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Low carbon, green, high quality refractories

Preventing Crack Formation in Magnesia Castables Using Novel Binder System and Drying Agent

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Cracking in MgO castables – a well-known problem

- MgO castables not widely used
- Limited work on MgO rich systems (pure MgO, MgO-SiO_2-H_2O gel bonded) and industrial scale samples
- Elkem started research (1989) on a binder system for basic castables
  - Reaction between MgO fines, microsilica (SiO_2) and water

«Cement-free binder»

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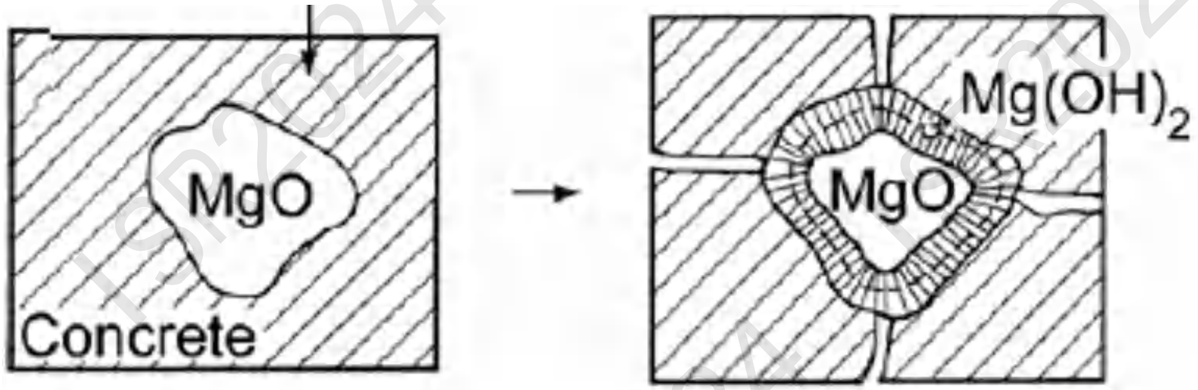
Root cause for cracking: MgO hydration

- When magnesium oxide hydrates to magnesium hydroxide an expansion will follow.

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

S.G. = 3,58 S.G. = 2,36

Vol $_{exp.}$ = 2.5 times

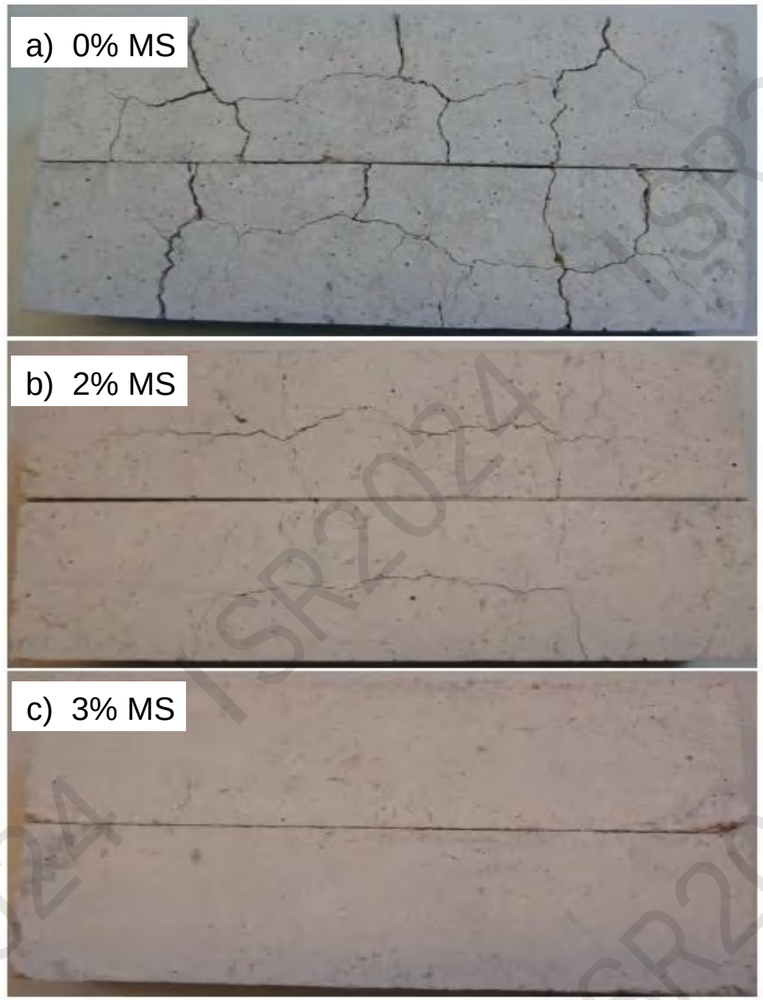


Crack formation (or slaking)

Crack formation (or slaking) caused by brucite formation takes place during both **curing and/or dryout process.**

BETTINA HEIDBERG1, 2, THOMAS BREDOW1, KLAUS LITTMANN2, KARL JUG1, Materials Science-Poland, Vol. 23, No. 2, 2005*

Microsilica as anti-hydration agent



40x40x160mm (lab-scale)

$MgO-SiO_2-H_2O$ gel bonded MgO castable

- Microsilica suppresses the hydration of MgO and subsequently avoids cracking in pure MgO system
- Min. 3 wt% microsilica is necessary to produce crack-free samples

H. Peng, B. Myhre and M. Luo, “New additive packages for self-flowing high-alumina and MgO based refractory castables.” Proceeding of ALAFAR 2012, Cancun, Mexico, Nov. 5-8, 2012

