

Copper in solidified copper smelter slags

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Abstract

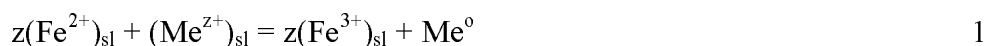
Appreciable amount of copper is slagged in high-grade matte smelting and converting. Major part of copper lost in slag is recovered through slag cleaning operations. Copper losses in slag are of two main types: copper is either dissolved in molten slag as cuprous oxide (or as sulphide) or forming a mechanical dispersion in slag. For slag cleaning by froth flotation mineralogy and morphology of solidified slag as well as chemical composition of copper bearing phases are of great interests. These phenomena are reviewed and discussed in this paper.

Introduction

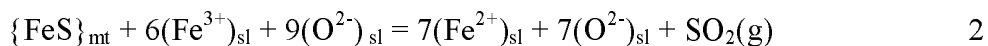
Copper smelting and converting slags contain appreciable amount of copper (Fig. 1) and are as a rule subjected to slag cleaning in order to recycle copper back to smelting stages. Alternative methods are traditional electric furnace smelting under reducing-sulphidising conditions and froth flotation of slowly solidified and cooled slag. Mineralogy, morphology and chemical composition of copper bearing phases in solidified slag, interesting characteristics from a flotation point of view, result in the chemical, thermal and mechanical processes taking place during smelting and solidification processes. The present paper is merely a superficial review of articles concerning copper in smelter slags and a retrospection on theses carried out on a theme “copper in copper smelting slags” at Helsinki University of Technology, Laboratory of Metallurgy.

On the formation of “copper losses” in slag

Copper content of matte smelting slags range around 1 wt-% up to 3-4 wt-% depending on the matte grade as well as smelting technology and praxis. Converter slags from slag blowing stages may contain copper few per cent up to 20 wt-%. Smelter slags from high grade matte smelting^{1,2,3,4,5} contain as a rule considerably more copper than could be expected on the base of results of equilibrium measurements^{6,7,8,9,10} (Fig. 1). Solubility of copper and sulphur in iron silicate slags is depending on matte grade (oxygen to sulphur potential ratio), temperature and slag composition. Results of equilibrium measurements on copper and sulphur solubility are somewhat scattered but the main mass of them are within the limits presented in Fig. 1. Upper limits^{6,7,8,9} correspond to pure iron silicate slags and high sulphur dioxide pressures, the lower limits to slags in which iron oxides and/or silica are partially substituted by calcia, magnesia or alumina^{6,7,8,10}. Contradiction between actual and equilibrium copper contents in iron silicate slags is usually attributed to the formation of mechanical dispersion of matte and copper in slag (see Fig.2¹¹). Mechanical dispersion of molten matte/copper, both denser than slag (accordingly, with tendency to separate by settling) might result in by mechanical mixing or by chemical interaction between slag and matte droplets settling through the slag. Based on their experimental investigations on lead and tin oxide containing iron silicate slags Vanyukov et al.¹² proposed a chemical mechanism of formation of fine metallic dispersion in slag. Authors suggest that reduction of oxides of more noble metals (relative to iron) dissolved in slag takes place through rapid disproportion reaction of type



that leads to formation of fine metallic dispersion in slag with very low settling rate. In suspension smelting of copper sulphide concentrates sulphide particules/droplets might be oxidised to different degrees ranging from copper-iron sulphide (matte) droplets with high iron sulphide content to magnetite and cuprous oxide that dissolve in slag. Iron sulphide containing matte droplets passing the slag layer react with slag



and reduce trivalent iron that leads further to the progress of disproportion reaction (1) with precipitation of fine dispersion of metallic copper.

For copper smelter slags another explanation for exceptionally high copper contents could be the difference in oxygen and cuprous oxide activity between slag and matte. Copper solubility in slag is in fact not directly controlled by matte grade but by oxygen (cuprous oxide) activity. If oxygen activity in slag is higher than in bottom matte solubility of copper might be shifted to the right in matte grade scale (see Fig. 3). Genevski et al¹³ investigated slag and matte samples taken from the settler of industrial FSF and reported decreasing oxygen activity through the slag layer to the bottom matte. Investigations of Fagerlund¹⁴ indicate high complexity of matte-slag formation reactions from oxidised reaction products of copper, silica and molten matte with rigorous gas evolution, dispersion and floating phenomena, that can lead both to the mechanical and chemical dispersion of matte and copper in slag.

Slags from slag blowing stages of copper matte converting are as a rule inhomogeneous containing solid magnetite and silica as well as great amount of suspended matte and metallic copper.

Solidification and cooling phenomena in copper slags

Mineralogical composition and morphology of copper in slags, important for slag flotation, is finally formulated in solidification and cooling of slag. Only metallic and sulphide particles can be flotated from ground slag, valuable metals dissolved in slag are not recoverable by froth flotation. On the other hand small particles not exposed in grinding of slag are lost with flotation residue. As the concentrate from slag flotation is recirculated back to smelting stages, chemical composition, especially impurity content of the floatable mineral section of slag is interesting.

