

**DISTRIBUTION OF SOME IMPURITY ELEMENTS BETWEEN HIGH
GRADE COPPER MATTE AND CALCIUM FERRITE SLAG**

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Synopsis: Equilibrium measurements of As, Sb, Pb and Bi distribution between high grade copper matte (60-80% Cu) and calcium ferrite slag were conducted at 1523 K under 1 bar SO₂ pressure at the Helsinki University of Technology, Laboratory of Metallurgy. The results are discussed on the basis of operating data obtained during industrial scale Peirce-Smith converting tests carried at the Outokumpu Harjavalta Copper Smelter. The distribution behaviour of As, Sb, Pb and Bi in laboratory and industrial tests was observed to be qualitatively similar. The values of As and Sb distribution coefficients tend to increase along with the increasing matte grade and oxygen potential of the system. Thermodynamically favourable conditions for As and Sb removal from copper matte using calcium ferrite slag were determined.

Key words: copper matte converting, distribution coefficients of impurity elements, impurity removal from copper matte, calcium ferrite slag, Peirce-Smith converter

1. INTRODUCTION

The high grade copper matte produced at Outokumpu Harjavalta Flash Smelting Furnace is treated in conventional Peirce-Smith converters to blister copper which is further subjected to fire refining and deoxidation in rotary anode furnaces. In the Flash Smelting Furnace (FSF) and the converters a silica flux is used to form slag. The process has a moderate ability to eliminate arsenic, antimony and bismuth mainly by evaporation during flash smelting and converting. A considerable amount of lead entering the process is eliminated with silica slag. Nowadays, impurities are not causing serious problems in the operation of the electrolytic refinery, but already a moderate increase of impurity level in imported concentrate might considerably harm the electrorefining process. As an important smelting technology supplier Outokumpu has put much effort to develop new processes for efficient elimination of impurities such as As, Sb, Bi and Pb from copper. Several procedures for effective impurity control in pyrometallurgical stages of copper processing have been developed and results of theoretical and laboratory studies on impurity behaviour have already been reported ^{16,17}). Also, the increasing importance of environmental protection and impurity control has reflected on the published reports of matte-slag impurity distribution behaviour ¹⁻¹⁰).

A test program was carried out recently at the Outokumpu Research Oy and Helsinki University of Technology with an aim to develop a process for elimination of arsenic and antimony from copper matte by using basic fluxes and existing commercial technology. Basic flux have already been utilised in continuous copper converting (Mitsubishi-process) and a number of copper producers have implemented the Elvas-method ¹¹) for converting of low grade copper matte using soda-lime mixture as a flux.

2. EXPERIMENTAL

A. Laboratory Tests

Several laboratory tests were conducted in a vertical electric furnace at the Helsinki University of Technology, Laboratory of Metallurgy using copper mattes ranging from 60 to 80 % Cu and calcium ferrite slag with two slightly different Fe/CaO ratio (55/25 and 57/22). The slag and copper matte doped with As, Sb, Bi and Pb were placed in a cylindrical magnesium oxide crucible (25 mm ID by 60 mm in height) and heated up to 1523 K. The equilibrium measurements were carried out at 1523 K under 1 bar SO₂ pressure for 10 hours. Samples of slag

were taken at regular intervals from the top of the crucible using vitreous silica tube (3 mm ID) and then rapidly cooled. The matte and the slag which remained in the magnesia crucible were left to solidify, then carefully separated and subjected to chemical analysis.

B. Industrial Tests

Industrial scale converting tests were carried out in one 120 t Peirce-Smith converter (3.7 m ID by 7.9 m in length) at the Outokumpu Harjavalta Copper Smelter. The test campaign contained of ten converting tests. Three "normal" converting tests were performed using iron silicate slag to obtain reference results for impurity distributions between slag and matte. Seven converting tests were performed by adding lime along with matte into the converter to form slag. The amount of added lime was approximately 10 % of the produced blister amount. In each test about 100 tons of high grade copper matte (average 65 % Cu) was charged and oxidised by blowing oxygen enriched air in two stages. The converter was periodically turned out to skim the slag.

