DESCRIPTION OF SLAGS FROM THE PROCESSES OF NON - FERROUS METALS METALLURGY

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ABSTRACT

In the paper the properties of slags formed by the metallurgical processes as manufacturing and refining of non - ferrous metals have been presented
The following slags have been studied: 1) slags from the shaft furnace process, 2) slags from Outokumpu flash smelting furnace, 3) slags from the rotary-rocking furnace, 4) slags from copper electrorefining anode slime processing 5) synthetic slags $PbO \cdot SiO_2$ *and* $4PbO * SiO_2$*. Density, and viscosity, as well as softening and melting points slags also structural examination using light microscope and SEM with X-ray microanalysis have been carried out. On the base of experimental results the description of physical - chemical properties of investigated slags have been performed.*

1 INTRODUCTION

The subject of this paper were non-ferrous metallurgy slags, in particular from copper, lead and silver production. By using a modern research methodology, the following essential physico-chemical parameters of the slags under investigation were determined:

-. softening and melting points, density, viscosity, phase composition, structure by applying coloured microphotography, microcomposition; additionally, a thermochemical analysis of formation reaction of the main slag-forming constituents of the slag under investigation.

For a differentiated chemical constitution and the structure of slags, each case had to be investigated separately. Be underlined, however, that the investigations of the slags phase composition were performed in a wide range of angles 2θ; therefore, the analysis precision could be elevated. SEM examinations with parallelly conducted analyses on the micro-area under investigations, are as well precise and accurate. The results obtained due to a modern investigation methodology allowed to analyse the slag characterization from the viewpoint of metallurgy; this characterization constitutes the framework for working out a correct technology [1-5].

2 EXPERIMENTAL PROCEDURE AND RESULTS

In the investigations the following method were applied:

- chemical analysis
- determination of softening and melting points

- determination of slag densities
- determination of viscosity
- investigations on the phase composition
- X- ray microanalysis
- thermochemical analysis of slag-forming reactions
- microscope observations.

The subject of the investigations was the following materials:

- shaft furnace slag (copper matte melting)
- flash-smelting slag (melting process of copper sulfide concentrates)
- electric furnace slag (after the reduction process of the reduction process of the flash
- smelting furnace slag), Fig 1
- slag from the 1st stage of refining of Cu-Pb-Fe alloy, Fig 2
- lead silicate $PbO \cdot SiO_2$ (synthetic)
- lead silicate $4PbO \cdot SiO_2$ (synthetic)
- slag from lead melting in the rotary-and-rocking furnace
- slags from copper electrorefining anode slime processing

As far as lead, copper and iron determination is concerned, the chemical analysis of slags [6] was carried out by means of an atom absorption spectrometer PERKIN-ELMER 3100 in an air-acetylene flame. The elements under investigation were determined according to the pattern series method basing upon linear (Pb) or non-linear ((Fe, Cu) calibration diagrams, worked out by using standard solutions. For each sample, the measurements of analytical signals were performed in the conditions as set for the solutions, whereas the looked for analyze concentrations in samples are calculated via apposite calibration functions. Instead, silicon determinations were carried out via a spectrophotometer UV/VIS SPEKOL 11 with the molybden-silicic acid method. The measurements were performed at the wave length 400 nm.

Results from determining the softening and melting points are given in Table 1. Investigations were performed with a high temperature HTM microscope.

Density of slags was computed from the formula:

$$r_t = \frac{m_o - m_t}{V_t} \qquad (1)$$

Where:

r_t – slag density (g/cm3) at temperature t
m_o – mass of a steel ball in air (g)
m_t – mass of the ball in slag at temperature t
V_t – ball volume (cm3) at temperature t

Results of slag density determinations are given in Table 2.

Slag viscosities were determined at temperatures corresponding to the liquid phase of the slags under investigation. Table 3 shows the results from viscosity determination.

