Endeavors to improve energy efficiency towards environmental-friendly production of manganese ferroalloys by CSIR-NML, Jamshedpur

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Outline of the presentation

- Introduction
- Process for LC-FeMn production
- Use of metallurgical residues in SiMn production
- SiMn slag in Geopolymers
- SiMn slag as cement materials
- Summary

Introduction

- Manganese is an essential alloying element in steel making.
- Many properties in steel derived by appropriate addition **of ferromanganese (FeMn) and silicomanganese (SiMn) alloys**.
- Ferromanganese classify as low carbon (LC-FeMn/0.2%Cmax), medium carbon (MC-FeMn/1-3%C) and high carbon (HC-FeMn/6-8%C) alloy by carbon content
- HC-FeMn is produced by Blast Furnace (BF) or Submerged Arc Furnace (SAF) method.
- Carbon act as reductant in the production of HC-FeMn

Carbothermic reduction of MANGANESE OXIDES

$2MnO_2 \rightarrow Mn_2O_3 + ½\ O_2$
$3Mn_2O_3 \rightarrow 2Mn_3O_4 + ½O_2$
$Mn_3O_4 \rightarrow 3MnO + ½O_2$

$3Mn_2O_3 + C \rightarrow 2Mn_3O_4 + CO$
$3Mn_2O_3 + CO \rightarrow 2Mn_3O_4 + CO_2$

$Mn_3O_4 + C \rightarrow 3MnO + CO$
$Mn_3O_4 + CO \rightarrow 3MnO + CO_2$

$MnO+CO \rightarrow Mn+CO_2$
(Due to high partial pressure requirement of carbon monoxide, the reduction of MnO by carbon monoxide does not occur.)

$MnO + {}^{10}/_{7}C \rightarrow {}^{1}/_{7}Mn_7C_3 + CO$
$MnO + {}^{10}/_{7}Fe_3C \rightarrow {}^{1}/_{7}Mn_7C_3 + {}^{30}/_{7}Fe + CO$

Mn_7C_3 reacts with excess MnO to form liquid manganese metal.

SAF for ferromanganese production

The MC- and LC-FeMn are basically produced by three methods:

Decarburization of HC-FeMn

The carbon is removed by oxygen lancing over liquid HC-FeMn in a converter.

Aluminothermic method

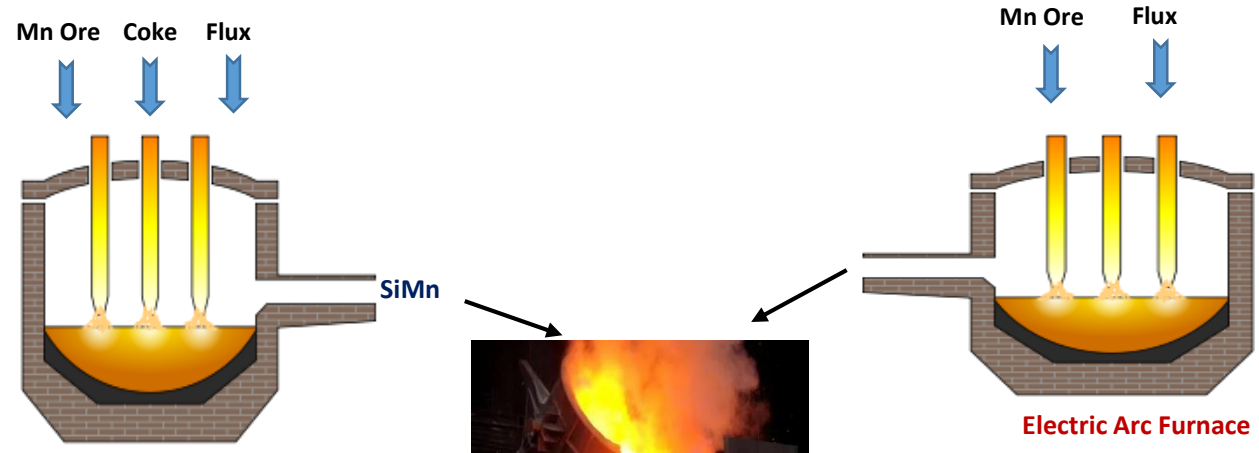
The pulverized manganese ore is reduced by aluminum in presence of flux.

Silicothermic method

The molten manganese ore-flux is mixed with liquid silicomanganese in a special ladle.

