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H_2 and H_2O - Challenges for the Refractory Lining Concepts of Aluminum Furnaces

83rd AMAP Colloquium, Sascha Stahl, Refratechnik Steel GmbH

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Agenda

- Short introduction of Refratechnik Group
- Lining concepts of Aluminum furnaces – State of the art
- Facts of using Hydrogen as alternative energy for combustion processes
- Wear mechanisms and effects due to the presence of H_2 / H_2O
- Estimated effects on the refractory lining
- Conclusion & Outlook

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Refratechnik worldwide

Largest family-Holding owned refractory producer

29 locations

> 2.000 employees

> 1 Mio. t production capacity

800 Mio. € turnover

Focus on two main pillars:

- High-quality refractory products and concepts
- Industry minerals

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Topics

The current situation

- Worldwide investigation programs to develop (heavy) industrial processes with significantly reduced carbon footprint and alternative fuels
- “Hydrogen shall be the new Carbon”, “Carbon Challenge”
- Starting theoretical, thermodynamical calculations for different scenarios
- Rapid set up of different test methods in lab and pilot plant scale
- Less possibilities for testing in industrial scale and a lot of NDAs

The questions of today:

- Are the state-of-the-art refractory concepts of Aluminium casthouse furnaces suitable for advanced Hydrogen rich burning processes?
- How will refractories be affected by these forthcoming transformations?

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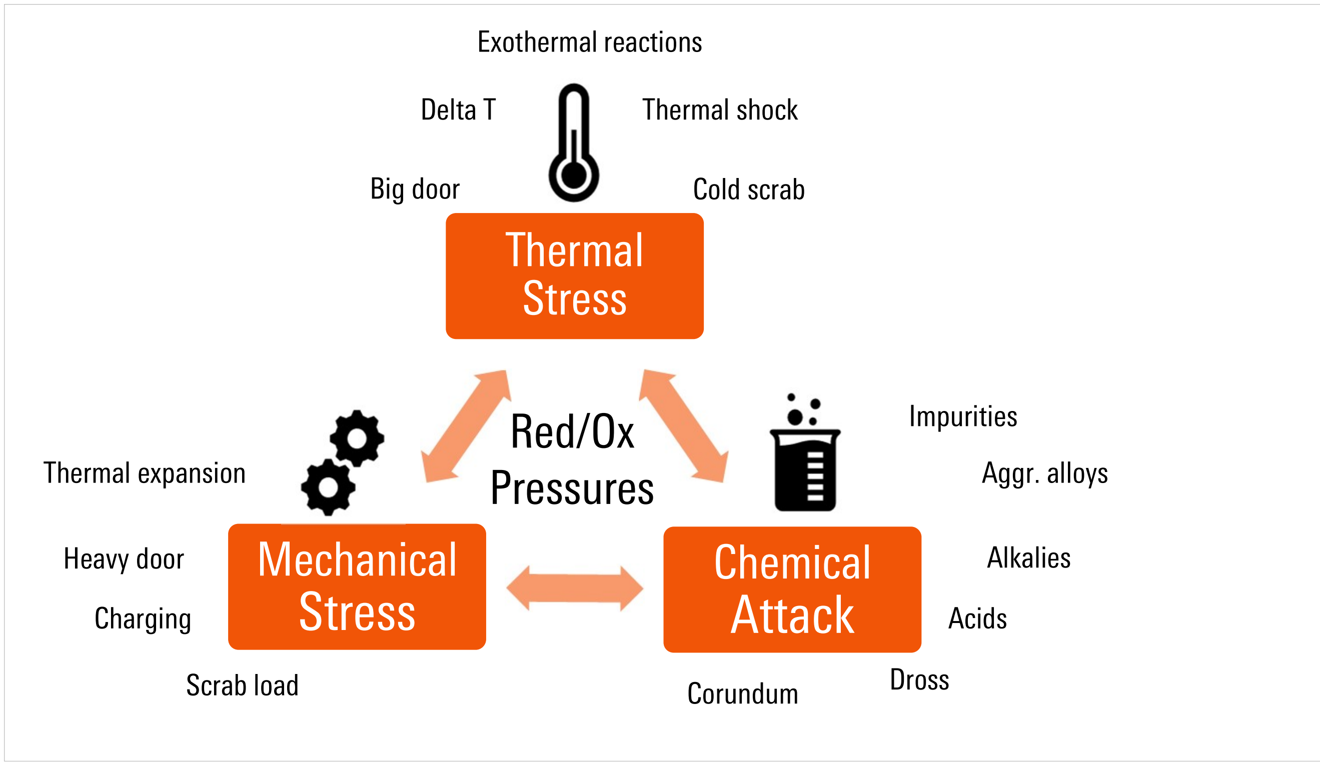
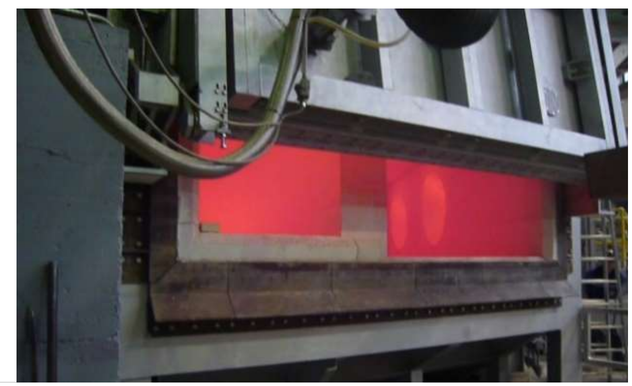
Refractory Linings – Challenges for Refractories





