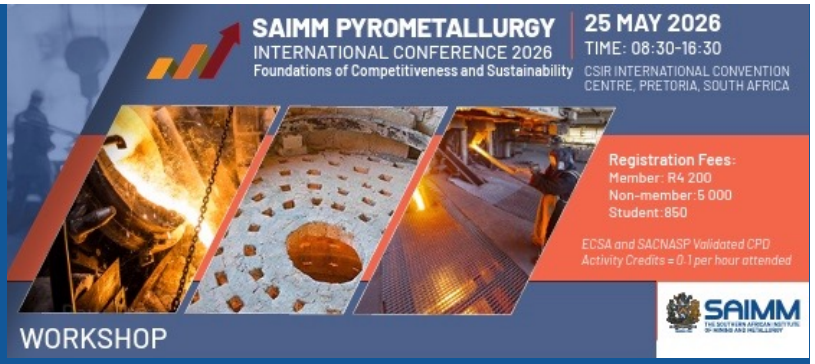
Types of Refractory Materials, their Properties and Use



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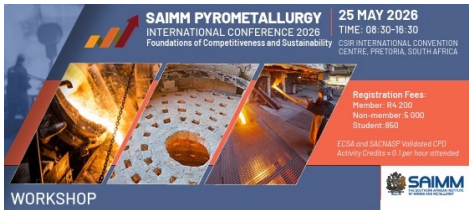
Centre for Pyrometallurgy, Dept of Materials Science & Metallurgical Engineering

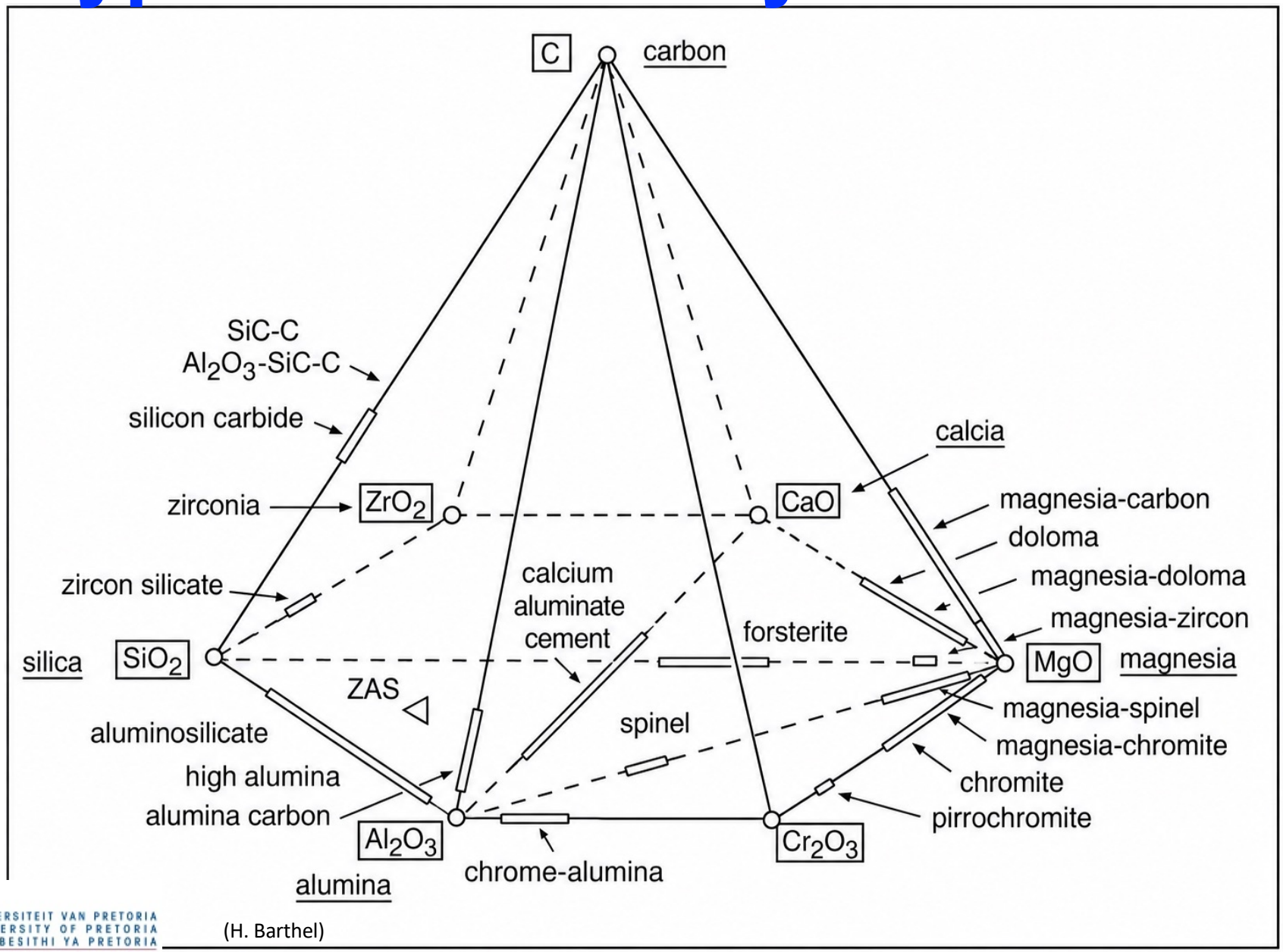
Outline



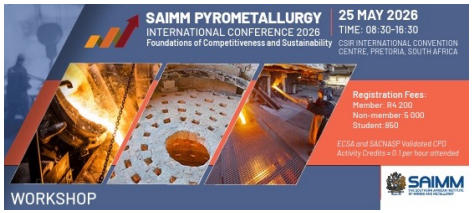
- **Refractory systems**:
  - Silica
  - Alumina-silicate & alumina & alumina-chromia (AZS)
  - Magnesia
  - Magnesia-chromite & magnesia-spinel
  - Doloma

- **Slag – refractory compatibility**
  - Freeze lining
  - Slag design (saturation)
  - Formation of interfacial layers
  - Structural spalling

Material pyramid defining different types of refractory materials



(H. Barthel)



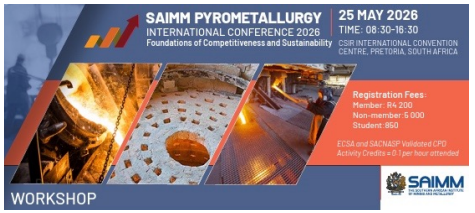
Classification based on composition

ISO classification:

NON-BASIC	BASIC	OXIDE-CARBON	SPECIAL MATERIALS
• silica	• magnesia	• MgO-C	• carbon & graphite
• alumina silicates	• forsterite	• Al_2O_3-C	• SiC
• high alumina	• doloma	• Al_2O_3-MgO-C	• $ZrSiO_4$
	• magnesia chromite	• doloma-C	• ZrO_2
	• magnesia spinel		

General brick definitions

Refractory	Limiting contents of major phase
Silica	$SiO_2 \geq 93\%$
Fireclay	$30\% \leq Al_2O_3 < 45\%$
High alumina	$Al_2O_3 \geq 56\%$
Magnesia	$MgO \geq 80\%$
Magnesia-chromite	$55\% \leq MgO < 80\%$
Chromite-magnesia	$25\% \leq MgO < 55\%$



Silica refractory materials

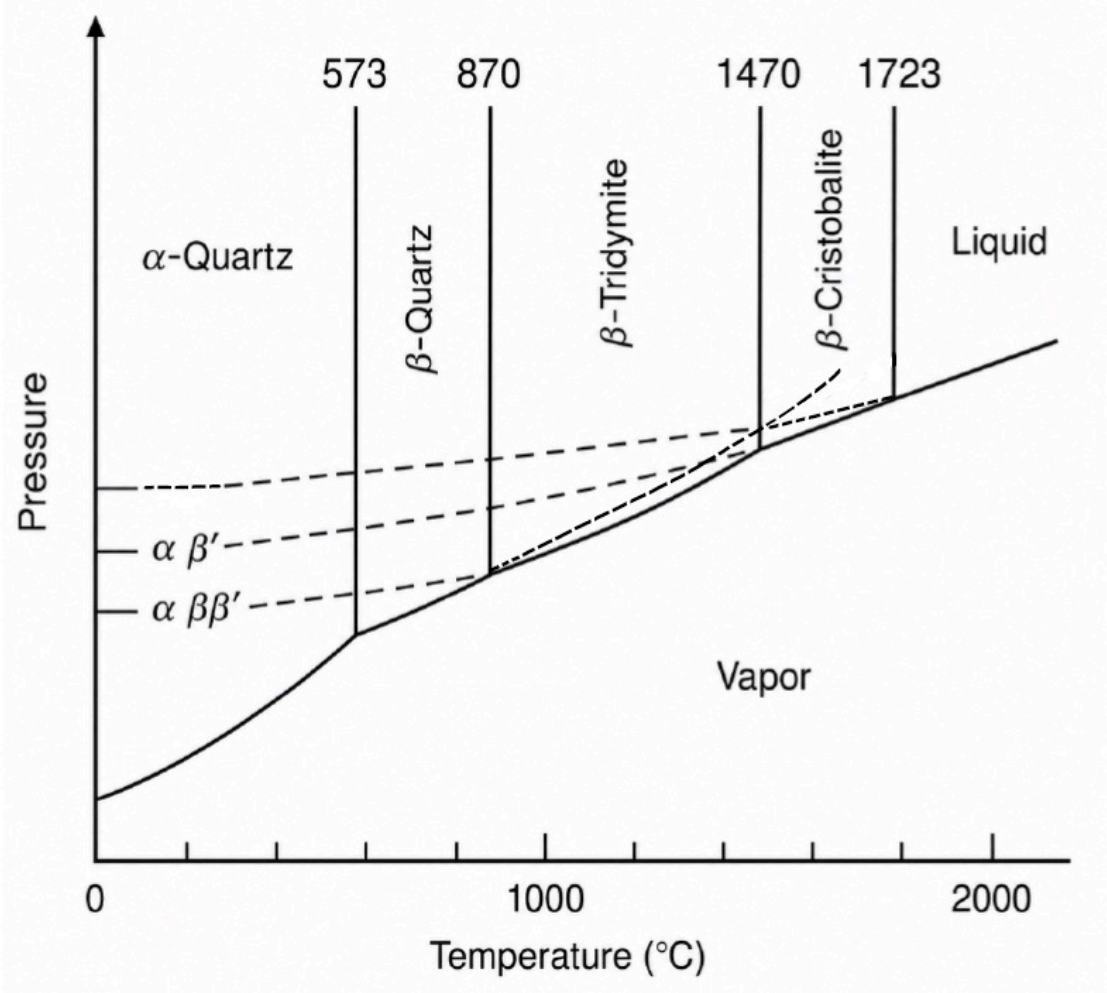
Silica refractories

- **Natural minerals:**
  - Quartzite
  - Diatomaceous earth (skeletons of single cell algae)

- **Artificially prepared:**
  - Fused silica

- Byproduct of Si and FeSi alloy production of :
  - Silica fume (diameter 0.1 – 1.0 μm)

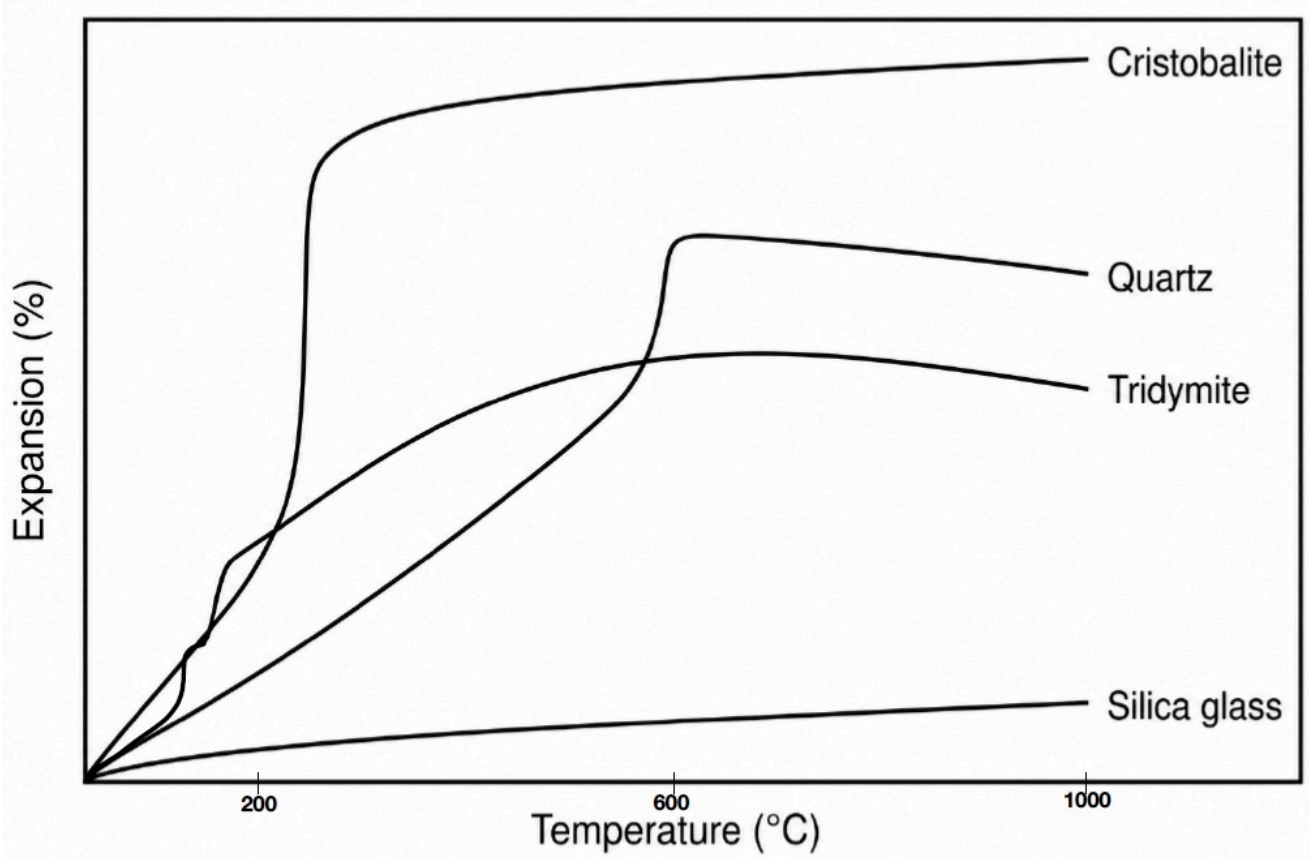
SiO_2: Polymorphic forms



- Quartz, cristobalite & tridymite
- Each polymorphic form has its own characteristic temperature range of stability and metastability
- Polymorphic transformations lead to changes in physical properties, e.g. density, crystalline structure, refractive index

Expansion when silica brick is fired

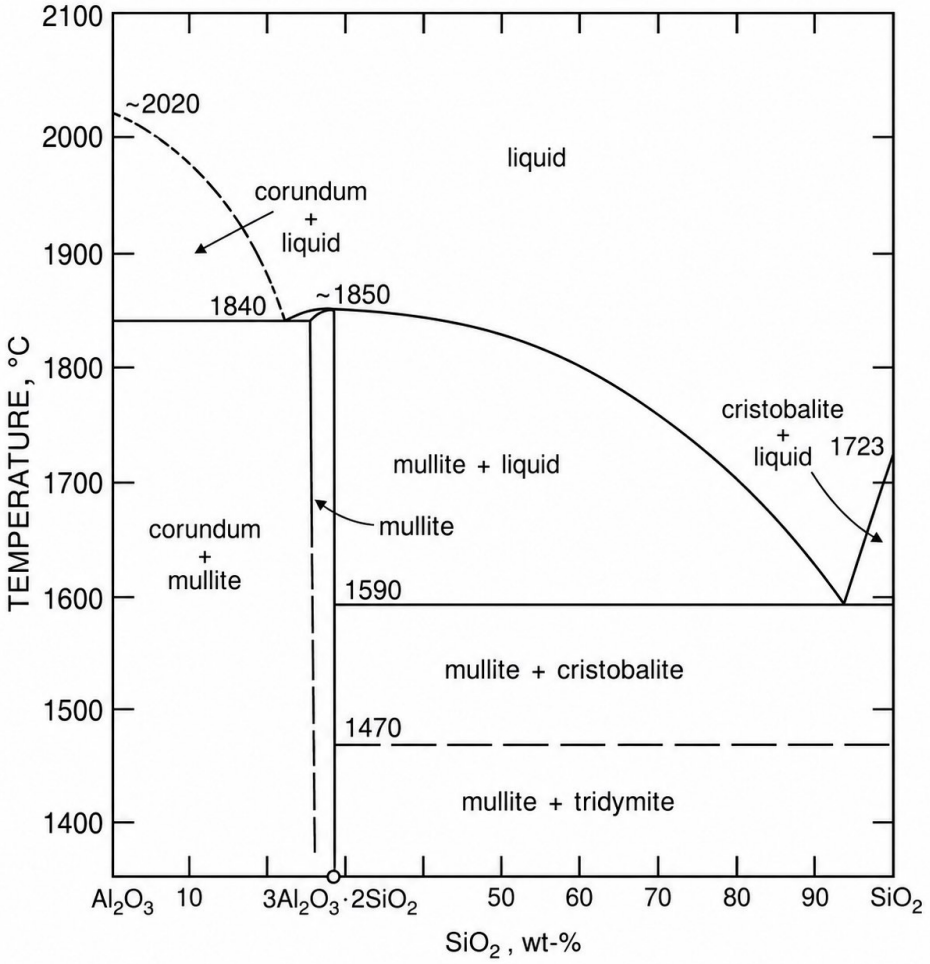
- Polymorphic transformations and volume changes with changes in temperature

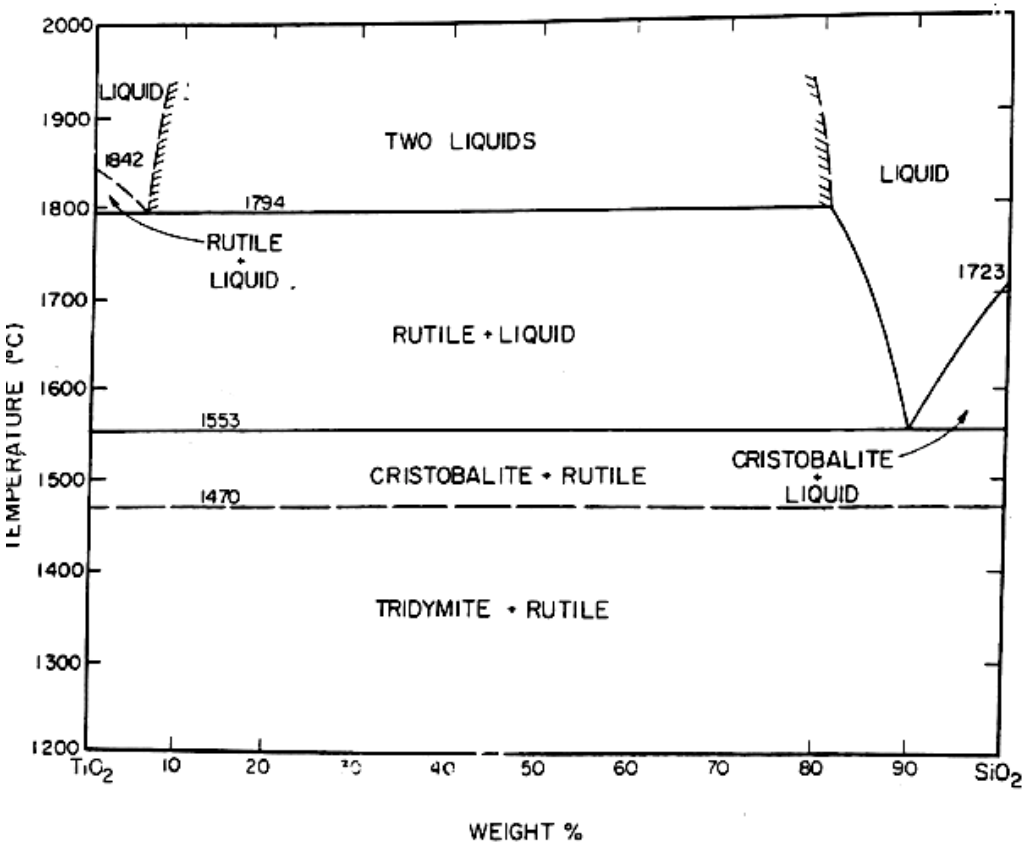


- 2% CaO is added as $Ca(OH)_2$ during firing
- CaO serves as a mineralizer (dissolving cristobalite and precipitating tridymite)

Silica bricks must be heated or cooled with extreme care in the temperature range where inversions take place

Effect of impurities on silica brick



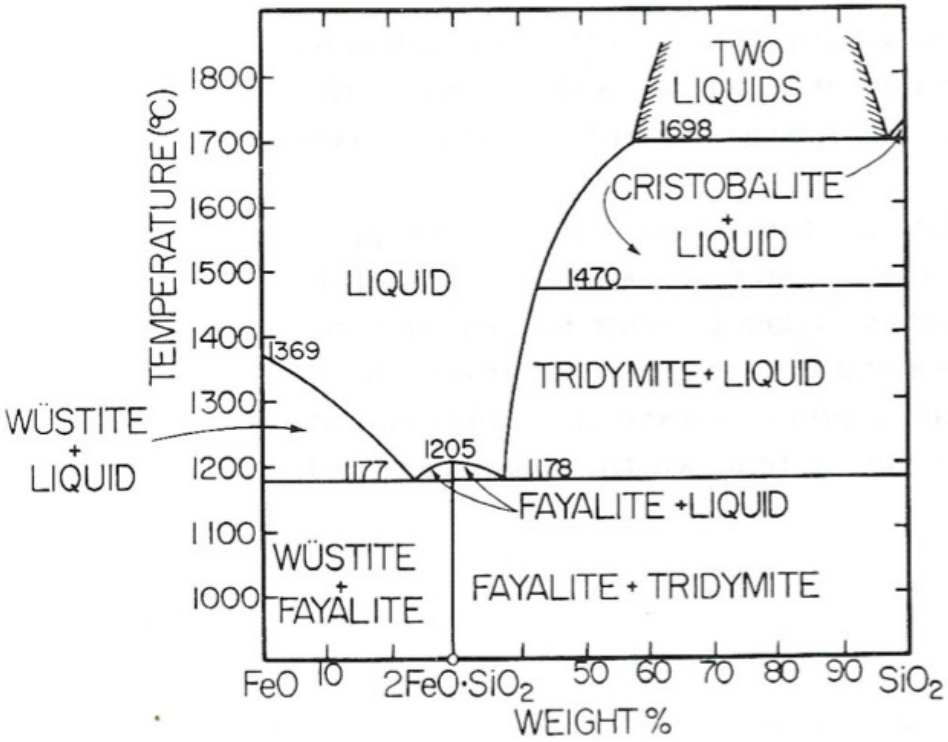


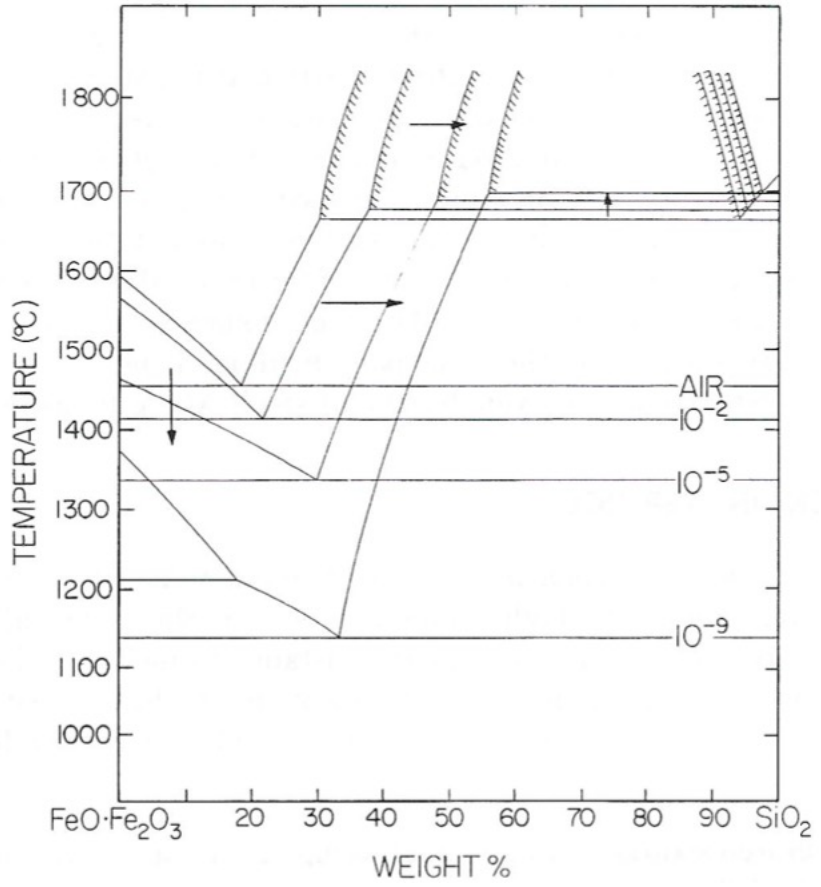
Al_2O_3 & TiO_2 severely corrode SiO_2 brick through formation of large amounts of liquid

Control over starting raw material and **impurities** are important criteria to avoid early failure in application temperature

Reaction of SiO_2 bricks with iron oxide

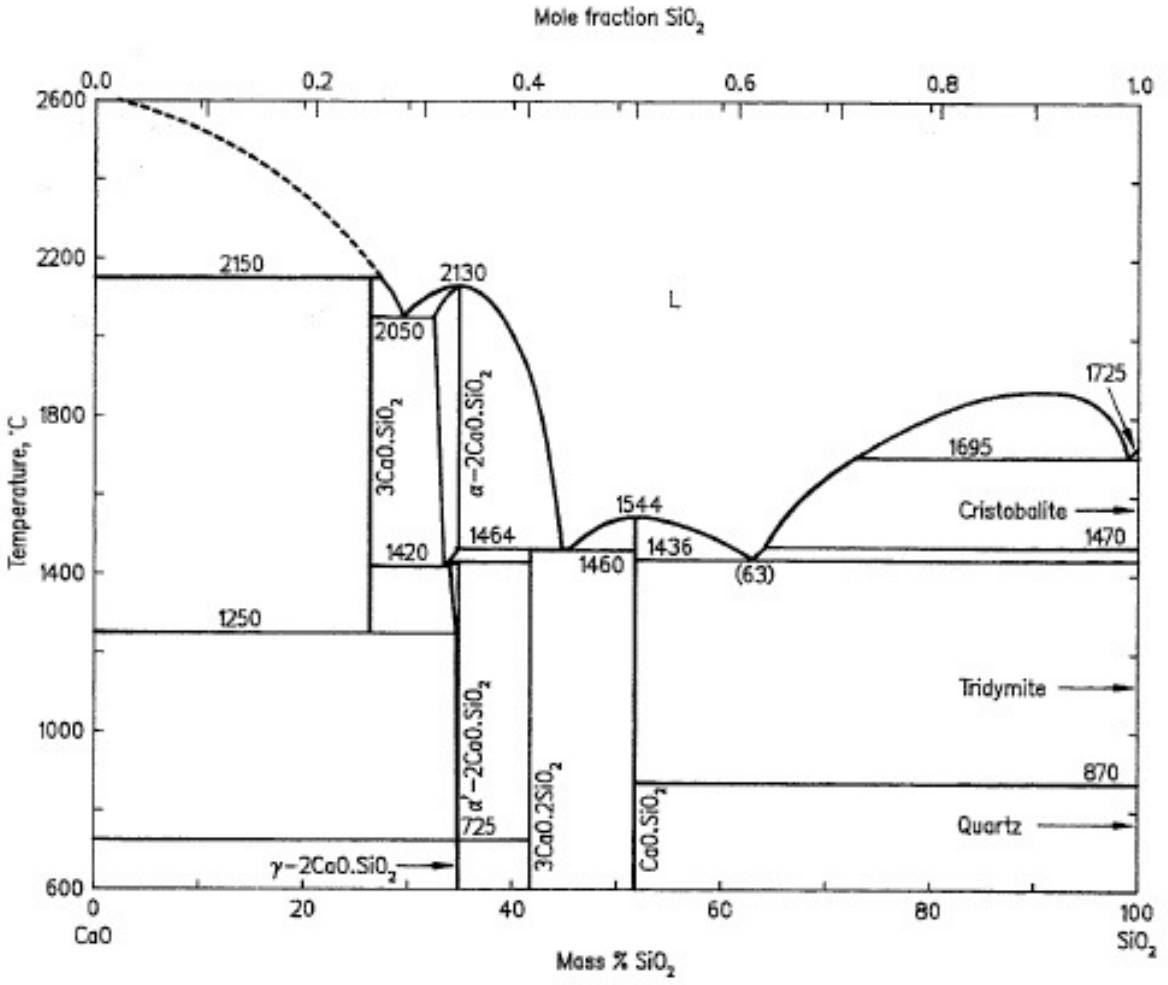
FeO – SiO_2
(in contact with Fe^0)





Iron oxides decrease solidus temperature of SiO_2 brick → more significant under lower oxygen potentials

