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Relationship between the common optical basicity models and the sulphide capacities of CaO-Al_2O_3-SiO_2-MgO slag

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Abstract

The correlations between the sulphide capacity and the optical basicity models available in literature are reviewed. The relationship between sulphide capacity and the optical basicity was investigated on plant data collected from the BOF plant in the temperature range of 1565–1650 °C. The goal of this work was to compare results given by applying common acceptable Young's, Sosinsky-Sommerville's, Tsao-Katayama's and Taniguchi's optical basicity as well as the KTH model for calculating the sulphide capacities. The present paper is focused on the thermodynamic aspect of sulphur refining CaO-Al_2O_3-SiO_2-MgO ladle slag during LF ladle treatment. Thirty one heats were employed in the present study in real production conditions of low carbon steels.

Key words: steels, thermodynamics, analytical methods, optical basicity, sulphide capacity

1. Introduction

In today's steelmaking industry, steel products with improved properties are in high demand. In the ladle refining process the knowledge of the slag phases in equilibrium with liquid steel is very important to the design and control of the results of steelmaking operations, in particular deoxidation and desulphurisation [1]. In order to produce steel with higher performance it is important to know how different process parameters of ladle refining affect the steel quality. Slag composition and sulphur content in the steel should usually be kept at certain levels during ladle refining [2].

Slag-steel reactions play an important role during secondary refining operations carried out in ladles. Generally, the slag is the most important factor for ensuring the quality of molten steel in the ladle. Ladle slag is formed from the products of deoxidation of the steel, the added mixtures and from the corrosion products of the ladle lining, particularly at the slag line [3]. The effectiveness of basic slag acting as a desulphuriser, is often measured by the sulphide capacity C_S. The sulphide capacity, C_S, correlates well with optical basicity, and hence slag compositions conducive to desulphurisation can be determined from knowledge of the optical basicity of individual components [4]. Basic principles of steel desulphurisation are now well understood and the thermodynamic and kinetic requirements are well established [5].

Chemical compositions of metallurgical slag, basicity and temperature have a strong influence on the ability of slags to remove sulphur from the steel. This work is an attempt to compare the relationship between optical basicity and, in literature, available models of calculating sulphide capacity of ladle slag [6–9].

1.1. Optical basicity

The concept of optical basicity was developed by glass scientists Duffy and Ingram [10] and introduced

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Table 1. Sulphide capacity prediction models

C_s model	Slags	Formulas of models	Ref.
Sosinsky-Sommerville	$CaO-SiO_2-MgO-Al_2O_3$ etc.	$\log C_S = (22690 - 54640\Lambda)/T + 43.6\Lambda - 25.2$	[6]
Young et al.	$CaO-SiO_2-MgO-Al_2O_3$ etc.	$\Lambda < 0.8$ $\log C_S = -13.913 + 42.84\Lambda - 23.82\Lambda^2 - 11710/T - 0.0223\ (\%\ SiO_2) - 0.2275\ (\%\ Al_2O_3)$	[7]
Taniguchi	$CaO-SiO_2-MgO-Al_2O_3$	$\log C_S = 7.350 + 94.89\log \Lambda - 10051 + \Lambda\ (-338\ (\%\ MgO) + 287\ (\%\ MnO))/T + 0.2284\ (\%\ SiO_2) + 0.1379\ (\%\ Al_2O_3) - 0.0587\ (\%\ MgO) + 0.0841\ (\%\ MnO)$	[8]
Tsao-Katayama	$CaO-SiO_2-MgO-Al_2O_3$	$\log C_S = 14.2\Lambda - 9894/T - 7.55$	[9]
KTH	$CaO-SiO_2-MgO-Al_2O_3$	$RT(\ln C_S) = 58.8157 \cdot T - 118535 - \{X_{Al_2O_3} \cdot 157705.28 - X_{CaO} \cdot 33099.43 + X_{MgO} \cdot 9573.07 - X_{MnO} \cdot 36626.46 + X_{SiO_2} \cdot 168872.59\} - \{\xi^{Al_2O_3-CaO}_{Interaction} + \xi^{Al_2O_3-SiO_2}_{Interaction} + \xi^{Al_2O_3-MnO}_{Interaction} + \xi^{CaO-SiO_2}_{Interaction} + \xi^{MgO-SiO_2}_{Interaction} + \xi^{MnO-SiO_2}_{Interaction} + \xi^{CaO-FeO}_{Interaction} + \xi^{MnO-FeO}_{Interaction} + \xi^{FeO-SiO_2}_{Interaction} + \xi^{Al_2O_3-CaO-MgO}_{Interaction} + \xi^{Al_2O_3-CaO-SiO_2}_{Interaction} + \xi^{Al_2O_3-MgO-SiO_2}_{Interaction} + \xi^{Al_2O_3-MgO-MnO}_{Interaction} + \xi^{Al_2O_3-MnO-SiO_2}_{Interaction} + \xi^{CaO-MgO-SiO_2}_{Interaction} + \xi^{CaO-MgO-SiO_2}_{Interaction} + \xi^{CaO-MnO-SiO_2}_{Interaction} + \xi^{MgO-MnO-SiO_2}_{Interaction} + \xi^{Al_2O_3-FeO-SiO_2}_{Interaction} + \xi^{CaO-FeO-SiO_2}_{Interaction} + \xi^{MgO-FeO-SiO_2}_{Interaction} + \xi^{MnO-FeO-SiO_2}_{Interaction}\}$	[21]

