

Distribution Equilibria of Sn, Se and Te Between FeO-Fe₂O₃-SiO₂-Al₂O₃-CuO_{0.5} Slag and Metallic Copper

M. NAGAMORI AND P. J. MACKEY

The distribution of tin, selenium and tellurium between alumina-containing fayalitic slags and metallic copper was measured at 1200 and 1300°C under controlled CO-CO₂ atmosphere with oxygen partial pressure (p_{O_2}) in the range $p_{O_2} = 10^{-6}$ to 10^{-11} atm (1 atm = 1.013×10^2 kPa). The solubility of Sn in slag was observed to increase linearly with increasing $p_{O_2}^{1/2}$. It was deduced that Sn is present in the slag in the form of SnO or Sn²⁺ and the activity coefficient of SnO in the slag was calculated to be 1.9 at 1200°C and 0.8 at 1300°C. The solubility of Se in the slag decreases with increasing oxygen partial pressure up to $p_{O_2} = 4 \times 10^{-8}$ atm, but above this oxygen partial pressure it becomes practically constant and the ratio (pct Se in slag/pct Se in copper) = 0.018 (at 1200°C) and 0.036 (at 1300°C). The solubility of Te shows a similar variation with oxygen partial pressure and the ratio (pct Te in slag/pct Te in copper) = 0.026 (at 1200°C) and 0.032 (at 1300°C) above $p_{O_2} = 10^{-8}$ atm. A concept of molecular dissolution of chalcogen elements in slag was developed on the basis of thermodynamic properties of slag, and the observed solubility of Se and Te was explained in terms of the chemical stability of the molecular cluster FeSe and FeTe in the slag.

COPPER concentrates usually contain a number of minor elements, the control of which in copper smelting processes is often a key to the quality of the anode copper produced and may also have a bearing on the overall economics of the process. Selenium and tellurium may be important by-products of copper smelting and refining and the process should be operated in such a way that the highest recovery possible of these elements is achieved. Tin is not usually a by-product and efforts are made to eliminate tin during smelting.

Minor elements are eliminated in copper smelting processes by both slagging and volatilization. Knowledge of the thermodynamic properties of the minor elements in slag is very important in the control of the slagging reactions, although to date very little is known regarding these properties.

This study is an extension of previous work¹ on the distribution of Pb, Bi, Sb and As between slag and metallic copper and was undertaken to investigate the distribution equilibria of Sn, Se and Te as a function of temperature and oxygen potential.

EXPERIMENTAL

The apparatus, starting materials and experimental technique used in the study were the same as described in previous papers.^{1,2} The only change was that the charges were doped with small amounts of reagent grade Sn, Se and Te (Table I). Equilibration was carried out for 20 h (1200°C) and 10 h (1300°C). The attainment of equilibrium was based on the previously^{1,2} established experimental conditions under which the

equilibration between the melt and CO-CO₂ gas was confirmed. The slag and copper were analyzed for Sn, Se and Te at the end of each experiment. In addition, the copper was analyzed for Fe, and the slag was analyzed for Cu, SiO₂, Al₂O₃ and Fe₂O₃. Selenium and tellurium in copper and slag were determined using X-ray fluorescence spectrometry after a pre-concentration step by precipitation with arsenic as collector. Tin in the copper and slag was analyzed by polarographic techniques.

RESULTS

Experimental results are summarized in Table I.

DISCUSSION OF RESULTS

Copper Solubility of Slag

It has been well established that copper dissolves in fayalite slag as CuO_{0.5} (Refs. 1, 3-5) in the absence of sulfur. The metallic copper phase in the present study is practically at unit copper activity, or $a_{Cu} \approx 1.0$, in view of the low levels of minor elements (<1.0 pct). Therefore,

$$a_{CuO_{0.5}} = K_2 \left(\frac{CO_2}{CO} \right)^{1/2} \quad [1]$$

where K_2 is given in Table II.⁶⁻¹²

The activity of CuO_{0.5} calculated by Eq. [1] is plotted against the observed copper concentration in slag in Fig. 1, which also includes the previous values by Nagamori, Mackey and Tarassoff.¹ No distinction is made between the experimental data of this investigation and the previous study,¹ since all measurements were made using the same procedures, and the analytical techniques were the same in each case. Although the data show considerable scatter in the high CuO_{0.5} activity range, it appears reasonable to approximate the experimental points from both studies by the temperature-independent relations:

M. NAGAMORI is with Centre de Recherche Industrielle du Québec, Ste-Foy, Quebec and P. J. MACKEY is Smelter Technical Superintendent, Noranda Mines Limited, Noranda, Quebec, Canada. Both authors were formerly with Noranda Research Centre, Pointe Claire, Quebec.

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$$\left. \begin{aligned} [\text{Cu}]_{\text{Sl}} &= 27 a_{\text{CuO}_{0.5}}; R = 1.5 \\ [\text{Cu}]_{\text{Sl}} &= 35 a_{\text{CuO}_{0.5}}; R = 2.0 \end{aligned} \right\} [2]$$

where [] refers to weight pct (see Symbols).

The CO₂/CO ratios which correspond to magnetite saturation in the fayalitic slags are presumably about 30 and 60 at 1200 and 1300°C respectively.² These CO₂/CO ratios correspond to $a_{\text{CuO}_{0.5}} = 0.10$ and 0.21 at 1200 and 1300°C, respectively. Those experimental points at 1200°C which are found in the range where $a_{\text{CuO}_{0.5}} > 0.09$ (or pct Cu > 2.5) may therefore be considered to indicate the magnetite saturation, which is marked by the almost constant copper concentration while the activity of copper oxide increases (Fig. 1). Copper contents at magnetite saturation are

about 2.5 pct (or $a_{\text{CuO}_{0.5}} \approx 0.09$, line A in Fig. 1) and 2.9 pct (or $a_{\text{CuO}_{0.5}} \approx 0.08$, line B in Fig. 1) corresponding to $R = 1.5$ and 2.0, respectively. The experimental points at 1300°C which are found all in the range $a_{\text{CuO}_{0.5}} < 0.191$ do not seem to indicate the effect of magnetite saturation.

