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Materialkonzepte für Spüler – getempert und gebrannt

Steel meets Refractory – 28.04.2022

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Steel ladle purging plugs

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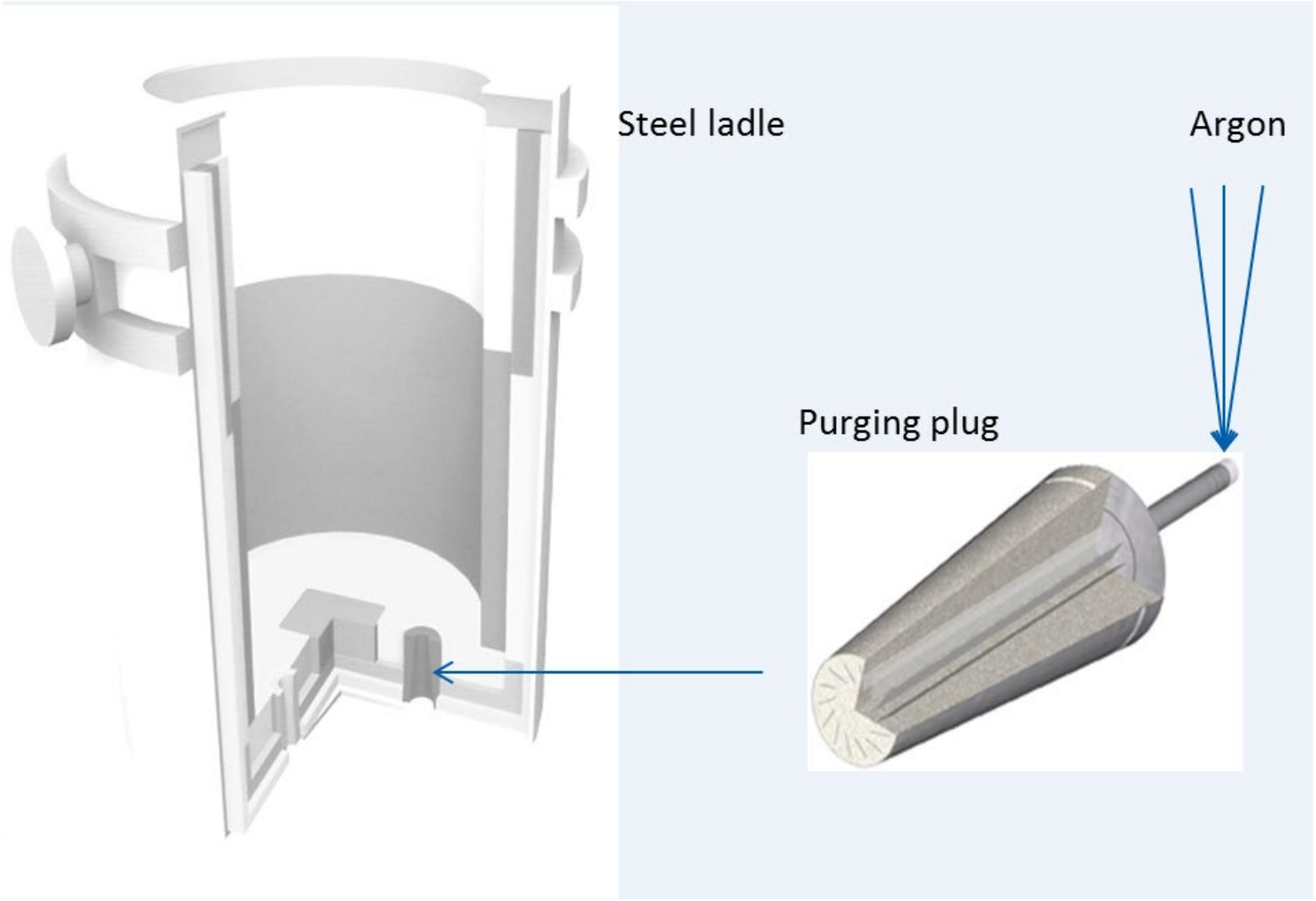
Essential for ladle metallurgy and high quality steel grades



Homogenization of steel composition and temperature

Enables reactions between steel and slag to perform metallurgical work (strong stirring)

Remove non-metallic inclusions e.g. alumina from Al-killing of steel (soft stirring)

Clogged PP require costly recycle of steel

Safety: PP (bottom) breakouts are disasters!

Possible: Plug exchange during bottom campaign

Purging plugs – major wear factors

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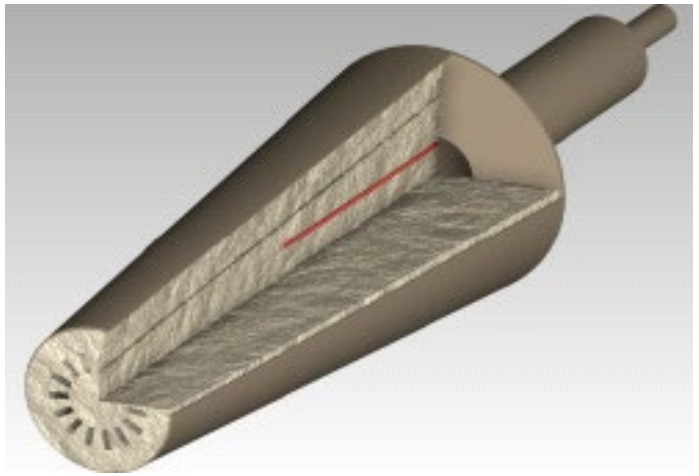
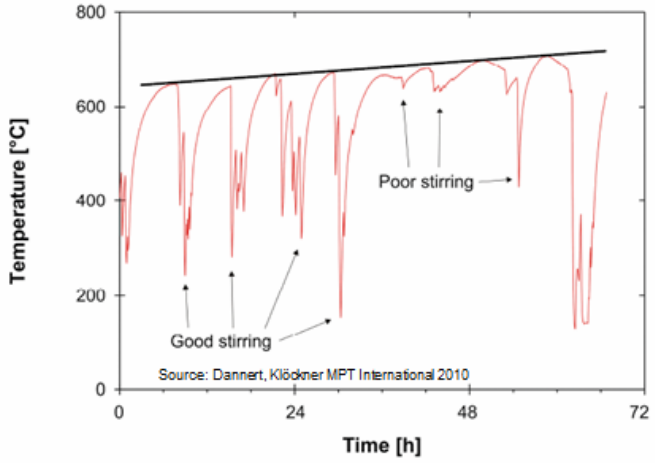
Erosion

