

Activities of cobalt and copper oxides in silicate and ferrite slags

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ABSTRACT

The distribution of cobalt and copper between a copper-cobalt alloy and a variety of slags was determined by a levitation melting technique at oxygen potentials fixed by CO/CO₂ gas mixtures and at temperatures from 1250 to 1350°C. The activities of CoO and Cu_{0.5} in the slags were calculated from these data.

SUMMARY

The activities of CoO and Cu₂O (as Cu_{0.5}) in slags were determined by equilibrating Co-Cu alloys with melts of varying compositions in a levitation melting apparatus in which the atmosphere was controlled to produce known oxygen potentials at temperatures from 1250-1350°C. The slags used were of compositions similar to those encountered in industrial furnaces, based on 'FeO'-SiO₂, 'FeO'-CaO-SiO₂, 'FeO'-CaO-Al₂O₃-SiO₂, and 'FeO'-CaO melts.

The melts and slags were analysed for their principal elements after equilibration: the iron in the slags was analysed for Fe²⁺ and Fe³⁺ but the small samples available made this differentiation difficult.

The activity coefficient of CoO at high dilution in 'FeO'-SiO₂ slags was found to be close to unity. Some slight decrease in its values was observed as the 'FeO' content of the slag was increased.

The activity of Cu₂O, expressed as Cu_{0.5}, was in good agreement with previous studies in 'FeO'-SiO₂ melts.

The activities of both CoO and Cu_{0.5} were found to increase with the addition of CaO to 'FeO'-SiO₂ slags, the effects being slight and marked, respectively.

The activity of CoO in CaO-'FeO' slags was found to be somewhat greater than in 'FeO'-SiO₂ slags.

These results are discussed in terms of the slag/metal and slag/matte distributions encountered in industrial practice.

INTRODUCTION

The principal source of primary cobalt is as a by-product of copper and nickel smelting, as cobalt is

found in copper and nickel deposits. The copper and nickel concentrates are first treated pyrometallurgically to enrich the cobalt content in either a matte, speiss or a metal phase. The bulk of concentrates are thus reduced for further treatment by hydrometallurgical methods. A high retention of cobalt in the matte, speiss or metal phases is therefore advantageous for a good recovery of cobalt by subsequent processes.

Copper concentrates are smelted to produce two immiscible liquid phases, i.e. slag and a copper-rich matte. One purpose of the matte smelting is to ensure a complete sulphidization of all the copper and other recoverable elements such as Co, Ni etc. During smelting the conditions are more reducing in order to produce a discard slag containing low percentages of copper, cobalt, nickel etc. Matte is then treated in a converter where it is blown with air or oxygen enriched air. The slag produced from the converting is high in copper and other valuable recoverable metals such as cobalt, nickel etc. which is either returned to the matte smelting (first stage) or is smelted separately in an electric furnace to recover a copper-cobalt-iron alloy[1,2].

Although an Ellingham diagram (Figure 1) is useful in interpreting smelting processes as described above, it relates only to pure phases as standard states. A knowledge of activity coefficients of the components in various phases would be advantageous in order to control the process conditions for a minimum loss of cobalt in the discard slag. At the time of commencement of this work very little data was available for the activity coefficient of cobalt oxide in the slag and speiss phases[3,4]. The present work was undertaken to study the slag/metal/gas equilibria between liquid copper-cobalt alloys and various slags encountered in the smelting processes which would assist the elucidation of the distribution of cobalt between slag/matte, slag/metal and slag/speiss phases encountered in the industrial processes.

EXPERIMENTAL

The gas/slag/metal equilibrium studies were carried out using a levitation melting technique. A sketch of the levitation apparatus is shown in Figure 2. The levitation cell consisted of a 15mm o.d., 150mm long transparent silica tube with both ends open. The tube was mounted on a fixed brass platform and was sealed with O-rings and brass couplings at both ends. Inlet and outlet holes for the incoming and outgoing

gases were located in the brass couplings. The top end of the brass coupling had a viewing glass through which temperature was recorded by means of a two colour pyrometer. A full account of the levitation apparatus has been given elsewhere[5].

Preliminary levitation experiments showed that lower temperatures in the range 1250-1400°C could only be obtained with an alloy containing less than 5% cobalt. The design of levitation coils was as recommended by Jahanshahi and Jeffes[6] which gave stable and lower temperatures. The temperature of the levitated droplet was further controlled by varying the power supply of the RF generator set and by varying the helium gas flow rate through the levitation cell. To reduce the temperature of the droplet, the power supply was increased which lifted the droplet in the upper coil, the upper coil acting mainly as a magnetic "stopper". Temperature of the droplet was further controlled by passing up to 700 ml/min of helium gas through the levitation cell. At the temperature of investigations and up to 700 ml/min of helium flowrate, the enhanced vaporization of copper-cobalt alloy was insignificant and no copper fumes were observed in the gas stream.

Stocks of copper-cobalt alloys and slags used for the equilibration studies were prepared prior to the experiments. Slag was encapsulated in the alloy to produce samples weighing approximately 1.0±0.1g of alloy and 85±15mg of slag made by ramming the slag into a drilled copper-cobalt alloy cylinder. The compositions of stock slags are given in Table 1.

The oxygen potential at the slag/metal interface was controlled by using a mixture of carbon monoxide and carbon dioxide. All the gases viz CO, CO₂ and He were dried and freed of oxygen by passing them through drying agents and the helium passed through a 'getter' furnace. Further details of drying agents and oxygen removal are given in reference 5. The gases were metered and the oxygen potentials of the incoming and outgoing gases through the levitation cell were measured with a solid electrolyte probe of lime stabilized zirconia. The levitation cell was found to be 'leak free' as the oxygen potential of the incoming and outgoing gases was the same.

A high impedance electrometer was used for obtaining the emf signals from the solid electrolyte probe. The CO/CO₂ ratio was not determined analytically but the values calculated from the emf measurements were in good agreement with the values of CO/CO₂ measured by orifice flowmeters.

The emissivities of metal droplets were fairly constant at up to 5% cobalt content in the copper; the temperature recorded by the two colour pyrometer agreed to within ±3°C with that of a Pt-Pt/13%Rh thermocouple.

Previous investigators[7,8] have shown that equilibrium between gas/metal/slag phase was attained within one minute. A series of experiments were conducted by varying the equilibration time from 5 minutes to 20 minutes. As there was no significant difference in the results obtained, an equilibration time of ten minutes was chosen for most of the experiments.

The slag sampling technique was similar to that used by Taylor[9]. The slag was sampled by touching the levitated droplet with an alumina rod and the metal droplet was subsequently quenched in a copper mould. Previous work[9] has shown that this slag sampling technique gave a minimum disturbance of the

equilibrium during sampling as it allowed the slag to cool out of contact with the metal phase.