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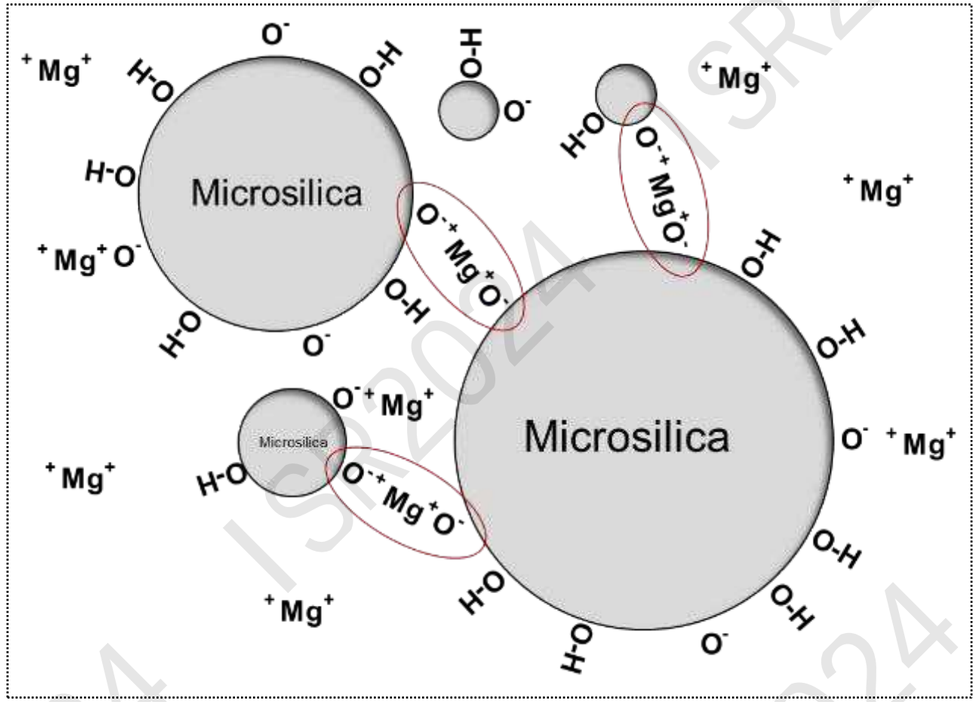
The role of microsilica in MgO castables: green binder and anti-hydration agent



MgO-SiO_2-H_2O gel bond

- Negatively charged silanol groups are covering the microsilica surface and in the presence of water/humidity will react with dissolved Mg^{2+} to form silica gel bond
- Microsilica partly dissolves at high pH and reacts with $Mg(OH)_2$ to form a protective coating on the MgO particles

$$\mathbf{HSiO_3^- + Mg(OH)_2 + H_2O \rightarrow MgHSiO_4 \cdot 2H_2O}\ \text{(M-S-H)}$$

- This compound (M-S-H) promotes resistance to brucite formation and is the precursor of forsterite, which provides mechanical strength after firing.

H. Peng, B. Myhre, Elkem, Norway: The hydration behaviour of MgO-SiO_2-H_2O gel bonded MgO castables Presented at the ALAFAR Congress 2014, Santiago, Chile, Oct. 28-31, 2014

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Objectives

- Understand the hydration mechanism of MgO in Magnesia castables based on **industrial** scale samples
- Investigate the drying behaviour of industrial-scale MgO specimens by using **Macro-TGA** and a **speciality drying agent**
- Develop **sustainable MgO castables** by **controlling hydration and drying behaviour**

MgO hydration/crack-formation in MgO castables based on industrial-scale samples

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Experimental

(Weight %)		SF-8	SF-6	SF-6*	VF-6
Synthetic DBM	0-5 mm	65	63	63	71.5
	100 mesh	6	10	10	11
	325 mesh	19.5	19.5	21	10
Elkem Microsilica®	971U	7.5	5.5	6	5.5
SioxX®-Mag		2	2		2
Dispersant-A				0.25	
Water		5.5	5.5	5.5	4.5
q-value		0.24	0.26	0.26	0.28

Variables

- Microsilica dosage/q-value
- Dispersant: SioxX®-Mag vs. Dispersant-A
- Dimensions (sizes and thickness)

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Novel Green Binder System (Cement-free)

- Binder system: $MgO\text{-}SiO_2\text{-}H_2O$ gel bond
- SioxX®-Mag, purposely designed to overcome the cracking problem of magnesia castables; the dosage is 2wt%, which brings the silica content of the mixes to a total of 6wt% for SF-6 and VF-6, and to 8wt% for SF-8

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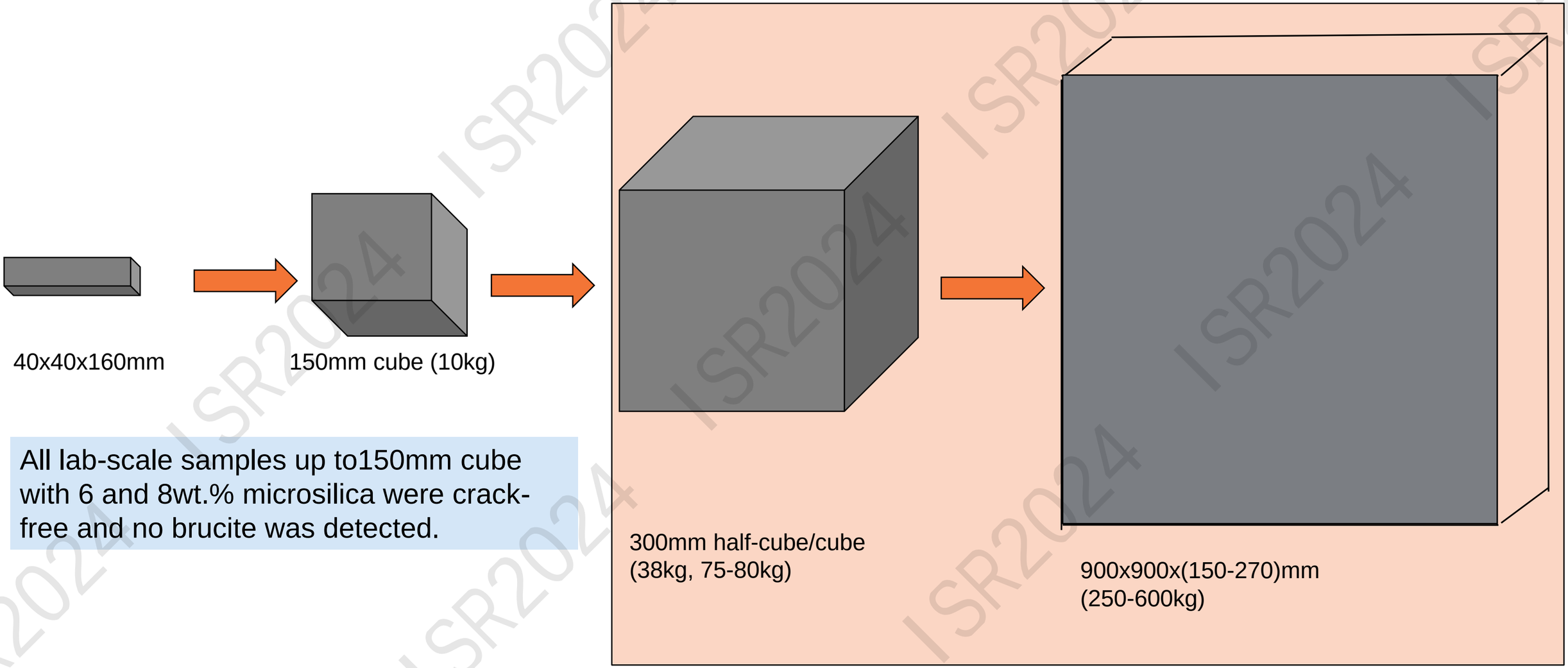
Sample preparation: various sizes



All lab-scale samples up to150mm cube with 6 and 8wt.% microsilica were crack-free and no brucite was detected.