Thermal shock & cracking



Temperature changes due to cold stirring gas



Oxygen lancing (FeO slag >2000°C)

Purging plug material technology

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- Regional differences:
  - China 1600 °C pre-fired
  - Europe/America 350-450°C tempered
- Thermal shock cracking / spalling
  - Major topic in China but not e.g. in Europe!
- Wear resistance, erosion resistance
  - Driver for high temperature pre-firing in China?
  - Trials: Tempered Chinese PP lower wear resistance, but no problem in Europe
- Other aspects high temperature pre-firing vs. tempering
  - Additional processing steps for high temperature pre-firing vs. casting in steel can directly and tempering
  - Even tolling (external firing) needed?
  - Higher energy consumption and CO_2 emission
  - Additional cost for pre-firing?
  - Different formulations of castable matrix in China vs. Europe

Purging Plug

I. Influence of matrix design and tempering on physical properties

Composition of test castables (1)

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PP castable	C2S26	C5S26	C5S0
Tabular T60/T64	%	%	%
3-6mm	25	25	20
1-3mm	18	18	20
0.5-1mm	6	6	10
0.2-0.6mm			10
0-0.5mm	10	7	
0-0.2mm			15
0-0.02mm			7
Spinel AR78			
0.5-1mm	7	7	
0-0.5mm	10	10	
0-0.045mm	9	9	
Reactive alumina			
CL370	13	13	13
Binder			
CAC CA-14M	2	5	5
Alphabond300			
Additives			
ADS3/ADW1	1	1	1
Water demand	3.9	4.1	4.2

General technical research on the factors (Binders & Spinel) in the formulation:

- Spinel containing ULCC and LCC
- Pure tabular LCC

Composition of test castables (2)

	Reactive alumina	
T60/T64	C2S15R6	C2S15R13
3 - 6 mm	25	25
1 - 3 mm	18	18
0,5 - 1 mm	10	10
0-0,5 mm	17	17
-45MY	7	0
AR78		
0.5-1mm	3	3
0-0.5mm	3	3
-45MY	9	9
Reactive Alumina		
CL370	6	13
CAC		
CA-270	2	2
Additive		
ADS 3	0.6	0.6
ADW1	0.4	0.4
Water demand		
	4.2	4.0

Optimize the matrix for tempered PP

- Reactive alumina content
- Erosion- Hot MoR

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Thermal shock resistance

Influence of reactive alumina content

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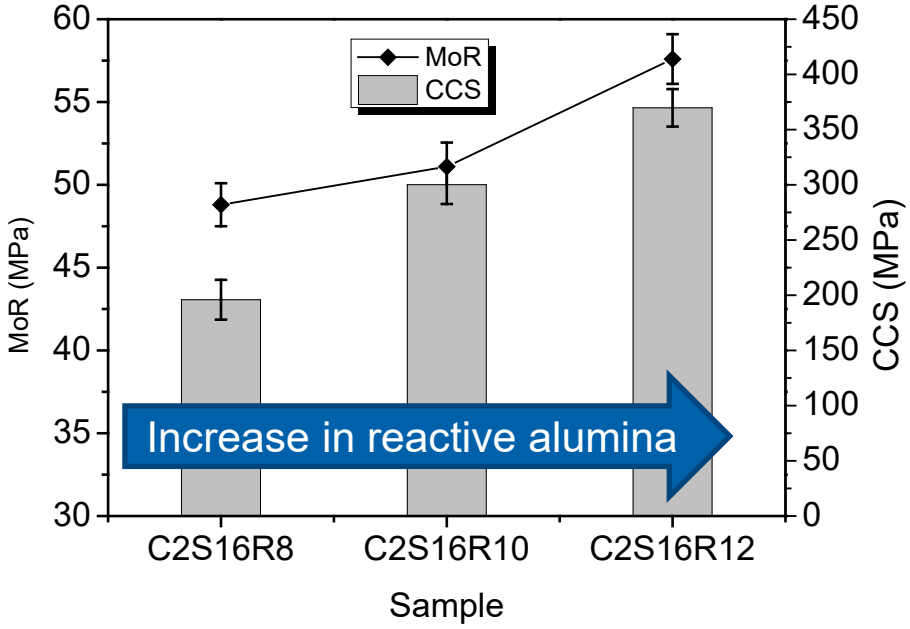
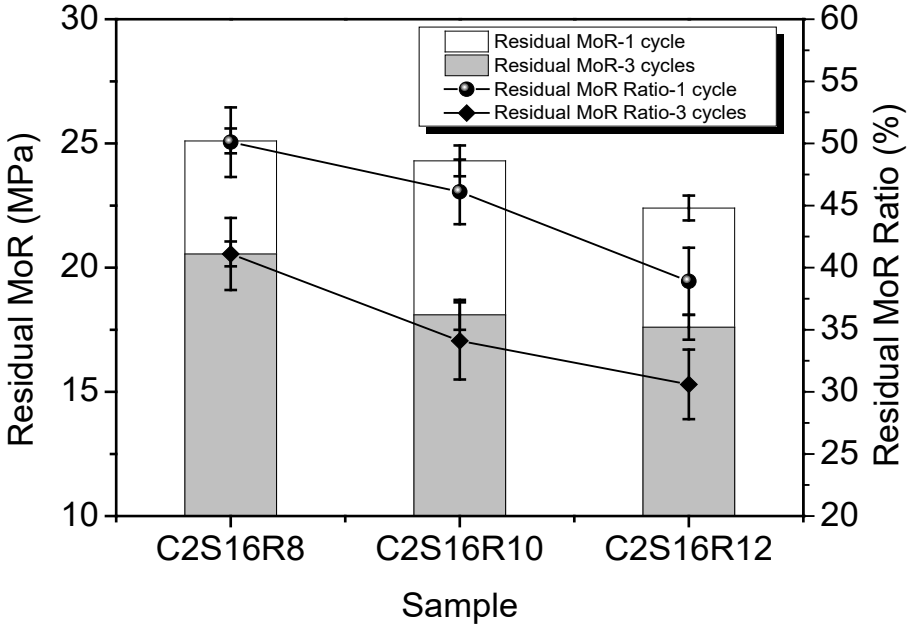
Pre-fired at 1600°C- Influence of reactive alumina amount

High tempered Fired PP- TSR by air quenching





- Higher content of reactive alumina beneficial to the sintering of castables
- Castables with too intense sintering reduce thermal shock resistance and performance of fired PP.

