New glass making processes and their impact on refractories

Dr B.Mishra

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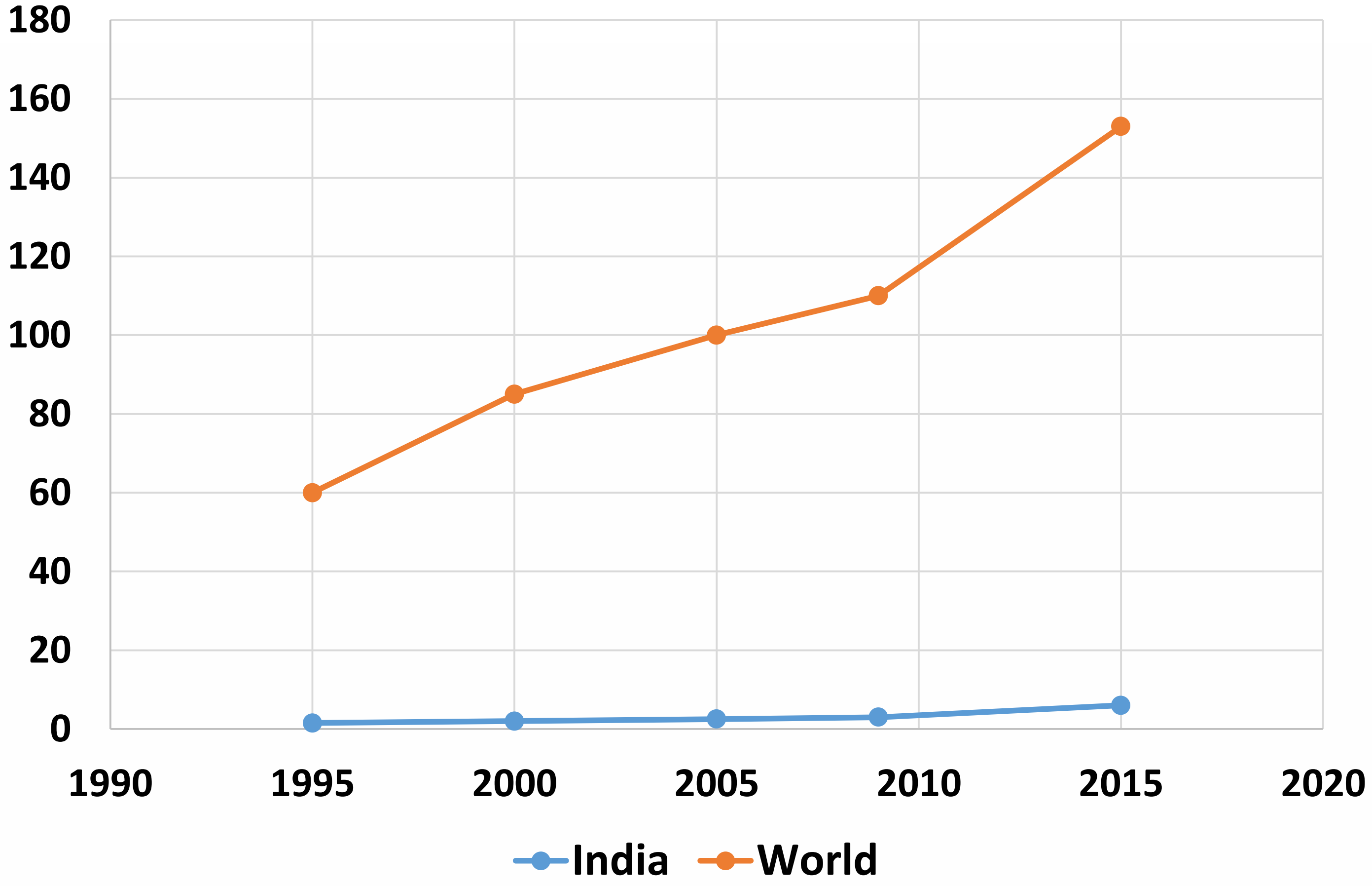
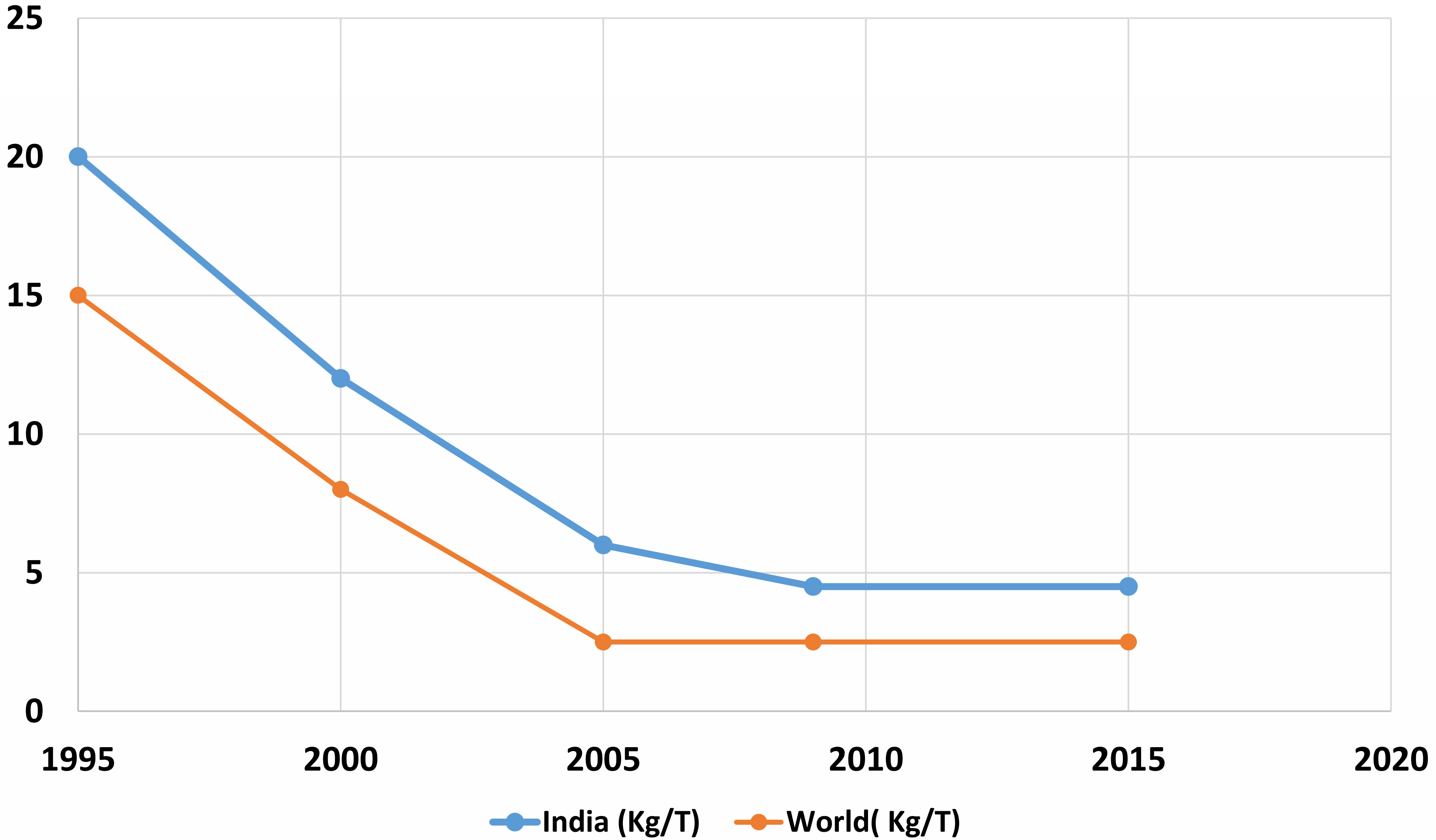
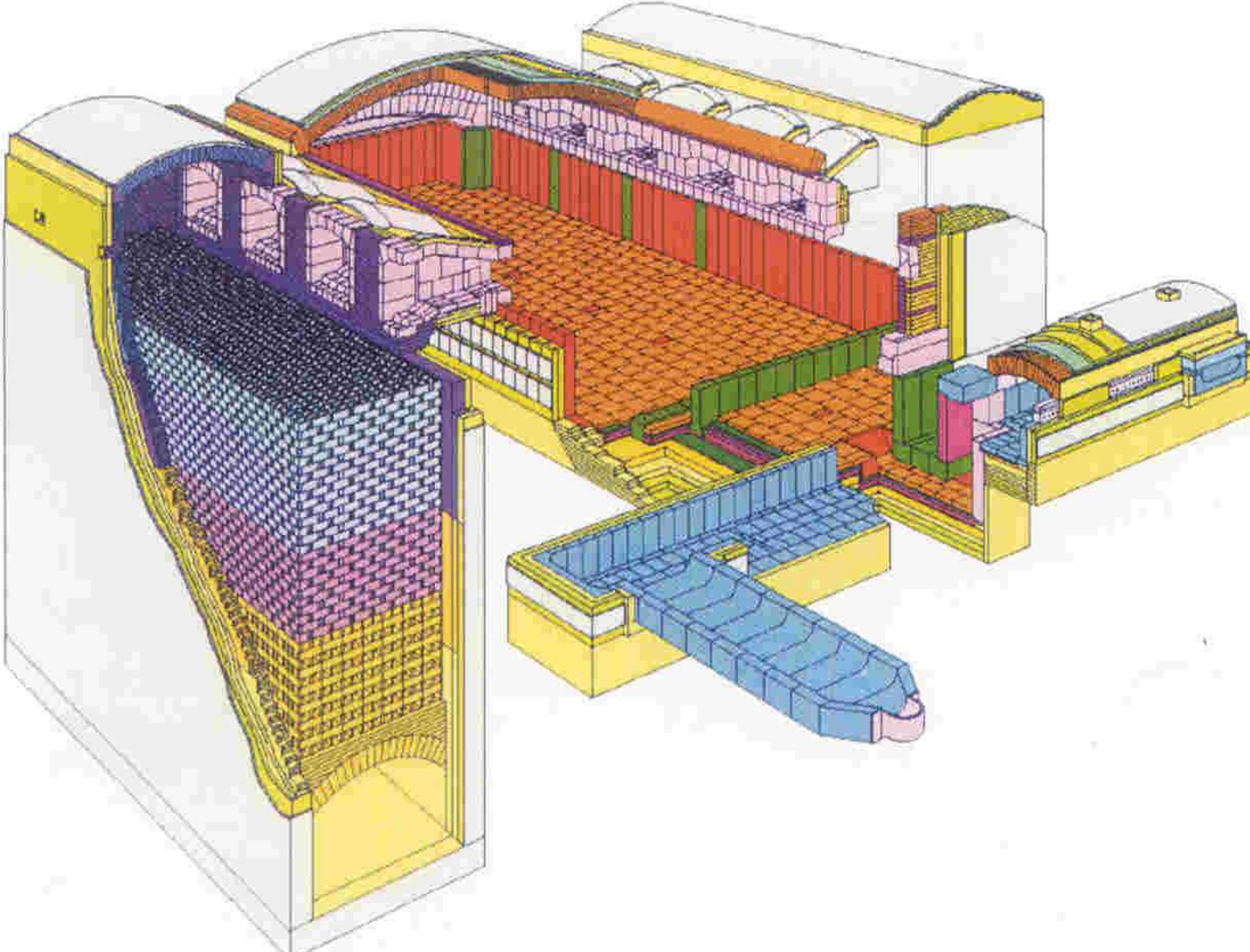
GLASS PRODUCTION

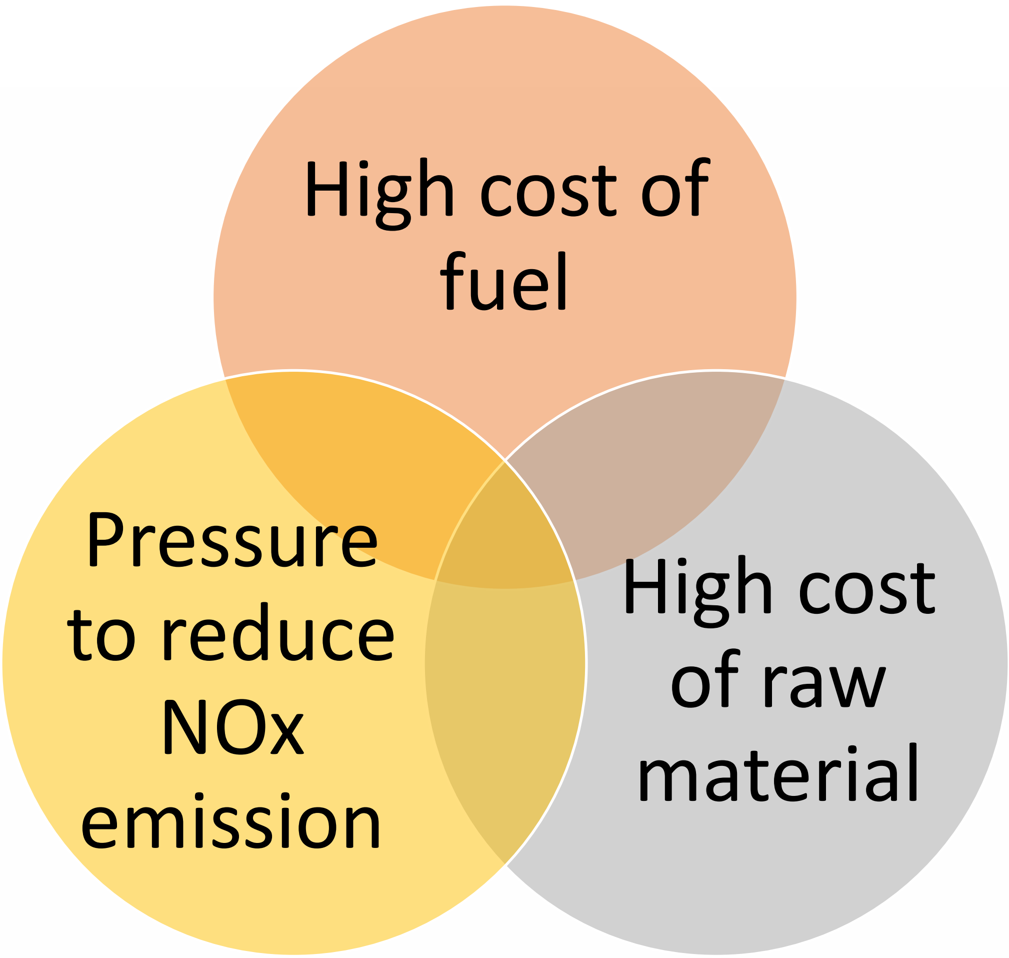


REFRACTORIES CONSUMPTION





PRESENT REALITY…



CHALLENGES OF GLASS INDUSTRIES

Reduce energy consumption	Increase the use of alternative fuels	Use of alternative raw materials
Reduce emissions of CO_2 –reduce greenhouse gas emissions	Great concern how to protect the environment .	Strong research in the sphere of sustainability