The slag sampled was weighed and was generally of 20 to 30 mg. Sometimes a second sample of slag was taken if the quantity of slag collected was small, before quenching the droplet.

Both the slag and metal samples were analysed for all the components (viz Cu, Co, Fe, Si, Ca, Al) after equilibration. A Perkin Elmer atomic absorption spectrophotometer was used for analyses. Ca, Si and Al were not detected in the metal samples. The mutual interference of the elements in the analytical instrument used was checked and was found to be negligible. Approximately 50% of the metal samples were analysed in duplicate and the reproducibility was within ±2% of the determined value. A complete bead of slag sample was taken for analysis in order to avoid any errors due to inhomogeneity on cooling.

The ferric analyses were carried out on several slag samples using a colorimetric method[10]. As the ferric iron was determined by taking a difference between total iron and ferrous iron, the accuracy of ferric iron was low and is estimated to be ±20%.

CALCULATION OF RESULTS

The results of the levitation experiments are summarised in Table 2. Full details are available in reference 5.

The metal analyses for Cu, Co and Fe usually totalled 100±1%. The iron content of the metal was always less than 1% and its effect on the activity of Co in the alloy was considered to be small. The oxygen contents of the alloys were not determined. Estimation of oxygen contents from thermodynamic calculations indicated that its effect on the activity of Co and of Cu would be negligible.

The activities of Co and Cu in the metal were calculated from the data of Taskinen[11]. Copper contents in the alloys lay in the region where the Co activities are a linear function of its atom fraction so that Cu behaves ideally.

The oxygen pressures at equilibrium with CO/CO₂ gas mixtures at various temperatures were calculated from the relationship:

$$\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$$

$$\Delta G^0 = -66950 + 20.2T \text{ cal/mol} \quad [1]$$

Slag mol fractions were calculated on the assumption that the species were CoO, CuO(0.5), FeO, CaO and SiO₂. Analysis of the slags for FeO(1.5) caused serious problems because of the small amounts of slag available and of preventing changes in Fe(2+)/Fe(3+) ratios of the samples during preparation for analysis. In most cases the Fe(3+) contents of the slags varied from 2-6%, with an error margin of ±20%. In such a slag, the presence of Fe(3+) would cause an underestimate of N(CoO) and N(CuO_{0.5}) of less than 1%. In the case of the calcium ferrite slag (slag E) the presence of Fe(3+) was taken into account in calculating mol fractions.

The slag analyses totalled to within 2.5% of 100%. In the case of slags C and D the lime to silica ratio was adjusted to that of the initial slag composition. This was calculated from:

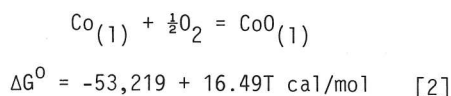
$$100 - (\text{wt}\% \text{CuO}_{0.5} + \text{wt}\% \text{CoO} + \text{wt}\% \text{FeO}) = \text{wt}\%(\text{CaO} + \text{SiO}_2)$$

$$\text{CaO/SiO}_2 = R$$

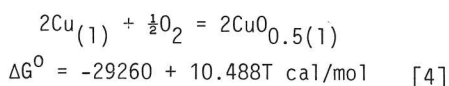
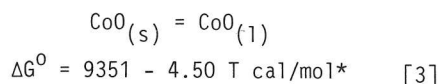
where R is the original ratio of the slag.

The activities of copper and cobalt oxides are expressed in terms of $\text{CuO}_{0.5}$ and CoO . The former was chosen rather than Cu_2O since two separate Cu^+ ions are formed in slag solutions as shown by the fact that the copper content of slags is proportional to $p\text{O}_2^{1/4}$ and to a_{Cu} [13,14,15]. Using $a(\text{CuO}_{0.5})$ gives constant values of $\gamma(\text{CuO}_{0.5})$ as $N(\text{CuO}_{0.5})$ approaches zero whereas $\gamma(\text{Cu}_2\text{O})$ approaches zero as $N(\text{Cu}_2\text{O})$ approaches zero.

Activities of $\text{CuO}_{0.5}$ and CoO were calculated relative to the pure liquid states using the equations:



based on [16] and [17]. The entropy of fusion of CoO was estimated as 4.50 cal/mol deg in agreement with the value used by Wang, Santander and Toguri[4] leading to



This equation is that used by Altman and Kellog[18] based on the data of Mah et al[19]

RESULTS

All activities are calculated relative to the liquid standard state.

FeO-SiO₂ slags

$a(\text{CuO}_{0.5})$ is plotted as a function of $N(\text{CuO}_{0.5})$ in slag A (FeO/SiO₂ ratio = 3.0) and slag B (FeO/SiO₂ ratio = 1.85) in Figure 3. No systematic difference between the two slag compositions could be observed. The limiting slope at infinite dilution gives a value of $\gamma(\text{CuO}_{0.5}) = 2.89$, there being some evidence that at higher copper concentrations it falls appreciably below this value.

$a(\text{CoO})$ is plotted against $N(\text{CoO})$ in Figure 4. As with $\text{CuO}_{0.5}$ there is little obvious difference between the results in slag A at slag B. The value of $\gamma(\text{CoO}) = 0.91$ is obtained for slag A and 1.00 for slag B.

FeO-SiO₂-CaO slags

The results for slags C and D are given in Figs. 5 and 6. In these slags FeO in slag B was replaced by 28-29% CaO and $\gamma(\text{CuO}_{0.5})$ was more than doubled to 7.81 and $\gamma(\text{CoO})$ to 2.08.

The effects of smaller additions of CaO to FeO-SiO₂ slags of FeO/SiO₂ weight ratios of 1.20 and 1.85 are shown in Figures 9, 10, 11, and 12. The resulting values of $\gamma(\text{CoO})$ and $\gamma(\text{CuO}_{0.5})$ are given in Table 1. It will be noted that the scatter in these experimental results produces some anomalies but the effect of increasing the CaO content of the slags is, in general, to increase the activity coefficients of both $\text{CuO}_{0.5}$ and CoO .

*NOTE:

Since writing this, some evidence has indicated that an entropy of fusion of 6.0 cal/mol deg may be more appropriate[20].

FeO-CaO slags

The results for a 'calcium ferrite' slag, E, are shown in Figures 7 and 8. The values of $\gamma(\text{CoO})$ are slightly higher than in iron silicate slags but $\gamma(\text{CuO}_{0.5})$ is lower than in iron silicate slags.