to the metallurgical community by Duffy, Ingram and Sommerville in the late 1970s [11]. Although it is not a frequently used parameter in the steelmaking practice, it is a valuable tool for designing slags or fluxes, and an alternative approach to estimate the slag's sulphide capacity. Optical basicity (denoted by Λ) refers to a measure of basicity determined by spectroscopic methods that have been shown to be predictable from Pauling's electronegativity of the individual elements in slag. The advantage of using optical basicity lies in the observation that it is simply extended to a multicomponent system such as ladle steelmaking slags. The values of optical basicity for common steelmaking oxides are available in literature [6, 7, 12]. Hence it is possible to estimate the sulphide capacities for ladle steelmaking slags knowing in many cases just their chemical composition, temperature and the oxygen activity $[a_O]$ in steel [13, 14]:

$$\Lambda = X_{AO}\Lambda_{AO} + X_{BO}\Lambda_{BO} + \cdots + X_{NO}\Lambda_{NO}. \quad (1)$$

In Eq. (1), X is the equivalent cation fraction that can be obtained by Eq. (2):

$$X = (\text{mole fraction of component } \times \text{ No. of oxygen atoms in oxide molecule}) \Big/ \sum (\text{mole fraction of component } \times \text{ No. of oxygen atoms in oxide molecule}). \quad (2)$$

1.2. Sulphide capacity models

The sulphide capacity is a property of the slag, which is dependent only on the temperature and the slag composition. The sulphide capacity can be used to describe the potential ability of an arbitrary homogeneous molten slag to remove sulphur and to compare the desulphurisation characteristics of different slags.

Fincham and Richardson [15, 16] have defined the sulphide capacity as:

$$C_S = K \times \frac{a_{(O^{2-})}}{f_{(S^{2-})}} = (\%S) \times \sqrt{P_{O_2}/P_{S_2}}. \quad (3)$$

The sulphide capacity such defined is a measurable parameter that characterises the desulphurising ability of the slag and depends only on slag composition and temperature. A more useful reaction for consideration of ladle steel desulphurisation is:

$$[S]_{metal} + {}^1\!/_2\,\{O\}_{gas} = [O]_{metal} + {}^1\!/_2\,\{S\}_{gas}. \quad (4)$$

Based on the optical basicity the five models were selected out of the numerous models provided in literature and compared with the values of the KTH model. The six sulphide capacity C_S prediction models with high acceptance are summarised in Table 1, and include S-S model by Sosinsky and Sommerville [6], Young's model [7], Taniguchi's model [8], T-K's