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MgO blocks (38kgs) with 6% microsilica content

300mmx300mmx150mm dried at 150ºC for 12 hours.

- After demoulding, all blocks were perfect.
- After drying, cracks were only observed in the block of SF-6*; no cracks were observed in other blocks containing SioxX®-Mag.

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H. Peng and B. Myhre, “Cracking of MgO based castables – a challenge of the past?” The 63rd International Colloquium on Refractories (ICR), Aachen, Germany, Sept. 2020.

Blocks (75kg) with different microsilica content

300x300x300mm @ 150˚C for 12 hrs

- After demoulding, all blocks were perfect;
- After dry-out at 150 ° C for 12 hours, the block containing 8 wt% microsilica was perfect; whereas cracks were observed in the blocks with 6 wt% microsilica

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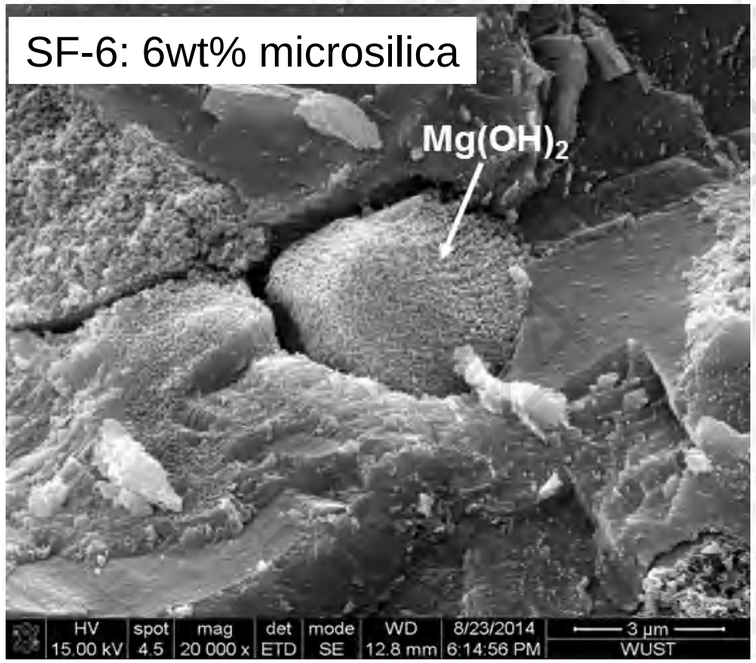
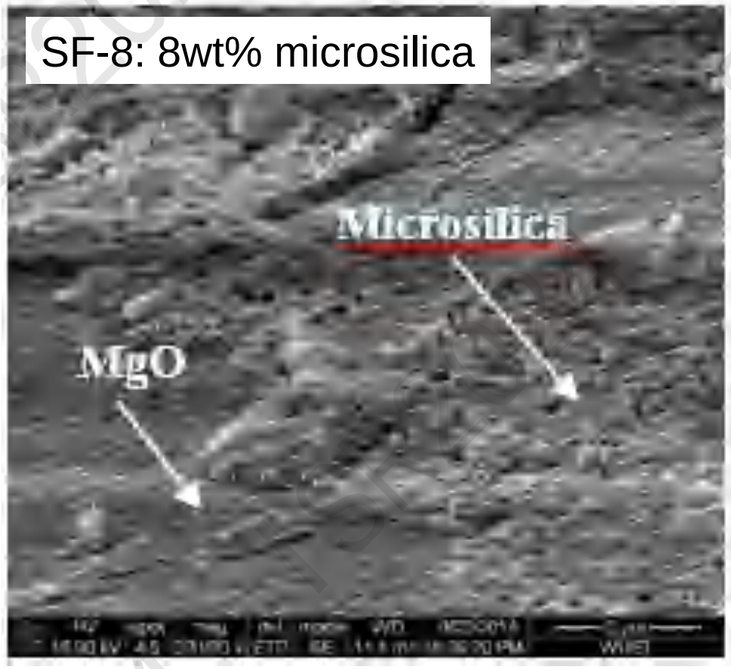
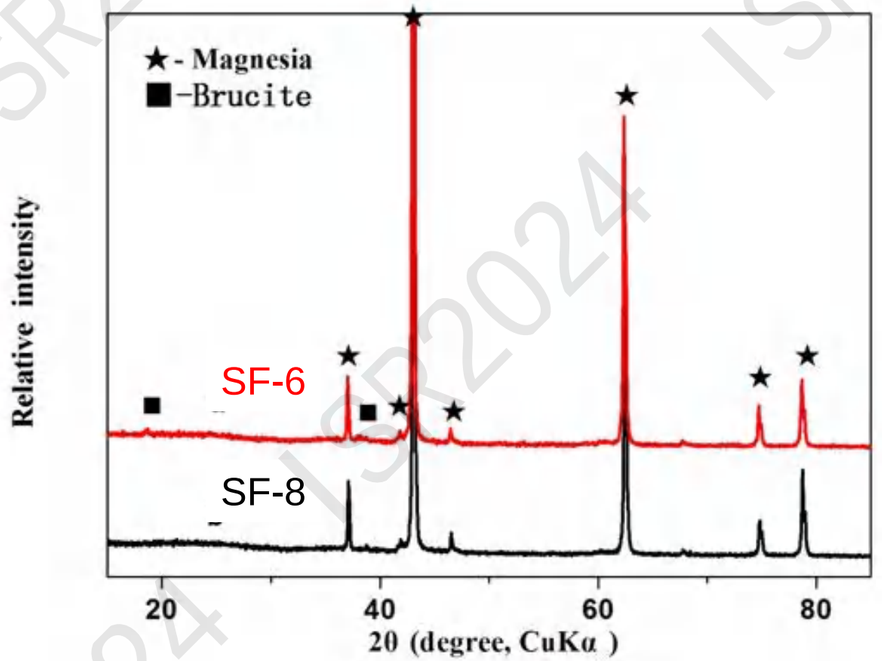
SEM and XRD characterization after dry-out at 150°C for 12hrs







- In sample SF-6 (6wt% microsilica), fibrous, rosette-like, brucite ($Mg(OH)_2$) is observed in the boundary area between the MgO aggregates and the matrix; no brucite is observed in sample SF-8 containing 8wt% microsilica

