PHYSICOCHEMICAL CHARACTERIZATION AND INDUSTRIAL EVALUATION OF CONVERTER SLAGS.

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ABSTRACT

Research works developed many decades ago inform us in plentiful form about results obtained for copper metallurgical slags. It is common to find many relationships between copper and magnetite content in function of other operational parameters linked to pyrometallurgical processes. However, most of these results concern laboratory researches and currently don´t show connection with industrial data.

Supervisors and workers in charge of copper smelting converters can daily confirm the very wide range of variation for the copper and magnetite concentrations in slags. So it has become very difficult to anticipate melt´s behaviour, and consequently to reproduce the operation´s best results.

However, making an adequate management of data obtained from chemical analyses for industrial slags it is possible to establish some correlation that could improve the smelting operation. The ratio Fe/SiO2 is of considerable importance. The addition of flux to the smelt in the proper quantity and opportunity contributes to diminish the magnetite production and hence, copper losses.

INTRODUCTION

The air injected into the converter reacts with iron and sulphur, not only in the melting phase but also in concentrate fed (in PS receiving concentrate during the slag blowing step). Slag and metallic phases are permanently under strong agitation due to the air´s high pressure. This allows an intimate contact between silica and iron oxide. Before slagging, melt remains without agitation during some minutes. This improves the phases separation; therefore, it could be considered that the metallic and slag phase will reach compositions very close to the equilibrium. Chemical equilibrium calculations among reactants are always of great interest, because they represent the ideal situation to which a reactor can tend (1).

A proper selection of the adequate slag is very important to obtain the best results during operation. The use of a phase diagram based on the ternary system FeO-Fe2O3-SiO2 is a good approximation in making this selection. If equilibrium conditions are reached, it will form a unique relationship linking the oxygen pressure, metal content, gas composition and temperature.

By applying the Gibbs rule to the smelting- converting process, using for instance a Peirce Smith converter and making an approach with five components in the system (Cu, Fe, S, O, SiO2) and three phases (slag, matte and gas phases), we will find four independent parameters which must be fixed in order to establish thermodynamically the equilibrium. Selecting the temperature and partial pressure of SO2 as fixed parameters (being SO2 directly related to enriched air in the process); it seems reasonable to select the SiO2 content in the slag and metal content in the matte as the last two independent variables.

The link between matte and slag can be expressed through the equation related to main components of these phases:
$FeS_{(l)} + 3Fe_3O_4 = 10FeO_{(l)} + SO_{2(g)}$

From the above equation it can be concluded, that in order to calculate the magnetite content in the slag, it is necessary to know the partial pressure of SO_2, the temperature and activities of FeS and FeO.

In the work already referred to (1), the way how the activities of FeS and FeO can be estimated from relationships obtained from Nagamori and Mackey(2) and from Diaz(3) was clearly explained. According to (1) the final expression to calculate the magnetite activity will be:

$$a_{Fe3O4}=(((A+B*a_{Fe3O4}+C*a^2_{Fe3O4})*p_{SO2})/(a_{FeS}* K))^{1/3}$$

As a result of an iterative calculation in the system FeO-Fe3O4-SiO2 we can obtain the relation of magnetite with silica content when temperature, oxygen enrichment and metallic phase grades are set. Results shown for different metallic phase grades are very similar to the results obtained by Korakas (4).

It is important to make clear that all the information obtained, considers thermodynamic equilibrium conditions between the different phases contained in the ternary already reffered to.

Similar conclusions are obtained when observing the classical graphic representation from Yazawa(5), that shows the fundamentals for continuous smelting. In this case, Yazawa considers the oxygen and partial sulphur pressures as independent parameters.

There is acceptance regarding the chemical formula that shows the thermodynamic balance between the copper dissolved in the slag and the white metal, as the following:

$Cu_2S_{(l)} + FeO_{(l)} = Cu_2O_{(l)} + FeS_{(l)}$

This relation reveals that the Cu_2O content increases when there is an increase in the Cu_2S concentration (matte high in copper and low FeS concentrations), which makes the equation move to the right(6).

It is accepted that when copper is directly produced from one-phased concentrate, having the metal phases 72% law orders of more or less 5%, the slags should have 9 to 12% of copper, whereas more than half correspond to dissolved copper (chemical loss) and the rest to a mechanic trap (physic loss)(7).

