The hydration of MgO-based refractory materials

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OUTLINE

- Background
- Literature
- Projects completed at UP
- Work in progress
- Acknowledgements

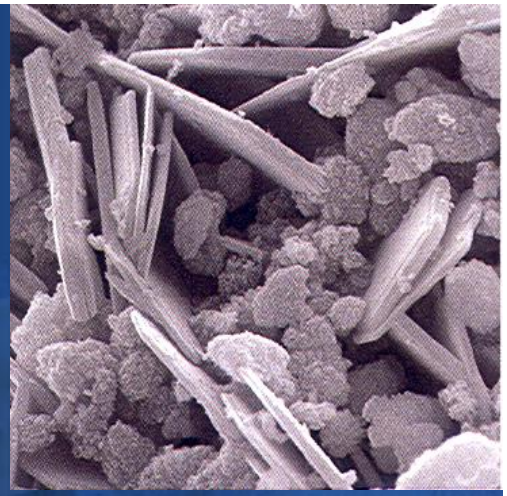
BACKGROUND

- **MgO-based refractory materials are widely used**
  - E.g. steel, titania, ferroalloy, copper, platinum, foundry, glass, cement industries
- **MgO-based refractory materials can potentially hydrate**
  - During transport, storage, installation, commissioning and operation, but also when water is mixed with refractory castables
- **Costs associated with replacing a MgO-based lining** amount to tens of millions of rands, depending on the size of the smelter
- **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

BACKGROUND (cont.)

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

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



Brucite crystals, 1:3000 (RHI)

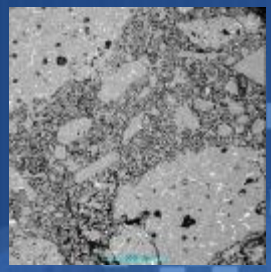
- **Brucite formation increases pH, allowing CO_2 to dissolve in water, generating H_2CO_3, and forming $MgCO_3$:**

$$MgO + H_2O + CO_2 \rightarrow MgO + H_2CO_3 \rightarrow MgCO_3$$

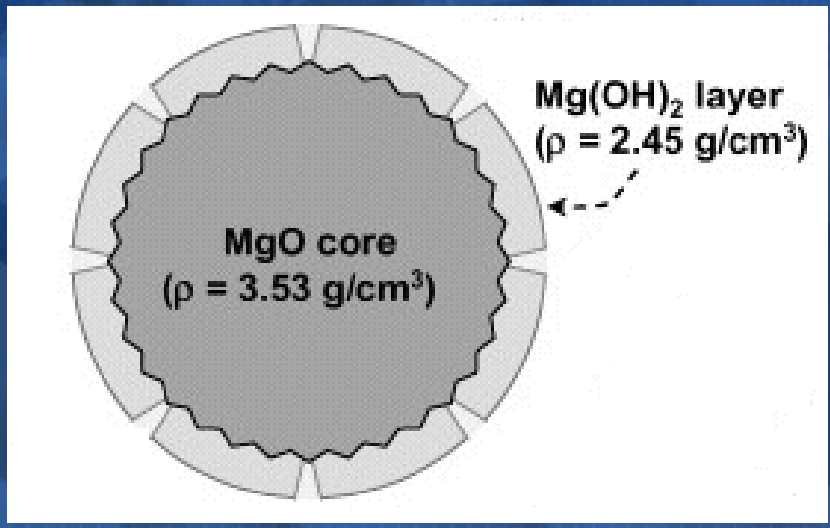
- **Also reports of white film of hydro-magnesite:**

$$Mg_5(CO_3)_4(OH)_2.4H_2O$$

BACKGROUND (cont.)