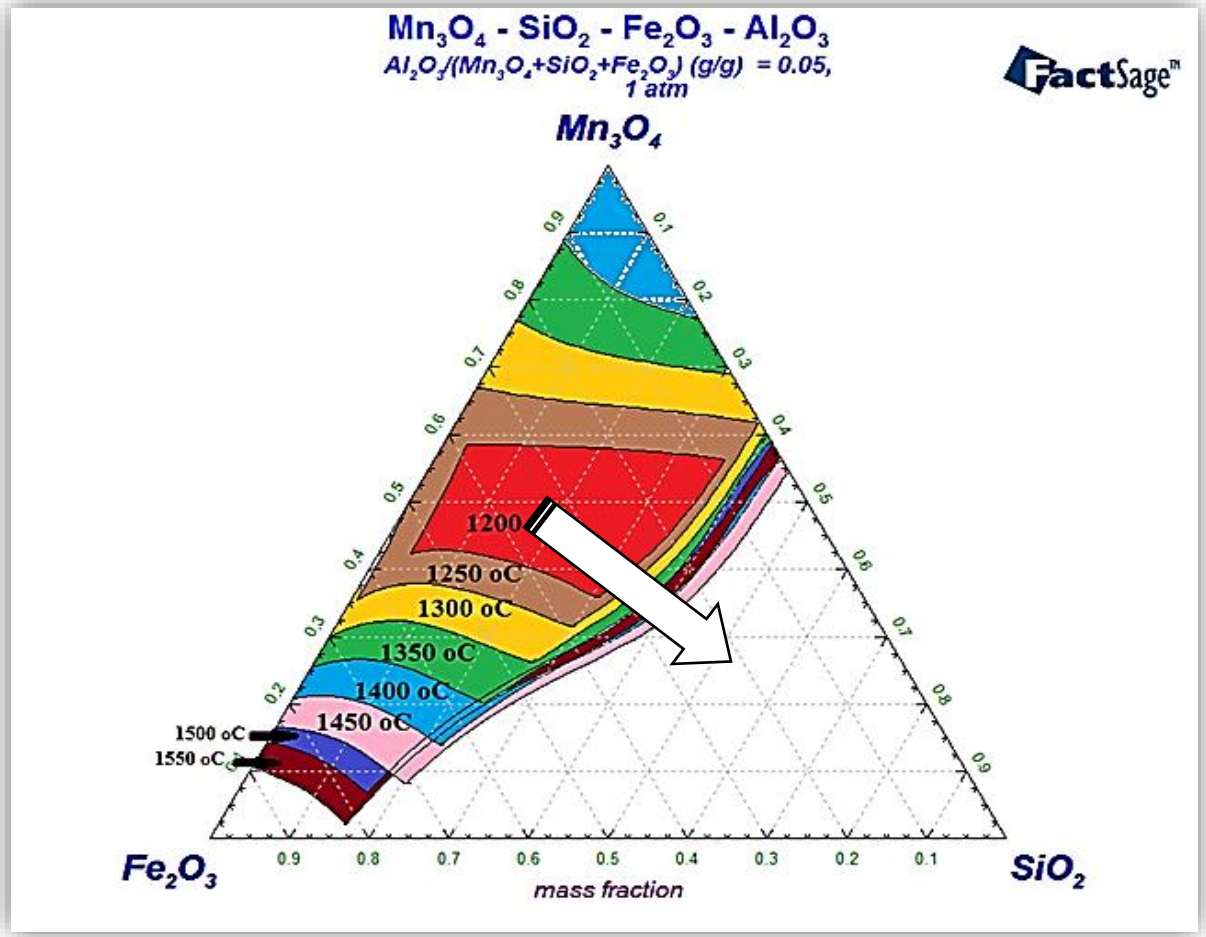
Silicothermic method

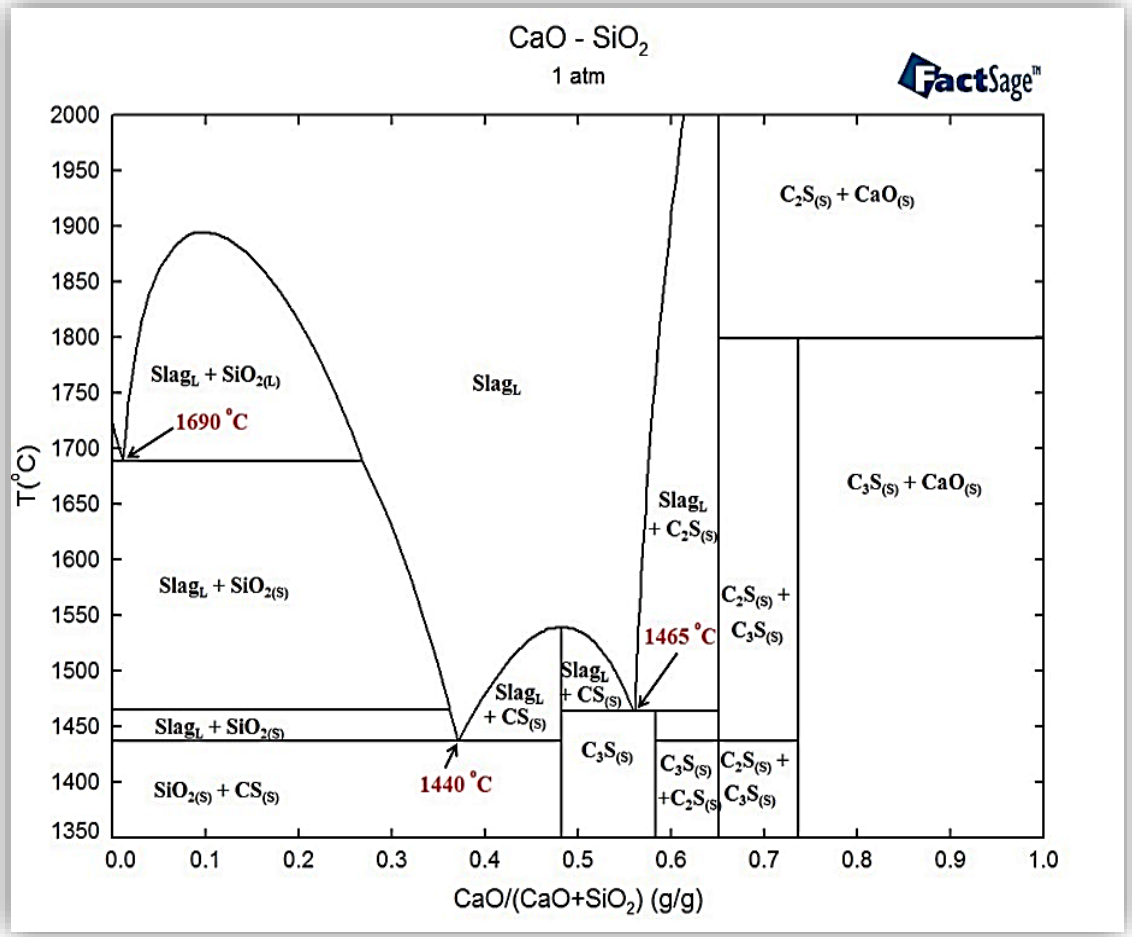
SiMn + Mn ore + Lime → **LC/MC Ferromanganese**



