

## CALCIUM AND CALCIUM SILICATE SLAGS IN COPPER PROCESSES

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Because its wide liquid area, high solubility of ferric iron and affinity for acidic elements such as arsenic, etc., calcium ferrite slags have proved a suitable alternative to iron silicate slag in copper pyrometallurgical processes. Its use in converting and fire refining is a standard practice at Chuquicamata, as well as in other smelters.

Since long ago in the smelting stage the tendency is to produce matte grade in the range 60% - 75% in copper content. However, because the restricted solubility of magnetite even at temperatures over 1573 K, the traditional  $\text{SiO}_2 - \text{FeO}_n$  system results in high viscosity high copper content in slag and loss of smelting capacity. Furthermore, the converting of high matte grades presents similar problems when using silica flux. Therefore, for the production of high matte grades and/or during converting, where high oxygen potentials are involved, the use of silicate slag is rather inconvenient.

In the case of smelters dealing with dirty concentrates minor elements behaviour imposes restrictions on the matte, blister and anode copper quality. Eventhough, the chemical quality of the matte, blister and anode copper may be improved it would be at the expenses of the mass of slag and/or the recovery of copper. Similarly, in the case of high grade concentrates the direct production of blister copper is desirable but its processing via silica flux presents several disadvantages.

In industrial operations, no matter special precautions are taken for the preparation of the charge, the presence of significant contents of lime or silica in silica or calcium base slags, respectively, is unavoidable. Therefore, in the converting of high matte grades or the direct production of blister, because the limited solubility of silica in calcium ferrite melts, a different slag system has to be considered.

By properly selecting the lime to silica ratio different sulfidic materials mixtures were processed to blister copper within encouraging slag fluidity, low copper content in slag and reasonables arsenic and sulfur contents in metal.

## INTRODUCTION

Lime or calcium oxide is a wellknown basic component in the slags used in iron and steelmaking, as for example reported by Hillenbrand et. al. <sup>(1)</sup>. However, its application in the nonferrous industry has not been as fast and/or wide application as it should be desirable. Its behaviour as a modifier of the viscosity in  $\text{SiO}_2\text{-FeO}_x$  slags, under coexistence of matte or copper phases, has been the matter of numerous studies, i. e. Altmann et. al. <sup>(2)</sup>, Kowalczyk et. al. <sup>(3)</sup> and Acuña et. al. <sup>(4)</sup>. Nevertheless, it was just in the 70's when Mitsubishi, as reported by Goto et. al. <sup>(5)</sup> considered its use as a major component of the slag system in equilibrium with copper metal. Also in the late 90's Kennecott turned to lime based slag in its flash converting process, Hanniala et. al. <sup>(6)</sup>. Despite this situation, no further industrial applications have been reported, eventhough it has been considered by most of the companies, i. e. Outokumpu, Noranda, Ausmelt, Robilliard et. al. <sup>(7)</sup> etc.

Phase equilibria in the  $\text{CaO-FeO-Fe}_2\text{O}_3$  ternary system coexisting with matte and/or copper phases have been studied by Takeda et. al. <sup>(8)</sup> and Nikolov et. al. <sup>(9)</sup>, at high sulfur dioxide partial pressures by Roghani et. al. <sup>(10)</sup> and the mutual solubility for two and three liquid phase equilibria, matte-slag and copper-matte-slag, respectively, has been reported by Acuña et.al <sup>(11)</sup> and by Roghani et.al. <sup>(12)</sup> for slag-matte equilibria under high partial pressures of sulfur dioxide. From these studies is clear the wide liquid area of the  $\text{CaO-FeO-Fe}_2\text{O}_3$  system, allowing to operate under very low and high oxygen potentials, i. e.  $10^{-12}$  to  $10^0$ .

The effect of silica upon the liquid area of the  $\text{CaO-FeO-Fe}_2\text{O}_3$  system at low oxygen potentials was reported by Osborn et.al <sup>(13)</sup> and the dissolution of silica under iron and magnetite saturation by Acuña et.al <sup>(14)</sup>. Furthermore, physical properties have been compiled by Diaz et. al. <sup>(15)</sup>, Okamoto et. al. <sup>(16)</sup> studied density and surface tension and Sakai et. al. <sup>(17)</sup> reported the effect of oxygen and sulfur pressures and lime content on surface and interfacial tensions in copper-calcium ferrite slag systems. Kucharski et. al. <sup>(18)</sup> reported activity data for copper oxide and wustite in the system  $\text{CaO-Cu}_2\text{O-SiO}_2\text{-Fe-O}$  at 1523 K and Hino et. al. <sup>(19)</sup> and Acuña et. al. <sup>(20)</sup> studied the effect of silica on the  $\text{CaO-Cu}_2\text{O-FeO}_n$  ternary. From these studies is concluded that the dissolution of silica increases with the sulfur dioxide partial pressure and a similar effect is reported for surface and interfacial tensions at fixed oxygen potential, but they are slightly dependent on lime content in the slag.

Distribution behaviour of impurities in the  $\text{CaO-FeO}_n$  system have been reported by Park et. al. <sup>(21)</sup> for lead and by Acuña et. al. <sup>(22)</sup> for arsenic, antimony, lead in two and three liquid phase equilibria and the effect of silver, bismuth, arsenic, antimony and lead under high sulfur dioxide partial pressures slag-matte equilibria by Roghani et. al. <sup>(23)</sup>. The capacity of this system to concentrate acid impurities, while rejecting those of basic character to the coexisting matte phase, has been established over any reasonable doubt.

The strong affinity of basic, i.e. calcium, sodium, barium, etc., for acidic, i.e. arsenic, antimony, etc, presents a reasonable approach for the treatment of dirty concentrates. Eventhough slagging of these impurities during smelting and/or converting proceeds at a large extent, they also reports to the coexisting matte and/or metal phases and stronger flux mixtures have to be used, specially in the fire refining stage. In such situations slagging by lime-soda slag is possible and the system may be represented by the  $\text{CaO-Na}_2\text{O-Cu}_2\text{O/FeO}_n$  pseudoternary. Despite this fact it has to be

kept in mind that the use of soda slag is restricted to applications where a strong effect is required, i.e. fire refining of high content arsenic, antimony, etc., blister copper. Basic relations in the copper-lime soda slag system have been reported by Fukuyama et. al. <sup>(24)</sup> and Yokokawa et. al. <sup>(25)</sup>, among others. From these results is concluded that acidic impurities are strongly concentrated in the slag phase when lime soda flux is used.

