

## Article

# Specific Features of Using High-Silica Flux Ore in Copper Smelting Units

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## Abstract

This study explores the application of high-silica flux ore in copper smelting and converting processes at the Zhezkazgan Copper Smelting plant. Pilot-scale experiments and SEM analyses were performed to assess its influence on slag composition, temperature regime, and metal recovery. The results demonstrated that replacing conventional flux with high-silica ore reduced flux consumption by 19%, increased converter slag temperature from 1124 to 1174 °C, and decreased copper content in converter slag from 10% to 4.5%. SEM micro-analysis revealed the formation of lead-containing silicate rims around matte inclusions, which hinder their settling at low temperatures. However, when the slag temperature exceeded 1400 °C, these rims were destroyed, facilitating separation and reducing residual copper. These findings highlight the potential of high-silica fluxes (>90% SiO<sub>2</sub>) to improve both energy efficiency and metal recovery in process of copper matte converting, offering practical recommendations for industrial operations.

**Keywords:** high-silica flux; copper losses; slag smelting; converting; magnetite; scanning electron microscopy (SEM)



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## 1. Introduction

An analysis of developments in copper smelting technology and theoretical research in this field has revealed a general trend towards an increase in the proportion of energy-saving autogenous processes for smelting copper ore and producing crude copper [1]. At the same time, it was shown that there is a practical lack of research on developing a theory of fluxing properties of quartz ores used in these processes. The latter does not allow for a quantitative assessment of the quality of fluxes and classifying the material according to their fluxing ability, taking into account impurities and their effect on the copper content in slags. Copper pyrometallurgy is currently mainly developing in the direction of mastering and implementing autogenous smelting processes, which are the most profitable and allow processing of sulfide concentrates that are relatively poor in copper [2–10], including Vanyukov smelting (VS).

The fluxing capacity of silicate ores used in smelting of the charge and converting processes is low, which is associated with the preferred use of gold-bearing ores containing a significant amount of oxide impurities, and requires feeding a greater excess of it into the furnace to obtain a homogeneous melt, which leads to decrease temperature of the melt and the production of heterogeneous slag melts with a high copper content both in dissolved form and in the form of a mechanical suspension [11–14]. At the same time, the output of

slag itself increases, which means that the total copper losses also increase [15–18]. The use of quartz-containing materials as fluxes in copper smelting production is effective due to their ability to bind iron oxides, forming low-melting slags [19–21]. This helps to lower the melting point and makes it easier to separate the metal from the waste rock. However, it should be taken into account that in addition to silicon dioxide ( $\text{SiO}_2$ ), other oxides present in the flux can increase the volume of slag, which leads to losses of non-ferrous and precious metals [22–25].

Recent studies have shown that high silica activity can increase the viscosity of the slag and strengthen the silicate network, which can reduce the fluidity of the melt and make it difficult to separate the matte (copper) and slag [26,27]. At the same time, the effect depends on the overall composition of the slag. Increasing the Fe content can break down the silicate structure, lower the crystallization temperature, and improve the fluidity of the slag [28].

In practice, the use of flux with a high silica content should be carefully controlled: a small, balanced addition reduces the volume of slag and, naturally, increases the temperature of the slag, reducing its viscosity, which improves separation and reduces copper losses [29]. When converting copper matte, the main purpose of the silicate flux is to bind iron oxide ( $\text{FeO}$ ) into fayalite and prevent overoxidation of iron oxide into magnetite, which increases the viscosity of the slag and contributes to higher copper content. To improve the heat balance of smelting and converting and reduce the copper content in smelting and converting slags, it is necessary to develop options for charge smelting and matte conversion technologies using rich siliceous fluxes with a silicon dioxide content of more than 90%.

## 2. Materials and Methods

The processing scheme for copper concentrates includes: the preparation of the charge, which includes a combination of concentrates and fluxes, the electric smelting of the charge to obtain copper matte and dump furnace slag. The subsequent step is the converting of copper matte to produce blister copper and converter slag, which is poured in liquid form into the electric furnace.

The converting process at the plant involves the preliminary loading of a portion of liquid matte (containing 47–50% copper). After a brief heating of the matte for 10 min through air blowing, the first batch of flux is introduced. Air blowing continues thereafter. The operations of adding new portions of matte and loading flux are repeated several times (typically 4–5 times).

During the initial period of converting, several discharges of converter slag are performed. During each discharge, several samples of liquid converter slag are collected. Subsequently, all samples collected during the first period of converting are combined and averaged. The objective of the flux introduced for melting is to bind the iron oxide generated during the blowing process into fayalite. Based on the operational experience of the smelting plant, the optimal silicon dioxide content in the converter slag is 25%. This ensures minimal copper and magnetite content in the converter slag and minimizes its volume.

