

Influence of slag composition on reduction control and operations of the slag-cleaning furnace at KCM, Zambia

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Abstract - This paper presents the results of linear regression analysis of the influence that each component of slag has on the losses of copper in slag-cleaning-furnace slag. Data used for the analysis are actual plant data collected over the past two years of operation. Facts obtained from the study will be helpful for smelter management to control these components in the flash smelting furnace feed and slag, to levels which will enable better control of copper in slag, and smoother operation of the KCM slag-cleaning furnace.

INTRODUCTION

Konkola Copper Mines plc of the Vedanta group (KCM) operates a 112 t/h Outotec direct-to-blister copper smelter at its Chingola operations in Zambia. Sulphide copper concentrates are oxidized by a concentrate burner at 75% air enrichment to produce blister containing up to 99.4% copper, which is tapped to anode furnaces for fire refining. The environment in the flash smelting furnace (FSF) is highly oxidizing; recovery of sulphur to the gas phase is high, but the slag contains high amounts of copper, both as dissolved oxide and mechanically entrained metallic prills (18 to 21%). The gases are channelled to the boiler and ESP for energy- and dust-recovery before final cleaning in the gas-cleaning plant for sulphuric acid preparation. Slag is cleaned in two stages, by carbothermic reduction, in the electric slag-cleaning furnaces (ESCF). In the first electric furnace (20 MVA), called the SCF (slag-cleaning furnace), copper oxide is reduced to produce blister copper (98.25% Cu) and slag containing 3 to 5% Cu, 0.78% Co. The slag from the first furnace is transferred to the second electric furnace, called the CRF (cobalt-recovery furnace). The CRF (15 MVA) offers a more reducing environment for the recovery of Cu and Co, together with Fe, forming a product known as cobalt alloy, and a slag containing as low as 0.45% Cu and 0.32% Co. Because of the high Fe content, the alloy has a high melting point; to lower the liquidus temperature, sulphur is introduced to the alloy by injection of FSF feed mixture to the bath¹. The two-stage process of slag cleaning employed at KCM, where copper oxide is first partially reduced in one electric furnace and more comprehensively in a second furnace, results in very high recovery of both copper and cobalt².

SLAG-CLEANING OPERATIONS AT NCHANGA SMELTER

Slag is tapped every 4 hours from the FSF to the SCF via water-cooled copper launders at 1290°C. A typical slag analysis from the FSF is shown in Table I. The objective of the SCF operation is to reduce copper in the FSF slag to 3–5% by the addition of an appropriate amount of metallurgical coke, to ensure minimal precipitation of iron and cobalt to the blister phase. Slag temperature is maintained around 1350°C, while blister temperature is kept above 1200°C.

Table I: Typical analysis of Flash Smelting Furnace (FSF) slag, mass %

Cu	Fe	SiO ₂	CaO	MgO	Co	S	Al ₂ O ₃	Fe ₃ O ₄
19.46	22.52	25.69	5.89	2.46	0.64	0.29	3.94	20.79

Control of copper in the SCF slag within the 3 to 5% range has been a challenge, due to changes in size and quality of metallurgical coke, and slag chemistry. Table II shows the average composition of SCF slag from March 2009 to December 2010.

Table I: Typical analysis of Slag Cleaning Furnace (SCF) slag, mass %

Cu	Fe	SiO ₂	CaO	MgO	Co	S	Al ₂ O ₃	Fe ₃ O ₄
5.48	27.03	30.93	8.09	3.242	0.76	0.38	6.39	14.02

Control of copper transferred to the CRF at between 3 to 5% has been very important in recent months, as the LME copper price is estimated to reach US \$12 000 per ton in 2011. The idea is to send minimum copper to the alloy phase in the CRF, because payables on copper in alloy are lower than in the anodes that go to the refinery for copper cathode production.

Sampling of slag for chemical analysis

Three samples are collected from the SCF slag launders during transferring of slag to the CRF, to make a composite sample for chemical analysis. Tapping times depend on the number of tap-holes opened, the level of slag in the furnace, and its viscosity. The samples are allowed to cool in air, and are then sent to the laboratory for chemical analysis using an X-ray fluorescence (XRF) method for components other than magnetite, which is determined by the magnetic saturation method in the Satmagan analyser.

Control of copper in SCF slag

Metallurgical coke for reduction reactions in the SCF is charged from the roof of the furnace to the surface of the slag. The amount of coke to charge to a slag batch is calculated using a coke-addition model, which takes into account the percentage of copper in the slag, the degree of copper reduction required, and the amount of slag received. Figure 1 shows the degree of control of SCF operations with respect to copper in slag.

