

## Thermodynamic Study on Process in Copper Converters (The slag-making stage)

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**Abstract:** The so-called Goto's model was modified by introducing a parameter of the oxygen efficiency from industrial trials, as well as the selected and newly re-assessed thermodynamic data. The application of the model to copper converters in Guixi Smelter has been carried out by the combination of thermodynamic calculations with the mass and heat balance using the plant data obtained in industrial trials for many heats. For the slag-making stage, good agreements have been reached between the calculated and measured temperature, blowing time as well as the contents for main elements in the matte and the slag. Relatively large deviations for contents of Zn and Pb in the slag may be caused by the complex chemical composition of the real molten slag, which may result in a large difference of  $\gamma_{Zn}$  and  $\gamma_{Pb}$  adopted with their real values. It is noted that the model can simulate the slag-making stage of copper converting process in industrial Pierce-Smith converters well.

**Key words:** copper converter; thermodynamic study; slag-making stage

It is known that the chemical composition in a multi-phase and multi-component system in equilibrium can be calculated using two approaches: Gibbs free energy minimization as well as the so-called the equilibrium constant method by Binkley. Combining the composition evaluation in a multi-phase and multi-component system with the method by Binkley with the mass and heat balance, Goto proposed a thermodynamic model for the process of copper flash smelting process [1]. Assuming that the oxygen blown into the converter was entirely consumed in the reactions of oxidation, Goto's model was extended to simulate the process in copper converters lately [2]. In the application, the calculated results were employed to analyze the converting process, however only the calculated blowing time, copper and  $Fe_3O_4$  contents of the slag in slag-making stage were compared with the plant data for one heat of the operation in Naoshima [3]. It was shown that with very close blowing time, the differences between the plant data and calculated results were quite large. It is questionable that such a simple comparison could provide a proper measure indicating in what a level the model can simulate the processes in copper converters.

In this study, Goto's model was modified by introducing a parameter of the oxygen efficiency determined statistically from the plant data of a series of heats with stable converting operations [4] and using re-assessed thermodynamic data. The modified model has been applied to interpret the converting process in the converters in Guixi Smelter. A systematic comparison between the calculated and the plant data in slag-

making stage is illustrated in this paper.

### 1 Model Modification

It is known that the converting process is strongly affected by oxygen efficiency. In the present study, the above mentioned model was modified by introducing a parameter of the oxygen efficiency. The definition of oxygen efficiency,  $\eta_{O_2}$ , is presented as

$$\eta_{O_2} = (Q_{O_2, \text{rea}} / Q_{O_2, \text{air}}) \times 100\%$$

where  $Q_{O_2, \text{rea}}$  is the oxygen amount consumed in the reactions for producing the matte or blister copper with chemically analyzed grades of matte or copper, and  $Q_{O_2, \text{air}}$  is that supplied by air-blowing into the molten bath. Based on the industrial trials of stable converting operation practice, in Guixi Smelter, the oxygen efficiency of each converting period in each heat was obtained from the mass balance calculations, and its arithmetic mean values of all the testing heats are listed in table 1 [4].

**Table 1 Oxygen efficiency data obtained from industrial trials in Guixi Smelter**

Converting period	Oxygen efficiency · %
Slag-making stage, first slag	93
blowing	90
Slag-making stage, 2nd slag	—
blowing	—
Copper-making stage	81

The newly re-assessed standard Gibbs free energies of formation [5, 6, 7, 8] were employed in this study

rather than those in Goto's work [3] which are listed in **table 2**. The following correlation for activity coefficient of

**Table 2** The newly reassessed Standard Gibbs free energy of formation using in this work different from those used by Goto *et al.* [3]

