Workshop of 3rd IRS, Oct. 23, 2017, Tehran, Iran

Lower Consumptions by Making Refractories Lighter

Ningsheng ZHOU

E-mail: nszhou@ 163.com

High Temperature Materials Institute,
Henan University of Science and Technology, China

To learn about and understand:

Why — Necessities of making refractories lighter

How — Technological approaches to weight reduction

What — Practices and applications

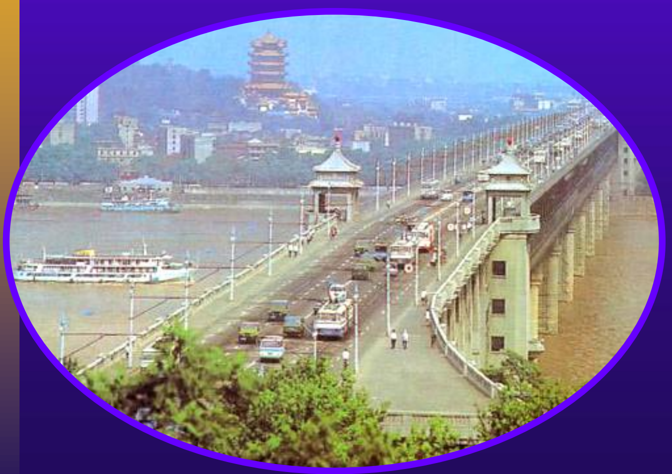
- Newly developed lightweight aggregates
- New castables using new ideas
- Some industrial trails

Prospects

Challenges that refractories are facing

- Energy and resource shortages are calling for efforts to realize energy conservation and consumption reduction.
- Properly weight reducing is beneficial to thermal shock resistance and spalling resistance of refractory linings.
- Thermal insulating performance of refractory linings is challenged by energy saving and lower consumption of user industries.
- R & D and application of weightreduced refractories are drawing attentions and efferts.

From heavy to light



Ancient lightweight brick

The embodiment of "lightening"

Under the premise of safety and durability in service, to realize：

- Reducing bulk density
- Reducing solid volume ratio in a specific total volume
- Reducing lining thickness

How to make refractories lighter?

- **Improvement and optimization in material system and microstructure**
- **Making aggregates lighter**
- **Inserting more pores in both aggregate portion and in matrix of refractories**
- **Lining structure optimization to avoid overweight**
- **More adoption of high performance lightweight bricks and monolithics**

Requirements for high performance?

"4 highs"

- High purity
- High strength
- High service temperature
- High resistance to furnace gas

"2 lows"

- Low thermal conductivity
- Low shrinkage

How to achieve high performance?

- **For LW aggregate: pore structure optimization → high strength and low thermal conductivity.**

Closed, micro-sized and spherical pores are suggested.

- **For material system: New material systems, e.g. Al_2O_3-SiO_2-CaO, MgO-SiO_2, MgO-Al_2O_3, Al_2O_3-CaO, etc..**

- **For property design: Better synergy of aggregate and matrix.**

Why to micro-size pores in refractory aggregates?

- Pore size ↓ → convective heat transfer ↓ → therm. insulation ↑
- Spherical pore ↑ → convective and radiative heat transfer ↓ → thermal insulation ↑
- Closed pore →convective heat transfer ↓ → thermal insulation ↑
- Pore size ↓ → strength ↑
- Pore size ↓ → chemical attack ↓

Three different lightweight aggregates

LW-1

Prepared by using saw-ash as pore-maker

BD/cm^3

$Al_2O_3 \geq 60\%$

$Fe_2O_3 \leq 2.0\%$

LW-2

Prepared by using polypropylene balls as pore-maker

BD/cm^3

$Al_2O_3 \geq 65\%$

$Fe_2O_3 \leq 0.8\%$

LW-3

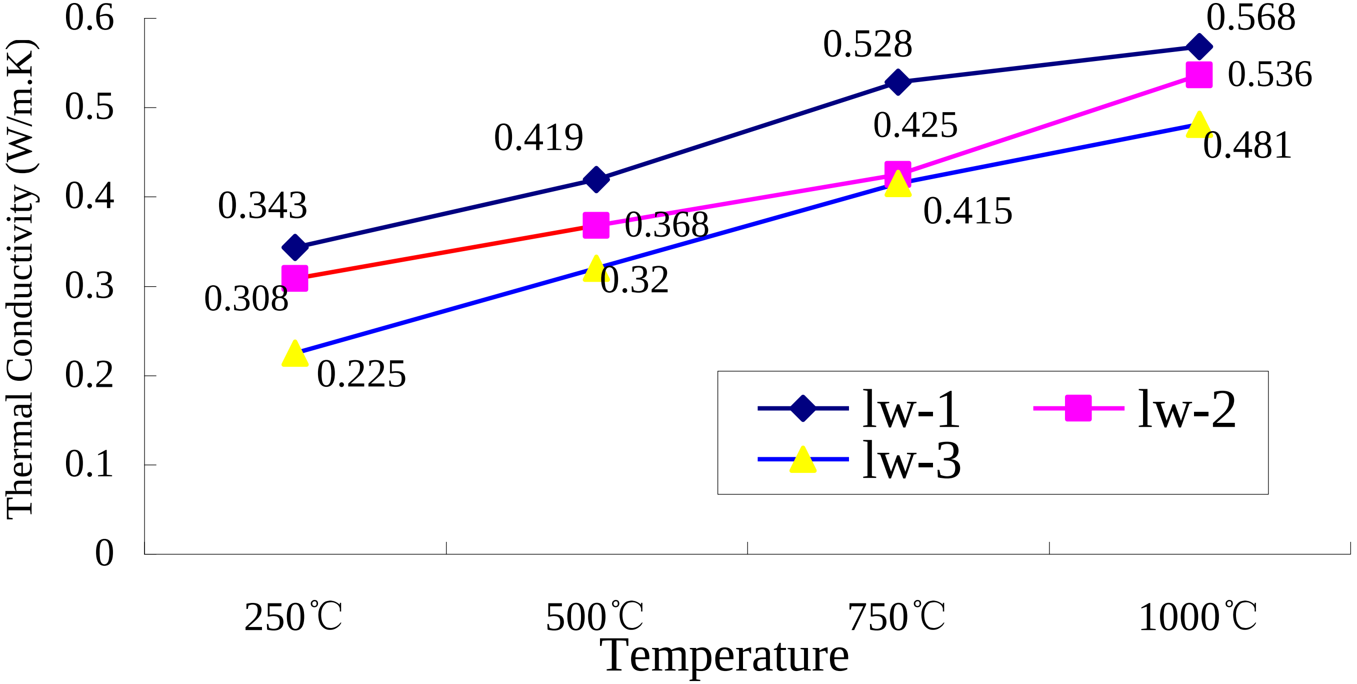
Micro-pored by special way

BD/cm^3

$Al_2O_3 \geq 65\%$

$Fe_2O_3 \leq 0.72\%$

Evidence of insulating advantage of micro-porous aggregate



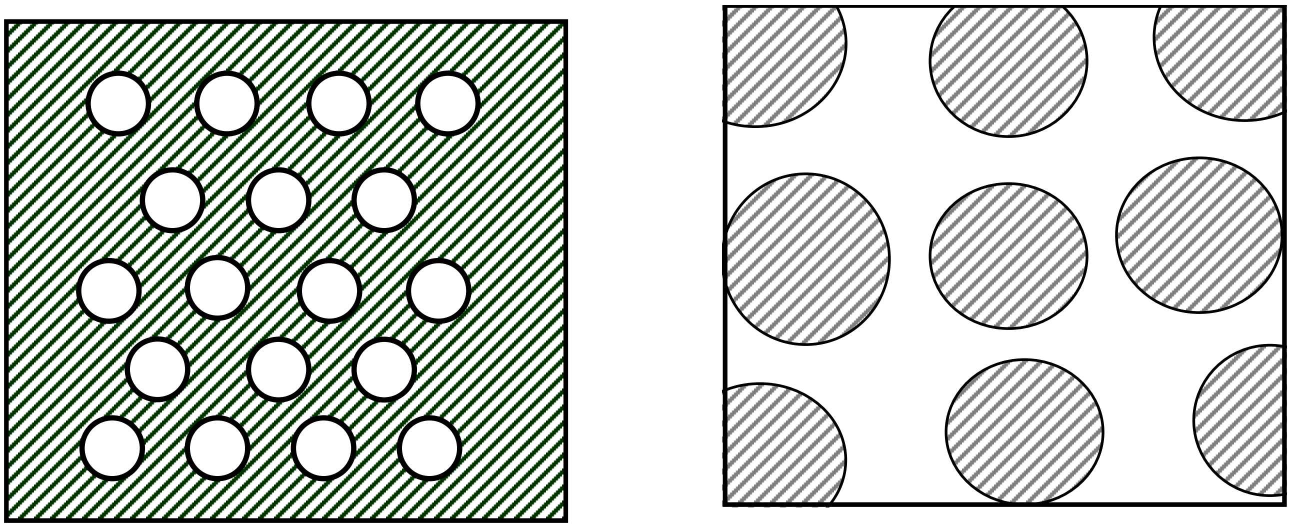
Thermal conductivity of the three lightweight castables with different aggregates

BD of the three castables were controlled at ~1.5g/cm^3

A theoretical analysis

on

Thermal conductivity in relationship with phase composition for a multi-phase material



(a)

Continuous dominant phase

(b)

Discontinuous dominant phase

Two modes of two-phase model

The total thermal conductivity of a two-phase material can be calculated by：

$$\lambda_m = \lambda_0 \frac{1 + 2V_d(1 - \frac{\lambda_0}{\lambda_d})/(\frac{2\lambda_0}{\lambda_d} + 1)}{1 - V_d(1 - \frac{\lambda_0}{\lambda_d})/(\frac{\lambda_0}{\lambda_d} + 1)}$$

Where, V_d—volumetric percentage of the dispersed phase, %

λ_0— thermal conductivity of the continuous phase

λ_d— thermal conductivity of the dispersed phase

If $\lambda_0 >> \lambda_d$, the formula can be simplified as:

$$\lambda_m \approx \lambda_0 \frac{(1 - V_d)}{(1 + V_d)}$$

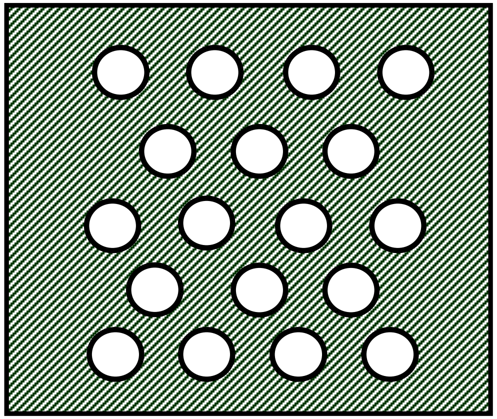
It indicates that **increased** V_d leads to thermal conductivity ↓.