Eq. [2] may be compared with the data at 1300°C for alumina-containing silica-saturated fayalitic slags by Toguri and Santander¹³ expressed by,

$$[\text{Cu}]_{\text{Sl}} = 29.7 a_{\text{CuO}_{0.5}} \quad [3]$$

The data for alumina-free silica-saturated fayalite slags by Ruddle, Taylor and Bates,¹⁴ and Altman and Kellogg⁴ at 1200 to 1400°C are given³ by the equation,

$$[\text{Cu}]_{\text{Sl}} = 35.9 a_{\text{CuO}_{0.5}} \quad [4]$$

Table I. Experimental Conditions and Results

Number	Temperature, °C	Fe/SiO ₂	CO ₂ /CO	Equilibration Time, h	$p_{\text{O}_2}^{1/2}$ (atm) ^{1/2}	Phase*	Analysis							Reciprocal Distribution Coefficient		
							Pct Cu	Pct SiO ₂	Pct Al ₂ O ₃	Pct Fe ₂ O ₃	Pct Fe	Sn ppm	Se ppm	Te ppm	$\frac{1}{L_{\text{Sn}}}$	$\frac{1}{L_{\text{Se}}}$
16	1200	1.5	2	20	6.61×10^{-6}	MC	—	—	—	0.28	1800	1600	1060	—	0.110	0.033
						SL	0.70	27.2	9.0	2.3	—	—	170	35	—	—
17	1200	1.5	5	21	1.65×10^{-5}	MC	—	—	—	0.096	2100	1300	920	0.021	0.065	0.040
						SL	1.22	27.5	8.3	3.6	—	44	84	37	—	—
18	1200	1.5	10	20	3.31×10^{-5}	MC	—	—	—	0.027	1500	2080	1080	0.039	0.040	0.031
						SL	2.20	27.5	9.2	11.4	—	58	84	34	—	—
19	1200	1.5	20	22	6.61×10^{-5}	MC	—	—	—	0.008	1920	1960	1250	0.073	0.032	0.028
						SL	2.73	24.2	10.0	12.3	—	140	62	34	—	—
20	1200	1.5	40	23	1.32×10^{-4}	MC	—	—	—	0.01	1800	2300	1010	0.140	0.023	0.028
						SL	2.69	—	7.5	—	—	250	53	35	—	—
21	1200	2.0	2	20	6.61×10^{-6}	MC	—	—	—	0.31	2400	1890	1010	0.024	0.100	0.032
						SL	0.85	27.1	7.1	4.0	—	58	190	32	—	—
22	1200	2.0	10	20	3.31×10^{-5}	MC	—	—	—	0.029	2400	1940	1160	0.092	0.050	0.028
						SL	2.48	25.0	6.4	7.7	—	220	97	32	—	—
25	1200	2.0	20	20	6.61×10^{-5}	MC	—	—	—	—	1500	2230	1370	0.130	0.030	0.026
						SL	3.00	24.8	4.5	8.3	—	200	66	36	—	—
23	1200	2.0	40	19	1.32×10^{-4}	MC	—	—	—	0.013	1700	2090	1010	0.220	0.025	0.026
						SL	2.81	24.7	5.0	9.4	—	370	52	26	—	—
30	1300	2.0	2	11	2.87×10^{-5}	MC	—	—	—	—	1000	1970	840	—	0.063	0.036
						SL	1.31	22.5	15.1	3.4	—	—	120	30	—	—
31	1300	2.0	10	10	1.43×10^{-4}	MC	—	—	—	—	1300	1980	1150	0.140	0.039	0.031
						SL	3.50	22.4	10.0	7.8	—	180	78	36	—	—
33	1300	2.0	20	10	2.87×10^{-4}	MC	—	—	—	—	1000	2080	—	0.250	0.038	—
						SL	6.08	21.6	7.4	6.6	—	250	78	40	—	—
32	1300	2.0	40	10	5.74×10^{-4}	MC	—	—	—	—	1100	1910	890	0.570	0.037	0.034
						SL	5.60	21.0	8.2	—	—	630	70	30	—	—

Charge: 8g slag, 8g Cu, 20 mg Sn, 30 mg Se, 20 mg Te.

*MC = metallic copper; SL = slag.

