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Thermodynamics of Sulphur Distribution between Slag and Hot Metal in Blast Furnace

S. S. Abd Elmomen

Tabbin Institute for Metallurgical Studies, Helwan, Egypt

Abstract

Daily average analysis of slag and the corresponding hot metal samples were collected on a 1033 m^3 blast furnace of the Egyptian Iron and Steel Company (EISCO) over a period of 50 days during May to June 2019. The measured temperature is that of liquid hot metal. The data obtained are used to study sulphur distribution between slag and metal using the concept of slag capacity. The partial pressure of oxygen is indirectly estimated by applying the thermodynamics of manganese oxidation reaction. The results show that the activity coefficients of Sulphur and manganese in the metal are 3.575 and 0.5193 respectively. There is a linear relationship between activity and concentration of MnO in the slag. Calculated and measured sulphur distribution coefficients are in satisfactory agreement.

Keywords**:** Blast furnace; Slag capacity; Sulphur distribution.

Introduction

The integrated iron and steel industry based on the blast furnace (BF) for hot metal production and Thomas converter steel making started in Egypt in the middle of the 20^{th}century. The selection of Thomas converter was due to the high phosphorous content of the hot metal produced. The iron content of the ore from Aswan was in the range of about 38 to 40% [1]. The ore was crushed to lumps and charged in the blast furnace. EISCO started with two small BF، s having a useful volume of 575m^3 each. Later on, another iron ore deposit was discovered in Bahariya region. The iron content of Baharyia ore is in the range about of 50 to 52% [1]. The plant was expanded by adding two relatively larger BF، s having 1033m^3 useful volumes each. The ore is transported from the mines to the plant by railway, crushed ground to sinter mix size. After sintering, crushing and screening to proper size, the sinter is charged in the BF as self-fluxing sinter. Baharyia ore however has high manganese content (2-3%) and relatively high sulphur content [1]. Sulphur present in the burden of the blast furnace comes from coke and iron ore.

In the BF about 90% of sulphur is removed mostly through slag and about 2-3% through dust and top gas. The remaining sulphur 10-11%ends up in the HM [2, 3]. In the BF, part of the sulphur dissolves in the HM.

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According to the reaction (1) Most of the dissolved sulphur is removed by the lime present in the slag.

$$CaO(s) + [S]_{Fe} = CaS(s) + [O]_{Fe} \quad (1)$$

This means that sulphur distribution ratio between slags and hot metal is a common parameter to describe desulphurization ability during blast furnace (BF) iron making process [4, 5].

The aim of the present work is to study the main parameters affecting sulphur slagging in BF by using the principle of sulphide capacity. This shows the ability of the slag to capture to Sulphur.

Experimental

Daily average analysis of test heats conducted on a 1033m^3 blast furnace of the Egyptian Iron and Steel Company (EISCO) over a period from May to June 2019. The data include the analysis of hot metal and the corresponding slag of 50 samples. The temperatures used in the present investigation are those of the hot metal. They are the average of at least 10 readings taken during metal tapping from the furnace. The metal samples were collected cast by cast and their analysis was averaged over the whole day. Slag samples were collected for analysis. The slag samples were ground and metallic iron was removed by a hand magnet. After preparation of hot metal and slag samples, they were analyzed by using XRF (Shimadzu-MXF 2400).

*Corresponding author e-mailSanaa.said@hotmail.com .; (S. S. Abd Elmomen).
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Table 1: The analysis of slag and the corresponding hot metal samples

