National Seminar on "Desulphurisation of Hot Metal & Utilisation of Torpedo", Bokaro Steel City November 18-19, 2011

1. De-Sulphurisation : Principles & Practices – Key Note Lecture (Dr Deepak Majumder)
2. Comparison of Mg Based Desulphurization Techniques And Role of Automation Systems
3. Introduction of Hotmetal Desulphurisation At Bokaro Steel Plant
4. Introduction of CaC2 & Magnesium Based Co-Injection Type De-Sulphurisation Unit In SMS-II of RSP
5. Hot Metal Desulphurization Benefits of Magnesium Lime Co-Injection
6. Technological Development of External Hot Metal Desulphurization In India
7. Total DS Management - An Innovative Model For External Desulphurisation of Hot Metal
8. Thermodynamic And Kinetic Aspects of Desulphurisation In Hot Metal
9. Improvement In Slag Skimming Efficiency For CaC2 – Mg Based Hot Metal De-Sulphurisation
10. Improvements In Process Technology For External Hot Metal Desulphurisation At RSP

De-sulphurisation : Principles & Practices

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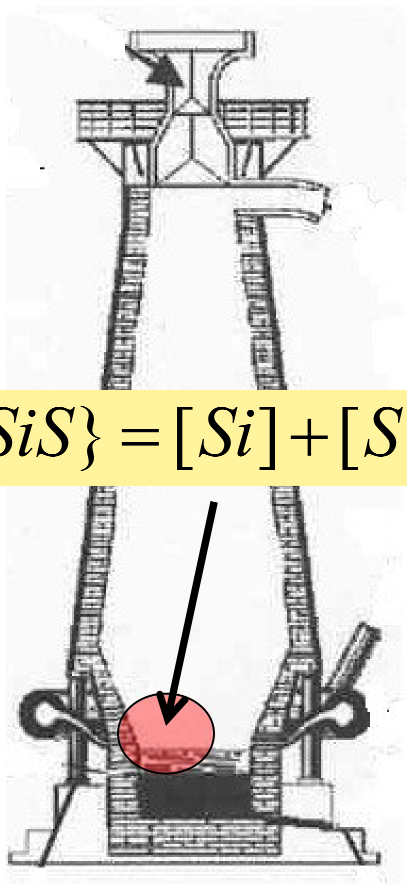
• 25 years in teaching & research • 3 Text books • 120 Publications • 13 National and International awards/ honors • Consultant for 8 Indian steel plants

Introduction: sources & reason for high sulphur content of Indian pig iron



$$\{SiS\} = [Si] + [S]$$

Hot metal temp range: 1280-1350 °C; Hot metal sulphur range=0.055 to 0.08 %

- Primary source of Sulphur in hotmetal is coke (~90%)
- Higher coke rate is one of the many factors leading to high sulphur hot metal
- Indian coking coal has one of the lowest Sulphur content (~0.6%), yet, in general, the sulphur content of hotmetal in India is high (0.045 to 0.080%)
- One of the reasons for high sulphur is due to low tap slag basicity
- Hot metal temperature in India is generally low and

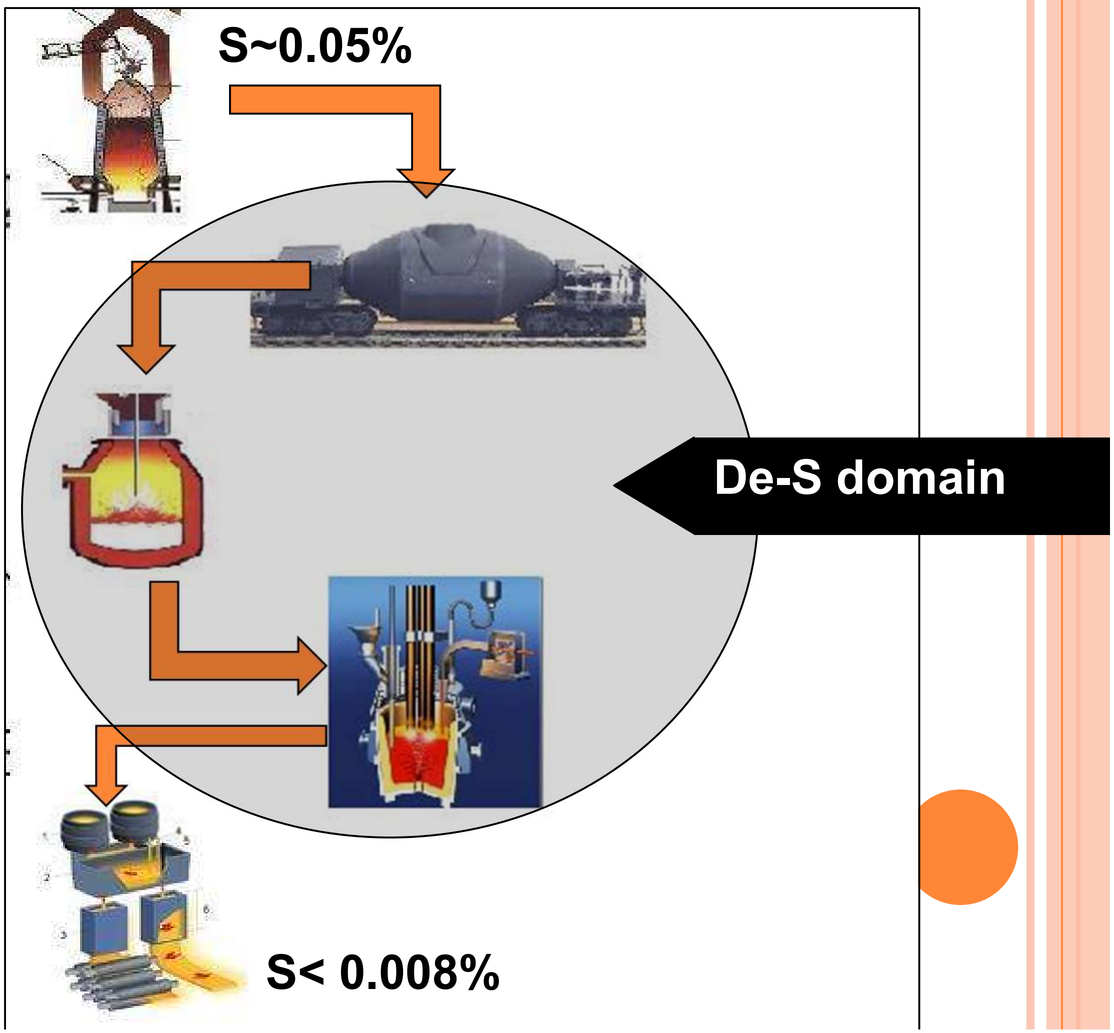
Detrimental roles of sulphur

Sulphur exists in both dissolved and combined state in finished steel. Castability is greatly influenced by sulphur content of molten steel. Sulphides are known to initiate cracking. Cracks in continuous cast slabs have been directly correlated with sulphide inclusion content. For high load application as well unfriendly environment, even very small sulphur content can be potentially dangerous and lead to structural failure. Toughness is greatly impaired due to the presence of sulphur.

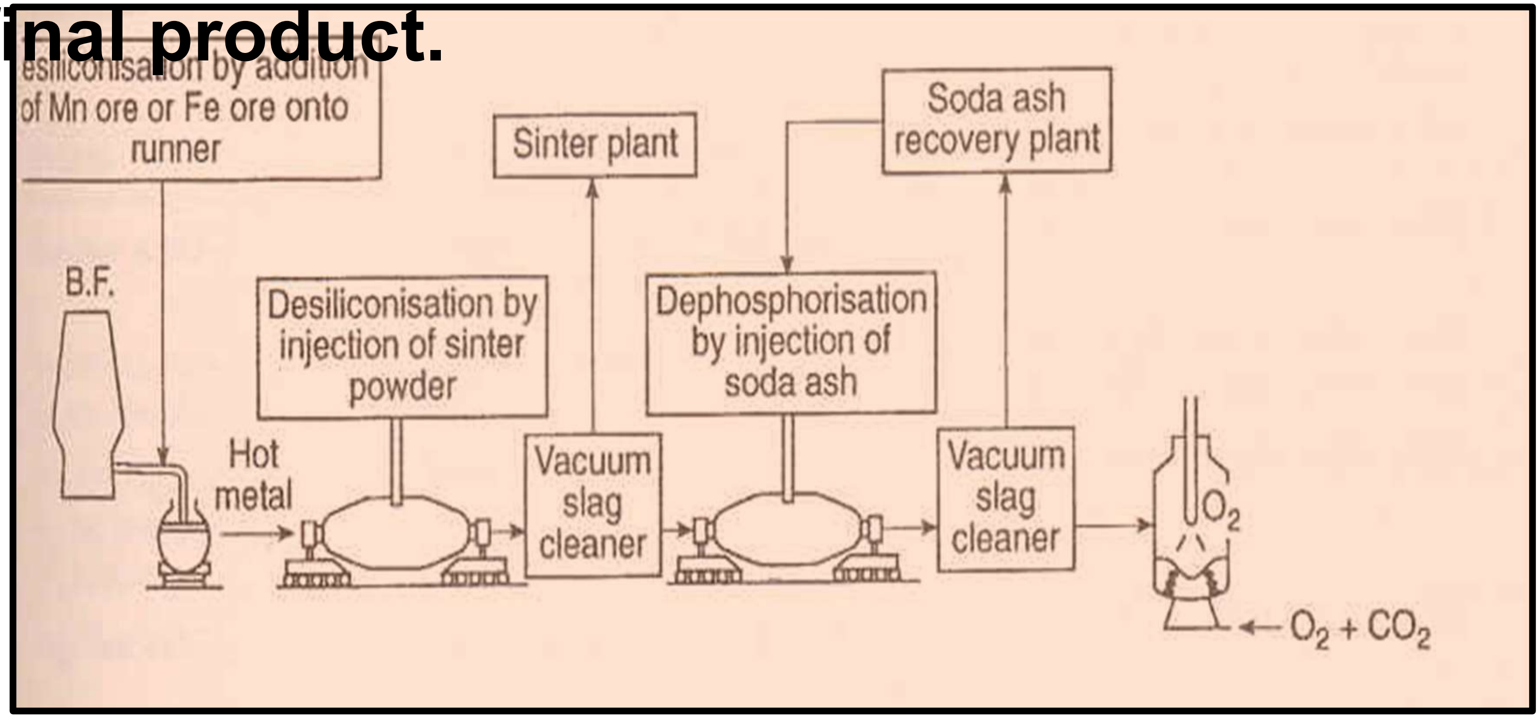
Allowable sulphur content in steel depends on application area. In general, sulphur in finished product is aimed at ~0.008 to 0.005 wt%. In stringent applications, (viz., armor plate, line pipe steel with resistance to hydrogen induced cracking) one is required to bring this down to <0.001%

There is an imperative need to control sulphur contamination of steel beyond blast furnace

Sulphur control strategy: Possibilities



Hot metal pre treatment and ladle metallurgy steelmaking are viable options to contain sulphur in the final product.



For superior process economics and more stringent requirements on the composition of steel , globally there is an increasing tendency to utilize primary steelmaking vessels (BOF and EAF) solely for melting and de-carburisation . This has lead to enormous growth in hot metal pre-treatment as well as ladle metallurgy

(A) DESULPHURISATION THERMODYNAMICS

SULPHUR REDISTRIBUTION BETWEEN SLAG AND METAL PHASES AND THE CORRESPONDING EQUILIBRIUM IS REPRESENTED VIA:

$$[S] + (O^{2-}) = (S^{2-}) + [O]$$

$\Delta H = +ve; \textit{weakly endothermic}$

IN STUDYING SLAG –METAL REACTION WITH RESPECT TO DE-SULPHURISATION, THE SULPHIDE CAPACITY, C_S ,FOR A LIQUID SLAG IS AN IMPORTANT PARAMETER AND DEFINED AS:

$$C_s = \frac{K_1 (a_{O^{2-}})}{(f_{s^{2-}})} = (\%S)_{slag} \left(\frac{p_{O_2}}{p_{S_2}} \right)^{1/2}$$

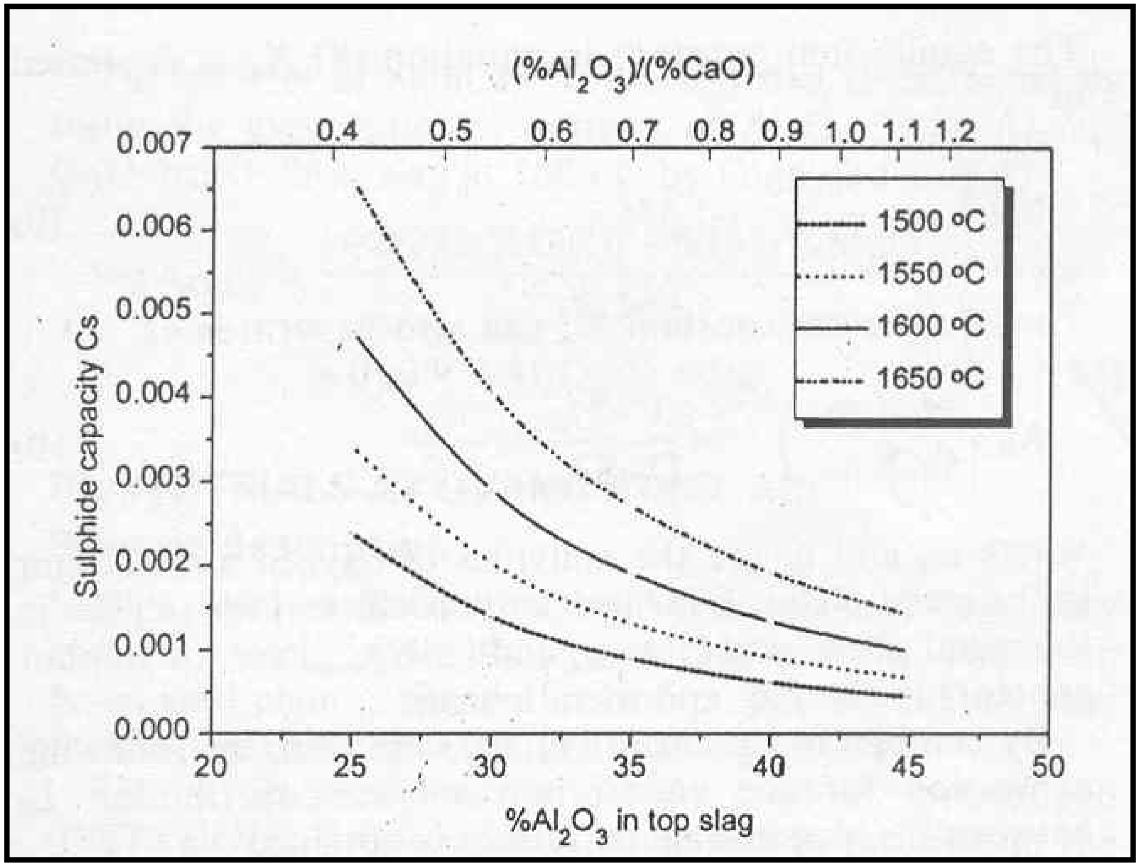
K_1 IS THE EQUILIBRIUM CONSTANT FOR THE REACTION:

$$\{0.5S_2\} + (O^{2-}) = \{0.5O_2\} + (S^{2-})$$

SULPHIDE CAPACITY AS DEFINED BY :

$$C_s = \frac{K_1\left(a_{O^{2-}}\right)}{\left(f_{s^{2-}}\right)} = \left(\%S\right)_{slag}\left(\frac{p_{O_2}}{p_{S_2}}\right)^{1/2}$$

DEPENDS ONLY ON THE COMPOSITION OF THE SLAG AND TEMPERATURE OF THE SYSTEM



DESULPHURISATION THERMODYNAMICS CONTD.

To relate sulphide capacity to the equilibrium sulphur distribution between slag and metal phases, we consider the simultaneous equilibrium of the following reaction as well

$$[S] + \{0.5O_2\} = \{0.5S_2\} + [O]$$

$$\log K_2 = -\frac{935}{T} + 1.375$$

By definition

$$K_2 = \frac{[h_O]}{[h_S]}\left(\frac{p_{S_2}}{p_{O_2}}\right)^{1/2} = \frac{(\%S)}{[\%S]}\frac{[h_O]}{[f_S]C_S}$$

since

$$C_s = (\%S)_{slag}\left(\frac{p_{O_2}}{p_{S_2}}\right)^{1/2}$$

Defining the equilibrium partition coefficient, L_S ,= (%S)/[%S],

Desulphurisation thermodynamics contd.

$$\log L_s = \log \frac{(\%S)}{[\%S]} = -\frac{935}{T} + 1.35 + \log C_S + \log[f_s] - \log[h_o]$$

Therefore necessary thermodynamic conditions for low sulphur steel are:

High sulphide capacity of slag (i.e., higher basicity of slag and lower activity coefficient of sulphur in slag

Higher activity coefficient of sulphur in the metal phase and

Low oxygen potential (implying a reducing environment)

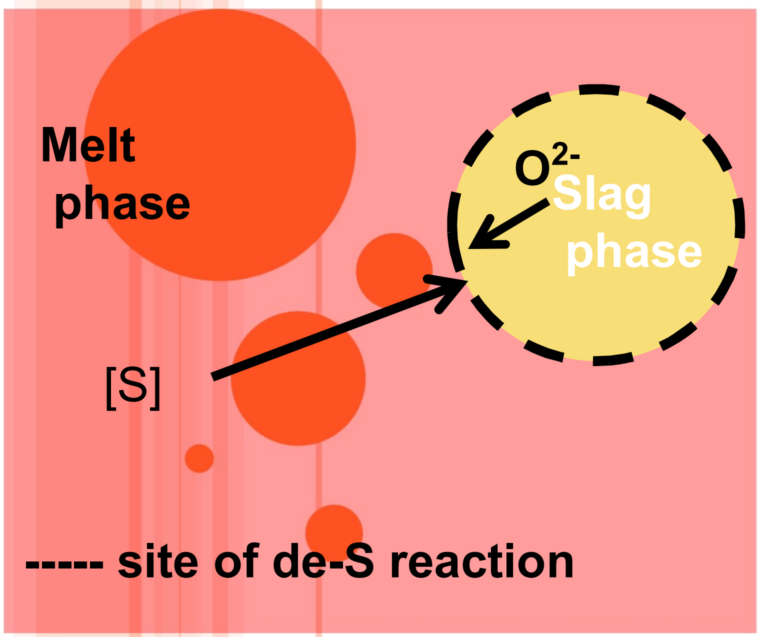
The influence of temperature on L is not obvious

Desulphurisation kinetics

The de-sulphurization reaction i.e.,

$$[S]+(O^{2-})=(S^{2-})+[O]$$

is a heterogeneous chemical reaction and therefore takes place at the slag –metal interface.



The rate of heterogeneous reaction is greatly influenced by (i) surface area and (ii) mass transport rates. Temperature has indirect influence since viscosity which depends strongly on temperature, affects mass transfer rate

Desulphurisation kinetics

Desuphurisation is a mass transfer controlled process (melt phase transport is often the rate limiting kinetic step). Mass transfer is a first order process i.e.,

$$N_S = kA\left(C^{eq.} - C_b(t)\right)$$

The following rate equation applies

$$\ln\frac{[\%S]-[\%S]^{eq.}}{[\%S]_{in}-[\%S]^{eq.}} = -kt$$

As *k* assumes a large value, exp(-kt)→0 and hence [%S]→%S$^{eq.}$, maximizing desulphurization in the system.

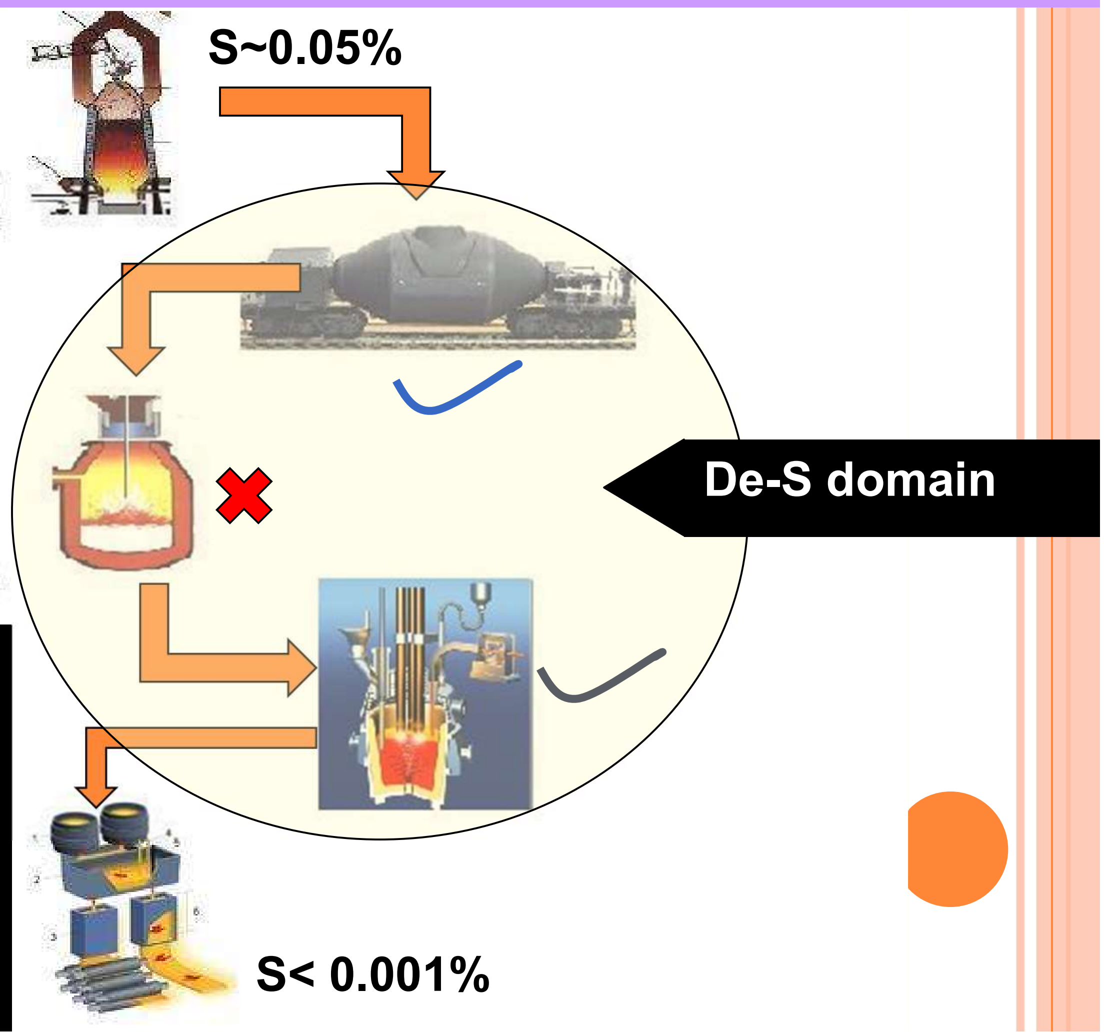
k in the above is the mass transport coefficient and is influenced profoundly by

From thermodynamic view points, torpedoes/transfer ladles as well as LF appear attractive for de-S, since $[h_o]$ is significant in BOF

$$\log L_s = \log\frac{(\%S)}{[\%S]} = -\frac{935}{T} + 1.35 + \log C_S + \log[f_s] - \log[h_o]$$

Due to the presence of carbon, relatively high L_S (wrt LF) is possible in torpedoes (since $[f_S]$ increases with $[C]$ content

Pre treatment ensures less S load in BOF & enables one to move towards slag-less refining leading to better process control & economics



De-sulphurisation statistics: pre treatment vs.

Parameter	Pre treatment	Steelmaking	LF
Oxygen potential	Low	High	Low
Activity coefficient	High (4-6)	Low (~1)	Low (~1)
Temp. °C	1300-1500	>1600	1550-1600
Cost of de-S	Low	high	moderate
Efficiency	High	Low	reasonable

External de-S offers many advantages (higher BF productivity, smoother and improved BOF operation). For large scale sulphur control (<0.01%) it is widely practiced. For ultra low sulphur steel (~10 to 20ppm) a final & further de-S is advocated in LF

Desulphurisation in torpedoes and ladles: Pretreatment of hot metal

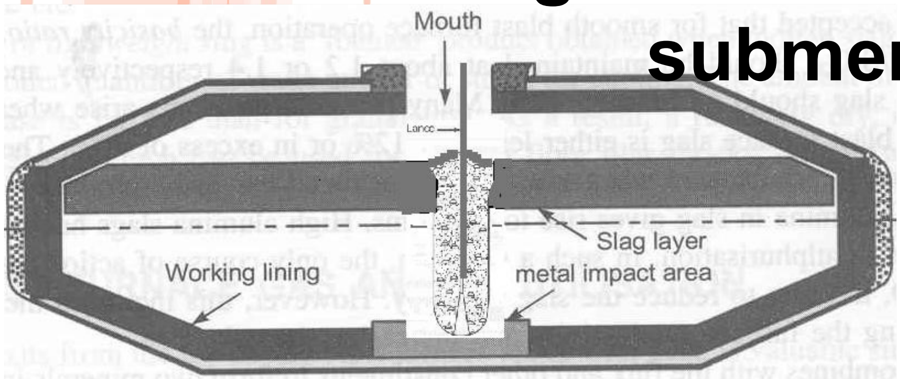
In the entire iron and steelmaking circuitry, De-S can be most effectively and economically carried out immediately following iron making, in transfer vessels such as a torpedo car or a ladle. From a thermodynamic stand point, favorable conditions (high sulphide capacity slag, lower oxygen potential etc.) can be easily ensured in a torpedo / ladle

However whether desirable degree of De-S is achieved at the end of torpedo/ladle treatment depends on how effectively different kinetic parameters were maneuvered during the process.

Desulphurization in torpedoes and ladles

contd………

De-S in transfer ladles/torpedoes involve injection of powder materials such as lime + spar, lime plus magnesium, calcium carbide plus magnesium or calcium carbide plus limestone etc. Desulphurizing agents are injected via a carrier gas such as Nitrogen through a submerged lance.



$Mg(g)+[S]\rightarrow MgS(s)$

$CaC_2 \rightarrow Ca(g)+2[C]$

$Ca(g)+[S]\rightarrow CaS(s)$

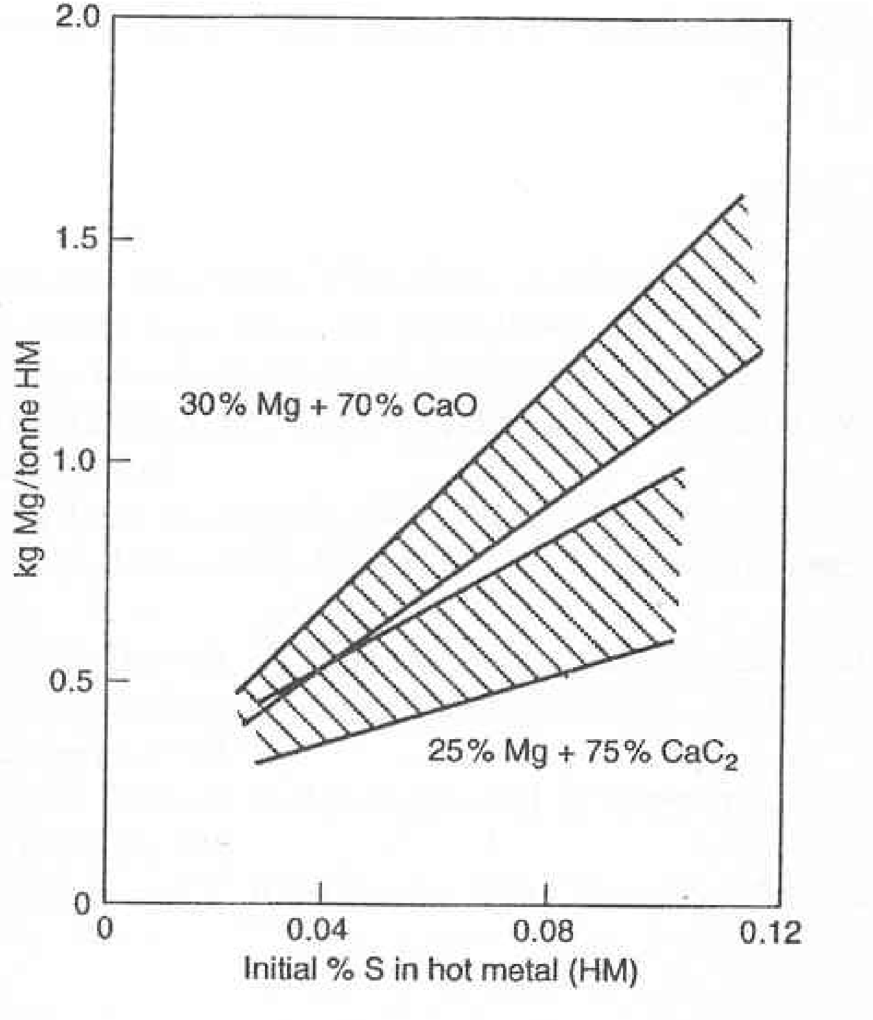
$MgS(s)+(CaO)\rightarrow (MgO)+(CaS)$

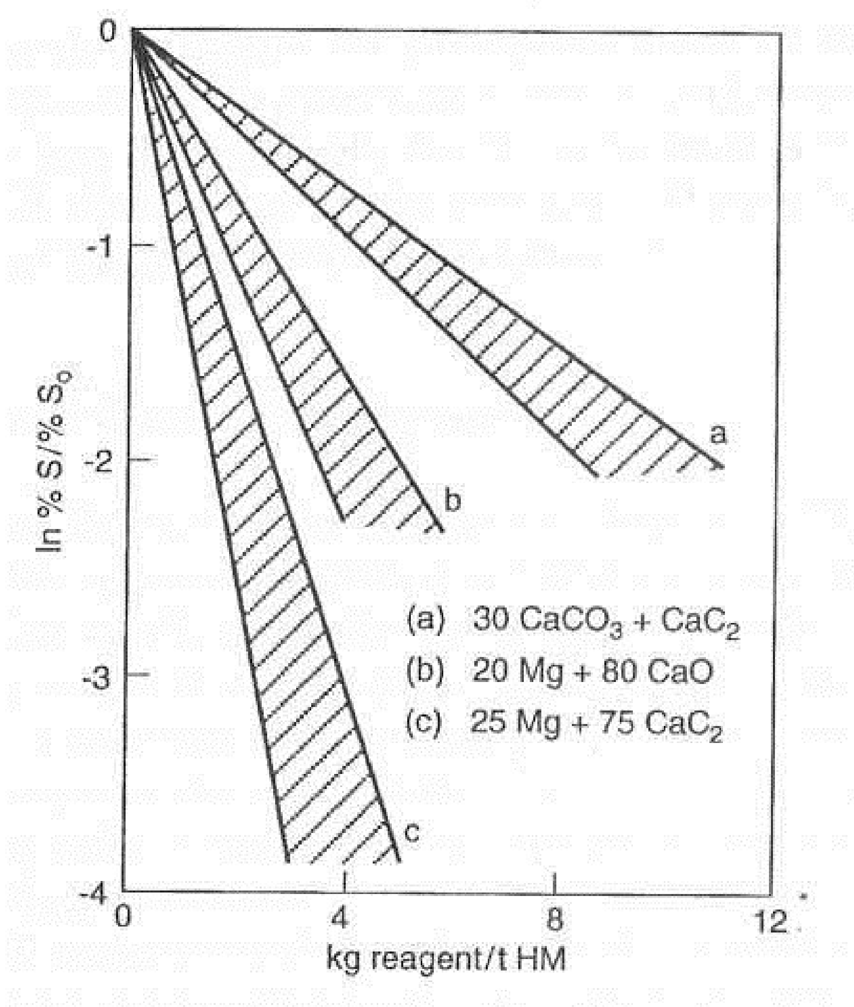
Most de-s is done by Mg (g). It is reported that a final sulphur level in the range of 20 to 60 ppm during the process is possible.

