Presenter Name: **Dr. Jyoti Prakash Nayak**

Paper name: **Alumina Rich Spinel Refractories for Steel Ladle Application – A Complete Solution by TRL Krosaki**

PRESENT AFFILIATION	**TRL Krosaki Refractories Ltd**
AREAS OF INTEREST	**Aluminosilicate Refractories**
Education	o **Ph.D. (Bio ceramics)** o **B.E. & M.Tech. (Chemical Engineering)**

Experience	• **12 yrs.**
Projects:	❖ **Ph.D. (01 - continuing) - As co-guide : NIT, Rourkela** ❖ **M.Tech. (02-nos. - completed) – As co-guide :** *Govt. College of Engg. & Ceramic Tech., Kolkata (2016)*
Publication / Patent	✓ **08-nos. in high impact factor journals** ✓ **11-nos. in refractory based Technical articles / Journals** ✓ **02-nos. patent (*Applied*)**

Alumina Rich Spinel Refractories for Steel Ladle Application

– A Complete Solution by TRL Krosaki

Dr. Jyoti Prakash Nayak

Contents

Background

- In early 1960s, increases of crude steel production and growth of demand for higher-purity steel.

  (Adoption of MgO-Cr_2O_3 Brick)

- In 1972, established stable operating technology for stainless steel production.

- In 1980s, demand for higher-purity steel increased.

- In 1990, demand for ultralow-carbon steel - Adoption of (Al_2O_3 + Spinel + Magnesia/Dolomite Brick)

- From 1995 onwards, demand for ultralow-carbon steel - Adoption of (Al_2O_3 rich + $MgAl_2O_4$ Spinel brick)

Introduction

Characteristics of Alumina Rich Spinel Brick

- High Chemical Purity (Al_2O_3 + MgO) > 99.0 %
- High Refractoriness
- Suppressing slag penetration
- High corrosion resistance
- Withstand on operational changes such as increasing tapping temperatures & longer holding times
- No carbon pick up by steel from the lining

Hence, Spinel based refractories are now being used widely in steel, glass, lime, and cement industries.

Mechanism

STEEL PROCESSING

CaO–FeO–SiO_2 slag penetrates into the matrix

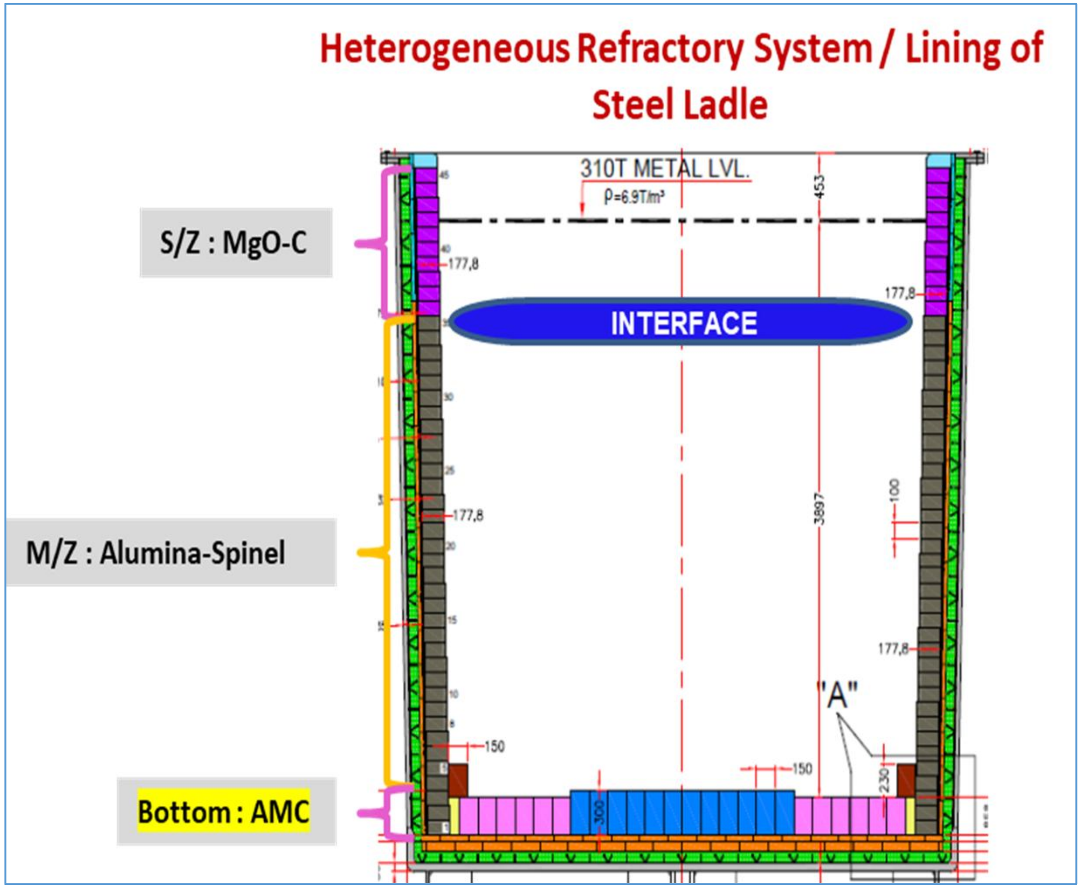
CaO in the slag reacts with Al_2O_3 to form CaO–Al_2O_3 compounds such as CA_6

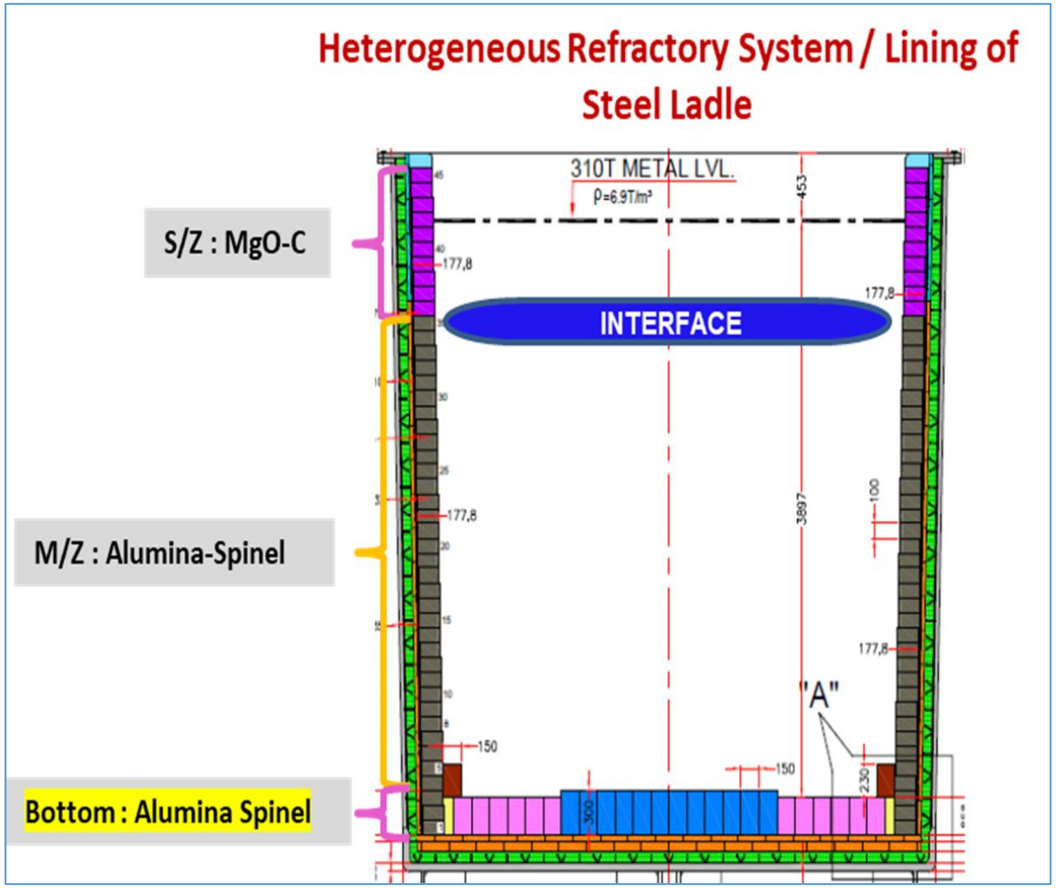
FeO forms a solid solution in the spinel

The slag composition moves to a SiO_2-rich composition as the penetration proceeds and liquid phase becomes more viscous