Chemical analysis of hot metal [wt.%]						Chemical analysis of slag [wt.%]						
Si	Mn	P	C	S	t	SiO_2	CaO	MgO	Al_2O_3	MnO	FeO	S
1.3	2.49	0.44	4.24	0.023	1450	38.79	35.17	7	9.68	3.06	0.58	1.33
1.32	3.1	0.34	4.19	0.023	1450	36.27	33.15	7.56	14.38	2.99	0.58	1.23
1.62	3.46	0.34	4.35	0.041	1480	36.36	32.67	7.72	12.4	4.44	0.94	1.21
0.61	2.07	0.32	4.04	0.064	1400	37.62	31.88	7.44	11.94	4.99	0.74	1.15
1.16	2.45	0.33	4.23	0.044	1420	37.19	31.95	7.26	13.1	4.28	0.76	1.19
0.94	2.08	0.35	4.04	0.055	1410	38.38	31.48	6.98	12.18	4.03	0.74	1.82
1.26	2.22	0.33	4.1	0.082	1420	38.42	31.71	6.2	10.76	5.18	2.01	1.86
1.02	1.81	0.36	4	0.1	1420	40.52	31.83	5.99	10.23	4.41	1.06	2
1.01	1.63	0.41	4	0.102	1420	40.01	33.67	5.54	9.5	4.07	1.13	1.89
1.44	2.35	0.39	4.17	0.044	1450	38.87	35.83	5.5	10.59	2.93	0.61	2.14
0.57	2	0.52	4.03	0.04	1398	36.88	35.24	6.83	11	3.9	0.39	1.2
0.37	1.65	0.51	3.82	0.058	1388	36.42	34.56	6.72	11.4	4.26	0.52	1.18
0.4	1.65	0.49	3.85	0.067	1382	36.5	33.54	6.6	12	4.38	0.52	1.2
0.34	1.94	0.43	3.93	0.048	1389	34.93	34.27	7.64	12.1	4.13	0.52	1.13
0.42	2.36	0.45	4.03	0.037	1397	35.78	33.61	7.55	11.02	4.8	0.39	1.27
0.54	2.16	0.48	4.04	0.042	1387	36.07	33.54	6.9	11.62	4.6	0.52	1.27
0.56	2.14	0.48	4	0.043	1395	36.43	34.58	6.76	11.22	4.29	0.39	1.28
0.48	1.47	0.47	3.72	0.084	1340	37.7	31	8.62	12.2	3.87	0.26	1.1
0.41	2.1	0.48	3.9	0.034	1412	37.05	36.07	6.25	11	3.12	0.26	1.28
0.49	2.08	0.52	4.02	0.038	1407	35.96	36.97	5.02	11.8	3.9	0.26	1.4
0.43	2.1	0.5	4	0.043	1400	36.67	35.86	5.12	11.2	4.39	0.26	1.38
0.42	1.67	0.48	3.8	0.077	1376	36.99	35.55	3.53	10.77	5.68	0.39	1.29
0.36	1.72	0.51	4	0.06	1387	35.52	36.32	6.36	9.4	5.5	0.77	1.36
0.46	1.91	0.51	4.04	0.049	1380	35.73	36.45	5.86	10.2	5.16	0.77	1.35
0.44	1.34	0.46	3.72	0.099	1378	37.83	32.23	5.31	11.2	5.8	0.77	1.37
0.48	1.59	0.49	3.8	0.088	1398	37.73	33.65	5.45	11.4	4.2	0.52	1.33
0.58	2.14	0.49	3.98	0.042	1400	37.4	34.92	6.33	11.2	3.6	0.52	1.29
0.5	1.96	0.5	4	0.05	1407	36.92	33.92	6.32	12.11	4.33	0.52	1.34
0.45	1.64	0.48	3.86	0.076	1401	37.81	32.82	4.85	13.1	4.8	0.52	1.15
0.4	1.34	0.48	3.78	0.098	1380	37.73	31.22	6.67	10.7	6.39	1.42	1.06
0.54	1.75	0.52	3.93	0.069	1404	37.1	32.55	7.43	10.88	4.84	0.65	1.29
0.55	1.9	0.53	3.96	0.054	1409	36.91	35.09	6.66	10.5	4.2	0.39	1.27
0.51	1.61	0.51	3.82	0.078	1407	37.27	31.23	6.04	13	5.8	0.39	1.24
0.26	1.43	0.46	3.7	0.077	1385	35.96	33.79	6.54	12.54	5.41	0.77	1.25
0.32	1.19	0.5	3.66	0.122	1381	36.98	31.41	6.84	12.7	6.12	1.03	1.08
0.54	1.78	0.5	3.86	0.066	1400	36.8	32.52	7.28	11.9	4.8	0.52	1.17
0.39	1.95	0.52	4	0.038	1385	34.91	36.54	6	11.84	4.2	0.65	1.31
0.45	1.98	0.5	3.98	0.055	1399	35.61	32.84	7.43	12.84	4.83	0.39	1.15
0.39	2.02	0.51	3.39	0.035	1396	34.74	34.92	8.04	11.9	3.2	0.39	1.24
0.22	1.39	0.55	3.81	0.074	1378	35.97	33.51	8.15	11.05	5.85	0.39	1.14
0.62	2.25	0.54	4.1	0.023	1402	32.78	37.58	6.63	13.3	2.97	0.65	1.31
0.45	2.2	0.53	4.02	0.053	1401	36.53	32.27	7.6	13.36	4.85	0.65	1.15
0.5	1.68	0.5	3.7	0.104	1363	39	29.12	7.42	11.48	6.45	0.77	1.11
0.67	1.62	0.51	3.82	0.088	1381	37.41	29.7	6.87	13.5	5.81	0.52	1.13
0.58	1.7	0.52	3.67	0.102	1397	37.81	30.82	8.26	11	4.6	0.52	1.22
0.62	1.99	0.52	3.44	0.052	1404	37.03	32.3	7.47	11.1	4.3	0.39	1.18
0.53	1.63	0.5	3.79	0.089	1395	38.7	32	7.33	11.38	4.61	0.39	1.15
0.51	1.78	0.5	3.81	0.079	1382	37.9	33.08	7.76	11.04	4.6	0.52	1.17
0.41	1.52	0.49	3.79	0.093	1390	38.91	32.11	7.76	11.18	4.6	0.39	1.13

