An Investigation on the Copper Content of Matte Smelting Slag in Peirce-Smith Converter

Chunlin CHEN[*], Jiayun ZHANG[*], Meng BAI[**], Shoukun WEI[*]

Dept. Physical Chemistry, University of Science & Technology Beijing, Beijing, China 100083

** Guixi Smelter, Jiangxi Copper *Co. Ltd.,Jiangxi, China, 335424*

Abstract The copper contents in the slags during the slag-making stage of Peirce-Smith converters with their existing forms have been investigated in this work. The investigation was based on plant trials in Guixi Smelter in Jiangxi Province, China, the corresponding thermodynamic calculations and kinetic considerations.

From the plant data, the total copper content in the slags was in a range between 2% and 8 %(mass). The mechanical entrainment of matte drops has been found to be the main cause of the copper loss from the converter slags. A parameter, the suspension index, defined as the ratio of the mass percent of copper in suspended matte drops in the slag to that in bulk of the matte phase, has been adopted to quantify the matte entrainment. The values of this parameter estimated in this work have been found mainly within a range of 2.5%-8%.

The Fe_3O_4 content in the slag has been estimated to be the most important factor, among others, influencing the separation of slag with matte and, consenquently, the copper loss from the slag.

1. Introduction

The higher total copper content in the slag formed during the slag-making stage in a Peirce-Smith converter (for brevity, "converter" is used bellow in the context) has long been focused in the copper production industry. The slag has to be poured out at the end of every slag-making stage, hence causing a considerable copper loss. Formally, the total copper content in the slags was reported within a range of 2%-15% (mass) [1]. In the plant practice in Guixi Smelter, a lower content range, 2%-8%, was maintained in recent years[2]. Recycling the copper from slags in solid state results in a remarkable raise in production cost. Although instructions to reduce the copper contents in the molten slag have been frequently presented in technical reports and monographs, still detailed investigation on this topic from fundamental as well as technical viewpoints would be favorable and feasible.

Based on industrial trials of two converters in Guixi Smelter and thermodynamic calculations, the copper content in the slags formed in slag-making stage was investigated with their existing forms in this study. As reported earlier, the matte drop suspension in the molten slags has been found to be the main cause for the copper loss. The factors influencing matte-drop suspension have also been investigated with thermodynamic as well as kinetic considerations.

2. Outline of industrial trials and process simulation

The purpose of the industrial trials carried out in Guixi Smelter was to obtain necessary quantitative information from the plant practice of the copper converters under stable operational conditions[2]. The plant data gained from the trials were, in turn, applied to the mass and heat balance, as well as to the process simulations [3].

In conventional plant practice of a converter, molten matte and slag samples are taken at the end of the slag-making stage. X-ray spectrometric method is adopted to determine the contents of Cu, Fe, S and SiO_2 in quenched samples. In the present work, Zn and Pb contents

in samples were also analyzed; temperature was measured using a Pt-Rh thermocouple as long as the melt stream was tapped. Furthermore, mineral composition analyses were taken for all the input and output materials with the aid of necessary XRD and EDS examinations after their chemical compositions had been analyzed.

Simulations of the converter operations were carried out for seven charges based on chemical equilibrium along with the heat and mass balance. A parameter, called oxygen efficiency was introduced in the calculations to take the process kinetics into consideration. However, during a slag-making stage, the corresponding oxygen efficiency value is close to unity, therefore the effects of the same were considered not significant. The temperature and composition variations in dense phases as well as partial pressures in the gas phase with time were calculated for each blowing period in the seven charges. As an example, Table 1 gives calculated chemical composition data for molten slag and matte at end of each blowing period in the slag-making stage of Charge 173 along with the corresponding plant data. It can be seen from the table that calculated mass percents of Cu and S in molten matte, and those of Fe and SiO_2 in molten slag are in good agreements with the relevant plant data. Also, deviations between calculated and measured values such as temperature and blowing time in slag-making stages are within reasonable levels. The information obtained, which will be reported elsewhere, would be useful to the operation optimization as well as process dynamic control of copper converters.