To evaluate the feasibility of using high-silica flux in the converting of copper matte, industrial tests were conducted. At stage 1, ordinary ore was fed to the converter as a flux, at stages 2 and 3, experimental high-silica ore, and at stage 3, high-silica ore of reverberatory furnace class was additionally added to the smelting furnace charge in the amount of 3.0%.

Chemical composition of flux ores currently used in copper plant and slags was taken from ZhCSP chemical control cards. During the tests, the temperature of the converter and waste slags at the outlet was monitored using pyrometry Raynger Series 3i Plus (Raytek Corp, Santa Cruz, CA, USA). Temperature measurements were performed at the hottest

point, i.e., at the converter outlet. Multiple readings were taken to improve accuracy, and the highest value was used for analysis.

In addition, the composition of slags and the forms of non-ferrous metal content in them were studied using electron microscopy. The microstructure and composition of mineral phases were studied using a JEOL JXA 8230 Electron Probe electron probe microanalyzer (JEOL Ltd., Tokyo, Japan). Electron probe study of the samples was carried out in the following modes: COMPO–image in backscattered electrons; EDS–wave-dispersive spectroscopy with determination of elemental composition; WDS–qualitative wave-dispersive spectroscopy with a clearer and more sensitive image. Artificial polished sections of materials for electron probe analysis were prepared using epoxy resin and polystyrene as binders. Grinding and polishing were carried out both by the standard method and using oil. To conduct studies using EDS-WDS microanalysis methods, a carbon film was applied to the polished surface of the samples using thermal spraying. EPMA measurements were performed in “Standardless” mode with automatic corrections on ZAF-method with high reproducibility of results.

### 3. Results and Discussion

Figures 1 and 2 show photographs of converter slag samples taken during tests of high-silica ore in converters at a temperature of 1200 °C. The presence of unmelted inclusions of quartz ore in them may indicate a low temperature of the conversion process and/or an excess of quartz ore additives, which do not have time to be melted.

Chemical composition of flux ores is presented in Table 1, and it was revealed that the consumption of high-silica flux ore during conversion decreased from 434 to 351 kg/t of blister copper, which led to an increase in the temperature of the converter slag from 1124 °C to 1174 °C, and the temperature of the waste slags from 1285 °C to 1335–1409 °C. The increase in temperature (Tables 2 and 3) contributed to a decrease in the magnetite content in the slags, which improved their physical and chemical properties.

**Table 1.** Chemical composition of the flux ores used.

| Name                                         | Chemical Composition of Flux Ores, % |      |       |      |      |                                |       |      |
|----------------------------------------------|--------------------------------------|------|-------|------|------|--------------------------------|-------|------|
|                                              | SiO <sub>2</sub>                     | Cu   | Pb    | CaO  | Fe   | Al <sub>2</sub> O <sub>3</sub> | Zn    | S    |
| Ordinary ore                                 | 64.20                                | 0.59 | 0.10  | 4.30 | 2.45 | 11.3                           | 0.07  | 0.21 |
| High silica ore, reverberatory furnace class | 96.90                                | 0.02 | <0.01 | 0.92 | 1.49 | 0.35                           | <0.01 | 0.02 |
| High silica ore, converter class             | 95.90                                | 0.09 | <0.01 | 1.17 | 1.07 | 0.29                           | 0.01  | 0.05 |

**Table 2.** Temperature parameters of converter and waste furnace slag.

| Stage | Converter Slag Temperature, °C | Temperature of Waste Furnace Slag, °C |
|-------|--------------------------------|---------------------------------------|
| 1     | 1124                           | 1285                                  |
| 2     | 1167                           | 1344                                  |
| 3     | 1174                           | 1409                                  |

For the successful slagging of the formed iron oxide, the converting temperature should be at least 1200 °C. The use of a flux rich in SiO<sub>2</sub> contributed to a slight increase in the process temperature due to a reduction in its volume. The main task of the flux during conversion is to ensure the most complete possible transition of oxidized iron to fayalite. To do this, it is sufficient to maintain the average SiO<sub>2</sub> content in converter slags at a level of 24–26%. An increase in the process temperature will contribute to a decrease in the magnetite content in the converter slag and an increase in the degree of lead transfer into converter dust.

As can be seen from Table 3, the copper content in the converter slag decreased from 10% to 4.5%, and the lead content decreased from 12% to 10%. However, the silicon dioxide concentration increased to 31% (with a target value of 26%), which is explained by the overconsumption of ore at the stage of adaptation to the use of high-silica ore.

