

## **Olivine slags - the ultimate solution to low copper slags?**

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### **Abstract**

Background of direct blister copper smelting is discussed, especially copper solubility to iron silicate and calcium ferrite slags. The use of olivine type of slags has been introduced in the literature, and the theoretical possibilities to decrease copper solubility using these slags is shown. From practical and economical point of view the problem in blister copper making is with high amount of fluxes needed and thus high amount of slag produced when trying to reach the minimum copper solubility area for normal type of copper concentrates. However, for concentrates with low iron content and high copper content olivine type of slags are one interesting option to be used.

## **BACKGROUND OF BLISTER COPPER MAKING**

The dream for every copper metallurgist is to produce blister copper from copper concentrates continuously in one single stage. This would result to simplified process flowsheet, the converter aisle with converter and ladle emissions is a history, gas flow rate would be constant, less manpower is needed etc. The Outokumpu flash smelting process [1], which dominates modern copper production is a process where continuous process demands can be fulfilled. However, the main concept is to produce copper matte in flash smelting furnace, and then to convert the matte either continuously in a flash converting process or as a batch process in Peirce-Smith converters. Production of blister copper in one single stage has commercially been implemented in few special cases.

The dream to produce blister copper continuously in one single stage was thoroughly studied at the Outokumpu Research Center already in late 1960's. Extensive pilot test campaigns were carried out, and know-how about direct blister making was improved significantly. During several years the knowledge was deepened and the process became fully understood both theoretically and technically. It was proven that blister copper can be produced from chalcopyrite type of copper concentrate, however high gas streams and high heat load complicate commercial applications. The other possible drawbacks in blister copper making were notified such as significantly increased copper content in blister copper slags and decreased elimination of certain harmful elements. Increased copper content in the slag necessitates the use of a slag cleaning unit. One way to improve the economics of the blister copper making would be to somehow decrease the copper content in the slags.

Increased copper content in highly oxidising conditions is especially true when iron silicate slags are used in blister copper making. The copper content is inevitably above 20 wt-% Cu, when the target for sulphur content in blister copper is about 0.2 % S. These oxidising conditions increase the ferric iron content in slag and thus precipitation of magnetite due to limited solubility of ferric iron in iron silicate slags might cause problems in the furnace. This is true especially if temperature of the slag is not high enough.

Using calcium ferrite slags in highly oxidising conditions, problems with magnetite can be avoided. Calcium ferrite slags are able to dissolve ferric iron and precipitation of magnetite is no longer a problem. Calcium ferrite slags are liquid on a wide oxygen potential range with proper control of lime content in the slags. The other benefit using these slags is that the solubility of copper in calcium ferrite slag is considerably lower than in iron silicate slag. However, still the copper contents are quite high (about 17 wt-% Cu) and cause significant copper load in slag and thus blister copper making becomes economically unfeasible. One unwanted feature of calcium ferrite slags is also its limited ability to dissolve silica, and also these slags can cause problems for the refractories in the furnace.

## OLIVINE SLAGS

So what are options for a metallurgist to achieve the dream on blister copper making? Obviously a big problem in blister copper making conditions is the high solubility of copper as well into iron silicate slags as into calcium ferrite slags. One solution is to be found studying the literature. In the late 80's and early 90's several papers were published about the use of olivine type slags in copper metallurgy [2-4]. This idea has been refined and generally these olivine slags or ferrous calcium silicate slags are one option for a new type of copper smelting slag [5]. Regarding to blister copper making the low copper solubility to these slags is an interesting observation, and thus these slags are discussed in this paper.

Olivine type of slags are a combination of iron silicate slags and calcium ferrite slags, and can partly be described using  $\text{CaO-FeO}_n\text{-SiO}_2$  phase diagram. These ferrous calcium silicate slags are in the range of wollastonite  $((\text{Ca,Fe})\text{O}\cdot\text{SiO}_2)$  and olivine  $(2(\text{Fe,Ca})\text{O}\cdot\text{SiO}_2)$  and have a low melting point as can be seen from Figure 1 [6]. Olivine type of slags are used extensively for years in ferrous metallurgy. When these slags are in equilibrium with iron, one of the main concern is to avoid the area of dicalcium silicate  $(2\text{CaO}\cdot\text{SiO}_2)$ . This silicate has a very high melting point and can cause operational difficulties.

The effect of ferric iron can be seen from Figure 2 where a quaternary projection of system  $\text{FeO-SiO}_2\text{:CaO-Fe}_2\text{O}_3$  is shown at temperature 1300 °C with constant  $\text{CaO}/(\text{CaO}+\text{SiO}_2)$  -ratio (*i.e.*  $Q\text{-ratio} = 0.35$ ) [7]. The liquidus area is wide when ferric iron content is low, but by increasing ferric iron content in the slag the formation of spinel phase (magnetite) is evident. This would cause difficulties in practical operations due to increased viscosity of slags. However, in blister copper making conditions, the copper in slag is in oxidic form and constrains the formation of magnetite. Thus liquidus region in these slags is much wider than in Figure 2 for olivine slags, where copper is not present. This phenomena has been verified as well in laboratory scale studies [8,9] as in pilot plant and industrial scale by Outokumpu.

In pure calcium ferrite slags there is no silica present. Operational difficulties arise in furnaces using calcium ferrite slags if too much silica comes with the feed. Only about 5 wt-%  $\text{SiO}_2$  is enough in the slag system when the saturation of dicalcium silicate precipitation is reached. If more silica is added the viscosity of the calcium ferrite slag increases dramatically and the removal of slag from the furnace becomes difficult. Because most copper concentrates contain even up to 10 %  $\text{SiO}_2$  in the gangue minerals, calcium ferrite slags cannot be used in primary smelting. Another reason is high solubility of sulphur in matte making conditions to these slags. Calcium ferrite slags are therefore used today only in converting stage, when the amount of incoming silica can be kept in minimum.