- **Why is MgO hydration a major concern in refractory formulations?**
  - 3-fold volumetric expansion due to differences in densities between MgO and $Mg(OH)_2$
    - Generates stress leading to severe mechanical damages, and premature degradation
    - Cracking increases available surface areas and further promotes the hydration process
    - Microstructure of the brick is not restored during re-firing
      - Loss of bond between aggregate and matrix
      - Increased porosity



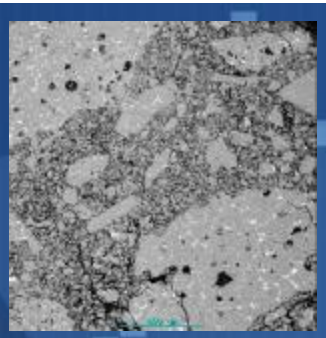
Salamao & Pandolfelli, 2008

BACKGROUND (cont.)

RHI

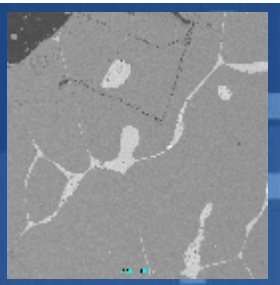
- **Partially hydrated MgO particles in castables**
  - Pre-cast shapes become distorted and brittle
  - Consequences on drying schedule
    - Decomposition of $Mg(OH)_2$ layer generate porosity, high surface area and reduced mechanical strength
- **Hydration protection**
  - $MgSO_4$ (kieserite), tar impregnation
  - Research on inhibiting hydration through additives, surface modification of grains
- **The Big Question**
  - **When can a MgO-based lining which had some hydration damage be used & when must it be replaced?**

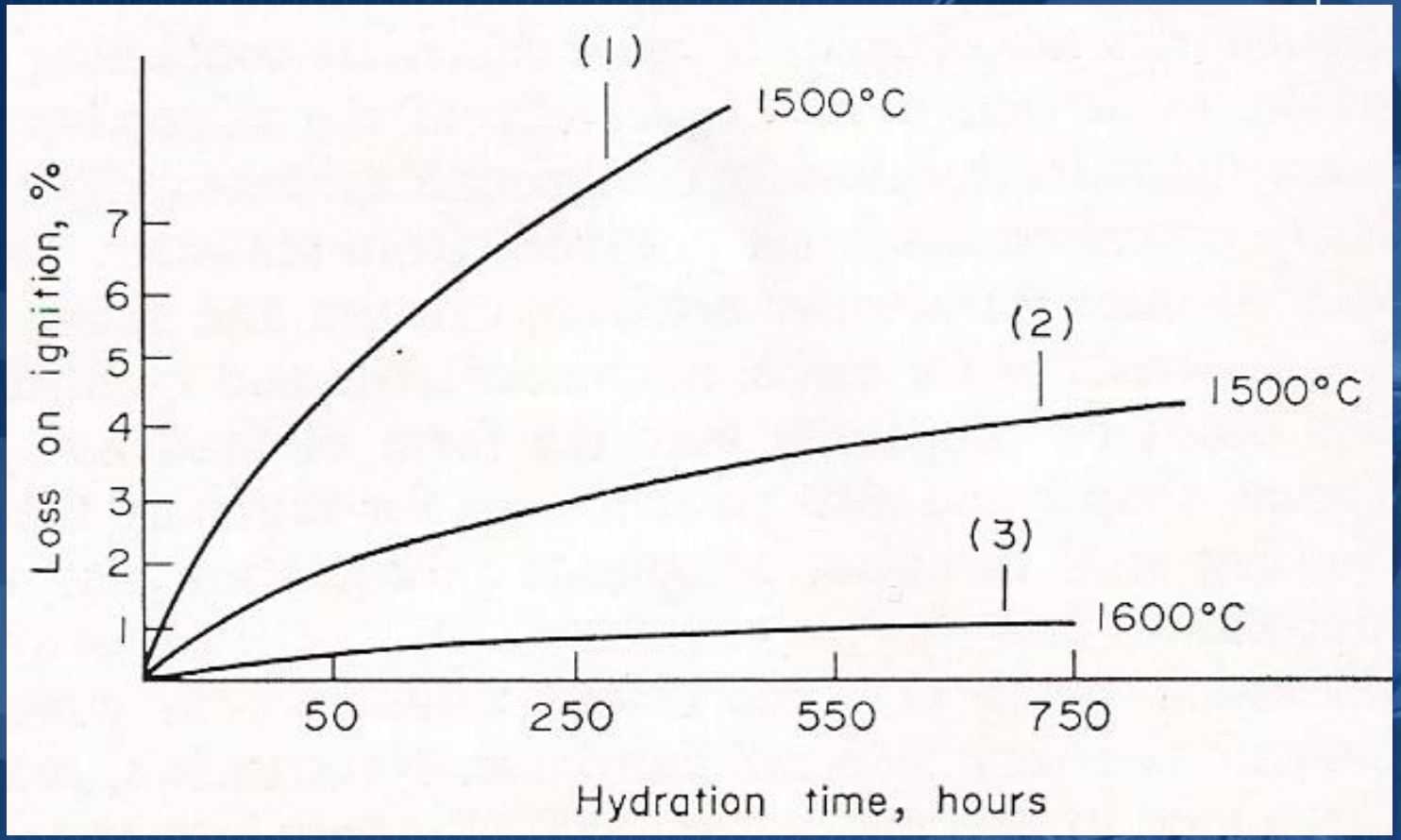
LITERATURE: Factors affecting hydration resistance of MgO-based refractories