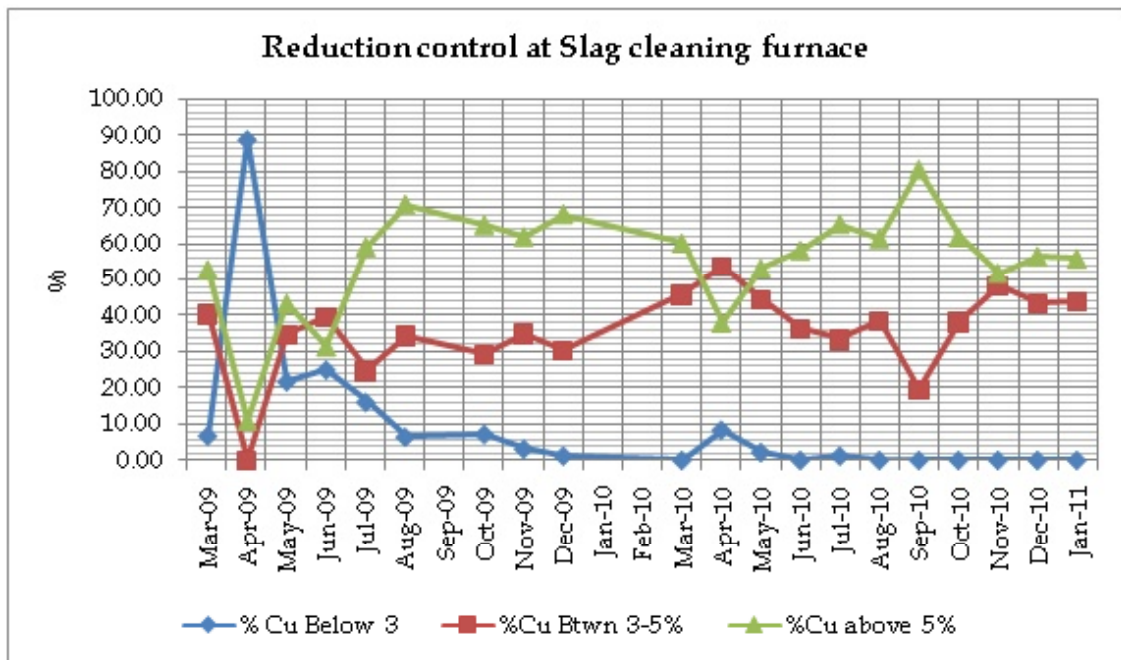


Figure 1: Control of copper in SCF slag within the desired range

Best control achieved was in April 2010, with 53.4% of the values being within the desired range of 3-5%. September 2010 was the worst month, because 80.5% of the values were above the upper control limit.

EFFECT OF SLAG COMPOSITION ON CONTROL OF COPPER IN SCF SLAG

Many investigations have shown that the composition of a particular slag system has the major influence on control of copper losses to the slag^{3,5,8,9,10,11}. This is due to the effect that chemical composition has on the liquidus temperature of the slag and its fluidity⁷. This paper uses simple linear regression analysis to determine the impact that the major components (Fe_3O_4 , SiO_2 , Al_2O_3 , MgO , and CaO) of the slag have on losses of copper to slag, because it is the appropriate method for this kind of analysis². Losses of copper in the slag may be in the form of dissolved oxides or mechanically entrained metal prills⁴. The data used in this investigation are actual plant data collected over a period of two years. The temperature of SCF slag has varied from 1320 to 1400°C over the period analysed in this paper.

Change in composition of FSF slag (KCM)

Due to changes in supply, mineralogy, and chemical composition of individual concentrates, it has been very difficult to make FSF slag that has a composition close to design values. SCF operations have likewise changed with the change in FSF slag, and operational challenges have been different for each of these changes. For example, Figure 1 shows that in the first six months of the period under consideration, there were a significant number of 'copper in SCF slag' values below the low limit of 3%, and there were almost none in the last 10 months of 2010. This is due to the fact that, in the last part of the period considered here, slag was more difficult to reduce because, as Figure 2 shows,

the important components of slag which determine its ease to be reduced have changed significantly.

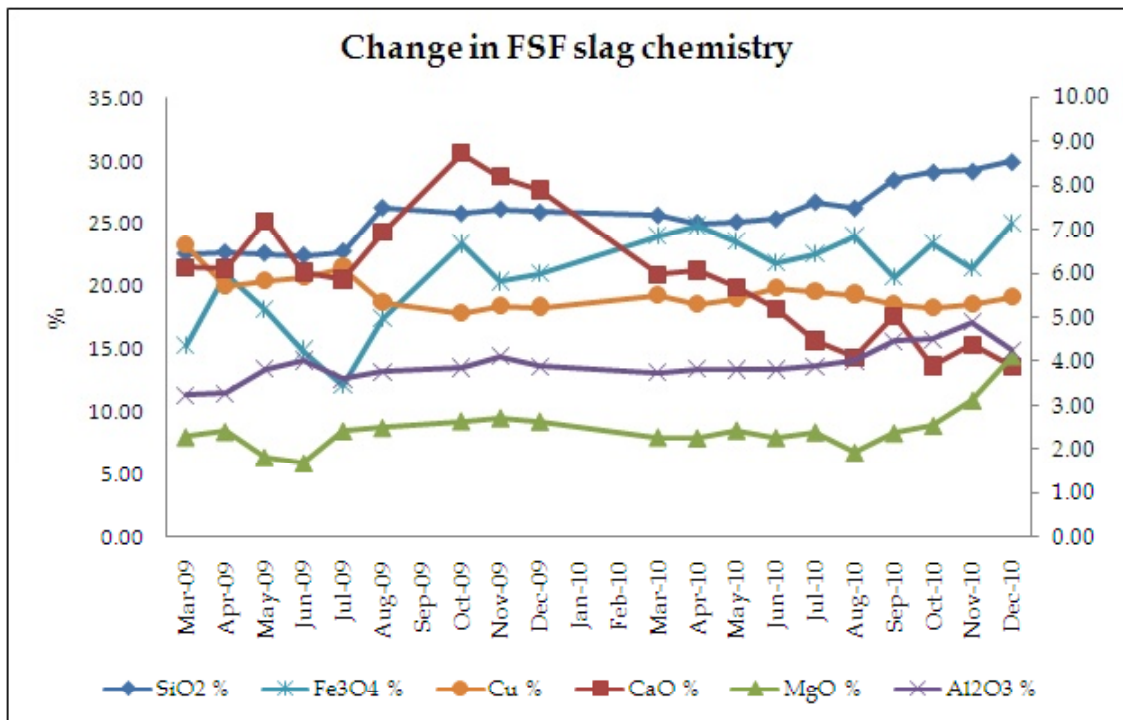


Figure 2: Change in FSF slag composition over a period of two years

Carbothermic reduction chemistry, and mechanisms of copper losses in slag

When coke is charged to the surface of slag in the furnace, there is very rapid direct reduction of copper oxide and magnetite by metallurgical coke⁸.