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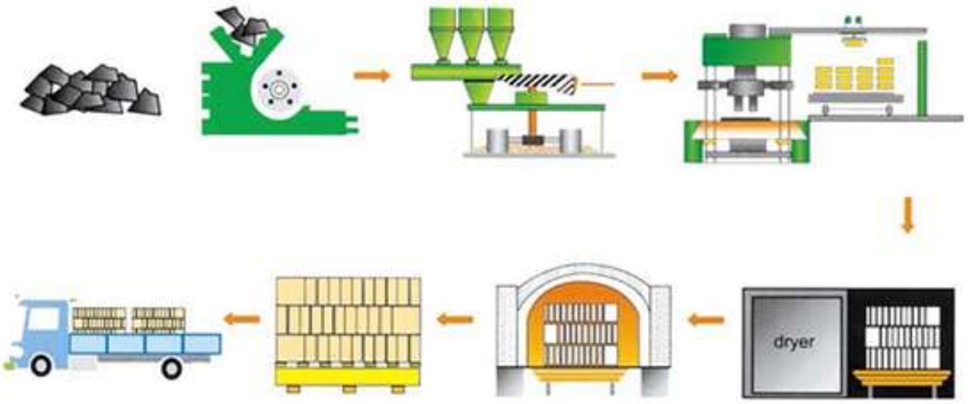
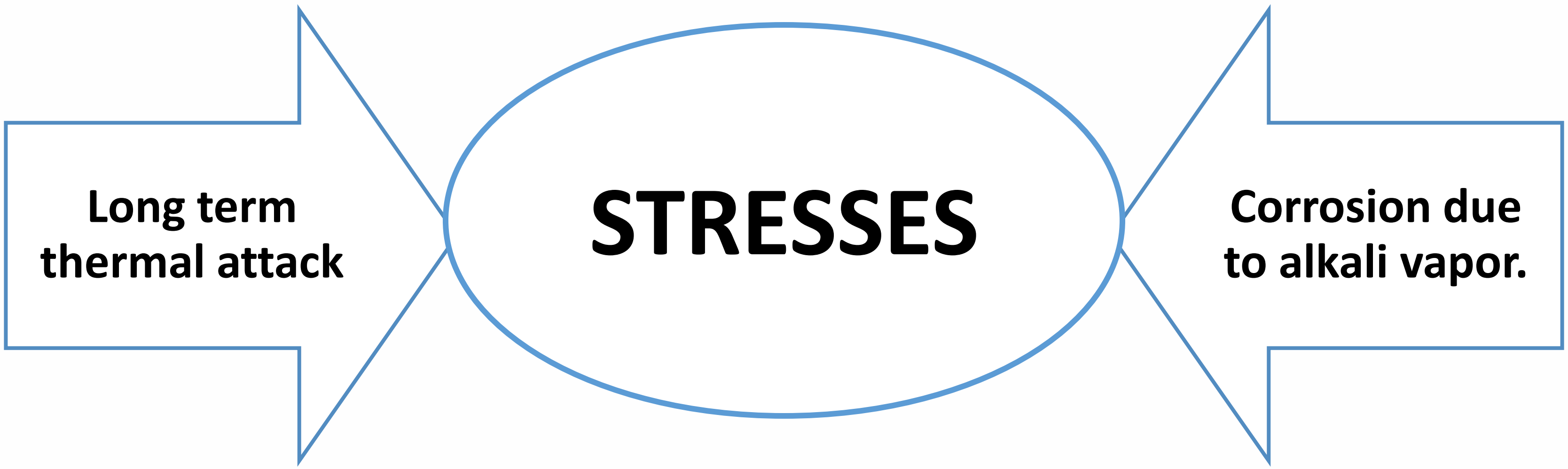
FOCUS SHIFT TOWARDS…

- High temperature of operation
- High pulling rate
- Oxyfuel burner
- Use of alternating fuel like pet coke

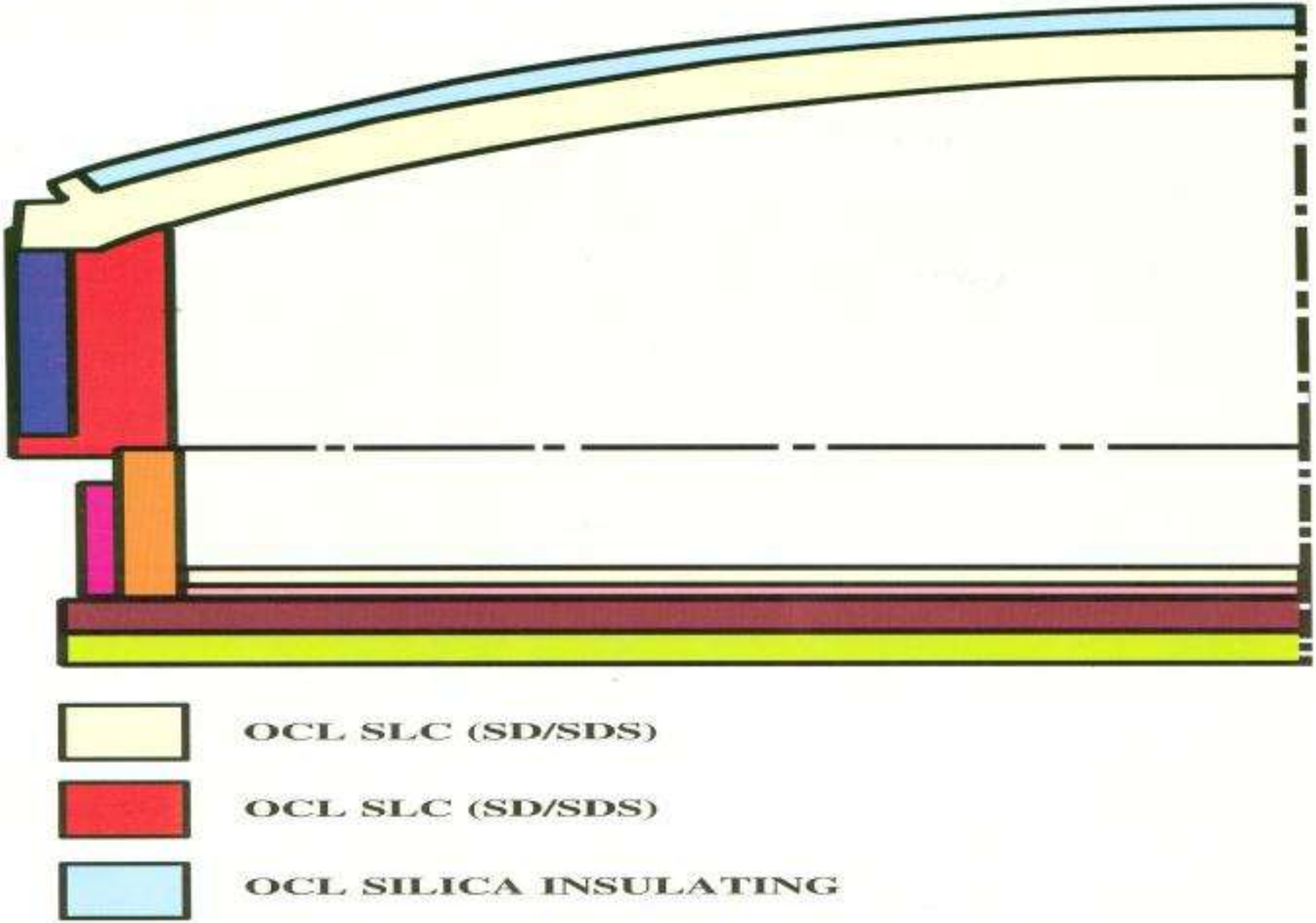
REFRACTORIES FOR GLASS INDUSTRY



REFRACTORIES FOR CROWN



GLASS MELTING TANK



SALIENT FEATURES OF SILICA BRICKS

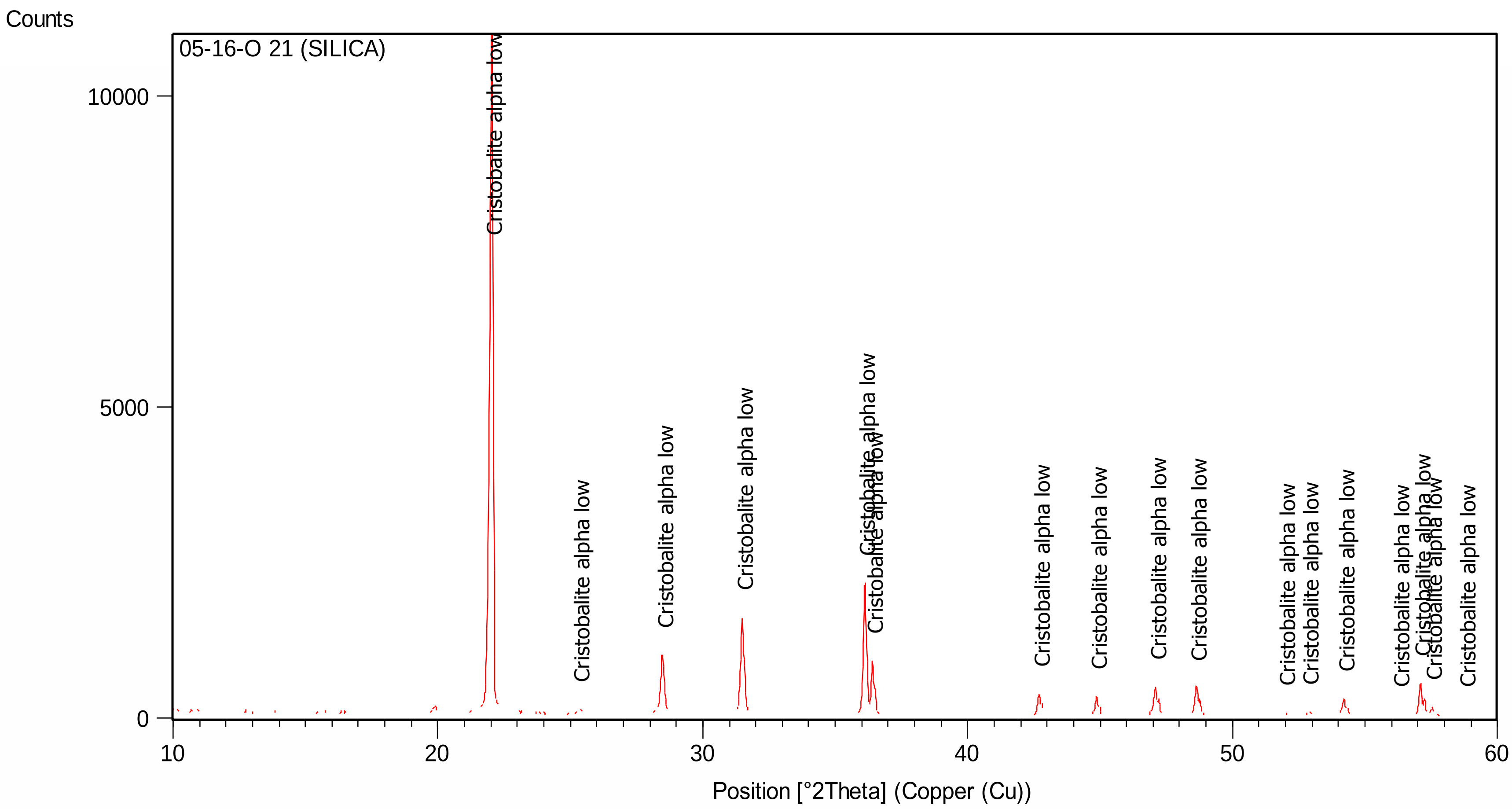
- VOLUME STABILITY ABOVE 1000 °C
- LOW FLUX FACTOR
- MINIMUM INFILTRATION OF ALKALIES
- LOW RQ
- COMPARATIVELY LOWER COST