Optical and microanalytical investigations of solidified slags (X-ray microanalysis using Cameca Microsonde MS 46) show that major part of copper dissolved in slag precipitates as metallic copper from the slag even in quenching^{15,16,17} (Fig 4.). Residual copper in the slag matrix is not only copper oxide remaining in the solution but also, probably predominantly, fine precipitate of metallic particles. Fine dispersion of copper can be seen in LOM micrographs of large magnification (Fig. 5 and 8) but particles are too small to be avoided by the electron beam in EPMA. Accordingly, a predominant part of dissolved copper is precipitating in the form of metallic particles during solidification and cooling of slag.

Observations by optical microscopy reveal as well, how copper is precipitated from iron silicate slag even in water quenching. In quenched slags copper is evenly distributed as small size precipitate (Fig. 5 and 8). Particle size of the precipitate increases with decreasing solidification and cooling rate (Figs. 6, 7 and 8). Copper particles in quenched slag are regularly surrounded by dark sphere (= no fine precipitate, low cuprous oxide content?) clearly distinguished from the reddish slag matrix (see Figs. 5, 6 and 8).

The disproportion reaction of cuprous oxide has been proposed to proceed through an electron exchange reaction¹⁸



that explains the rapid disproportion of cuprous oxide and precipitation of copper in quenching. This assumption is supported by the observations suggesting that copper particles are often surrounded by magnetite¹⁹. For quantitative confirmation of the phenomena, however, it would be necessary to make a statistical analysis on great number of slags and copper precipitates. Such investigation was not carried out.

On the particle size distribution and impurity content of copper precipitate

Flash smelting furnace (FSF) and Peirce Smith converter (PS) slags at Outokumpu Harjavalta Metals, Harjavalta Smelter are tapped in large 20 ton molds and slowly cooled. Size distribution of copper/matte particles in one FSF-slag cast and in one PS-slag cast were determined by LOM image analyser (resolution +5 µm) on samples taken from different height and axial position in the 20 ton slag cast.¹⁹ Results are presented in Fig. 10. No significant differences by slag type or sample position was observed. The result was not surprising as the aim of particle size distribution analysis was only to obtain a qualitative picture on differences in size distribution between the different types of slag and between the central and outer part of slag cast. For a statistically significant result much larger number of casts, samples per one cast and site should have been scrutinized.

Not only the form of the occurrence of copper in solidified slag and size distribution but also the chemical composition of metallic precipitate in the smelter slags is of some interest from slag cleaning, environmental and impurity elimination points of view. Copper particles in slowly cooled flash smelter and slag blowing converter slags (for approximate analysis, see Table I) were analysed for their arsenic, antimony and tin content. Samples subjected to EPMA/EDS analysis were the same as in particle size analysis.¹⁹ In all more than 1100 individual particles were investigated. Distribution ratio between copper particles and slag matrix for the mentioned impurity elements could not been obtained as their contents in slag proved to be too low for reliable analysis using EPMA.

Results presented in Table I and in Figs. 11 to 13 show, that arsenic, antimony and tin, all, are strongly concentrating in copper particles. No clear dependence on position in slag cast or on particle size was observed. Scatter in contents of all impurity elements in copper particles is amazingly large, ranging from practically zero to several percent. Coke charged to the converter before slag pouring seems to increase the absorption of As, Sb and Sn by copper particles (Fig. 11 vs. 12).

Concluding remarks

Articles and reports, reviewed, imply that mineralogy and morphology of copper in solidified smelter slags is formed in complex chemical, mechanical and physical processes taking place during smelting, solidification and cooling of slag. It is obvious that copper is in solidified smelting and converting slags mainly in metallic state in the form of evenly distributed beads ranging from sub-micron level up to few hundreds of microns (not so rare exception is highly stiff, solid-liquid converter slag with high content of mechanically entrapped copper and matte). In slow cooling chemically dissolved copper is dissociating more or less substantially to metallic copper and could be in principle recovered completely by flotation. Mechanically mixed or precipitated copper in slag “absorbs” substantial part of slagged arsenic, antimony and tin during its the route from molten state to room temperature that are, accordingly, recycled back to smelting with concentrate from flotation cleaning of smelter and converter slags.

