THERMODYNAMIC INVESTIGATION OF COPPER REMOVAL FROM LIQUID SLAGS

M. H. Abbasi

Department of Materials Engineering
Isfahan University of Technology
Isfahan, Iran

Abstract The removal of copper dissolved in liquid slags by pyrometallurgical means such as gaseous reduction and sulphidization is thermodynamically investigated. The lowest level possible for copper content is theoretically determined and compared. The results show that gaseous reduction is not as effective as sulphidization. Slags with very low levels of dissolved copper can be obtained with sulphide treatment. Effects of temperature, slag and matte composition have also been investigated.

چکیده   حذف مس حل شده در سرباره های مذاب به روش های پیرومتالورژی ازقبیل احیـا کردن با گاز و سـولفوره کردن مورد بررسی ترمودینامیکی قرار گرفته است. پائین ترین حدی که امکان حذف مس وجـود دارد، بطور تئوری تعیین و مقایسه شـده است. نتایج نشان میـدهد که احیا با گاز درمقـایسه با سولفوره کردن چـندان موثر نیست. با سـولفوره کردن، سرباره با درصـد مس بسیار پائینی مـی توان بـدست آورد. اثرات دما و تر کیـب شیـمیائـی سرباره و مات نیز مـورد تحقـیق و بررسی قرار گرفته است.

INTRODUCTION

During the conventional copper smelting operations which involve smelting in a reverberatory furnace and converting the matte produced, copper is lost to some extent in the slags produced. The copper concentration in smelter slags varies from 0.2 to 1% depending on the particular type of operation. In converter slags the copper level is higher usually in the range of 2-15%. According to Yazawa[1], slags in equilibrium with white metal will contain 7-8% copper as copper oxide. Slags produced during continuous copper making processes such as Noranda, Workra, etc., also contain at least 7-8% copper [2].

The smelter slags are usually discarded directly without further treatment. The converter slags and the slags produced in continuous coppermaking processes are high in copper content and they must be treated for copper recovery. Copper is almost removed from these slags by slow cooling, milling and froth flotation.

In this paper the removal of dissolved copper from liquid slags by pyrometallurgical means such as gaseous reduction and sulphidization is thermodynamically investigated and the maximum recovery possible is determined under different conditions of temperature and slag composition.

COPPER IN SLAG

Copper losses in slags may be of two kinds:

(a) mechanical losses

(b) chemically dissolved losses

Mechanical losses are due to the entrained sulphide or metal particles in the slag. The amount of entrained material in a slag depends on physical factors such as densities, surface tension and viscosities of the phases. As far as one can judge, about half of the copper losses in industrial copper smelting slags are in the form of dispersed matte droplets or metal particles. This part can be recovered by settling. The velocity of movement of materials through the slag, v, is given by stokes law [3].

$$V = gd^2(\rho p - \rho s) / 18\mu$$

where g is the gravitational constant, d is the particle diameter, ρp is the density of entrained particles, ρs is the slag density and μ the slag viscosity.

For a slag of viscosity 4 poise with matte and slag densities differing by one g/cm³, a matte drop of 1mm diameter will fall through a slag layer of one meter in about 10 minutes, while for a matte drop of 0.1 mm diameter, the time taken will be about 19 hours. Thus, the settling of fine

matte drops from slags will require a very long time under quiescent conditions. Also, it can be seen that when the diameter of the particles are constant, the main factor influencing the rate of settling is the slag viscosity which should be kept as low as possible by working at high temperature and by avoiding the formation of magnetite and Cr_2O_3. As this paper is concerned with the removal of dissolved copper, entrained copper will not be discussed further.

The chemically dissolved copper is caused by the solubility of copper mainly in the form of oxide. According to the ionic theory of liquid slags, chemically dissolved copper is present as cuprous ions which are in equilibrium with copper oxide according to:

$$2Cu^+ + O^{2-} = Cu_2O(1)$$
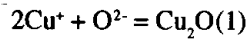
For a slag of essentially constant composition, the activity of O^{2-} is approximately constant and with the assumption of dilute solution conditions, the activity of Cu^+ is proportional to the copper concentration. This leads to the relation:

$$(wt\% \text{ Cu in slag}) = K(aCu_2O)^{1/2} \quad (1)$$

where K is the proportionality constant. It can be seen that copper solubility approaches zero as the activity of copper oxide approaches zero. So copper can only be dissolved after being oxidized. This relation has been confirmed by several investigators and the values of constant K have been obtained for a number of slag systems (Table 1). As one expects, K is a function of slag composition. Using K values from Table 1 and calculating copper oxide activity thermodynamically, it will be possible to predict the minimum copper content in the slag achievable from equation(1).