3. Results and discussion

The data obtained from Egyptian Iron and Steel Company (ESICO) is used to study sulphur distribution between slag and metal using the concept of slag capacity. The partial pressure of oxygen is indirectly estimated by applying the thermodynamics of manganese oxidation reaction.

The data obtained from Egyptian iron and steel company (EISCO) for blast furnace no.3 are given in Table 1. These data are used to study the effect of temperature and basicity on the sulphide capacity and sulphur distribution between slag and hot metal.

3.1 Sulphide capacity

The capacity of slag to remove sulphur from hot metal is defined by sulphide capacity of slag C_S, which is given by the equation [6]

$$C_{S=}(S)\left(\frac{p_{O_2}}{p_{S_2}}\right)^{1/2} \quad (2)$$

The partial pressure of oxygen is indirectly estimated by applying the thermodynamics of the following manganese oxidation reaction.

$$[Mn] + \tfrac{1}{2}O_{2(g)} = MnO_{(s)} \quad (3)$$

The standard free energy change, ΔG_o, of this reaction is [7]

$$\Delta G_o = -399154 + 120.54\,T \quad (4)$$

Equilibrium constant of this reaction can be calculated [7]

$$K_{Mn} = \frac{(a_{(MnO)})}{a_{[Mn]}(p_{O_2})^{1/2}} \quad (5)$$

The equilibrium constant K_{Mn} dependence on the temperature is given by [7]

$$lnK_{Mn} = \frac{48014}{T} - 14.506 \quad (6)$$

3.1.1 Activity of manganous oxide in slag

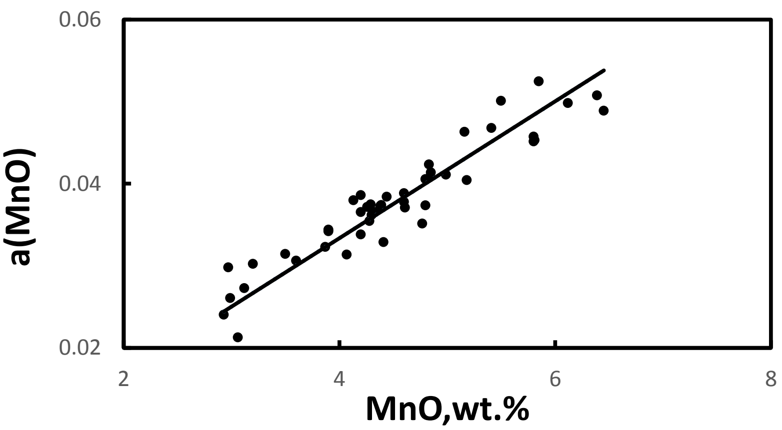
The activity of manganous oxide in slag $a_{(MnO)}$ may be given by this equation [7]

$$a_{(MnO)} = 10^{-3}\,(MnO)\left[1.6 + 5.9\,\frac{(CaO)+1.4(MgO)}{(SiO_2)}\right] \quad (7)$$