PROPERTIES OF SILICA BRICK

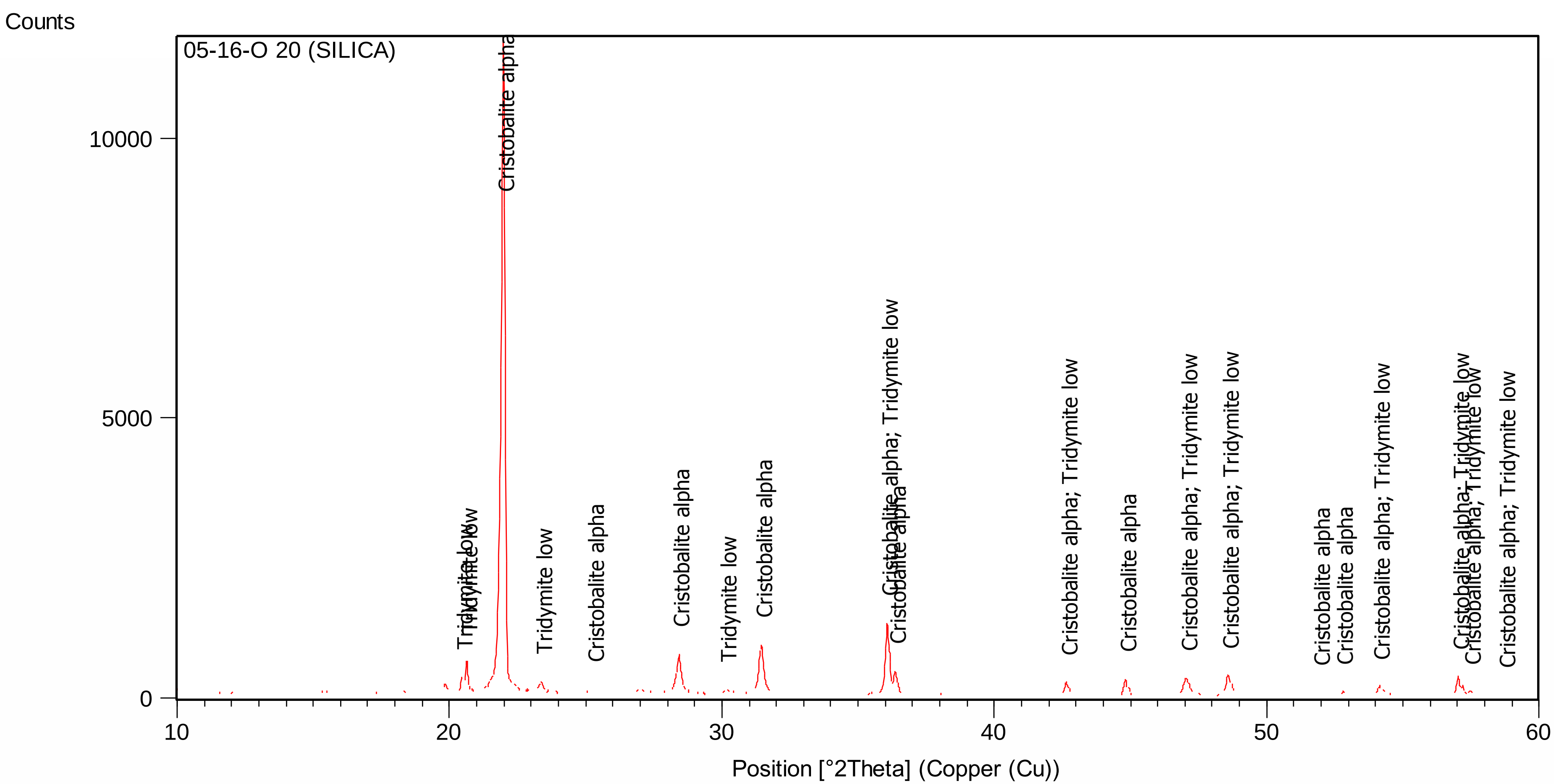
Quality	Silica SD	Silica SDS
SiO_2	96.2	96.5
Fe_2O_3	0.4	0.4
Al_2O_3	0.43	0.3
CaO	3	2.8
Flux factor	0.5	0.4
PCE SK	33	33
Specific Gravity	2.32	2.33
A.P. %	18.5	18.7
B.D (gm/cc)	1.87	1.86
CCS (kg/cm^2)	635	642
TE coefficient X 10^{-6}	13	14
RUL ta°C	1680	1690
Crystobalite content%	40	60
Residual Quartz %	0.8	0.5

USED VS ORIGINAL SILICA BRICK

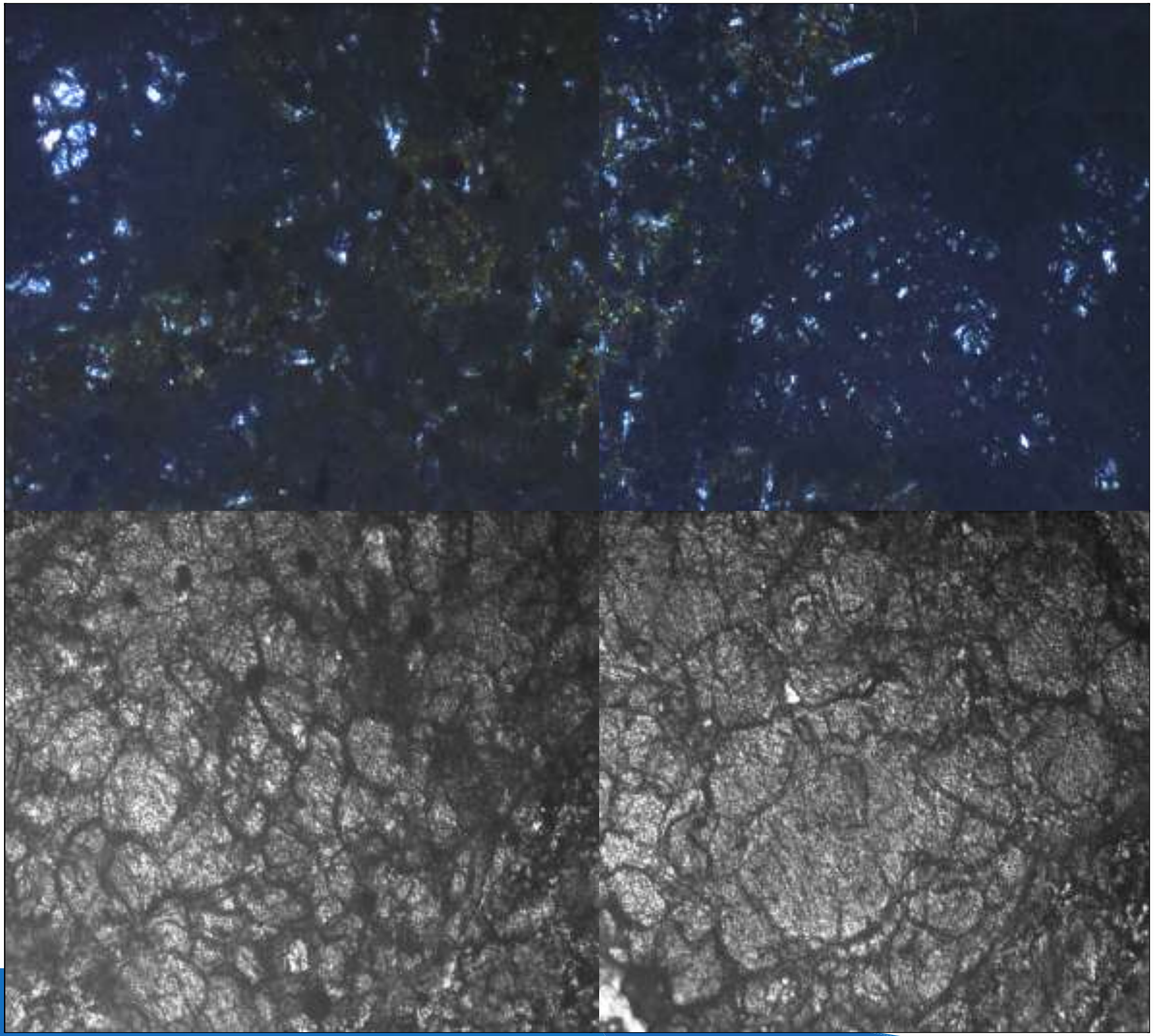
X-ray diffractogram of used silica brick Hot face



X-ray Diffractogram of used Silica brick Cold Face



Photomicrograph of Used Silica Brick



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INFERENCE

- Specific gravity of silica brick increases with crystobalite content with similar glass and quartz content.
- During use the hot face is completely converted to crystobalite and glass and impede further infiltration of alkali.
- The higher crystobalite content makes it higher resistant to alkali .
- Thermal expansion increases as crystobalite content increases.

PROPERTIES OF SILICA BRICK

Quality	Silica LLS	Silica ZLS
SiO_2	98.2	99.2
Fe_2O_3	0.2	0.1
Al_2O_3	0.3	0.05
CaO	3	2.8
Flux factor	0.4	0.1
PCE SK	33	33
Specific Gravity	2.32	2.29
A.P. %	18.5	18.7
B.D (gm/cc)	1.82	1.80
CCS (kg/cm^2)	435	**340**
TE coefficient X 10^{-6}	13	14
RUL ta°C	1690	1700
Crystobalite content%	50	20
Residual Quartz %	0.8	-

SILICA INSULATION

- HIGH APPARENT POROSITY.
- LOW THERMAL CONDUCTIVITY.
- LOW BULK DENSITY.
- HIGH STRENGTH.

Brand Name	SLC INS A	SLC INS B
SiO_2	90	91
CaO	6	4.5
A.P.	72	64
B.D. (gm/cc)	0.64	0.85
CCS (kg/cm^2)	20	40
Thermal conductivity (w/mk) at 400°C	0.23	0.26

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FUSED SILICA BRICK

- **NEGLIGIBLE THERMAL EXPANSION**
- **HIGH CHEMICAL PURITY**
- **HIGH STRENGTH**

Quality	**Fused silica brick**
SiO_2	98
Fe_2O_3	0.1
Al_2O_3	0.4
CaO	0.1
A.P.%	18.5
B.D (gm/cc)	1.8
CCS (kg/cm^2)	300
RUL ta 2 (kg/cm^2)	1690°C

ZIRCON REFRACTORIES

- HIGH RESISTANCE TO THERMAL SPALLING
- HIGH REFRACTORINESS UNDER LOAD
- HIGH RESISTANCE TO ALKALI ATTACK
- NEUTRAL IN CHARACTER

PROPERTIES DATA OF ZIRCON REFRACTORIES

Quality	Zircon	Zircon Chrome
Chemical (wt.%)		
ZrO_2	65	62
SiO_2	32	30
Fe_2O_3	0.3	0.3
Cr_2O_3	-	5
Al_2O_3	0.2	0.2
A.P .%	19	17.5
B.D (gm/cc)	3.70	3.74
CCS (kg/cm^2)	1000	1000
RUL ta °C	1600°C	1650°C
TSR(DIN 51068/1)	30	40

ZIRCON BRICK AFTER ALKALI TEST AT 1500°C/6 HOURS

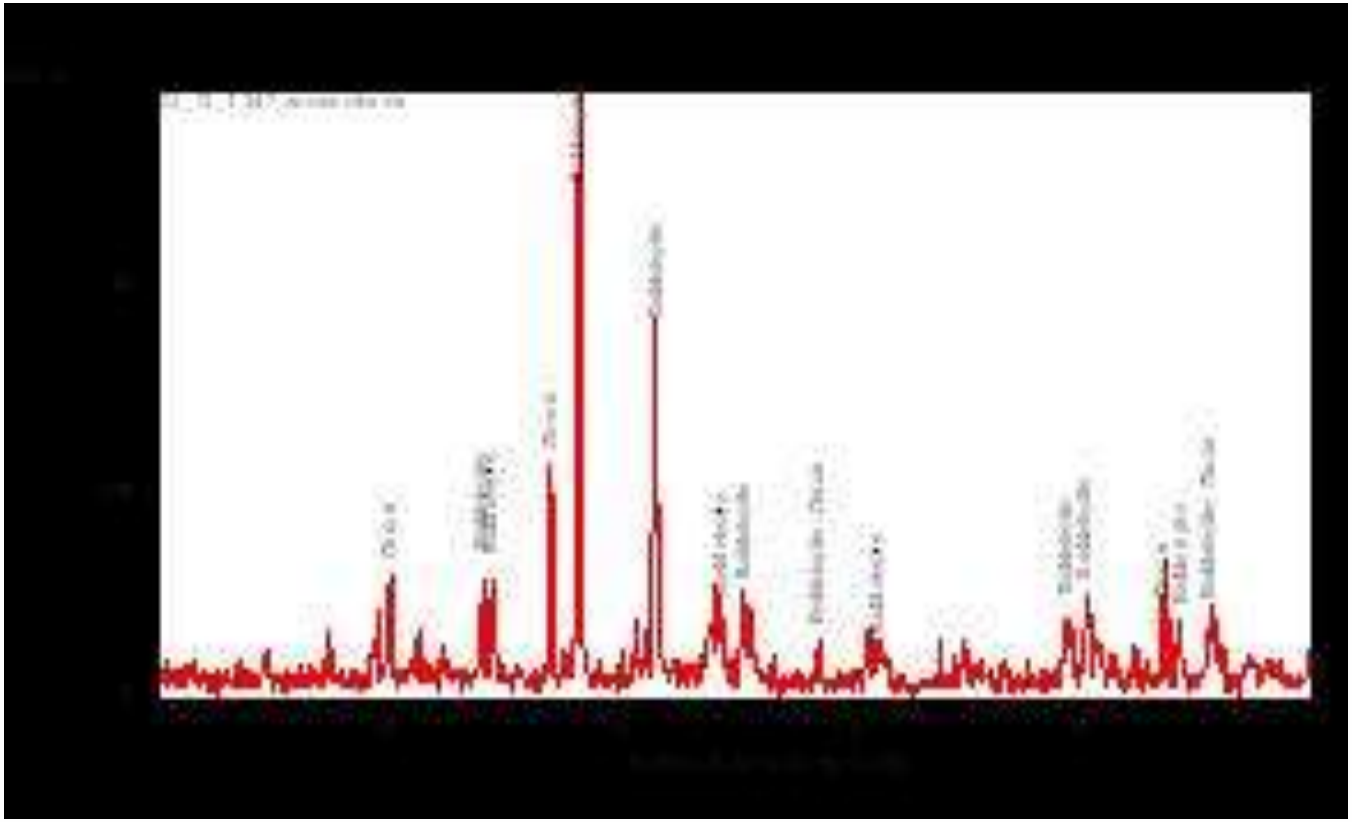
ZIRCON SILICA CONTACT AREA

ZIRCON SILICA INTERFACE WITH ALKALI

ZIRCON WITH ALKALI

- ALKALI VAPOUR ATTACK WAS SEVERE IN THE INTERFACE OF ZIRCON AND SILICA BRICK
- ALKALI VAPOUR ATTACK IS MODERATE OVER ZIRCON BRICK
- NO REACTION IS FOUND BETWEEN SILICA AND ZIRCON WHERE IT DOES NOT CONTACT WITH ALKALI VAPOUR.