The calculated relative deviations for the Zn and Pb contents, either in matte or in slag phase in Table 1 are greater than those for the main elements. Furthermore, the errors do not exhibit systematic tendencies. For the total copper content in the slags, negative deviation can be found between calculated values and plant data. This will be discussed in the following section.

3. Copper content in slag

The mineralographic examination has shown that Cu_2S particles exist in a diameter range of 0.002-0.2 mm in the slag samples. The mechanical entrainment of the matte drops within the molten slag is thus confirmed. As the matte drop suspension was not considered in some of the calculations, this, as mentioned above, would result in negative deviation of the calculated total copper content in the slag from the relevant plant data.

Cu_2O, Cu_2S as well as metallic copper phase (Cu^0) in the slag samples were found from their X-ray diffraction patterns. A question may arise from how the pure copper phase is being formed in the slag samples. For the reaction,

$$Cu_2S_{(l)}+2Cu_2O_{(l)}=6Cu_{(l)}+SO_{2(g)} \qquad (1)$$
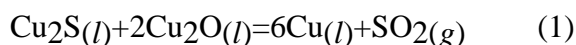
the temperature dependence of standard Gibbs energy change is as follows

$$\Delta G_1^0 =1260\text{-}35.61T , \text{ J} \qquad (2)$$

Eq.(2) gives negative ΔG_1^0 values in the temperature range of converter operations. However, Cu_2O may react with FeS as shown in the following equation

$$2FeS_{(l)}+ 2Cu_2O_{(l)} =2Cu_2S_{(l)}+2FeO_{(l)} \qquad (3)$$

The temperature dependence of ΔG_3^0 is given by Eq. (4).

$$\Delta G_3^0 = -194700 + 40.08T, \quad \text{J} \qquad (4)$$

Eq.(4) yields much more negative values for ΔG_3^0 than those of ΔG_1^0. Even if the partial pressure of SO_2 as well as activities of the components in molten slag and matte phases in the converter are considered, thermodynamic calculation can still give more negative ΔG_3 values when the FeS content in matte exceeds 1%. Since Cu_2O in the slag reacts with FeS prior to Cu_2S, the copper phase observed in slag samples might be formed due to the over cooling of the sample quenching in air rather than the reaction expressed by Eq.(1) at high temperature. The standard Gibbs energies for the compounds involved in Eqs.(1) and (3) are listed in Table 2.

3. 1 Copper existing as dissolved forms in slag

In the theoretical calculations, Cu_2S and Cu_2O have been regarded as the dissolved components in the slag during the slag-making stage. The calculations have indicated the increase of the dissolved Cu_2S and Cu_2O contents in the slags with the copper grade of the molten matte, $(Cu\%)_{matte}$. As an example, the calculated variations for Charge 173 are illustrated in Fig. 1. The calculated total contents of copper existing as dissolved forms, $(Cu\%)_{slag, dis}$ *versus* $(Cu\%)_{matte}$ for the seven charges are plotted in Fig. 2. The correlation of $(Cu\%)_{slag, dis}$ with $(Cu\%)_{matte}$ being fitted is as follows

$$(Cu\%)_{slag, dis} = 0.1107 - 0.3224 \times (Cu\%)_{matte} + 0.2380 \times (Cu\%)_{matte}^2 \quad (5)$$

3. 2 Copper loss caused by matte entrainment in slag

The total copper mass percents, $(Cu\%)_{slag, tot}$, in the slag at the end of each blowing period in slag-making stage are listed in Table 3, with a range of 2%-8%. For comparison, the calculated $(Cu\%)_{slag, dis}$ values along with the corresponding $(Cu\%)_{matte}$ are included in this table. It is noted that about 85% of the total amount of copper has been estimated to be contained in matte drops mixed in the slag.