Fears on the effect of basic slags upon the refractory lining has prevented its wider application at industrial scale. However, the real reason for this effect might lay on the reactivity of some process products, i.e. the extremely fluid and aggressive copper oxide, towards the lining, the chemical/physical properties of the refractory bricks and/or operational conditions.

## LIME IN COPPER PYROMETALLURGICAL PROCESSES

To talk about pure silicate or calcium slags does not make sense since normal concentrates always contain some percentages of silica, lime and others. Assuming silica flux is used, i. e. in the smelting stage, the lime in the concentrate and in the flux reports to the slag phase and certainly its effect has to be assessed. A similar situation happens when lime flux is used.

In the event in the productive chain a combination of fluxes is used, i. e. silica in smelting and lime in converting, carryover of these from one to the next stage is unavoidable. For example during tapping of matte its contamination with the equilibrating slag is wellknown in industrial operations. Therefore, if in the next step a different flux is used, the effect of silica or lime, whatever it applies, on the liquid area of the new slag system has to be considered.

## LIME IN COPPER SMELTING

The use of lime in matte smelting is not widely practiced mainly because of economical reasons, i. e. higher price in comparison to silica and fears of its effect on the refractory lining. Despite this fact, in low concentrations it can be used as a viscosity modifier, as shown in Figure 1 for three types of slags produced at the Chuquicamata smelter. The tendency observed in these curves is a minimum in viscosity for a range 4%-9%CaO content in the case of low and/or intermediate oxygen potentials, i. e. in slag cleaning operations (SCF) and matte grades about 60%Cu in the Flash Outokumpu reactor (FSF), and 7%-15%CaO in the case of high oxygen potentials, as for the case of El teniente Converter producing matte grades about 75%Cu. Furthermore, it is observed that the effect of lime on viscosity is much deeper when operating at high degree of oxidation, i. e. two times lower in the case of the CT operating at approximately  $10^{-7.2}$  in oxygen potential, when doing at reduced degrees, i. e. 1.1 times lower in the case of the SCF at about  $10^{-10}$  in oxygen potential.

The CaO-FeO-Fe<sub>2</sub>O<sub>3</sub> ternary, corresponding to the pure calcium ferrite slag system is shown in Figure 2, where for comparison purposes also the SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub> ternary is included. From these diagrams the effect of lime upon the extent of the liquid area is clear, a wide zone allowing to operate under extreme conditions of oxygen potentials without the problems associated to viscous slags and magnetite precipitation. Similarly, from these diagrams is evident that silica restricts the liquid area and the same effect is shown by decreasing the temperature of the slag. Furthermore, it is observed that working at a fixed oxygen potential, i. e. at -9 or 0 as represented

by dashed-dotted lines for the log of the sulfur dioxide partial pressure at 1573 K in Figure 2, an increase in lime content allows to operate under more oxidizing conditions (higher  $\text{Fe}^{+3}$  over  $\text{Fe}^{+2}$  ratio), while the opposite occurs if silica slag is used.

The distribution behaviour of impurities between condensed phases may be defined by:

$$L^{s/m}_X = (\text{wt\% X}) / \{\text{wt\% X}\} \quad [1]$$

where wt% means the mass percentage of the impurity X and ( ) and { } represent two coexisting phases, i. e. slag and matte. In Figure 3 the distribution coefficients for arsenic, antimony, lead and bismuth for matte–slag equilibria is presented with full lines for the equilibria involving calcium ferrite slags and dashed lines for silicate slags, Yazawa et. al. <sup>(26)</sup> and Johnson et. al. <sup>(27)</sup>. By comparing these distribution behaviours is clear that acidic impurities, i.e. arsenic and antimony, concentrates strongly in calcium ferrite slags when compared to silicate slags. Similarly, rather basic impurities concentrate mainly in silicate in comparison to calcium slags.

Based on the values presented in Figure 3, i. e. for the distribution coefficient of arsenic and antimony for slags coexisting with a matte grade 70%Cu, is concluded that acid impurities are approximately two order of magnitude higher while basic impurities, i. e. lead, concentrate at least ten times higher in matte.

## LIME IN COPPER CONVERTING

Depending on the matte grade to be converted one or two process step is required. Low matte grades may go through slag blowing, with intermediate slagging and matte charging, until white metal composition is reached. From here on, blister blowing with minimum slag formation and high magnetite production is done. At the end of the slag blowing and during blister blowing the oxygen potential has to be raised resulting in “mushy” highly viscous and high magnetite slags, which precipitate on the furnace’s hearth. As a result high copper content slags are produced, which requires its further treatment for copper recovery, and intensive furnace cleaning for magnetite remotion, to keep furnace capacity.

The effect of temperature on the liquid area of the ternary  $\text{CaO-FeO}_n\text{-Cu}_2\text{O}$  system is shown in Figure 4. Decreasing temperature results in shrinking the liquidus area towards the  $\text{Cu}_2\text{O}$  corner of the ternary, it means that under such situation high copper content slags will be produced. On the other hand, it is observed that at a fixed temperature, i.e. 1573 K by properly selecting the composition of the slag might be possible to produce copper free slags. However, if some silica dissolves in the system, as shown in Figure 5 for the  $\text{Cu}_2\text{O-FeO}_n\text{-CaO-12\% SiO}_2$  pseudoternary, the liquidus area is reduced towards the  $\text{Cu}_2\text{O}$  corner and higher silica contents will further shrink the liquid region. In such situation the molten area would lay very close to the  $\text{Cu}_2\text{O}$  corner of the system and therefore high copper content slags will be produced.

The mineral ores in the Calama area are high in arsenic content and so are the concentrates. For this reason during the converting of the white metal produced in the Teniente Converters, limestone in a ratio 1:30, respect to the mass of the charge to process, is used. By this procedure arsenic slagging was increased from let say 30% to 60%, in comparison to the old procedure of

using silica flux. Furthermore, slag fluidity increased with no signs of refractory wear over that caused by the use of silica. In the case of the Caletones smelter limestone is being tried successfully in the semicontinuous converting of white metal, resulting in the avoidance of “mushy” and high copper content silicate slags.

