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Paper name: Refractory Raw Materials: Problems and Prospects

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Experience	• Industry experience of 6 years at H&R Johnson (I) Ltd, Mumbai in the field of ceramic tiles and ceramic colour • Joined CSIR-CGCRI, in the year 2007 • Experience in the field of refractory raw materials, synthetic refractory aggregates, castables, reaction sintering
Projects:	• Participated in 30 nos. of projects on refractory raw materials, synthetic aggregate, high alumina castable, carbon-containing refractories, chemically bonded ceramics etc.
Publication/ Patent	Publications: Journals: 21, Conference paper: 20, Patent: 2

Refractory Raw Materials: Problems and Prospects

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Introduction

- Bauxite and magnesite are two most important refractory raw materials
- Expected increase in requirement due to target steel capacity enhancement
- India endowed with both the materials
- Indian resources: impure, not suitable
- Mostly imported: Import cost for 2018-19: Mullite- 27 Cr, Bauxite-1336 Cr, Magnesite- 1112 Cr

Value addition of Indian refractory raw materials is essential

Indian Bauxite

- Bauxite is one of the primary raw materials for refractory
- 5th in bauxite production in the world
- Bauxite resources: 3,896 million tons (656 million tons reserves & 3,240 million tons other resources)
- Major reserves are Odisha, Andhra Pradesh, Gujarat, Maharashtra, Madhya Pradesh, and Chattishgarh
- Only ~ 4% of total production is refractory/chemical grade

Impurities: iron oxide; silica; titania and lime

Source: Indian Bureau of Mines, Mineral Year Book 2020

Indian Bauxite

Chemical Composition

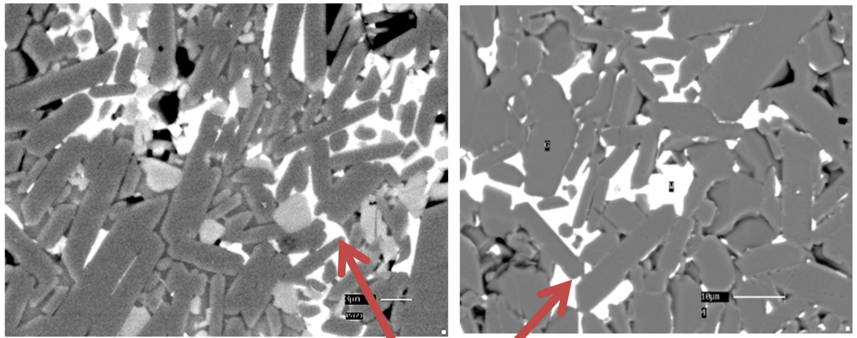
Constituent, wt%	Variety 1	Variety 2
SiO_2	3-6	5-10
Al_2O_3	51-55	51-55
Fe_2O_3	5-8	2-5
TiO_2	5-8	2-5
CaO	0.1-0.3	2-4
LOI	23-25	25-27
RUL, ta, °C	1440-1460	1440-1450

Possible Impurities phases:

