



# 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  $\sim 270^\circ\text{C}$  to form brucite:



Brucite crystals,  
1:3000 (RHI)

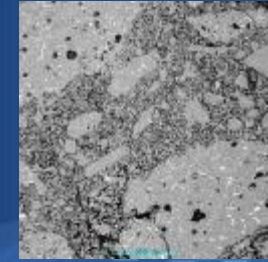
- Brucite formation increases pH, allowing  $\text{CO}_2$  to dissolve in water, generating  $\text{H}_2\text{CO}_3$ , and forming  $\text{MgCO}_3$ :



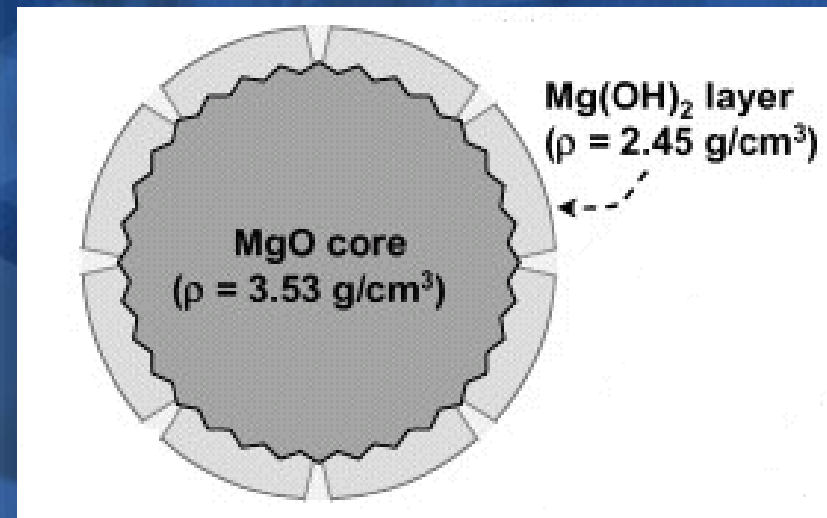
- Also reports of white film of hydro-magnesite:



# 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)<sub>2</sub>
    - 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

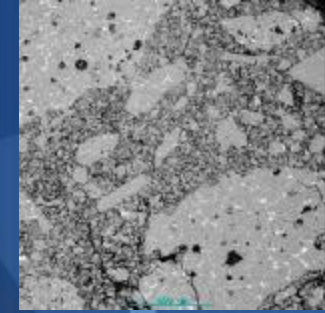
# BACKGROUND (cont.)



