Study of LF slag composition and its correlation with the desulphurisation and cleanliness aspect of liquid steel

Minal Shah[1] , Shoumodip Roy[2]
Dept. of Metallurgy and Materials Engineering , NIT Jamshedpur, India

ABSTRACT:

Over the past few decades the demand for steel around the world has been increasing at a rapid rate, coupled with an increase in steel quality. One major technique for improving the quality of steel is to reduce its sulphur content. Sulphur is one of the most detrimental impurities in the steelmaking process, affecting both internal and surface quality.

Desulphurization of steel at ladle furnace depends on temperature, amount of oxygen and sulphur in the steel, but mainly on chemical composition and physical properties of slag. Necessary requirement for effective desulphurization is also minimum amount of easy reducible oxides in the slag. There are many correlations for expression of slag desulphurization capacity, where their functional dependency on each other can be found. This paper presents graphical correlation of sulphur capacity with different parameters, correlation of slag colour with composition of slag (FeO and MnO mainly) ,ternary diagram of slag having CaO , Al_2O_3 and SiO_2 at constant 5% MgO from set of approximately 30 heats and area occupied by slag in ternary plot based on these, the parameters responsible for slag desulphurization capability are expressed using regression analysis of industrial data.

Keywords –Desulfurization, sulphur capacity, ternary diagram, regression analysis

I. INTRODUCTION

Over the past few decades the demand for steel around the world has been increasing at a rapid rate, coupled with an increase in steel quality. Steel producers are required to maximise throughput, minimise production outages and maintain high quality standards while all the time minimising costs. The modern metallurgy of iron and steel is first of all oriented in quality improvement, effectiveness and competitiveness of its production.

One major technique for improving the quality of steel is to reduce its sulphur content. Sulphur is one of the most detrimental impurities in the steelmaking process, affecting both internal and surface quality.

Desulphurization of steel at ladle furnace depends on temperature, concentrations of oxygen and sulphur in the steel, but mainly on chemical composition and physical properties of slag. The refining of molten steel in the ladle furnace to meet the required compositional range requires the optimisation of the process parameters. For sulphur removal control, parameters such as argon gas flow rate through the porous plugs, inductive stirring effect, and vacuum pressure of the tank degasser in case of tank degasser, amount & composition of the top slag should be optimised.

In present work; thermodynamics and kinetics of desulphurization and impact of slag properties on desulphurization is studied.

II. SULPHUR IN STEEL

2.1 EFFECT OF SULPHUR ON CONTINUOUS CASTING OF STEEL

- Formation of undesirable sulphides which promotes granular weaknesses and cracks in steel during solidification.
- It lowers the melting point and intergranular strength.
- Sulphur contributes to the brittleness of steel and thus acts as stress raiser in steel .
- Hot shortness

.

2.2 THERMODYNAMICS OF DESULFURIZATION

A simplest approach to this issue is to recognize that the CaO in slag is the predominant desulfizer. For the reaction,

$$CaO(s) + \underline{S} \rightarrow CaS(s) + \underline{O} \quad (1)$$

With the data of analysis,

$$\log K_{12} = -5140/T + 0.961 \quad (2)$$

K_{12} is equilibrium constant for reaction (2) is same as K_{MS} for a CaO-CaS reaction. At 1600˚C Eq (3) gives $K_{12} = 0.013$.

Carlsson et al have proposed an alternative correlation,viz.

$$\log K_{12} = -5304/T + 1.191 \quad (3)$$

$$K_{12} = (a_{CaS})[h_O]/(a_{CaO})[h_S] \quad (4)$$

Proceeding similarly as in the derivation

$$m\, K_{12}(a_{CaO}) = (W_s).[h_O]/[h_S] = C_s' \quad (5)$$

where m is a constant of proportionality.

$$\log C_s = \log m + \log(a_{CaO}) - 4204/T - 0.184 \quad (6)$$

Tsao et al performed equilibrium measurements and proposed the following correlation :

$\log C_s = 3.44(X_{CaO} + 0.3X_{MgO} - 0.8X_{Al2O3} - X_{siO2}) - 9894/T + 2.05$ (7)

Andersson et al studied the distribution of sulfur and the extent of sulfur removal using

$[S] + 1/2O_{(g)} = [O] + 1/2S_{(g)}$ (8)

$K_7 = a_{\underline{O}} / a_{\underline{S}} . \sqrt{(P_{S2}/P_{O2})} = (\%S)/[\%S]. a_{\underline{O}} / f_S . Cs$ (9)