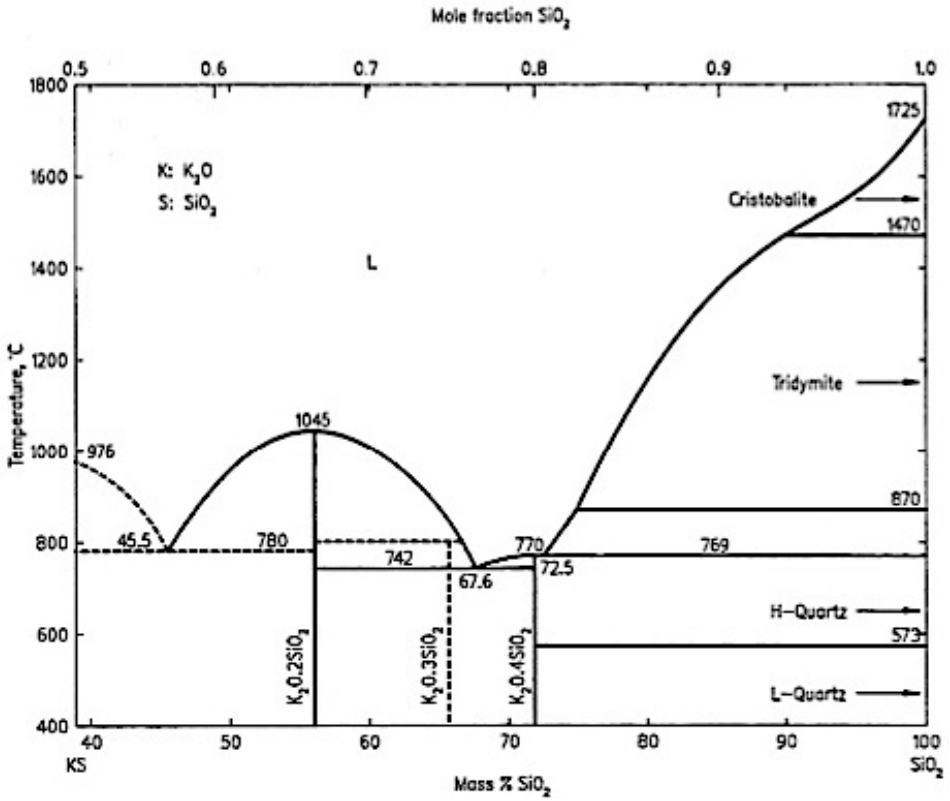
Reaction of SiO_2 with CaO



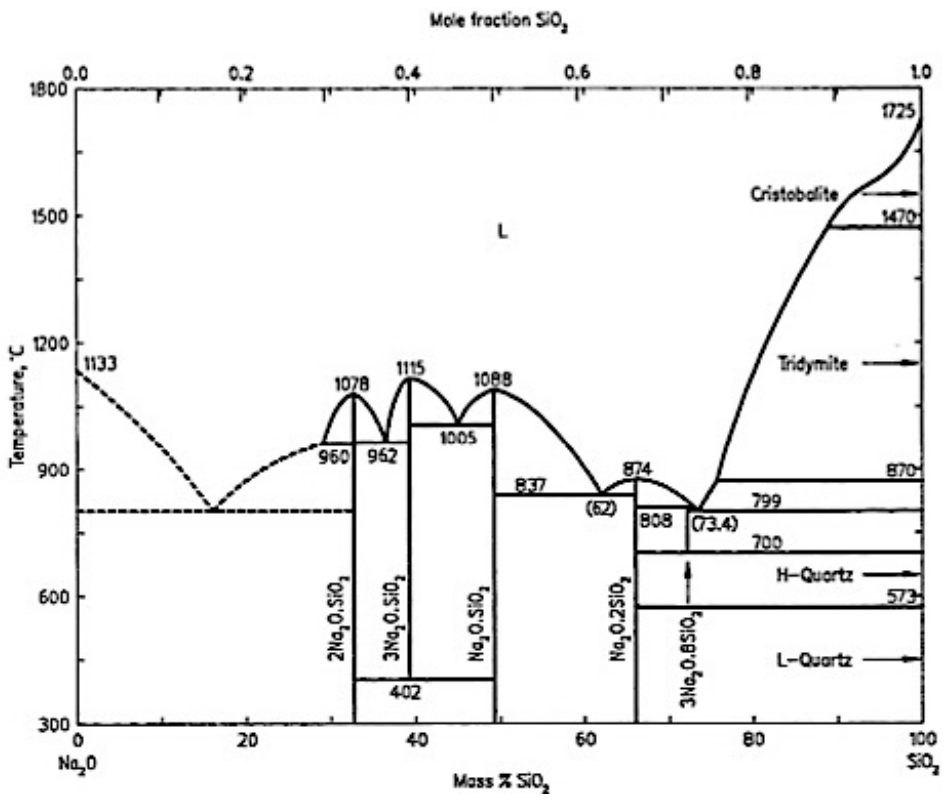
SiO_2 brick not severely corroded by CaO

Reaction of SiO_2 with alkali oxides

K_2O – SiO_2



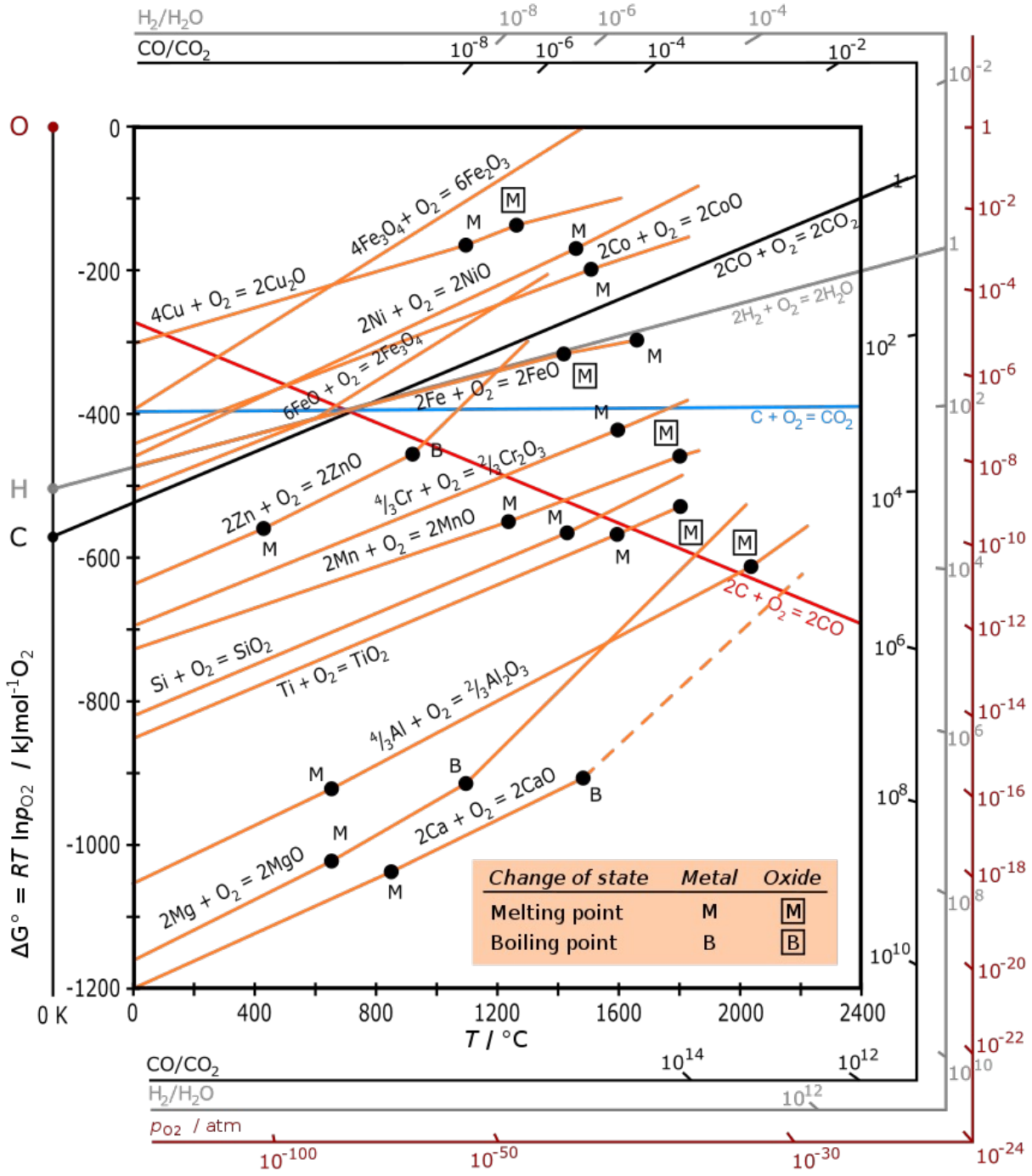
Na_2O – SiO_2



Alkali oxides severely corrode SiO_2 brick

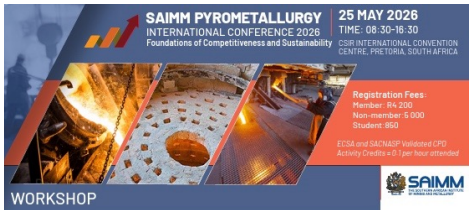
Ellingham diagram for metallurgical important oxides

Reduction of silica by e.g. $H_2(g)$, aluminium

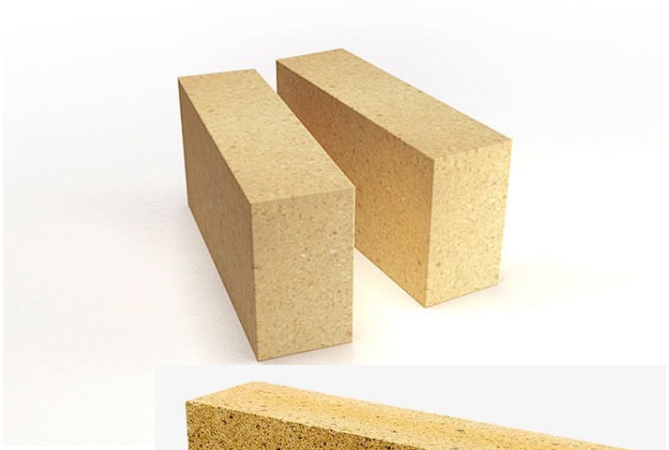


Properties of silica bricks

- Beneficial properties:
  - Ability to carry a load to within a few degrees of its melting point (~1723°C)
  - Long service lives under continuous high-temperature operation
  - Relatively high resistance to attack by iron oxide
- Limitations:
  - Crack when subjected frequent temperature fluctuations
  - Intense corrosion by vapours containing alkalis
  - Easily reducible (high up on Ellingham diagram)
- Applications:
  - Coke ovens, glass melting furnaces, hot blast stoves



Alumina-silicate and high-alumina refractory materials



Al_2O_3 – SiO_2 and high-alumina materials

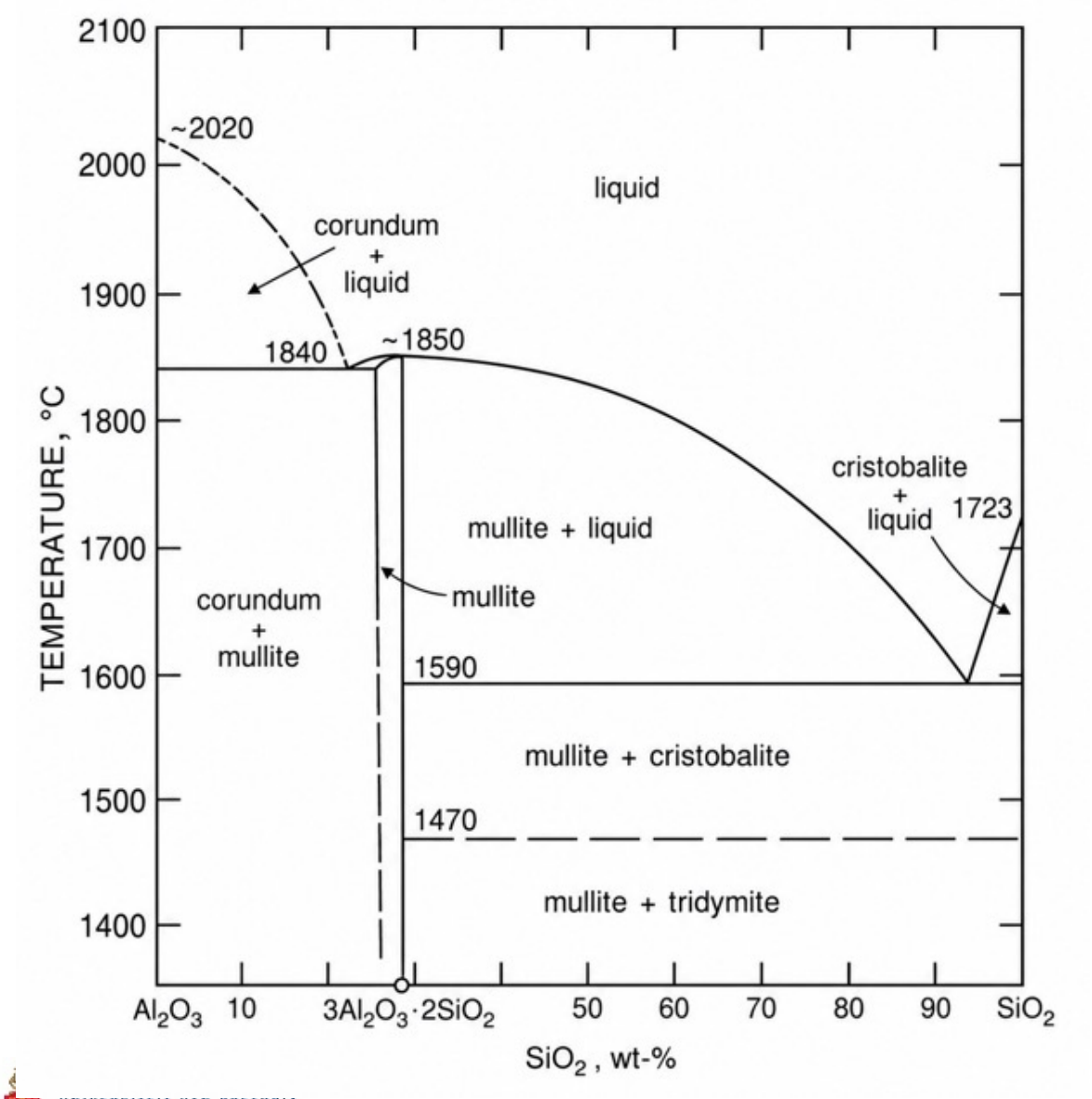
Range of materials:

- < 50% Al_2O_3: Kaolinite ($Al_2O_3.2SiO_2.2H_2O$)
- 50% Al_2O_3: Kaolinite ($Al_2O_3.2SiO_2.2H_2O$) & Gibbsite ($Al(OH)_3$)
- 60% Al_2O_3: Andalusite / kyanite / sillimanite ($Al_2O_3.SiO_2$)
- 70% Al_2O_3: Corundum & sillimanite (Al_2O_3 + $Al_2O_3.SiO_2$)
- 85% Al_2O_3: Bauxite (Gibbsite ($Al(OH)_3$) & boehmite (AlO(OH))
- 95% Al_2O_3: Corundum (Al_2O_3)

ALUMINA- SILICATE RAW MATERIALS

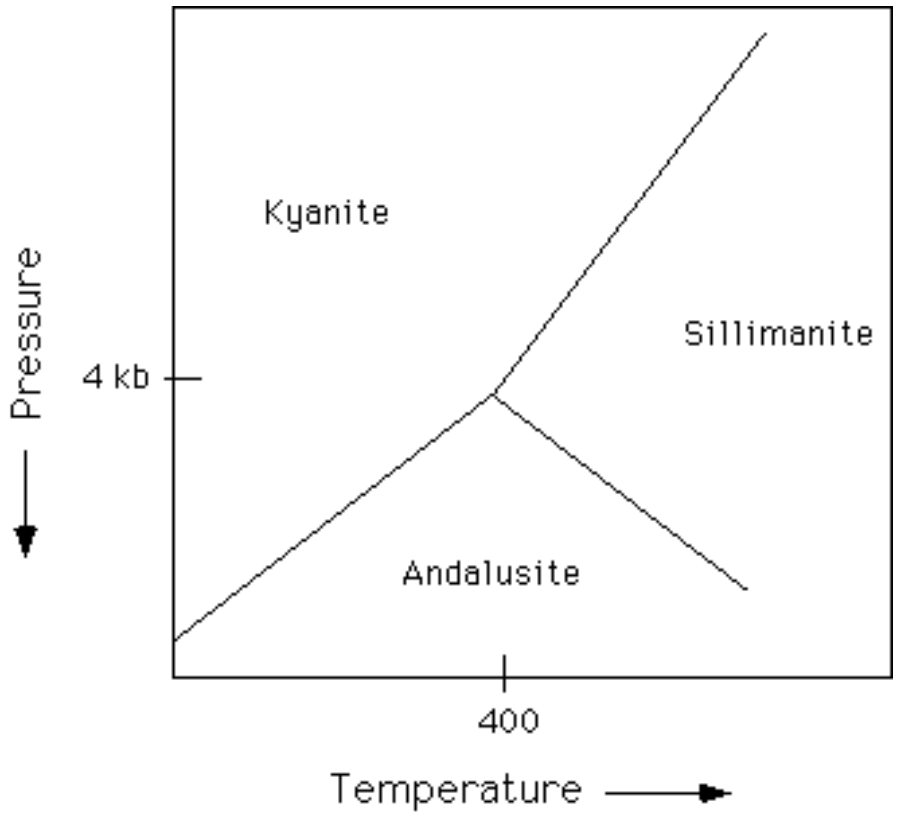
- **Alumina silicate hydrates:**
  - Clay minerals (kaolinite structure ($Al_2(Si_2O_5)(OH)_4$ / $Al_2O_3.2SiO_2.2H_2O$)
  - Decompose into
    - Mullite ($3Al_2O_3.2SiO_2$) and cristobalite when heated at 1100 – 1300ºC
    - Mullite ($3Al_2O_3.2SiO_2$) and glass when heated at 1300 – 1400ºC
- **Alumina silicate anhydrates:**
  - Polymorphic forms: sillimanite, andalusite and kyanite ($Al_2O_3.SiO_2$)
  - Decompose into mullite ($3Al_2O_3.2SiO_2$) and silica when heated
- **Secondary raw material:**
  - Grog (recycled bricks) / chamotte (fired clay)
  - Artificially synthesized mullite ($3Al_2O_3.2SiO_2$)
    - Sintered or fused

Alumina – Silicate Refractories: Al_2O_3 – SiO_2 system



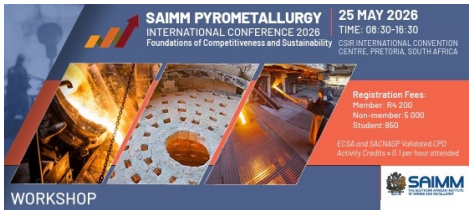
- SiO_2-rich materials such as fireclay materials: $T_{solidus}$ = 1590ºC
- High alumina-based materials: $T_{solidus}$ = 1840ºC

ALUMINA- SILICATE ANHYDRATES



- **Polymorphic forms of $Al_2O_3.SiO_2$:**
  - Kyanite
  - Sillimanite
  - Andalusite
- **Volume expansion** on decomposition to mullite and SiO_2

$$3Al_2O_3.SiO_2 \rightarrow 3Al_2O_3.2SiO_2 + SiO_2$$



Volume expansion of polymorphic forms

Mineral	Decomposition temperature (°C)	Volume expansion (%)
Andalusite	1350-1500	4.9
Sillimanite	1540-1625	5.6
Kyanite	1325-1410	18.8

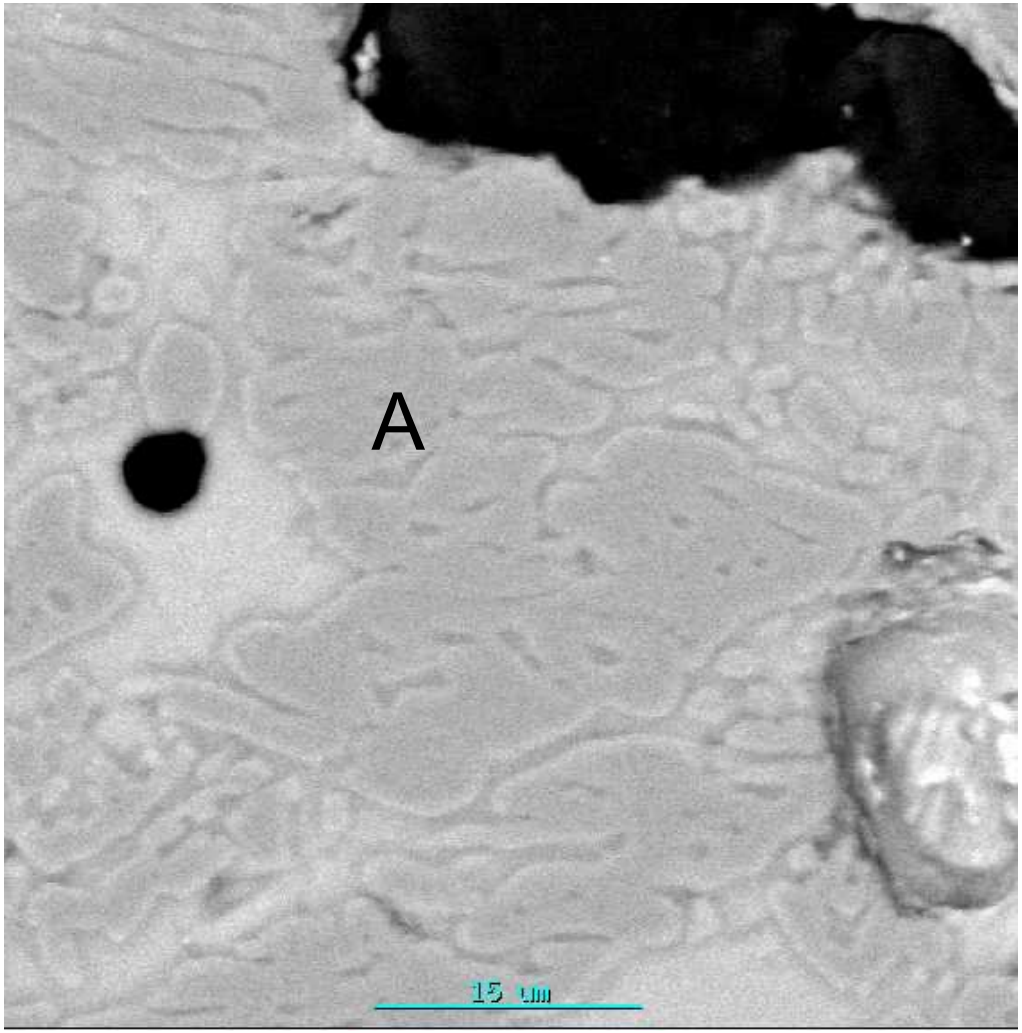
- Kyanite grains tend to crack on firing because of the large expansions, therefore need to be pre-calcined
- Andalusite or sillimanite can be added to shaped refractories in the unfired state

Schacht, CA. Refractories Handbook, 2004

Mullite

- **Stoichiometric mullite ($3Al_2O_3.2SiO_2$)**
  - 71.8 wt.% Al_2O_3
- **Commercially available mullite**
  - 71-76 wt.% Al_2O_3, 23-24 wt.% SiO_2,
    - Impurities: small quantities of TiO_2, Fe_2O_3, CaO and MgO
- **Mullite is a desirable phase in refractories**
  - Abrasion resistant
  - Slag resistant
  - Has a small coefficient of thermal expansion
  - Withstands high temperatures under load
- **Mullite content in chamotte differs from that contained in andalusite**
  - Less mullite and more glass/cristobalite in chamotte
  - Morphology of mullite has great impact on properties

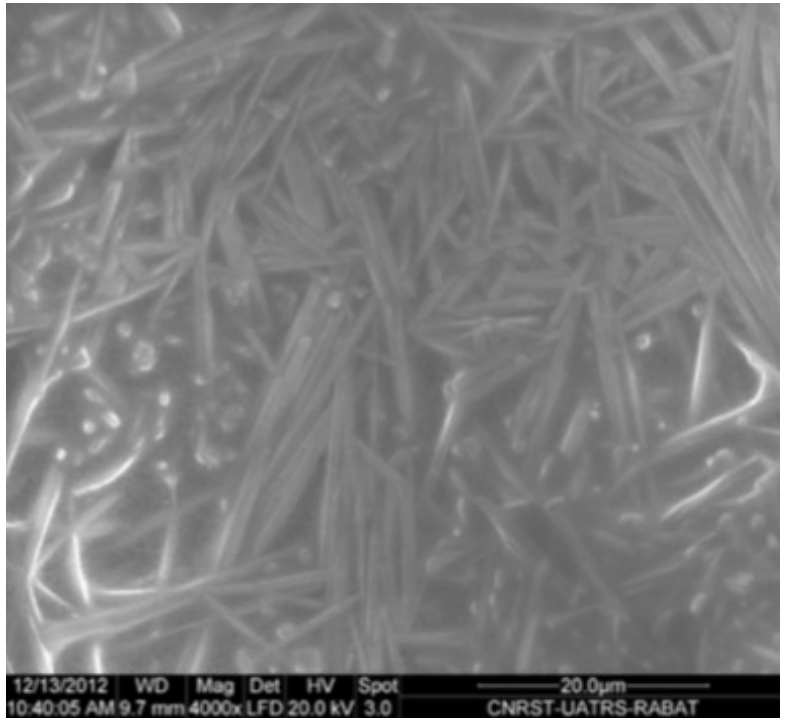
Fired Andalusite / mullitised andalusite

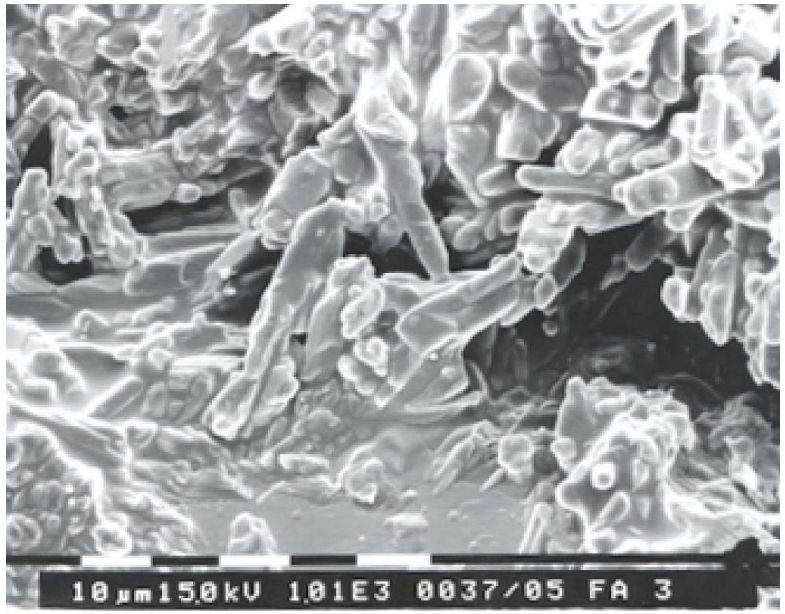


- Interlocking, blocky mullite crystals (A) form in andalusite during transformation and isolate interstitial silicate/glassy phase
- Mullitised andalusite has better thermal shock resistance compared with monocrystalline mullite

- Mullite is needle-like in chamotte, surrounded by silicate / glassy phase

Mullite bond

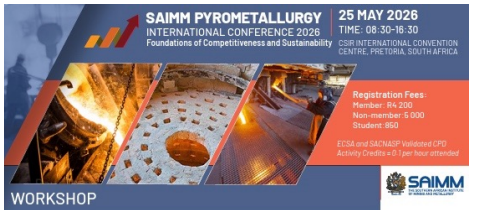




Needle-like crystals

- Established when SiO_2 and Al_2O_3 reacts in matrix, or between grains and matrix
- Good thermal stability
  - High hot-strength, remains stable up to 1850ºC
- Good thermal shock resistance
  - Low thermal expansion coefficient; moderate thermal conductivity helps it dissipate heat relatively well, minimizing temperature gradient within material
- Needle-like microstructure helps crack deflection and energy dissipation, which enhances resistance to thermal shock-induced cracking
- Excellent creep resistance
  - Resist deformation during thermal cycling

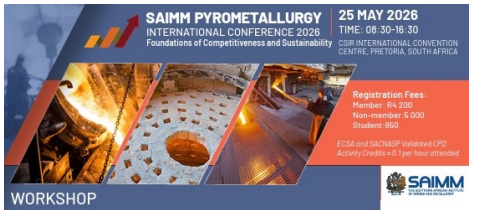
ALUMINA



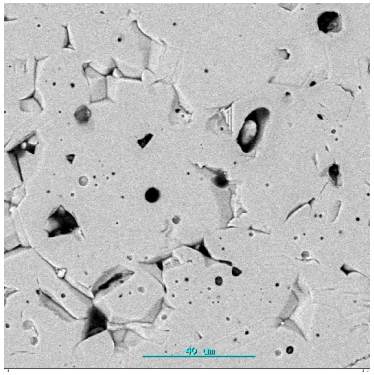
- **Natural raw materials:**
  - Bauxite (mixture of boehmite (monohydrate, $Al_2O_3.H_2O$) and gibbsite (trihydrate, $Al_2O_3.3H_2O$))
    - Iron oxide, aluminosilicates and titania as impurities
  - Calcined bauxite: Corundum as main component, mullite and a small amount of a glassy phase (due to impurities)

- **Artificially prepared**
  - $Al(OH)_3$ made by Bayer process, produce α-alumina (corundum) when fired
    - High purity (> 99% Al_2O_3)