- $FeAlTiO_5$
- Ca- containing low melting phase

Not suitable for high temperature application

Microstructure of sintered bauxite

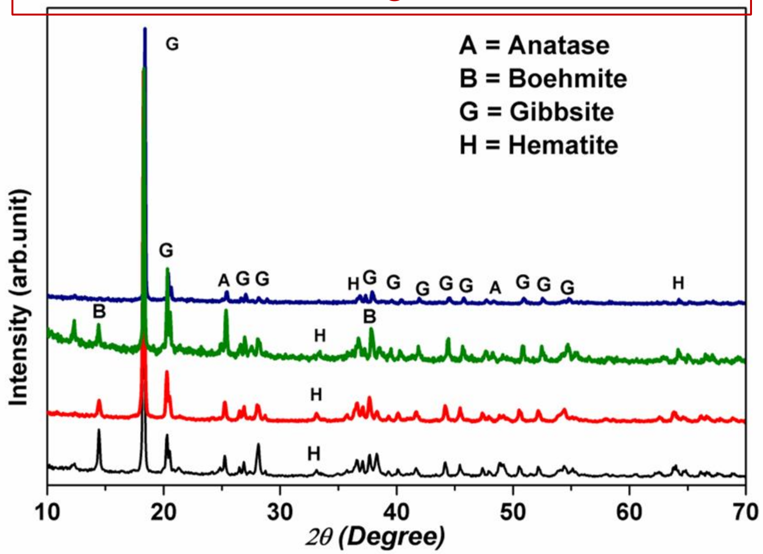


Contains CaO

CaO content low

Low melting phases

Phase assemblage: raw bauxite



Methodologies for Value Addition

Beneficiation
- Physical separation
- Reduction roasting followed by magnetic separation
- Flotation separation
- Segregation by fusion