Ruddle (8) experimentally found that the cuprous oxide´s solubility in the saturated magnetite slag reaches 8%, which corresponds to 7% of copper.

Altman (9) states that up to 2.1% of soluble copper in magnetite was found in the saturated slag in silica and in equilibrium with an axis of 1250 ºC in that $pO_2=3.3*10^{-8}$.

Mihalop (10) obtained results simulating a 60% matte, that show correlation for the copper to magnetite content for the FeO-Fe_2O_3-SiO_2-Cu_2S-FeS system.

Robilliard (11) shows a parabola relation for the total content of copper in the slag as a function of the ratio Fe/SiO_2, this shows a minimum copper loss of the ratio=0.95.

Themelis (12) also shows- due to the process of results obtained from an investigation performed on 34 smeltings plants - a relation similar to one above (Fe/SiO_2), but a minimum displacement to 1.5 (calculated as Fe/SiO_2).

It is interesting to know that the results presented by Komkov (13), who shows a clear minimum of the copper content in the slag in a 31 to 32 % range of slag in a Vanyukov oven and points out that lower amounts conduce to an increase in the total loss of copper, while with amounts over 32% a dispersion of data is seen, which is caused by the increase of the copper´s viscosity. The explanation of the positive desplacement of silica contents over 32 to 33% can be obtained starting with the fayalitic slag´s physical properties, where it is known that the viscosity can increase at 150cP to 32% of SiO_2 and at 400cP to 36% of Si O_2 (14).

Mackey (7) points out that for reverberatory slag, an increase of silica content conduces to a permanent decrease of the copper content in the slag. This indicates that though the viscosity increases for higher silica content, it helps to separate the slag - matte phases and so the copper loss decreases.

The results stated in the paragraph above show apparent contradiction with those in reference with 11, 12, 13. If there is a permanent decrease a parabola form result would not show a minimum copper loss. Nevertheless, the results given by Mackey concur with those cited by Geveci and Rosenquist (15) in the zone where the ratio Fe/SiO_2 is larger than 1.6.

The apparent contradiction is caused only if the existence of two zones are considered when carrying out the analysis:

$1.7 < Fe/SiO_2 < 2.0$
$1.3 < Fe/SiO_2 < 1.7$

The results shown in 11, 12, 13 are confirmed by Healy (16), who explains the loss in relation to slags physical properties. Healy indicates that the amount of white metal trapped in the slags depends on the viscocity, the grade of agitation performed on the slag phases, and the white metal. It also depends on density differences between both phases and their interfacial tension. In addition, he states that the settling time influences on the copper trapped. Healy defines the relative index of suspension as the ratio (viscosity/delta density) for the range $-9<\log pO_2<-7$ and 75% of copper in the white metal. Considering the ratio Fe/Si as an independent variable in the Noranda case, the relative index value could be considered as 0.5, which corresponds to the plateau of the curve shown. Concludes stating that the copper loss is large until the ratio Fe/Si reaches 3.5. If the this ratio increases , the loss decreases, combining the effect of lowering the relative index of suspension and the slag amount (due to the effect of adding less silica).

Healy´s conclusions are also in contradiction with the one´s stated on (7), but concur with the one´s obtained by Robilliard, Themelis and Komkov.
With everything stated above and after three decades of searching for the knowledge already found, one would say that the industrial equipment works in stable condition and is controlled.

But this is not true.

Operational practice shows that the slags discharged from the CPS have oscillating values, and it is very difficult for the worker to repeat good results.

RESULTS
As an example, the following graphic shows in a sequence of 100 samples taken at the end of the first blowing, the oscillating amounts for copper and magnetite content in slags.

The objective of this work is to make a critically analyse for slags discharged from converters so workers can make their job in optimum conditions with helpful tools.

Slag samples are normally extracted from the converter and are inspected visually by the operator. The slag samples are then sent to a metallurgical laboratory for a chemical analysis. The report includes data for copper content, magnetite, silica, sulfur and the total amount of iron. The chemical results made can only be considered as historic data since its identification is found a long period after extraction has taken place.

Analysing a group of slag data and taking in consideration the analysis of silica content as an independent variable –like shown in figures 2, 3, 4, 5, and 6- is practice normally used in the industry, but must be made carefully as explained later.

Figures 2 and 3 show the result obtained for a group of 200 chemical analyses of slag samples. Here, the analysis of silica content has been sketched as an independent variable.