Fig. 1 represent the variation of the activity of manganous oxide in slag$a_{(MnO)}$ with the concentration of (MnO) for all samples investigated from (EISCO) over a period of 50 days during 2019.

$$\boldsymbol{a_{(MnO)} = 0.0083(MnO) \quad r = 0.9366} \quad (\mathbf{8})$$

Figure1: variation of activity of manganous oxide in slag with concentration of (MnO)



3.1.2 Activity of manganese in hot metal

The activity of manganese in hot metal is determined by this equation

$$a_{[Mn]=}f_{[Mn]}[Mn] \quad (9)$$

where $f_{[Mn]}$ is given by

$$logf_{[Mn]} = e_{Mn}^{(Mn)}[Mn] + e_{Mn}^{(Si)}[Si] + e_{Mn}^{(C)}[C] + e_{Mn}^{(S)}[S] + e_{Mn}^{(P)}[P] \quad (10)$$

Table 2 contains the values of interactions parameters [8]

Fig. 2 describes the relation between the activity of manganese in hot metal and its concentration as given by this equation

$$a_{[Mn]=0.5193\,[Mn]} \quad r{=}0.9889 \quad (11)$$

$$f_{[Mn]} = 0.5193 \quad (12)$$

Which is nearly the same value obtained in a previous paper [9].

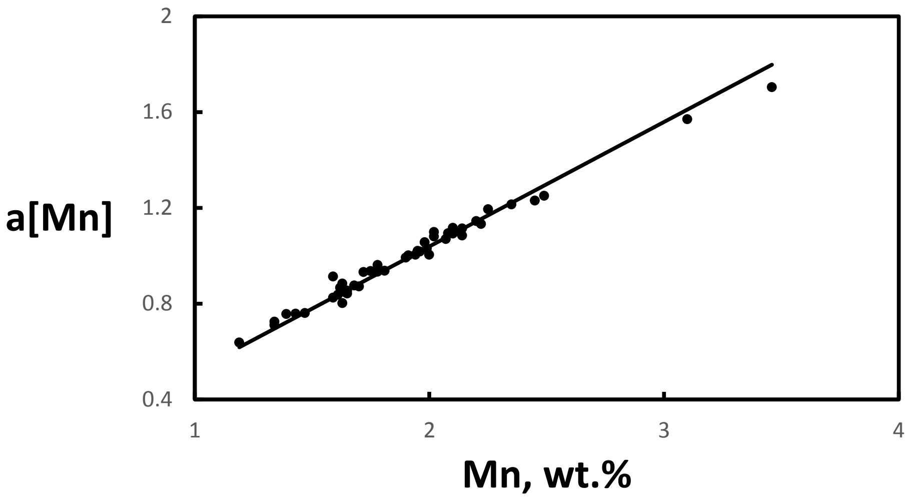
From Eq. (6, 7 and 9) the partial pressure of oxygen can be calculated from Eq. (5) the values obtained are on average of $1*10^{-15}$ atm.

which is in accord with the magnitude of oxygen pressure in the blast furnace hearth [10]

Table 2: Values of interaction parameter of the element i and Mn

$e_{Mn}^{(Mn)}$	$e_{Mn}^{(Si)}$	$e_{Mn}^{(C)}$	$e_{Mn}^{(S)}$	$e_{Mn}^{(P)}$
0	0	-0.07	-0.048	-0.0035

Figure2: activity of manganese in hot metal and its concentration



3.1.3 Activity of Sulphur in hot metal

Activity of sulphur in hot metal can be calculated according to this equation

$a_{[S]}= f_{[S]}[S]$ (13)

where $f_{[S]}$ is given by

$$logf_{[S]} = e_S^{(S)}[S] + e_S^{(Si)}[Si] + e_S^{(C)}[C] + e_S^{(Mn)}[S] + e_S^{(P)}[P] \quad (14)$$