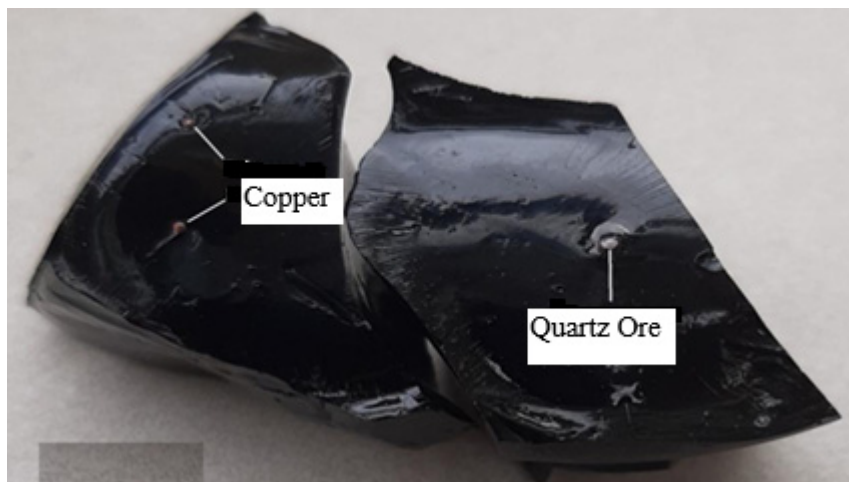


**Figure 1.** Samples of converter slag with inclusions of unmelted quartz ore and metallic copper.

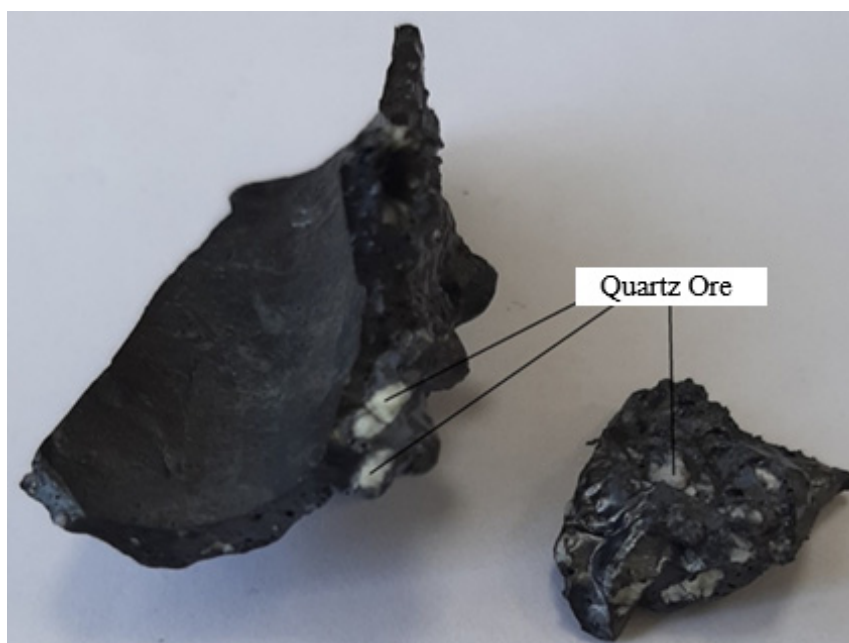


**Figure 2.** Samples of converter slag with inclusions of unmelted quartz ore.

**Table 3.** Change in the chemical composition of converter slag, %.

| Test Stages | Cu    | SiO <sub>2</sub> | Fe <sub>total</sub> | CaO  | Pb    |
|-------------|-------|------------------|---------------------|------|-------|
| 1           | 10.05 | 23.79            | 22.37               | 2.06 | 12.8  |
| 2           | 4.49  | 25.73            | 26.10               | 0.96 | 11.97 |
| 3           | 4.42  | 31.04            | 27.44               | 1.74 | 10.11 |

In test stages 1, 2, and 3, the content of Fe<sub>3</sub>O<sub>4</sub> was 33.93%, 9.36%, and 8.42%, respectively. More than half of the total slag produced by smelting furnaces is converter slag. Thus, converter slag, which has a lower temperature than the slag melt in the furnaces, an

increased content of magnetite and lead, has a negative effect on the copper content in the waste furnace slags (Table 4).

**Table 4.** Chemical composition of waste furnace slag at different stages of testing, %.

| Test Stages | Cu   | SiO <sub>2</sub> | Fe    | CaO  | Pb   |
|-------------|------|------------------|-------|------|------|
| 1           | 1.22 | 44.57            | 14.99 | 6.5  | 3.64 |
| 2           | 1.00 | 50.49            | 15.65 | 7.05 | 2.83 |
| 3           | 0.88 | 48.35            | 15.97 | 7.46 | 2.74 |

The obtained dependences of the content of Cu, Fe<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> in the slags were compared with the known phase diagrams of the Cu-Fe-Si-O system. According to the literature data, the region of magnetite stability at 1200–1250 °C corresponds to high FeO activity and low SiO<sub>2</sub> activity. Our results show that an increase in the SiO<sub>2</sub> fraction to 25–31% decrease the content of magnetite in the slag, which is described in the work [30]. This confirms that the activity of silica is a key factor in reducing magnetite and residual copper in slags.