ALUMINA

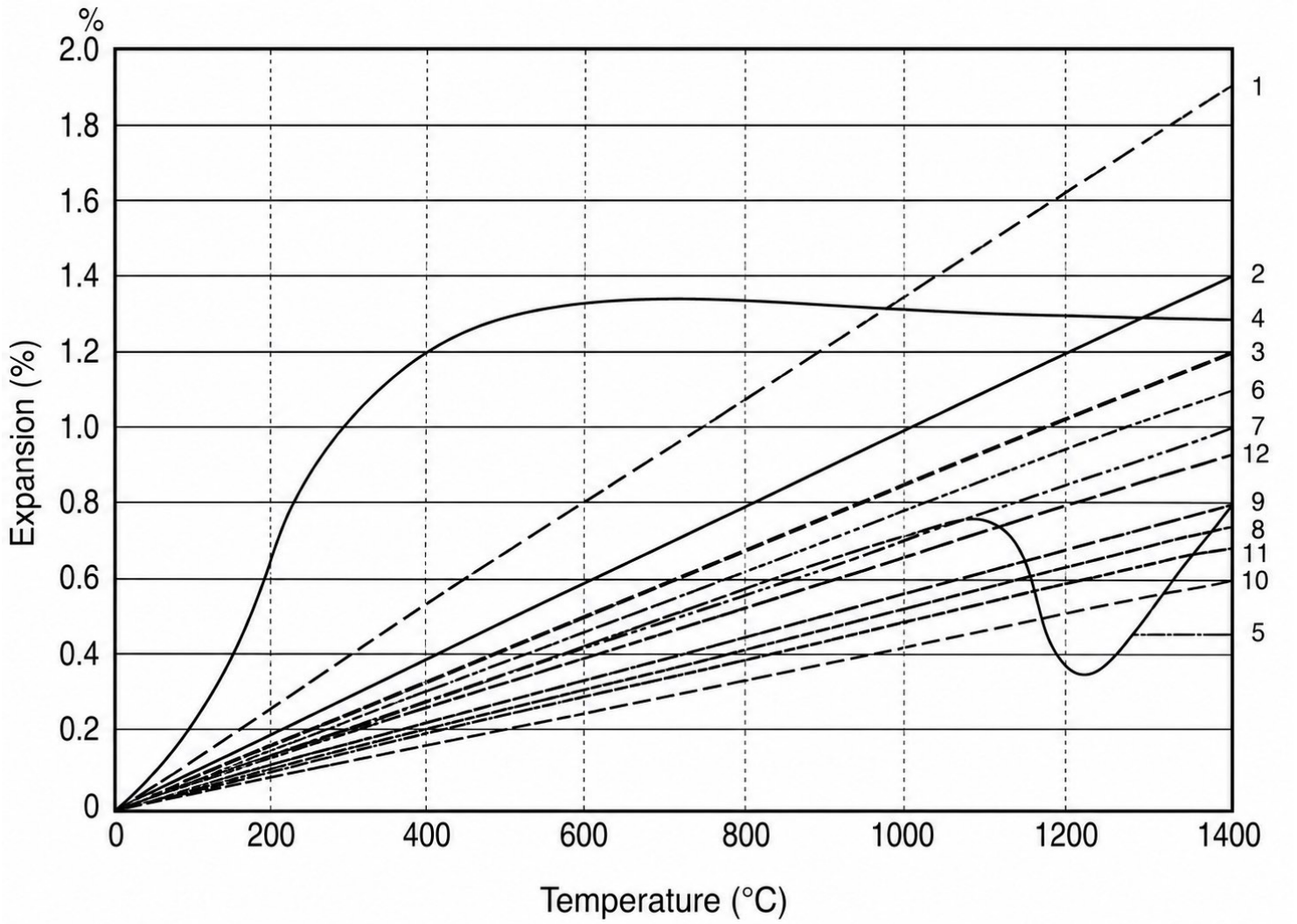


- **Sintered alumina:**
  - Fired in a kiln or furnace at temperatures typically between 1500 – 1900°C
  - Tabular alumina:
    - High purity calcined alumina produced in the Bayer process (can contain traces of Na_2O), fired 1800 – 1950ºC
    - Designed for excellent resistance to thermal shock
      - Pores are stress concentrators and attract cracks
      - Work of fracture increases and crack has difficulty to propagate through closed pore



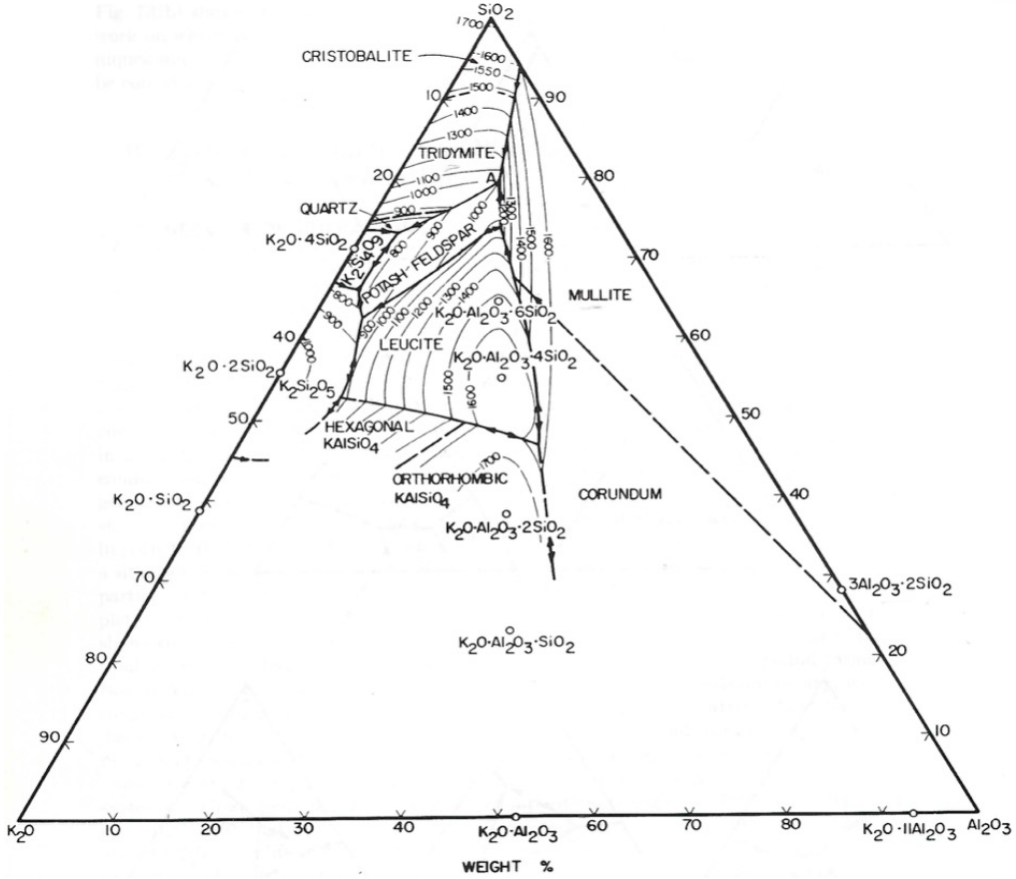
- **Fused alumina:**
  - Brown fused alumina (94-97% Al_2O_3): Produced from bauxite (titanium oxide as impurity)
  - White fused alumina (>99%): Produced from alumina produced in the Bayer process (Na_2O as impurity)

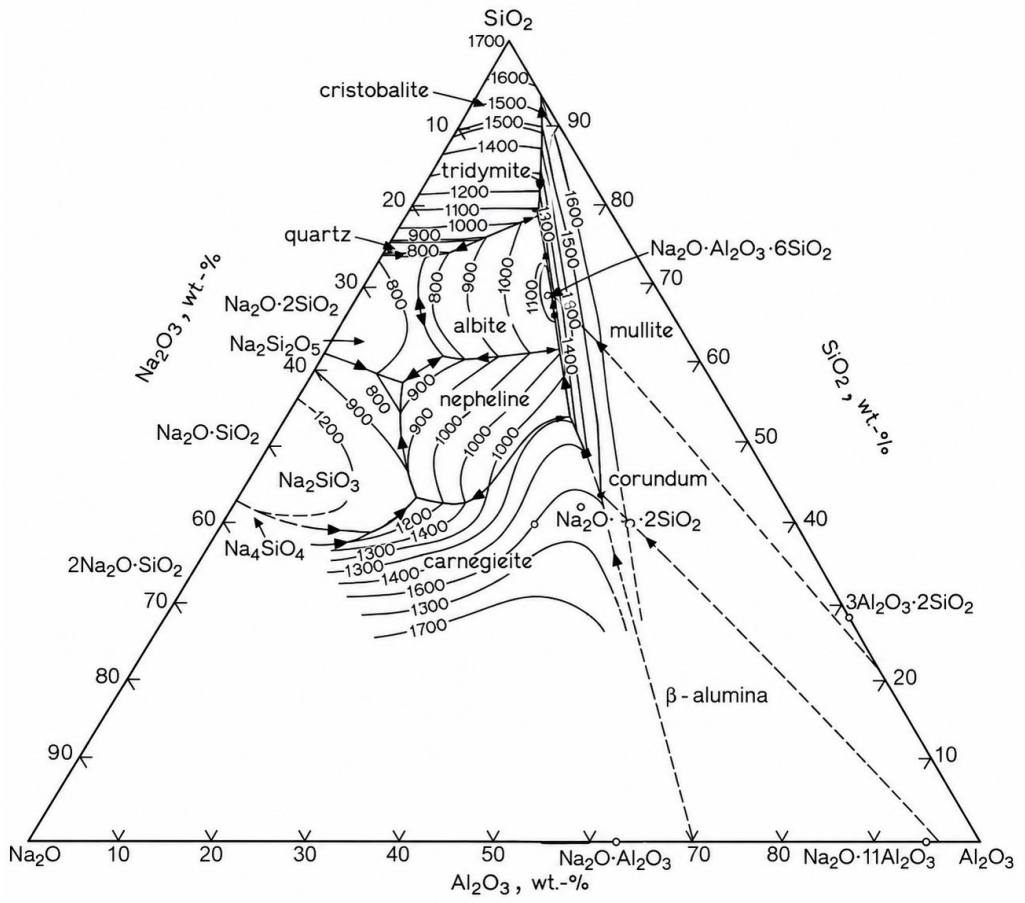
Reversible thermal expansion of fireclay and sillimanite



1 = magnesia;
2 = chromite-magnesia;
3= chromite;
4 = silica;
5 = zirconia;
6 = corundum 99%;
7 = corundum 90%;
8 = fireclay;
9 = sillimanite;
10 = zircon;
11 = silicon carbide

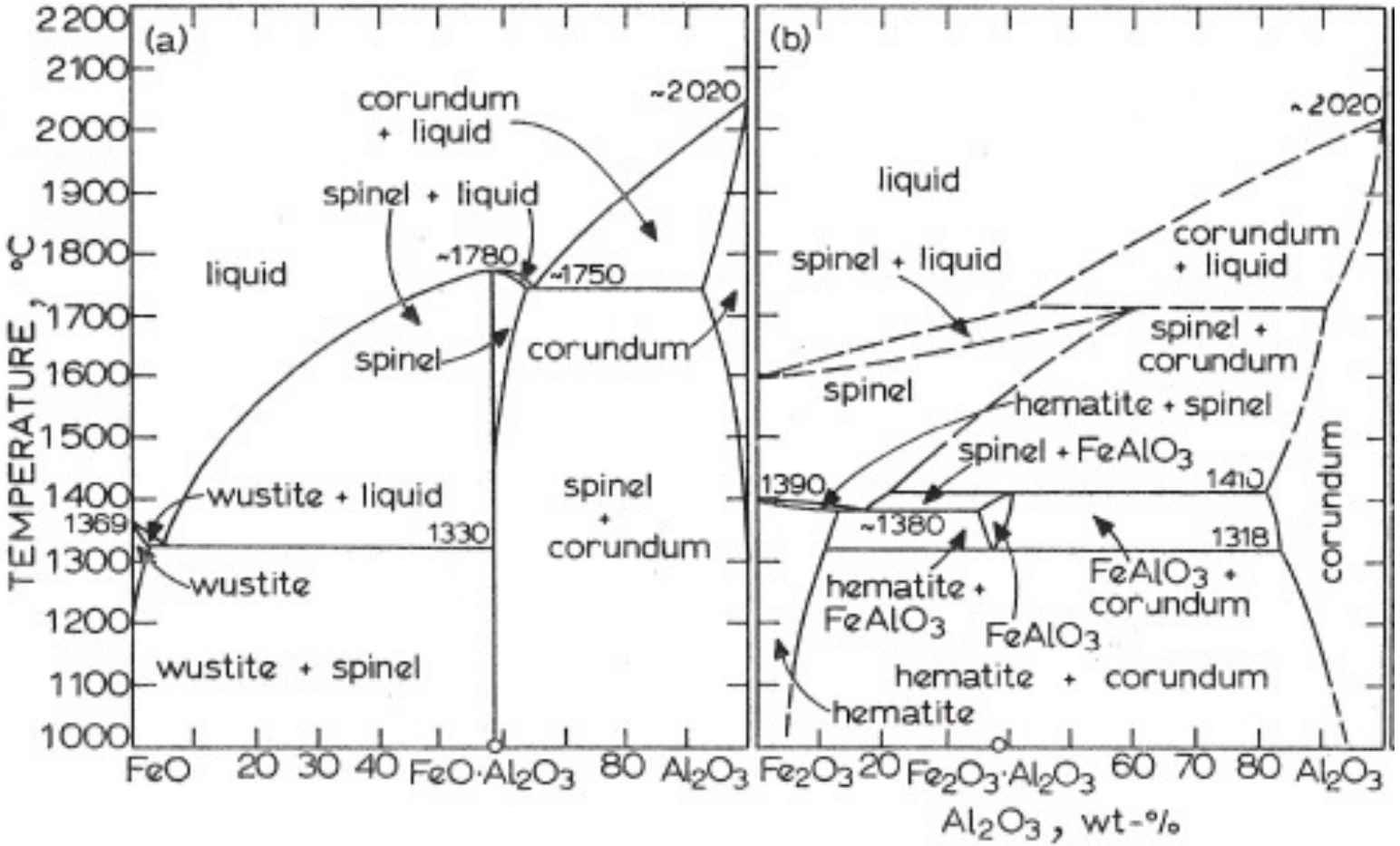
Fluxing of alumina silicate & alumina bricks by alkali oxides





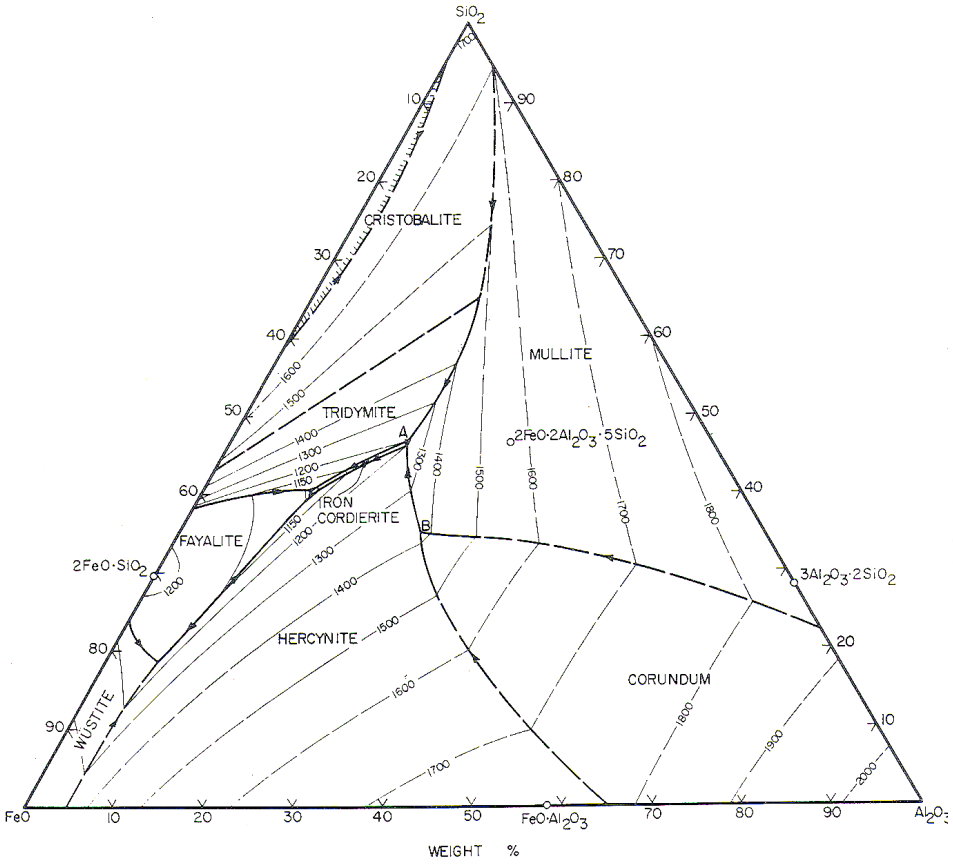
Al_2O_3 – iron oxide system

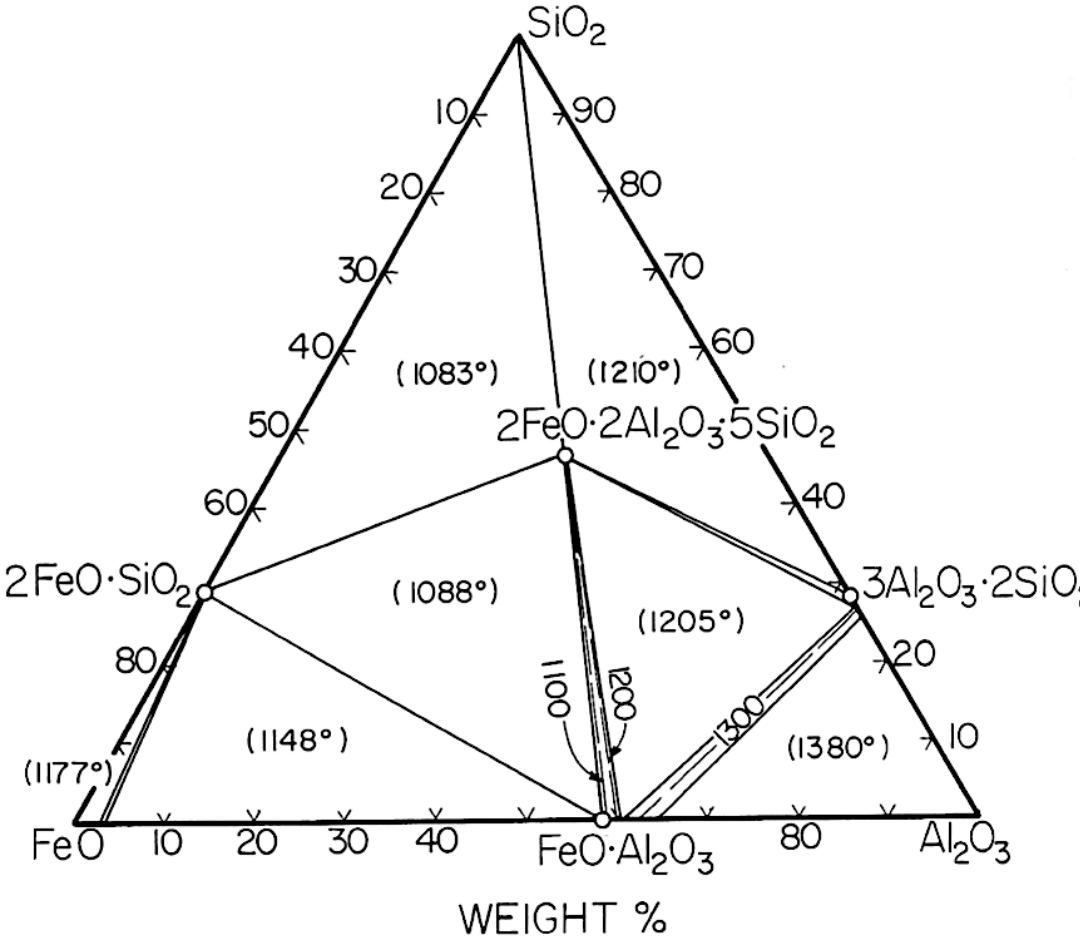
In contact with Fe^0 **In air**



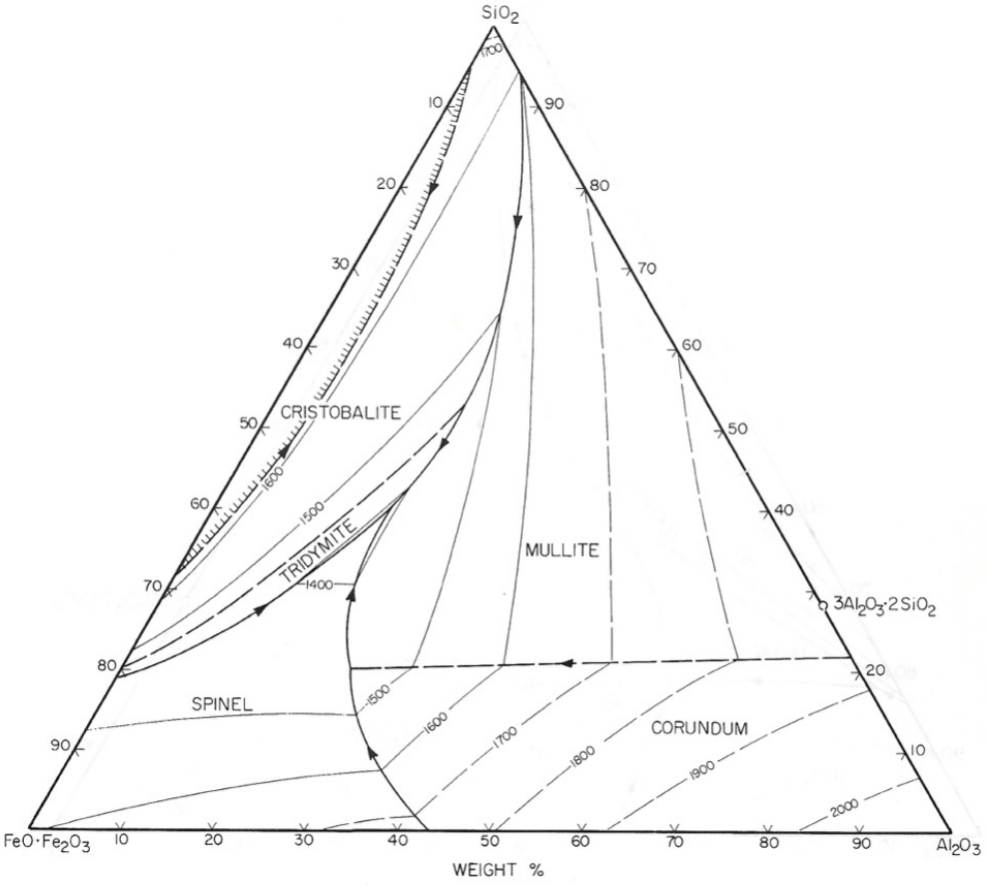
Al_2O_3-based materials have good corrosion resistance with respect to iron oxides ➞ more corrosion resistant under oxidizing conditions

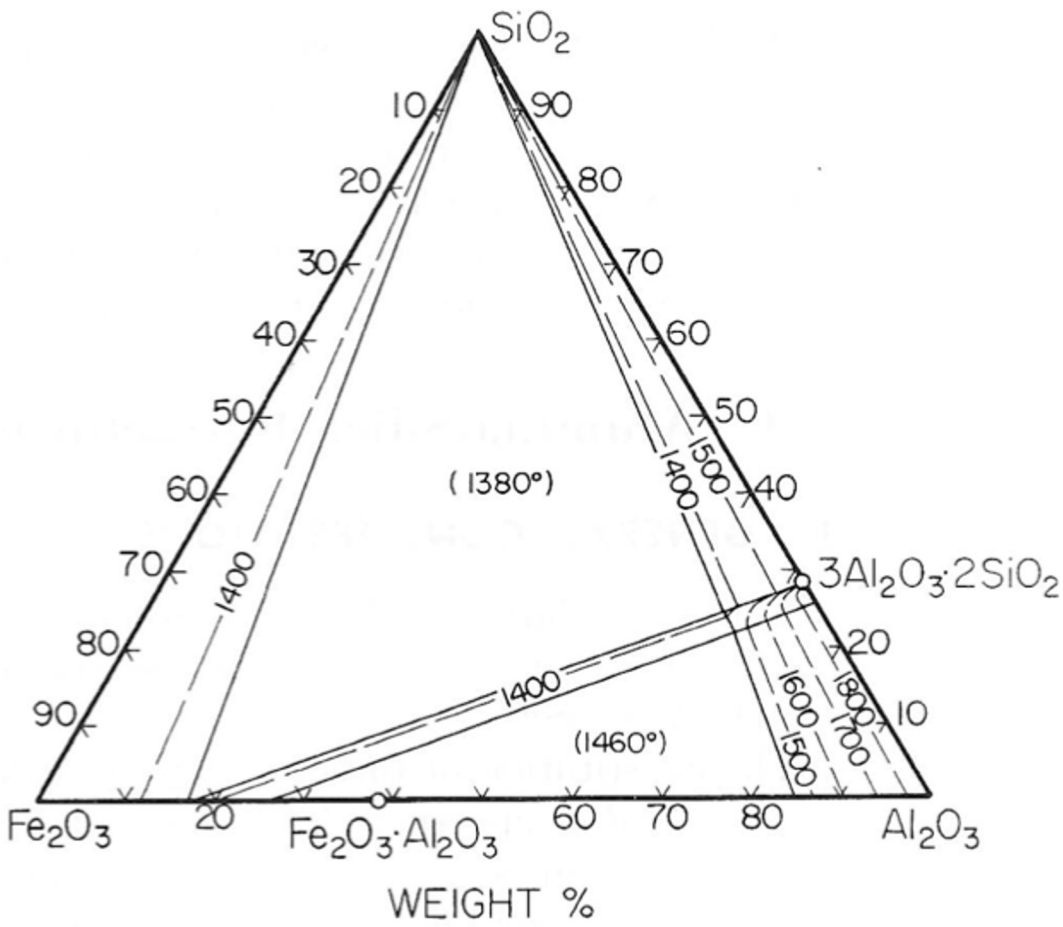
Fluxing of alumina silicate & alumina bricks by FeO
(reducing conditions)



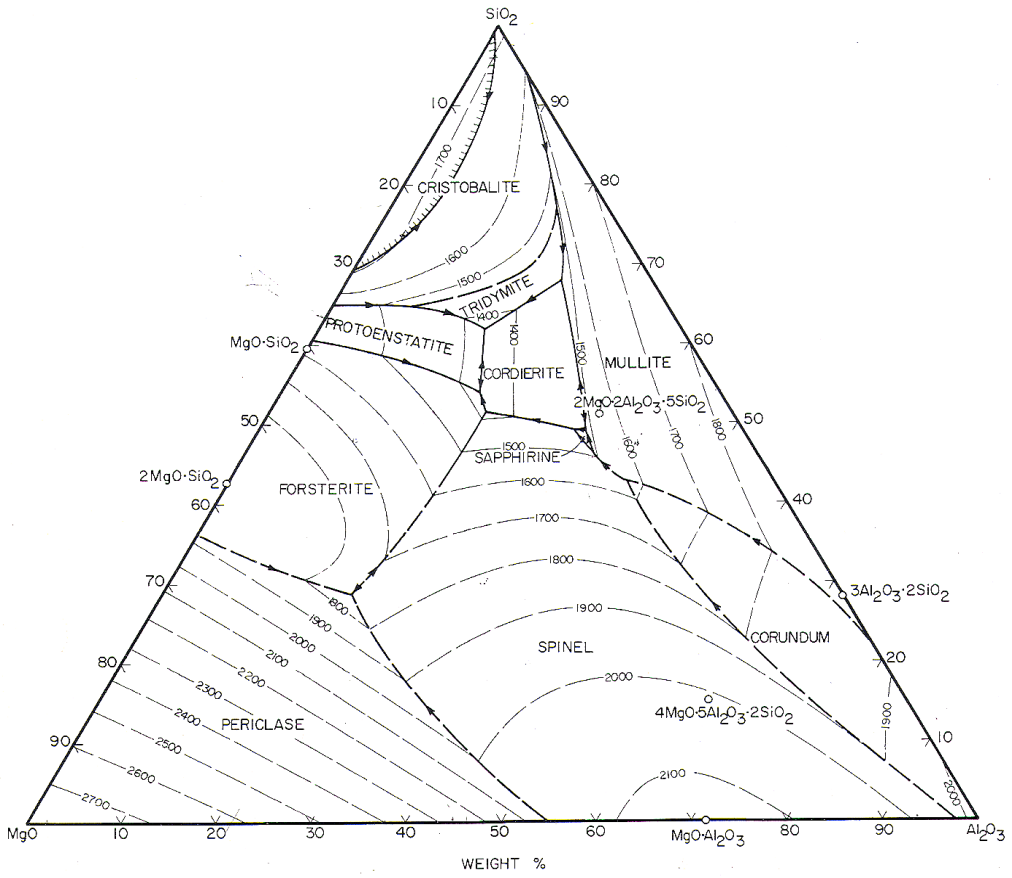


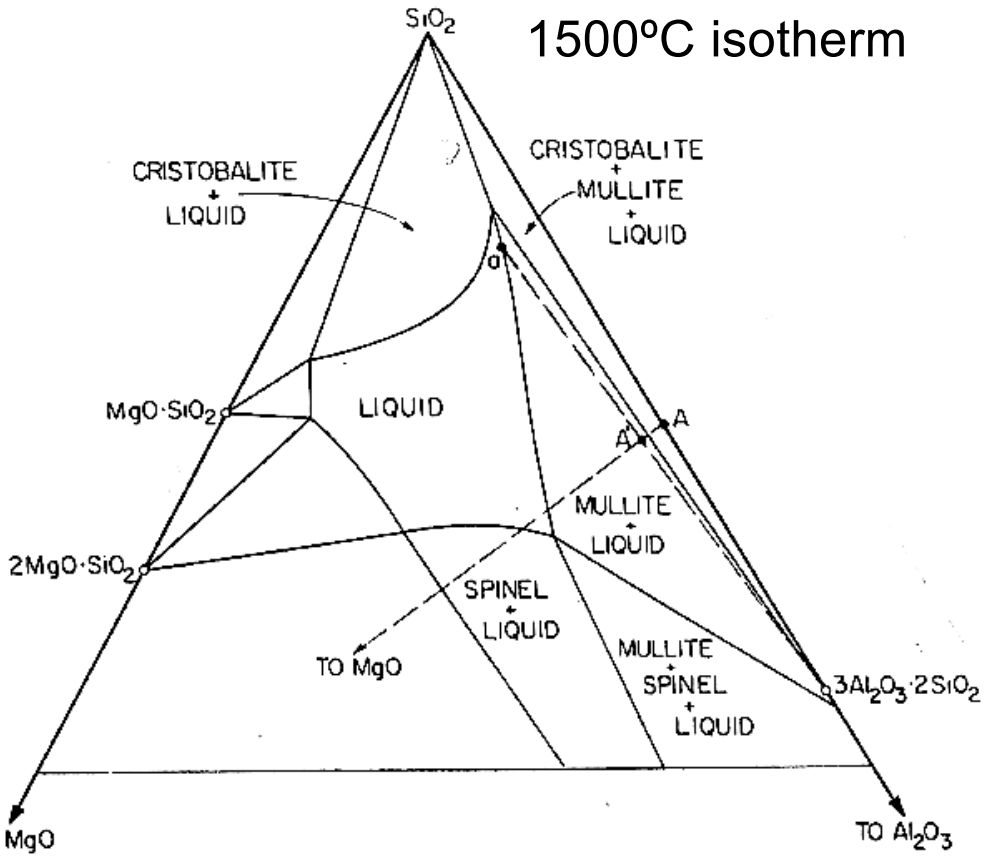
Fluxing of alumina silicate & alumina bricks by iron oxides (oxidising conditions)