Component	$\Delta_f G^\ominus / \text{J} \cdot \text{mol}^{-1}$	Reference
FeO	$-232\,714 + 45.31 T$	[5]
ZnS	$-375\,382 + 191.57 T$	[6]
PbS	$-111\,838 + 51.04 T$	[6]
Cu <sub>2</sub> O	$-195\,200 + 92.58 T$	[7]
SO <sub>2</sub>	$-361\,665 + 72.68 T$	[5]
SO	$-57\,780 - 4.98 T$	[5]
CO <sub>2</sub>	$-395\,350 - 0.54 T$	[8]

FeS in matte [9, 10] with its mole fraction has been used in this study

$$\gamma_{\text{FeS}} = 0.882(1 - x_{\text{FeS}})^{0.5}$$

The calculated  $\alpha_{\text{FeS}}$  values for the matte agree well with those published by Bale and Toguri [11] and differ from Goto's early publication [3]. These alternations could enable the present thermodynamic calculations more precisely.

Regarding the calculation procedure, please refer to

reference [2].

## 2 Industrial Trials

The industrial trials of copper converting operations for the converters No.1 and No. 3 were simultaneously carried out in Guixi Smelter in Aug. of 1996. The time schedule for the trials was registered. All the charged materials, products as well as by products such as molten matte, blister copper were sampled, quenched and then chemically analyzed. The mineralographical analysis was employed to give the composition for all the cold charge materials, quenched slag, matte as well as blister copper samples for 2 representative heats [12]. Temperatures of the melts were measured every time when the molten matte or blister was tapped using Pt-Rh thermocouple. The initial temperatures of the matte at pouring into the converter at a start of the 1st and 2nd slag blowing period have been estimated ( $1100 \pm 15$ ) °C. The temperature drop of the melts which remained in the converter during the rest between the 1st and 2nd slag blowing was estimated about 100 °C.

As an example, the chemical composition of materials charged in heat 173 is presented in **table 3**, and the corresponding time schedule of the operation in **table 4**.

**Table 3** Chemical composition of materials charged for heat 173 of converter No.3 (mass fraction in %)

Elements	Matte in 1st slag blowing	Matte in 2nd slag blowing	O <sub>2</sub> 1st slag blowing	O <sub>2</sub> 2nd slag blowing	Residue	Silica flux	Skull	Recycled white matte
Cu	59.52	57.43	0.000	0.000	19.52	0.00	58.94	54.25
S	21.34	21.86	0.000	0.000	0.29	0.00	12.19	13.97
Pb	0.28	0.32	0.000	0.000	2.19	0.00	0.52	0.26
Fe	14.68	15.13	0.000	0.000	39.81	1.40	12.75	15.70
Zn	0.42	0.63	0.000	0.000	2.29	0.00	0.41	0.32
O	1.30	1.00	26.560	24.760	16.61	0.00	6.08	5.12
N	0.00	0.00	73.320	75.120	—	0.00	0.00	0.00
H	0.00	0.00	0.070	0.070	0.00	0.00	0.00	0.00
C	0.00	0.00	0.001	0.001	0.00	0.00	0.00	0.00
SiO <sub>2</sub>	0.00	0.00	0.000	0.000	11.67	93.97	5.52	6.60
T / K	1373	1373	298	298	1373	298	298	1373