Carbon monoxide from the above reactions forms a gas film between the coke and the slag. From this point, oxides in the molten slag are reduced by carbon monoxide, and the Boudouard reaction (Equation [3]) becomes the reaction-rate-controlling factor⁸.



Equations 1 and 2 take place at the same time; one cannot take place without the other¹³. A dispersion of very fine copper droplets formed, from Equation 2, coalesce to form bigger particles, which then settle to the bottom of the furnace¹¹. Mass transfer amongst fine copper droplets is therefore very important for nucleation to take place¹². In the slag-cleaning furnace, mixing of small particles is intensified by the stirring action caused by the inflow of slag during FSF-slag tapping. The biggest droplets of metallic copper are formed during this time¹³. After FSF-slag tapping, there is less turbulence in the SCF;

therefore reactions and droplet formation are slow¹³. Movement of slag in this period is mainly by electromagnetic forces (magneto-hydrodynamics), enhanced by high electrode-current-densities and temperatures^{12,13}.

Copper losses in slag can be divided between electrochemical losses (chemical and physical) and mechanical losses (unsettled droplets) whose percentages depend on the degree of oxidation or reduction, temperature, and composition of the slag (which affects its viscosity)¹¹. The effect of slag viscosity on the loss of copper by entrainment (mechanical) is shown by the effect it has on the settling rate of a metal droplet, as given by Stokes law (Equation 4)¹¹.

$$u = \frac{(\rho_{Cu} - \rho_{slag})}{18\eta_{slag}}gd^2 \quad [4]$$

where u = settling rate, m s⁻¹

g = acceleration due to gravity, m s⁻²

d = diameter of copper droplet, m

ρ_{Cu}, ρ_{slag} = density of copper and slag respectively, kg m⁻³

η_{slag} = viscosity of slag, Pa s

Equation 4 shows that the settling of copper droplets is very much dependent on the viscosity of the slag. Slag viscosity plays a vital role in the formation of copper droplets big enough to settle at the desired rates. The lower the viscosity, the better the coalescence of fine blister particles to form bigger particles, and, according to Equation 4, the faster the settling¹².

Other mechanisms may be responsible for suspending copper particles in the slag¹¹. Gases formed during reactions may also transfer some metal droplets to the slag zone¹¹. In the SCF, bath agitation keeps copper droplets in suspension in the slag, and, if this happens a few minutes before skimming, copper mechanical losses to the SCF slag will be high.

The effects of Fe₃O₄ content in SCF slag on control of copper in SCF slag

Magnetite (Fe₃O₄) is formed in the flash smelting furnace by oxidation of iron in the concentrates. Both the extent of oxidation and the amount of iron in the concentrate has an influence on the amount of Fe₃O₄ in the FSF slag. It has been found that losses of valuable metals (Cu, Co, and Ni) to slag increase with increasing magnetite in the slag⁵. Figure 3 shows a strong dependency of copper on the amount of Fe₃O₄ in SCF slag. Increasing the amount of Fe₃O₄ in SCF slag will result in precipitation of Fe₃O₄ crystals, therefore increasing the viscosity of the slag and the entrainment (mechanical losses) of molten copper droplets in the slag³. As demonstrated by Stokes law above, this will result in slow settling of molten copper droplets.

Over-heating of the slag decreases its viscosity, and accelerates reduction of Fe₃O₄, and this liberates suspended copper droplets^{9,11}. Operation of the SCF has recently shown that, at high Fe₃O₄ levels in FSF slag, good control of Cu in

SCF slag has been achieved, when the SCF slag temperature was kept above 1380°C during FSF-slag tapping.

It is, therefore, important that Fe_3O_4 in FSF slag is controlled at levels that can be reduced in the SCF within the design cycle time and plant feed rate to give copper in SCF slag within the required range. For example, the data used in this study show that, if Fe_3O_4 in FSF slag is kept below 18%, it is possible for the SCF to reduce Fe_3O_4 to 10% within the design cycle time to produce slag with 4% Cu.