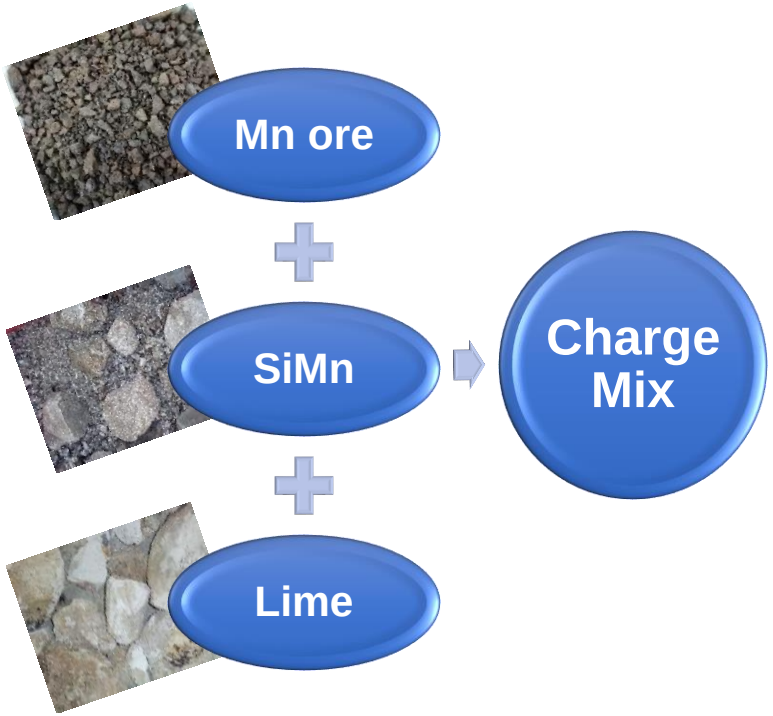
LC Ferromanganese

Liquid Phase boundaries and phase relations in Mn_3O_4-Fe_2O_3-SiO_2 system





Smelting tests

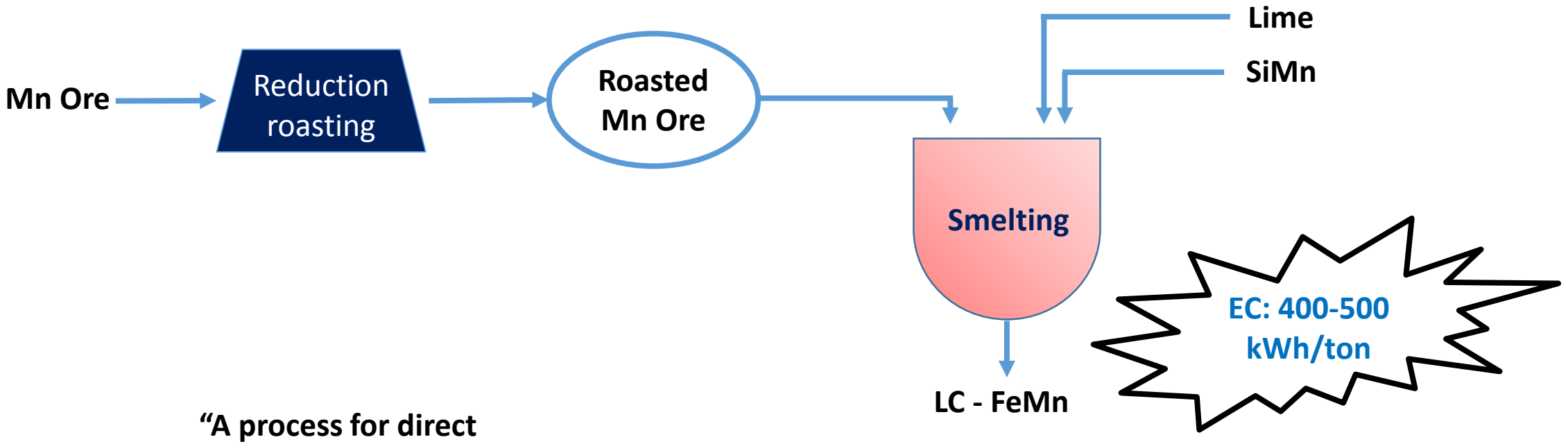


Raw material

Silicothermic reduction in 50 kVA EAF

Products

Process flow-sheet



"A process for direct production of low and medium carbon ferromanganese in electric arc furnace" Application no. 201811046956

READY FOR DEMONSTRATION AND VALIDATION ON INDUSTRIAL SCALE

Innovation/Advantages

- One step smelting process.
- Low power consumption
- High throughput per unit volume of reactor per unit time
- Silicomanganese alloy already available in market
- Existing EAF sufficient
- Utilizes established protocol of EAF
- Possible customization to continuous mode

Silicomanganese production using MANGANESE NODULE RESIDUE

Alternative resource of strategic metals

Chemical Composition of Sea Nodule

Component	% (w/w)
Cu	0.86
Ni	0.94
Co	0.08
Mn	25.0
Fe	7.32
SiO_2	17.06
Al_2O_3	3.84