X-RAY DIFFRACTOGRAM OF ZIRCON BRICK AFTER ALKALI ATTACK



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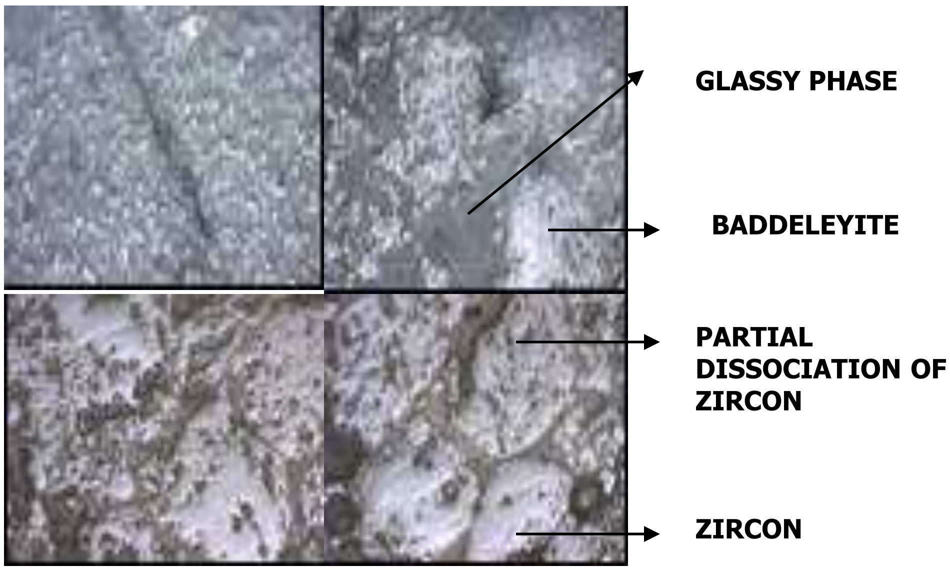
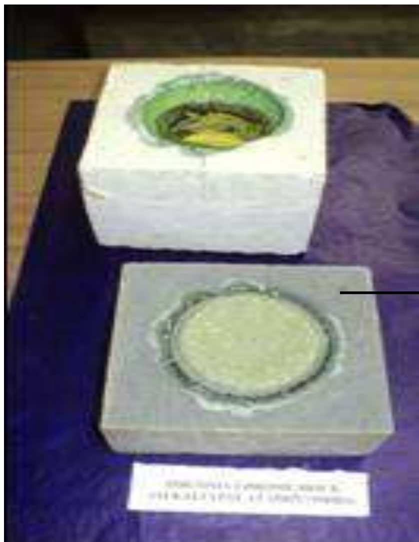
X200 PHOTOMICROGRAPH OF ZIRCON AFTER ALKALI ATTACK



- HOT FACE IN CONTACT WITH ALKALI VAPOUR IS DISSOCIATED IN TO BADDELEYITE AND GLASSY PHASE.
- AWAY FROM THE ALKALI VAPOUR ZONEPARTIAL DISSOCIATION OF ZIRCON IS FOUND.
- IN THE ZONE NOT IN CONTACT WITH ALKALI VAPOUR UNDISSOCIATED ZIRCON GRAINS ARE FOUND.

ZIRCON CHROME AFTER ALKALI TEST

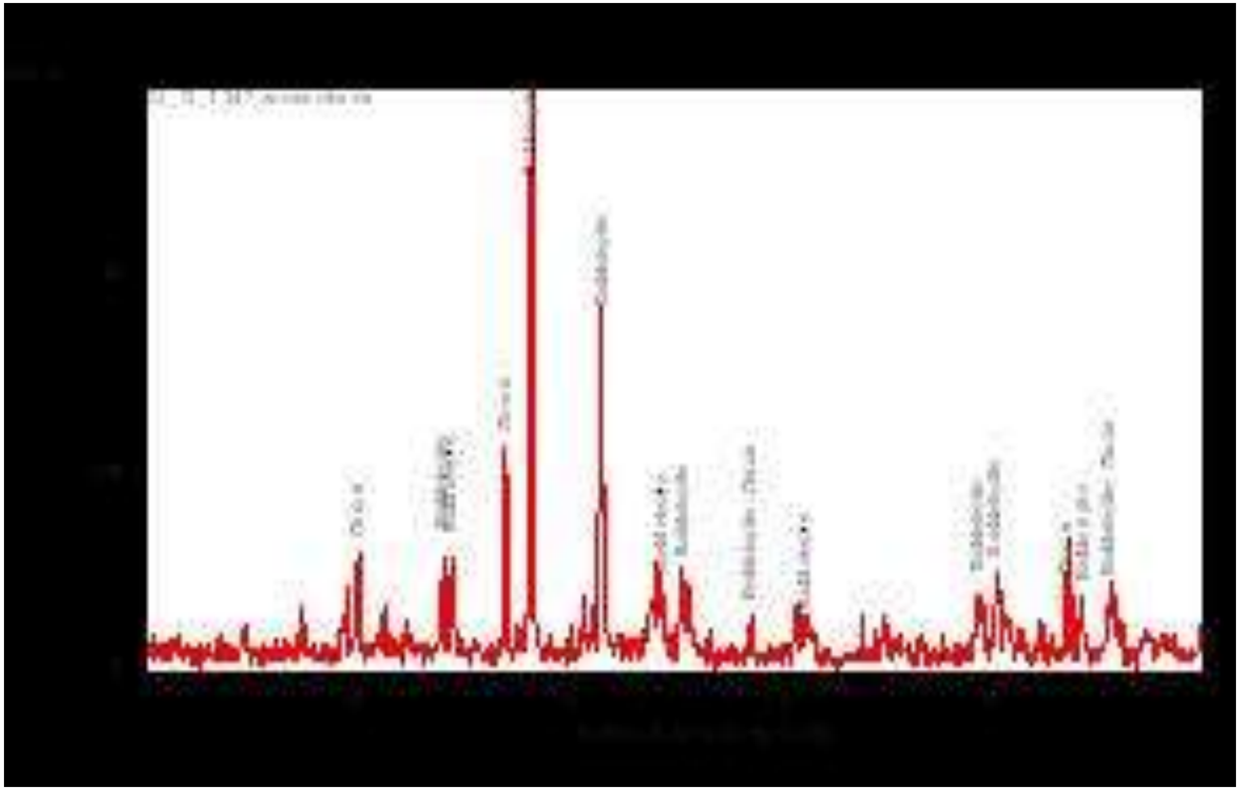


CONTACT AREA OF ZIRCON CHROME AND SILICA WITH OUT ALKALI VAPOUR

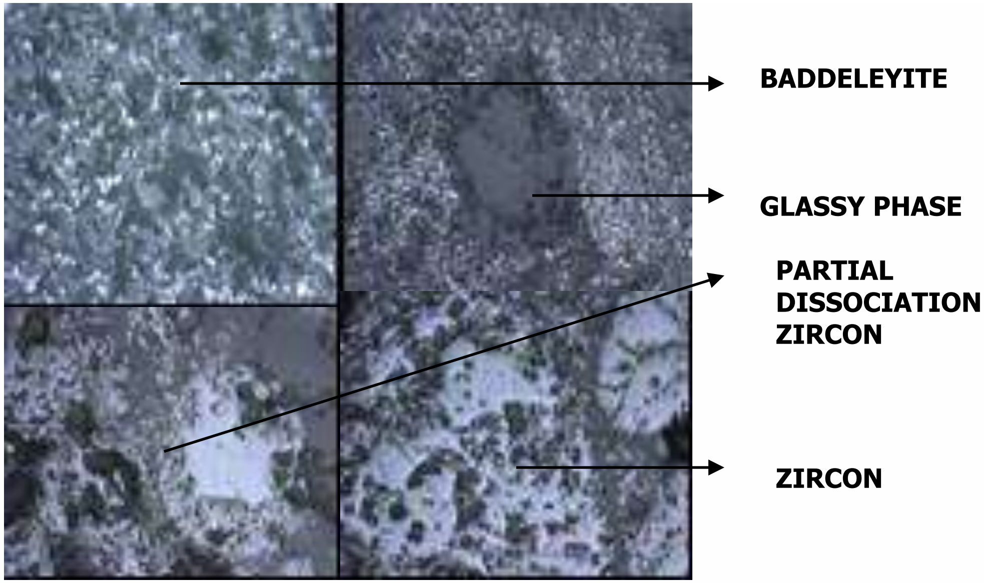
CONTACT AREA OF ZIRCON CHROME AND SILICA WITH ALKALI VAPOUR

- ALKSALI ATTACK IS FOUND TO BE SEVERE IN THE INTERFACE OF SILICA AND ZIRCON CHROME BRICK
- ALKALI ATTACK IS LESS SEVERE THAN ZIRCON BRICK
- NO RECATION IS FOUND BETWEEN SILICA AND ZIRCON CHROME(NO ALKALI VAPOUR ZONE)

X-RAY DIFFRACTOGRAM OF ZIRCON CHROME BRICK

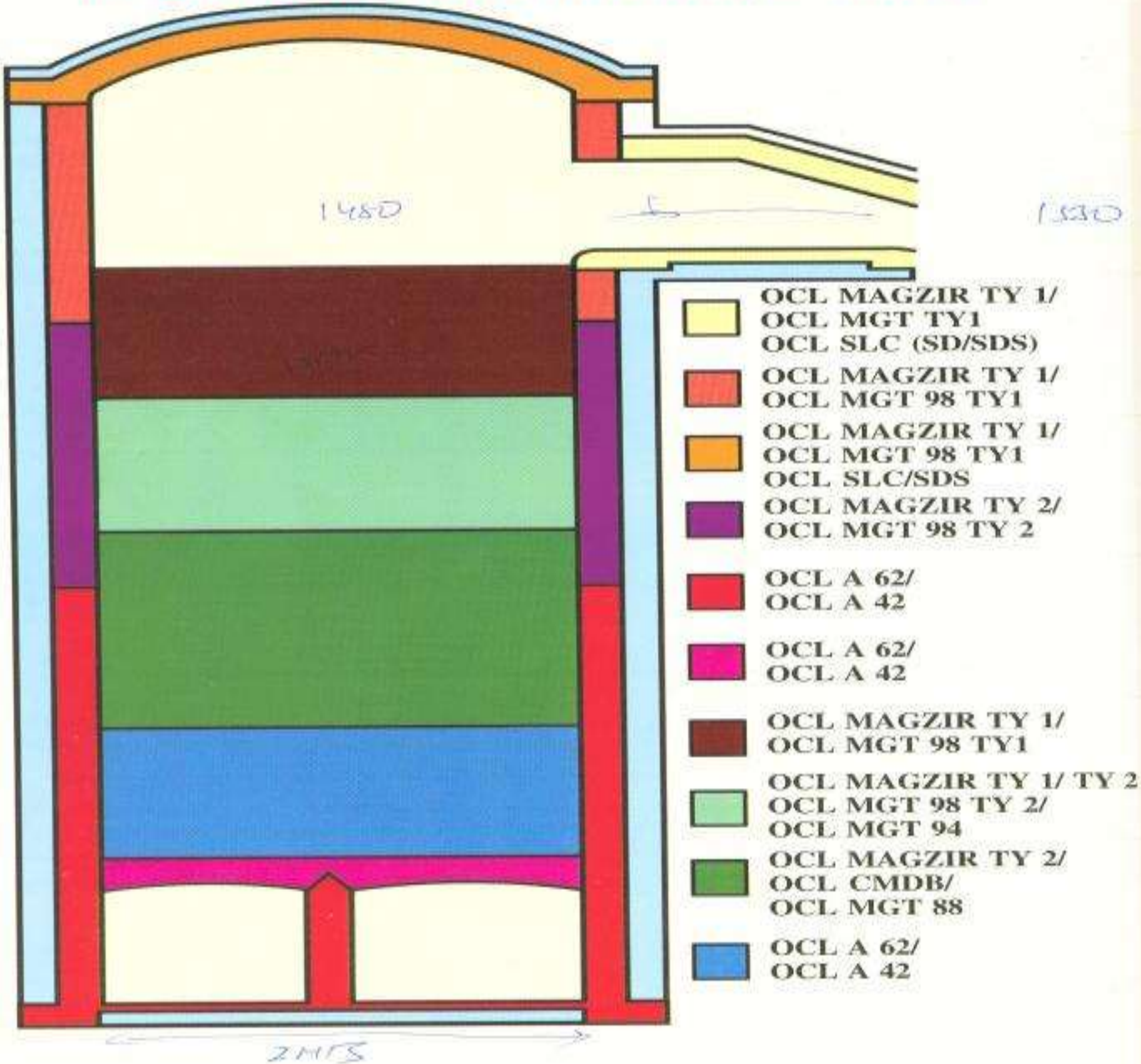


X200 PHOTOMICROGRAPH OF ZIRCON CHROME AFTER ALKALI TEST



- HOTFACE IN CONTACT WITH ALKALI IS ALTERED TO BADDELEYITE AND GLASS.
- 10MM AWAY FROM ALKALI VAPOUR ZONE PARTIAL DISSOCIATION OF ZIRCON IS FOUND.
- 15MM AWAY FROM ALKALI VAPOUR ZONE UNDISSOCIATED ZIRCON GRAIN S ARE FOUND.