## COPPER SOLUBILITY IN OLIVINE SLAGS

The solubility of copper in olivine slags (ferrous calcium silicate slags) has been studied by Yazawa, Takeda and co-workers [2-5]. Takeda presented Figure 3, where copper solubility at 1300 °C is as a function of oxygen partial pressure. Some of these copper solubility values are quite low, so could these slags be used in blister copper making?

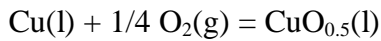
The solubility of copper is dependent on slag composition (basicity of slag), and the slag composition can be described using ratios Q and R (weight percent ratios), which are defined as follows

$$Q = \frac{CaO}{CaO + SiO_2} \quad R = \frac{FeO_n}{FeO_n + CaO + SiO_2}$$

The Q-ratio is thus the connection line from CaO-SiO<sub>2</sub> binary with various CaO compositions towards FeO<sub>n</sub> corner, and R-ratio is FeO<sub>n</sub> composition in the slag. These ratios are used in this paper to describe the composition of the CaO-SiO<sub>2</sub>-FeO<sub>n</sub> slags.

From Figure 3 it can be concluded, that at blister copper making conditions (sulphur content of blister 0.20 wt-% S, oxygen partial pressure  $p_{O_2} = 10^{-4.74}$  bar and  $p_{SO_2} = 1$  bar, the copper solubility in iron silicate slags (Q = 0.10-0.20) is about 21 wt-% Cu, with calcium ferrite slags (Q = 1.0) copper solubility is less being about 17 wt-% Cu, and with two ferrous calcium silicate slags the copper solubility is as low as 9.5 and 6 wt-% Cu. So these two latter values of copper contents would mean that copper solubility to the slags might be reasonable in blister copper making conditions.

The oxidic dissolution of copper is described by reaction



The equilibrium constant is defined by equation

$$K = \frac{a_{CuO_{0.5}}}{a_{Cu} \times p_{O_2}^{1/4}}$$

and the activity coefficient of oxidic copper in slag by following equation [2]

$$(\gamma_{CuO_{0.5}}) = \frac{K \times M_{Cu} \times a_{Cu(l)} \times n_T \times p_{O_2}^{1/4}}{(\%Cu)}.$$

Thus solubility of copper is inversely proportional to the activity coefficient of oxidic copper.

The equilibrium studies of Takeda [4] showed high activity coefficients when Q-ratio is between 0.45-0.55 and R-ratio about 0.20 as presented in Figure 4. The highest value for activity coefficient is 13. The corresponding copper solubility values in blister copper making conditions

were then calculated. The sulphur content in the blister copper was chosen to be 0.20 wt-% S, at 1300 °C oxygen partial pressure is  $p_{O_2}=10^{-4.74}$  bar and as discussed above the copper content is then 6.0 % Cu. Assuming further that activity coefficients in Figure 4 have same behaviour also on higher oxygen partial pressures than the measured range ( $p_{O_2} = 10^{-8} \dots 10^{-6}$  bar), copper contents in the whole slag range can be approximated from activity coefficients at oxygen partial pressure  $p_{O_2}=10^{-4.74}$  bar from the ratio

$$(\%Cu)_i \approx \frac{(\gamma_{CuO_{0.5}})_A}{(\gamma_{CuO_{0.5}})_i} \times (\%Cu)_A = \frac{13 \times 6.0}{(\gamma_{CuO_{0.5}})_i}$$

As activity coefficient value range of oxidic copper in Figure 4 is from 13 to 4, the corresponding calculated copper content range is from 6 to 19.5 wt-% Cu. The copper solubility values calculated from activity curves are presented in Figure 5. Curves were calculated using SigmaPlot ® -software, and the isocurve values are valid near shown points (these points correspond the points in Figure 4). As can be seen the copper solubility values are lowest at high Q-ratio and low R-ratio, and highest copper solubility values is with low Q-ratio and high R-ratio.

## MINIMUM COPPER SOLUBILITY AREA – THE ANSWER?

One obstacle in blister copper making is the high solubility of copper as well in iron silicate as calcium ferrite slags. Therefore according to Figure 5 it looks interesting to use a slag composition range where copper solubility is lowest ( $Q = 0.50\text{-}0.55$ ;  $R = 0.20\text{-}0.24$ ), about 6 wt-% Cu in the slag. A simple flash smelting material balance calculation procedure was carried out to study the blister copper making using this particular olivine type slag. Concentrate and fluxes (silica and lime) were inputs and blister copper and slag outputs.

To study the effect of smelted concentrate composition in blister copper making conditions, copper to iron ratio in the concentrate was varied and other components (sulphur, silica and other gangue oxides) kept as constant. The results are shown in Figure 6. According to the calculations the amount of fluxes needed to fix the composition of the slag to the lowest copper solubility composition drastically increases as copper to iron ratio is less than  $Cu/Fe = 3$  (concentrate composition about 45 wt-% Cu and 15 wt-% Fe). The amount of flux needed is then more than 70 % compared to the amount of concentrate feed. This big amount of fluxes has economical drawbacks. If flux addition is high, the amount of formed slag is also high. Although the content of copper in this kind of slag is low, the total amount of copper in the slag is high. Thus the direct recovery of copper to blister copper is poor and a great amount of copper goes into the slag. The slag needs a slag treatment unit and when amount of slag is more than three times the amount of blister copper, the cost of slag treatment becomes too high.