Table II. Free Energy Data and Equilibrium Constants

i	Reaction	ΔG° , cal/mole*	K_i		Reference
			1200°C	1300°C	
1	$\text{Cu}(l) + \frac{1}{4}\text{O}_2(g) = \text{CuO}_{0.5}(l)$	$-17,490 + 7.21 T$	1.047×10	7.158	1
2	$\text{Cu}(l) + \frac{1}{2}\text{CO}_2(g) = \text{CuO}_{0.5}(l) + \frac{1}{2}\text{CO}(g)$	$16,260 - 3.16 T$	1.893×10^{-2}	2.695×10^{-2}	1
3	$\text{Sn}(l) + \frac{1}{2}\text{O}_2(g) = \text{SnO}(l)$	$-62,690 + 20.69 T$	6.058×10^4	1.551×10^4	6
4	$\text{Sn}(l) + \text{O}_2(g) = \text{SnO}_2(s)$	$-140,180 + 51.52 T$	3.503×10^9	1.665×10^8	7
5	$\frac{1}{2}\text{Se}_2(g) = \text{Se}(g)$	$32,780 - 13.12 T$	1.006×10^{-2}	2.051×10^{-2}	8, 9
6	$\frac{1}{2}\text{Se}_2(g) + \frac{1}{2}\text{O}_2(g) = \text{SeO}(g)$	$-4,050 - 1.23 T$	7.417	6.792	8, 9, 10
7	$\frac{1}{2}\text{Se}_2(g) + \text{O}_2(g) = \text{SeO}_2(g)$	$-43,110 + 16.10 T$	7.573×10^2	2.968×10^2	8, 9, 10
8	$\frac{1}{2}\text{Te}_2(g) = \text{Te}(g)$	$27,160 - 12.15 T$	4.215×10^{-2}	7.606×10^{-2}	11
9	$\frac{1}{2}\text{Te}_2(g) + \frac{1}{2}\text{O}_2(g) = \text{TeO}(g)$	$-2,780 - 1.48 T$	5.449	5.130	11, 12
10	$\frac{1}{2}\text{Te}_2(g) + \text{O}_2(g) = \text{TeO}_2(g)$	$-35,050 + 15.08 T$	8.050×10	3.758×10	11, 12
11	$\text{Fe}(\gamma) + \frac{1}{2}\text{O}_2(g) = \text{FeO}(l)$	$-54,890 + 10.55 T$	6.947×10^5	2.107×10^5	3
12†	$\text{Fe}(\alpha) + \frac{1}{2}\text{Se}_2(g) = \text{FeSe}(s)$	$-35,500 + 19.1 T$	1.240×10	5.734	7, 11
13†	$\text{Fe}(\alpha) + \frac{1}{2}\text{Te}_2(g) = \text{FeTe}(s)$	$-35,100 + 19.3 T$	9.781	4.561	7, 11

*1 cal = 4.19 J.

†Extrapolated to higher temperatures.

As previously noted¹ and evident from the above comparison Al_2O_3 lowers the oxidic copper solubility in fayalite slags.

Minor Elements in Slag

As discussed previously,¹ the interaction between minor elements in the metallic copper phase may be neglected due to their very low levels in the present experiments. The activity coefficient of an element X can then be assessed based solely upon data for the binary Cu-X system.

The distribution coefficient of element X between metallic copper and slag phases, L_X , was previously¹ defined by concentration of element X in metallic copper over that in slag. Namely,

$$L_X = \frac{[X]_{\text{Cu}}}{[X]_{\text{Sl}}} \quad [5]$$

where the concentrations are expressed in terms of weight percent in the present study rather than mole fraction in the previous paper.¹ In this paper, the reciprocal of L_X is most often used and written as L_X^{-1} .

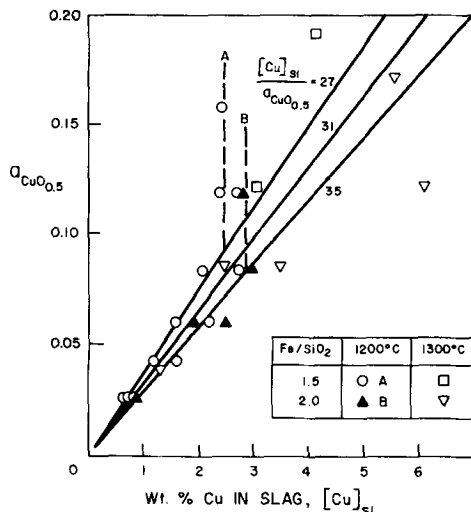


Fig. 1—Solubility of copper in alumina-bearing fayalitic slag at 1200 and 1300°C. A and B—estimated magnetite saturation limits at 1200°C for slags with $R = 1.5$ and 2.0 , respectively.

Tin

Tin may dissolve in fayalite slag in monatomic (gaseous) or oxidic form. Since both $\text{SnO}(l)$ and $\text{SnO}_2(s)$ are known to be stable between 1200 and 1300°C (Ref. 15), these two oxidic forms (or Sn^{2+} and Sn^{4+} ions, respectively) may be assumed. The technique for determining the form of tin dissolution in the present slag is based on a somewhat similar method developed previously¹ for other minor elements. In the following, the dependency of L_{Sn}^{-1} on $p_{\text{O}_2}^{1/2}$ is examined for various types of dissolution mechanisms in slag.

a) **Monatomic (Sn^0).** When an element is present in slag in monatomic form, the concentration of the element in the slag is assumed to be independent of the oxygen partial pressure over the system. Accordingly, if the slag composition does not vary greatly, then at constant temperature,

$$L_{\text{Sn}}^{-1} = \text{constant}. \quad [6]$$

b) **SnO (Stannous, Sn^{2+}).** When $[\text{Sn}]_{\text{Sl}}$ is given, the mole fraction of SnO can be calculated by,

$$\begin{aligned} N_{\text{SnO}} &= \frac{[\text{Sn}]_{\text{Sl}}/W_{\text{Sn}}}{\sum([\text{MeO}]_{\text{Sl}}/W_{\text{MeO}})} \\ &= 5.65 \times 10^{-3} [\text{Sn}]_{\text{Sl}}. \end{aligned} \quad [7]$$

In this case the slag is considered to be a molecular mixture of the $\text{FeO}-\text{FeO}_{1.5}-\text{SiO}_2-\text{AlO}_{1.5}-\text{CuO}_{0.5}-\text{SnO}$ system and the summation in the denominator is found to be practically constant, being about $1.50 (\pm 0.05)$ for the slags in the present work.