Converting with calcium ferrite slag was easy to control, no major failures occurred and steady state conditions were established during the whole test campaign. The viscosity of calcium ferrite slag was low which allowed easy slag tapping and handling of the converter. It was easy to blow the melt and tuyere blockages did not occur. Converting time was reduced by approximately 15 % compared to the tests where silica slag was used. The average amount of calcium ferrite slag per one converting was approximately 50% less compared to the corresponding amount of iron silica slag. In addition, copper content in calcium ferrite slag was half of the amount contained in silica slag. Thus, copper slag losses and the amount of recycled copper during the calcium ferrite slag tests were considerably low.

Some of the reverts added into the converter contained comparatively high amount of silica. In order to avoid undesirable increase of silica content in calcium ferrite slag the amount of the reverts rich in silica was reduced. In regard to impurity elimination it was important not to allow large amounts of calcium ferrite slag to be tapped along with blister into the anode furnace in order to avoid reversion of arsenic and antimony from slag to copper.

During the test campaign 113 tons of silica slag and 157 tons of calcium ferrite slag were produced. Blister copper and slag were tapped to ladles. Blister was fire refined and cast. The slag was left to solidify, then crushed and sent to the slag flotation plant. Samples were taken periodically from all incoming, circulating and outgoing material flows of the converter. After the tests, an examination of the converter showed no visual damages or severe refractory wear.

3. RESULTS AND DISCUSSION

A. Distribution Ratios of As, Sb, Bi and Pb Between Slag and Copper Matte

The laboratory and industrial test results are summarised in Figures 1 to 4. The distribution coefficients of As, Sb, Bi and Pb between calcium ferrite slag and copper matte are presented as a function of matte grade.

In Figure 1 the distribution coefficient values L_s/m of arsenic obtained during the laboratory tests show a steady trend of increase with increasing matte grade and oxygen potential up to 78 % copper in matte. Approaching the copper saturation near 80 % copper in matte, affects drastically the distribution behaviour of arsenic resulting in 50-60 % drop of the distribution coefficient values. The values of the arsenic distribution coefficient obtained during the industrial tests show the same trend of increasing along with the increasing matte grade. Maximum is, however, reached at lower copper content near 72 % copper in matte followed by decline as matte grade approaches the area of 80 % copper.

In Figure 2 the distribution values of antimony between calcium ferrite slag and matte steadily increase with the increasing matte grade and oxygen potential reaching maximum at matte grade near 77 % copper. During the industrial tests high distribution coefficients of antimony were observed at matte grades ranging near 70 % copper.

The distribution behaviour of antimony and arsenic demonstrate the contradictory role of increasing oxidation degree on matte-slag distribution. Increasing oxygen activity itself shifts the oxidation-slagging

equilibria of impurities to the right. However, a simultaneous decrease in activity coefficients of arsenic and antimony in matte reported in literature 3,6,7,10), give the reverse effect near copper saturation. During the industrial tests the influence of kinetic conditions on the activities of the main bath constituencies is obvious. Due to the vigorous conditions near the converter blowing area it can be assumed that copper saturation is achieved before the completion of iron slagging and some copper exists in the melt at relatively earlier stages of matte converting, which inevitably influences on arsenic and antimony distribution behaviour.

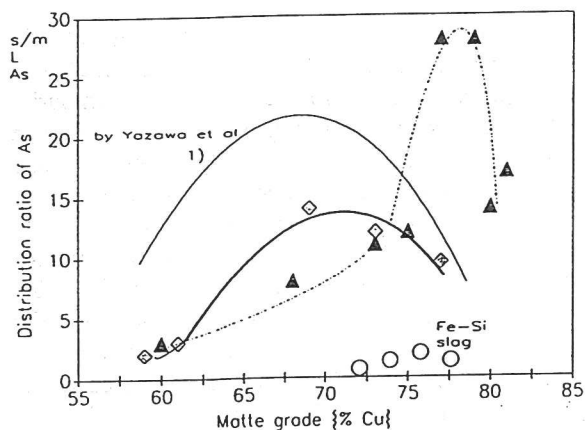


Figure 1. Distribution ratio of arsenic between calcium ferrite slag and copper matte as a function of matte grade.