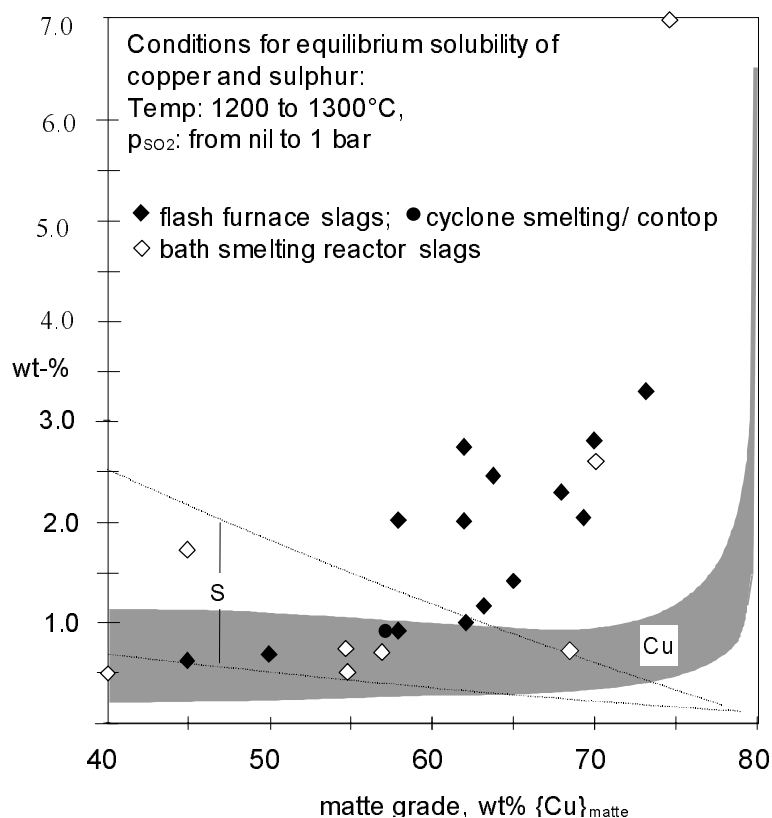


Fig. 1 Solubility of copper and sulphur in molten iron silicate slags^{6,7,8,9,10} and copper content of some industrial matte smelting reactor slags^{1,2,3,4,5}.

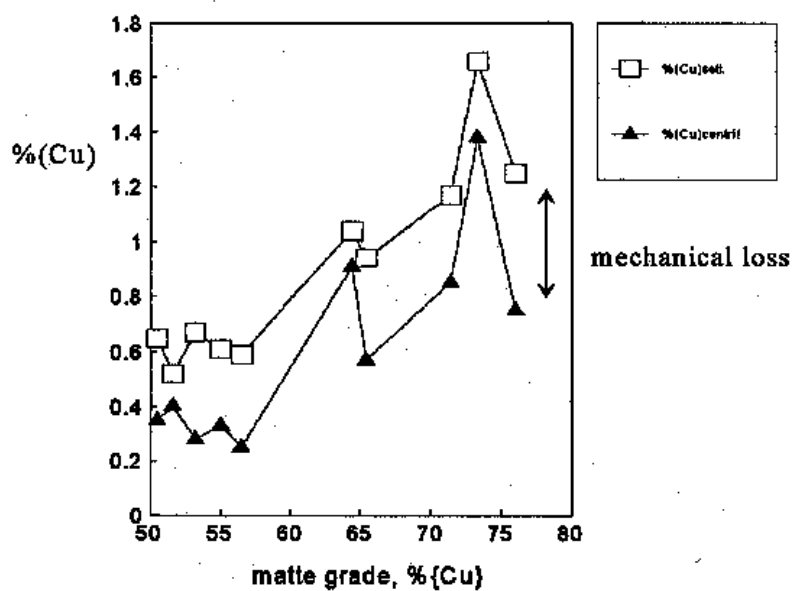


Fig. 2. Comparison of copper content of slags from pilot scale suspension smelting reactor after settling and centrifuging. Figure is redrawn from a figure in ref.¹¹.