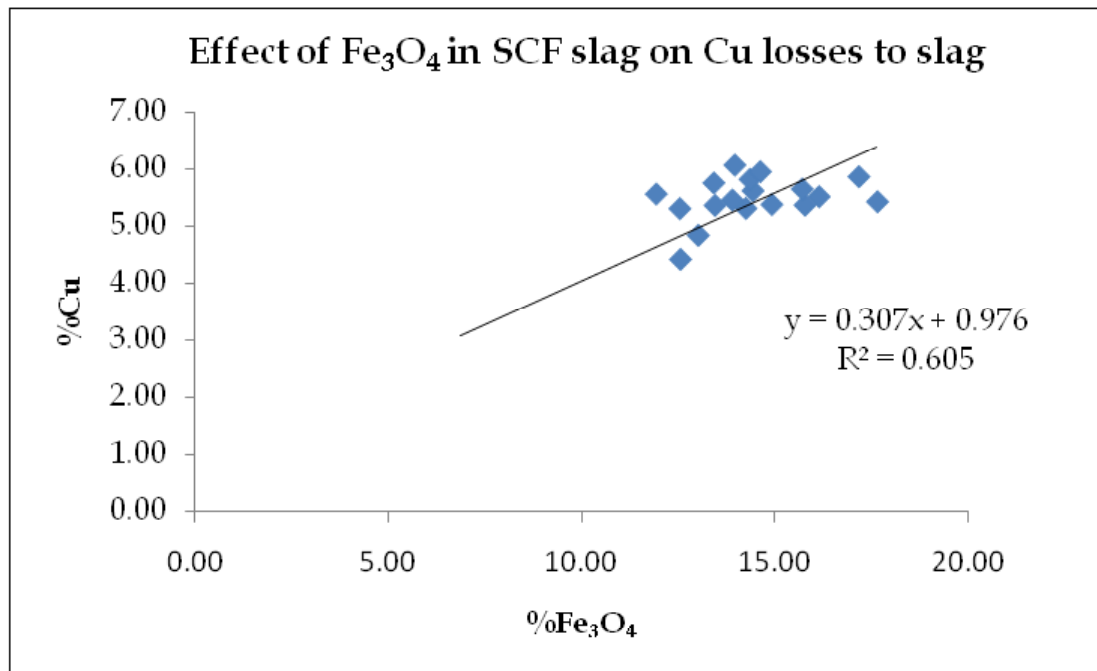


Figure 3: Influence of Fe_3O_4 on control of Cu in SCF slag

The effects of Fe_3O_4 in FSF slag on slag-cleaning operations

Apart from the above influence of Fe_3O_4 on SCF degree of reduction control, Fe_3O_4 causes other operational issues. Firstly, precipitation of Fe_3O_4 at high levels leads to formation of an intermediate layer (50 to 200 mm) between the blister copper and slag phase during reduction. The intermediate phase insulates the transfer of energy and Cu droplets to the blister phase. Temperatures of blister copper in the SCF under such conditions drop below 1130°C, making transfer of blister to the anode furnaces difficult, because of poor flow, and the metal cools easily. Removal of solidified copper from blister launders, and the repair of blister launders, also becomes frequent at low blister tapping temperatures. This also increases the amount of scrap copper generation that has to be re-melted in the anode furnaces.

To increase the transfer of energy from the slag phase to the blister, air agitation of the bath is employed, using steel pipes to disturb the intermediate phase. Use of agitation pipes is an extra cost, and the operation itself requires additional manpower. An increase in the Fe_3O_4 content of the slag also results

in increased metallurgical coke consumption, because Fe_3O_4 is also reduced by copper during slag cleaning⁶.



Figure 4: Intermediate phase formation and entrainment of copper droplets

The pictures in Figure 4 were taken from the SCF furnace during the high Fe_3O_4 conditions. When the intermediate phase is too dense, the product elemental copper will form a layer on top of this phase, and sometimes blister copper will run out of the slag launders during skimming. This is not desirable, because slag launders are made out of copper, and so blister copper will naturally stick in the launders, and it is very difficult to remove, and may damage the launders.

The influence of silica on control of copper in SCF slag

Silica content in the slag has an impact on the viscosity of slag¹⁰. An increase in silica, as Figure 5 shows, increases the amount of copper in the SCF slag, because of silica saturation at Fe/SiO_2 ratios less than 1, which results in high slag viscosity⁶. Because of the glassy nature of the high-silica slag, its porosity to gases decreases, which adversely affects the reduction reaction rates at the slag/gas interface⁵.

A new phenomenon was observed in September 2010 in SCF operations, when the bath was expanding during slag tapping from the FSF, from gas evolution that is highest in this phase of the cycle. For this reason, SCF slag volumes, as calculated from level measurements, were about 150 t more than the FSF slag calculation, leading to excess consumption of coke. This phenomenon was also verified with mass-balance calculations.