The calculated slag composition in Figure 6 corresponds 38 wt-% CaO, 21 wt-%  $FeO_n$ , 35 wt-%  $SiO_2$  and 6.5 wt-%  $CuO_{0.5}$ . To produce blister copper in a single stage using this kind of slag is only feasible if iron content in the concentrates is low enough. In the world copper concentrate market there are only few concentrates where copper to iron ratio is high enough, *i.e.* some concentrates in USA, Australia, Poland, Chile, and Congo. Normally copper to iron ratio in

copper concentrates is from 1 to 2, and with these kind of concentrates the amount of flux needed is far too high to reach a composition where copper content in the slag is lowest as can be seen from Figure 6. So next interesting question in our seek for a proper blister copper making slag is, if a certain slag composition could be found for a normal type of concentrate to produce blister copper in one single stage in a flash smelting furnace.

## **FINDING AN OPTIMUM SLAG COMPOSITION**

When results from the calculations with minimum copper content range in the olivine slag were not satisfactory, the next step was to study on wider slag range, if there could be an area where copper content and amount of flux needed would make a compromise. The calculations were carried out for concentrates where iron content in the concentrate varied from 25 to 14 wt-% Fe, and sulphur content from 30 to 22 wt-% S, and copper content in the concentrate was correspondingly from 30 to 45 wt-% Cu. Silica content was kept constant, 5 wt-% SiO<sub>2</sub>.

The calculations for blister copper were carried out when copper content in the olivine type of slag was from 6 to 19.5 wt-% Cu (see the points in Figure 5) with corresponding Q and R ratios. The results were similar with all concentrate grades, only the scale was different when copper content changed. With lowest copper content in the concentrate the iron content in the concentrate is highest and thus the amount of fluxes needed to form an iron containing slag is greatest, thus the behaviour is same as in Figure 6 where copper to iron ratio was studied for a specific slag composition.

### ***Amount of flux***

The graphs for amount of fluxes needed from calculations with 40 wt-% Cu in concentrate are shown in Figure 7. From copper solubility data (Figure 5) it is known that minimum copper content can be reached when Q-ratio is high and R-ratio is low. On the other hand copper content in the slag is highest when Q-ratio is low and R-ratio is high. Comparing this information to Figure 7, it can be seen that the amount of fluxes needed is less than 20 % of the amount of concentrate when R-ratio is above 0.5. This would be reasonable from practical point of view in blister copper making. Unsatisfactory flux amount is reached with lower R-ratio region. The flux amount strongly increases when R-ratio is less than 0.3, and this increase is promoted with increasing Q-ratio.

### ***Copper recovery to blister copper in flash smelting furnace***

Another important aspect when seeking for an optimum slag composition is direct copper recovery in the flash smelting unit. The calculations of direct copper recovery to blister copper in flash smelting unit is presented in Figure 8. The recovery describes the portion of the incoming copper, which is directly recovered to blister copper. Thus the copper content in the slag and the amount of the slag are involved in copper recovery calculations. According to the results direct copper recovery is best with high Q-ratio ( $Q = 0.50-0.55$ ) and low R-ratio ( $R = 0.20-0.40$ ), where

direct copper recovery is over 80 %. Also quite good direct recovery is with higher R-ratio,  $R = 0.58$  when  $Q = 0.45$ . This latter region is also a place where flux amount is not too high.

In blister copper making the amount of copper in the slag is inevitably high, and a separate slag cleaning unit is needed. Slag cleaning could be carried out in an electric furnace, where copper content is lowered for further cleaning. The final slag cleaning would be carried out in a slag concentrator, and the recovered copper slag concentrate would be recycled back to the flash smelting unit. Thus the total recovery of copper in the whole process concept is quite high because copper losses would occur only in the slag concentrator, where copper content in the tailings is about 0.3-0.4 wt-% Cu.

### ***Circulation of copper in blister copper making process***

Calculations were also made taken into account the whole circulation of copper in the blister copper making process. The amount of fluxes needed is the same also in this case as without copper slag concentrate circulation, if the recovery of silica and lime in the slag concentrator is assumed to be same order of magnitude. The general behaviour of flux amount as a function of slag composition is then same as in Figure 7. The consequences are that copper slag concentrate recycling increases the amount of the flash smelting slag. The amount of circulating copper as a function of slag composition is shown in Figure 9, and as can be seen the analogue is same than with amount of fluxes needed in Figure 7. The lower the R-ratio is (less iron in the slag, thus more fluxes are needed to reach low R-ratio values), the higher is the amount of circulating copper. The circulation of copper is lowest in the same region where the amount of fluxes is smallest, although solubility of copper in the slag is then highest. This means that in blister copper making with olivine type of slags the amount of fluxes needed and thus the amount of slag is more determining than low solubility values of copper.

### ***Economically optimum composition***

Still one possibility to find an optimum composition in blister copper making for olivine type of slags is to be checked. The question is, what happens when economical aspects are taken into account. For fictitious, simplified economical calculation, the cost of fluxes (silica 13 USD/t, lime 88 USD/t), electricity (total consumption in electric furnace and slag concentrator 150 kWh/t slag, cost of electricity 42 USD/MWh) and price of copper (copper revenues from blister copper taken into account the lost copper in tailings, price level 1600 USD/t Cu) were considered. Operating and other costs were not included in this simplified calculation. The calculated fictitious profit is shown in Figure 10 as a function of slag composition.

High amount of fluxes result to high amount of flash smelting slag and further to high copper losses into slag concentrator tailings. The economics do follow the same pattern. Best economical results are achieved when R-ratio in the slag is high. If R-ratio is constant, the economical result slightly improves with decreasing Q-ratio (decreasing lime additions). So from economical point of view it can as well be concluded that in the liquid slag region there isn't any superior slag composition to be found.

