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Magnetite behaviour in Peirce Smith converters slag at Ilo copper smelter plant, Peru

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The slag produced in the Peirce Smith converters at the Ilo smelter of Southern Peru Copper Corporation has shown a wide range of magnetite content, which introduces an additional problem in the smelting units due to materials' recirculation. However, the operation data analysis and the application of thermodynamic concepts have made it possible to produce slag with magnetite content between 18 and 20%. The results have suggested that matte grade enhances magnetite formation while silica controls its precipitation, and they are also influenced by the increasing temperature of the slag. Thus, in order to obtain the required magnetite content in the slag, matte grade is gradually enriched in equilibrium with slag containing from 25 to 32% silica.

Introduction

The Southern Peru Copper Corporation smelter is located in southern Peru 17 km from the Ilo Port, and it started its operation on 1960. Currently, the smelter operation includes two Reverberatory furnaces, seven Peirce Smith converters, one Teniente converter, an acid plant, an oxygen plant, and two casting wheels.

At the moment, 1 150 000 Mt/year of copper concentrate are smelted and 285 000Mt/year of blister copper are produced in the Peirce Smith converters. The schematic diagram of the smelting and converting process is shown in Figure 1.

The magnetite and silica content of the converters slag at the Ilo smelter is in the range 10.23% to 22.69%, and 24.04% to 27.00% respectively, as shown in Table I. These slag characteristics show serious operational problems in the reverberatory furnace due to materials' recycling. The influence of magnetite content on the melt is well known:

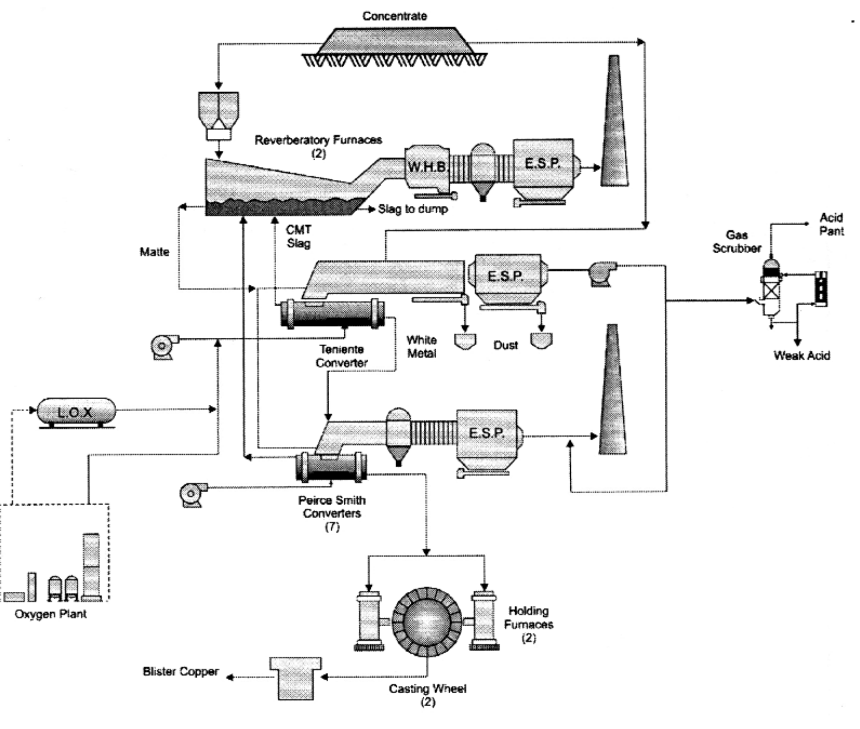

Figure 1. Schematic diagram of the smelting and converting process at the Ilo smelter

Table I
Characteristics of the Peirce Smith slag converters de SPCC (*)

Content	% Cu	% Fe	% S	% Fe_3O_4	% SiO_2	% Al_2O_3	% CaO
Average	2.85	46.48	0.20	16.46	25.52	1.30	0.08
Standard Deviation	0.88	1.50	0.33	6.23	1.48	0.35	0.12
Maximum	5.72	52.16	2.27	31.96	29.10	3.62	0.81
Minimum	0.52	41.37	0.00	6.40	20.75	0.30	0.00

(*) Analysis of slag data obtained between January and May 2000.

matte-slag separation difficulties, false bottom, and increasing copper loses in the discard slag.