Also, $\log K_{12} = -935/T + 1.375 + \log C_S + \log f_{\underline{S}} - \log a_{\underline{O}}$ (10)

III. LADLE FURNACE OPERATIONS AND PARAMETERS

3.1 PROCESS STEP AT LF:

- Transfer of ladle from OLP to LF
- Auto coupling for purging or manual purging hose connection & start purging.
- Lowering of roof & take temperature.
- If temp> 1560˚C, then take the sample.
- If temp> 1560˚C, then start arcing by swiveling of the electrode arms.
- Now start Fe- alloy addition as per grade requirement.
- Al-wire feeding should be done to keep %Al >0.08%
- Take the sample & temperature.
- Again Fe-alloy addition for minor correction.
- Mild purging for inclusion floatation.
- CaSi /café wire addition as per grade requirement.
- Again mild purging before lifting the ladle.
- Take final sample & temperature.

3.2 ANALYSIS PROCEDURES AND TECHNIQUES:

- **TEMPERATURE**: The temperature of the molten steel was measured at each sampling occasion. In some occasions for the purpose the temperature was measured using the electro nite Celox 6000
- **CHEMICAL COMPOSITION STEEL SAMPLES**: Slag and steel samples were collected before and after arcing and after the stirring period. Steel samples were taken using the automatic sampling equipment installed at the ladle furnace. A dual thickness ('lollipop') sampler from Rescon-Electro Nite was used to sample the liquid steel to determine the amount of sulphur as well as other elements that dissolved in the steel. The pin (with diameter of 6 mm) of each lollipop sample was used for the determination of the C and S contents in steel using the combustion method with a Leco CS-230 instrument. The body of the lollipop sample was used to determine the chemical composition of elements like Mg, Ca, Al, Ti, Sn and B using the Optical Emission Spectroscopy (OES) method. The remaining elements were analyzed using the XRF method.
- **CHEMICAL COMPOSITION OF SLAG SAMPLES**: The composition of slag samples were analyzed using X-ray fluorescence (XRF). First, the slag samples were crushed into small particles. Thereafter, homogeneous discs were prepared by sintering and pressing of the crushed particles. Then, the chemical composition of the slag components was determined. Also, the content of main oxides (such as CaO, Al_2O_3 , MgO, SiO_2 ,CaF_2 , Cr_2O_3 , MnO,P_2O_5 ,TiO_2 and some other) in slag were analyzed by a Thermo ARL 9800XP instrument. In addition, Sulphur in the slag was determined based on a combustion and Infra Red (IR) technology using CS-444LS Leco equipment.

3.3. USEFUL PROPERTIES OF SLAG IN LADLE REFINING:

- It insulates the bath, reduces temperature losses
- It desulphurizes the steel
- It helps control the types of inclusions and traps them in the ladle.
- It controls the steel oxygen levels and chemistry of the steel.
- Can protect steel from oxygen and N_2 pickup. It can influence H_2 pickup.
- It protects the ladle from arc flare and refractory erosion

IV. RESULTS

1. The ternary plot between Al_2O_3, SiO_2,CaO system at a constant MgO -5% is shown below:

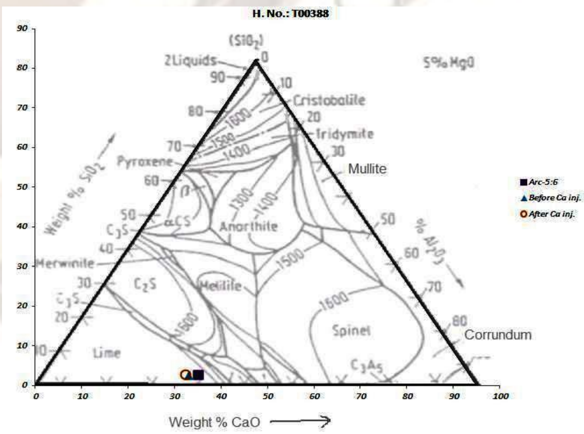


Fig1.Ternary diagram for CaO, Al_2O_3 , SiO_2 system at constant 5% MgO

2. Composition of CaO, Al_2O_3 and SiO_2 and its position has been correlated with Sulfide capacity, it has been found that the slag having

less sulphide capacity lies more near to liquidus temperature of lime.