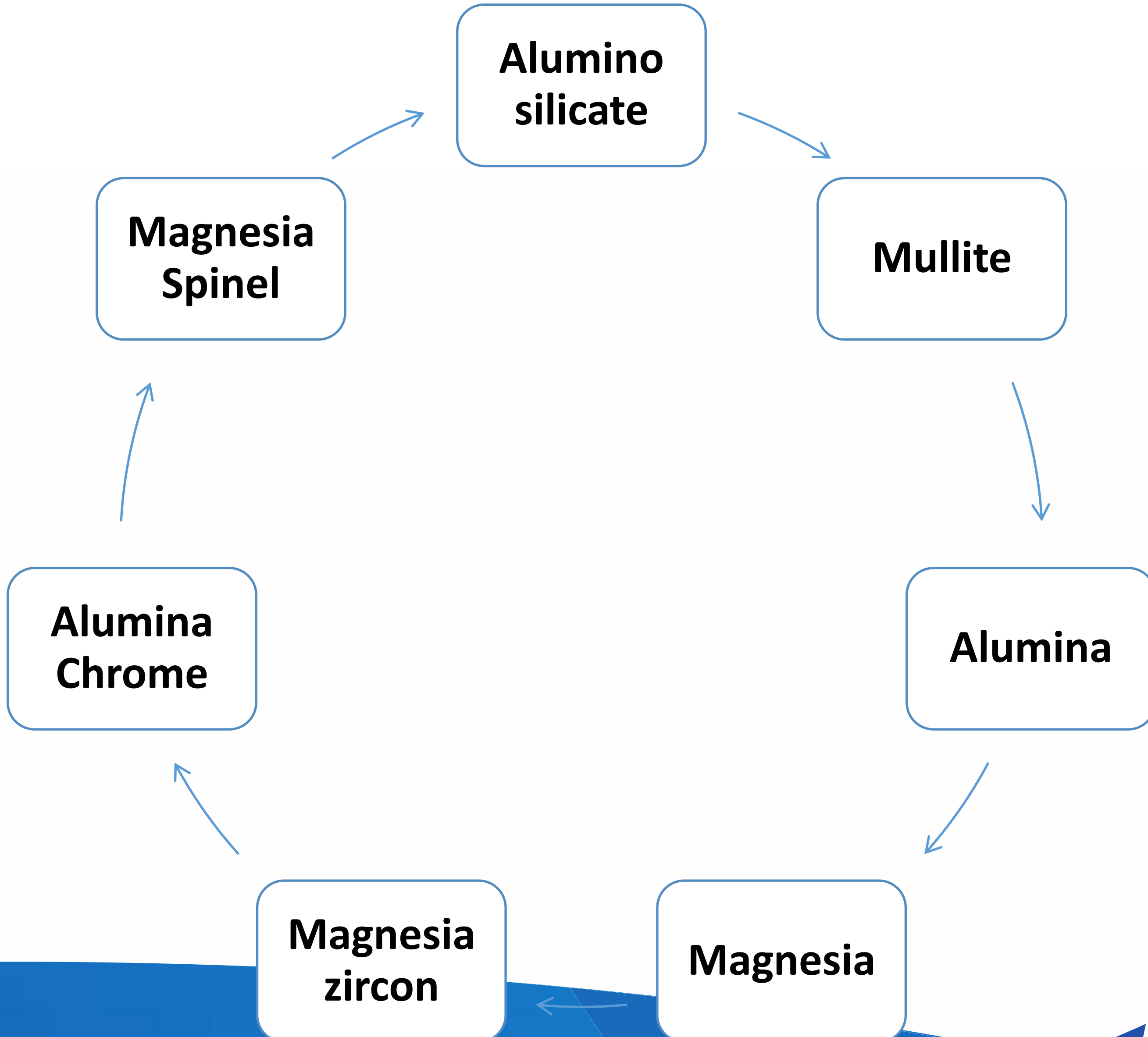
REGENERATOR FOR GLASS TANK



STRESSES ENCOUNTERED BY REGENERATOR

- **Mechanical and Chemical stresses from solid carryover.**
- **Thermo-mechanical stresses from temperature variation and thermal shock that occurs within the packing.**
- **Chemical corrosion from aggressive batch constituents, vapors and alkali condensation.**

DIFFERENT QUALITIES USED IN REGENERATOR



DIFFERENT PACKING OPTIONS…

TOP COURSE
1. 98 MGT
2. MAGZIR
3. ALUMINA
4. ALUMINA CHROME

CONDENSATION ZONE
1. MAGZIR 2
2. Frosterite Bonded 88% Magnesite
3. Spinel Bonded Magnesite
4. ALUMINA ZIRCON
5. 62% & 42% Alumina

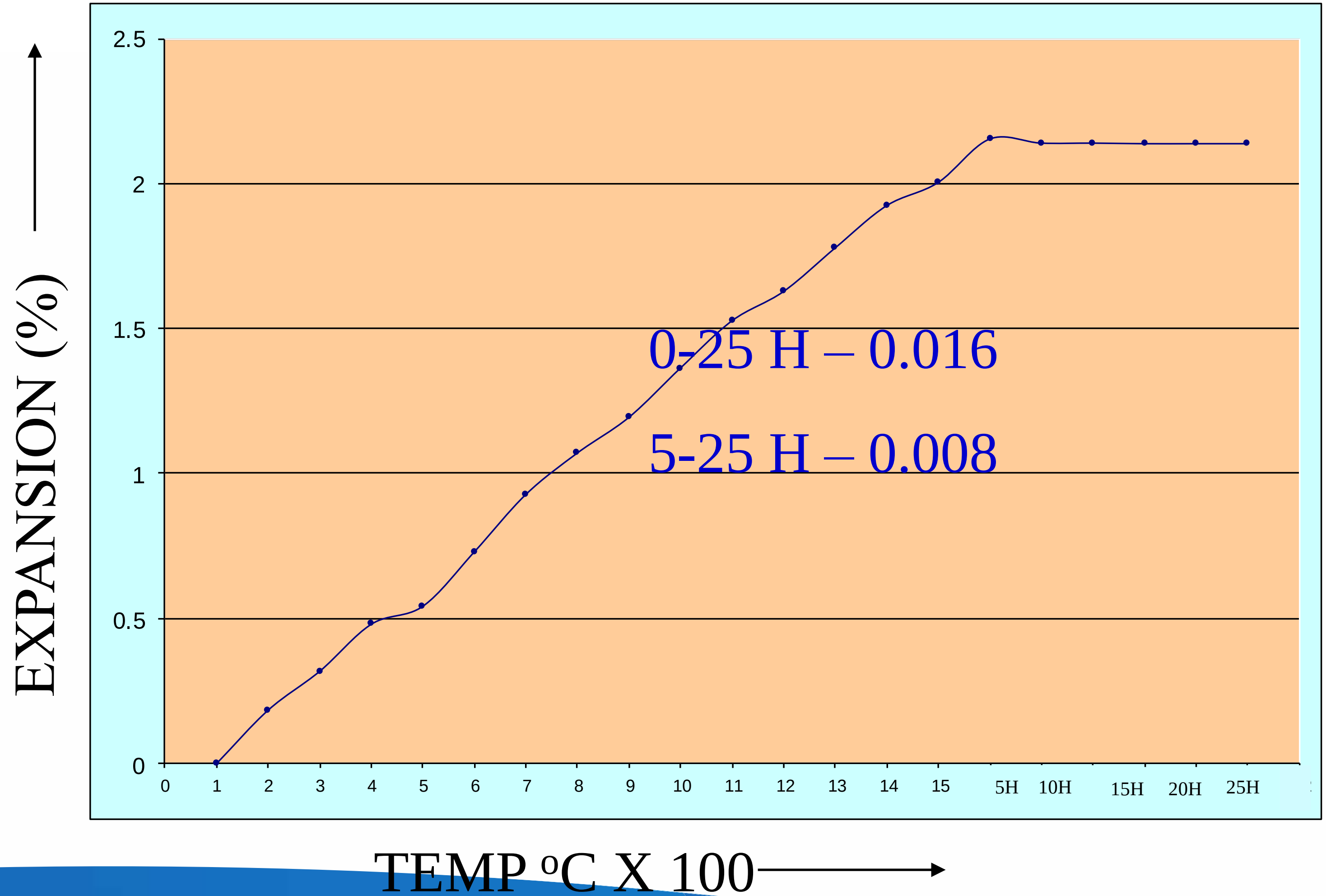
MAGNESIA BASED REFRACTORIES

- High refractoriness under load
- High resistance to creep under compression at elevated temperature
- High thermal conductivity
- High heat capacity

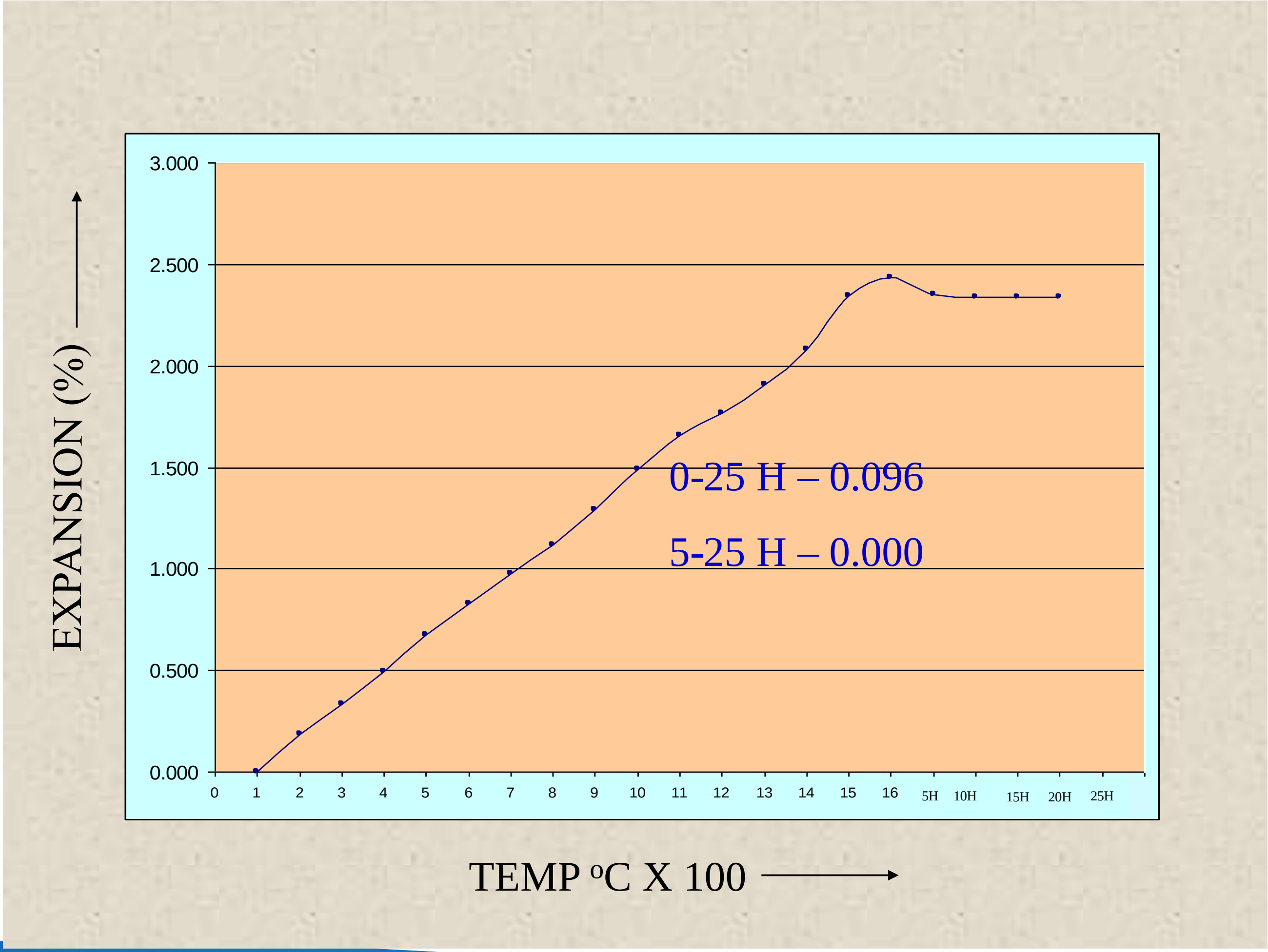
MAGNESIA BASED REFRACTORIES

Property	MGT 98	MGT 98	MGT 97	MGT88
MgO %	97.8	99.2	97	90.2
CaO %	0.9	0.6	1.2	-
SiO_2 %	0.5	0.O5	0.6	5.6
Fe_2O_3 %	0.4	0.05	0.6	0.3
A.P %	15	15	16	15
B.D (gm/cc)	3.05	3	2.97	2.95
CCS (kg/cm^2)	900	900	850	800
RUL ta°C	1750°C	1750°C	1750°C	>1600
HMOR 1400°C(kg/cm^2)	98	135	112	90
HMOR at 1500°C (kg/cm2)	72	92	76	84
Creep 1500°C 5-25hrs	0.05	0.05	0.25	73
Creep 1600°C 5-25 hrs.	0.1	0.1	0.5	0.2

CREEP UNDER COMPRESSION OF MGT 98 BASED ON SWM AT 1600°C/25HRS



CREEP UNDER COMPRESSION OF MGT 98 BASED ON FUSED GRAIN AT 1600°C/25HRS



PROBLEMS WITH MAGNESIA BASED REFRACTORIES FOR REGENERATOR

- Poor resistance to carryover attack
- Poor resistance to sulphate attack
- High thermal expansion
- Poor resistance to thermal spalling
- Poor resistance to hydration

Brick Component	**+Sand**	**→**	**Reaction Product**		**Volume increase**
$3C_2S + 2M$	+ S	→	$2C_3MS_2$	Merwinite	13%
$C_2S + 2M$	+ S	→	2CMS	Monticellite	30%
2M	+ S	→	M_2S	Forsterite	96%
C = CaO, M = MgO, S = SiO_2					

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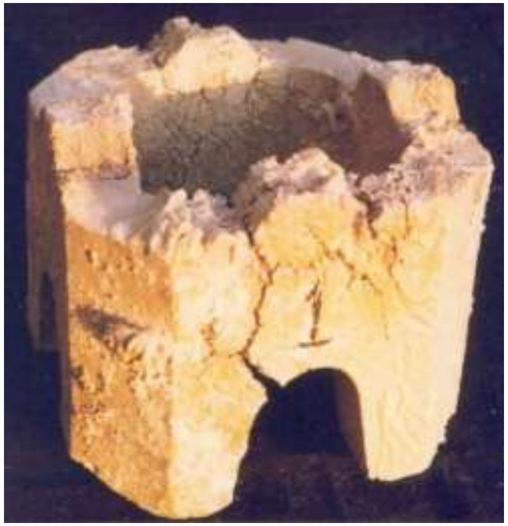
PROBLEMS WITH MAGNESIA BASED REFRACTORIES FOR REGENERATOR



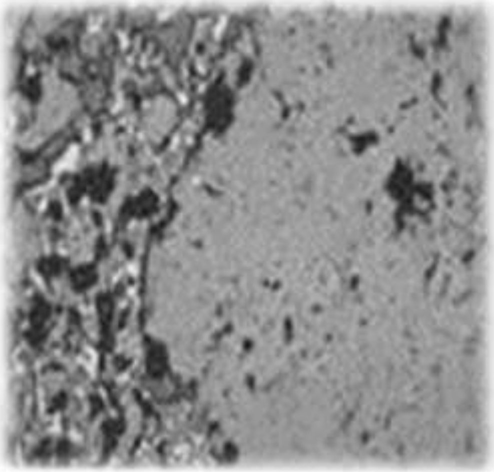
Magnesite brick – Condensation zone

PROPERTIES DATA OF MAGNESIA ZIRCON REFRACTORIES

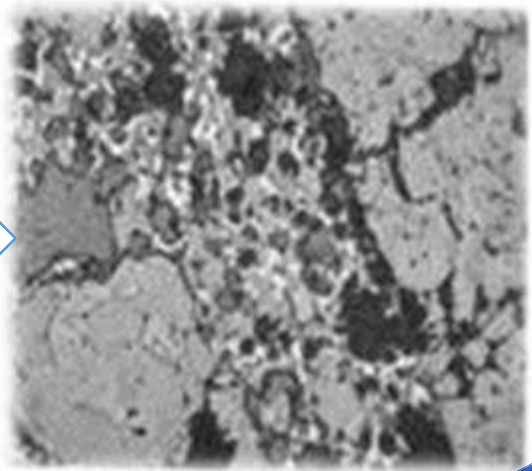
	Magzir I	Magzir II	Magzir III
Chemical Properties			
MgO %	77.4	76	72
ZrO_2 %	12.6	12.4	16
SiO_2 %	7.2	9.4	10
Fe_2O_3 %	0.4	0.5	0.46
Physical Properties			
A.P %	12.1	12.6	12.4
B.D (gm/cc)	3.19	3.16	3.23
CCS (kg/cm^2)	900	900	850
RUL ta	1710°C	1620°C	1670°C
HMOR 1400°C(kg/cm^2)	128	119	126
HMOR 1400°C after alkali sulplate attack (kg/cm^2)	96	92	101
Spalling (BRRA) cycle	+30	+30	+30