Table 2. Chemical composition of analysed slags

Heats	% CaO	% SiO_2	% Al_2O_3	% MgO	% MnO	T (K)
1	54.32	4.82	30.50	7.81	0.06	1851
2	57.00	8.20	27.70	4.10	0.09	1851
3	55.03	3.69	31.88	4.40	0.24	1865
4	55.20	2.90	34.21	8.88	0.03	1869
5	53.80	2.96	34.38	8.55	0.02	1854
6	52.49	3.85	32.51	9.05	0.13	1857
7	54.37	4.38	30.01	7.74	0.04	1845
8	56.72	5.65	27.51	5.22	0.07	1850
9	54.60	5.01	29.71	5.06	0.11	1860
10	54.62	3.71	29.83	8.19	0.06	1838
11	52.63	4.07	30.49	12.16	0.51	1851
12	54.85	3.38	28.92	8.31	0.08	1866
13	58.05	1.77	38.80	7.05	0.05	1865
14	54.64	2.38	31.05	9.28	0.08	1851
15	57.93	4.29	31.18	3.79	0.13	1870
16	57.09	8.46	25.43	7.76	0.10	1852
17	54.23	2.47	32.73	5.71	0.08	1853
18	53.34	3.88	33.36	6.33	0.06	1884
19	55.77	1.09	40.67	10.36	0.07	1847
20	58.24	3.57	33.31	3.32	0.18	1855
21	57.90	2.24	34.12	4.03	0.08	1865
22	57.78	5.00	30.72	4.24	0.11	1828
23	55.15	3.59	31.13	5.43	0.13	1862
24	58.32	4.49	32.12	3.53	0.08	1869
25	57.38	4.26	31.71	5.22	0.11	1868
26	60.37	4.44	29.92	3.58	0.11	1844
27	53.23	3.19	33.26	6.92	0.05	1857
28	59.58	3.02	31.52	3.92	0.12	1858
29	52.12	2.17	35.28	7.71	0.06	1844
30	58.01	3.72	31.74	4.43	0.13	1868
31	56.11	3.49	28.45	7.37	0.07	1872

model by Tsao-Katayama [9] based on optical basicity Λ and the KTH model [17–19] in terms of defined interaction coefficient of component i to $j\xi^{i-j}_{\text{Interaction}}$ is used in this work for comparison.

2. Experimental

2.1. Process of plant trial

Plant data used in this work was obtained at Dillinger Hütte Steel-plant in Dillingen, Germany. During the tapping, aluminium and FeSi were added as the deoxidisation agents, Fe-Mn as the ferroalloy, and the synthetic slag. The samples of metal and slag were taken after the LF treatment. The oxygen activity in the steel bulk was not measured. Finally, the steel was cast on the radial casting machines.

In Table 2 is presented the temperature and the chemical composition of slag for thirty-one analysed heats. The slag compositions used in the calculations were normalised to a four-component system of CaO-SiO_2-Al_2O_3-MgO, since the sum of all the oxides in the Table 2 does not always reach 100 %.

The values of optical basicity were calculated using the following coefficients for each oxide reported by Young et al. [6]: CaO-1.0, Al_2O_3-0.605, SiO_2-0.48, MnO-0.59, MgO-0.78 and FeO-0.51. The calculated values of the optical basicity Λ for all analysed heats were less than 0.8.

In order to calculate the oxygen activity in steel in this study the following equations were used:

$$2\,[\mathrm{Al}] + 3\,[\mathrm{O}] = (\mathrm{Al_2O_3}), \tag{5}$$

$$[\mathrm{Si}] + 2[\mathrm{O}] = (\mathrm{SiO_2}), \tag{6}$$

$$\Delta G^0_{\mathrm{Al}} = -1205115 + 386.7T, \tag{7}$$

$$\Delta G^0_{\mathrm{Si}} = -581900 + 221.8T. \tag{8}$$

The equilibrium constants of Eqs. (5) and (6) are:

$$K_{\mathrm{Al}} = \exp\frac{-\Delta G^0_{\mathrm{Al}}}{RT} = \frac{a_{(\mathrm{Al_2O_3})}}{[a]^3_{\mathrm{O}} \cdot [a]^2_{\mathrm{Al}}}, \tag{9}$$

$$K_{\mathrm{Si}} = \exp\frac{-\Delta G^0_{\mathrm{Si}}}{RT} = \frac{a_{(\mathrm{SiO_2})}}{[a]^2_{\mathrm{O}} \cdot [a]_{\mathrm{Si}}}. \tag{10}$$

From Eqs. (9) and (10) it is possible to derive an expression for the oxygen activity:

$$a_{\mathrm{O}} = \sqrt[3]{\frac{a_{\mathrm{Al_2O_3}}}{a^2_{\mathrm{Al}} \cdot \mathrm{e}^{-\frac{\Delta G^0}{RT}}}}, \tag{11}$$

$$a_{\mathrm{O}} = \sqrt{\frac{a_{\mathrm{SiO_2}}}{a_{\mathrm{Si}} \cdot \mathrm{e}^{-\frac{\Delta G^0}{RT}}}}. \tag{12}$$