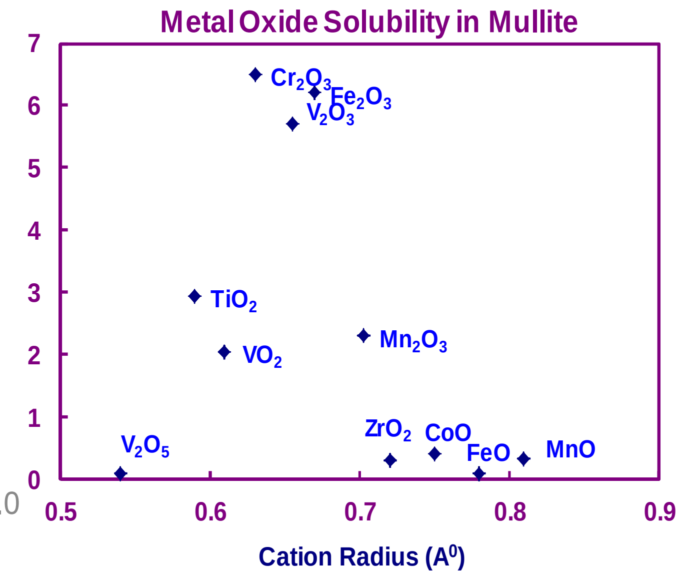
Removes Fe_2O_3, SiO_2

Leaching
- Bio leaching
- Acid leaching

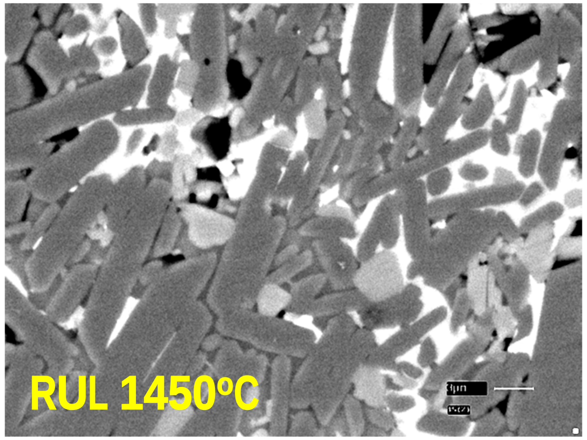
Removes Fe_2O_3, SiO_2, CaO

Phase modification
Mullite-corrundum composite

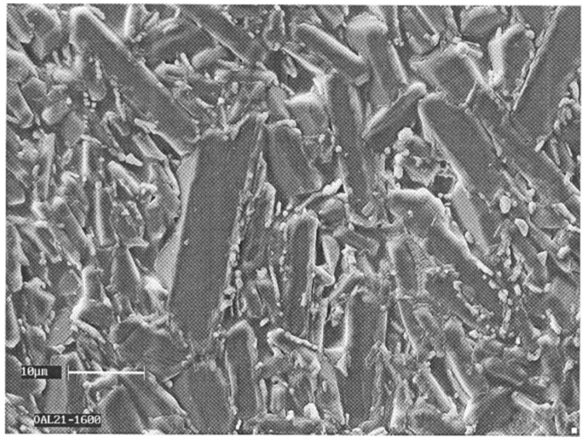
High temperature applications



Bauxite Containing CaO

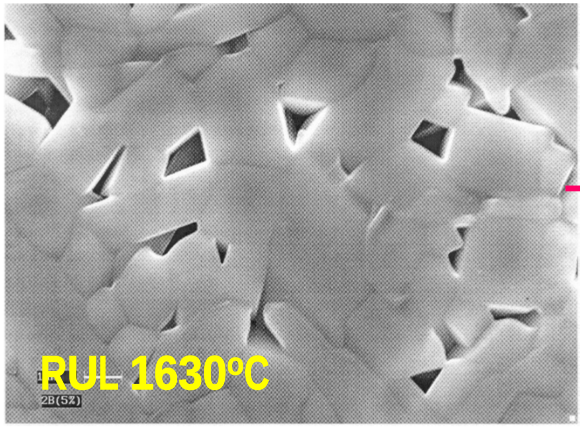


As received bauxite containing CaO

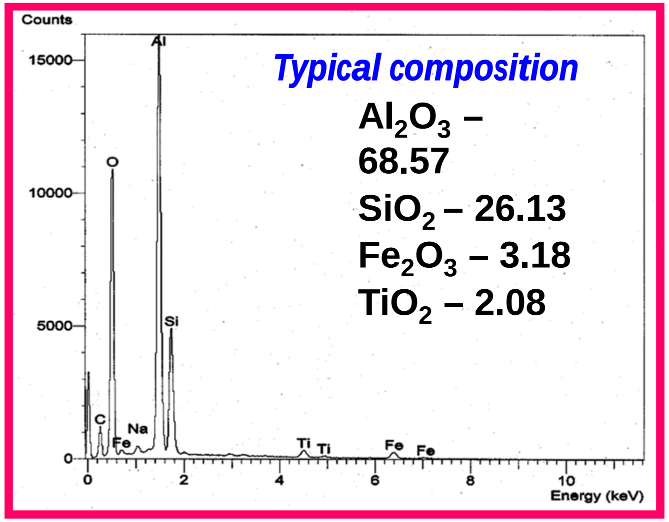


Mullite from bauxite

Acid leaching followed by sintering



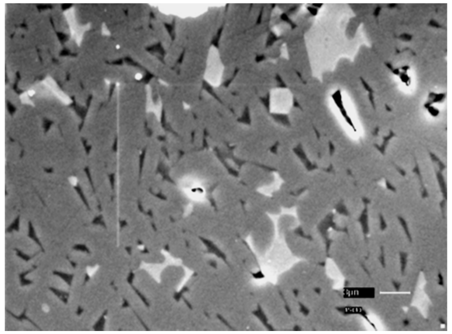
Mullite from bauxite with minor beneficiation