Thus, high magnetite production in the Peirce Smith converters is not desirable. Therefore, the objective of this work is to understand the mechanism of magnetite formation during the blowing to slag and its dispersion in the slag in order to obtain the magnetite content in the range of 18% to 20% in the converter slag.

Fundamentals

Thermodynamic of magnetite formation

The magnetite behaviour in slag during the smelting and converting processes has been reported by several authors[1,2,3], and it can be discussed according to reaction [1].

$$3Fe_3O_{4(slag)} + FeS_{(matte)} = 10FeO_{(slag)} + SO_{2(gas)} \qquad [1]$$

The equilibrium constant can be written according to equation [2]

$$K_{(1)} = \frac{(a_{FeO})^{10} p_{SO_2}}{(a_{Fe_3O_4})^3 a_{FeS}} \qquad [2]$$

and the activity of magnetite is described by equations [3] and [4]:

$$(a_{Fe_3O_4})^3 = \frac{(a_{FeO})^{10}}{a_{FeS}} \frac{p_{SO_2}}{K_{(1)}} \qquad [3]$$

$$\log a_{Fe_3O_4} = \frac{1}{3}\begin{pmatrix} 10\log a_{Feo} - \log a_{FeS} + \\ \log p_{SO_2} + \dfrac{\Delta G^\circ_{(1)}}{2.303RT} \end{pmatrix} \qquad [4]$$

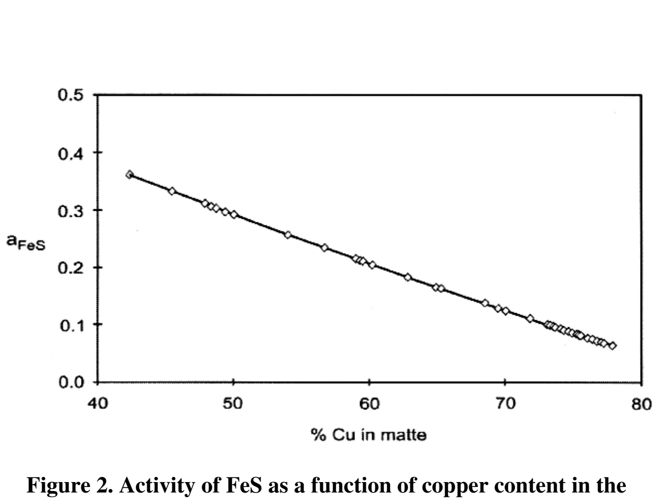

Figure 2. Activity of FeS as a function of copper content in the matte

In order to evaluate the magnetite behaviour, one must know the FeS activity in the matte and the FeO activity in the slag. The activity of FeS and Cu_2S were measured by Asano[4] as a function of Cu_2S mol fraction at 1300°C. The effect of temperature on the activity of FeS and Cu_2S was determined in the range of 1200°C to 1350°C by comparing data calculated by Gaskell *et al.*[5] and those measured by Krivsky and Schuhmann[6], and it was found that temperature does not have a strong influence on the FeS and Cu_2S activities. The activity of FeS was correlated as a function of the mol fraction of Cu_2S by using data reported by Asano[4] and equation [5] was obtained with a correlation coefficient of 0.9998.

$$a_{FeS} = 0.2904 \cdot 10^{-5}(N_{Cu_2S})^2 - 0.9472(N_{Cu_2S}) + 0.66 \qquad [5]$$

The mol fraction of Cu_2S in the matte was computed from a mixture of Cu_2S-FeS; the excess sulphur was dissolved in the matte, and iron is present as Fe_3O_4 and FeO in the slag. The activity of FeS as a function of the copper content in the matte was correlated as a function of copper content in enriched matte by using data of the Ilo smelter. The results are shown in Figure 2 and equation [6]. The activity of FeS was determined with a 0.9271 correlation coefficient.