As known, the differences of physical property values, such as the density and viscosity, between the molten matte and slag in a converter are relatively low. Fine size matte drops may suspend easily in the molten slag layer. A so called suspension index proposed to quantify the matte drop entrainment in the slag for Noranda process[4] has been employed in this work. This parameter has been defined by the mass ratio of copper in suspended matte drops in slag to that in the matte phase, and designated by S_{matte}^{slag} in this paper. Nagamori estimated[4] that for the slag-making stage in Noranda process S_{matte}^{slag} was around 6%. From its definition, the following equation was used to estimate the suspension index values of matte drops in a converter.

$$S_{matte}^{slag} = \frac{(Cu\%)_{slag, tot} - (Cu\%)_{slag, dis}}{(Cu\%)_{matte}} \times 100\% \qquad (6)$$

The plant data for $(Cu\%)_{slag, tot}$ and $(Cu\%)_{matte}$ could be obtained from daily production records, while $(Cu\%)_{slag, dis}$ values in the present work were theoretically calculated. The S_{matte}^{slag} values evaluated from the operational practice of converters in Guixi Smelter were

mainly distributed between 2.5%-8% with their mean value of 4.7%. The $S_{\text{matte}}^{\text{slag}}$ data are listed in column 6, Table 3.

Using Eq. (6) with known $S_{\text{matte}}^{\text{slag}}$ and the calculated $(Cu\%)_{\text{slag, dis}}$ data, one may roughly estimate the variation of $(Cu\%)_{\text{slag, tot}}$ with $(Cu\%)_{\text{matte}}$ during a slag-making stage. Fig. 3 is an example showing such a variation for Charge 173.

4. Discussion

In order to reduce the copper loss for a converter, optimized operation parameters are desirable. To meet the demand, a better approach is to apply a non-linear method in numerical analyses, like pattern recognition or artificial nerval-networks, to the optimization. In such calculations, much more amount of plant data would be required. In the present work, a simple linear regression method has been adopted to investigate the factors influencing $S_{\text{matte}}^{\text{slag}}$. The ratio of the mass pct of Fe to that of SiO$_2$ in the slag, designated by r_{SiO2}^{Fe} is an important operation parameter for the slag-making stage. The r_{SiO2}^{Fe} values obtained in the industrial trials are listed in column 7, Table 2. A plot of $S_{\text{matte}}^{\text{slag}}$ *versus* r_{SiO2}^{Fe} is illustrated in Fig. 4. It is apparent that no explicit correlation could be derived from this scattered-data distribution. Similarly, a scatter could be noted from $S_{\text{matte}}^{\text{slag}}$ values *versus* the measured temperatures listed at column 8, Table 2.

It is known that the falling velocity of a matte drop in a molten slag layer can be evaluated using Stokes law as follows

$$V = \frac{1}{18} \times g \times (\frac{r_{\text{drop}} - r_{\text{slag}}}{m_{\text{slag}}}) \times d_{\text{drop}}^2 \qquad (7)$$

where r_{slag} and m_{slag} stand for the density and viscosity of the molten slag , r_{drop} and d_{drop} denote the density and diameter for matte drop respectively, g is gravity acceleration. The measures to increase r_{drop}, d_{drop}, and to reduce m_{slag} and r_{slag} may simply be proposed to improve matte and slag separation. As the chemical reactions and physical phenomena in an industrial converter are complicated, considerations should be taken more carefully.

The rate of r_{drop} variation with $(Cu\%)_{\text{matte}}$ and temperature when the copper grade of matte exceeds about 60 % has been estimated to be relatively low. In this case, the effect of r_{drop} variation on the separation between the molten slag and matte during the slag-making stage could be neglected. It should be mentioned that the mean drop size depends on the differences between r_{slag} and r_{drop}, m_{slag} and m_{drop}, as well as the interfacial tension between the molten slag and matte, $s_{\text{slag-matte}}$ [5]. This again emphasizes that physical properties of the slag may pay an important role in the matte drop suspension. As known, the increasing Fe$_3$O$_4$ contents in the slag would raise the slag viscosity dramatically and affect other physical properties, like $s_{\text{slag-matte}}$ and r_{slag}. Accordingly, the matte-drop suspension in the slag could be expected to be sensitive to the Fe$_3$O$_4$ content in the slag. This can be seen from the plot of $S_{\text{matte}}^{\text{slag}}$ values *versus* the mass pct of Fe$_3$O$_4$ in Fig. 5. Due to the random and fluctuation nature of the plant data, the plot also shows a scatter. However, a rising tendency of $S_{\text{matte}}^{\text{slag}}$ with the mass pct of Fe$_3$O$_4$ is still revealed clearly in Fig. 5.