▲ laboratory tests ◆ industrial tests
○ Fe-Si slag, laboratory tests

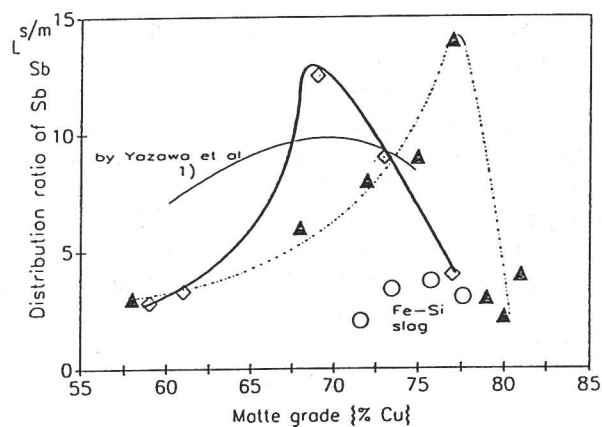


Figure 2. Distribution ratio of antimony between calcium ferrite slag and copper matte as a function of matte grade.

▲ laboratory tests ◆ industrial tests
○ Fe-Si slag, laboratory tests

During the laboratory tests, changes in matte grade had no effect on bismuth distribution (Figure 4). At matte grades ranging from 60 to 80 % copper the distribution coefficients of bismuth between slag and matte remained near 0.1. The distribution coefficients of bismuth obtained during the industrial test campaign were slightly higher compared to the laboratory test values. During the laboratory and industrial tests the effect of oxygen potential on the distribution coefficients of lead was obvious (Figure 3). Lead distribution ratio showed clear tendency of increasing at matte grades above 75 % copper.

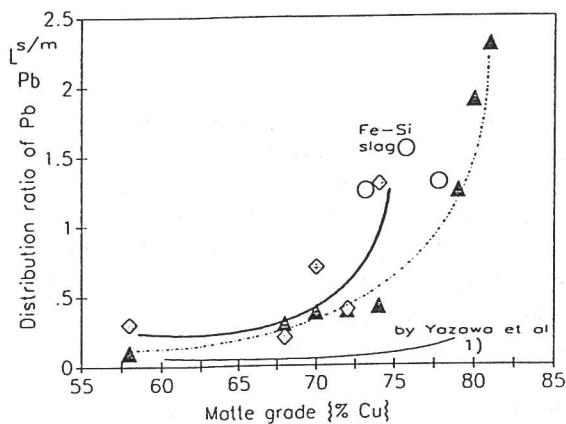


Figure 3. Distribution ratio of lead between calcium ferrite slag and copper matte as a function of matte grade.

▲ laboratory tests ◆ industrial tests
○ Fe-Si slag, laboratory tests

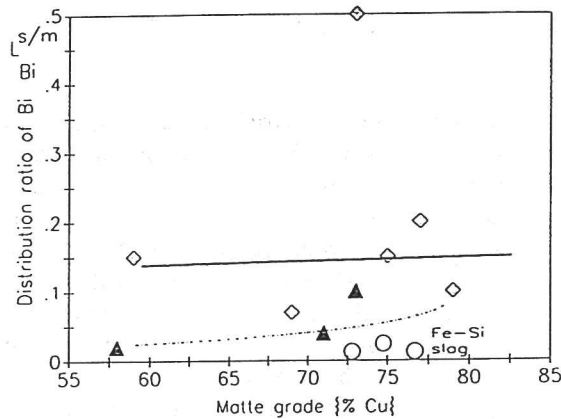


Figure 4. Distribution ratio of bismuth between calcium ferrite slag and copper matte as a function of matte grade.