FeO-SiO₂-Al₂O₃ slag

The effect of replacing half of the CaO in slag G by Al₂O₃ (slag K) is shown in Figures 11 and 12. This appears to have the opposite effect to CaO and to cause a slight lowering of $\gamma(\text{CoO})$ and $\gamma(\text{CuO}_{0.5})$.

DISCUSSION

The above results are summarised in Table 1. In this table are also given the initial slag compositions, calculated in terms of FeO, SiO₂, CaO and Al₂O₃ species. As stated above, analysis for Fe₂O₃ caused serious difficulties because of the small slag samples available. The figures for Fe₂O₃ in Table 1 represent the approximate Fe₂O₃ contents of the slags after equilibration experiments. Only in the case of slag E, calcium ferrite, is the Fe₂O₃ content of the slag greater than 5 wt %.

It is clear from Figures 3 and 4 that the effect of varying the FeO/SiO₂ ratio of an iron silicate slag has little effect on the activities of $\text{CuO}_{0.5}$ or CoO although a slight trend to lower activity coefficients in higher FeO slags may be detected. This is in accord with the values obtained by Taylor and Jeffes[7,21] on $\text{CuO}_{0.5}$ and NiO in such slags.

The effect of additions of CaO are, however, quite striking in increasing $\gamma(\text{CuO}_{0.5})$ but the effect on $\gamma(\text{CoO})$ appears to be positive but much less so than for $\gamma(\text{CoO}_{0.5})$. These are illustrated in Figure 13.

It is interesting to speculate on the reason for these observed effects and to relate them to the stabilities of the compounds formed between the slag components.

In Table 3 are listed the heats of formation from the oxides of some silicates and ferrites. It has been noted[7] that the slight but definite lowering of $\gamma(\text{NiO})$ in iron silicate slags by increased 'FeO' content is due to the stability of NiFe_2O_4 compared with Ni_2SiO_4 and because Fe₂O₃ becomes progressively more important as the FeO content of the slag increases. The slight effect observed on $\gamma(\text{CoO})$ may be due to the smaller difference in the stabilities of Co_2SiO_4 and CoFe_2O_4 .

The addition of lime to an iron silicate slag would strongly lower the activity of SiO₂ and correspondingly increase the activity of FeO and promote the formation of Fe₂O₃. If this were the case, the activity coefficient of $\text{CuO}_{0.5}$ would decrease but in fact it increases. This effect is well documented in other work by Elliot et al[22] and Altmann[23] and presents something of a conundrum in terms of the stabilities of the binary compounds. Turkdogan[24] points out that this is analogous to increase in activity coefficients of FeO and MnO in slags, but in these cases the silicates involved are much more stable than the non-existent copper silicates.

The authors suggest that this could be fruitful field for study by theoreticians.

Comparison with other results

Wang, Santander and Toguri[4] measured the solubility of NiO and CoO in iron silicate slags. Their results indicate a value of $\gamma(\text{CoO})$ of 1.14 in silica saturated

slag, which has an FeO/SiO₂ ratio of 1.3. This is in fair accord with the present values given in Table 1.

Yazawa[25] has calculated values of $\gamma(\text{CoO})$ of 1.7 and 2.0 in calcium ferrite and iron silicate slags. These values are relative to the solid CoO standard state, and recalculated to the liquid standard state these values are changed to 0.85 and 0.98 respectively. The value for iron silicate slags is in good agreement with the present work but the value for calcium ferrite is appreciably lower than ours.

Matte-Metal distribution of cobalt

Imris[2] has given an account of the distribution of cobalt between matte and slag in the Rokana smelter in which a matte containing 59.6% Cu and 0.99% Co was in co-existence in a reverberatory furnace with a slag containing 0.46% Co. Using values of $p(\text{O}_2) = 1.2 \times 10^{-4}$ and $p(\text{S}_2) = 1 \times 10^4$ atm. to define conditions at the slag/matte interface, assuming $\gamma(\text{CoO}) = 1.2$ and ideal behaviour of cobalt sulphide in matte. The predicted slag/matte distribution ratio of 0.88 w/w comes very close to the distribution observed at Rokana with a 60% copper matte.

Slag-Metal distribution of cobalt

The behaviour of cobalt in partitioning between metal and slag during the fire refining of copper was discussed by Jeffes and Jacob[26] who concluded that it could be explained if CoO(s) had an activity coefficient of 0.94 in the slags involved. Converting this to the liquid standard state would give a value of $\gamma_{\text{CoO}(l)} = 0.46$. The higher values obtained in the present work means that cobalt will be retained in the metal about twice as well as was concluded by Jeffes and Jacob.