RHI

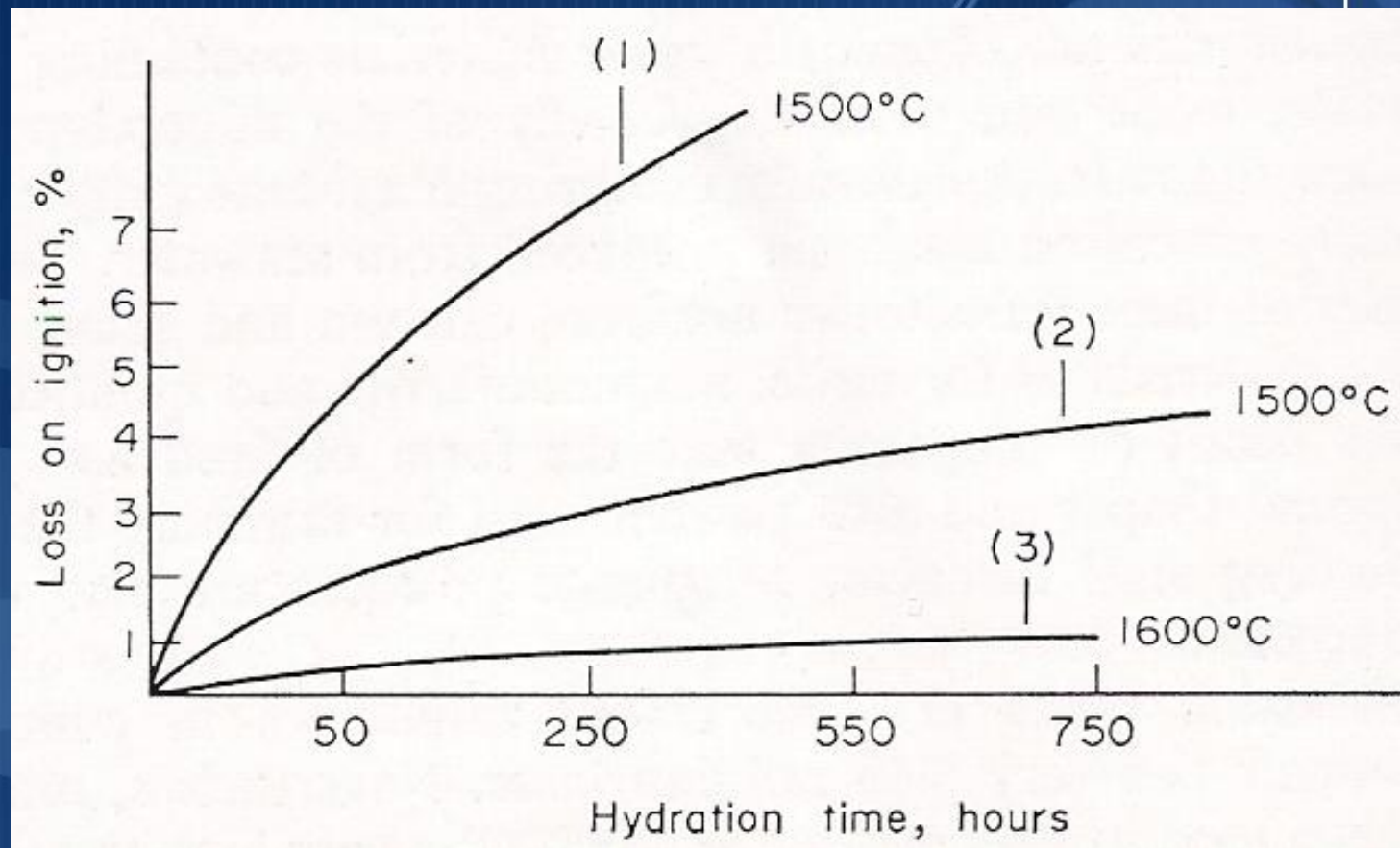
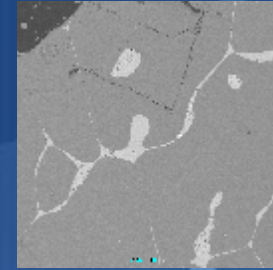
- **Partially hydrated MgO particles in castables**
  - Pre-cast shapes become distorted and brittle
  - Consequences on drying schedule
    - Decomposition of  $\text{Mg}(\text{OH})_2$  layer generate porosity, high surface area and reduced mechanical strength
- **Hydration protection**
  - $\text{MgSO}_4$  (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



