The Effect of Silica, Alumina, Calcia and Magnesia on the Activity Coefficient of Cobalt Oxide in Iron Silicate Slags

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ABSTRACT

Iron silicate slags with varying contents of silica (14 wt % to 43 wt %), or alumina (up to 16 wt %), or calcia (up to 13 wt %) or magnesia (up to 11 wt %) were equilibrated with solid-iron alloys or liquid cobalt-gold-iron alloys in cobalt, alumina, or silica crucibles at oxygen pressures of either 10^{-9} or 10^{-10} atm. (1 atm. = 1.013 x 10^5 Pa) at 1573 K. The solubility of cobalt oxide was measured in the slags and the activity coefficient calculated relative to pure solid cobalt oxide as standard state. The activity coefficient of cobalt oxide was found to increase with an increase in either alumina, or calcia or magnesia in the slag and decrease with an increase in the silica content of slag.

1. INTRODUCTION

Cobalt is often a by-product from nickel and copper smelting operations[1]. The recovery depends on the distribution of cobalt between matte and discard slag in the smelting stage and an important factor affecting this distribution is the activity coefficient of cobalt oxide in slag. The authors have previously measured the activity coefficient for silica saturated slags at 1573 K, and report a constant value of 0.91 $\pm$ 0.09 relative to pure solid cobalt oxide, for slags containing up to 10 percent cobalt oxide[2]. This value is significantly lower than reported by others[3-5] for silica saturated iron silicate slags, although similar to that reported for alumina saturated slags[6]. These comparisons, dealt with in some detail previously[2], highlight significant inconsistencies in the published data.

In industrial practice, iron silicate slags are not silica saturated and the Fe/SiO_2 ratio is an important variable. At the WMC Kalgoorlie Nickel Smelter, for example, the Fe/SiO_2 ratio in the flash furnace was increased from 1.0 to 1.7 over a ten year period, in order to decrease the slag mass and to increase its fluidity[7]. The distribution of cobalt from matte to slag ((%Co in slag)/[%Co in matte]) increased by about 35 percent as a result[7]. Zakharov and Tikhonov[8] reported a similar trend, with the distribution of cobalt to iron silicate slags equilibrated with mattes under argon, being doubled as the percent silica in slag decreased from 40 to 13 percent.

Takeda et al.[9] measured the oxygen pressure of liquid Cu-Ni-Fe alloys equilibrated at 1573 K with iron saturated slag with between 20 and 36 percent silica. The distribution of cobalt from alloy to slag was reported to increase around 40 percent as the silica in slag was increased over this range. These results imply that the activity coefficient of cobalt oxide decreases with an increase in silica content of slag, since the alloys contained essentially content amounts of cobalt (0.28-0.30%) over a narrow range of oxygen pressures.

Fontana et al.[10] reported the solubilities of cobalt in iron silicate slags containing lime and equilibrated with Cu-Co alloys by levitation at 1623 K, and at oxygen pressures of between 10^{-7} and 10^{-10} atm. Although no activity coefficients were calculated, the solubility of cobalt reported for slags of constant Ca/Si ratio increased with increase in Fe/Si ratio, but the effects of silica and calcia could not be isolated.

Katyal and Jeffes[11] equilibrated iron silicate and ferrite slags with liquid Co-Cu alloys at temperature between 1523 and 1623 K by the levitation technique. The activity coefficient of cobalt oxide in silica unsaturated iron silicate slag increased slightly with increase of silica content in slag.

In addition to being unsaturated with silica, industrial slags also contain oxide contaminants such as magnesia, calcia and alumina. No data are

available for the effect of magnesia on activity coefficient of cobalt oxide. The work of Katyal and Jeffes[11] showed that while the activity coefficient of cobalt oxide increased slightly from calcia-free iron silicate slag to 20 percent calcia in slag, it nearly doubled from 20 percent to 30 percent calcia in slag.

Reddy[6] equilibrated alumina saturated fayalite slags (Fe/SiO_2 of 1.34) with liquid Co-Cu alloys at temperatures of 1473 and 1573 K and reported an activity coefficient for cobalt oxide very similar to that reported by Grimsey and Liu[2] for alumina-free silica saturated slags. This comparison implies that alumina in slag has little effect on the solubility of cobalt oxide. In contrast, the addition of alumina to iron silicate slags in contact with nickel mattes[12], may have substantially increased the activity coefficient of cobalt oxide, as evidenced by the reported enhancement in the matte/slag distribution for cobalt.