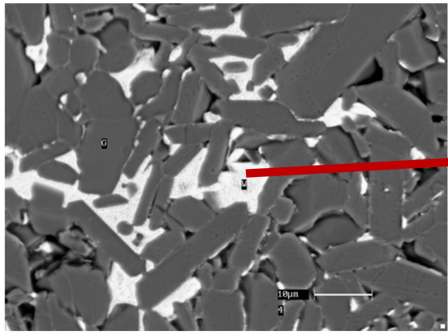


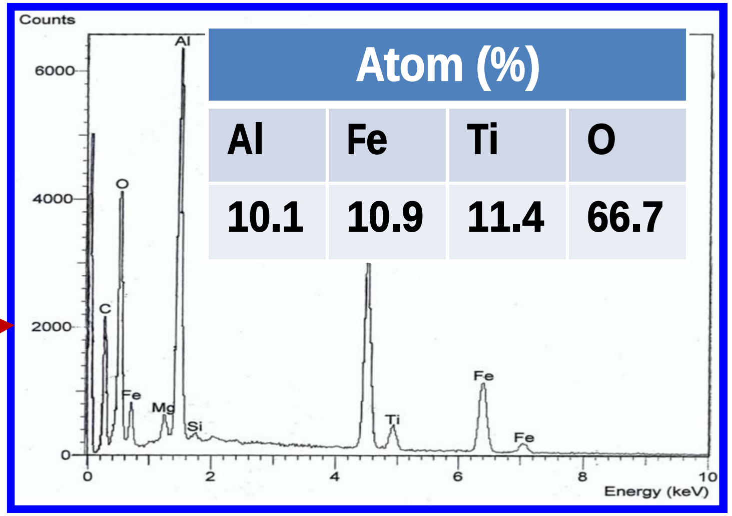
EDX spectra of mullite grain

Bauxite with Low CaO

- Detrimental impurities: Fe_2O_3, TiO_2
- Low melting phase: $FeAlTiO_5$



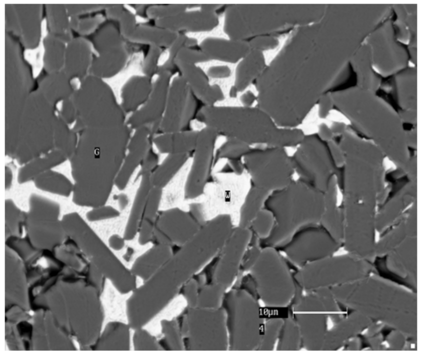




Atom (%)			
Al	Fe	Ti	O
10.1	10.9	11.4	66.7

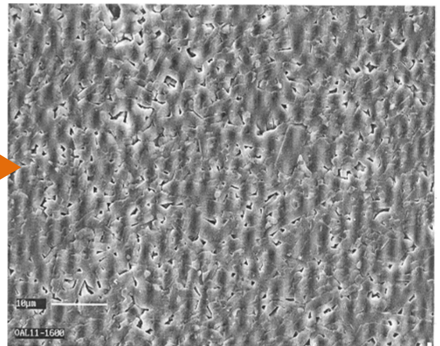
➢ **Phase modification with or without minor beneficiation**

➢ **Formation of mullite-corundum composite**



Sintered bauxite

RUL: 1450-1460 °C



Value added product

RUL: > 1600 °C

Typical composition from EDX

Atom (%)				
Al	Si	Fe	Ti	O
33.47	10.18	1.60	0.96	53.79

Refractory aggregates from Indian and Foreign Origin

Properties	Indian Bauxite	Processed aggregates	Imported Bauxite
Bulk Density, g/cm^3	2.90	2.80	3.06
App. Porosity, %	12.4	10.1	13.9
RUL, t_a °C	1450	1600-1630	1610

- Up-scaled at a level of 30 Tons at the industry
- High temperature properties are similar with lab scale product

Sillimanite Beach Sand

Sillimanite Beach Sand

- Sillimanite beach sand is generated as by product during rare earth extraction process from beach sand
- Pure form of alumino silicate with very low amount of impurities.
- Reserve: 131 Million Tonnes

Chemical constituents (%)	Quilon	OSCOM
SiO_2	37.1	38.0
Al_2O_3	59.3	56.6
Fe_2O_3	0.5	0.4
TiO_2	0.4	0.25
CaO	0.6	0.4
MgO	-	0.31
ZrO_2	1.5	-

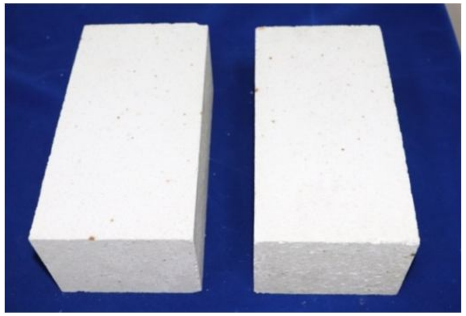
Sillimanite Beach Sand

Value added to form mullite aggregate using calcined alumina and sintering additives

Properties of refractory aggregates	
Apparent porosity (%)	0.74
Bulk Density (g/cc)	3.04
Specific Gravity	3.13
Flexural strength (MPa)	140

Fired briquettes

Nodules



Refractory bricks from developed aggregates

Properties	Standard brick	Developed brick
A.P. (%)	20	19.9
B.D. (g/cc)	2.5	2.51
CCS (kg/cm^2)	500	462
Hot MOR at 1400°C (kg/cm^2)	-	52
RUL (°C)	1700	> 1640

Magnesite

Magnesite

- Magnesite is the most important basic refractory raw material

- Indian magnesite reserve is 82 million tonnes and resource is 312 million tonnes