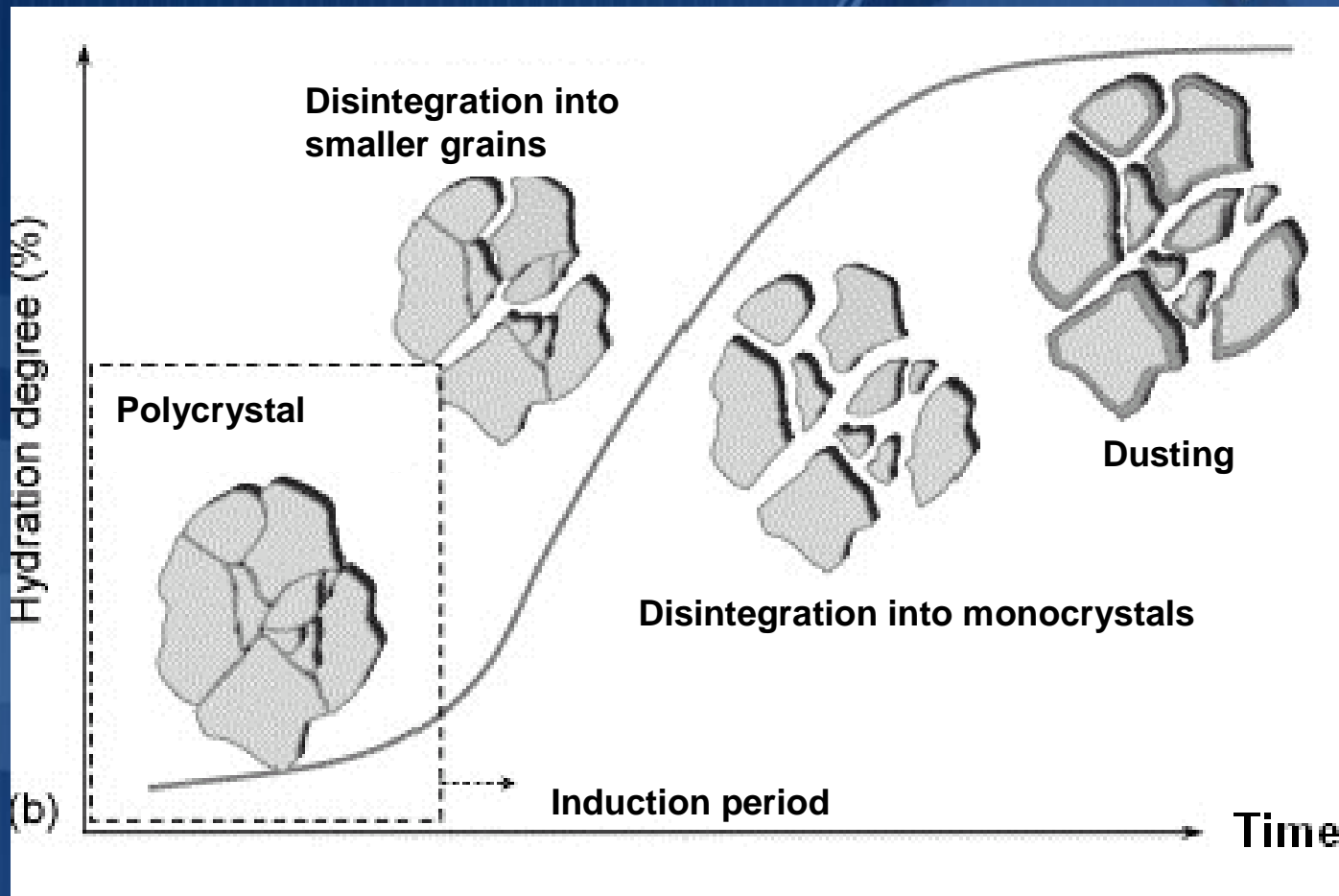
(Shaw, 1972)

(1): Stored at 60°C

(2): Stored at 40°C

(3): Stored at 20°C

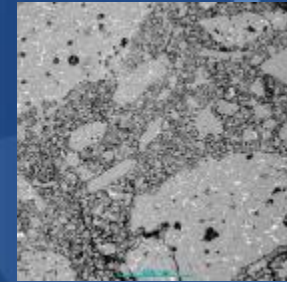
# LITERATURE: Hydration mechanism of polycrystalline magnesia (Kitamura, Onizuka & Tanaka (1995))



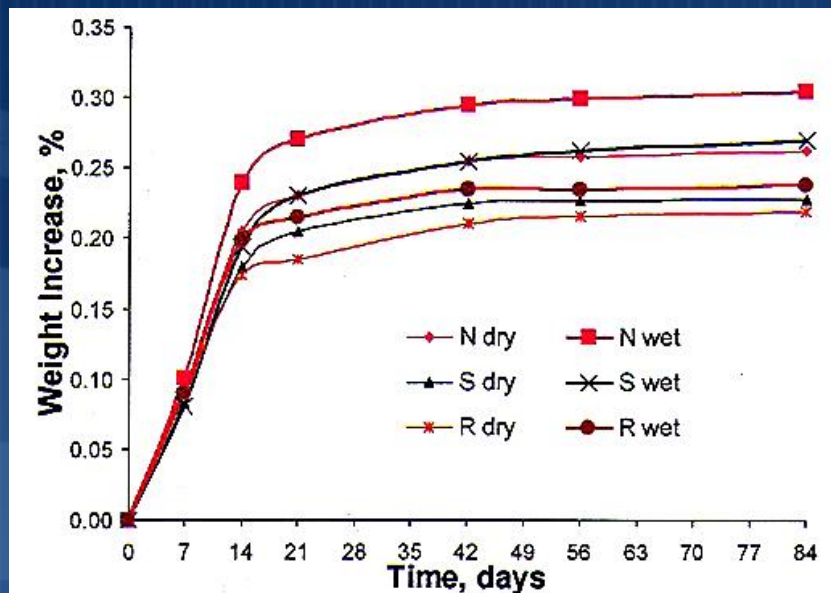
(Kitamura et al., 1995; Salomão et al., 2007)