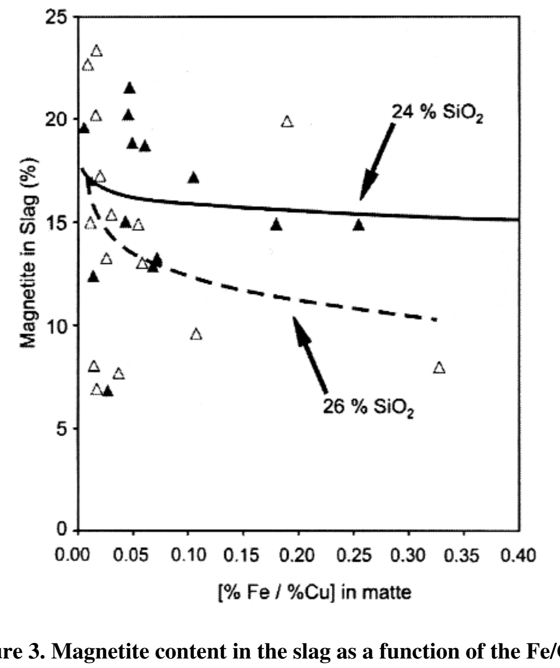

Figure 3. Magnetite content in the slag as a function of the Fe/Cu ratio in the matte

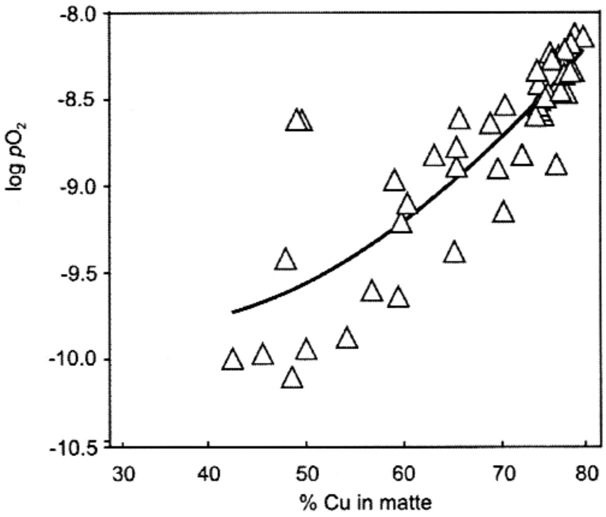

Figure 4. Effect of the oxygen potential on the copper content in the matte

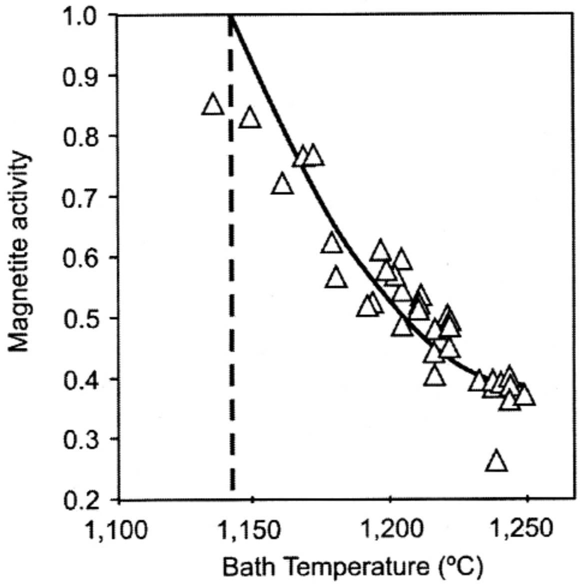

Figure 5. Effect of temperature on the magnetite activity

$$a_{FeS(PS)} = 2 \cdot 10^{-5} \left(\%Cu_{(PS)}\right)^2 - 0.0108 \left(\%Cu_{(PS)}\right) + 0.7844 \qquad [6]$$

In Equation [6], the $a_{FeS(PS)}$ and $\%Cu_{(PS)}$ are the activities of FeS and the copper content, respectively, in the enriched matte produced in the Peirce Smith converter of Southern Peru Copper Corporation.

