THE PREDICTION OF COPPER AND IRON ACTIVITIES IN COPPER PYROREFINING SLAGS

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ABSTRACT

The composition of copper pyrorefining slags as a function of gaseous oxygen potentials under refining furnace operation conditions (temperature range 1100-1300 °C) was investigated. Based on isotherms slag phase composition, experimentally obtained at oxygen pressures of 1, 0.21, 0.01 and 0.0001 atmospheres, a prediction method for copper and iron activities was established by using an integration of Gibbs-Duhem equation in the ternary Cu-Fe-O system. This approach, similar to that used by Krivsky and Schuhmann for the Cu-Fe-S system, supposes the constant Cu/Fe ratio.

Possibilities for compound activities prediction are presented and the advantages and limitations of the described method as well as the utilization for the pyrometallurgical process analysis are discussed.

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1. INTRODUCTION

During copper pyrorefining process, the composition of liquid metallic and oxidized phases are usually represented by the Copper-Iron-Oxygen system\(^{(1)}\). Nevertheless, this ternary has not been treated extensively in the literature and generally it has only been estimated from the boundary binary systems in the temperature range of interest for copper pyrometallurgy\(^{(2,3)}\).

Some experimental works by Gadalla and White\(^{(4)}\), Kulkarni\(^{(1)}\), Jacob\(^{(5)}\) and Floyd\(^{(6)}\) may be utilized to estimate this system by extrapolating these data. Acuña\(^{(7,8,9)}\) has presented a phase composition study and the thermodynamic behaviour of this melt in the copper-slag region, giving more light on the subject.

Figure 1, shows an estimation by Luraschi for the Cu-Fe-O system\(^{(2)}\), by compilation of the existing data. Here de ABCD region corresponds to the liquid slag \(^{(12)}\). The AB line represents the composition of this slag in equilibrium with liquid copper \(^{(11)}\) and the CD line represents the composition of the slag in equilibrium with a 1 atmosphere oxygen gas phase.

The present work gives the experimental determination of the slag composition in the ABCD region, under oxygen pressures of 1, 0.21, 0.01 and 0.0001 atmospheres, at 1100, 1200 and 1300°C. Under these conditions, the Copper and Iron activities are calculated by the integration of the Gibbs-Duhem equation, considering the experimental data already given by Acuña\(^{(7,9)}\) for the AB line.

2. EXPERIMENTAL APPARATUS

The experimental apparatus has been described in published papers\(^{(8,9)}\) and
it consists of a reactor which allows the equilibrium between the liquid and the gas phase at high temperatures. The different partial oxygen pressures are obtained by blowing pure oxygen, air or air/argon mixed in the desired ratio.

The sample, contained in an alumina crucible, was prepared from the oxides CuO and Fe₂O₃, both reagents grade chemicals and in such proportions to assure a final composition in the single phase range 12(ABCD region in Figure 1), under the fixed partial oxygen atmosphere.

Kinetic studies demonstrated that equilibrium is reached after 8 hours at the temperature. At the end of the experiment, the sample is quenched and then analyzed for Cu, Fe, O and Al₂O₃.

3. EXPERIMENTAL RESULTS

The experimental results are presented like oxygen molar fraction content, \( X₀ \), versus iron content, \( M_{Fe} \), in the melts, at temperatures of 1100, 1200 and 1300°C (Figures 2, 3 and 4 respectively).

The results extrapolated from Gadalla and White(4) for oxygen pressures of 1 and 0.21 atmospheres (\( Y = 0 \) and \( Y = 0.68 \) respectively), and the results obtained by Acuña(7,8) for AB line (\( Y = Y \) curve) at the three studied temperatures are also indicated in the different diagrams.

4. COPPER AND IRON ACTIVITIES DETERMINATION

The Gibbs-Duhem relation applied to a ternary system at constant pressure and temperature can be written(10):

\[
 n₁ dδ₁ + n₂ dδ₂ + n₃ dδ₃ = 0
\]  

(1)
where $n_i$ represents moles of component $i$ and $\bar{G}_i$ its partial molar free energy or chemical potential.