2.2. Activity of oxygen in the slag and steel

It is well known that a control of the desulphurisation process is impossible if the oxygen activity is not known. As mentioned above, the oxygen activity in steel $[a_{\mathrm{O}}]$ at the end of the LF treatment was calculated using several existing online process data sets such as the temperature and the chemical composition of metal and slag. It was assumed that one of the reactions which took place during ladle treatment such as $2[\mathrm{Al}] + 3[\mathrm{O}] = (\mathrm{Al_2O_3})$ and $[\mathrm{Si}] + 2[\mathrm{O}] = \mathrm{SiO_2}$ was in equilibrium. Because of the fact that silicon controls the oxygen activity in steel prior to the aluminium deoxidation, in this study, the oxygen activity $[a_{\mathrm{O}}]$ was calculated using both Eqs. (5) and (6). In the present work, Ohta and Suito [20] expressions in Eqs. (13) and (14) were used to calculate the Al_2O_3 and the SiO_2 activities in slag, while Wagner's expression

Table 3. The calculated optical basicity, alumina $a_{(\mathrm{Al_2O_3})}$ and silica $a_{(\mathrm{SiO_2})}$ activities in slag, and oxygen activities $[a_\mathrm{O}]$ in steel for analysed heats

Heats	Λ	$a_{(\mathrm{Al_2O_3})}$	$a_{(\mathrm{SiO_2})}$	Case A $[a_\mathrm{O}]_{\mathrm{c,from\ Eq.\ (10)}}$ (%)	Case B $[a_\mathrm{O}]_{\mathrm{c,from\ Eq.\ (11)}}$ (%)
1	0.78	4.42E-04	1.98E-04	2.16E-05	7.74E-05
2	0.78	3.58E-03	2.47E-04	7.34E-05	9.84E-05
3	0.77	4.42E-05	1.57E-04	9.27E-06	9.08E-05
4	0.78	6.69E-06	1.75E-04	5.68E-06	1.04E-04
5	0.78	1.16E-05	1.94E-04	5.01E-06	7.94E-05
6	0.77	1.50E-04	2.20E-04	2.03E-05	1.22E-04
7	0.78	2.22E-04	1.74E-04	1.24E-05	6.37E-05
8	0.79	6.16E-04	1.51E-04	1.92E-05	7.58E-05
9	0.78	4.46E-04	1.80E-04	3.29E-05	1.05E-04
10	0.79	6.01E-05	1.48E-04	8.77E-06	5.86E-05
11	0.78	2.49E-04	2.06E-04	1.54E-05	7.72E-05
12	0.79	2.42E-05	1.27E-04	1.25E-05	9.27E-05
13	0.78	1.99E-09	1.63E-04	2.30E-07	1.05E-04
14	0.79	6.67E-07	1.28E-04	2.09E-06	7.39E-05
15	0.78	8.56E-05	1.38E-04	1.29E-05	9.10E-05
16	0.78	3.86E-03	2.31E-04	6.90E-05	9.58E-05
17	0.78	8.29E-07	1.41E-04	2.47E-06	8.74E-05
18	0.78	1.16E-04	2.13E-04	2.00E-05	1.23E-04
19	0.78	1.60E-13	2.00E-04	7.45E-09	9.42E-05
20	0.78	1.68E-05	1.38E-04	5.13E-06	7.07E-05
21	0.79	5.99E-08	1.17E-04	8.47E-07	6.94E-05
22	0.78	2.76E-04	1.57E-04	9.65E-06	4.96E-05
23	0.78	3.54E-05	1.47E-04	9.34E-06	9.34E-05
24	0.78	1.19E-04	1.51E-04	1.40E-05	8.02E-05
25	0.78	1.00E-04	1.53E-04	1.25E-05	8.51E-05
26	0.79	6.92E-05	1.10E-04	7.90E-06	6.18E-05
27	0.78	2.23E-05	1.87E-04	9.15E-06	1.05E-04
28	0.79	1.96E-06	1.00E-04	1.84E-06	7.24E-05
29	0.78	4.24E-07	1.96E-04	1.53E-06	9.32E-05
30	0.79	2.63E-05	1.30E-04	8.84E-06	8.19E-05
31	0.79	2.26E-05	1.13E-04	1.20E-05	9.53E-05