Both figures have been obtained by drafting the set of values of the analysis (%Cu_{slag} ** %SiO_2) and (%Fe3O4 ** % SiO_2) as the Chemical Laboratory reports; although they are separated into two subsets that contain equal amount of reported data (low silica level, high level +).

By just observing both figures, it may be concluded that it is difficult to give clear instructions to the operator for him to work under conditions that may minimize the content of copper in the slags.

When the set of data (%Cu_{slag} ** %SiO_2) reported by the laboratory is organized according to the silica value and grouped in subsets of 4 elements (neighboring values for Si02), the result shown in Figure 4 is obtained. For every of these subsets, the average of the variable is estimated and the corresponding Si02 average value is associated with it. Figure 5 corresponds to the result obtained for the set of data (%Fe3O4 ** % SiO_2).

When these new sets are under statistical analyses, it is normally observed that there are no correlations in the variables.

As previously mentioned, Figures 4 and 5 correspond to a routine that is frequently used in industry. It is wrongly concluded that the copper content in the slag and the content of the magnetite are always lower; at greater silica content, which leads to oversaturation of the slags in silica, the efficiency of the process decreases due to the presence of an excess of flux that does not benefit the operation (it absorbs energy and occupies space).

Organizing the data, though this time according to the parameter $Fe/Si0_2$ and grouping them in the same way as before, the following graphic is obtained showing a comparatively higher correlation with respect to the one shown before.

Upon observing Figure 6, it may be concluded that the set of highly dispersed values shown in Figures 1, 2, and 3, has been orderly organized, making it possible to give a “clearer instruction” to the operator to minimize the copper content in the slags.

When the corresponding magnetite content data is processed, it is advisable to do it using fayalite content (estimated from the value of Fe_{Total} and magnetite), since in its value two independent measurements intervene. Figure 7 shows the result obtained.

So as to facilitate the analysis of the data presented, the following graphic is included, containing the result obtained when the value of $Si0_2$ is related to the parameter $Fe/Si0_2$.

When comparing the results shown in Figures 4 and 5 with those in Figures 6 and 7, it is concluded that there exists an apparent contradiction in their interpretation.

- Figures 4 and 5 induce to oversaturate the slags with silica, since a “permanent improvement” in the levels of copper and magnetite is observed. It is usual to find values higher than 30% as operational practice.

- While Figures 6 and 7 suggest selecting the range of values extending from $1.6 < Fe/Si0_2 < 1.8$ the optimum value $Fe/Si0_2$, which, according to what Figure 8 shows, corresponds to slags with silica content lower than 27%.

An analysis of the data that only considers the value of silica is weak to the extent that it does not do any correction by default of the excess of mass. When there is oversaturation of silica, it is possible to obtain lower values of copper and magnetite content, not only because of a beneficial metallurgical effect, but also because its excess dilutes the presence of other components. When the slag is highly contaminated due to copper dragging, the silica values reported may be low due to the same effect.

The analysis of the data that considers the parameter $Fe/Si0_2$ corrects the error referred to.

Figures 9, 10 and 11 show the result obtained for slags of continuous conversion.

CONCLUSIONS

1. The silica content reported by the Chemistry Laboratory does not explicitly account for the copper content in the slags, so the assumption that increasing contents of silica will diminish the copper content in the slags does not always hold true.
2. The parameter $Fe/Si0_2$ may be regarded as a useful parameter to control the losses of copper in the slags.
3. There exists the possibility of giving more explicit instructions to optimize the operation.
4. Slags coming from batch or continuous conversion have a similar behavior.