If $\lambda_d >> \lambda_0$, the formula can be simplified as:

$$\lambda_m \approx \lambda_0 \frac{(1 + 2V_d)}{(1 - V_d)}$$

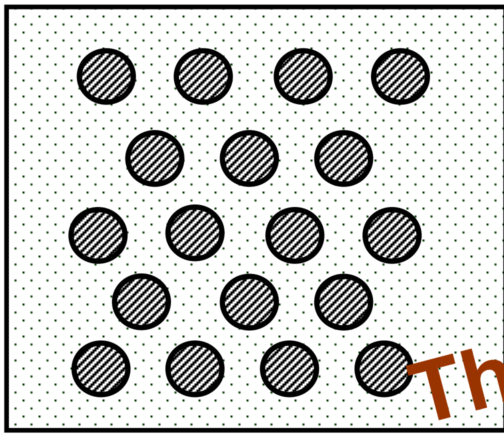
It indicates that **reduced** V_d leads to thermal conductivity ↓.

Three approaches to making lightweit castables



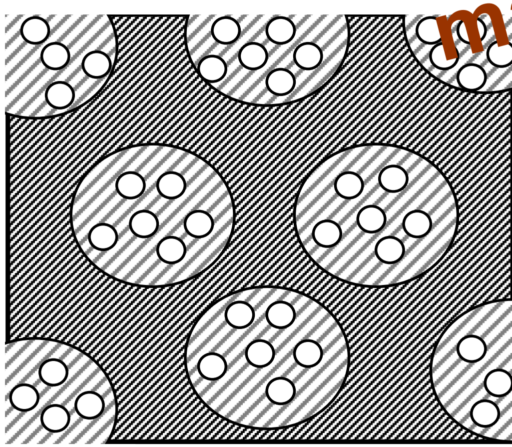
Dense matrix, hollow aggregates or big pores as dispersing phases

Type I



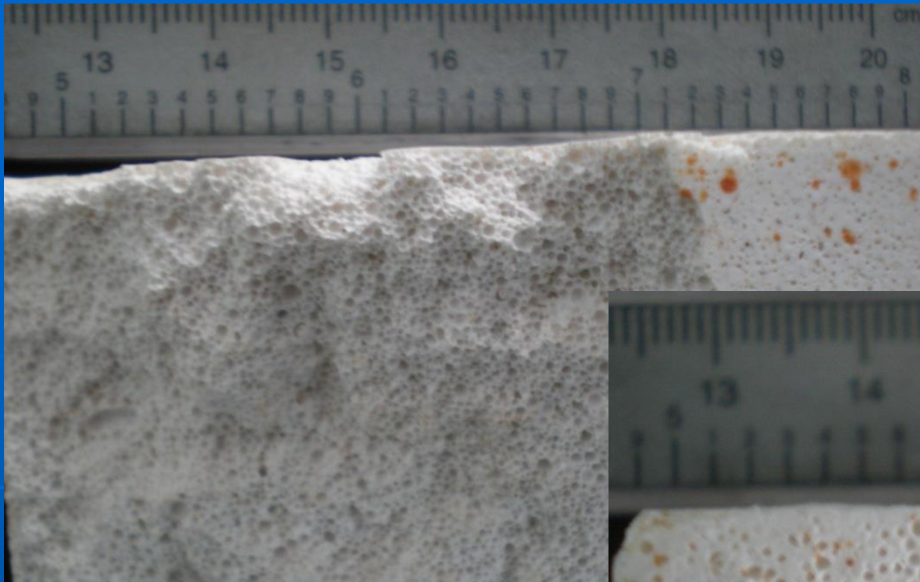
Dense aggregates, micro-pored matrix

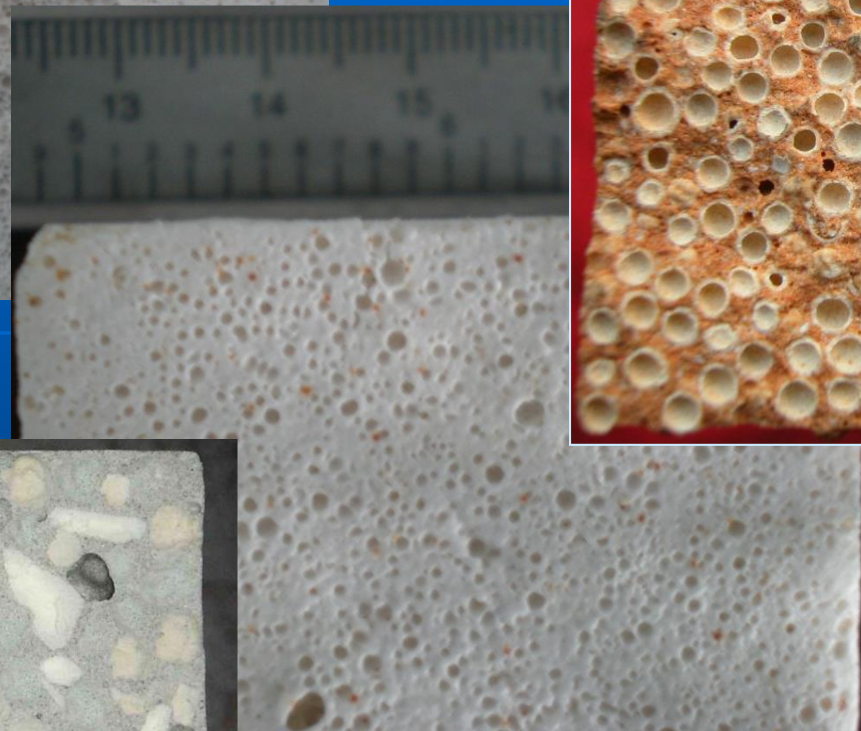
Type II



Dense matrix, micro-pored aggregates

Type III





Closed pores

Micro-pored aggregates

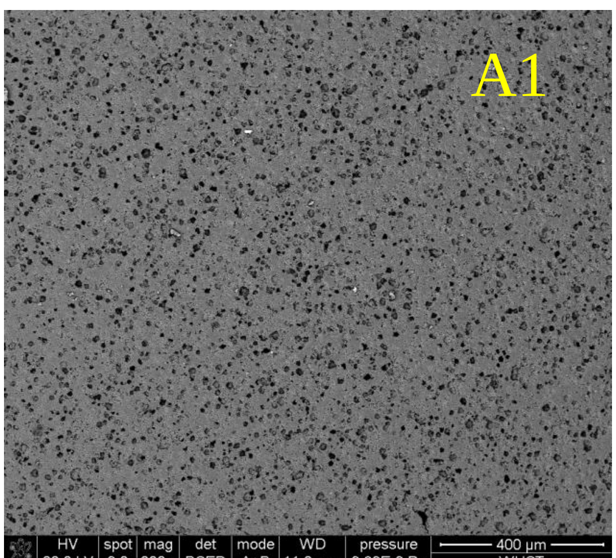
Newly developed weight reduced castables

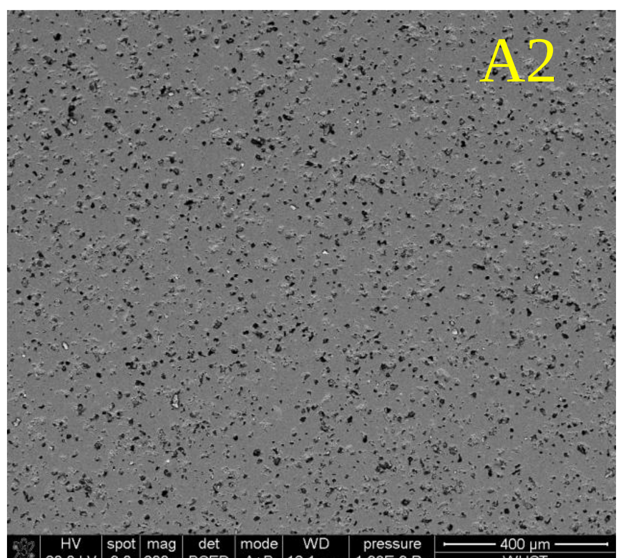
- Micro-pored sintered alumina and its castables
- Micro-pored and hollow mullite based aggregates and their castables
- LW forsterite and MgO-SiO_2 LW castables
- Mullite and Al_2O_3-MgO LW pre-cast shapes
- LW CA_6-MA clinker and the Al_2O_3-CaO-MgO LW castables
- Multi-layer concept

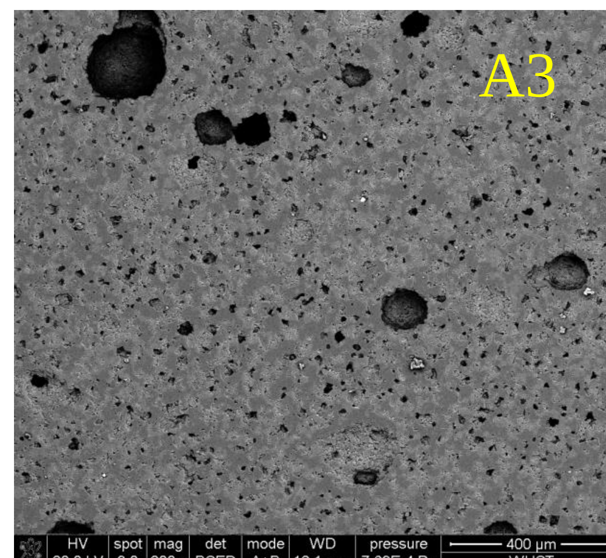
Microporous sintered alumina (MSA)

Three kinds of MSA in comparison with conventional one (A_0)

Code	BD, g/cm^3	TD, g/cm^3	AP, %	Closed porosity, %
A_0	**3.63**	**3.94**	**2.8**	**5.0**
A_1	**3.31**	**3.97**	**4.4**	**12.2**
A_2	**3.47**	**3.96**	**3.9**	**8.4**
A_3	**3.14**	**3.91**	**8.3**	**11.1**







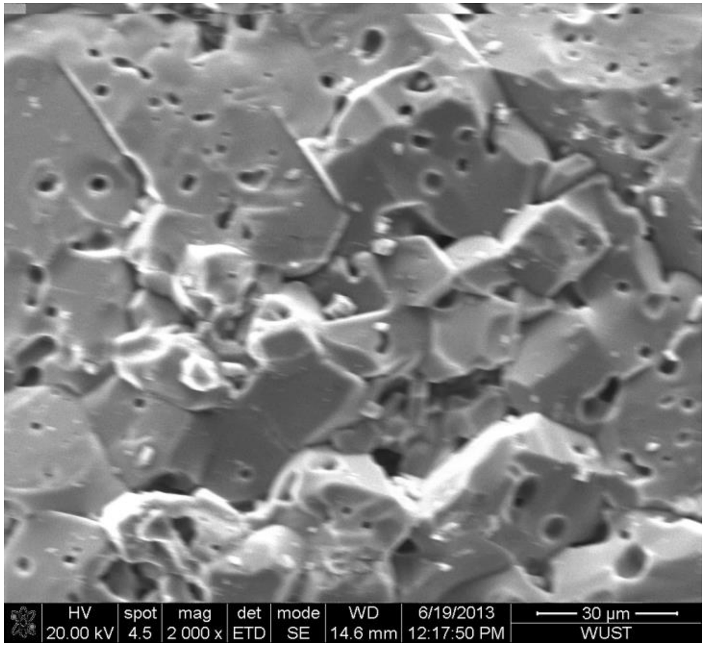
Thermal conductivity at 800℃
(by laser flash method)

Specimen	A_0	A_1	A_2	A_3
T. C., $W\cdot(m\cdot K)^{-1}$	11.13	6.47	8.36	9.05

Thermal conductivity of the MSAs is less than that of the conventional one (A_0), e.g., A_1 is reduced by ~42%, as compared to A_0.