## LIME IN DIRECT COPPER PRODUCTION

In the case of the direct production of blister from concentrates, as for example in Glogow, Plucinski et. al. <sup>(28)</sup>, and Olympic Dam, Hunt et. al. <sup>(29)</sup> the traditional silica flux is unsuitable. In spite of the fact that the concentrates are chalcosite type the mass of slag is low, but because the high oxygen potentials involved and in the event of using silica flux, it would result in highly viscous and extremely high copper content slags. Furthermore, if the concentrates are high in impurity contents, as for example lead and arsenic at Glogow, these would report mainly to the metal phase imposing an intensive slagging operation at the fire refining stage. If at refining no intensive slagging is desired, in the melting/converting stage a higher oxidation has to be done resulting in huge mass of slag.

By using a calcium base slag is possible to decrease the precipitation of magnetite and to increase slagging of acidic impurities. Despite this fact, basic and/or neutral character impurities, as for example lead and bismuth, will concentrate in the metal phase. Furthermore, due to the strong affinity of these impurities with metals significant levels of them will report to the metal phase producing a high impurity blister or semiblister copper, which has to go intensive slagging/oxidation to produce the quality of anode copper required at the tankhouse.

Continuous direct production of copper from sulfide mixtures were done by top blowing at the level of 100 kg/h at approximately 1523 K and under coexistence of white metal phase. The results obtained in terms of the distribution coefficient of arsenic between slag and blister copper is defined by:

$$L^{s/c}_{As} = (\%As) / [\%As] \quad [2]$$

with the same meaning as in equation 1, but c and [ ] represent the copper phase, in relation to the CaO to SiO<sub>2</sub> ratio in slag are shown in Figure 6. The tendency observed is an increase in distribution coefficient with increasing slag basicity or lime to silica ratio, suggesting that the arsenic content in blister copper may be reduced by the use of high lime slags. Regarding the order of magnitude of the distribution coefficient of arsenic between slag and copper phases, it is similar to that corresponding to three liquid calcium ferrite slag-high matte grade-copper equilibria, i. e. Acuña et. al. <sup>(22)</sup>.

Industrial tests on continuous copper production were done by injecting a sulfide mixture, high in arsenic content, under molten white metal. The level of the tests was about 65 ton of charge per hour, corresponding to the sulfide mixture plus a lime/silica flux, and the process temperature was in the order 1523 K. The results, in relation to sulfur and oxygen and copper content in blister, are presented in Figure 7. The tendency observed is a decrease in sulfur with increasing oxygen and copper content in blister. Similarly, the relation among arsenic, oxygen and copper content in blister is presented in Figure 8, resulting in the same tendency, i. e. higher dissolution

of oxygen produces a decrease in arsenic and increase in copper content in blister. These results indicate that arsenic and sulfur compete for the oxygen dissolved in the melt, increasing the copper content in blister.

In respect to the results from the industrial test and the blister quality required at fire refining some comments have to be done. For example at Chuquicamata a typical blister contains about 2,500 ppm arsenic, 300 ppm sulfur and 7,000 – 8,000 ppm oxygen, which requires approximately three quarter an hour oxidation, half an hour complexing by soda-lime mixtures and one hour and a half reduction. No doubt the blister quality obtained in the industrial direct copper production will result in extensive oxidation, complexing and reduction, in order to comply with the requirements at the fire refining stage. In such situation to maintain anode copper production additional refining capacity, i. e. to increase the number of reactors, must be considered.

### LIME IN COPPER REFINING

In the fire refining of copper a standard practice is to use a mixture of soda and lime and from the point of view of the slag it may be considered as the  $\text{Cu}_2\text{O}-\text{Na}_2\text{O}-\text{CaO}$  system. Despite there is no much information on this system, the lime to soda ratio, which depends on the specie to be slagged and its desired content in blister copper, is normally 3:1 or 1:1.

Isothermal lines for the  $\text{Cu}_2\text{O}-\text{CaO}-\text{Na}_2\text{O}$  system, corresponding to test run under air atmosphere, are presented in Figure 9. It is observed that decreasing the temperature the liquidus area shrinks towards the  $\text{Cu}_2\text{O}-\text{CaO}$  axis, while higher temperatures expands the area suggesting a tendency for  $\text{CaO}*\text{Na}_2\text{O}$  interaction. From the tendency depicted in this figure is clear that low copper slag, i. e. below 50%  $\text{Cu}_2\text{O}$ , are only possible at temperatures over 1523 K and high soda and/or lime contents. From the curves in Figure 9 might be deduced that soda has a deeper effect than lime in widening the liquidus area or that, at the same temperature, copper in the slag decreases at the expenses of soda rather than lime. However, similar copper contents in slag may be obtained by a proper selection of the lime to soda ratio, as for example 1:1  $\pm$  10% for a 50%  $\text{Cu}_2\text{O}$  at a range in temperature between 1493 K to 1573 K. In this way the aggressiveness of soda is replaced by the milder lime resulting in a lower probability of attack on the refractory lining.

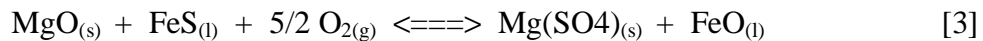
At Chuquicamata smelter a standard practice consists of using a 1:2 ratio of soda to partly roasted limestone, which at a temperature of 1473 K results in slagging between 140-180 kg of arsenic per ton of injected flux mixture.

### SLAG REFRACTORY INTERACTION

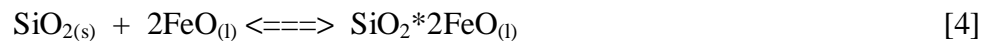
In copper pyrometallurgy a standard procedure for lining the inner refractories with a magnetite layer is followed. This practice has its origin when acid character bricks were used and nowadays its use responds to the necessity of extending the refractory lifetime. From the physicochemical point of view a stronger interaction basic refractory (chromium-magnesite) acid slag (silicate type) should be expected when compared to a basic refractory basic slag (calcium or calcium silicate type). However, if physicomechanical effects predominates the situation might be different.

Due to the reduced capacity of silicate slag to dissolve magnetite, the brick magnetite layer can endure for long time abrasive environments, such as viscous slag, waving, etc. In spite of the high capacity of calcium ferrite slag to dissolve magnetite the refractory protective magnetite layer is meaningless and decrease in its lifetime has to be expected. To reduce this effect the slag line is heavily protected by water refrigerated copper blocks.