## 3 Results of Simulation and Discussion

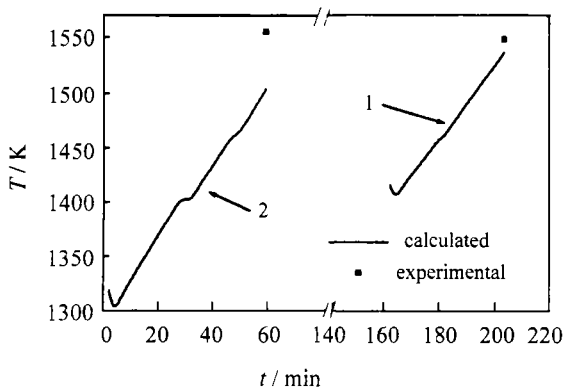
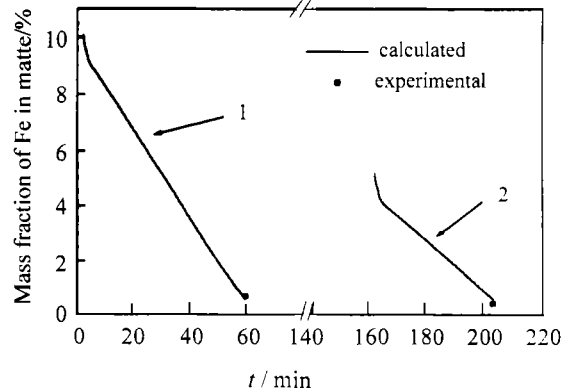
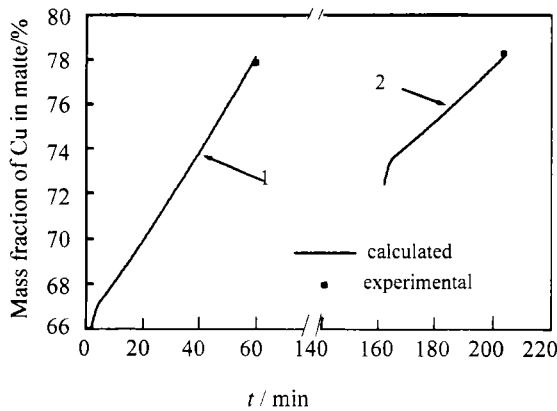
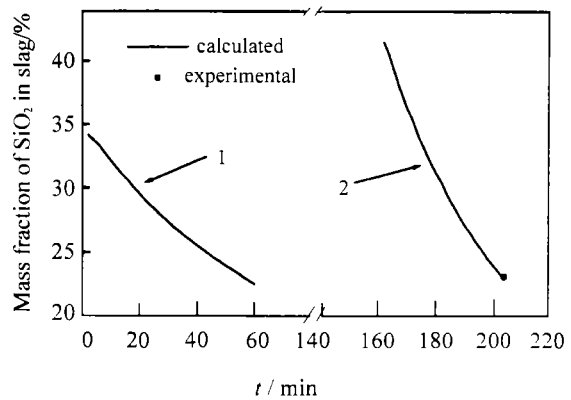
### 3.1 Result of heat 173 in converter No. 3

The results of the calculation using the model described above with the input data of heat 173 of converter No. 3 are illustrated in figures 1~7. For a comparison, the measured temperature and composition values in matte and slag are also marked in figures 1~5.

**Figure 1** shows that the temperature of the matte continuously increases with time due to the oxidation of Fe in slag-making stage. The initial temperature drops at the start two minutes in the 1st and 2nd slag-blowing period were caused by the cold charge-silica flux. **Figure 2** and **figure 3** respectively show the continuous decrease of the content of Fe and the increase of the content of Cu. The increase of the content of Cu in the matte is due to the oxidation of Fe to 'FeO' and

**Table 4** Time schedule of the operation in heat 173 of converter No. 3

Period	Time (min) Operation steps
1st slag-blowing	0 Charge: matte 118.5 t, silica flux 3 t, skull 11 t, recycled white-matte 8 t, residue 5 t and 30 300 m <sup>3</sup> (STP)
	2 Charge: silica flux 5.25 t
	60 (end): The 1st slag blowing is stopped at about 77.83% (mass fraction) Cu in matte, 52.5 t slag is tapped. The temperature of slag is 1 555 K.
	Rest time: 90 min
2nd slag-blowing	0 Charge: matte 61 t, skull 5.5 t and air 23 290 Nm <sup>3</sup>
	2 Charge: silica flux 4 t
	45 (end): The 1st slag blowing is stopped at about 78.26% (mass fraction) Cu in matte. 50 t slag is tapped. The temperature of slag is 1 548 K.
	Rest time: 30 min

**Figure 1** Variation of furnace temperature, 1– 1st slag blowing; 2– 2nd slag blowing.**Figure 2** Variation of copper content in matte, 1– 1st slag blowing; 2– 2nd slag blowing.**Figure 3** Variations of iron content in matte, 1– 1st slag blowing; 2– 2nd slag blowing.**Figure 4** Variations of SiO<sub>2</sub> content in slag, 1– 1st slag blowing; 2– 2nd slag blowing.