The X-ray phase analysis was carried out by means of diffractometry as fully computer-aided, basing upon PC-APD system. A selected group of compounds, most likely to occur in the slags under investigation, was taken out for analysis from the database. The selection of the group area was performed basing upon the chemical analysis of those slags. In particular, attention was paid to the basic compounds occurring in the slags under investigation, for example: PbO, FeO, Fe_2O_3, Fe_3O_4, SiO_2, Cu_2O, Cu and, of course, complex compounds like:

$Pb \cdot Fe_2O_3$
$Pb \cdot FeOy$

$(SiO_2)_2$
$FeO \cdot (SiO_2)y$
$Cu_2O \cdot (SiO_2)y$
$PbO \cdot (Si_2O_2)y$
$PbO \cdot (Fe_2O_3)y$

Diffraction patterns of investigated slags are illustrated in Figs 3-5. Structural examinations were performed by means of an light microscope in normal and polarized light, with magnifications from 125x to 800x. The results of the microscope observations made are presented in Figs. 6, 7 as (exemplary) coloured microphotographs.

Observations of slags with a scanning microscope (SEM), in conjunction with an analysis performed simultaneously, were carried out on a JEOL microscope and a micro-X- ray analyser IXA-50A, provided additionally with a system of X-ray radiation dispersion spectrometer KEVEX. The microstructure of the materials under investigation was observed in the secondary electron image (SEJ) and photographed. At the same time, there were performed quality analyses of the chemical constitution within the micro-area under observation, as well as local analyses so as to obtain an X-ray radiation spectrum of the elements constituting the sample under investigation.

3 DISCUSSION

The softening and melting points, determined by means of a high temperature microscope, are as follows:

- shaft furnace slag (copper matte melting),
- t soft = 1065^{o}C , t melt 1120^o C.

The abovesaid temperature values, especially the melting point, correspond with the slag phase composition based upon fayalite $2FeO \cdot SiO_2$ whose melting point, according to the equilibrium diagram FeO-SiO_2, amounts to 1250^{o}C. This slag represents an extended fayalite – apart from FeO there occur as well CaO, MgO and Al_2O_3. Those are the constituents which affect changes in the slag melting point (equilibrium diagrams FeO-SiO_2-CaO; FeO-SiO_2-Al_2O_3).

Flash smelting furnace slags are characterized with lower levels of both the softening point (1015^{o}C) and of the melting point (1055^{o}C). Apart from the principal slag-forming constituents (FeO, SiO_2, CaO, Al_2O_3, MgO), this slag contains high contents of copper (approx. 14%) in both metal and oxide forms, and of lead (about 3.5%). Therefore, it constitutes a separate phase system.

Electric furnace slag (from the reduction process of the flash melting slag) has its softening point and melting points values as high as, respectively, 1040^{o}C and 1105^{o}C. So they are similar to those of the shaft furnace. As distinct from the flash smelting slag, its contents are different and the main constituents are as follows: SiO_2 - about 38%, CaO about 23-25%, Al_2O_3 about 10%, MgO about 8% and Fe about 6%). Instead, its phase composition resembles that of the shaft furnace.

The slag from the Cu-Pb-Fe alloy refining process exhibits the following temperature values: softening point 960^{o}C and melting point 1035^{o}C. Its composition is completely different, for example: copper (16-35%), lead (17-35%), SiO_2 (12-27%), iron (7-26%), CaO (about 4%). The levels of the said constituents fluctuate within a wide range.

A synthetic slag $PbO \cdot SiO_2$ has the following parameters: softening point 505^{o}C and melting point 680^{o}C. The lowest melting point, in comparison with the equilibrium system $PbO \cdot SiO_2$, should be attributed to the phase composition of the slag under investigation, this is to say, to the eutectic occurring in the system mentioned ($PbO \cdot SiO_2 + 2PbO \cdot SiO_2$).

A synthetic slag 4 $PbO \cdot SiO_2$ characterizes by the following properties: softening point 620^{o}C

and melting point 700^oC.
However, the melting temperature is lower than in the equilibrium system $PbO-SiO_2$ and corresponds with the temperature of the eutectic $4PbO·SiO_2$ + $2PbO·SiO_2$, occurring in the system $PbO-SiO_2$.
Investigations on synthetic lead silicates refer to copper slags from the flash smelting process, converting of the Cu-Pb-Fe alloy and slags from the KALDO converter (processing of anodic slimes) characterized, among others with contents of lead silicates.
The slag from the rotary-and-rocking furnace has the following parameters: softening point 1180^oC and melting point 1320^oC.
The said values regard slag samples taken at random; their phase composition is as follows: FeO 20-38%, SiO_2 25 – 33%, CaO 6-15%, MgO 2-7%, Al_2O_3 approx. 8%
Thus, the slag is based on fayalite and the softening point almost corresponds to the levels from the system FeO- CaO – SiO_2.
The phase analysis of copper slags (from the shaft, flash smelting, Cu-Pb-Fe alloy converting processes, of lead slags (from the melting process in the rotary-and rocking furnace, finally of those from the anodic slime processing, comprises the complete documentation of the X-ray phase analysis with the following data:

- results of the X-ray diffraction analysis according to the PC-APD PHILIPS data base
- probability of occurrence of a diffraction line of the compound given (FORMULA), however, in compliance with some strict limitations
- diffraction patterns.

The investigated slags exhibited a clear differentiation in their phase composition in accordance with the type of the technological process. In the case of copper slags there are observed different phase compositions while comparing the slags respectively, from the shaft and flash smelting furnace processes. The proportions of the chief slag constituents (oxides of Fe, Pb, Cu, Si, Al and other) are subject to changes. The phase analysis has revealed the occurrence of many phases based upon oxides of Fe, Pb, Cu and SiO_2, as well as their differentiation depending upon the slag type. A separate phase composition is revealed in the slag from the converting of the Cu-Pb-Fe alloy in which, among others, the following compounds have been found: Fe_3O_4, Fe_2O_3, Cu_2O, SiO_2, PbO, $3PbO·2SiO_2$, $2PbO·SiO_2$, $PbO·2Fe_2O_3$, $2PbO·Fe_2O_3$, $PbO·Fe_2O_3·SiO_2$.
The viscosity values of the investigated copper slags, slags coming from the shaft furnace process, flash smelting process, electric furnace and the alloy refining process, are appreciably different one from another. This differentiation can be attributed to the chemical and phase composition of slags. The shaft furnace slag exhibits the highest viscosity [37 (P) at 1357^oC]. That from the flash smelting furnace has a viscosity value far and out lower: 3.7 P at 1356^oC; finally, in the case of the slag from the electric furnace – 12,5 P at 1356^oC.
The lowest value has the slag from the converting of the Cu-Fe-Pb alloy: 0,3 P at 1113^oC. The slag from the lead melting process, held in the rotary and-rocking furnace, is characterized with a viscosity value of about 3 (P) at 1347^oC. Instead, synthetic lead silicates exhibit higher viscosities, namely:

$4PbO·SiO_2$ – 1,6 [P] at 923^oC

$PbO·SiO_2$ – 3,4 [P] at 1207^oC.

While comparing the said values, it should be stressed that the occurrence of lead silicates in the slag can appreciably reduce the viscosity levels. It has been unequivocally reflected in the case of the slag coming from the converting of the Cu-Pb-Fe alloy.
The coloured microphotographies, obtained in the microscope observations (Figs 6, 7) can attest to a complex structure of the slags under investigation. The proportions of the structural constituents are distinctly changed, depending upon the slag type. Typical spherical inclusions of metal copper, which have not been coagulated and precipitated from the slag, are

characteristic for the flash smelting process slag. In turn, in the shaft furnace slag (copper matte melting) in the micro-picture there can be observed sporadic inclusions of copper matte. In the case of the Cu-Fe-Pb refining process there occurs a multi-constituent structure, containing among other, interesting needle-like crystallites of Fe and Cu silicates.

However, the coloured microphotographs of the slag coming from the lead smelting performed in the rotary-and rocking furnace, illustrate a complex system in which, apart from the main slag-forming constituents, there appear sporadic inclusions of metal lead and unreacted batch constituents (lead sulphides, metal iron, according to the course of the lead melting process.

A particular structure is revealed in the slag from the classic cupellation process and the BOLIDEN technology (Fig 6c) – of remelting of silver-bearing anodic slimes. In other slags, silver inclusions assume various forms. It can be generally stated that the performed microscope investigations lead to a detailed description of the microstructure of the slags under examination and constitute an important factor that is complementary to the X-ray phase analysis from the view-point of the distribution of the structural constituents (phases) found in the materials subject to investigations. The enclosed coloured microphotographs corroborate the said remarks.