From Table 3 it is clearly seen that the magnetite content in converter slag can reach 30% or more. With such a content, it turns out that almost all the iron in converter slags is in the form of magnetite. That is, there is practically no fluxing of iron oxide into the form of fayalite. And all this magnetite goes into the smelting furnace. The same with lead. During smelting, lead almost completely passes into matte, during conversion, about 80% of lead passes into converter slag (the lead content in converter slag reaches 17%). Its distillation into the gas phase is difficult due to the low temperature during conversion.

The content of non-ferrous metals in slag is affected by many factors—the composition of the matte under the slag, the temperature during slag formation, the cooling rate of the slags under study, the melting method, but the most significant factor is the slag composition, including the content of harmful impurities.

The effect of zinc and magnetite on the properties of slag has been studied in sufficient detail. The zinc content in slag of more than 5% leads to an increase in the melting temperature, slag viscosity and deterioration of the conditions for separating slag and matte. Magnetite in slag also increases the melting temperature and viscosity of the slag. Under optimal conditions during smelting, the magnetite content may vary within 3–7%, while in converter slags it can exceed 20%. At lower smelting temperatures, the solubility of magnetite decreases, leading to its deposition on the furnace bottom and the formation of an intermediate slag layer enriched with magnetite.

The effect of lead, with a content of more than 5%, on copper losses with slag has practically not been considered in the available literature. To consider the effect of lead on the slag structure and the content of non-ferrous metals in them, electric smelting slag with an increased lead content of more than 6% was used. The production of such slags is associated with an increase in the lead content in the raw materials, as well as its accumulation in converter slags up to 15–17%. During electric smelting of copper sulphide raw materials with increased lead content, lead sulphide is almost completely converted into matte and its content in matte, taking into account the pouring of the entire volume of converter slag into the electric furnace, is 12–15%. During conversion, about 20% of lead is converted into sublimates and dusts, while the rest enters converter slags and cycles back into the furnaces.

At relatively low temperatures in electric furnaces (up to 1300 °C), large matte particles do not have time to pass from slag to matte, causing increased copper losses with waste slags. The composition of the sample studied using microprobe analysis at individual points in Figure 3 is given in Table 5. A matte particle larger than 800 µm did not pass

into matte. This matte particle is surrounded by a rim consisting mainly of lead silicate. Apparently, this rim is firmly connected to the slag matrix and prevents the precipitation of such a large particle of matte.