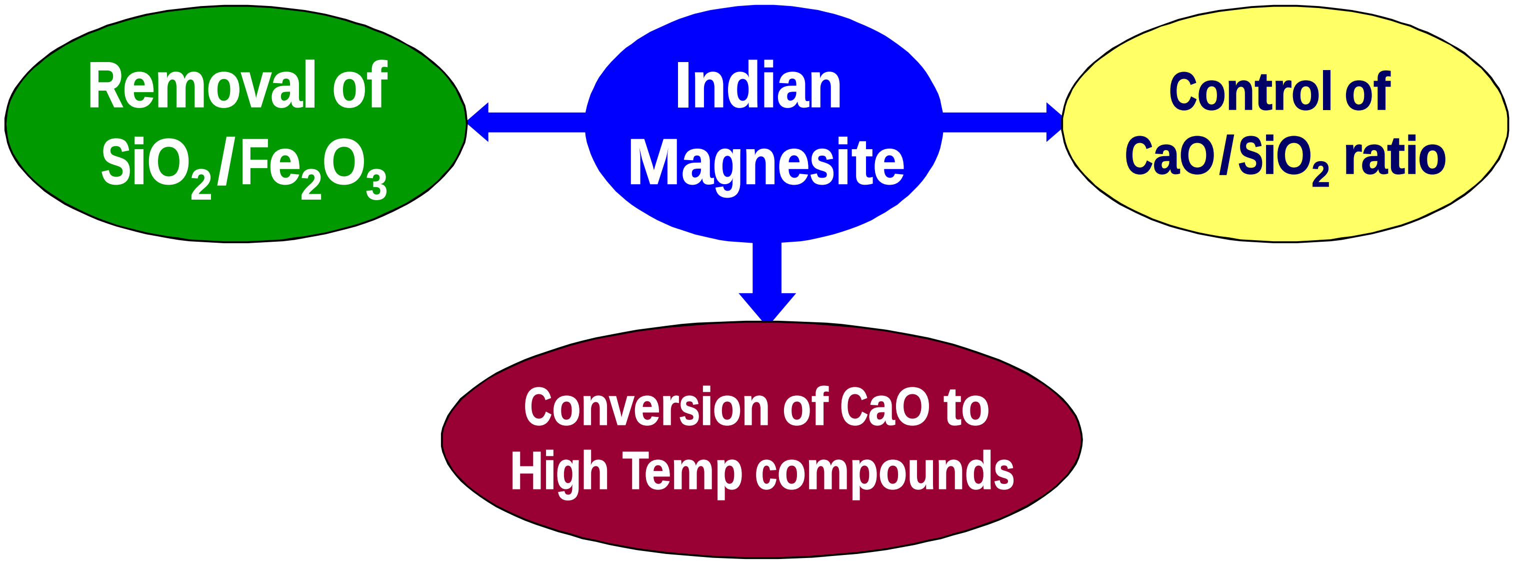
- Major magnesite resources are available in the state of Uttarakhand, Tamil Nadu and Rajasthan

- In spite of having good reserve of natural magnesite, India has to depend on imported magnesite for refractory production

Problems with Indian magnesite

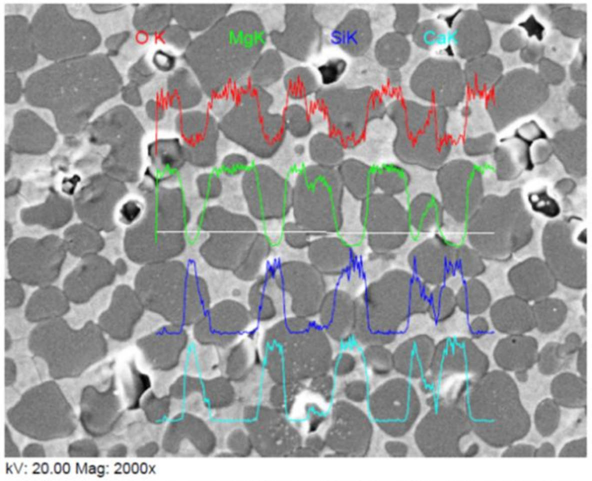
Constituents (%)	Magnesite source	
	Salem	Almora
MgO	88-90	82-84
CaO	2-7	5 (max)
SiO_2	4-8	4.5 (max)
Fe_2O_3	Tr.	4-6