Taking into consideration that the slags under investigation constitute valuable metal-bearing intermediate products (as batch constituents) in the metal winning processes, there was performed a thermodynamic analysis [7] of the main reactions of slag-forming and of reduction of metal oxides occurring in slags, by emans of carbon and CO.

The following reactions have been regarded:

Silicate formation:

$$2FeO + SiO_2 \rightarrow 2FeO \cdot SiO_2 \qquad (2)$$

$$nPbO + SiO_2 \rightarrow nPbO \cdot SiO_2 \qquad (3)$$

n = 1, 2 i 4

$$Cu_2O + SiO_2 \rightarrow Cu_2O \cdot SiO_2 \qquad (4)$$

$$2Na_2O + SiO_2 \rightarrow 2Na_2O \cdot SiO_2 \qquad (5)$$

Reduction of metal oxides:

$$XMeO + yC \rightarrow xMe + yCO_2 \qquad (6)$$

$$XMeO + yCO \rightarrow xMe + yCO_2 \qquad (7)$$

Where: MeO: Cu_2O, PbO, Sb_2O_3, Sb_2O_5
As_2O_3, As_2O_5, SeO_2

Silicate reduction:

$$nMeO \cdot SiO_2 + C \rightarrow nMe + SiO_2 + xCO_2 \qquad (8)$$

$$nMeO \cdot SiO_2 + CO \rightarrow nMe + SiO_2 + yCO_2 \qquad (9)$$

Where MeO: FeO, PbO, Cu_2O i Na_2O

Thus, there have been regarded main constituents of copper and lead slags. The thermodynamic analysis of such complex systems (like slags) was carried out with a certain simplification, with a limitation to the examination of the basic systems occurring in slags.

The enclosed diagrams show the change in free enthalpy according to the temperature of the said reactions and determine the priority of the reaction in the given system from the theoretical viewpoint.

For example, in the case of the slag from the process of Cu-Fe-Pb alloy refining, the following reduction reactions were investigated:

$$Cu_2O + CO \rightarrow 2Cu + CO_2 \qquad (10)$$

$$PbO \cdot SiO_2 + CO \rightarrow Pb + SiO_2 + CO_2 \qquad (11)$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \qquad (12)$$

A change in free enthalpy as a temperature function can suggest a possible course of the said reactions. The Cu_2O reduction reaction should be the fastest.

The above mentioned remarks regard, as said previously, the investigation of the aforesaid reactions at certain simplifications (for the complex systems reflected in the slags). For instance, the Cu_2O reduction reaction should be considered in compliance with the following scheme:

$$(Cu_2O) + CO \rightarrow 2[Cu] + CO_2 \qquad (13)$$

Where: the symbols in round brackets ( ) represent a slag constituent, whereas in square brackets - a constituent of a metallic alloy.

The computed values of changes in free enthalpy of the reactions under investigation are presented in the enclosed diagram (Fig 8).

Taking into consideration the results obtained for the investigations of the slags under investigation, there were performed examinations on the course of the reduction reaction of copper slags (from the converting process of the Cu-Pb-Fe alloy) and lead-bearing slags (processed in the rotary-and-rocking furnace). The reduction of copper slag, coming from the refining of the Cu-Fe-Pb alloy, containing 20-35% Cu, 30-38% Pb, 5-10% Fe, 35-42 % SiO_2 (hence – an appreciable range of the principal slag constituents), was being carried out at 1200^oC [1473 K] within a 2 hours time, in the presence of wood coal as a reducing agent. The reduction effects were 3 products, distributed along the vertical section of the crucible, namely:

Fayalite slag (upper zone)

- copper (with lead contents) (middle zone),
- lead [with copper contents] (lower zone).

So, during the reduction process there occurred a typical process of segregation.

Below are given the results of the analysis in the respective zones:

- the top zone is the fayalite slag (2FeO, SiO_2, Fe_2O_3, dispersed copper and lead inclusions),
- middle zone (a copper and lead alloy: about 70% Cu and 21 % Fe),
- bottom zone (lead-based alloy containing about 90% Pb and 5% Cu.

All 3 melt products were subject to a chemical, X-ray, phase analyses and to microscope observations [8].