Desulphurization in torpedoes and ladles

contd…………

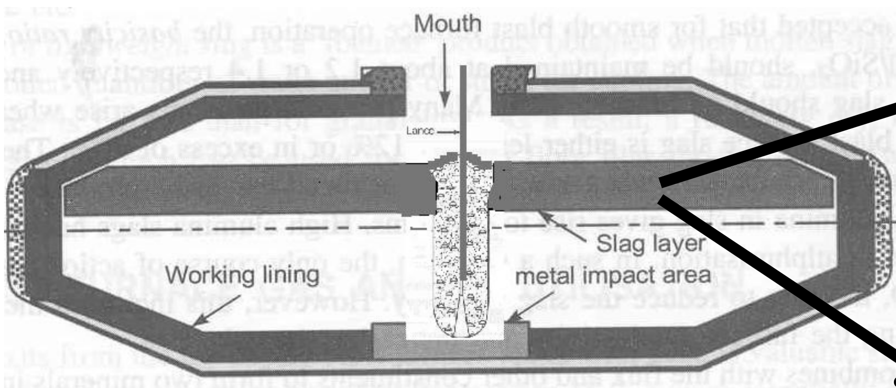
Reagents type, loading and magnesium content all exert profound effect on the final e





Desulphurisation in torpedoes and ladles

contd…..



Slag before de-S: BF slag, spalling from runner; worn out lining material and oxidation

Post de-S slag :It is a mixture of the above plus high melting point oxides such as,

Viscosity and melting temperature of slag produced during de-S continuously increase posing problem for efficient de-S. Also for low final sulphur, a low operating temperature is desirable which makes it difficult to keep the slag molten. This calls for slag conditioning

Desulphurization in torpedoes and ladles

contd……….

Temperature drop: The reaction Mg(g)+[S]→MgS(s) is exothermic and by and large compensates for the heat demand of external de-S (heating of gas + powder solids etc.). Heat loss in torpedoes are of the order of 0.25 to 0.3 °C / min as opposed to 0.5 °C /min for transfer ladle.

Solubility of MgS: Solubility of MnS in steel decreases with decreasing temperature. Therefore from the view point of high sulphur partitioning, it is desirable that bath temperature is kept low. This however make it difficult to kep the slag molten.

Desulphurization in torpedoes and ladles

contd……….

Slag conditioning

1. Improve fluidity by decreasing its viscosity and melting temperature
2. Smooth and quick skimming and
3. Reduce iron los entrapped in the post de-S

Common conditioning agents

Various proportions of fluorspar, dolomitic lime, silica, alumina, cryolite, soda ash, calcium

Al_2O_3 –SiO_2 based agents use for CaO based de-S decrease slag basicity

Fluorspar based agents create environmental problems

Soda ash based agents lead to excessive alkali

Typical composition of slag conditioning agents

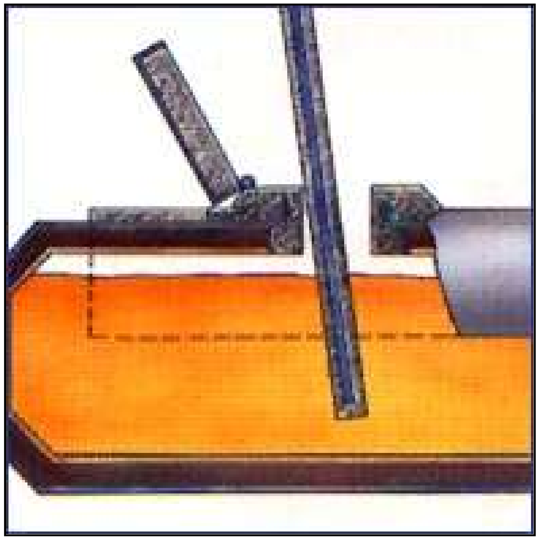
Plant	SiO_2	Al_2O_3	CaO	CaF_2	$Na_2O + K_2O$
A	50	2.5	5.7	20	21
B	50-70	20-36			10-15
C	56-70	5-19	1-12		6-11
D	36		1	32	10
E		<30		1-10	

De-S agent: 80CaO+20Mg and $80CaO+15MgO+5CaF_2$

Injection time: 4-8 minutes

De-S efficiency: 70 – 82%

Desulphurization: torpedo vs. ladle ladles

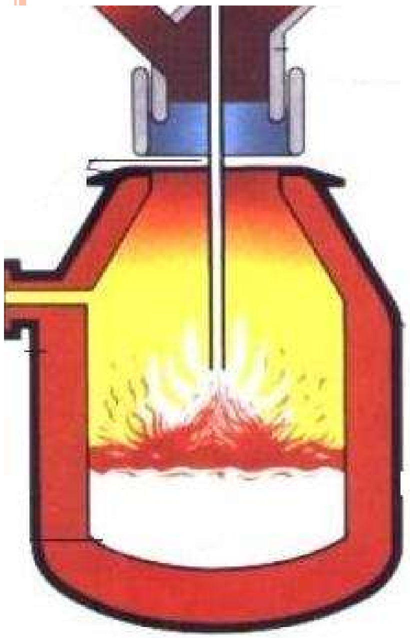


Shallow vessel; stirring is not adequate (large dead zones in melt expected), residence time of Mg bubbles small; Efficiency of Mg utilization is 60~70%. Temperature drop small.

Deep vessel; stirring is relatively intense (average speed ~0.5m/s), residence time of Mg bubbles somewhat better; Efficiency of Mg utilization is relatively high. Temperature drop

Engineering of injection system (i.e., lance design) is needed to harness the potential of torpedo de-S

Desulphurization in BOP



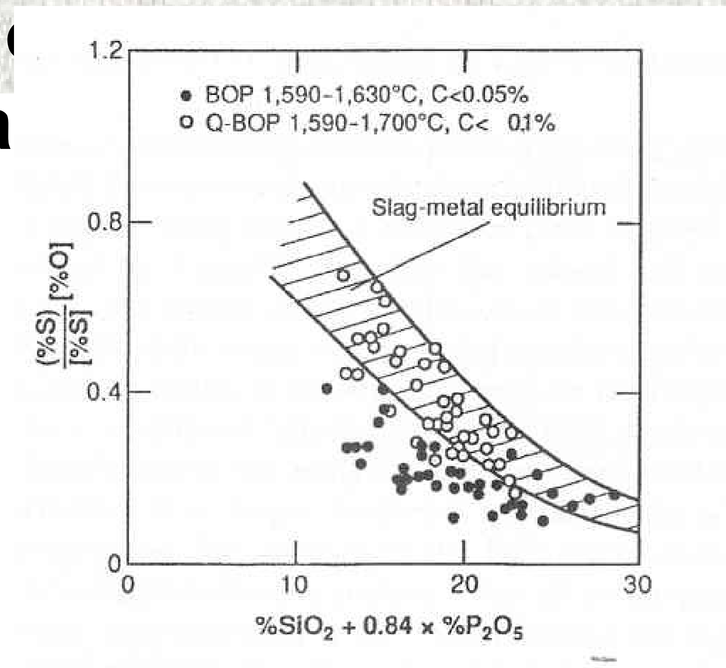
Thermodynamic conditions essential for de-S are not largely satisfied in BOP. Some de-S is achieved (largely due to high basic slag and intense slag metal mixing).

Slag metal sulphur distribution ratios at turn down are about

half of the slag meta

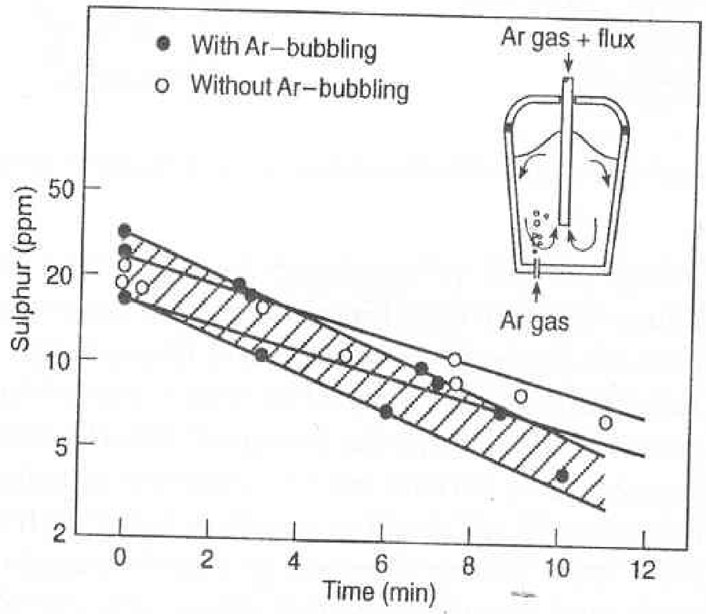
SiO_2 and P_2O_5 contents of slag has significant influence on L_S

In some cases, sulphur pickup has been reported



Desulphurisation in ladles

$80\%CaO+20CaF_2$



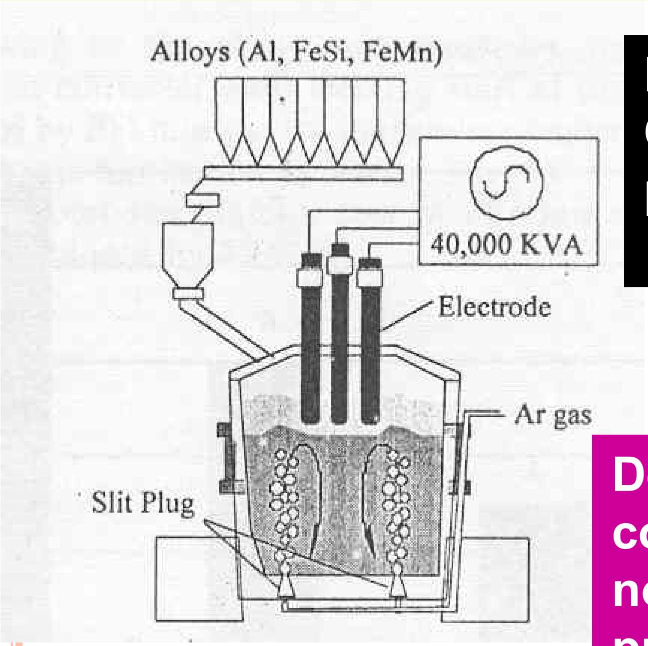
Less than 10 ppm [S] is possible only by desulphurisation of the fully killed steel in ladle. The ladle slag is generally lime saturated calcium aluminate containing less than 10% silica. Overall de-S reaction is :

$$(CaO)+[S]+\frac{2}{3}[Al]=(CaS)+\frac{1}{3}(Al_2O_3)$$

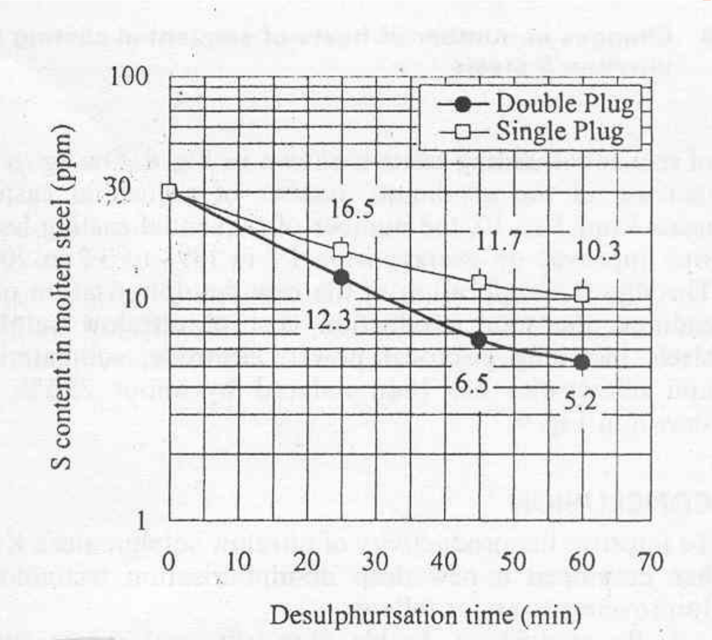
Hard argon injection in presence of lime rich aluminate slag can reduce [S] level up to about 20-30 ppm. For desulphurization level below 10 ppm, flux injection is practiced. Flow is intensified by injecting argon through a separate porous plug

Desulphurization in ladles

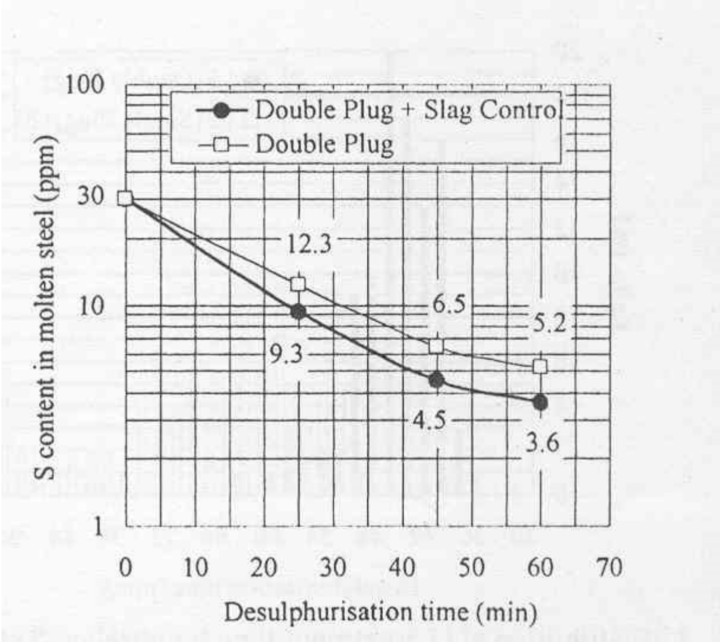
Argon flow rate plays decisive role on the sulphur content of ladle refined steel



De-S efficiency: One vs. two porous plugs



De-S efficiency: conditioned vs. normal ladle slag practice



Desulphurisation in ladles

De-S during the final stages of steelmaking is at times tricky since this has the potential to destroy steel quality through re-oxidation and nitrogen pick

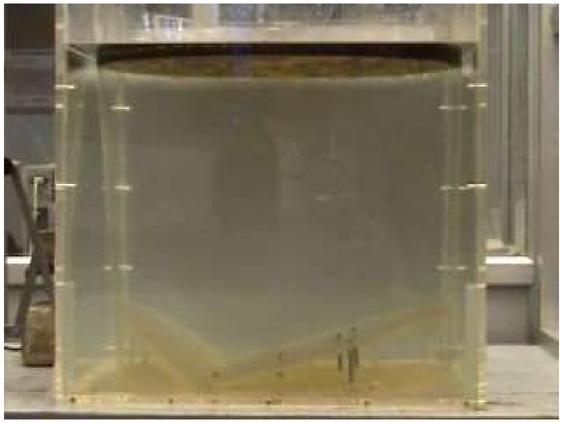
Ladle cover, reasonable free board and continuous argon flushing below the lid are mandatory

Engineering of argon flow rate for adequate slag metal mixing is important since it is not practical to use more than the desired flow rate

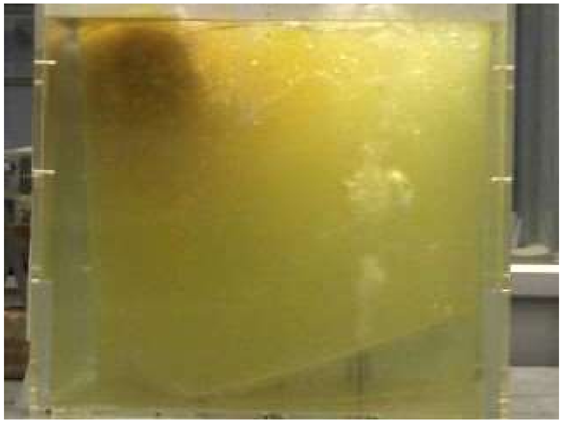
Desulphurization in ladles: our for at Ispat industries , Dolvi

Simulation of slag metal mixing through water modeling

Gas flow rate equivalent to 100 Nm^3 /hr./plug



Without stirring and 0.64R



Plug at -0.64R and 0.64R

Plug at -0.5R

Estimation of the required argon flow rate for actual industrial

$$Q_{crit} = 3.8x10^{-3} L^{1.81} \left(\frac{\sigma \Delta \rho}{\rho_{slag}^{2}} \right)^{0.35}$$

SUMMARY

1. BF in principle is capable of producing sulphur as low as 0.005%. However due to many operating reasons , the [S] content of steel is significantly high (0.04~0.08 wt%)

2. For high end application, it is therefore necessary to remove sulphur from hotmetal through subsequent treatments.

3. Pre treatment (De-S in torpedo/transfer ladle) as well as during subsequent refining in BOF and LF are viable options. Their efficiency varies

4. Thermodynamically , de-S conditions are most favorable in torpedoes followed by LF and BOP. Therefore, if kinetic factors are maneuvered well, highest L_S is likely to result during pre treatment.

5. Pre treatment offers many advantages apart from ensuring low [S]. Blast furnace performance as well as BOP performance can be significantly improved if Pre treatment of HM is practiced to

6. Mg injection along with CaO etc. provides best de-S results during pre treatment. It is possible to attain a [S] level as low as 0.005% following correct external de-S practice.

SUMMARY.....contd

7. Conditioning of slag with soda ash, fluorspar etc. are required to harness the maximum potential of external de-S.

8.Stiring of the bath is very important and from such a stand point torpedo looses out to ladles since the bath in the former is shallow.

9. Some de-S in BOP is possible despite hostile thermodynamic conditions.   A highly fluid and basic slag ensures some [S] removal. In the worst scenario, when DRI is used, [S] content

SUMMARY…..contd

10. For ultra low S steel, treatment in LF is necessary. In the presence of a highly basic slag , hard argon bubbling can produce steel having [S] as

11. For further De-S up to about 2 to 5 ppm [S], powdered lime injection in LF is necessary. Auxiliary stirring improves efficiency of powder injection.

12. Preventive measures are needed to protect steel from re-oxidation and nitrogen pick up, during de-sulphurization in LF.

Comparison of Mg based desulphurization techniques and role of automation systems

Ronanki Sriharsha
SMS-2 (Operations)
SAIL – Bokaro Steel Plant

Introduction to Mg based desulphurisation (also disadvantages of using pure Mg)

- Desulphurisation- An important aspect in today's steel making.
- Emphasis on lesser sulphur content in steel demands efficient desulphurization techniques.
- Against the conventional CaO-based desulphurisation, Mg-based desulphurisation techniques have proven to be very effective and consistent in reducing sulphur levels and very cost-effective .
- Affinity of magnesium for oxygen has resulted in development of blended reagent-based techniques.

Blended CaC_2 based Mg reagent

- CaC2 is roughly 8 times as effective as lime and Mg is around 20 times as effective as lime.
- Mg in its powder form as an industrial reagent is expensive so it is blended with CaC2
- Mg utilization efficiency= theoretical Mg consumption/actual Mg consumption.
- Use of reagent enables efficient Mg utilization, minimising input costs.
- Angle of repose ~35-40 deg, which is a function of torpedo ladle design, bulk density of powder, and reagent blend composition.

Disadvantages of Pre-blended reagents based techniques

- Dynamic adjustment of reagent injection rates not possible; affects quality, costs, in some cases both.
- Quality deterioration during storage of pre-blended materials in vessels.

CO-INJECTION BASED MG - CAC2 DESULPHURISATION

- Slightly modified from pre-blended reagents-based technique.
- Developed to enable more dynamics in operations; gives more flexibility to the treatment processes.
- The reagents are stored in separate storage silos and introduced variably through the lance.
- Benefits arise from scale of operations, over longer periods.

Co-injection based Mg - CaC2 desulphurisation - benefits

- Better utilisation of materials, leading to lower heat losses, decreased input costs over longer periods.
- Improved quality control, hence lesser rejects.
- Improved equipment life from better process control → lower downtime → higher productivity.

THE OTHER SIDE OF THE COIN

- Problems with CaC_2 include :
  - Inflammable reagent.
  - High affinity to moisture or vapours (steam), releasing C_2H_2 which is also explosive. This renders water-based safety measures useless.

$$CaC_2 + H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

  - Unutilised CaC_2 enters slag, which has complicated disposal issues relating to environmental and pollution norms.
  - Lack of scalability of the treatment unit (to a different unit), when the laws are subject to change, leading to obsoletion.
  - CaC_2 in slag leads to precipitate layer formation, causing difficulties in treatment at metal-slag interface. Also leads to CaC_2 losses – input losses.

ALTERNATIVE TECHNIQUES OF MG BASED DESULPHURISATION

- Lime is being considered as an excellent alternative to CaC2, because :
  - Though lime is very less effective than CaC2, it is also much cheaper than industrial reagents (18 times cheaper than Mg, 10 times cheaper than CaC2).
  - Being insoluble in hot metal unlike CaC2 or Mg, it provides precipitation sites for MgS, enabling better slag formation.
  - It generates stirring action, helping to dissolve the magnesium vapours and reducing bubble diameter, enabling better utilisation of Mg reagents. Thus compensation for CaC2 can be done through combined CaO + Mg inputs to yield simlar results.

Role of automation – Diff levels

- Automation Systems : electronic or computer-based process control mechanisms that eliminate human intervention to extents possible.
- In cost-competitive world, cost and quality are both concerns : automation brings in consistency to the products delivered through predictability and superior process control.

Role of automation – Diff levels (contd…)

- Level 0: Digital devices, sensors, and other hardware.
- Level 1: This is the base automation level and includes programmable controllers like PLC's, microprocessors, etc. that manage functional logic and operate interlocks for safety.
- Level 2: This is process automation, which consists of servers, operator workstations and mini-computers to handle the schemes of material flow and production targets, as well as providing the necessary tools for monitoring and diagnosis.
- Level 3: This relates to plant-wide automation that defines the production schedules and keeps record of past activities for monitoring, reporting and event-tracking.
- Level 4: Organisation-wide automation that integrates various Level 3 systems. Thus, it facilitates integration of operations and production systems, corporate systems and business systems.

Benefits of automation

- No human intervention, hence standardisation of product quality and better control over costs.
- Enable better quality through rigorous quality control, and tracking of input costs, and better support for research and quality control facilities with relevant and accurate data.
- Such tasks can be performed by automation which cannot be performed manually like :
  - Series of fast and spontaneous activities;
  - Activities where superior timeliness is needed, than can be achieved by manual performance;
  - Such activities where human limitations and risks to life cannot be ignored.
- Safety interlocks and scheduled activities ensure a high level of safety to everyone working on production lines.
- They enable reporting of daily business activities in a much efficient and predictable manner, and support tracking of costs to activities, thus supporting cost control measures.

FUTURE PROSPECTS/MY OPINIONS/ WHAT COULD HAPPEN

- Though CaC_2 is much more effective than lime, clearly, lime is the co-reagent of the future due to:
  - ease in its disposal, and safety concerns with CaC_2.
  - Lime is easily available, cheaper and available in sizeable deposits.
- Importance of automation can never be underscored. The benefits it offers are many. Through these, automation systems bring a high level of consistency to the quality of products, thus bringing predictability in cost-appropriation and enabling focus on cost-reduction,

Thank you

Good Day.

INTRODUCTION OF HOTMETAL DESULPHURISATION AT BOKARO STEEL PLANT

P Kumar*, S K De**, Sachin*, S Mallik* & R K Rathi*

*BSL, SAIL, ** RDCIS, SAIL

ROAD MAP OF PRESENTATION

- EXISTING FACILITY
- PRODUCTION PLANNING
- FACILITIES FOR HM DeS UNITS
- PROCESS & DESIGN PARAMETERS
- PROCESS DESCRIPTION

EXISTING FACILITY

- **BSL has two steel melting shops SMS –I and SMS – II.**
- **Crude steel production in SMS II through BOF-CC route - 2.7 Mt/Yr of conventional slabs.**
- **Two independent desulphurisation stations, facilitating latest technology of co-injection of desulphurisation reagents, are coming up.**

PRODUCTION PLANNING

- **The new desulphurisation stations will treat 100% hot metal to be sent to BOF shop of SMS – II.**
- **About 37 heats of ladle capacity 300 t will be treated per day.**
- **Based on 365 operating days, about 3.154 Mt of hot metal will be treated in the two desulphurisation stations.**

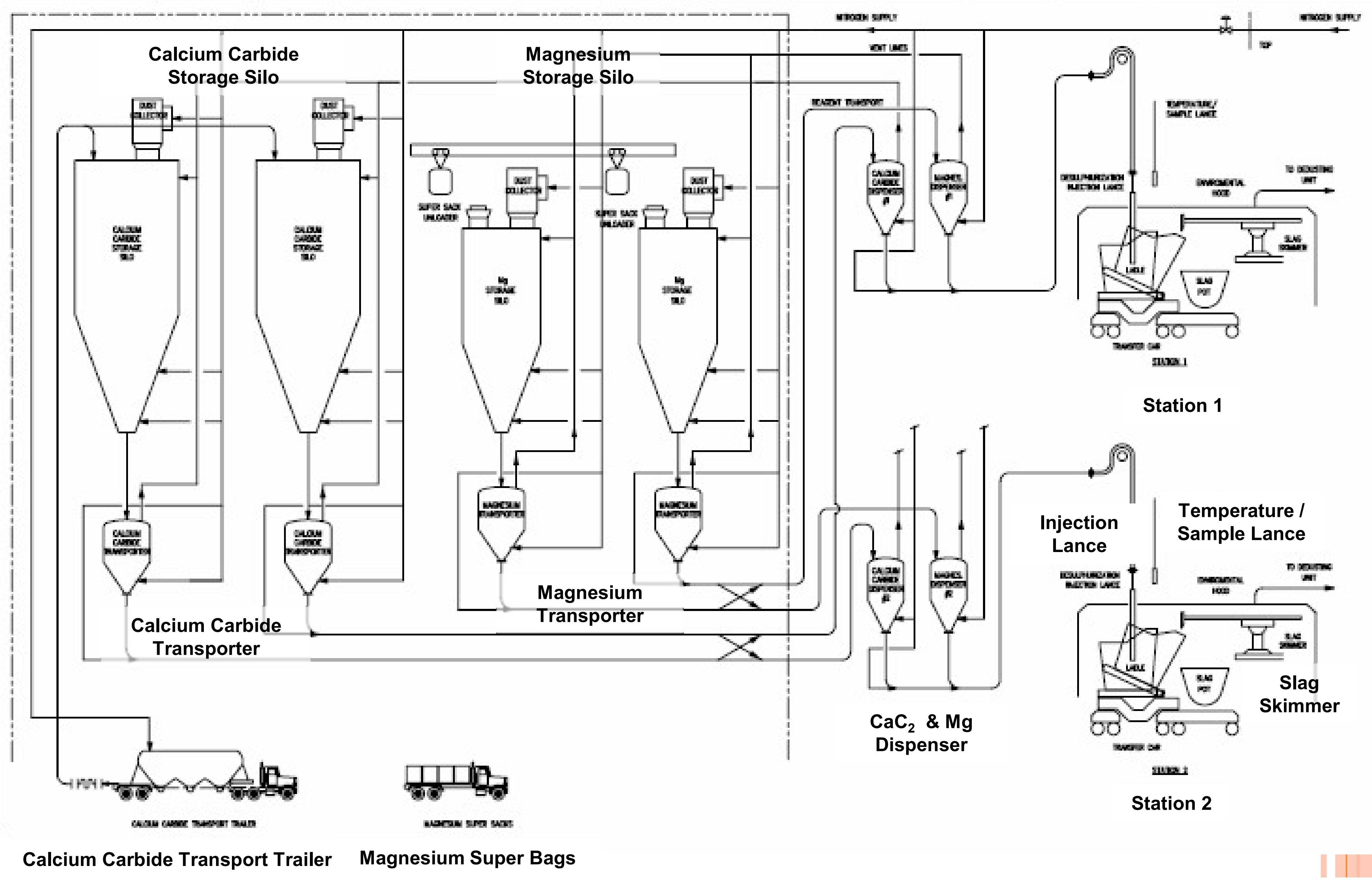
FACILITIES FOR HM DeS UNITS

- **Desulphurisation equipment proper**
- **Silos**
- **Fume extraction system, Pollution control, Air conditioning and ventilation system**
- **N_2 supply system, pressure reducing station and buffer vessel (16m^3)**
- **Electrics, controls, automation including Level-I automation, instrumentation, communication and process control models (Level - II)**

FACILITIES FOR HM DeS UNITS - contd.