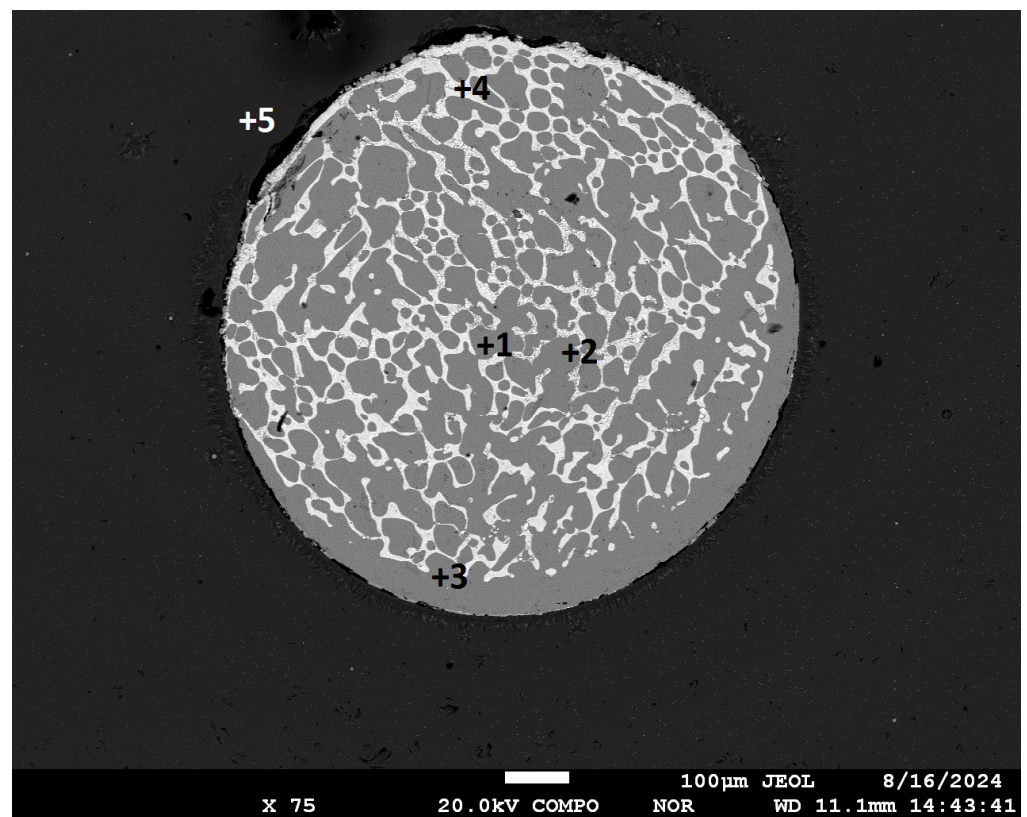


**Figure 3.** Micrograph of a slag sample, 75×. 1–5—points at which elemental analysis of the slag sample was carried out.

**Table 5.** Content of components in the studied points of the slag sample (Figure 3), %.

| Point No. | S     | Fe    | Cu    | Pb    | O     | Na   | Mg   | Al   | Si    | Ca   | Ti   |
|-----------|-------|-------|-------|-------|-------|------|------|------|-------|------|------|
| 1         | 24.92 | 7.85  | 67.23 | -     | -     | -    | -    | -    | -     | -    | -    |
| 2         | 24.71 | 7.34  | 67.95 | -     | -     | -    | -    | -    | -     | -    | -    |
| 3         | 24.47 | 5.47  | 70.07 | -     | -     | -    | -    | -    | -     | -    | -    |
| 4         | 15.34 | 3.25  | 30.43 | 43.00 | -     | -    | -    | -    | -     | -    | -    |
| 5         | 16.76 | 3.51  | 32.75 | 46.98 | -     | -    | -    | -    | -     | -    | -    |
|           | -     | 17.20 | -     | 4.24  | 43.53 | 2.29 | 0.99 | 4.16 | 20.04 | 3.93 | 0.35 |

It turned out that the same lead silicate rim also surrounds copper sulfide inclusions. Figure 4 shows a micrograph of a chalcocite particle surrounded by a lead silicate rim in the form of a serrated crown, which also prevents the precipitation of such a particle into the matte phase. The composition of the sample studied using microprobe analysis at individual points is given in Table 6.

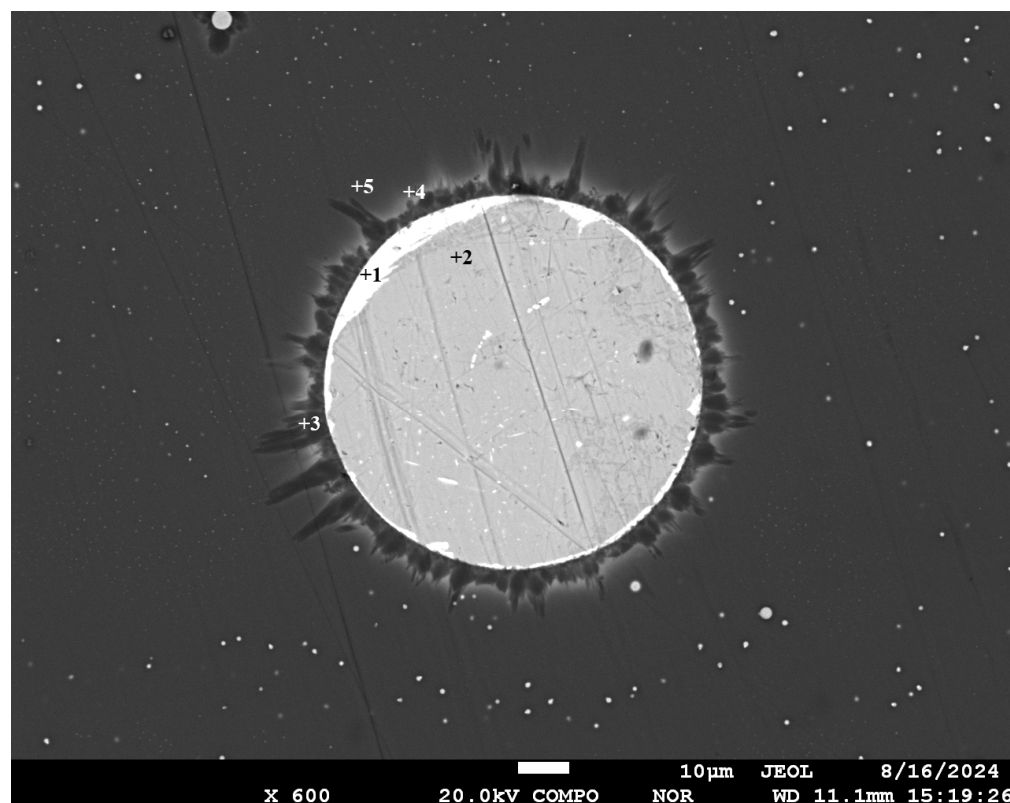


**Figure 4.** Micrograph of a slag sample, 600 $\times$ . 1–5—points at which elemental analysis of the slag sample was carried out.