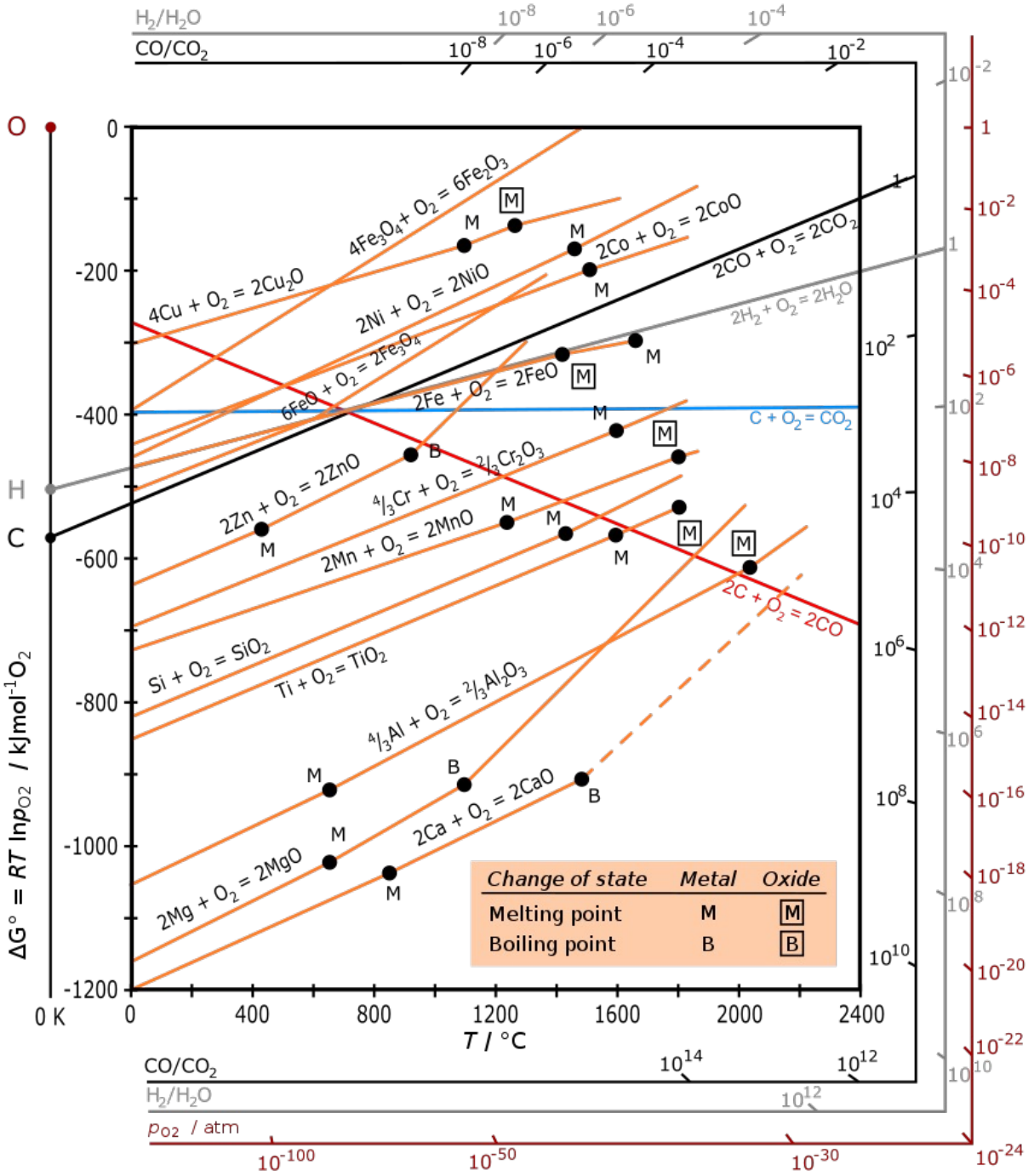
Compatibility of alumina-silicate brick with a typical basic brick (MgO)





Ellingham diagram for metallurgical important oxides

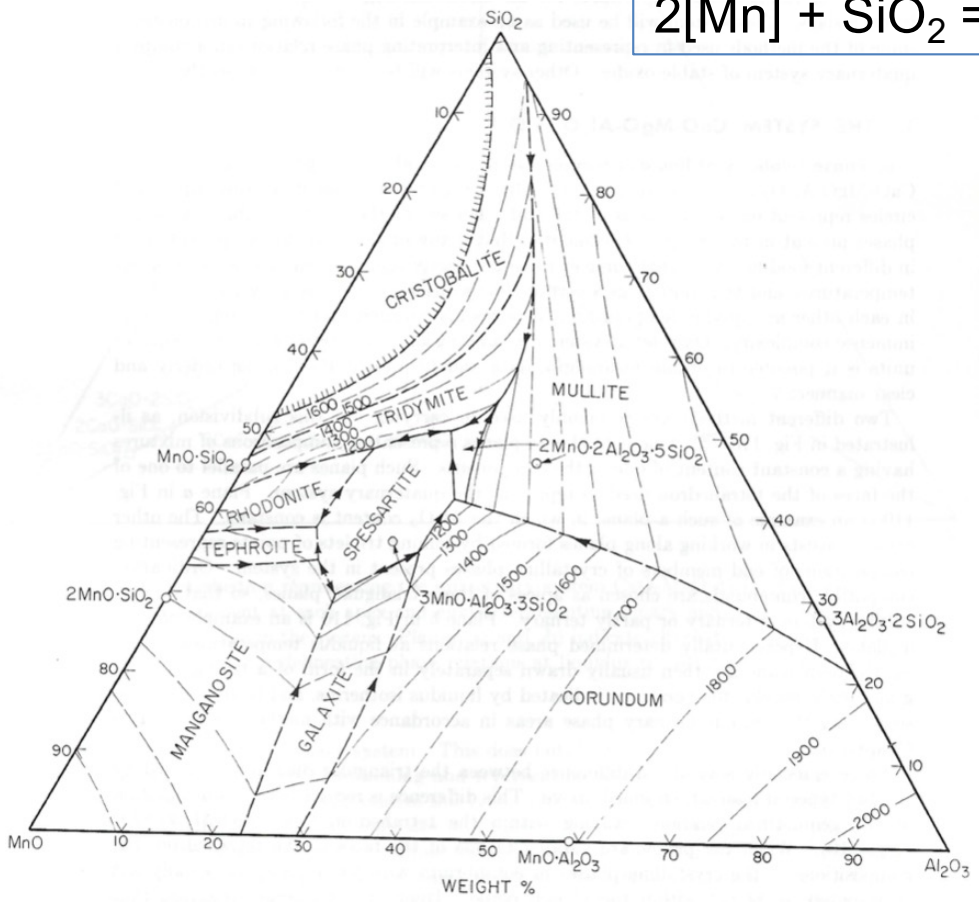
Reduction of silica in alumina-silicate refractories by Fe-Mn alloys

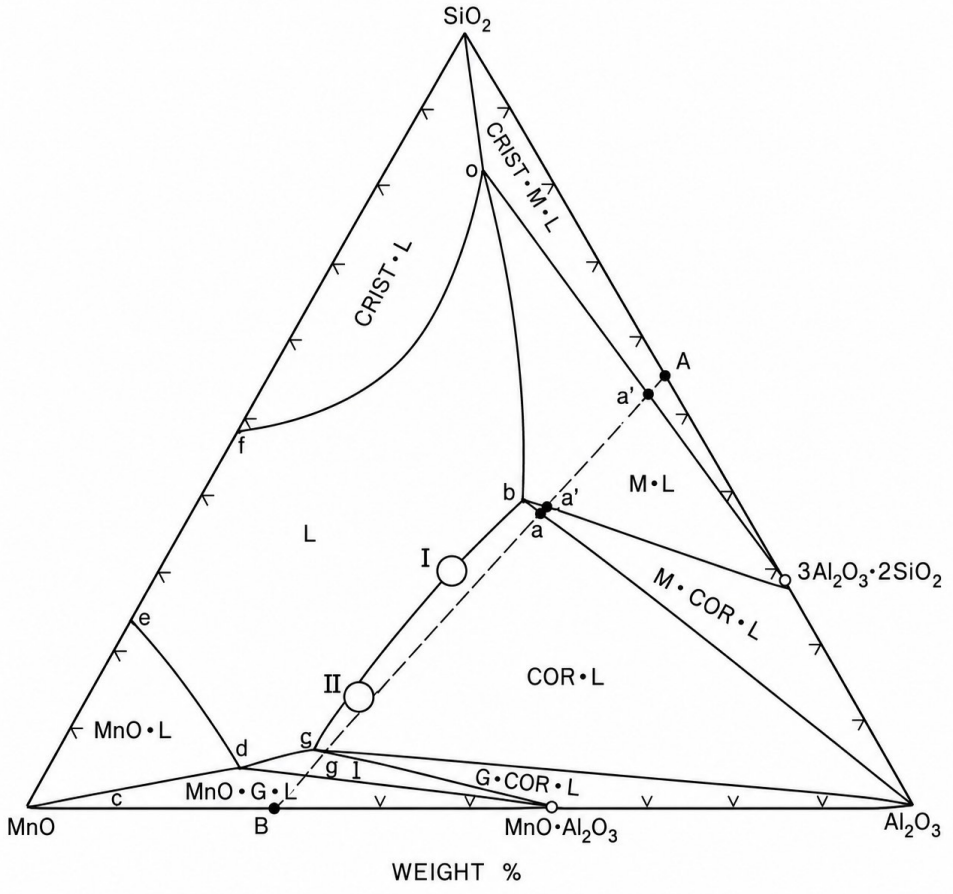


Reaction between alumina-silicate refractories with Fe-Mn alloys

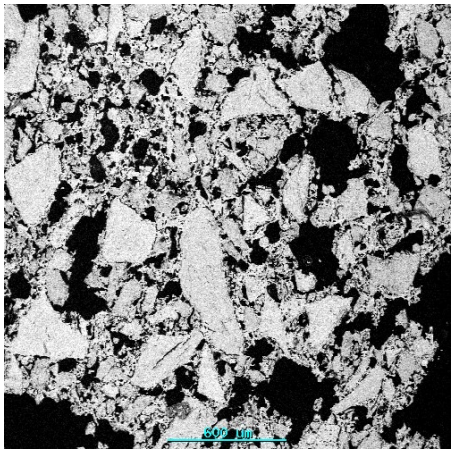
1500ºC isotherm

$2[Mn] + SiO_2 = [Si] + 2MnO$





Properties of fireclay bricks



- Beneficial properties:
  - Low thermal conductivity (insulating)
  - Low thermal expansion coefficient (good thermal shock resistance)
  - Low cost
- Limitations:
  - Not suitable for use at very high-temperatures
  - SiO_2 in brick is easily reducible (high on Ellingham diagram)
  - Severely attacked by alkalis
- Applications:
  - General-purpose, wide application range
    - E.g. Insulating and backup linings glass furnaces, ladles, aluminium industry
    - Burner blocks, combustion chambers, cooler areas in rotary kilns, pizza ovens

Properties of andalusite-based bricks

- Beneficial properties:
  - Resulting from the mullitisation of andalusite:
    - Good hot strength
    - Good dimensional stability
    - Enhance thermal shock resistance
    - Good spalling resistance
- Limitations:
  - Limited corrosion resistance to basic slags
  - Lower corrosion resistance than high-alumina refractories
  - Limited maximum service temperature
  - Unsuitable in alkali-containing environments
- Applications:
  - Widely used: Steel ladles, tundishes, blast furnace troughs, reheating furnaces, rotary kilns, glass furnaces, kiln furniture.

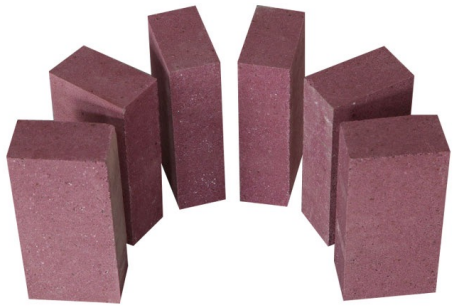
Properties of alumina refractories

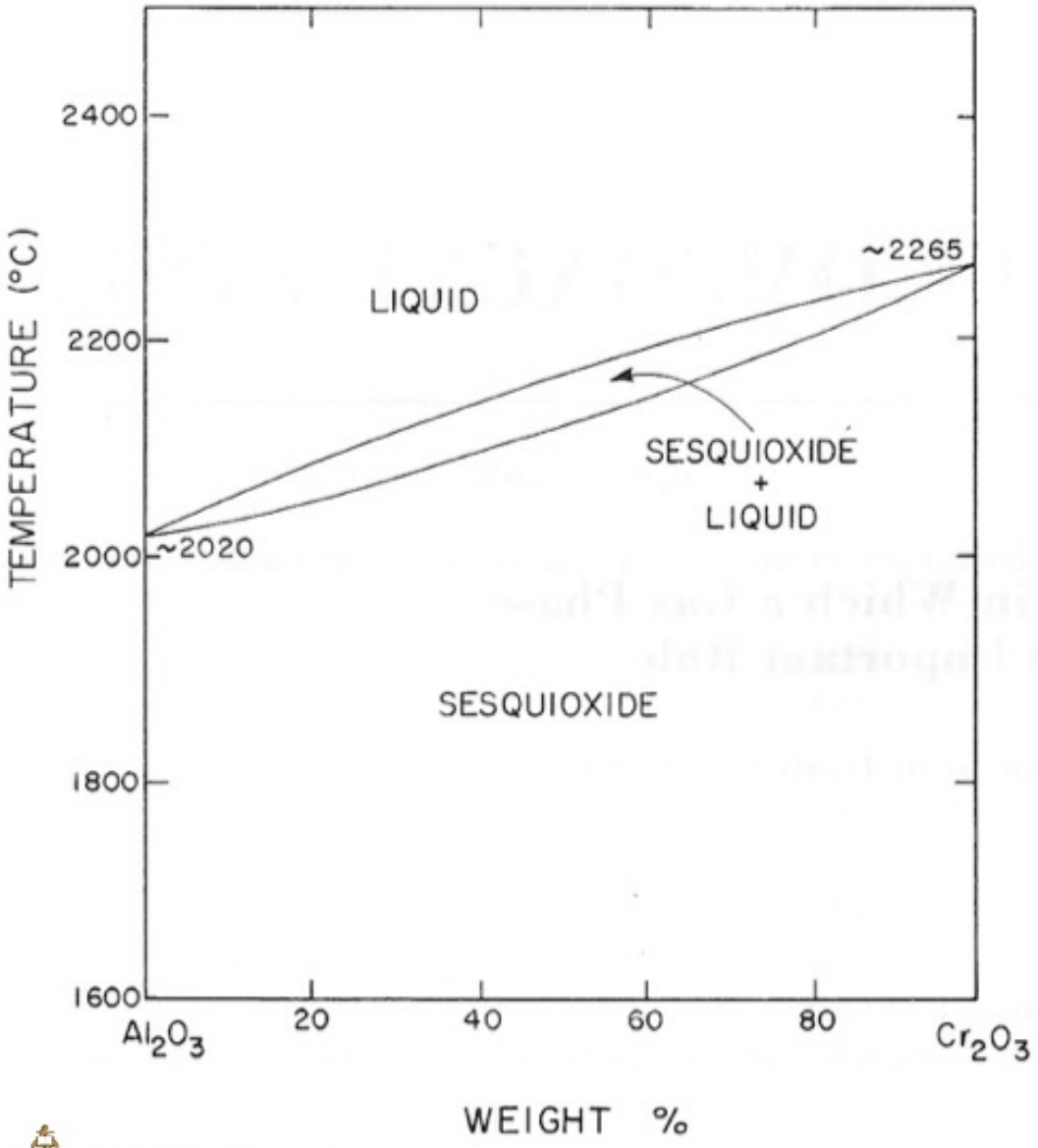
- Beneficial properties:
  - Excellent cold & hot strength
  - Good corrosion resistance to acidic and neutral slags
  - Good abrasion and erosion resistance
  - Perform well under reducing conditions
- Limitations:
  - Poor corrosion resistance to CaO-rich (highly basic) slags
  - Sensitive to thermal shock
- Applications:
  - Widely used: Iron and steel industry, ferroalloy industry, foundry industry, cement and lime industry, petrochemical industry, aluminium industry

Cr_2O_3 addition to refractory formulations

- Added to **establish bonding**:
  - Added to Al_2O_3 – based materials to establish $(Al,Cr)_2O_3$ bonding phase
    - Trace amounts of Cr_2O_3 in Al_2O_3 accounts for a ruby colour
  - Added to magnesia-chromite bricks to enhance formation of a spinel bonding phase
- Added for **enhanced corrosion resistance**:
  - Cr_2O_3 readily reacts with oxides such as iron oxide, manganese oxides, MgO to form spinels

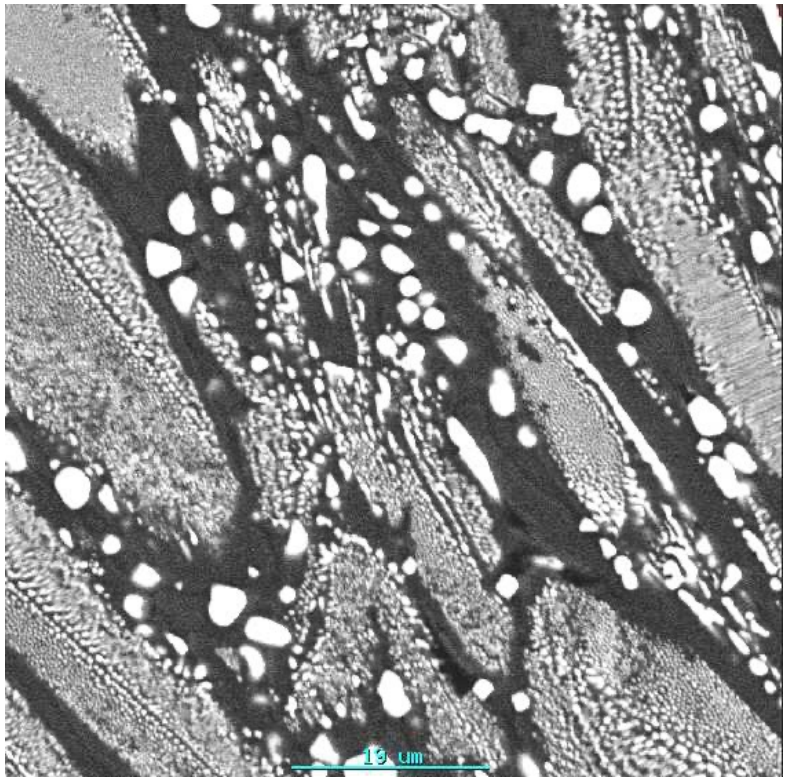
$Al_2O_3 – Cr_2O_3$ materials



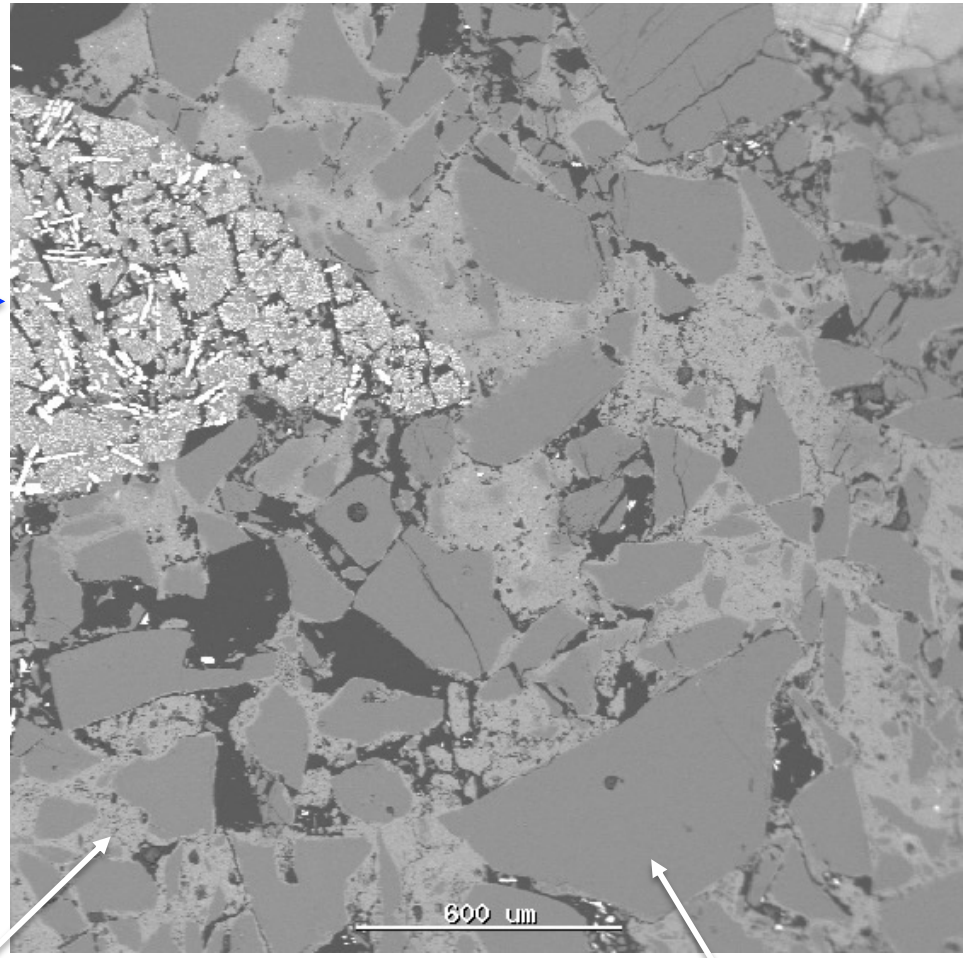


- Very high $T_{solidus}$ in this system
- $(Al,Cr)_2O_3$ solid solution bonding phase forms
  - $T_{solidus}$ of bonding phase is > 2000°C
- Possibility of Cr(VI) formation

$Al_2O_3 – Cr_2O_3$ brick microstructure



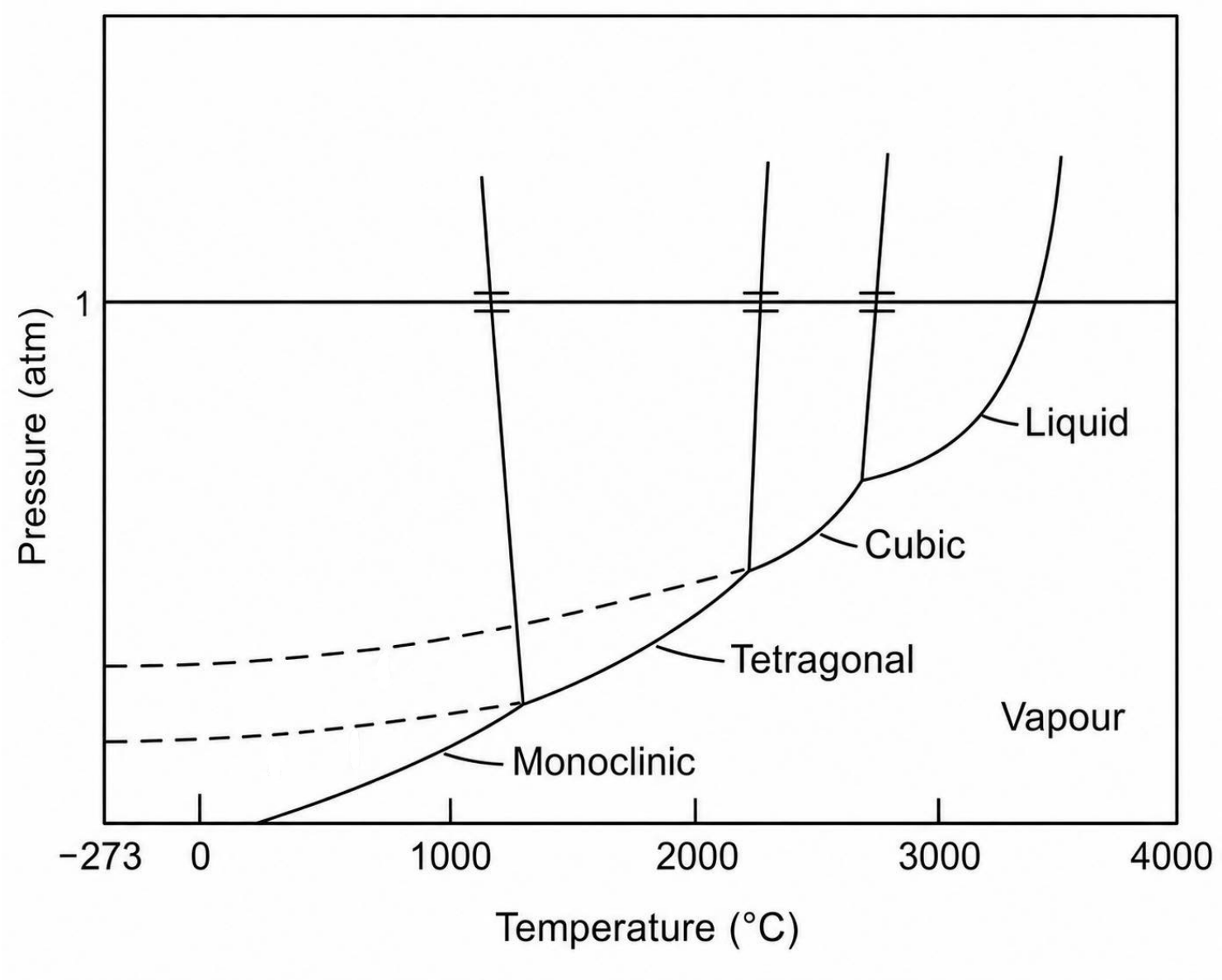
AZS (Al_2O_3-ZrO_2-SiO_2) grains for improved thermal shock resistance



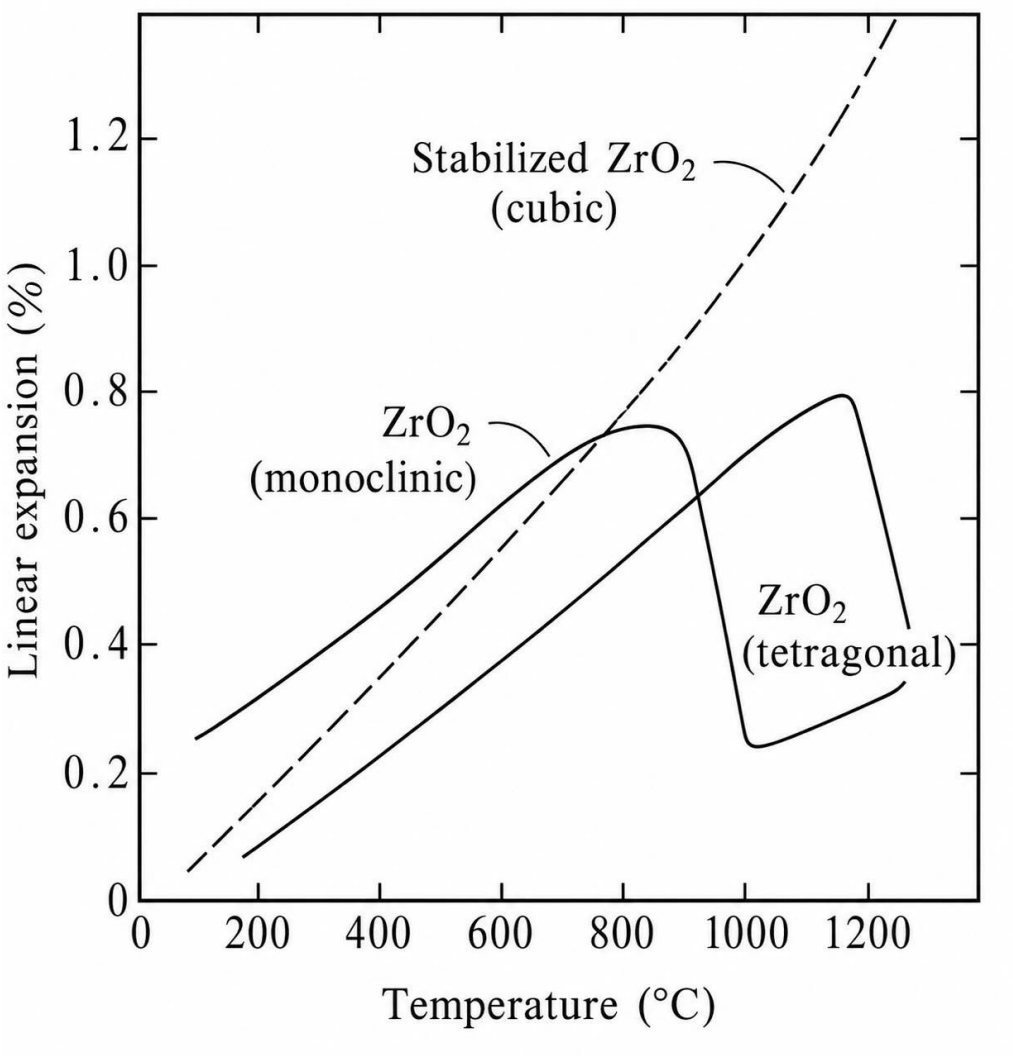
$(Al,Cr)_2O_3$ solid solution bonding phase