Purging plugs: Fracture behaviour

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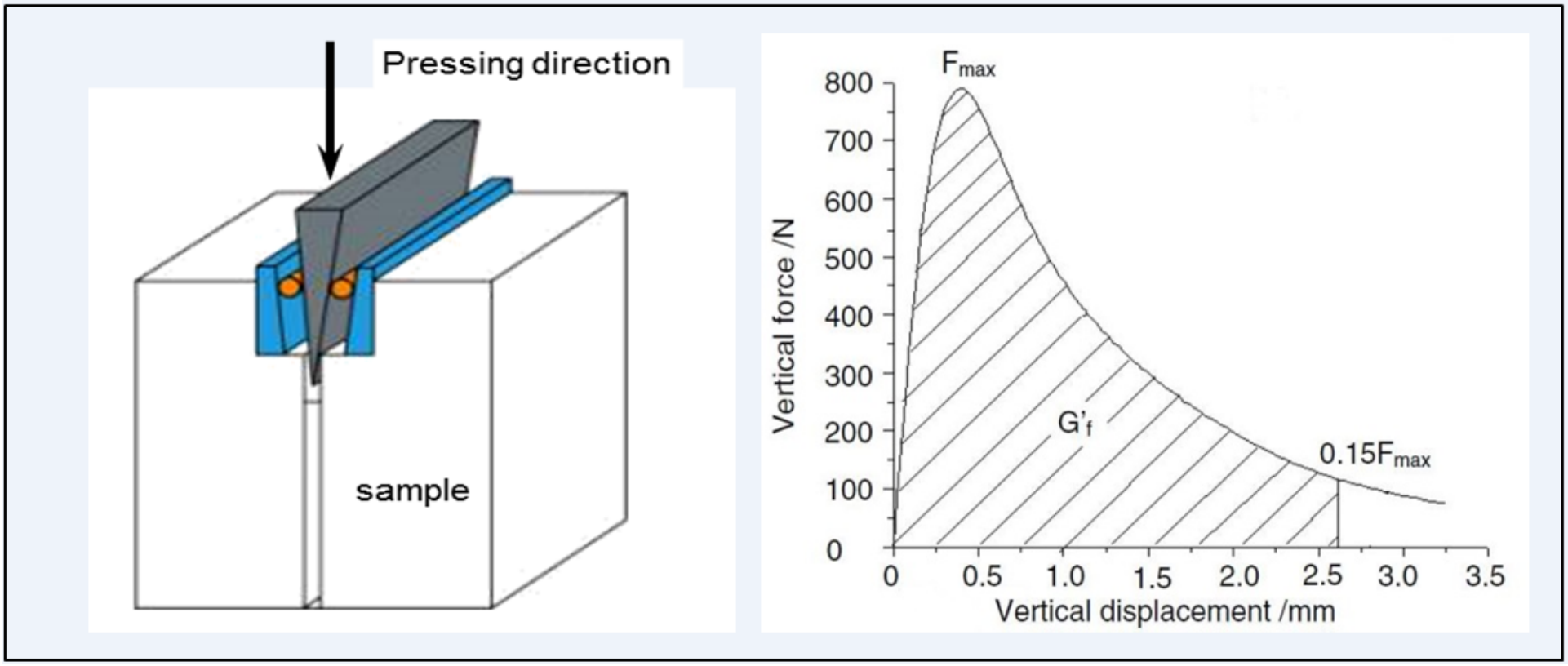
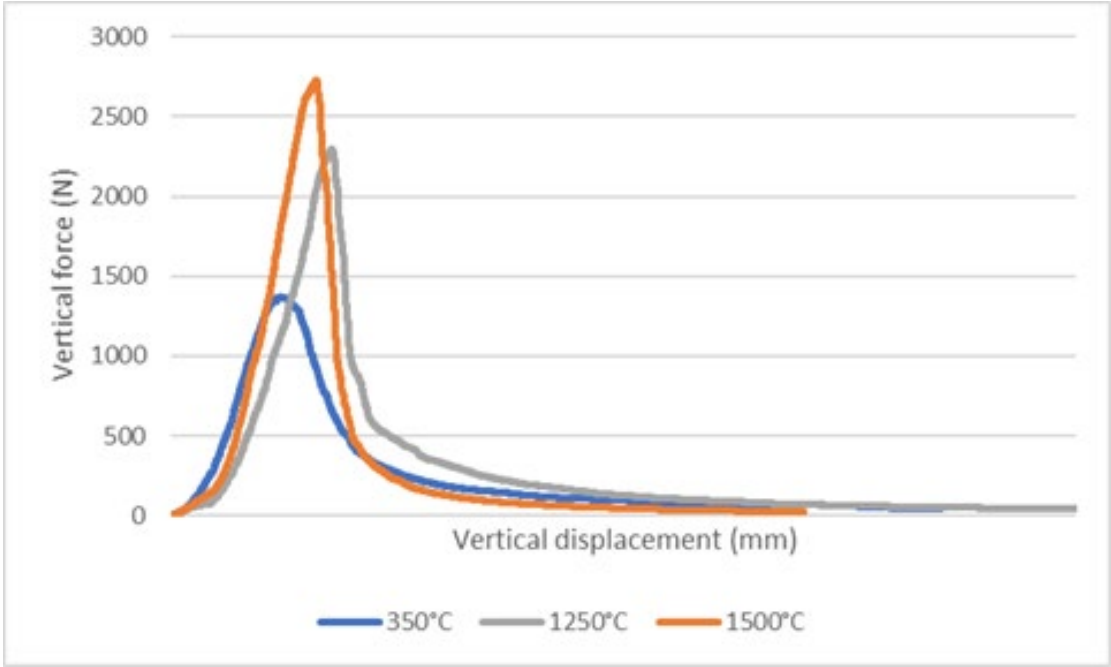
Wedge splitting test UNI Leoben



- Pre-firing at 350, 1250, and 1500°C

Purging plug wedge split test; 350°C

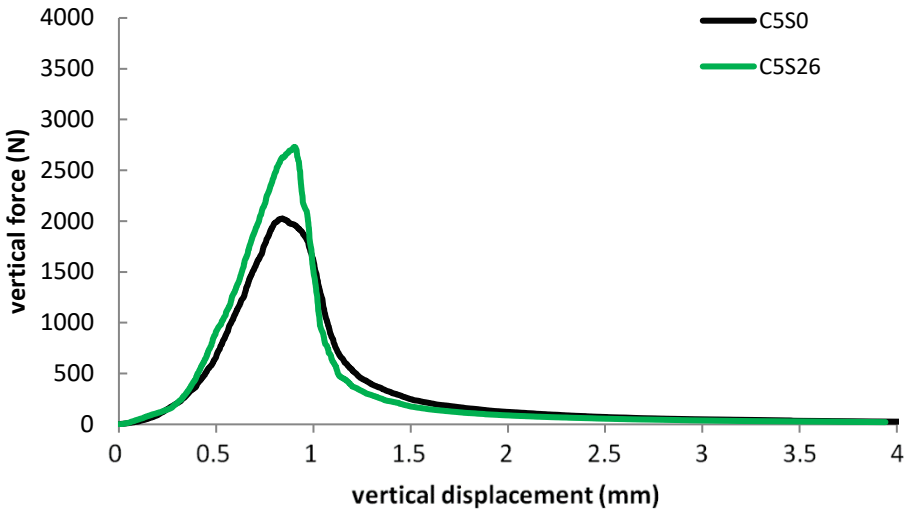
Low cement Alumina-Spinel castables with different pre-firing temperatures