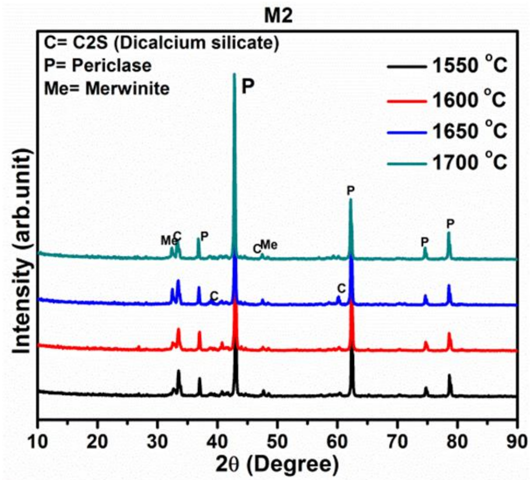
Low melting phases like monticellite, merwinite , di-calcium ferrite may be formed

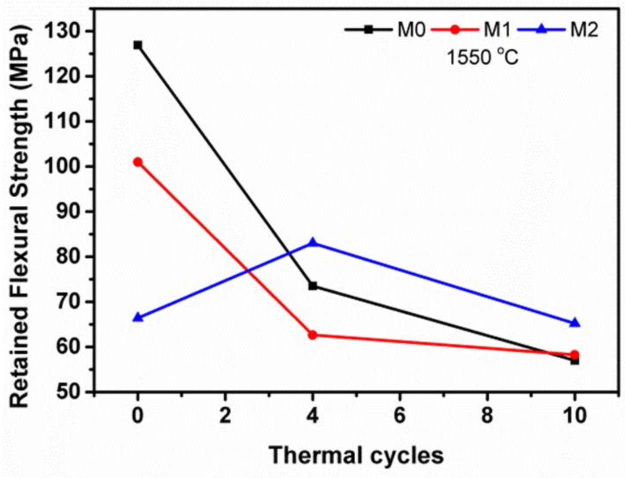


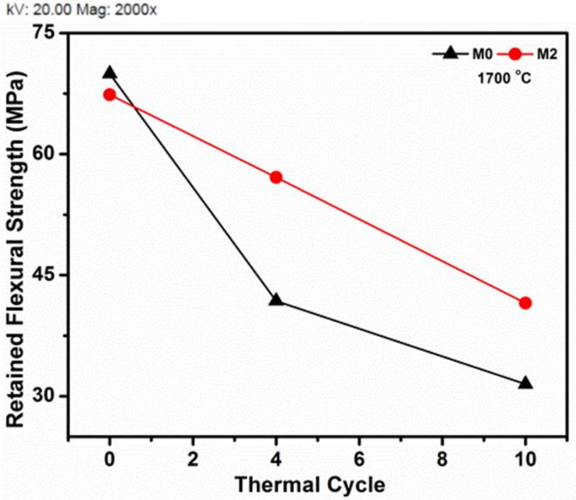
Changing lime/silica ratio

- Phase formation in CaO-MgO-SiO_2 is controlled by CaO-SIO2 ratio.
- Lime/silica ratio was adjusted to minimise the low melting phase formation







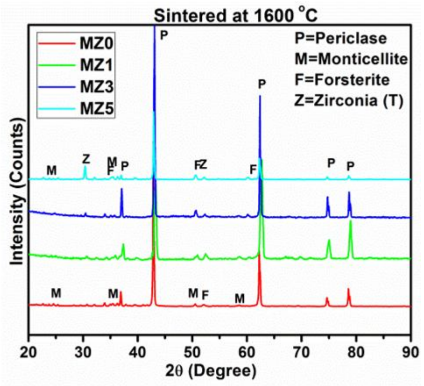


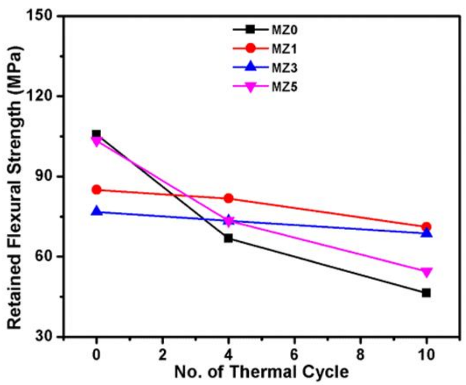
Lime/silica ratio of 2:1 is beneficial in terms of thermo-mechanical properties due to the formation of C_2S phase