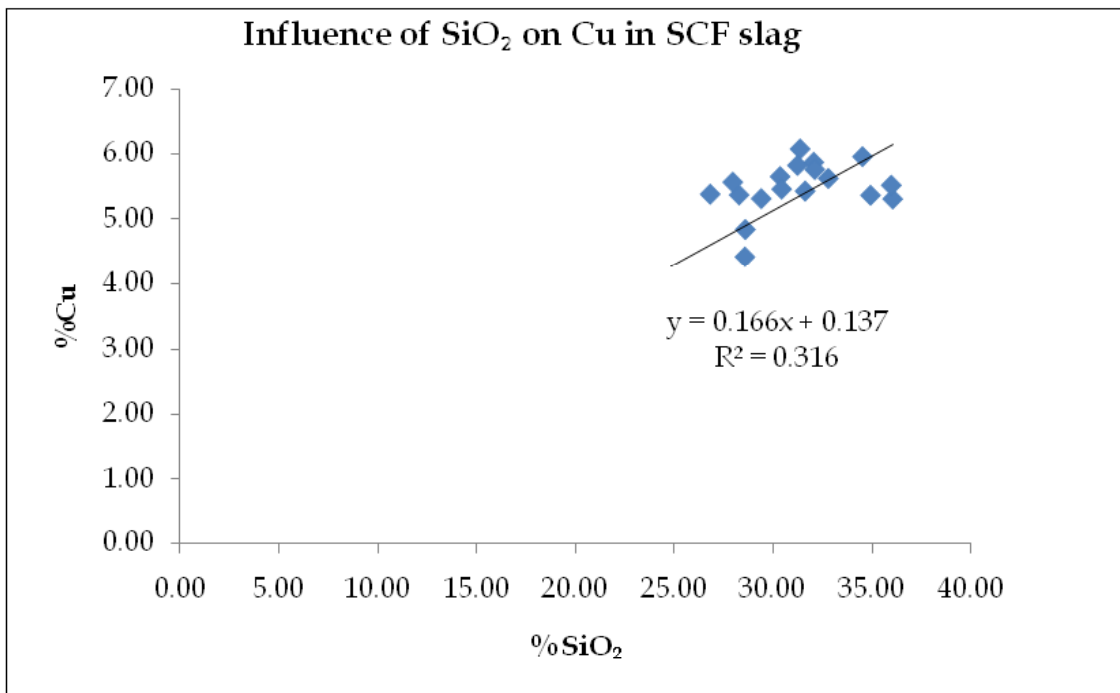


Figure 5: Influence of SiO₂ on control of Cu in SCF slag

SCF slag samples taken in September 2010 for mineralogical analysis also indicated entrainment of both metallic copper droplets and Fe₃O₄ in the *glassy phase* (as per lab report), as shown in Figure 6.

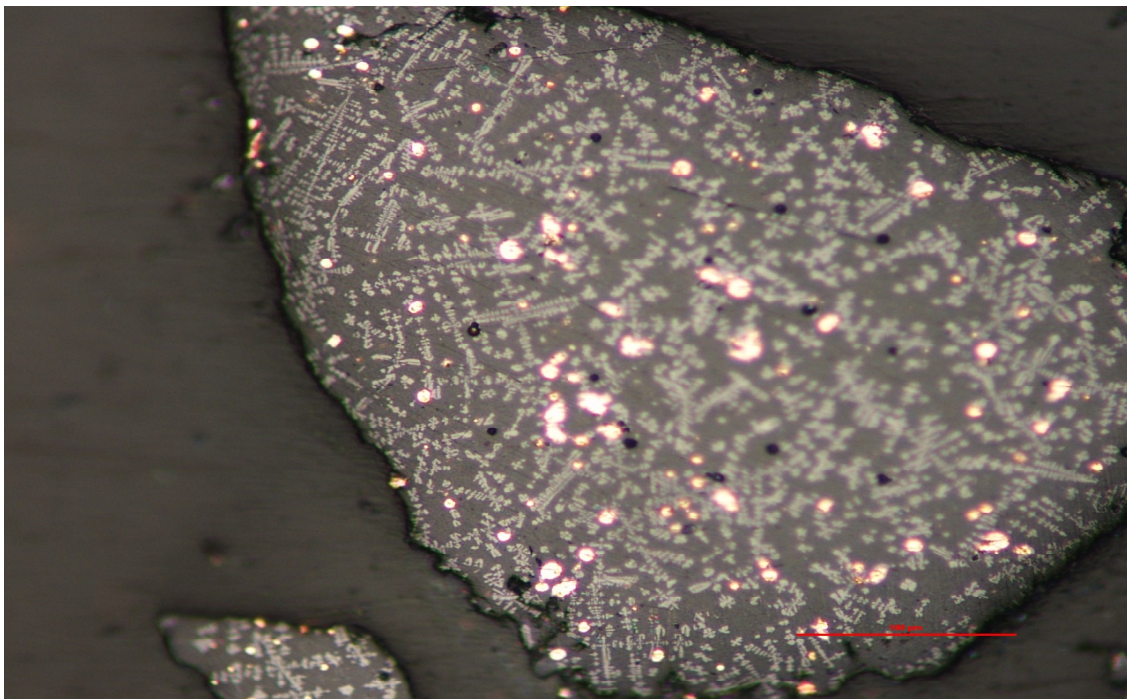


Figure 6: Grains of elemental copper (< 5 μm) with secondary magnetite in glass phase in SCF slag

The influence of alumina on control of copper in SCF slag

Alumina forms high-melting compounds with FeO_x and SiO_2 , which are solid at copper-smelting temperatures⁶. It has also been shown that an increase of alumina in the calcium silicate slag enlarges the spinel (Fe_3O_4) saturation area and this increases mechanical losses of copper as Figure 7 shows⁴.