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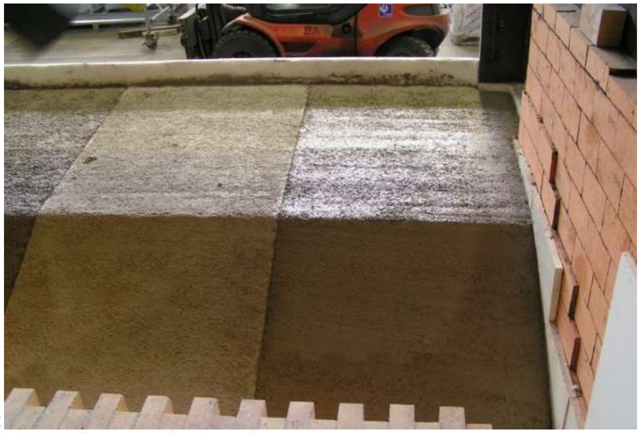
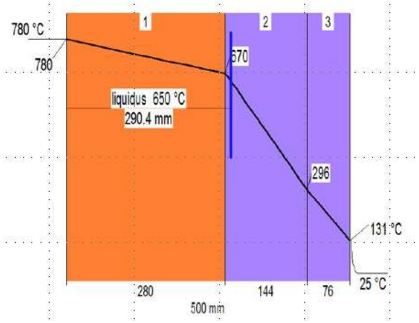
Refractory Linings – State of the Art Wear Lining

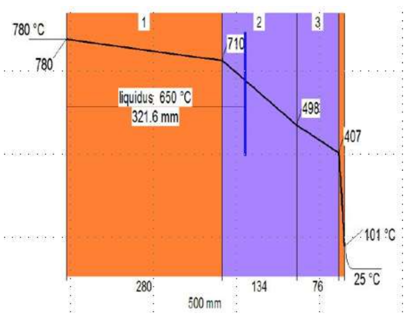
- Upper furnace, burner blocks and roof: Monolithics or Phosphate bonded bricks with 50-80% Al_2O_3 usually without special anti-wetting additives focus on high temperature resistance, TSR and mechanical strength
- Furnace hearths, bath area and belly band: Dense Microsilica free Monolithics/pre-shaped blocks or bricks with 70-90% Al_2O_3 and reactive anti-wetting additives (e.g. P_2O_5, $BaSO_4$, CaF_2)
- Suitable metal or ceramic anchors

Refractory Linings – State of the Art Safety Lining and Insulation

- Upper furnace, burner blocks and roof: Semi insulating Monolithics and bricks with 30-40% Al_2O_3
- Furnace hearths, bath area and belly band: Semi-insulating Monolithics and bricks with 30-40% Al_2O_3 and anti-wetting additives (liquidus temperature)
- Insulation with (microporous) board or brick
- Focus on TSR, heat transfer and thermal process stability according to the given heat transfer calculation/shell temperature.







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Combustion and Furnace Process – State of the Art vs. Transformation

State of the Art

- Dried (natural) gas fuels for burners with ambient air, Oxygen or recuperated process heat/gas
- Stable and well-known process parameters
- (Natural) gas fuels produce a lot of CO_2 during combustion
- Plans for substitution!

▸ Stoichiometric combustion of Methane:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

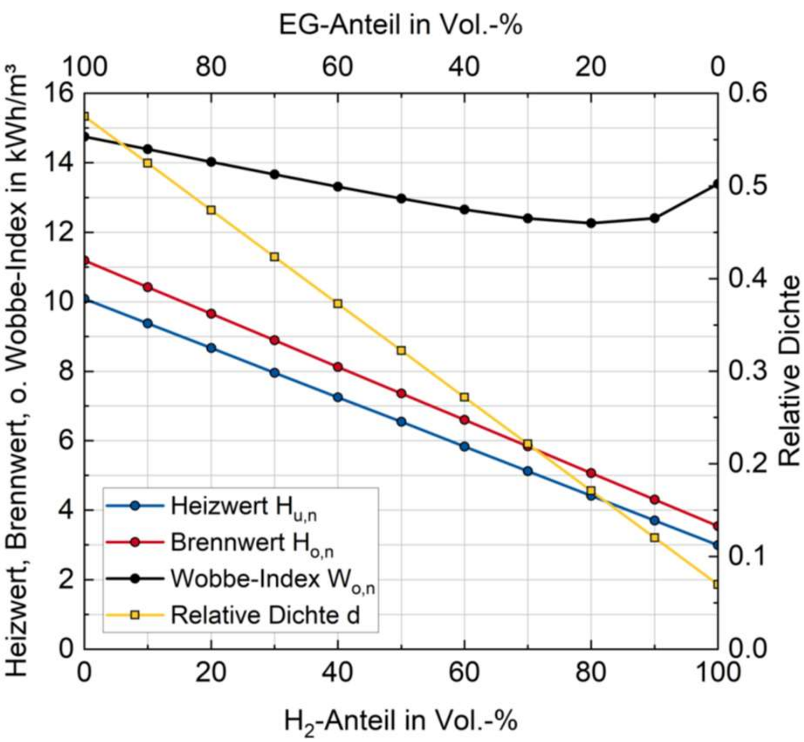
Transformation

- Combustion of 4-75% H_2 with air is free of CO_2 $\rightarrow$ H_2O
- Near future: natural gas enriched with H_2
- Distant Future: H_2 should substitute natural gas, other fossil and all CO_2 forming combustion fuels