Next stage of investigations regarded a lead-bearing slag from the cupellation process (containing about 68% Pb, approx. 6,6% Cu and 4% Ag). It was subject to a reduction process at 1100^oC for 2 hours.

And in this case there were performed indispensable investigations on the reduction products, viz. on the metal phase and slag, incl. the chemical analysis, microscopic and X-ray examinations. The performed investigations on the reduction of the cupellation process slag refer to obtaining of lead anodes which are directed to the lead electrorefining (BETTS method).

4 CONCLUSION

The completed investigations on slags from the non-ferrous metallurgy have enabled to have the slags characterized from the metallurgical viewpoint. Such a characteristics is indispensable for working out a technology related to metal recovery.

5 REFERENCES

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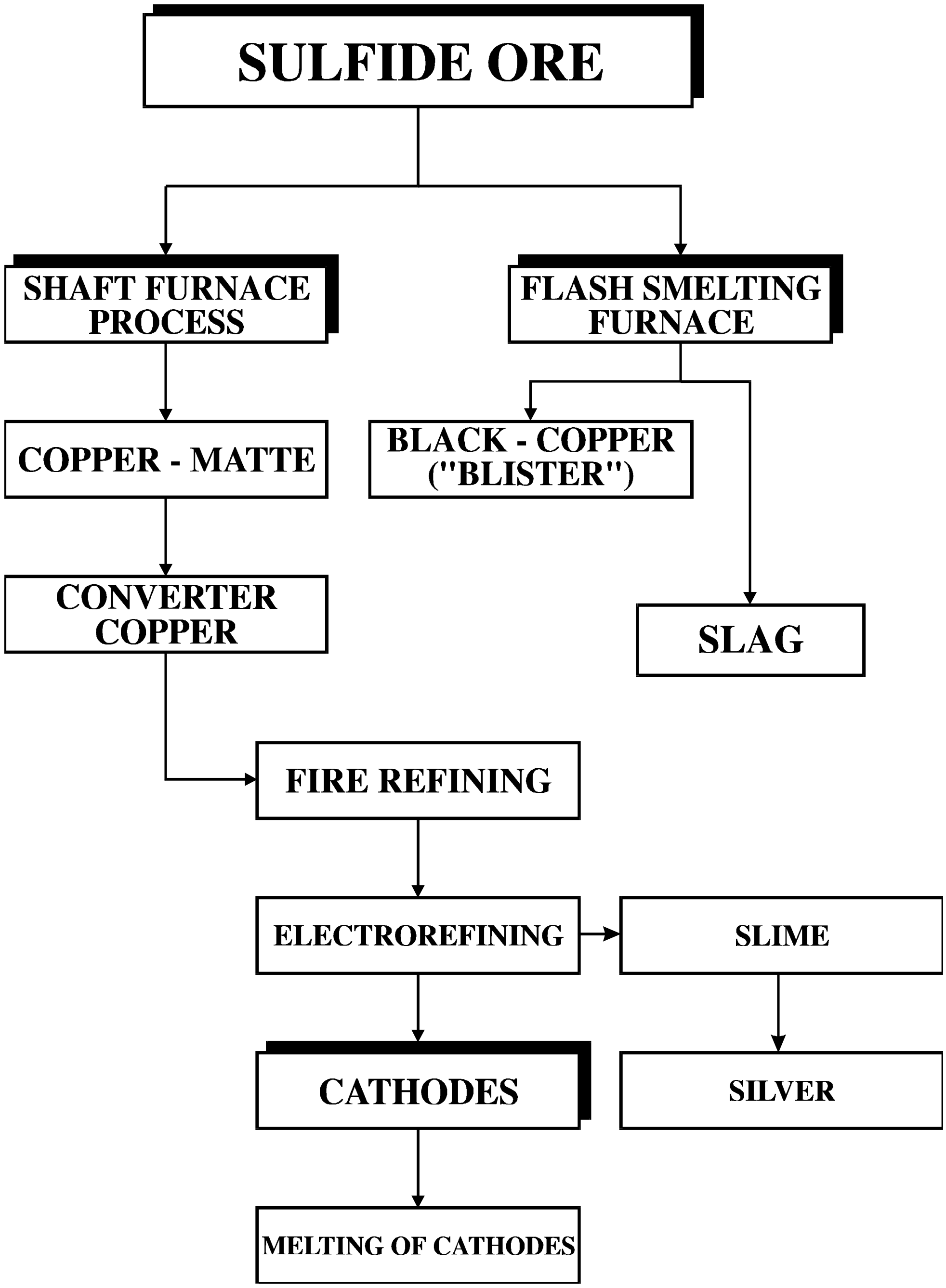