Fe<sub>3</sub>O<sub>4</sub> to enter the slag during the slag-making stage. It can be seen in figure 2, 3 that the predicted contents of Fe and Cu in matte are in a good agreement with those of measured. As shown in **figure 4** and **figure 5**, the increase of Fe in slag results in the decrease of SiO<sub>2</sub> during the slag-making stage. The calculated contents of SiO<sub>2</sub> and Fe in slag agree well with the plant data.

**Figure 6** and **figure 7** respectively show the constant partial pressure of SO<sub>2</sub> and the gradual increase of the

partial pressure of O<sub>2</sub> in gas phase during the slag-making stage. These may imply the decrease of the oxygen efficiency in the same period. Due to the limitation of the equipment conditions in the workshop, the composition of gas phase could not be measured, therefore a similar comparison for gas phase could not be provided.

### 3.2 Other heats

In addition to heat 173, the model has been applied

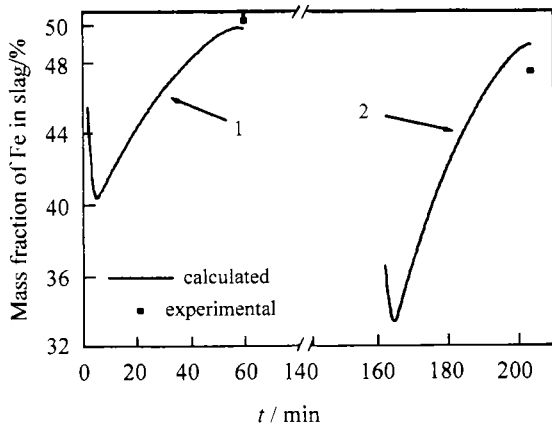


Figure 5 Variations of iron content in slag, 1- 1st slag blowing; 2- 2nd slag blowing.

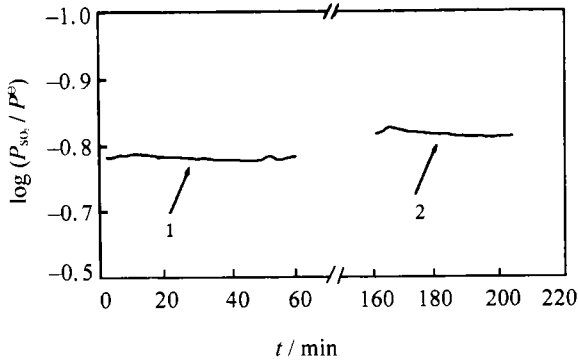


Figure 6 Variations of  $\text{SiO}_2$  partial pressure in gas phase, 1- 1st slag blowing; 2- 2nd slag blowing.

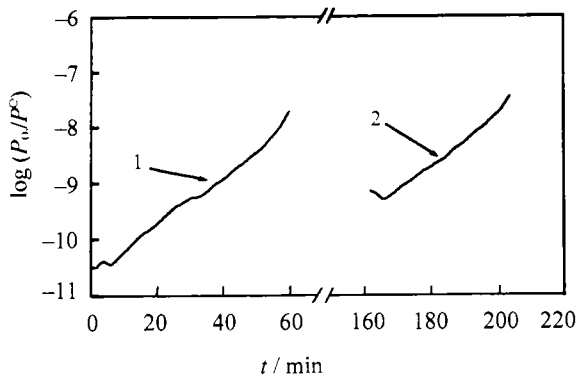


Figure 7 Variations of  $\text{O}_2$  partial pressure in gas phase, 1- 1st slag blowing; 2- 2nd slag blowing.

to calculate the other heats. For comparison, the calculated results with the relevant plant data are listed in Appendix 1 and 2.