Two points might be mentioned. First, both the Fe_3O_4 content and r_{SiO2}^{Fe} are affected by temperature in a certain degree, and are not independent each other. Secondly, the scattered data distribution of S_{matte}^{slag} with r_{SiO2}^{Fe} or temperature might be attributed to characteristics of the fluctuation and random present in plant data. These experimental facts may imply that a more complex relationship of S_{matte}^{slag} with r_{SiO2}^{Fe} or temperature might exist.

The foregoing analysis also indicates that to diminish the copper loss from the slag in a converter, the necessary technical measures should be considered comprehensively. Among all these considerations, a proper control of the Fe_3O_4 content in the slag may play a key role.

5. Conclusions

From the plant practice of Peirce-Smith converters in Guixi Smelter, the total copper content in the molten slags was found to be in a range of 2%-8%(mass) at the end of the slag-making stage. Nearly 85 % of total copper content in slags could be found in mechanically suspended matte drops, while the remaining portion is the copper existing as Cu_2O and Cu_2S dissolved in the slags.

The mechanical entrainment of matte drops could be quantified by a suspension index defined as the ratio of the mass content of copper in matte drops in the slag to that in molten matte. The values of the suspension index estimated in this work are within a range of 2.5%-8%.

Usually, converter temperature, viscosity as well as Fe_3O_4 content in the slag are considered to diminish the matte drop entrainment in the slag and, therefore, the copper loss from the converter. The present work has indicated that proper control of the Fe_3O_4 content may play a predominant role in this regard.

Acknowledgment

References

[1] A. K. Biswas, Davenport: Extractive Metallurgy of Copper, 3rd.Edition, Pergamon Press, Oxford, 1994.
[2] Internal Report of Industrial Trials on the Copper Converters in Guixi Smelter. Dec. 1997.
[3] Chunlin Chen: Doctoral Thesis, Department of Physical Chemistry of Metallurgy, University of Science and Technology Beijing, 1999.
[4] M. Nagamori, P. J. Mackey, Metallurgical Transactions, 1978, 9B. 255-265.
[5] R. Clife, J. R. Grace, M. E. Weber, Bubbles, Drops and Particles, Chapters. 3 and 7, Academic Press, New York, 1978.
[6] R. Jr. Schuhmann, Trans. AIME, 1950, 188: 873-884
[7] S. Rainer, Metall. Trans. B. 1983, 14B: 473-481.
[8] O. Knacke, O. Kubaschewcki, K. Hesselman, Thermochemistry Properties of Inorganic Substances, 2nd. Edition, Springer Verlag, Berlin, 1991.
[9] C. E. Sims: Electric Furnace Steelmaking, Vol. II, 134-137, Interscience, 1963.
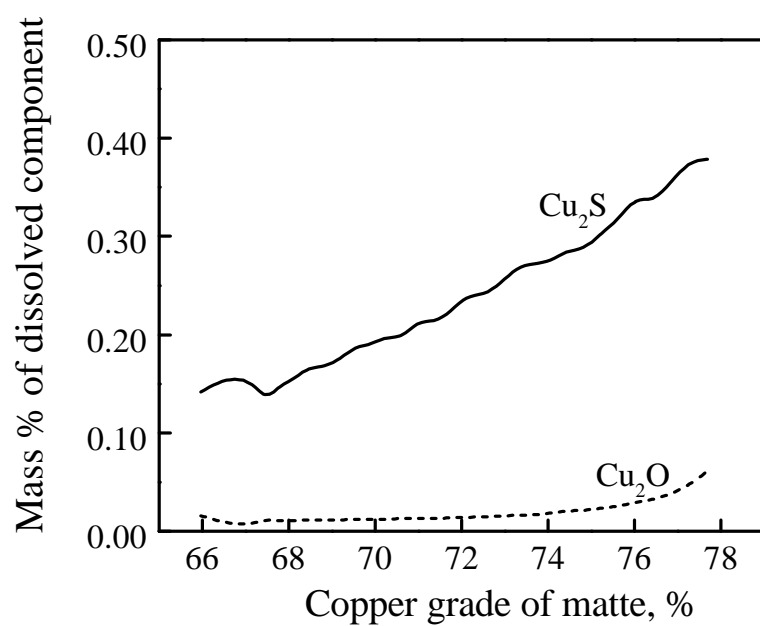
Fig. 1   Content variations of dissolved components
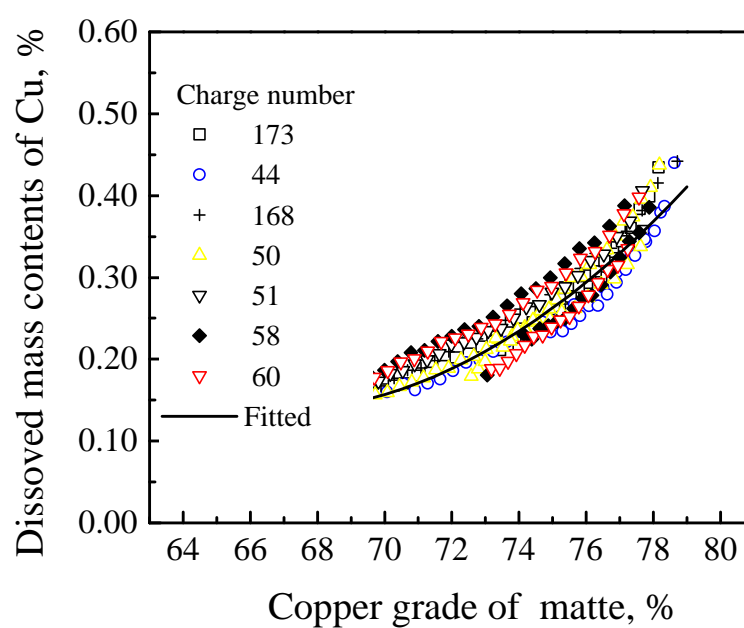with copper grade of matte for Charge 173