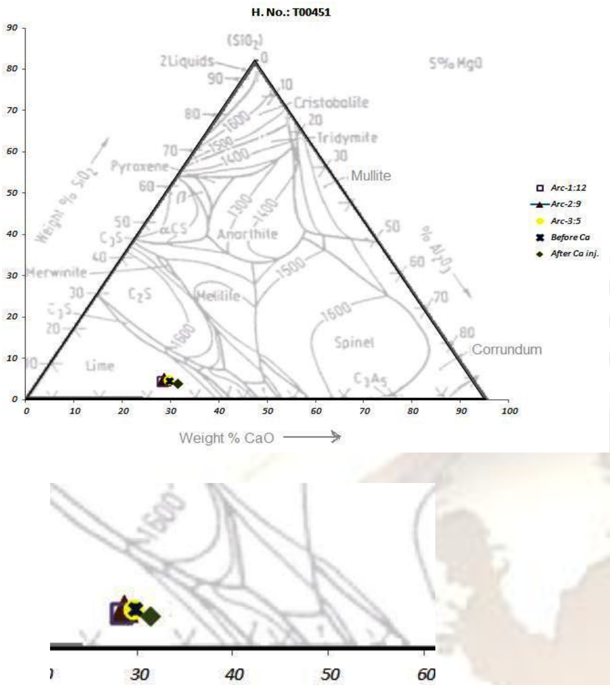


Fig2.Ternary diagram for CaO, Al_2O_3, SiO_2 system at constant 5% MgO for correlation with sulphide capacity

Table 1.Shows the composition of above given slag sample at different stages after 1st ,2nd arcing ,before and after Ca treatment.

Sample _id	**CaO**	**Al_2O_3**	**SiO_2**	**C_s**
LFS-1	64.08	26.01	4.91	0.09
LFS-2	63.56	25.83	5.60	0.10
LFS-3	62.70	26.95	5.34	0.09
LFS-4	62.48	27.23	5.28	0.09
LFS-5	61.27	29.22	4.51	**0.08**

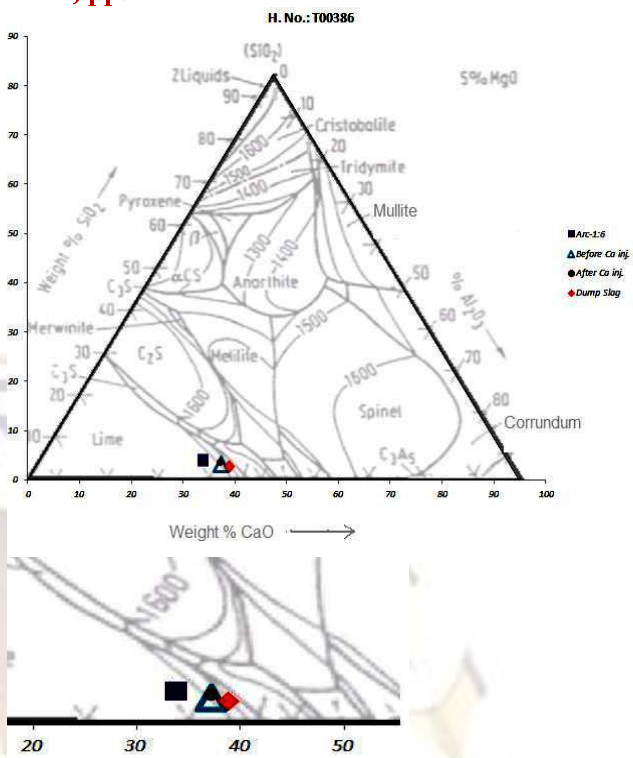
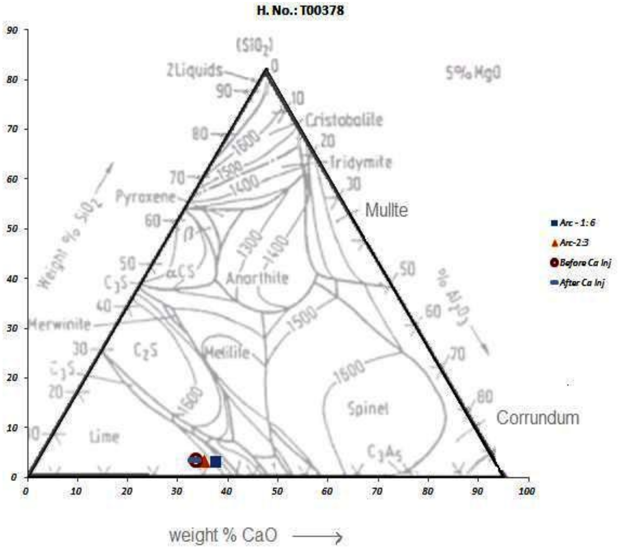


Fig3.Ternary diagram for CaO, Al_2O_3 , SiO_2 system at constant 5% MgO for correlation with sulphide capacity(having low C_s)

Table 2: Shows the composition of above given slag sample at different stages after 1st arcing ,2nd ,before and after Ca treatment.