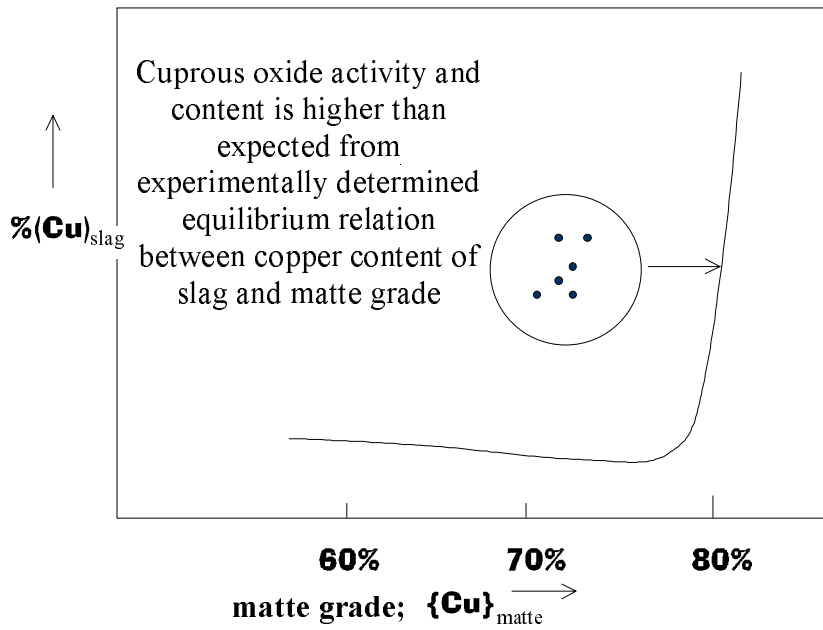


Fig. 3 Schematic explanation of “high” copper contents of smelter slags

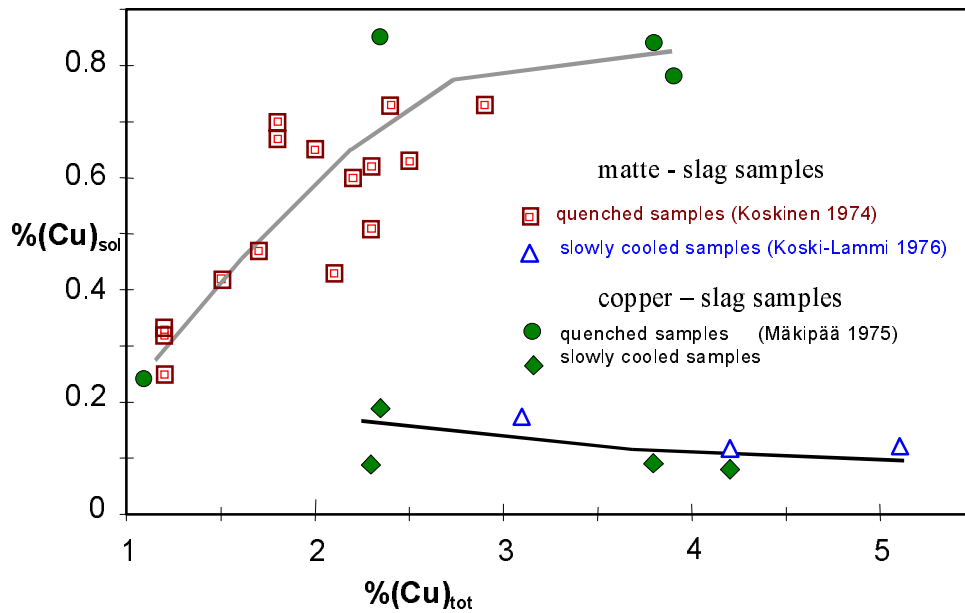


Fig. 4. Residual copper in silicate phase (in $< 1\mu$ metallic particles) after solidification as a function of total copper content of slag. Iron silicate slags containing $15 \text{ wt}\% \pm$ % alumina are equilibrated either with high-grade mattes (75 to 80 wt% Cu)^{15,16}, or with metallic copper¹⁷ at 1250 to 1270°C under controlled atmosphere.

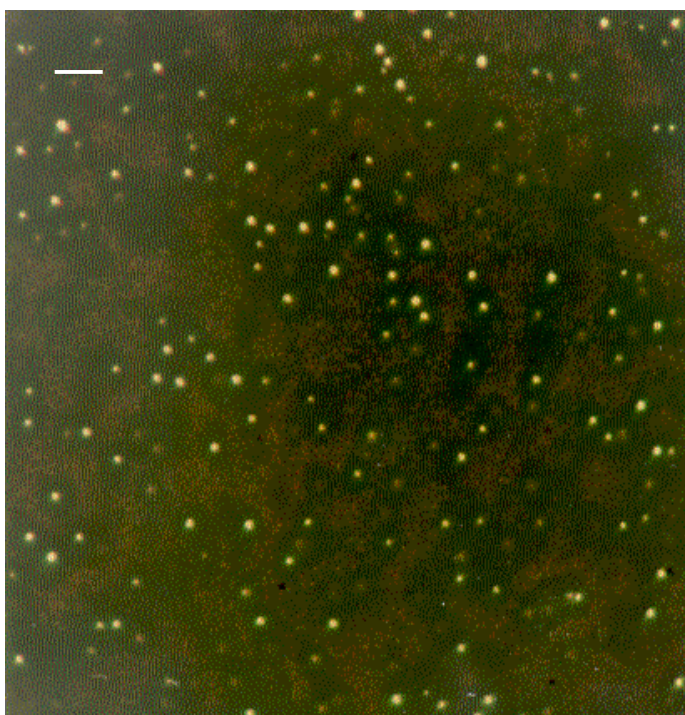


Fig. 5

LOM image of iron silicate slag equilibrated with copper at 1270°C under CO₂/CO-flow of $p_{O_2}/\text{bar} = 6.3 \cdot 10^{-10}$. Sample was quenched in nitrogen flow at the end of the furnace – medium cooling rate. Bar - 10 μm

$\text{Cu}_{\text{sl}} = 1.2 \%$ (ref.¹⁷)