In the present work, solid Fe-Co alloys have been equilibrated with silica unsaturated iron silicate slags at an oxygen pressure of 10^{-10} atm. to evaluate the effect of Fe/SiO_2 ratio on cobalt oxide activity coefficient. Further, liquid Co-Fe-Au alloys have been equilibrated with silica saturated slags containing alumina, calcia or magnesia, as well as alumina saturated slags, at 10^{-9} or 10^{-10} atm. oxygen pressure, to evaluate the effect of either alumina, calcia or magnesia on the activity coefficient of cobalt oxide in the slags.

2. EXPERIMENTAL

When equilibrium is reached between an alloy of Co-Fe or Co-Fe-Au, an iron silicate slag containing cobalt oxide and a CO_2/CO gas which sets a specific oxygen pressure, the relevant equilibria are:

$$[Co] + CO_2 = (CoO) + CO \quad (1)$$
$$[Fe] + CO_2 = (FeO) + CO \quad (2)$$
$$CO + 1/2\ O_2 = CO_2 \quad (3)$$

where [ ] and ( ) represent the metal and the slag phase respectively. Iron is transferred from slag to alloy, and cobalt from alloy to slag, when equilibrium is achieved using initially iron free alloys and iron silicate slags.

The experimental technique has been described in detail previously[13,14]. Equilibrations with solid Co-Fe were carried out by containing approximately two grams of pure iron silicate slag within an 8 mm diameter by 25 mm high crucible of welded 0.1 mm thick (99.5 wt % Co) foil. A sheet of foil (4 mm x 15 mm) also was placed within the slag, to monitor the composition of the alloy at equilibrium.

Equilibrations with liquid Co-Fe-Au alloys were carried out by containing two grams of initially Co-Au alloy and two grams of slag mainly in pure recrystallised alumina crucibles or silica crucibles; one experiment was carried out with a magnesia crucible. The Co-Au alloys were prepared in an induction furnace from 99.9 wt percent cobalt and 99.99 wt percent gold, where the latter lowered the melting point of the alloy and also allowed the cobalt activity to be varied. Slags of the required composition were made from mixtures of two master slags of low ferric iron content, containing 38 and 12 percent silica respectively, which were prepared by melting iron , silica and ferric oxide powders in an iron crucible at 1573 K. Additions of alumina, calcia and magnesia powder were made as necessary.

The crucible, containing the alloy and iron silicate slag, was held at 1573 K in a vertical, silicon carbide tube furnace and under a stream of purified and dried CO_2 - CO gas, controlled at set ratios by capillary flow meters, and at a total flow of 200 cm^3/min. The temperature was measured by an alumina-sheathed Pt/Pt-13% Rh thermocouple placed directly under the crucible, while the oxygen pressure was monitored by a stabilized zirconia solid electrolyte cell placed just above the surface of molten slag. After equilibration times of between 36 and 48 hours the crucible with the alloy and slag was quenched into an argon filled, water-cooled, copper chamber. The solidified slag was pulverized under ethanol to minimize secondary oxidation, and analysed[15,16] for Co, ferrous Fe, total Fe and SiO_2. The alloy was analyzed for Co and Fe by atomic absorption[16].

A frustrating aspect of the work was the high percentage of the experiments which failed when using cobalt crucibles, especially when the equilibrium iron content of the alloy exceeded 20 percent. This occurred when the silica in the slag fell below 30 percent. The combination of a high level

of iron diffusing into the alloy, and of cobalt dissolving from the alloy into slag, pitted the metal and allowed the slag to leak from the crucible. This problem was not encountered to the same extent when using nickel crucibles in similar experiments[14], presumably since nickel has a lesser tendency to dissolve into slag and corrosion is less severe.

3. RESULTS

The composition of equilibrated slags and alloys are listed in Table I where all compositions have been smoothed to 100 percent except for the Co-Fe-Au alloys, where the gold content was obtained by difference. The alloy compositions for solid Co-Fe alloys at a given temperature, oxygen pressure, percent silica in the slag and a total pressure of one atm. are unique since the system has four degrees of freedom. In contrast, the addition of gold to provide for liquid Co-Fe-Au alloys, increases the degrees of freedom by one, and allows the cobalt content of the alloy to be varied when the four previous variable are defined.