▸ Stoichiometric combustion of Hydrogen:

$$2\,H_2 + O_2 \rightarrow 2H_2O$$

Combustion and Furnace Process – Some known Facts



Combustible	Calorific value kWh/kg	Calorific value kWh/m³
Natural Gas	8,9 – 12,5	8,6 – 11,4
Methan CH_4	13,9	9,94
Hydrogen H_2	33,3	3,0

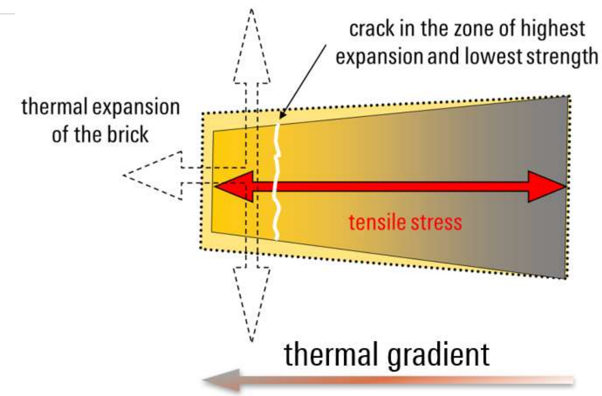
- Lower density and calorific value, higher volume of combustion gas to reach the same heat input (3x)
- Different flow rate, heat-flow and pressure parameters in the furnace
- Flame will change color, size, temperature (+200K)
- Different parameters for the security systems and the refractories
- Reactions with particles in the atmosphere

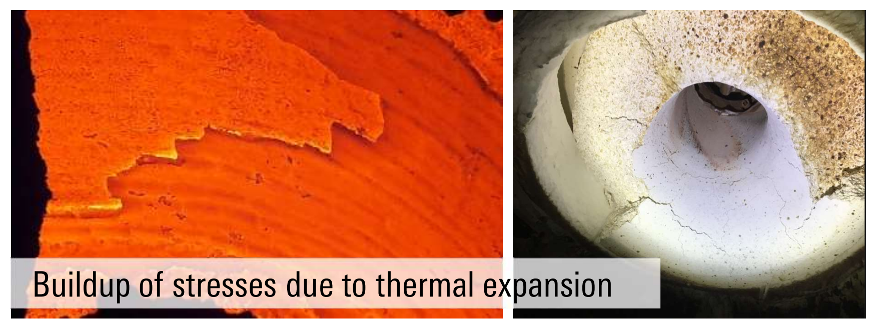
Quelle: Brennertechnologie beim Einsatz von Wasserstoff, Nico Schmitz –Herbert Pfeifer

Wear Mechanisms + Effects due to changed Combustion/Burner Settings

Thermal shock

- Higher flame temperature leads to higher thermal stress around the stressed/impact area (on/off)
- Damage caused by temperature related increase in volume (irreversible/reversible)
- Formation of stresses in single bricks or networks
- Refractory lining need to perform at high temperatures, attack by:
  → impacts - flexural stress - pressure





Buildup of stresses due to thermal expansion

General Wear Mechanisms and Effects due to H_2 / H_2O Reaction with Refractories - Thermodynamic point of view

1. Thermodynamic instability due to reduction of the oxide according to the schematic equation

$$MeO\,(s) + H_2(g) \rightarrow Me\,(s, l) + H_2O\,(g)$$

2. Active corrosion through the formation of gaseous reaction products according to the schematic equation

$$MeO_2(s) + H_2(g) \rightarrow MeO\,(g) + H_2O\,(g)$$

3. For non-oxidic refractory materials such as SiC or Si_3N_4, in addition to a reaction with H_2, corrosion as a result of oxidation by the residual water vapor in the H_2-atmosphere:

Hydrothermal corrosion

$$5SiC\,(s) + H_2O\,(g) \rightarrow SiO\,(g) + C\,(s) + H_2(g)$$

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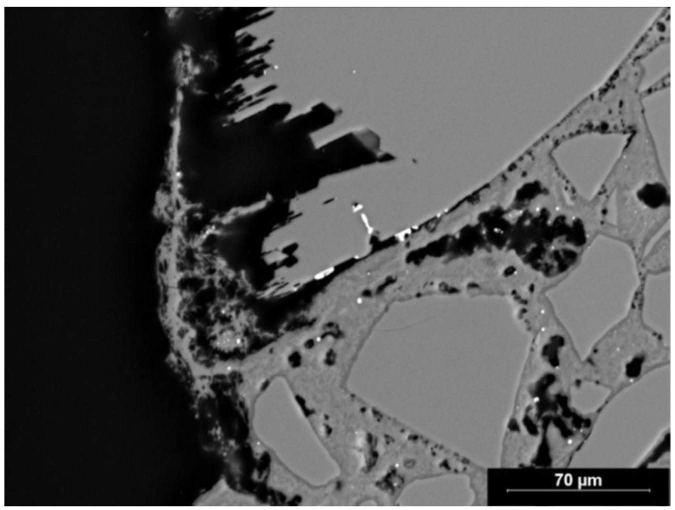
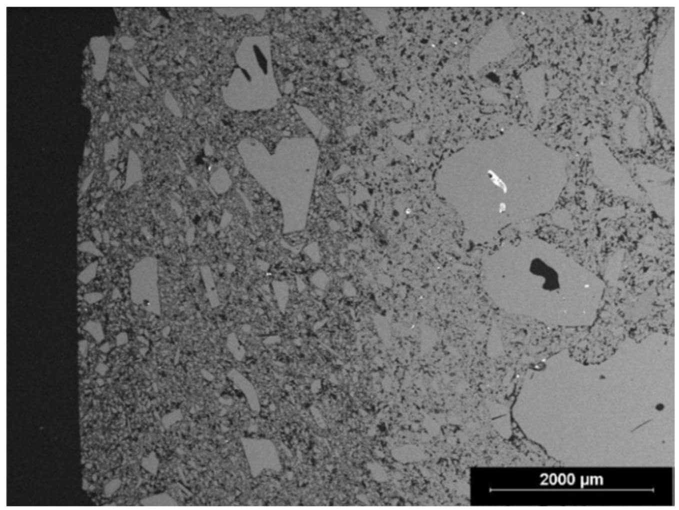
Wear Mechanisms and Effects due to residual H_2 as Reduction Gas

General kinetic and hydrothermal corrosion of SiC



Corroded SiC-grain on sample surface,1200°C, H_2 3.0, 50h,
(RE, x500, 25kV)



Surface SiC-rich material,1300°C, H_2 5.0, 50h,
(RE, x20, 25kV)

General kinetic of corrosion:

- Weight change
- Volume change
- Layer formation

Source: Dr.-Ing. Almuth Sax, „Verschleißmechanismen Feuerfester Erzeugnisse"

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Wear Mechanisms and Effects due to residual H_2 as Reduction Gas

Dissolving of SiO_2 by H_2 in Al_2O_3/SiO_2 ceramic bonded bricks

REFRAL S 62, cross section, Lab. test: 100% H_2, 1400°C, before and after testing

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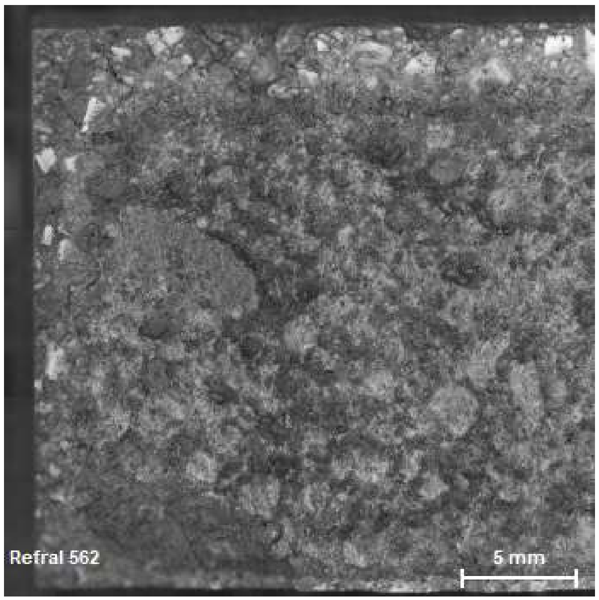
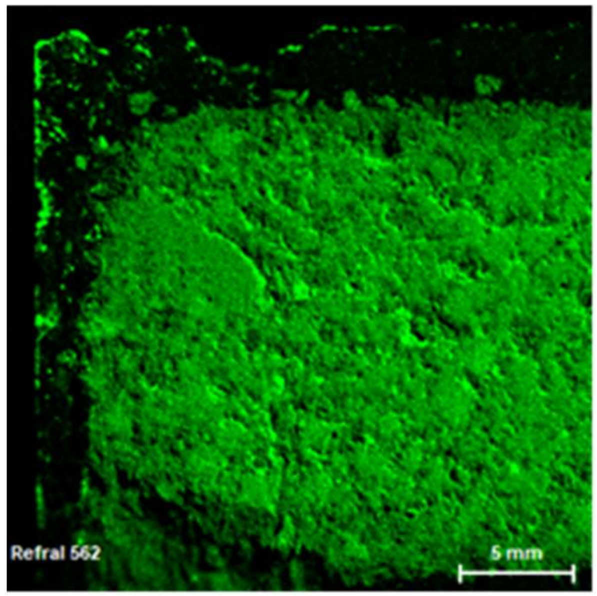
Wear Mechanisms and Effects due to residual H_2 as Reduction Gas