[21] in Eq. (15) was used to calculate the alumina $[a]_\mathrm{Al}$ and silicon $[a]_\mathrm{Si}$ activities in the steel. All used oxides are in weight percent.

$$\begin{aligned}\log a_{\mathrm{Al_2O_3}} =& \{-0.275(\%\ \mathrm{CaO}) + 0.167(\%\ \mathrm{MgO})\}/ \\ & /(\%\ \mathrm{SiO_2}) + 0.033(\mathrm{Al_2O_3}) - 1.560, \qquad (13)\\ \log a_{\mathrm{SiO_2}} =& 0.036(\%\ \mathrm{MgO}) + 0.061(\mathrm{Al_2O_3}) + \\ & + 0.123(\%\ \mathrm{SiO_2}) - (\%\ \mathrm{SiO_2})/(\%\ \mathrm{CaO}) - \\ & - 6.456. \qquad (14)\end{aligned}$$

The activity coefficients of sulphur, aluminium and silicon in the metal were calculated by using Wagner's equation as follows:

$$\log f_i = \sum (e_i^j[\%j]), \qquad (15)$$

where e_i^j is interaction coefficient of j on i, f_i is Henry's activity coefficient for species i in the metal.

The interaction coefficients used in this work are: $e_\mathrm{S}^\mathrm{S} = (-0.153 + 233/T)$, $e_\mathrm{S}^\mathrm{C} = 0.113$, $e_\mathrm{S}^\mathrm{Si} = 0.063$, $e_\mathrm{S}^\mathrm{Al} = 0.035$, $e_\mathrm{S}^\mathrm{Mn} = -0.026$, $e_\mathrm{Al}^\mathrm{Al} = (0.011 + 63/T)$, $e_\mathrm{Al}^\mathrm{C} = 0.091$, $e_\mathrm{Al}^\mathrm{Si} = 0.056$, $e_\mathrm{Al}^\mathrm{S} = 0.030$, $e_\mathrm{Si}^\mathrm{C} = 0.18$, $e_\mathrm{Si}^\mathrm{Si} = (0.089 + 34.5/T)$, $e_\mathrm{Si}^\mathrm{S} = 0.056$, $e_\mathrm{Si}^\mathrm{Al} = 0.058$, $e_\mathrm{Si}^\mathrm{Mn} = 0.002$ [22–24].

The results of calculated optical basicity, alumina activities $a_{(\mathrm{Al_2O_3})}$ and silica activities $a_{(\mathrm{SiO_2})}$ in the slag, and calculated values of oxygen activities in the steel $[a_\mathrm{O}]_\mathrm{Si}$ and $[a_\mathrm{O}]_\mathrm{Al}$ at the end of ladle treatment are shown in Table 3.

3. Results and discussion

As can be seen in Table 3 the calculated values of alumina activities $a_{(\mathrm{Al_2O_3})}$ are generally very low, i.e. below 10^{-3} and 10^{-4} (wt.%) and sometimes even lower than 10^{-5} in the case of heats with the content of $[\%\ \mathrm{S}] \leq 0.0005$. On the other hand, in the case of heats with the sulphur content in the range $[\%\ \mathrm{S}] = 0.0006$–$0.001$ the values of alumina activities are spread well below 10^{-5} (wt.%). However, since the $\mathrm{SiO_2}$ contents at the end of vacuum treatment were between 1.09 and 8.46 wt.% and the fact that Eq. (14) is only valid for a $\mathrm{SiO_2}$ content of 10 to 50 wt.%, there could be

Table 4. Compared results of relationship between optical basicity and sulphur capacities