- **Quality of MgO**
  - Microstructure and purity (type and amount of impurities)
  - Relative density, Porosity & Pore size distribution
  - Grain size, crystallite size & surface area
    - Processing parameters
      - Calcination and sintering temperatures
      - Holding time
- **Water vapour pressure**
- **Hydration temperature**
  - Cooling of calcined grains must be under lowest possible RH

LITERATURE: Hydration of magnesia refractories with different firing parameters

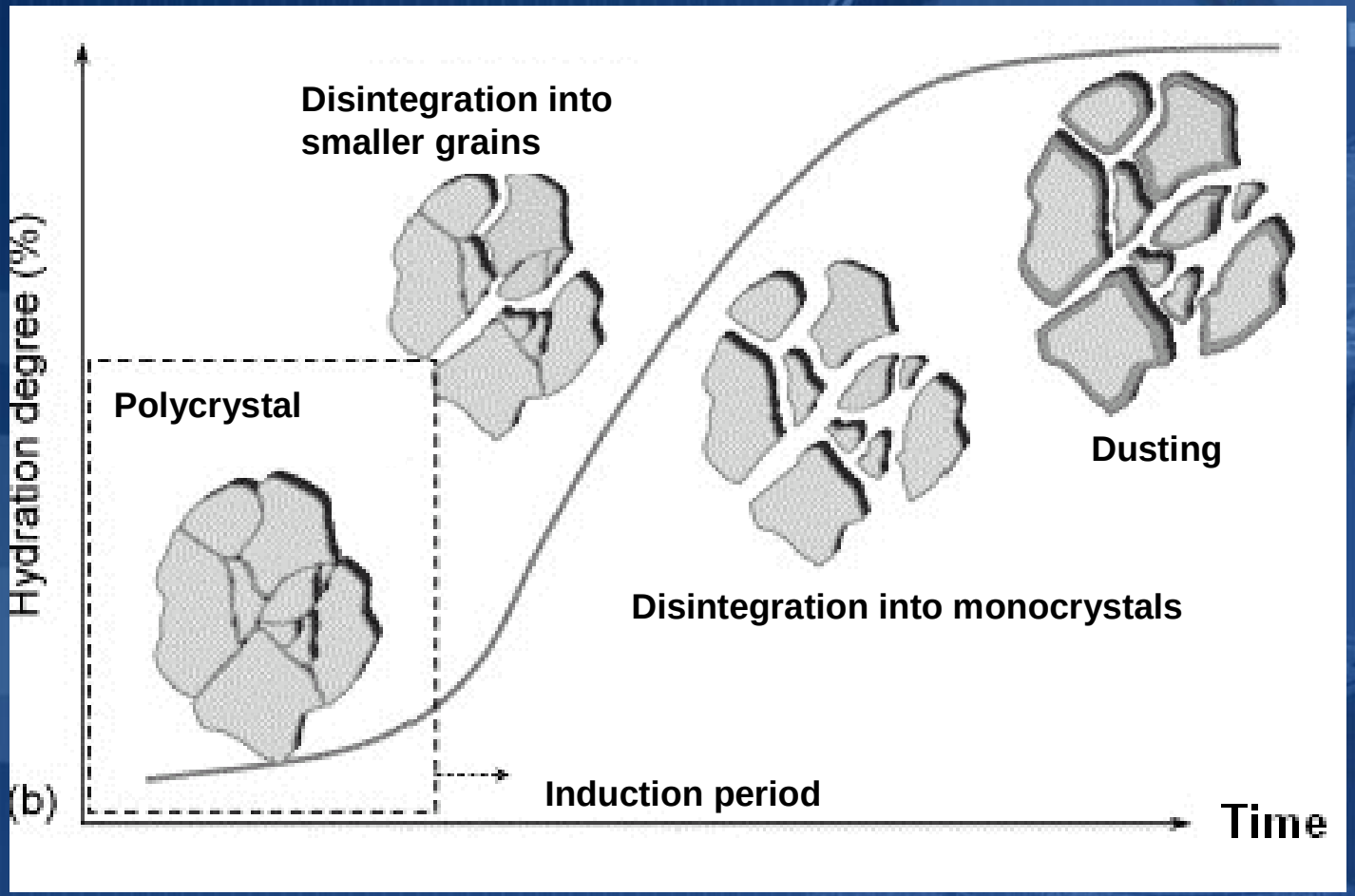




(Shaw, 1972)

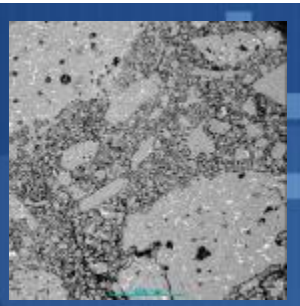
(1): Stored at 60°C (2): Stored at 40°C (3): Stored at 20°C

LITERATURE: Hydration mechanism of polycrystalline magnesia (Kitamura, Onizuka & Tanaka (1995))

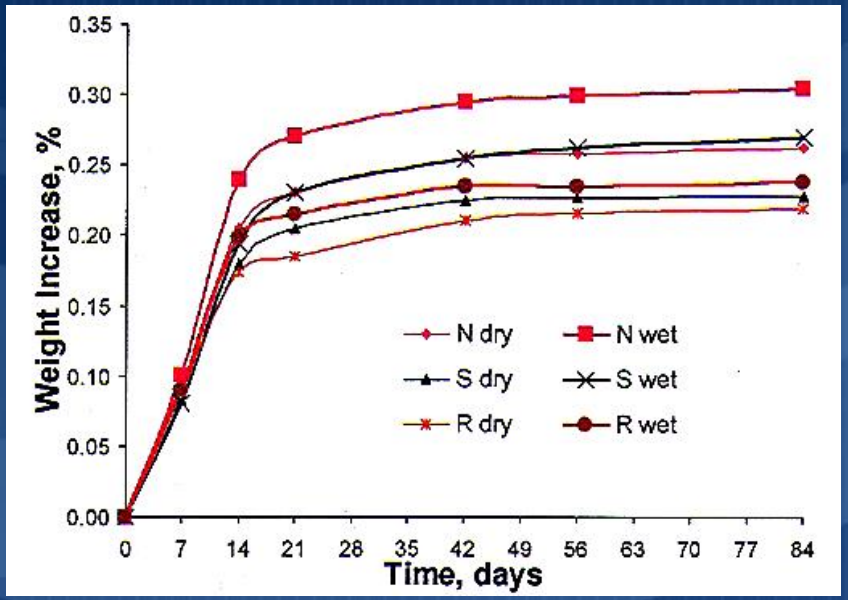


(Kitamura et al., 1995; Salomão et al., 2007)