**Table 6.** Content of components in the studied points of the slag sample (Figure 4), %.

| Point No. | S     | Fe    | Cu    | Pb    | O     | Na   | Mg   | Al   | Si    | Ca   |
|-----------|-------|-------|-------|-------|-------|------|------|------|-------|------|
| 1         | 18.65 | 2.88  | 48.00 | 30.47 | -     | -    | -    | -    | -     | -    |
|           | 16.56 | 2.59  | 43.54 | 27.07 | -     | -    | -    | -    | -     | -    |
| 2         | 22.82 | -     | 77.18 | -     | -     | -    | -    | -    | -     | -    |
| 3         | -     | 17.18 | 0.77  | 4.47  | 43.11 | 1.33 | 1.57 | 4.13 | 20.38 | 4.65 |
| 4         | -     | 15.72 | 0.57  | 12.83 | 38.07 | 2.15 | 0.62 | 4.09 | 19.04 | 3.48 |
| 5         | -     | 17.56 | -     | 5.32  | 42.94 | 2.13 | 1.00 | 4.07 | 19.91 | 4.01 |

Figure 5 shows the mapping of a slag section containing a copper sulfide inclusion with a lead silicate rim, where between the copper sulfide and the serrated rim the surface of the copper sulfide particle is covered with an alloy of copper sulfide and lead sulfide. The migration of metals and their sulfides to the surface of the matte particle (Point 1) may be attributed to the combined effects of surface tension forces and gravitational forces. Point 1 (edge zone of the droplet)—this is a Cu-Pb-S sulfide phase (close to  $\text{Cu}_2\text{S-PbS}$ ). Lead reduces the surface tension which explains the observed enrichment of lead and sulfur at the droplet boundary, indicating the migration of lead toward the surface. Point 2 (center of the droplet)—consists of nearly pure  $\text{Cu}_2\text{S}$ , where the surface tension is higher than that of  $\text{PbS}$ ; therefore, this zone tends to remain in the center, forming the core.

In addition, it can be seen that the lead silicate is uniformly distributed over the main silicate matrix of the slag. It should be noted that the presence of such a rim could only be established by electron microscopy; mineralogical analysis could not identify it. Figure 6 shows copper sulfide inclusions with a particularly developed rim. Figure 7 shows matte inclusions in slag with a lead content of more than 6% and slag with a lead content of less than 2%.