Cobalt is assumed to be present in the slag as CoO, in agreement with previous studies[2-4,6]. The activity coefficient can be calculated from the equilibrium

$$Co + 1/2\ O_2 = CoO\ (s) \qquad (4)$$

where for the metal-slag-gas system:

$$\gamma_{CoO} = \frac{K_4 pO_2^{0.5} a_{Co}}{X_{CoO}} \qquad (5)$$

X_{CoO} is the mole fraction of cobalt oxide in slag, pO_2 is the oxygen pressure in atmospheres, γ_{CoO} and a_{Co} are the activity coefficient of cobalt oxide in slag and activity of cobalt in alloy respectively. The value of the equilibrium constant K_4 is taken as 1.209×10^4 at 1573 K[5] when the solid cobalt standard is used for solid Co-Fe alloy and as 1.386×10^4 when the liquid cobalt standard is used for liquid Au-Co-Fe alloy[13]. Oxygen pressure is calculated from the CO_2/CO ratio in the gas through the equilibrium constant for (3), which is taken as 6.981×10^4 at 1573 K[17].

The activity of cobalt in solid Co-Fe alloys at 1573 K, with atom fraction of cobalt greater than 0.7 is essentially ideal[18], while the activity of cobalt in liquid Co-Fe-Au alloys can be calculated[19] using the four suffix Margules equation[2] with interaction parameters based on the binary systems Co-Au[20] Au-Fe[21] and Co-Fe[22].

The activity coefficient of cobalt oxide relative to pure solid cobalt oxide was calculated from equation (5) and is listed in table II, along with data associated with the calculation. The activity coefficient of cobalt oxide for silica unsaturated, alumina-free slags is plotted against percent silica in Figure 1. The figure shows that the activity coefficient decreases with an increase the concentration of silica in the slag for the range of 28 to 38 weight percent silica.

A description of the behaviour of γ_{CoO} versus percent silica or mole fraction of silica in the alumina-free slag is given by the least-square fitted equation:

$$\gamma_{CoO} = 1.70 - 0.021\ SiO_2\ (wt\ \%) \qquad (6)$$

or

$$\gamma_{CoO} = 1.55 - 1.35\ X_{SiO2} \qquad (7)$$

The fitted lines include the previous data for silica saturated slags[2] containing 37 to 41 percent silica and apply for the range of 30 to 40 percent silica in slag.

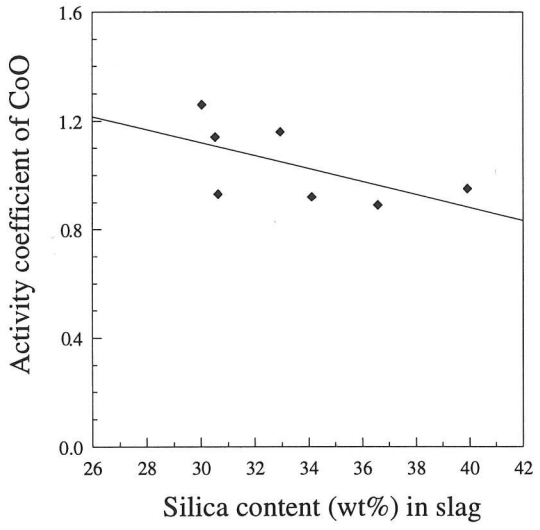

Fig. 1: The activity coefficient of cobalt oxide at 1573 K as a function of silica content in alumina-free slag.