▲ laboratory tests ◆ industrial tests
○ Fe-Si slag, laboratory tests

B. Impurity Removal From Copper Matte

The distribution of impurity elements in the main incoming and outgoing flows of the converter based on material balance calculations from the industrial tests are shown in Figures 5 to 8. The converter flow sheet is divided in two stages, slag blowing and blister blowing, where impurity distributions are presented as incoming and outgoing flows of the total impurity amount fed along with matte and reverts into the converter. The amount of impurities contained in FSF matte corresponds to 100. The content of impurities in matte before blister blowing is based on matte analyses after slag blowing and the estimated amount of impurities contained in the added reverts. After blister tapping, some amount of slag is normally left in the converter until the next matte converting. The amount of impurities contained in this slag is calculated and shown in Figures 5 to 8 as one circulating the converter flow sheet.

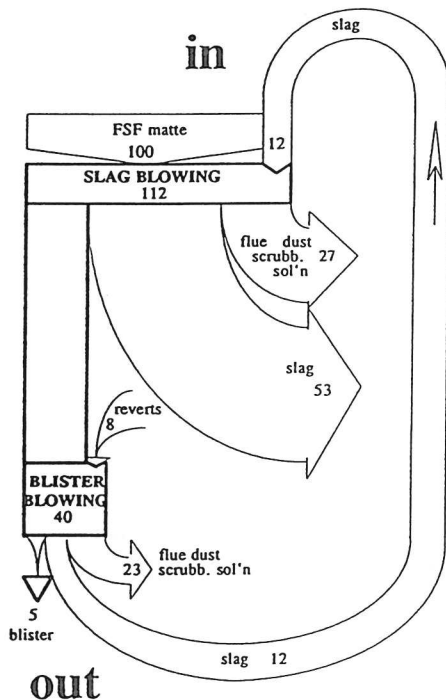


Figure 5. Arsenic distribution in the incoming and outgoing flows of PS-converter.

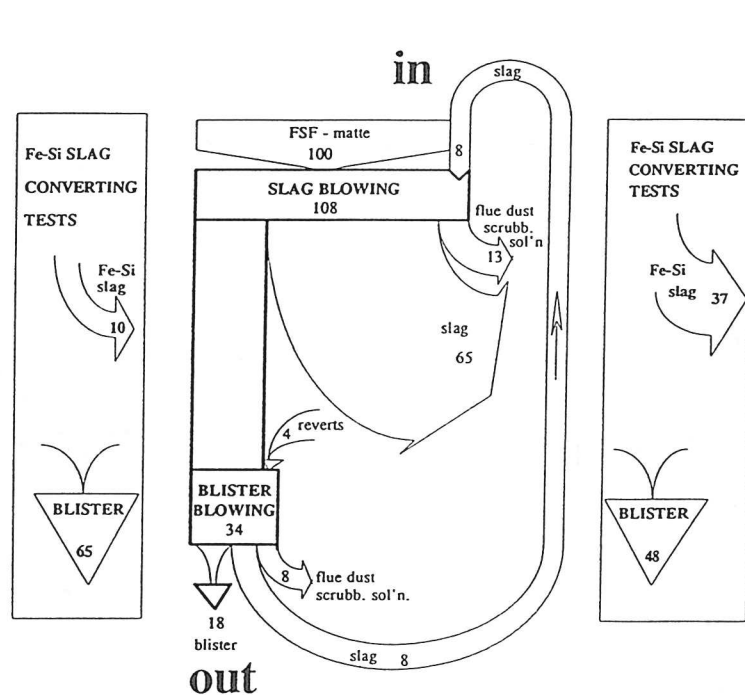


Figure 6. Antimony distribution in the incoming and outgoing flows of PS-converter.

The distribution of arsenic between matte, calcium ferrite slag and flue dust obtained during the industrial tests is shown in Figure 5. More than half of the total arsenic amount fed into the converter along with FSF matte is eliminated with calcium ferrite slag formed during slag blowing stage and one third is removed with flue dust. Before blister blowing some amount of arsenic enters the converter along with reverts. During blister blowing, due to the higher oxygen potential a considerable amount of arsenic left in matte is eliminated with flue dust and some amount remained in slag left in the converter. At this stage of the converting, however, the amount of arsenic transferred to slag is relatively small. The analyses made before the anode furnace treatment showed that less than five percent of the total arsenic load remained in blister. For comparison, during the silica converting tests the amount of arsenic removed with slag after slag blowing was ten percent of the arsenic feed, and more than a half of the total arsenic load remained in blister.