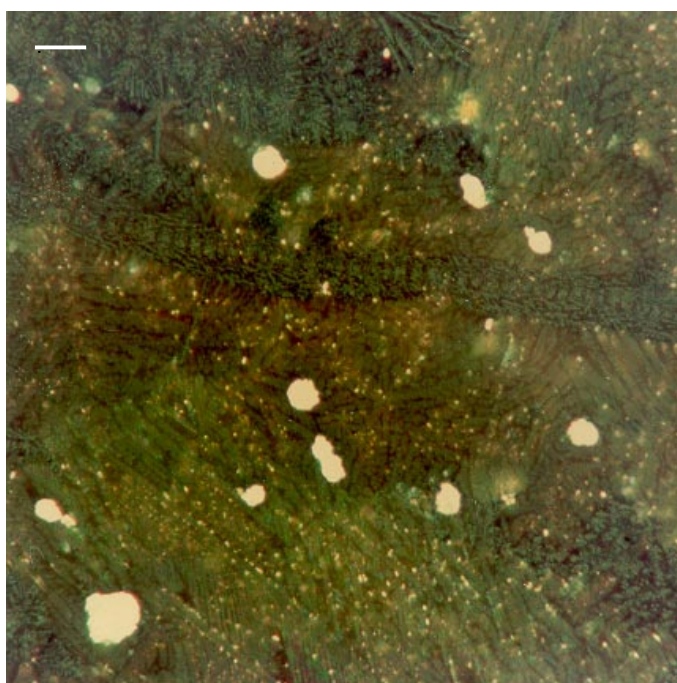


Fig. 6

LOM image of iron silicate slag equilibrated with copper at 1270°C under CO₂/CO-flow of $p_{O_2}/\text{bar} = 6.5 \cdot 10^{-9}$. Sample was quenched in nitrogen flow at the end of the furnace – medium cooling rate; Bar - 10 μm

$\text{Cu}_{\text{sl}} = 2.5 \%$ (ref.¹⁷)

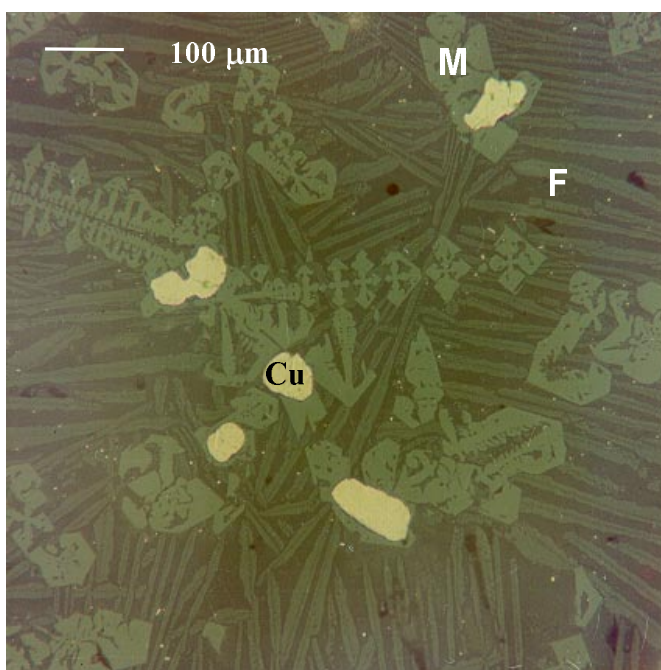


Fig. 7

LOM image of iron silicate slag equilibrated with copper at 1270°C under CO₂/CO-flow of p_{O2}/bar = 6.5*10⁻⁹. Sample was cooled slowly, with the furnace, Cu_{sl} = 2.3%; (ref.¹⁷)

Bar - 100 μm

Cu – copper, M – magnetite (Al-containing spinel), F – crystallised iron silicate (fayalite) with glassy silicate slag between the crystals