For the condition that $\bar{G}_1$ and $n_3$ are constant, division by $dn_2$ gives

$$n_2 \left( \frac{\partial \bar{G}_2}{\partial n_2} \right) \bar{G}_1, n_3 + n_3 \left( \frac{\partial \bar{G}_3}{\partial n_2} \right) \bar{G}_1, n_3 = 0 \quad (2)$$

Differentiation of (2) with respect to $\bar{G}_1$ while $n_2$ and $n_3$ are constant gives:

$$n_2 \left( \frac{\partial \bar{G}_2}{\partial \bar{G}_1 \partial n_2} \right) n_3 + n_3 \left( \frac{\partial \bar{G}_3}{\partial \bar{G}_1 \partial n_2} \right) n_3 = 0 \quad (3)$$

Now, dividing (1) by $d\bar{G}_1$, considering a path where $n_2$ and $n_3$ are constant, we have:

$$n_1 + n_2 \left( \frac{\partial \bar{G}_2}{\partial \bar{G}_1} \right) n_2, n_3 + n_3 \left( \frac{\partial \bar{G}_3}{\partial \bar{G}_1} \right) n_2, n_3 = 0 \quad (4)$$

Differentiation of (4) with respect to $n_2$, with $\bar{G}_1$ and $n_3$ constant leads to:

$$\left( \frac{\partial n_1}{\partial n_2} \right) \bar{G}_1, n_3 + \left( \frac{\partial \bar{G}_2}{\partial \bar{G}_1} \right) n_2, n_3 + n_2 \left( \frac{\partial \bar{G}_2}{\partial \bar{G}_1 \partial n_2} \right) n_3 + n_3 \left( \frac{\partial^2 \bar{G}_3}{\partial n_2 \partial \bar{G}_1} \right) n_3 = 0 \quad (5)$$

Combining (3) and (5), it appears:

$$\left( \frac{\partial \bar{G}_2}{\partial \bar{G}_1} \right) n_2, n_3 = - \left( \frac{\partial n_1}{\partial n_2} \right) \bar{G}_1, n_3 \quad (6)$$

This is the form of the Gibbs-Duhem equation used by Krivsky and Schuhmann in activity determination of copper, iron and their compounds in the Cu-Fe-S system(11).

Equation (6) can be integrated along a path of constant $n_2$ and $n_3$; i.e. a compositional path of constant $X_2/X_3$. On the ternary composition diagram, such as a path follows a straight line through the corner for component 1.
The differentials ratio of partial molar free energies may be related to the activities of components 1 and 2 by:

\[
\left( \frac{\partial G_2}{\partial \ln a_1} \right)_{n_2, n_3} = \left( \frac{\partial \ln a_2}{\partial \ln a_1} \right)_{n_2, n_3} \tag{7}
\]

Using the Schuhmann tangent-intercept method, we can do \((\partial \ln a_1/\partial n_2)_{n_3}\) equal to the mole ratio \(X_1/X_2\) representing the required composition of the binary mixture 1-2, which may be added in infinitesimal amount to the ternary mixture without changing the activity of component 1.

Doing: oxygen = 1, copper = 2 and Iron = 3, then we have the following formula for copper:

\[
\ln a_{Cu}^{Y=Y*} = \ln a_{Cu}^{Y=Y} - \left[ \int \frac{Y* (X_o/X_{Cu}) a_o x_{Fe}=0 d\ln a_o}{X_{Cu}/X_{Fe}} \right] x_{Cu}/x_{Fe}
\]  

The formula already indicated is similar for iron:

\[
\ln a_{Fe}^{Y=Y*} = \ln a_{Fe}^{Y=Y} - \left[ \int \frac{Y* (X_o/X_{Fe}) a_o x_{Cu}=0 d\ln a_o}{X_{Cu}/X_{Fe}} \right] x_{Cu}/x_{Fe}
\]  

A scheme of the graphic calculation for Copper is shown in Figure 5 where the values corresponding to \(Y=Y\) were obtained by Acuña in the slag-metal region. We calculate the copper and iron activities for \(Y* = 0.0, 0.68, 2\) and 4, corresponding to oxygen partial pressure of 1, 0.21, 0.01 and 0.0001 atmospheres (oxygen activities of 1, 0.458, 0.1 and 0.01 respectively).

Figures 6 and 7 show the copper and iron activities obtained at temperatures of 1100, 1200 and 1300°C, following this procedure. For copper, the activities are given directly in function of iron content in the metallic distribution \((\eta_{Fe})\), and for iron it was more interesting to give the logarithm of the activity values.
5. DISCUSSION

The experimental results presented in Figures 2, 3 and 4 are in agreement with those extracted from literature data, i.e., the points on the Cu-O binary joints (on the straight line AD in figure 1), the points extrapolated from Gadalla and White (4) for equilibrium with the spinel solid solution at 0.21 and 1 atm O_2 pressure (corresponding to BC line in Figure 1) and the results obtained by Acuña (7,8,9) for the saturated slag (AB line in Figure 1).

Since all the experiments were performed with alumina crucibles, the solubility of Al_2O_3 in the slag was measured by atomic absorption spectrometry of Al in the melt. The detailed data is presented elsewhere (13). The maximum solubility average was 1.33, 2.30 and 3.18% Al_2O_3 for 1100, 1200 and 1300°C respectively with the tendency to increase as a function of the iron content of the slag. These results are in agreement with those obtained by Acuña for the slag under inert atmosphere (8).