Table 3 include the values of the interaction parameters of sulphur $f_{[S]}$ [8]

Fig. 3 represents the variation of activity with the concentration of sulphur in hot metal. The equation obtained from this figure is satisfied by.

$$\boldsymbol{a}_{[S]} = 3.575[S] \quad r = 0.9891 \quad (15)$$

$$f_{[S]} = 3.575 \quad (16)$$

This value agrees well with 3.9, the activity coefficient of sulphur in an alloy contaning: 1.5%Si, 4.0%C, 1.0%Mn, and 0.06% S [11]

The partial pressure of sulphur can be calculated from this reaction

$$\frac{1}{2} S_2(g) = [S] \quad (17)$$

The equilibrium constant of this reaction is given by

$$K_S = \frac{a_{[S]}}{(p_{S_2})^{1/2}} \quad (18)$$

The standard free energy change and equilibrium constant of Sulphur depends on the temperature calculated as follows [12]

$$\Delta G_S^o = 131461 + 22.05\ T \quad (19)$$

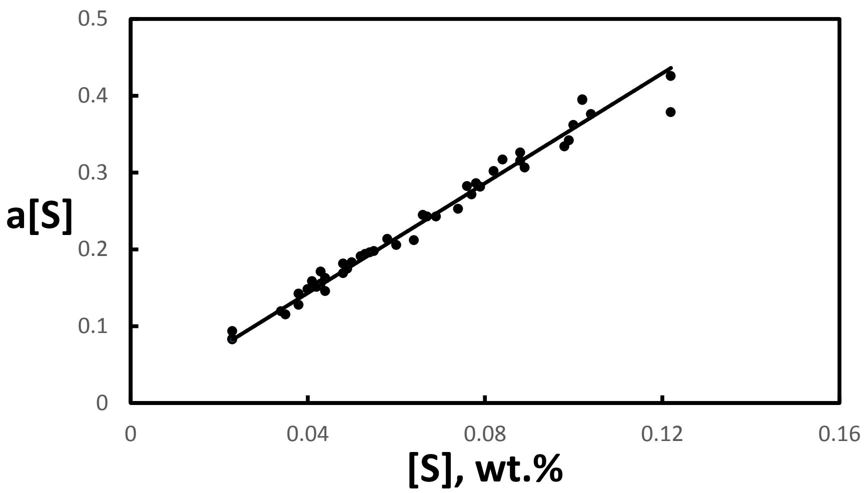
$$lnK_S = \frac{15814}{T} - 2.653 \quad (20)$$

The partial pressure of sulphur can be obtained from Eq. (15, 18 and 20).

Table 3: Values of interaction parameter of the element i and S

$e_S^{(Mn)}$	$e_S^{(Si)}$	$e_S^{(C)}$	$e_S^{(S)}$	$e_S^{(P)}$
-0.026	0063	0.11	-0.028	0.029

Figure 3: variation of activity and the concentration of sulphur in hot metal



3.2 Effect of slag composition on sulphide capacity

The effect of slag composition on sulphide capacity can be estimated by plotting log C_S as calculated by Eq. (2) against basicity, B at constant average temperatures1383, 1405 and 1458ºC respectively as shown in Fig. 4. The straight lines are more or less parallel and have an average slope equal to 0.7424. The results may be described by the following equations:

$$logC_S(1383) = 0.7171B - 4.4914, r = 0.9703 \quad (21)$$

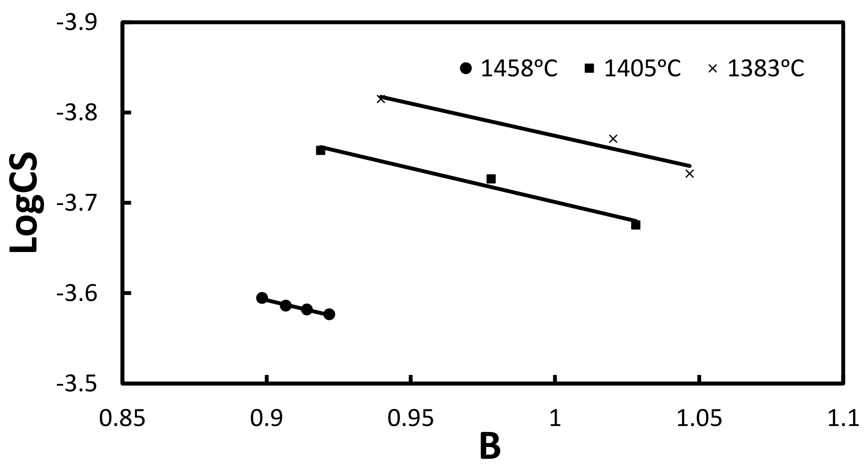
$$logC_S(1405) = 0.7491B - 4.4501, r = 0.9829 \quad (22)$$

$$logC_S(1458) = 0.7614B - 4.42777, r = 0.9917 \quad (23)$$

Basicity is defined by

$$B = \frac{CaO}{SiO_2} \quad (24)$$

Figure 4: variation of log C_S against basicity, B at constant average temperatures1383, 1405 and 1458ºC respectively



3.2.1 Combined effect of both temperature and basicity on sulphid capacity

The combined effects of both basicity and temperature on sulphide capcity can be represented by the general Eq. (25).

$$logC_S(B,T) = 0.7424B + b \quad (25)$$

The value of the slope depends on the basicity whereas the values acquired by intercept, b, of the three lines with the ordinate are dependent on the temperature as follows.

$$b = 0.7171 \quad at \quad t = 1383^{o}C \quad (26)$$

$$b = 0.7491 \quad at \ t = 1405 \ ^{o}C \quad (27)$$

$$b = 0.7614 \quad at \ t = 1458 \ ^{o}C \quad (28)$$

Fig. (5) represents the variation of the intercept, b, with the reciprocal of the corresponding absolute temperature. The straight line can be described by the equation

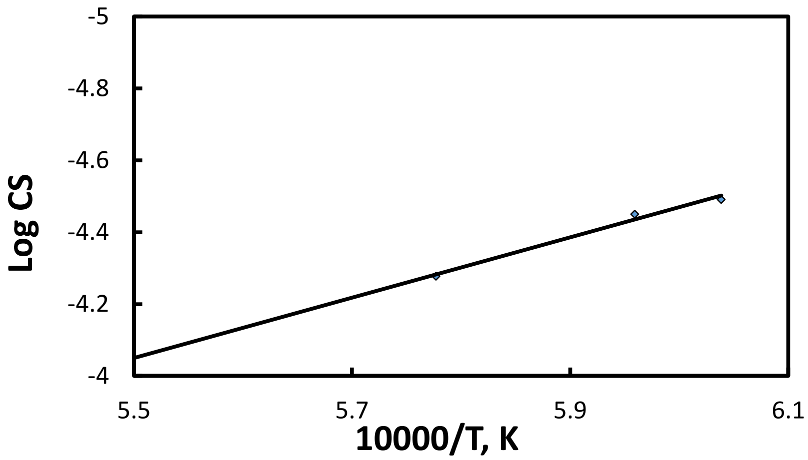
$$b = -\frac{8391}{T} + 0.5654 \ , \quad r = 0.997 \quad (29)$$

From Eqs. (25) and (29) Eq. (30) can be obtained which represents the effects of both basicity and temperature on sulphid capacity.

$$logC_S(B,T) = 0.7424B - \frac{8391}{T} + 0.5654 \quad (30)$$

This equation shows the increase of sulphid capacity of slag by increasing both basicity and temperature. For example, if the basicity of slag increases from 0.8 to 0.9 the sulphid capacity increases from 0.000195to 0.000231. On the other hand, when the temperature increases by 50 k the sulphid capacity increases from 0.000234 to 0.000279.