Thus, suppressed the rate of slag penetration in Al_2O_3–spinel refractories

Refractory Lining Pattern of Steel Ladle





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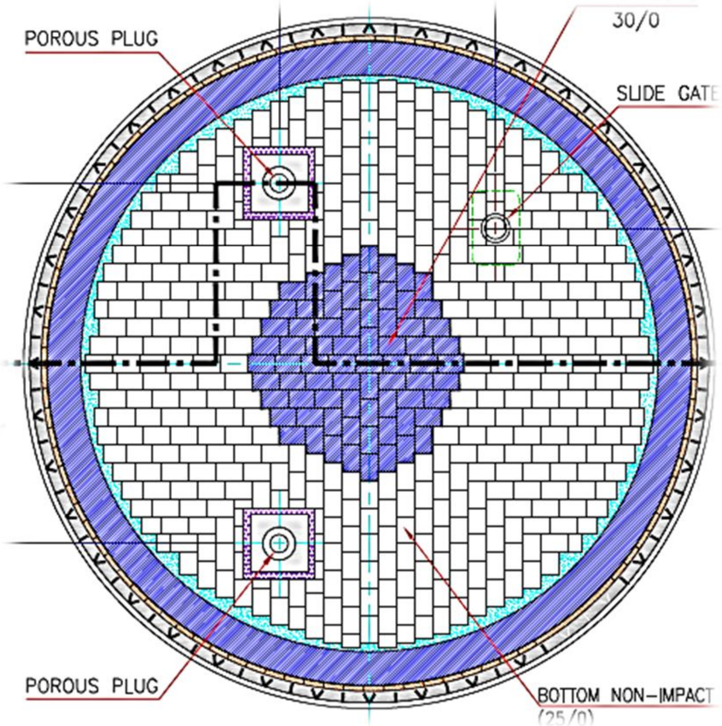
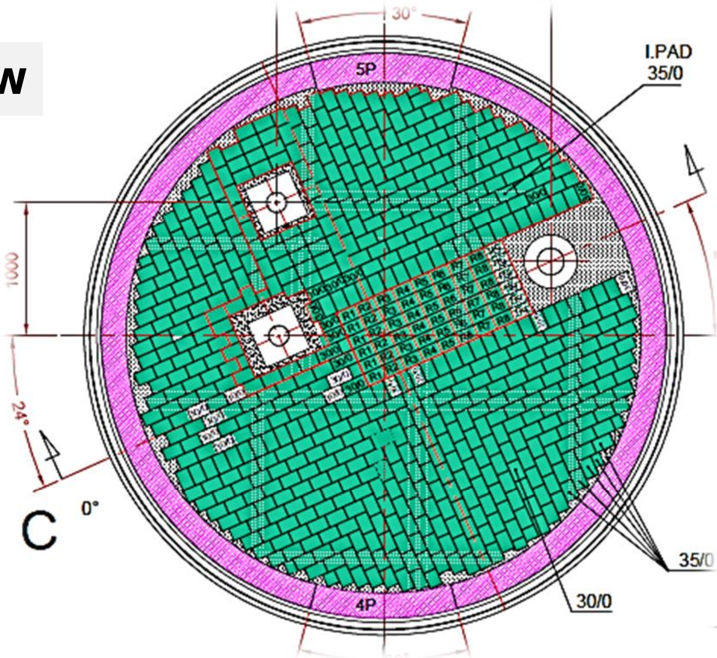
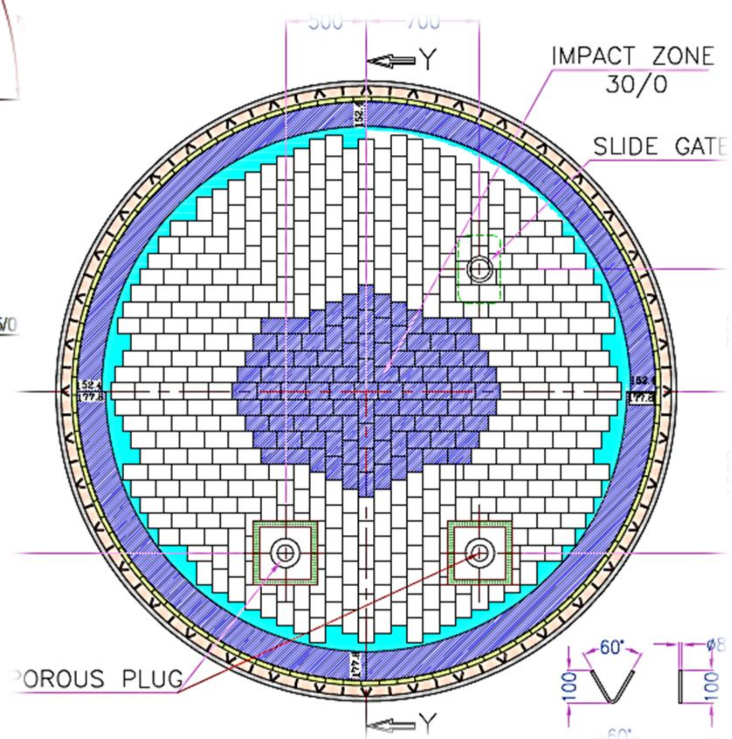
Different design of Steel Ladle - Top View







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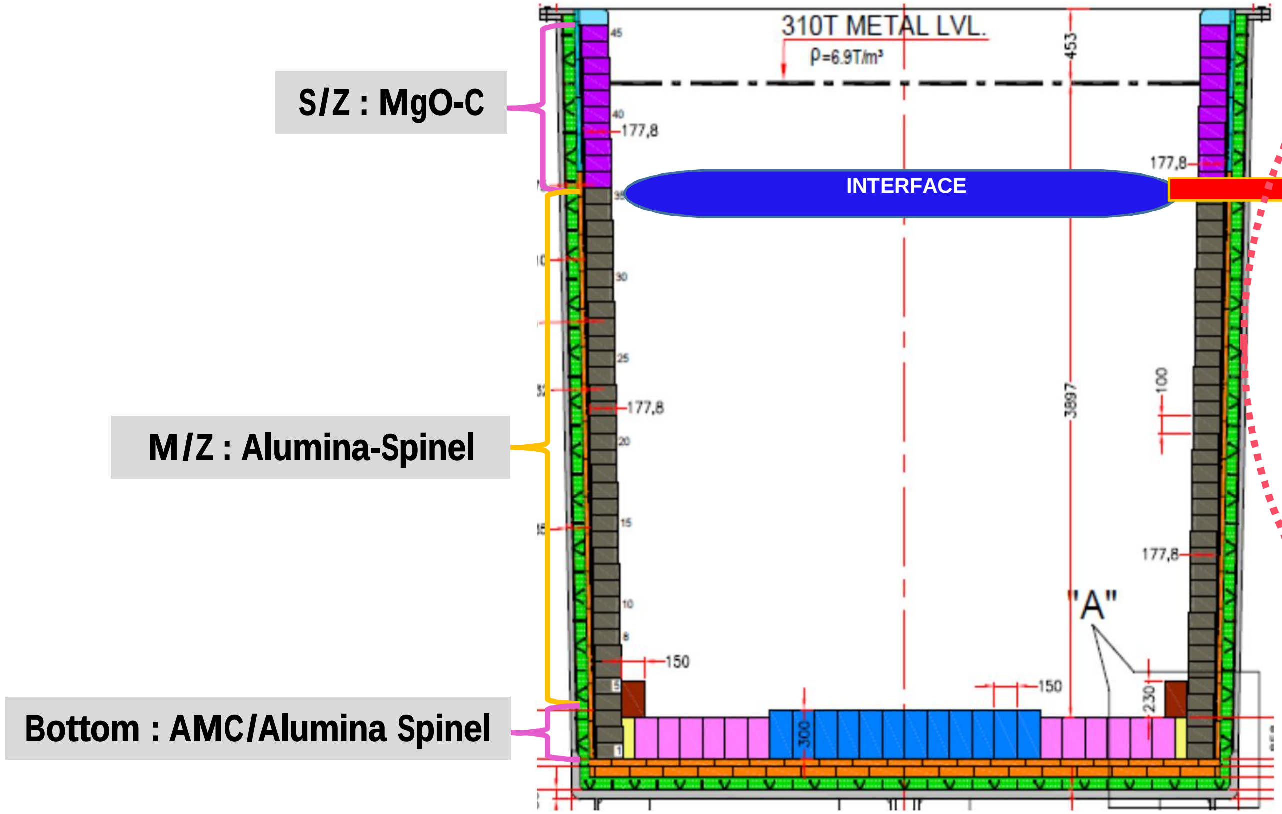
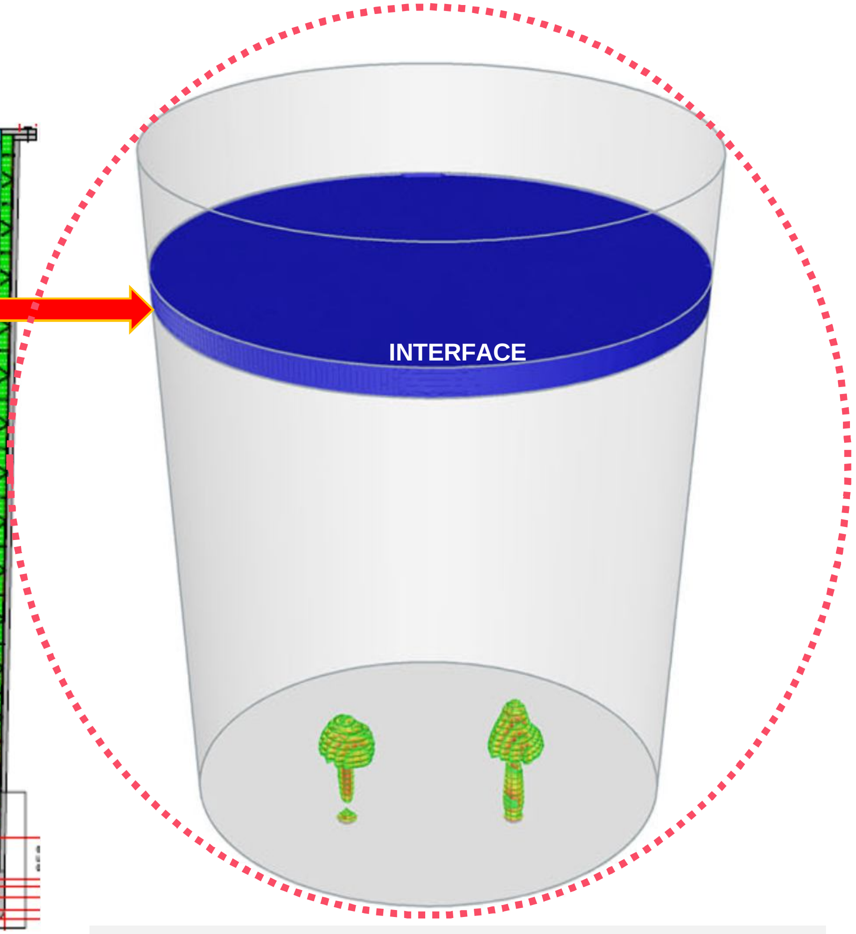
Steel Ladle





Model representation of Steel ladle

Mechanism of Steel Processing *via* Refractory Lining

During production of steel, the degree of oxide inclusions partly depends on the reaction of the melt with the furnace lining, the ladle lining and the pouring system. The refractory may be eroded by the molten steel and slag as well as corroded through chemical reaction with the slag and molten steel and the deoxidation of products.