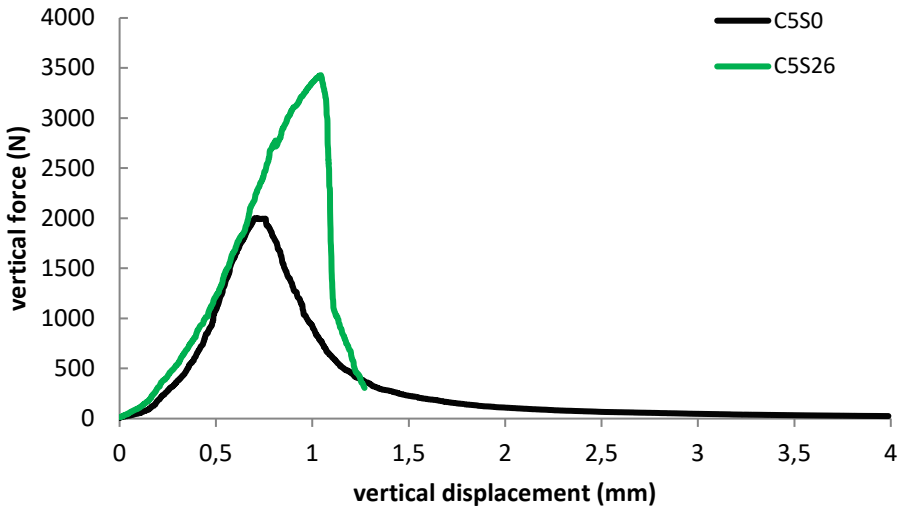
Lower pre-firing temperature → Lower vertical forces but less steep curve during descending load process → material is less brittle

Purging plugs: wedge split test 1250 & 1500°C

1250°C



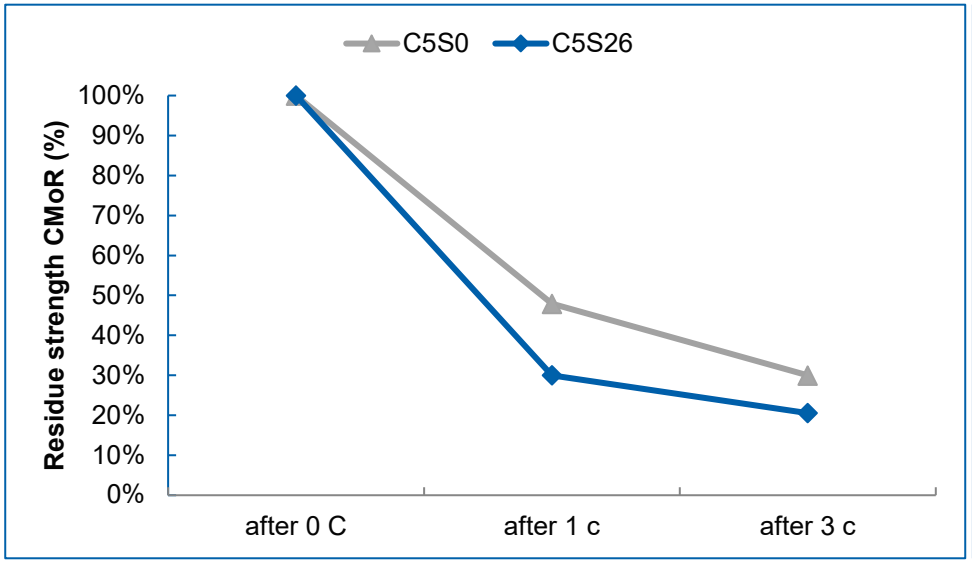
1500°C

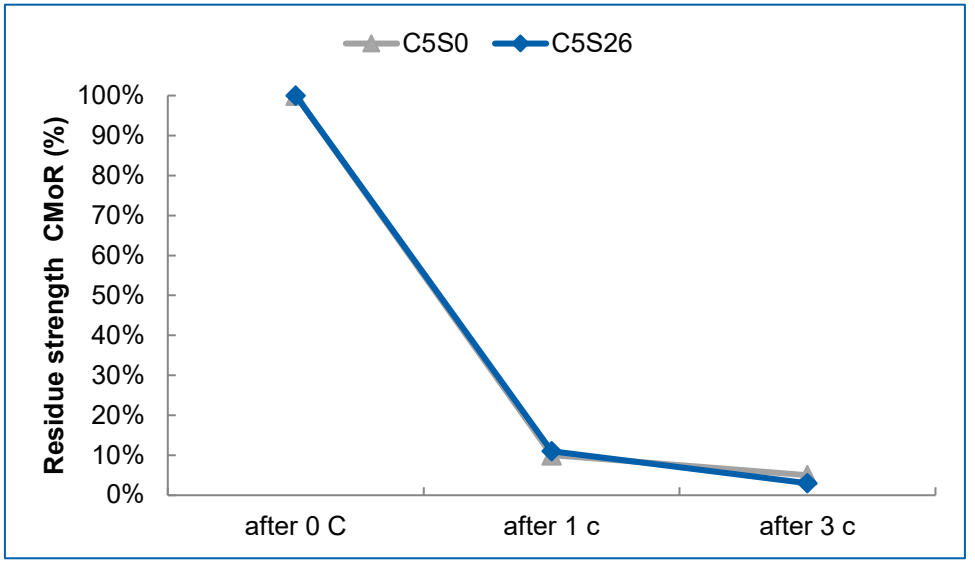


- Sintering = higher strength = higher vertical forces
- Higher vertical forces: Increase in brittleness of the material
- Spinel CAC bonded has higher strength but also higher brittleness

Purging plugs: TSR testing water quenching

Pre-firing at 400°C and 1650°C





- Clearly higher strength loss at 1650°C pre-firing vs. 400°C
- Higher strength loss for spinel containing castable fired at 400°C