Sample _id	**CaO**	**Al_2O_3**	**SiO_2**	**C_s**
LFS-1:	58.88	31.48	4.64	0.07
LFS-2(before Ca inj.)	56.01	35.33	3.65	**0.06**
LFS-3(after Ca inj.)	55.86	35.06	4.06	0.07
Dump slag	54.62	37.20	3.17	-

3. Composition of CaO, Al_2O_3 and SiO_2 and its position has been correlated with basicity, it has been found that the slag having less basicity lies more near to liquidus temperature of lime.



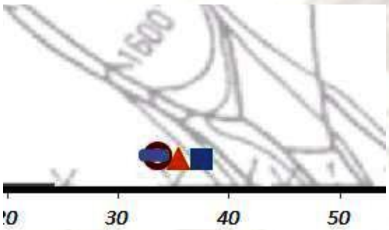


Fig4.Ternary diagram for CaO, Al_2O_3 , SiO_2 system at constant 5% MgO for correlation with sulphide capacity

Table 3. Shows the composition of above given slag sample at different stages after 1st arcing ,2nd ,before and after Ca treatment.

Sample _id	CaO	Al_2O_3	SiO_2	Basicity
LFS-1	55.61	35.78	3.60	**1.52**
LFS-2	57.76	33.45	3.78	1.66
LFS-3	59.34	31.47	4.19	1.79
LFS-4	59.65	31.18	4.17	1.81

4. Sulphide Capacity has been correlated with CaO, MgO and Al_2O_3 content of the slag as shown below.

The various graphs are being plotted by **MATLAB SOFTWARE**.

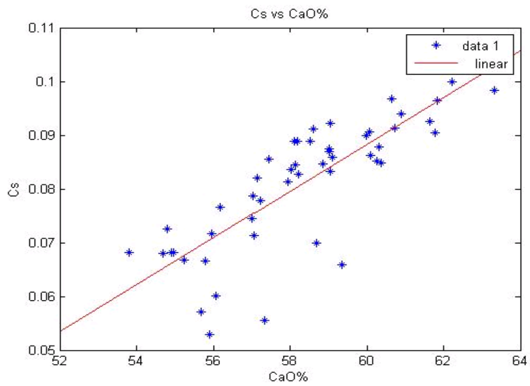


Fig 5. Sulfide Capacity as a function of CaO content of slag

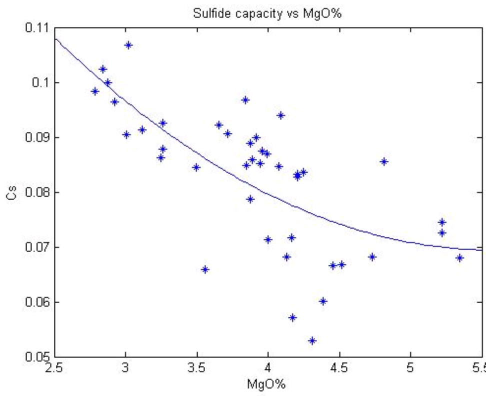


Fig 6. Sulfide capacity as a function of saturated MgO It shows that for better desulfurization reaction rate, it will be very effective to decrease the MgO content. Likely effect on increasing viscosity

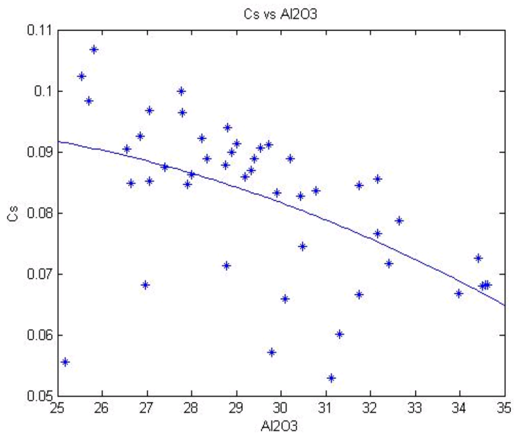


Fig 7. Sulfide Capacity as a function of Alumina in slag

5. Basicity

Basicity is defined as ratio of (CaO+Mg0/(Al_2O_3 +SiO_2) . Significant relation have been made between sulphide capacity and basicity.