Although the slag line is the major concern when using calcium base slags, the refractory lining along and beneath the matte and blister copper areas has been detected to be affected at a similar degree that when using silicate slags. In the first case this effect may be explained by the sulphatation action of the matte, which can be represented by:



favoured thermodynamically, specially at low matte grades and high temperatures. Practical evidence has been found in the inner and lower brick rows in the form of magnesium sulfate, but not chromium sulphate, the other major brick component. Some brands of the serie chromite 40%-magnesite 60% of wide application in copper pyrometallurgy, contains significant levels of silica as binding agent. On service this silica may react with specie of iron oxides in the slag to produce low points compounds, as for example fayalite, according to the reaction:



Reaction products will change the temperature profile and therefore infiltration of the refractory lining by slag, matte and or blister copper, would be enhanced. The situation may be even worse when bricks of poor physical characteristics are used, as for example high open porosity, low density, etc. In such situation, even in absence of reaction products, the bricks will be easily impregnated and the whole temperature profile will change, causing interlayer accretions and hearth/bottom raising, effect which has been ascribed to hearth raising in flash furnaces.

One example of brick degradation ascribed to slags is shown in the Micrographs 1 and 2, where Micrograph 1 and Micrograph 2 correspond to a brick in contact with molten white metal and calcium silicate slag, respectively. In both cases by SEM X-Ray analysis the presence of magnesite, chromite, sulfides, a silicate matrix and a Ca-Mg-S-O compound were detected. Because of the similarity of both morphologies/microstructures may be advanced that the mechanism of infiltration in the bricks is consistent with their high open porosity. Furthermore, the presence of a "silicate matrix", independently if the bricks were in contact with molten copper, white metal or slag, denotes the existence of silica over reasonable levels for this application.

Because its surface finishing bricks facing the melt constitute favourable sites for bubble nucleation and therefore erosion-abrasion effects are enhanced. Similarly, specially at high oxygen potentials, metal surface tension decreases and the refractory lining is much easier infiltrated/impregnated by the melts.

At Caletones Smelter during the semicontinuous converting of white by calcium silicate slag was found that the refractory lining decreased at a rate of 0.013 mm per 40 tons of charge, while in

batch mode and use of silicate slag it did at 0.026 mm. These results suggest that refractory wearing by calcium and/or calcium silicate slags might be lower, or at least similar, to that produced by the use of silicate slags.

## CONCLUSIONS

High matte production, as well as the direct production of blister copper, by calcium base slags presents several advantages over the use of silica flux, specially from the point of view of magnetite precipitation, and therefore copper content and distribution of acid impurities to the slag. Despite these facts, typical copper concentrates contains significant levels of silica which reports to the slag phase and consequently its effect on the slag system must be assessed. Assuming the full benefits of lime are obtained in the smelting-converting step, less intensive slagging via refractory aggressive soda base slag is required at the fire refining stage.

In spite of the attractiveness in using lime flux its interaction with the refractory bricks need to be clarified, specially as a function of its chemical stability against copper oxide, iron sulfide and physical properties, i. e. density, surface finishing, open porosity, etc.

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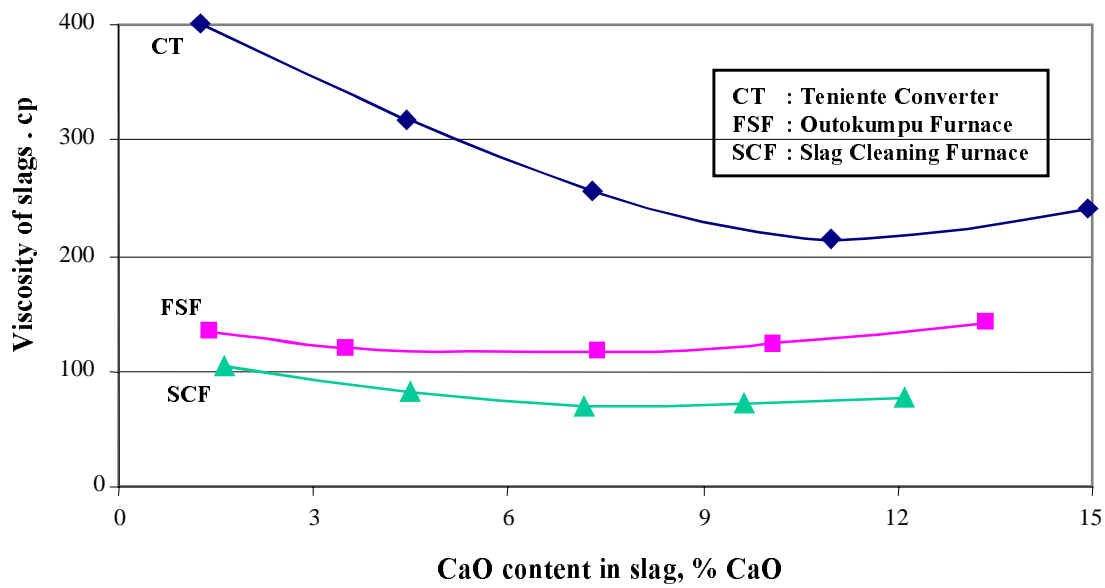


Figure 1 : Effect of lime content on the viscosity of various Chuquicamata slags at 1523 K.