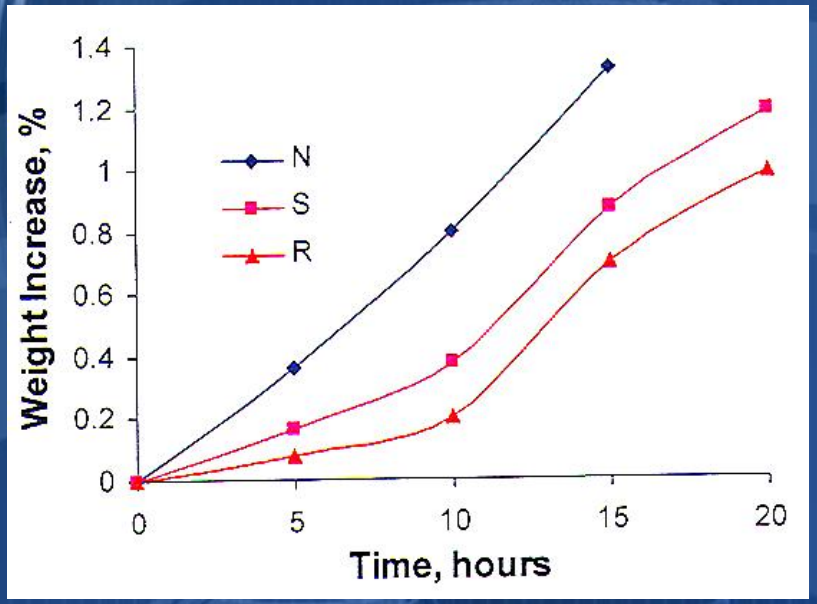
LITERATURE: Mechanisms of hydration (Lauzon, Rigby, Oprea, Troczynski, Oprea (2003))



Hydration under room conditions



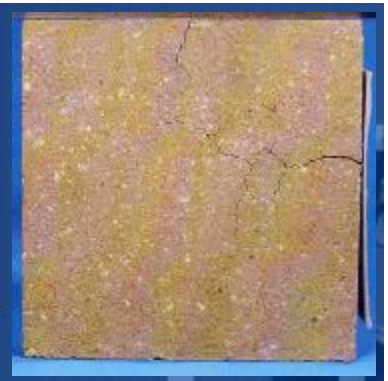
Hydration in autoclave under steam at 34.5 kPa



N: 96.2% MgO, C/S = 2.4; **S: 97.7% MgO, C/S = 2.2**

R: 95% MgO, C/S = 0.6

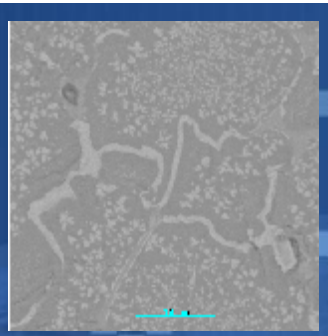
EXPERIMENTAL


RHI

- **Most common methods whereby hydration is evaluated:**
  - Measurement of LOI
  - XRD
  - TG / DTA
  - Infrared Spectroscopy
  - Young's modulus of elasticity (MOE)
- **Hydration tests are performed in**
  - Steam ovens / Hydration chambers
  - Autoclaves

FIRST FACT FINDING PROJECT:

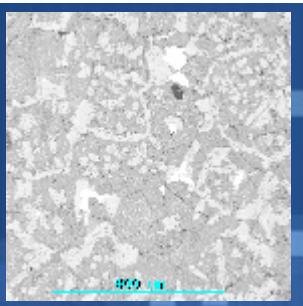
(D Swanepoel, 2008)