Table I: Composition of iron silicate slags and equilibrated solid Co-Fe and liquid Co-Fe-Au alloys at 1573 K.

pO_2 (atm.)	Slag Compositions (wt%)							Alloy Compositions (wt%)		
	SiO_2	FeO	Fe_2O_3	CoO	Al_2O_3	CaO	MgO	Co	Fe	Au
10^{-10}	30.0	60.2	1.76	8.02	-	-	-	74.3	19.1	-
	30.5	57.7	2.73	9.08	-	-	-	83.1	19.4	-
	30.6	55.9	2.25	11.3	-	-	-	79.0	17.0	-
	32.9	57.0	0.89	9.19	-	-	-	83.4	16.9	-
	34.1	52.1	1.84	11.9	-	-	-	82.9	13.0	-
	36.6	48.9	1.71	12.8	-	-	-	86.6	10.5	-
	39.9	46.9	1.02	12.2	-	-	-	87.4	9.40	-
	17.4	63.6	1.24	1.81	16.0	-	-	5.00	9.31	85.7
	22.6	58.4	1.24	1.90	15.9	-	-	4.86	8.77	86.4
	23.7	58.1	1.21	1.76	15.3	-	-	4.55	8.41	87.0
	27.2	55.0	1.17	1.77	14.9	-	-	4.17	7.44	88.4
	32.5	50.3	2.02	1.71	13.4	-	-	4.43	6.37	89.2
	35.4	46.4	1.43	2.01	14.7	-	-	3.88	5.54	90.6
	42.9	36.8	1.75	2.86	15.6	-	-	5.46	3.76	90.8
	42.3	47.1	1.30	3.67	5.71	-	-	5.01	4.27	90.7
	39.9	47.8	0.91	3.79	7.65	-	-	4.97	4.17	90.9
	40.7	47.1	0.95	3.85	7.37	-	-	5.26	3.87	90.9
	40.9	39.6	1.48	2.79	15.3	-	-	5.89	3.94	90.2
10^{-9}	14.2	61.6	5.28	3.02	16.0	-	-	2.28	3.92	93.8
	19.8	54.6	6.25	3.80	15.5	-	-	3.03	3.58	93.4
	24.9	51.5	5.27	3.49	14.8	-	-	2.42	3.13	94.5
	27.8	48.9	4.30	4.16	14.8	-	-	2.88	3.05	94.1
	34.9	40.9	5.97	3.64	14.6	-	-	2.20	2.77	95.0
	39.4	37.1	7.02	2.96	13.5	-	-	2.07	2.54	95.4
	40.5	44.4	5.05	6.25	3.84	-	-	3.27	2.09	94.6
	42.2	39.3	3.97	4.51	10.0	-	-	2.98	2.12	94.9
	37.2	39.5	5.76	3.51	14.1	-	-	2.22	2.76	95.0
	43.9	40.6	4.69	7.87	-	2.93	-	2.24	1.91	95.9
	40.2	46.6	2.92	5.98	-	4.29	-	2.11	2.37	95.5
	39.4	44.6	2.84	5.40	-	7.72	-	2.31	2.01	95.7
	40.3	42.0	3.08	5.91	-	8.68	-	1.89	2.26	95.9
	40.7	37.9	2.70	7.34	-	11.4	-	2.36	2.26	95.4
	39.0	39.3	3.11	5.85	-	12.7	-	2.54	1.90	95.6
	40.4	49.3	2.43	4.01	-	-	3.88	2.05	2.36	95.6
	40.5	45.5	2.77	3.97	-	-	7.28	2.44	2.22	95.3
	40.8	41.9	3.16	3.57	-	-	10.5	1.91	2.60	95.5

Table II: Activity coefficient of cobalt oxide in iron silicate slag at 1573 K and data associated with the calculation.