Two types of sintered alumina

	BD /g/cm^3	Al_2O_3 %	SiO_2 %	Fe_2O_3 %	Na_2O %
Conv. S.A.	3.55	99.15	0.11	0.12	0.34
MSA	3.42	99.05	0.14	0.12	0.37

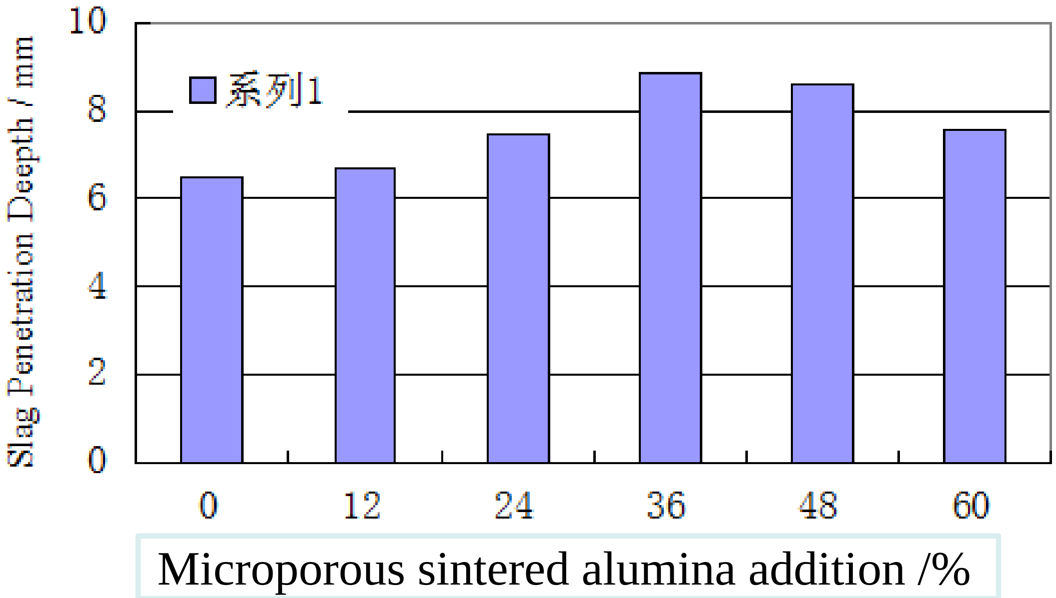


Microstructure of the industrialized MSA

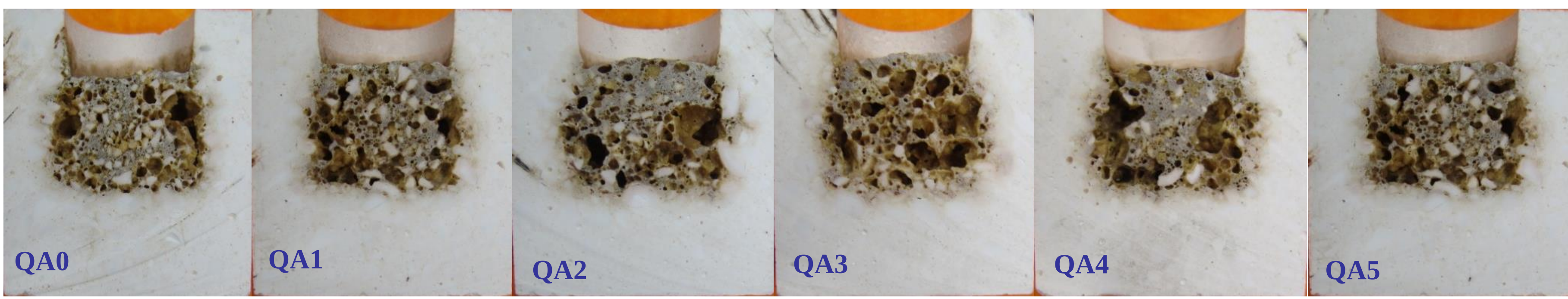
Experimental formula of Al_2O_3-Sp. Castables, %

Material	Size	Code					
		QA_0	QA_1	QA_2	QA_3	QA_4	QA_5
Conv. TA	10-0mm	60	48	36	24	12	0
	-320 mesh	8	8	8	8	8	8
Fused spinel	1-0mm	10	10	10	10	10	10
	-200 mesh	10	10	10	10	10	10
MSA	10-0mm	0	12	24	36	48	60
Untra-fine alumina powder		7	7	7	7	7	7
CA Cement		5	5	5	5	5	5

Slag resistance by crucible slag test



Increased MSA addition does not show significant negative influence on static slag resistance.

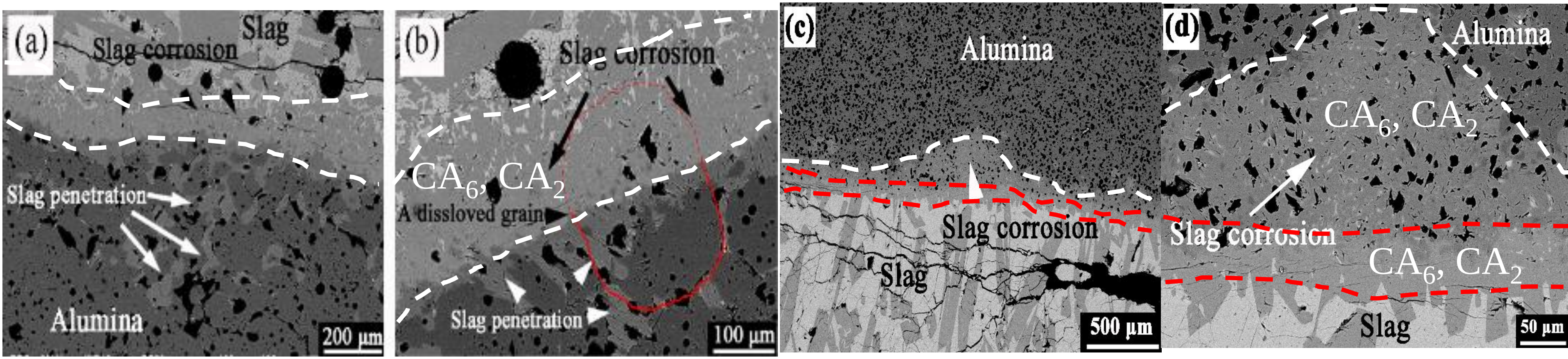


The influence of MSA addition on slag resistance

Slag corrosion test

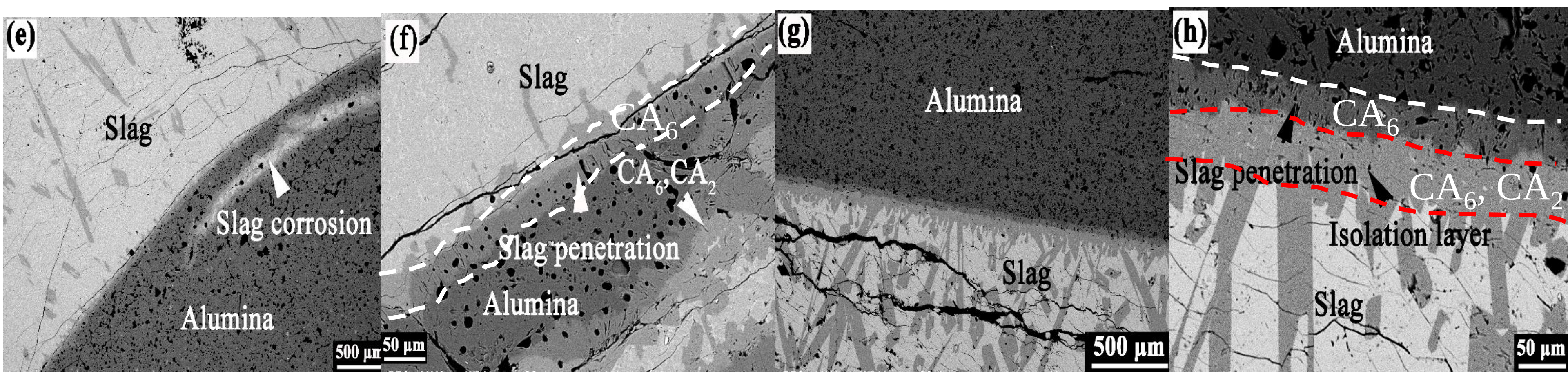
Common sintered alumina

Immersion method, 1600°C×3h



Slag 1 | **60 wt% CaO; 20 wt% Al_2O_3; 20 wt% SiO_2**

Slag 2 | **48 wt% CaO; 36 wt% Al_2O_3; 16 wt% SiO_2**



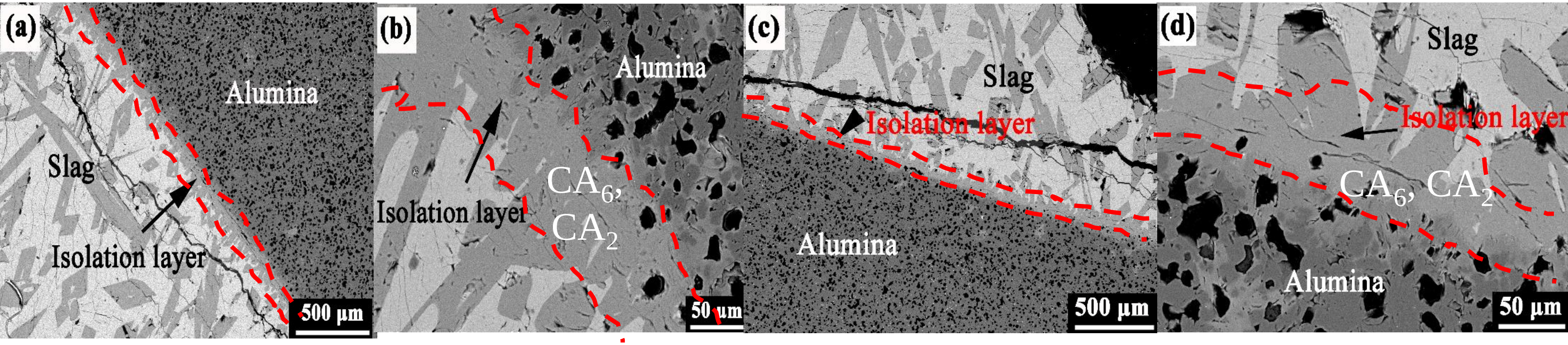
Slag 3 | **55 wt% CaO; 42 wt% Al_2O_3; 3 wt% SiO_2**