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FIGURES 1 - 11

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FIGURE 1

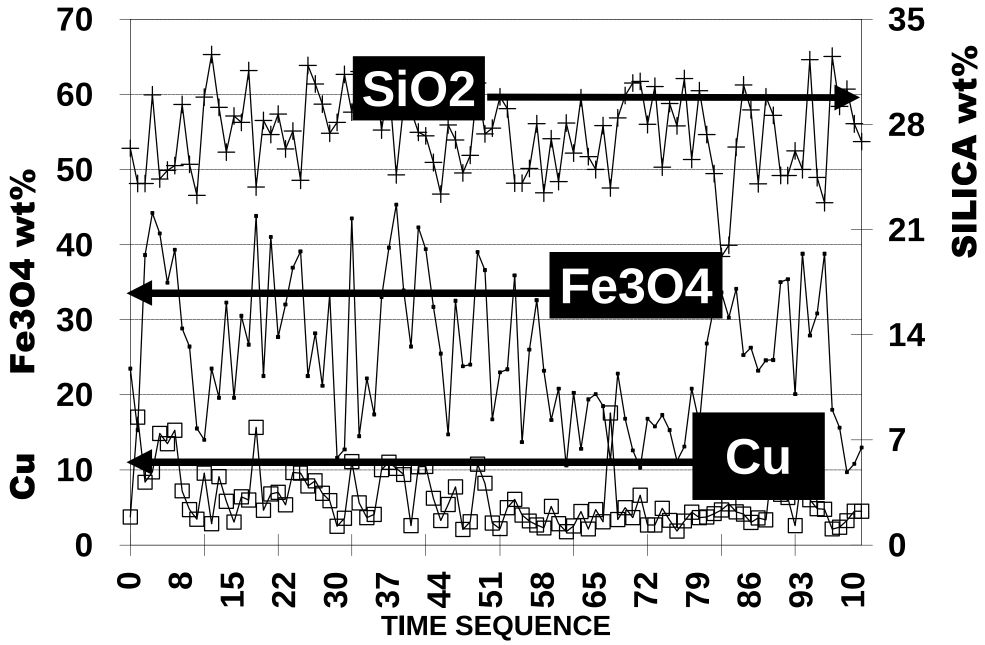

FIGURE 2