Al_2O_3 grains

ZrO_2: Polymorphic forms

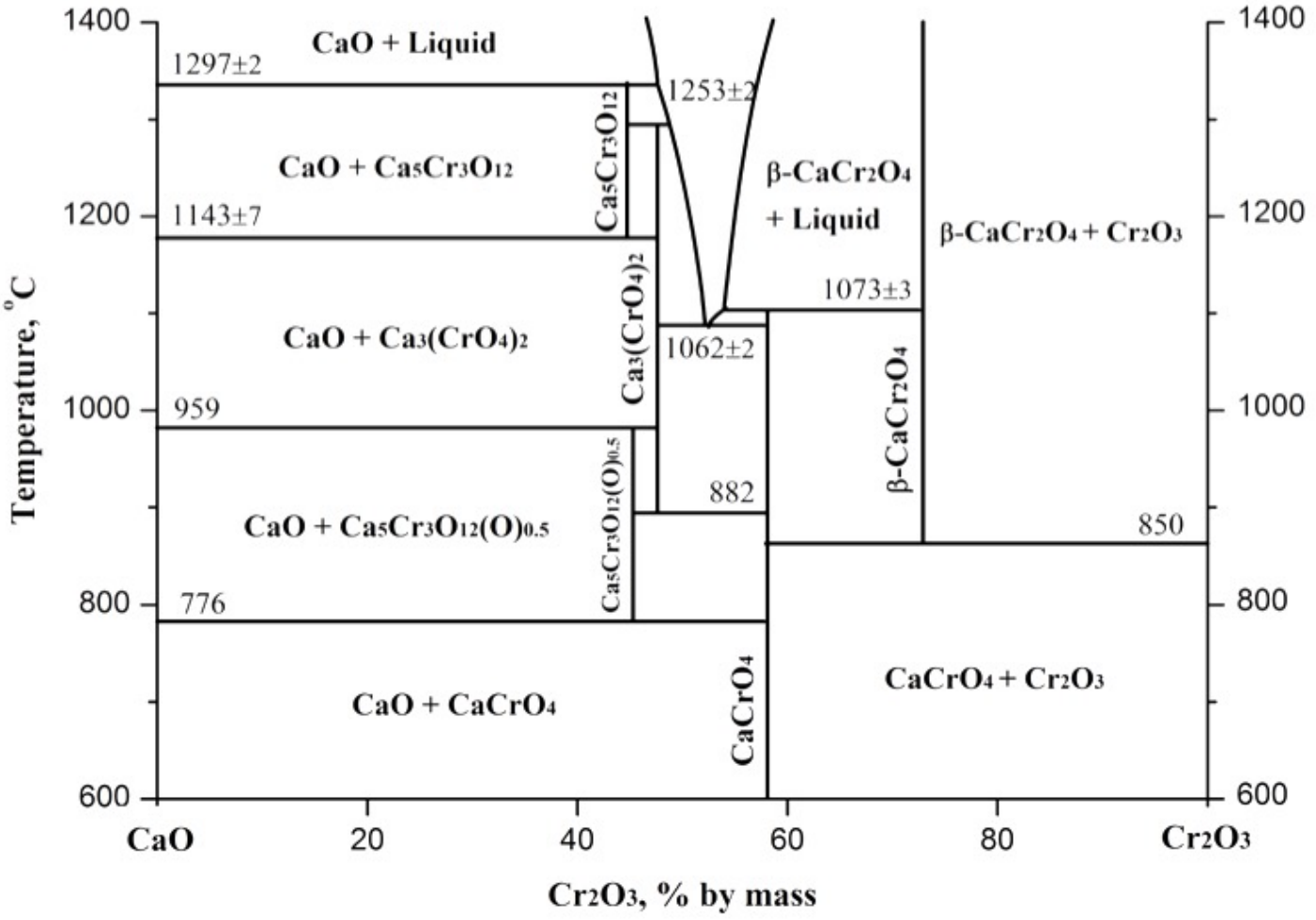


Linear thermal expansion of ZrO_2



Large volume change (approximately 9%) accompanies the monoclinic – tetragonal inversion

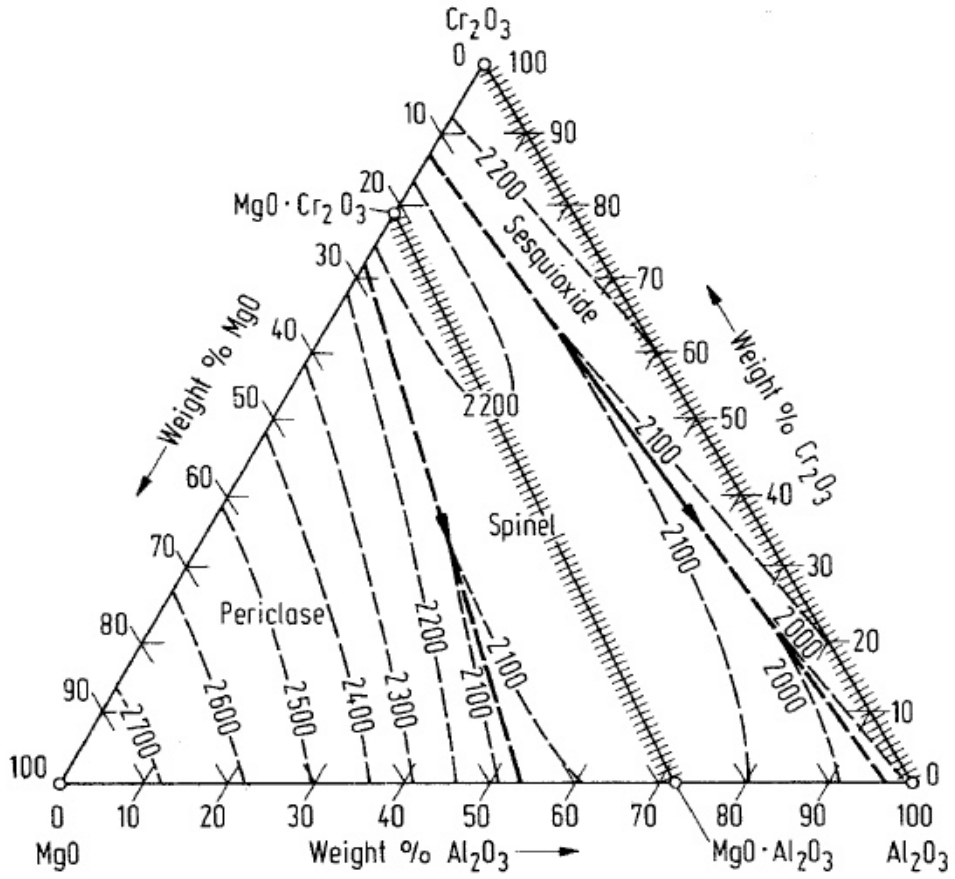
Reactions of the CaO component of doloma with Cr_2O_3 (in air)

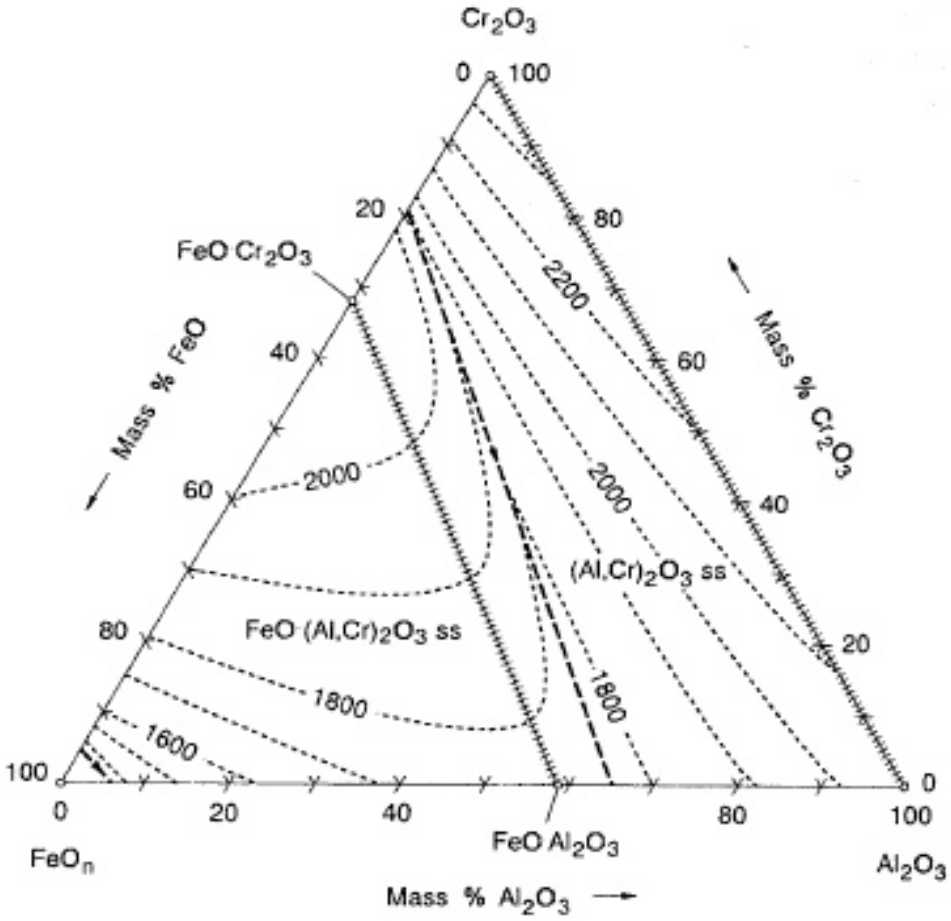


<u>Oxidising conditions in the presence of CaO / Na_2O</u>

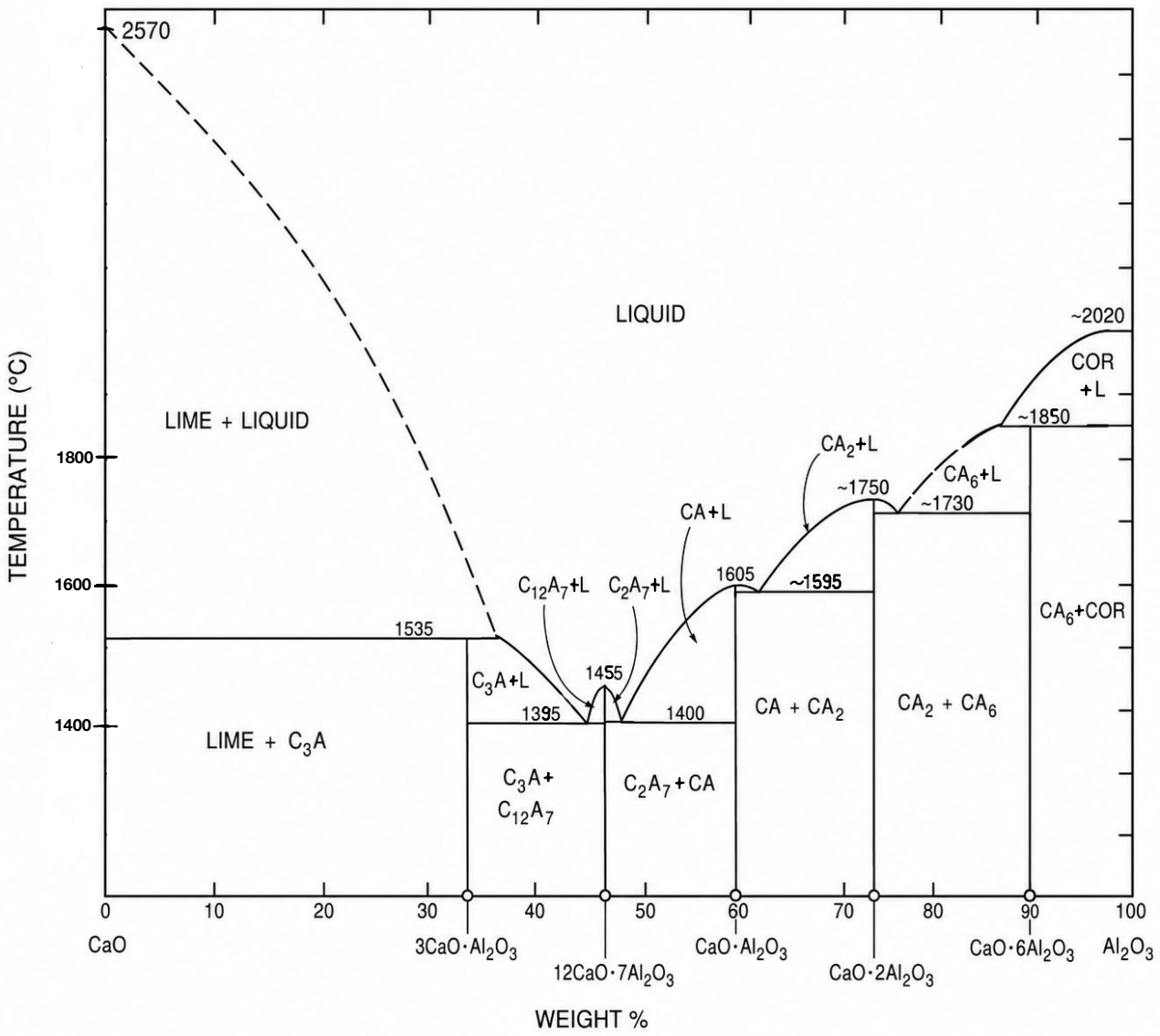
- Cr(VI) formation:
  - $CaCrO_4$
  - Na_2CrO_4
  - $Ca_4Al_6CrO_{16}$, (hauyne)
- Highly soluble in water
- Carcinogenic

Spinel formation when MgO & FeO in slag reacts with $(Al,Cr)_2O_3$





Fluxing action of CaO on Al_2O_3



Properties of Al_2O_3-Cr_2O_3 refractories

- Beneficial properties:
  - Can be used at very high temperatures
    - Excellent hot strength
  - Excellent penetration resistance
  - High corrosion resistance
    - Protective spinel layer slows down further corrosion
  - Good abrasion and erosion resistance

- Limitations:
  - Potential formation of Cr(VI)
  - Cost associated with Cr_2O_3 raw material
  - Poor performance in CaO-rich slag (attack Al_2O_3)
  - Possible thermal expansion mismatch between phases

- Applications: Non-ferrous smelting furnaces, slagging gasifiers, glass furnaces, converters

Basic refractory materials

Magnesia refractory materials

MgO

- MgO = periclase ≠ magnesite
- Main sources:
  - Magnesite ($MgCO_3$) is a weathering product of olivine
    - Calcined to MgO at ~1850°C
    - MgO-CaO-SiO_2-based impurities
  - Brines and seawater

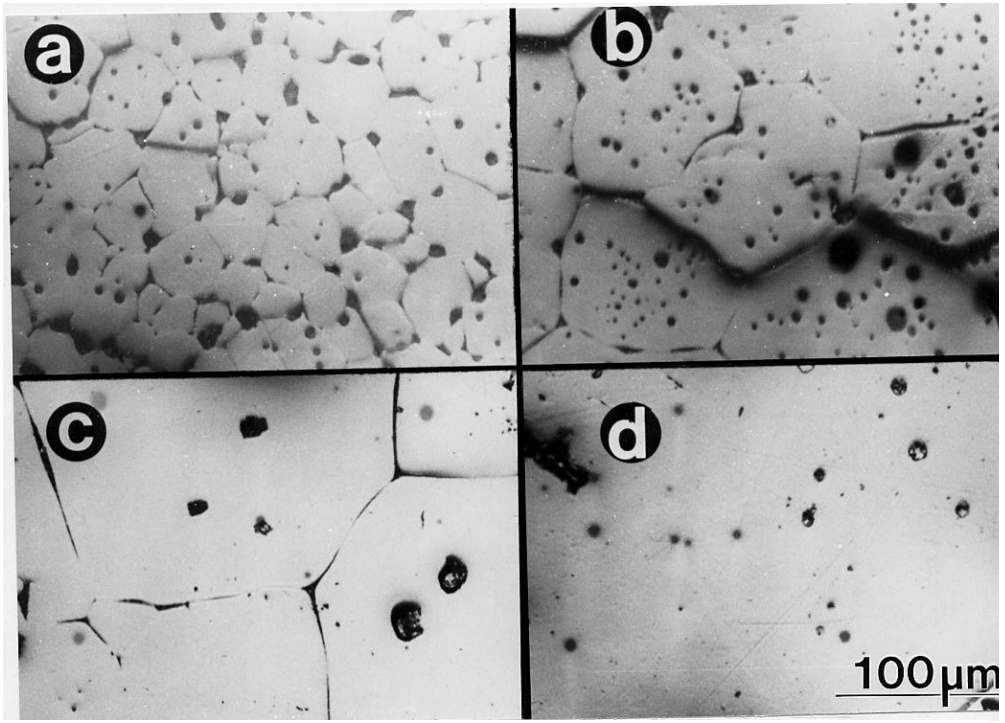
$$MgO.Ca(OH)_2 + Mg^{2+} \rightarrow MgO.Mg(OH)_2 + Ca^{2+}$$

$$Ca(OH)_2 + Mg^{2+} \rightarrow Mg(OH)_2 + Ca^{2+}$$

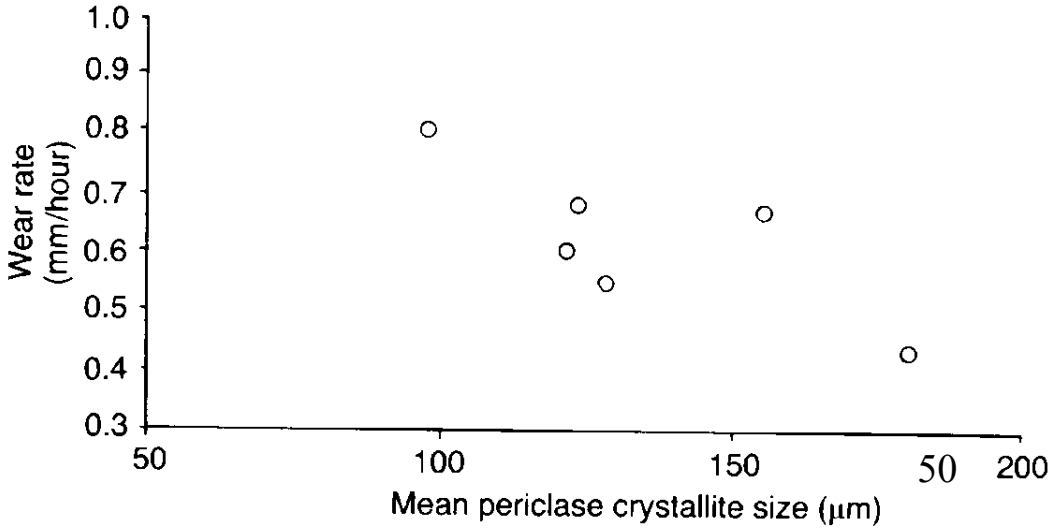
    - Calcined at ~1850°C to MgO
    - B_2O_3 as potential harmful impurity
- Sintered and fused grain MgO

MgO: Fused or Sintered Grain?

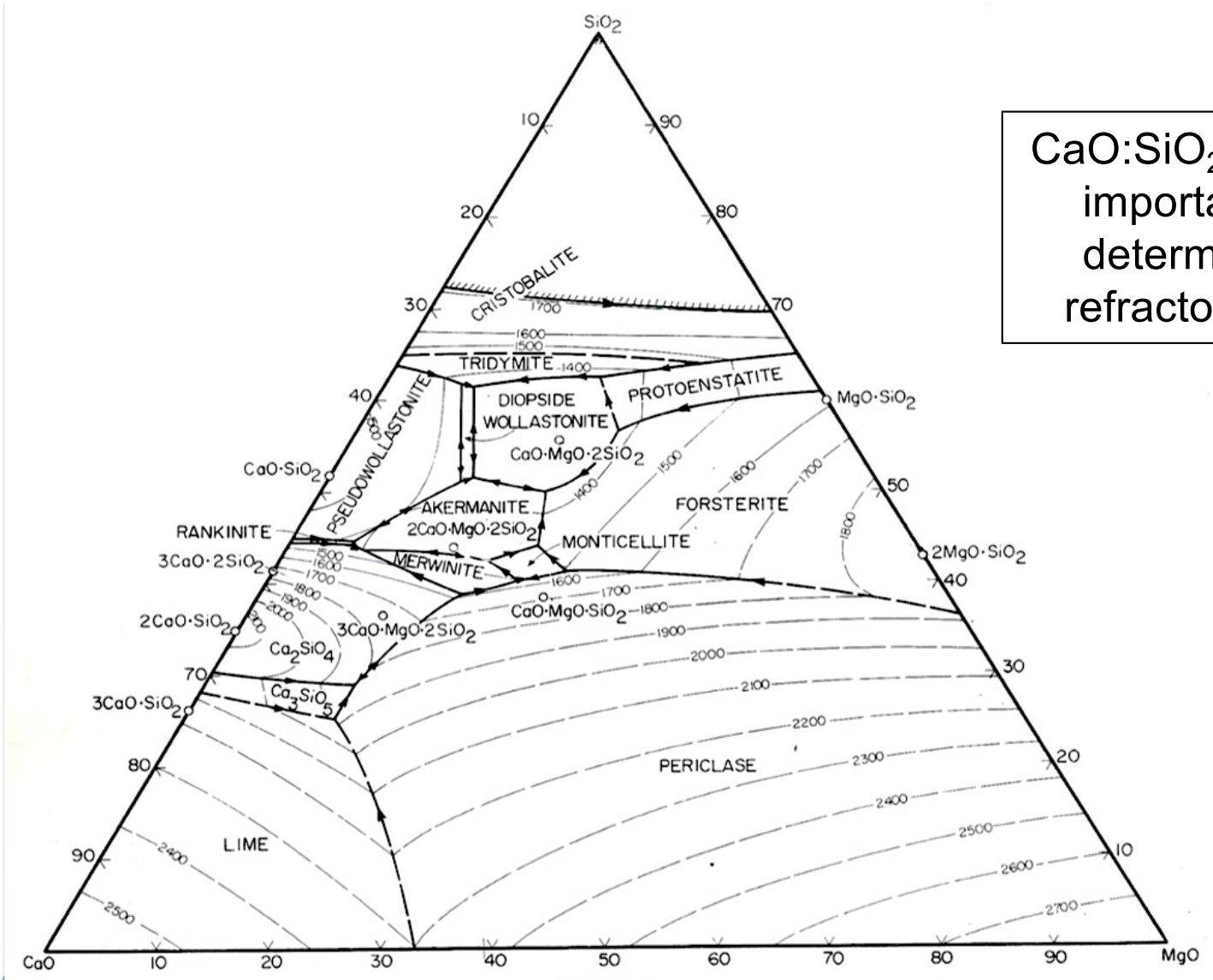
- (a) – (c): Sintered MgO with increasing crystallite size (phase boundaries are clearly visible)
- (d): Fused MgO grain



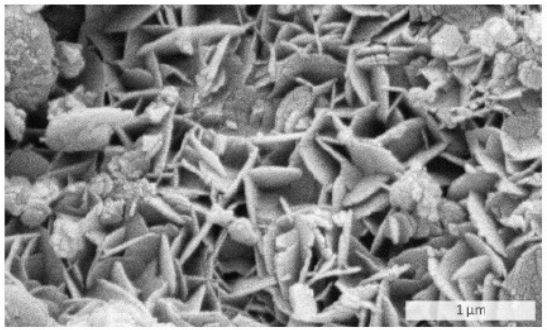
- Reduced wear with
  - Fused MgO
  - Greater crystallite size as less weakening due to second phases at grain boundaries



Silicate impurities in magnesia refractory materials



$CaO:SiO_2$ ratio is important in determining refractoriness



Hydration of MgO

- MgO-based refractory materials hydrate at temperatures below ~270°C to form brucite:

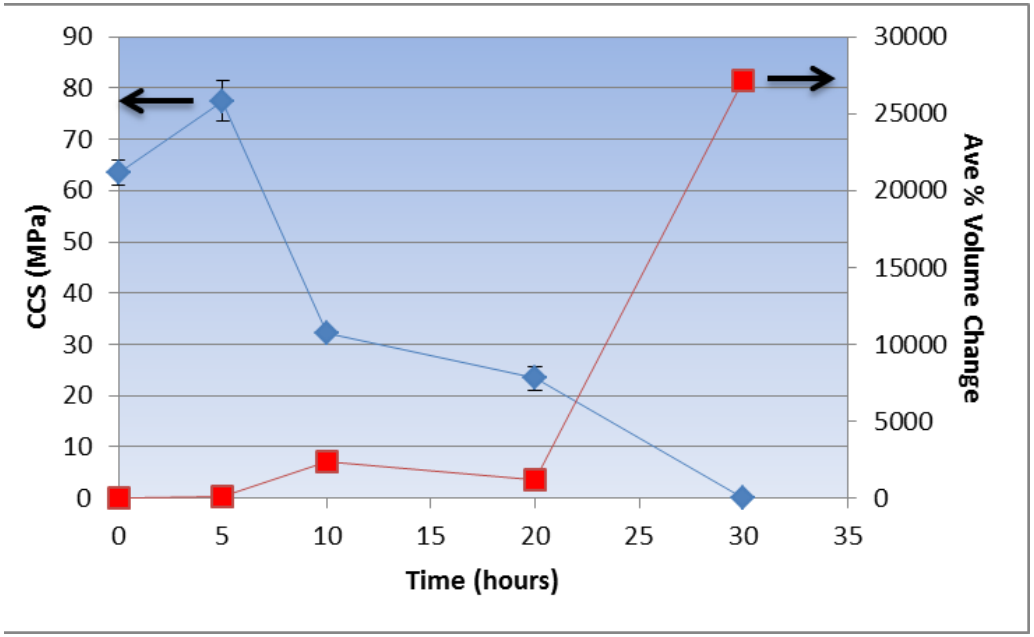
$$MgO + H_2O \rightarrow Mg(OH)_2$$

  - 3-fold volumetric expansion, causes cracking, eventually dusting

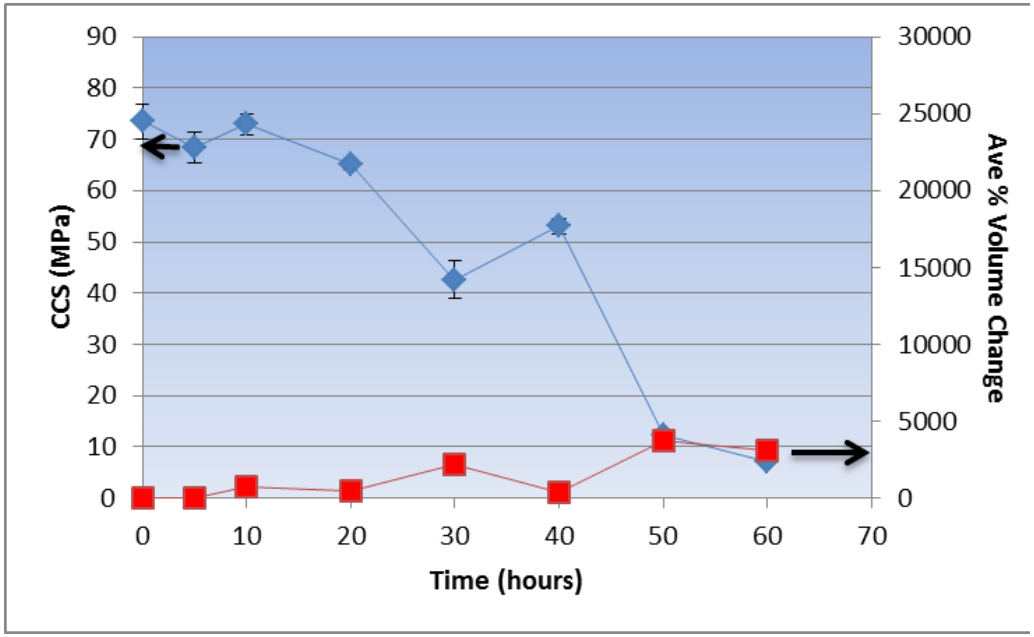
- Risk of hydration of MgO-based materials is minimised by
  - Storing in closed rooms at 10-30°C with good ventilation
  - Avoiding condensation under shrink wrapping
  - Installing bricks as close to heat-up as possible
  - Protective coatings such as $MgSO_4$ are used to slow down or prevent hydration