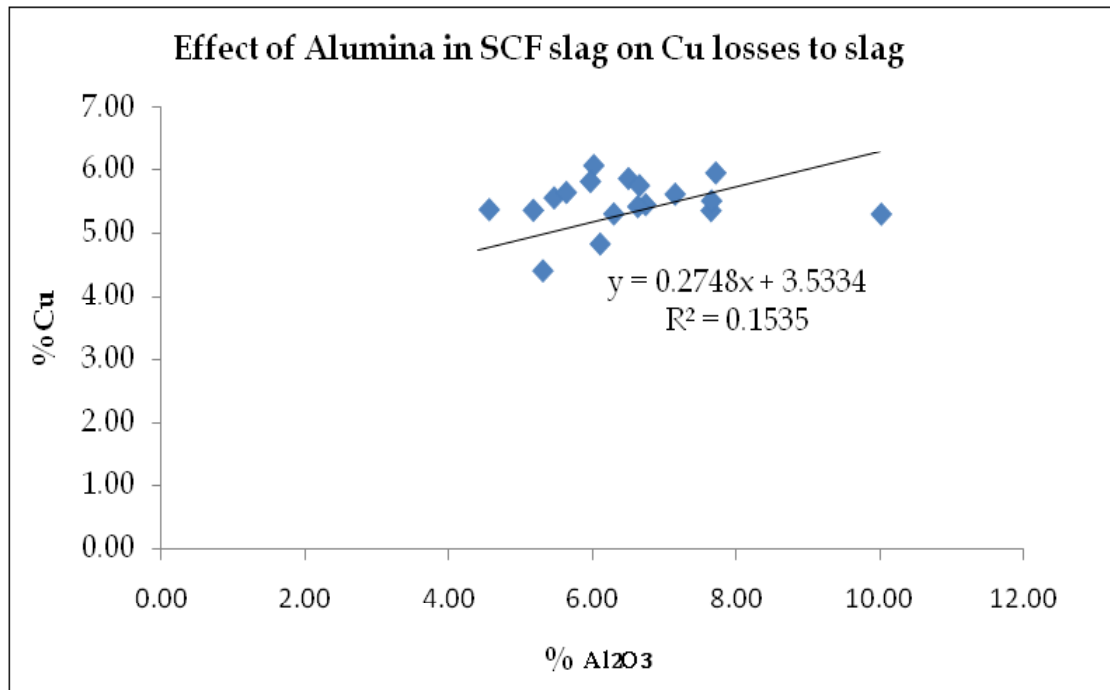


Figure 7: Influence of Al_2O_3 on control of Cu in SCF slag

The influence of magnesia on control of copper in SCF slag

The MgO forms a thermally stable (solid) silicate called olivine ($\text{Mg}_2\text{SiO}_4 - \text{Fe}_2\text{SiO}_4$) at concentrations greater than 3-4% in the KCM slag (FSF slag), resulting in high-viscosity slags^{4,6}, and its systems with FeO_x or Fe_2O_3 are solid at copper smelting temperatures⁶.

Figure 8 shows the influence MgO has on the amount of copper in SCF slag. The coefficient of determination of 0.191 indicates that the influence of MgO on copper in SCF slag is low at average concentrations seen in the period studied.

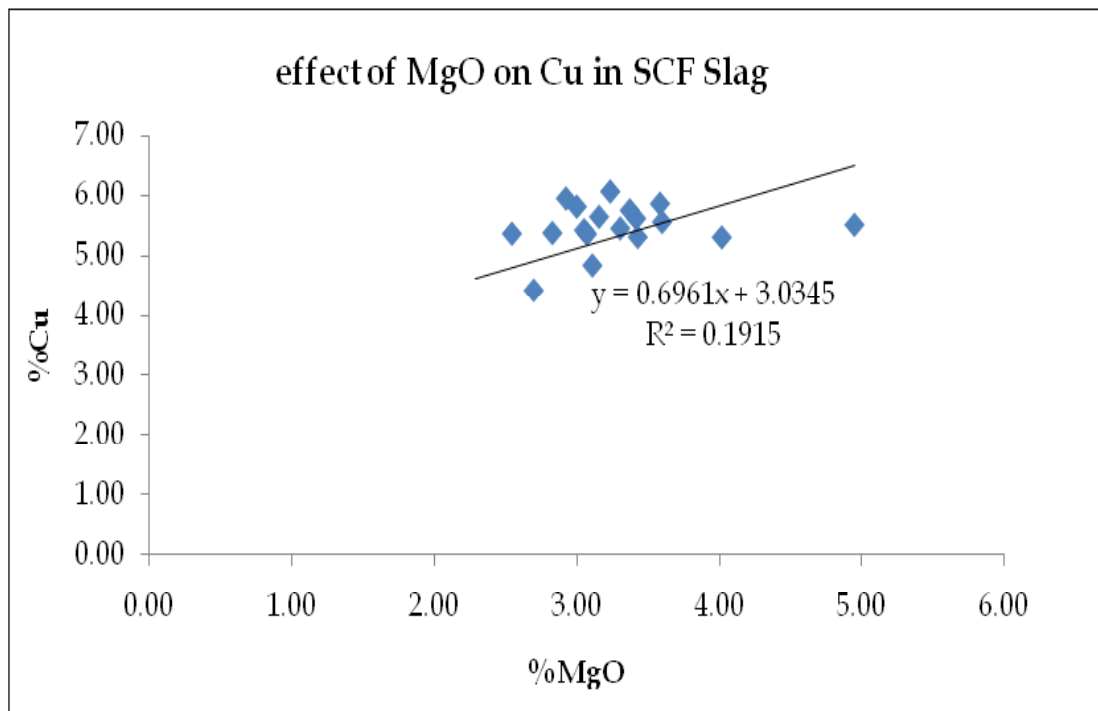


Figure 8: Influence of MgO on control of Cu in SCF slag

Effect of lime on control of copper in SCF slag

Lime (CaO) is used as a flux in the flash smelting furnace to prevent the formation of solid substances such as magnetite (Fe_3O_4) and olivine ($\text{Mg}_2\text{SiO}_4 - \text{Fe}_2\text{SiO}_4$), and to flux the solid silica⁶. It has an influence on the viscosity of the slag; the more the CaO, to a certain extent, the less the viscosity, and the easier it becomes for copper droplets to settle. Variation of CaO in the SCF slag has, however, had little impact on the control of copper levels in slag, as shown in Figure 8.