Cu and SiO_2 ANALYSIS IN SLAGS

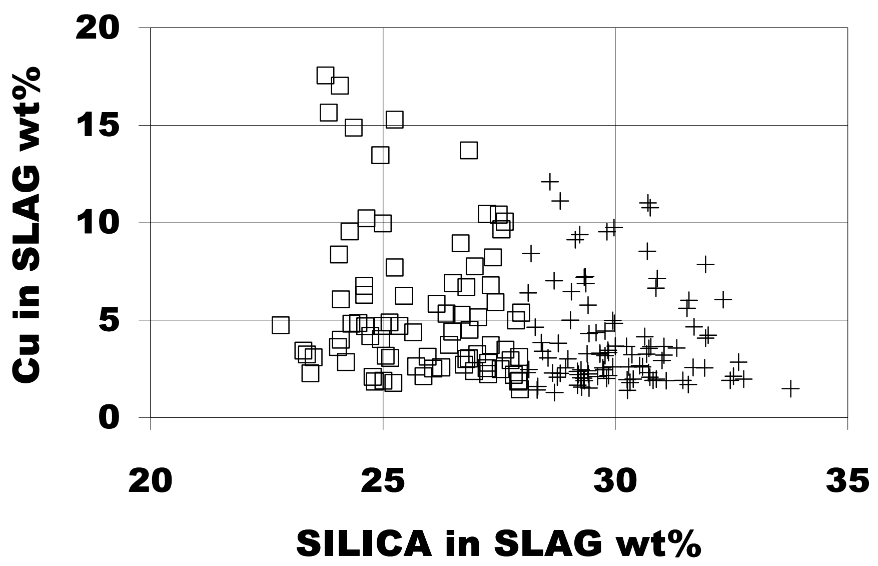

FIGURE 3

Fe_3O_4 and SiO_2 ANALYSIS IN SLAGS

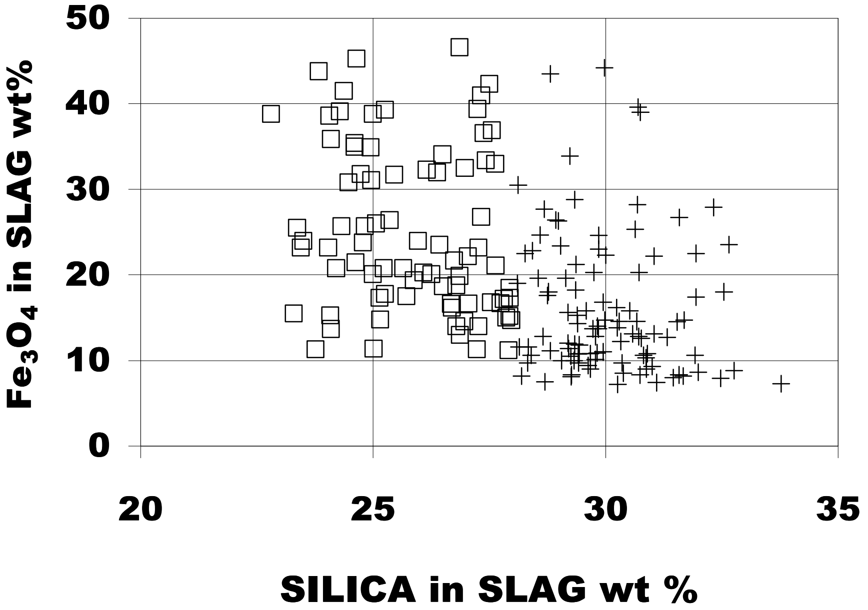

FIGURE 4