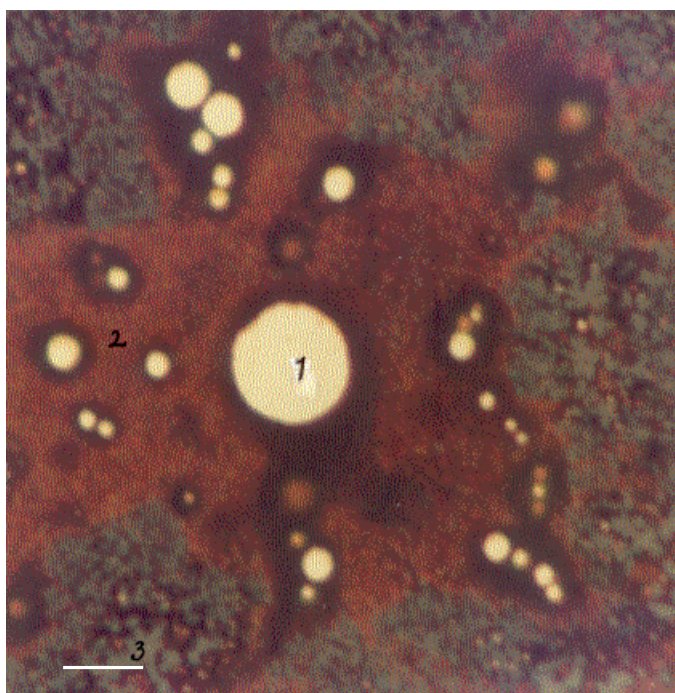


Fig. 8

Water quenched iron silicate slag equilibrated with copper matte at 1250°C 72 h under CO₂/CO-flow of p_{O2}/bar = 2.2*10⁻⁸; Bar - 10 μm
Cu_{sl} = 2.2%,
S_{sl} = 0.19% (ref.¹⁵)

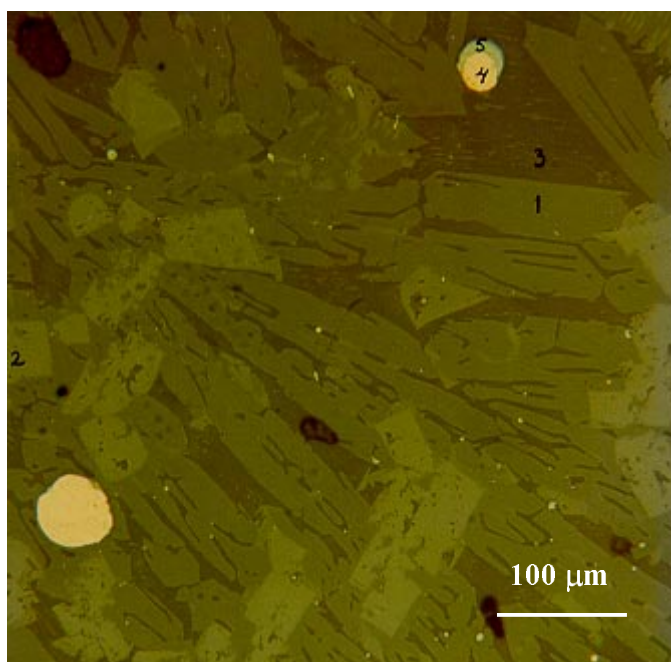


Fig. 9

Slowly, with the furnace cooled iron silicate slag equilibrated 40 h with copper matte at 1250°C under CO₂/CO-mixture with $p_{O_2}/\text{bar} = 2.2 \cdot 10^{-8}$;

Bar - 100 μm

Cu_{sl} = 1.8%, S_{sl} = 0.18% (ref.¹⁷)

1 - crystalline fayalite,

2 – magnetite (spinel)