The industrial tests showed that a considerable amount of antimony is removed from matte by calcium ferrite slag. Over sixty percent of the antimony contained in FSF matte was eliminated with calcium ferrite slag during slag blowing and thirteen percent reported to flue dust (Figure 6). The calcium ferrite slag contained nearly two times more antimony than the corresponding silica slag.

Lead distribution in the main outflows of the converter is shown in Figure 7. Over 50 % of the initial lead load was removed from matte during slag blowing and one third was removed during blister blowing stage. During the lime tests, an increase of lead content in scrubber solution sediment was noticed at the Sulphur acid

plant. Calcium ferrite slag tapped after slag blowing contained eight percent of the total lead feed. Nearly one fifth of the total lead load circulated the converter flow sheet along with slag left after blister blowing. The amount is high having in mind, that comparatively small amount of slag was left in the converter. During the silica tests, nearly ninety percent of the lead contained in FSF matte was eliminated with slag.

The addition of lime did not particularly affect bismuth distribution in the outgoing flows of the converter (Figure 8). In both silica and lime tests the amount of bismuth eliminated with slag was negligible. Considerable amount of bismuth was removed from matte along with flue dust during slag blowing (over 60 %) and some during blister blowing stage. Nearly one third of the total bismuth load remained in blister.

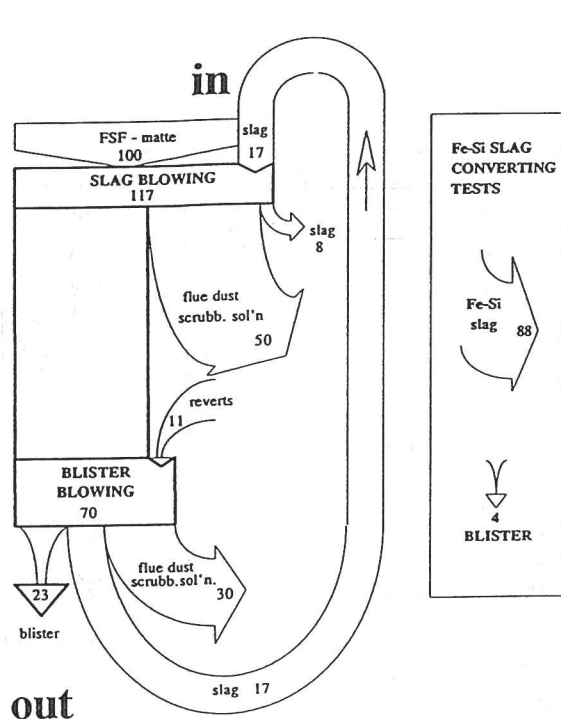


Figure 7. Lead distribution in the incoming and outgoing flows of PS-converter.

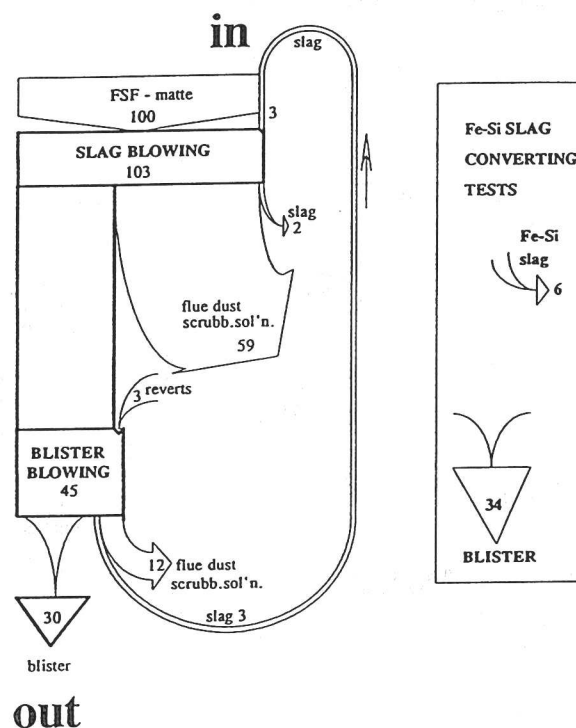


Figure 8. Bismuth distribution in the incoming and outgoing flows of PS-converter.