Slag 4 | **72 wt% CaO; 4 wt% Al_2O_3; 24 wt% SiO_2**

Slag corrosion test

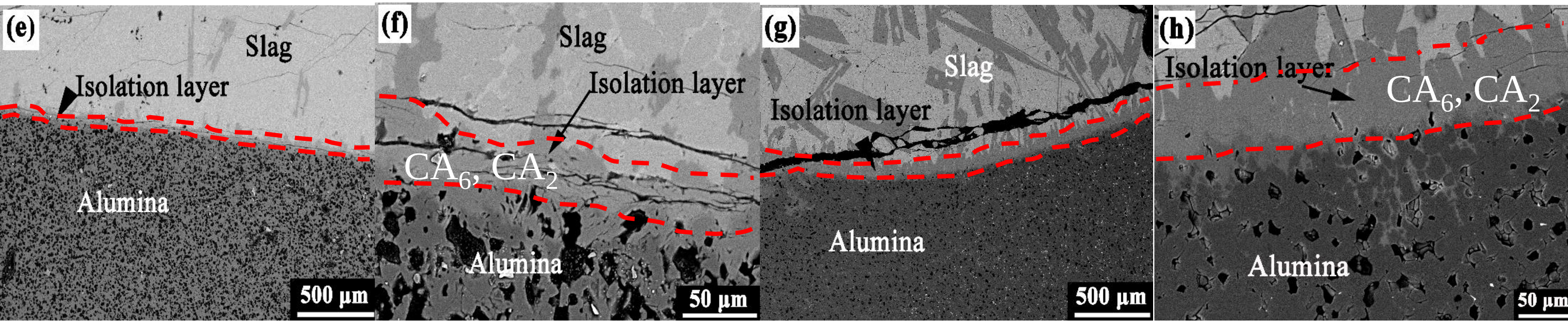
Micro-pored sintered alumina

Immersion method, 1600°C×3h



Slag 1 60 wt% CaO; 20 wt% Al_2O_3; 20 wt% SiO_2

Slag 2 48 wt% CaO; 36 wt% Al_2O_3; 16 wt% SiO_2

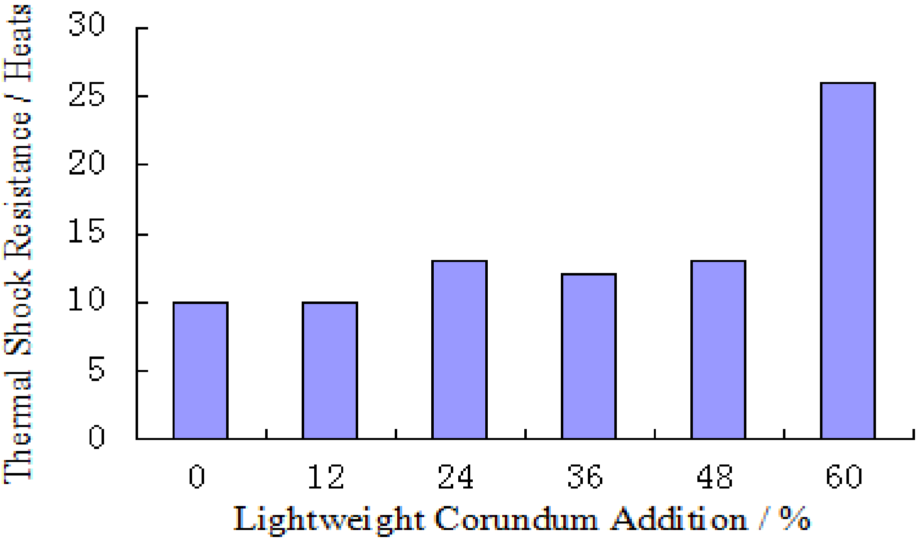


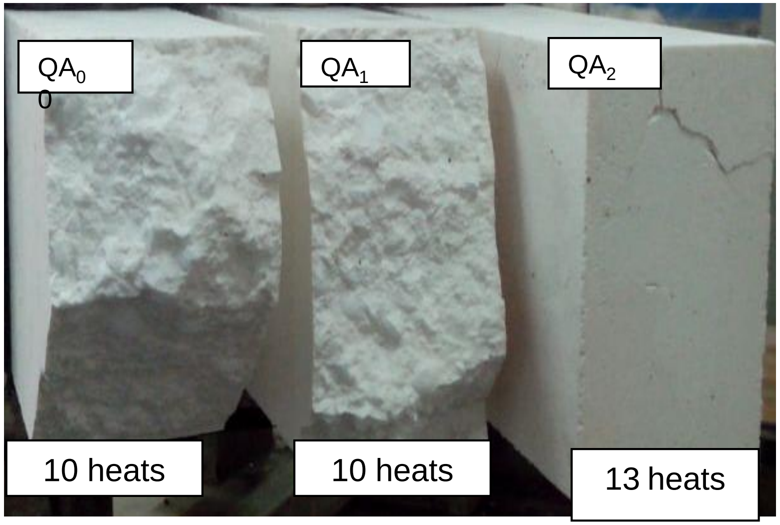
Slag 3 55 wt% CaO; 42 wt% Al_2O_3; 3 wt% SiO_2

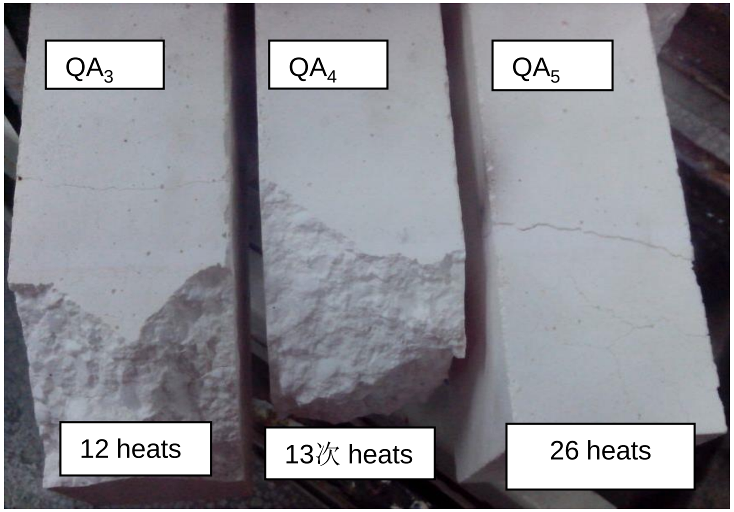
Slag 4 72 wt% CaO; 4 wt% Al_2O_3; 24 wt% SiO_2

TSR comparison by water quenching

MSA addition↑→ TSR↑, 26 heats at a MSA addition of 60%.







Advantages of Microporous sintered alumina

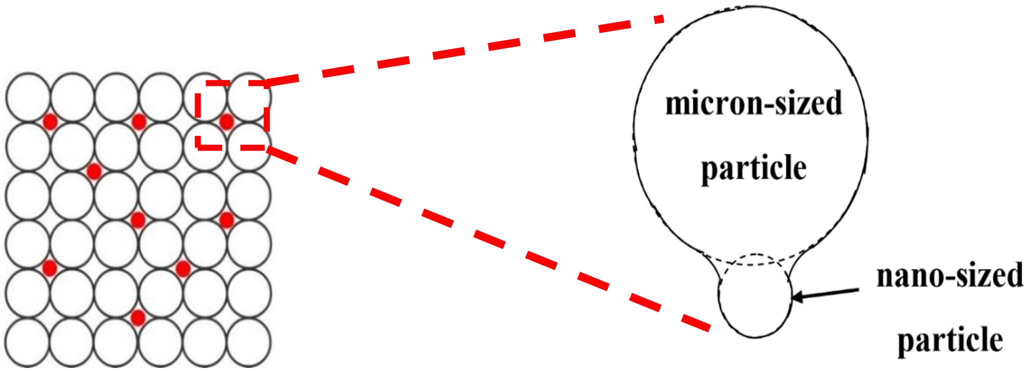
The following advantages can be provided by using MSA to partially or completely replace conventional sintered alumina aggregates:

- Reduced thermal conductivity, contributive to insulating and energy saving
- Reduced material consumption, helpful to lighten refractory linings
- No degradation in strength and resistance to corrosive media attack, due to enhanced grain-matrix bonding.
- Significantly improved thermal shock resistance.

Fabrication principle

Pores $v_p = F_p M_p$ — $v_b > v_p$ → **Closed pores**

Grain boundaries $v_b = (F_b - NF_p) M_b$ — $v_b < v_p$ → **Apparent pores**



Superplasticity is defined as the ability of a material to exhibit substantially large elongation under stress. Furthermore, superplastic materials deform by means of **grain boundary sliding**.

$$\dot{\varepsilon} = \frac{AGb}{kT}\left(\frac{b}{d}\right)^{p}\left(\frac{\sigma}{G}\right)^{n} D$$