CCS vs. volume change of $MgSO_4$ impregnated MgO bricks

Untreated

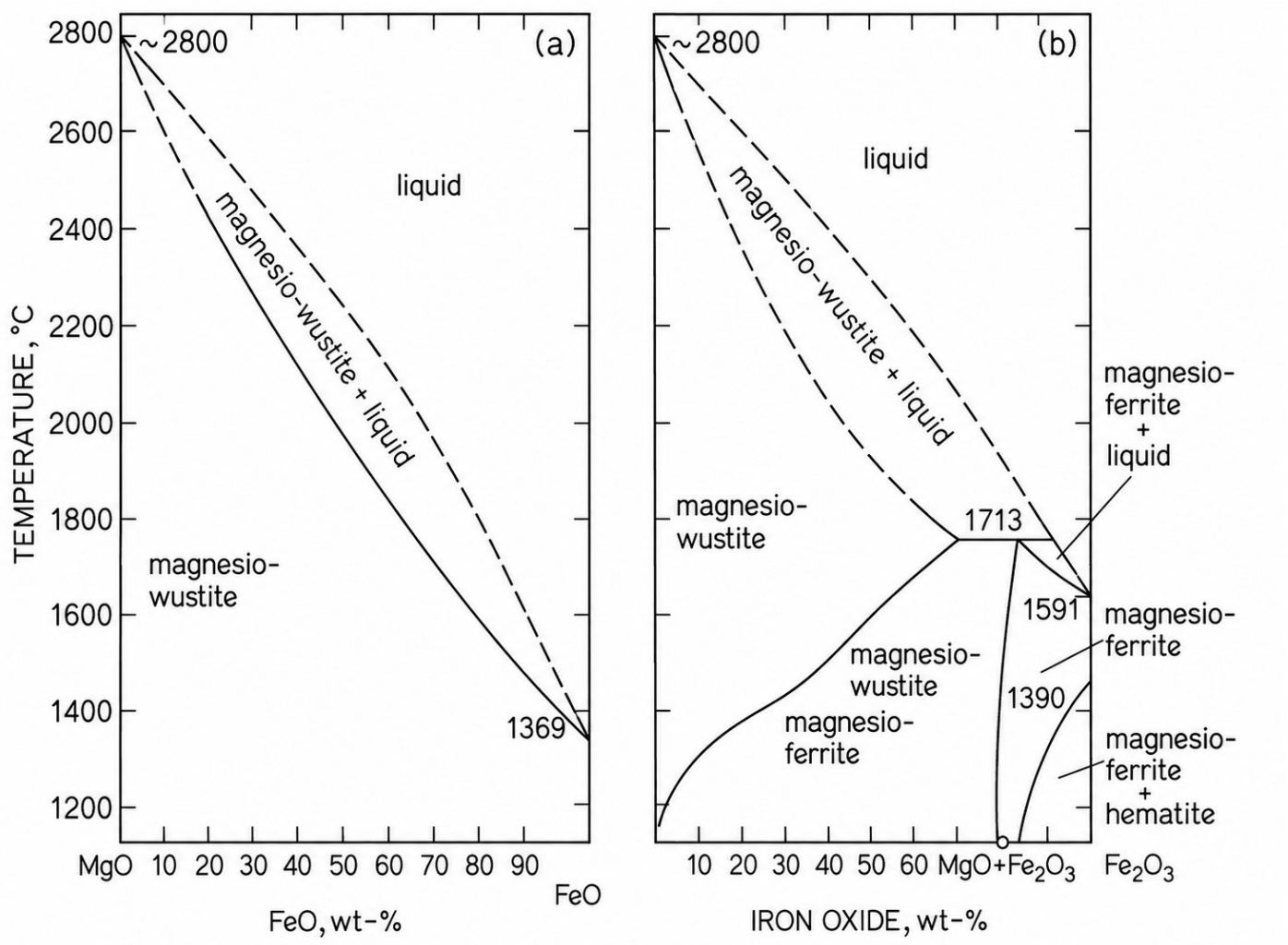


Treated



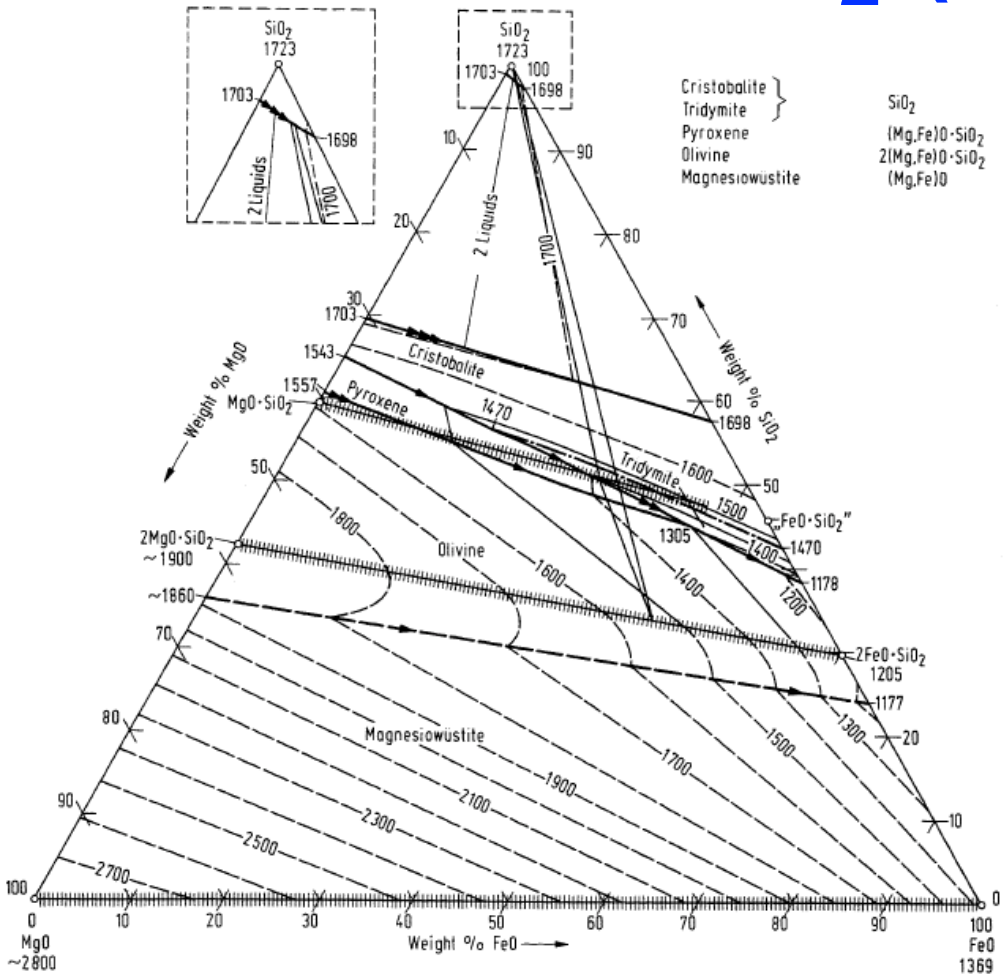
MgO – iron oxide

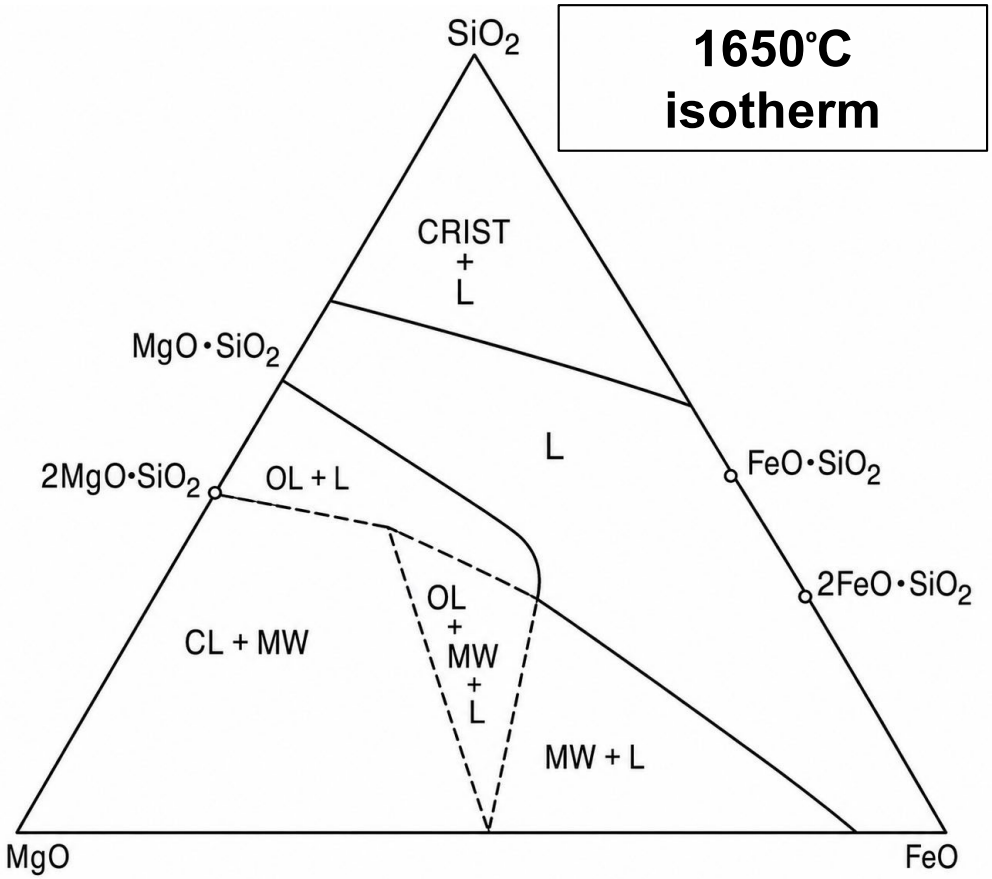
In contact with Fe^0 **In air**



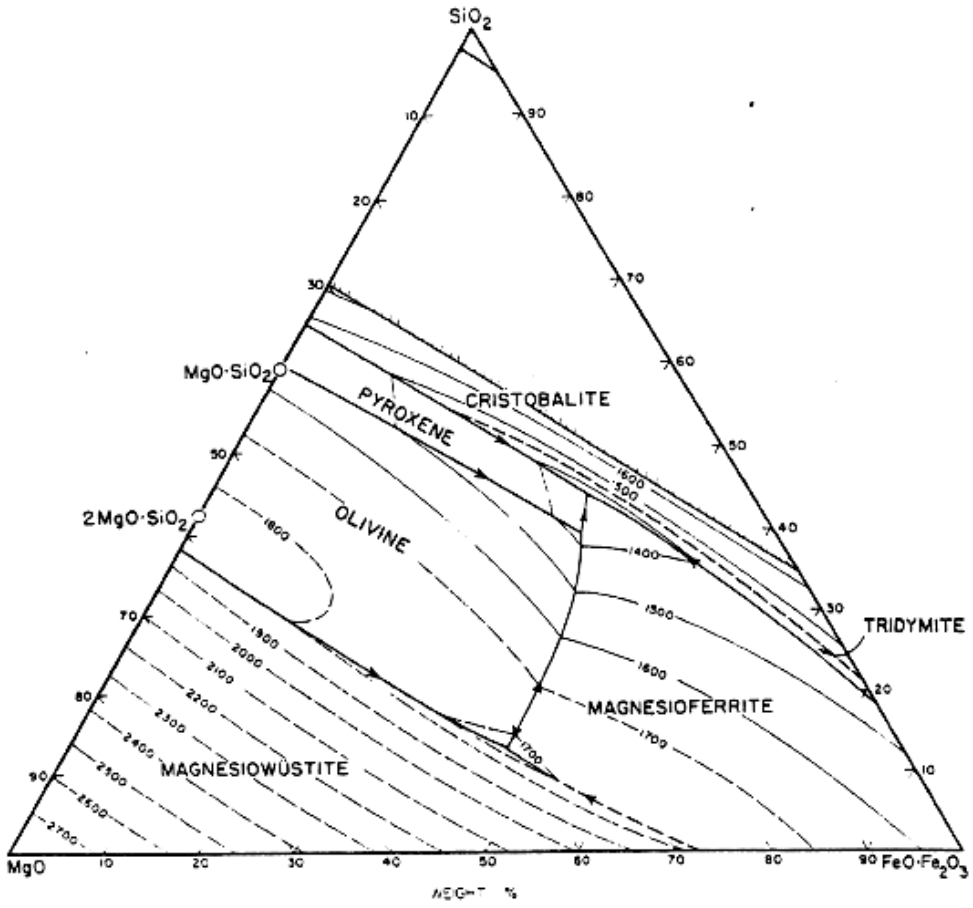
- Significant solid solution phase formation
- MgO – iron oxides phase diagrams already motivate why MgO-based materials perform the best in contact with FeO-rich slags

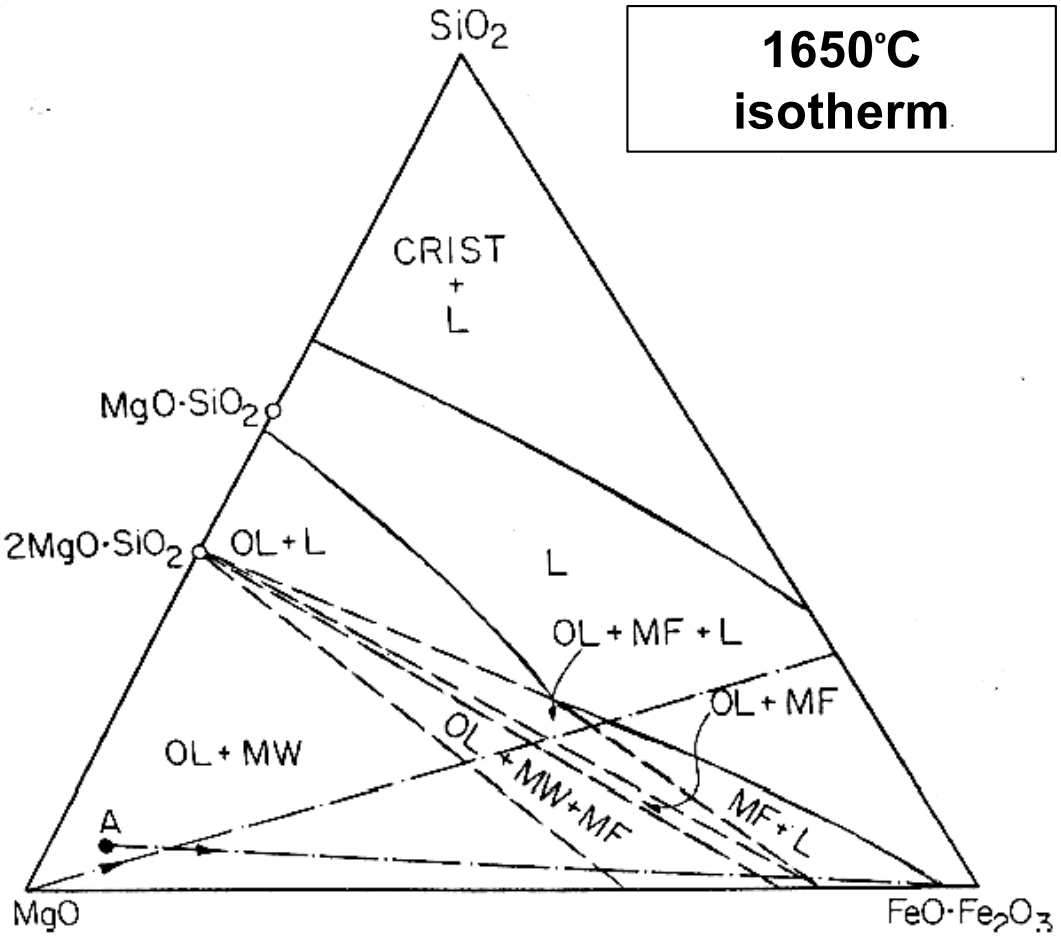
Phase relations in the system MgO – FeO – SiO_2 (in contact Fe^0)





Phase relations in the system $MgO – Fe_3O_4 – SiO_2$ (in air)





Magnesia-chromite refractory materials

Magnesia-chromite / Chromite-magnesia

- Prepared from mixes of:
  - magnesia grain and chromite ore
  - fused magnesia and chromite ore
  - fused magnesia-chromite grain

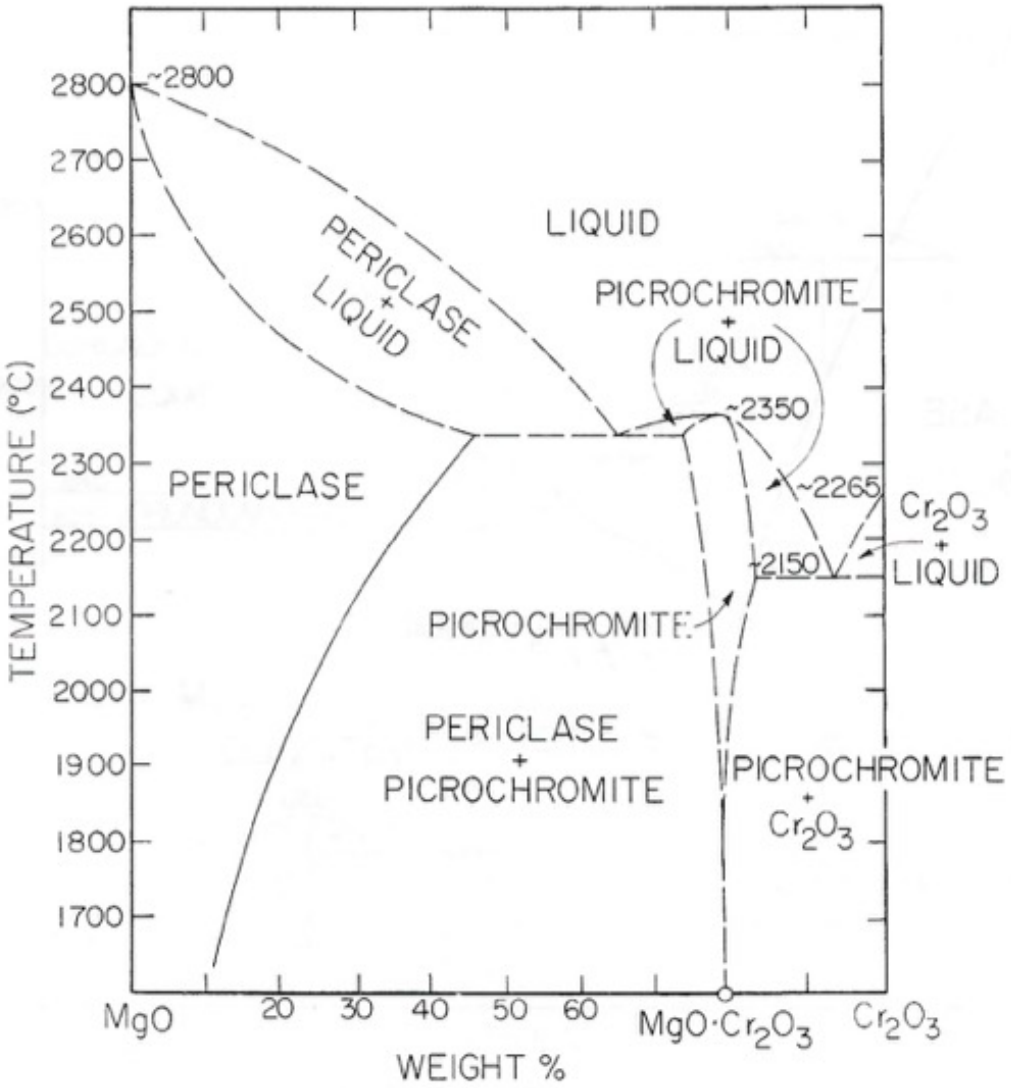
- Chromite ore consists of:
  - Spinels in solid solution: $(Mg,Fe^{2+})O.(Cr,Al,Fe^{3+})_2O_3$
    (rich in spinel ($MgAl_2O_4$) and picrochromite ($MgCr_2O_4$))
  - Low in iron oxide and SiO_2

- Developed due to the bad thermal shock resistance of magnesia

Magnesia-chromite / Chromite-magnesia

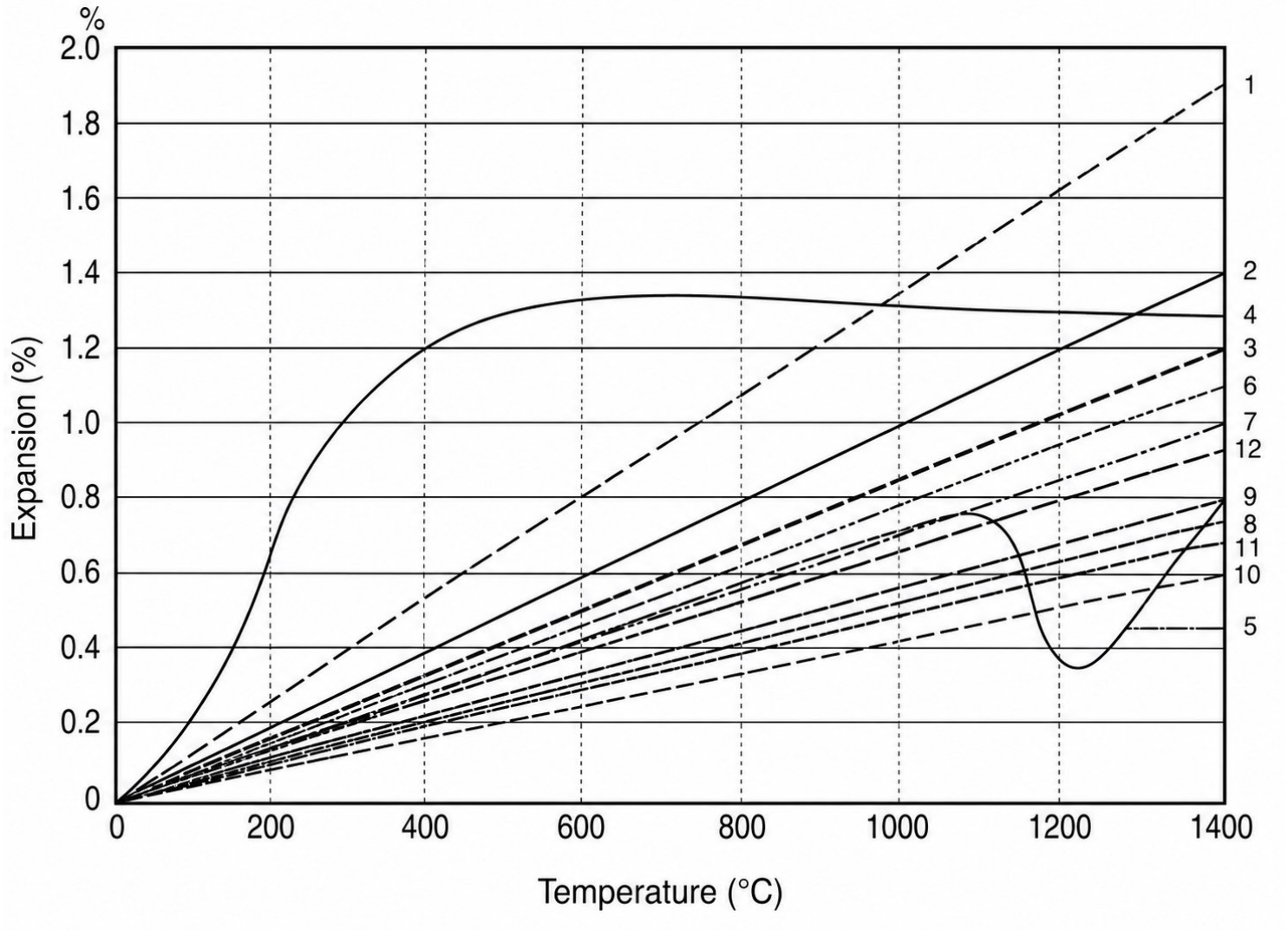
- Direct-bonded vs. silicate-bonded bricks have
  - Lower impurity content
  - Improved hot strength and corrosion resistance
- In general, magnesia-chromite refractories have:
  - A lower thermal conductivity, as well as thermal expansion coefficient than that of MgO
  - Very good slag resistance
- Environmental restrictions due to Cr(VI) formation under oxidising conditions (e.g. cement kilns)

$MgO - Cr_2O_3$



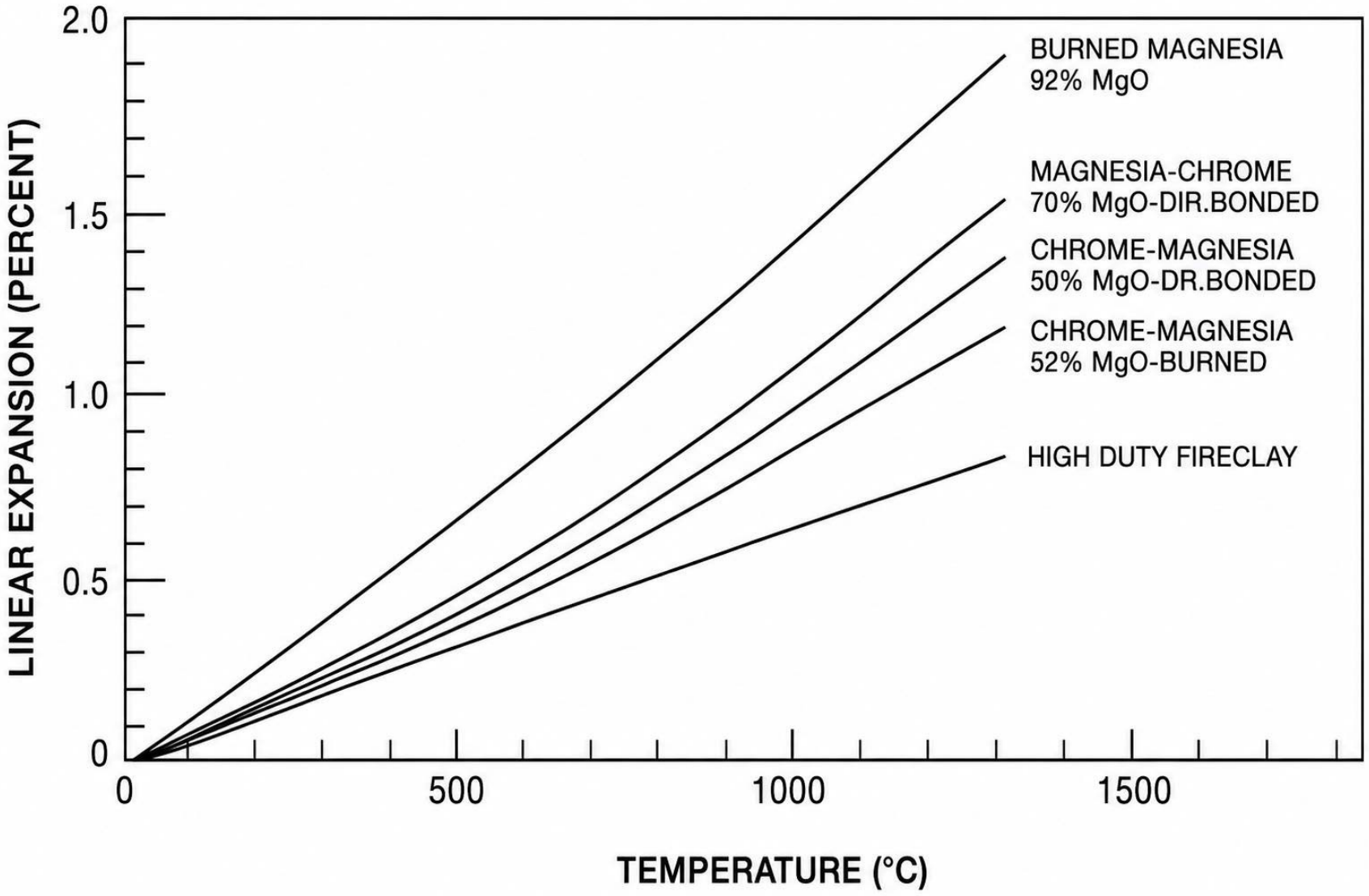
- Diagram serves as motivation for the use of MgO-chromite refractories
- Chromite adds thermal shock resistance to MgO materials
- Chromite is sensitive to Po_2 fluctuations

Reversible thermal expansion of MgO



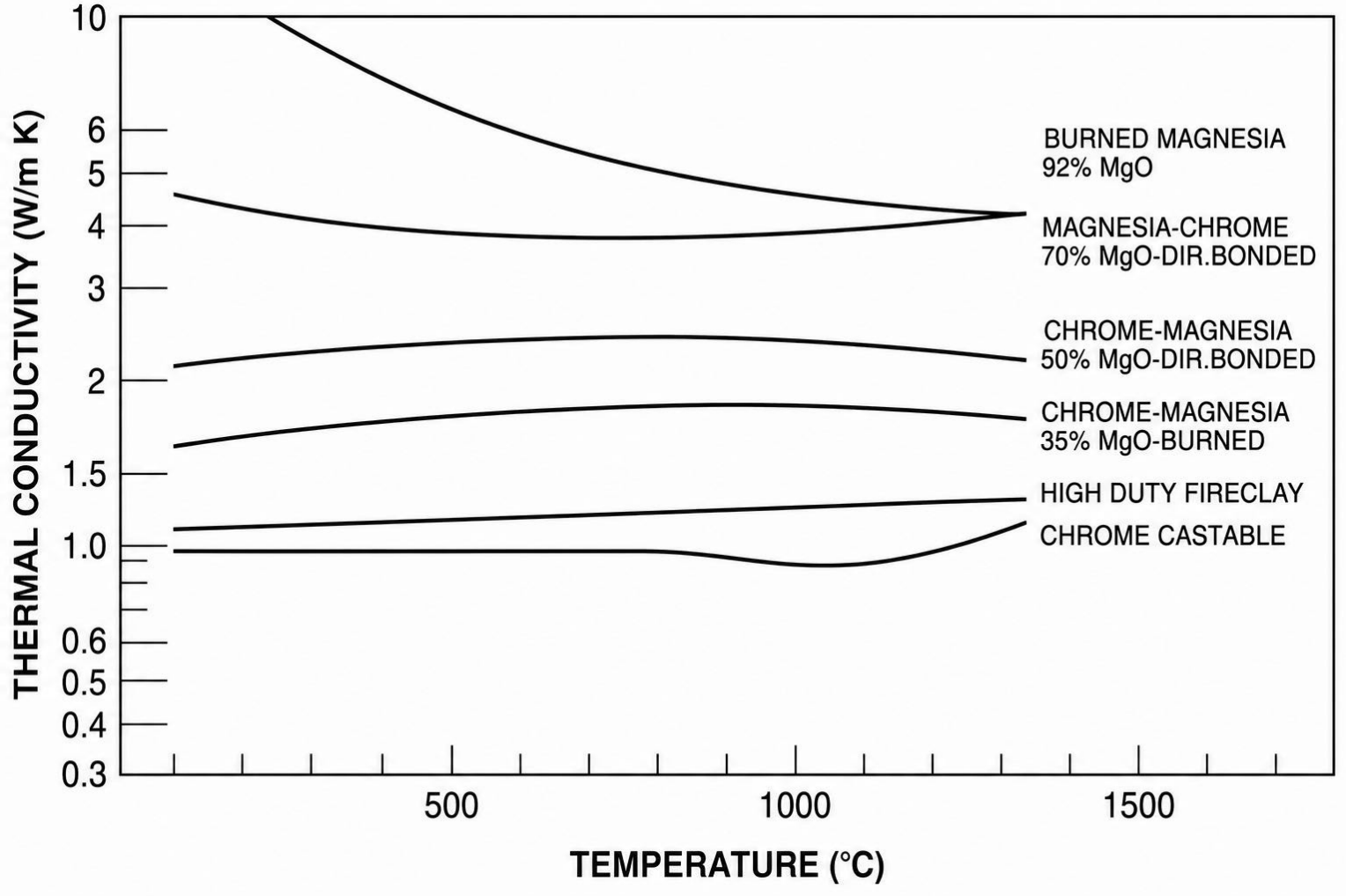
1 = magnesia;
2 = chromite-magnesia;
3= chromite;
4 = silica;
5 = zirconia;
6 = corundum 99%;
7 = corundum 90%;
8 = fireclay;
9 = sillimanite;
10 = zircon;
11 = silicon carbide

Thermal expansion of electric furnace refractories



(Donaldson et al.)