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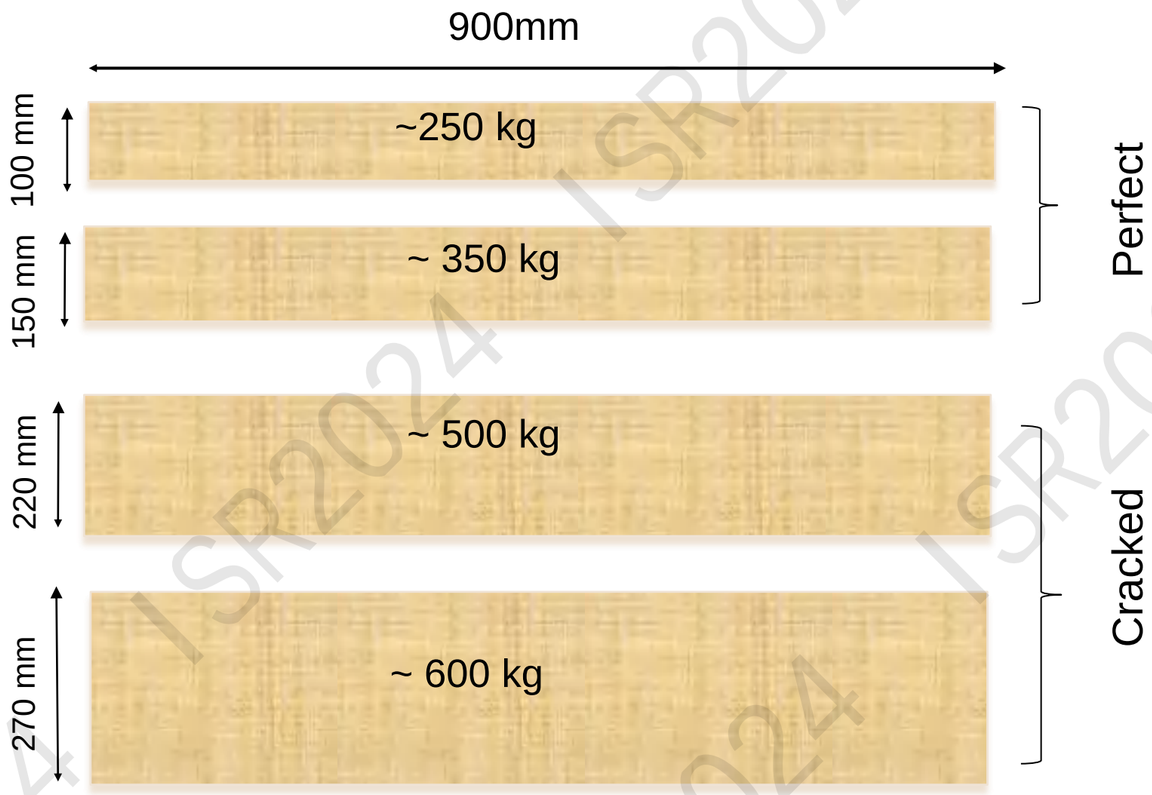
Castable SF-8: Block dimensions and cracking tendency after dry-out



- Castable SF-8 was selected for production of larger specimens (250 to 600kgs)
- At demoulding after one day, all blocks were perfect, no cracks were observed
- After air-curing for another day at ambient temperature, all blocks were dried at 350 ° for 10hrs

- The thickness of castable block has a strong impact on the crack formation during dry-out

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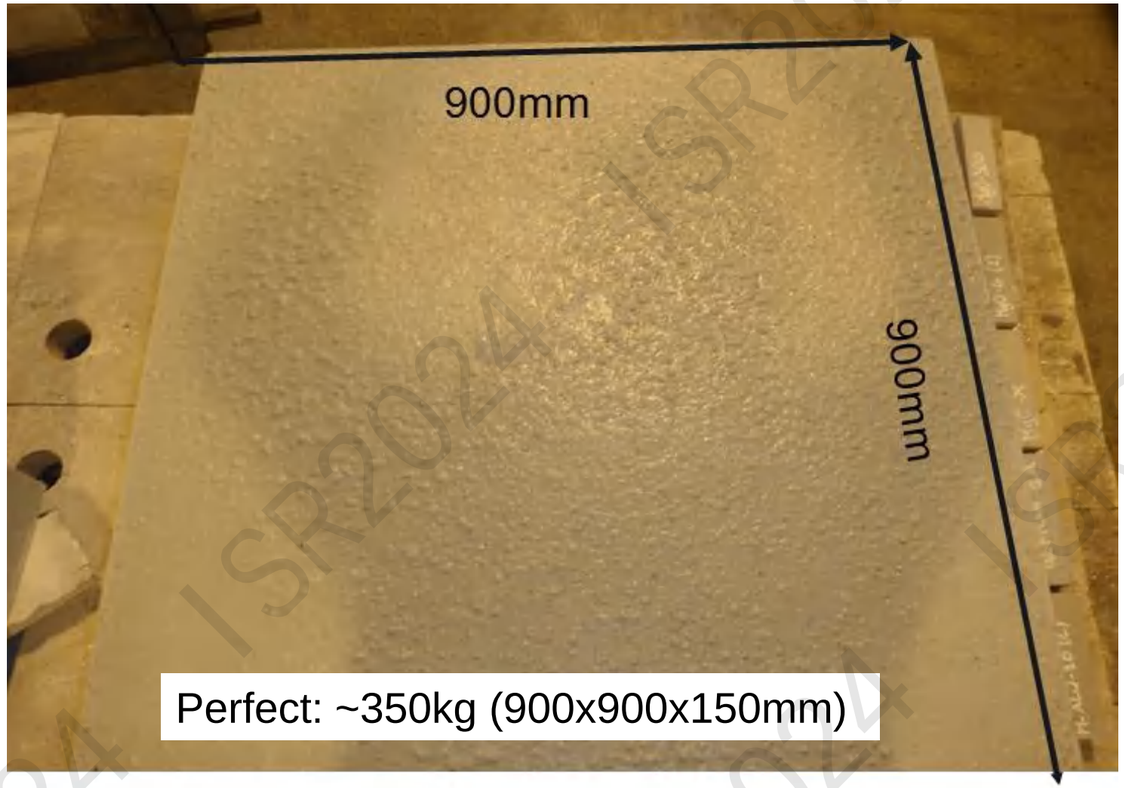
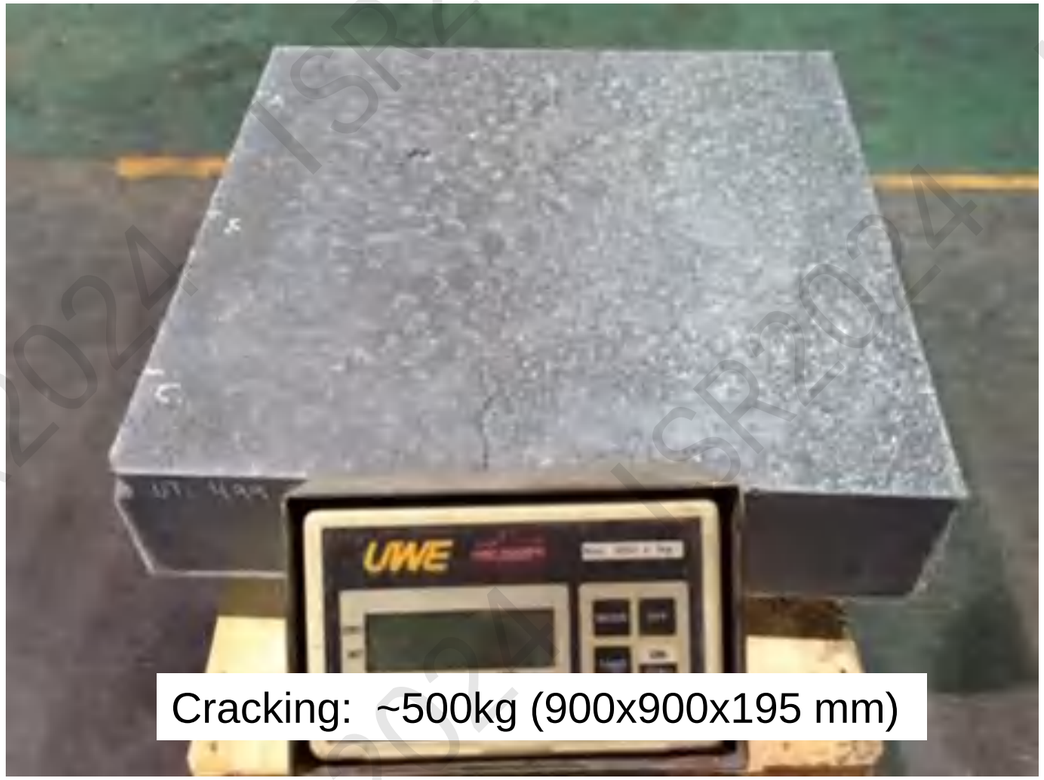
Castable SF-8 blocks with 8wt% microsilica after dry-out