Dissolving of SiO_2 by H_2 in Al_2O_3/SiO_2 ceramic bonded bricks



Cross section, Lab. test: 100% H_2, 1400°C



Si-Mapping

$$SiO_{2(s)} + 2\,H_{2(g)} \rightarrow Si_{(s,l)} + 2\,H_2O_{(g)}$$

- Ceramic bonded Andalusite brick
- Reduction of Oxides
  → color change
- Massive weight loss detected
- Increasing porosity
- Weak structure
  → premature wear
- Condensation of SiO below 850°C

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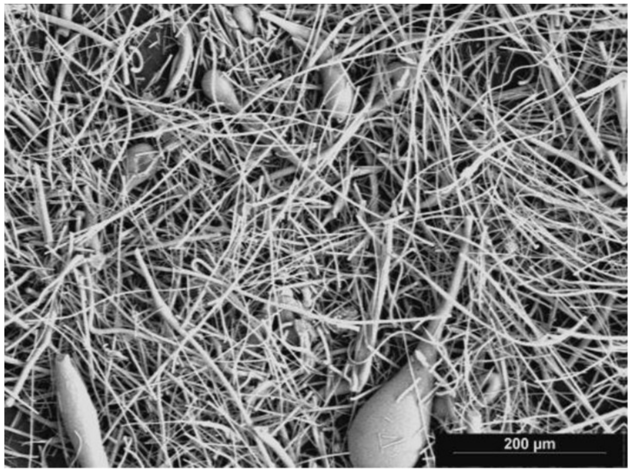
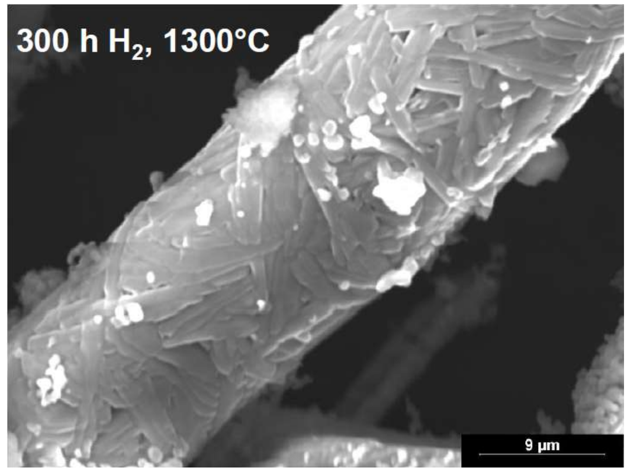
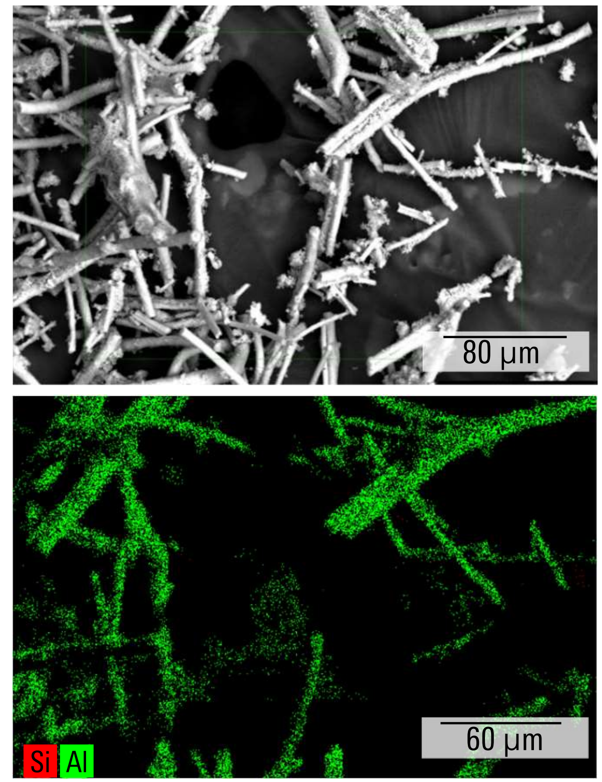
Wear Mechanisms and Effects due to residual H_2 as Reduction Gas

Dissolving of Alumosilicate insulating wool







- Evaporation of SiO_2 and Corundum formation
- Changing the thermal conductivity and flexibility