Thus, it is important to understand the mechanism involved during processing of steel through steel ladle by using refractories via;

(i) Thermodynamics and thermo physical phenomena

- **Diffusion of gaseous components to the boundary layer**
- **Chemical reaction at the interface**
- **Diffusion of dissolved components to the bulk and the growth of the oxide at the interface**

(ii) Kinetic reactions

Contd…

(i) Thermodynamics and thermo physical phenomena

- **Diffusion of gaseous components to the boundary layer**
- **Chemical reaction at the interface**
- **Diffusion of dissolved components to the bulk and the growth of the oxide at the interface**

According to Lee & Zhang, the motion of the slag film caused by surface tension phenomena (wettability) between the refractory and slag essentially causes the local corrosion of refractories at the slag surface (Fig 1). This is because the slag film motion accelerates the dissolution rate of the refractory and also induces the abrasion of some refractories.

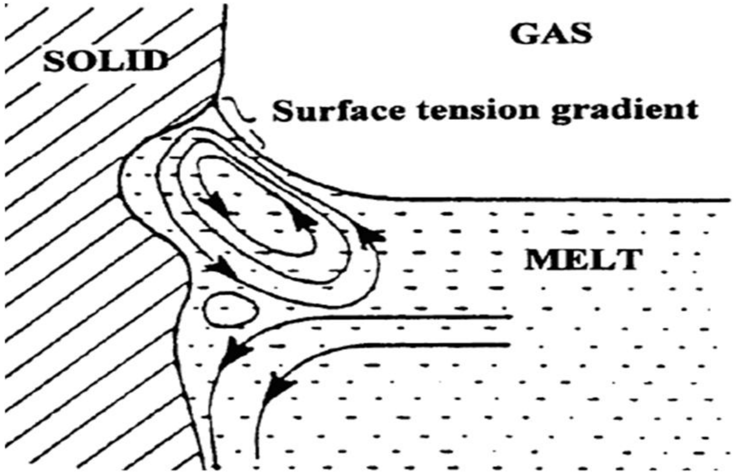


Fig. 1: Motion of the slag film caused by the surface tension phenomena between the refractory and slag.

Note:

The active film motion is dominantly induced by the Marangoni effect and/or change in the form of the slag film due to the variation of the surface tension and the density of slag film.

Lee W. E.; Zhang S.: Melt Corrosion of Oxide and Oxide-Carbon Refractories, International. Materials Reviews, Vol. 44, No. 3, (1999) pp 77-104.

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(ii) Kinetic Reactions

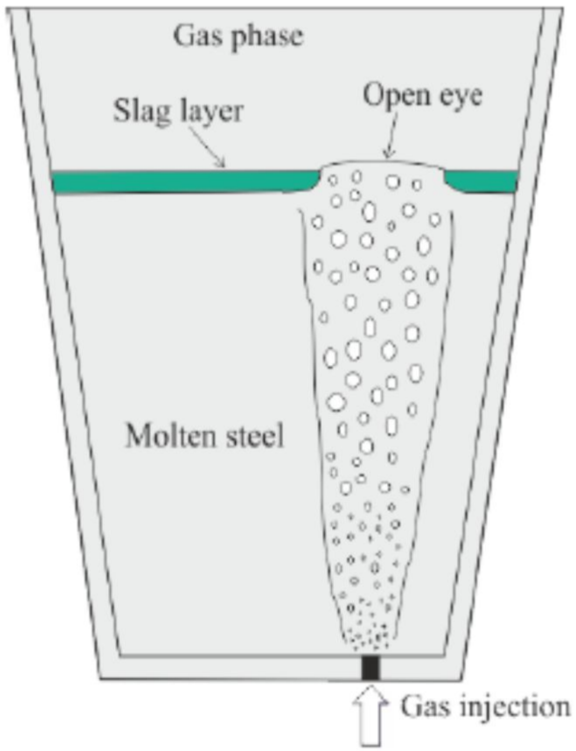
Corrosion of the lining material in contact with slag during ladle refining of steel is usually described in three major categories:

- ***Dissolution, or diffusion, which is a chemical process by which the refractory material is continuously dissolved***
- ***Penetration, by which the slag penetrates into the refractory and causes mechanical effects***
- ***Erosion, which is the abrasion process of the refractory material exposed to gas and slag movement***

Erosion of the refractory material in contact with the slag is dependent on the abrasion, which is determined by the high-velocity slag and gases. It is common opinion that the erosion effects are not so high when alumina or magnesia linings are used. However, the corrosion rate is typically higher for a polycrystalline ceramic (refractory) than for a single crystal, due to grain boundary effects.

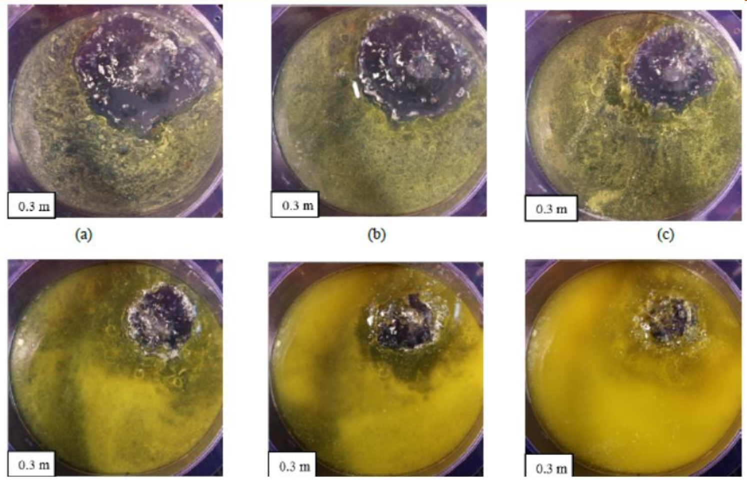
Note: Viscosity is an important factor also that affects the penetration. At the boundary layer, where the slag dissolves some refractory oxide, the viscosity of the slag will increase and further attack by the slag is then possible by diffusion through a viscous slag layer at the interface.

Impact of Slag Eye on Performance of Steel ladle

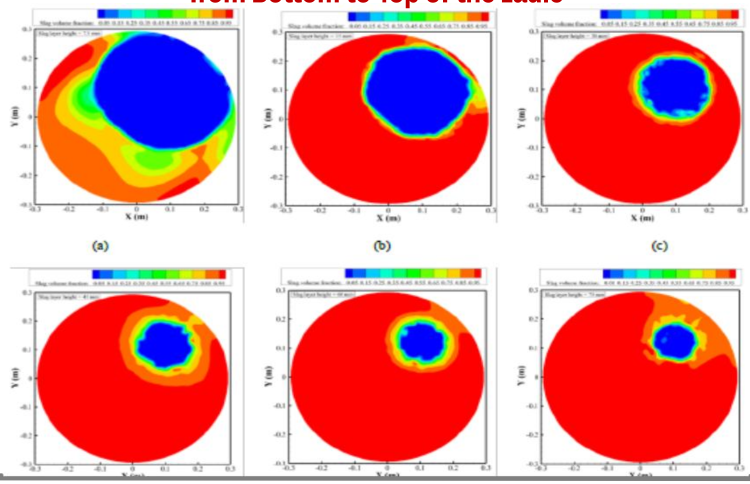


Schematic gas stirring process (single Plug) in a Ladle

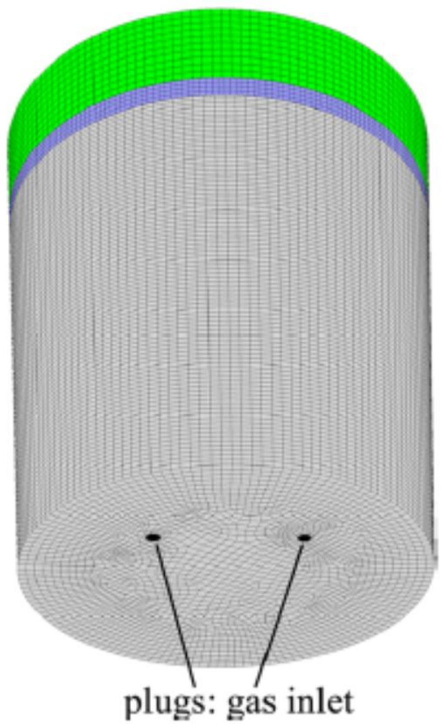
21st Australasian Fluid Mechanics Conference
Adelaide, Australia
10-13 December 2018