3 – glassy slag, 4 – metallic copper,

5 – cuprous sulphide

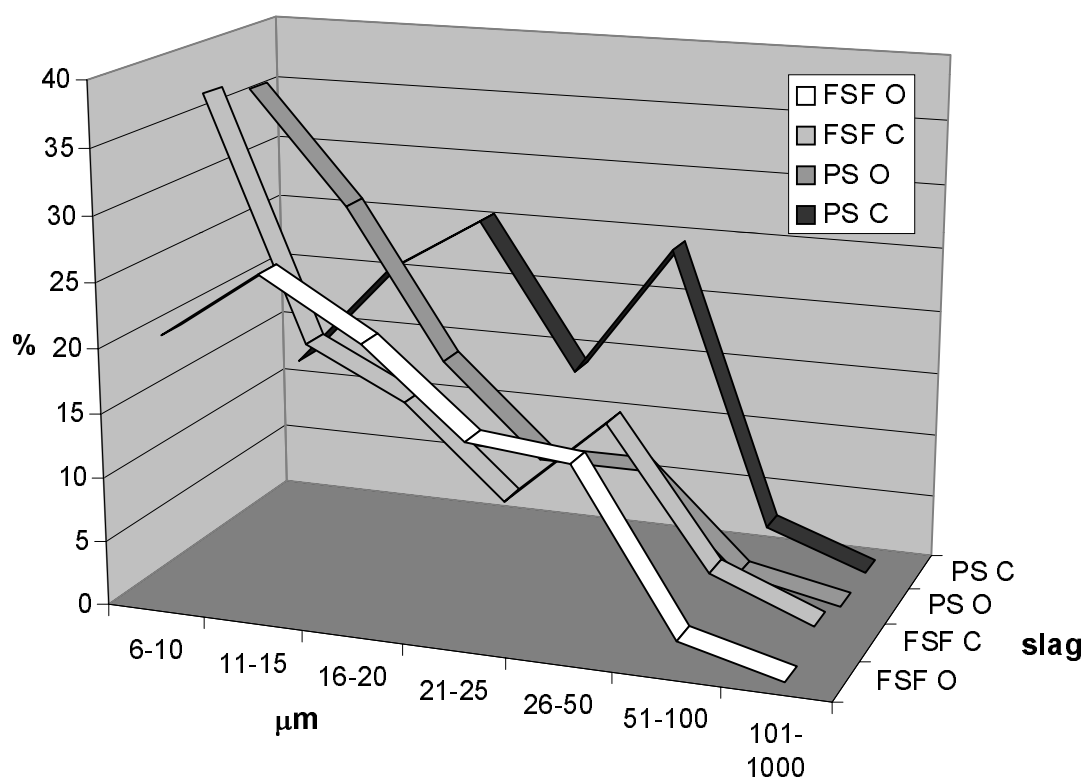


Fig. 10 Particle size distribution of copper/matte particles in slowly cooled FSF- and PS-converter slags; for average see Table I
 O – sample taken 1 cm beneath of the surface of slag cast
 C – sample taken from the centre of cast

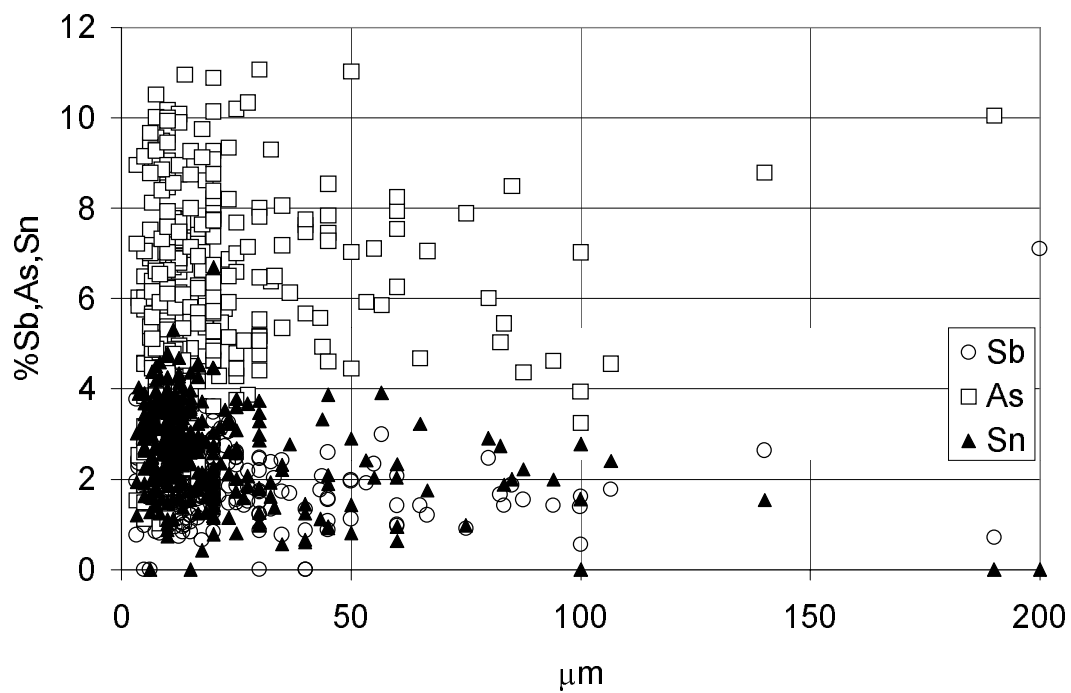


Fig. 11 Antimony, Arsenic and Tin content of copper precipitates in FSF-slag as a function of particle size of precipitate