Thermal conductivity of electric furnace refractories



Alumina-chromia ~2.9 W/mK @ 1000°C

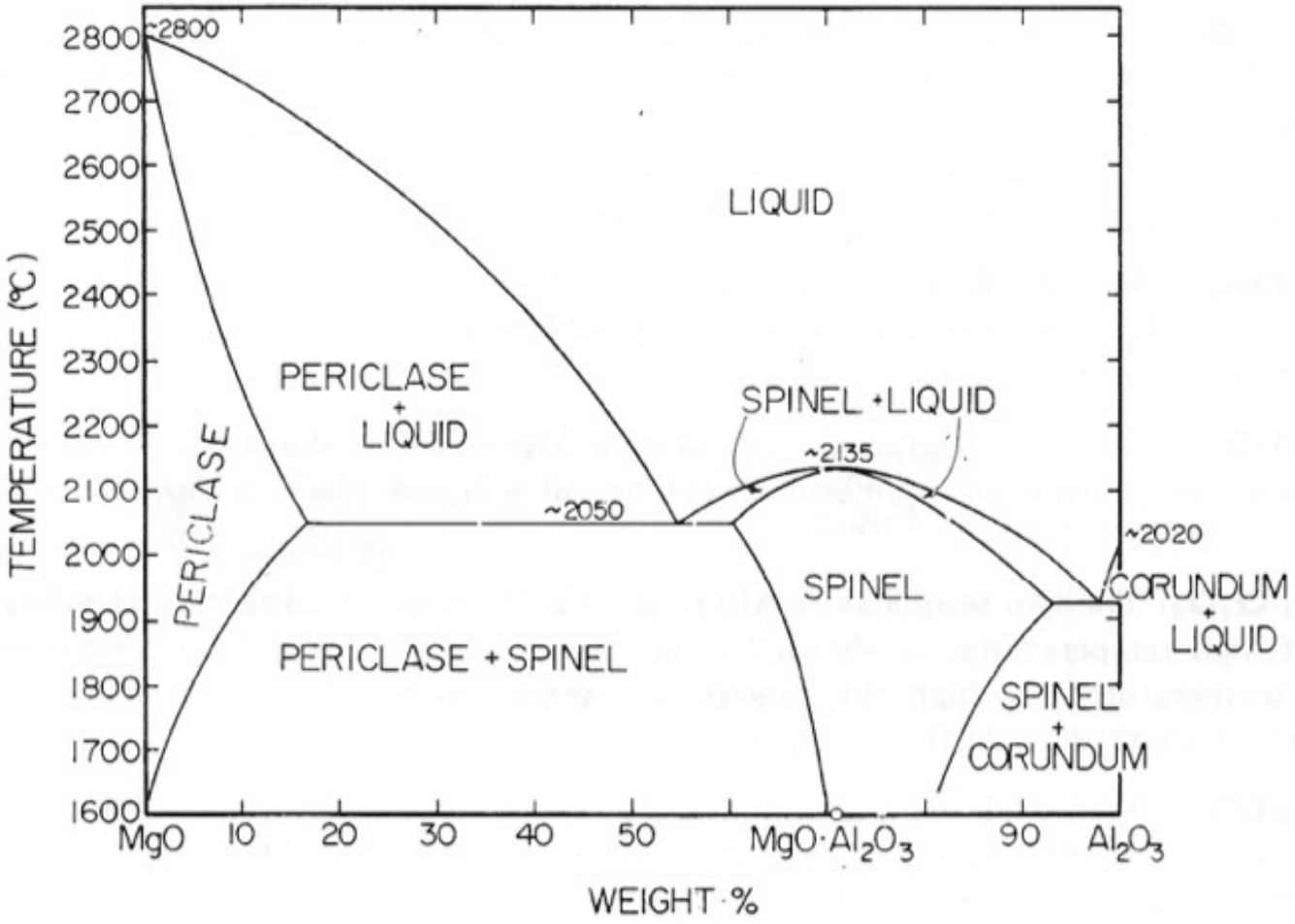
(Donaldson et al.)

Magnesia spinel refractory materials

MAGNESIA SPINEL ($MgAl_2O_4$)

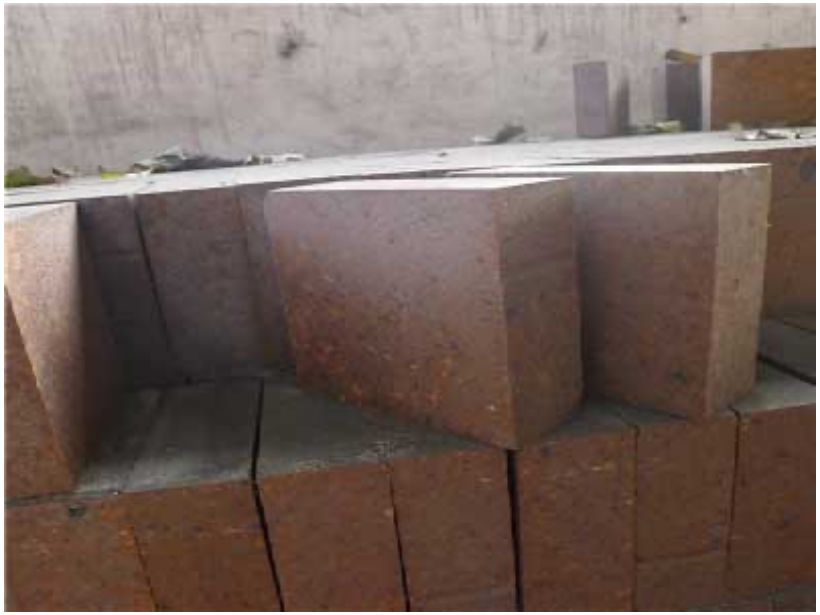
- Developed as
  - An environmentally safer alternative to magnesia–chromite bricks
  - Not sensitive to Po_2 fluctuations
- Very refractory compound (m.p. = 2135°C)
- Good bonding agent for both MgO and Al_2O_3
  - Added to refractories as a pre-prepared grain, or
  - Formed in-situ (> 1500 °C), where it forms a bonding phase

$MgO - Al_2O_3$



Can produce magnesia-rich and Al_2O_3-rich spinels

Doloma refractory materials



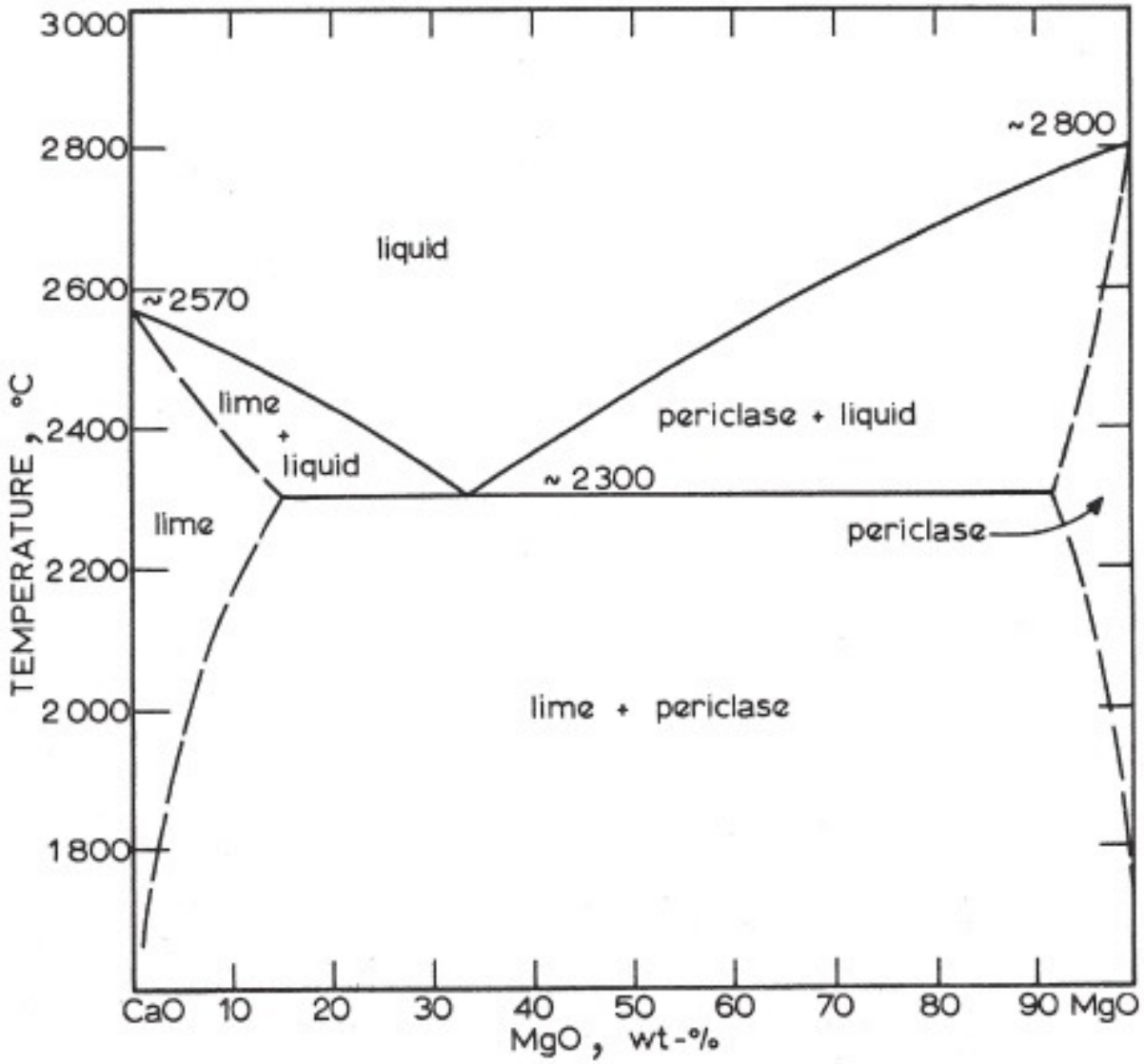
DOLOMA

- Calcined product of dolomite ($(Ca,Mg)CO_3$)
  - $MgCO_3$ decomposes first into MgO (700-800ºC)
  - $CaCO_3$ decomposes into CaO (800-900ºC)

- CaO.MgO easily forms hydroxides, especially CaO
  - Large volume increase with formation of $Ca(OH)_2$
  - Can be protected against hydration through resin bonding

- Silicate impurity phases (MgO-CaO-SiO_2-based)

CaO – MgO system

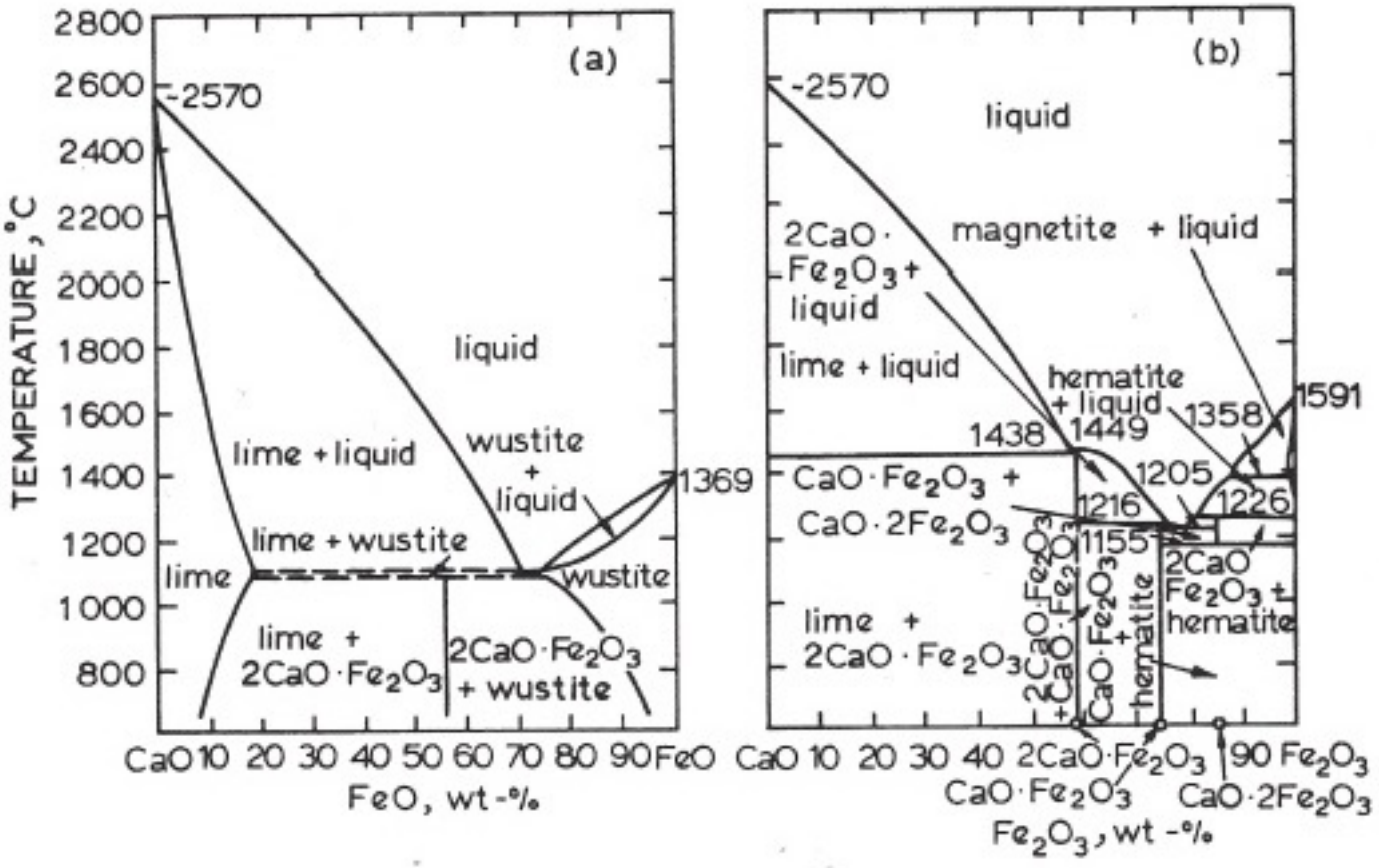


Very high $T_{solidus}$

Reactions of the CaO component of doloma with iron oxide

In contact with Fe^0

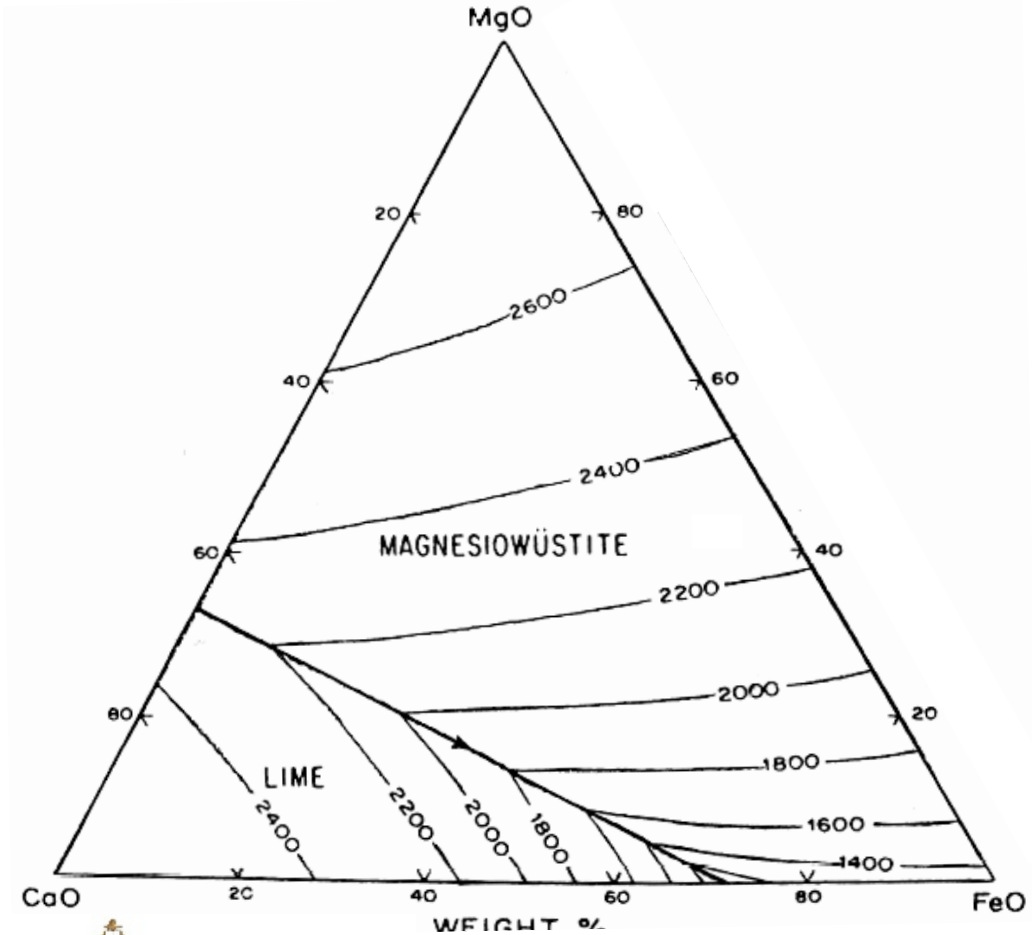
In air

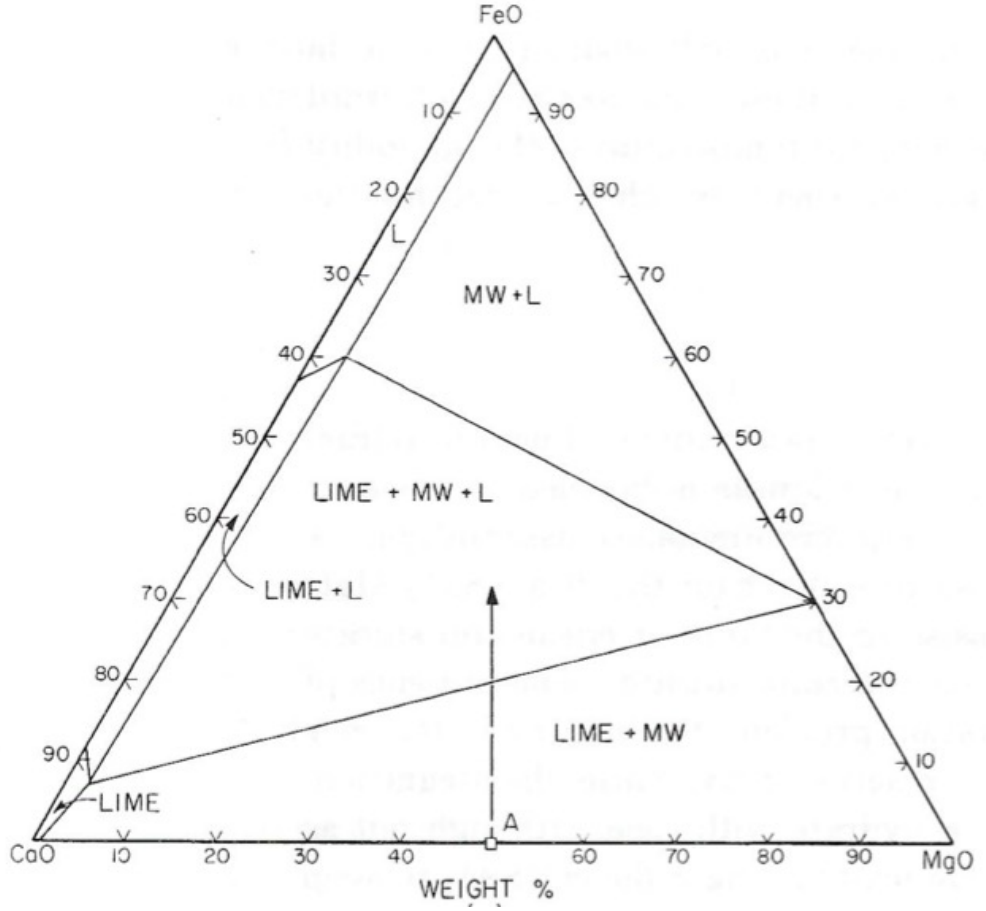


- CaO part of doloma refractory material has low corrosion resistance to iron oxides

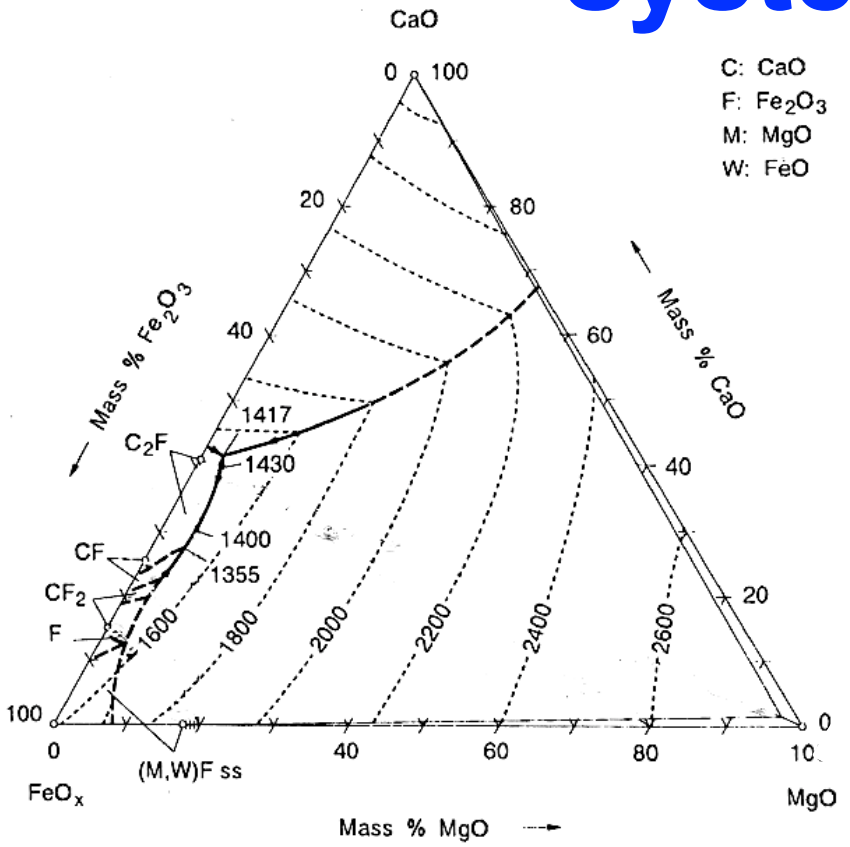
Reaction of doloma refractories with iron oxide: CaO – MgO – FeO system (CO_2/H_2 = 1)

1500^{0}C isotherm

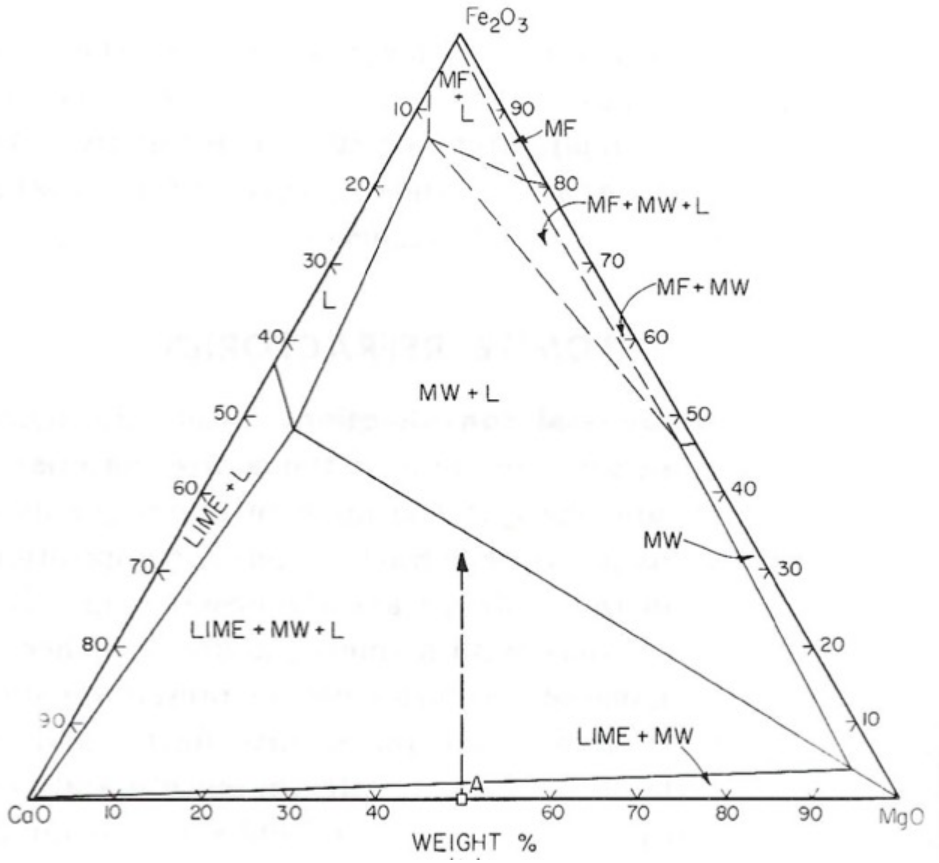




Reaction of doloma refractories with iron oxide CaO – MgO – Fe_2O_3 system (in air)

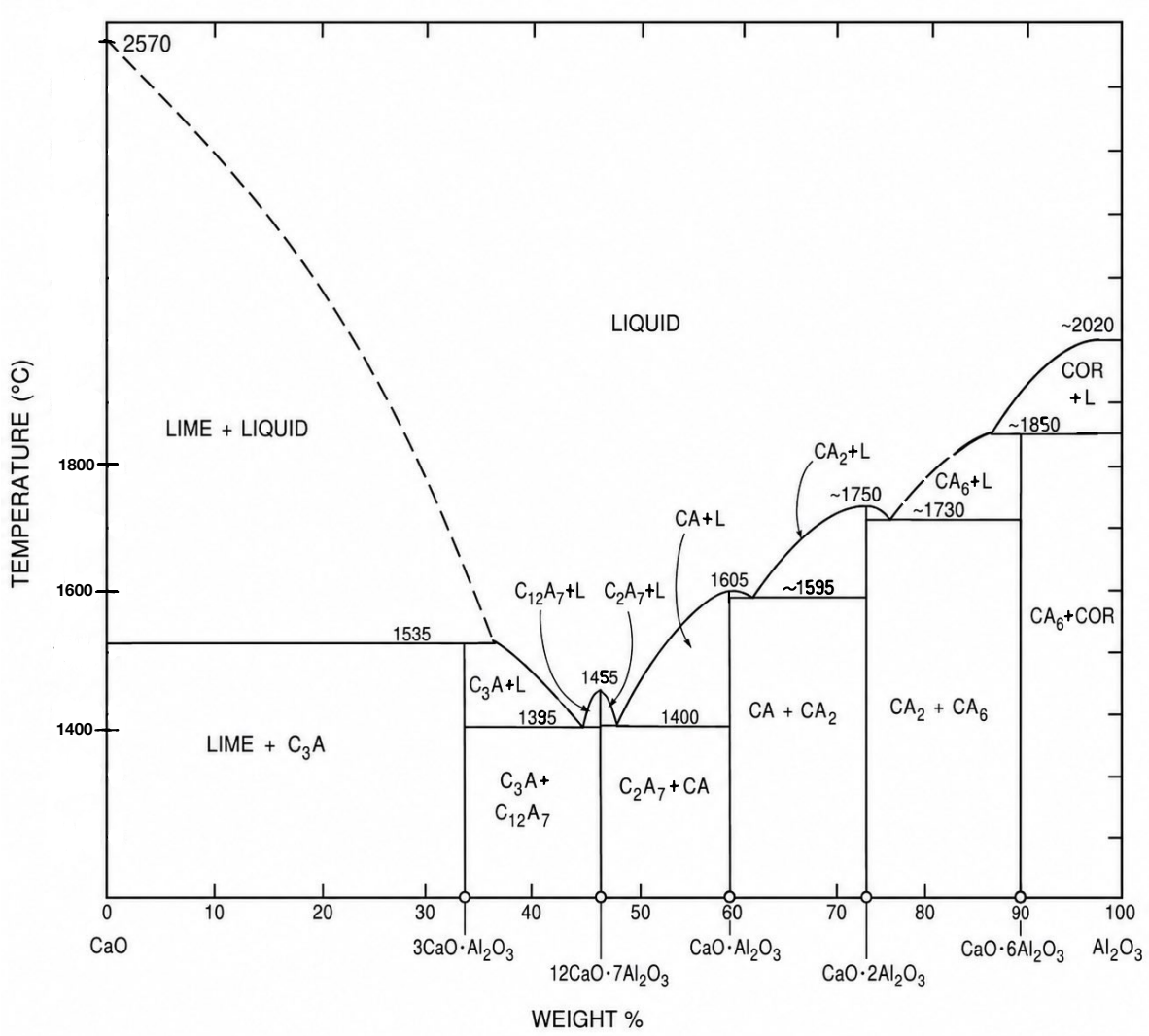


1500^{0}C isotherm



Doloma has higher corrosion resistance to iron oxide under reducing conditions

Reactions of the CaO component of doloma with Al_2O_3



Doloma slag line will be corroded by slag produced from Al killed steel

Properties of MgO refractories

- Beneficial properties:
  - Good resistance to iron oxide
  - High hot strength
- Limitations:
  - High thermal expansion (∴ poor thermal shock resistance)
  - High thermal conductivity, which necessitates the use of insulating refractories
  - Hydrates
  - Prone to spalling
- Applications:
  - Electric arc furnaces, basic oxygen furnaces
  - Safety linings
  - Basic gunning for EAF, BOF and tundish,
  - Hearth ramming and fettling in EAF