The activity of FeO was determined graphically considering almost no influence of oxygen partial pressure in silica saturated slag[7], the FeO activity in the FeO-Fe_2O_3-SiO_2 system reported by Korakas[1] at 1270°C, and the average ternary composition of Peirce Smith converter slag produced at the Ilo Smelter, as shown in Table II.

Effect of matte grade on the magnetite formation.

The behaviour of magnetite as a function of the Fe/Cu ratio in enriched mattes was determined using data obtained in the Peirce Smith converter operation at the Ilo smelter. The magnetite content in the slag increases with the increasing of wt% of copper in the matte or the Fe/Cu ratio decreases in the matte, and the increasing of magnetite in slag is higher when the Fe/Cu ratio is lower than 0.05, as shown in Figure 3. The results shown in this figure are in agreement with those reported by Korakas[1] for smelting and converting of synthetic mattes. The higher increase of magnetite content in the slag when the Fe/Cu ratio is lower than 0.05 is explained by the the increased oxygen potential in the system at high matte grade. The effect of the oxygen partial pressure on the copper content in the enriched mattes smelted in the Ilo smelter is shown in Figure 4, and it can be observed that oxygen potential increases with increasing of wt% Cu in the matte. The oxygen partial pressure was calculated according to reaction [7] and Equation [8].

$$FeS_{(1)} + \frac{3}{2} O_{2(g)} = FeO_{(1)} + SO_{2(g)} \qquad [7]$$

$$\log p_{O_2} = \frac{2}{3}\left(\log \frac{a_{FeO}}{a_{FeS}} + \log p_{SO_2} + \frac{\Delta G^{\circ}_{(7)}}{2.303RT} \right) \qquad [8]$$

Equation [8] was evaluated using the free standard energy reported by Hayashi[3] and the FeO activity considered by Korakas[1] as 0.39. The SO_2 partial pressure was determined as 0.1212 from data obtained at the Ilo smelter and the temperature was considered as that indicated in Table II.

Table II
Chemical analysis of Peirce Smith converter slag at SPCC(*)

Sample No.	Temp. °C	Chemical Analysis (%) Cu	Fe	S	Fe_3O_4	SiO_2	Al_2O_3	CaO	Ternary Diagram (%) FeO	Fe_2O_3	SiO_2
270	1243	2.20	44.84	0.00	9.10	27.75	1.60	0.00	60.46	7.30	32.25
271	1243	3.22	46.10	0.00	16.62	25.70	1.48	0.00	56.85	13.31	29.83
272	1238	2.06	46.21	0.00	8.25	26.89	1.74	0.00	62.50	6.55	30.94
273	1227	3.26	47.32	0.00	20.43	24.66	1.40	0.00	55.42	16.22	28.37
274	1227	2.32	46.00	0.00	15.51	27.78	1.34	0.00	56.28	12.16	31.56
275	1243	3.32	44.77	0.00	18.46	28.34	1.36	0.00	52.89	14.61	32.50
276	1227	2.06	47.95	0.00	9.79	24.14	1.51	0.00	64.28	7.81	27.91
277	1232	3.01	45.97	0.10	13.11	24.86	1.19	0.00	60.06	10.66	29.28
278	1216	1.93	47.59	0.69	20.31	24.11	1.47	0.15	56.04	16.16	27.80
279	1232	2.24	48.79	0.08	16.25	23.65	1.55	0.00	60.17	12.81	27.02
280	1242	4.77	45.85	0.00	24.86	25.31	1.22	0.00	50.62	19.95	29.43
281	-	4.00	44.96	0.00	28.19	26.09	1.44	0.00	46.96	22.65	30.38