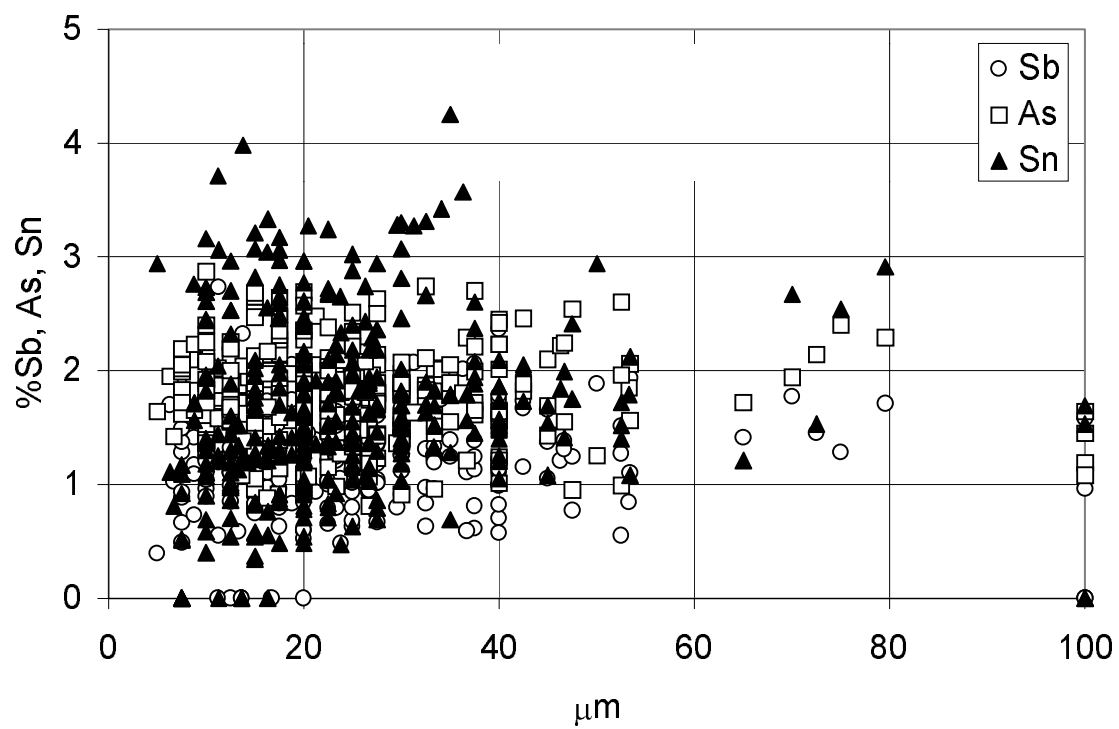


Fig. 12 Antimony, arsenic and tin content of copper precipitates in converter slag

as a function of particle size of precipitate; coke charged onto the slag

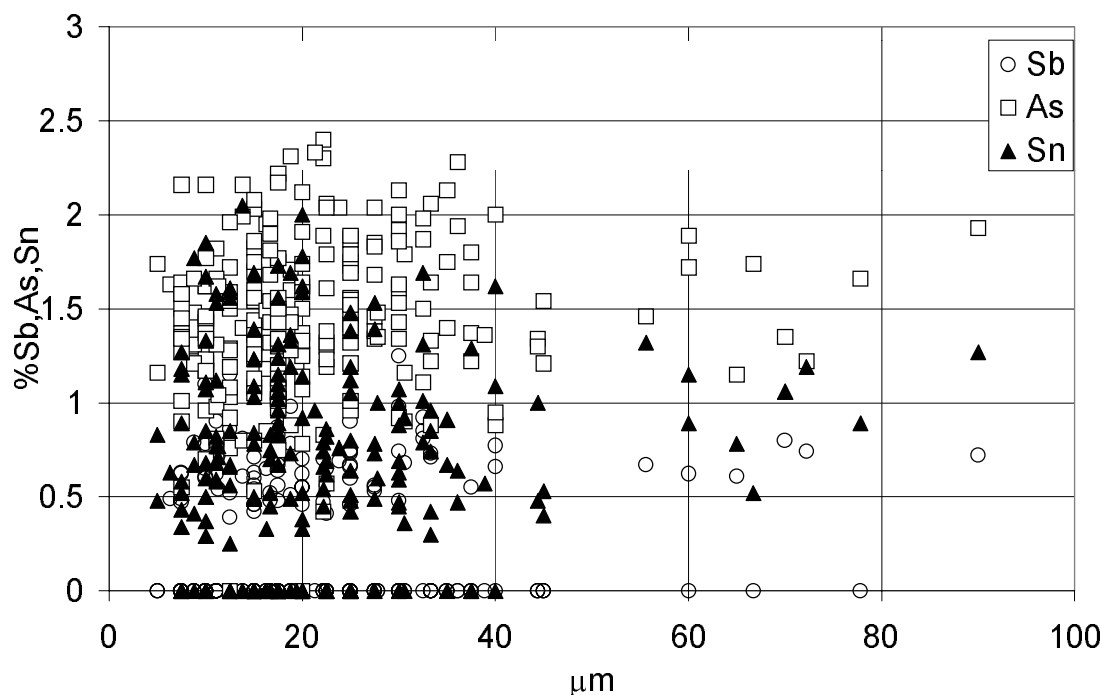


Fig. 13 Antimony, arsenic and tin content of copper precipitates in converter-slag as a function of particle size of precipitate; no coke addition

Table 1

Average EDS-analysis of copper particles in converter and FSF-slugs and chemical analysis of parallel slag samples

<i>Copper particles in</i>	<i>Cu</i>	<i>Sb</i>	<i>As</i>	<i>Sn</i>	<i>S</i>	<i>Average Size (μm)</i>
FSF slag I	86,5	1,6	6,1	2,8	0,2	20,5
FSF slag II	85,7	2,0	6,3	2,6	0,4	20,9
Converter slag I	91,4	1,3	1,8	1,7	0,4	24,1
Converter slag II	91,3	0,3	1,5	0,6	0,2	21,5
Slag total						
FSF slag I	1.7	0.07*	0.2*	0.2*	0.17	
FSF slag II	1.5	“	“	“	0.13	
Converter slag I	8.4	-	-	-	1.0	
Converter slag II	10.0	-	-	-	1.1	

*Long term average analysis of FSF slags covering the period of the investigation;

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