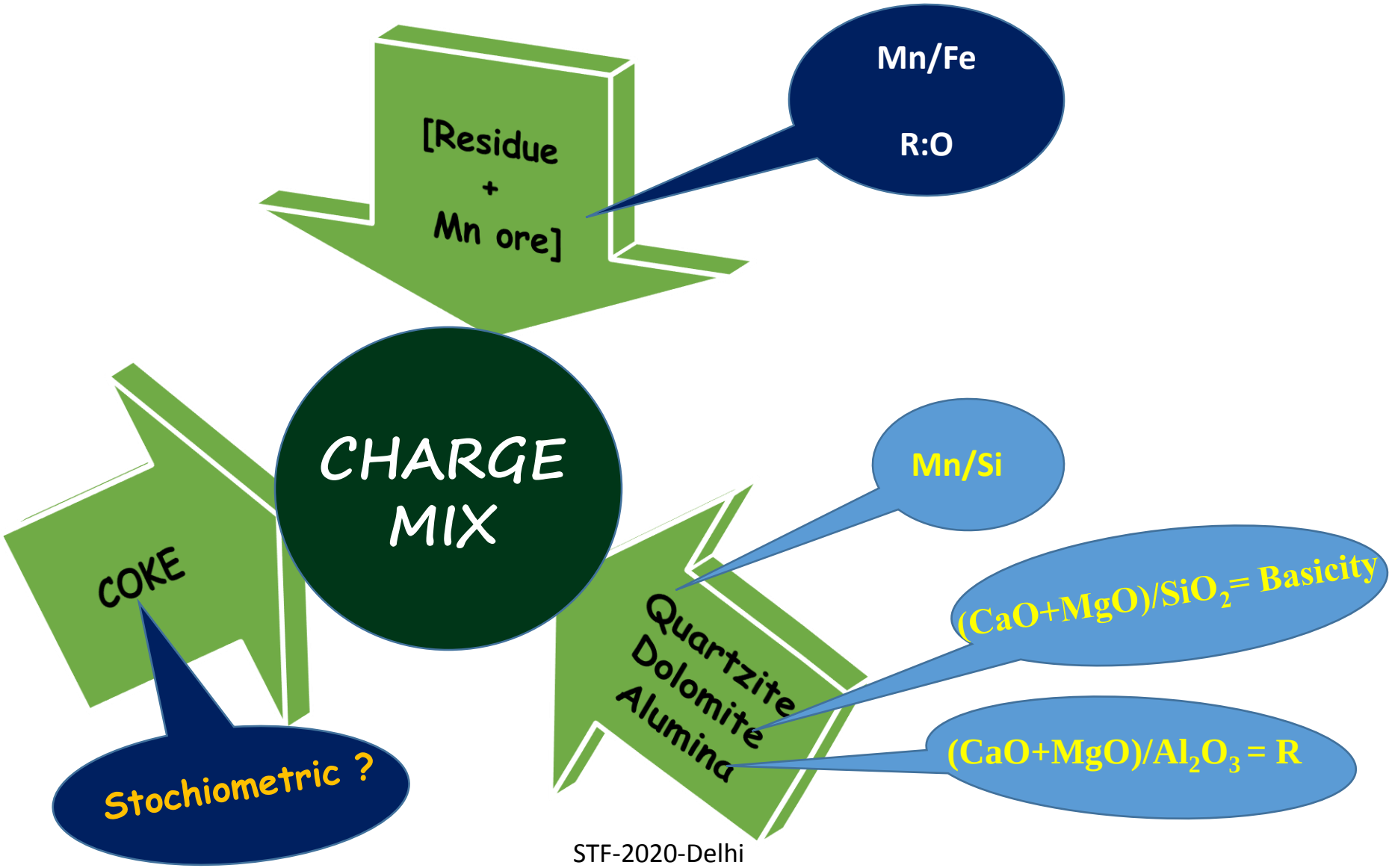
CSIR-NML's Process

Reduction roasting – Ammonia leaching – Solvent extraction – Electrowining route

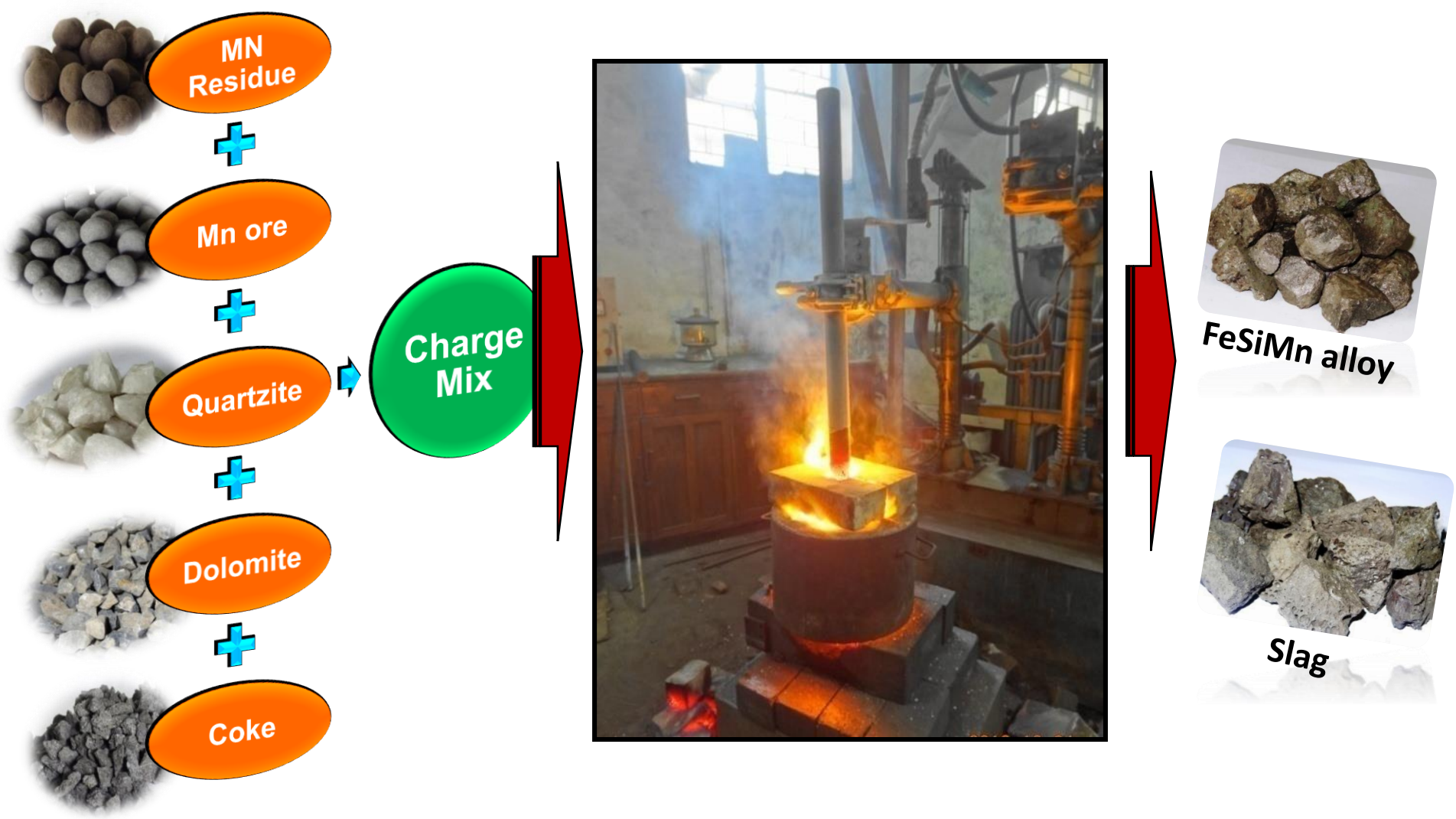
Mn/Fe = 2.5

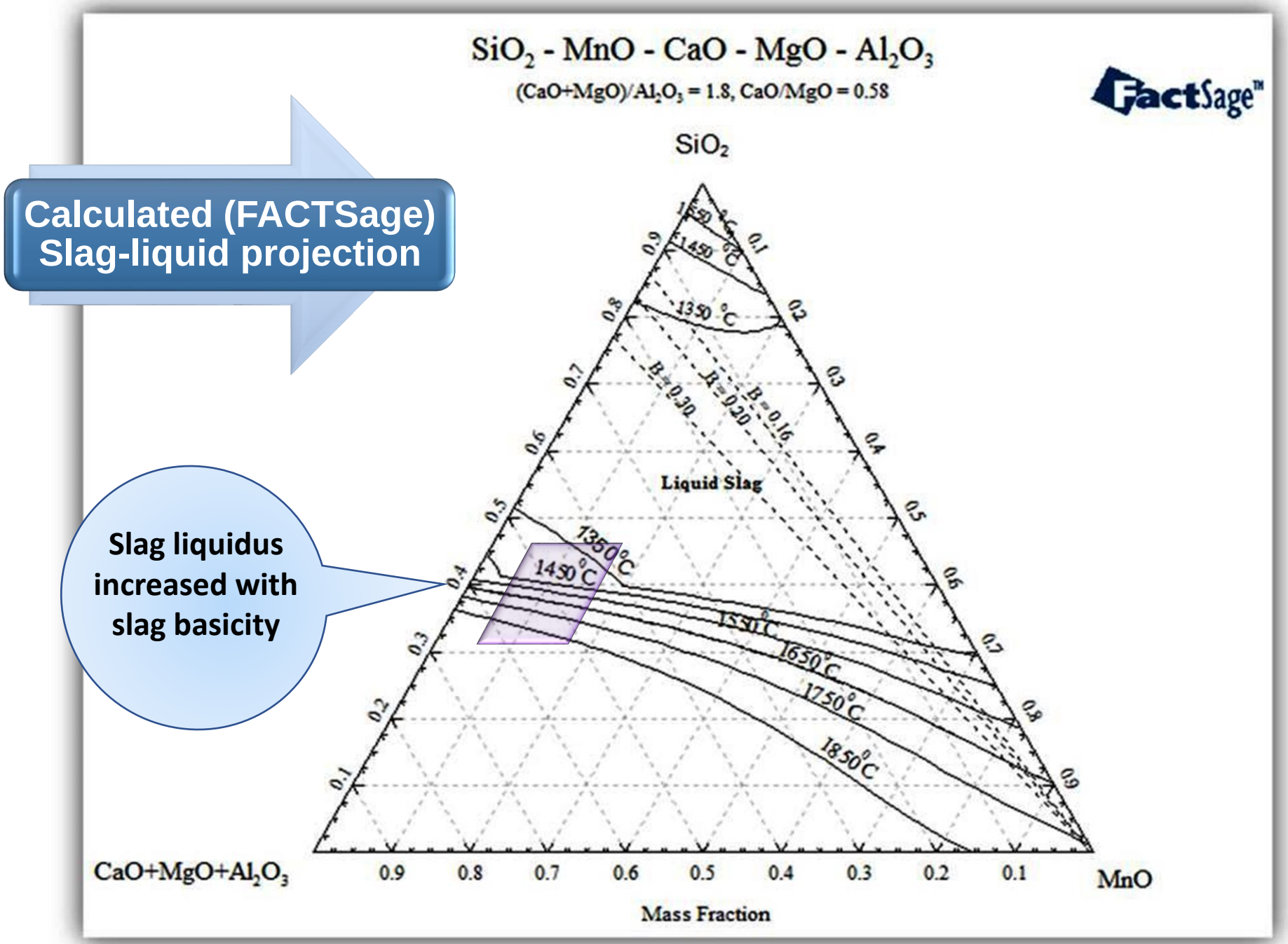
Powdery residue contains MnO_2, Fe_2O_3, SiO_2, Al_2O_3 etc.

Charge Mix Preparation



Smelting tests




Calculated (FACTSage)
Slag-liquid projection
Slag liquidus increased with slag basicity
SiO2 - MnO - CaO - MgO - Al2O3
(CaO+MgO)/Al2O3 = 1.8, CaO/MgO = 0.58
FactSage
SiO2
Liquid Slag
B=0.30
B=0.20
B=0.16
1350 °C
1450 °C
1550 °C
1650 °C
1750 °C
1850 °C
CaO+MgO+Al2O3
MnO
Mass Fraction