Source: Dr.-Ing. Almuth Sax, „Verschleißmechanismen Feuerfester Erzeugnisse“

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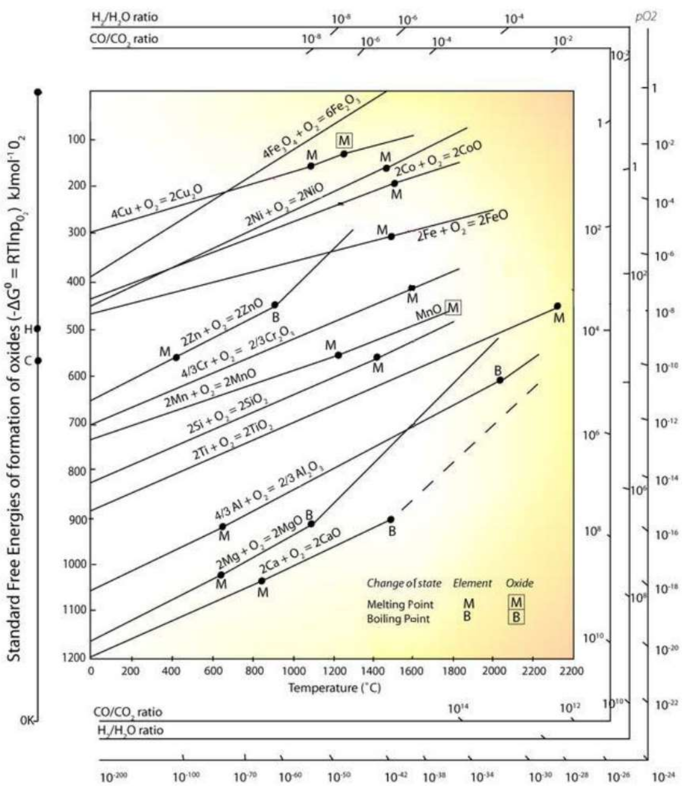
Wear Mechanisms and Effects due to residual H_2 as Reduction Gas

Dissolving and reduction of oxides - Richardson-Ellingham-Diagramm and Crowley



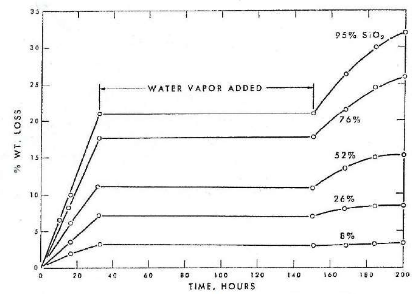
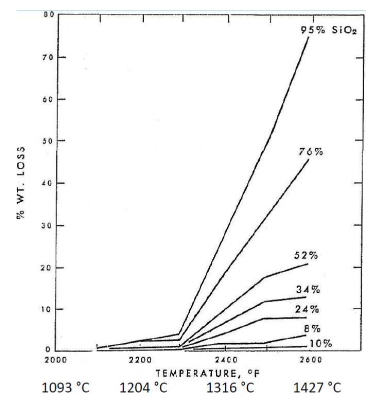


Fig. 3. Weight loss of brick at 1371 °C in 75%H₂-25%N₂ atmosphere. After 32 hr water vapor was added for 150 hr.



Source: Crowley (1970); "Hydrogen- Silica reactions in refractories"

Used for the estimation of the resistance of metal oxides under diff. reducing conditions

Reactions dependent of:

- Temperature
- H_2/H_2O and CO/CO_2 ratio
- Water vapor content
- Pressure and flow rate

Wear Mechanisms and Effects due to residual H_2 as Reduction Gas

Thermodynamical calculations via FactSage™7.3 (University of Koblenz)

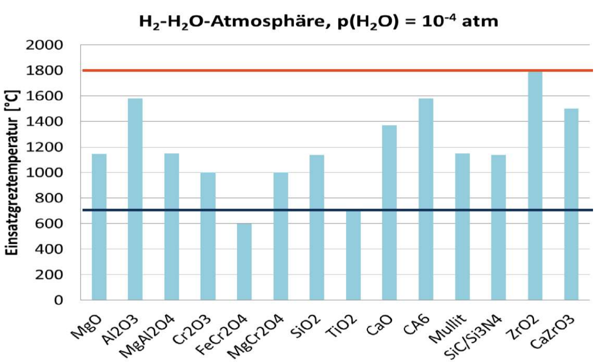
The following common refractory materials were investigated

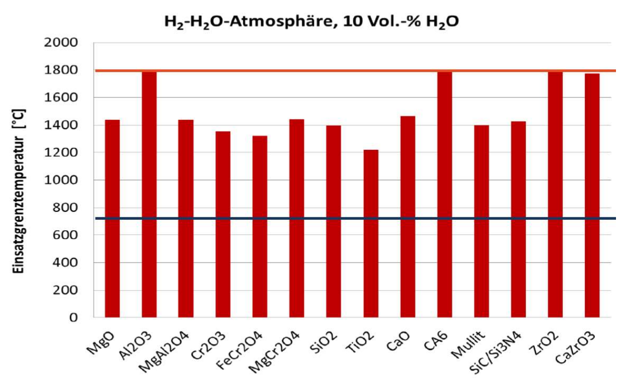
MgO	Cr_2O_3	SiO_2	ZrO_2
Al_2O_3	$MgCr_2O_4$	TiO_2	CaO
$MgAl_2O_4$	C	CA_6	$CaZrO_3$
$FeCr_2O_4$	SiC / Si_3N_4	Mullite	$AlPO_4$