Properties of magnesia-chromite refractories

- Beneficial properties:
  - Improved thermal shock resistance to MgO bricks
  - Good resistance to attack by more acidic slags
- Limitations:
  - Under fluctuating temperature and Po_2 chromite grains expand and contract
  - Under oxidising conditions, in presence of CaO and Na_2O, Cr(VI)-containing compounds form
- Applications:
  - Non-ferrous metal smelting furnaces
  - Incinerators and waste-treatment furnaces
  - Ferroalloy production furnaces

Properties of magnesia-spinel refractories

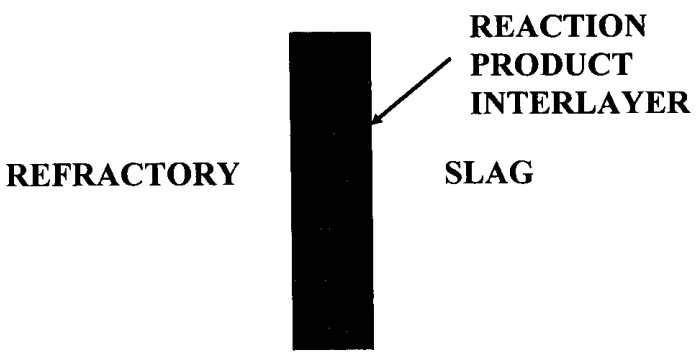
- Beneficial properties:
  - Excellent thermal shock resistance (does not expand under alternating temperature and Po_2)
  - Formation of carcinogenic compounds in contact with CaO not a problem
- Limitations:
  - Expansion associated with spinel formation must be controlled
  - Higher cost
- Applications:
  - Cement & lime rotary kilns
  - EAF roofs
  - Steel ladles

Properties of doloma refractories

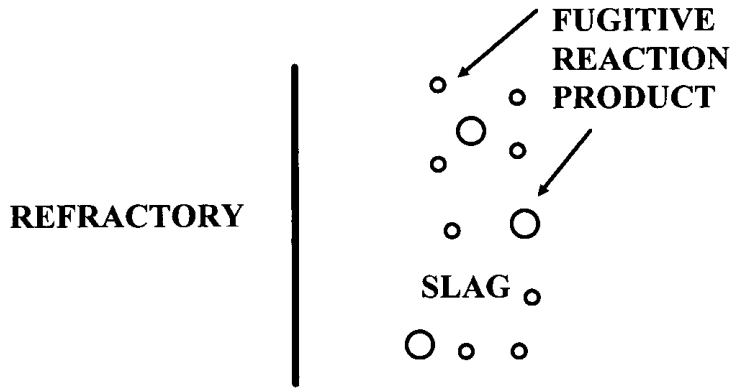
- Beneficial properties:
  - Improved steel quality (clean steel due to very stable oxides)
  - Very good corrosion resistance to highly basic slags
- Limitations:
  - High thermal conductivity (must keep ladles warm)
  - Hydration of free lime (can get dusting)
  - Tendency to form β–Ca_2SiO_4 which convert to γ – Ca_2SiO_4 during cooling (~ 10% volume increase)
  - Corrosion due to FeO in slag
- Applications:
  - Lime kilns, Argon Oxygen Decarburization (AOD) converters, electric arc furnaces, steelmaking ladles

Slag-refractory compatibility

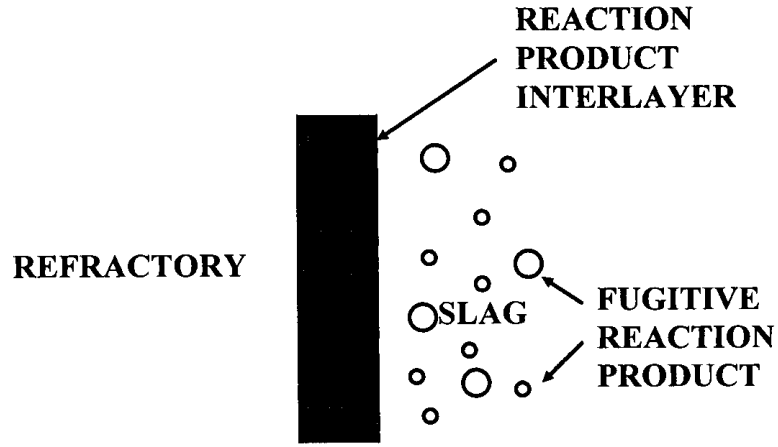
Slag-refractory compatibility



- Freeze lining
  - More aggressive slags become manageable where suitable refractory materials are not available

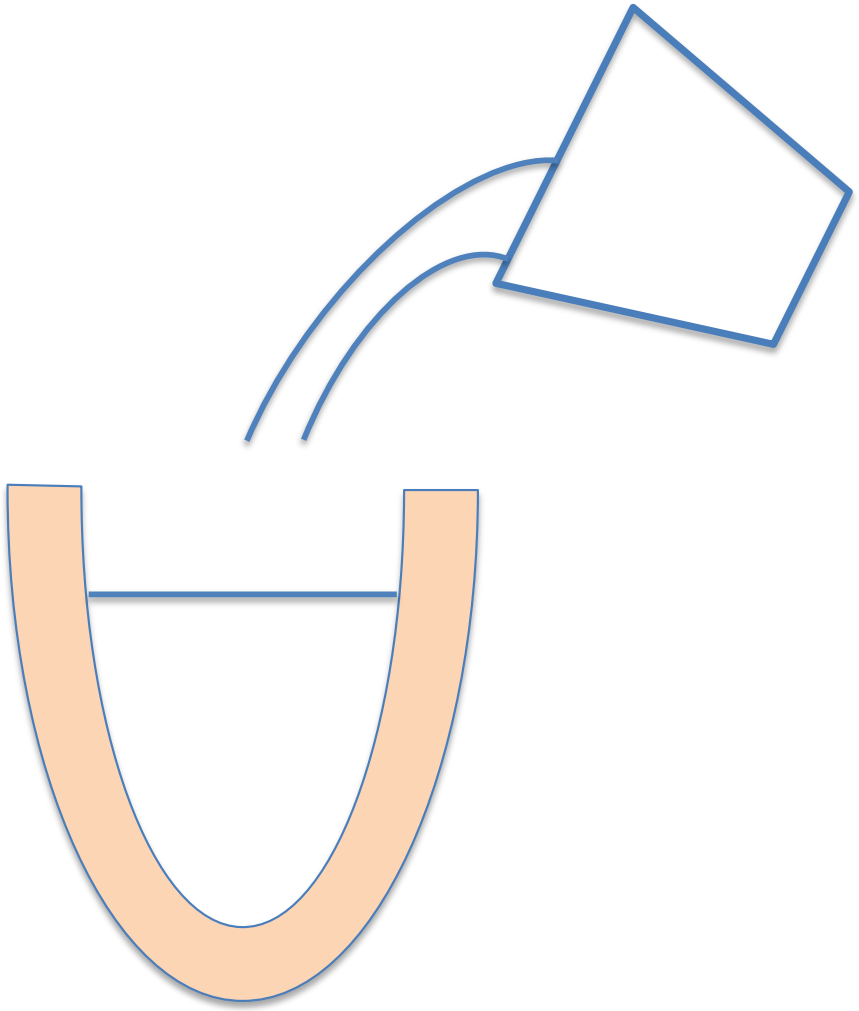


- Saturate slag with main refractory component



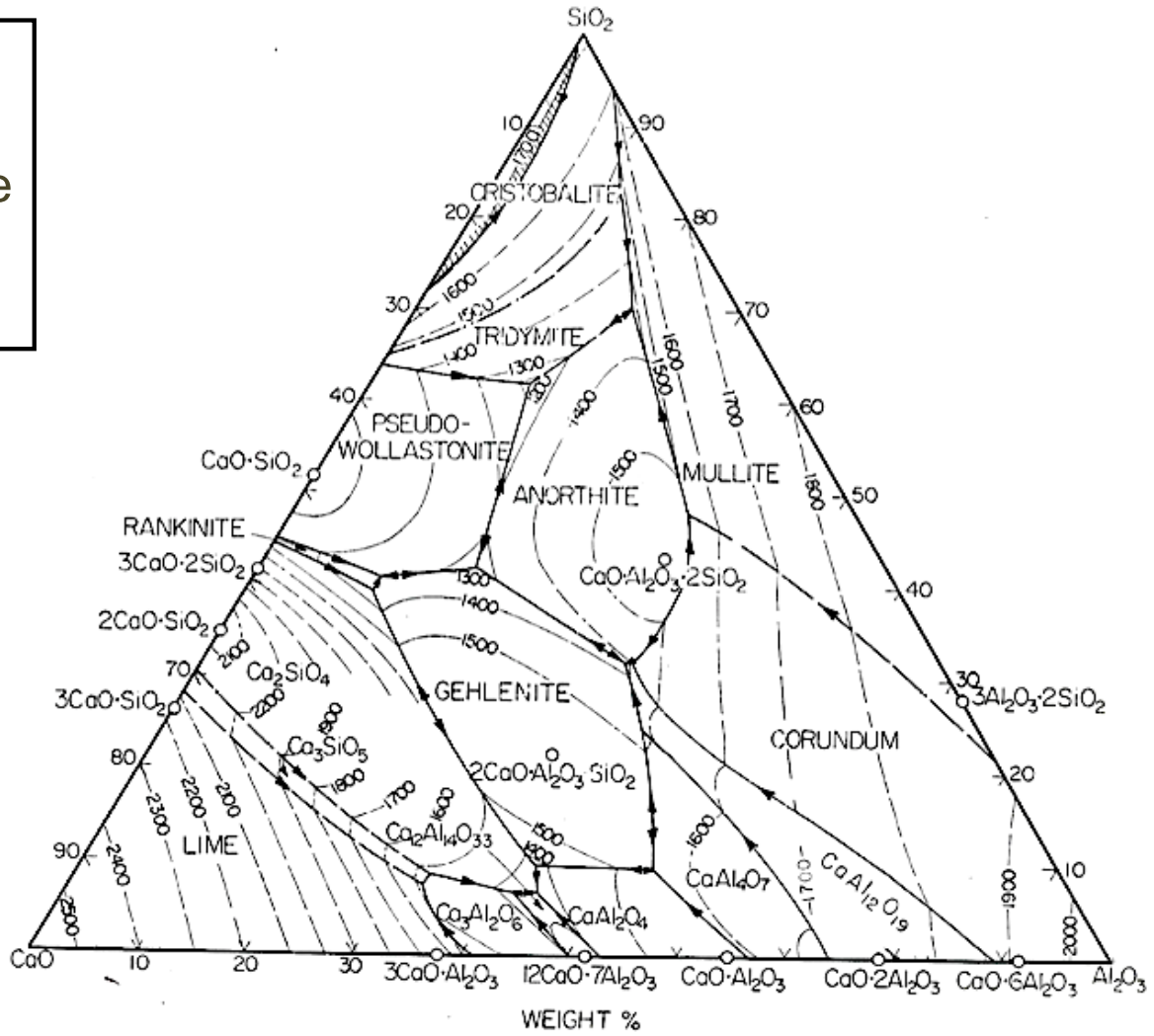
- Reaction product forms which slows down wear
  - Selective corrosion may occur, only certain phases in the refractory are attacked

Concept of saturation of slag with main refractory component



Prevent refractory corrosion:
Saturate slag with main refractory component

SiO_2-CaO-Al_2O_3-based slags with compositions in the all liquid phase field @ 1600˚C



Al_2O_3-based lining

Saturate slag with Al_2O_3 (since lining is Al_2O_3-based), i.e. move slag composition to phase boundary of (liquid & Al_2O_3) phase field

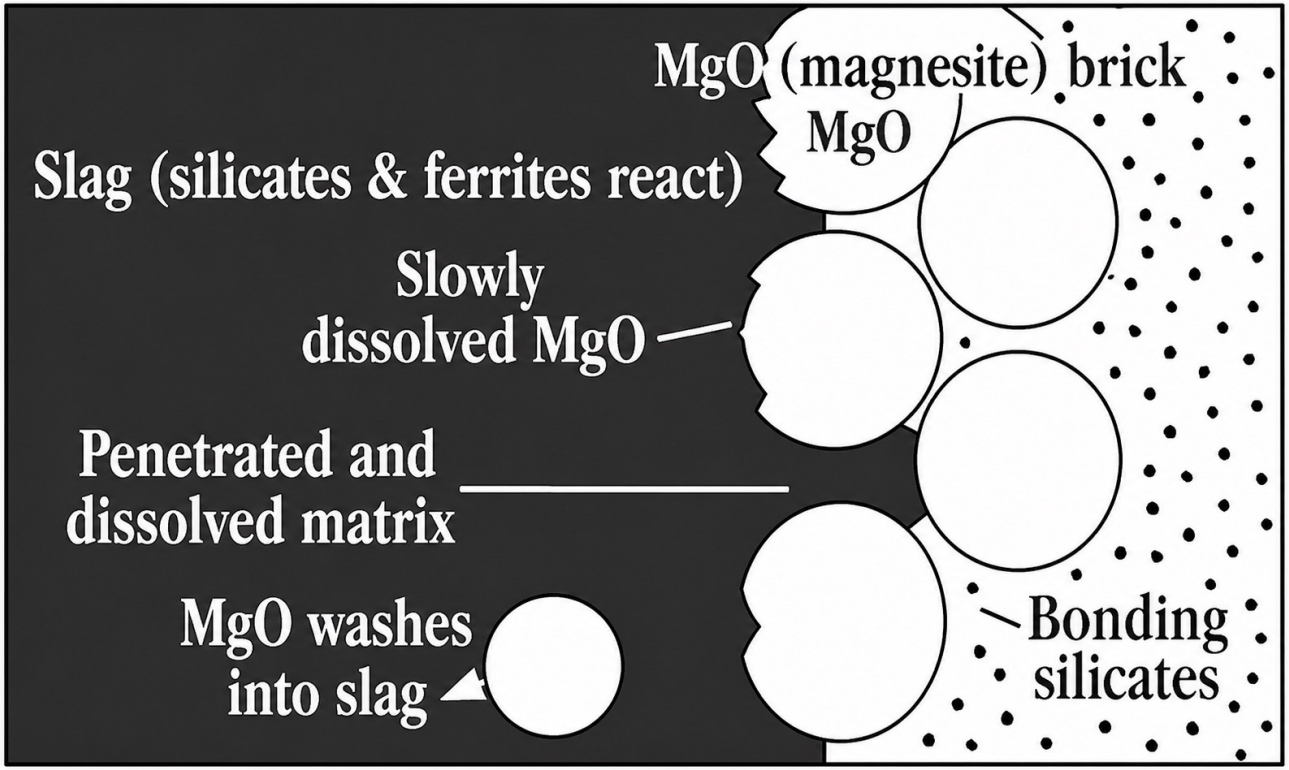
Refractory – slag reaction mechanisms: Alumina

- Refractory consists of Al_2O_3 or mullite with mixtures of Al_2O_3, mullite ($3Al_2O_3.2SiO_2$) and glass in the matrix phase
- Al_2O_3 brick in contact with MgO-saturated slag:
  - Wear is retarded through the formation of a spinel ($(Mg,Al,Fe)_3O_4$) boundary layer
- Al_2O_3 brick in contact with basic slags (lime bearing):
  - Wear by dissolving the glassy and mullite phases in the matrix
  - Corrosion is controlled by the CaO-Al_2O_3 reaction
- Al_2O_3 brick is much more resistant to a slag of lower basicity and MgO saturated

Refractory – slag reaction mechanisms: Alumina-chromia

- Refractory consists of Al_2O_3 and $(Al,Cr)_2O_3$ bonding phase
- Al_2O_3-Cr_2O_3 brick in contact with MgO-saturated slag:
  - Wear is retarded through the formation of a spinel ($(Mg,Al,Cr)_3O_4$) boundary layer
- Al_2O_3 brick in contact with basic slags (lime bearing):
  - Wear by attacking Al_2O_3 in grains and $(Al,Cr)_2O_3$ bonding phase
  - Corrosion is controlled by the CaO-Al_2O_3 reaction
- Al_2O_3 brick in contact with acidic slags:
  - Limited slag penetration and reaction

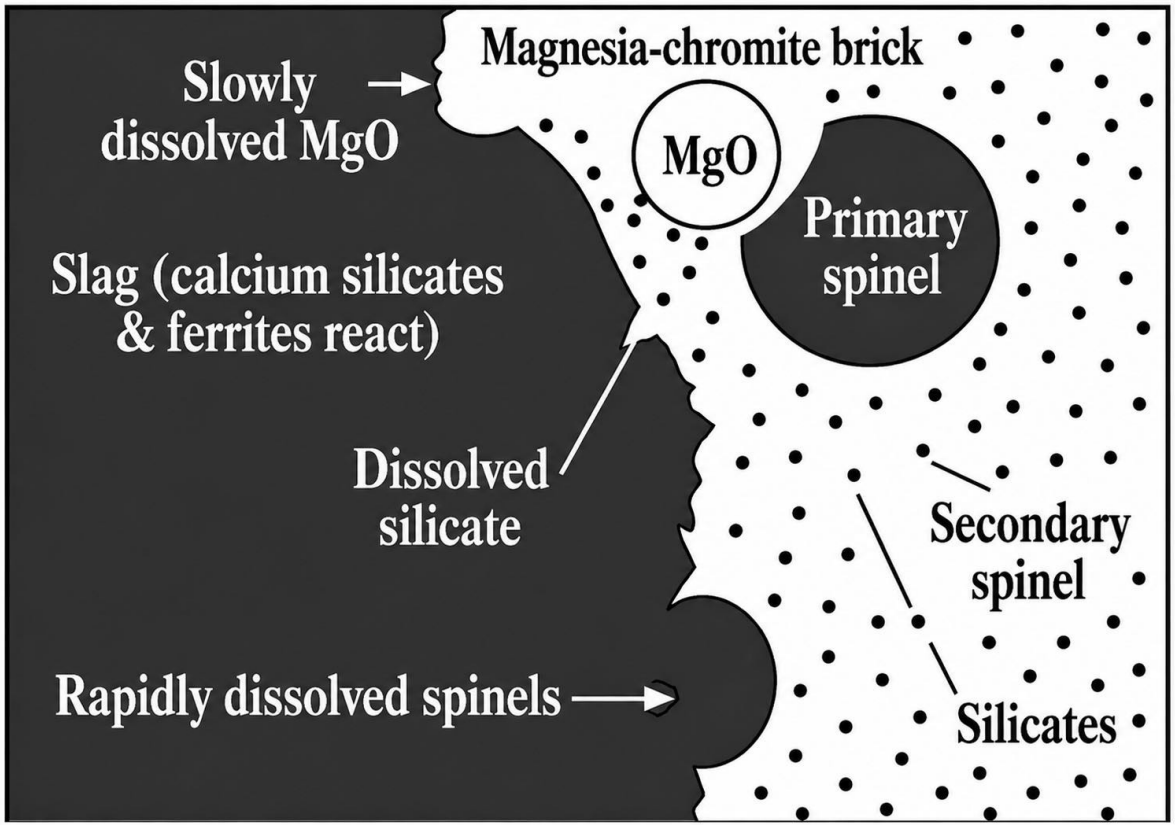
Refractory – slag reaction mechanisms: MgO



MgO refractories are more resistant to moderately basic and highly basic slags than magnesia-chromite refractories, provided the slag is saturated with MgO

- MgO bricks are **resistant to wear by ferritic slags**
- MgO bricks mainly **wear** by the dissolution of the **silicate bonding phase**
  - MgO grains can also dissolve if slag is not saturated with MgO
- MgO bricks are susceptible to penetration by fluid slags, which leads to **densification and spalling**

Refractory – slag reaction mechanisms: MgO-chromite brick



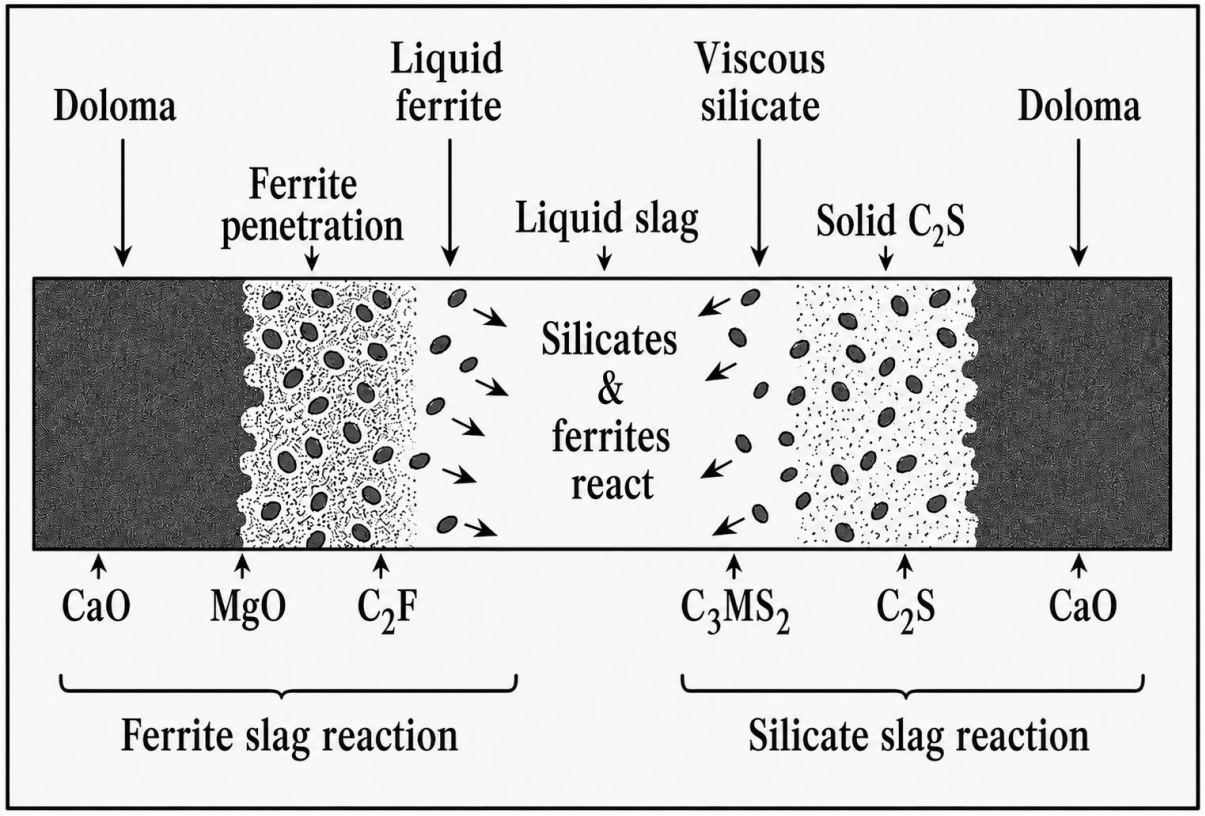
- Magnesia-chromite bricks are **less basic** than MgO or doloma bricks
- Bricks are bonded by and contain spinels
  - **Lime-rich slags dissolve bonding spinel phases**
- Magnesia-chrome bricks are resistant to slags of lower basicity when the slag is saturated with respect to MgO

Refractory – slag reaction mechanisms: MgO-$MgAl_2O_4$ bricks

- **Alumina-spinel brick vs. magnesia-chrome brick**:
  - Less subject to oxidation/reduction reactions
  - Better refractoriness and slag resistance, but more effort to produce

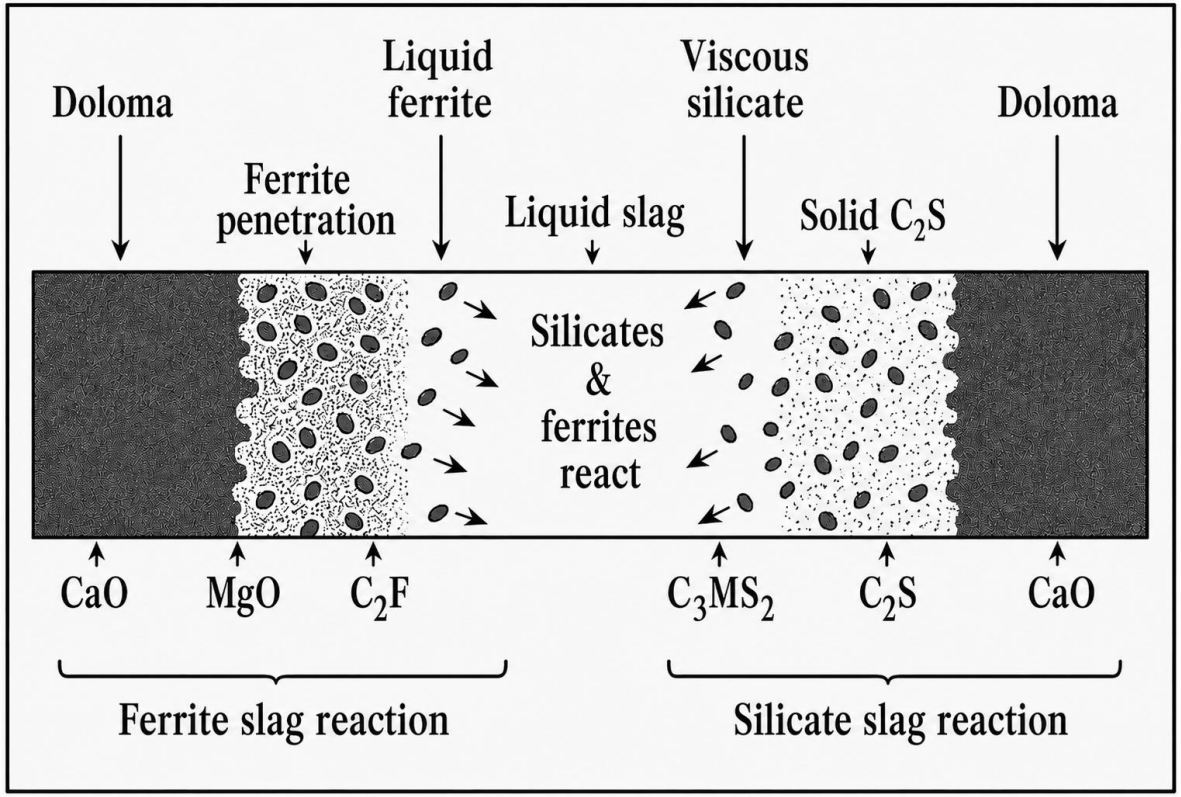
- General slag **wear mechanism is similar to magnesia- chromite** refractories:
  - High-lime slags preferentially dissolve the spinel phase
  - Lower lime, higher magnesia basic slags are most compatible with bricks that contain spinels

Refractory – slag reaction mechanisms: Doloma



- **Mainly wear through dissolution of the CaO**
- Doloma bricks can be used in contact with **silicate slags** that are not lime saturated, because **Ca_2SiO_4 / Ca_3SiO_5 boundary layer** forms
  - Corrosion reaction becomes boundary layer controlled, and wear rates are lowered

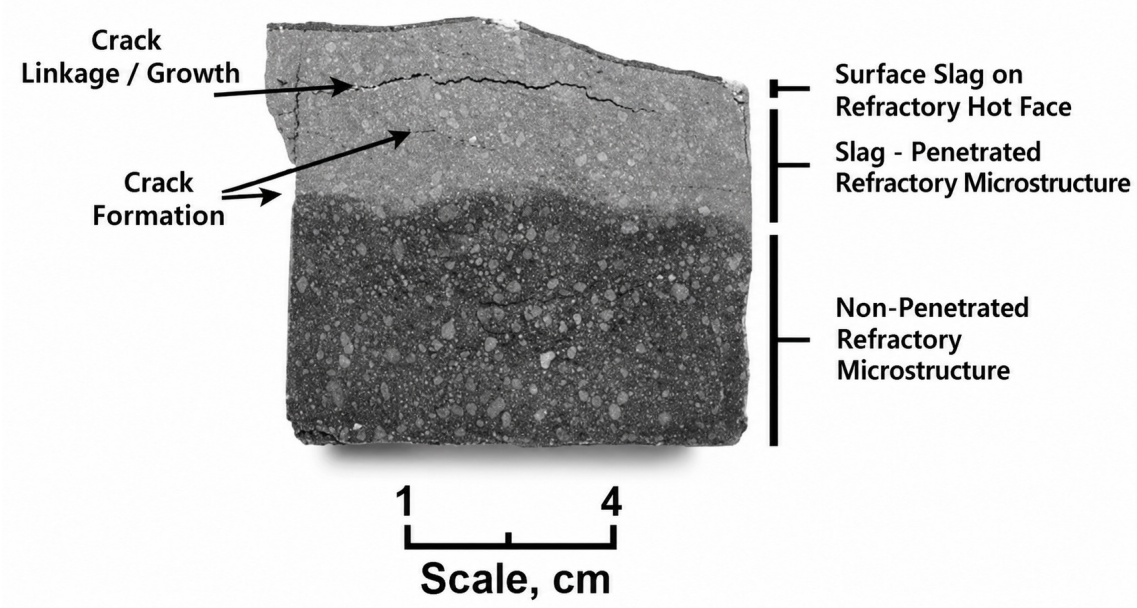
Refractory – slag reaction mechanisms: Doloma (cont.)



Ferritic slags: Reaction of the R_2O_3's with CaO forms liquid phases, i.e. no boundary layer, and slag can penetrate deep into the brick

- **CaO-deficient ferritic slag**:
  - Addition of **MgO** will reduce refractory wear by forming **spinels** with the unreacted R_2O_3's
  - Fluidity of the slag will be reduced
- **Calcium-aluminate ladle furnace slags**:
  - Will dissolve CaO from the brick, no boundary layer will form
  - Minimize refractory wear by limiting turbulence and ensuring MgO saturation is maintained

Structural spalling



(Bennett & Kwong, Met Trans A, 2011, 42A, p. 895)

- When **penetration** is more important than dissolution, spalling becomes a major wear mechanism

- Consequence of a corrosion penetration
  - Change in the texture of the refractory
  - Slag reduces the apparent porosity, causes differential expansion & development of stresses
  - Formation of microcracks, eventual disruptive cracks parallel to hot face
  - Cracking at interface between altered area and unaffected material