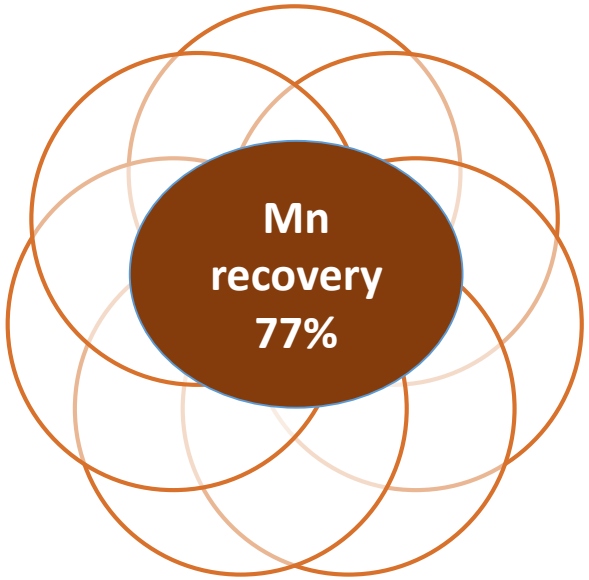
Optimum smelting conditions

for producing standard grade silicomanganese alloy

***w*MNR:Mn Ore = 1:0.6**

15 min holding time

Mn/Fe = ≥3.5



Coke = 110% of stoichiometry

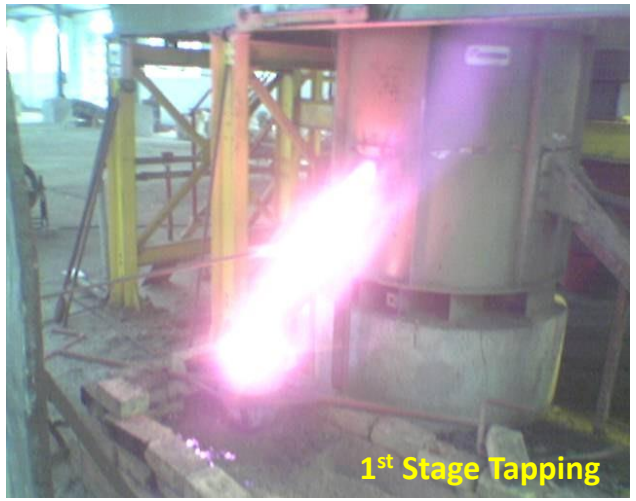
Mn/Si = ≤2.5

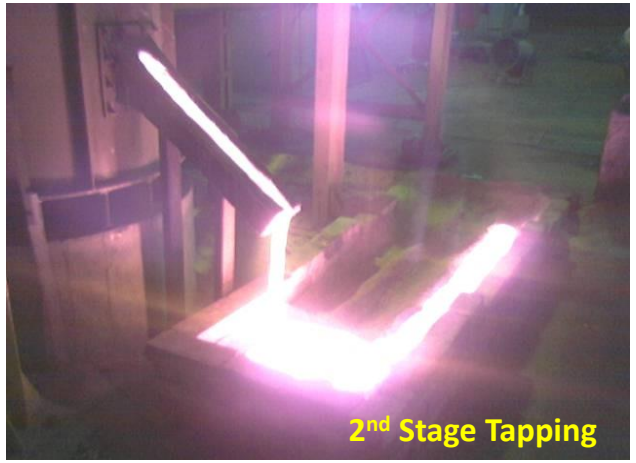
R($CaO+MgO/Al_2O_3$) = 1.8

B ($CaO+MgO/SiO_2$) = 0.2

Randhawa et al. (2012) Min. Proc. Extr. Metal.

Work at Sea Nodule Residue Treatment Pilot Plant for Silicomanganese Production



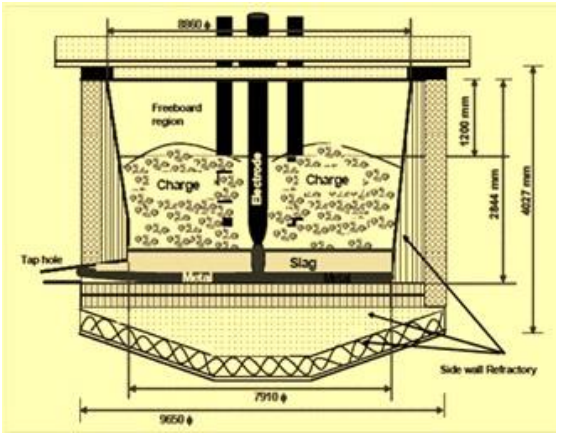


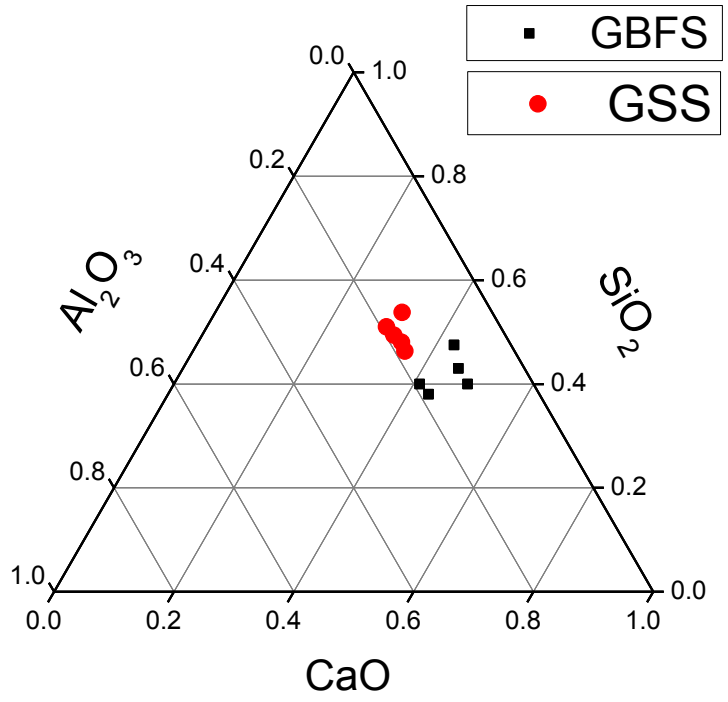
SiMn slag

By-product of SiMn production in submerged arc furnace

Worldwide annual generation is 14.8 million metric ton

Chemical composition similar to GBFS, except high MnO





Waste to Resource

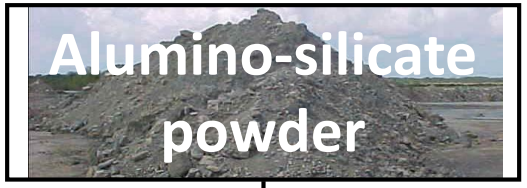
With geopolymerization
convert into a useful product