Within the dilute solution range where Henry's law prevails,

$$\begin{aligned} a_{\text{SnO}} &= \gamma_{\text{SnO}}^0 N_{\text{SnO}} \\ &= 5.65 \times 10^{-3} \gamma_{\text{SnO}}^0 [\text{Sn}]_{\text{Sl}}. \end{aligned} \quad [8]$$

The concentration of Sn in the liquid copper phase is converted to activity by

$$\begin{aligned} a_{\text{Sn}} &= \gamma_{\text{Sn}}^0 N_{\text{Sn}} \\ &= 5.35 \times 10^{-3} \gamma_{\text{Sn}}^0 [\text{Sn}]_{\text{Cu}} \end{aligned} \quad [9]$$

where the value of γ_{Sn}^0 is given in Table III.^{16,17} When the slag and metallic copper phases are in equilibrium under a known oxygen potential, insertion of Eq. [9] into the equilibrium constant relationship for Reaction [3], Table II, yields

$$a_{\text{SnO}} = K_3 p_{\text{O}_2}^{1/2} a_{\text{Sn}} \\ = 5.35 \times 10^{-3} K_3 \gamma_{\text{Sn}}^0 p_{\text{O}_2}^{1/2} [\text{Sn}]_{\text{Cu}} \quad [10]$$

Combining Eqs. [8] and [10], the reciprocal distribution coefficient for tin is given as,

$$L_{\text{Sn}}^{-1} = \frac{[\text{Sn}]_{\text{Sl}}}{[\text{Sn}]_{\text{Cu}}} \equiv c_1 p_{\text{O}_2}^{1/2} \quad [11]$$

where c_1 is a constant at constant temperature and given as,

$$c_1 \equiv \frac{0.95 K_3 \gamma_{\text{Sn}}^0}{\gamma_{\text{SnO}}^0} \quad [12]$$

The activity coefficient γ_{Sn}^0 is given in Table III. Consequently, the activity coefficient of SnO in slag can be calculated from the slope c_1 of a linear plot of L_{Sn}^{-1} vs $p_{\text{O}_2}^{1/2}$. Then,

$$\gamma_{\text{SnO}}^0 = \frac{0.95 K_3 \gamma_{\text{Sn}}^0}{c_1} \quad [13]$$

Eq. [11] indicates that if tin dissolves as SnO in the slag, the value of L_{Sn}^{-1} will be linear with $p_{\text{O}_2}^{1/2}$.

c) SnO_2 (Stannic, Sn^{4+}). When tin dissolves in slag in the form of SnO_2 , it can be demonstrated by a procedure similar to the above case of SnO, that the values of L_{Sn}^{-1} should be linear with p_{O_2} rather than $p_{\text{O}_2}^{1/2}$ as for stannous dissolution. That is,

$$L_{\text{Sn}}^{-1} = c_2 p_{\text{O}_2} \quad [14]$$

where

$$c_2 = \frac{0.95 K_4 \gamma_{\text{Sn}}^0}{\gamma_{\text{SnO}_2}^0} \quad [15]$$

It is therefore evident that by examining the dependency of the values of L_{Sn}^{-1} upon $p_{\text{O}_2}^{1/2}$, the form in which tin dissolves in the slag can be determined. In Fig. 2 these hypothetical cases are shown schematically. Each of the lines in Fig. 2(a) corresponds to only one type of dissolution mechanism. It is possible that two or more dissolution mechanisms can occur simultaneously, as shown in Fig. 2(b) corresponding to simultaneous dissolution in monatomic and oxidic forms.

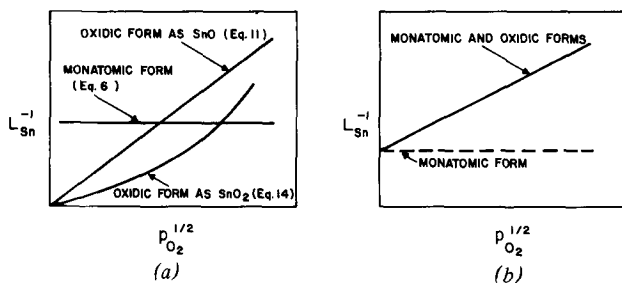


Fig. 2—Possible forms of Sn dissolution in fayalitic slag.

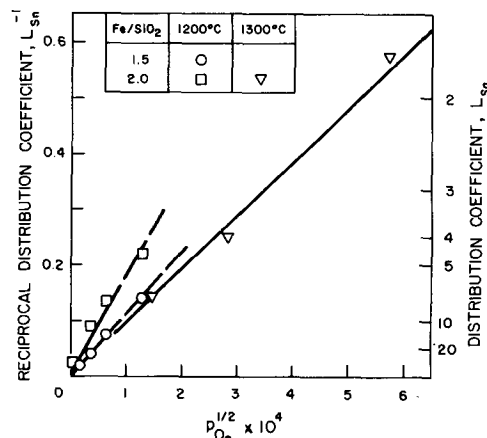


Fig. 3—Reciprocal distribution coefficient of tin between alumina-bearing fayalitic slags and metallic copper as a function of oxygen partial pressure.

Fig. 3 is a plot of the actual values of L_{Sn}^{-1} against $p_{\text{O}_2}^{1/2}$. A marked linearity of the data rules out both monatomic and quadravalent dissolution of tin in the slag, and tin apparently dissolves as SnO (Sn^{2+}) in the slag under the present conditions. Namely,

$$\left. \begin{aligned} L_{\text{Sn}}^{-1} (R = 1.5, 1200^\circ\text{C}) &= 1.1 \times 10^{-3} p_{\text{O}_2}^{1/2} \\ L_{\text{Sn}}^{-1} (R = 2.0, 1200^\circ\text{C}) &= 1.8 \times 10^{-3} p_{\text{O}_2}^{1/2} \\ L_{\text{Sn}}^{-1} (R = 2.0, 1300^\circ\text{C}) &= 0.96 \times 10^{-3} p_{\text{O}_2}^{1/2} \end{aligned} \right\} \quad [16]$$