## **CAN OLIVINE TYPE OF SLAGS BE USED IN BLISTER COPPER MAKING?**

All the preceding examples have shown that our problem with great copper load in slags in blister copper making is not solved with olivine type of slags, although the laboratory scale equilibrium results from literature seemed to be promising. There are possibilities to use olivine type of slags in blister copper making, however from copper solubility point of view the most interesting area with minimum copper content in slag (high Q-ratio, low R-ratio) means for normal concentrates too high amount of fluxes and thus slag amount increases too much. For few special type of concentrates (very high copper to iron ratio) olivine slags can be used and then the amount of fluxes needed is not too high.

The whole preceding argumentation changes if impurities are taken into account. It is well known that calcium ferrite type of slags are better than iron silicate slags to remove impurities such as arsenic and antimony in blister copper making conditions. This same impurity removal ability applies also to olivine type of slags (ferrous calcium silicate slags) [5]. The removal of lead is contrary to pure calcium ferrite slags reasonably good with these ferrous silicate slags. So with impure concentrates the olivine type of slags are still an option in blister copper making

## **SUMMARY**

The dream to produce blister copper in single stage still has not yet come true for every type of copper concentrates, and the use of olivine type of slags is not the ultimate solution. The problem is with high amount of fluxes needed and thus high amount of slag produced when trying to reach the minimum copper solubility area for normal type of copper concentrates. However, for concentrates with low iron content and high copper content olivine type of slags are one interesting option to be used.

## **References**

1. Hanniala, P., Helle, L., Kojo, I.V., Competitiveness of the Outokumpu Flash Smelting Technology Now and in the third Millennium, Copper 99, Volume V – Smelting Operations and Advances, Ed., D.B. George, W.J. (Pete) Chen, P.J. Mackey, A.J. Weddick, TMS, 1999, 221-218.
2. Takeda, Y., Yazawa, A., Dissolution loss of copper, tin and lead in  $\text{FeO}_n\text{-SiO}_2\text{-CaO}$  slag. Productivity and Technology in the Metallurgical Industries, Ed. M. Koch, J.C. Taylor, TMS, 1989, 227-240.
3. Takeda, Y., Oxidic and sulfidic dissolution of copper in matte smelting slag. 4th International Conference on Molten Slags and Fluxes, Sendai, ISIJ, 1992.
4. Takeda, Y., The effects of basicity on oxidic dissolution of copper in slag. Metallurgical Processes for Early Twenty-First Century, Ed. H.Y. Sohn, TMS, 1994, 453-466.



5. Yazawa, A., Takeda, Y., Nakazawa, S., Ferrous calcium silicate slag to be used for copper smelting and converting, Copper 99, Volume VI – Smelting, Technology Development, Process Modelling and Fundamentals, Ed., C. Diaz, C. Landolt, T. Utigard, TMS, 1999, 587-599.
6. Schlackenatlas – Slag atlas, Verlag Stahleisen M.B.H., Düsseldorf, 1981.
7. Taskinen, P., MTDATA – an advanced program for thermodynamical equilibrium calculations, Internal Report, Outokumpu Research Oy, 24.1.2000
8. Geveci, A., Elliott, J.F., Formation of Slag Phase in the System Cu-Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>, Second International Symposium on Metallurgical Slags and Fluxes, Ed. Fine, H.A., Gaskell, D.R., AIME, NY, 1984, 547-559.
9. Rosenqvist, T., Thermodynamics of Copper Smelting, Advances in Sulfide Smelting, Vol. I, Basic Principles, Ed. Sohn, H.Y. et al. TMS-AIME, Warrendale, 1983, 239-255.

# CaO-FeO-SiO<sub>2</sub>

Bild 87: System CaO-FeO-SiO<sub>2</sub> bei Sättigung an Eisen nach Osborn und Muan [VII].  
Figure 87: The system CaO-FeO-SiO<sub>2</sub> given iron saturation after Osborn and Muan VII

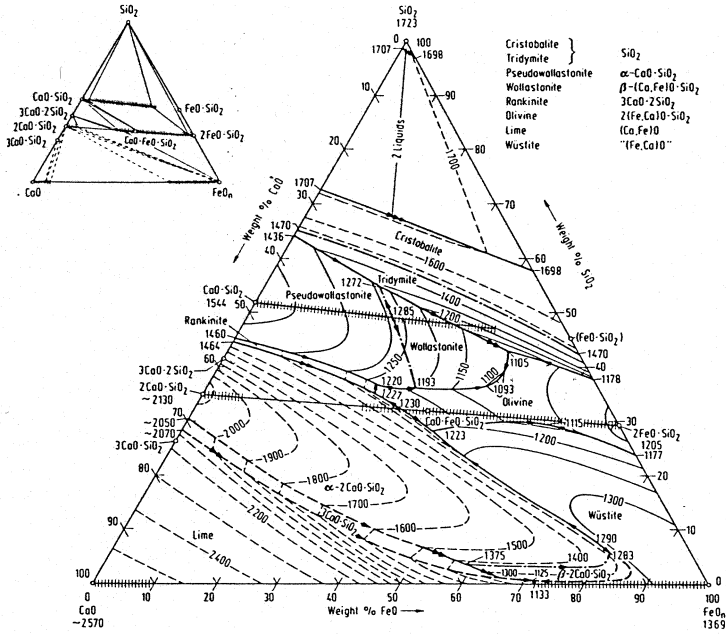


Figure 1. System CaO-FeO<sub>n</sub>-SiO<sub>2</sub> [6].