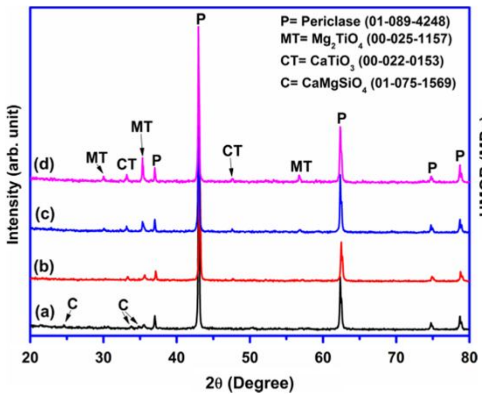
- C Ghosh *et al.* Ceram. Int. 40 (2014) 16791-98.
- *M K Haldar, C Ghosh, A Ghosh*, J Mat. Sc. Chem. Engg. 2 (2014) 1-8.

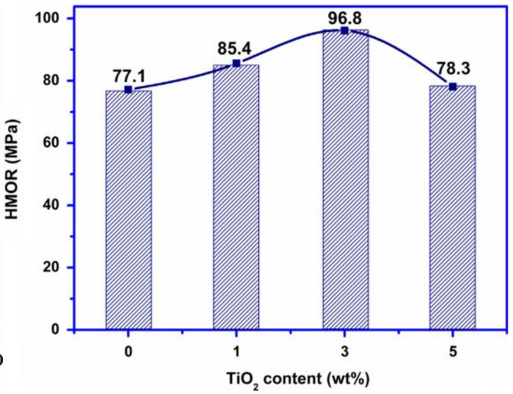
Conversion of CaO to High Temperature Compounds

- ZrO_2, TiO_2, Y_2O_3 were used as additives to contain the low melting phase
- Formation secondary phases restricts low melting phase formation









With ZrO_2 With TiO_2

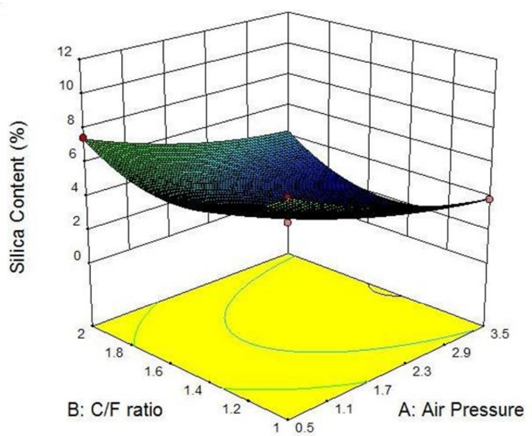
- CaO is used by zirconia for *tetragonal phase stabilization* thus reducing the formation of monticellite phase
- Formation of *$CaTIO_3$* with addition of TiO_2 reduces low melting phase formation
- 1 & 3 wt% addition showed better properties

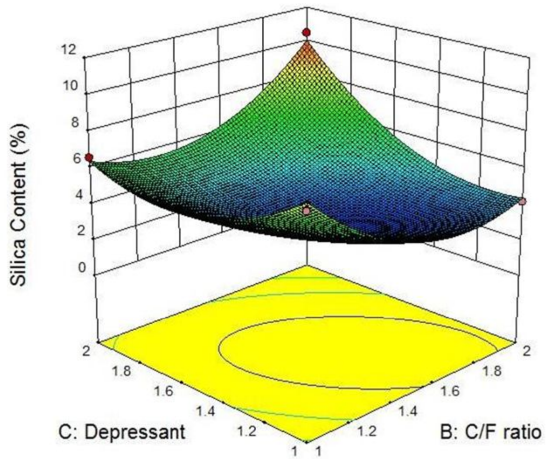
C Ghosh et al. *Int. J. Appl. Ceram. Technol*., 16 (2019) 410-417.
Burhanuddin et al. *Int. J. Miner. Process.*, 144 (2015) 40-45.
P. Kumar et al. *Ceram. Int*. 41 (2015) 9003–9008.