For activity determination, a large discussion was brought earlier by Schuhmann (12) and later by Richardson (10) around the calculation method, and the first researcher applied it to Cu-Fe-S system (11). Figure 5 shows the "tangent - intercept" procedure for copper, where the tangent \( \frac{\delta X_o}{\delta X_{Cu}} \) for a specific oxygen potential, corresponds to the \( X_o/X_{Cu} \) values on the binary Cu-O. The calculated results in Figure 6 and 7 show the activity values for copper and iron at the temperatures indicated. Those figures show a decrease of copper activities and an increase of those corresponding to iron, as a function of the iron content, \( \gamma_{Fe}=1-\gamma_{Cu} \) the change being more important for smaller values of O_2 partial pressure, which correspond to the longer penetration to the ternary system.

Both copper and iron activities corresponding to the saturated slag (Y=Y curve)
increase with the iron content. For copper it is caused by equilibrium with the metallic phase (Cu corner in ternary Cu-Fe-O, figure 1) which is higher while it is nearer the pure copper.

Note that, for the oxygen partial pressures in this study, there is an increase of two metals activities with the temperature of the melts.

By knowing the oxygen, copper and iron activities; those of oxidized compounds can be calculated. For instance, cuprous oxide for copper and magnetite for iron, according to the equilibrium relationship:

\[ 2Cu + \frac{1}{2} O_2 = Cu_2O \]

and

\[ 3Fe + 2O_2 = Fe_3O_4 \]

where it is only sufficient to find the standard states and free energies values to fix the equilibrium.

The "tangent-intercept" procedure is a method depending on the careful measurement of the slope \( \partial X_i / \partial X_j \) \( (i = \text{oxygen}, j = \text{copper, iron}) \), then it is necessary to repeat a sufficient number of measured points to permit a good construction of the curve \( \partial X_i / \partial X_j \) against \( \log a_i \). The integral is simply the area under the curve between the limits \( Y = Y \) and \( Y = Y^* \) (\( Y^* = 0, 0.68, 2 \) or 4). So, the exposed method is very simple to apply in activity determination, when a certain accuracy for graphic measure is taken.

During copper pyrometallurgical process under the studied temperatures, there is an oxidized phase in contact with a metallic phase and the first one, must be ideally free from copper and charged of existing impurities, with the purpose to reach the highest copper content in the metallic phase. In fact, the oxidized phase is, at the same time, in contact with a gaseous phase, under
a given oxygen partial pressure. So, it is very important for the metallurgical process, to find the relationship between slag and gaseous phase behaviour. In this work, these relationships were established for a Cu-Fe-O system which are not far from the last stages of copper pyrorefining process. Certainly, it would be of interest to use an approximation of this method to more components of the melt system.

6. CONCLUSIONS

Measurements on the slag-gas equilibrium in the Cu-Fe-O system, at temperatures of 1100, 1200 and 1300°C have been reported.

The experimental results of the research were compared only with other authors in the extremes of slag region composition range, that is to say, the Cu-O binary system, the slag-spinel solid solution equilibrium and the saturated slag in equilibrium with a metallic phase. In this comparison, the present data agree well with previous information.

Activities of copper and iron were determined from the data, using an integration of Gibbs-Duhem equation for the ternary Cu-Fe-O, and it was concluded that there was a great effect of oxygen potential, iron content and temperature on the activity values.

The information obtained allows to get a better knowledge of Cu-Fe-O system thermodynamic behaviour and it also contributes to know the pyrometallurgical operation to extract copper.

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REFERENCES


Figure 1 Estimated isotherm (1200°C) for Cu-Fe-O system under 1 atmosphere total pressure. (3)
Figure 2. Slag region in the Cu-Fe-O system (1100°C).

\[ P_{O_2} = 10^{-Y} \]

- \( \times \) \( Y = 0 \)
- \( \circ \) \( Y = 0.68 \)
- \( \square \) \( Y = 2 \)
- \( \triangle \) \( Y = 4 \)
- \( Y = Y \) (8)
- \( Y \) (4)

(\( Q \)) BINARY Cu-O

\[ \gamma_{Fe} = X_{Fe}/(X_{Fe} + X_{Cu}) \]
Figure 3: Phase diagram of the Cu-Fe-O system in the O-200°C region.
Figure 4. Slag region in the Cu-Fe-O system (1300°C).
Figure 5. Scheme of Gibbs-Duhem integration in the Cu-Fe-O system for the Y values indicated.
Figure 6. Calculated copper activities (1100-1200-1300°C)
Fig. 7. Calculated iron activities (1100-1200-1300°C)

\[
\gamma_{Fe} = \frac{x_{Fe}}{x_{Fe} + x_{Cu}}
\]