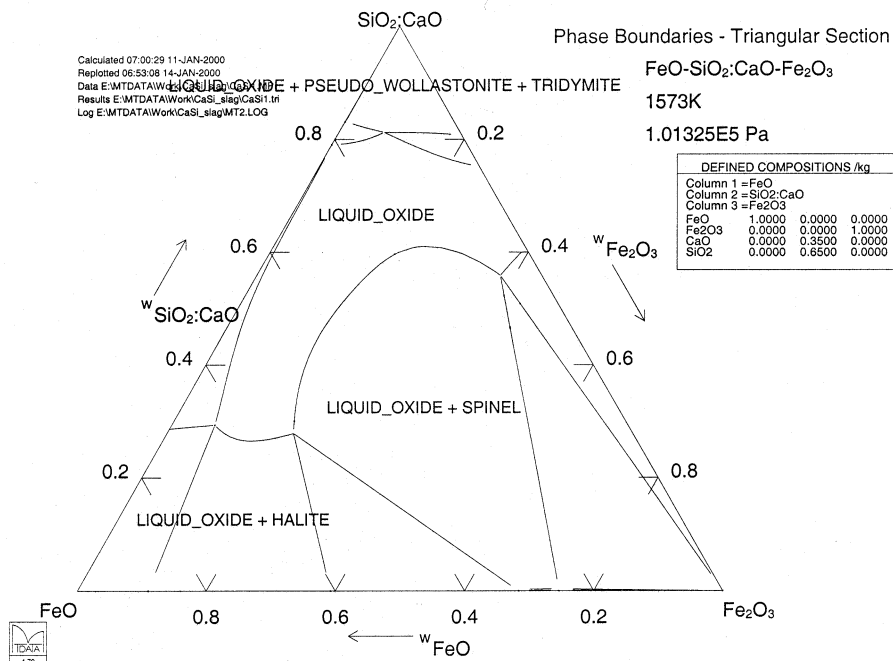


Figure 2. System CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with constant Q-ratio 0.35 at temperature 1300 °C [7].

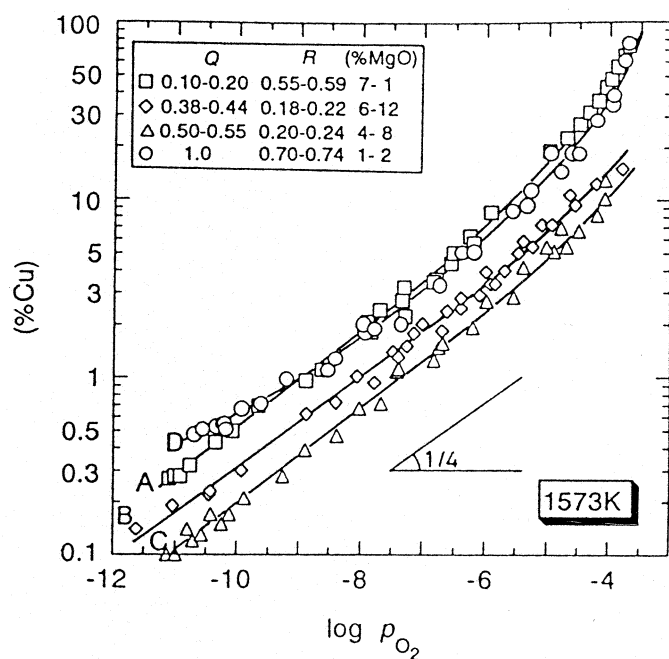


Figure 3. Copper solubility in  $\text{CaO-SiO}_2\text{-FeO}_n$  slags in oxygen potential range from iron saturation to  $\text{Cu}_2\text{O}$  saturation [4].

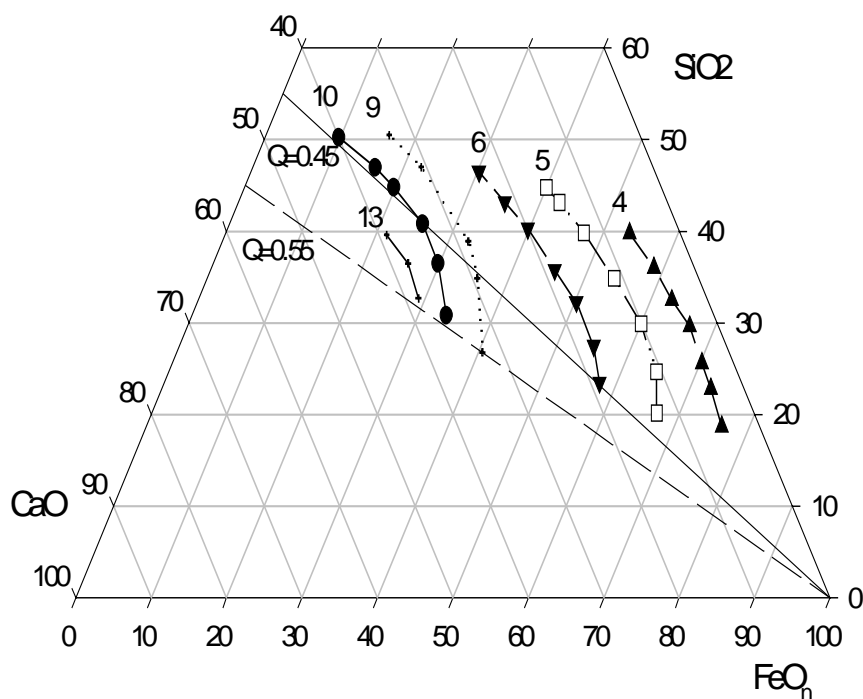


Figure 4. System  $\text{CaO-FeO}_n\text{-SiO}_2$  and activity coefficient of  $\text{CuO}_{0.5}$ , 1300 °C, oxygen partial pressure  $10^{-8}\dots 10^{-6}$  bar, data from [4]. Compositions in wt-%.