TSR according to Chinese national standard:
Heat treatment at 1100°C for 5 h and quenched in water for 3 min

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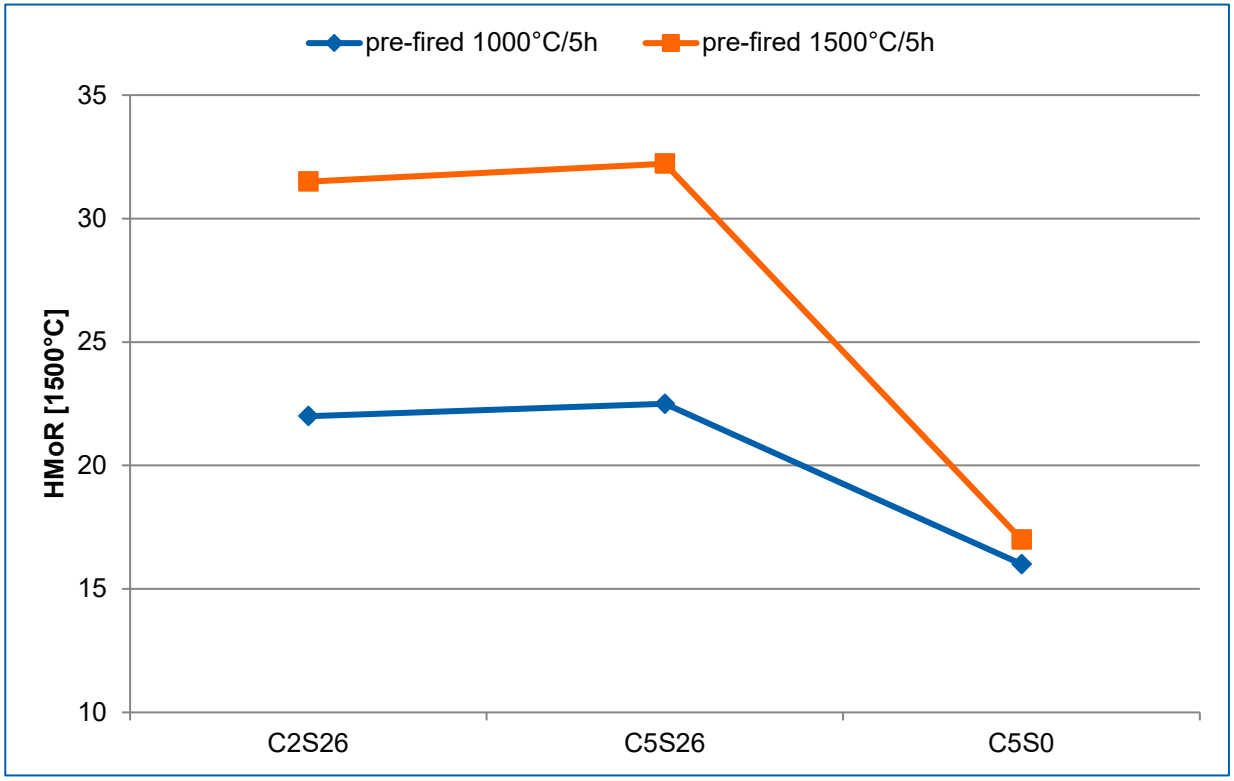
Erosion resistance

Indicator for erosion:
Hot Modulus of Rupture

Purging plugs: erosion resistance, HMoR



- HMoR 1500°C: Advantage of Spinel and CAC
- Increase in cement content from 2% to 5% does not result in HMoR benefit
- Advantage of higher pre-firing temperature