GASEOUS REDUCTION OF DISSOLVED COPPER

The copper oxide dissolved in slag can be reduced by injection of a reducing gas into the liquid slag. The reduction of copper oxide occurs by reaction such as:

$$Cu_2O \text{ (slag)} + R = 2Cu \text{ (metal)} + RO$$
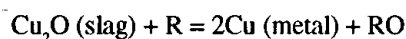
where R denotes a reducing gas like CO or H_2 or a mixture of both. At the same time dissolved iron will be reduced

according to the reaction:

$$FeO \text{ (slag)} + R = Fe \text{ (metal)} + RO$$
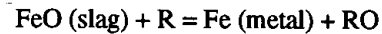
the relative amounts of these metals reduced will be

TABLE 1. K Values for Solubility of Copper in Slags.

slag system	T(oC)	K	Ref
Silica unsaturated			
$Fe/SiO_2=1.5$, $8\pm2\%Al_2O_3$	1200-1300	27	[4]
$Fe/SiO_2 = 2$, $8\pm2\%Al_2O_3$	1200-1300	35	[5]
Alumina saturated	1250	23.6	[6]
Silica saturated			
Iron silicate	1300	33.6	[7]
Iron silicate	1300	35.7	[8]
Iron silicate	1300	29.3	[9]
Iron Silicate	1224-1286	35.9	[10]
Iron silicate	1300-1450	32	[11]
Iron silicate(up to 11% CaO)	1300	35.02- 0.84X*	[12]
Iron silicate(up to 4%MgO)	1300	33.7	[12]
Iron silicate(up to 8% Al_2O_3)	1300	34.2	[12]
Iron silicate(11-14%Al_2O_3)	1300	30	[4]
Iron silicate(5%CaO,3%Al_2O_3)	1300	26.7	[13]
Iron silicate(9%CaO,12%Al_2O_3)	1300	22.7	[4]
Iron silicate	1217-1307	30b	[14]

a. X = CaO%
b. Estimated from plot

controlled by the equilibrium of the reaction :

$$Cu_2O(slag)+Fe(metal)=FeO(slag)+2Cu(metal) \quad (2)$$
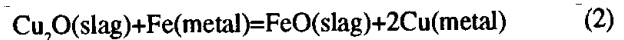
As a result of gaseous reduction a Cu-Fe alloy will be formed. Examination of the Cu-Fe phase diagram shown in Figure 1 indicates that the solubility of Fe in liquid copper is about 6 atom% at 1200°C and 10 atom% at 1300°C. Beyond these limits part of the alloy will be solid. Considering the equilibrium between slag and liquid alloy, the standard free energy change for reaction (2) when all the components are in liquid state, can be calculated using thermodynamic data from kubaschewski, Alock[15].

$$\Delta G°2(cal)= -26080 + 3.92T \log T-12.14T$$

$$\Delta G°2= -RT \ln (aFeO. a^2Cu / aFe. aCu_2O) \quad (3)$$

At elevated temperatures, liquid Cu-Fe alloys approximate a regular solution behaviour [16]. Activities in Cu-Fe liquid alloys at 1550°C are given by Hultgren et al [17].

SEIGHT PER CENT IRON
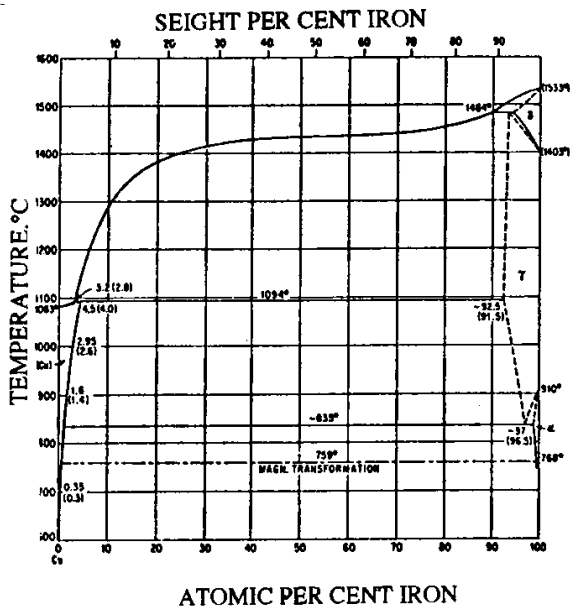
ATOMIC PER CENT IRON