(*) Analysis of slag data obtained between January and May 2000

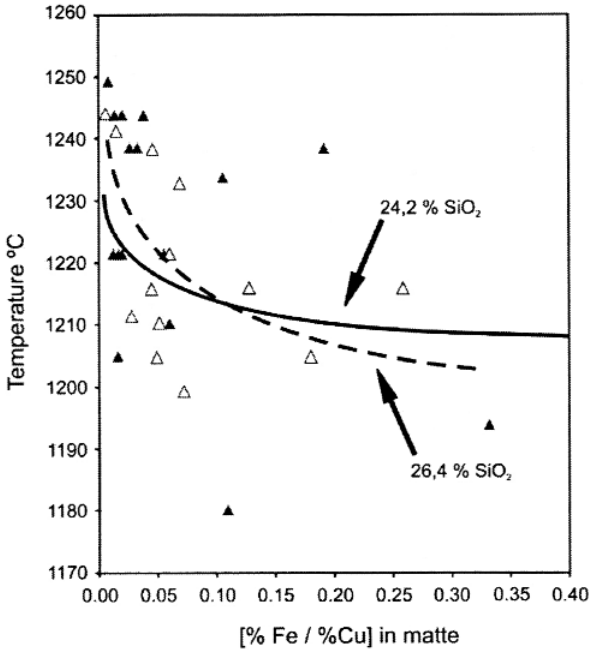

Figure 6. Effect of Fe/Cu ratio on the matte temperature

The copper content in slag increases with the oxygen potential increasing, as shown in Figure 4, and at over 70% copper in the matte the oxygen potential rate of increase is higher. The data plotted in this figure show agreement with those reported by Hayashi[3] for data obtained in the Mitsubishi smelting furnace of the Naoshima smelter. The magnetite activity increases when increasing the oxygen potential, and for silica saturated slag Michael and Schuhmann[7] have shown that it become higher when the oxygen potential reached values from 10^{-10} to 10^{-8} atm, which is in agreement with the results plotted in Figure 4.