pO_2 (atm.)	Alloy		Slag mole fraction					Activity coefficient
	X_{Co}	a_{Co}	SiO_2	Al_2O_3	CaO	MgO	CoO	γ_{CoO}
10^{-10}	0.762	0.762	0.341	-	-	-	0.0729	1.26
	0.776	0.776	0.346	-	-	-	0.0826	1.14
	0.787	0.787	0.348	-	-	-	0.103	0.93
	0.795	0.795	0.372	-	-	-	0.0832	1.16
	0.825	0.825	0.385	-	-	-	0.108	0.92
	0.850	0.850	0.411	-	-	-	0.116	0.89
	0.860	0.860	0.445	-	-	-	0.109	0.95
	0.124	0.220	0.211	0.114	-	-	0.0158	1.92
	0.122	0.221	0.271	0.112	-	-	0.0164	1.87
	0.115	0.214	0.283	0.108	-	-	0.0152	1.95
	0.108	0.209	0.322	0.105	-	-	0.0153	1.90
	0.117	0.231	0.381	0.0925	-	-	0.0147	2.18
	0.105	0.215	0.414	0.101	-	-	0.0171	1.75
	0.149	0.299	0.496	0.106	-	-	0.0240	1.73
	0.137	0.276	0.475	0.0378	-	-	0.0319	1.20
	0.136	0.275	0.453	0.0512	-	-	0.0329	1.16
	0.144	0.290	0.461	0.0492	-	-	0.0333	1.21
	0.159	0.315	0.473	0.104	-	-	0.0235	1.86
10^{-9}	0.066	0.145	0.174	0.116	-	-	0.0266	2.39
	0.087	0.187	0.240	0.111	-	-	0.0333	2.46
	0.071	0.156	0.298	0.105	-	-	0.0303	2.25
	0.084	0.181	0.331	0.104	-	-	0.0359	2.21
	0.066	0.144	0.410	0.101	-	-	0.0311	2.02
	0.062	0.137	0.458	0.0923	-	-	0.0253	2.37
	0.097	0.204	0.457	0.0255	-	-	0.0551	1.62
	0.089	0.188	0.482	0.0669	-	-	0.0387	2.13
	0.066	0.145	0.434	0.0969	-	-	0.0300	2.12
	0.068	0.147	0.483	-	0.0346	-	0.0695	0.93
	0.064	0.139	0.443	-	0.0506	-	0.0528	1.16
	0.070	0.151	0.431	-	0.0904	-	0.0473	1.40
	0.057	0.126	0.439	-	0.101	-	0.0516	1.07
	0.071	0.154	0.440	-	0.132	-	0.0636	1.06
	0.077	0.164	0.421	-	0.147	-	0.0507	1.42
	0.062	0.136	0.437	-	-	0.0626	0.0348	1.71
	0.073	0.158	0.427	-	-	0.115	0.0337	2.06
	0.057	0.127	0.422	-	-	0.162	0.0296	1.88

The effect of silica on the activity coefficient of cobalt oxide for alumina saturated slags can be evaluated for slags of approximately constant alumina content, since in this case the form of the Gibbs Duhem equation for slags containing silica, cobalt oxide, ferrous oxide, ferric oxide, and alumina becomes X_{SiO2} dln γ_{SiO2} + X_{CoO} dln γ_{CoO} + X_{FeO} dln γ_{FeO} + $X_{FeO1.5}$ dln $\gamma_{FeO1.5}$ = 0, which is identical to that for silica unsaturated, alumina-free slags.

Figure 2 shows the activity coefficient of cobalt oxide for alumina saturated slags containing similar levels of alumina within the range of 13-16 percent, versus percent silica in the slag. The activity coefficient appears to decrease with an increase in silica content, in agreement with the trend observed for alumina-free slag (Figure 1).

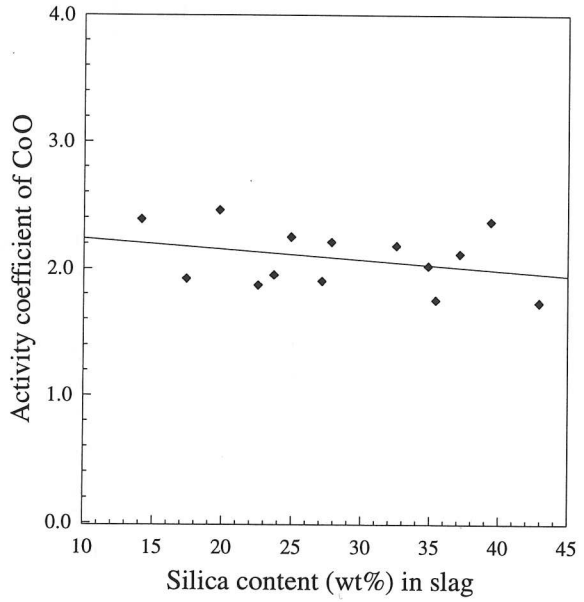

Fig. 2: The activity coefficient of cobalt oxide as a function of percent silica in alumina saturated slag with between 13 and 16 percent Al_2O_3 at 1573 K.