		log C_S measured		log C_S calculated				
Heats	Λ	Case A	Case B	Young et al.	S-S	Taniguchi	T-K	KTH
1	0.78	–2.02	–1.46	–2.13	–1.94	–2.15	–1.80	–2.25
2	0.78	–1.53	–1.40	–2.18	–2.02	–2.32	–1.88	–2.10
3	0.77	–2.56	–1.57	–2.16	–1.97	–2.75	–1.87	–2.02
4	0.78	–2.85	–1.59	–2.07	–1.82	–2.10	–1.73	–2.23
5	0.78	–2.93	–1.73	–2.16	–1.96	–2.22	–1.83	–2.33
6	0.77	–2.38	–1.60	–2.17	–2.01	–2.38	–1.89	–2.35
7	0.78	–2.46	–1.75	–2.12	–1.94	–2.12	–1.78	–2.22
8	0.79	–2.29	–1.69	–2.06	–1.85	–2.07	–1.70	–2.00
9	0.78	–2.17	–1.67	–2.11	–1.88	–2.21	–1.77	–2.08
10	0.79	–2.77	–1.94	–2.11	–1.92	–2.06	–1.74	–2.20
11	0.78	–2.59	–1.89	–2.11	–1.96	–2.17	–1.83	–2.37
12	0.79	–2.74	–1.87	–1.96	–1.69	–1.87	–1.59	–2.05
13	0.78	–4.27	–1.61	–2.13	–1.86	–2.22	–1.76	–2.20
14	0.79	–3.43	–1.88	–2.04	–1.81	–1.98	–1.67	–2.16
15	0.78	–2.67	–1.82	–2.06	–1.80	–2.35	–1.72	–1.90
16	0.78	–2.05	–1.91	–2.09	–1.95	–2.15	–1.81	–2.18
17	0.78	–3.24	–1.69	–2.12	–1.88	–2.22	–1.75	–2.11
18	0.78	–2.37	–1.58	–2.10	–1.82	–2.20	–1.77	–2.19
19	0.78	–5.81	–1.71	–2.24	–2.04	–2.34	–1.89	–2.47
20	0.78	–3.13	–1.99	–2.13	–1.89	–2.35	–1.76	–1.94
21	0.79	–3.64	–1.73	–2.06	–1.75	–2.16	–1.65	–1.92
22	0.78	–2.67	–1.96	–2.21	–2.06	–2.39	–1.85	–2.06
23	0.78	–2.77	–1.77	–2.09	–1.85	–2.29	–1.74	–2.05
24	0.78	–2.64	–1.88	–2.08	–1.80	–2.24	–1.71	–1.93
25	0.78	–2.74	–1.90	–2.06	–1.79	–2.16	–1.70	–2.01
26	0.79	–2.75	–1.85	–2.06	–1.82	–2.11	–1.65	–1.84
27	0.78	–2.82	–1.76	–2.15	–1.93	–2.23	–1.81	–2.25
28	0.79	–3.53	–1.93	–2.02	–1.72	–2.10	–1.60	–1.82
29	0.78	–3.72	–1.94	–2.23	–2.03	–2.29	–1.87	–2.37
30	0.79	–2.72	–1.75	–2.04	–1.75	–2.14	–1.66	–1.92
31	0.79	–2.75	–1.85	–1.93	–1.63	–1.89	–1.55	–1.95

some error in the calculated alumina activities. After LF treatment, the calculated values of silicon activity in the slag are steady at the level 10^{-4} (wt.%), which corresponds to a SiO_2 content of a few per cent. This is in accordance with the earlier published results [25].

3.1. Comparison of the sulphide capacity results

In this work, we applied the Young's et al. approach to calculate measured values of the sulphide capacity with calculated oxygen activity $[a_O]$ in the steel according to Eq. (11) (further called Case A) and Eq. (12) (further called Case B). Then results were compared with the calculated values of the sulphide capacity according to original parameters each above mentioned optical basicity concepts as well as the KTH model.

The results are shown in Tables 4, 5, 6a, 6b and Figs. 1, 2a,b. For the clarity of the presentation, in Fig. 1, all results are calculated for the same level of the final content of the sulphur, and then shown within Young's "S" curve contour. The optical basicity for all analysed slags was in the narrow range Λ = 0.77–0.79. It is evident from Fig. 1 that the results of measured and calculated values of the sulphide capacities by prediction of activity oxygen $[a_O]_{Si}$ (Case B) lay in the upper middle region of the basicity. On the other hand, there are big discrepancies between measured and calculated values of the sulphide capacities log C_S by prediction of oxygen activity $[a_O]_{Al}$ (Case A). Mostly, heats with the measured values of the sulphide capacity lie outside, in the lower region of the Young's "S" curve contour. As can be seen from Table 4 and Figs. 2a,b, the measured values of the predicted oxygen activities in the Case A are lower comparing with those in the Case B.