Figure 1. Cu-Fe phase diagram

Assuming regular solution behaviour to be valid down to 1200°C, it is possible to calculate the activity coefficient of Cu and Fe components at 1200 and 1300°C using the relations.

$$\overline{G}^{E}Cu = RT1 ln \; \gamma \; Cu(T1) = RT2 ln \; \gamma Cu(T2)$$

$$\overline{G}^{E}Fe = RT1 ln \; \gamma Fe(T1) = RT2 ln \; \gamma Fe(T2)$$

the results of these calculations are:

Cu-6%Fe(1200°C)   aFe = 0.640   aCu = 0.955

Cu-10%Fe(1300°C)   aFe = 0.756   aCu = 0.933

The FeO activity in silica-saturated slags is nearly constant and is taken to be 0.35[1,12,18]. Substituting these values in equation(3), it is possible to calculate the copper oxide activity in the slag which is in equilibrium with Cu-Fe liquid alloys.

$$aCu_2O(1200°C) = 8.20 \times 10^{-5}$$

$$aCu_2O(1300°C) = 12.3 \times 10^{-5}$$

Calculating the copper oxide activity, it is now possible to use K values from Table 1 and calculate the copper content

in silica saturated slags of different compositions. As Table 1 shows, most of the K values are measured in the temperature range 1200 - 1300°C and slag composition is the most important parameter. Table 2 represents the results of calculations for copper content of different silica-saturated slags. It can be seen that with gaseous reduction the amount of copper remaining in slag is 0.2-0.4% depending on temperature and slag composition.

As the reduction with gas continues, more iron oxide is reduced. According to Cu-Fe phase diagram in Figure 1, an alloy containing more than 6%Fe at 1200°C and 10%Fe at 1300°C is partly solid. However, within the liquidus region, equilibrium exists between solid and liquid phases. Therefore the copper and iron activities will remain constant as shown in Figure 2. As a result the copper content of the slag does not change. Thus gaseous reduction beyond 6% Fe at 1200°C and 10%Fe at 1300°C will not be effective in removing more copper from slag. So it can be concluded that the lowest level of copper in slag achievable with gaseous reduction is 0.2-0.4% depending on temperature and slag composition.

SULPHIDIZATION

As mentioned earlier, dissolved copper in slag is in the form of oxide. By equilibrating the slag with a low grade matte or pyrite, copper oxide is converted into sulphide according to reaction:

TABLE 2. Calculated Copper Content of Slags.

silica-saturated slags	K	wt%Cu	
		1200°C	1300°C
Iron silicate	33.6	0.30	0.373
Iron silicate	35.7	0.323	0.396
Iron silicate	29.3	0.265	0.325
Iron silicate	35.9	0.325	0.398
Iron silicate	32	0.29	0.355
Iron silicate(up to 11%CaO)	25.8	0.234	0.286
Iron silicate(up to 4%MgO)	33.7	0.30	0.374
Iron silicate(up to 8%Al₂O₃)	34.2	0.31	0.380
Iron silicate(11-14%Al₂O₃)	30	0.272	0.333
Iron silicate(5%CaO,3%Al₂O₃)	26.7	0.242	0.296
Iron silicate(9%CaO,12%Al₂O₃)	22.7	0.21	0.252
Iron silicate	30	0.272	0.333

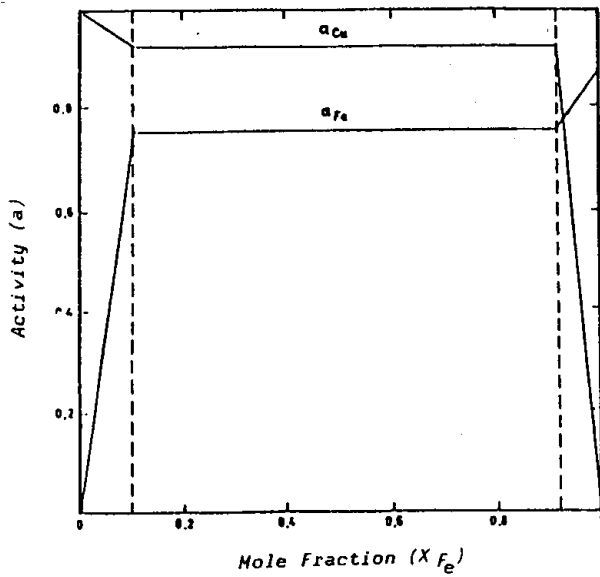$$FeS(matte)+Cu_2O(slag)=FeO(slag)+Cu_2S(matte) \quad (4)$$