MAGNESIA ZIRCON REFRACTORIES

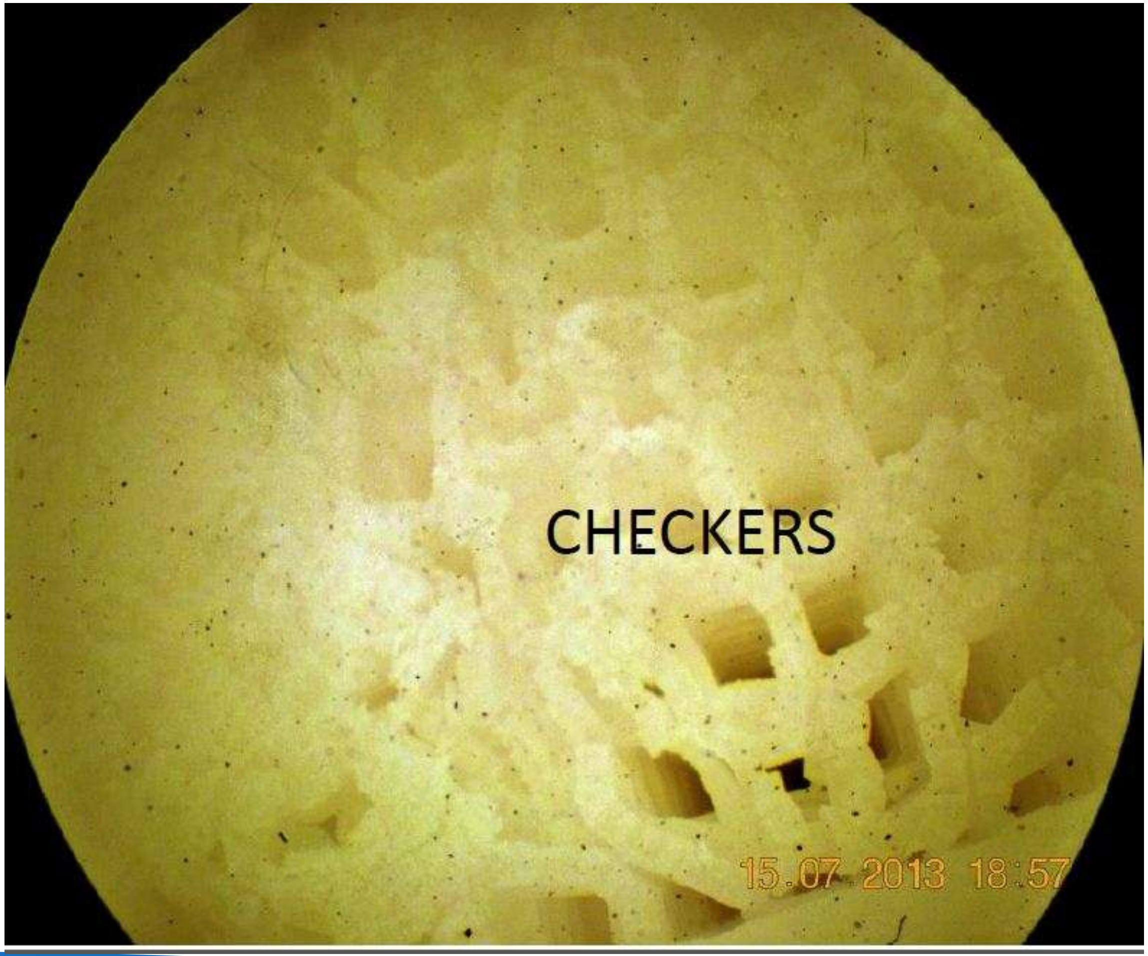
- High resistance to carryover attack.
- High resistance to sulphate attack.
- High resistance to thermal spalling.



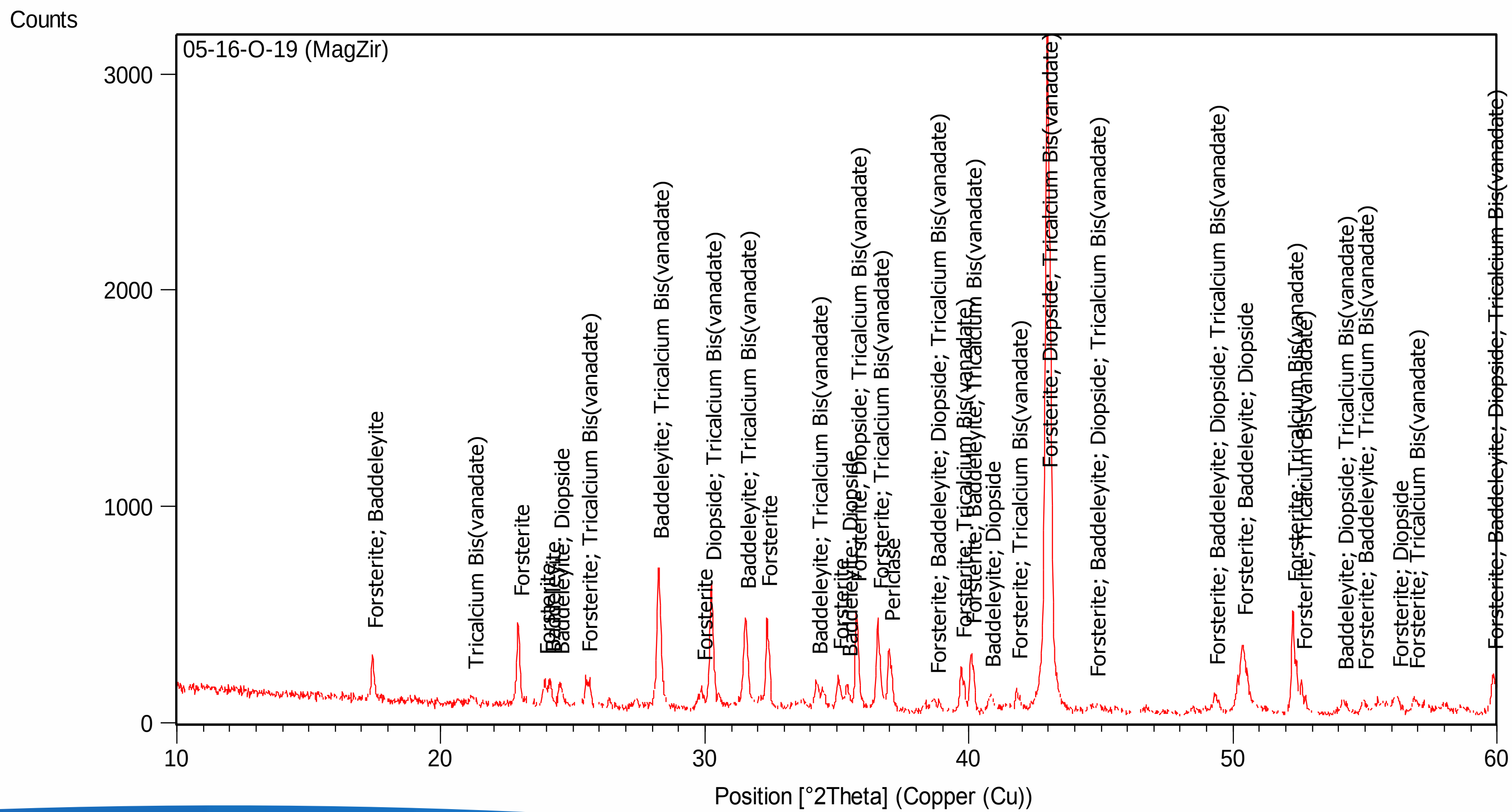
X200 PHOTOMICROGRAPH OF MAGNESIA ZIRCON REFRACTORIES



300TPD AFTER 4 YEARS



X-Ray Diffractogram Of Used Magnesia Zircon



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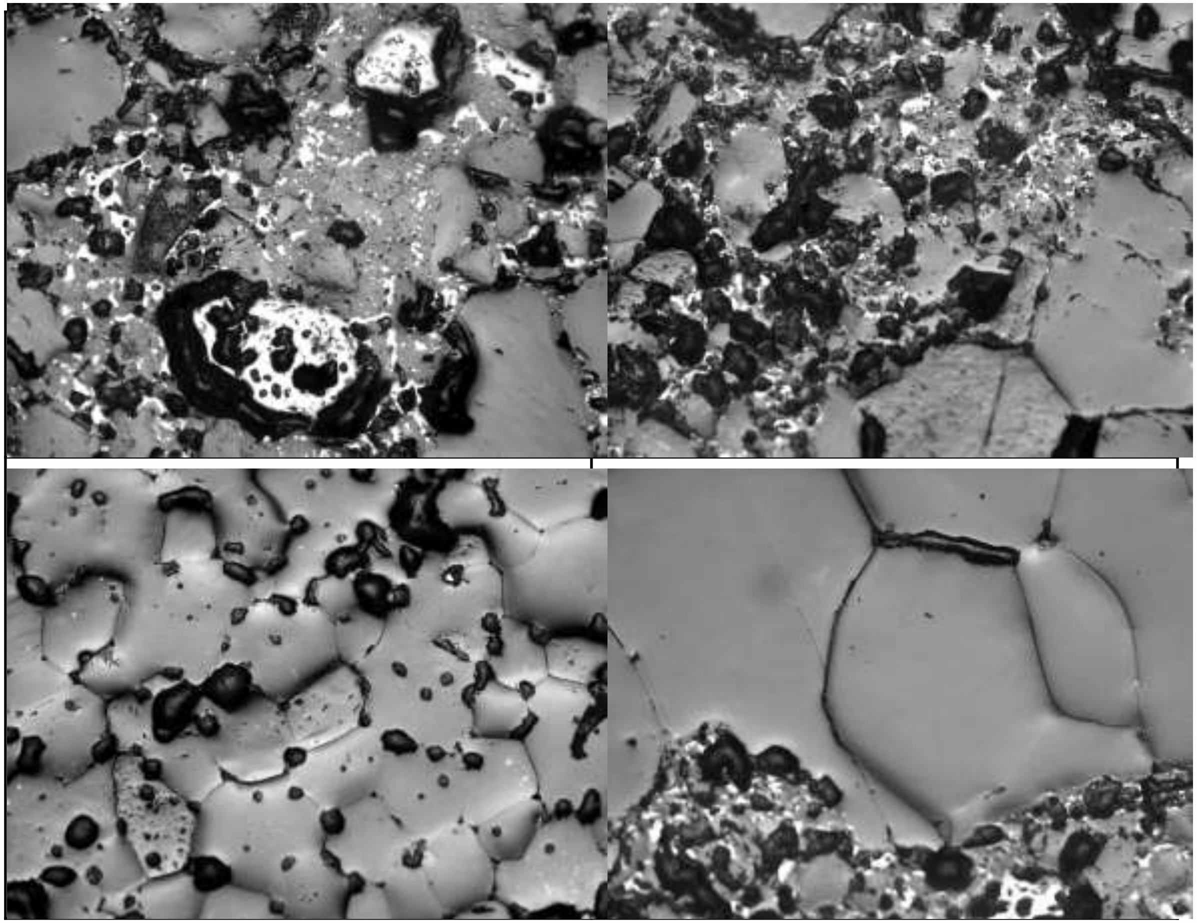
Photomicrograph of used Magnesia ZirconX200



ALUMINA, ALUMINA CHROME AND ALUMINA ZIRCON REFRACTORIES

- MOSTLY USED IN THE CRITICAL AREA OF REGENERATOR
- BASED ON FUSED ALUMINA
- HIGH HOT STRENGTH
- HIGH RESISTANCE TO THERMAL SHOCK
- HIGH RESISTANCE TO CARRY OVER AND SULPHATE ATTACK