Perfect: ~350kg (900x900x150mm)



Cracking: ~500kg (900x900x195 mm)

- Faster removal of water from inside of the block is an alternative to further minimize brucite formation and ultimately prevent cracking during dry-out.

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Further development of crack-free MgO castables by controlling the dry-out process

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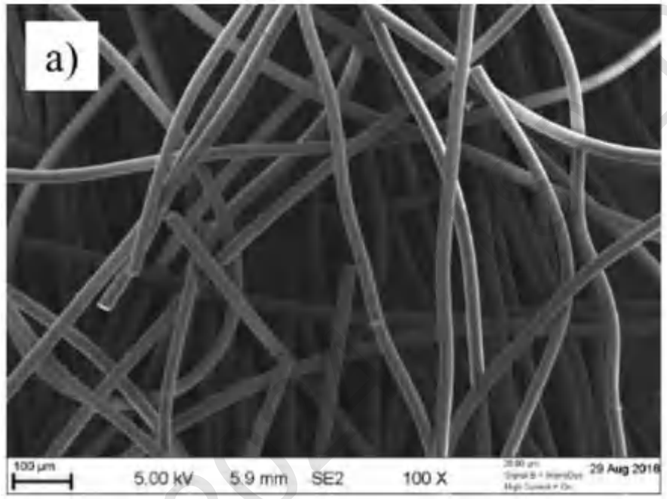
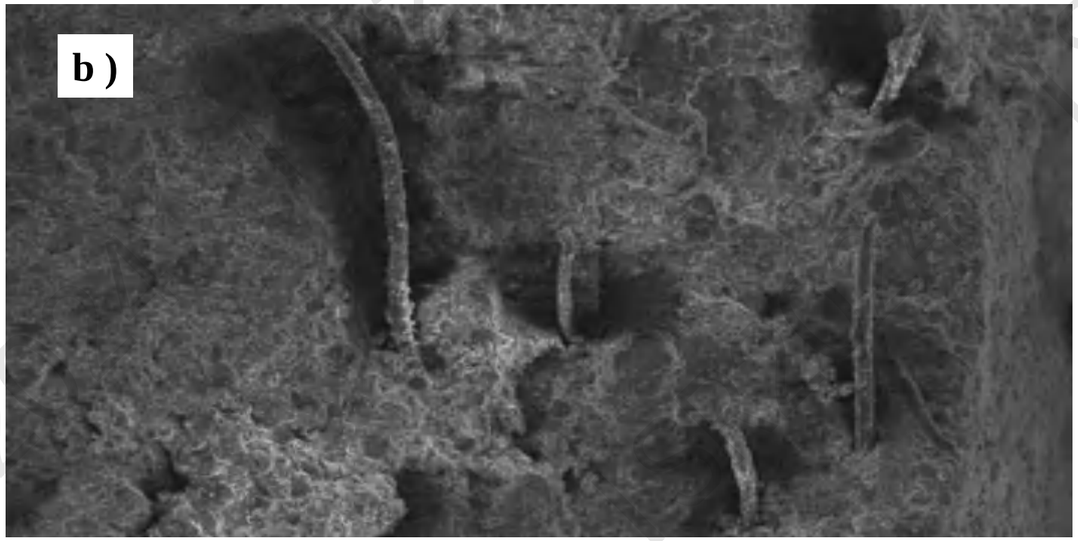
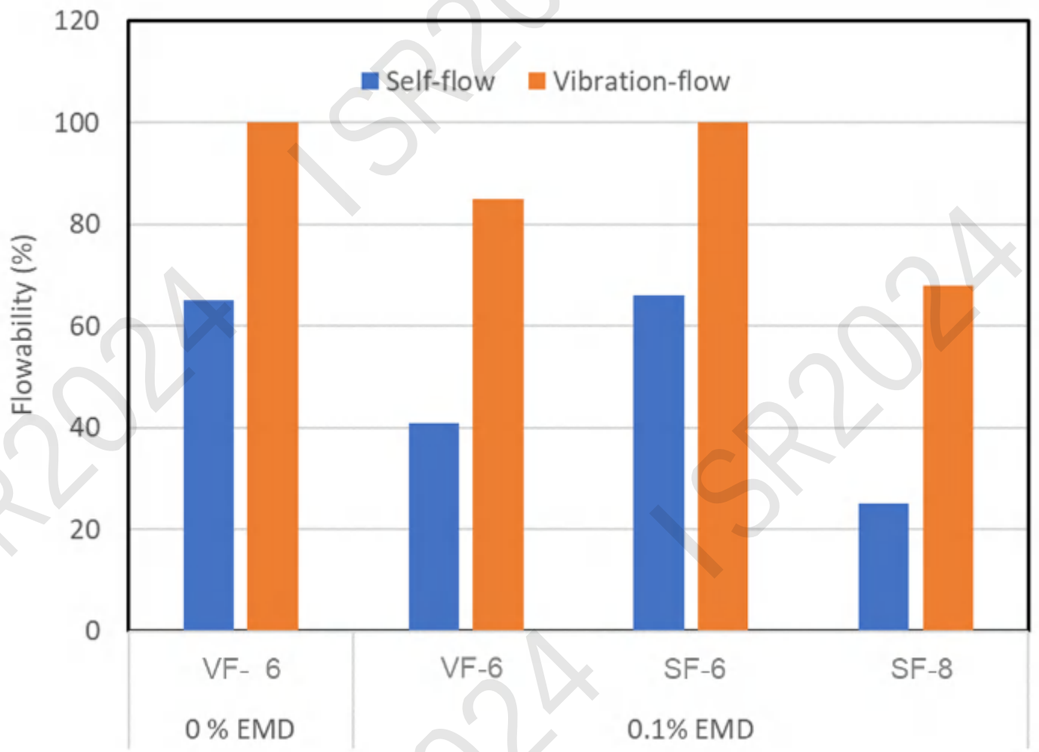
Further alternatives to solve the cracking challenge?