Fig 1 Flow-sheet of copper winning

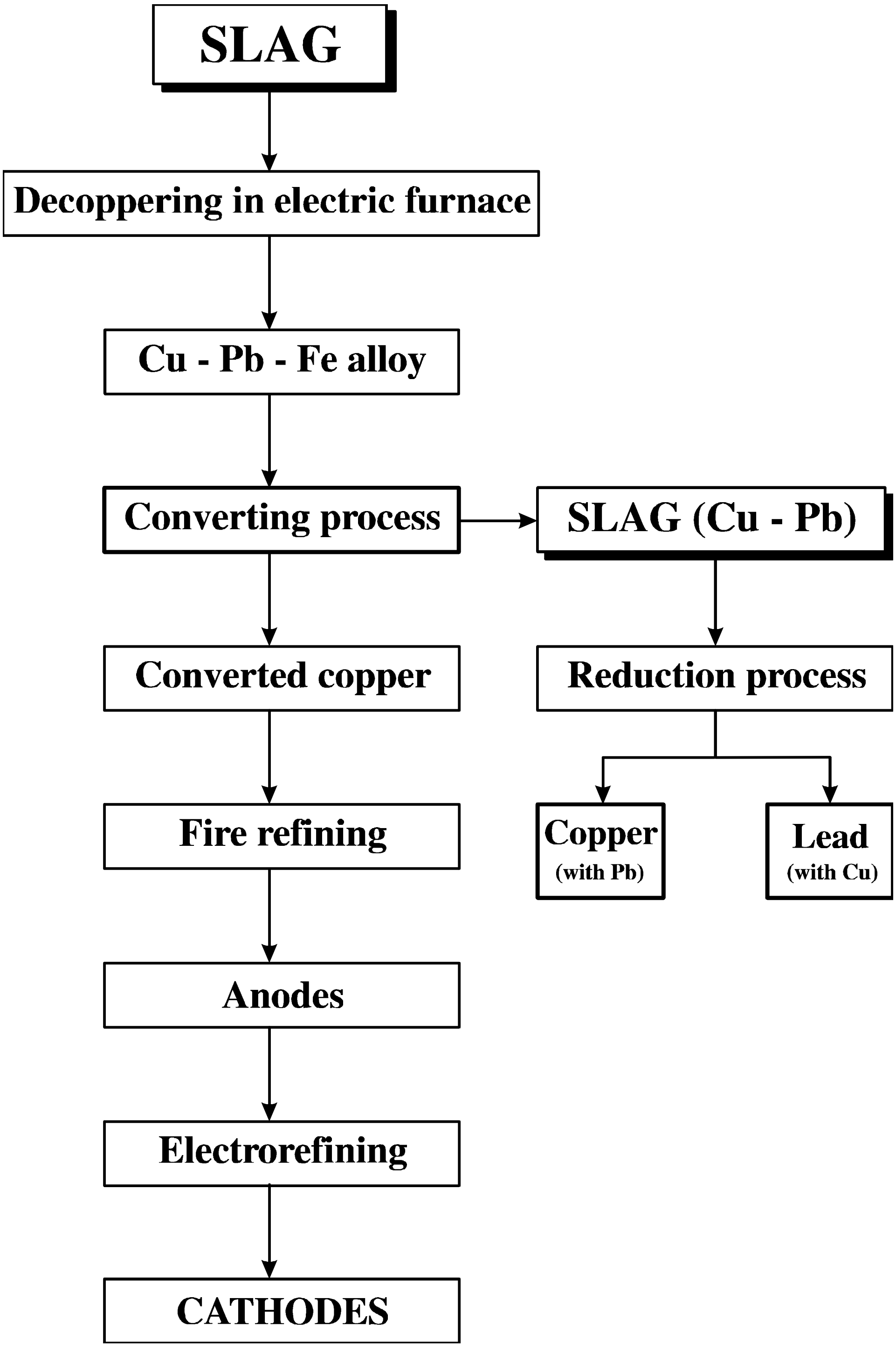


Fig 2 Flow-sheet of Outokumpu (flash smelting process) slag metal removal