Using the c_1 values in Eq. [16], the activity coefficient of SnO in the slag can be determined from Eq. [13] as,

$$\left. \begin{aligned} \gamma_{\text{SnO}}^0 (R = 1.5, 1200^\circ\text{C}) &= 2.4 \pm 0.3 \\ \gamma_{\text{SnO}}^0 (R = 2.0, 1200^\circ\text{C}) &= 1.5 \pm 0.3 \\ \gamma_{\text{SnO}}^0 (R = 2.0, 1300^\circ\text{C}) &= 0.8 \pm 0.1 \end{aligned} \right\} \quad [17]$$

Table III. Raoultian Activity Coefficients of Sn, Se and Te in Molten Copper at Infinite Dilution

Element	Temperature Dependency, (K)	γ^0		Reference
		1200°C	1300°C	
Sn(l)	$\log \gamma_{\text{Sn}}^0 = -1,300 T^{-1} - 0.45$	4.65×10^{-2}	5.29×10^{-2}	16
Se(l)	$\log \gamma_{\text{Se}}^0 = -3,770 T^{-1} + 0.25$	4.91×10^{-3}	7.13×10^{-3}	17, PW
Te(l)	$\log \gamma_{\text{Te}}^0 = -3,680 T^{-1} + 1.142$	4.40×10^{-2}	6.35×10^{-2}	17, PW*

PW = present work. The originally reported values¹⁷ were based on extrapolated vapor pressure data of pure Se and Te rather than the values measured by Baker.^{20,21} The activity data shown here have been recalculated by the present authors using the experimental values of Hino *et al*¹⁷ and the vapor pressure data established by Baker.^{20,21}

*Predel and Pichl²⁶ recently measured thermodynamic properties of Cu-Te alloys. However, their data at 1064°C point to a value of $\gamma_{\text{Te}}^0 \approx 100$ which the present authors consider too high.

Alternatively, neglecting the effect of (Fe/SiO₂), a simplified expression may be obtained,

$$\log \gamma_{\text{SnO}}^0 = 8,800 T^{-1} - 5.70 \quad [18]$$

which gives, $\gamma_{\text{SnO}}^0 = 1.88$ at 1200°C and $\gamma_{\text{SnO}}^0 = 0.78$ at 1300°C.

Rankin and Biswas⁶ reported the value of ($\gamma_{\text{FeO}} / \gamma_{\text{SnO}}$) to be between 4.5 and 5.5 for FeO-Fe₂O₃-SiO₂-Al₂O₃-SnO slags containing 7 to 43 pct SnO at 1250°C. Based on data for fayalitic slags^{2,3,18,19} one may assess the value of γ_{FeO} in the slags as being between 0.63 to 0.73. The data of Rankin and Biswas⁶ then suggest a γ_{SnO} value of 0.14 (± 0.02), which is only one tenth of the present values. The experiments by Rankin *et al* were carried out without controlling the oxygen potential and this may have prevented equilibrium conditions from being established. Rankin *et al* studied the concentrated solution range while the present work is concerned with the dilute solution range. It is possible that this difference also contributes to the variation in γ_{SnO} values.

Selenium

As in the case of Sn, the dependence of L_{Se}^{-1} on oxygen potential is analyzed.

a) Monatomic (Se⁰). When Se dissolves in slag in monatomic form, the Se concentration in slag is not affected by oxygen partial pressure, as discussed for the monatomic dissolution of tin in slag, and therefore,

$$L_{\text{Se}}^{-1} = \text{constant.} \quad [19]$$

b) Gaseous SeO. The oxide SeO is a stable gas at copper smelting temperatures and it is possible that this molecular form dissolves in slag. Assuming this type of dissolution, the dependence of the distribution coefficient on the oxygen partial pressure is examined to determine the dissolution form.

When $[\text{Se}]_{\text{Cu}}$ is known, the selenium activity in the dilute solution range is given as,

$$a_{\text{Se}} = \gamma_{\text{Se}}^0 N_{\text{Se}} = 8.05 \times 10^{-3} \gamma_{\text{Se}}^0 [\text{Se}]_{\text{Cu}} \quad [20]$$

where the value of γ_{Se}^0 can be calculated from the data shown in Table III. Also,

$$p_{\text{Se}_2}^{1/2} = (P_{\text{Se}_2}^0)^{1/2} a_{\text{Se}} = 8.05 \times 10^{-3} (P_{\text{Se}_2}^0)^{1/2} \gamma_{\text{Se}}^0 [\text{Se}]_{\text{Cu}} \quad [21]$$

where $P_{\text{Se}_2}^0$ is the partial pressure of Se₂ over pure liquid selenium and has been determined as shown in

Table IV.^{7,20,21} Substitution of Eq. [21] into the equilibrium constant for Reaction [6] gives,

$$p_{\text{SeO}} = K_6 p_{\text{Se}_2}^{1/2} p_{\text{O}_2}^{1/2} = 8.05 \times 10^{-3} K_6 \gamma_{\text{Se}}^0 (P_{\text{Se}_2}^0)^{1/2} [\text{Se}]_{\text{Cu}} p_{\text{O}_2}^{1/2}. \quad [22]$$

According to Henry's law, the concentration of gaseous SeO dissolved in the slag should be proportional to the partial pressure of SeO over the slag:

$$[\text{SeO}]_{\text{Sl}} = h_1 p_{\text{SeO}}. \quad [23]$$

Noting that $[\text{Se}]_{\text{Sl}} = 0.83[\text{SeO}]_{\text{Sl}}$, then:

$$[\text{Se}]_{\text{Sl}} = 0.83 h_1 p_{\text{SeO}} = 6.68 \times 10^{-3} h_1 K_6 \gamma_{\text{Se}}^0 (P_{\text{Se}_2}^0)^{1/2} [\text{Se}]_{\text{Cu}} p_{\text{O}_2}^{1/2}. \quad [24]$$