Purging plugs: erosion resistance, HMoR

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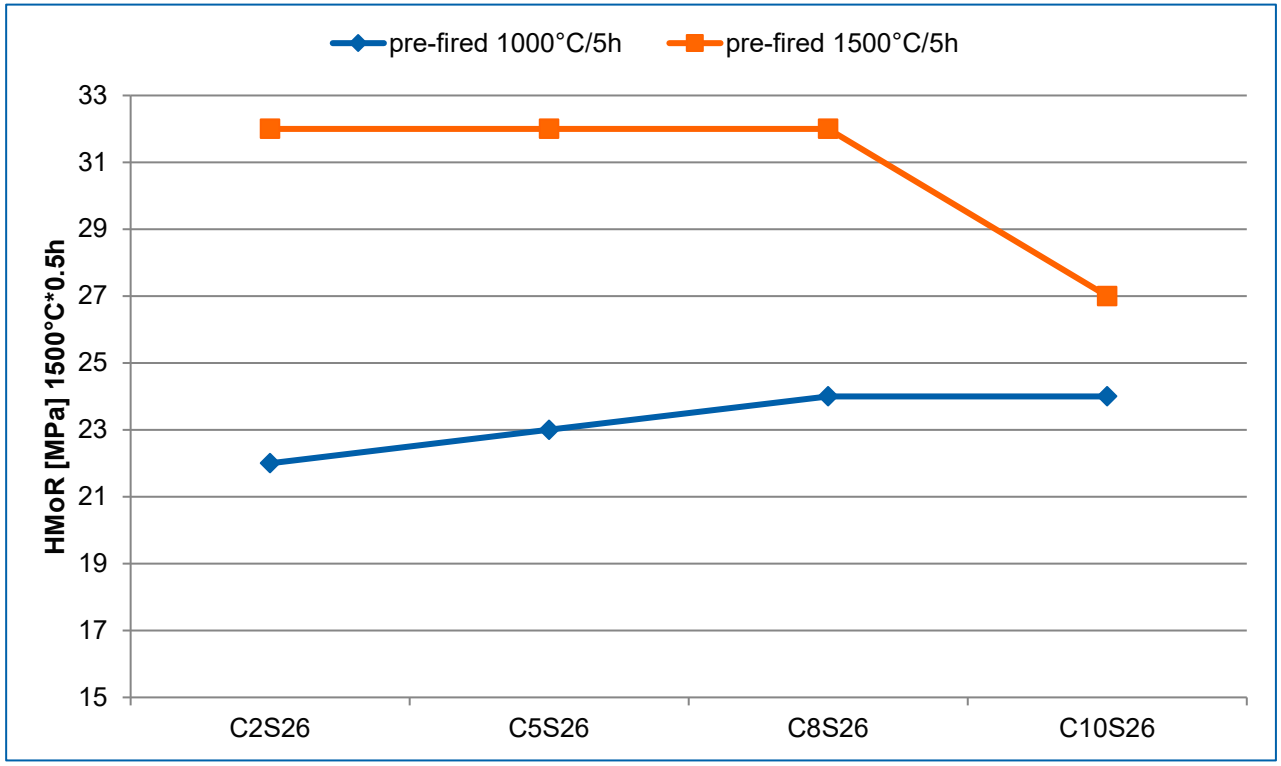
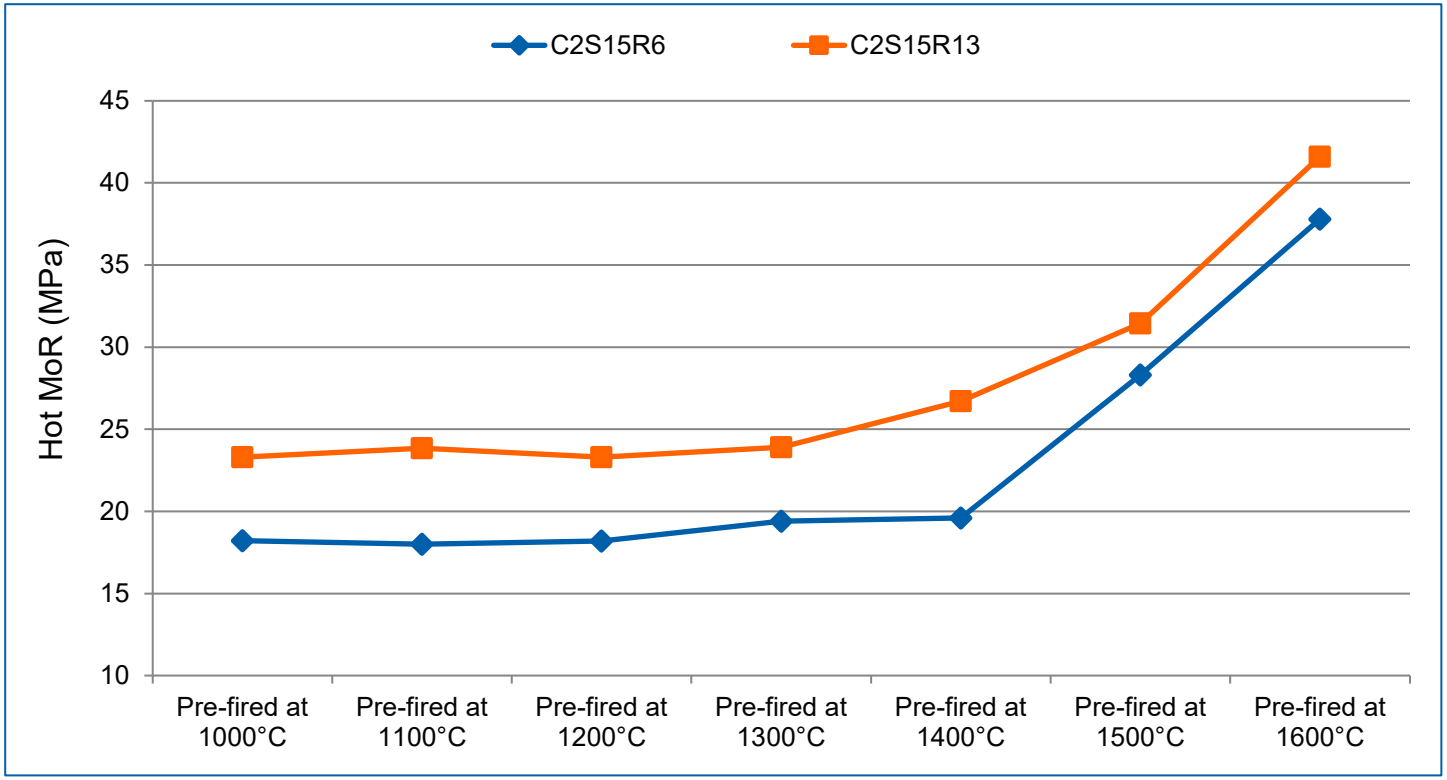
26% Spinel, 2 to 10% Cement



- No advantage by higher cement contents
- Higher pre-firing temperature beneficial for HMoR

Purging plugs: erosion resistance, HMoR

15% Spinel, 2% CAC: *6% vs 13% CL370*



- Hot MoR increases with pre-firing temperature above 1400°C
- Higher reactive alumina content increases Hot MoR (erosion resistance) also at intermediate temperature
- Good for tempered purging plug: sufficient strength in bulk of PP but material not as brittle as high temperature fired plug
- Strong sintering only at hot surface of PP where its needed for erosion resistance