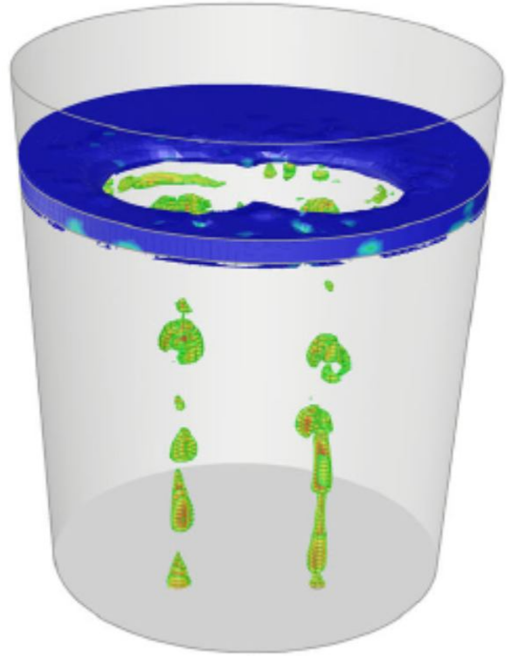
Slag-eye size variation when slag layer height is increased from Bottom to Top of the Ladle



Model of Fluid Flow, Mass Transfer and Slag-Steel interfacial behavior in Gas Stirred ladle



Schematic gas stirring process (Double Plug) in a Ladle

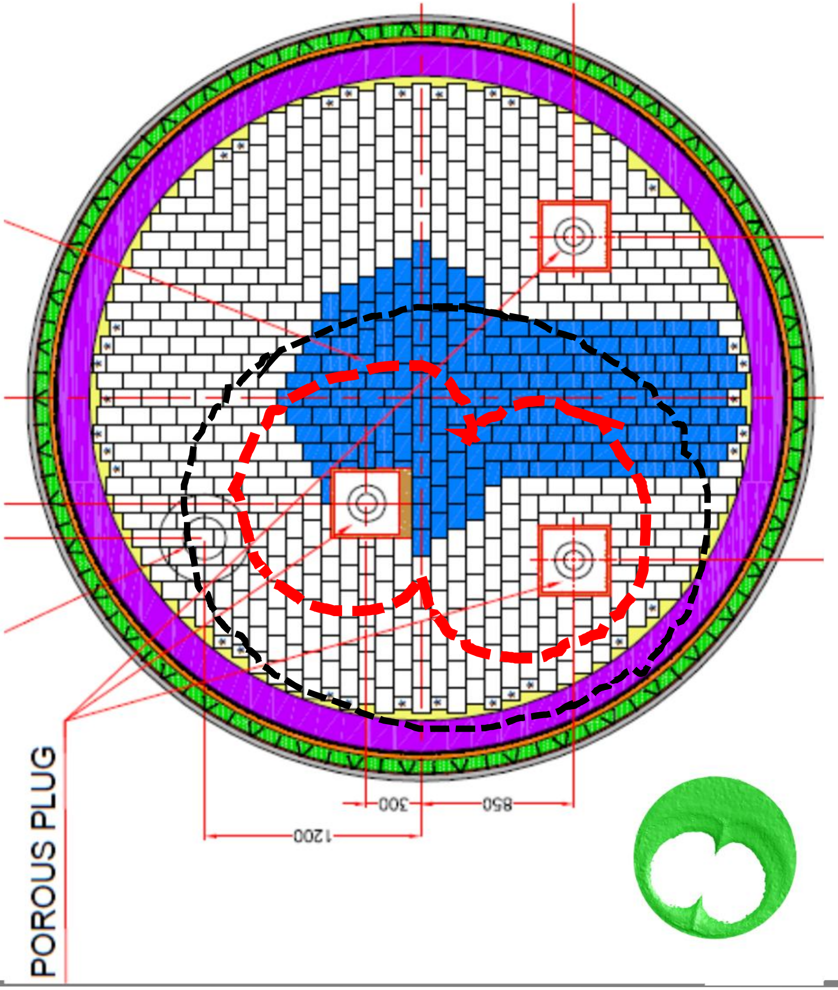


Article *in* Metallurgical and Materials Transactions B · February 2018

DOI: 10.1007/s11663-018-1206-y

… With Reality in Steel Ladle

- Interface of steel ladle gets damaged severely when **Two Plugs are being operated**.
- This may be due to mis-match of characteristics of refractories at the junction of S/Z and M/Z.



Extensive Study on Fired Spinel Brick by TRLK

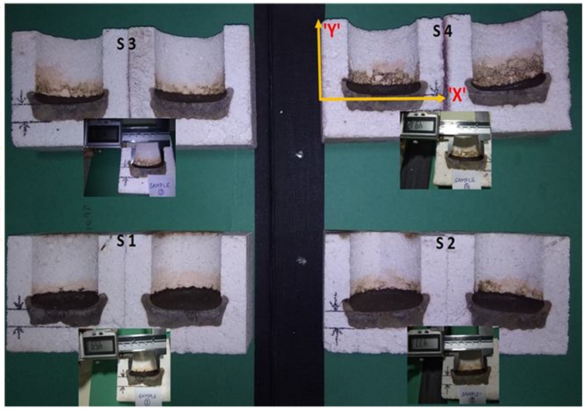
Slag Corrosion Study

(Static CUP Test Method - 1600 °C/3 hrs)

Sample No.	Cavity Corroded in 'X' Direction (mm)	Initial Diameter of Cavity in 'X' Direction (mm)	% of Corrosion
S1	45.91	45.71	0.44
S2	47.71	45.74	4.31
S3	47.93	45.75	4.77
S4	49.12	45.78	7.30

Slag Composition

Constituants	Weight (%)
CaO	62.3
SiO_2	9.16
Fe_2O_3	0.92
MgO	5.09
Al_2O_3	22.4

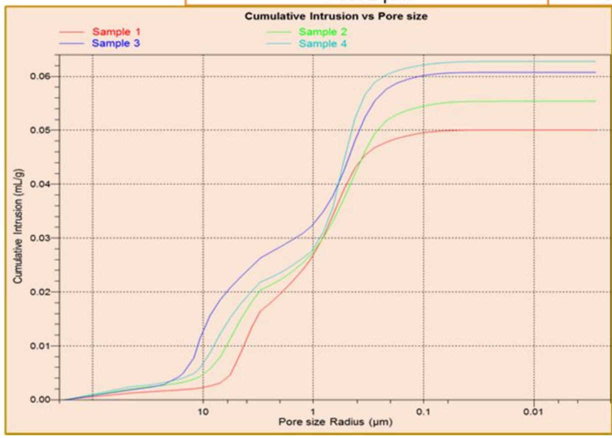


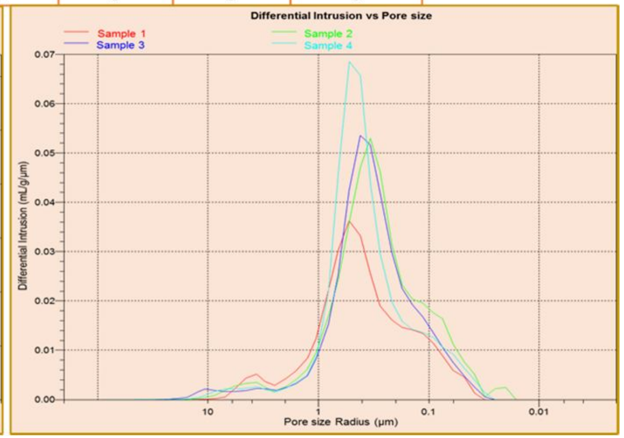
Thermal Shock Resistance Study of Spinel Brick Sample (DIN Method)

Sample No.	Nucleation of Micro fine Crack	Crack width increased	Spalled at	Nature of Spalling
S1	3rd Cycle	7th Cycle	14 Cycle	Circumferential
S2	5th Cycle	10th Cycle	15 Cycle	Circumferential
S3	8th Cycle	14th Cycle	Not Spalled (+ 20 nos.)	Crack Propagated Circumferentially
S4	11th Cycle	17th Cycle	Not Spalled (+ 20 nos.)	• Grains dislodging started from the test specimen at 6th Cycle onwards. • Network type crack propagation observed.