The comparisons show that the calculated contents of main elements such as Cu, Fe and S in the matte are in a good agreement with those of the plant data. The calculated contents of  $\text{SiO}_2$  and Fe in slag also agree with the measured data. The relative deviations between calculated and measured contents for Cu, Fe, S in matte respectively take the values of 0.6%, 0.3% and 0.1%, while for Fe,  $\text{SiO}_2$  in slag the reasonably higher

values of 1.7% and 1.6% were obtained.

As shown in appendix 1 and 2, the calculated mass fraction values of Cu in the slag are about 3% lower than the measured data. This difference may be caused by the ignorance of the mechanical entertainment of the matte droplets in the slag.

The differences between the predicted and measured contents for Zn, Pb in the slag are relatively high. These differences may be attributed to that the activity coefficients of  $\gamma_{\text{ZnS}}$ ,  $\gamma_{\text{PbS}}$ ,  $\gamma_{\text{ZnO}}$ ,  $\gamma_{\text{PbO}}$  used in the model differ from those in the real systems. Clearly, the accuracy improvements of the thermodynamic data for the molten slag and matte systems with a complex composition are desirable.

There are two forms of iron, ferrous and ferric ions, existing in the molten slag. Only the total iron amount in slag could be chemically analyzed in the industrial tests. For this reason, the amounts of the  $\text{Fe}_3\text{O}_4$  calculated could not be compared with the relevant plant data. The range of the predicted results of  $\text{Fe}_3\text{O}_4$  in the slag is from 28.56% to 36.54%, which agree with the data using the slag samples taken from the representative heats by means of mineralographic analysis [12].

## 4 Conclusions

The so-called Goto's model was modified by introducing oxygen efficiency of copper converter and newly re-assessed thermodynamic data. The modified model has been applied to the converter operations in Guixi Smelter. For the slag-making stage, the comparison of the model predicted results with the plant data shows a good agreement in blowing time, bath temperature as well as the main elements Cu, Fe, S in the matte, Fe and  $\text{SiO}_2$  in the slag.

The calculated mass contents of Cu in slag were about 3% lower than the measured values, which may be caused by the ignorance of the mechanical mixing of matte droplets on the slag. Rather large deviations between the calculated and measured contents of Zn and Pb in the slag were attained. The deviations may be reduced by the improvements of the accuracy for the relevant activity coefficients of components, such as ZnS, PbS in the matte and ZnO, PbO in the slag.

The modified model may provide a tool to analyze the slag-making stage of the process in copper converters and could be applied to monitor and optimize the operation practice of this period in industrial copper converters.

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Appendix 1 Comparison between model predicted and plant data for Slag-making stage ( I )