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TABLE 1

S. No	Type of Slag	Temp °C	-log pO ₂	a _{Cu} x10	a _{Co} x10	a _{Fe} x10 ²	N Cu _{0.5} x10 ²	N Co ₀ x10 ²	N Fe ₀ x10 ²	N SiO ₂ x10 ²	N CaO	% Cu Slag x10 ²	a Cu _{0.5} x10 ²	% Co Slag	a Co ₀ x10 ²	% Fe Slag	a Fe ₀	Y Cu _{0.5}	Y Co ₀
1	Slag	1310	9.0582	9.48	5.09	7.60	1.26	9.63	63.46	25.64		1.16	3.90	8.26	8.26	51.39	0.4836	3.10	0.86
2	'A'	1360	8.4920	9.70	2.84	6.90	1.83	5.63	65.06	27.48		1.70	4.77	4.87	5.48	53.24	0.4781	2.61	0.97
3	I	1380	8.2750	9.73	2.62	5.09	1.62	5.93	66.69	25.75		1.49	5.14	5.07	5.44	53.87	0.3634	3.17	0.92
4	R	1255	9.7238	9.74	3.37	8.41	1.01	5.44	66.05	27.50		0.92	3.22	4.83	4.74	53.12	0.4843	3.18	0.87
5	O	1270	9.5376	9.76	2.66	8.92	1.43	4.46	66.41	27.69		1.32	3.42	3.83	3.90	53.87	0.5265	3.39	0.88
6	N	1260	9.6614	9.76	3.49	8.85	1.17	5.33	66.62	26.87		1.09	3.28	4.61	4.98	54.46	0.5127	2.80	0.93
7		1342	8.1117	9.69	3.04	2.43	2.30	11.83	62.46	23.41		2.13	6.24	10.19	10.60	50.86	0.3175	2.71	0.90
8	S	1368	7.8244	9.39	4.22	3.92	2.34	18.49	56.37	22.79		2.10	6.75	15.46	15.79	44.55	0.5346	2.88	0.86
9	I	1305	8.5366	9.75	2.62	3.32	2.50	8.61	62.05	26.84		2.28	5.36	7.38	8.82	50.23	0.4069	2.14	0.96
10	I	1325	8.3044	9.59	3.56	2.55	2.17	15.26	55.18	27.28		1.98	5.84	12.92	11.89	44.18	0.3242	2.68	0.78
11	L	1270	8.9574	9.78	2.50	3.75	2.26	6.43	64.94	26.37		2.04	4.77	5.40	7.16	51.58	0.4318	2.11	1.11
12	I	1315	8.4198	9.65	4.28	3.48	2.07	16.95	59.43	21.54		1.84	5.62	14.06	13.91	46.61	0.4349	2.72	0.82
13	C	1395	7.5356	-	3.68	2.80	2.69	15.40	56.00	25.91		2.47	7.45	13.14	14.74	45.83	0.3994	2.77	0.96
14	A	1325	7.9584	9.74	3.82	1.81	2.85	20.40	51.98	24.73		2.61	7.18	17.37	19.01	41.77	0.3430	2.52	0.93
15	T	1335	7.8445	9.60	3.98	1.60	2.88	22.32	49.81	24.99		2.65	7.35	19.06	20.35	40.21	0.3087	2.55	0.91
16	E	1370	7.4566	9.67	3.45	1.76	4.91	23.97	49.34	21.77		4.38	8.36	19.78	19.33	38.61	0.3601	1.70	0.81
17		1285	8.4287	9.59	3.92	2.33	2.80	20.46	51.06	25.67		2.59	6.12	17.64	17.46	41.59	0.4109	2.19	0.85
18		1355	7.6208	9.65	3.33	2.34	3.23	20.84	48.97	26.95		2.92	7.96	17.51	17.95	38.90	0.4666	2.46	0.86
1	Slag	1350	8.6024	9.45	4.62	6.16	1.52	8.58	53.05	36.84		1.43	4.51	7.50	8.46	43.80	0.4188	2.96	0.99
2	'B'	1378	8.2966	9.33	4.36	5.79	1.56	9.24	52.33	36.86		1.42	4.10	7.80	8.58	41.79	0.4254	2.62	0.93
3		1320	8.9422	9.57	4.78	8.21	1.22	8.56	53.71	36.51		1.12	4.04	7.37	7.79	43.69	0.5302	3.31	0.94
4	I	1308	9.8016	-	4.77	7.16	1.55	8.27	52.75	37.42		1.42	3.88	7.04	7.80	42.47	0.4526	2.50	0.91
5	R	1345	8.0782	9.54	4.07	2.45	2.58	16.85	47.38	33.20		2.39	6.22	14.49	14.34	38.52	0.3221	2.41	0.85
6	O	1370	7.8028	9.63	3.47	1.68	2.81	13.22	47.56	36.44		2.62	6.86	11.48	13.05	-	0.2300	2.45	0.99
7	N	S 1325	8.3046	9.56	3.86	2.95	2.07	14.59	52.22	31.12		1.89	5.82	12.38	12.89	41.89	0.3748	2.81	0.88
8	I	1320	8.3620	9.57	3.17	3.78	2.62	11.51	51.65	34.21		2.41	5.76	9.83	10.45	41.71	0.4760	2.20	0.91
9	L	1325	8.3046	9.78	2.43	2.66	2.38	7.76	52.81	37.04		2.16	5.90	6.54	8.12	42.03	0.3376	2.48	1.05
10	I	1285	8.7750	9.67	3.53	3.47	2.31	10.82	54.01	32.86		2.11	5.04	9.16	10.55	43.24	0.4109	2.18	0.98
11	C	1280	8.8354	9.70	2.49	3.29	1.79	7.42	57.46	33.32		1.68	4.98	6.47	7.34	47.32	0.3854	2.78	0.99
12	A	1330	7.9012	9.50	3.12	-	2.93	22.27	44.92	29.88		2.71	7.29	19.13	15.74	36.44	-	2.49	0.71
13	T	1370	7.4566	9.70	3.41	1.61	3.22	19.68	47.85	29.24		2.97	8.38	16.81	19.11	-	0.3392	2.60	0.97
14	E	1320	8.0159	9.65	3.67	2.07	2.61	19.99	46.09	31.40		2.41	6.99	17.08	18.02	37.41	0.4903	2.68	0.90
1	Slag	1290	9.2160	9.60	4.46	8.26	1.69	7.06	66.83		24.43	1.55	3.81	6.00	7.06	53.73	0.5543	2.26	1.08
2	'E'	1330	8.7487	9.49	3.99	9.29	1.89	6.39	66.95		24.77	1.74	4.44	5.47	7.59	54.16	0.6685	2.35	1.19
3	C	1300	9.0970	9.68	3.76	9.28	2.31	6.07	68.82		22.79	2.12	3.98	5.17	6.59	55.47	0.6335	1.72	1.09
4	A	1270	9.4588	9.51	4.13	9.15	1.68	5.82	67.62		24.88	1.53	3.55	4.92	6.64	53.99	0.5914	2.11	1.14
5	L	1250	9.7080	9.55	4.22	10.01	1.79	5.51	68.54		24.15	1.63	3.27	4.67	6.40	54.84	0.6231	1.82	1.16
6	C	F 1350	8.5236	9.61	3.35	6.14	2.05	5.52	68.46		23.97	1.86	4.81	4.66	6.72	54.61	0.4574	2.34	1.21
7	I	E 1315	8.0201	9.71	3.05	3.09	2.57	13.76	63.39		20.28	2.34	7.13	11.67	15.70	50.80	0.6106	2.77	1.14
8	U	R 1255	8.7440	9.79	3.62	2.81	2.36	15.11	63.18		19.36	2.10	5.63	12.48	15.70	49.32	0.4991	2.39	1.04
9	M	R 1275	8.4964	9.83	3.18	2.95	2.79	12.11	65.44		19.67	2.45	6.11	9.88	14.63	50.52	0.5425	2.19	1.21
10	I	1355	7.5672	-	3.30	2.32	3.16	15.45	63.11		18.24	2.83	8.24	12.85	18.91	49.61	0.4921	2.61	1.22
11	T	1360	7.1736	9.73	2.54	1.29	4.09	19.72	58.21		17.98	3.63	10.62	16.28	21.76	45.42	0.4074	2.60	1.10
12	E	1300	7.8574	9.78	3.18	2.01	3.12	24.35	55.03		17.50	2.80	8.18	20.36	23.22	43.50	0.5712	2.62	0.96

TABLE 1 (continued)