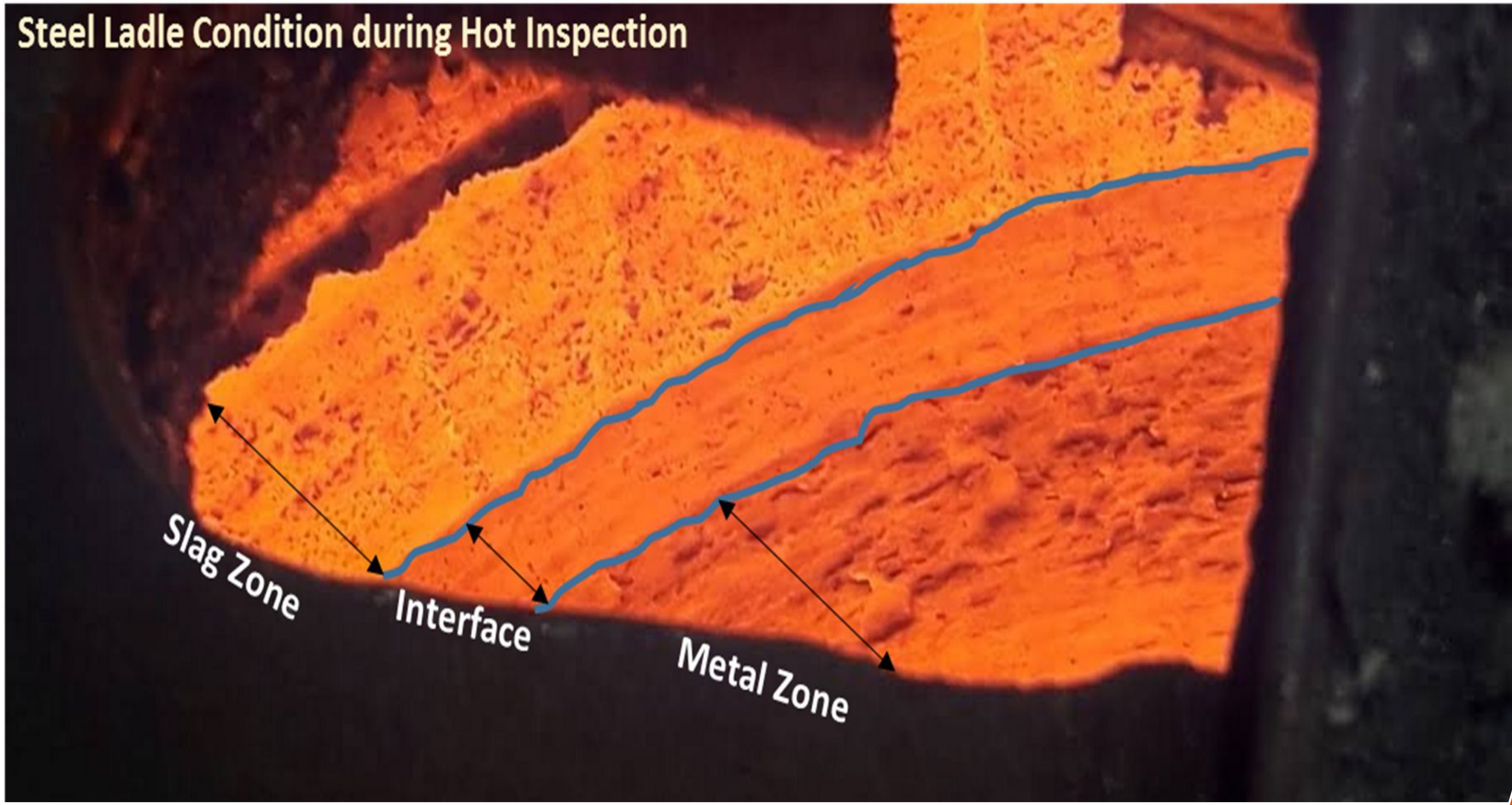
Porosimetry Study of Spinel Brick Sample

Sample No.	S1	S2	S3	S4
Total Intrusion Volume(ml/g)	0.0501	0.0554	0.0607	0.0627
Total Pore area (m^2/g)	0.137	0.187	0.175	0.187
Medium pore dia (v) micron	2.3064	1.9588	2.7153	1.5993
Medium pore dia (A)micron	0.8671	0.6312	0.6915	0.849
Average Pore dia micron	1.4647	1.1846	1.3865	1.3403
AP (%)	15.6	17	18.5	18.9
BD (g/cc)	3.1109	3.078	3.0446	3.0109
ASG	3.6846	3.7105	3.7354	3.712
Permeability (mdarcy)	3.7347	7.0095	28.119	11.9327
Distribution	**Volume (%)**			
> 100 µm	2.2	3.1	2.1	5.5
> 10 µm	11.4	21.1	30.2	22.8
> 1 µm	66.3	46.0	31.5	48.5
> 0.5 µm	14.6	21.5	29.4	18.6
> 0.1 µm	5.5	8.3	6.8	4.6
< 0.01 µm	0	0	0	0





Major Issue with Steel Ladle



- Weakening of S/Z & M/Z interface
- Premature Ladle Life
- Customer Dissatisfaction

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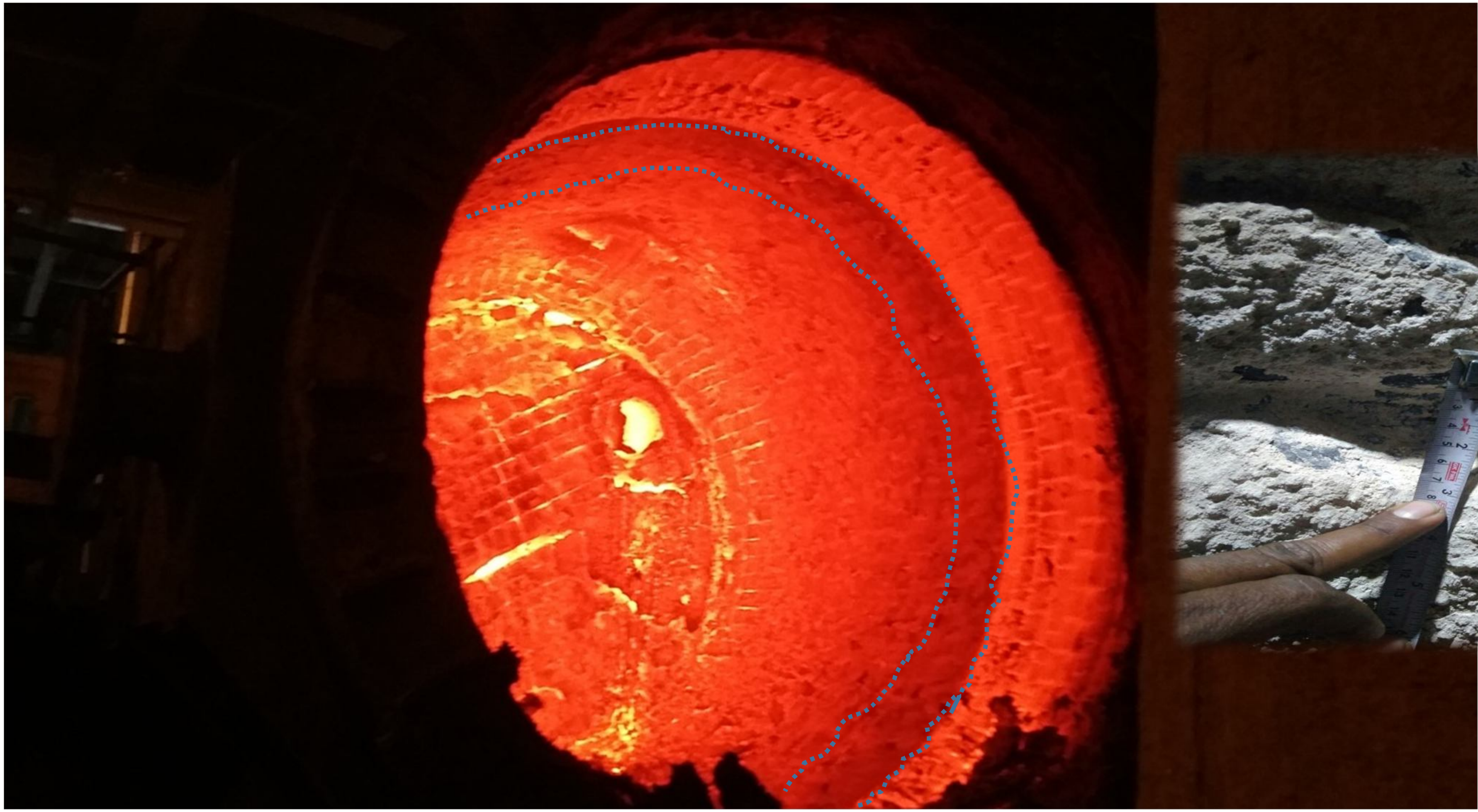


Weakening of Slag Zone & Metal Zone Interface of Steel Ladle

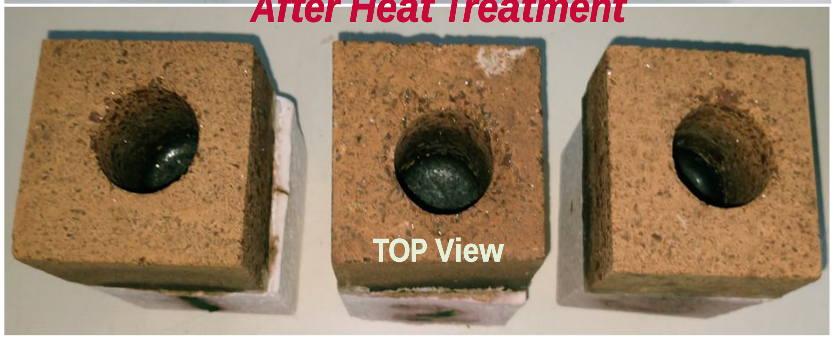
Prototype Slag Corrosion Study

Before Heat Treatment

"X" TRLK "Y"