# LITERATURE: Mechanisms of hydration

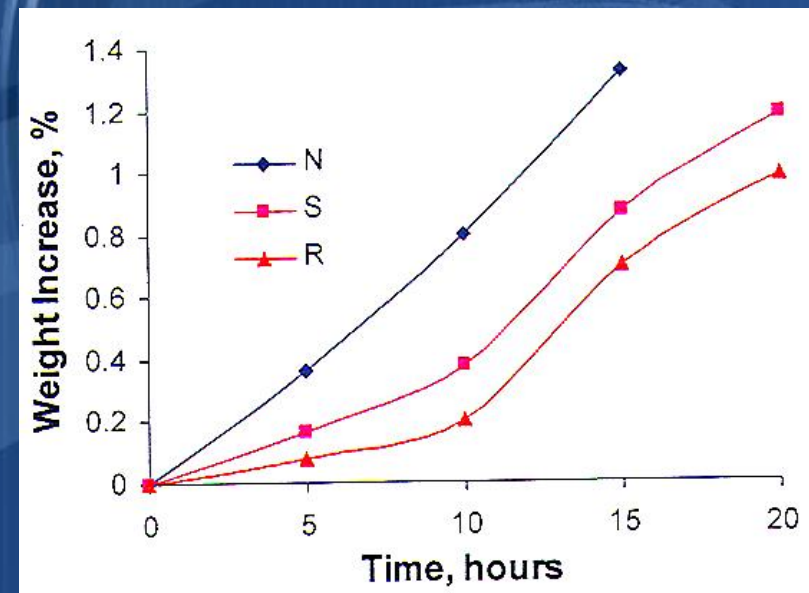
(Lauzon, Rigby, Oprea, Troczynski, Oprea (2003))



## 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

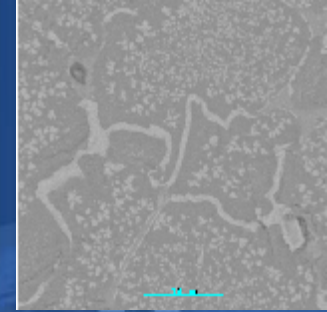


RHI

- **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:

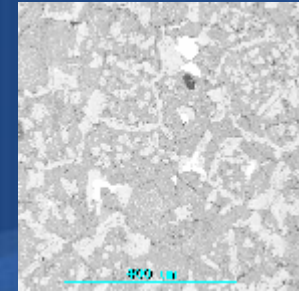
(D Swanepoel, 2008)