Blowing period	Molten phase	Element or component	Mass fraction of <i>i</i> / % (Heat 173, converter No. 3)		Mass fraction of <i>i</i> / % (Heat 50, converter No. 1)		Mass fraction of <i>i</i> / % (Heat 51, converter No. 1)	
			Measured	Predicted	Measured	Predicted	Measured	Predicted
the 1st	Matte	Cu	77.83	78.14	76.86	77.59	76.14	77.99
		S	19.02	18.92	18.64	19.18	18.90	18.77
		Fe	0.72	0.63	0.74	1.17	0.77	0.44
		Zn	0.052	0.20	0.021	0.18	0.014	0.05
		Pb	0.33	0.34	0.15	0.35	0.14	0.14
	Slag	Cu	3.34	0.36	3.57	0.30	3.11	0.46
		S	0.32	0.07	0.27	0.07	0.27	0.07
		Fe	50.42	49.96	49.64	51.01	51.33	48.37
		Fe <sub>2</sub> O <sub>3</sub>	—	31.60	—	31.18	—	30.79
		Zn	1.77	1.18	0.98	0.40	0.97	0.68
		Pb	0.49	0.49	0.13	0.19	0.28	0.48
		SiO <sub>2</sub>	20.63	22.38	22.57	24.68	21.40	22.56
		<i>T</i> / K*	1555	1505	1532	1484	1550	525
	the 2nd	Matte	Cu	78.26	78.14	79.25	78.89	76.83
S			18.60	19.02	18.36	18.88	18.90	18.93
Fe			0.46	0.62	0.58	0.51	1.16	0.50
Zn			1.18	0.029	0.014	0.006	0.042	0.09
Pb			0.20	0.30	0.14	0.04	0.21	0.15
Slag		Cu	3.92	0.40	3.74	1.73	2.63	0.47
		S	0.30	0.08	0.27	0.09	0.29	0.10
		Fe	47.50	49.07	52.28	51.43	51.99	48.51
		Fe <sub>2</sub> O <sub>3</sub>	—	28.60	—	35.52	—	28.56
		Zn	1.53	1.40	0.90	1.78	0.93	0.005
		Pb	0.44	0.50	0.28	1.86	0.22	0.22
		SiO <sub>2</sub>	23.15	22.87	21.05	17.44	21.51	22.35
		<i>T</i> / K*	1548	1536	1573	1585	1550	1562

Note: \* the temperature refers to that measured when start the tapping at the end of blowing, *i* represent element.

Appendix 2 Comparison between model predicted and plant data for Slag-making stage (II)

Blowing period	Molten phase	Element or component	Mass fraction of $i$ / % (Heat 58, converter No. 1)		Mass fraction of $i$ / % (Heat 60, converter No. 1)		Mass fraction of $i$ / % (Heat 168, converter No. 3)	
			Measured	Predicted	Measured	Predicted	Measured	Predicted
the 1st	Matte	Cu	78.08	77.73	77.24	77.69	79.05	79.07
		S	18.80	18.89	19.31	18.92	18.59	18.92
		Fe	1.12	0.68	1.00	0.63	0.60	0.43
		Zn	0.064	0.24	0.079	0.24	0.025	0.004
		Pb	0.33	0.39	0.37	0.28	0.21	0.02
	Slag	Cu	2.37	0.37	2.94	0.37	4.26	2.0
		S	0.27	0.07	0.39	0.07	0.24	0.08
		Fe	50.90	48.41	50.09	49.23	50.60	49.04
		Fe <sub>3</sub> O <sub>4</sub>	—	28.06	—	30.16	—	29.54
		Zn	1.18	0.28	1.61	1.40	1.15	0.014
	$T / K^*$	Pb	0.35	1.20	0.34	0.40	0.44	1.12
		SiO <sub>2</sub>	21.27	23.88	21.41	22.77	20.23	20.72
			1568	1528	1534	1515	1543	1552
the 2nd	Matte	Cu	77.77	78.79	77.06	77.21	78.11	79.03
		S	18.68	18.86	18.89	19.08	18.56	18.91
		Fe	1.43	0.49	1.00	1.16	0.77	0.50
		Zn	0.083	0.007	0.062	0.24	0.035	0.005
		Pb	0.36	0.06	0.32	0.28	0.25	0.20
	Slag	Cu	7.87	1.72	3.79	0.40	6.38	2.10
		S	1.00	0.09	0.69	0.10	0.60	0.07
		Fe	50.68	51.69	50.37	51.10	51.10	50.19
		Fe <sub>3</sub> O <sub>4</sub>	—	36.45	—	31.26	—	30.43
		Zn	1.28	2.19	1.36	0.80	1.12	1.63
	$T / K^*$	Pb	0.24	2.70	0.30	0.24	0.34	1.34
		SiO <sub>2</sub>	18.48	17.47	20.84	21.96	19.45	17.89
			1534	1594	1542	1575	1543	1531

Note: \* the temperature refers to that measured when start the tapping at the end of blowing,  $i$  represent element.