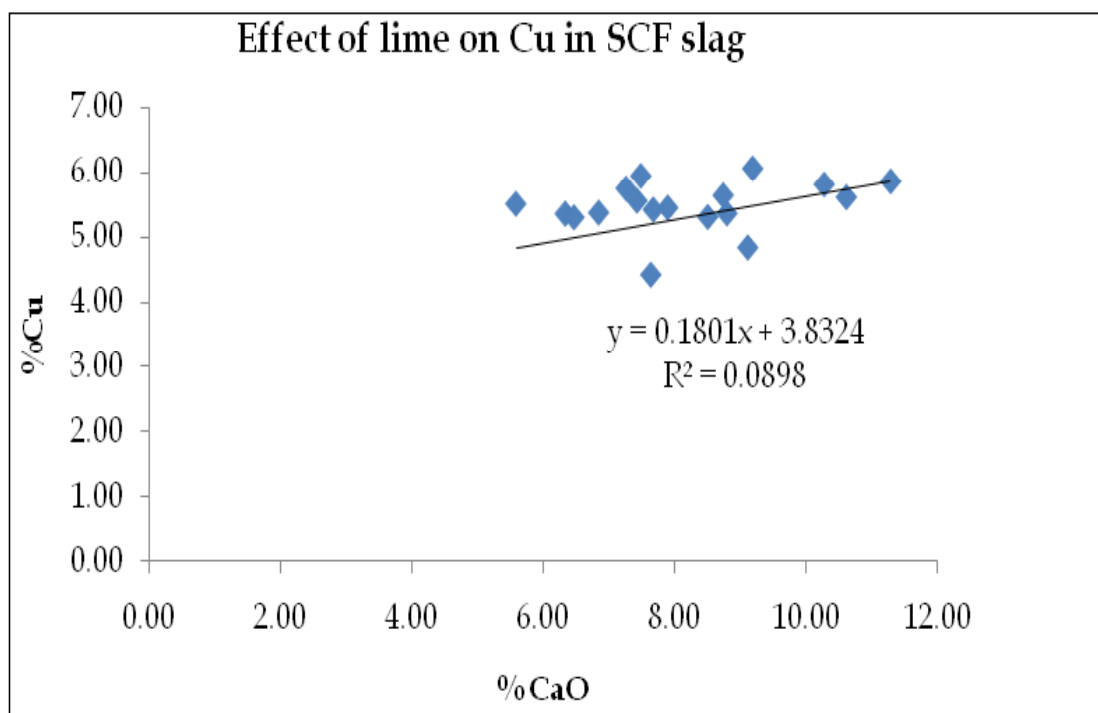


Figure 9: Influence of CaO on Cu in SCF slag

Linear regression analysis of the data collected for this study shows something that is contrary to the common belief that CaO decreases losses of copper to slag. It should be pointed out here that data given by ternary diagrams should not be generalized, because it usually applies to a given set of conditions⁴. The coefficient of determination for the CaO/Cu relationship is low, but shows that an increase in CaO content of the SCF slag has slightly increased the content of copper in SCF slag. The plant (SCF) experienced difficulties raising temperatures when the lime suddenly increased in the FSF slag. CaO is refractory, and, if present in more than required quantities, will increase the liquidus temperatures of the slag and reverse the effect it has on copper losses in slag.

Application of the R^2 for the Fe_3O_4 and Cu in the SCF slag relationship

The relationship between Fe_3O_4 and Cu in slag has come out very important for every metallurgist working in the SCF because it has the highest coefficient of determination ($R^2 = 0.605$) of all components of slag considered in this study. Magnetite, therefore, has the highest influence on copper in the slag that is tapped to the cobalt recovery furnace (CRF). The significance here is not really the value of R^2 for the Fe_3O_4 - Cu relationship calculated in this study. However, it is in the fact that in months where Fe_3O_4 had the major influence on copper in SCF slag, values of R^2 were very close to 0.6. The author concludes that when Fe_3O_4 is the major controlling component of copper in SCF slag, R^2 for the Fe_3O_4 - Cu relationship will be close to 0.6. This is valid for SCF (KCM) operations only.

Figure 10 demonstrates how the R^2 can be used to analyse the SCF slag-cleaning operation. An important observation made from the data was that for months which had other components of slag increase their influence on copper in SCF slag the coefficient of determination R^2 for the Fe_3O_4 - Cu relationship was less than 0.6; for example, September 2010. In this month, the effect of SiO_2 on copper in SCF slag was amplified by the increased concentration of silica in the slag, and the effect was weakening the strength of the correlation between Fe_3O_4 and Cu in slag. For this reason, the September 2010 slag was tough to clean, because both SiO_2 and Fe_3O_4 had an influence on copper losses. Slag with a coefficient of determination R^2 above 0.6 tended to be easily reduced, and cases of over-reduction were higher than for slags with a coefficient of determination R^2 value less than 0.6.