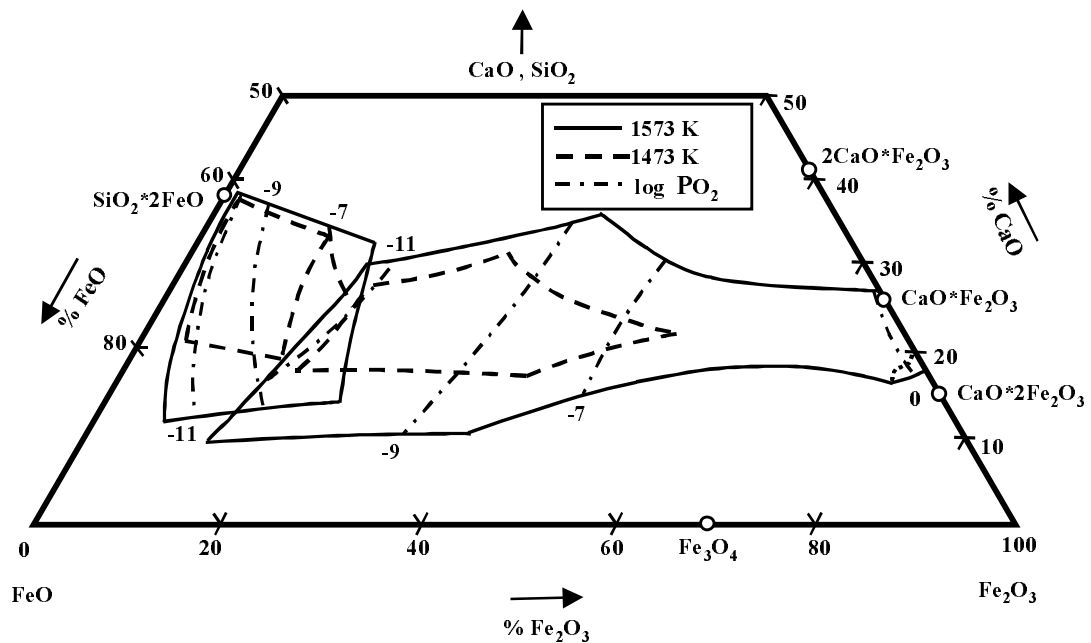


Figure 2 : Liquidus surface of the FeO-Fe<sub>2</sub>O<sub>3</sub>-CaO and FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems at various oxygen potentials, denoted by dashed-dotted lines at 1573 K.

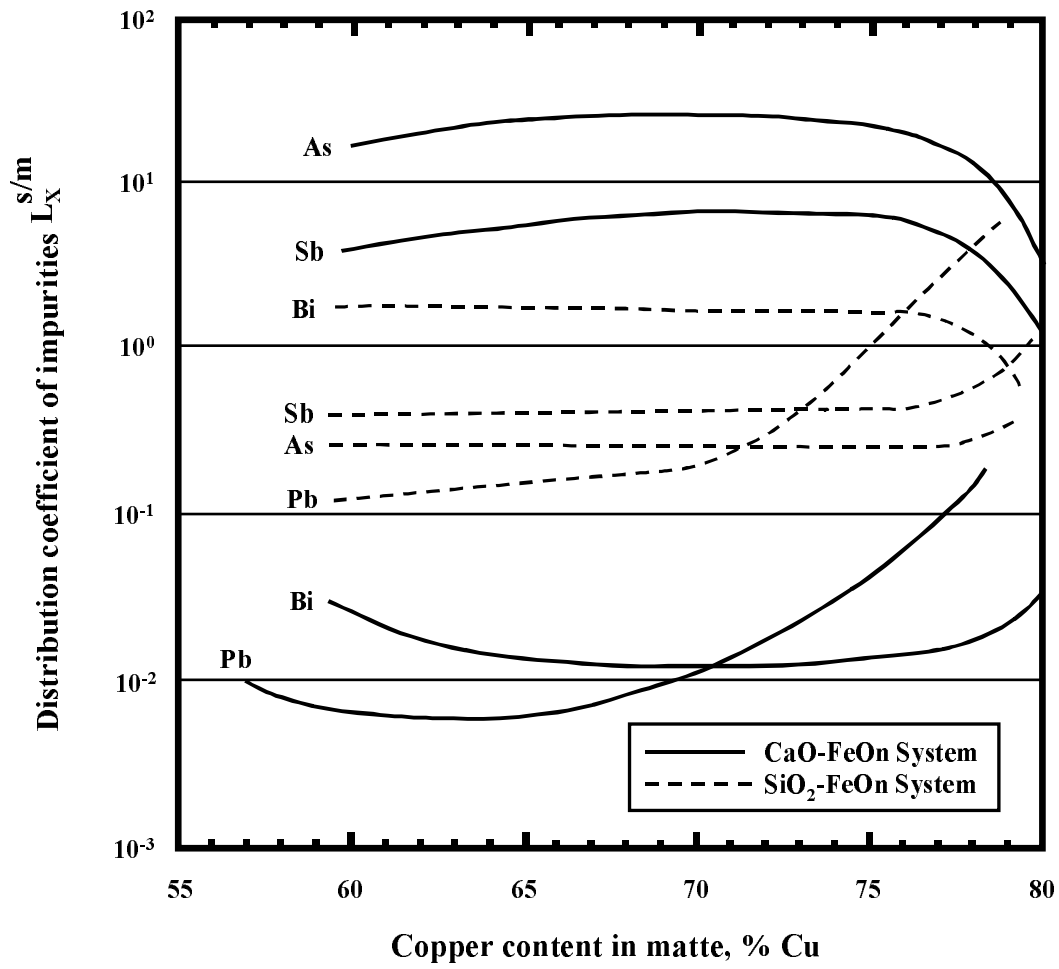


Figure 3 : Effect of matte grade on distribution coefficient of various impurities between calcium ferrite<sup>(22,23)</sup> and silicate<sup>(26,27)</sup> slags and matte at 1523 K and  $P_{SO_2} = 0.1$  atm.

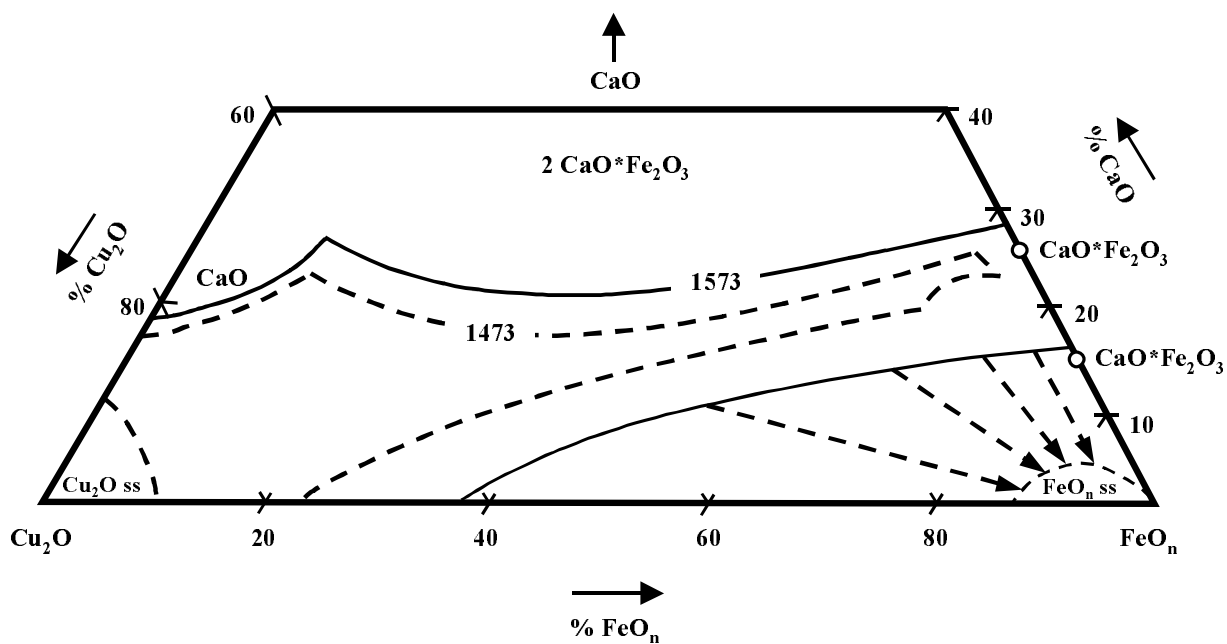


Figure 4 : Liquidus surface of the  $\text{Cu}_2\text{O}$ - $\text{FeO}_n$ - $\text{CaO}$  system at 1473 K and 1573 K <sup>(18)</sup>.