Thus it is evident that when selenium dissolves in slag as the gaseous molecule SeO, the selenium concentration in slag should be proportional to $[\text{Se}]_{\text{Cu}}$ and $p_{\text{O}_2}^{1/2}$. Consequently,

$$L_{\text{Se}}^{-1} = \frac{[\text{Se}]_{\text{Sl}}}{[\text{Se}]_{\text{Cu}}} = 6.68 \times 10^{-3} h_1 K_6 \gamma_{\text{Se}}^0 (P_{\text{Se}_2}^0)^{1/2} p_{\text{O}_2}^{1/2} = c_3 p_{\text{O}_2}^{1/2}. \quad [25]$$

Eq. [25] indicates that if selenium dissolves in slag as the gaseous molecule SeO, L_{Se}^{-1} will be proportional to $p_{\text{O}_2}^{1/2}$.

c) Gaseous SeO₂. A calculation similar to the case for gaseous SeO leads to the following relation,

$$L_{\text{Se}}^{-1} = 5.73 \times 10^{-3} h_2 K_7 \gamma_{\text{Se}}^0 (P_{\text{Se}_2}^0)^{1/2} p_{\text{O}_2} = c_4 p_{\text{O}_2} \quad [26]$$

where,

$$[\text{SeO}_2]_{\text{Sl}} = h_2 p_{\text{SeO}_2}. \quad [27]$$

d) Molecular FeSe. First consider the equilibrium of Reaction [11] in Table II.

$$a_{\text{Fe}} = \frac{a_{\text{FeO}}}{K_{11} p_{\text{O}_2}^{1/2}}. \quad [28]$$

For fayalitic slags studied in the present work, the FeO concentration in the slag ranges between 50 and 60 pct, which corresponds to an FeO activity of 0.45 to 0.55 at 1300°C, and 0.43 to 0.50 at 1200°C. Accordingly, as an approximation, it may be assumed that $a_{\text{FeO}} = 0.5$ (± 0.05). Then,

$$a_{\text{Fe}} = 0.5 K_{11}^{-1} p_{\text{O}_2}^{-1/2}. \quad [29]$$

Table IV. Vapor Pressure of Pure Liquids

Element	Temperature Dependency (atm, K)*	P° (atm)*		Reference
		1200°C	1300°C	
Sn(l)	$\log P_{\text{Sn}}^0 = -15,500 T^{-1} + 5.35$	6.72×10^{-6}	3.13×10^{-5}	7
Se(l)	$\log P_{\text{Se}_2}^0 = -5,540 T^{-1} + 5.57$	6.44×10	1.12×10^2	20
Te(l)	$\log P_{\text{Te}_2}^0 = -5,900 T^{-1} + 4.64$	4.31	7.75	21

*1 atm = 1.013 × 10² kPa.

Assuming that selenium dissolves in the slag as molecular FeSe, or that selenium in the slag results in short-range ordering or clustering with the iron atom (ion), then from Henry's law,

$$[\text{FeSe}]_{\text{Sl}} = 1.71 [\text{Se}]_{\text{Sl}} \\ = h_3 a_{\text{FeSe}} \quad [30]$$

or,

$$a_{\text{FeSe}} = 1.7 h_3^{-1} [\text{Se}]_{\text{Sl}} \quad [31]$$

From the equilibrium constant for Reaction [12] in Table II,

$$a_{\text{FeSe}} = K_{12} a_{\text{Fe}} p_{\text{Se}_2}^{1/2} \quad [32]$$

Inserting Eqs. [21] and [29] into Eq. [32], we have,

$$a_{\text{FeSe}} = 4.0 \times 10^{-3} K_{11}^{-1} K_{12} (P_{\text{Se}_2}^0)^{1/2} \gamma_{\text{Se}}^0 p_{\text{O}_2}^{-1/2} [\text{Se}]_{\text{Cu}} \quad [33]$$

From Eqs. [31] and [33],

$$L_{\text{Se}}^{-1} = \frac{[\text{Se}]_{\text{Sl}}}{[\text{Se}]_{\text{Cu}}} = 2.4 \times 10^{-3} h_3 K_{11}^{-1} K_{12} (P_{\text{Se}_2}^0)^{1/2} \gamma_{\text{Se}}^0 p_{\text{O}_2}^{-1/2} \\ \equiv c_5 p_{\text{O}_2}^{-1/2} \quad [34]$$

The slag is an oxidic mixture primarily of ionic or molecular nature. However, for fayalitic slags there is an increase in metallic character (metallicity) with increasing ferrous oxide as well as decreasing ferric oxide contents. Eq. [34] implies that oxygen (or ferric oxide) in the slag tends to render selenium unstable in the slag, whereas the metallicity of the slag tends to stabilize selenium in the slag. In Fig. 4(a), this hypothetical dissolution of selenium in slag as molecular FeSe is schematically shown, whereas in Fig. 4(b) a composite case of the molecular and monatomic dissolution is demonstrated. The composite dissolution is assumed to be expressed as the sum of the molecular and monatomic mechanisms, or namely,

$$[\text{Se}]_{\text{Sl}}^{\text{to}} = [\text{Se}]_{\text{Sl}}^{\text{ml}} + [\text{Se}]_{\text{Sl}}^{\text{mn}} \quad [35]$$

Accordingly,

$$L_{\text{Se}}^{-1} = c_5 p_{\text{O}_2}^{-1/2} + c_6 \quad [36]$$

The actual experimental data for L_{Se}^{-1} are plotted against $p_{\text{O}_2}^{1/2}$ in Fig. 5 and exhibit the composite dissolution of Se by the molecular and monatomic mechanisms discussed above. The experimental points at 1300°C more clearly indicate the relationship. The data may be represented by the equations,

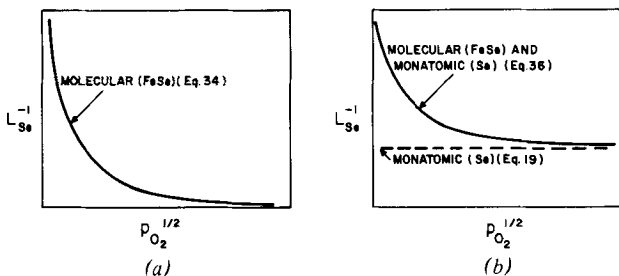


Fig. 4—Possible forms of Se dissolution in fayalitic slag.