- Complete hydraulics and lubrication systems
- All material handling facilities such as jib crane, monorail, underslung hoists, etc.
- Temperature measurement-cum-sampling lance at torpedo reladling station
- Other accessories related to the desulphurization stations

HOT METAL DESULPHURISATION FACILITY – BASIC FLOW DIAGRAM



BASIC PROCESS PARAMETERS

Heat size	300 t
Ladle free board	500 mm (minimum)
Sulphur level	Initial S – (0.07% avg., 0.10% max.) Final S – (0.005% avg., 0.002% min.)
Hot metal temperature	1,300-1400 °C

DESIGN PARAMETERS

Number of stations	Two
Process vessel	Hot metal ladle
Reagents	• Calcium carbide • Magnesium
Reagent conveying medium	Dry nitrogen

DESIGN PARAMETERS

Desulphurisation process	Co-injection based process. However, the same equipment can be used without any modification for mono injection of CaC_2 or co-injection of Mg & lime.
Maximum injection rate	For CaC_2 : 48 kg/min For Mg : 16 kg/min

DESIGN PARAMETERS

Injection time	Injection time depends on initial and final S in hot metal. On average, it will vary from 12 to 15 min.
Allowable temperature drop during entire desulphurization operation	25°C (max)

DESIGN PARAMETERS

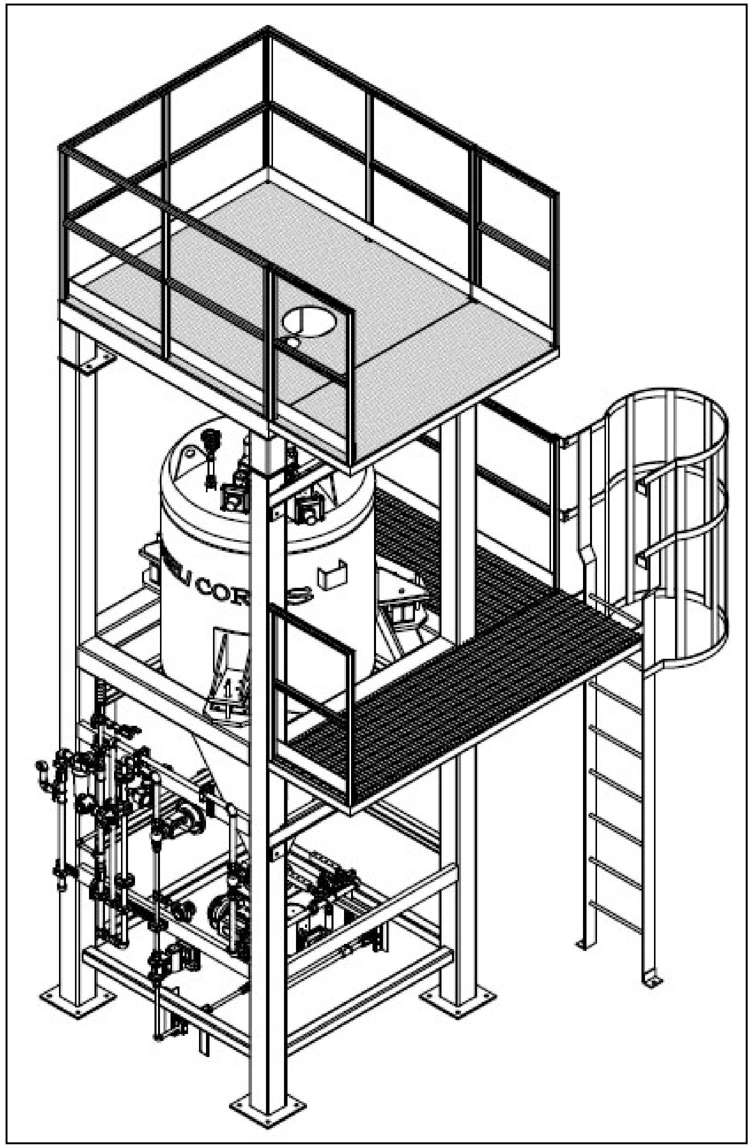
Capacity of storage silo for CaC_2	2 x 120 m^3
Capacity of storage silo for Mg	2 x 40 m^3
Capacity of CaC_2 injection dispenser	2 x 2.2 m^3
Capacity of Mg injection dispenser	2 x 2.2 m^3
Capacity of HM treatment ladle	Same as existing ladle of SMS-II of BSL (with modification)

DESIGN PARAMETERS

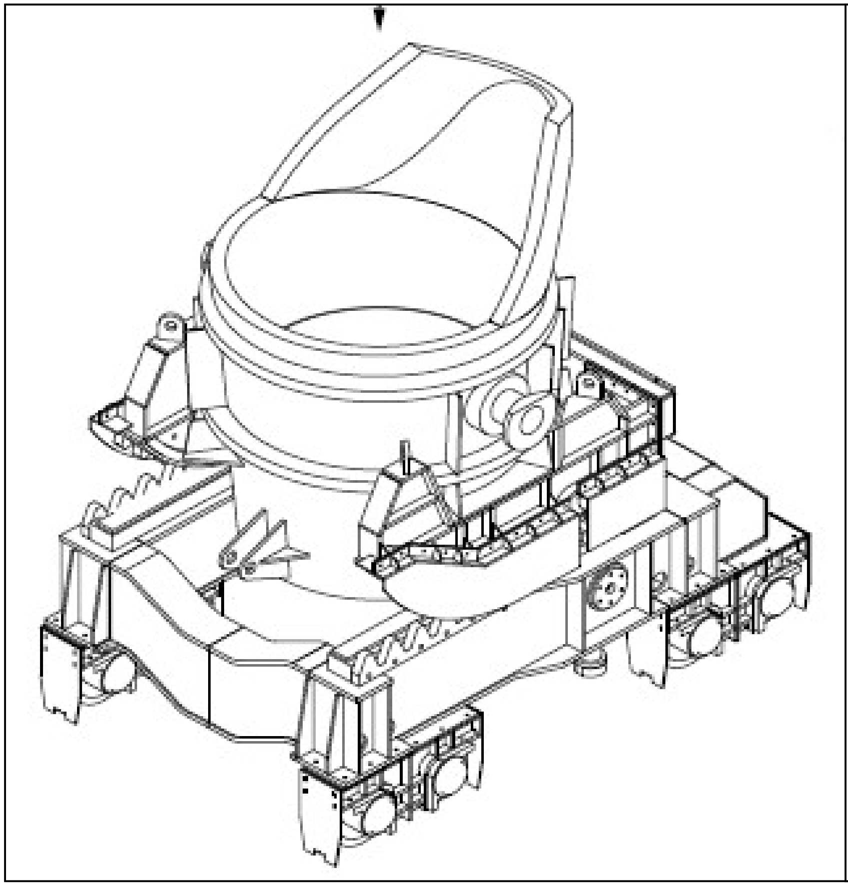
Deslagging operation	By tilting of HM ladle into the slag pot with slag skimmer
Placement of HM treatment ladle	On a tiltable type ladle transfer car
Tilting mechanism of car	By hydraulic power pack system
Placement of Slag pot	On the same HM treatment car

DESIGN PARAMETERS

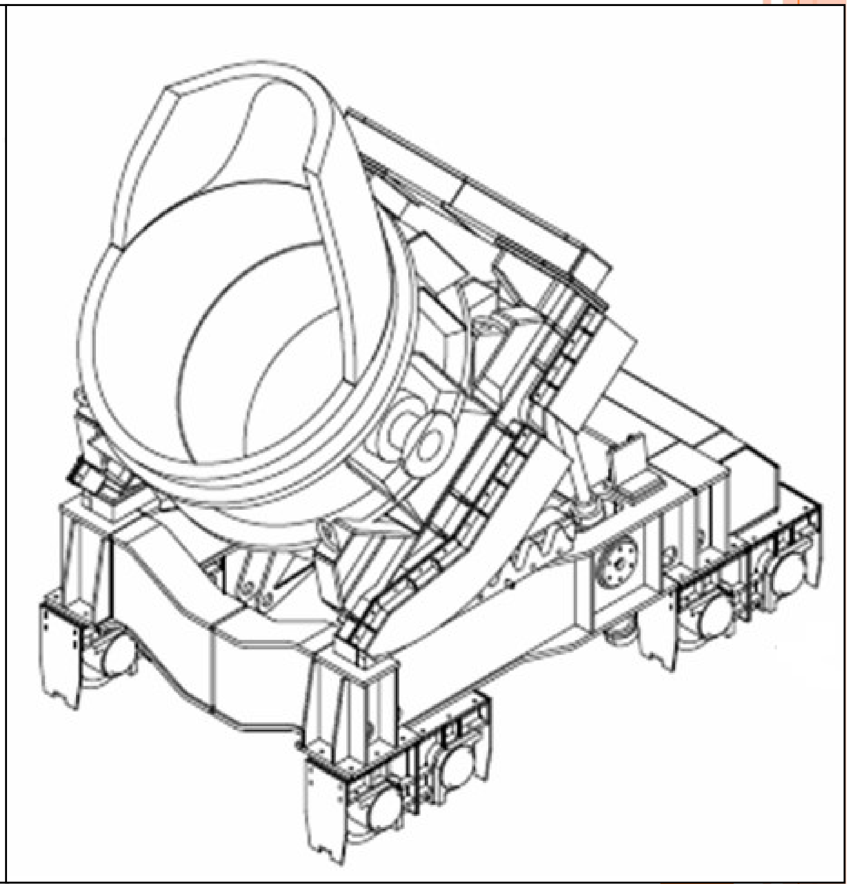
Desulphurisation enclosure	Reagent injection and slag skimming will be completed in the environmental enclosure, which will ensure that all fume generated during the process are captured and extracted from the work area.



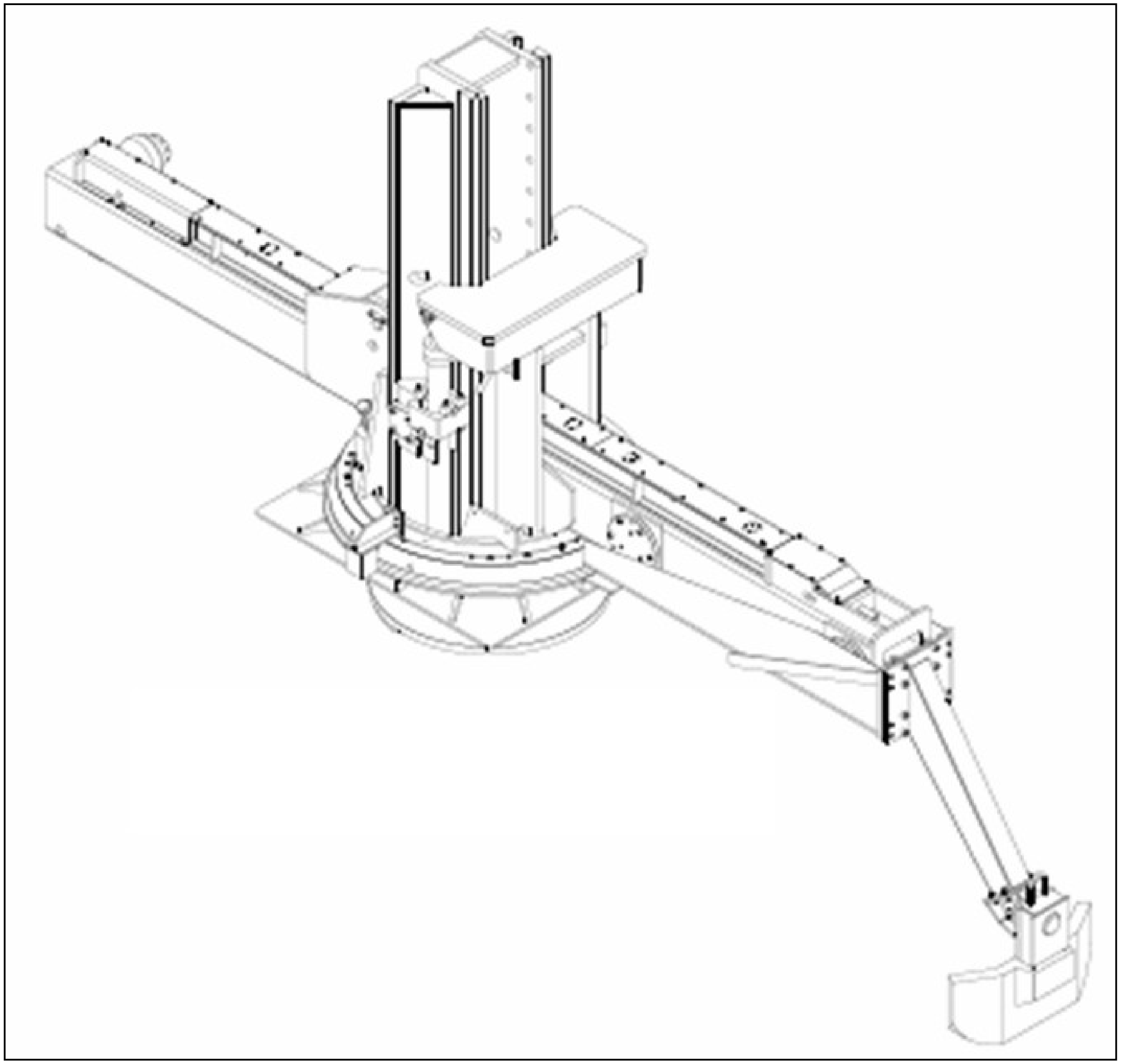
REAGENT DISPENSER



TRANSFER CAR INJECTION POSITION



TRANSFER CAR SKIMMIMG POSITION



SLAG SKIMMER

PROCESS DESCRIPTION

Hot metal will be received in torpedo cars. Hot metal ladle filled with hot metal will be placed on to the transfer car. The transfer car will be taken inside desulphurisation chamber before start of operation.

PROCESS DESCRIPTION

The granulated magnesium and calcium carbide will be used as desulphurising reagents and will be co-injected in pre-set ratio as per extent of desulphurisation requirement with the help of an refractorty coated injection lance. Blending of reagents will be in reagent injection line.

PROCESS DESCRIPTION

At the end of the DeS process, the lance will be withdrawn. The slag layer will be removed by tilting the car with the help of a hydraulic tilter. A hydraulically operated slag raking machine will be used for skimming the slag from top of the ladle into the slag pot. After deslagging, the ladle will be brought back into the open bay and transferred to BOF.

PROCESS DESCRIPTION

Both activities, reagent injection and slag skimming, will take place in the environmental enclosure to prevent fumes escaping into the working area. The fumes will be dedusted in ESP based Fume Extraction System prior to release into the environment.


Thank You!

Introduction of CaC_2 & Magnesium based Co-Injection type De-sulphurisation Unit in SMS-II of Rourkela Steel Plant, Rourkela

(Authors : AJIT KUMAR JAISWAL & B. DEBNATH)

(DGM(Steel) & AGM(RSC), Steel Authority of India Ltd./Centre For Engg. & Technology, Ranchi)

Introduction

- Increasing demand for high quality steel, particularly for application in off shore, transport and structural sectors calls for adhering to strict specifications in terms of high strength, low temperature, toughness, cold forming and weldability.
- SAIL also on the development of high performance steel for auto, gas pipelines, electrics and construction steels.
- S with the exception of free cutting steels adversely affects mechanical properties of steel, internal & surface quality
- Desired sulphur level < 0.015 %
- An unavoidable major task for the steel
- Best stage for De-S just before charging HM into BOFs.
- CET provided consultancy services for RSP & DSP DE-S projects like FR & TSs preparation, Contract Specification finalization, detailed engineering drawings & approval of vendor's engineering and designers' supervision

A BRIEF INTRODUCTION OF SMS –II, RSP

- **SMS–II has**
  - 2 nos. of BOFs
  - 1 LF
  - 1 no. 150 tonne Argon Rinsing Unit (ARU)
  - 2 nos. of single strand Slab Casters and
  - had only one hot metal desulphurization unit with mono injection facility to inject caclium carbide/lime based reagent and now with help of CET one more De-S unit.
- **Initially designed for ½ operation and for 1.35 Mtpa production with an average heat weight of 150t**

During 2008 – 2011, the facilities in SMS-II have been augmented to facilitate Simultaneous blowing and produce steel @ 1.85 Mtpa

- **Problems with old De-S Unit :**
  - jamming too during the injection of reagent powders.
  - This unit was from the problems of frequent valves and pipes failure and For the slag skimming operation, converter charging crane
  - Suffers designed for meeting the selective heat requirements
- **Feeling a need of installing a latest and most efficient De-S Unit for 100%de-sulphurisation treatment, second one came.**

SELECTING THE BEST PROCESS FOR NEW DE-SULPHURISATION UNIT

Following options exit for producing low S steel:

- Produce low 'S' hot metal in the blast furnace
- Desulphurise the hot metal before steel making process
- Secondary treatment of steel

Presently 'S' in the hot metal from BFs is around 0.056 %. Exercising control on the 'S' output in the blast furnace means maintaining in BFs:

- High basicity slag regime
- High hot metal temperature regime

But, this leads to :

- Increased slag volume,
- High coke consumption
- Lower blast furnace production.

With the spiraling non coking coal prices, reduction in the coke requirements is prime concern for the steel makers.

Moreover, seeing the above disadvantages, no option was left other than external de-sulphurisation.

Alternatives w.r.t. external de-sulphurisation

Comparison of the processes for HM vs Steel de-sulphurisation is given below :

Parameters	HM	Steel
Oxygen potential	Low	High
Temperature of HM/Steel	1300 °C	> 1600 °C
Activity coefficient (FS)	4.5 – 6.0	1.5
Cost of reagent	Low	High
De-sulphurisation efficiency	High	Low
Temperature drop	Little (Adjusting possible)	High
Steel (final) cleanliness	More	Less
Sulphide shape control	No (Can be done)	Yes (By injection)

Considering the above data, external De-sulphurisation of hot metal is always preferred to steel De-sulphurisation.

Benefits of Hot Metal De-sulphurisation

Hot metal De-sulphurisation also gives some additional benefits in blast furnace operations and during steel making :

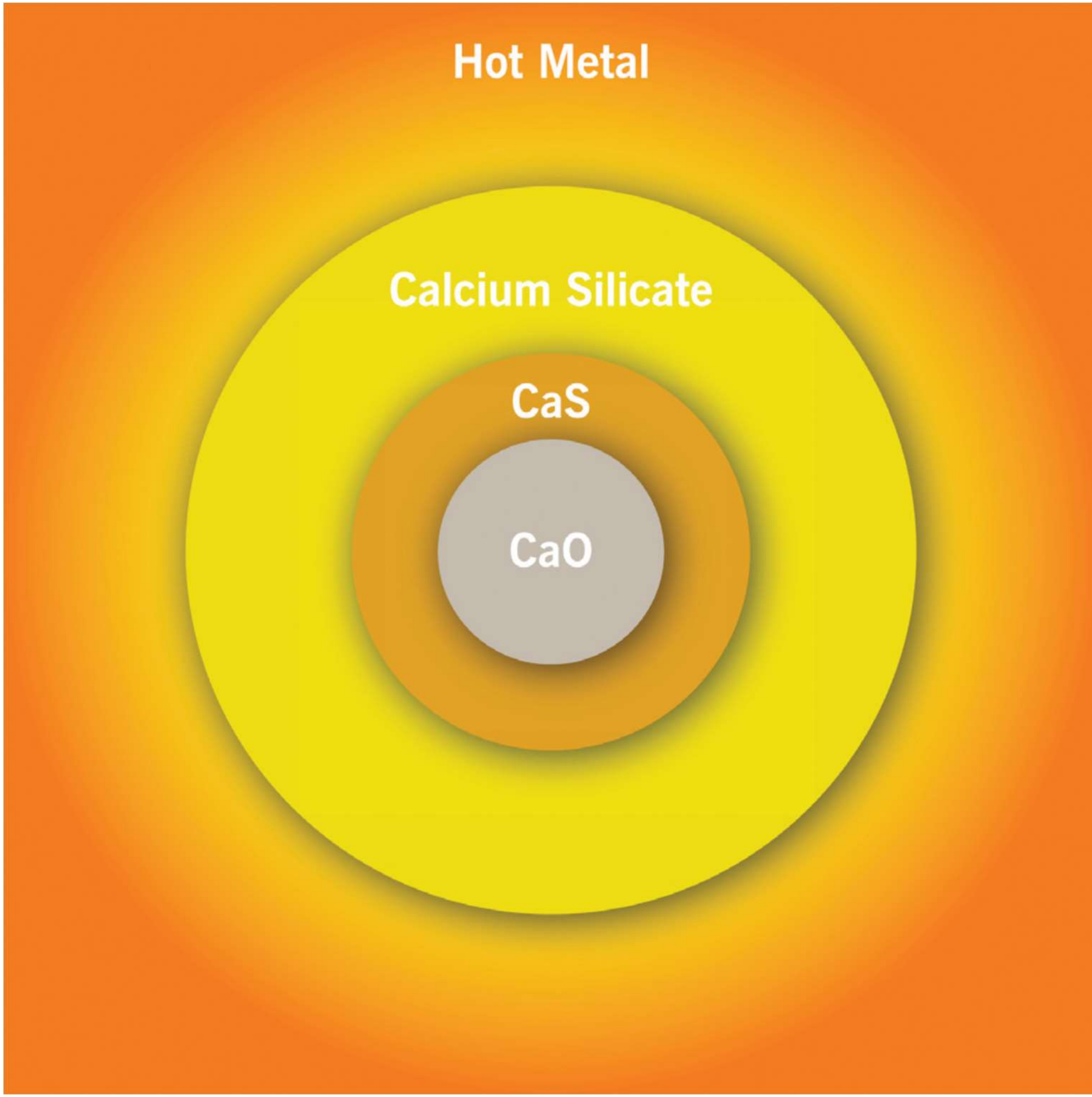
- **Blast furnace productivity increases, because of lean slag practice.**
- **Coke and flux consumption decrease in blast furnace.**
- **Alkali build up in blast furnace comes down.**
- **Reduction in energy requirement per ton of hot metal.**
- **Higher lining life of BOF vessels**
- **Flexibility to maintain desired 'S' levels for steel making as per specific heat requirement**

As oxidizing conditions during steelmaking do not favour De-sulphurisation. The choice, therefore, rests on external De-sulphurisation of hot metal.

Cost of reagents	Lowest	Low & readily available	Medium cost	High
Generation of fumes, dust, etc.	Large (oxidation of Na vapour & C to CO)	Negligible	Negligible	Large
Specialty w.r.t. precautions and actions	Added while filling ladles at BF Cast House or at the steel works. Abandoned for difficult process control & environmental management	Has to be: no carry over slag. HM temp (1400 ^{0}c) If O not controlled with Mg, S may revert back in contact with O.	Safety in handling, storage & use (inflammable acetylene with moisture) Full ladle required for higher residence time. No carry over slag	Very volatile , if used alone at high temperature No problem with carry over slag & O content. Lime/CaC2 with Mg reduces the size of Mg bubbles and provides precipitation sites for MgS.
Efficiency of De-S	Cannot bring down `S' very low	10% when lime alone. (CaS & CaSiO4 impede the De-S process) Therefore, size to 45µm. maxm.	8 times the capacity of lime based. (Precipitate impedes the De-S process, but Co2 of Limestone helps in mixing CaC2 powder)	20 times the capacity of lime (boils and then dissolves by 85%) S down to less than 0.005% very fast. However, its consumption increases when `S' becomes very low.
Slag generation & temp loss	High	Large	Less	Less

Alternatives w.r.t modes of reagents delivery

Criteria	Mechanical stirring	Mono injection	Co-injection
Problems	Complicated equipment required.	Pre-mixes suffer from segregation of Mg resulting in sudden violence in reaction & lance choking. S reversal is more due to absence of lime.	Lance blockage has been completely eliminated. Violence of Mg alone is controlled once co-injected with carbide.
Used with or when	Used when availability of Mg is restricted, otherwise not popular.	Mono-injection of Mg alone successful with a bell-type vaporizing lance.	Used with individual dispenser
Flexibility	Optimisation of process depends upon rotation speed, immersion depth & eccentricity of the impeller much more than the addition of the reagents	Lower control of changing the proportions of the reagents	Flow rates can be adjusted quickly & reliably by adjusting the position of orifice valve via the PLC Control as per process phase
Space requirement	High	Low	Low
Reagents consumption rate	High	High	Drastically reduced


Hot Metal
Calcium Silicate
CaS
CaO

Alternatives w.r.t modes of reagents delivery (contd.)

Criteria	Mechanical stirring	Mono injection	Co-injection
Refractory cost of ladles per thm	High as more freeboard for accommodating impeller & vortex and also for high treatment time.	Low as same ladle can treat more of metal for reduced freeboard and that too in lesser time.	Very low as same ladle can treat more of metal for reduced freeboard and that too in least time.
Slag generation and iron loss	Both high for large amount of reagents. Iron loss from 2% to 3%	Both medium for medium amount of reagents	Both low. Foamy easily removal slag generation around 3 t for 150 t HM and Iron loss 1%
Temperature loss	25- 50 °C. Temp loss can be restricted to 30 °C by use of more lime.	Medium	10-20 °C
Total cost of the process	High on account of above two in spite of lower cost of reagent	Medium	Low on account of above two in spite of high cost of reagent

RECOMMENDATION

The use of Mg based reagent definitely helps in achieving lower final `S' level, but the cost of these reagents are much higher than that of the carbide based reagents.

Therefore, depending upon the requirements of final `S' level

- Carbide alone first till it becomes uneconomical & slow
- Then Mg injection maintaining an optimum carbide flow level
- Then gradually reducing Mg flow
- Finally, the carbide is stopped after Magnesium.

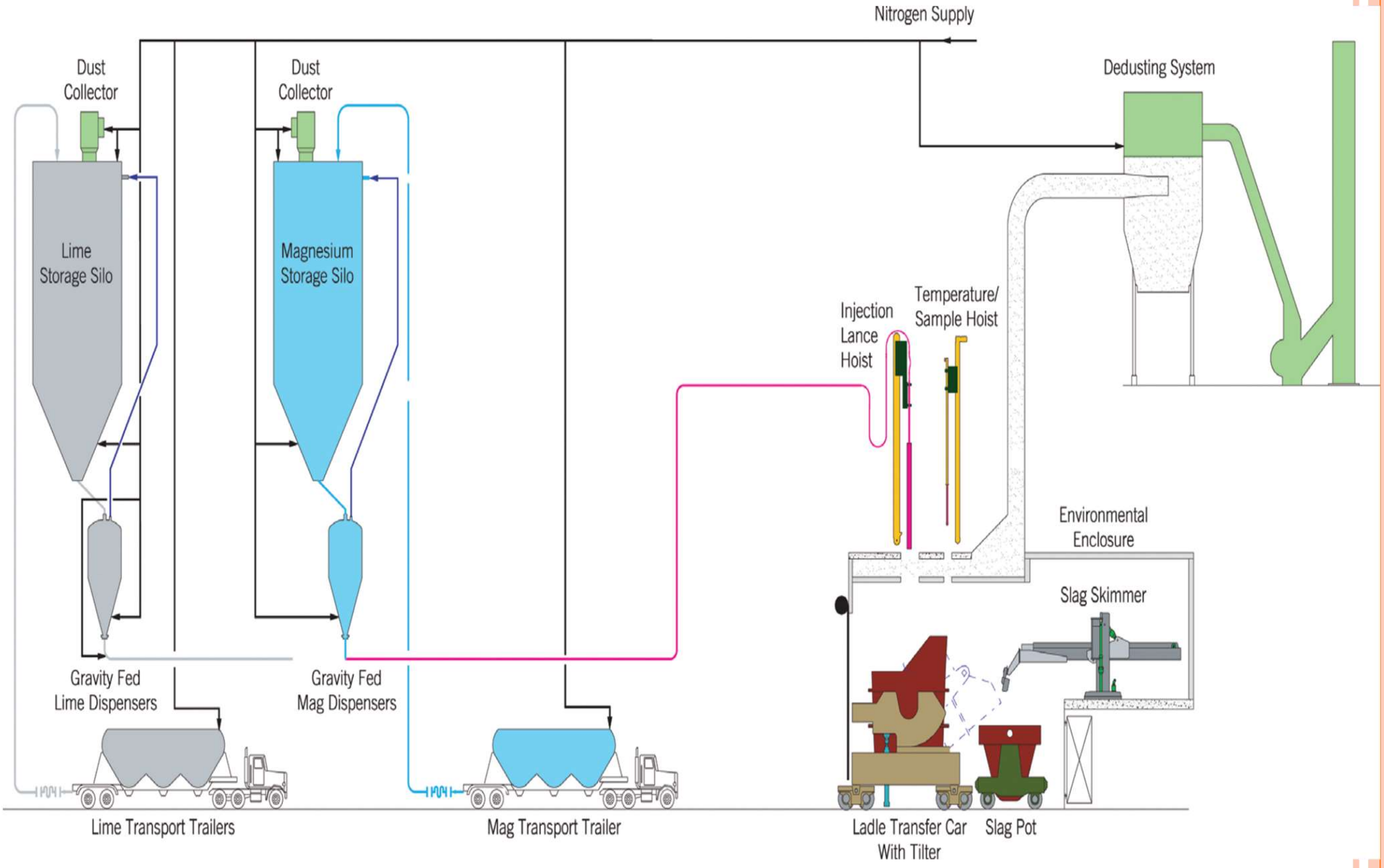
Considering the above mentioned points, co-injection facility using mixture of CAC2 & Magnesium powders for De-sulphurisation of HM was recommended for implementation.