Fig. 2   Correlation of mass % of copper in dissolved
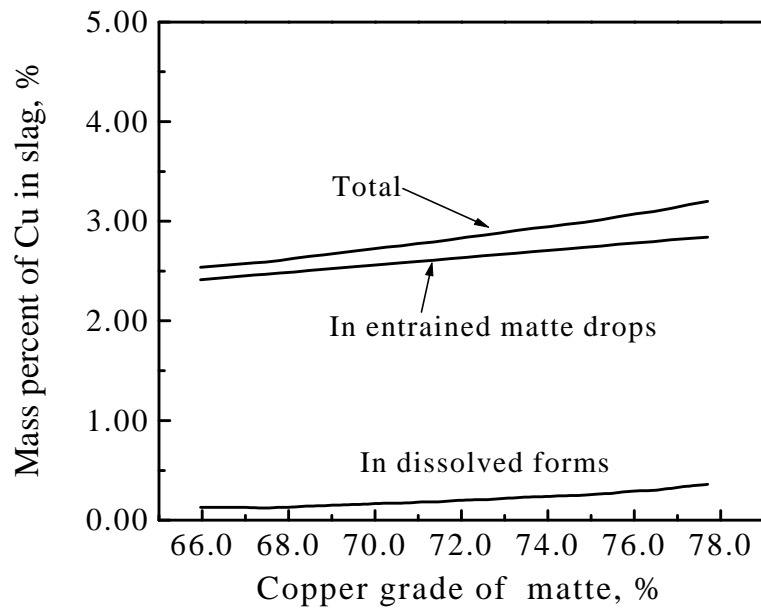forms in slag with copper grade of matte