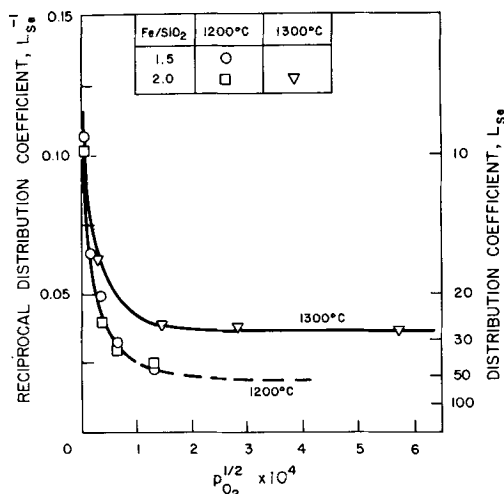


Fig. 5—Reciprocal distribution coefficient of selenium between alumina-bearing fayalitic slags and metallic copper as a function of oxygen partial pressure.

$$\left. \begin{aligned} L_{\text{Se}}^{-1} (1200^\circ\text{C}) &= 8.0 \times 10^{-7} p_{\text{O}_2}^{-1/2} + 0.018 \\ L_{\text{Se}}^{-1} (1300^\circ\text{C}) &= 6.0 \times 10^{-7} p_{\text{O}_2}^{-1/2} + 0.036 \end{aligned} \right\} \quad [37]$$

More generally, for the temperature range between 1200 and 1300°C,

$$L_{\text{Se}}^{-1} = (7.0 + 2.0 t) \times 10^{-7} p_{\text{O}_2}^{-1/2} + 0.027 + 0.018 t \quad [38]$$

where,

$$t = 0.01 (T - 1523). \quad [39]$$

Tellurium

A similar treatment is followed for Te. The dissolution of gaseous TeO can be formulated in a similar manner to the case for gaseous SeO. Namely,

$$L_{\text{Te}}^{-1} = 4.42 \times 10^{-3} h_4 K_9 \gamma_{\text{Te}}^0 (P_{\text{Te}_2}^0)^{1/2} p_{\text{O}_2}^{1/2} \\ \equiv c_7 p_{\text{O}_2}^{1/2} \quad [40]$$

For the dissolution of gaseous TeO₂,

$$L_{\text{Te}}^{-1} = 3.98 \times 10^{-3} h_5 K_{10} \gamma_{\text{Te}}^0 (P_{\text{Te}_2}^0)^{1/2} p_{\text{O}_2} \\ \equiv c_8 p_{\text{O}_2} \quad [41]$$

For the molecular or cluster dissolution of FeTe,

$$L_{\text{Te}}^{-1} = 1.7 \times 10^{-3} h_6 K_{11}^{-1} K_{13} \gamma_{\text{Te}}^0 (P_{\text{Te}_2}^0)^{1/2} p_{\text{O}_2}^{-1/2} \\ \equiv c_9 p_{\text{O}_2}^{-1/2} \quad [42]$$

The experimental data for L_{Te}^{-1} are plotted against $p_{\text{O}_2}^{1/2}$ in Fig. 6 indicating that tellurium exhibits composite dissolution by molecular and monatomic mechanisms, as in the case for selenium. The data may be represented by the equations,

$$\left. \begin{aligned} L_{\text{Te}}^{-1} (1200^\circ\text{C}) &= 6.0 \times 10^{-8} p_{\text{O}_2}^{-1/2} + 0.026 \\ L_{\text{Te}}^{-1} (1300^\circ\text{C}) &= 1.0 \times 10^{-7} p_{\text{O}_2}^{-1/2} + 0.032 \end{aligned} \right\} \quad [43]$$

More generally, for the temperature range of 1200 to 1300°C,

$$L_{\text{Te}}^{-1} = (8.0 + 4.0 t) \times 10^{-8} p_{\text{O}_2}^{-1/2} + 0.029 + 0.006 t \quad [44]$$

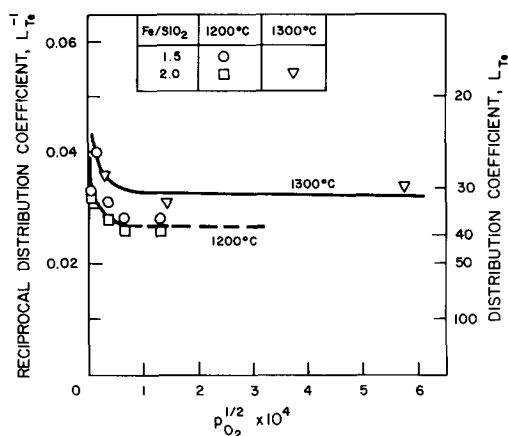


Fig. 6—Reciprocal distribution coefficient of tellurium between alumina-bearing fayalitic slags and metallic copper as a function of oxygen partial pressure.