The activity coefficient of cobalt oxide in silica saturated slag is plotted against percent alumina in the Figure 3, which includes the data[2] for alumina-free silica saturated slag at the oxygen pressure of either 10^{-9} or 10^{-10} atmospheres. The Figure shows that activity coefficient of cobalt oxide in the slag increases from 0.9 to about 2.0 as the concentration of alumina increases from 0 to about 16 weight percent, which indicates that alumina has a strong effect on the activity coefficient of cobalt oxide. This result is consistent with a previous report[12] that alumina may reduce the solubility of cobalt oxide in slag.

The relationship between activity coefficient of cobalt oxide and percent alumina in slag which includes all slags containing alumina from this study, as well as the data for twenty silica saturated slags containing no alumina[2] is given as:

$$\gamma_{CoO} = 0.90 + 0.085\ Al_2O_3\ (wt\ \%) \qquad (8)$$

or

$$\gamma_{CoO} = 0.90 + 6.2\ X_{Al2O3} \qquad (9)$$

The fitted lines include the previous data for silica saturated slags[2] containing 37 to 41 percent silica and apply for the range of up to 16 percent alumina in slag.

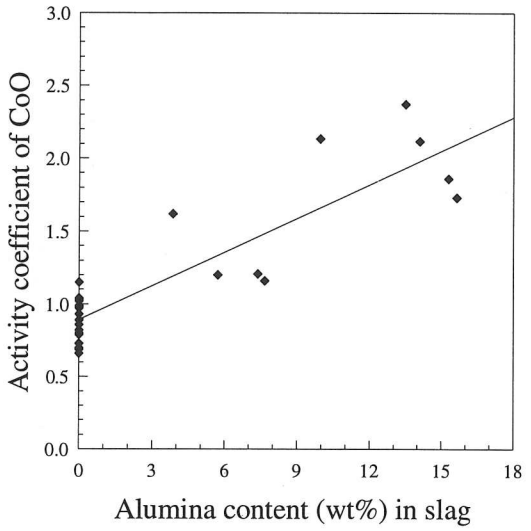

Fig. 3: The activity coefficient of cobalt oxide as a function of percent alumina in silica saturated slag, for all slags of this study, as well as twenty silica saturated slags[2] at 1573 K.

Figure 4 shows the activity coefficient of cobalt oxide as a function of concentration of calcia in weight percent in slag. As can be seen, the activity coefficient increases slightly as the concentration of calcia increases. The trend can be quantified by following least square regression equations:

$$\gamma_{CoO} = 0.90 + 0.036\ CaO\ (wt\ \%) \qquad (10)$$

or

$$\gamma_{CoO} = 0.90 + 2.9\ X_{CaO} \qquad (11)$$

The fitted lines include the previous data for silica saturated slags[2] containing 37 to 41 percent and apply for the range of up to 13 percent calcia in slag.

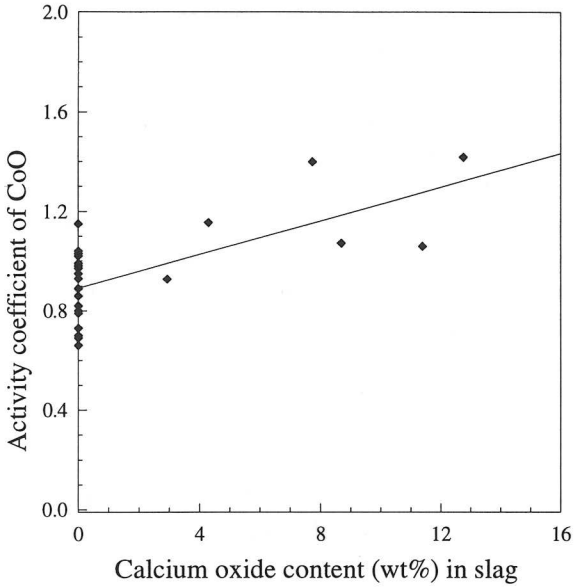

Fig. 4: The activity coefficient of cobalt oxide as a function of percent calcia in silica saturated slag, for all slags of this study, as well as twenty silica saturated slags[2] at 1573 K.

Figure 5 shows that the activity coefficient appears to increase as the mole fraction of magnesia increases. The relationship between activity coefficient of cobalt oxide and concentration of magnesia as weight percent in slag can be quantified by following least square regression equations:

$$\gamma_{CoO} = 0.90 + 0.13\ MgO\ (wt\%) \qquad (12)$$

or

$$\gamma_{CoO} = 0.90 + 7.9\ X_{MgO} \qquad (13)$$

The fitted lines include the previous data for silica saturated slags[2] containing 37 to 41 percent and apply for the range of up to 11 percent magnesia in slag.