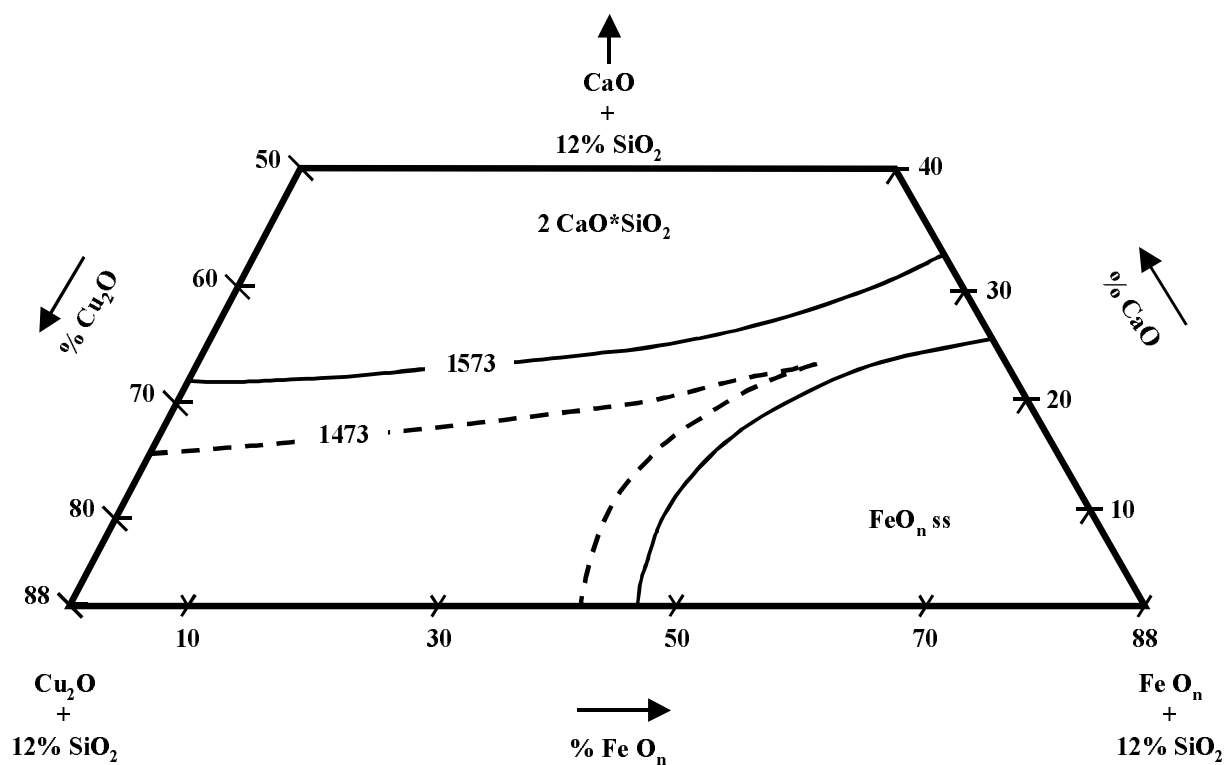


Figure 5 : Liquidus surface of the  $\text{Cu}_2\text{O}$  -  $\text{FeO}_n$  -  $\text{CaO}$  / 12 %  $\text{SiO}_2$  pseudoternary system at 1473 K and 1573 K <sup>(18,19)</sup>.

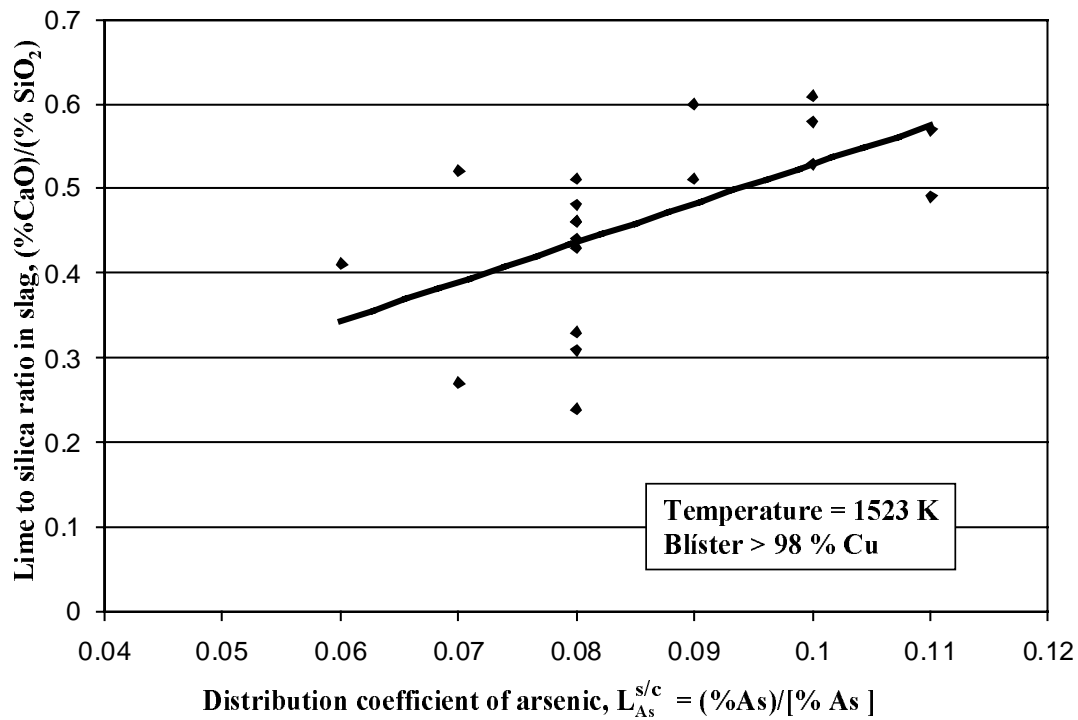


Figure 6 : Relationship between the lime to silica ratio in slag and distribution coefficient of arsenic between slag and copper phases.