Grain size

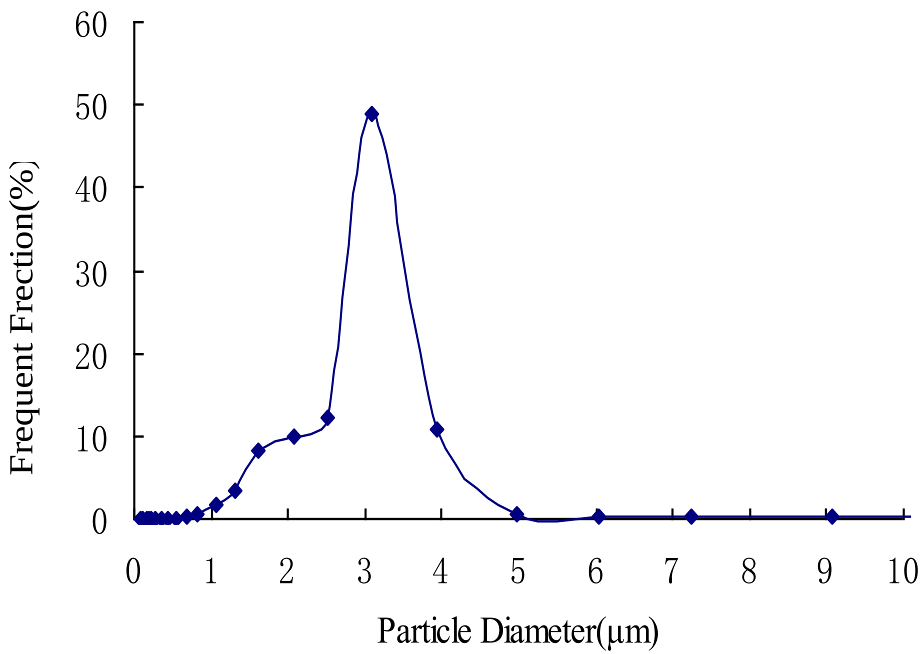
Diffusion coefficient

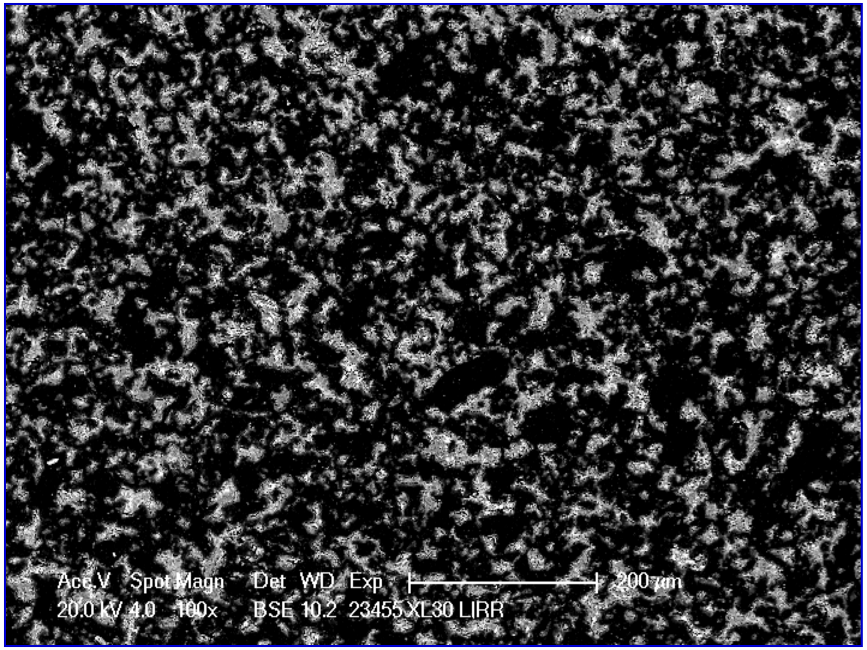
In-situ stress ⇄ Superplasticity

Newly developed weight reduced castables

- **Micro-pored sintered alumina and its castables**
- **Micro-pored and hollow mullite based aggregates and their castables**
- **LW forsterite and MgO-SiO_2 LW castables**
- **Mullite and Al_2O_3-MgO LW pre-cast shapes**
- **LW CA_6-MA clinker and the Al_2O_3-CaO-MgO LW castables**
- **Multi-layer concept**

Micro-pored mullite

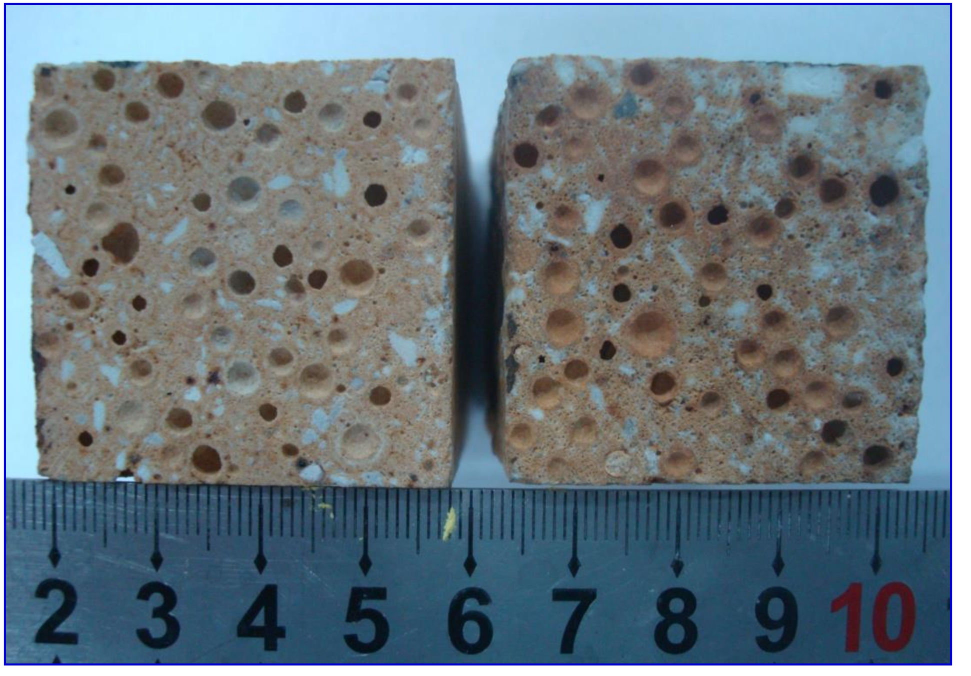




- **70% Al_2O_3 content**
- **AP above 50%**
- **BD under 1.2g/cm^3**

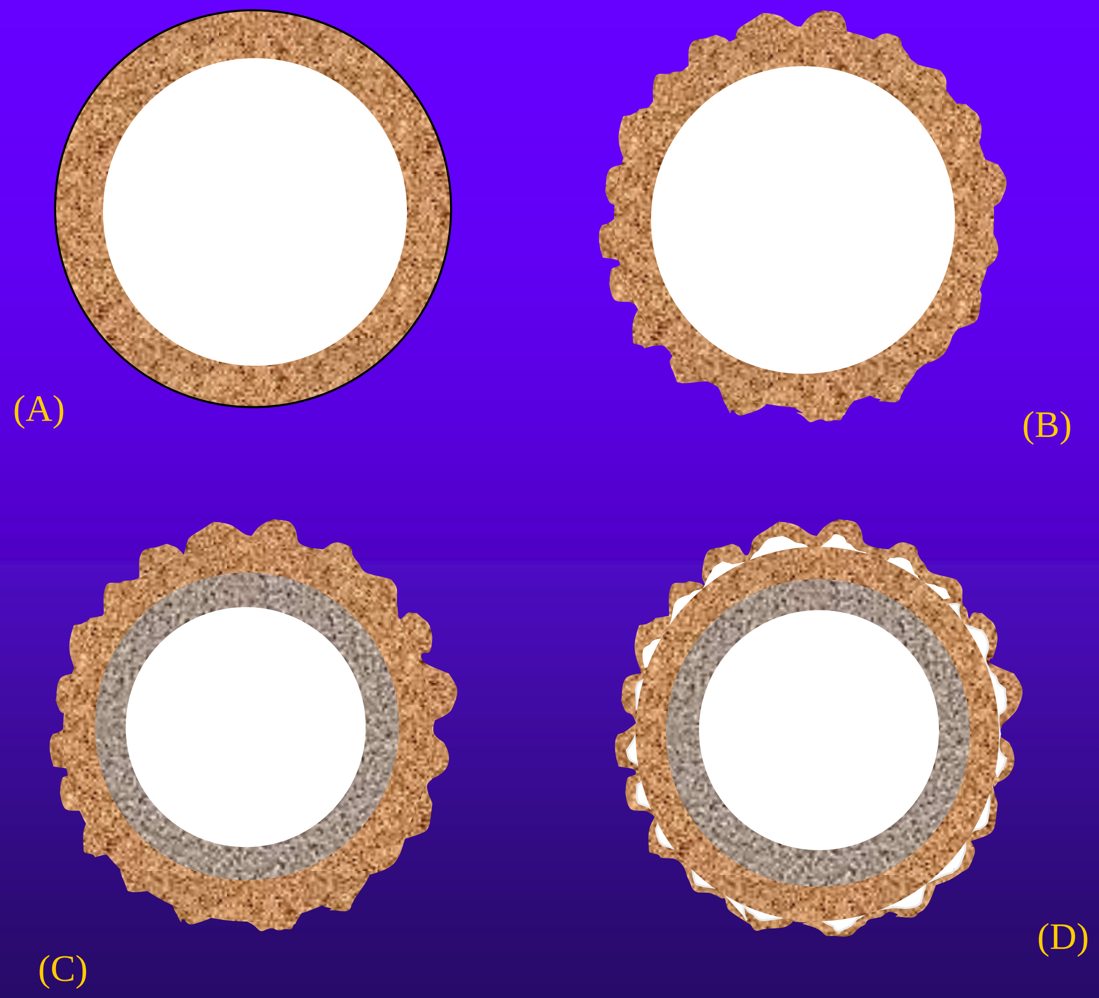
Micro-pored mullite castables

Combined utilization of two LW aggregates

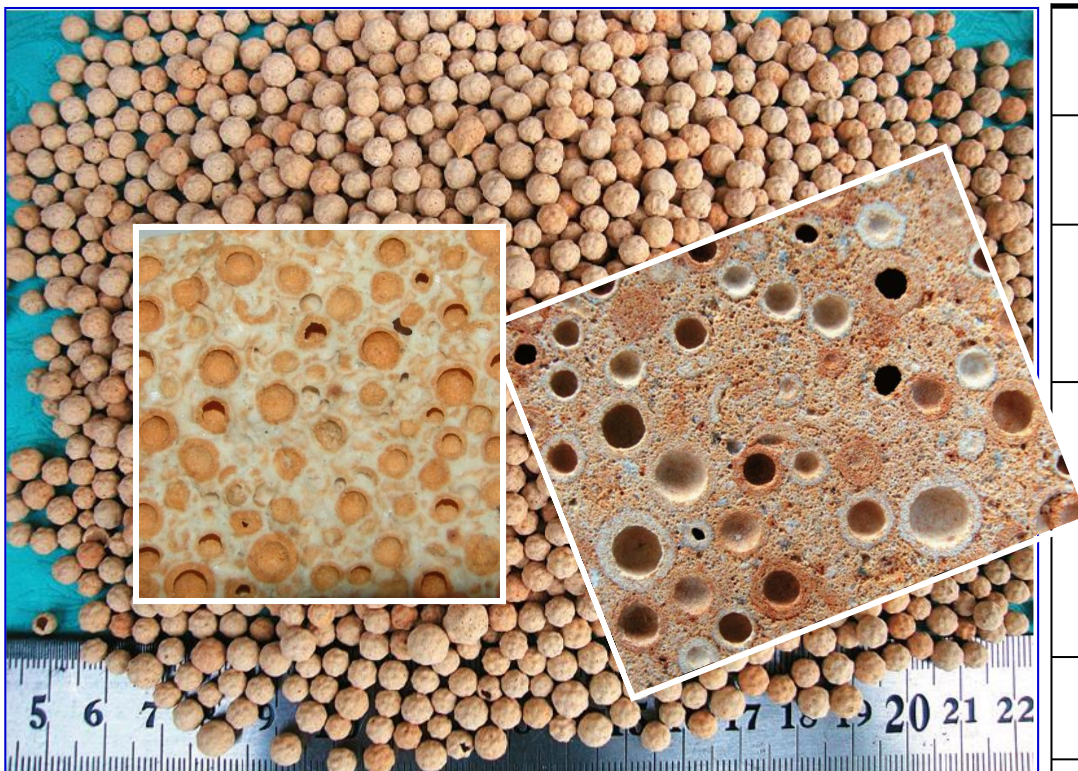


- **Featured by low thermal conductivity**
- **Micro-pored mullite + MHB → low TC + high strength**