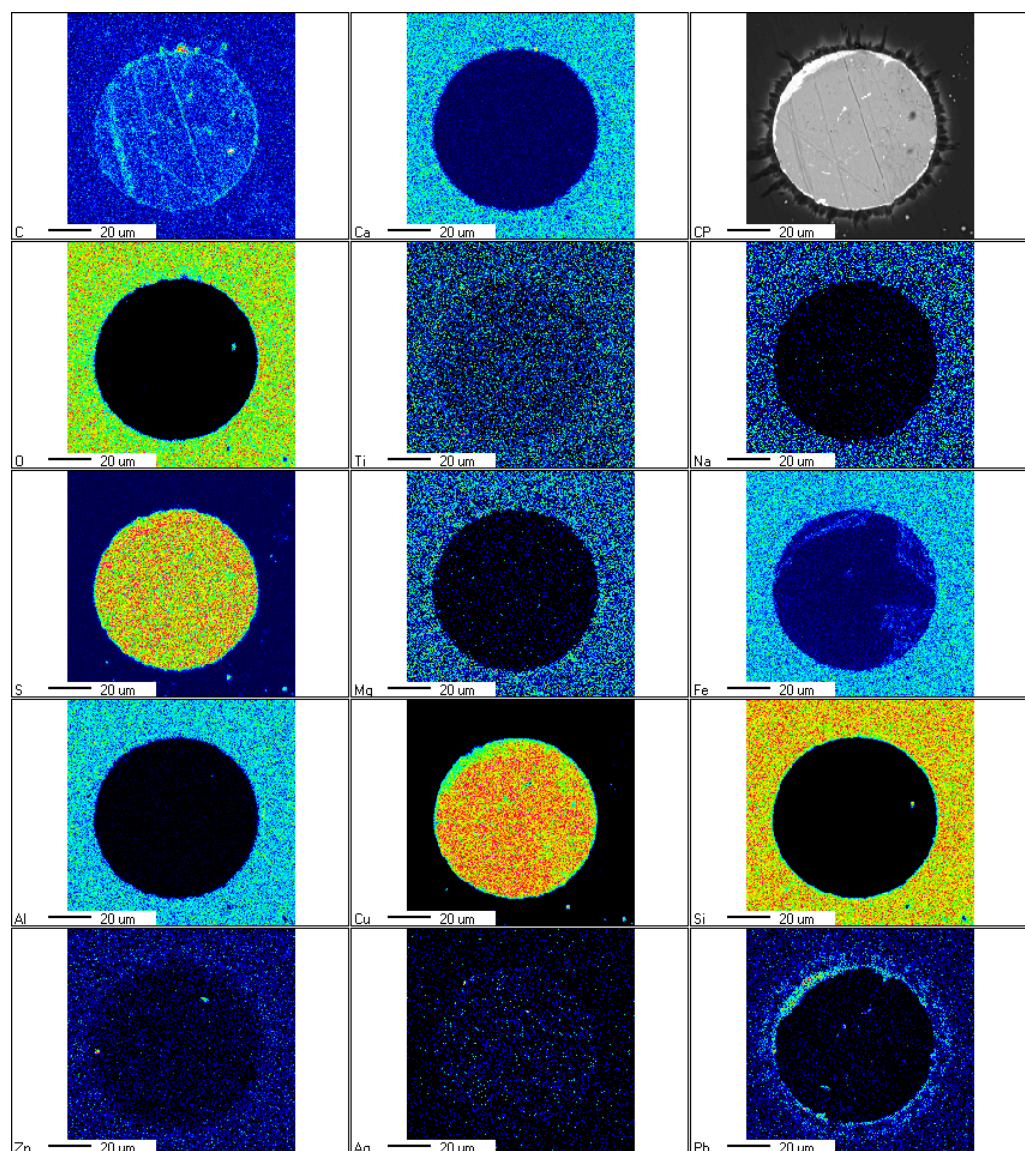


**Figure 5.** Mapping of a slag area with fine suspension of copper and lead sulfides.

Figure 7 shows a sulfide inclusion with an area saturated with lead sulfide (distinguished by a lighter color), near which the rim is more developed. From this, we can conclude that lead sulfide, released on the surface of the copper sulfide inclusion, is a kind of rim crystallization center.

Thus, the experimental results not only show the practical effectiveness of the high-silica flux, but also confirm the patterns predicted by the Cu-Fe-Si-O phase diagrams: an increase in  $\text{SiO}_2$  activity shifts the equilibrium to the formation of fayalite, reduces magnetite and residual copper, and facilitates the separation of matte-slag. And the increased lead content in the slag can lead to the formation of a shell consisting of lead silicate around a drop of copper sulfide, which hinders its deposition in the slag. It should be noted that when the slag temperature was increased to 1400 °C (Table 2) and more during tests of high-silica flux on converters, this led to the disappearance of the rim around the matte inclusions and a decrease in the copper content in the slags.