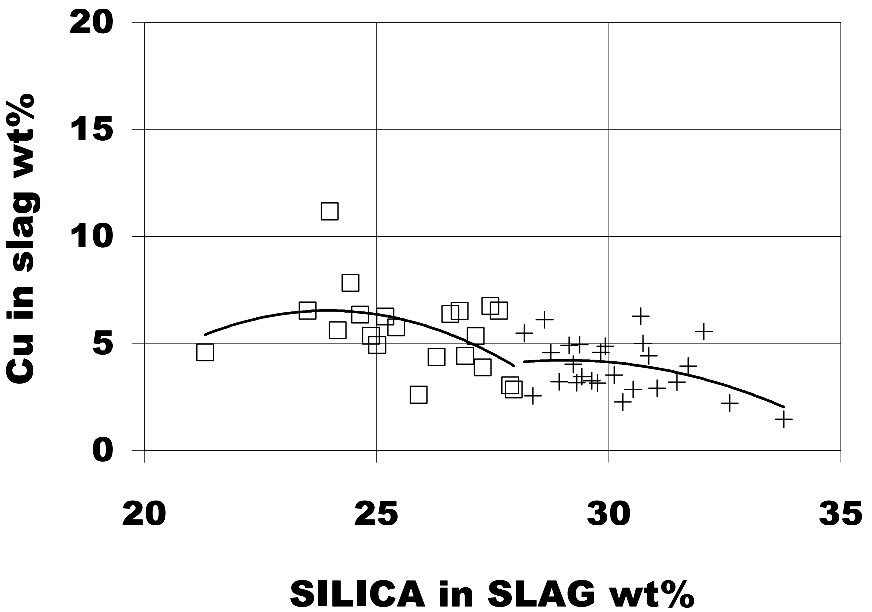

FIGURE 5

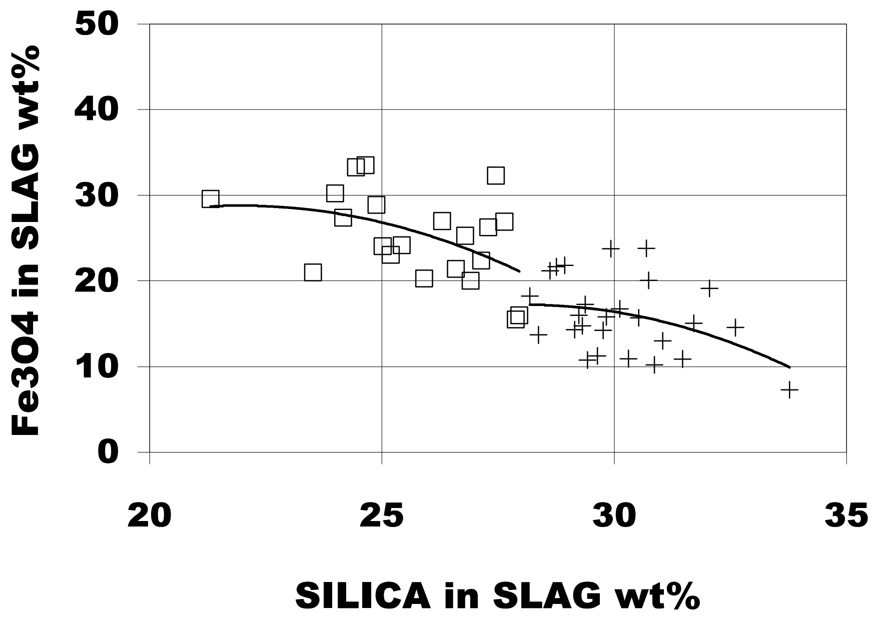

FIGURE 6

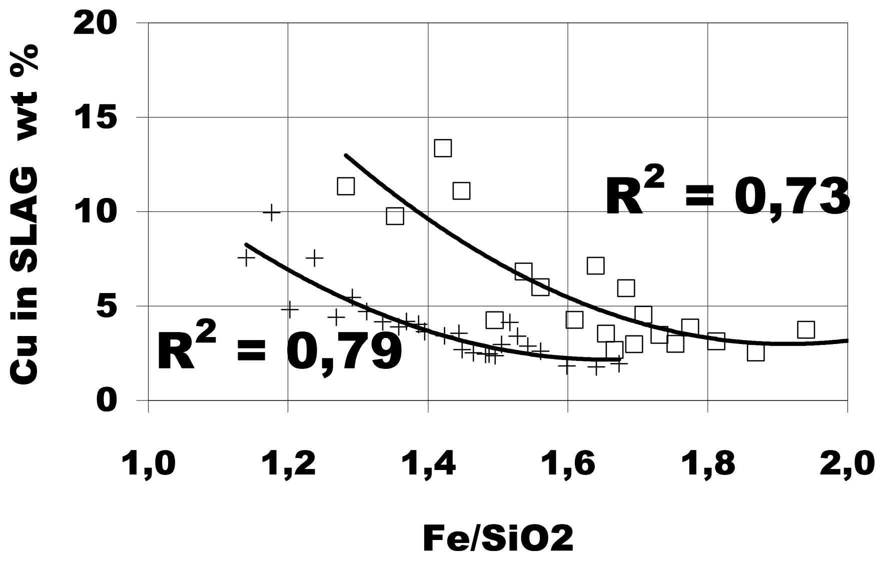

FIGURE 7

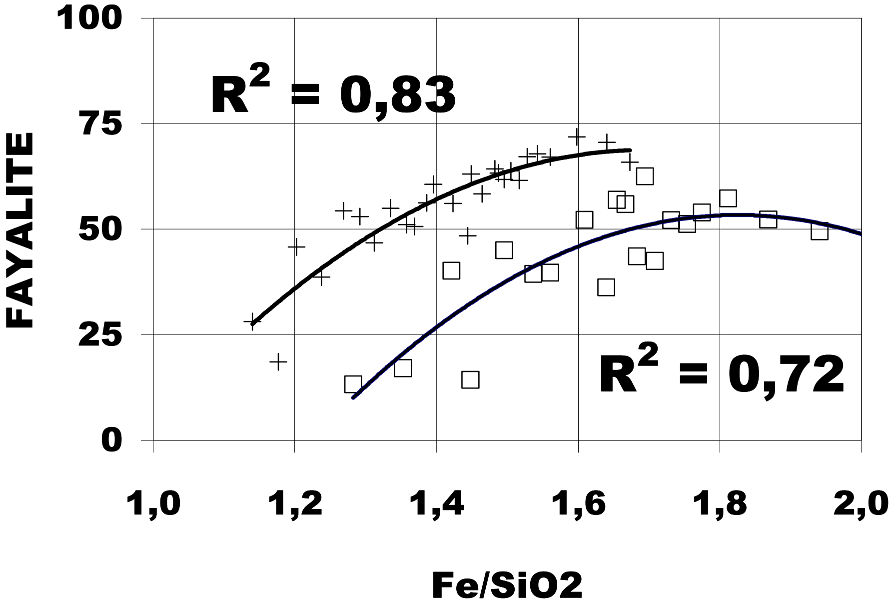