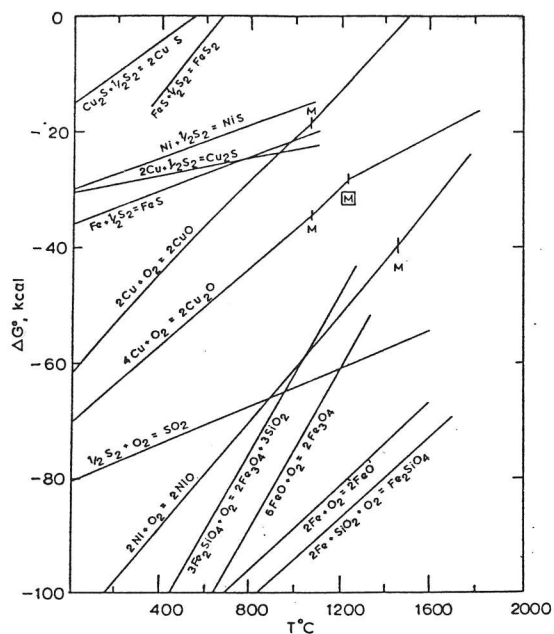
S. No.	Type of Slag	Temp °C	-log P _{O₂}	a _{Cu} x 10 ²	a _{Co} x 10 ²	a _{Fe} x 10 ²	N _{Cu30.5} x 10 ²	N _{Co0} x 10 ²	N _{Fe0} x 10 ²	N _{SiO2} x 10 ²	N _{Ca0} x 10 ²	% Cu Slag	a _{Cu0.5} x 10 ²	% Co Slag	a _{Co0} x 10 ²	% Fe Slag	a _{Fe0}	Y _{Cu0.5}	Y _{Co0.5}
1	Slag 'C'	1305	9.1614	9.29	4.52	10.06	4.94	3.09	23.88	36.80	35.74	0.51	3.75	2.94	6.97	21.50	0.6016	7.60	2.25
2		1355	8.5916	9.61	3.44	8.68	6.10	2.97	26.48	35.49	34.45	0.62	4.54	2.81	6.06	23.71	0.5659	7.45	2.05
3		1310	9.1029	9.49	4.41	9.98	5.54	3.18	23.04	37.15	36.07	0.57	3.83	3.04	6.89	20.77	0.6020	6.92	2.16
4	CaO	1340	8.7590	9.55	4.03	9.23	5.25	3.03	27.98	34.74	33.72	0.53	4.29	2.86	6.83	24.96	0.5862	8.17	2.25
5	FeO	1295	9.2797	9.60	4.37	8.46	5.21	3.42	24.68	36.21	35.16	0.53	3.62	3.25	6.54	22.16	0.4968	6.95	1.91
6	SiO ₂	1295	9.2797	9.59	3.83	10.48	4.91	3.12	28.81	34.29	33.29	0.50	3.65	2.93	5.73	25.65	0.6156	7.43	1.84
7		1365	7.5827	9.84	2.88	-	18.20	7.33	30.44	30.65	29.76	1.81	7.96	6.78	14.68	26.63	-	4.37	2.00
8		1320	8.0875	9.56	3.67	3.74	11.03	7.54	29.63	31.32	30.41	1.10	6.73	6.99	16.61	25.98	0.6469	6.10	2.20
9		1375	7.3758	9.64	3.73	2.42	15.07	9.66	30.59	29.55	28.68	1.49	8.16	8.89	19.50	26.60	0.4584	5.42	2.02
10		1330	8.5916	9.65	4.20	4.31	14.24	11.43	30.65	28.66	27.84	1.40	6.93	10.46	19.52	26.52	0.7569	4.86	1.71
11		1260	8.8068	9.48	4.91	3.42	9.59	10.20	29.91	29.89	29.04	0.95	5.29	9.39	18.74	26.03	0.5300	5.51	1.84
12		1325	8.0300	9.52	4.36	2.93	10.65	10.72	32.29	28.37	27.55	1.05	6.77	9.80	19.99	27.93	0.5120	6.36	1.87
13		1280	8.5608	9.57	4.87	3.44	17.90	10.44	30.68	28.97	28.12	1.77	5.72	9.57	19.67	26.60	0.5537	3.20	1.88
14		1295	8.3805	9.66	4.43	1.92	9.65	10.10	28.57	30.62	29.74	0.96	6.07	9.33	18.71	24.98	0.3170	6.29	1.85
15		1315	8.1454	9.43	4.67	2.49	13.33	10.93	27.95	30.33	29.46	1.32	6.51	10.08	20.84	24.37	0.4259	4.89	1.91
16	Slag 'D'	1375	8.2865	9.46	4.75	5.90	6.42	4.65	22.14	39.58	32.98	0.66	5.03	4.42	9.74	19.88	0.4389	7.83	2.09
17		1360	8.4496	9.62	4.19	7.20	5.49	3.55	24.94	38.70	32.26	0.56	4.80	3.36	8.28	22.34	0.5223	8.74	2.33
18		1310	9.0159	9.76	3.92	8.53	5.20	2.90	22.94	40.16	33.47	0.53	4.06	2.76	6.77	20.67	0.5687	7.81	2.33
19	CaO	1330	8.7851	9.81	3.01	8.29	5.47	2.87	24.38	39.38	32.83	0.56	4.38	2.72	5.48	21.89	0.5721	8.01	1.91
20	FeO	1310	9.0159	9.60	3.48	7.04	4.85	2.97	22.98	40.12	33.44	0.50	4.06	2.83	5.99	20.70	0.4690	8.37	2.01
21	SiO ₂	1335	8.7283	9.43	4.90	7.46	5.45	4.73	20.65	40.41	33.66	0.56	4.37	4.51	9.06	18.62	0.5086	8.00	1.92
22		1375	7.3461	-	4.81	2.08	26.08	20.20	25.37	28.27	23.56	2.53	8.63	18.21	29.14	21.60	0.4561	3.31	1.44
23		1365	7.4546	9.65	4.24	2.61	13.79	14.66	26.22	31.50	26.24	1.36	8.42	13.42	25.03	22.68	0.5637	6.10	1.71
24		1325	7.9019	9.53	4.34	2.45	11.81	14.37	26.59	31.56	26.27	1.16	7.30	13.16	23.03	23.02	0.4940	6.18	1.60
25		1300	8.1931	9.78	3.38	4.26	10.61	9.97	27.29	33.64	28.04	1.06	6.73	9.23	16.76	23.87	-	6.34	1.68
26		1345	7.6755	9.54	4.40	2.26	12.24	15.29	24.97	31.92	26.60	1.21	7.81	14.02	24.63	21.65	0.4720	6.28	1.61
27		1350	7.6198	9.53	4.23	2.72	13.83	15.78	26.25	30.87	25.72	1.36	7.96	14.40	24.00	22.66	0.5738	5.75	1.52
1	Slag 'F'	1420	7.7334	9.02	5.59	4.93	12.80	12.81	34.63	42.72	8.78	1.22	5.80	11.57	14.03	29.68	0.4325	4.52	1.10
2	FeO/SiO ₂	1370	8.2595	9.13	5.77	6.53	10.40	10.20	35.22	41.44	12.10	0.98	5.00	8.93	12.80	29.28	0.5291	4.82	1.26
3	1-2	1430	7.6319	8.79	6.39	5.88	13.80	13.99	32.20	43.61	8.81	1.31	5.86	12.35	16.45	26.95	0.5238	4.23	1.18
4	CaO 10%	1320	8.8187	-	6.10	4.67	13.90	18.55	29.37	41.32	9.36	1.32	4.19	16.39	11.86	24.24	0.3478	3.01	0.64
5		1320	8.8187	9.40	5.85	3.58	10.40	18.52	34.83	41.46	4.15	1.00	4.22	16.60	11.37	29.63	0.2666	4.05	0.62
1	Slag 'G'	1370	8.2595	9.13	5.57	5.02	10.10	14.31	31.00	34.43	19.24	0.98	5.05	12.92	12.35	26.55	0.4068	5.03	0.87
2	FeO/SiO ₂	1330	8.7041	8.98	6.76	6.56	10.30	12.22	29.70	35.90	21.15	1.00	4.28	11.05	13.50	25.49	0.4971	4.16	1.10
3	1-2	1350	8.5336	9.58	3.81	6.13	8.90	5.64	32.87	38.19	22.40	0.87	4.71	5.11	7.54	28.24	0.4513	5.27	1.33
4	CaO 20%	1335	8.7018	9.62	3.30	6.55	9.50	4.68	31.14	39.47	23.76	0.93	4.50	4.23	6.27	26.66	0.4701	4.74	1.34
1	Slag 'H'	1380	8.1518	9.32	7.07	6.47	13.70	18.62	31.72	34.87	10.01	1.37	4.84	15.20	16.10	33.56	0.5329	3.55	0.87
2	F/Si ₂ CaO	1300	9.0523	9.57	6.26	6.38	11.10	16.95	31.61	35.44	9.46	1.29	3.91	5.57	11.52	38.06	0.4855	3.51	0.68
3	10% Al ₂ O ₃	1370	8.3141	9.81	2.90	7.61	14.20	5.53	32.81	42.20	12.49	1.24	5.13	2.52	6.04	38.39	0.5509	3.63	1.10
4	10%	1340	8.6454	9.48	3.30	12.90	12.90	5.83	31.90	42.42	13.11	1.08	4.59	6.49	6.35	36.22	-	3.57	1.09
1	Slag 'H'	1360	8.3686	9.93	5.92	6.06	14.50	17.40	40.50	29.48	10.79	1.55	4.85	0.00	12.79	38.33	0.4830	3.33	0.74
2	F/S 1.85	1350	8.5336	8.44	3.47	6.36	13.50	6.27	45.10	35.76	11.52	1.33	4.76	14.28	6.86	30.16	0.4682	5.53	1.10
3	CaO 10%	1360	8.4232	9.02	1.29	6.21	13.30	2.88	46.36	35.99	13.43	1.51	5.03	12.62	2.63	31.85	0.4648	3.80	0.91
4		1365	8.3685	8.99	3.79	5.49	11.40	7.41	43.57	35.68	12.18	1.18	4.99	11.40	7.80	34.56	0.4144	4.38	1.05
1	Slag 'J'	1320	8.9347	8.39	0.00	7.50	15.60	0.00	44.09	32.22	22.13	1.24	4.53	15.76	0.00	25.49	0.5586	2.90	0.00
2	F/S 1.85	1410	7.8362	9.31	6.88	7.56	14.10	16.27	36.20	29.94	16.17	1.02	5.36	14.27	16.86	25.22	0.6529	3.80	1.04
3		1360	8.3686	-	6.29	5.43	16.00	14.43	38.38	28.05	17.53	1.29	4.80	4.68	13.59	26.32	0.4328	2.99	0.94
4	CaO 20%	1320	8.8187	9.55	6.40	6.36	12.70	13.22	42.26	25.89	17.34	1.17	4.17	4.94	12.42	25.65	0.4737	3.27	0.94