Hollow spherical aggregates



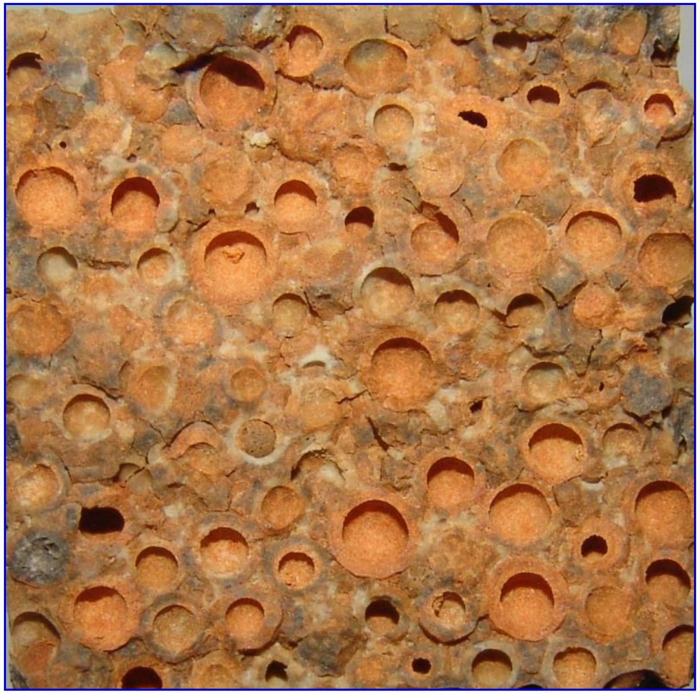
Mullite hollow ball (MHB)

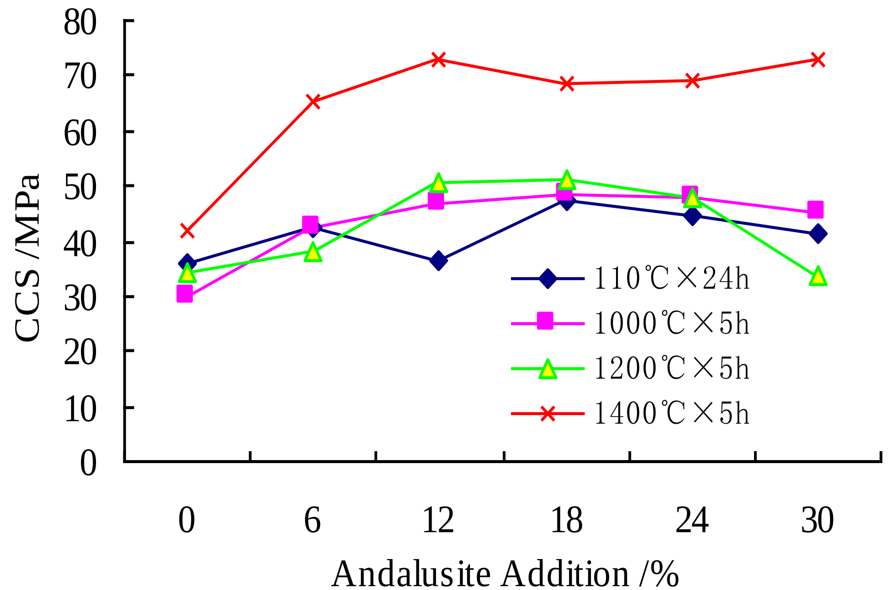


Al_2O_3 content	55 - 60 %
K_2O+Na_2O content	≤1.0%
Stacking density	0.68 - 0.76 g/cm^3
Refractoriness	≥1770℃
Cylinder compressive strength	2.2 - 2.8 MPa
Size in diameter	3 - 8mm
Wall thickness	0.5 - 3 mm

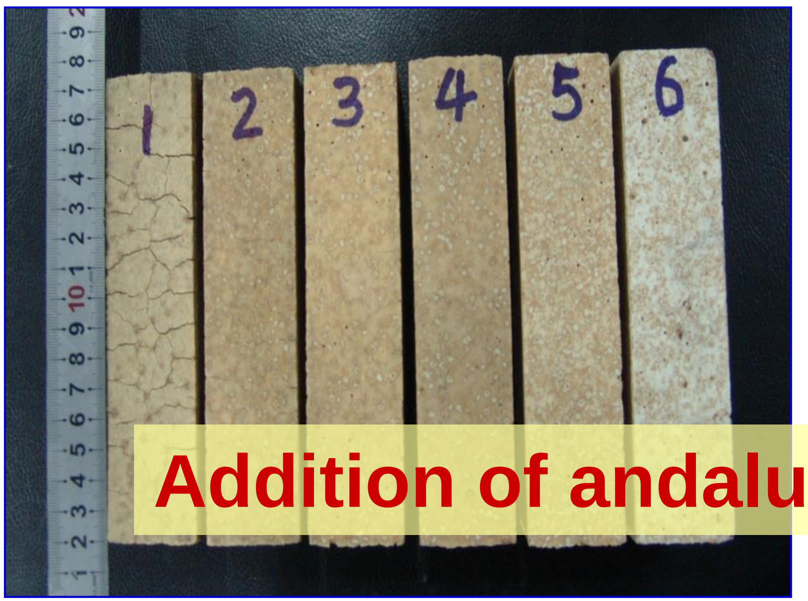
- **Hard shell and hollow core.**
- **Sizes: Φ3mm, Φ5mm and Φ8mm.**

LW castables using MHB as aggregates





- Lightweight
- High strength
- Service temp. can go up to 1450°C

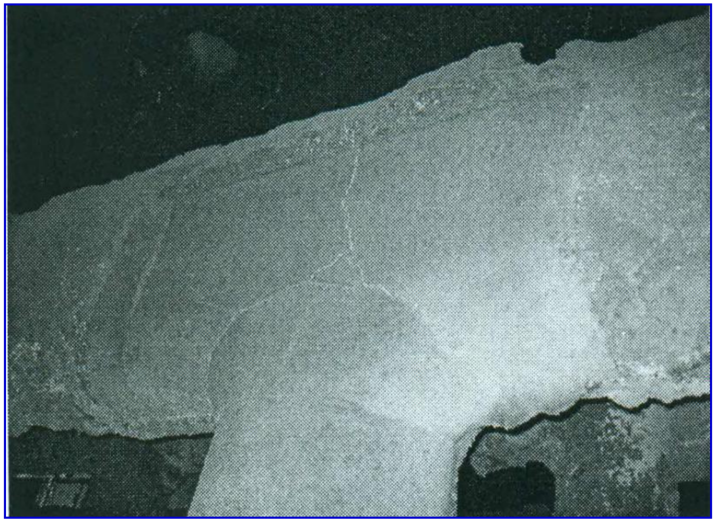


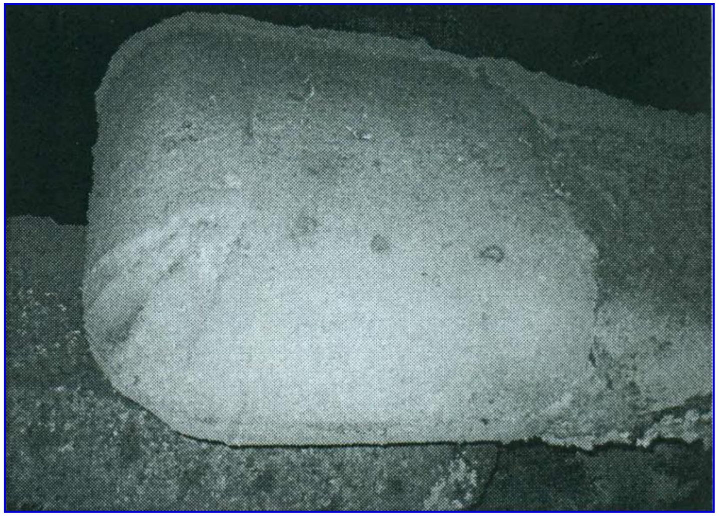
Addition of andalusite!

LW castables for water cooled skid and post lining of stepping beam reheating furnace at BaoSteel

After installation

After 9 month service





MHB LW castables for annular heating furnace in Maanshan Steel

- **Wheels of steel rolling heating furnace with an outer diameter of 28m and an inner diameter of 24m.**
- **Installed in Aug 2011 by a LW castable with BD of 1.8g/cm^3.**

Metal Magnesium Reduction Furnace

Pre-cast LW burners

Other applications

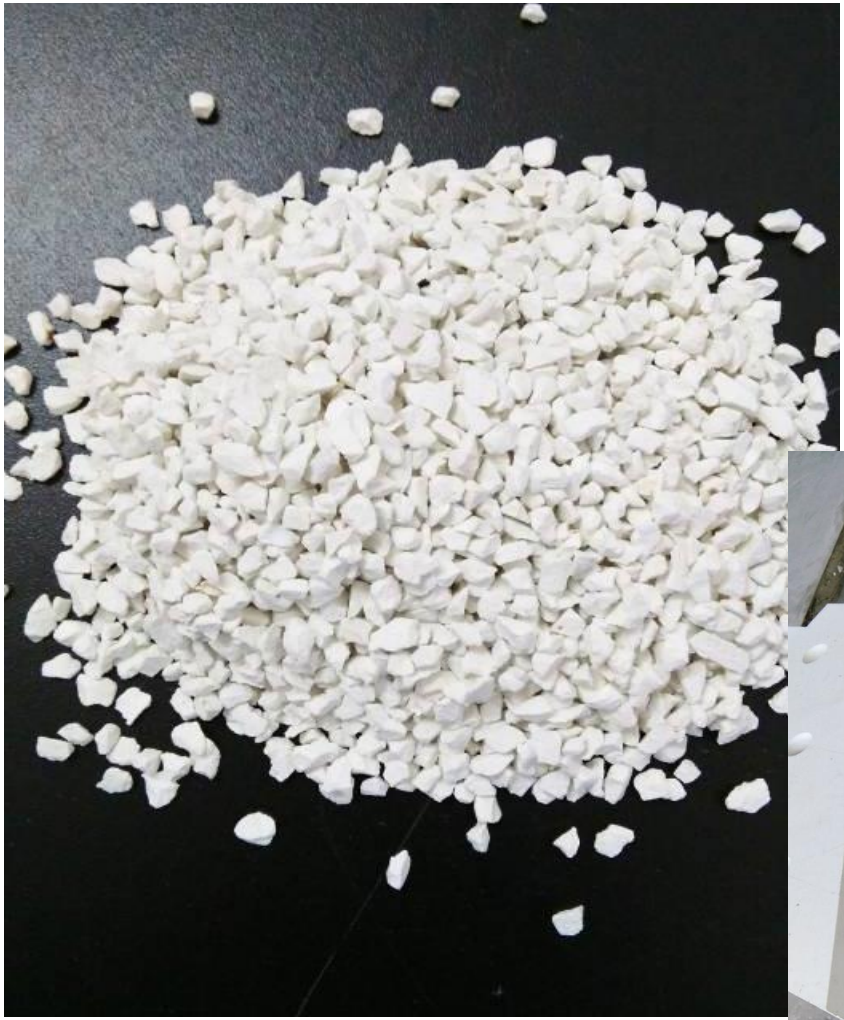
Properties of the LW vs. dense castable for ladle back lining