C. Effect of Silica Content in Slag on Impurity Distribution

The formation of calcium ferrite slag and the changes in slag viscosity were followed closely during the converting tests. An important item was to avoid rapid increase of silica content in calcium ferrite slag which could have led to the formation of dicalcium silicate phase.

Although the addition of large amounts of reverts rich in silica and slag from the FSF was avoided to some extent, silica content especially in slag formed after blister blowing was high in some of the tests which inevitably affected the distribution behaviour of impurities.

In Figures 9 and 10 are shown the distribution ratios of As, Sb, Bi and Pb as a function of slag basicity ratio CaO/SiO_2 . High silica content in slag reduced considerably the ability of slag to bind arsenic and antimony (Figure 9). The distribution ratios of arsenic and antimony between slag and matte (72-78 % Cu) were several times lower as SiO_2 content in slag exceeded six percent. The increase of silica content in slag had some effect on lead behaviour (Figure 10). A considerable amount of lead left in matte after slag blowing reported to silica rich slag during blister blowing stage.

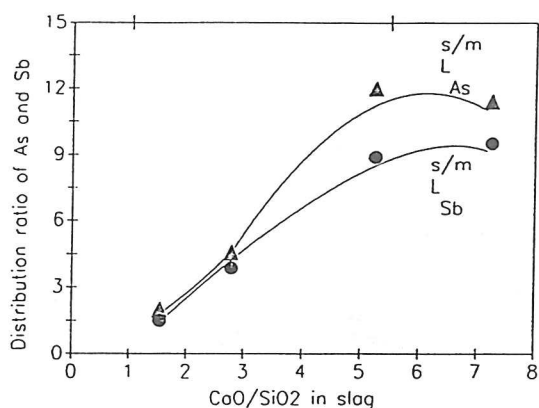


Figure 9. Distribution ratio of As and Sb between slag and matte (72-78 % Cu) plotted against slag CaO/SiO₂ ratio.

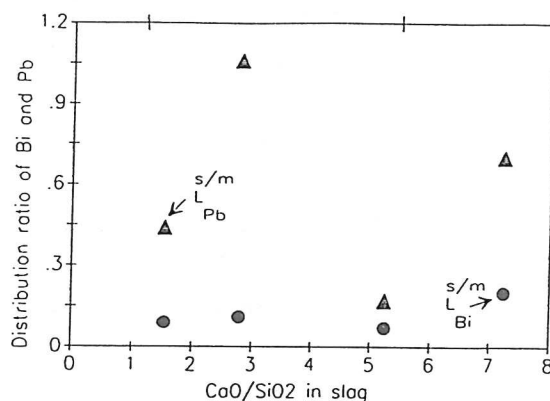


Figure 10. Distribution ratio of Bi and Pb between slag and matte (72-78 % Cu) plotted against slag CaO/SiO₂ ratio.

4. SUMMARY

Laboratory and industrial scale tests were conducted to determine the distribution behaviour of As, Sb, Bi and Pb between calcium ferrite slag and copper matte. Impurity element distributions in the main outflows of the Peirce-Smith converter are presented based on material balance calculations from the industrial test campaign.

The treatment of high grade matte in Peirce-Smith converter offers favourable conditions for impurity removal, but low contents of As and Sb in matte can not be achieved without appropriate flux formulation. Calcium ferrite slag removed effectively As and Sb from matte and the content of these elements in blister copper produced was reduced considerably compared to converting tests where silica flux was used. The effectiveness of As and Sb removal with calcium ferrite slag during matte converting was found to be highly dependent on SiO₂ content in slag. Easy controlled existing technology was applied at reasonable cost.

5. REFERENCES

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