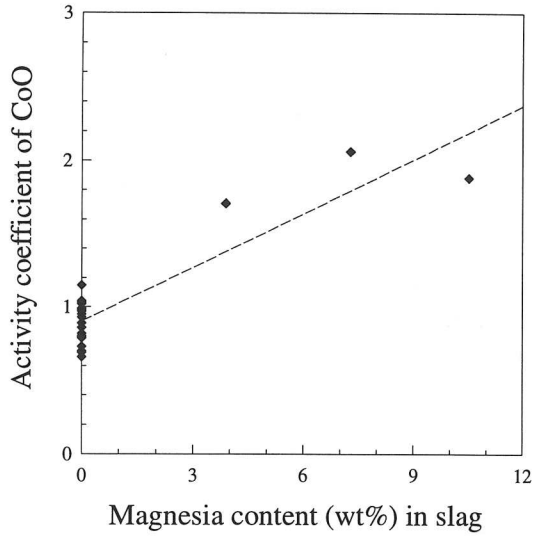

Fig. 5: The activity coefficient of cobalt oxide as a function of percent magnesia in silica saturated slag, for all slags of this study, as well as twenty silica saturated slags[2] at 1573 K.

The experimental results can be combined to provide a general equation to estimate the solubility of cobalt in slag. Equation (5) can be rewritten as:

$$X_{CoO} = \frac{K_4\, pO_2^{0.5}\, a_{Co}}{\gamma_{CoO}} \qquad (14)$$

Since the solubility, expressed as cobalt (wt %) is approximately proportional to its mole fraction, rearrangement of equation (14) shows that a plot of cobalt (wt %) versus $pO_2^{0.5}\ a_{Co}/\gamma_{CoO}$ should be linear with a zero intercept at the origin. This leads to a relationship between cobalt (wt %) in slag, cobalt activity, activity coefficient of cobalt oxide and oxygen pressure, namely:

$$wt\%\,Co = \frac{1.13\times10^{6}\, pO_2^{0.5}\, a_{Co}}{\gamma_{CoO}} \qquad (15)$$

pO_2 represents oxygen pressure in atmospheres, and γ_{CoO} and a_{Co} represent the activity coefficient of cobalt oxide and activity of cobalt respectively.

Equation (15) quantifies the increase in solubility of cobalt which occurs in slag with either an increase in oxygen pressure or cobalt activity in the system or a decrease in activity coefficient of cobalt oxide.

When the activity coefficient equations (8, 10, or 12) are incorporated into equation (15) the solubility of cobalt in slag can be calculated at different conditions. Figure 6 summarises the present experimental values, and those from a previous work[2], as a plot of the cobalt wt percent in slag, calculated by using equation (15). The predicted values are in reasonable agreement with the experimental data; the slope of the best fit for the calculated values versus measured values is only 3 percent from unity.

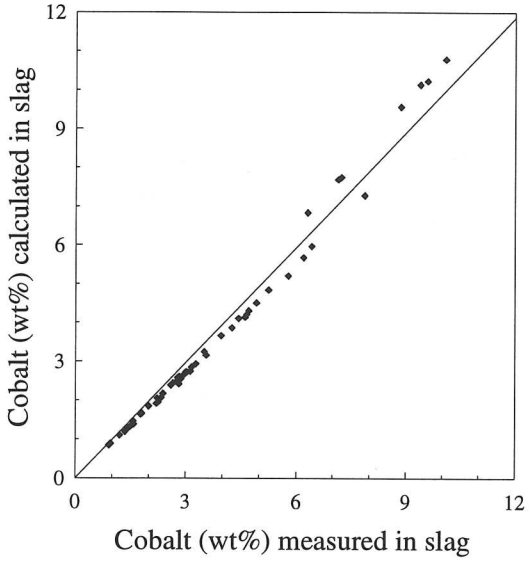

Fig. 6: The relationship between the predicted solubility of cobalt in slag and that measured by experiments at 1573 K.