Slag Corrosion at 1600 ºC/3 hrs

After Heat Treatment

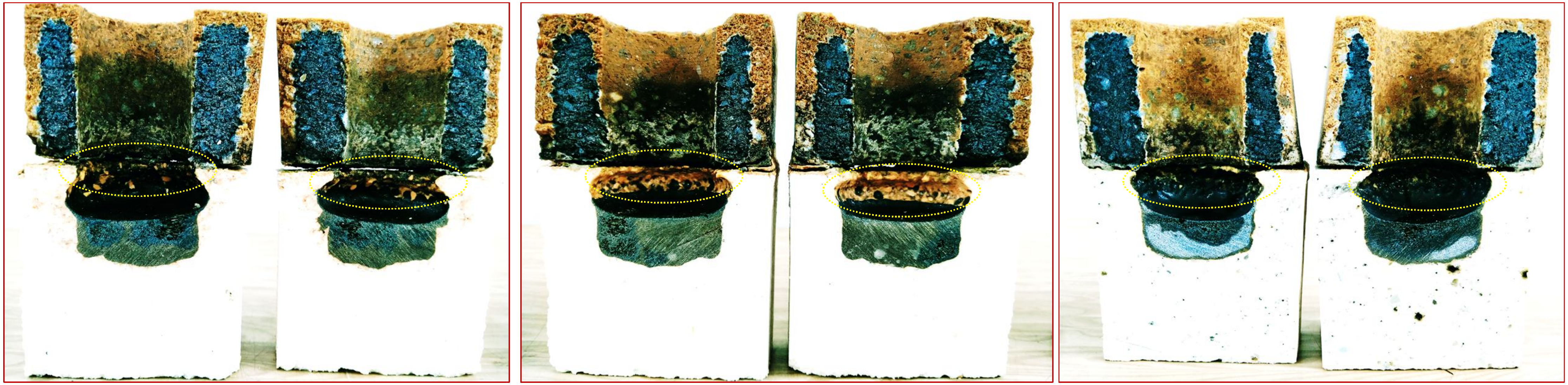


- **CUPs of both quality joined by using thin layer of >90% mortar.**
- **Two CUPs are aligned such a way that - as if having one cavity.**
- **LF-Out slag has been used for corrosion study.**

Contd…

Prototype Slag Corrosion Study : at 1600

Contd…



Raw material Properties Related with Steel Ladle Refractories

Properties	MgO	Graphite	Al_2O_3	$MgAl_2O_3$
Melting Point (ºC)	2852	+3550	2054	2135
Thermal Expansion (.10-6/ºC)				
at 500 ºC	11 - 13		7.3 - 8.0	7.6
at 1000 ºC	13 - 15	2.7 – 3.7	8.7 - 9.3	8.4
at 1500 ºC	15 - 19		9.3 - 9.9	10.2
Thermal Conductivity (W/mK)				
at 25 ºC	40	133.02	38	15
at 100 ºC	38	128.54	36	13
at 500 ºC	16	88.61	11	8
at 1000 ºC	7	64.26	7	5
Density (g/cm^3)	3.65	1.637	3.99	3.58

Mean Thermal Expansion Coefficients*

Material Linear Expansion Coefficient, 0-1000F in./in. ºc x 10 $^{-6}$

Alumina (Al_2O_3)	8.8
Magnesia (MgO)	13.5
Spinel ($MgOAl_2O_4$)	7.6

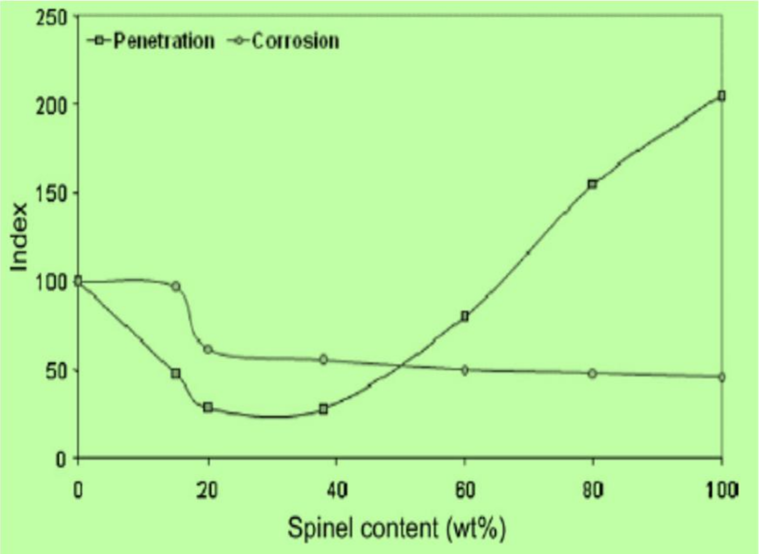
*Source: Kingery, W. D., Introduction to Ceramics, 1976, John Wiley ~ Sons, Inc.

INTERFACE

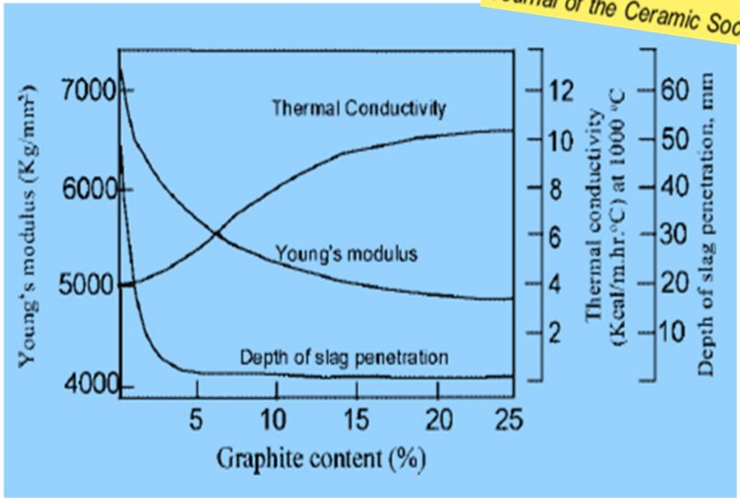
- Mismatch of Thermal Gradient
- Mismatch of Thermal Expansion Ratio-Leads stress development
- Susceptible area to generate low contact angle (θ_c) by molten material
- Vulnerable area for development of Eutectic phases.
- Most attacking area of Slag Eye.

Concept to Reality

- It is concluded that to balance the Thermal gradient, Thermal Expansion ratio, and Non wettability characteristics of refractory between S/Z and M/Z interface area; an equivalent grade of refractory, which is nearer (Characteristics wise) to MgO-C and Al_2O_3-Spinel grade should be developed for steel ladle interface application, which can suppress the Marangoni effect on refractory lining.
- Thus, Alumina-Spinel refractory having optimized “C” content should be preferred to counter such issue for steel ladle application.

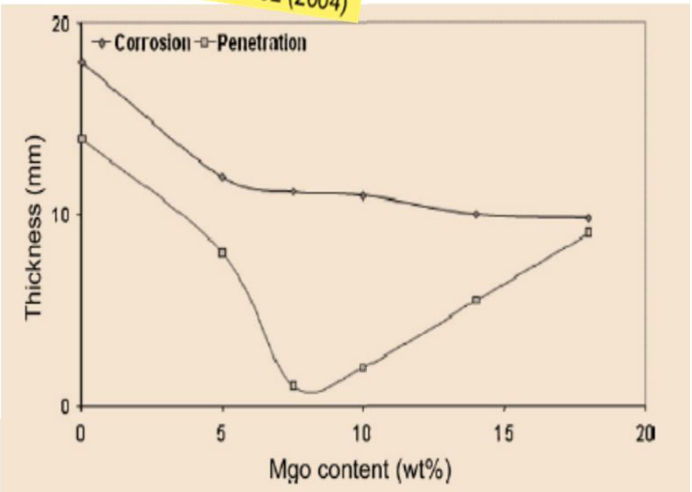


Spinel-containing alumina-based refractory castables; Ceramics International 37 (2011) 1705–1724



Effect of Graphite content in magnesia-carbon refractory on the Thermal conductivity and slag penetration resistance

Journal of the Ceramic Society of Japan 112 [10] 517–532 (2004)



Effect of MgO content in magnesia-carbon refractory on the corrosion and slag penetration resistance

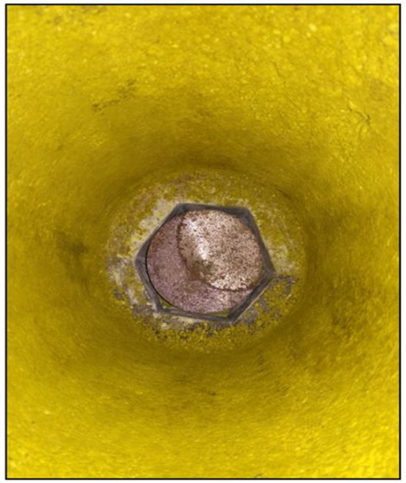
TRL SLM 3 @
Steel Ladle Transition Zone Refractory

Product Description: Resin Bonded Al_2O_3-Spinel Baked Product

Special Features:

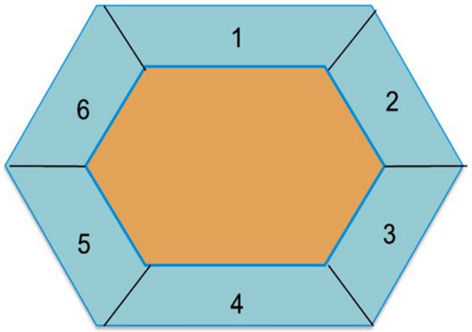
- Low porosity
- High Cold Crushing Strength
- High HMoR in Reducing atm.
- Excellent Corrosion Resistance

Slag Corrosion Test of Spinel Products



Induction Slag Furnace (inside view) after lining

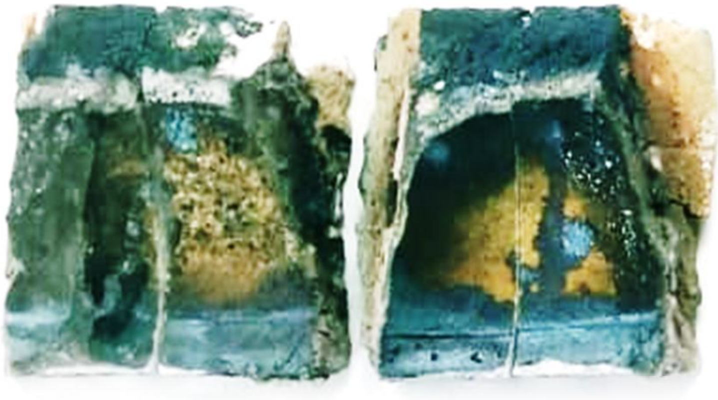
Induction Slag Furnace (top view) after lining



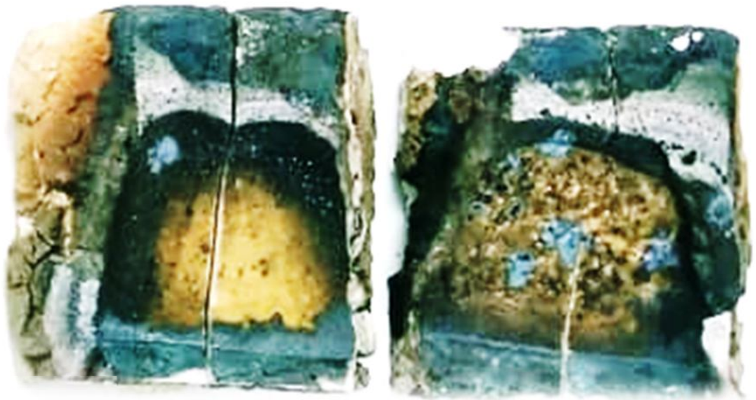
Induction Furnace Slag Corrosion test @ at 1600 ^{o}C, soaking 1 hr

1. **SLM 2 (MG)- Fired Product**
2. **SLM 2 (MG)- Fired Product**
3. **TRL SLM 3 - Baked Product**
4. **TRL SLM 3 – Baked Product**
5. **SLM 2 (I) – Fired Product**

Contd…



TRL SLM 2 (MG)

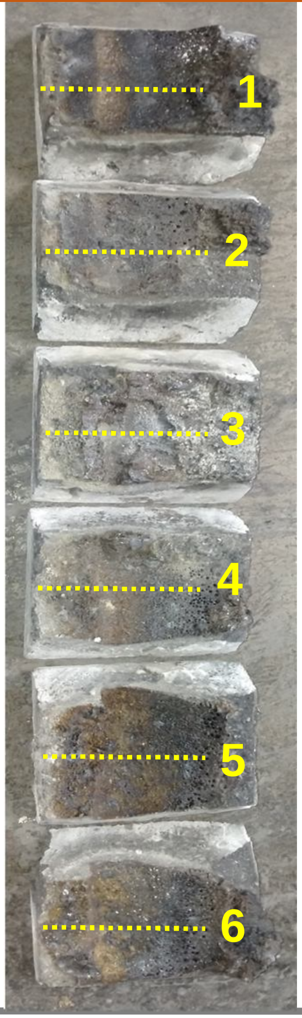


TRL SLM 2 (I)

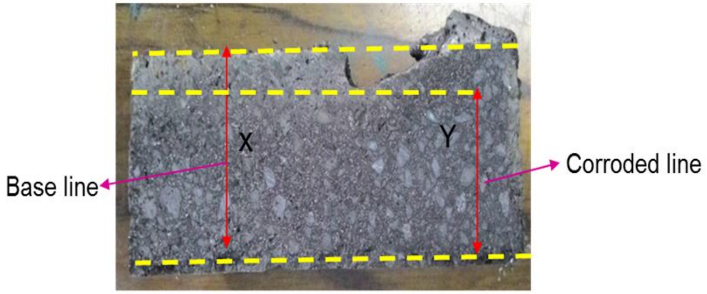
TRL SLM 3

Corrosion Test Results

Tested Sample ID		Base line	Corrode Line	% Corrode
1. SLM 2 (MG) – Fired Product	A	38.40	20.78	45.88
	B	38.40	20.97	45.39
2. SLM 2 (MG) - Fired	A	39.34	21.87	44.40
	B	39.34	21.68	44.89
3. SLM 3 - Baked Product	A	37.90	25.13	33.69
	B	37.90	25.42	32.92
4. SLM 3 - Baked Product	A	37.40	24.83	33.60
	B	37.40	24.89	33.45
5. SLM 2 (I) – Fired Product	A	38.14	20.10	47.29
	B	38.14	20.17	47.11
6. SLM 2 (I) – Fired Product	A	38.80	20.83	46.31
	B	38.80	20.77	46.47



% Corrosion=[(X-Y)/X]*100



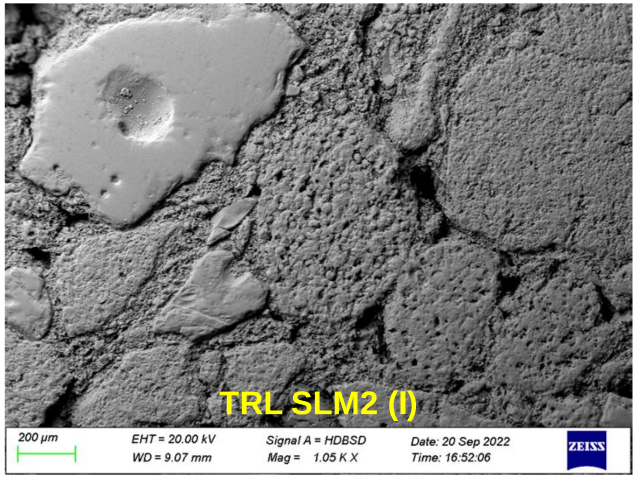
A & B : Two parts of sample after slicing

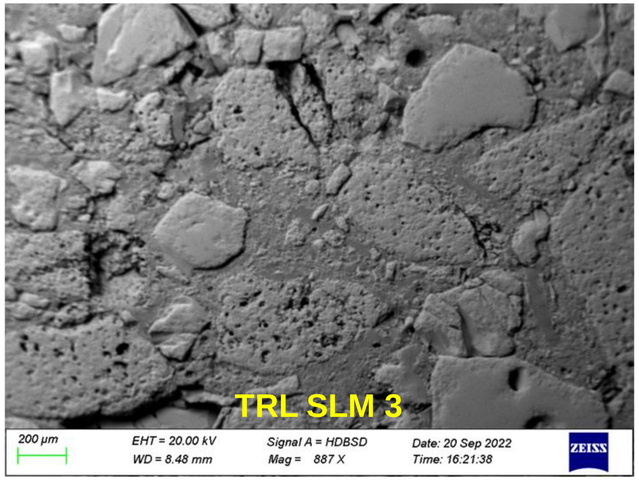
Corrosion Resistance:

TRL SLM 3 (Resin bonded spinel brick > SLM2 (MG) > SLM 2 (I)

Properties of Alumina Rich Spinel Bricks

Properties	Fired Spinel Brick	Baked Spinel Product
AP (%)	16.7	5.6
BD (g/cc)	3.13	3.21
CCS (kg/cm^2)	520	663
RUL (t_a) °C	1750+	1750+
PLC at 1450°C/2hrs (%)	+0.05	+0.14
HMoR at 1500°C (MPa)	4.5 – 6.8	2.9 - 4.4
Spalling Resistance	****	***
Slag Corrosion Resistance	***	*****
Microstructure (SEM)	• Pores between grain boundary. Spinel aggregates are well distributed. • Corundum grains are surrounded by Spinel materials.	• Very compact, and Corundum grains are surrounded by Spinel materials. • Matrix part is quite rigid.