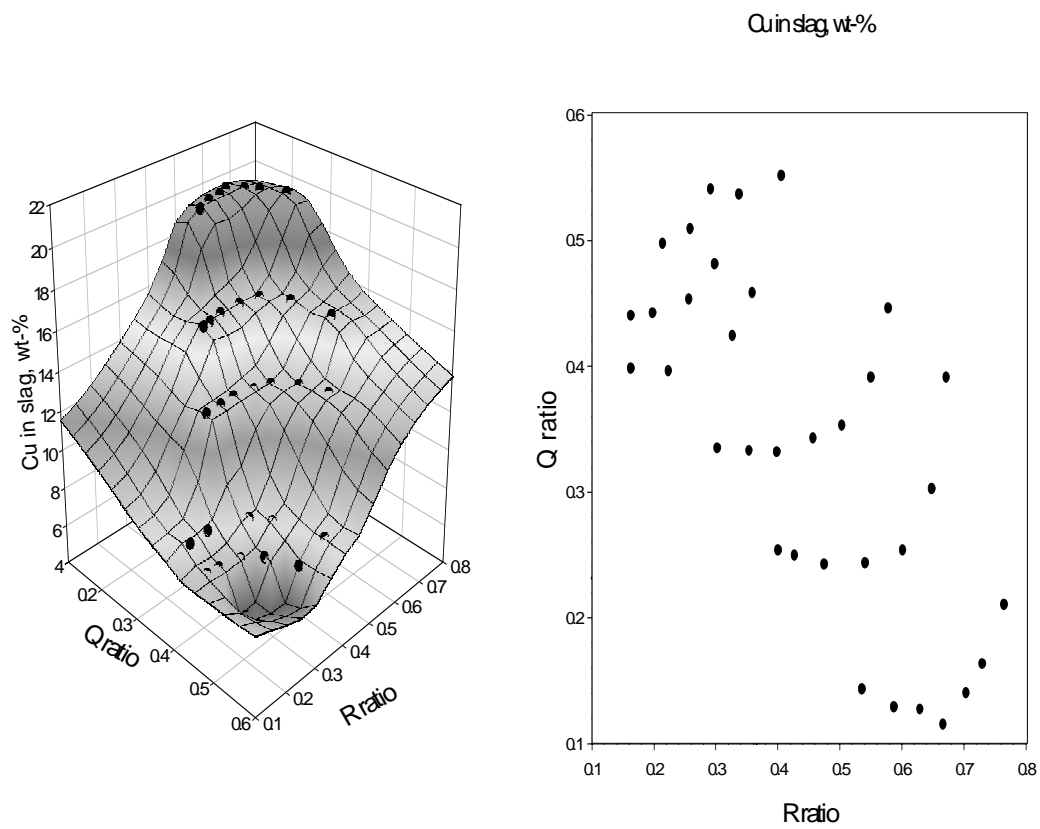


Figure 5. Calculated copper solubility in  $\text{CaO-FeO}_n\text{-SiO}_2$  slag in blister copper making conditions from activity coefficient values. Calculations are valid near marked points, and slag may not be homogeneous in the whole composition range in true blister copper making conditions.

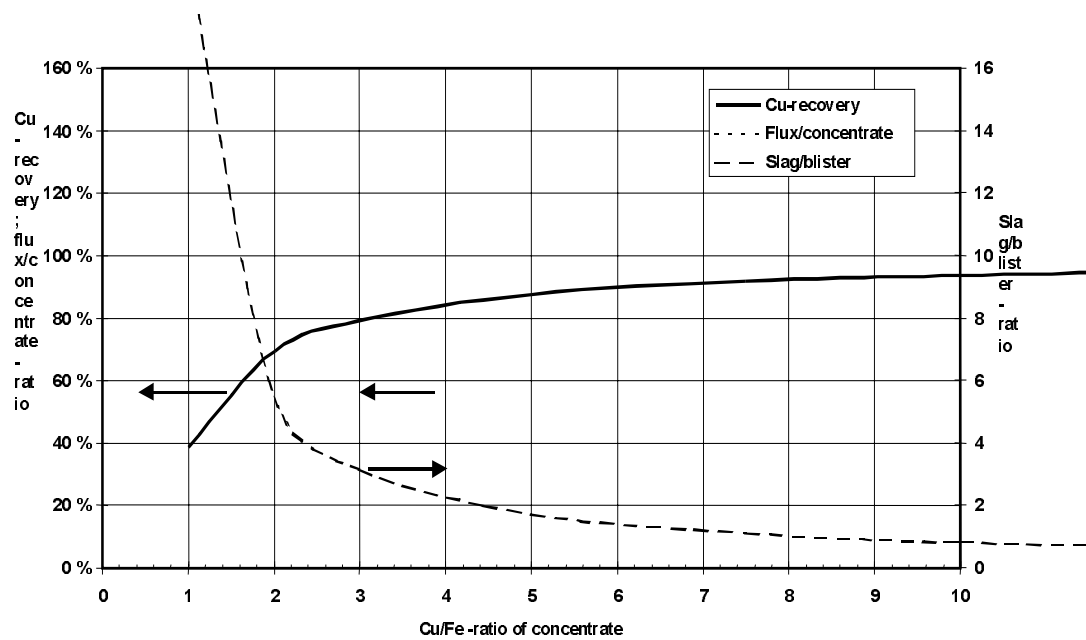


Figure 6. The effect of copper to iron ratio in copper concentrates to flux amount, copper recovery and slag amount.  $Q = 0.50-0.55$ ,  $R = 0.20-0.24$ , 6 wt-% Cu in  $\text{CaO-FeO}_n\text{-SiO}_2$  slag.