4. DISCUSSION

4.1 Effect of Silica

The observed decrease in the activity coefficient of cobalt oxide with increase in the silica content of silica unsaturated, iron silicate slags, and those saturated in alumina, can be interpreted thermodynamically by considering that cobalt oxide forms a relatively stable orthosilicate, compared say, to ferrous oxide; The standard free energy of formation of cobalt and iron orthosilicates are respectively -10 kJ/mol[23] and -4 kJ/mol[24] at 1573 K. It is therefore reasonable to expect that the activity coefficient of cobalt oxide would decrease with an increase in the silica content of iron silicate slags. The result is consistent with the evidence from a previous experimental study[9,10].

However, this does not necessarily imply that the activity coefficient of cobalt oxide in slag increases with an increase in silica content (which would be contrary to the results from this work). As explained by Grimsey, the cobalt distribution between matte and slag depends on the activity coefficient ratio of ferrous oxide to cobalt oxide ($\gamma_{FeO}/\gamma_{CoO}$) as well as the percent iron in slag, and does not depend simply on the activity coefficient of cobalt oxide. When the percent silica in slag increases, the cobalt solubility will decrease mainly as a consequence of the related decrease in the iron content of slag, since the activity coefficient ratio ($\gamma_{FeO}/\gamma_{CoO}$) would be expected to remain relatively constant for these chemically similar oxides. Thus the industrial observations are not inconsistent with the present experimental results.

4.2 Effect of Alumina

A comparison of Figures 1 and 2 shows that the activity coefficient of cobalt oxide in alumina saturated slag is virtually doubled compared to that in alumina free slag. Alumina is amphoteric and may be expected to act as acid relative to both cobalt and iron oxides in silica unsaturated slags. Thus the strong effect of alumina on the activity coefficient is unexpected.

If alumina were to simultaneously act as acidic oxide relative to ferrous oxide and cobalt oxide, this might explain its effect in increasing the activity coefficient of CoO, since ferrous aluminate is chemically more stable than cobalt aluminate; the respective free energies of formation from the constituent oxides are -51 kJ for $FeO \cdot Al_2O_3$ and -28 kJ for $CoO \cdot Al_2O_3$ at 1573 K[26]. Thus cobalt oxide may be rejected from the melt, relative to ferrous oxide, in the presence of alumina, resulting in an increase in its activity coefficient as observed. However, the two fold magnitude of the observed increase is difficult to explain.

4.3 Effect of Calcia

An increase in calcia in slag was shown to increase the activity coefficient of cobalt oxide but to a lesser extent than alumina. Calcia is a stronger

base, relative to silica, than alumina and should preferentially interact with silica to strongly reject cobalt oxide and ferrous oxide[27]. The cobalt oxide activity coefficient may be expected to increase significantly therefore as calcia is added to the slag, with the effect greater than for alumina addition. However, the relative stability of $FeO \cdot Al_2O_3$ may have to be considered also, such that the present observations cannot be interpreted based on a comparison of oxide-silica interactions alone.

4.4 Effect of Magnesia

Since only three data points were observed for the effect of magnesia on cobalt oxide in slag, the magnitude of the increase in the activity coefficient with magnesia addition needs further investigation. However, the observed increase was expected since magnesium silicate is more stable than either iron or cobalt silicate, that is, MgO is a much stronger base relative to silica than either FeO or CoO, and preferentially interacts with it.

5. CONCLUSIONS

The activity coefficient of cobalt oxide relative to pure solid cobalt oxide was measured in iron silicate slags over a range of silica, alumina, calcia and magnesia contents through the equilibrium of slags with either solid Co-Fe or liquid Co-Au-Fe alloys at oxygen pressure of either 10^{-10} or 10^{-9} atm. at 1573 K. It was found that:

(1) The activity coefficient of cobalt oxide decreases with an increase in silica content over the range of 15 to 41 percent silica in slag.

(2) The activity coefficient of cobalt oxide increased with the addition of either alumina (up to 16 wt%), calcia (up to 13 wt%) or magnesia (up to 11 wt%) into the slag.

(3) The level of enhancement of the activity coefficient in the presence of alumina was significantly greater than in the presence of calcia. This was unexpected from a thermodynamic standpoint. The magnitude of the effect of magnesia requires further experimental confirmation.

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