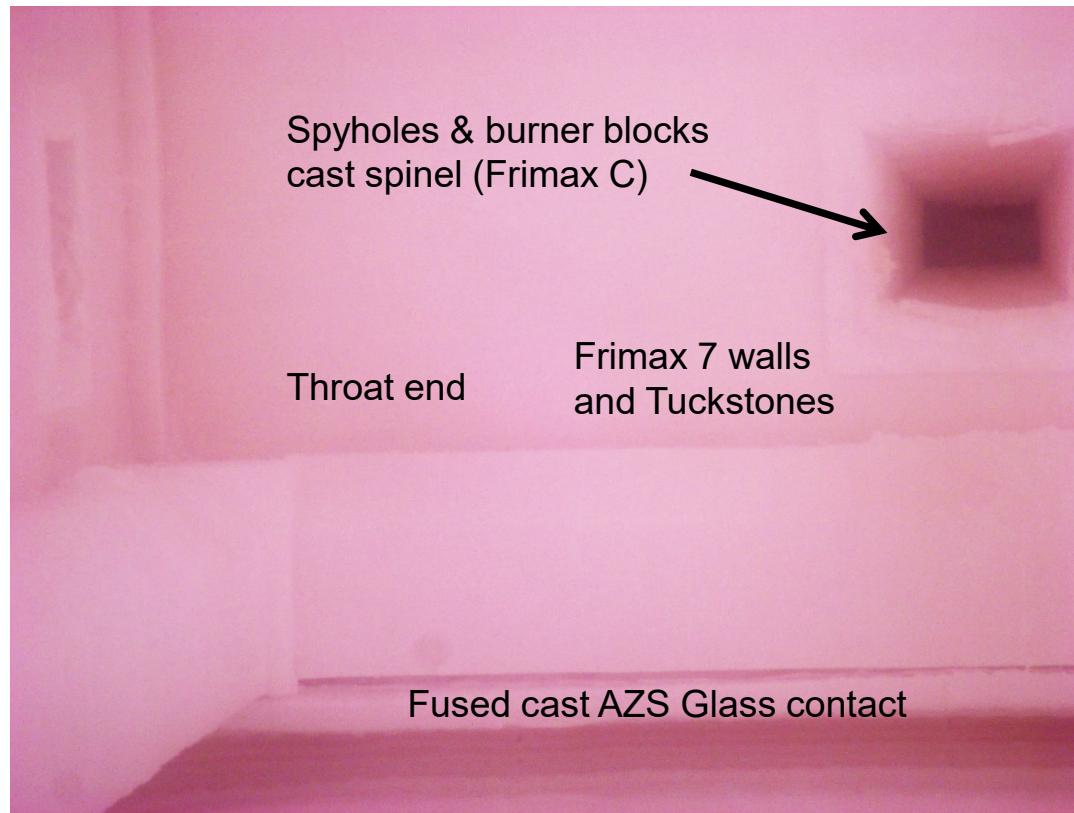


Identical furnace showing unreacted spinel crown after 6 years

### Case Studies

Soda Lime Glass, 1550°C,  
15x6m tank

Spinel (Frimax 7) in Throat  
& Throat end side walls  
lasting 16.5 years



Photograph after 13.5 years

## Case Studies

**Spinel (Frimax 7) has been used in the melter sidewalls of an oxy-fired float tank for 18 years, showing minimal 0-10mm wear.**

(No photographs allowable)

## Possible design change?

### Flat Roof Construction for temperature changing Hybrid Furnaces

To avoid the crown stresses changing superstructure temperature on maximum electric to maximum gas an interlocking flat suspended roof could be adopted





Possibly the first ever hydrogen firing of Refractory bricks

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