FIGURE 8

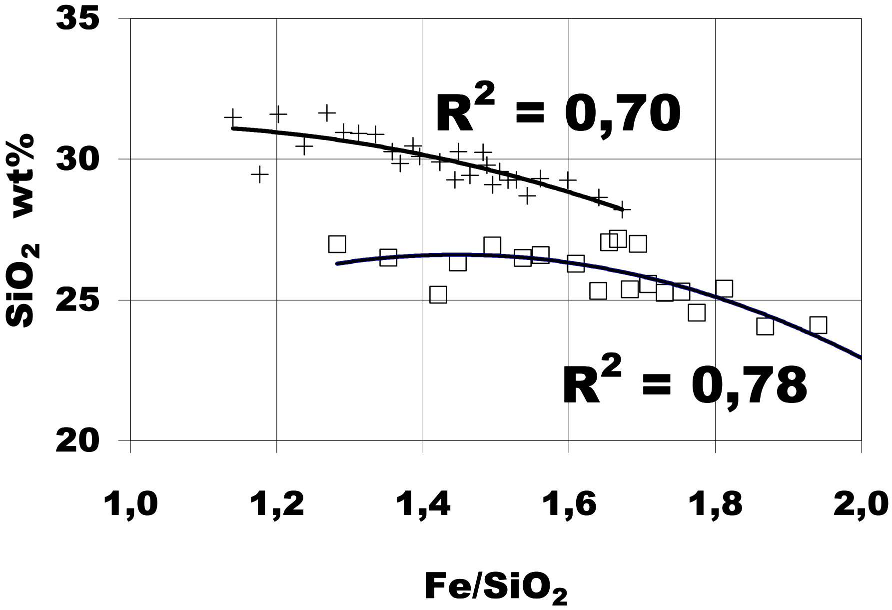

FIGURE 9

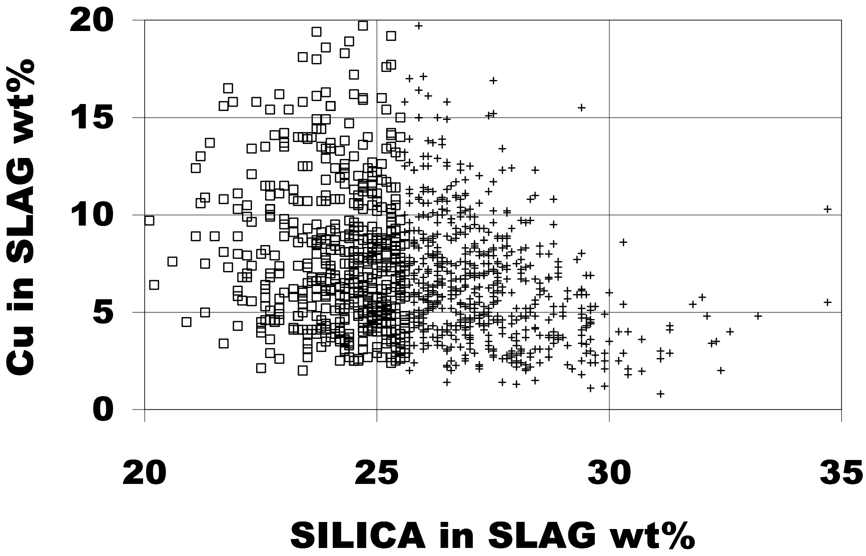

FIGURE 10

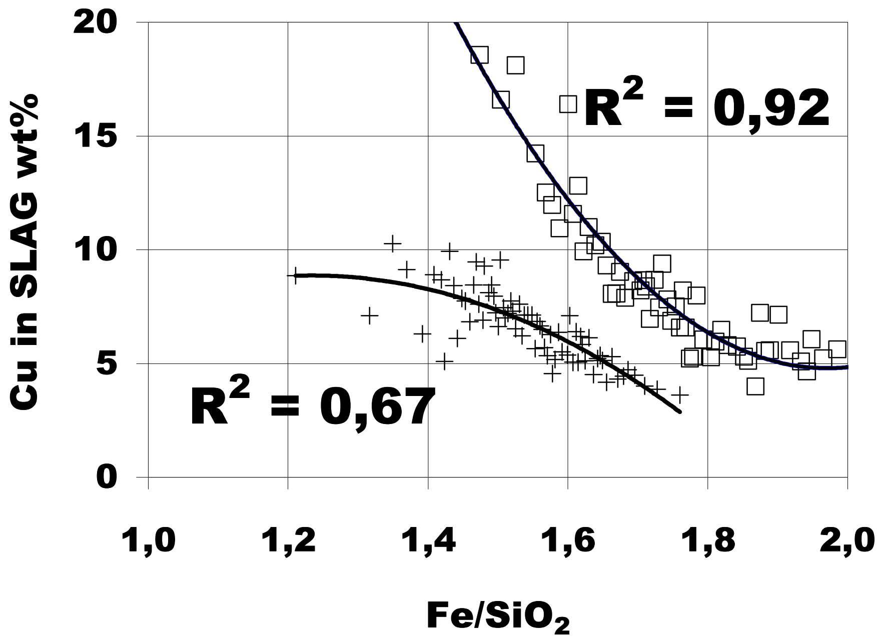

FIGURE 11