Location : the site finally selected was towards the end of Converter Charging (EF) Bay between axis 21-22. The existing EF Bay was extended by 36 m towards CP-11.

This installation was equipped with :

- slag raking facility for removal of slag before and after
- Extraction, cleaning & discharging of fumes generated during the process.

Schematic Drawing



DESIGN PARAMETERS

- Injection rate :
  - For CaC_2 : 40-60 Kg/min
  - For Mg : 15-20 Kg/min
- Injection time : 10-15 min.
  (Depending on initial "S")
- Capacity of storage silo for CaC_2 : 100 m^3 for 10 days storage
- Capacity of CaC_2 injection dispenser : 2 m^3 , 2 no.
- Capacity of storage silo for Mg : 20 m^3 for 10 days storage
- Capacity of Mg dispenser : 1 m^3 , 2 no.
- Temperature drop during injection : 0.5 – 1.00 °C/min.
- Capacity of ladle stand : 180t
- Tilting angle : (+) 45° to (-) 5°
- Control system : PLC based
- Lifting and tilting mechanism : Hydraulic system

NITROGEN AS A CARRIER GAS

- Quality : Dry filtered (free from oil and grease)
- Dew point : – 40° C
- Pressure at Take over point (TOP) : 16 bar (Approx.)
- Operating pressure : 6-12 bar (Approx.)
- Total requirement at pick time : 1700 Nm^3 /hr.

Consumption pattern of Nitrogen:

- Silo blanking : 30 Nm^3 /h
- Dispenser pressurization : 320Nm^3 /h
- Reagent injection : 15Nm^3 /h
- Reagent unloading : 500Nm^3 /h
- To meet the requirement of Nitrogen on uninterrupted supply basis, it was tapped from take over point (TOP) of the LP Nitrogen header (at 18 kg/cm2g). Necessary Pressure Reducing Station (PRS) was installed .

Typical cycle time for the De-sulphurisation process

1	Lifting of ladle by EOT Crane and placement of loaded Ladle on transfer car	: 3 Minutes
2	Transfer of ladle to the DS enclosure	: 3 Minutes
3	De-Slagging (optional)	: 3 Minutes
4	Sampling and temperature	: 1 Minutes
5	Injection of reagent	: 12-15 Minutes
6	Sampling and temperature	: 1 Minutes
7	De-Slagging	: 10 Minutes
8	Movement of ladle out of the enclosure	: 3 Minutes
9	Lifting of ladle by EOT Crane for charging to BOF Converter	: 3 Minutes
10	Other works on an Average basis e.g slag pot changing, lance changing, etc	: 3 Minutes
11	Total time	: 42-45 minutes

Packages & Implementation

Package No. 1 : Bay Extension & Allied Facilities – Strl.(NTK)

Package No. 2 : Bay Extension & Allied Facilities – Civil (NTK)

Package No. 3 : De-sulphursiation Unit (Global TK)

Package No. 4 : LT & HT Sub-stations (TK)

Package No. 5 : Supply items like charging metal ladles, slag pots, etc. (TK)

- The project completion schedule was 22 months from Stage-II approval i.e by May'2008.
- Main De-Sulphurisation package (Pkg.no.3) was awarded to M/s SMS Mevac UK .
- The Project was commissioned after completing the commissioning test done during 28.07.2008 to 31.07.2008 with just overrun of 2 months only.

1. Performance Test Results: – REAGENT CONSUMPTION

No. of Heats	Start 'S' Average (Before DS)	Final 'S' Average (After DS)	Average consumption of CAD 9 (In Kg/T of Hot Metal)		Average consumption of Mg-97 (In Kg/T of Hot Metal)	
			As per PG Parameters	Achieved during PG Test	As per PG Parameters	Achieved during PG Test
100	0.042 %	0.006 %	1.791	1.301	0.359	0.342

2. Performance Test Result : TEMPERATURE DROP RATE

PG Value	Average Temperature drop rate achieved during PG Test	Remarks
≤ 1.2°C / min.	0.442°C/min	Average Temperature drop rate is ≤ 1.2°C / min. PG against Temperature Drop Rate is achieved

3. Performance Test Result : CYCLE TIME

PG Value	Average Cycle Time Achieved during PG Test	Remarks
≤ 30 minutes	28 Minutes	Average Cycle Time is ≤ 30 minutes. PG against Cycle Time is achieved

4. Performance Test Result : Lance Life

PG Value	Achieved during PG Test	Remarks
≥ 600	622 minutes (Was Still running)	Lance Life ≥ 600 minutes. PG against Lance life is achieved.

5. Performance Test Result : Pollution Control

PG Value	Achieved during PG Test	Remarks
40 mg/ Nm^3	8.16 mg/ Nm^3	Performance guarantee achieved

PRODUCTION & DE-SULPHURISATION PERFORMANCE FOR 2010-11

Sl.	Parameters	Unit	Performance
1	Crude steel production	Tonne	1759684
2	Heats made	Nos	11688
3	Heats cast	Nos	11648
4	Capacity utilisation	%	129.87
5.	Nos. of heats blown	Nos.	11688
6.	De-sulphurisation done on heats	Nos.	1138 (9.74%)
7.	Avg. life of lance	Min.	600
8.	Avg Injection rate of CaC_2	kgs/min	30 ag. Envisaged 40-60
9.	Avg Injection rate of Mg reagent	kgs/min.	10 ag. Envisaged 15-20
10.	Initial S and aimed S	%	0.056 and 0.01
11.	Sp. Consumption of CaC_2 reagent	kg/thm	0.050
12.	Sp. Consumption of Mg reagent	kg/thm	0.010
13.	Injection time & Total Cycle time	Min.	7-8 , 35-37 ag. Envisaged 7-85, 42-45
14.	Temperature drop during injection	Deg.	10 deg. In 7-8 min. (slightly higher than 1 deg./min.)
15.	Nitrogen pressure at Take over point	bar	16.79
16.	Peak requirement of Nitrogen	nm3/hr.	2192 ag. Envisaged 1700

CONCLUSION

- It is, therefore, required to streamline the operation cycle to get the maximum benefit from De-sulphurisation Unit.

THANK YOU

HOT METAL DESULPHURIZATION
BENEFITS OF MAGNESIUM LIME CO-INJECTION

Danieli Corus

Bart vd Berg

Contents

- The Company
- The Process
- KR versus Co-injection
- Level-1 and 2 System
- Conclusion

The Company

Danieli Corus is a joint venture between

Danieli

- Established in 1914 as an Italian based equipment manufacturer
- One of the first Italian companies to use EAF
- Pioneer of the "Mini-mill" concept

Corus

- Founded in 1918 as the Dutch Blast Furnace & Steel Works
- Later became known as Hoogovens
- 1999 merger with British Steel then named Corus
- 2006 purchase by Tata Steel Group, now known as Tata Europe

THE COMPANY

Danieli Corus

- Formerly names HTS Hoogovens Technical services
- Established in 2000 as a stand alone company
- Head office in IJmuiden, the Netherlands
- Currently, 39 offices in 31 countries around the world

Experise:

Blast furnace:

- design
- Stoves
- PCI

Steelmaking:

- desulphurization
- sublances,
- Bottom stirring,
- waste gas analysis
- Level-1 & Level-2 systems

Aluminium industry

- FTC & GTC

THE COMPANY

<u>Tata Europe (the Netherlands):</u>

- 2 Blast Furnaces
- 1 Steelplant
- 2 De-S Mg/Lime
  (From 1999)
- 3 converters 330 ton
- 2 LFs
- 1 VD
- 2 CCMs
- 1 Thin slab caster

Output 7,5 M ton steel

The Process

Intial facts

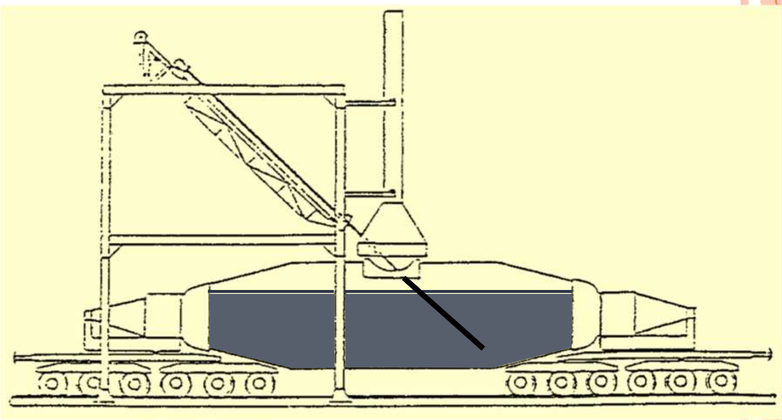
Sulphur is added through cokes/coal in Blast furnace

Sulphur is unwanted in many steelgrades

Typically 75% - 100% of hot metal is treated

Sulphur removal before steelplant possible

- In Troughs (at Blast furnace)
- In Torpedo

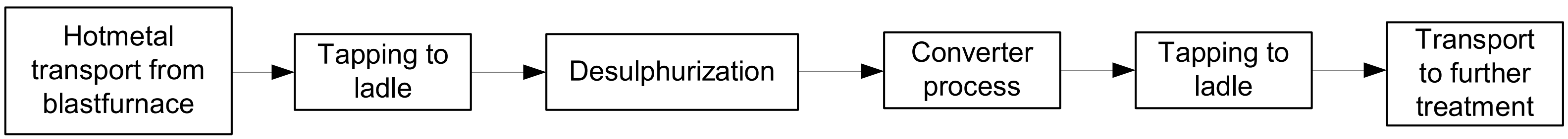


Important factors are:

- Fast Process
- Low cost (minimum amount of materials/ no overshoot)
- Low temperature loss of hot metal
- Removal of sulphur rich slag Preventing sulphur return
- Low Hot metal Loss

THE PROCESS

General process flow Steelplant:



General process steps:

- Hot metal ladle is placed (by crane) on ladle transfer car
- Temperature and analysis is (can be) determined
- (Injection) Lance is lowered into the hot metal ladle
- An amount of material is added
- Temperature and analysis is determined again
- (Repeat treatment if necessary)
- Ladle is tilted and slag is removed by skimmer
- Ladle is moved back for transport to converter
- Removal of Ladle by crane

The Process

Materials used:

- Soda Ash (Na_2CO_3)
- Calcium Fluoride (CaF_2)
- Calcium Carbid (CaC_2)
- Lime (CaO)
- Limestone $CaCO_3$
- Magnesium (Mg)

Reactions:

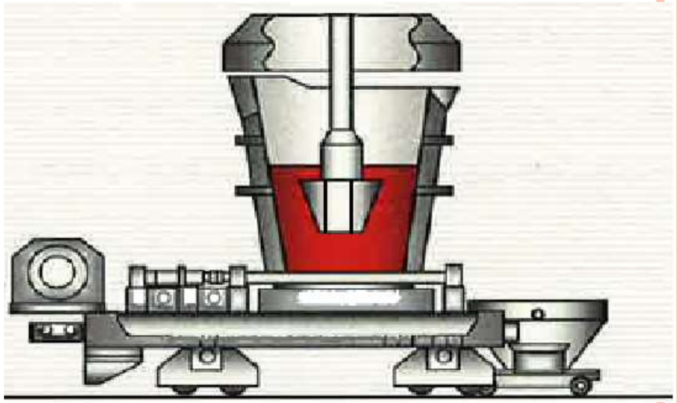
$Mg + S \rightarrow MgS$	reaction in steel
$2MgS + O_2 \rightarrow 2MgO + 2S$	reverse reaction
$2Mg + O_2 \rightarrow 2MgO$	Fireworks! 3000 oC
$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$	Explosive situation
$CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$	acetylene
$C_2H_2 + O_2 \rightarrow CO_2 + H_2O$	3500 oC!
$CaO + MgS \rightarrow CaS + MgO$	stable reaction of S
$CaC_2 + MgS + \frac{1}{2}O_2 \rightarrow CaS + MgO + 2C$	stable reaction of S
$CaO/CaC_2/CaF_2 + S \rightarrow CaS + C/F/O$	desulph mono injection
$CaO + H_2O \rightarrow Ca(OH)_2$	Clotting of Lime
C + "O" $\rightarrow$ CO and/or CO_2	Oxidation
$CaO(CO_2)$ better $CaCO_3 \rightarrow CaO + CO_2$	Burnt Lime and LOI

The Process

Main Process Types:

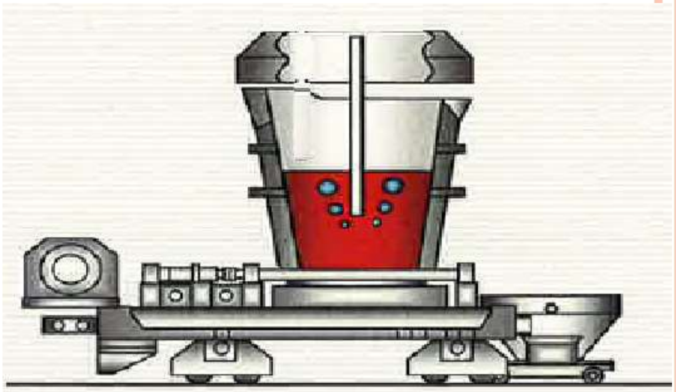
KR = Kanbara Reactor (stirring system)

- Materials added from top
- Materials injected



Mono / Co-injection

Mono Injection	Co-Injection	Sequential Injection
• Mg • CaC_2 • Blends	• Mg / Lime • Mg / CaC_2	• pre and/or post injection



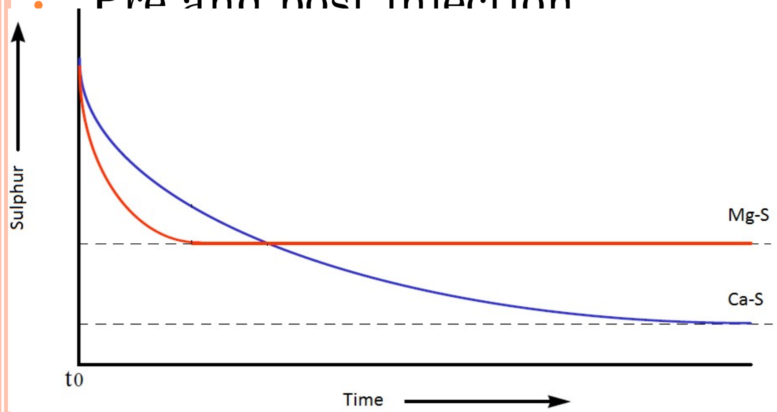
THE PROCESS

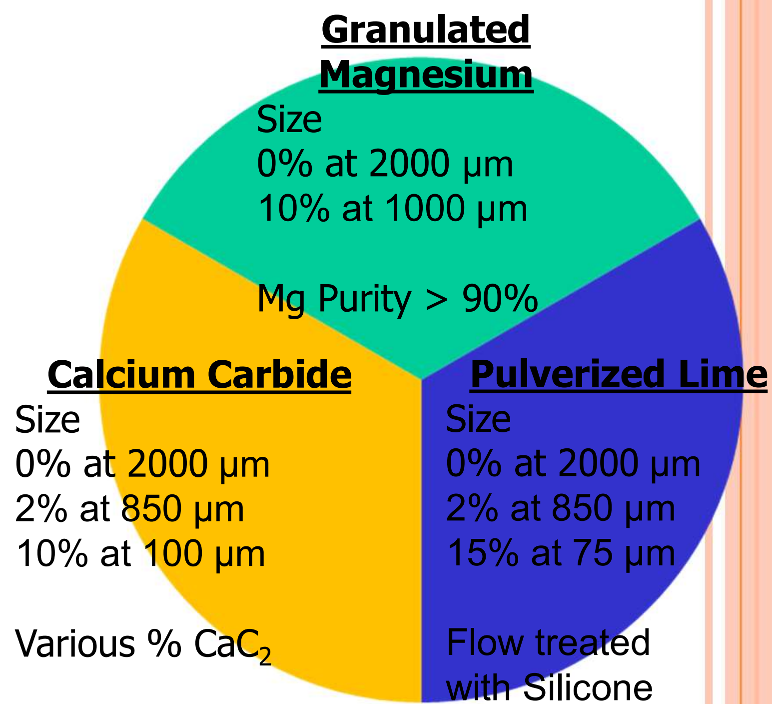
DC co-injection Technology

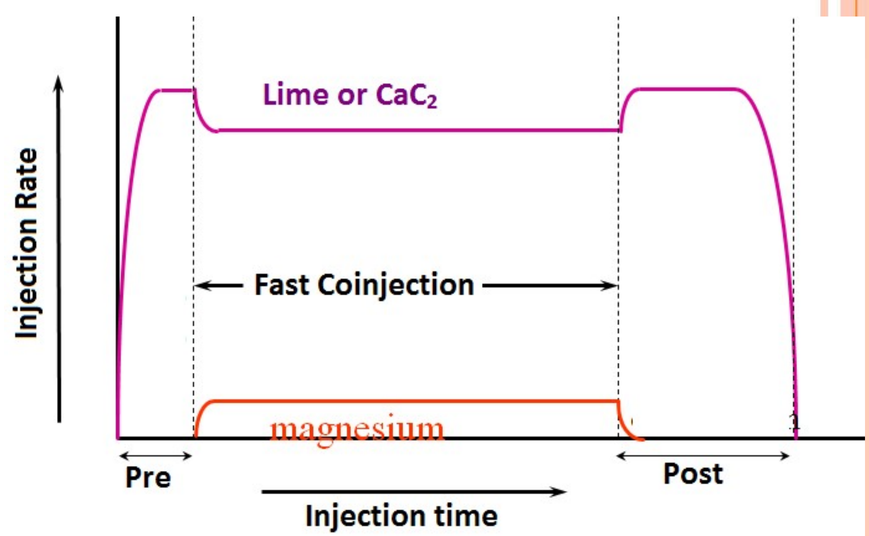
- Mg/Lime
- Mg /CaC_2
- Mg/Lime/CaC_2

also supports:

- monoinjection CaC_2 and Blends
- Pre and post injection



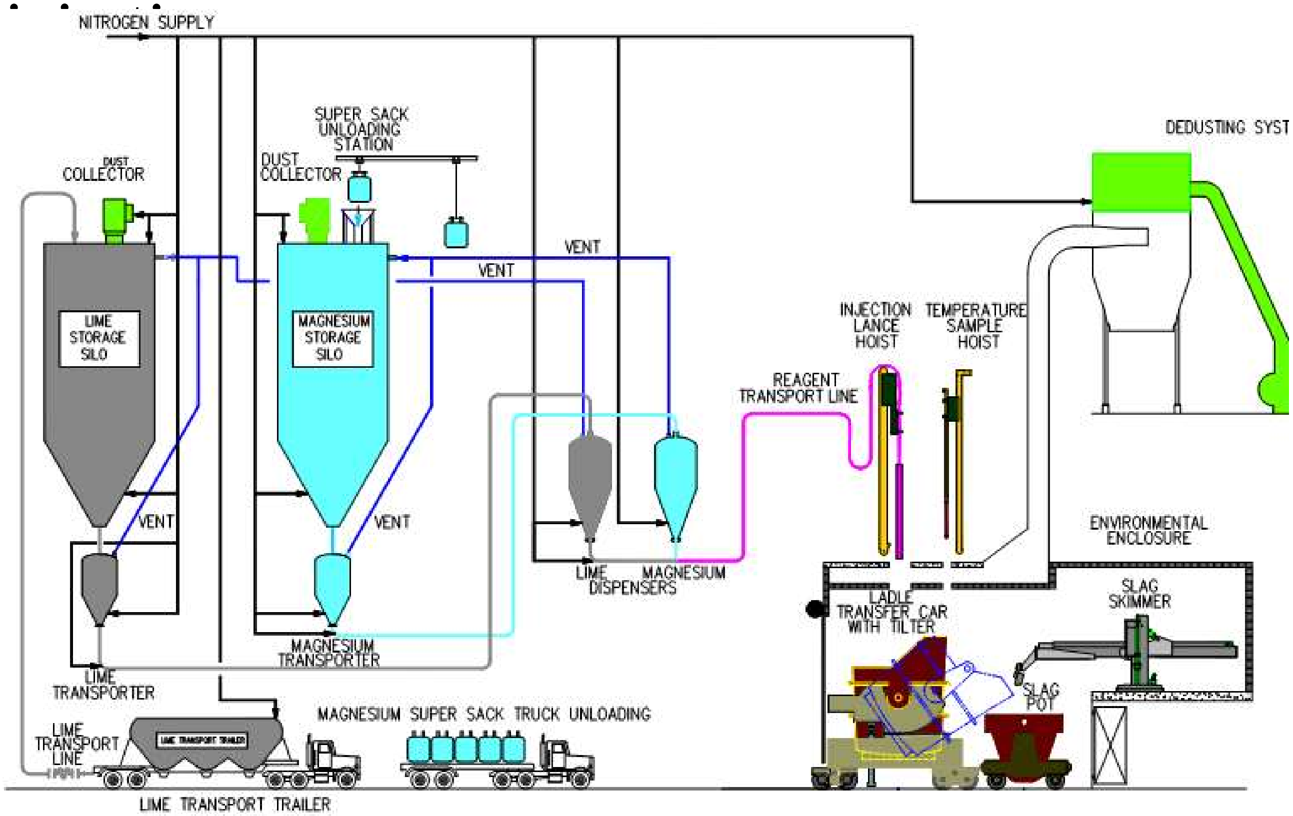




Lime: good,cheap but slow, high slag volume
CaC_2: good desulphurizer but environmental /safety issues
Magnesium: fast but very violent reaction (expensive)

The Process

Typical Layout DC co-



However many variations exist:

- Amount and layout of stations
- Transfer car / removable hood
- Truck/Sack loading

- Transporters yes/no
- Amount of dispensers
- Materials used
- Amount of Skimmers

KR versus Co-injection

Typical Figures:

	Coinjection	**KR Process**
Sulphur [S] before	0.03 – 0.05 %	same
Sulphur [S] after	0.001 – 0.010 %	same
Temperature hot metal	1300 – 1400 ^{O}C	same
Mg consumption	0.7 kg/ton hot metal	none
Lime consumption	2.4 kg/ton hot metal	6 kg/ton
Temperature Loss	10 - 20 ^{O}C	25 - 40 ^{O}C
Hot metal loss	1 %	2.5 %
Injection rate Mg	10 kg/min	none
Injection rate Lime	40kg/min	none
Injection ratio Lime/Mg	3-7 (4) Lime : 1 Mg	none
Injection(stir) time	8-12 min	same or more
Skimming time	7 min	same or more
Total cycle time	28 – 33 min	same or more

KR versus Co-injection

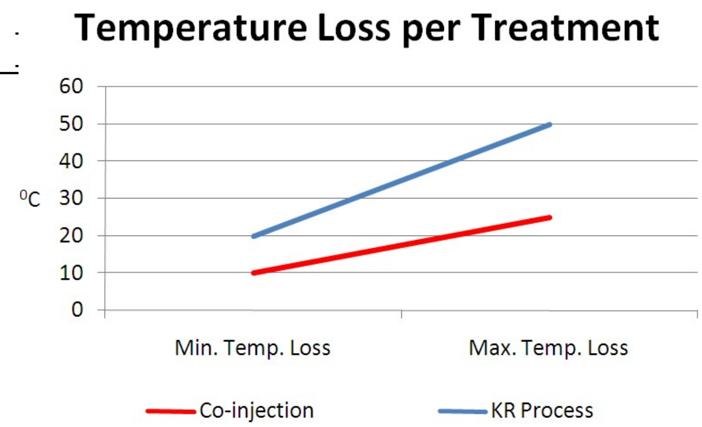
Comparison between Co-injection and

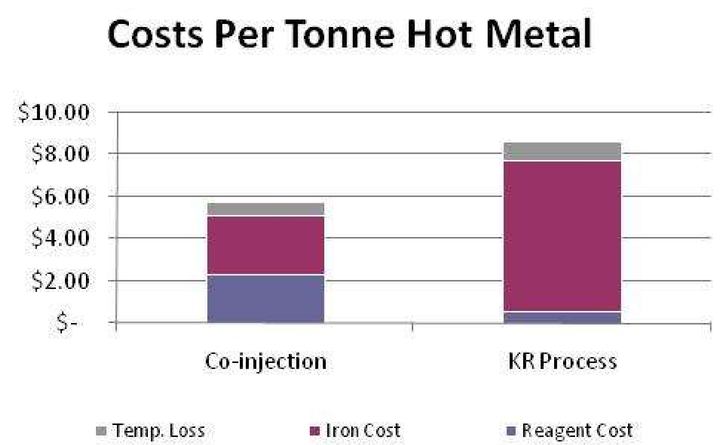
Cost	USD/THM
Co-Injection	$ 2.26
KR	$ 0.53

Cost	USD/THM
Co-Injection	$ 0.61
KR	$ 0.92

Cost	USD/THM
Co-Injection	$ 2.88
KR	$ 7.21

Loss





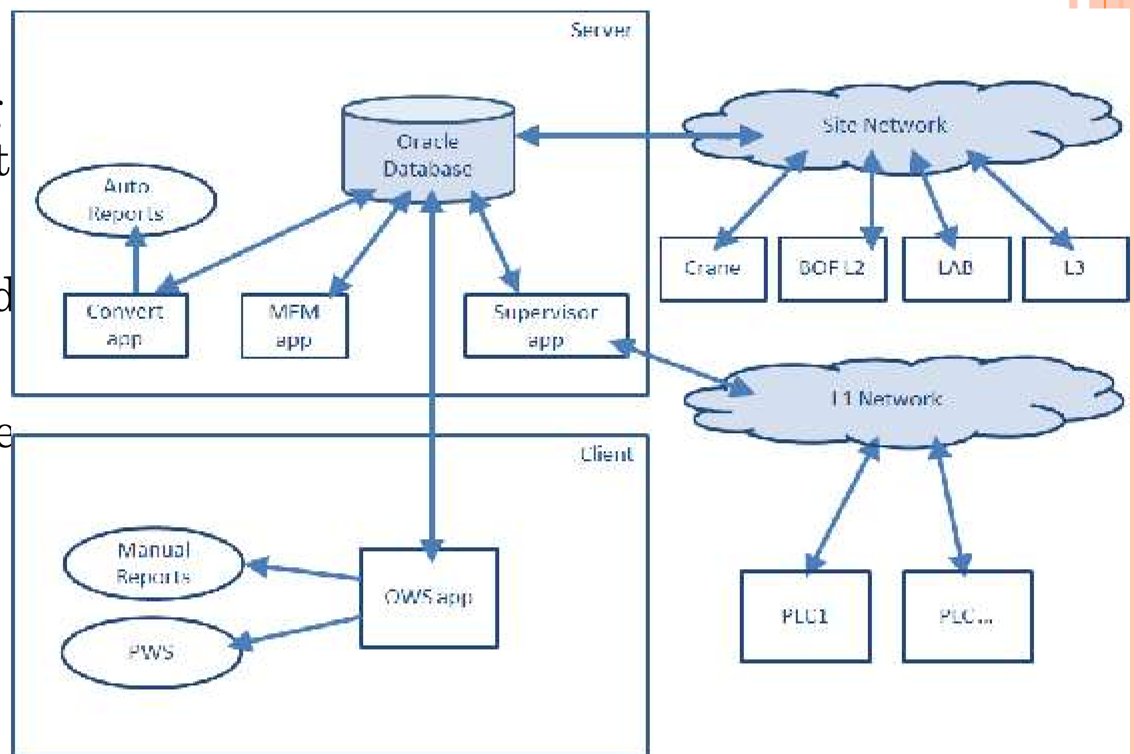
Level-1 and 2 system

<u>The Level system:</u>

Level-1 consists of measuring HMI interaction on comput

Level-2 collects from and send data to other systems Hardware is a computer serve and 1 client computer per operating station

Level-3 system is a planning system that collects from and sends data to level-2 on production



Level-1 and 2 system

The Level-2 software is made of two main components:

- The Environmental shell
- The Process model (also in level-1)

Environmental Shell:

- HMI for displaying operational info and "adjusting"
- HMI for inputting process settings
- Inventory management
- Data management and reports

Process model:

Input - Material properties (Lime, Mg, CaC_2)
- Heat properties (Weight, Temp., analysis)
- Process settings (Final S, conformance, Lance setpoint, ratio)

Output - Amount Materials needed
- Temperature (Loss)
- Weight Loss

CONCLUSION

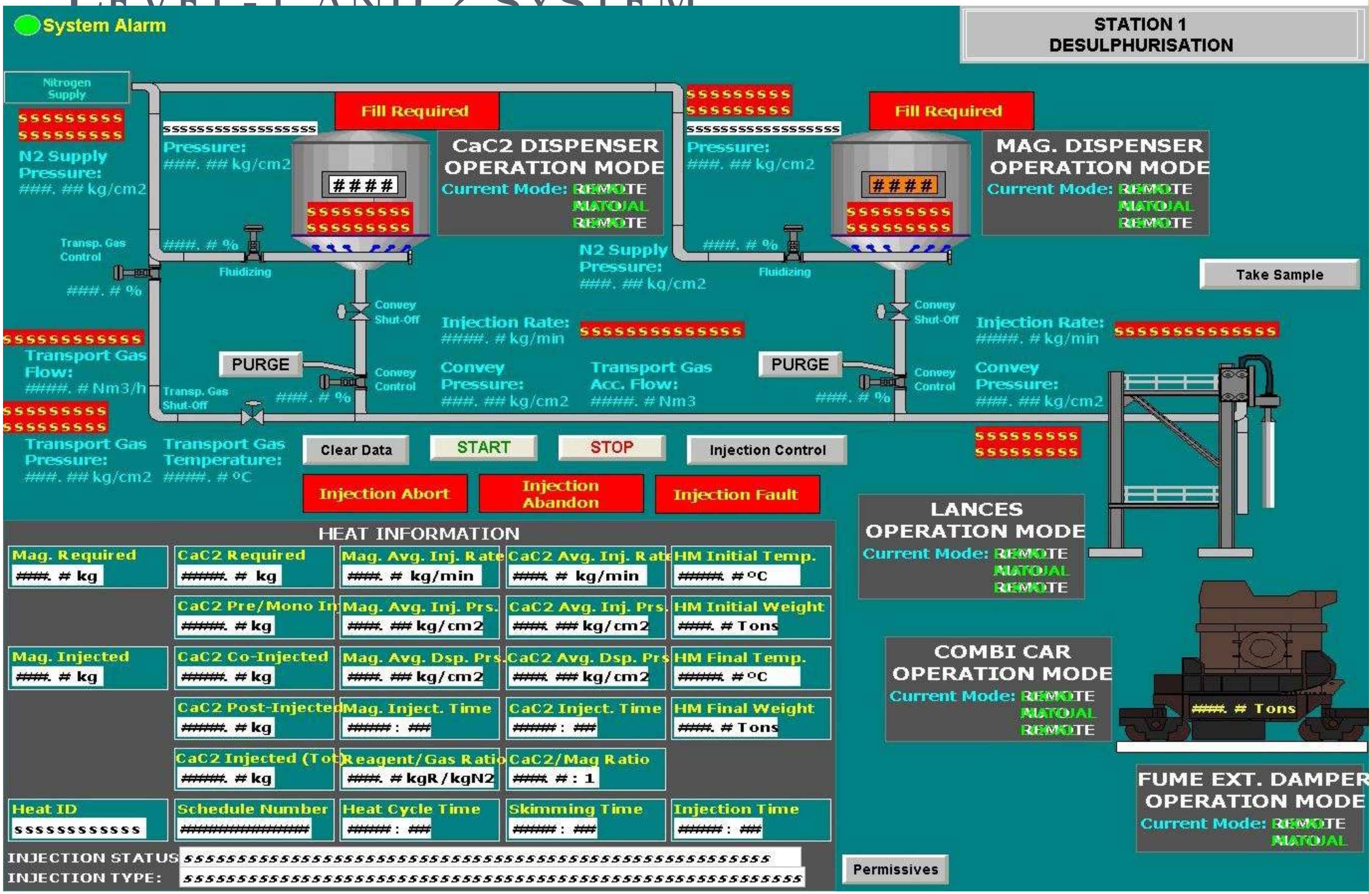
<u>Desulphurization by co-injection:</u>

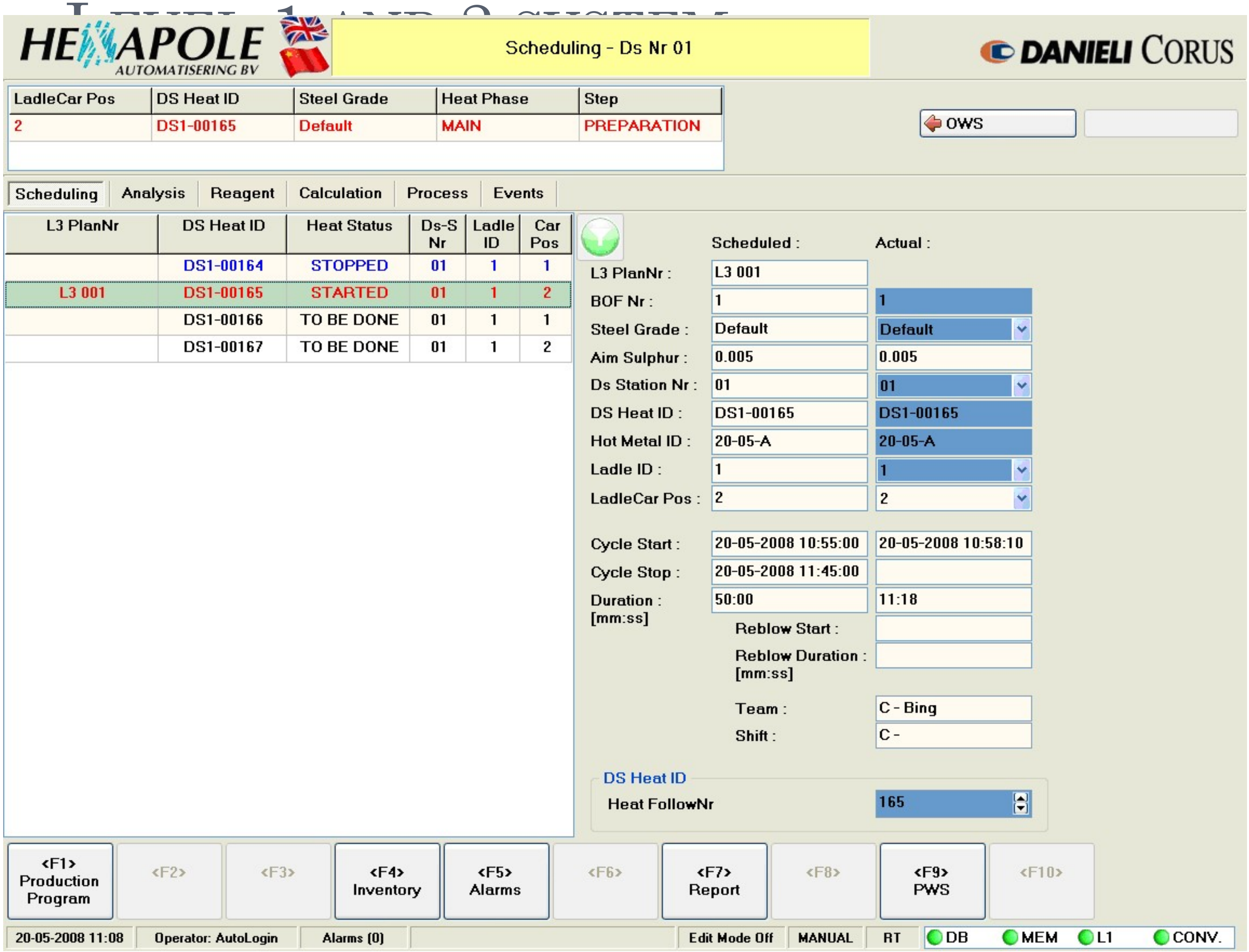
- Excellent hitrate with level-2 system and process model
- Low Nitrogen and Energy consumption
- Small slag amount
- Low Temperature loss
- Flexible layout due to pneumatic transport
- Smaller ladles required per ton Hot Metal/Less freeboard
- Easy and fast to replace injection lance
- Fast desulphurization process
- Flexible reagent ratio and rate
- Very cost effective process

Therefore it can be concluded coinjection is a superior process to KR.

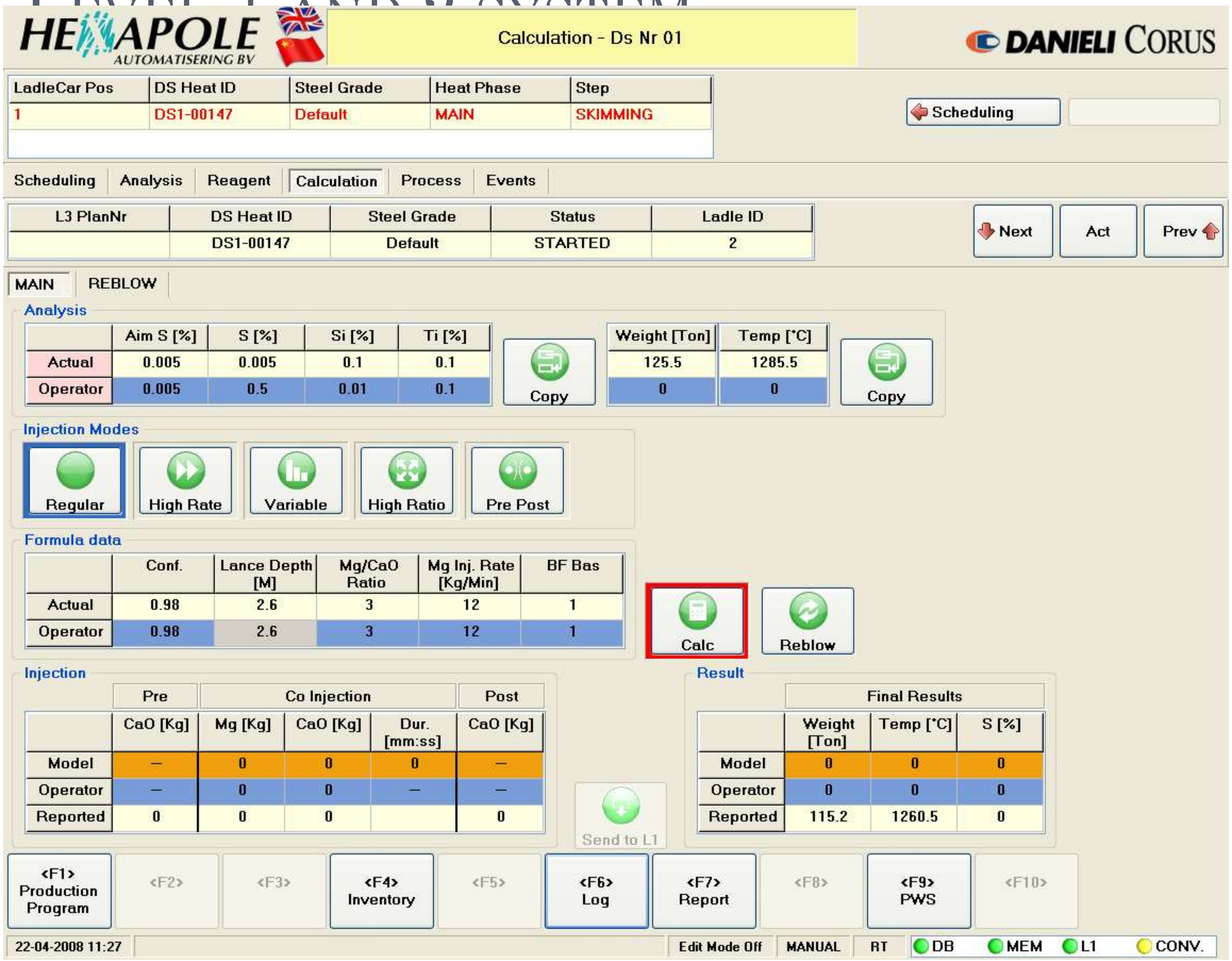
Danieli Corus supplied over 38 desulphurization stations all

Level-1 and 2 system



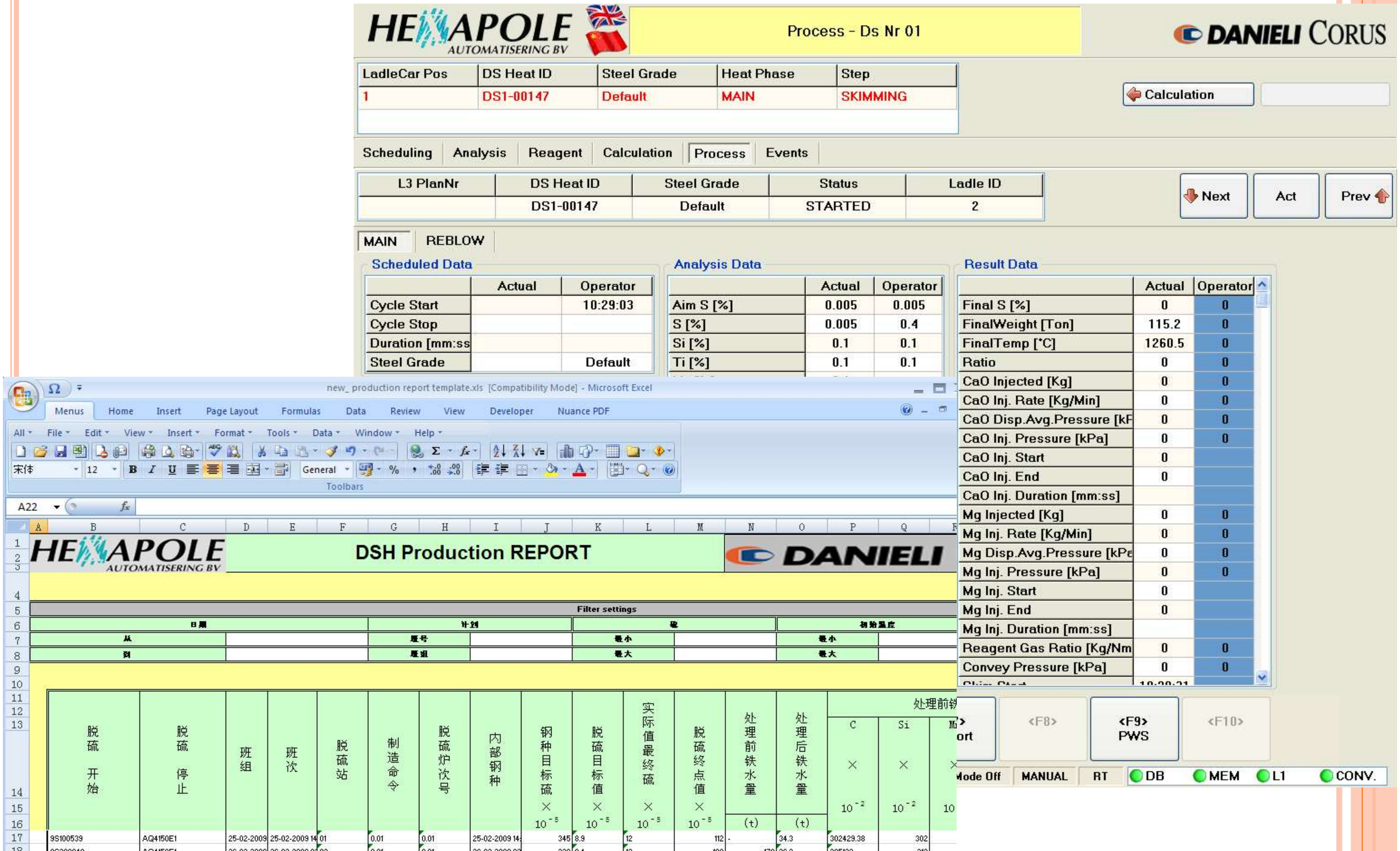

HEXAPOLE AUTOMATISERING BV
Scheduling - Ds Nr 01
DANIELI CORUS
LadleCar Pos | DS Heat ID | Steel Grade | Heat Phase | Step
2 | DS1-00165 | Default | MAIN | PREPARATION
OWS
Scheduling
Analysis
Reagent
Calculation
Process
Events
L3 PlanNr | DS Heat ID | Heat Status | Ds-S Nr | Ladle ID | Car Pos
DS1-00164 | STOPPED | 01 | 1 | 1
L3 001 | DS1-00165 | STARTED | 01 | 1 | 2
DS1-00166 | TO BE DONE | 01 | 1 | 1
DS1-00167 | TO BE DONE | 01 | 1 | 2
Scheduled :
Actual :
L3 PlanNr : L3 001
BOF Nr : 1 1
Steel Grade : Default Default
Aim Sulphur : 0.005 0.005
Ds Station Nr : 01 01
DS Heat ID : DS1-00165 DS1-00165
Hot Metal ID : 20-05-A 20-05-A
Ladle ID : 1 1
LadleCar Pos : 2 2
Cycle Start : 20-05-2008 10:55:00 20-05-2008 10:58:10
Cycle Stop : 20-05-2008 11:45:00
Duration : [mm:ss] 50:00 11:18
Reblow Start :
Reblow Duration : [mm:ss]
Team : C - Bing
Shift : C -
DS Heat ID
Heat FollowNr 165
<F1> Production Program
<F2>
<F3>
<F4> Inventory
<F5> Alarms
<F6>
<F7> Report
<F8>
<F9> PWS
<F10>
20-05-2008 11:08
Operator: AutoLogin
Alarms (0)
Edit Mode Off
MANUAL
RT
DB
MEM
L1
CONV.

Level 1 and 2 system



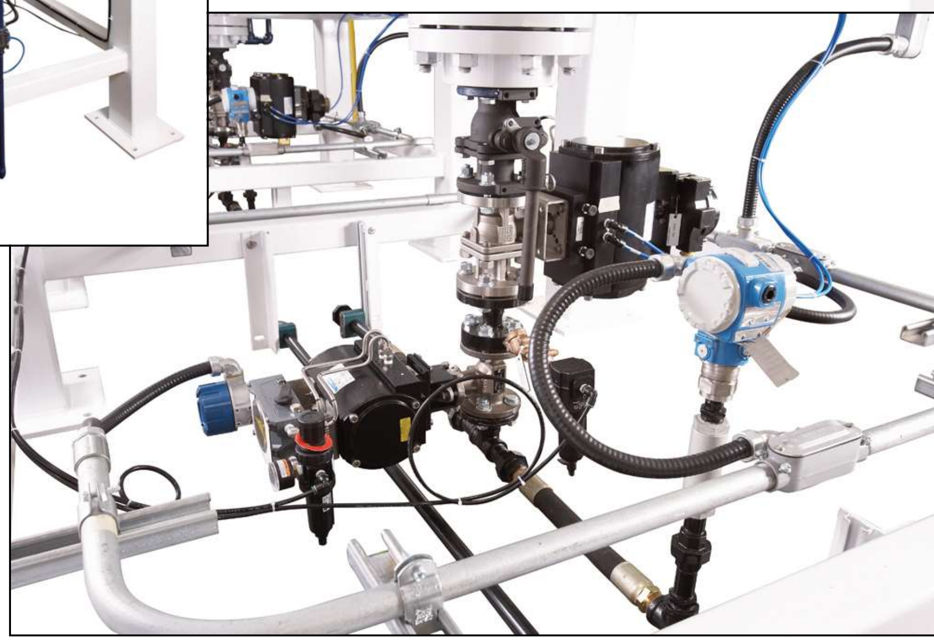
SCREENSHOTS (PROCESS DATA)

Screenshot Level-2 Process data and Reports



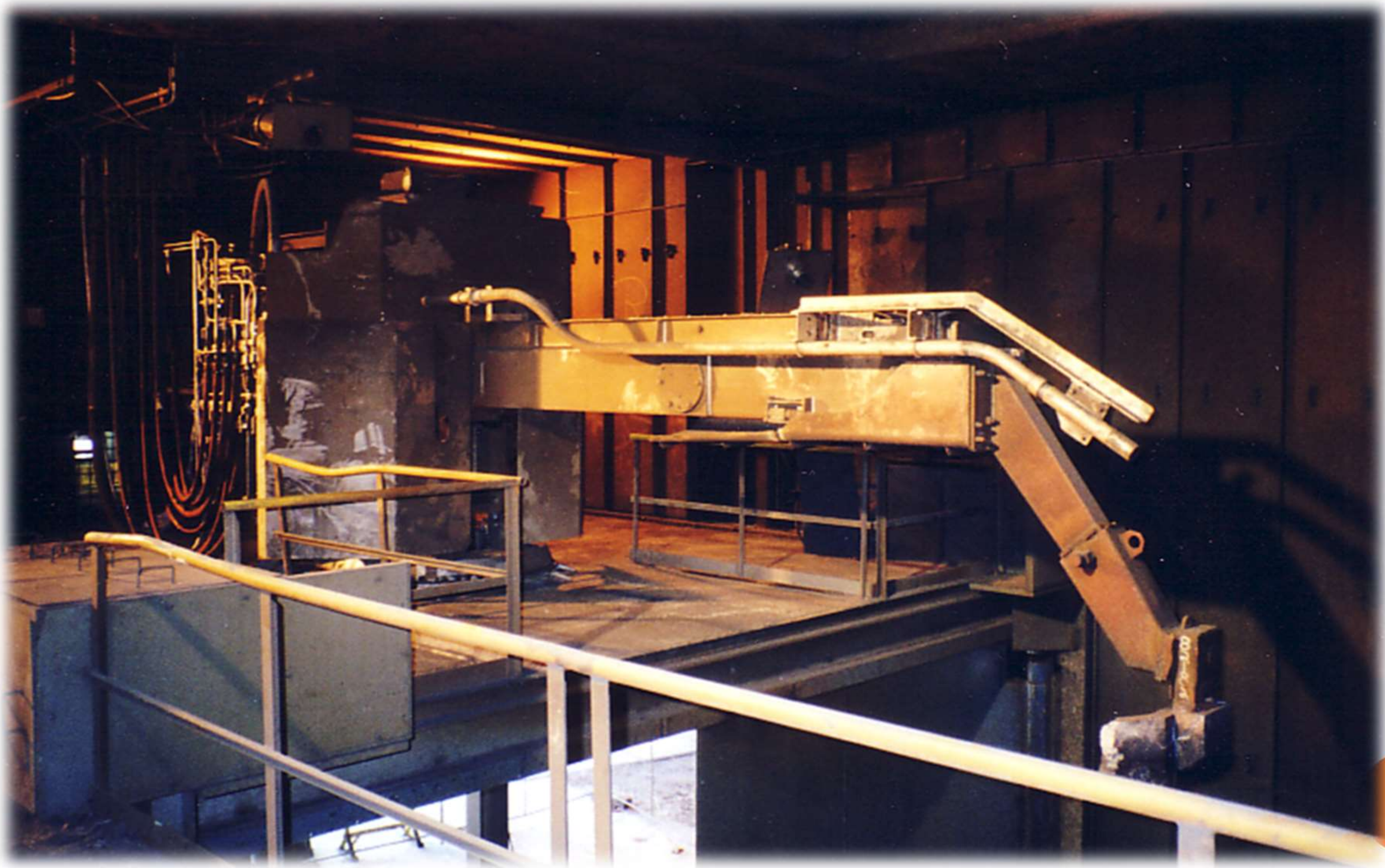
Reagent Storage Silos

Dispensers



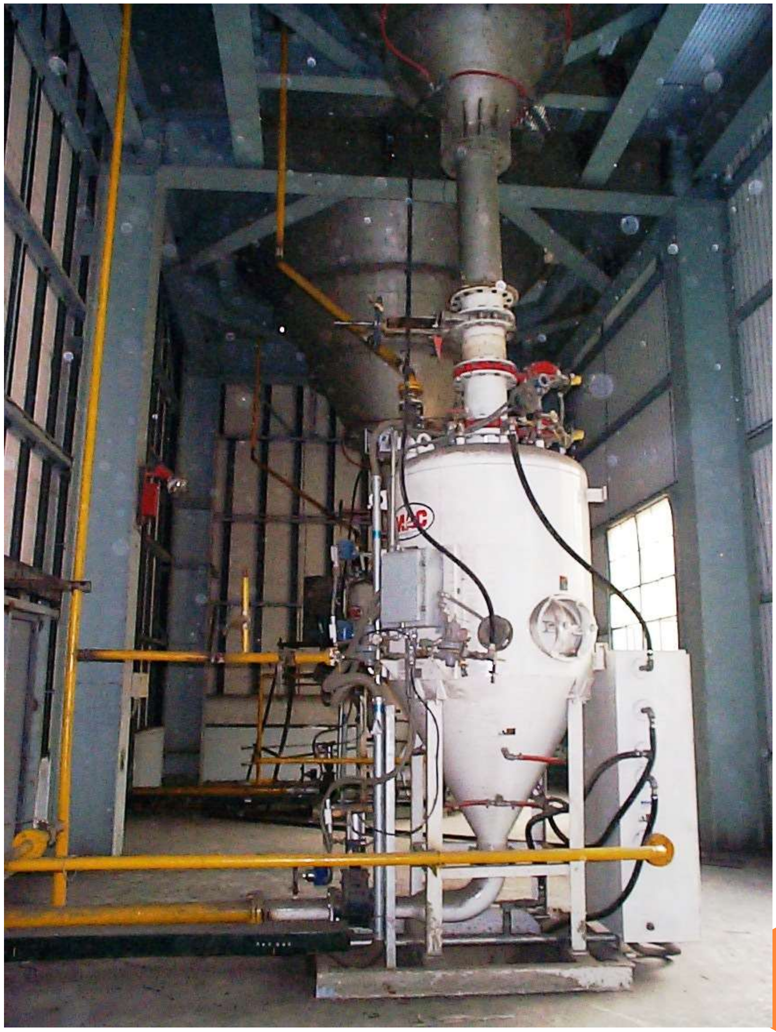
Control room

Slag Skimmer



Slag Skimmer

Injection lance and Transporter



Lances and transfer car

Questions?