- Introducing a special drying agent: EMSIL-DRY®
- Optimising dryout profile by Macro-TGA

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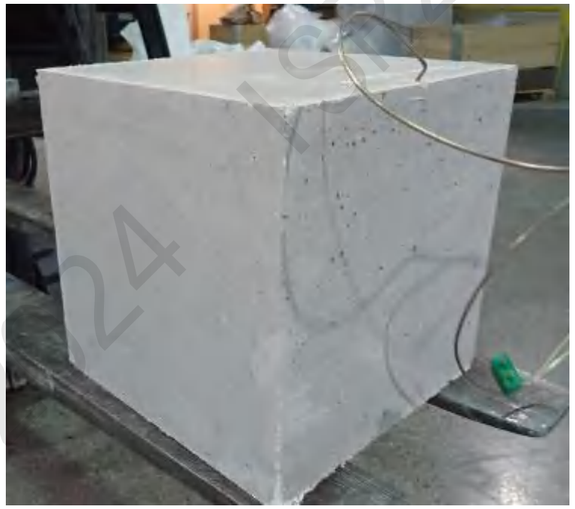
Macro-TGA: unique tool for dryout behaviour characterision of industial scale specimens

Heating profile: 40°C/hr from room Temp. to 600° C



300mm cube (~75kg)

$$W = 100\% \times (M_0 - M)/(M_0 - M_F) \quad (1)$$

$$(dW/dt)_i = (W_i - W_{i-10})/(t_i - t_{i-10}) \quad (2)$$

Where:
M is the instantaneous mass recorded at time t_i during the heating stages of the samples,
M_0 is the initial mass and
M_F is the final (dry) mass of the sample.

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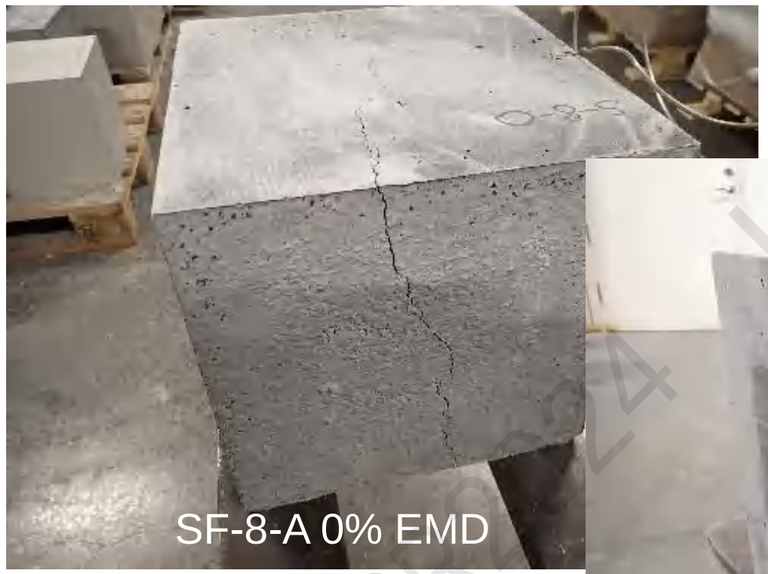
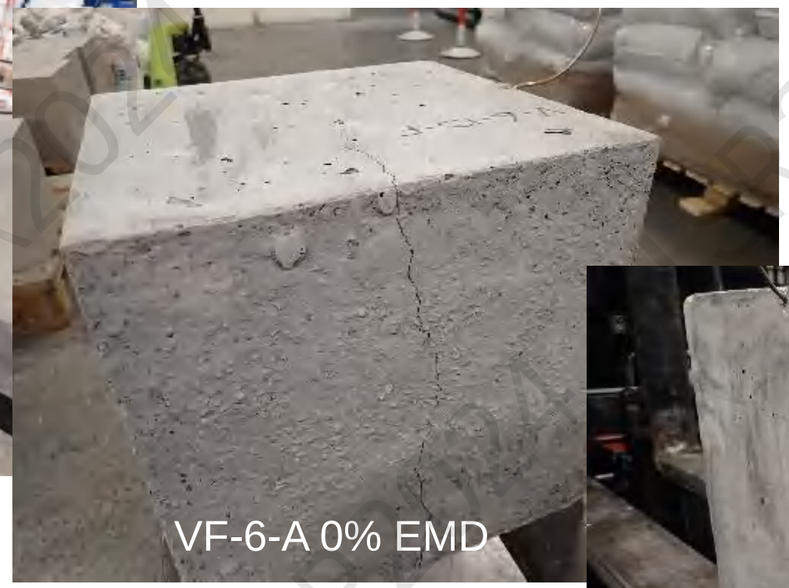
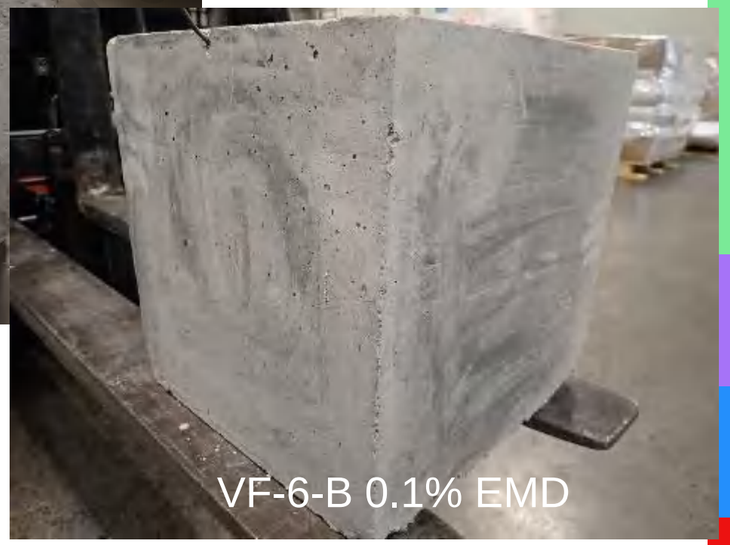
Photos after Macro-TGA test (Heating rate: 40°C/hrs)