Purging plugs: HMoR & microstructure

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Spinel + CAC

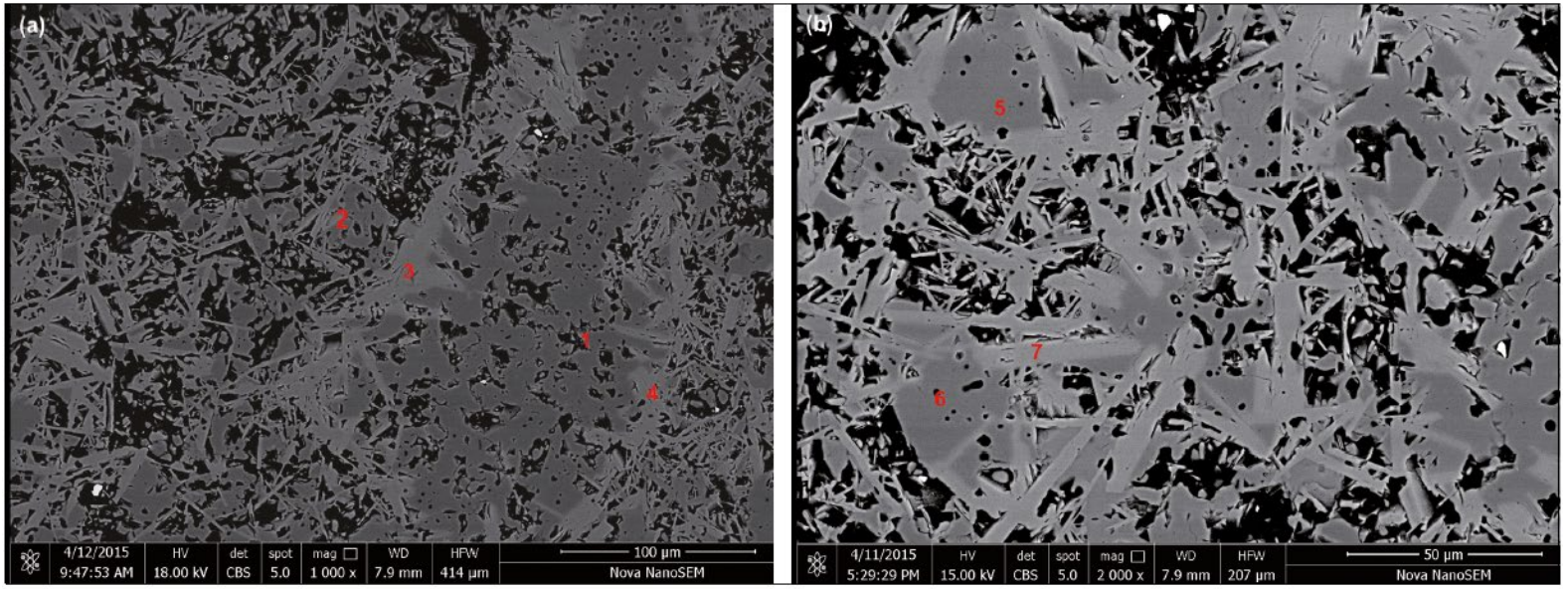


Fig. 23 a–b Microstructure and EDS analysis of C5S26 sintered at 1650 °C for 5 h; EDS analyses are given in Tab. 2

Tab. + CAC

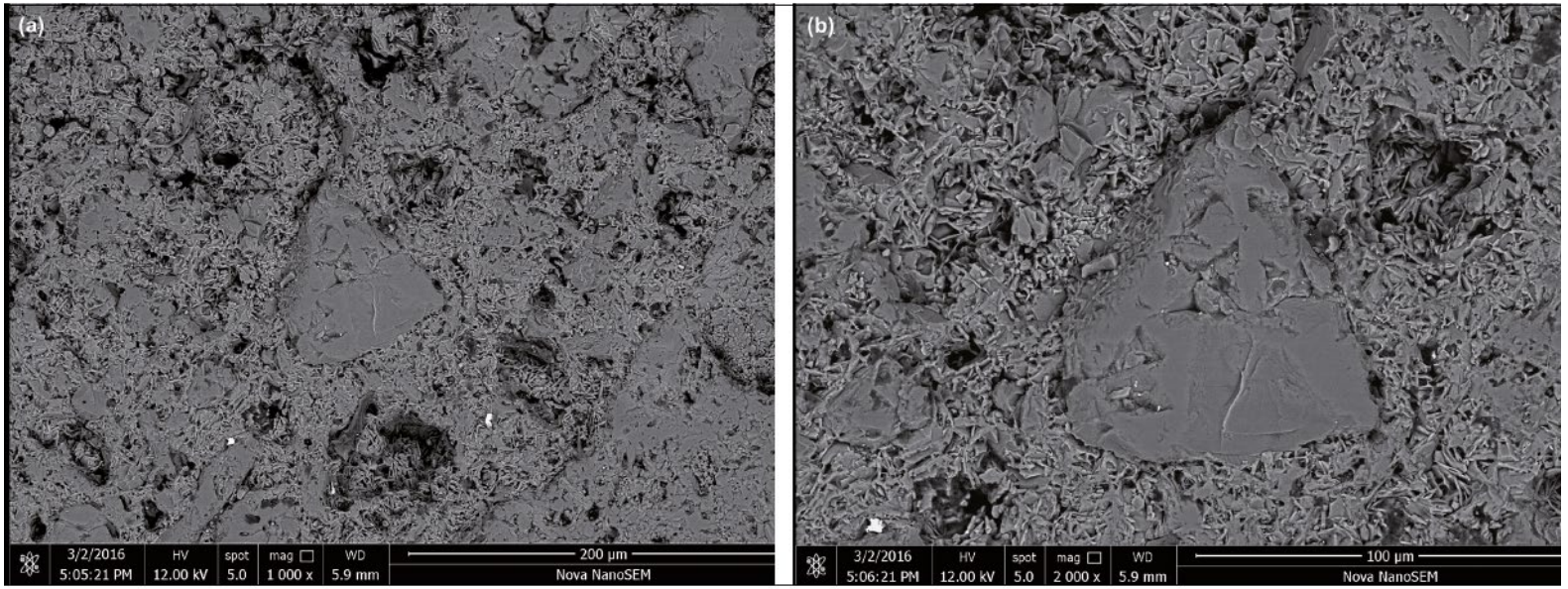
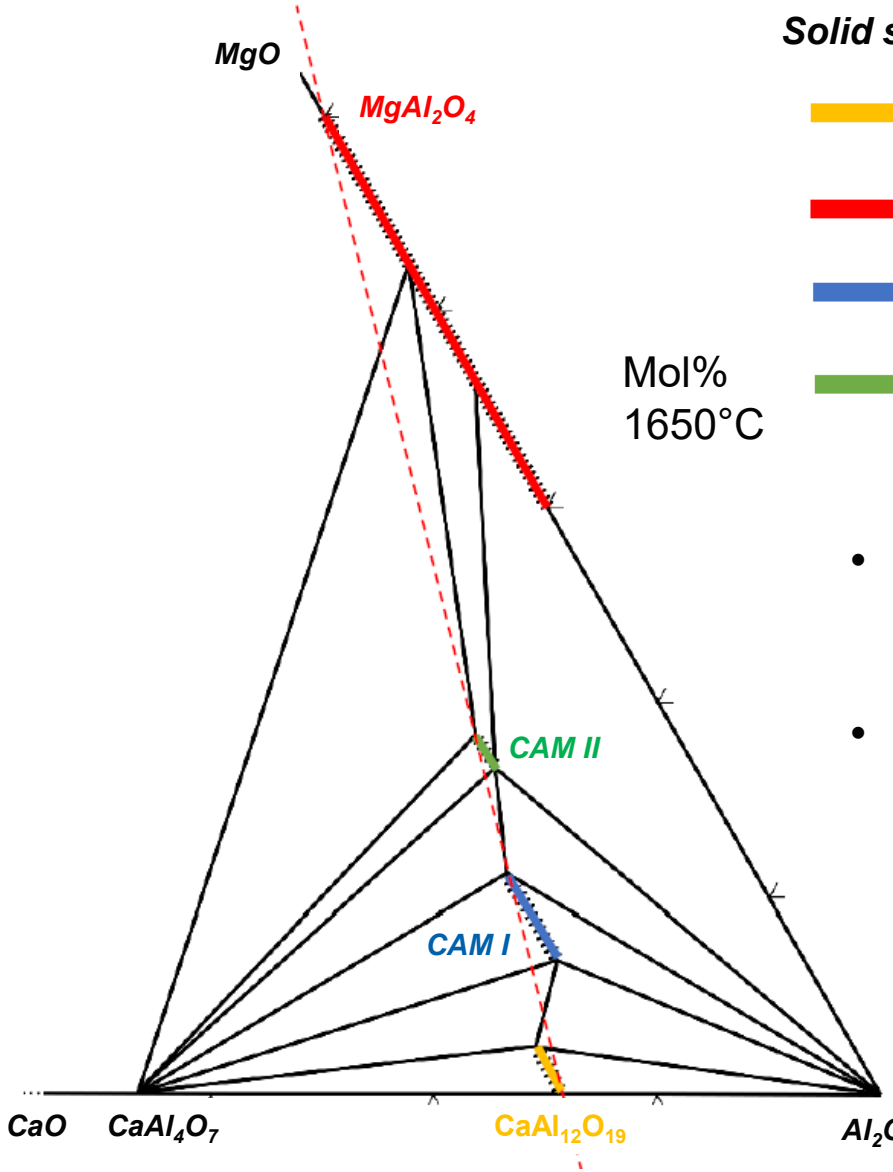