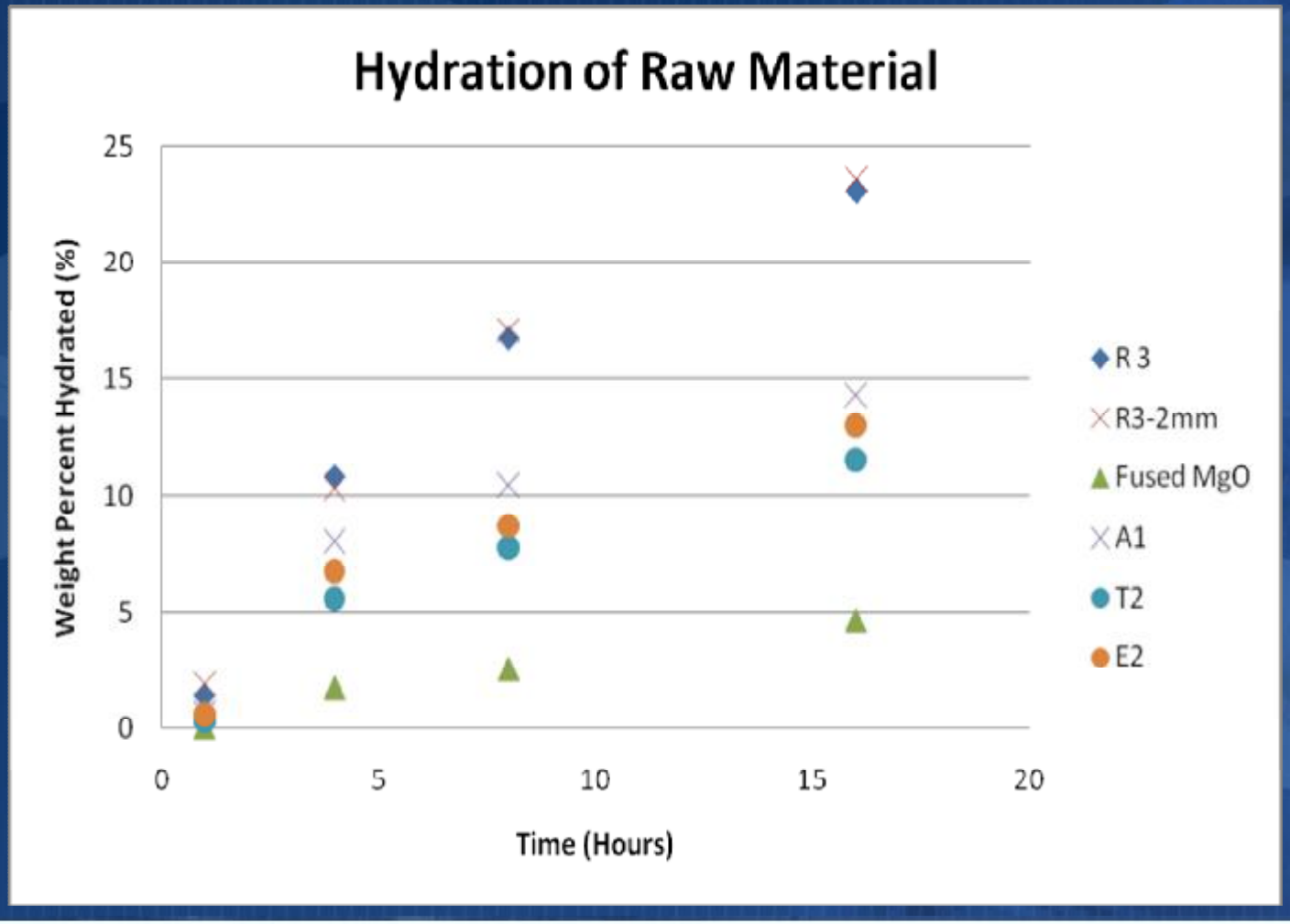


- **Hydration of various MgO-based raw materials:**
  - Sintered MgO
  - Fused grain MgO
  - Fused grain MgO-chrome
- **Hydration of refractory bricks:**
  - MgO-based bricks
  - MgO-chrome bricks