OVERALL DISCUSSION

The present experimental method of doping the melt with minor elements under a controlled oxygen potential has the remarkable advantage of simplifying an otherwise very difficult and complicated experimental procedure for determining the activity coefficient of elements dissolving oxidically in the slag. It should, however, be noted that the method theoretically can produce reliable results only when the element has no significant volatile species. In the present work, volatile species are present and the effects of volatilization must therefore be discussed. In the case of tin, SnO is known to be quite volatile at copper smelting temperatures. As can be determined from the data in Table I, the final amount of tin present in the slag and copper phases at the end of an experiment indicates that the evaporation of gaseous species containing tin was quite low at 1200°C, while as much as one third of the tin in the initial charge volatilized at 1300°C. Reference to Table I also shows that there were some losses of Se and Te, especially Te.

If the doped element volatilizes from the slag surface at a faster rate than the metallic copper phase can supply the element to the slag across the copper/slag interface, a situation could occur in which the minor element concentration in the slag is lower than the equilibrium value. This could result in a larger L_X value being observed in the present experiments, and the real activity coefficient could be slightly lower than the values presented here. By the same token, the solubilities of Se and Te in the slag observed in the present experiments could be lower due to volatilization of the species SeO and TeO from the slag.

Clarification of the effect of volatilization from the slag and the resulting concentration gradients would require detailed data on kinetic and diffusional transfer in the liquid and gaseous phases.

The effect of magnetite saturation which was observed in the copper solubility (Fig. 1) should be expected for tin in runs with $\text{CO}_2/\text{CO} = 40$ at 1200°C. The two runs with $p_{\text{O}_2}^{1/2} = 1.32 \times 10^{-4}$ at 1200°C, however, failed to deviate from linearity prevailing in the lower oxygen pressure range ($p_{\text{O}_2}^{1/2} < 7 \times 10^{-5}$). Although a similar deviation may also be expected

in L_{Se} and L_{Te} of the two runs, the experiments failed to indicate the saturation effect. It might be that experimental scatter has masked the saturation effect, which may not be sufficiently large at $\text{CO}_2/\text{CO} = 40$ anyway.

As pointed out previously,¹ industrial slags contain entrained copper and/or matte and a correction for these suspended phases is required to determine the apparent distribution coefficient for industrial slags. The possible volatilization during equilibration is considered not to affect the application of the present data in analyzing the behavior of minor elements in industrial processes. In some copper smelting processes such as converting in the Peirce-Smith converter or the Noranda process,²² the melt undergoes turbulent contact with injected tuyere gas. It is to be noted that the CO-CO₂ gas volume per unit mass of melts in the present experiments is 2 to 4 times larger than the specific air volumes per unit mass of melts in an industrial converting vessel. However, the efficiency of minor element volatilization into the gas atmosphere in the present study is considered to be much lower than that in the industrial processes. This is because in the present experiments, the CO-CO₂ gas simply sweeps the melt surface whereas in the industrial vessels, submerged jets give rise to high gas/liquid contacting and turbulence.

Slags are often considered as simple mixtures of various oxides, where all the constituents are present as an oxide. The results of the present and previous studies^{1,3} indicate that especially for minor element dissolution, the slag is far from being a simple oxidic mixture. Oxidic dissolution is applicable to minor elements such as copper,^{1,3} lead,^{1,23} cobalt,²⁴ and tin (present work). However, some portion of the dissolved copper in sulfur-containing fayalitic slag is now considered to be sulfidic in terms of the molecular theory of slag.³ Sulfidic dissolution of lead and tin is possible for a sulfur-containing slag. Molecular dissolution is assumed to be true of sulfur as well as selenium and tellurium. This follows since FeSe and FeTe are as stable as FeS (Table II), while it is known from previous work^{3,25} that FeS is stable under copper smelting conditions. The previous investigation¹ of sulfur-free silica-unsaturated slags at $p_{\text{O}_2} = 10^{-6}$ to 10^{-11} atm indicated that bismuth, antimony and arsenic dissolve in the atomic form. Sulfidic and oxidic dissolution of these elements might become significant under certain conditions. In the present study it has been shown that selenium and tellurium dissolve as the selenide and telluride of iron in slag at low oxygen potential ($p_{\text{O}_2} < 10^{-8}$ atm) in addition to atomic dissolution.

Thus, in commercial copper smelting processes the slag is a rather complex melt, particularly for minor element dissolution. The various dissolution concepts discussed here offer an improved basis for control of commercial smelting process, since it is the minor elements and almost they alone that determine the quality of anode copper.

SYMBOLS

a_i

= activity of component i . Reference state indicated in Table II,

c_i	= constant at constant temperature,
ΔG°	= Gibbs free energy of formation, cal/mole (1 cal = 4.19 J),
h_i	= Henrian activity coefficient,
K_i	= equilibrium constant of Reaction i ,
L_X	= distribution coefficient of component X between slag and copper, see Eq. [5],
L_X^{-1}	= reciprocal distribution coefficient = $1/L_X$,
N_i	= mole fraction of component i ,
p_i	= partial pressure of component i , atm (1 atm = 1.013×10^5 kPa),
P_i^0	= partial pressure of component i over pure element, atm,
R	= $[\text{Fe}]_{\text{Sl}}/[\text{SiO}_2]_{\text{Sl}}$,
t	= see Eq. [39],
T	= temperature, K,
W_i	= atomic weight of component i ,
$[X]_{\text{Cu}}, [X]_{\text{Sl}}$	= weight percent of component X in metallic copper and slag phases respectively,
$[X]_{\text{Sl}}^{to}, [X]_{\text{Sl}}^{ml}, [X]_{\text{Sl}}^{mn}$	= weight percent of component X in slag, superscripts to , ml and mn referring to total, molecular, and monatomic respectively.
γ_i	= Roaultian activity coefficient of component i ,
γ_i^0	= Roaultian activity coefficient of component i at infinite dilution.

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