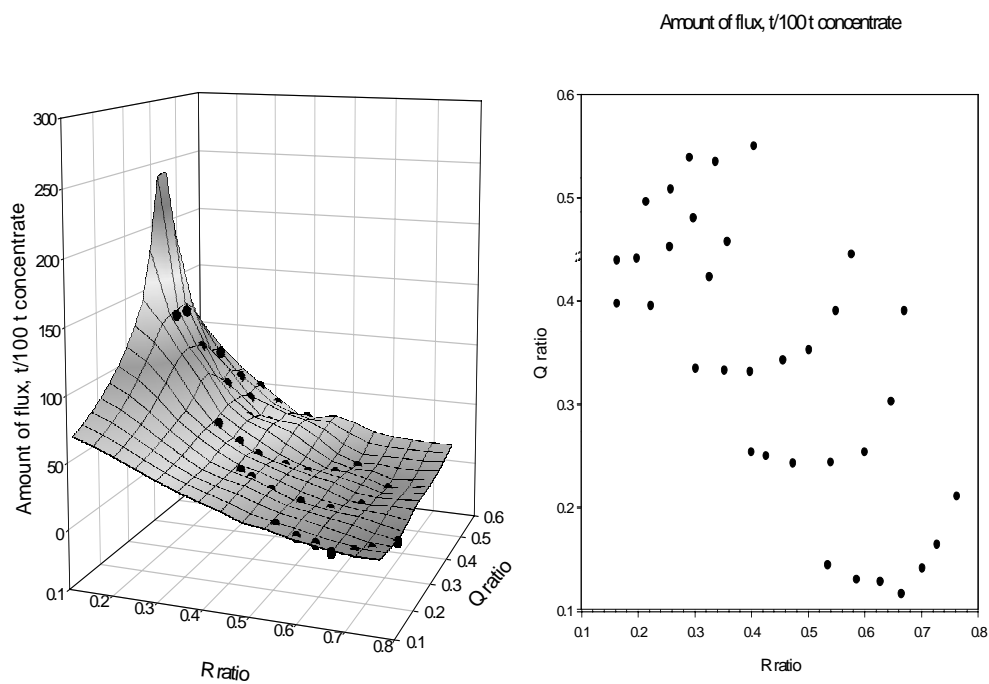


Figure 7. Amount of flux compared to the amount of concentrate with various  $Q$  and  $R$  ratios in  $\text{CaO-FeO}_n\text{-SiO}_2$  slag in direct blister flash smelting of copper concentrates with 40 wt-% Cu. Calculations are valid near marked points, and slag may not be homogeneous in the whole composition range in true blister copper making conditions.

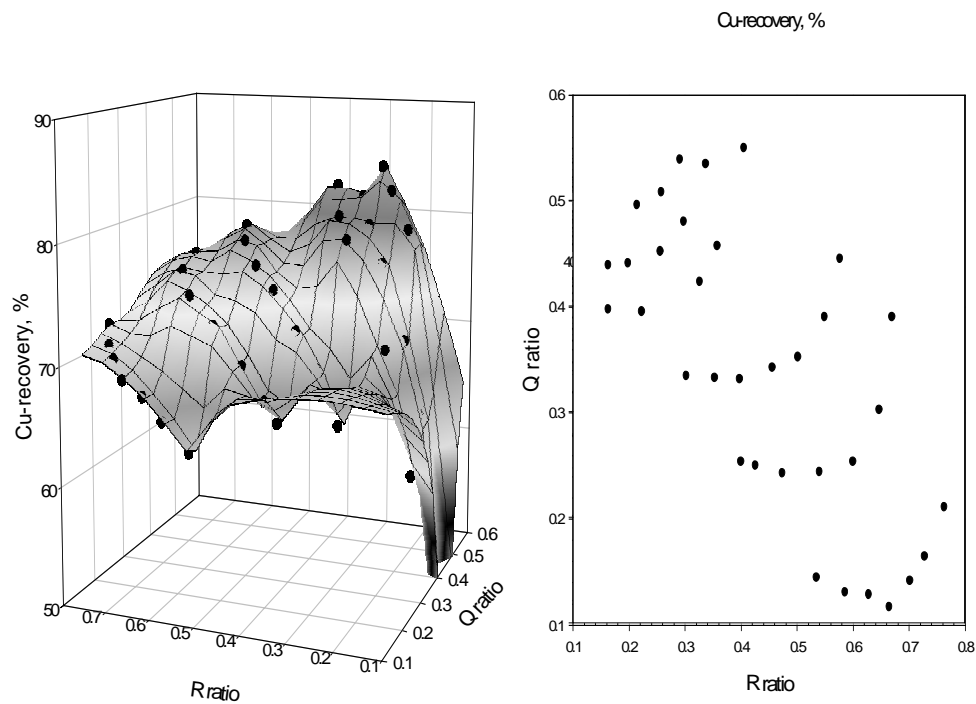


Figure 8. Direct copper recovery to blister copper with various Q and R ratios in  $\text{CaO-FeO}_n\text{-SiO}_2$  slag in flash smelting of copper concentrates with 40 wt-% Cu. Calculations are valid near marked points, and slag may not be homogeneous in the whole composition range in true blister copper making conditions.