Fig. 3 Variation of copper contents in slag
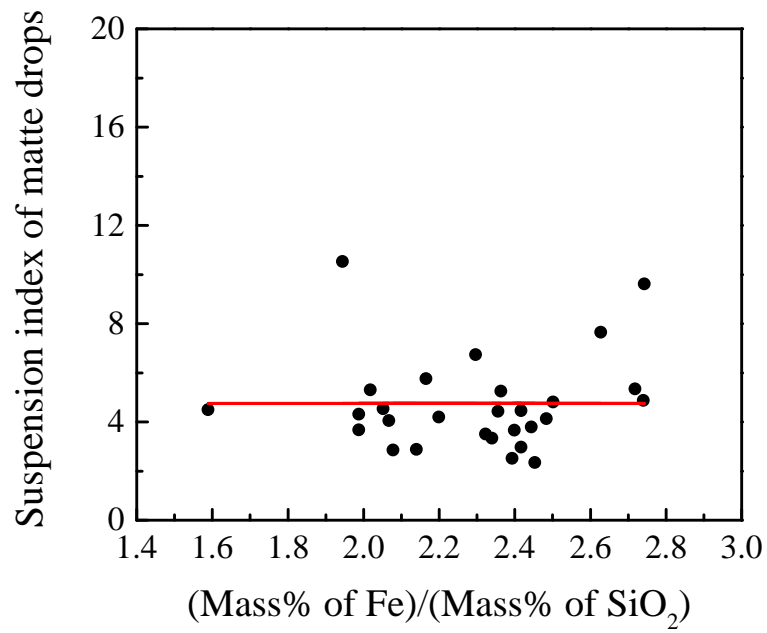with copper grade of matte for Charge 173

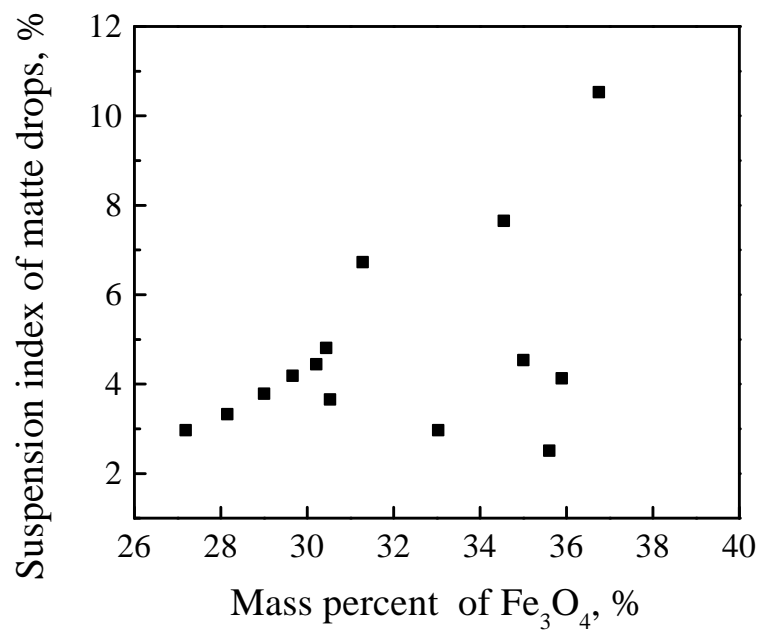Fig. 4   Plot of $S_{\text{matte}}^{\text{slag}}$ *versus* $r_{\text{SiO}_2}^{\text{Fe}}$

Fig. 5   Plot of $S_{\text{matte}}^{\text{slag}}$ *versus* Fe$_3$O$_4$ content

Table 1 Calculated and measured mass percents of main elements, SiO₂ and temperature at end of blowing period in slag-making stage of Charge 173

Period	Phase		Cu	S	Fe	SiO$_2$	Zn	Pb	T(K)
SL 1*	Matte	Expl.**	77.83	19.02	0.72	-	0.052	0.33	1555
SL 1	Matte	Calc.	78.53	18.78	0.48	-	0.11	0.23	1556
SL 1	Slag	Expl.	3.34	0.32	50.42	20.63	1.77	0.49	1555
SL 1	Slag	Calc.	0.48	0.09	49.82	22.33	1.40	0.73	1556
SL 2	Matte	Expl.	78.26	18.60	0.46	-	0.029	0.20	1548
SL 2	Matte	Calc.	78.96	18.80	0.36	-	0.007	0.04	1554
SL 2	Slag	Expl.	3.92	0.30	47.50	23.15	1.53	0.44	1548
SL 2	Slag	Calc.	0.52	0.09	48.81	22.29	1.84	0.86	1554

* SL 1 and SL 2 respectively correspond to the 1st and 2nd blowing period in the slag-making stage in
   operational practice of converters in Guixi Smelter.