Figure 5: variation of the intercept, b, with the reciprocal of the corresponding absolute temperature



3.3 Sulphur distribution between slag and hot metal

Sulphur distribution between slag and hot metal is defined as

$$\eta_S = \frac{(S)}{[S]} \quad (31)$$

From Eqs.(2, 5,13,18,20 and 30) sulphur distribution between slag and hot metal can calculated

$$\eta_S(B,T) = C_S \frac{K_{Mn}}{K_S} \frac{f_{(S)} f_{Mn}[Mn]}{a_{(MnO)}} \quad (32)$$

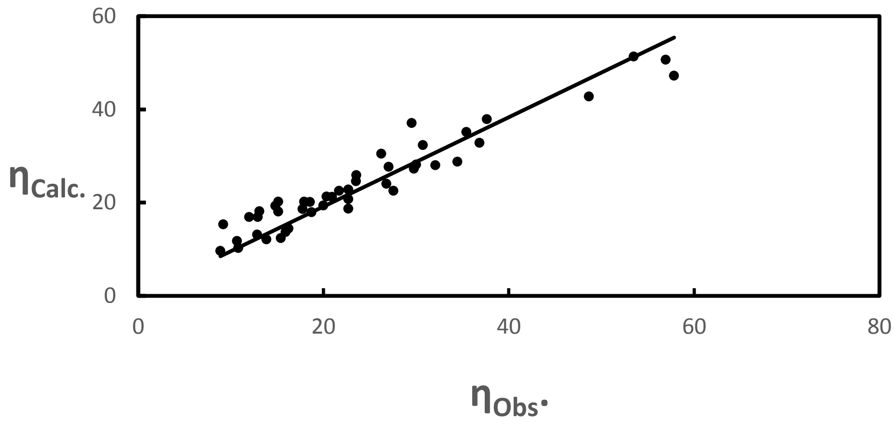
By substituting the values of manganese and sulphur coefficients obtained from Eqs.(11) and (15)Eq. 33 become

$$\eta_S(B,T) = C_S \frac{K_{Mn}}{K_S} \frac{1.8588[Mn]}{a_{(MnO)}} \quad (33)$$

$$\eta_{calc} = 0.9587\eta_{obs} \quad (34)$$

Fig, 6 represents the relationship between calculated and observed sulphur distribution. The value of the slop obtained from Fig. 6 is nearly one and the correlation coefficient is0.941 this confirms the applicability of using the concept of sulphid capacity to estimate the sulphur distribution between slag and metal. Furthermore the Eq. (34) obtained can be used in a computer program to controls sulphur distribution between slag and metal in blast furnace.

Figure 6: relationship between calculated and observed sulphur distribution ratio



Conclusions

Daily average data on slag and the corresponding hot metal analyses of BF No.III of (EISCO) ($1033m^3$) were used to investigate the effect of temperature and basicity on the sulphide capacity and sulphur distribution between slag and hot metal.
The following conclusions can be made:

1. The activity of manganese oxide is linearly related to the concentration.
2. The activity coefficient of manganese dissolved in the metal 0.5193 and the activity follows a linear trend with manganese concentration.
3. Activity of Sulphur in hot metal correlates linearly with concentration over the whole concentration range (0.023 -0.122wt %) and activity coefficient of Sulphur in hot metal of is 3.575
4. The sulphide capacity increases with increase of temperature and basicity.
5. The possibility of using the sulphid capacity principals in a computer program to controls sulphur distribution between slag and metal in blast furnace

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LIST OF ABBREVIATIONS:

$a_{(MnO)}$: manganous activity in slag
$a_{[Mn]}$: manganese activity in hot metal
B: basisty
b: intercept
d: intercept
C_S :sulphide capacity
$f_{[Mn]}$ activity coefficient of manganese in hot metal
e^i_{Mn} Interaction parameters
$f_{[S]}$ activity coefficient of Sulphur in hot metal
e^i_S Interaction parameters of Sulphur
K_{Mn} equilibrium constant of manganese
K_S :equilibrium constant of sulphur
P_{O_2}: oxygen partial pressure
P_{S_2}: sulphur partial pressure
T: Absolute temperature
t : hot metal temperature
η_S: sulphur distribution ratio

η_{calc} sulphur distribution calculated

η_{obs}sulphur distribution observed from the practical

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