TABLE 2

Activity coefficients of CuO(0.5) and Co in dilute solution in various slags

No	Initial Slag Compositions (w %)							
	FeO/SiO ₂ w/w ratio	FeO	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	γ° CoO	γ° CuO _{0.5}
A	3.0	75	25	-	-	4.52	0.91	2.89
B	1.85	65	35	-	-	1.35	1.00	2.89
C	1.20	39	32	29	-	1.92	2.08	7.81
D	1.0	35	36	28	-	NA (1.9)	2.08	7.81
E	-	79	-	19	-	14.4	1.16	2.32
F	1.20	49	41	10	-	2.3	1.49	4.03
G	1.20	43.6	36.3	20	-	2.69	1.29	4.54 ^x
H	1.85	58.5	31.5	10	-	(2.3)	1.05	3.94
J	1.85	51.9	28.1	20	-	(2.7)	1.00	3.04 ^x
K	1.20	43.6	36.3	10	10	(2.3)	1.14	3.62

FeO 71.85
SiO₂ 80.09

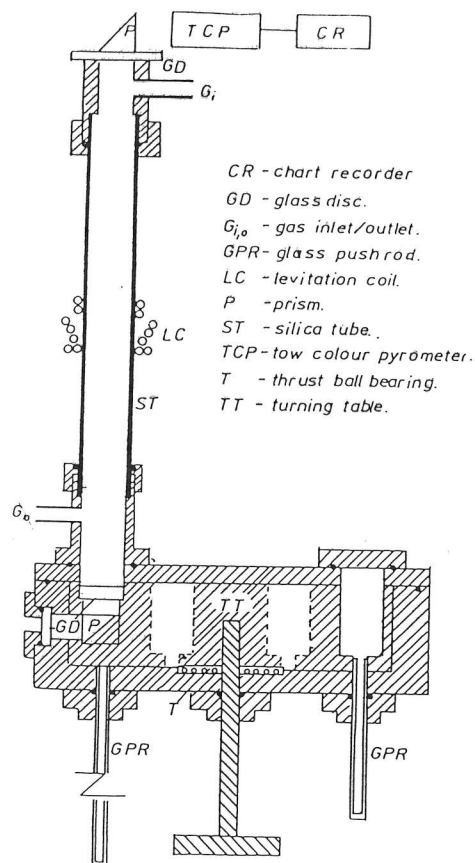


1) Standard Gibbs free energies of formation of oxides and sulphides of iron, copper, nickel and cobalt