“Technological Development of External Hot Metal Desulphurization in India”

Samiksha Saxena, Animesh Sengupta, Jayanta Roy, Amitava Baksi

National Seminar on Desulphurization of hot metal & utilization of torpedo.
18th -19th Novemver 2011 , Bokaro

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CONTENTS

1. Introduction
2. Advantages of External DS
3. HMDS Technology
4. Changing trends of HMDS in India
5. Conclusion

Introduction

- Indian Steel industry is witnessing significant growth
- Day by day demand of quality steel is growing
- With the scarcity of good quality coking coal, external desulphurization will play an important role for producing quality steel
- Presently ~ 20% hot metal in India is desulphurised through external DS route
- Expected Growth: 30-35 % hot metal in India will be treated through external DS by 2013-14
- Several developments have taken place in the area of external DS during the last decade in ISPs & MSPs

Advantages of External DS

- **Reduces constraints in Raw Material selection for Blast Furnace Operations**
  S in Coke, fluxes, ores

- **Improves Blast Furnace Productivity**

- **In Steel Making**

- Allows use of cheaper scrap
- Lower Flux rate – higher scrap charge
- Consistent 'S' - high strike rate in Steel Making
- Improve Caster Speed

- **Ensures Lower S in Products**

- **Helps in Overall Cost Reduction**

HMDS TECHNOLOGY

Typical Steel making Route

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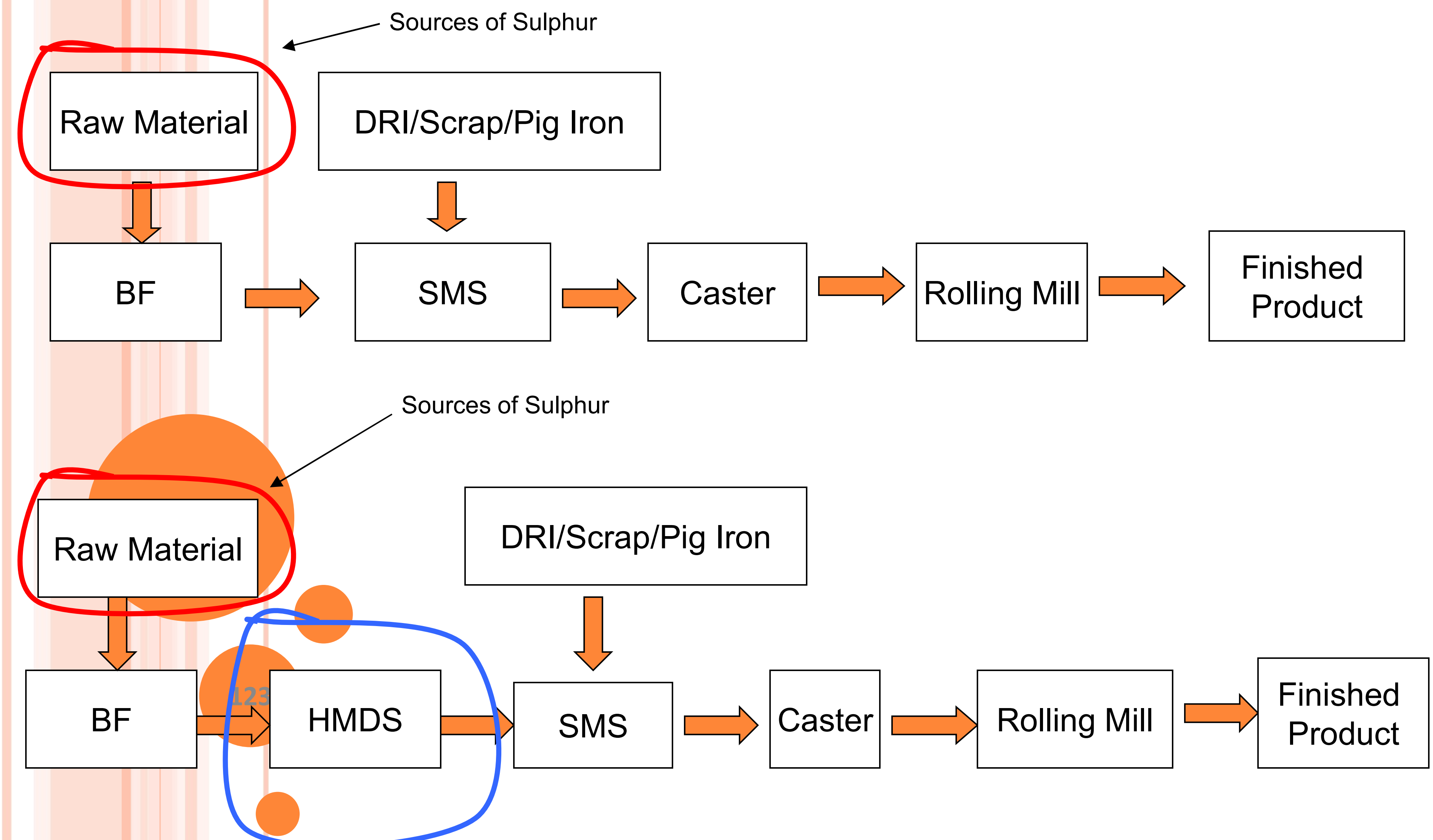

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SELECTION OF DS COMPOUNDS

Desulphurising Compounds (DCs)

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- Magnesium based Desulphurising Compounds (MAGs)
- Calcium Carbide based Desulphurising Compounds (CADs)
- Fluidised Lime (Jet Lime)

Additives

- Slag Conditioners
- Hydrocarbons

Indexed Cost

MAG : CAD : Jet Lime = 10 : 3 : 1

Magnesium Based DC

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$$Mg + S \longrightarrow (MgS)$$

- Gas/Liquid reaction
- Solubility loss at low ‘S’ levels $\leq$ 0.012% and high temperatures
- Used as passivated granules
- Generally not used as single reagent

Advantages	Disadvantages
▪ Low consumption rate ▪ Low injection time ▪ Low slag volume & therefore low iron losses	▪ High Cost ▪ Low melting (650^{o} C) & Vapourising Temp (1105^{o} C) ▪ Not suitable at high HM temperatures ▪ More liquid slag, difficult to skim

Calcium Carbide Based DC

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$$CaC_2 + S \rightarrow (CaS) + 2C$$

High melting point of CaC_2

-Solid/liquid reaction

-S removal thro' diffusion process

-Requires bath agitation & dispersed carbide particles

Advantages	Disadvantages
▪ Cost effective & efficient ▪ Exothermic reaction; low temperature loss in DS ▪ Can be used as single reagent	▪ Fire & explosion risk if not handled with care ▪ Low efficiency at HM temp $<1250^{o}$ C

Fluidized Lime

CaO + S → (CaS) + O

- Characteristic of progressive reduction in rate of DS due to increased oxygen activity

Advantages	Disadvantages
▪ Low material cost ▪ Available locally	▪ Large Slag volume ▪ High Iron Losses ▪ Lower efficiency at HM temp <1350° C ▪ Fresh, reactive and soft burnt required ▪ Loss in HM temperature

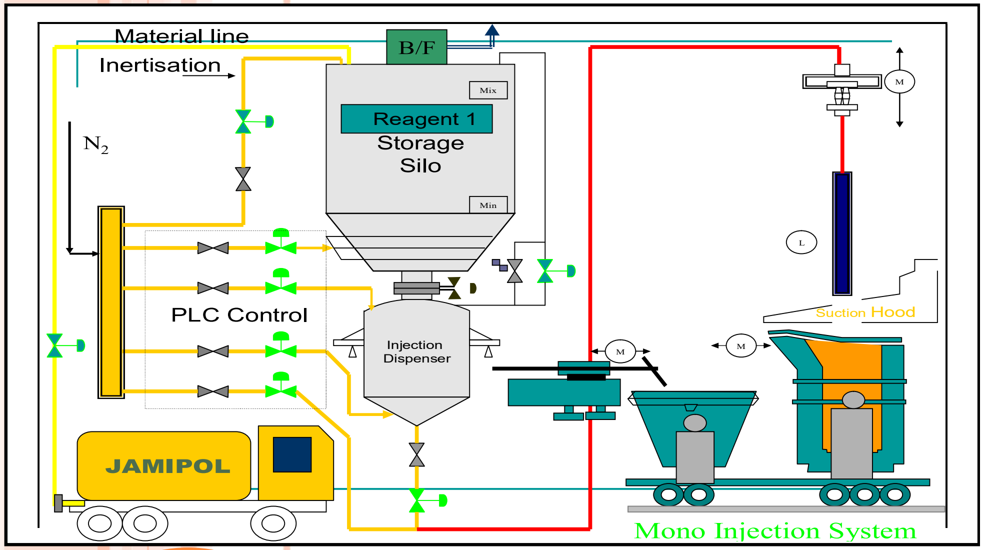
Deep Injection Systems

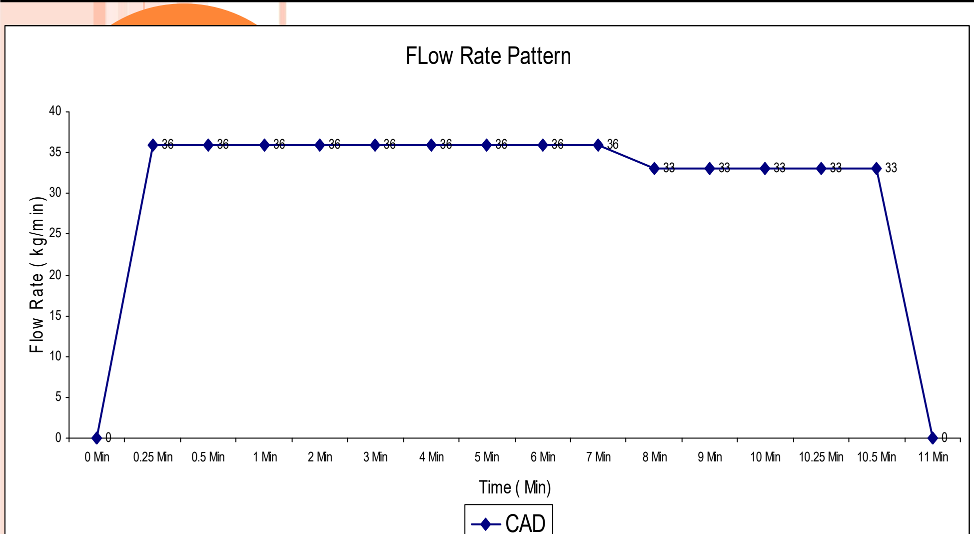
Important Performance Parameters

- Specific Consumption of DS Compound
- Cycle Time
- Temparature loss
- Sulphur reversal
- Metal Loss
- Strike rate
- Lance life

130

Mono Injection System





- Uses single reagent/mixtures
- Low capital and maintenance cost
- Higher injection time
- Simple operation

Mono Injection System

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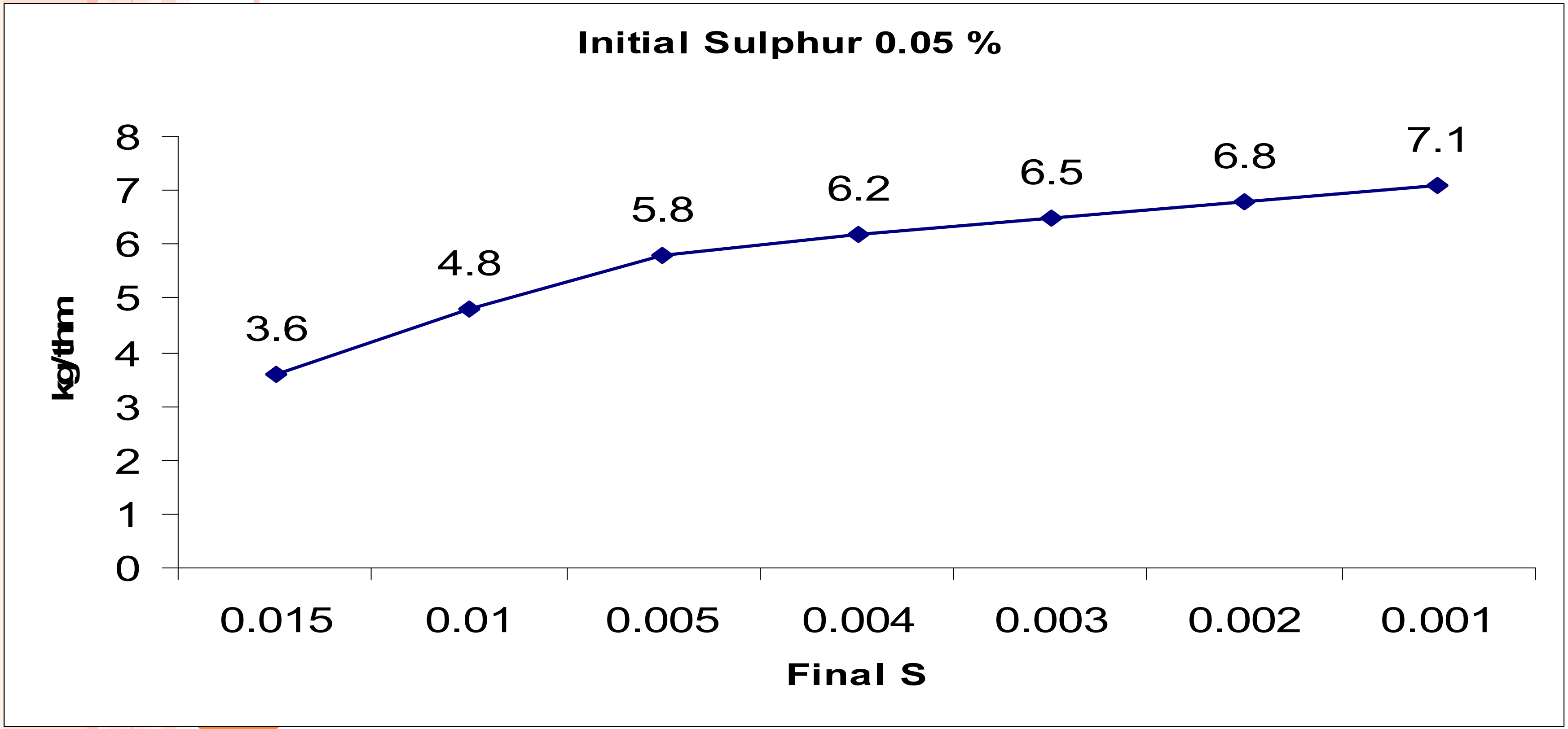
Sp. Consumption of CAD (kg/thm):



Heat Size 140-150 Tons

HM Temp > 1300 Deg C

Mono Injection System

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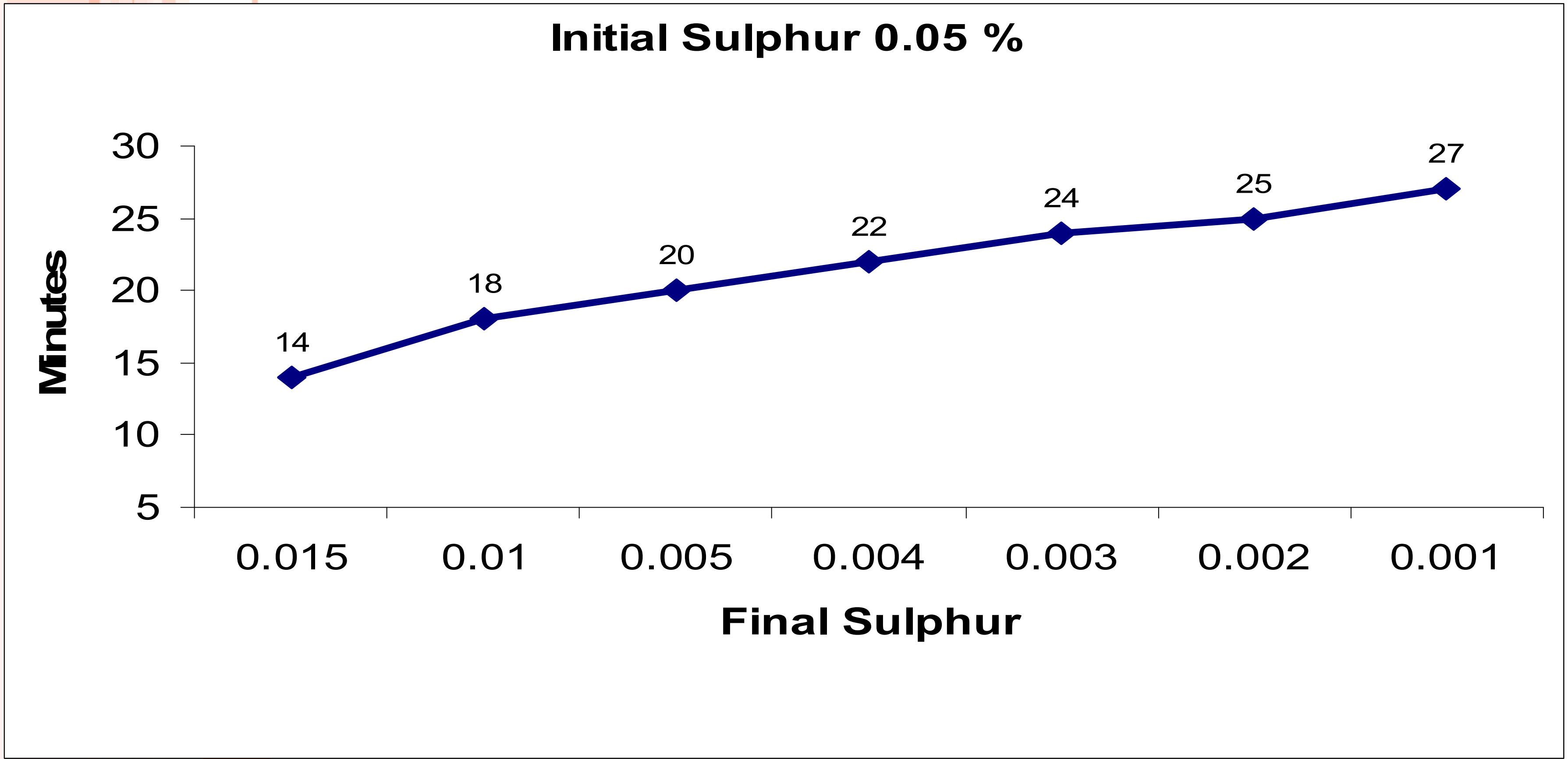
Injection Time :

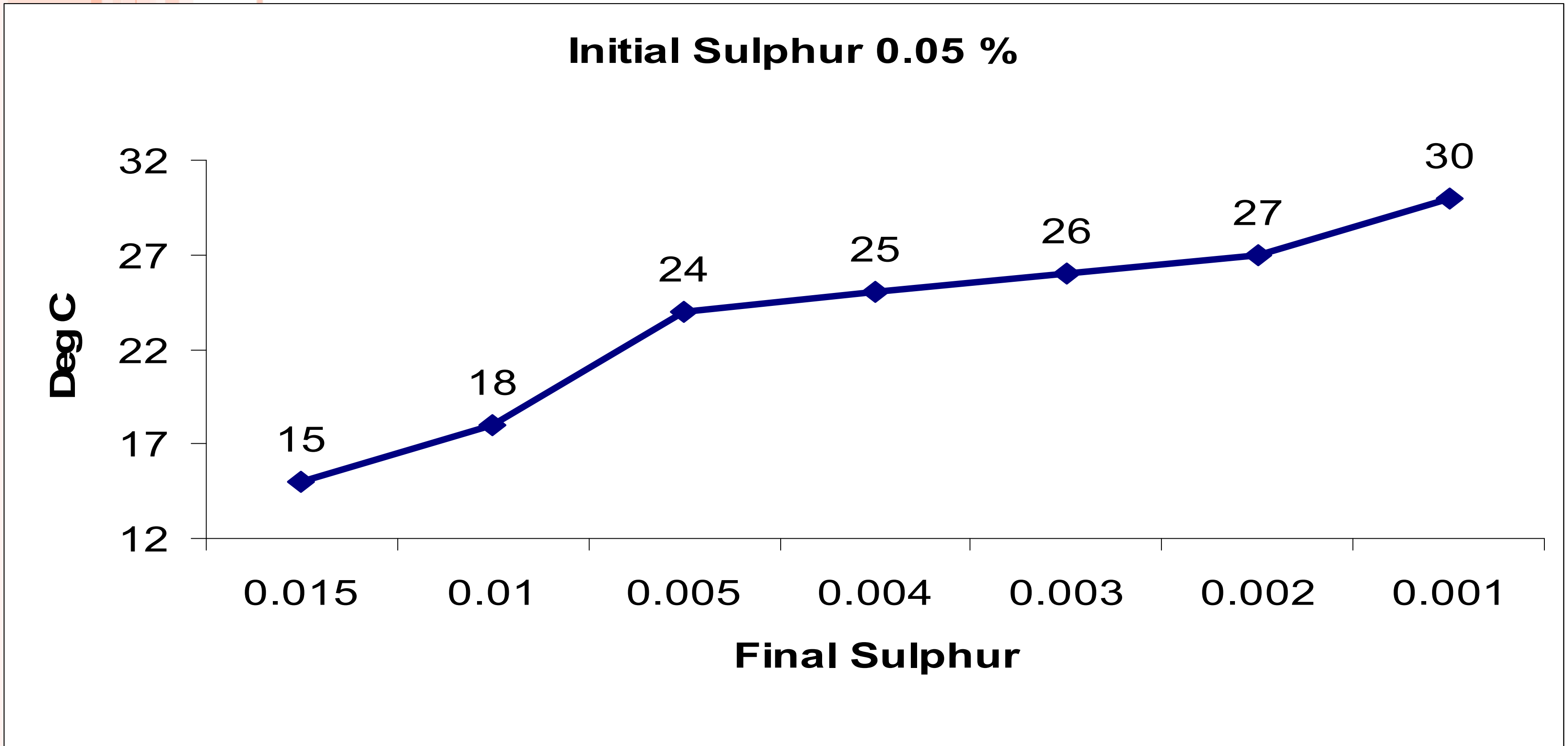


Heat Size 140- 150 Tons

HM Temp > 1300 Deg C

Mono Injection System

Temperature Loss:



Heat Size 140- 150 Tons

HM Temp > 1300 Deg C

Co Injection System

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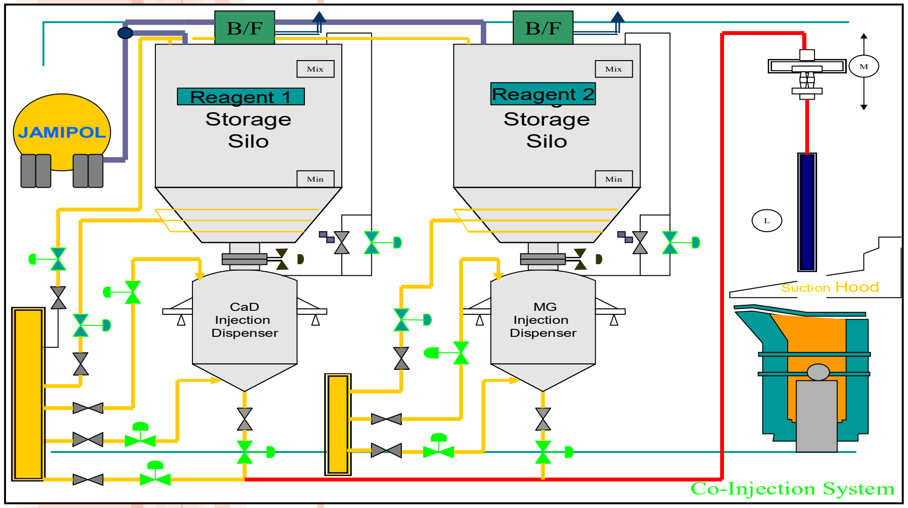
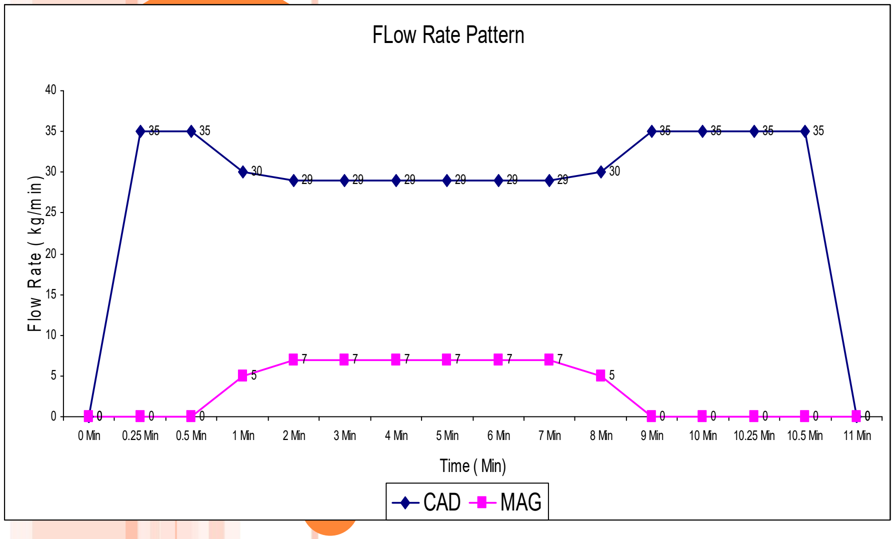
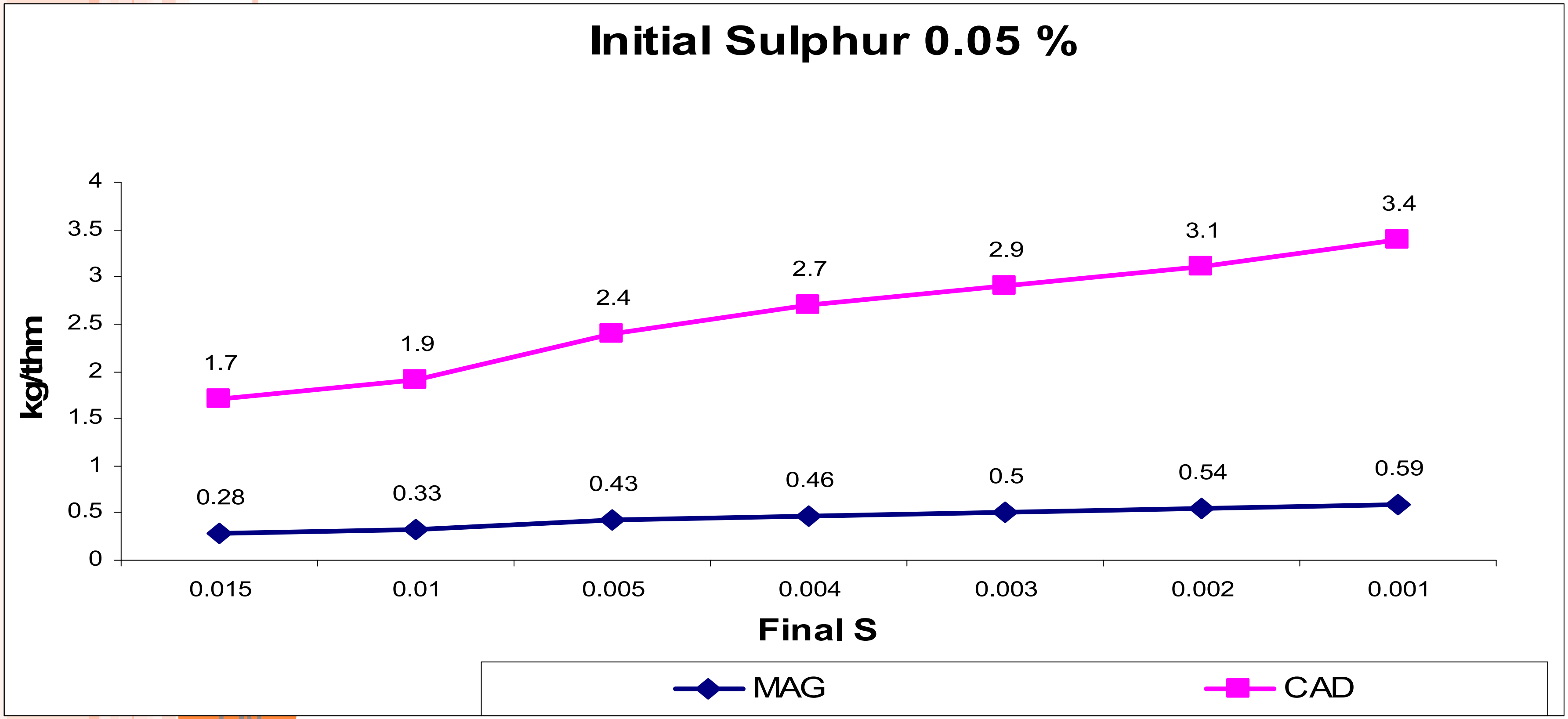




- Facilitates injection of two reagents with variable ratios
- Consistency of injection
- No segregation
- Lower cycle time
- Lower operating cost

Co Injection System

Sp. Consumption of CAD & MAG (kg/thm):



Heat Size 140-150 Tons

HM Temp > 1300 Deg C

Co Injection System

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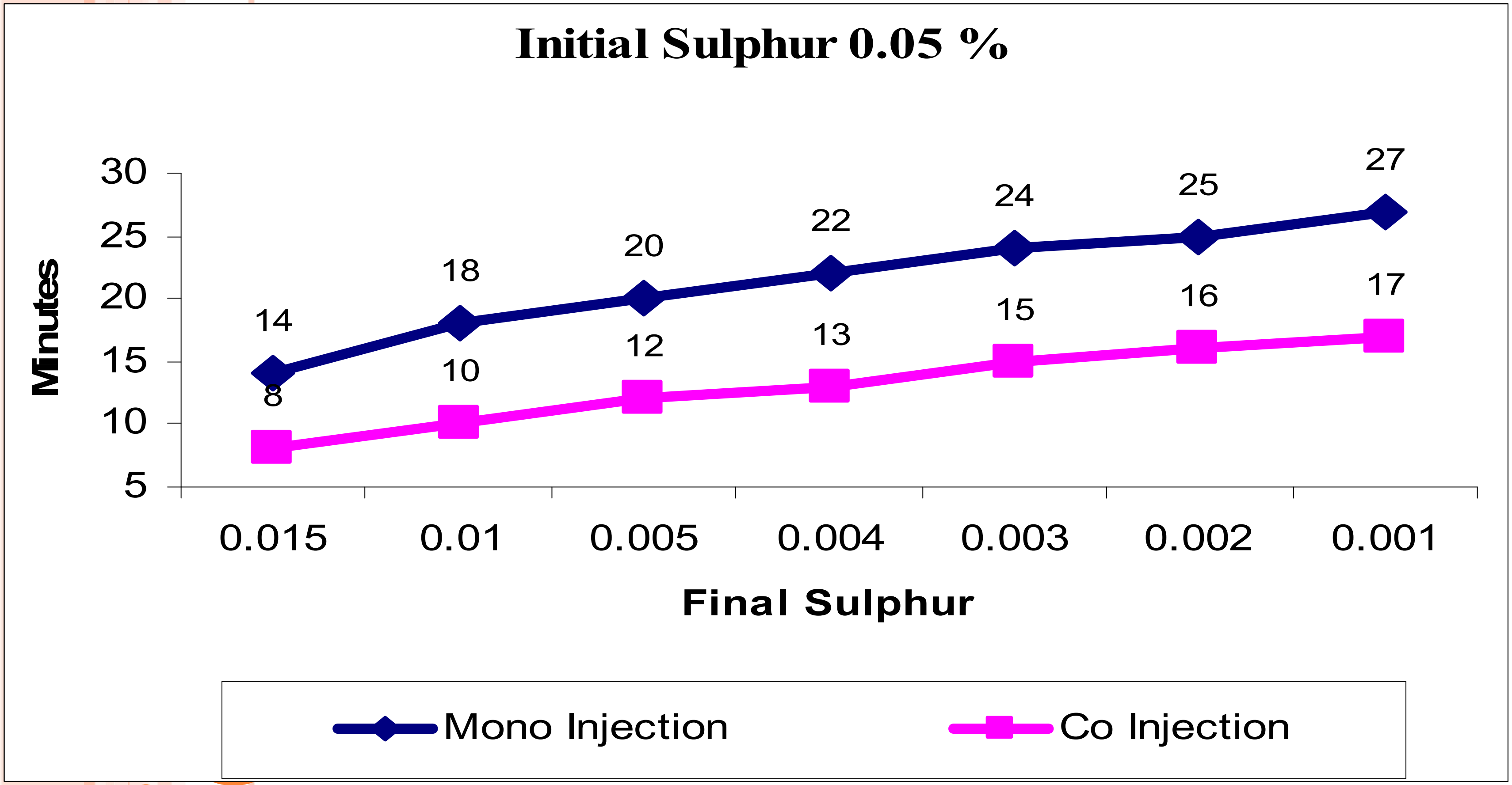
Injection Time :