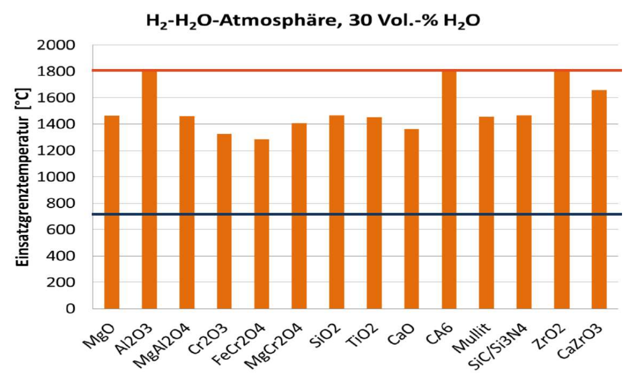
Relevant refractories in Aluminum furnaces

Wear Mechanisms and Effects due to residual H_2 as Reduction Gas

Thermodynamical calculations via FactSage™7.3 (University of Koblenz)







- Active corrosion in pure H_2 atmosphere reduces the maximum service temperature (0.01% H_2O)
- Vapor reduces the active corrosion of Oxides
- Vapor creates new problems e.g. (re)hydration or hydrothermal corrosion

20% H_2 content → 86% energy of pure nat. gas → +14% gas volume for the same energy output

Wear Mechanisms and Effects due to H_2 / H_2O in the Atmosphere

Other known and estimated reactions

- Na_2O is already attacked from 600°C
- No free iron (Fe) in the refractories, total Fe_2O_3 content <1,5% (<1,0% at temp. >1150°C)
- CH_4 shows instability with H_2 in the combustion gas → $C_{(s)}$ stable
- Carbon instability→ CH_4 formation or oxidation
- Potential (re)hydration of sensitive components in the refractories
- Free and reactive Phosphates (e.g. $AlPO_4$) should be attacked
- >1300°C 99% of Alumina might be the goal (example POX-reactors for Syn-Gas production)

▸ Unknown conditions of significantly increased water vapor pressure with unknown influence on the alloy quality – get rid of the vapor!

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Wear Mechanisms and Effects due to H_2 / H_2O in the Atmosphere

C-Deposit / “CO Bursting”

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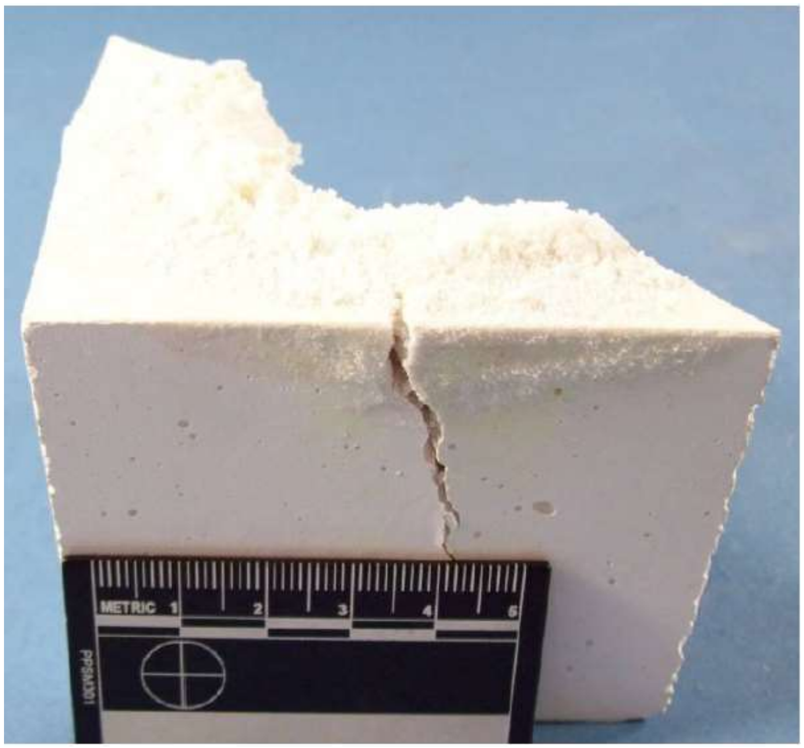
Wear Mechanisms and Effects due to H_2 / H_2O in the Atmosphere

Alkali Bursting e.g. Potassium-Oxide (K_2O) or Sodium-Oxide (Na_2O) rich vapor



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Possible Impacts on Refractories and Furnace Processes by H_2 / H_2O

1. Direct effects of H_2 and H_2O atmosphere on refractories along the entire process chain
    - Resistance to reduction / vapor?
    - Permeability / Thermal conductivity?
    - New and unknown reactions between conditions, steam and process impurities.
    - Unintended condensation/deposit of gaseous components, salts, alkalis or acids.
    - Higher flame temperature → burning alloy components from the open bath + TSR?

2. Indirect effect due to changed properties of Aluminum process chain and process plants
    - Higher gas Volume (pipes, burners, peripheral devices)
    - What happens with the huge amount of water vapor → Influence of Aluminum?
    - Burner and exhaust duct issues?
    - Gas recovery? Safety precautions?