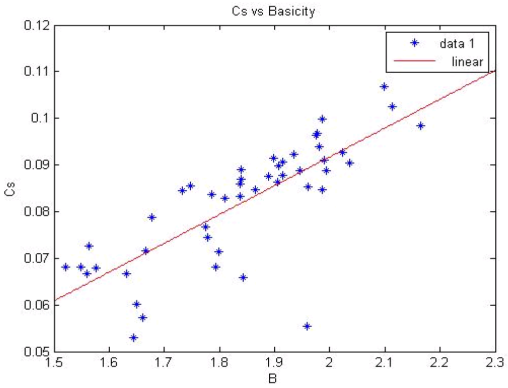


Fig 8. Sulfide Capacity values as a function of Basicity

6. Temperature

Sulfide capacity is plotted as a function of temperature. Figure shows that sulphide capacity is improved at higher temperature.

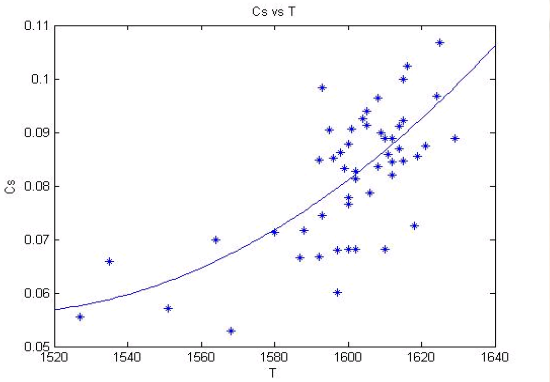


Fig 9. Sulfide capacity as a function of Temperature

7. Fe Concentration

Sulphide Capacity has been correlated with Fe content in slag.

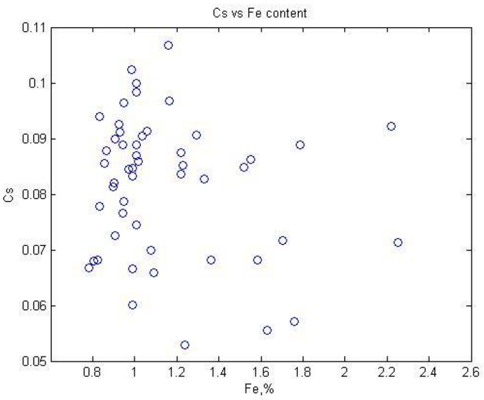


Fig 10.. Sulfide capacity as a function of Fe content in slag
;,

8. Regression Analysis

The Cs actual and predicted were plotted against each other by mathematical regression

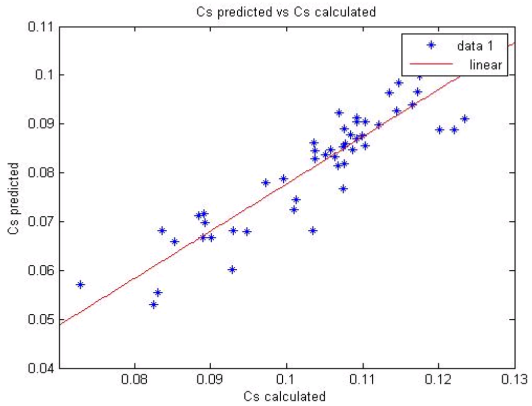


Fig 11. Sulphide capacity predicted as a function of Sulphide Capacity calculated

9. Colour Analysis

It has been found through experiment that the colour of slag is mainly dependent on the Fe% in slag as shown in following Table 4