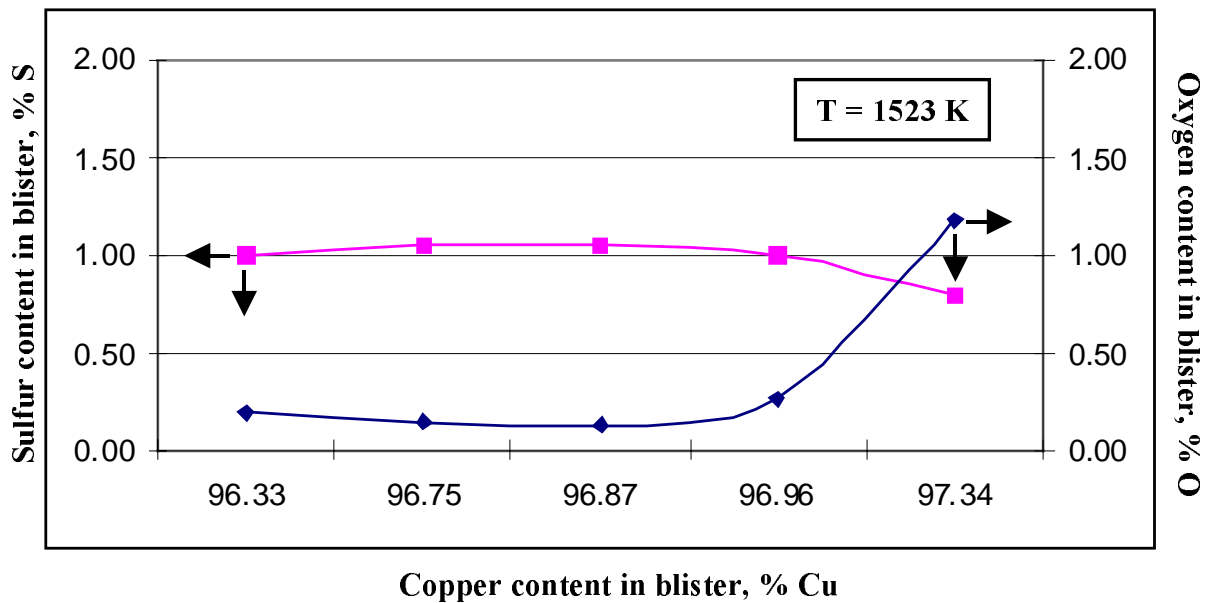


Figure 7 : Relationship among copper, sulfur and oxygen contents in blister.

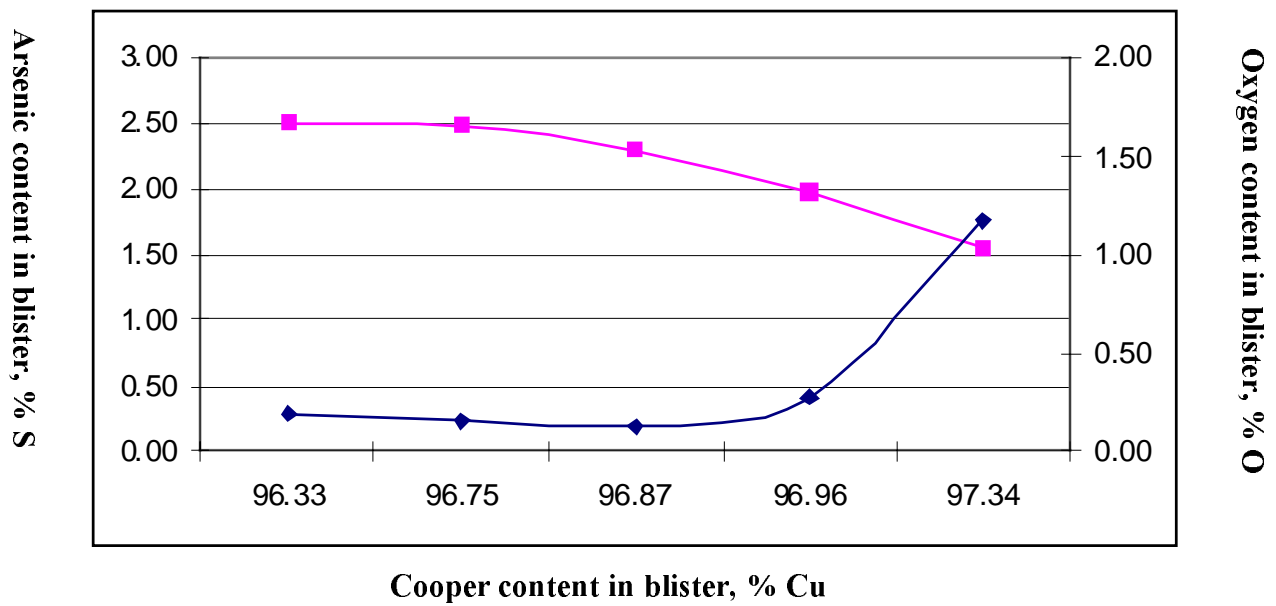


Figure 8 : Relationship among copper, arsenic and oxygen contents in blister.