Fig. 25 Microstructure of C5S0 sintered at 1650 °C for 5 h

Formation of CAM phases

$CaO-Al_2O_3-MgO$ phase diagram



Solid solution at 1650°C

Hibonitess	$CaMg_xAl_{12-x}O_{19}$	with	$0 \le x \le 0.18$
Spinellss	$Mg_{1-3w}Al_{2+2w}O_4$	with	$0.07 \le w \le 0.12$
CAM Iss	$Ca_2Mg_{2-3y}Al_{28+2y}O_{46}$	with	$0 \le y \le 0.30$
CAM IIss	$CaMg_{2-z}Al_{16+2z}O_{27}$	with	$0 \le z \le 0.20$

- Hibonite can incorporate up to ~2.5 mol% MgO at 1650°C
- Further increase in MgO leads to CAM-phase or spinel formation

Phase diagram after:
Göbbels, M.; Woermann, E. & Jung, J.
The Al-rich part of the system $CaO-Al_2O_3-MgO$ Part I. Phase relationships
Journal of Solid State Chemistry, Elsevier, 1995 , 120 , 358-363

PP summary: tempered vs. HT pre-fired

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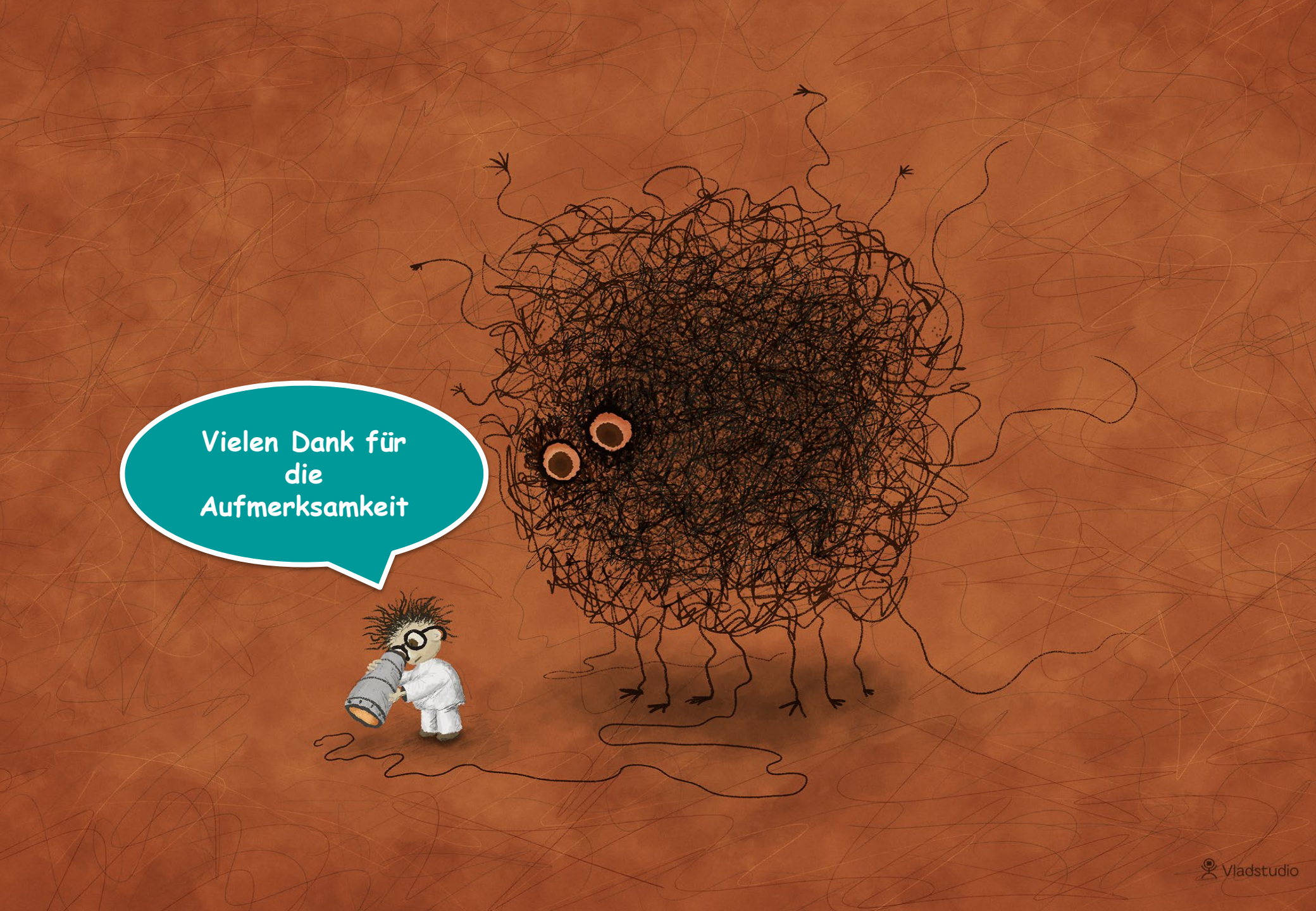
Ultra-low cement castable with 15 % spinel

	Matrix sinter reactivity	Erosion resistance HMoR as indicator	Thermal shock resistance Fracture behaviour	Matrix recommendation
Tempered (350-450 °C)	low	o	+	Higher amount of high quality bi-modal reactive alumina Spinel in fines
	high	+	+	
Pre-fired (1600°C)	low	+	o	Lower amount of reactive alumina and not too fine PSD
	high	+	-	

- Depending on the specific challenges in a steel plant, the optimum solution can be different!


Vielen Dank für die Aufmerksamkeit
Vladstudio