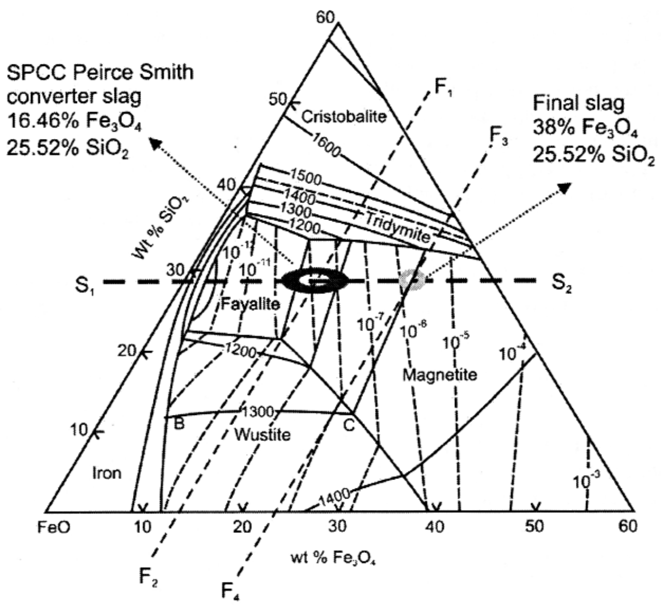

Figure 7. Ternary system FeO-SiO$_2$-Fe2O$_3$

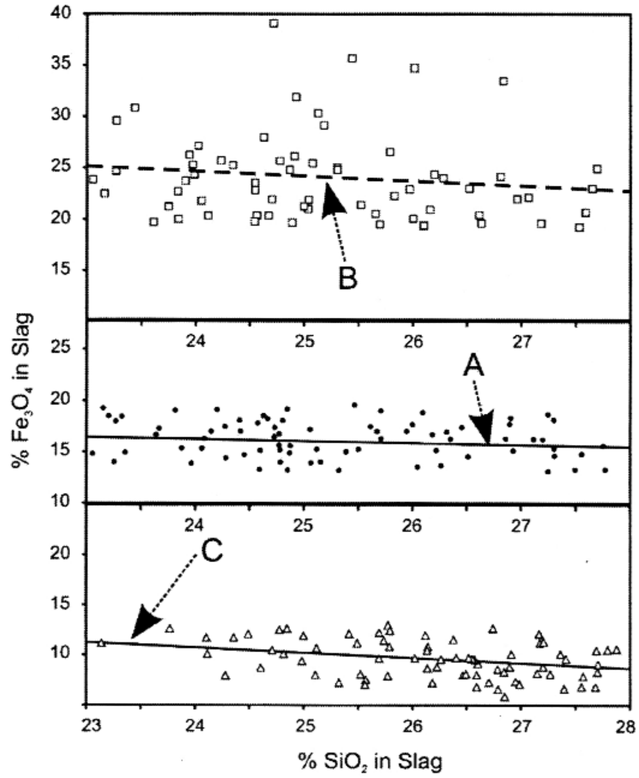

Figure 8. Effect of silica on the magnetite content in the slag

Therefore, one expects to find high magnetite content in the slag during the converting process at the Ilo Smelter, which is due to the oxygen potential when high matte grade is reached.

Temperature and matte grade

The effect of temperature on the magnetite activity is shown in Figure 5, and it can be observed that magnetite activity decreases when the temperature is higher than 1150°C during the blowing to slag converting process. The magnetite activity in Peirce Smith converter slag was determined based on Reaction [1] and Equation [4]. The magnetite activity decreasing with temperature is explained observing the variation of the standard free energy of magnetite formation with temperature, which suggests that magnetite is relatively more stable than SO_2 at temperatures lower than 1200°C so that sulphur would be oxidized to SO_2 rather than FeO to magnetite at temperatures higher than 1200°C. Therefore, the magnetite content in converting slag decreases when the process is conducted at temperatures higher than 1150°C.

The effect of the matte grade or Fe/Cu ratio on the temperature is shown in Figure 6, and it can be observed that the slag temperature increases with matte grade increasing or Fe/Cu ratio decreasing, especially for ratios lower than 0.05. This effect is explained by the presence of magnetite in the slag at constant silica content, which is described in the ternary system $FeO\text{-}SiO_2\text{-}Fe_2O_3$[8-13] shown in Figure 7. The average composition of the Peirce Smith converter slag produced at the Ilo smelter is indicated at the intersection of S_1S_2 and F_1F_2, and along the S_1S_2 line. The oxygen potential increases from the isotherm 1175°C to the isotherm 1300°C as does the magnetite content shown at the intersection of line S_1S_2 and F_3F_4.