Table 4 shows the deviation between measured and calculated sulphide capacity. It is evident that there are two groups of results where the deviation between obtained values of the measured and calculated values of the sulphide capacity was relatively small: one group for the S-S's and T-K's models, compared with the measured values in Case B, and the second group,

Table 5. The average values of the calculated sulphide capacities C_S for the average levels of final sulphur content

% S	C_S measured		C_S calculated				
	Case A	Case B	Young et al.	S-S	Taniguchi	T-K	KTH
0.0003	0.0042	0.0284	0.0072	0.0113	0.0053	0.0148	0.0063
0.0005	0.0031	0.0162	0.0084	0.0137	0.0085	0.0187	0.0073
0.0006	0.0008	0.0162	0.0083	0.0141	0.0070	0.0183	0.0081
0.0007	0.0002	0.0191	0.0072	0.0126	0.0053	0.0163	0.0073
0.0008	0.0013	0.0145	0.0080	0.0145	0.0058	0.0187	0.0103
0.0009	0.0006	0.0136	0.0078	0.0138	0.0067	0.0190	0.0098
0.001	0.0018	0.0159	0.0105	0.0208	0.0101	0.0251	0.0116

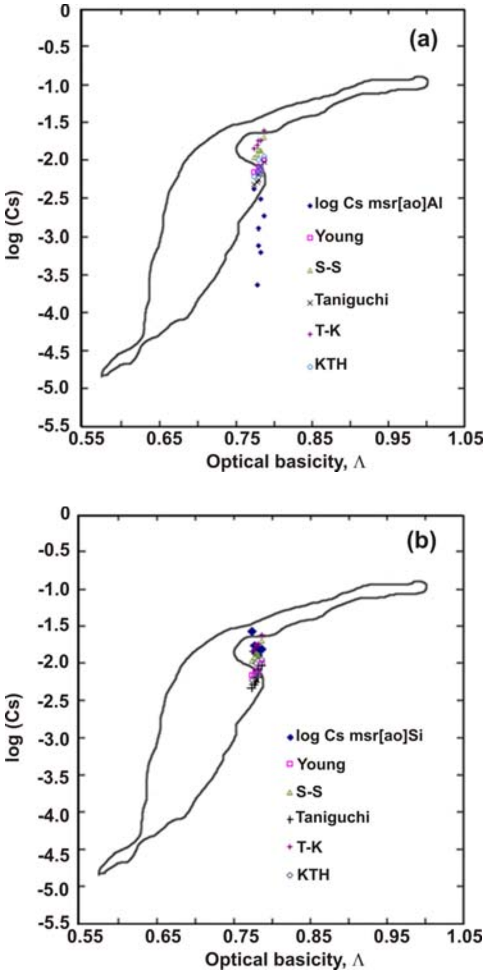

Fig. 1. Relationship between optical basicity and measured and calculated sulphur capacities log C_S for the different calculated values of oxygen activities: a) Case A $[a_O]_{Al}$, b) Case B $[a_O]_{Si}$.

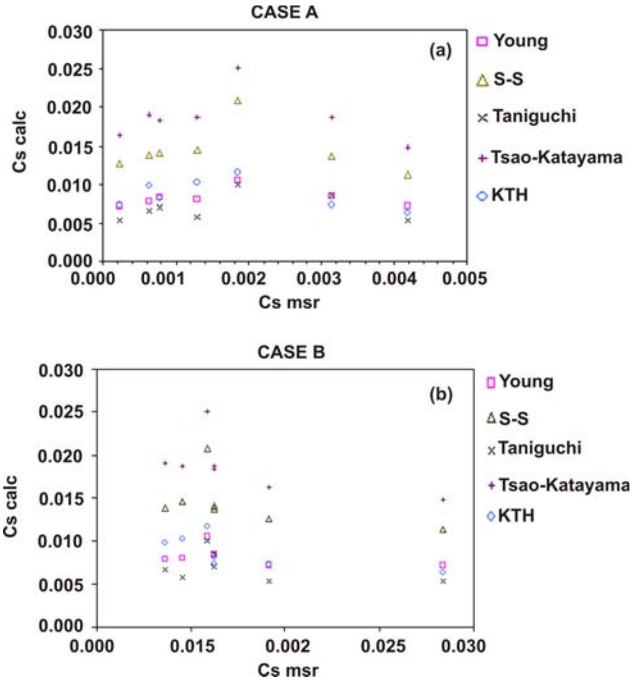

Fig. 2. a) Comparison of measured values of the sulphide capacity $C_{S\,msr}$ with that calculated $C_{S\,calc}$ using different optical basicity models (Case A). b) Comparison of measured values of the sulphide capacity $C_{S\,msr}$ with that calculated using different optical basicity models (Case B).

where Youngs's, Taniguchi's and KTH models are compared with the measured values in Case A.