Heat Size 140-150 Tons

HM Temp > 1300 Deg C

Co Injection System

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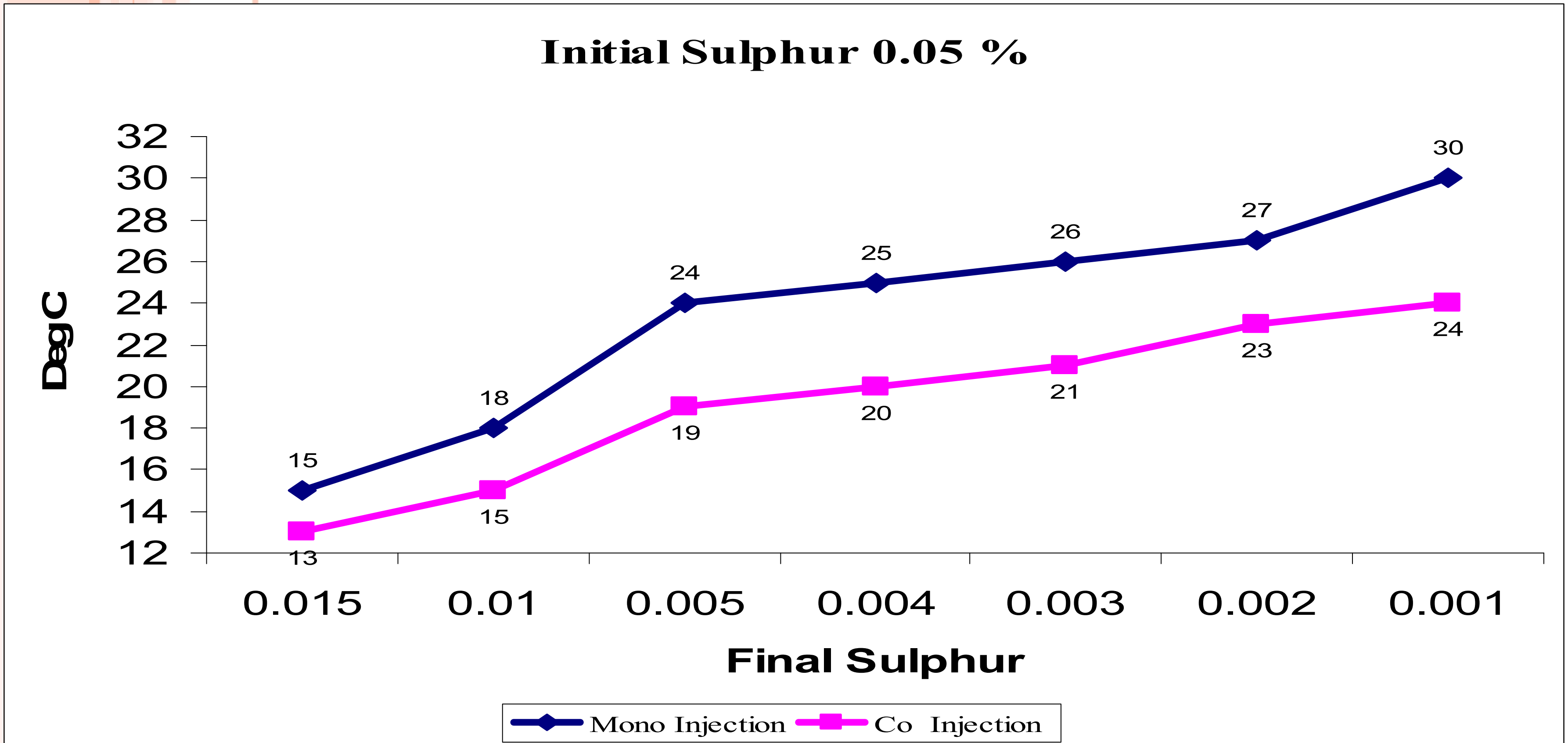
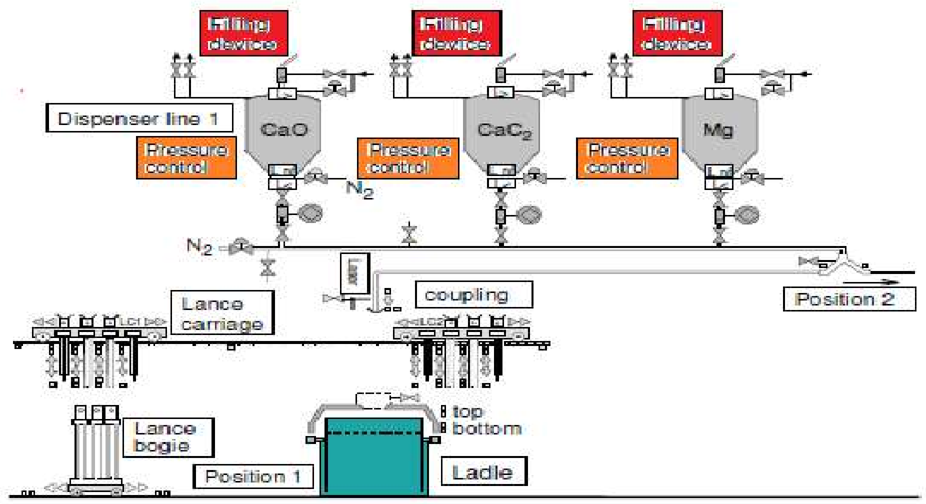
Temperature Loss:

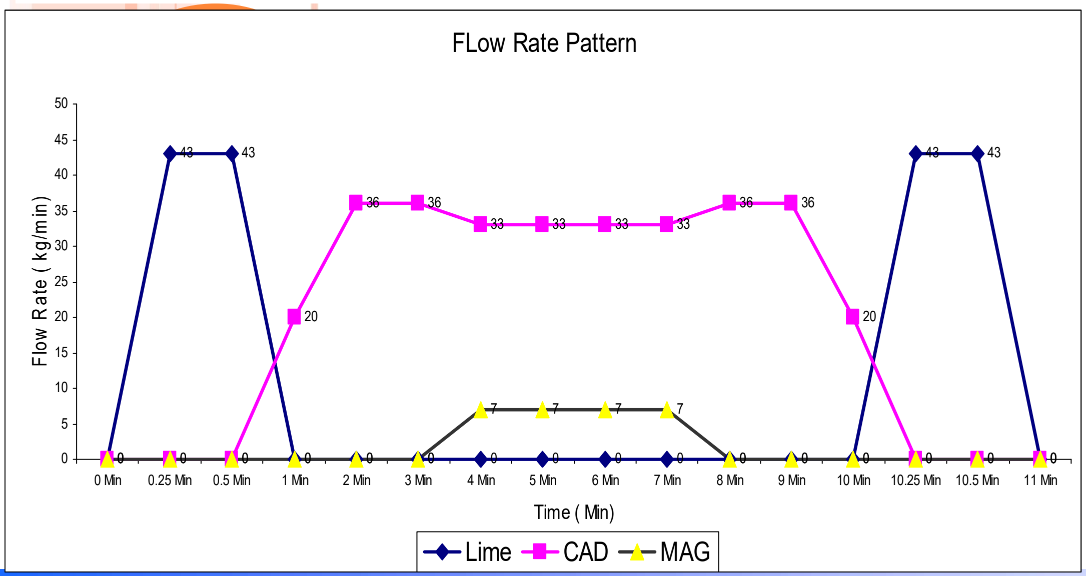


Heat Size : 140-150 Tons

HM Temp > 1300 Deg C

Multi Injection System

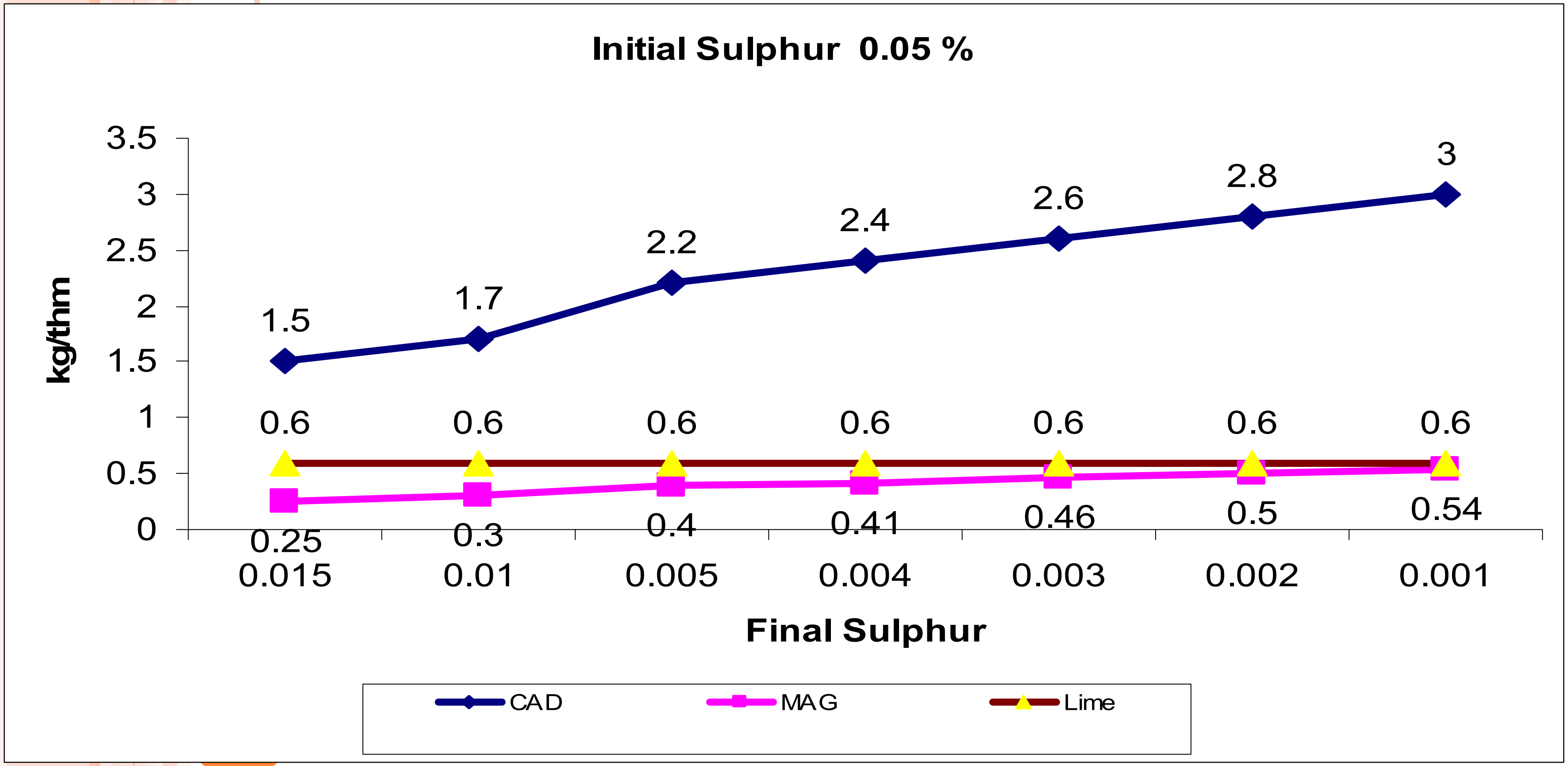




- Facilitates injection of multiple reagents
- Enables injection of slag conditioners
- Reduced operational cost

Multi Injection System

Sp. Consumption of CAD, MAG & Jet Lime:



Heat Size 140 -150 Tons

HM Temp > 1300 Deg C

Multi Injection System

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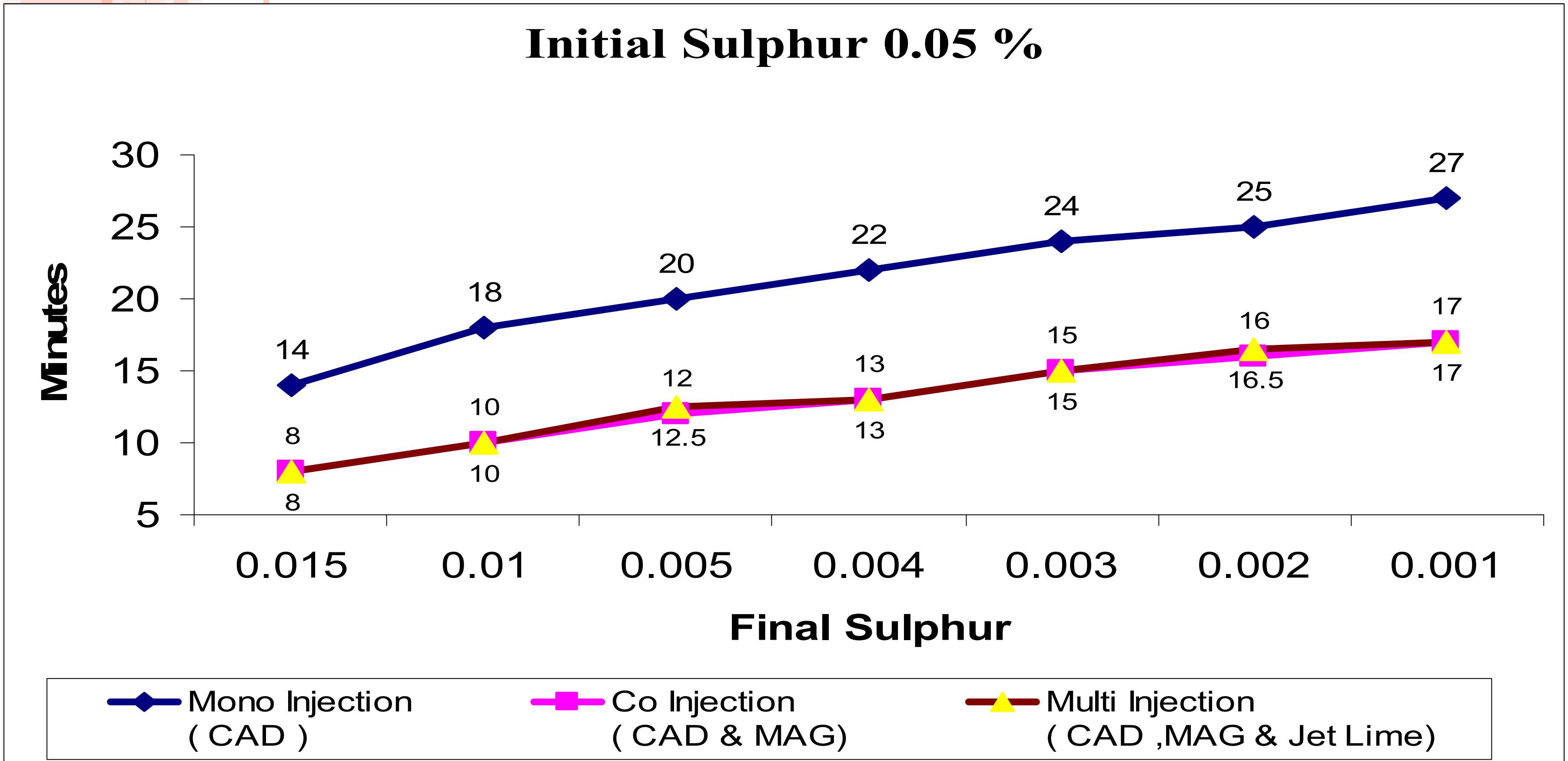
Injection Time :



Heat Size 140 -150 Tons

HM Temp > 1300 Deg C

Multi Injection System

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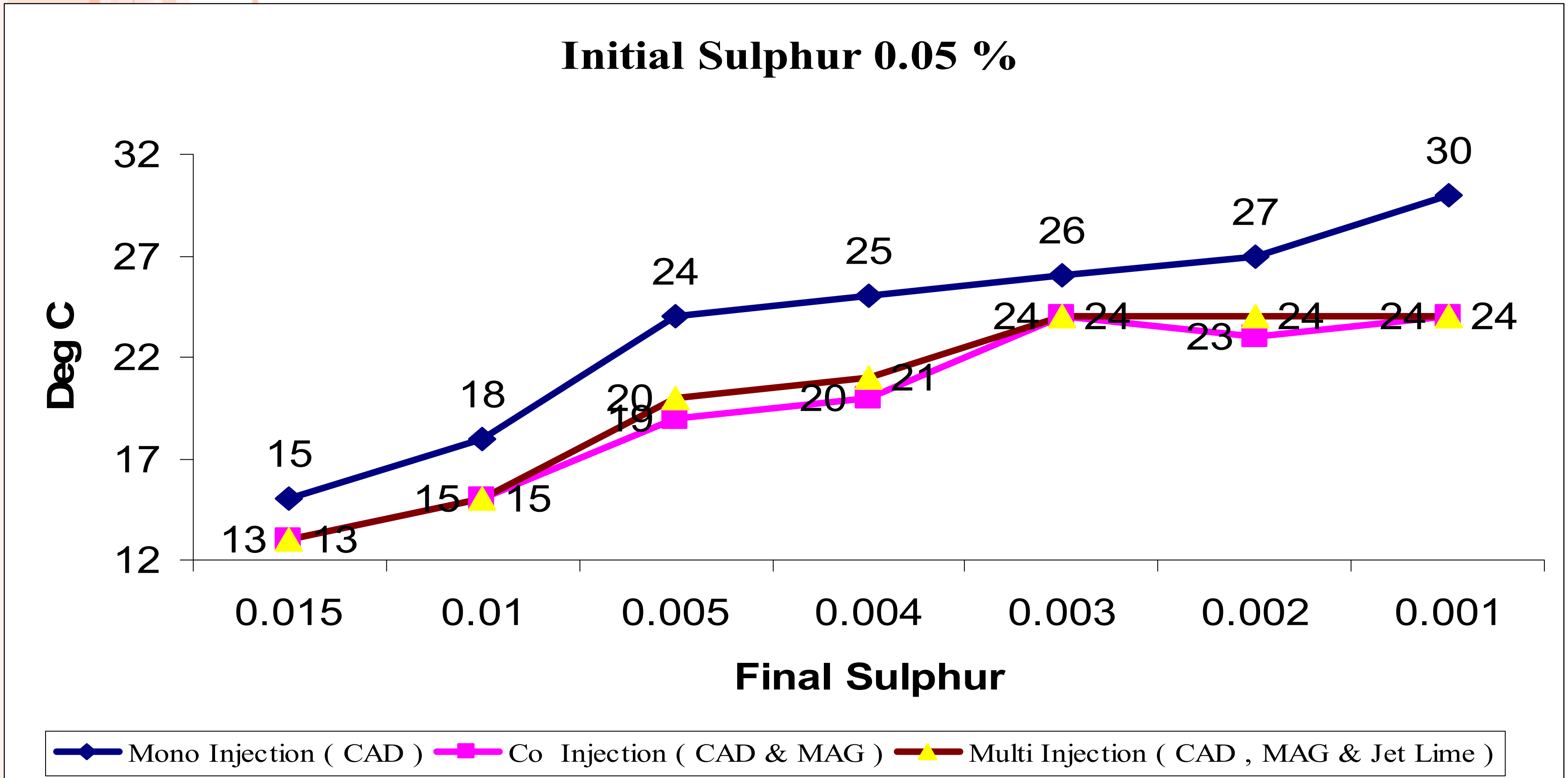
Temperature Loss :



Heat Size 140 -150 Tons

HM Temp > 1300 Deg C

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Comparison of Different Processes

Parameters \ Processes	Mono- injection	Co-injection	Multi injection
Capital cost	Low	Medium	High
Operational cost	High	Low	Low
Operational control	Low	High	High
Cycle time	High	Low	Low
Temperature losses	High	Low	Low
Max compound injected	1	2	>2
Flexible injection ratio	N.A	Yes	Yes
Compounds injected	Majorly carbide , Some places Lime	Carbide – magnesium, lime-magnesium	Carbide- magnesium-lime & slag fluidizers with additives if reqd.
Steel plants in India using injection technology	JSW, Tata Metaliks	Tata Steel, JSW, RSP, BSP	Bhusan Steel, Essar Steel

CHANGING TRENDS OF HMDS IN INDIA

Changing trends of HMDS in India

Future prospects

>2009

2005-2009

1995-2005

>1995

Conclusion

Conclusion

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- The demand for external desulphurization is continuously increasing
- Continuous development in technology to optimize the cost economics of external desulphurisation of Hot metal
- Several different varieties of DS compounds have been developed to address the customised needs of the Steel Plants
- There is a growing interest in external desulphurisation of Hot metal among MBFs
- Developments are in progress to build Low cost DS Stations for MBFs

Thank you

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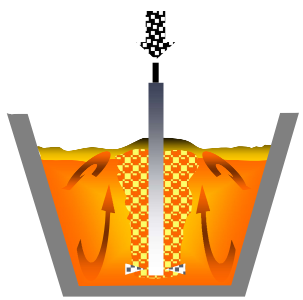
TDSM

Total DS Management

An Innovative Model for External Desulphurisation of Hot Metal



149

18th – 19th November 2011

National Seminar on Desulphurisation of hot metal & utilization of torpedo

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Contents

Introduction

- Hot metal picks up sulphur from various sources during production in blast furnace and corex.
- Sulphur in hotmetal is undesirable element for production of quality steel.
- It can be removed/ reduced at various stages
  - BF / Corex
  - Steel melting furnace
  - External desulphurisation between BF/ Corex to SMS.
- Today External desulphurisation of hot metal has become the most common process in steel industry.

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Two Processes of External Desulphurisation

- *Deep injection process*
- *Stirrer / KR Process*

Deep injection process is the most common process in Indian steel industries.

Requirements of Deep Injection Process

- *DS station plant / equipment- CAPEX Investment*
- *Carrier gas (Pure Nitrogen)- Available with most steel plants.*
- *Electricity – Available with most steel plants.*
- *Reagents – To be procured from the reagent suppliers,*
  - *This needs regular and repeated procurement activities.*
  - *Inventory stock to be maintained.*
  - *Increase OPEX for DS process.*
- *Operating Consumables*
  - *Injection lance,*
  - *Temperature measuring and sampling probes*
  - *Consumables for LECO machines*
- *Additional staff for regular procurement, plant operation and maintenance.*
- *Knowledge of process safety.*

Total DS Management Model

Hot Metal from BF/COREX

→

External Desulphurization under "Total DS Management" program

Outcome :
Desired level of sulphur within agreed cycle time & Cost

→

Sent to Steel Making Unit

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Concept of Total DS Management (TDSM)

Supply of Reagents as per process requirement

Supply of Process Consumables for DS process (Optional)

Deployment of work force for safe operations of DS equipment

Operation of Slag Raking Machines

Operation of torpedo for hot metal pouring

Operation of ladle cars

Routine check up of plant equipment

Identification & reporting of Problem /Breakdown

The responsibility excludes
EOT Cranes & HEME operations & Maintenance of equipment

OPERATION SEQUENCE AT DS STATION

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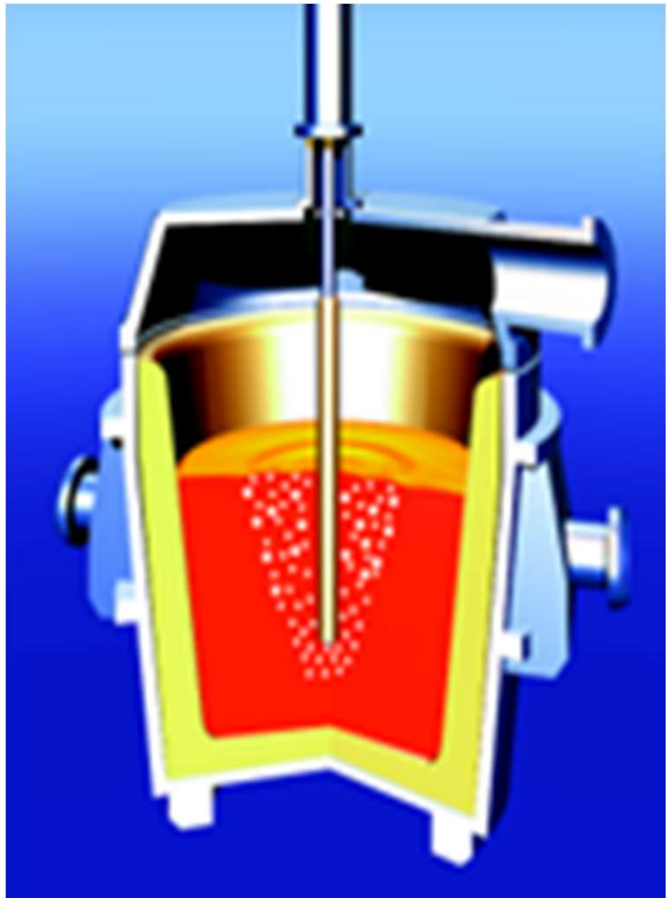
- Receiving Torpedo and Pouring Hot metal in Ladle on Transfer Car
- Temperature measuring & Sampling
- Positioning of Ladle Transfer Car to DS Station
- Sulphur Analysis
- Set Process Parameters
- **Start injection & monitor Process Parameter**
- Position Ladle for De slagging
- Sampling & Temperature Measuring
- Slag raking
- Sulphur Analysis
- Deliver desulphurised hot metal to SMS



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TDSM Model

- *This model has been developed by JAMIPOL for "Total DS Management" in steel plants.*
- *Under this model*
  - *JAMIPOL takes total responsibility of HMDS operation and delivers desired level of sulphur in hot metal to the customer for further processing.*
  - *JAMIPOL deploys it's own competent operating personnel and ensure proper utilisation of plant and equipment.*
  - *JAMIPOL maintains inventory of custom made own reagents for the DS process.*
  - *Injection lance and temp measuring cum sampling probes are also procured and stock maintained by JAMIPOL for the DS operation.*
  - *Plant maintenance is done by the common maintenance team of the customer.*
- *Customer pays the fixed amount to JAMIPOL @ per point sulphur drop in hot metal.*

Cost to customer under TDSM Model

Payments for the given billing periods are made by the customer in two parts

- *Cost of Reagent & Consumables @ R1x total sulphur points dropped in hot metal during the billing period*
- *Cost of services @ R2 for total sulphur points dropped in hot metal during the same billing period.*
- *No any other payment is made by the customer.* 158

Benefits of Total DS Management to steel plants

- *Guaranteed sulphur level in hot metal*
- *Improved Strike Rate*
- *Reduced Specific DS Cost*
- *No inventory cost of reagents*
- *No inventory cost of Lance, Combo/ Chiller probes and LECO Consumables.*
- *No additional work force for HMDS plant operation.*
- *Proper utilisation of plant and equipment*

Role of JAMIPOL in Total DS Management

- *JAMIPOL is the only company who provides total DS solution to the steel plants for external deulphurisation of hot metal.*
- *It has competent technical team for system and equipment design.*
- *JAMIPOL has designed and developed a DS station for ladle size <60T. The plant was successfully commissioned in 2007.*
- *It has two strategically located reagent manufacturing plants to manufacture and supply desired quantity of reagent on time.*
- *Technology team is also competent and backed up by world leader SKW, Germany.*
- *JAMIPOL has already started working with* ***ESSAR Steel Hazira*** *and* ***Bhushan Steel Angul*** *as per this program.*

Conclusion

With external DS facility it has been possible for the steelmakers to utilize the raw materials of whatever quality they have and then transform these to the desirable low sulphur steel products.

Now it is time for the DS compounds suppliers to become integral stakeholders with the Steelmakers in providing solution not only in the form of compounds but also in the development and running of the DS stations. The success of external desulphurization is driven by interference of machine, men, material and method related philosophies which need to update with the course of time.

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Thank You

THERMODYNAMIC AND KINETIC ASPECTS OF DESULPHURISATION IN HOT METAL

PRESENTED BY
SHRESHTHA KARMAKAR,
FINAL YEAR,
METALLURGICAL AND MATERIALS ENGG. DEPT,
NIT, DURGAPUR.

IMPORTANCE OF STEEL

- Iron and Steel Industry is the foundation of development
- Per capita consumption in the world is 200 kg while in India it is 50 kg
- Steel produced by oxygen steel making and electric steel making
- Quality is affected by the phosphorus and sulphur content

SULPHUR IN STEEL

- Sulphur causes hot shotness
- Primary source of sulphur is the coke ash containing iron sulphide, calcium sulphide and also organic sulphur.
- Ore has a little iron sulphide while fluxes has sulphides and sulphates.
- Desulphurisation is carried out in blast furnace, during pre-treatment of HM and secondary steel making.