		Micro-pored LW castables	Dense castables
BD, g/cm^3	110℃×24h	1.6~1.8	2.7~2.8
	1450℃×3h	1.6~1.8	2.7~2.8
PLC, %	1450℃×3h	-0.04	-0.06
CCS, MPa	110℃×24h	>20	>25
	1450℃×3h	>40	>60
CMOR, MPa	110℃×24h	>4	>4
	1450℃×3h	>8	>8
Thermal conductivity, W/m.K	800℃	0.65	0.98

Use effect of the LW castable as ladle back lining in two steel plants

		48t and 80t ladles at Xingtai Steel	160t Ladles at Benxi Steel
Ladle configuration and service condition	Bottom	MgO-C bricks, 300mm thick	MgO-C bricks, 320mm thick
	Wall	MgO-C bricks, 170mm thick	Low carbon bricks, 150~180mm thick
	Slag line	MgO-C bricks, 200mm thick	MgO-C bricks, 160mm thick
	Wall back lining	Micro-pored LW castables, 85mm in thickness	Micro-pored LW castables, 90mm in thickness
	Average shell temperature	200~230 ℃. 80~100℃ lower than that by using dense castables	180~220 ℃. 50~80℃ lower than that by using dense castables
	Tapping temperature	1600 ℃. Reduced by 15~20℃	1600~1630 ℃. Reduced by about 15 ℃
	Refining way	LF, 100%	LF, RH

Lightweight mullite based sintered clinker



Comparison of two types of mullite based sintered clinker

	Al_2O_3, %	Fe_2O_3, %	BD, g/cm^3	AP, %	WA, %	$K_2O + Na_2O$, %
CM45	46.66	0.73	2.56	3.3	1.27	0.23 + 0.12
LM45	46.79	0.71	2.18	18.4	8.44	0.26 + 0.13

Comparison of two castables using different aggregates

	Al_2O_3, %	Fe_2O_3, %	AP, %	BD, g/cm^3	T.C., W/m.K (Hot face temp.: 1000℃)	CCS, MPa	RUL, ° C (0.2MPa, $T_{0.6}$)
CM	50.86	0.85	16. 8	2.36	1.12	89	1426
LM	50.99	0.86	22. 9	2.14	0.76	83	1455

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LW forsterite and MgO-SiO_2 LW castables

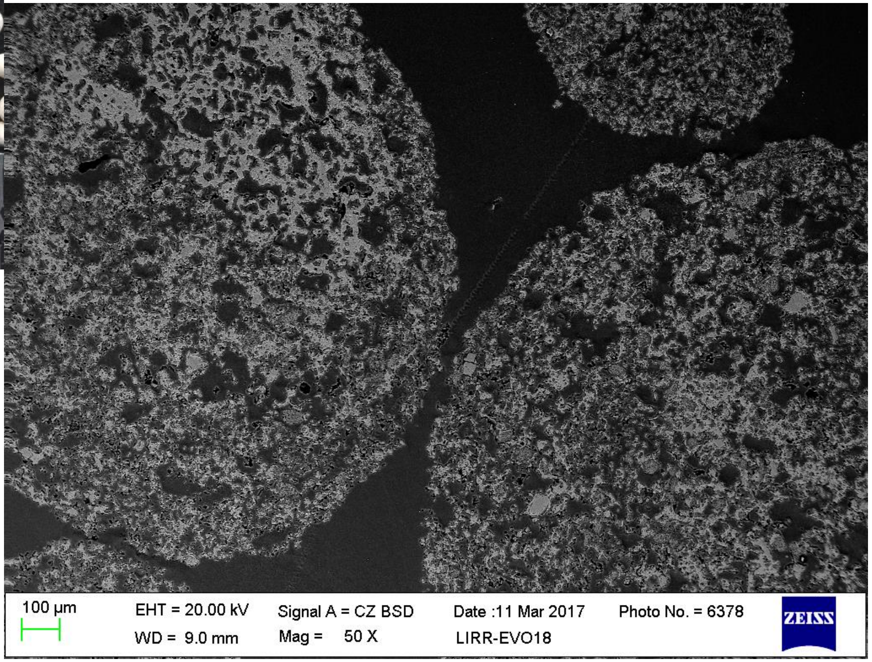
Basic LW castables
- **Higher service temp.**
- **Good resistance to furnace gas**
- **Rich resources**

LW and semi-LW MgO-SiO_2 castables

		1#	2#
BD of the adopted aggregates, g/cm^3		~1.4	~1.8
BD, g/cm^3	1400℃×3h	1.90	2.14
PLC, %	1400℃×3h	-0.07	+0.7
CMOR, MPa	1400℃×3h	3.9	5.7
CCS, MPa	1400℃×3h	23	35.95

Forsterite based porous spheres

Synthesized porous forsterite balls with sizes 2-5mm



Section of porous forsterite balls by SEM observation

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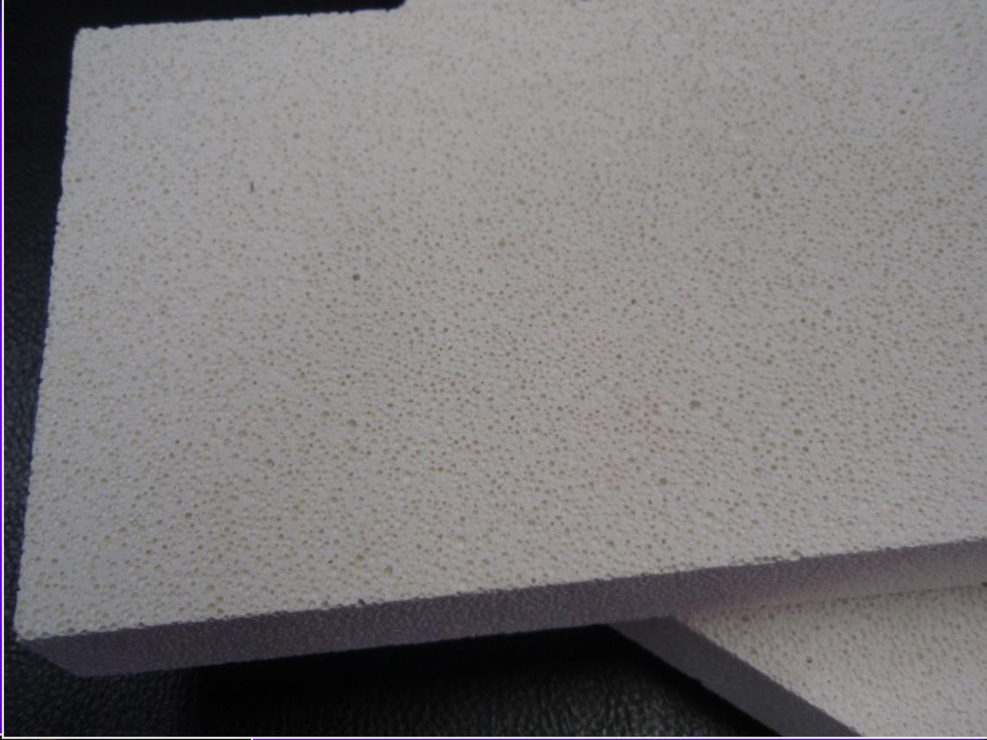


Pore sizes: under 1mm

Thickness: 18-25mm

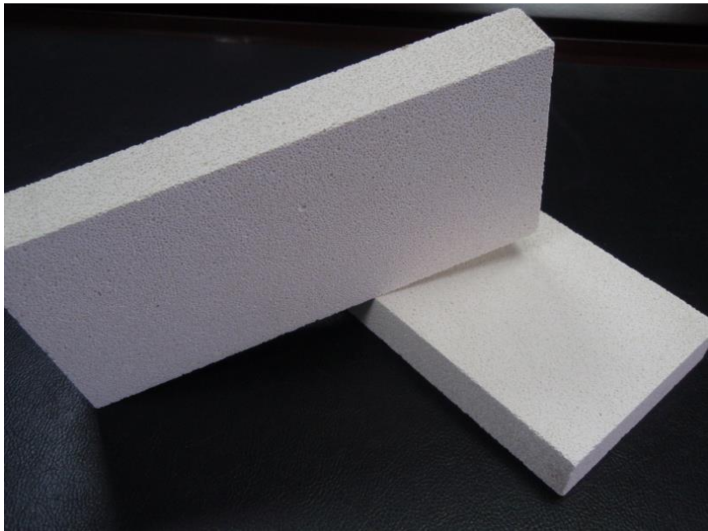
Mullite based close-pored insulating boards

		RF-IBAM	RF-IBBM	RF-IBCM
Chem. comp., %	Al_2O_3	72.28	71.56	50.82
	SiO_2	26.68	21.57	43.05
	Fe_2O_3	0.13	1.35	0.86
	TiO_2	0.08	1.69	0.48
BD, g/cm^3		1.05	0.98	0.92
CCS, MPa		18	15	13
PLC, % (1400°C， 3h)		-1.18	+0.28	-0.46
Thermal conductivity, W/m·K at 800°C on hot face		0.612	0.416	0.294

LW pre-cast shapes in Al_2O_3-MgO system

	Testing condition	Measured data
Chemical composition，%	Al_2O_3+MgO	89.56
BD，g/cm^3	110℃×24h	1.53
CMOR，MPa	1500℃×3h	8.7
CCS，MPa	1500℃×3h	43.6
PLC，%	1500℃×3h	+0.56
HMOR，MPa	1400℃×1h	0.15
Thermal conductivity，	700℃（Average T）	0.704
W/MK	900℃（Average T）	0.790

- **Service temperatures up to 1600°C**
- **Closed pore structure**
- **Suitable for high temp. back linings**



Newly developed weight reduced castables

- **Micro-pored sintered alumina and its castables**
- **Micro-pored and hollow mullite based aggregates and their castables**
- **LW forsterite and MgO-SiO_2 LW castables**
- **Mullite and Al_2O_3-MgO LW pre-cast shapes**
- **LW CA_6-MA clinker and the Al_2O_3-CaO-MgO LW castables**
- **Multi-layer concept**