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Effects on the Refractory Linings – Outlook

Wear lining

Furnace hearths, bath area and belly band

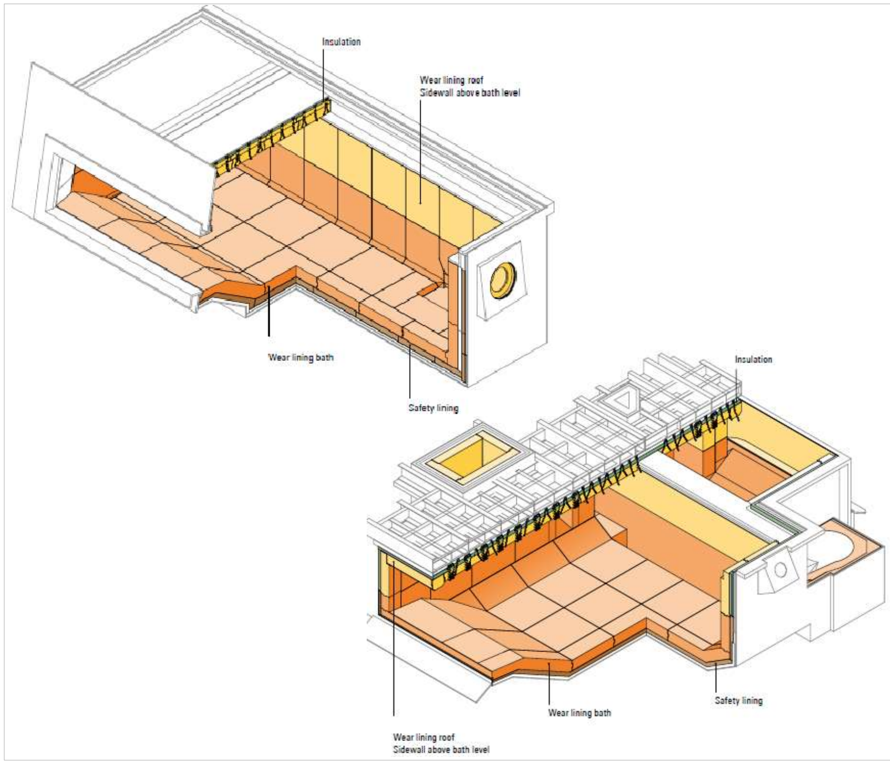
In case of normal conditions, dense Microsilica free products shall be save.

But: Unknown reactions on the reactive anti wetting agents and Phosphate-bonded materials

Upper furnace, burner blocks and roof

In case of higher temperatures, Silica/Mullite/SiC containing materials could reach their max. service temperature

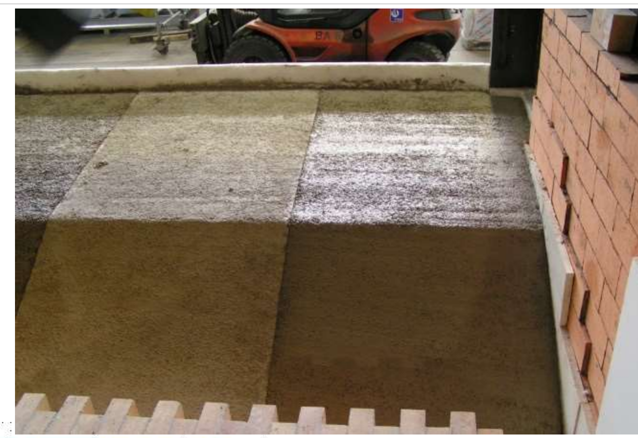
Anchoring with (other) suitable metal or ceramic anchors

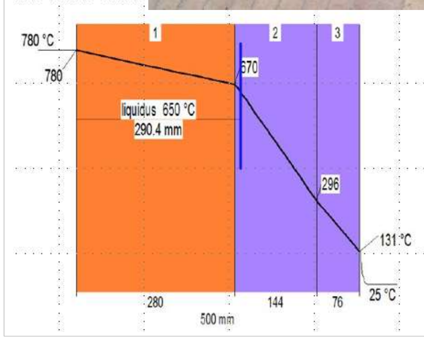


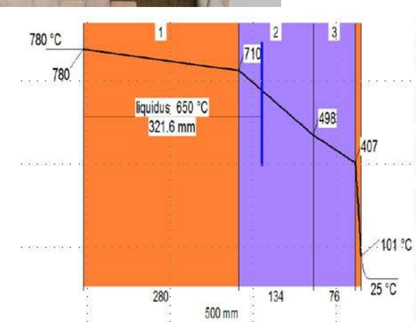
Effects on the Refractory Linings – Outlook

Safety lining and insulation – all areas

- Materials with higher porosity can absorb a lot of water vapor and dissolved impurities and thus change their properties.
- Unwanted condensation/deposit of salts, alkalis and harmful impurities in cold areas and close to the steel shell.
- Insulation with (microporous) board or brick according to the given heat transfer calculation/shell temperature should be vapor resistant.
- New conditions for the steel shell and anchors







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Conclusion & Outlook

- Many different potential mechanisms and reactions with it´s relations can cause premature failure of the refractory and cause process problems
- New processes bring new focus
- Understanding of potential wear mechanisms helps to take targeted countermeasures
- Generally suitable refractory materials for H_2 based transformation are available

▸ Talk to your reliable refractory producer

The knowledge of all blocks results in the optimal refractory product

Expect the best. REFRATECHNIK

Thank you for your interest.

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