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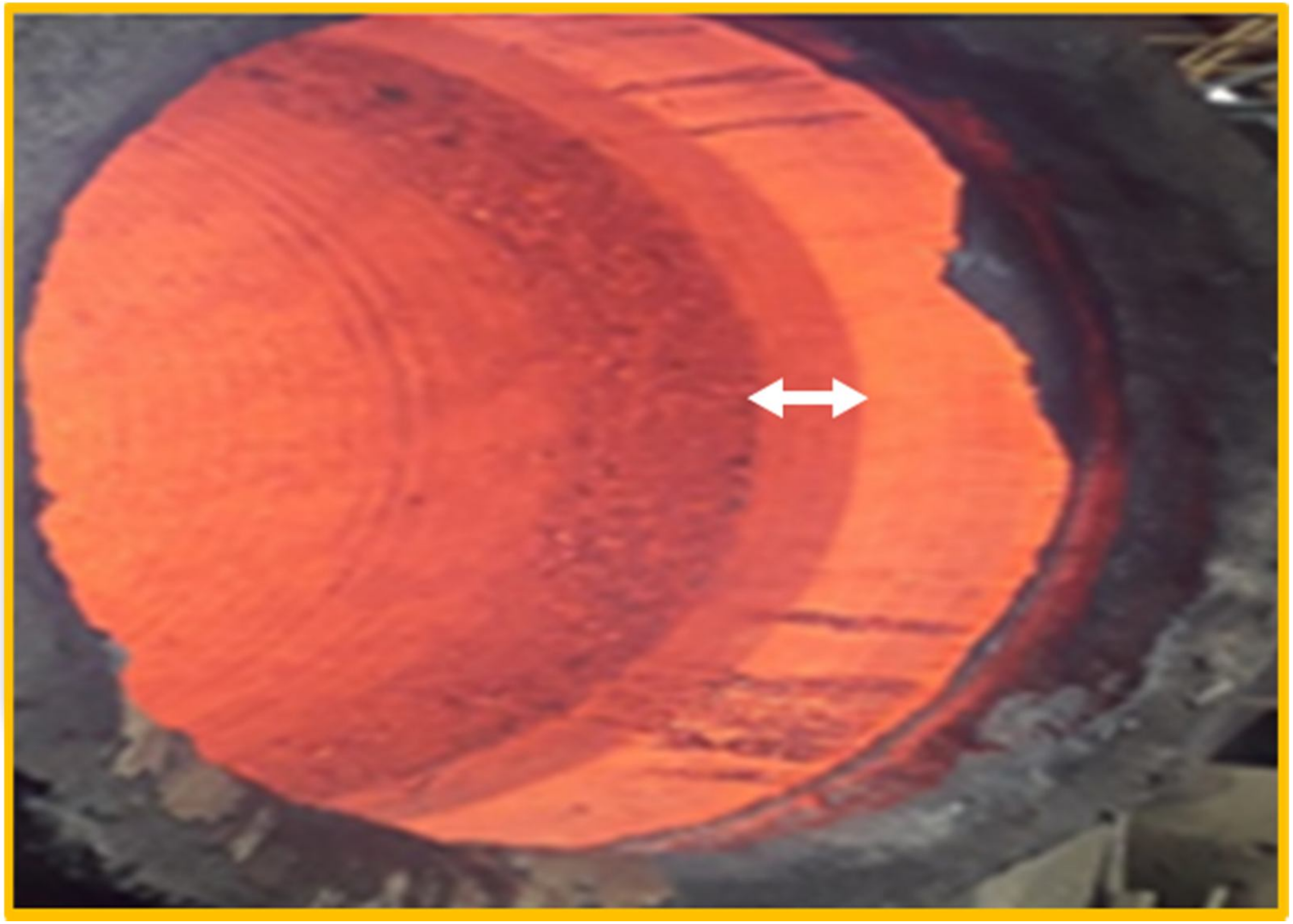
Lining of Steel Ladle with Spinel Products

Product Features:

Physical Properties
- Low Porosity
- High CCS

Thermo-mechanical Properties
- High HMoR®
- Low RTE

Wear Resistance
- Excellent corrosion resistance
- Less slag infiltration



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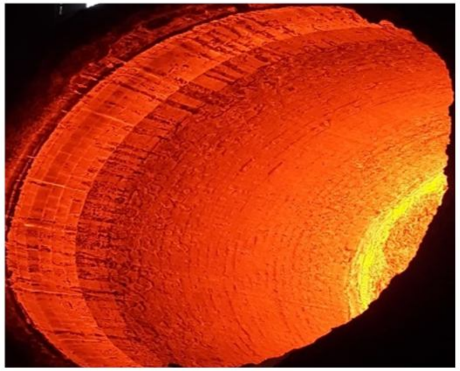
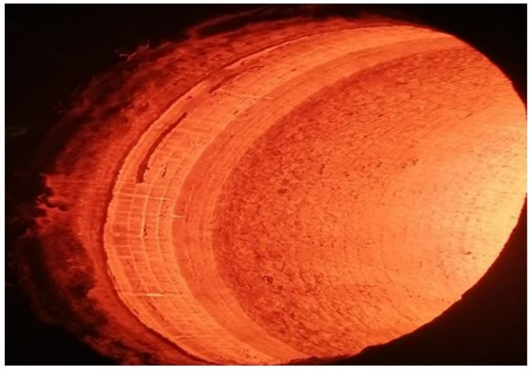
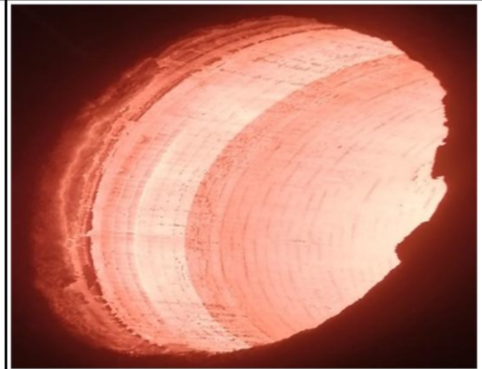
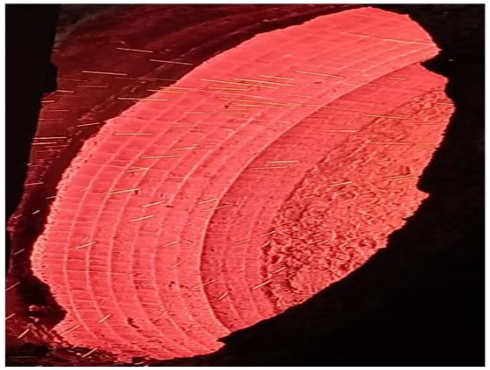
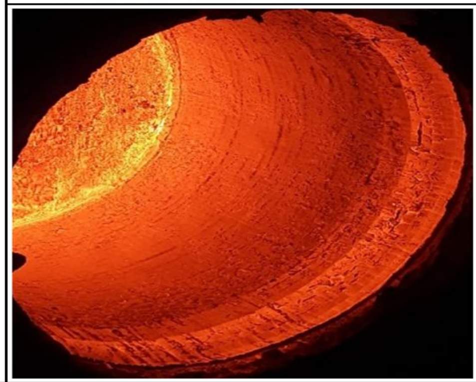
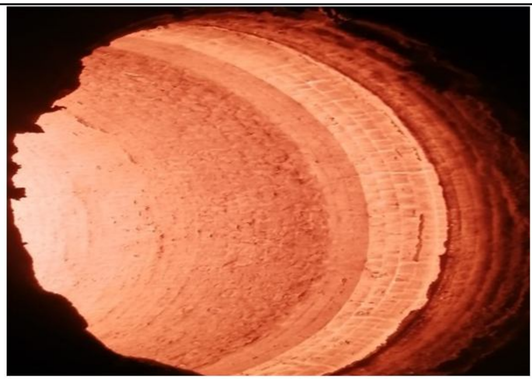
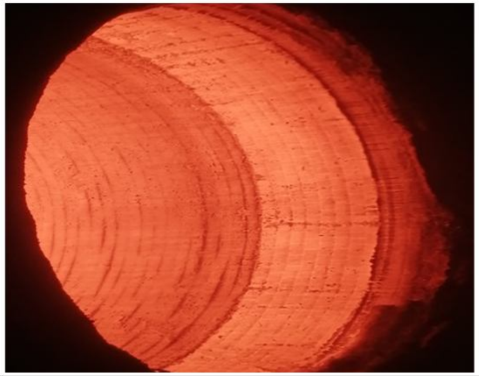
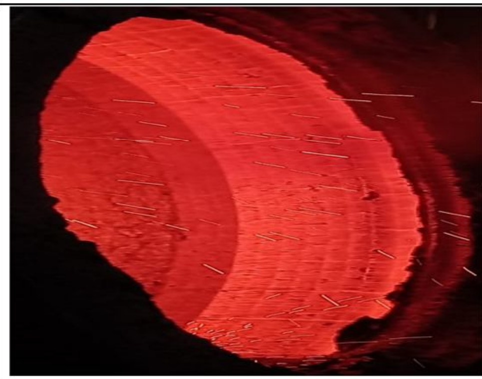
Performance of Spinel products

	Steel Ladle No-14 (Set-2) Transition Zone 3 layer Spinel Carbon Observation			Steel Ladle No-9(Set-3) Transition Zone 3 layer Spinel Carbon Observation	
Date	3-Feb-21	8-Feb-21		9-Feb-21	14-Feb-21
Heats	32	49		13	47
Status					
					
Remark	No abnormalities	No abnormalities		No abnormalities	No abnormalities
NB:	During the Circulation period In Spinel Carbon bricks Unlike fired spinel no chop-off, no abnormal erosion, no Slag-Metal zone gap generation observed.				

Concluding Remarks

- For steel ladle application, TRLK is providing complete refractory solution along with benchmark services.
- For spinel product category, high performance oriented baked product i.e., TRL SLM 3 has been developed and commercialized by TRLK successfully.
- By using TRL SLM 3 for steel ladle application, not only it will help steel maker to save time and money, but it will help a lot to reduce "Carbon Footprint", which is a global concern now a days.

Thank You