- **Using a steam oven at 80°C over extended periods of time**
- **Analyse samples:**
  - Calculation of % hydration vs. time
  - XRD
  - TG / DTA

Hydration of MgO-based raw materials: (D Swanepoel, 2008)





R3 = sintered MgO, C/S~3.7

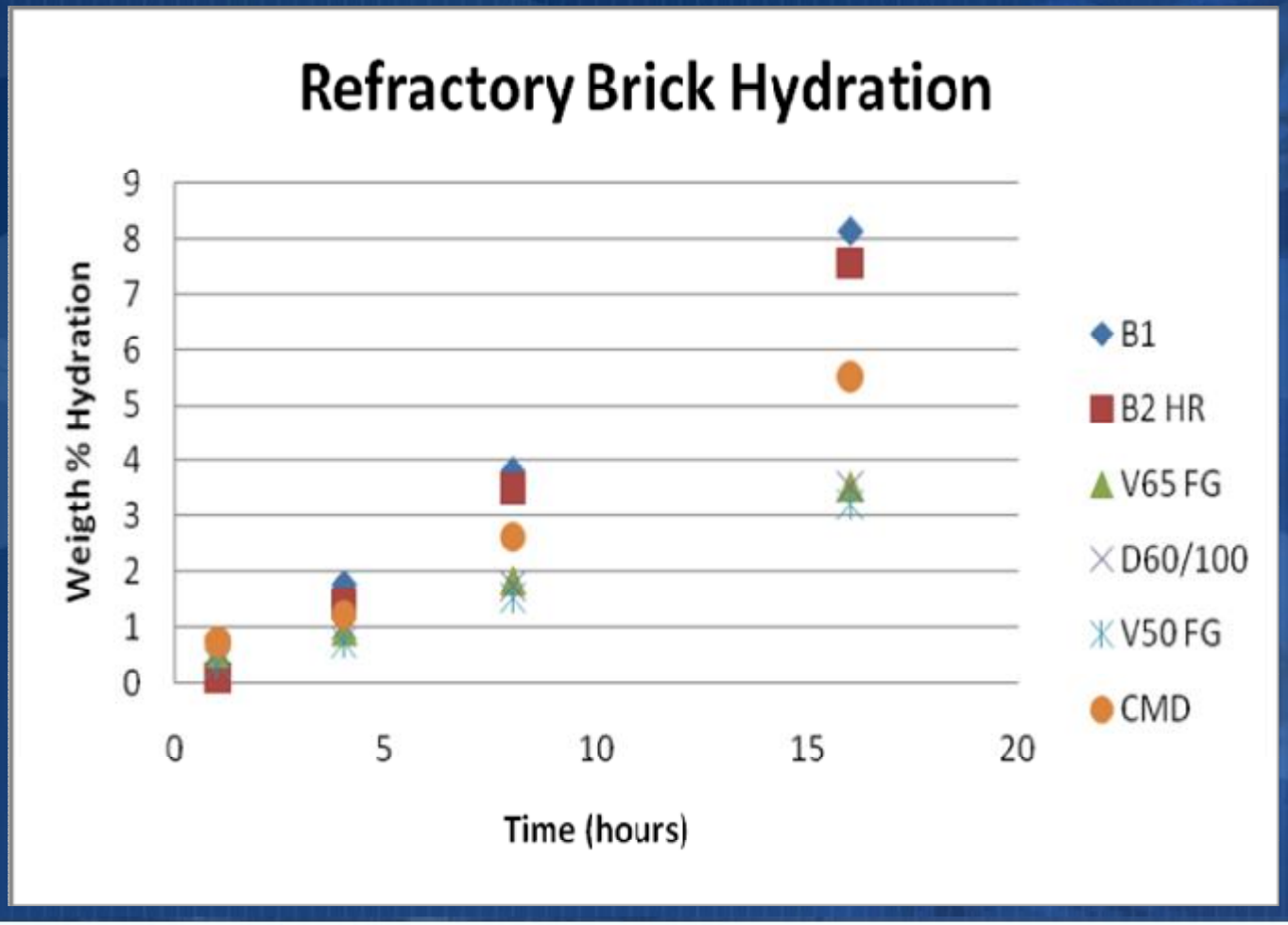
T2 = sintered MgO, C/S~1, high impurity content