** Expl. and Calc. designate the measured and calculated data respectively.

Table 2 Gibbs energy of formation of different

Formation of compounds	$\Delta G^0 = a + bT$ for compound formation	Reference
$2Cu_{(l)} + (\frac{1}{2})S_{2(g)} = Cu_2S_{(l)}$	$\Delta G^0_{Cu_2S(l)} = -106{,}630 + 12.55T$	[6]
$2Cu_{(l)} + (\frac{1}{2})O_{2(g)} = Cu_2O_{(l)}$	$\Delta G^0_{Cu_2O(l)} = -128{,}150 + 47.87T$	[7]
$(\frac{1}{2})S_{2(g)} + O_{2(g)} = SO_{2(g)}$	$\Delta G^0_{SO_2(g)} = -361{,}670 + 72.68T$	[8]
$Fe_{(l)} + (\frac{1}{2})S_{2(g)} = FeS_{(l)}$	$\Delta G^0_{FeS(l)} = -119{,}140 + 38.24T$	[6]
$Fe_{(l)} + (\frac{1}{2})O_{2(g)} = FeO_{(l)}$	$\Delta G^0_{FeO(l)} = -238{,}010 + 93.60T$	[9]

Table 3 Values of S_{matte}^{slag}, $(Cu\%)_{slag, tot}$, $(Cu\%)_{slag,dis}$, $(Cu\%)_{matte}$, r_{SiO2}^{Fe} and *T* at end of blowing period in slag-making stage obtained from the industrial trials

Charge	Period	$(Cu\%)_{slag, tot}$	$(Cu\%)_{slag, dis}$	$(Cu\%)_{matte}$	S_{matte}^{slag} (%)	r_{SiO2}^{Fe}	*T* (K)
44	SL2	5.74	0.44	78.74	6.73	2.30	1555
44	SL2	8.85	0.48	79.49	10.53	1.94	1561
50	SL 1	3.57	0.35	76.86	4.19	2.20	1532
50	SL 2	3.74	0.47	79.25	4.13	2.48	1573
51	SL 1	3.11	0.32	76.14	3.66	2.40	1550
51	SL 2	2.63	0.35	76.83	2.97	2.42	1550
58	SL 1	2.37	0.41	78.08	2.51	2.39	1568
58	SL 2	7.87	0.39	77.77	9.62	2.74	1538
60	SL 1	2.94	0.36	77.24	3.33	2.34	1534
60	SL 2	3.79	0.36	77.06	4.45	2.42	1542
168	SL 1	4.26	0.46	79.05	4.81	2.50	1543
168	SL 2	6.38	0.41	78.11	7.65	2.63	1542
173	SL 1	3.34	0.39	77.83	3.79	2.44	1555
173	SL 2	3.96	0.41	78.26	4.53	2.05	1548
64	SL 1	3.39	0.30	75.90	4.06	2.07	-
64	SL 2	3.90	0.40	77.90	4.50	1.59	-
175	SL 1	3.97	0.46	79.15	4.43	2.36	-
175	SL 2	4.45	0.38	77.48	5.26	2.36	-
176	SL 2	3.69	0.36	77.13	4.32	1.99	-
172	SL 1	3.72	0.20	72.29	4.87	2.74	-
172	SL 2	4.67	0.45	79.00	5.34	2.72	-
48	SL 1	3.14	0.33	76.41	3.68	1.99	-
177	SL 1	4.14	0.23	73.66	5.30	2.02	-
63	SL 1	1.98	0.24	74.00	2.35	2.45	-
163	SL 1	2.76	0.21	72.76	3.50	2.32	-
161	SL 1	4.67	0.30	75.77	5.76	2.17	-
155	SL 1	2.51	0.33	76.35	2.86	2.08	-
155	SL 2	2.58	0.36	77.06	2.88	2.14	-