Figure 2. Activities of Cu and Fe in Cu-Fe alloys at 1300°C·

The standard free energy change for reaction (4) can be calculated using data from kubaschewski and Alcock.

$$\Delta G^\circ 4(cal) = -32200 - 2.3T \log T + 10.02T$$

$$\Delta G^\circ 4 = -RT\ln(aFeO.aCu_2S/aFeS.aCu_2O) \qquad (5)$$

the Cu$_2$S-FeS binary system (matte) exhibits small negative deviations from ideality and can be well described by Temkin's model.

$$aCu_2S = (XCu^+)^2(XS^{2-})$$

$$aFeS = (XFe^{2+})(XS^{2-})$$

where:

$$XCu^+ = nCu^+/(nCu^+ + nFe^{2+})$$

$$XFe^{2+} = nFe^{2+}/(nCu^+ + nFe^{2+})$$

$$XS^{2-} = nS^{2-} / nS^{2-}$$

and nCu$^+$, nFe^{2+} and nS^{2-} represent the number of moles of copper, iron and sulphur ions respectively. The results of activity calculations in Cu$_2$S-FeS system with different compositions are shown in Table 3. the calculated values seem to agree well with the measured data of Krivsky and Schuhmann [19], Bale and Toguri[16] and Sinha and
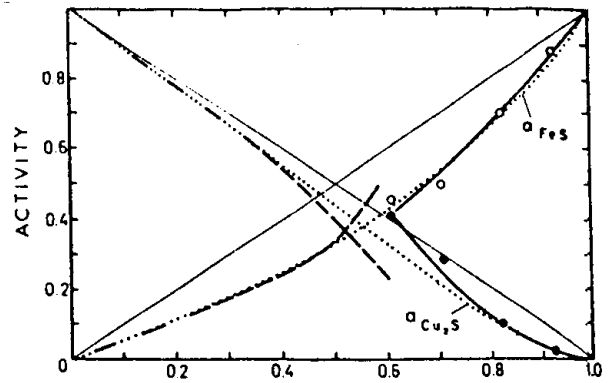

Figure 3. aCu$_2$S and aFeS in the Cu$_2$S - FeS pseudobinary at 1200°C.

...... Temkin Model

O   Measured aFeS

●   Measured aCu$_2$S

Nagamori [20] as shown in figure 3.

TABLE 3. Calculated Activities in Cu$_2$S-FeS Binary System Using Temkin Relation.

wt%Cu$_2$S	XCu$_2$S	XFeS	aCu$_2$S	aFeS
10	0.0578	0.9422	0.012	0.891
20	0.1214	0.8786	0.047	0.784
30	0.1914	0.8086	0.1033	0.679
40	0.2690	0.7310	0.180	0.576
50	0.3559	0.6441	0.276	0.475

Using activity values from Table 3 and assuming aFeO to be 0.35 for silica-saturated slags, it is possible to calculate the Cu$_2$O activity from equation (5). Table 4 summarizes the results of these calculations.

TABLE 4. Calculated Copper Oxide Activities in Liquid Slags Equilibrated with Mattes of Different Compositions.

wt%Cu$_2$S in matte	aCu$_2$Ox10^4	
	1200°C	1300°C
10	0.331	0.642
20	1.474	2.858
30	3.740	7.252
40	7.683	14.90
50	14.3	27.7

TABLE 5. Calculated Copper Content of Liquid Slags in Equilibrium with Mattes of Different Composition Using Minimum and Maximum K Values.

wt%Cu_2S in matte	wt%Cu in slag	
	1200°C	1300°C
10	0.013-0.021	0.018-0.029
20	0.027-0.044	0.038-0.061
30	0.044-0.07	0.061-0.097
40	0.063-0.099	0.088-0.138
50	0.086-0.136	0.119-0.189

Knowing the copper oxide activity, it is possible to use K values from Table 1 and calculate the copper content in different slags. For the sake of comparison, the minimum and maximum values of K have been used only.

Table 5 represents the results. It is clear from table 5 that equilibration with a low grade matte is very effective in removing dissolved copper from liquid slags.

CONCLUSION

The limit for the removal of dissolved copper from liquid slags by pyrometallurgical means such as gaseous reduction and sulphidization is investigated thermodynamically. The effects of temperature, matte and slag composition have been taken into account. The results show that gaseous reduction is not very effective and copper content levels in the range of 0.2-0.4% can be achieved. However, sulphidization of copper oxide in slag with a low grade matte is a much more effective method for the removal of dissolved copper. Very low levels of copper in slag can be obtained.

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