THERMODYNAMICS OF SULPHUR DISTRIBUTION BETWEEN SLAG AND HOT METAL IN BLAST FURNACE.

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ABSTRACT

Daily average analysis of slag and the corresponding hot metal samples were collected on a 1033 m³ 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.

1. 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 20th 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 575m³ each. Later on, another iron ore deposit was discovered in Bahariya region. The iron content of Bahariya ore is in the range about of 50 to 52% [1]. The plant was expanded by adding two relatively larger BF^s having 1033 m³ 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. Bahariya 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.

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

2. EXPERIMENTAL

Daily average analysis of test heats conducted on a 1033 m³ 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).

3. RESULTS AND DISCUSSION

The data obtained from Egyptian Iron and Steel Company (EISCO) 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.

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]

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

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 ₂ O 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

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

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

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]

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

Figure 1 represents 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.

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

Fig. 1: 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:

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

Table 2 contains the values of interactions parameters. [8]

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

Figure 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].

Fig. 2: Activity of manganese in hot metal and its concentration.

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]

3.1.3. Activity of Sulphur in hot metal

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

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

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

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

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

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

$$a_{[S]} = 3.575 [S] \quad r = 0.9891 \quad (15)$$

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

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

Fig. 3: Variation of activity and the concentration of sulphur in hot metal.

The partial pressure of sulphur can be calculated from this reaction:

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]

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

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

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

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 temperatures 1383, 1405 and 1458°C respectively as shown in figure 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:

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

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

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

Basicity is defined by:

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

Fig. 4: Variation of $\log C_S$ against basicity, B at constant average temperatures 1383, 1405 and 1458°C respectively.

3.2.1. Combined effect of both temperature and basicity on sulphide capacity

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

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

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:

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

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

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

Figure 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:

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

Fig. 5: Variation of the intercept, b , with the reciprocal of the corresponding absolute temperature.

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

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

This equation shows the increase of sulphide capacity of slag by increasing both basicity and temperatures. For example, if the basicity of slag increases from 0.8 to 0.9 the sulphide capacity increases from 0.000195 to 0.000231. On the other hand, when the

temperature increases by 50 k the sulphide capacity increases from 0.000234 to 0.000279.

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 be 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.32 becomes:

$$\eta_s(B, T) = C_s \frac{K_{Mn}}{K_s} \frac{1.8588 [Mn]}{a_{(MnO)}} \quad (33)$$

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

Figure 6 represents the relationships between calculated and observed sulphur distribution. The value of the slope obtained from figure 6 is nearly one and the correlation coefficient is 0.941 this confirms the applicability of using the concept of sulphide capacity to estimate the sulphur distribution between slag and metal. Furthermore the Eq. (34) obtained can be used in a computer program to control sulphur distribution between slag and metal in blast furnace.

Fig. 6: Relationship between calculated and observed sulphur distribution ratio.

4. CONCLUSIONS

Daily average data on slag and the corresponding hot metal analyses of BF No.III of (EISCO) (1033 m³) 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:

- The activity of manganese oxide is linearly related to the concentration.
- The activity coefficient of manganese dissolved in the metal 0.5193 and the activity follows a linear trend with manganese concentration.
- Activity of Sulphur in hot metal correlates linearly with concentration over the whole concentration range (0.023 - 0.122 wt %) and activity coefficient of Sulphur in hot metal is 3.575.
- The sulphide capacity increases with increase of temperature and basicity.
- The possibility of using the sulphide 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 : Basicity.
 b : Intercept.
 d : Intercept.
 C_S : Sulphide capacity
 $f[Mn]$: Activity coefficient of manganese in hot metal.
 e_{Mn}^i : Interaction parameters.
 $f[S]$: Activity coefficient of Sulphur in hot metal.
 e_S^i : 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.

CAPTIONS OF TABLES

Table 1: The analysis of slag and the corresponding hot metal samples.

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

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

CAPTIONS OF FIGURES

Fig. 1: Variation of activity of manganous oxide in slag with concentration of (MnO) .

Fig. 2: Activity of manganese in hot metal and its concentration.

Fig. 3: Variation of activity and the concentration of sulphur in hot metal.

Fig. 4: Variation of $\log C_S$ against basicity, B at constant average temperatures 1383, 1405 and 1458°C respectively.

Fig. 5: Variation of the intercept, b , with the reciprocal of the corresponding absolute temperature.

Fig. 6: Relationship between calculated and observed sulphur distribution ratio.