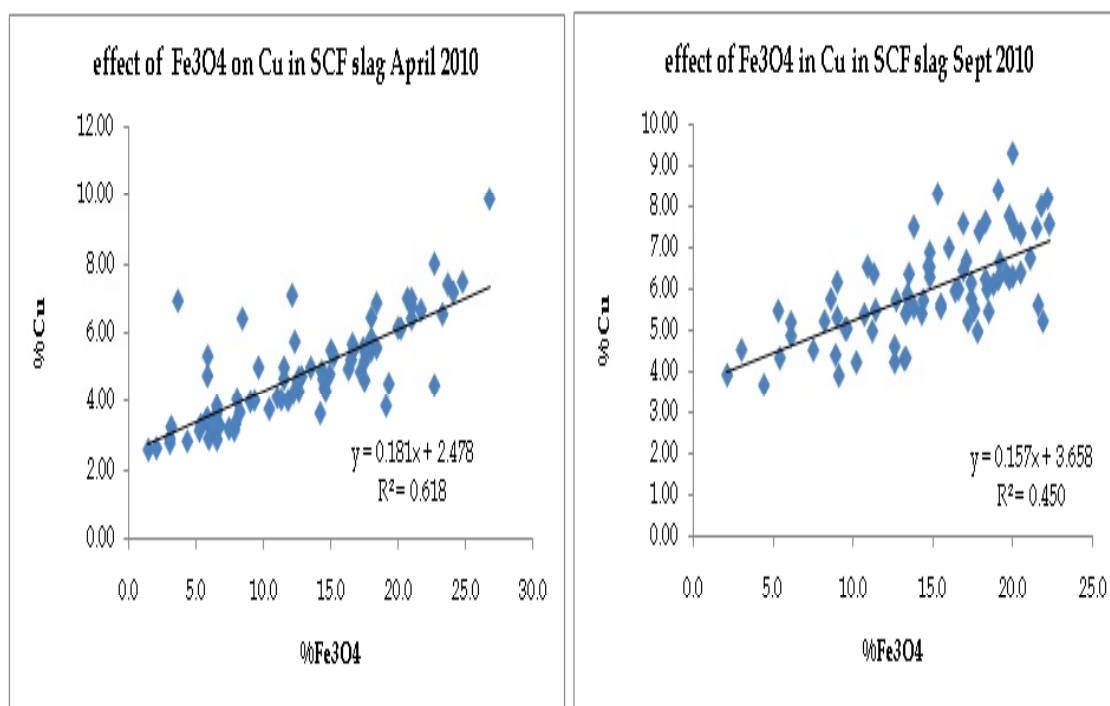


Figure 10: Comparison of factors affecting Cu in SCF by comparing Fe_3O_4 – Cu R^2 for slags

Therefore, if slag has an R^2 value for the Fe_3O_4 – Cu relationship close to 0.6 (e.g. the April 2010 slag), copper in the SCF slag will be effectively kept between 3 and 5%, if Fe_3O_4 in the slag is controlled between 8 and 10% under equilibrium conditions, *i.e.* not adding too much coke to the slag resulting in rapid reduction of Fe_3O_4 which increases Fe to the blister. This is only achievable if Fe_3O_4 in the FSF slag is below 18%. The control of Fe_3O_4 formation in the FSF is outside of the scope of this study.

Table III: Comparison of SCF slag composition between April 2010 and September 2010

	Cu %	Fe %	SiO_2 %	CaO %	MgO %	Co %	S %	Al_2O_3 %	Fe_3O_4 %	Fe/ SiO_2
Apr-10	4.84	31.34	28.58	9.11	3.11	0.79	0.13	6.10	13.01	1.10
Sep-10	5.95	24.31	34.52	7.49	2.93	0.68	0.08	7.71	14.61	0.70

To summarise the use and significance of the R^2 for the Fe_3O_4 – Cu relationship for SCF operation, the following will be important to a metallurgist's analysis or control of the slag-cleaning process in the SCF:

1. R^2 (Fe_3O_4 vs Cu) > 0.6: slag has low viscosity and easier to clean but over-reduction becomes easily possible.
2. R^2 (Fe_3O_4 vs Cu) = 0.6: Control of Fe_3O_4 in the SCF slag becomes the limiting factor for controlling Cu in SCF slag.
3. R^2 (Fe_3O_4 vs Cu) < 0.6: indicates influence of other components of slag, such as SiO_2 , increases Cu losses to the slag in SCF.

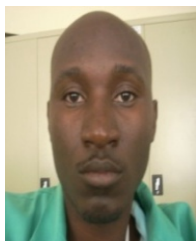
CONCLUSIONS

With a coefficient of determination of 0.605, Fe_3O_4 has the highest influence on copper content in SCF slag. Therefore, success in achieving the objective of SCF operation, in keeping copper in slag within the 3 to 5% range, will be realised if Fe_3O_4 in both the FSF and SCF slag is kept within the limits recommended in this paper. Reduced Fe_3O_4 in FSF slag will also result in improved control of SCF blister temperatures and less metallurgical coke consumption. Magnetite will be the determining factor of what should be the degree of reduction to get the required copper in SCF slag, as is the practice in most smelters⁷. The trends show that SiO_2 is second in influencing the control of Cu in SCF slag. The smelter should therefore control the amount of SiO_2 in the feed mixture, so that it is around 23.7% in slag. Amplified influence of SiO_2 and other slag components in the control of Cu in the SCF will be indicated by coefficients of determination for the Fe_3O_4 - Cu relationship below 0.6. FSF slag containing higher Fe_3O_4 than desired by SCF should be cleaned at higher than normal temperature, to liberate the entrained metal prills. It is very important to remember that this should be done during FSF slag tapping when the bath is turbulent. This will favour the formation of large Cu prills that will settle very fast, thereby minimizing copper entrainment in slag.

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