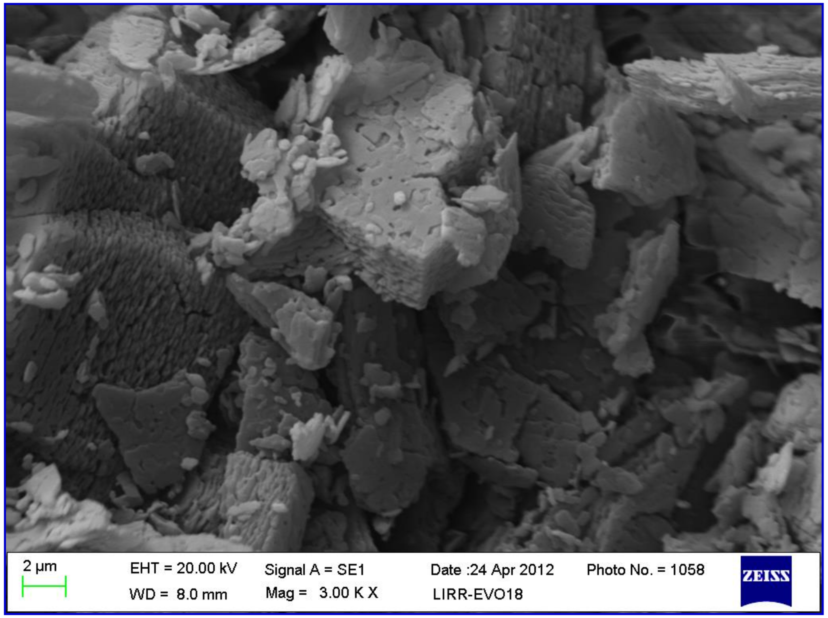
Features of CA_6, MA spinel & corundum

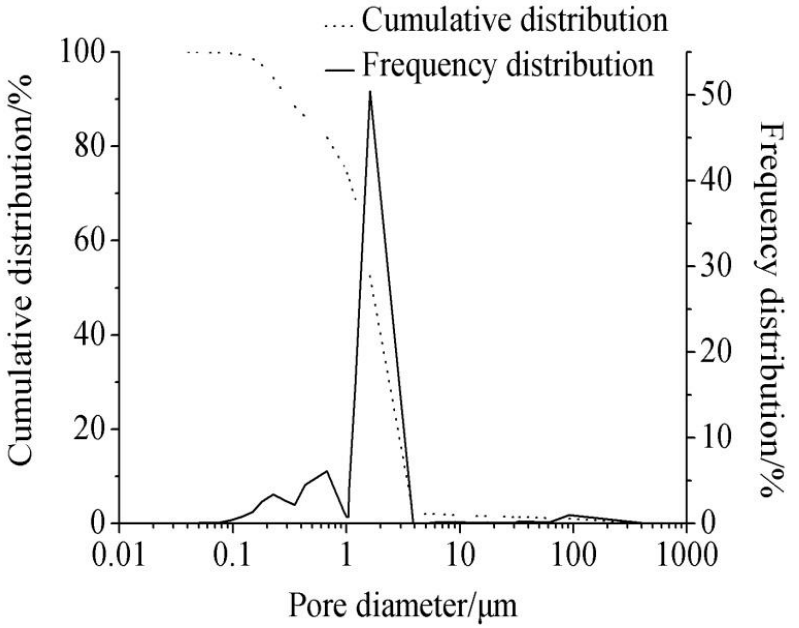
CA_6	MA
mp. 1860°C	**mp. 2135°C**
Therm. coef. 8.0×10^{-6} °C^{-1}	**Therm. coef. 8.9×10^{-6} °C^{-1}**
Good stability in reducing atmosphere	**Good stability both in oxygen and in reducing atmosphere**
Good resistance to alkali	**Good resistant to chem. attack**
Theo. density 3.38g/cm^3	**Theo. density 3.58g/cm^3**

Corundum

mp. 2050 °C, therm. coef. 8.0×10^{-6} °C^{-1}, good chemical stability

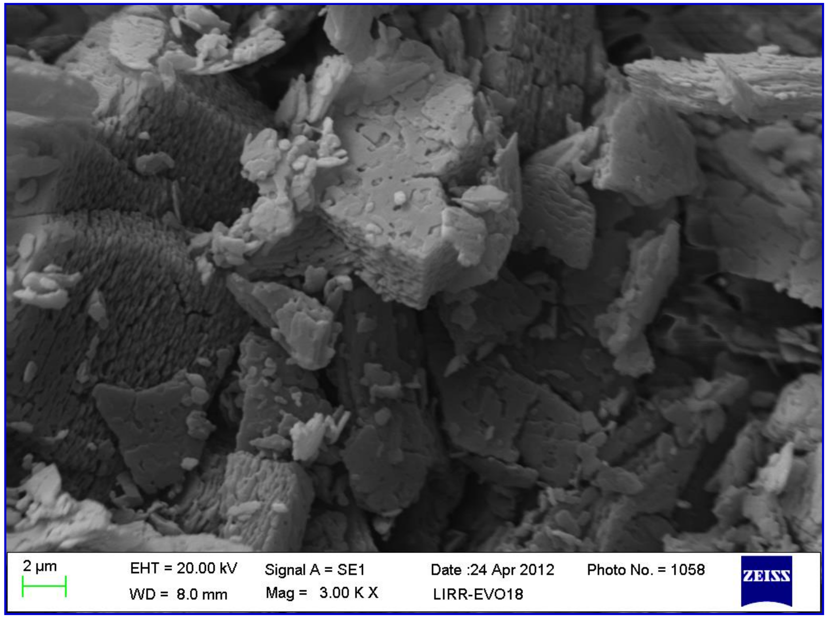
Microstructure and pore size distribution of porous CA_6-MA

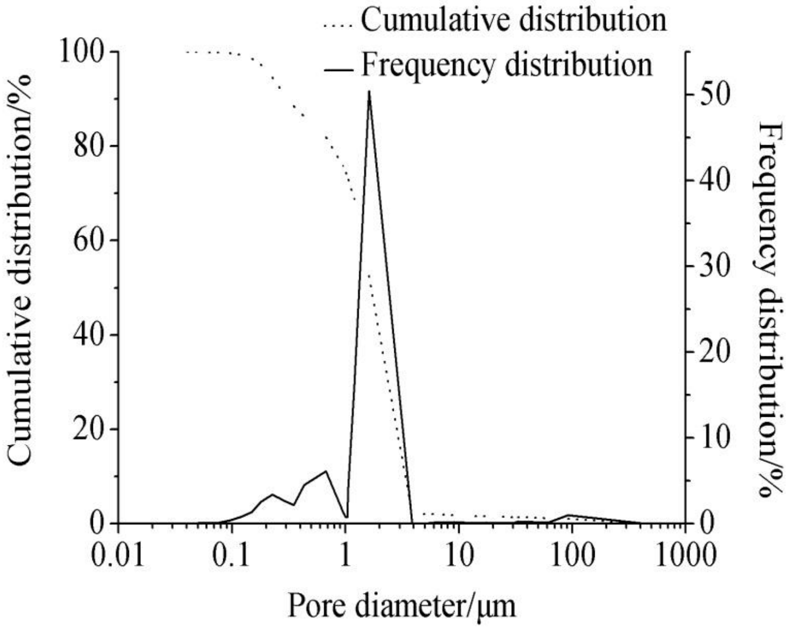




Phase composition: ~70% CA_6, ~30% MA

Microstructure and pore size distribution of CA_6-MA aggregate





Properties of Al_2O_3-CaO-MgO LW castables

BD, g/cm3	1600°C×3h	1.48
AP, %	1600°C×3h	60
PLC, %	1600°C×3h	+1.30
CMOR, MPa	1600°C×3h	5.2
CCS, MPa	1600°C×3h	14.0
HMOR, MPa	1400°C×0.5h	1.2
T. C., $W(m\cdot K)^{-1}$	1000°C at hot face	0.38

Newly developed weight reduced castables

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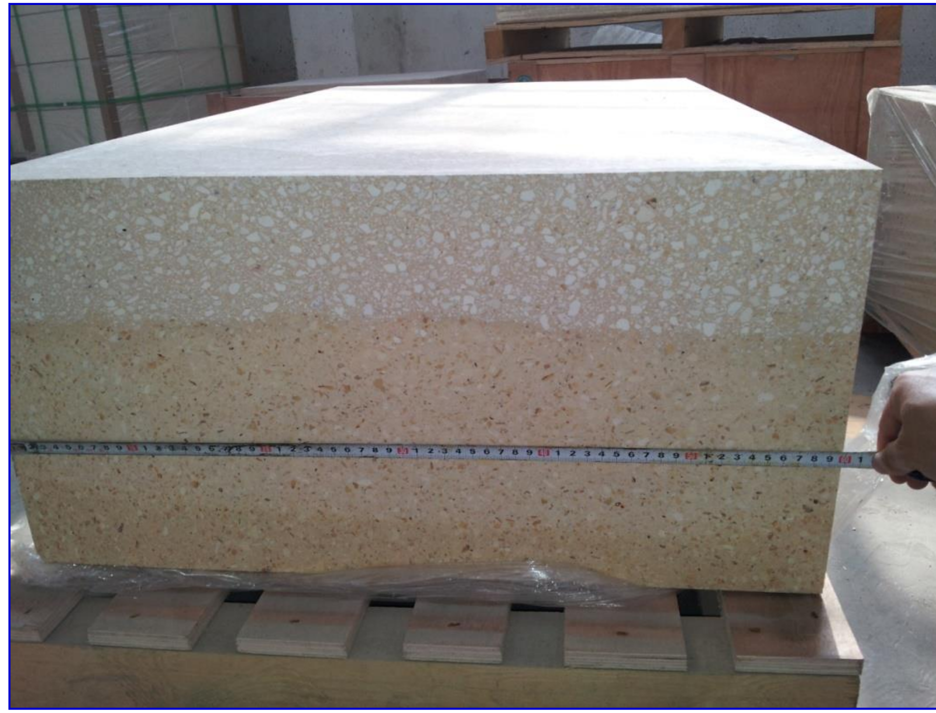
- **LW forsterite and $MgO\text{-}SiO_2$ LW castables**
- **Mullite and $Al_2O_3\text{-}MgO$ LW pre-cast shapes**
- **LW $CA_6\text{-}MA$ clinker and the $Al_2O_3\text{-}CaO\text{-}MgO$ LW castables**
- **Multi-layer concept**

Micro-pored mullite and its pre-cast blocks

QM45-1.8 Micro-pored mullite



Pre-cast block with combination of dense and LW castables

Application: back lining of tin bath bottom in glass industry

Two-layer brick for hot metal ladle lining

Multi-layer brick for cement kiln

Concluding remarks

— meaningfulness and prospets

- The development and application of weight reduced refractories can play an important role in energy saving and material consumption reduction for refractory linings. Experience sharing and application promotion are necessary to achieve lower consumptions.
- The relationship between pore structure and comprehensive properties of products is worth of careful investigation so that overall compromising various properties can be realized.

Concluding remarks

— meaningfulness and prospects

- It is not always reasonable and necessary to achieve "the lighter, the better". Lightweight concept and approaches to high performance can also be applied to dense refractories in favor of lowering energy and material consumptions.
- More available sources, better qualities and more competitive prices must be achieved during the preparation, optimization of new lightened aggregates and the manufacture and application of the related lightened products for increasing acceptance and adoption of them.

Thanks for your attention