On the other hand, it is obvious that the average values of sulphide capacity obtained by Sosinsky-Sommerville's and Tsao-Katyama's models are the closest to equilibrium as shown in Table 5. Also, comparing the results of calculated sulphide capacities by optical basicity concept and the KTH model between the heats 1–12 ([% S] $\leq$ 0.0005) and 13–19 ([% S] = 0.0006–0.001), the models of Young and Taniguchi as well as the KTH model show very similar results, however, all models predict that heats 1–12 have slightly lower average values of the sulphide capacities compared with heats 13–19 within all applied models.

Tables 6a and 6b show the differences between measured and calculated values of the sulphide capacities ΔC_S for the average levels of the final content of sulphur. The "–" means that calculated values of C_S are higher than measured. It is clear that in

Table 6a. The differences between measured and calculated values of the sulphide capacities ΔC_S for the average levels of final content of sulphur (Case A)

% S	Young	S-S	Taniguchi	Tsao-Katayama	KTH
0.0003	–0.003	–0.007	–0.003	–0.012	–0.001
0.0005	–0.005	–0.010	–0.005	–0.015	–0.004
0.0006	–0.008	–0.013	–0.006	–0.017	–0.007
0.0007	–0.007	–0.012	–0.005	–0.016	–0.006
0.0008	–0.007	–0.013	–0.004	–0.017	–0.009
0.0009	–0.007	–0.013	–0.006	–0.018	–0.008
0.001	–0.009	–0.019	–0.008	–0.023	–0.010

Table 6b. The differences between measured and calculated values of the sulphide capacities ΔC_S for the average levels of final content of sulphur (Case B)

% S	Young	S-S	Taniguchi	Tsao-Katayama	KTH
0.0003	0.021	0.017	0.023	0.014	0.022
0.0005	0.008	0.002	0.008	–0.002	0.009
0.0006	0.008	0.002	0.009	–0.002	0.008
0.0007	0.012	0.006	0.014	0.003	0.012
0.0008	0.006	0.000	0.009	–0.004	0.004
0.0009	0.006	–0.0002	0.007	–0.005	0.004
0.001	0.005	–0.005	0.006	–0.009	0.004

Table 7. The values of correlation coefficient R between measured and calculated sulphide capacity ($C_{S\ \mathrm{msr}}$–$C_{S\ \mathrm{calc}}$) for the average values of the final sulphur content

$C_{S\ \mathrm{msr}}$–$C_{S\ \mathrm{calc}}$	Young et al.	S-S	Taniguchi	Tsao-Katayama	KTH
			R		
Case A	0.80	0.75	0.76	0.80	0.87
Case B	0.43	0.45	0.43	0.56	0.74

Case A all models give the calculated values higher than measured while in Case B the Tsao-Katayama's model gives higher calculated values than measured for almost all average sulphur levels. Also, it can be seen that the correlation between measured and calculated values of the sulphur capacities are more or less scattered.

One possible reason for the increased deviation between measured and calculated values of sulphide capacity C_S was that the use of Eq. (12) to calculate the alumina activity might not be appropriate for those slags whose silica content was too far away from the specified lower limit of 10 wt.%. The second reason could potentially be dependent on the content of the both oxides, % SiO_2 and % Al_2O_3, at the end of LF treatment. Finally, the third reason is the relatively small number of analysed samples for the same level of the final sulphur content.

For the purpose of comparison between analysed models, the regression coefficient R between measured and calculated values of the sulphide capacities C_S has been calculated for the average values of the final sulphur content. The results are shown in Table 7. Generally, it is clearly seen that the KTH model gives better correlation than results obtained by optical basicity models.

4. Conclusions

1. It is possible to estimate the sulphide capacities for ladle steelmaking slags knowing its chemical composition, temperature and predicted the oxygen activity $[a_O]$ in steel.

2. Predicting the sulphide capacities of CaO-Al_2O_3-SiO_2-MgO ladle slags using the analysed expressions based on the optical basicity concept give the results in the field of middle and relatively high region of slag basicity.

3. The correlation between measured and calculated values of the sulphide capacities shows the better agreement between predicted and experimentally

determined sulphur capacity data based on the KTH model comparing with the optical basicity concept.

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