ALUMINA, ALUMINA CHROME AND ALUMINA ZIRCON REFRACTORIES

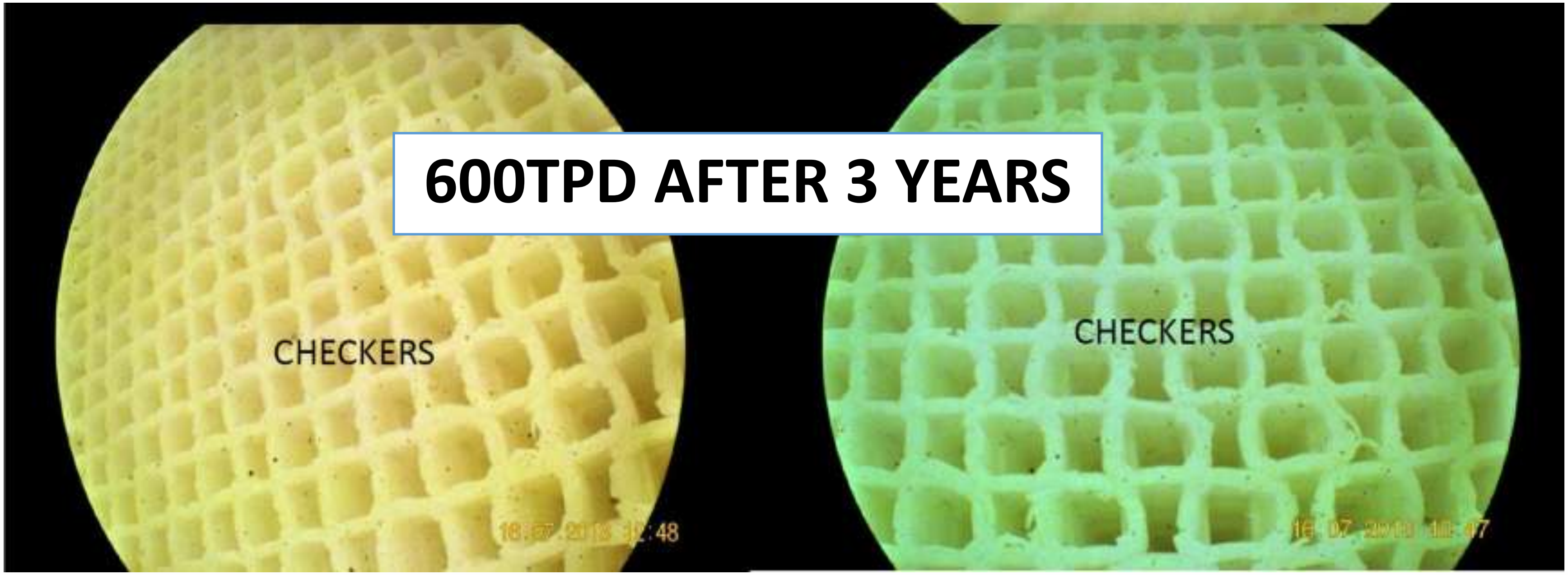
Quality	HA99	A85CRZ	Aluzir 80
Al_2O_3	99.1	84.1	79
ZrO_2	-	3.2	12.5
Cr_2O_3	-	9.8	-
SiO_2	0.14	1.9	7
Fe_2O_3	0.12	0.1	0.2
AP %	16	14	16
BD (gm/cc)	3.22	3.34	3.25
CCS (kg/cm^2)	1000	1800	1000
RUL ta °C	>1700	>1700	>1700
TE at 1400°C	1.12	1.08	1.05
HMOR at 1400°C (kg/cm^2)	135	173	148
HMOR 1400°C After Alkali sulphate attack (kg/cm^2)	122	170	120
HMOR at 1500°C (kg/cm^2)	88	123	
TC(W/Mk) At 700°C	3.2	3	2.4
TC(W/Mk) At 1000°C	3	2.8	2.4
Creep 1500°C 0-15hrs	0.14	0.19	-
Creep 1500oC 5-25 hrs	0.05	0.08	-
TSR Air cycle 1000°C	>25	>30	>50

COMPARISON FOR TOP COURSE PACKING

PROPERTIES	ALCHROME	MAGZIR 1	ALUMINA
AP%	14	14-16	16-18
BD(gm/cc)	3.34	3.12	3.22
CCS(kg/cm2)	1900	800	1200
RUL taoC	>1700	>1670	>1700
TE at 1400oC	1.12	1.74	1.12
HMOR at 1400oC(kg/cm2)	173	128	135
HMOR at 1400oC After Alkali sulphate attack(kg/cm2)	170	96	122
HMOR at 1500oC(kg/cm2)	123	-	88
TC(W/Mk) At 400oC	3.5	2.9	3.8
At 700oC	3.0	2.8	3.2
At 1000oC	2.8	2.8	3.0
Creep under compression at 1500oC/25 hrs 2 kg/cm2 load 0-25hrs	0.19	0.86	0.14
5-25hrs	0.08	0.32	0.05

COMPARISON FOR TOP COURSE PACKING

PROPERTIES	ALCHROME	MAGZIR 1	ALUMINA
TSR Air cycle 1000oC	>30	>15	>25
Specific heat(BTU/lb/oF)			
800oF	0.230	0.246	0.235
1000oF	0.232	0.252	0.242
1200oF	0.242	0.256	0.248
1400oF	0.248	0.261	0.252
1600oF	0.252	0.265	0.257
1800oF	0.255	0.271	0.260
2000oF	0.260	0.275	0.264
2200oF	0.262	0.280	0.267


600TPD AFTER 3 YEARS
CHECKERS
CHECKERS


600TPD AFTER 3.5 YEARS
CHECKERS
CHECKERS

ALUMINA CHROME REFRACTORIES

A85CRZ CHB in pet-coke fired 300 TPD furnace after 7 yrs service.

COMPARISON FOR CONDENSATION ZONE PACKING

PROPERTIES		MGT88	MAGNEL70	MAGZIR 2	HA 62	A42
AP%		13-16	16-18	14-16	14-17	13-18
BD(gm/cc)		2.99-3.04	2.90-2.92	3.05-3.10	2.40-2.45	2.20-2.24
CCS(kg/cm2)		550-800	500-700	600-800	500-600	600-800
RUL taoC		1650	>1700	1640	1520	1500
TE at 1400oC		1.89	1.82	1.72		
HMOR at 1400oC(kg/cm2) Alkali sulphate attack	Before	90	55	85		
	After	84	50	79		
Creep under compression at 1300oC/25 hrs Load 2kg/cm2	0-25 hrs	0.2	0.05	0.2	0.4	0.8
	5-25 hrs	0.1	0	0.1	0.2	0.55
Creep under compression at 1350oC/4kg/cm2 load	0-25 hrs	0.4	0.05	1.09		
	5-25 hrs	0.25	0	0.54		
TC(W/Mk)	At 400oC	6.2	3.4	2.9	1.65	1.2
	At 700oC	5.1	3.2	2.8	1.65	1.3
	At 1000oC	3.9	3	2.8	1.75	1.4
TSR Air Cycle 1000oC		>30	>75	>30	>50	>50

COMPARISON FOR CONDENSATION ZONE PACKING

PROPERTIES	MGT88	MAGNEL85	MAGZIR 2	HA 62	A42
Specific heat(BTU/lb/oF)					
800oF(427)	0.250	0.252	0.246	0.229	0.220
1000oF(538)	0.256	0.258	0.252	0.233	0.227
1200oF(649oC)	0.260	0.262	0.256	0.237	0.234
1400oF(760oC)	0.265	0.268	0.261	0.240	0.241
1600oF(871oC)	0.270	0.272	0.265	0.242	0.248
1800oF(982oC)	0.275	0.278	0.271	0.245	0.253
2000oF(1093oC)	0.280	0.282	0.275	0.247	0.258
2200oF(12040C)	0.284	0.286	0.280	0.249	0.262
2400oF(1315oC)	0.289	0.290	0.285	0.251	0.266
2600oF(1426oC)	0.293	0.294	0.290	0.253	0.269
Heat capacity at 760oC	0.79235	0.78256	0.79605	0.576	0.53261
Heat capacity at 871oC	0.8073	0.79424	0.80825	0.5808	0.54808

MULLITE REFRACTORIES

- Excellent high temperature creep resistance.
- High resistance to carryover attack.
- Low thermal conductivity
- Low coefficient of thermal expansion.
- High volume stability.

Quality	Fused Mullite	Sintered Mullite
Al_2O_3%	76	72
SiO_2%	22	26
Fe_2O_3%	0.1	0.5
Alkalies	0.3	0.35
A.P.%	18	18
B.D (gm/cc)	2.65	2.55
CCS (kg/cm^2)	500	600
RUL ta°C	>1700°C	>1700°C
TSR(DIN 51068/1)	35	35
Creep 1600°C 5-25 hrs	0.1	-
Creep 1500°C 5-25 hrs	-	0.15

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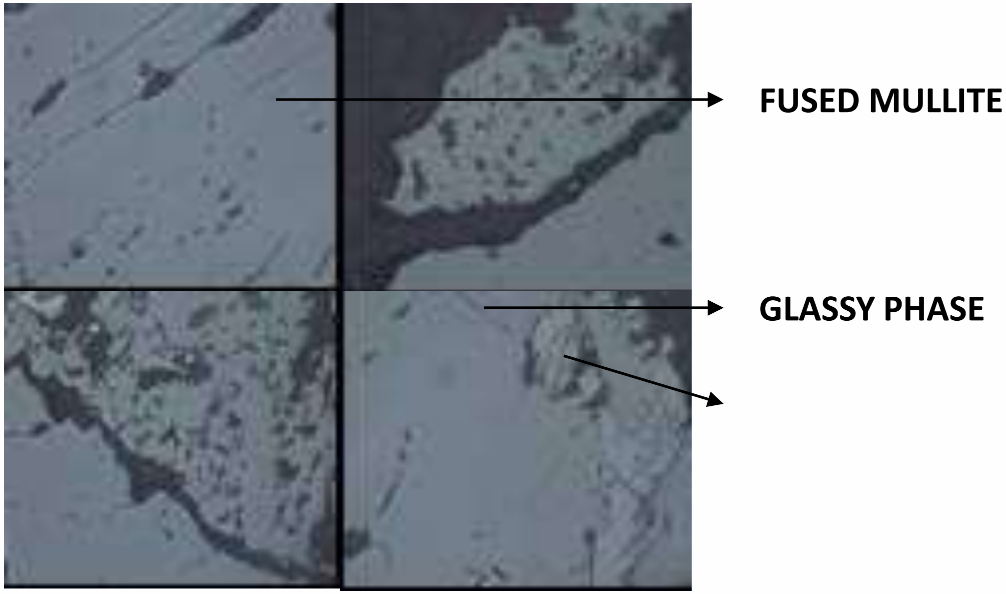
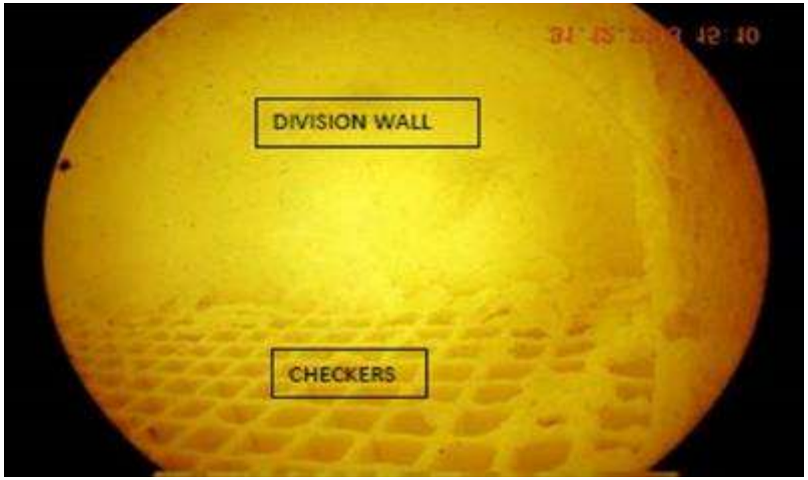
X200 PHOTOMICROGRAPH OF FUSED MULLITE BRICK

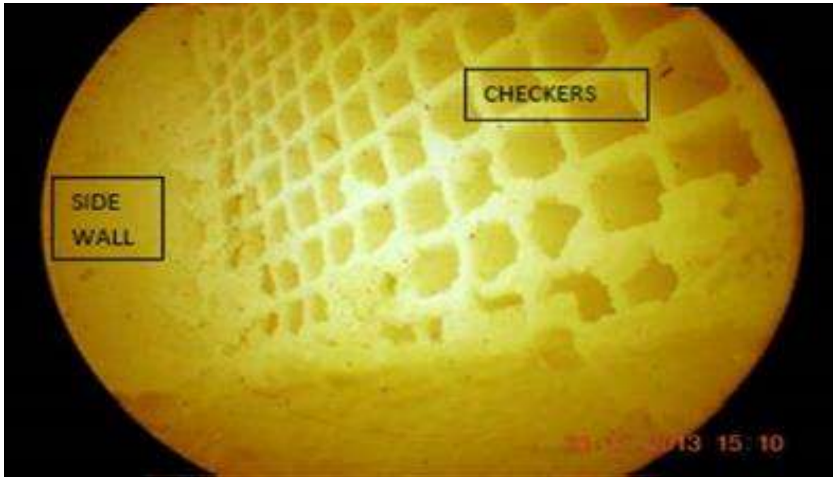


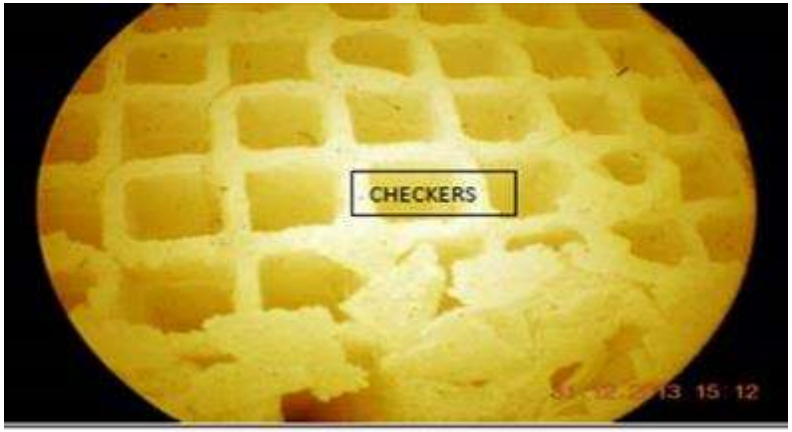
- Acicular interlocking grains.
- Large crystal size.
- Very less glassy phase.