Fused MgO, C/S~2

A1 = Mag-chrome, C/S~0.5

E2 = Mag-chrome, C/S~0.6

Hydration of MgO-based bricks: (D Swanepoel, 2008)



B1: MgO-based, C/S~3.5

B2HR: MgO-based, C/S~0.7

V65FG: Mag-chrome, C/S~0.6

D60/100: Mag-chrome, C/S~0.6

V50/FG: Mag-chrome, C/S~0.4

CMD: Mag-chrome, C/S~0.5

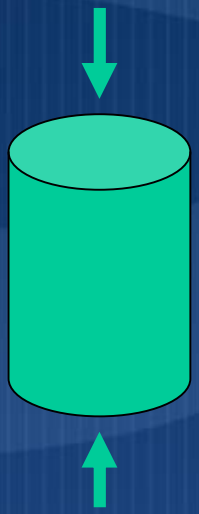
WORK IN PROGRESS:

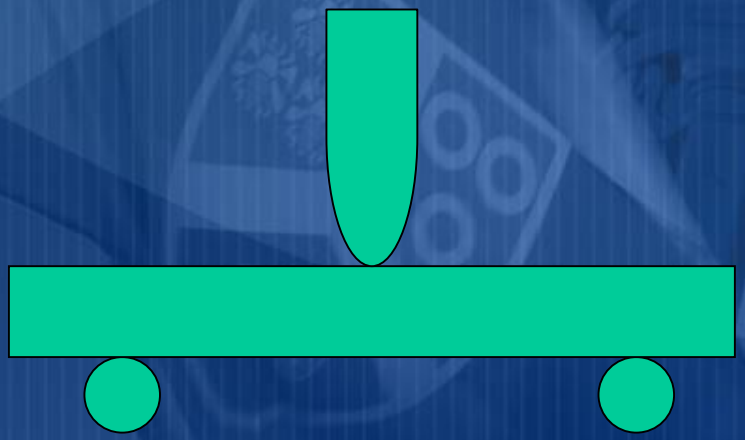
(Karabo Setlhare, 2009)

RHI

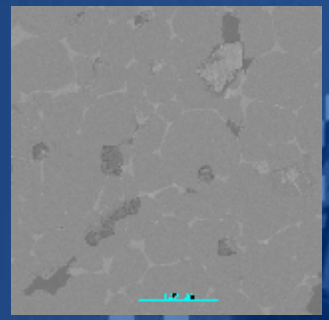
Relationship between the degree of hydration of MgO-based and kieserite-dipped MgO-based bricks and:

- CCS (cold crushing strength)
- Cold-MOR and Hot-MOR (modulus of rupture)





WORK IN PROGRESS:



- **'Time before hydration' test**
  - Role of adsorbed H_2O film in hydration reaction

- **'Find' a mobile, user friendly hydration testing device, whereby the extent of hydration of MgO-based refractory linings can be evaluated in a non-destructive manner**

  - MEng(Metallurgy), Starting Aug. 2009

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- **Students & UP:**
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  - Karabo Setlhare
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  - RHI
  - Vereeniging Refractories
  - Vesuvius SA