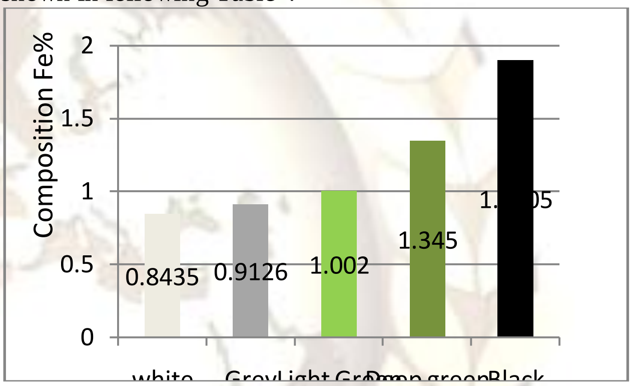


Table4

S. No.	Colour	Concentration, wt– % Fe total Min	Fe total Max	MnO total Min	MnO total Max	Fe + MnO Min	Fe + MnO Max
1.	White	0.82	0.86	0.05	0.07	0.86	1.1
2.	Grey	0.89	0.93	0.61	0.83	0.83	1.2
3.	Light Green	0.94	1.06	0.24	0.34	1.01	1.2
4.	Deep Green	0.16	1.52	0.46	0.56	1.08	1.9
5.	Black	1.55	2.25	0.8	1.04	2.62	3.1

V. CONCLUSIONS

5.1 It was seen from the Ternary diagram of CaO-Al_2O_3-SiO_2 system that all the slag samples lies in "Lime saturated region" i.e saturated with CaO content. This is to say that the melting points of these slag is going to be very high and the intense heat generated below the arc would only be able to keep it molten. To lower the melting point of the slag - an optimization of quantity of lime addition for slag making will be required.

5.2 Composition of CaO, Al_2O_3 and SiO_2 and its position has been correlated with the sulfide capacity, it has been found that the slag having less sulphide capacity lies more near to liquidus temperature of lime.

5.3 Composition of CaO, Al_2O_3 and SiO_2 and its position has been correlated with basicity, it has been found that the slag having less basicity lies more near to liquidus temperature of lime.

The sulphide capacity of the slag was found to obey the linear relation given as:

$$C_s = 0.000307\times T + 0.0011\times Al_2O_3\% + 0.007402\times MnO\% + 0.002848\times MgO\% - 0.0002\times S\% - 0.00074\times SiO_2 + 0.006067\times CaO\% + 0.001062\times Fe\% - 0.00645\times Basicity - 0.79608$$

where T is the temperature.

The Cs actual and predicted were plotted against each other by mathematical regression and it was seen that the result has a good accuracy with R^2 value 0.983334 which means that the above relation is valid with these compositions as well.

5.4 It has been concluded through experiment that the colour of slag is mainly depends on the composition of Fe% in slag.

5.5 It was concluded that sulphide capacity of steel slag has a strong effect on composition of CaO of the slag

5.6 It was concluded that sulphide capacity of steel slag has a poor effect on composition of Al_2O_3 of the slag

5.7 Also it was seen that sulphide capacity (Cs) decreases to a much lower value with increase in MgO. This can be attributed to the fact that MgO increases the viscosity of the slag which in turn decreases the sulphur partition ratio or in other words the ability to form sulphides decreases and correspondingly increases the sulphur content of the hot metal. A typical grade of the steel (SA103) was selected for the experimentation.

5.8 It is known that desulfurisation is improved with slags of higher basicity. Basic slag have high content of basic oxides which are network breakers with ability to release its oxygen ion (O^{2-}) in exchange for the dissolved sulphur in steel.

5.9 As essential parameter in desulfurization is the temperature at which the process is carried out. It influences the viscosity (favourable kinetic condition and sulphide capacity) of the slag and also sulphur distribution in the metal and slag.

5.10. Sulphide Capacity has poor correlation with Fe concentration in slag.

REFERENCES

Books

[1] Secondary Steelmaking by Dr. Ahindra Ghosh
[2] Fundamentals of Steelmaking by Dr. E.T.Turkdogan
[3] Principles of Steelmaking by Dr. Brahma Deo
[4] Slag Atlas by Verein Deutscher Eisenhuttenleute
[5] Steel Making by Dr. R.H.Tupkary
[6] Steel Plant Training Course

Software

[7] Math work by Matlab

Thesis

[8] Master Thesis on Improvement of the Desulphurisation Process in the Ladle Furnace by Slag Composition Control (Dr.Stephen Famurewa Mayowa).
[9] Optimisation Slag Composition in Ladle furnace considering to effective desulfurization (Bul'ko B., Kijac J, Domovec M.)

Journal Papers:

[10] Deep Steel Desulphurisation Technology in the Ladle Furnace at KSC (D.Takahashi, M.Kamo, Y.Kurose and H.Nomura).
[11] Use of Phase diagrams in studies of refractories corrosion (S.Zhang and W.E.Lee)
[12] Slag–metal reactions during ladle treatment with focus on desulphurisation (M. Andersson, M. Hallberg, L. Jonsson, and P. Jo ̈nsson)