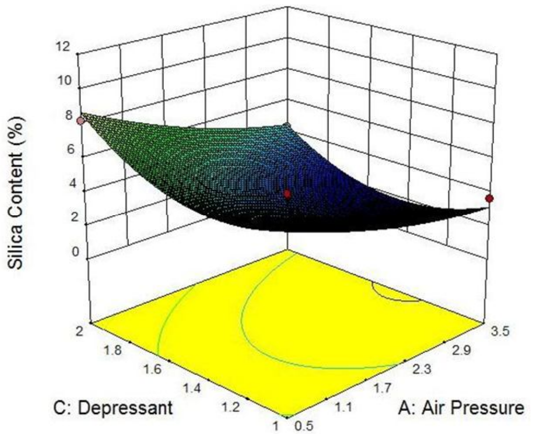
Beneficiation for Impurity Separation

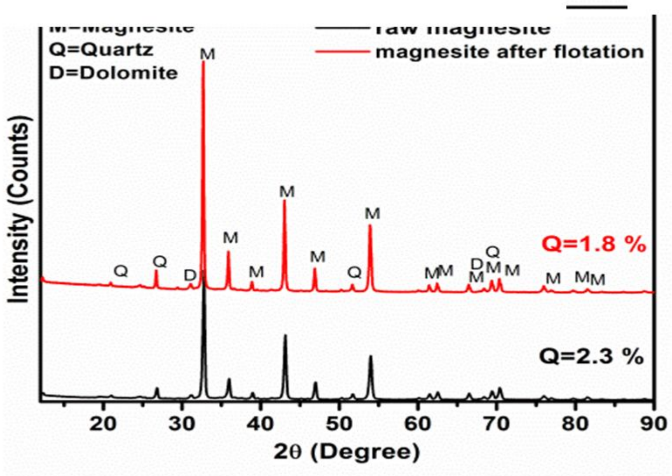
- Reverse froth flotation was used
- Air pressure, C/F ratio and depressant dosage was varied
- Optimum conditions were suggested by RSM

Materials Used	
Collector	Alkyl ether monoamine
Frother	Pine oil
Depressant	SHMP









•Amount of silica could be reduced by following this process

C Ghosh et al. Trans. Ind. Ceram. Soc. 79 (2020), 1, 23-29.

Superior Magnesia Through Fusion Process

- Development of superior magnesia aggregates from Indian magnesite through arc melting
- Separation of the impurities through gravity separation

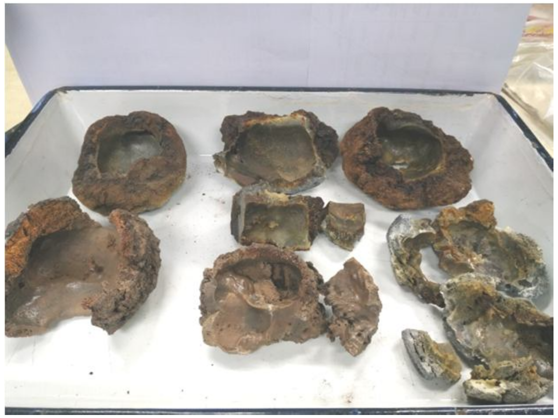
Impure Almora Magnesite

MgO-84.5

SiO_2- 3.36
Fe_2O_3- 4.70
CaO- 4.18

Melt processing through arc melting

Processed Almora Magnesite



MgO-91.81

SiO_2- 3.68
Fe_2O_3- 1.69
CaO- 1.92

Remarks

- India endowed with large reserves of bauxite and magnesite
- Low quality restricts their high temperature applications
- Nature of impurities and their content vary form one origin to another
- Improvement in high temperature properties of Indian bauxite and magnesite was achieved through different value addition process
- ***A multipronged approach involving beneficiation, arc melting and phase modification is the solution***


Thank You