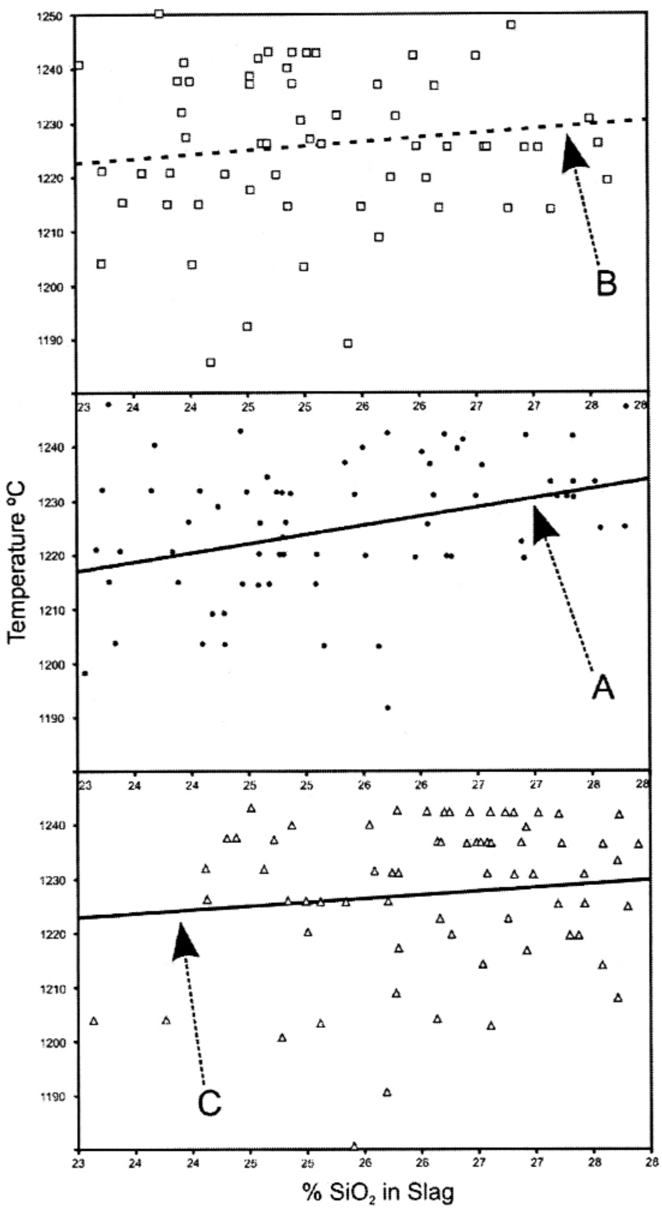

Figure 9. Effect of temperature on the silica content in the slag

Therefore, at the beginning of the blowing to slag operation during converting, magnetite formation is enhanced due to the lower temperature of processing, while at the end of this operation the temperature increases due to the higher magnetite content in the slag along with the higher oxygen potential caused by the matte grade increasing.

Effect of silica on the magnetite formation

The effect of silica on the magnetite content in converter slag is presented in Figure 8, and it shows that the increasing of silica content decreases magnetite formation (magnetite content for A>19.44, 19.44>B>12.38, and C<12.38 %). This observation is in agreement with Equation [3], which shows the strong influence of the FeO activity on the magnetite activity in the slag. The presence of silica in the slag enhances fayalite formation instead of magnetite due to its relatively higher stability, and fayalite fixes the activity of FeO in the slag controlling the magnetite activity and decreasing the magnetite content, as reported by Michael and Schuhmann[7] and Korakas[1].

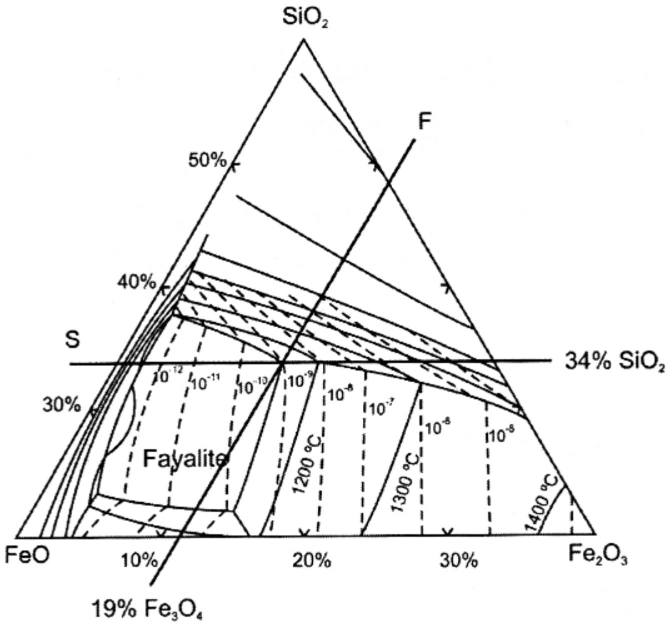

Figure 10. Polythermic surface of the FeO-SiO$_2$-Fe$_2$O$_3$ system

Temperature and silica content

The effect of temperature on the silica content in converting slag at the Ilo Smelter is shown in Figure 9. It can be observed the silica increases proportionally to the temperature (magnetite content for A>19.44, 19.44>B>12.38, and C<12.38 %). This behaviour is explained in the ternary system FeO-SiO$_2$-Fe$_2$O$_3$ shown in Figure 10, where fayalitic slag with silica content higher than 34% and magnetite lower than 19% increases silica content and oxygen potential with increasing temperature, as is presented at the intersection of lines S and F in Figure 10. Thus, temperature increases rapidly in converter silica saturated slag in equilibrium with high grade matte, and magnetite content decreases when silica in the slag increases during the blowing to slag in the converting process.