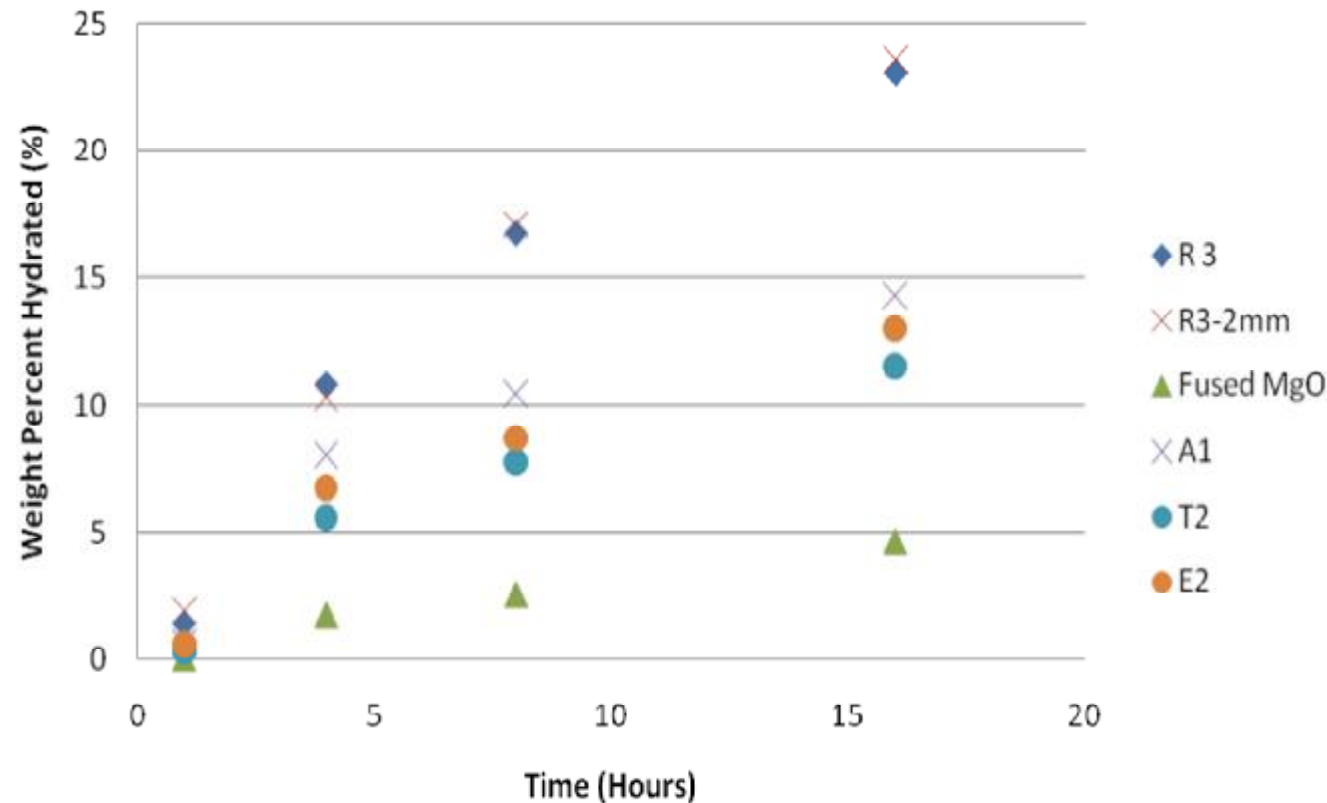
- **Hydration of various MgO-based raw materials:**
  - Sintered MgO
  - Fused grain MgO
  - Fused grain MgO-chrome
- **Hydration of refractory bricks:**
  - MgO-based bricks
  - MgO-chrome bricks
- **Using a steam oven at 80°C over extended periods of time**
- **Analyse samples:**
  - Calculation of % hydration vs. time
  - XRD
  - TG / DTA