SULPHUR REACTIONS

- The sulphur in coke ash undergoes the following reactions in the raceway:

$$CaS_{(\text{in coke ash})} + SiO(g) \text{ ----> } CaO + SiS(g)$$

$$FeS_{(\text{in coke ash})} + SiO(g) + C(s) \text{ ----> } SiS(g) + CO(g) + [Fe]$$

- In the bosh and belly regions, SiS decomposes as

$$SiS(g) \text{ ----> } [Si] + [S]_{metal}$$

- Sulphur absorbed by the slag by

$$SiS\ (g) + (MO) + CaO \rightarrow (SiO_2) + (CaS)_{slag} + M$$

Refer to Ironmaking and Steelmaking:Ahindra Ghosh & Amit Chatterjee

PARAMETERS FOR LOW SULPHUR HOT METAL

- Basicity and temperature of slag
- Slag bulk
- Contact surface and time

THERMODYNAMIC ASPECTS OF DESULPHURISATION

Slag metal sulphur reaction in the hearth:

$$[S] + (O^{2-}) \rightarrow (S^{2-}) + [O]$$

$$K_1 = (\%S)[\%O]/[\%S](a_{O2-}) \qquad \text{(eqn 1)}$$

$$[Fe] + [O] \rightarrow (FeO)$$

$$K_2 = (\%FeO)/[\%O] \qquad \text{(eqn 2)}$$

$$L_{S(eq)} = (\%S)/[\%S]$$

From eqn 1 and eqn 2

$$L_{S(eq)} = (a_{O2-})/(\%FeO)$$

Refer to
Ironmaking : A.K.Biswas

REMOVAL OF SULPHUR FROM HOT METAL

- An extensive pre-reduction of ore before it reaches the bosh
- Using oxygen enriched blast
- Highly basic and fluid slag by using MgO and low FeO content of bosh slag
- Lower sulphur load by decreasing the coke rate and replacing with hydrocarbon
- Injection of lime powder through the tuyeres or use of lime-bearing coke
- Using Granulated Coal Injection
- Using High Top Pressure and steam injection

SULPHUR REMOVAL DURING PRE TREATMENT OF HOT METAL:

- Soda ash is an effective reagent for desulphurisation

$$Na_2CO_3 + 2[C] + [S] \rightarrow Na_2S + 3CO\ (g)$$

- Injection of calcium carbide with lime, limestone, carbon in argon gas
- Injection of calcium carbide with magnesium granules

SULPHUR REMOVAL IN SECONDARY STEEL MAKING:

- Done in LF by IM
- Injection of desulphurising agents(Ca, Mg, Ca-Si, CaC_2, CaF_2+CaO)
- Cored Wire Feeding

CONCLUSION

- Review of the technological advancements shows the extent of improvement in hot metal quality attainable through systematic implementation of carefully formulated strategy.
- Environmental hazards and power consumption should be carefully considered before implementing any new technology.

IMPROVEMENT IN SLAG SKIMMING EFFICIENCY FOR CaC_2 – MG BASED HOT METAL DE-SULPHURISATION

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Hot Metal De-sulphurisation

Hot Metal De-Sulphurisation
(Two Stages)

↓

Injection of Hot Metal De-Sulphurising Reagents

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Slag Skimming: Removal of De-sulphurised product

Slag Skimming

- Slag skimming is essential for removal of post de-sulphurised slag from ladle
- Post de-sulphurising slag consists of BF slag and reaction product
- Residual slag due to poor skimming re-enter the steel at BOF which will nullify the de-S effort
- Slag skimming is an art and depends upon the operator's 'intuition' and skill
- It is a gravity – driven flow enhancing by mechanical agitation and raking that separates immiscible stratified liquid
- Movement of slag from interior 'remote' slag to ladle lip is prerequisite for good skimming

Slag Conditioner

- The formation of MgO increases the melting point and viscosity of the post de-Sulphurising slag
- Difficult to separate the viscous slag from the HM
- HM gets entrapped within the slag in emulsified form
- Total iron in the post de-S slag can reach 50 – 70%
- Addition of slag conditioning agent improves the fluidity and to reduces the amount of entrapped metal
- Various industrial raw materials can be used as slag conditioner (like CaF_2, K_2O, Na_2O, CaO, Na_2CO_3 etc)
- The composition and quantity of slag conditioning agents needs to be optimized depending upon the slag conditions

Background

- ☼ SMS-II, BSP equipped with two de-S stations based on co-injection of Mg and CaC_2 reagents
- ☼ The injection system has separate dosing systems for the two reagents
- ☼ Injection rate is about 30 kg / min in the ratio of 1:5
- ☼ The average initial HM S is ~ 0.045% (0.025 – 0.07%)
- ☼ The post de-S slag is viscous and difficult to skim out from HM
- ☼ Poor skimming leads to high S reversal (~ 0.01%) in BOF
- ☼ There was a need to improve the post de-S slag fluidity for easy skimming

Plant Trial

- ✶ Modified CaC_2 DS reagent was loaded in the carbide silo and trial of more than 80 heats were carried out
- ✶ The slag skimming procedure and its effectiveness were examined and compared for both kind of reagents
- ✶ Sulphur mapping was carried out to ascertain S content at different stages of steelmaking
- ✶ Slag samples were collected & an estimation was made for metal loss

De-sulphurising Reagents

EXISTING CaC_2 REAGENT

- Reagent composition:
  - Calcium carbide DS reagent
    - CaC_2 (chemical) – 52 ± 2%
    - CaO – rest
    - Grain Size – 85 % min, 63 micron

PROPOSED MODIFICATION IN CaC_2 REAGENT

- Calcium Carbide DS reagent with slag modifier
  - CaC_2 (chemical) – 52 ± 2%
  - Slag Conditioner – 3.5 ± 0.5%
  - Grain Size – 85 % min, 63 micron

Observations

Photograph of Post de-S Slag Sample

Base Period: Metallic & heavier

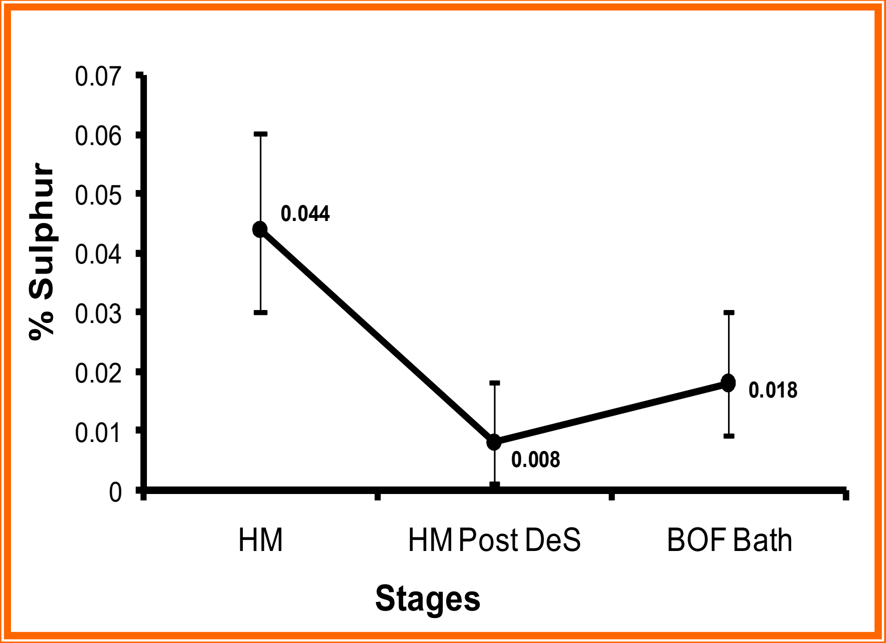
Trial Period: Brittle & light

- Improved slag characteristics results easy removal of slag and thereby improving the slag skimming efficiency & skimming time

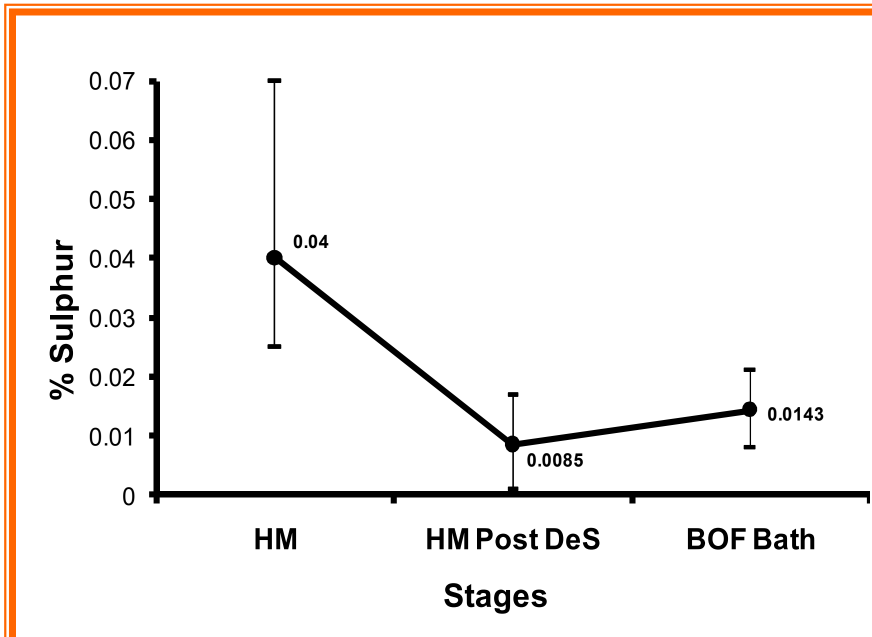
Role of Slag Conditioner

- Concentrated surfactants like O, S
  - Acts as emulsifiers,
  - Promotes wettability,
  - Stabilizes the emulsion and
  - Preventing coagulation to larger drops and separation
- Effective slag conditioner decreases the wetting angle between slag and iron granules & also increase the interfacial tension between hot metal granules
- Therefore, it helps to improve the slag fluidity and to decrease the entrapped metal

Sulphur Mapping

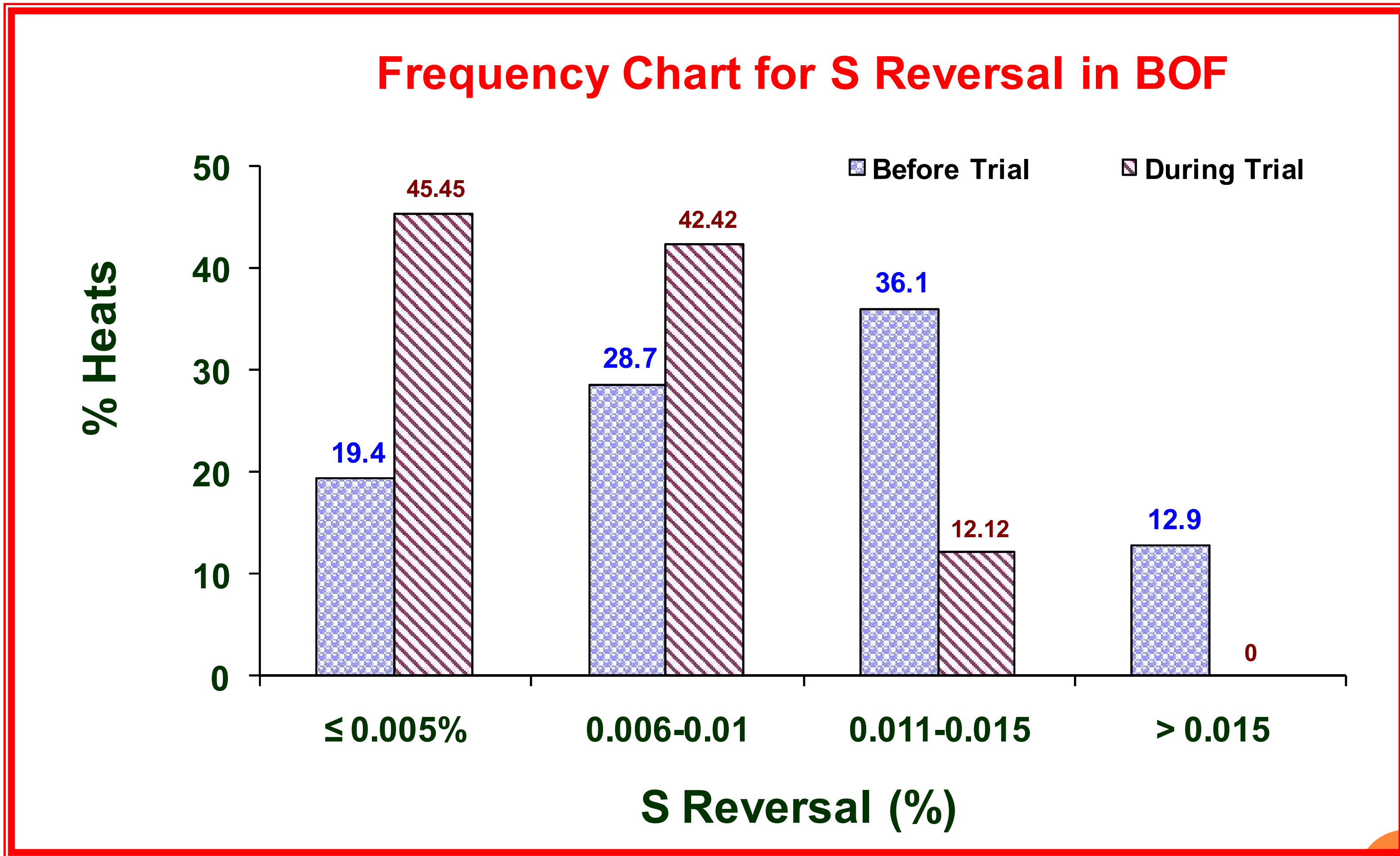


Sulphur mapping from mixer to BOF for base period



Sulphur mapping from mixer to BOF during trial

Analysis & Results



Frequency chart for S reversal from post de-S HM to BOF

Analysis & Results Contd…

Parameters	Base Period	Trial Period
HM Sulphur, %	0.044	0.040
Post De-S S, %	0.008	0.0085
BOF Bath S, %	0.018	0.0143
BOF Reversal, %	0.009	0.006
Post de-S Slag Density, g/cc	4.8 (3.4 – 6.0)	3.7 (2.8 - 5.4)
Entrapped Metal, %	68.6 (34.9 – 86.6)	34.9 (7.2 – 71.8)
Estimated Metal Saving, Kg/ton	-	~ 5

Comparative analysis of de-S parameters

Conclusions

¤ Use of slag conditioner with CaC_2 reagent does not have negative effect on de-sulphurisation efficiency

¤ It helps to improve the post de-S slag characteristics w.r.t. fluidity, amount of entrapped metal & density

¤ Easy removal of slag was noticed thereby improving the slag skimming efficiency and slag skimming time

There is little bit of SAIL in everybody’s life

Thank You

IMPROVEMENTS IN PROCESS TECHNOLOGY FOR EXTERNAL HOT METAL DESULPHURISATION AT RSP

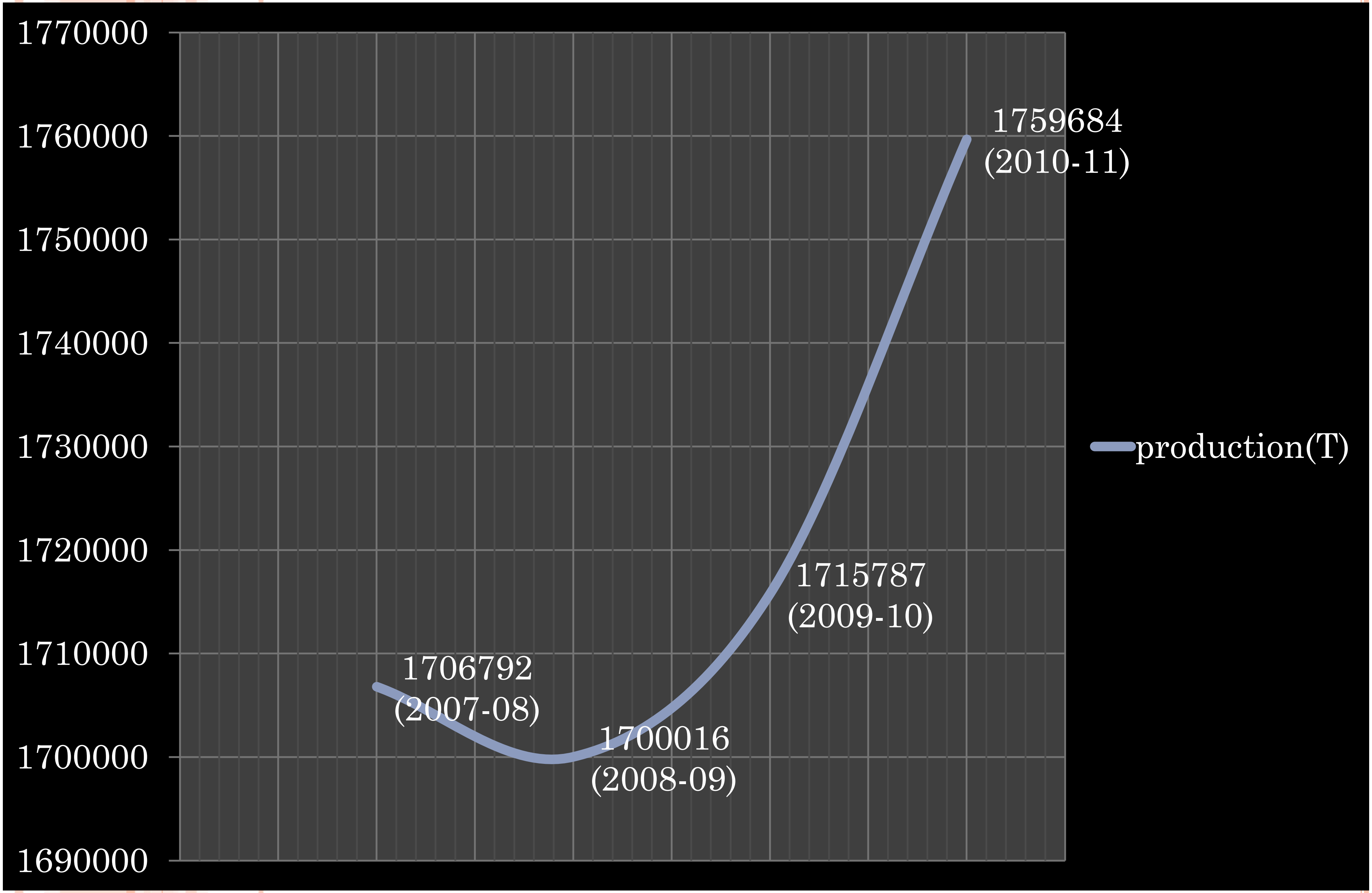
Name	S.L. Manjhi
Title	D.G.M.(O)
Dept	S.M.S-2
Company	SAIL, Rourkela Steel Plant

Material Flow at Steel Melting Shop-II, RSP

WHY DESULPHURISATION----

- Improvement in Steel Quality
- Improvement in Productivity

Grade	Max sulphur%
IS 3589	0.03
IS 5986	0.03
IS 2062 E 250A	0.035
API	0.01
IS 10748	0.04
WTCR	0.025
DSQ	0.025
TP-RSP	0.02
IS 513 D	0.03
IS 2002	0.03
LPG	0.02
SAE	0.025
SAILMA	0.015
SAPH-44	0.015
JISG	0.025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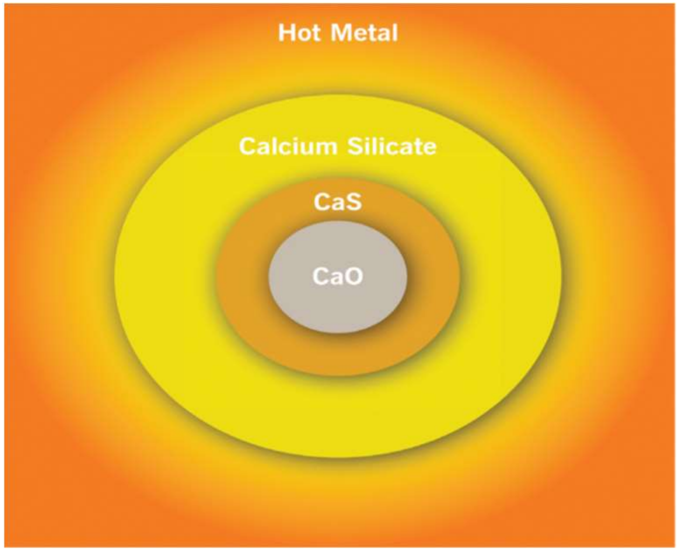
1700016 (2008-09)
production(T)

Year

Materials Used For Desulphurisation

- CaC_2
- Mg-Al + Lime
- CaC2 and Mg-Al

PRINCIPLES---

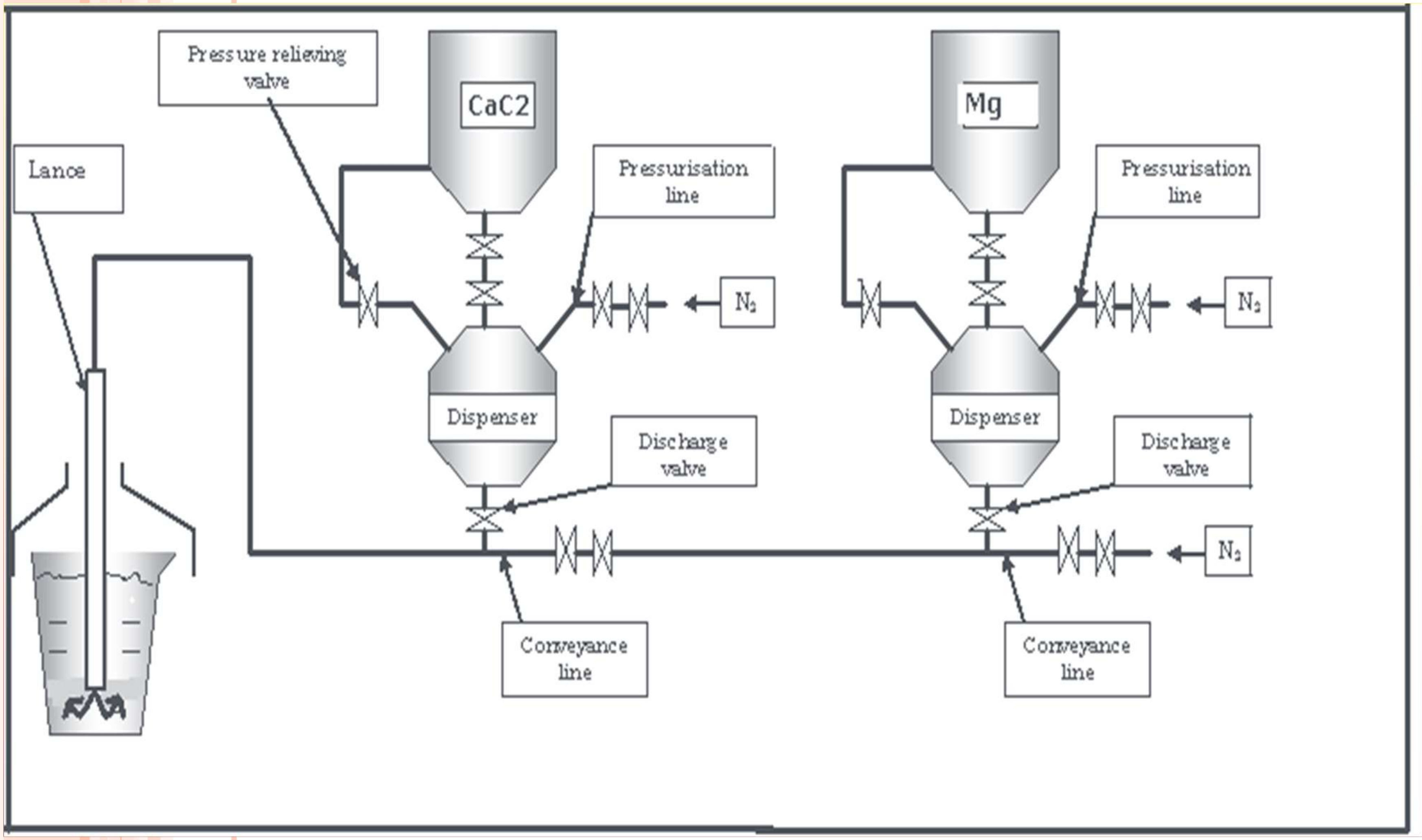


- Lime

CaC2 $CaC_2 + [S] = CaS + 2[C]$

- Mg $Mg + S \rightarrow MgS(s)$

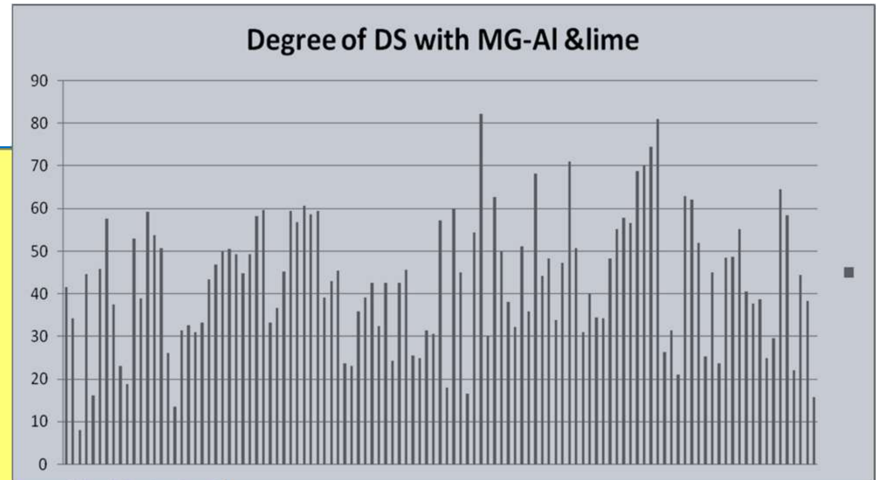
Layout of Desulphurisation Plant

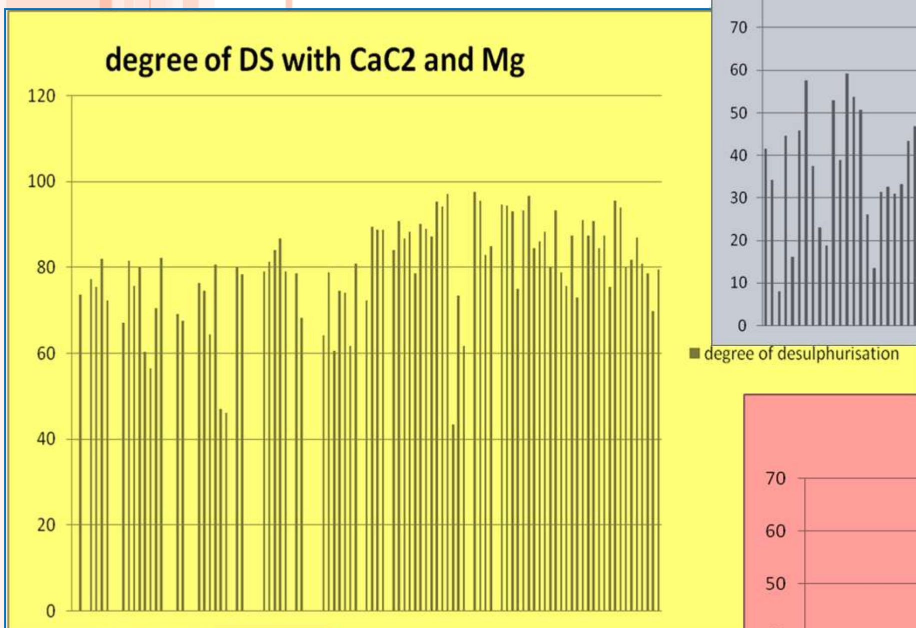


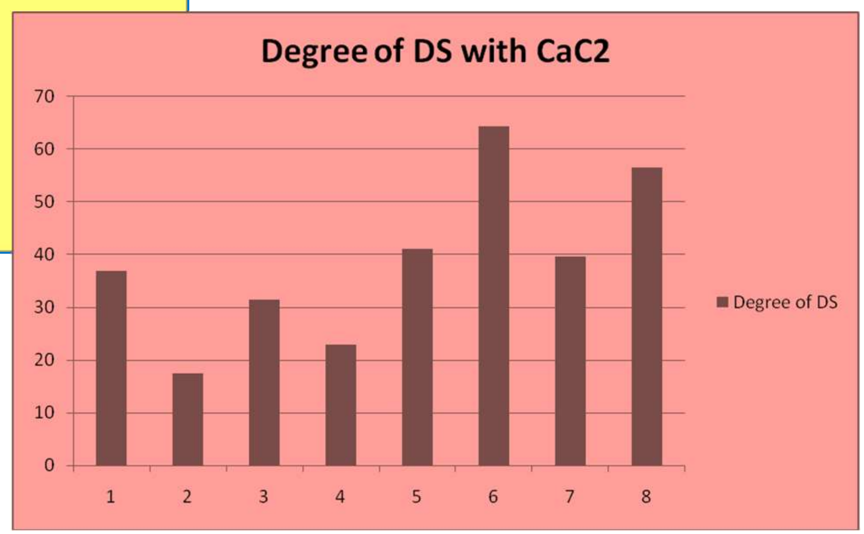
COMPARISONS---

Factors	CaC_2	Mg-Al	Co-injection of CaC2 & Mg
Reagent consumption per ton of metal for 0.001% drop of sulphur	0.12 kg/ton	0.033 kg/ton	0.05+0.009 =0.06 kg/ton
Cost of reagent per ton of metal for 0.001% drop of sulphur	4.32 Rs/ton	3.89 Rs/ton	1.83+1.44 =3.27 Rs/ton
Average Treatment Time	12.2 min	7.3 min	8.4 min

COMPARISONS---







RESULTS

- Average degree of desulphurization were found to be 80%, 43.5% and 38.8% for co-injection of CaC_2 and Mg, Mg-Al and CaC_2 respectively

- The specific compound costs for CaC_2, Mg-Al and co-injection of CaC_2 and Mg were found to be 0.12 kg/ton, 0.033 kg/ton and 0.06 kg/ton respectively

- The specific cost of CaC_2, Mg-Al and Co-injection of CaC_2 and Mg were found

CONCLUSIONS

The co-injection of CaC_2 and Mg based reagent is better than CaC2 or Mg-Al reagents.

THANK YOU