TYPICAL CURVE FOR CREEP UNDER COMPRESSION AT 1600°C/50HOURS

MULLITE PEELING FROM CROWN AND TARGET WALL







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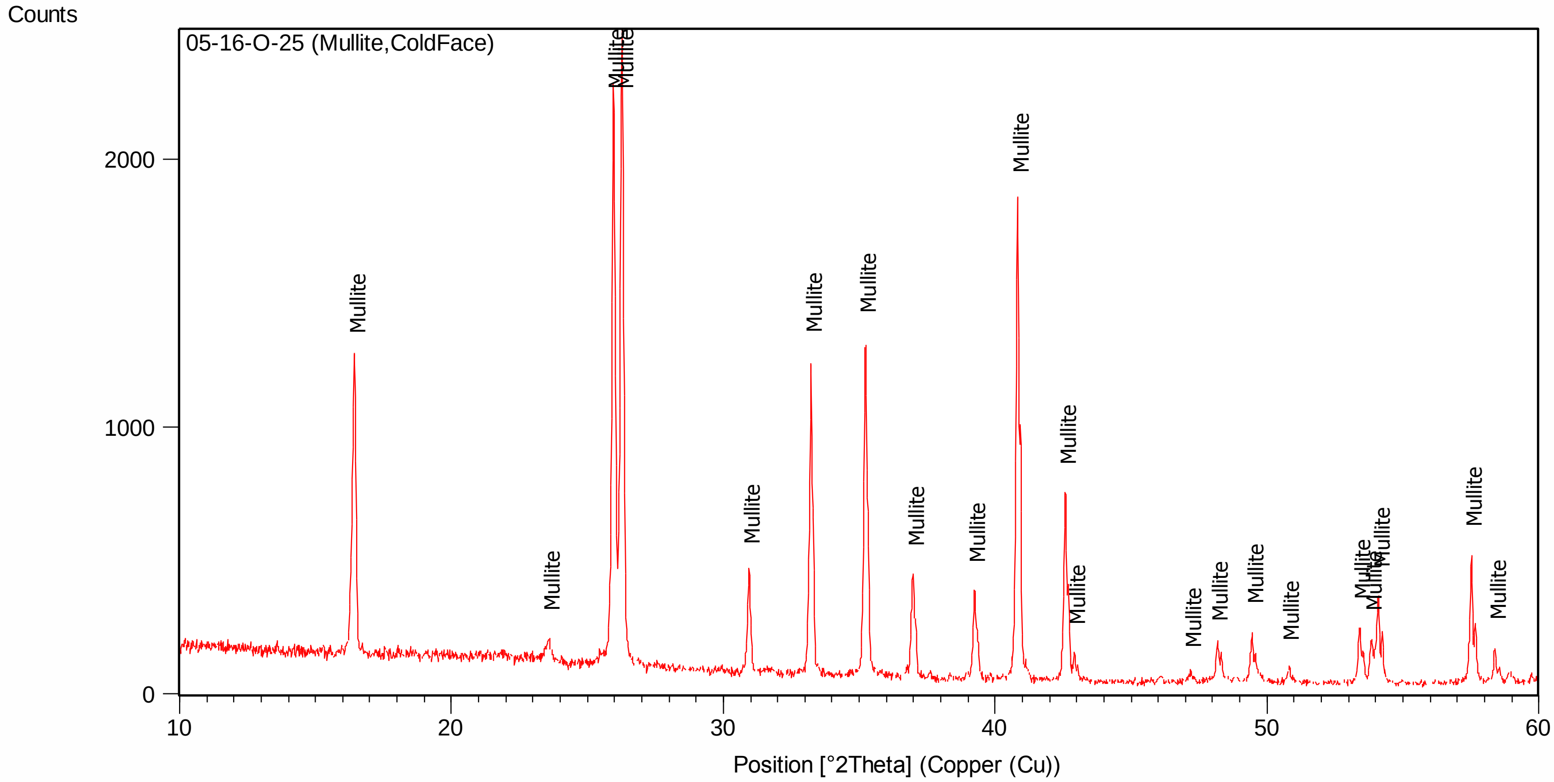
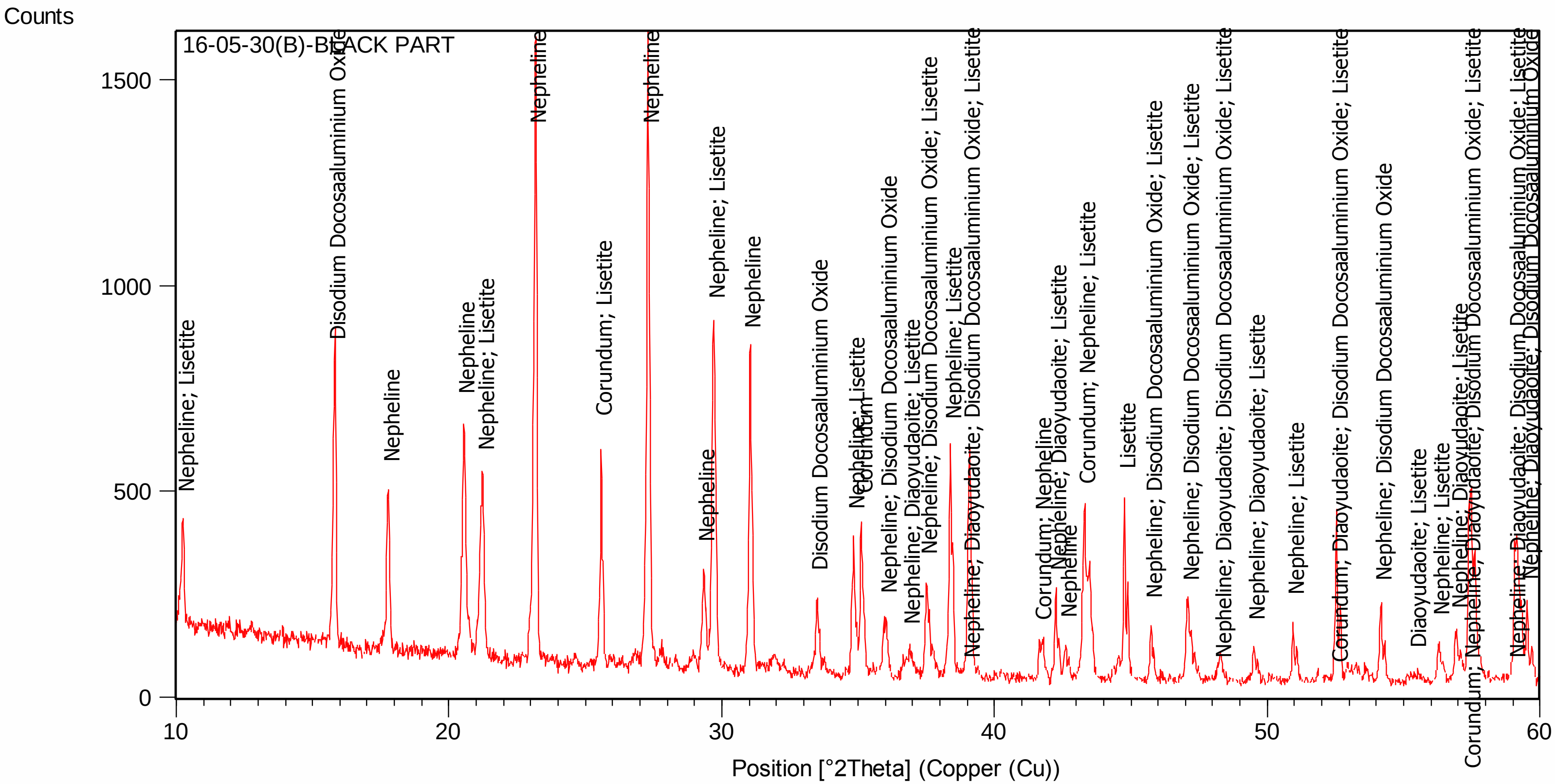
X-Ray Diffractogram of used Mullite brick cold face



Dalmia
Bharat Refractories

X Ray Diffractogram of used Mullite brick Hot face



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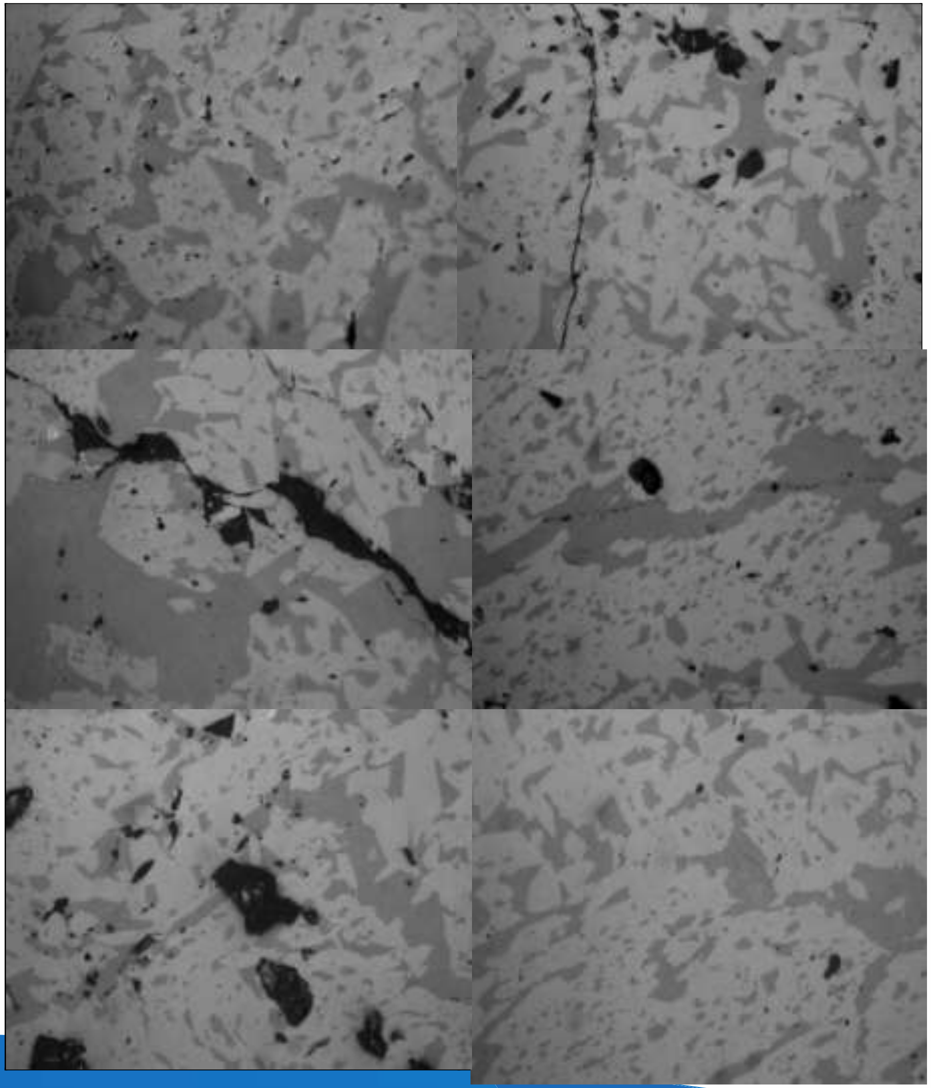
Bharat Refractories

Photomicrograph of used Mullite brick Cold face X200



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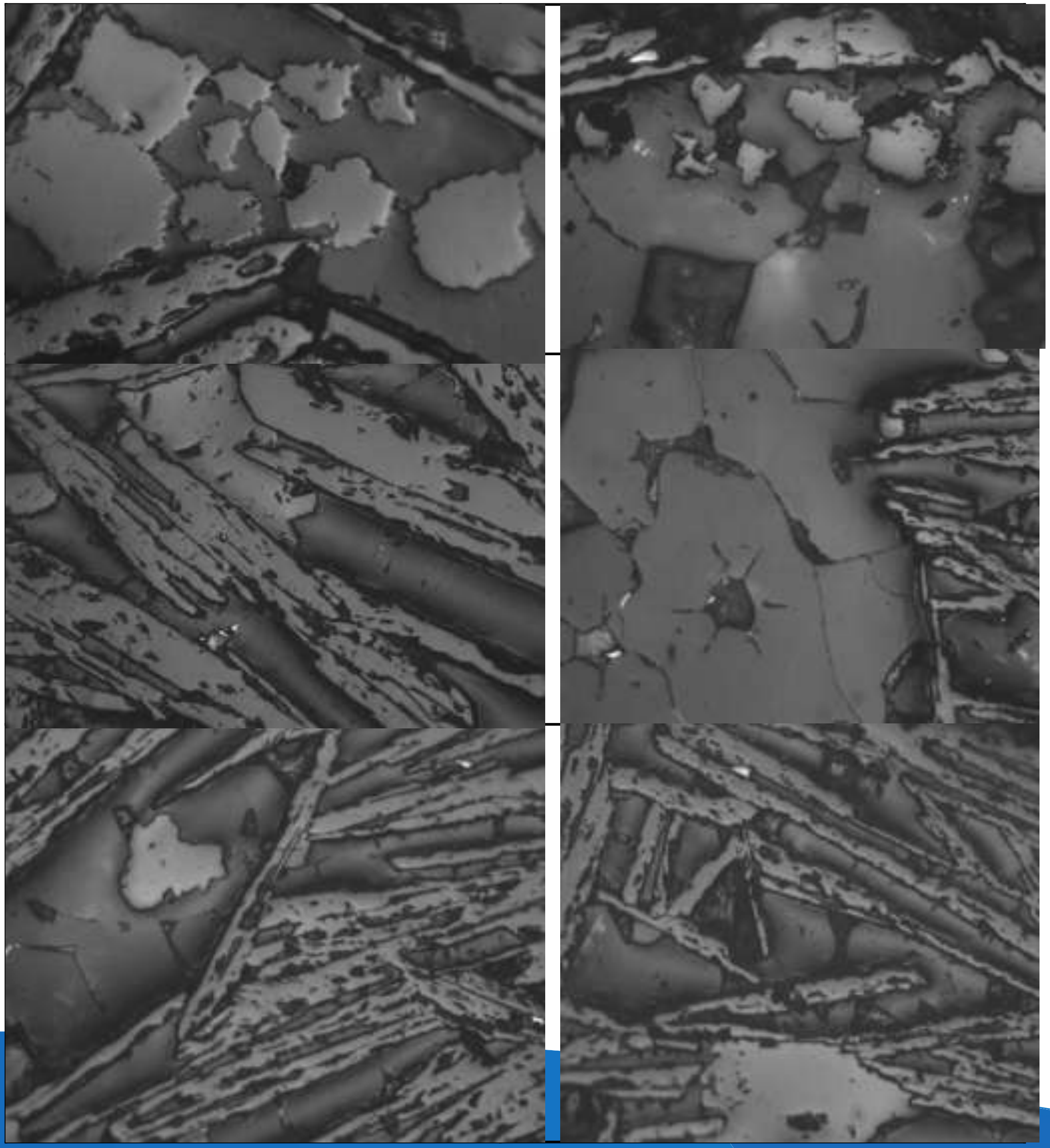
Photomicrograph of Used Mullite brick Hot face X200



CONCLUSION

Through the judicious selection of raw materials and manufacturing technique, bricks with controlled chemical, physical, thermo-mechanical, thermal and pyro-chemical properties can be made. The judicious selection of refractories gives superior performance to the furnace with increased productivity

THANK YOU