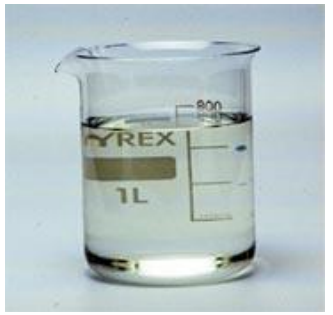
The Changing Mindset

Geopolymers

- Geopolymers are a class of inorganic (alumino-silicate) binders
- Formed by interaction between highly alkaline solution (activator) with reactive alumino-silicate powder (e.g. fly ash, metakaolin) materials
- Known by other term as inorganic polymers, geocements, hydroceramics, low temp. glass etc.
- Various industrial waste and by-products (fly ash, slags, mine tailing, volcanic ash) can be used as feed material

Process flow chart





Alkali Solution

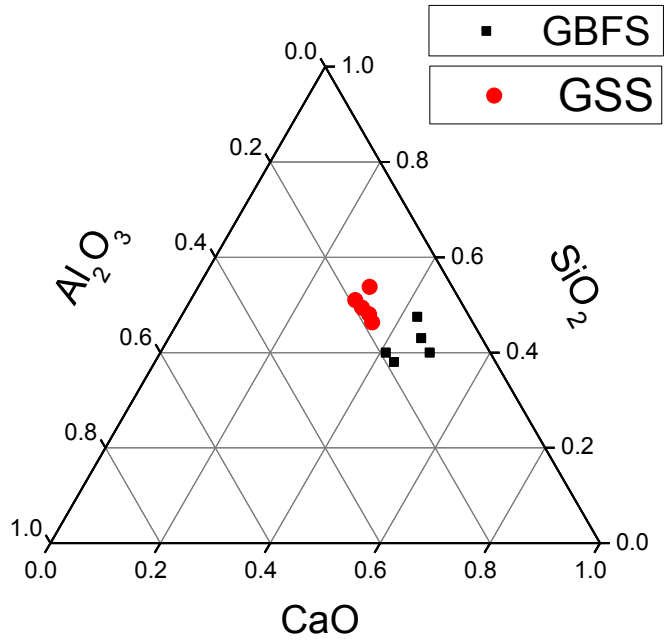
Mixing

Vibro-casting

Geopolymer

Geopolymerization of silico-manganese slag

- Resembles with GBFS
- Normal industrial practice is air cooling
- During alkali activation produces hydrogen bubbles due to presence of residual Si metal
- Structure becomes spongy like with non uniform porosity distribution
- With addition of fly ash rate of reaction is controlled and gases are escaped from body
- Inert fly ash particles positioned in pores and dense, uniform structure developed
- **40 MPa CS is achieved with 20 wt% fly ash and 80 wt% slag**



Application of SiMn slag in cement

Ordinary Portland Cement (OPC)

Made by mixing $CaCO_3$ containing substances with SiO_2, Al_2O_3 and Fe_2O_3 containing substances and heating them to form clinker which subsequently ground to powder and mix with 2-6 % gypsum.

Portland slag cement (PSC)

Made by blending Portland cement clinker with granulated blast furnace slag (*25-70% of the mass of the mixture*)

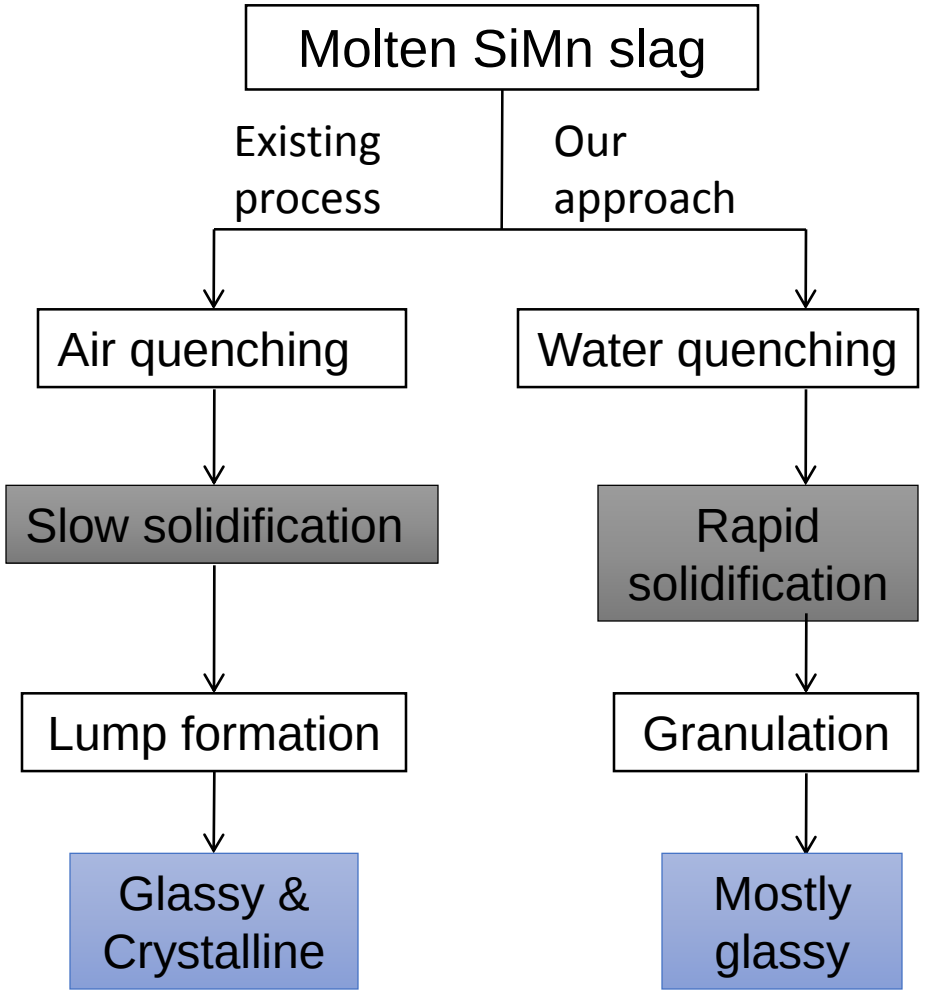
Modification of SiMn slag

Slag reactivity depends on its chemical constituents, mineralogy and glass content