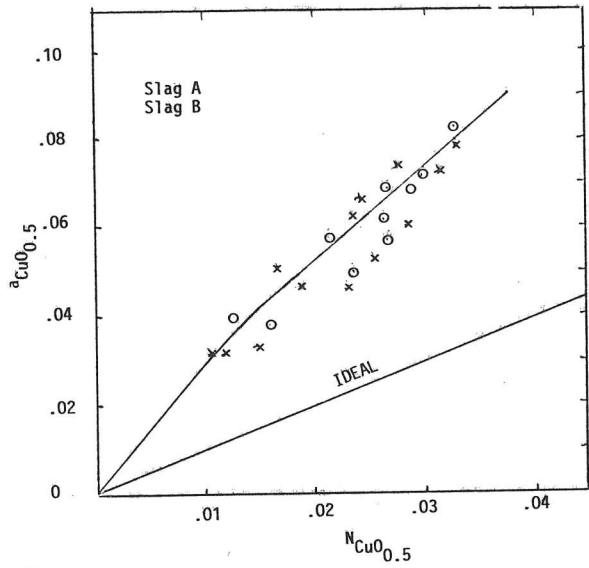
TABLE 3

ΔH₂₉₈ for orthosilicates and ferrites/mole basic oxide (Kcal)

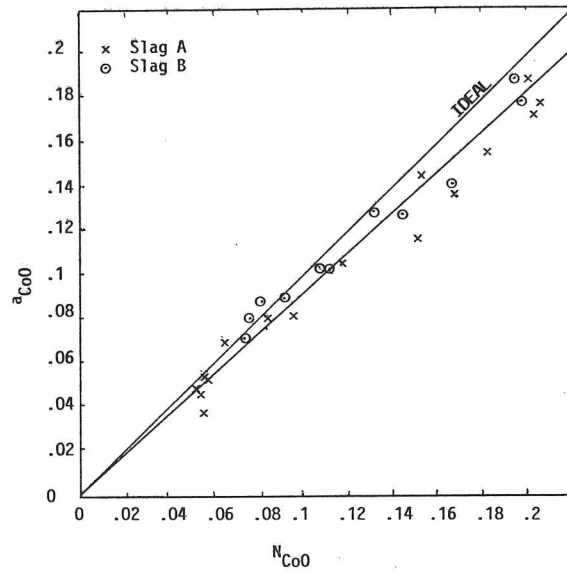
	SiO ₂	Fe ₂ O ₃
NiO	-1.8	-4.1
CuO _{0.5}	N/A	-8.7
FeO	-4.3	-5.3
CoO	-4.8	-5.9
CaO	-16.8	-4.8



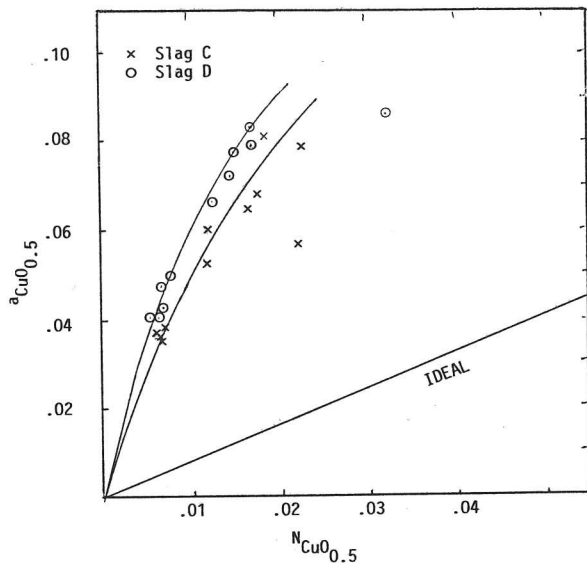
2) The levitation apparatus



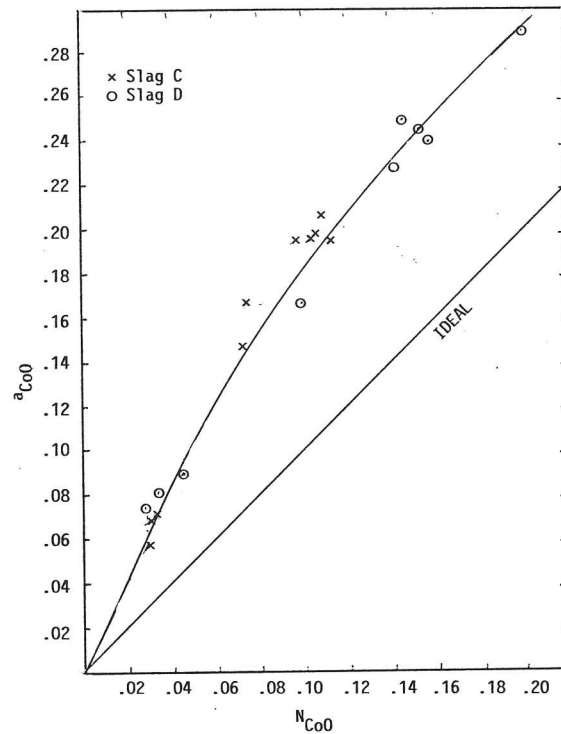
3) Activity of $\text{CuO}_{0.5}$ in slags A and B (Iron silicate)



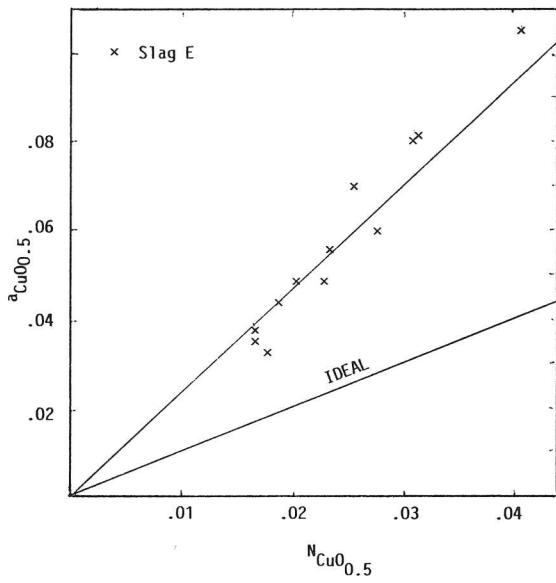
4) Activity of CoO in slags A and B (Iron silicate)