SF-8-A 0% EMD


SF-8-B 0.1 % EMD


VF-6-A 0% EMD


VF-6-B 0.1% EMD

- The addition of drying agent, EMSIL-DRY® (EMD), prevent cracking formation during dry-out process

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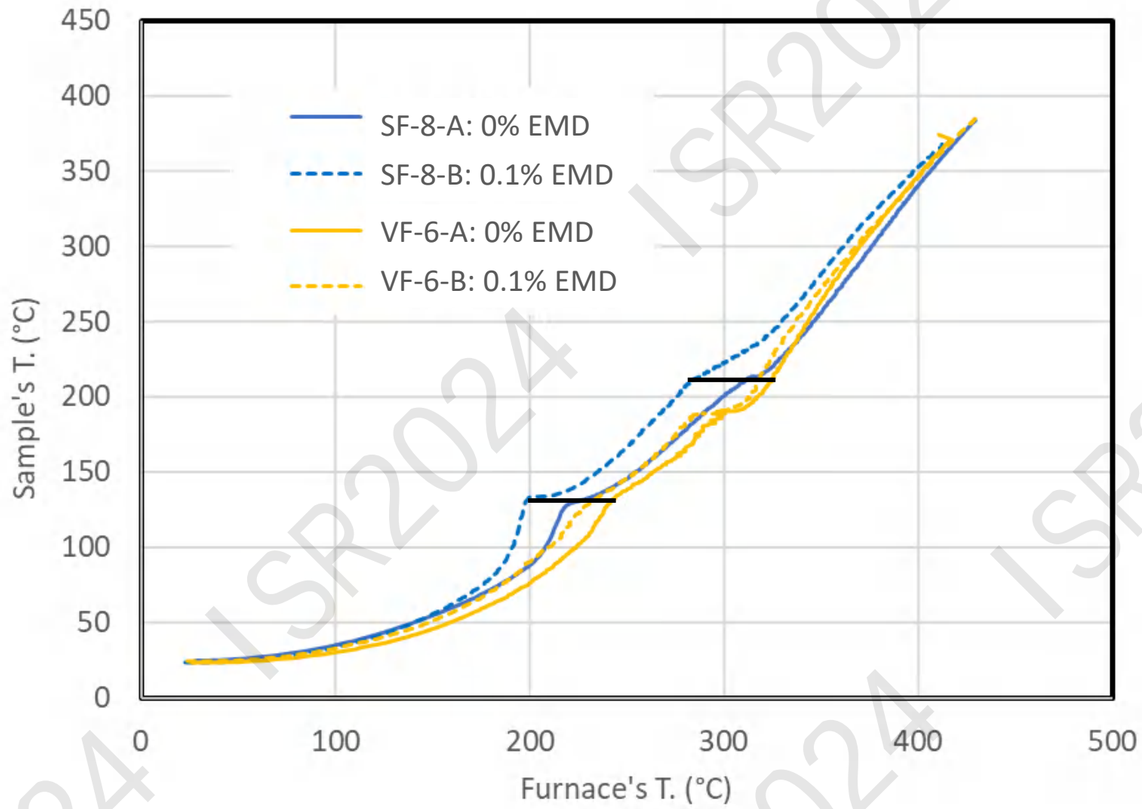
Temperature development: samples vs furnace



- Two plateaus/breaks were observed for all samples:
  - ~130ºC and ~ 210ºC respectively;
  - Corresponding furnace temperature ranges are 200-240ºC and 280-320ºC
- Dry-out profile for larger blocks (furnace temperature):
  - 20 to 220ºC, 30ºC/h;
  - 220ºC: 5hrs;
  - 220 to 320ºC, 50ºC/hr;
  - 320ºC, 8hrs