Normal industrial practice is air quenching of the molten slag, available in lumps with partly glassy and partly crystalline

Only the glassy part takes part in active reaction and crystalline part remains un-reactive

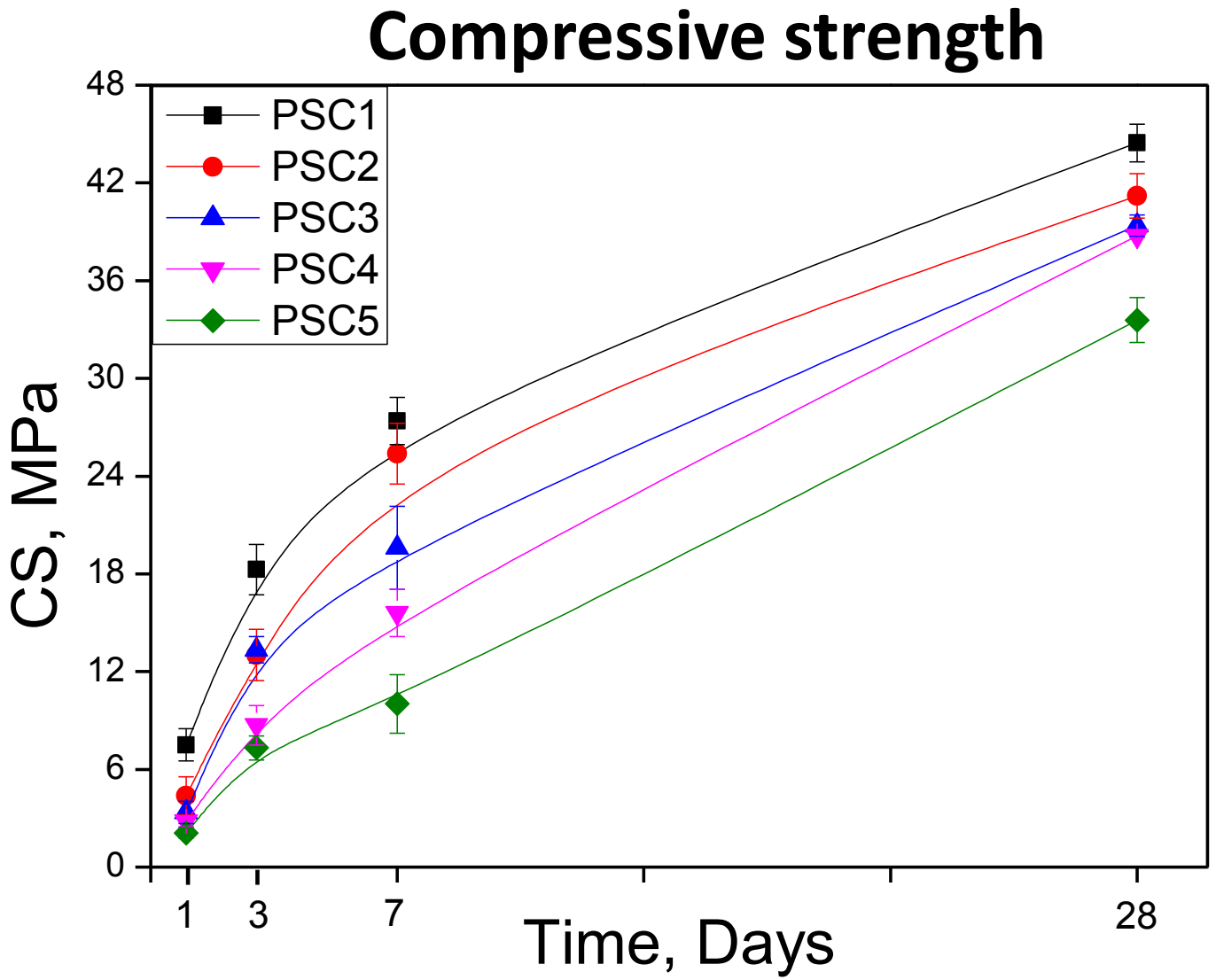
The reactivity of slag improves by water quenching method



Tests for cement application

Batch formulation

Batch ID	Comp. strength			
	Sand (wt.%)	Clinker (wt.%)	GBFS (wt.%)	GSS (wt.%)
PSC1	75	15	10	00
PSC2	75	15	7.5	2.5
PSC3	75	15	05	05
PSC4	75	15	2.5	7.5
PSC5	75	15	00	10



(Nath & Kumar, 2016, Cons. Build. Mater)

Summary

- We developed **AN IMPROVED PROCESS** for production of LC-FeMn in electric arc furnace by silicothermic reduction of manganese ore. Under optimum conditions the **ENERGY CONSUMPTION IN EAF SMELTING IS ABOUT 400-500 kWh/ton ALLOY.** The process is **READY FOR DEMONSTRATION AND VALIDATION** on Industrial scale.

- **The Manganese nodule residue used with or without blending of manganese ore to produce standard grade of silicomanganese.**

- **SiMn slag, a by-product of silico-manganese alloy production** and major oxide constituents are SiO_2, CaO, Al_2O_3 and MnO, could be successfully used in the production of **Geopolymers** with reasonable strength.

- **Granulated SiMn can be used as a component of slag cement.**

- The energy efficient and environmental-friendly process and effective usage of by-products for value addition are essential for sustainability of manganese ferroalloy Industry.

Acknowledgement

The Ministry of Steel

The Ministry of Earth Sciences

The Director, CSIR-National Metallurgical Laboratory

The organizing committee, STF-2020

Thank you!

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