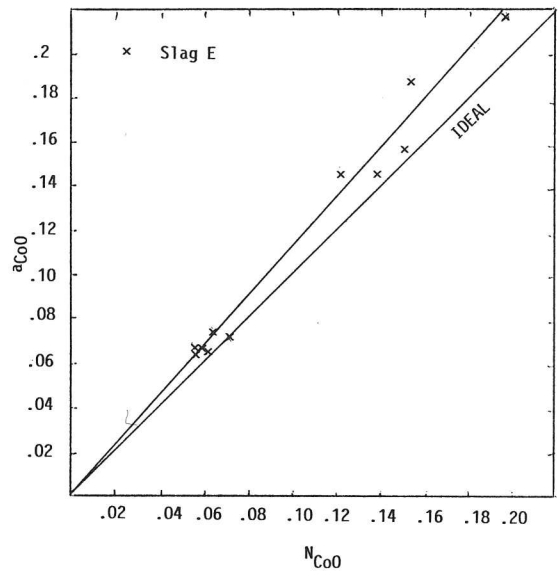
5) Activity of $\text{CuO}_{0.5}$ in slags C and D (Lime iron silicate)



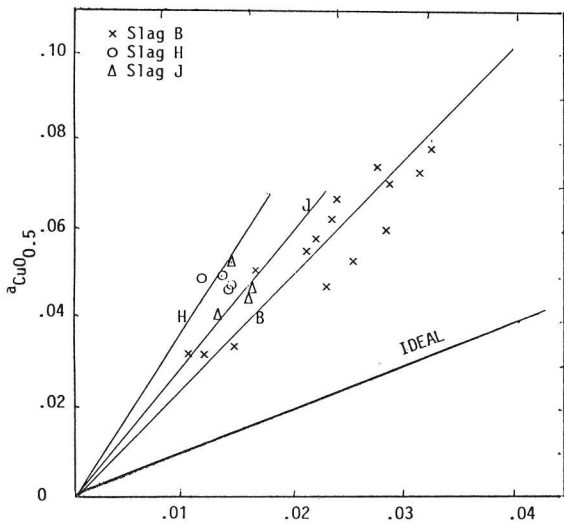
6) Activity of CoO in slags C and D (Lime iron silicate)



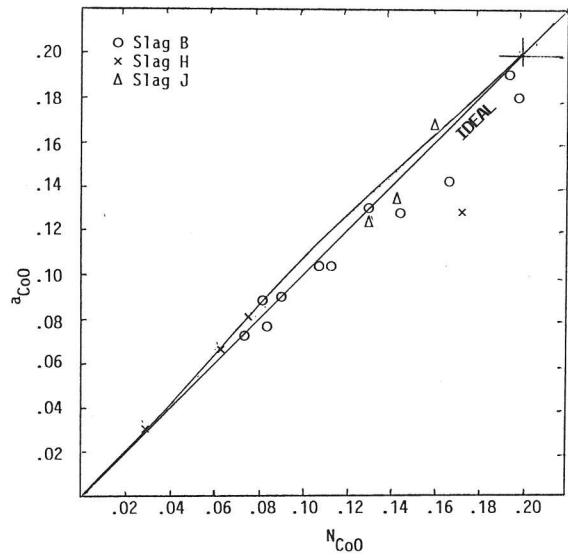
7) Activity of $\text{CuO}_{0.5}$ in slag E (Calcium ferrite)



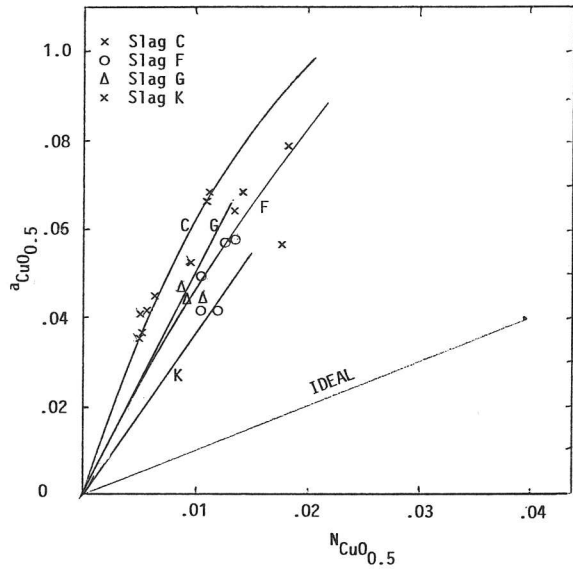
8) Activity of CoO in slag E (Calcium ferrite)



9) Activity of $\text{CuO}_{0.5}$ in slags B, H and J (Varying CaO contents)

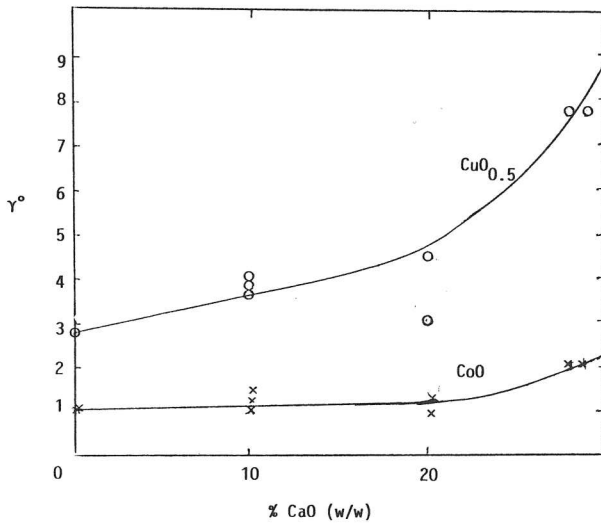
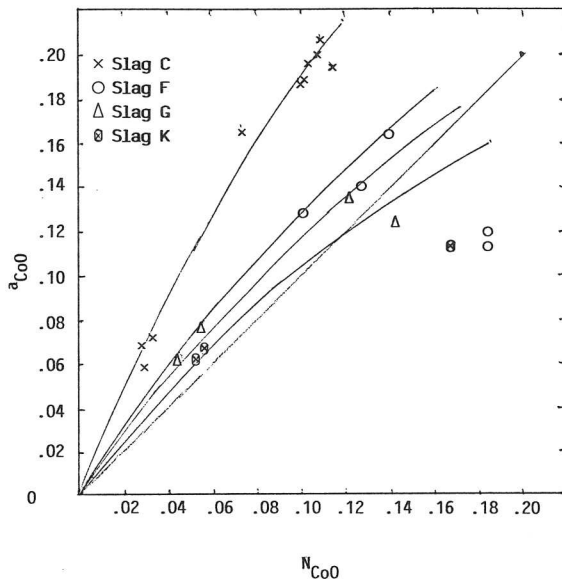


10) Activity of CoO in slags B, H and J (Varying CaO contents)



11) Activity of $\text{CuO}_{0.5}$ in slags C, F, G, K (Varying CaO and alumina contents)

12) Activity of CoO in slags C, F, G, K (Varying CaO and alumina contents)



13) Effect of CaO content of slags on activity coefficients of $\text{CuO}_{0.5}$ and CoO