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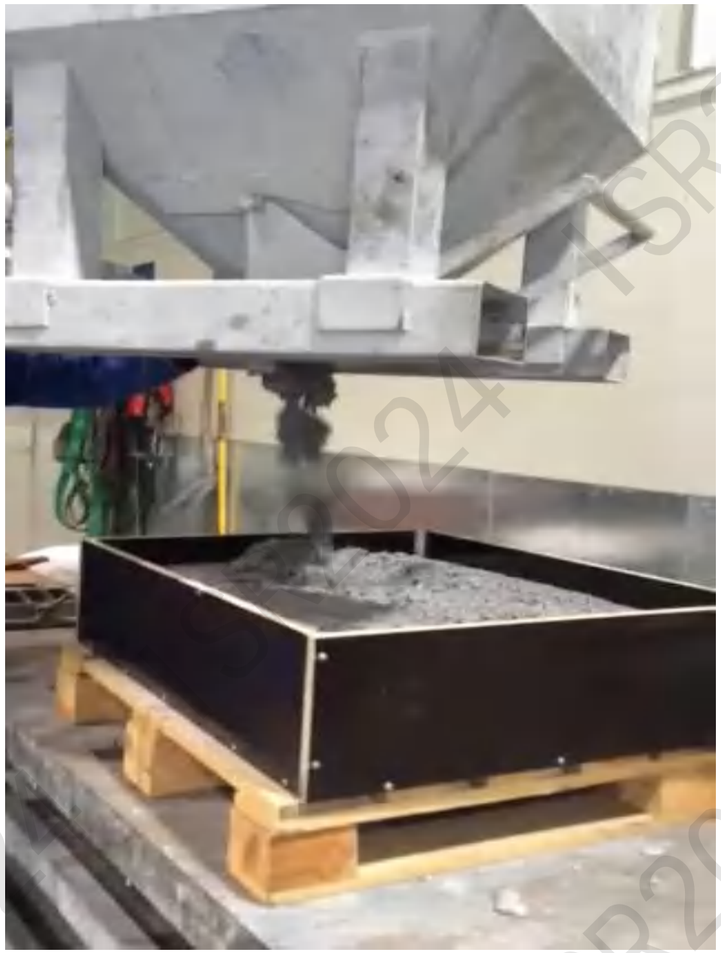
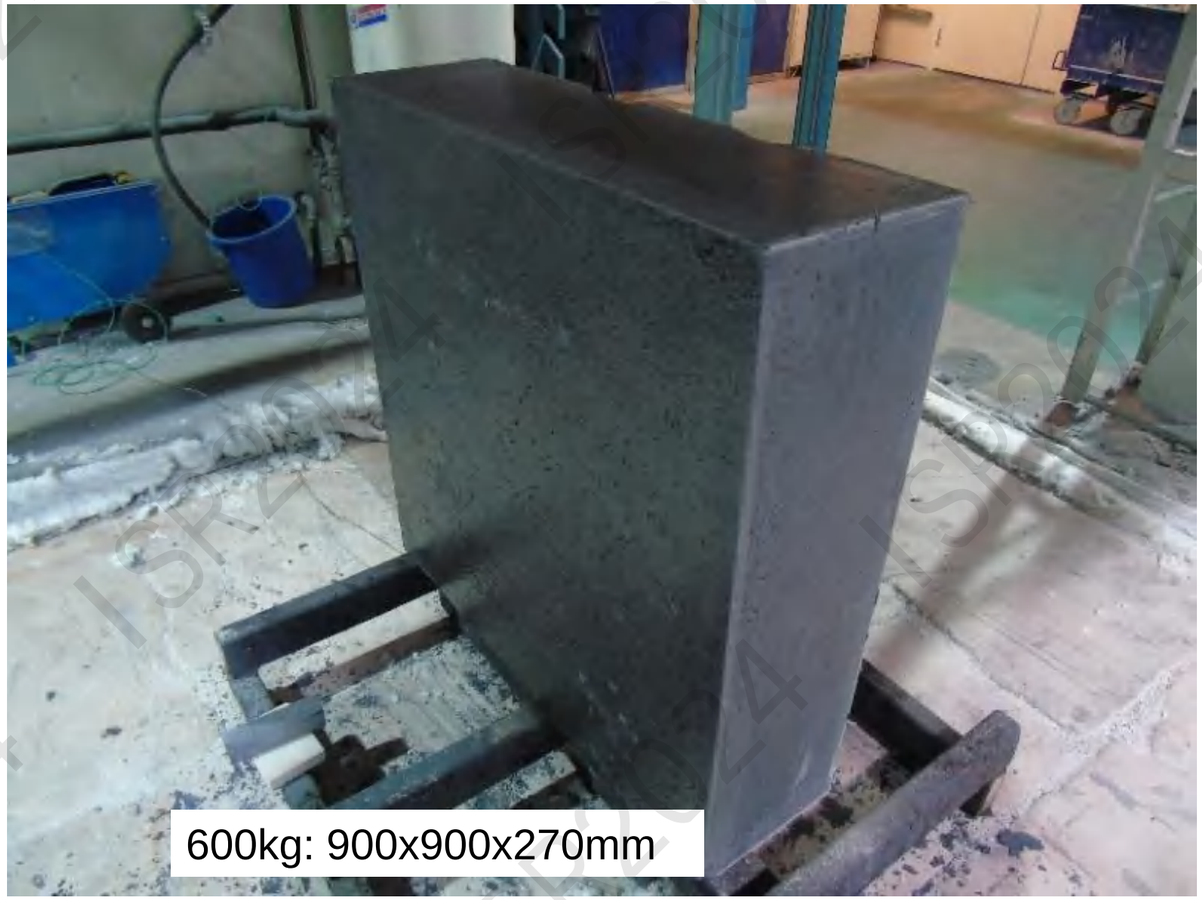
Video & Photo of the block at demolding





- All specimens are perfect at demolding

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Castable SF-8, 600 kg blocks, dry-out @ 320°C for 8hrs

No EMSIL-DRY®

0.1% EMSIL-DRY®

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Castable VF-6, 600 kg blocks, dry-out @ 320°C for 8hrs

0.05% EMSIL-DRY®

0.1% EMSIL-DRY®

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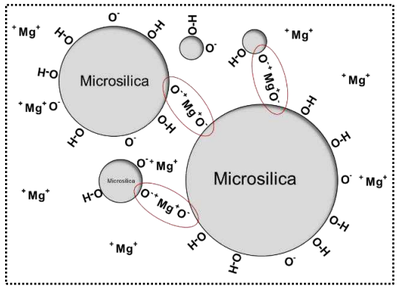
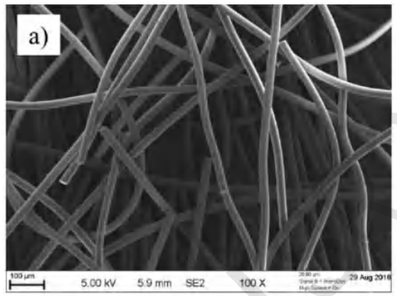
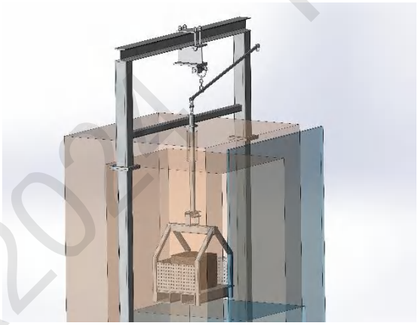
Summary



- The novel green binder, in combination with Microsilica and SioxX™-Mag, plays an essential role as an anti-hydration agent and in producing crack-free MgO castables.



The risk of cracking has been further minimized by selecting a suitable drying agent that can remove enclosed water at higher speed and at a lower temperature.

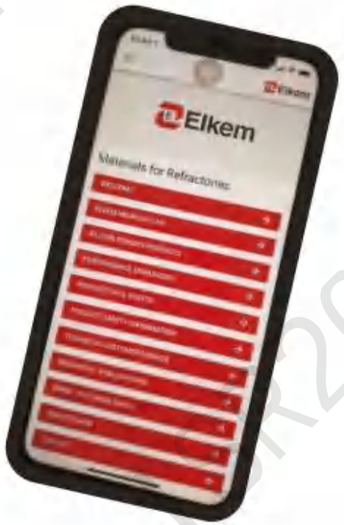


The Macro-TGA has proven to be a unique tool in facilitating the design of an optimized heating profile.

Sustainable MgO refractory castables with improved performance

Thank you for your attention!

Email:
hong.peng@elkem.com



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Delivering your potential