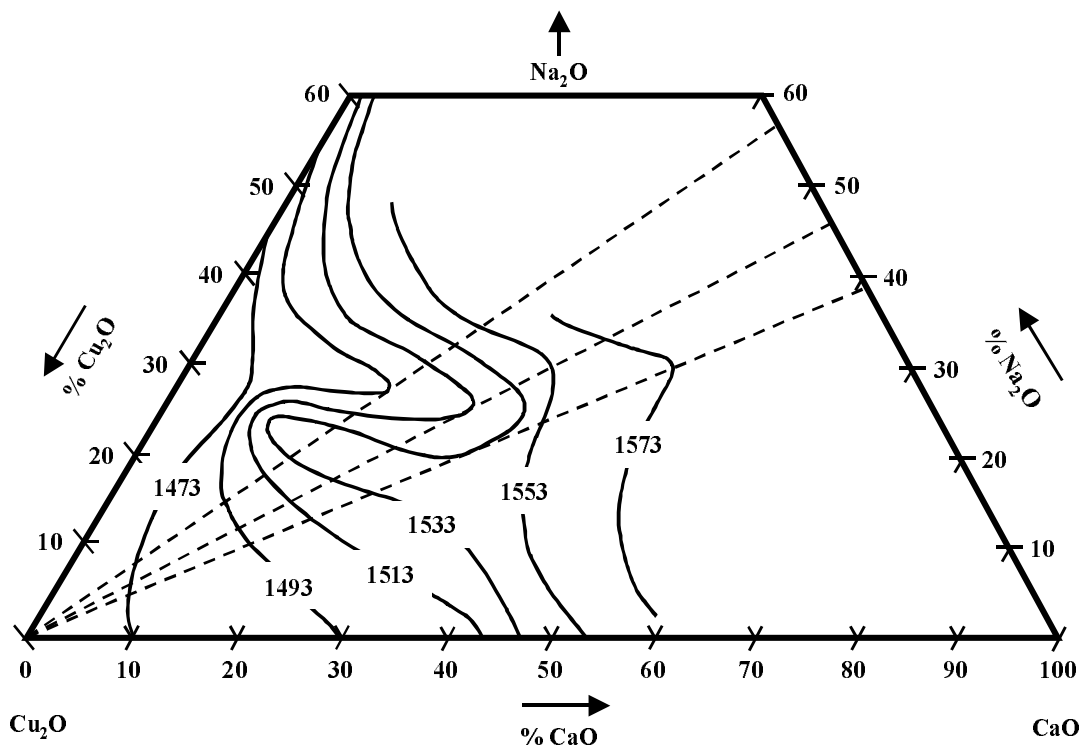
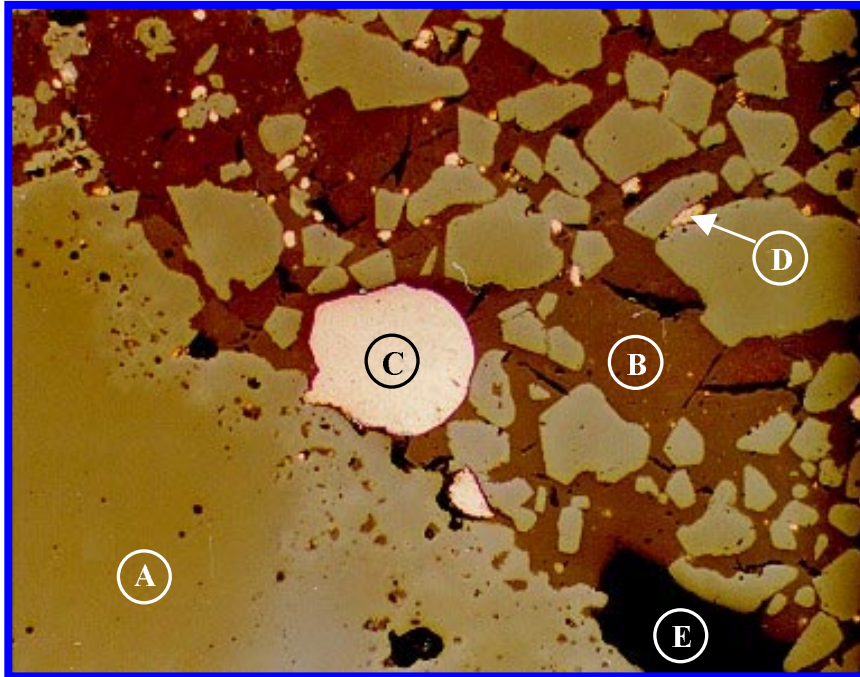
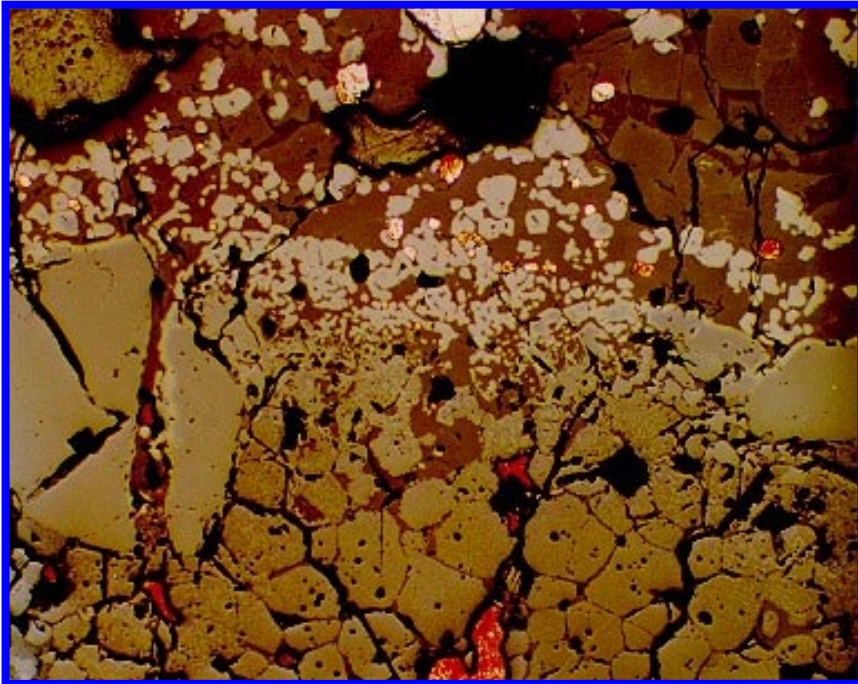


Figure 9 : Isothermal lines on the  $\text{Na}_2\text{O}$  -  $\text{CaO}$  -  $\text{Cu}_2\text{O}$  ternary system for test run under air atmosphere at several temperatures in Kelvin degrees (K).



Micrograph 1 : Refractory brick in contact with white metal showing chromite grains (A), silicate matrix (B), white metal (C) and copper (D). Infiltration is ascribed to the high open porosity (E) of the bricks, 200 X.





Micrograph 2 : Refractory brick in contact with slag showing a morphology similar to Micrograph 1, chromite grains (A), silicate matrix (B), white metal (C) and copper (D). Infiltration is ascribed to the high open porosity (E) of the bricks, 100 X.