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



## Hydration of Raw Material



**R3** = sintered MgO,  
C/S~3.7

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

**Fused MgO**, C/S~2

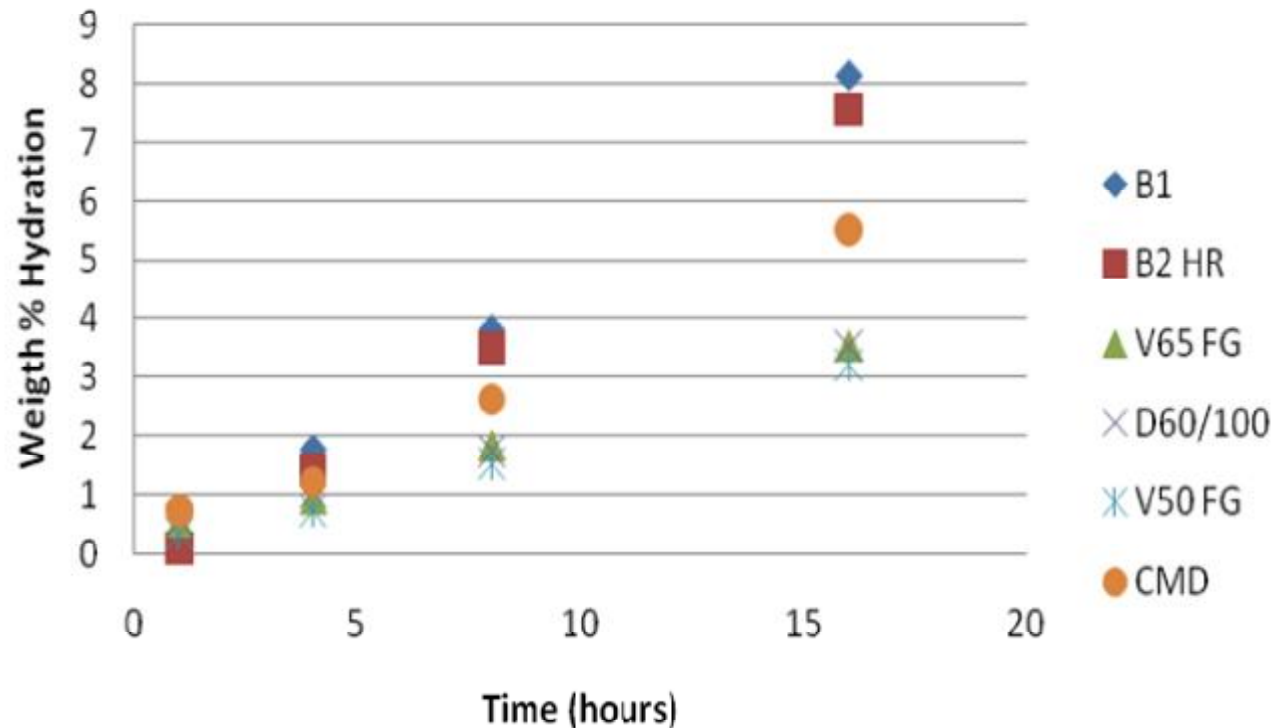
**A1** = Mag-chrome,  
C/S~0.5

**E2** = Mag-chrome,  
C/S~0.6

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



## Refractory Brick Hydration



**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:

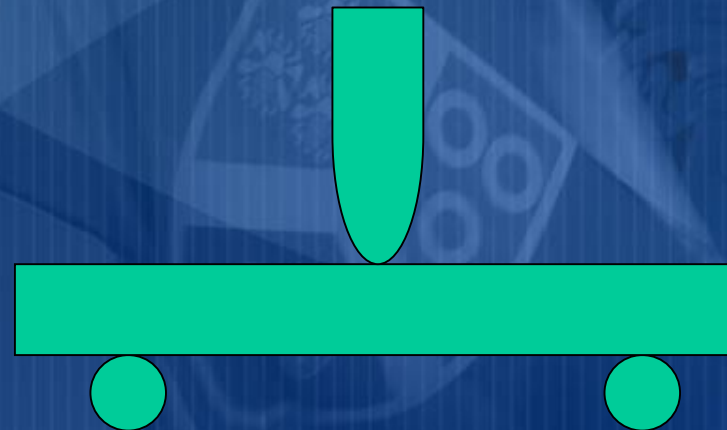
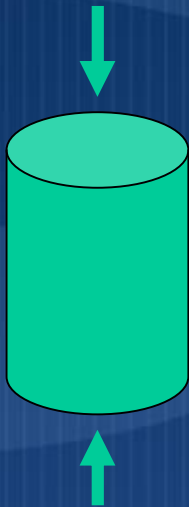
(Karabo Setlhare, 2009)



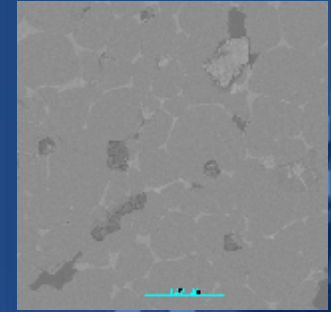
RHI

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<sub>2</sub>O 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

# Acknowledgements



- **Students & UP:**
  - Dewald Swanepoel
  - Karabo Sethlare
  - Department of Civil Engineering
  
- **Support from industry:**
  - Hatch SA & Lonmin
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  - Vereeniging Refractories
  - Vesuvius SA