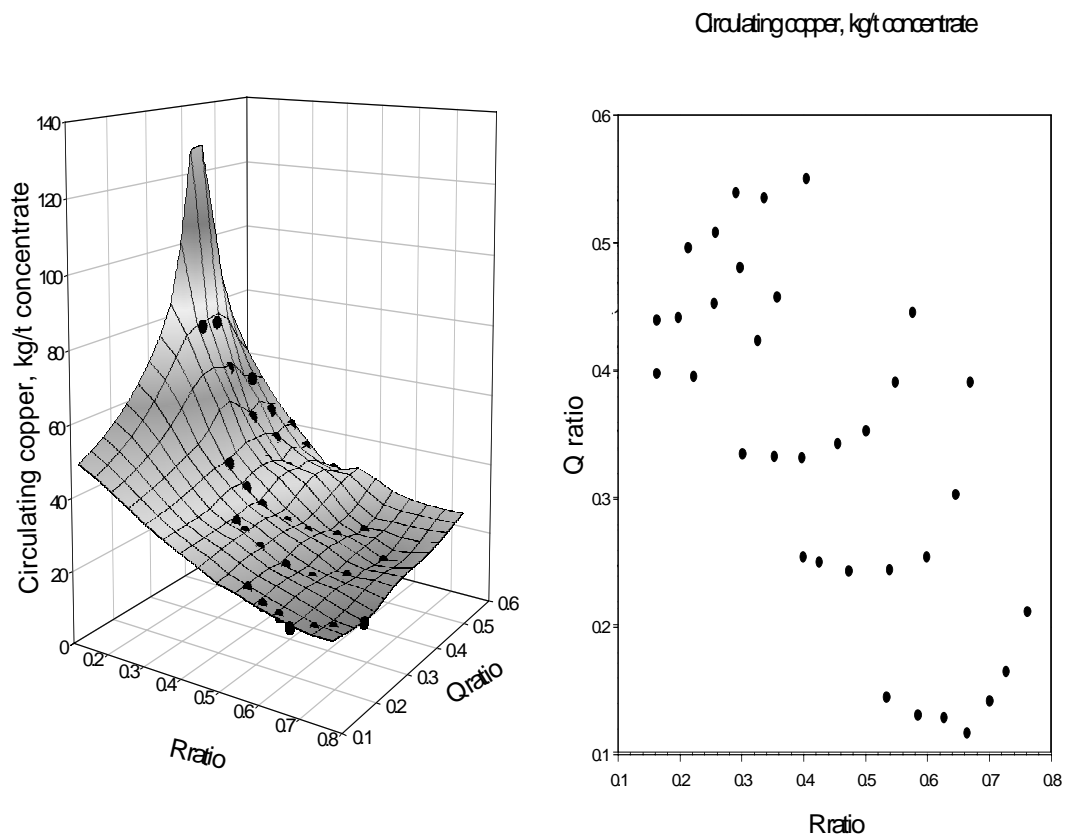


Figure 9. Circulating copper in blister copper flash smelting with slag cleaning and copper slag concentrate recycling with various Q and R ratios in  $\text{CaO-FeO}_n\text{-SiO}_2$  slag. 40 wt-% Cu in copper concentrate. Calculations are valid near marked points, and slag may not be homogeneous in the whole composition range in true blister copper making conditions.

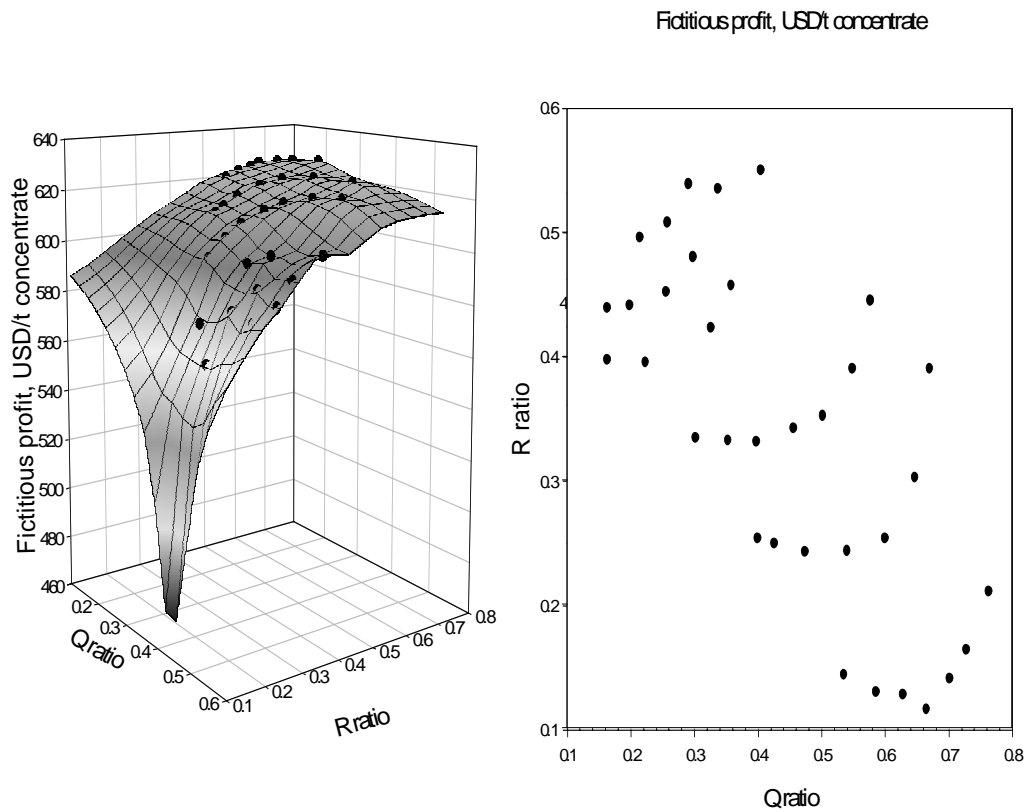


Figure 10. Fictitious profit, USD/t concentrate in blister copper flash smelting with slag cleaning and copper slag concentrate recycling with various Q and R ratios in  $\text{CaO-FeO}_n\text{-SiO}_2$  slag. 40 wt-% Cu in copper concentrate. Calculations are valid near marked points, and slag may not be homogeneous in the whole composition range in true blister copper making conditions.