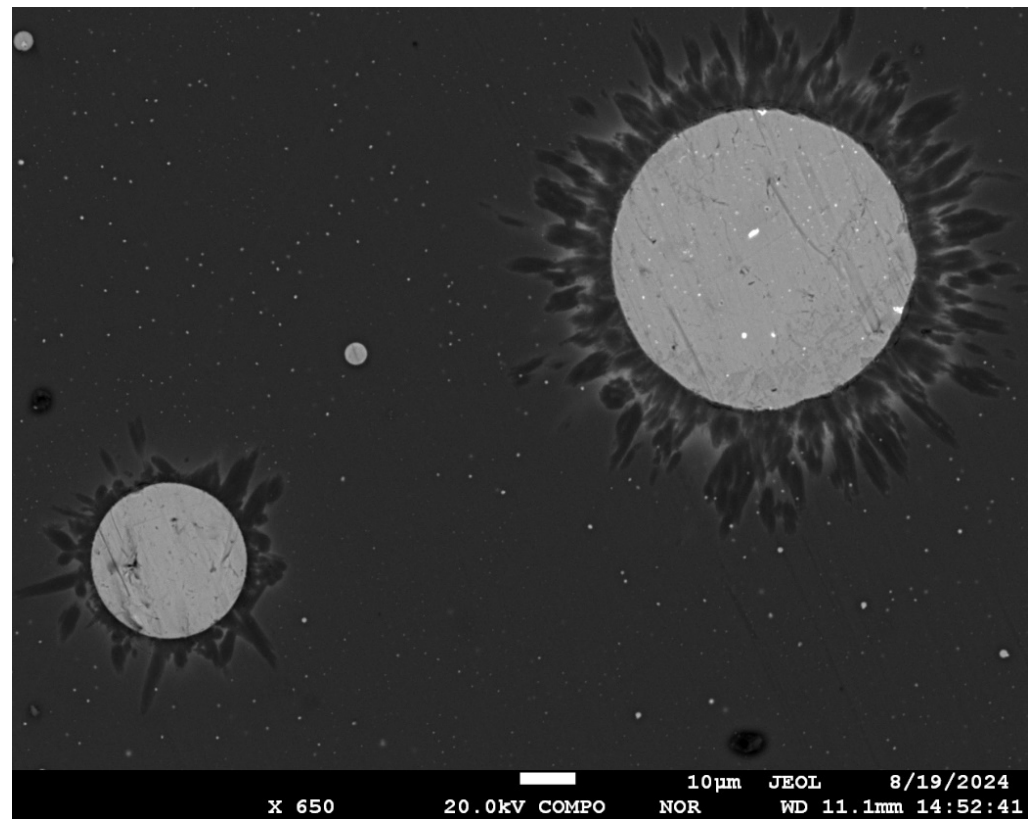


**Figure 6.** Copper sulfide inclusions with a particularly well-developed rim.

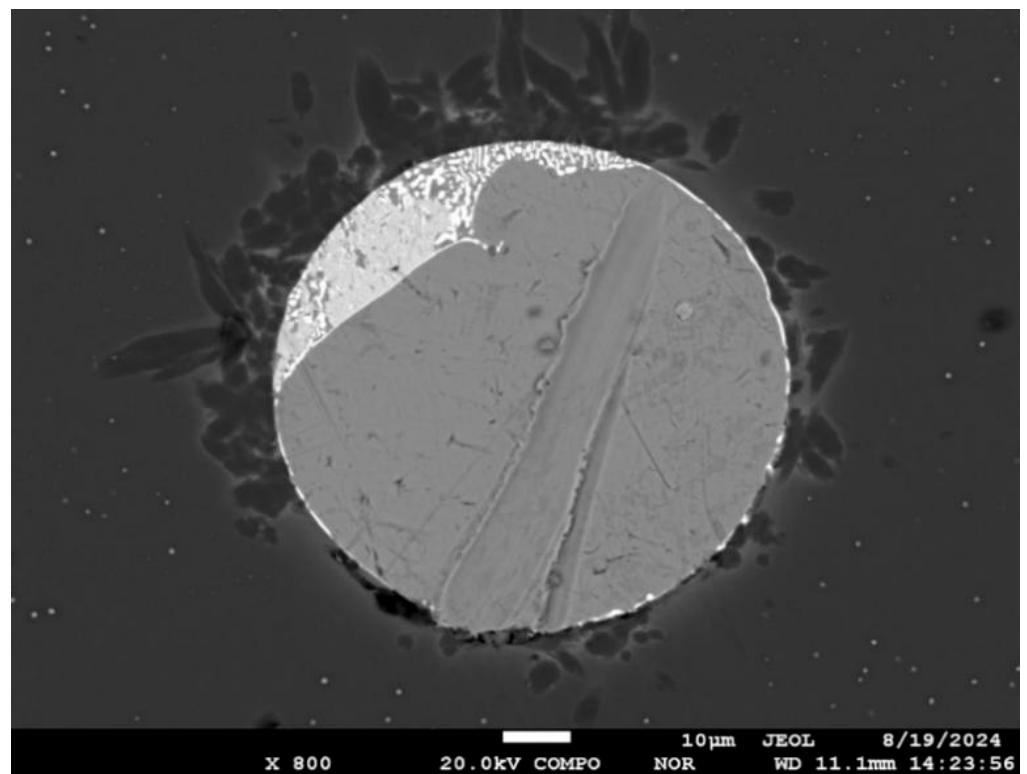


**Figure 7.** Local increase in lead sulfide concentration (light inclusion area) provokes more intense rim formation.

## 4. Conclusions

The use of silica flux in smelting furnaces and converters leads to significant technological and economic improvements. The temperature of converter slag increased from 1124 °C to 1174 °C, which improved fluidity and reaction kinetics. Copper losses were reduced by more than 50% (converter slag: 10 → 4.5 wt% copper; furnace slag: 1.22 → 0.88 wt% copper), while the Fe<sub>3</sub>O<sub>4</sub> content decreased from 30 to 15 wt% and SiO<sub>2</sub> increased to 31 wt%. Flux ore consumption decreased by 19% (434 → 351 kg/t of blister copper), and slag formation decreased to 20%, which led to a reduction in disposal and electricity costs.

These improvements lead to increased copper recovery, reduced flux costs and improved operational stability. The data obtained indicate potential cost savings of 10–15% per ton of blister copper. Observations of the microstructure revealed heterogeneous behavior of the matte droplets in the slag, indicating complex metal migration processes that merit further investigation for process optimization.

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**Data Availability Statement:** The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding authors.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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