Effect of operating 'lots' on the magnetite content

The copper enrichment of mattes by the converting process is accomplished by doing several blowing to slag or 'lots', and matte grade increases gradually in every blowing. The effect of operating lots is presented as a function of %Cu, %SiO$_2$ and %Fe$_3$O$_4$ in Figure 11. This figure shows magnetite varying in a wide range while silica content in the slag is kept almost constant, which is in agreement with observations reported by Korakas[1] who calculated %Fe$_3$O$_4$ as a function of %SiO$_2$ in converting slag in equilibrium with mattes at different FeS activities at 1270°C. Thus, in order to keep %Fe$_3$O$_4$ in the slag ranging from 18% to 20%, it is required to maintain a slag containing silica in a range of 25% to 32% in equilibrium with mattes of 70% to 78% of copper, as shown in Figure 12. This could be accomplished by operating the converter so as to reach a 70% Cu matte in equilibrium with a 25% SiO$_2$ slag during the first 'lot', and a matte of 78.8% Cu in equilibrium with a slag of 32% silica at the end of the blowing to slag operation during the converting process.

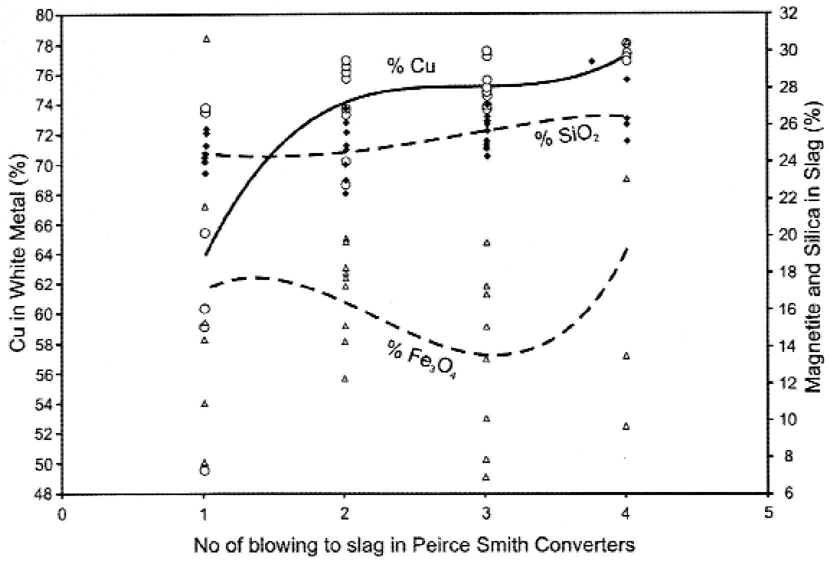

Figure 11. The effect of operating lots as a function of %Cu, %SiO_2 and %Fe_3O_4

Final remarks

The copper enrichment in Peirce Smith converters is accomplished by exposing the matte to a gradual oxygen potential increase, which also increases magnetite activity and, as a result, high magnetite content in the slag. However, the presence of silica controls magnetite formation, and to enrich the matte a silica saturated slag and temperature higher than 1150°C are required. Finally, for operating Peirce Smith converters to keep the slag with %Fe_3O_4 in the range of 18% to 25%, copper mattes should be kept in contact with slags which gradually increase silica content from 25% to 32% or maintain the saturated condition according to the matte grade.

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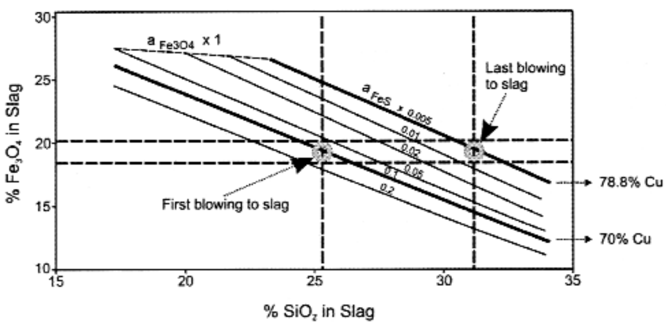

Figure 12. The effect of silica on the magnetite content in the slag

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