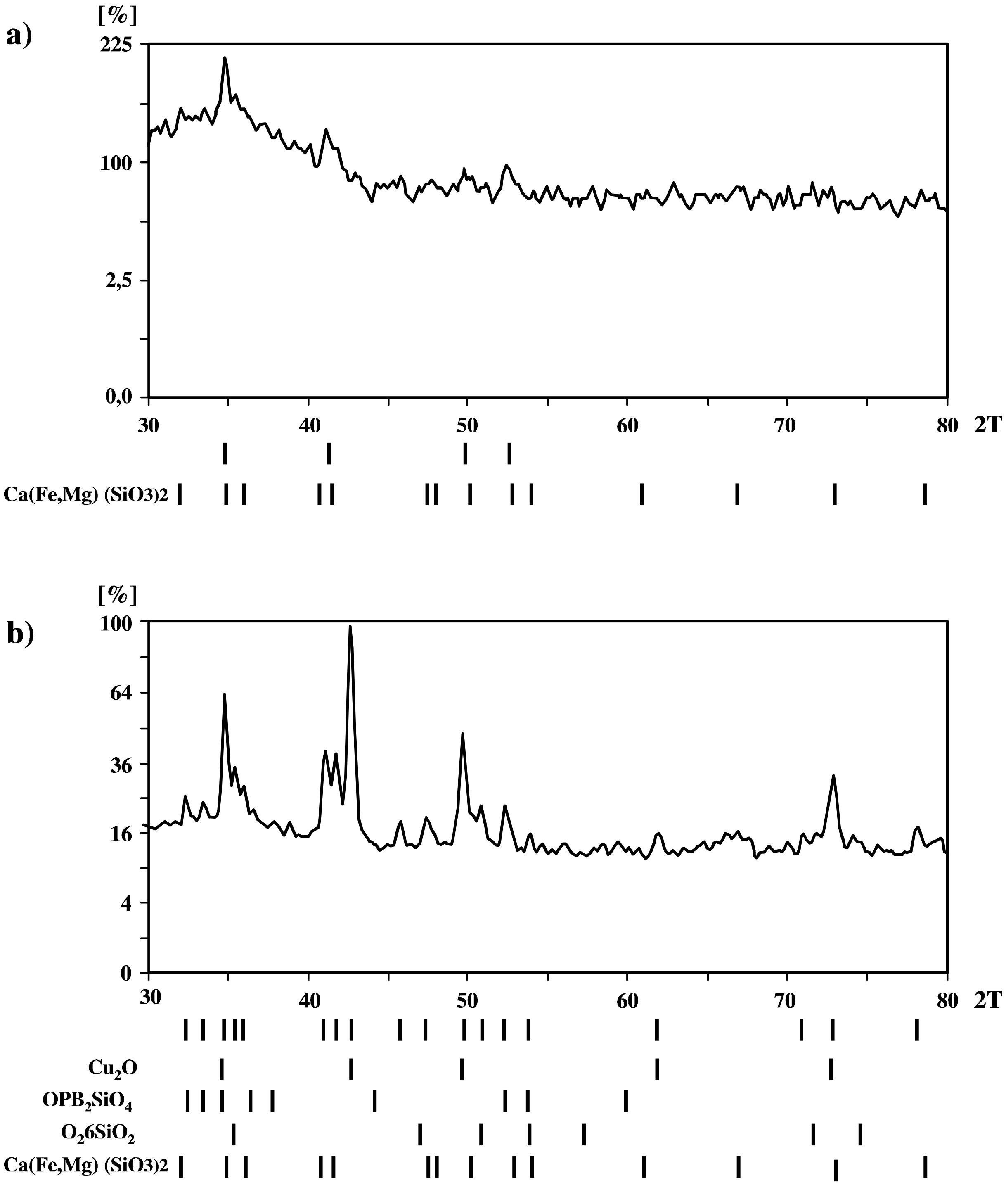


Fig 3 Diffraction patterns of slags obtained from the Cu matte melting shaft furnace (a) and flash smelting process (b)

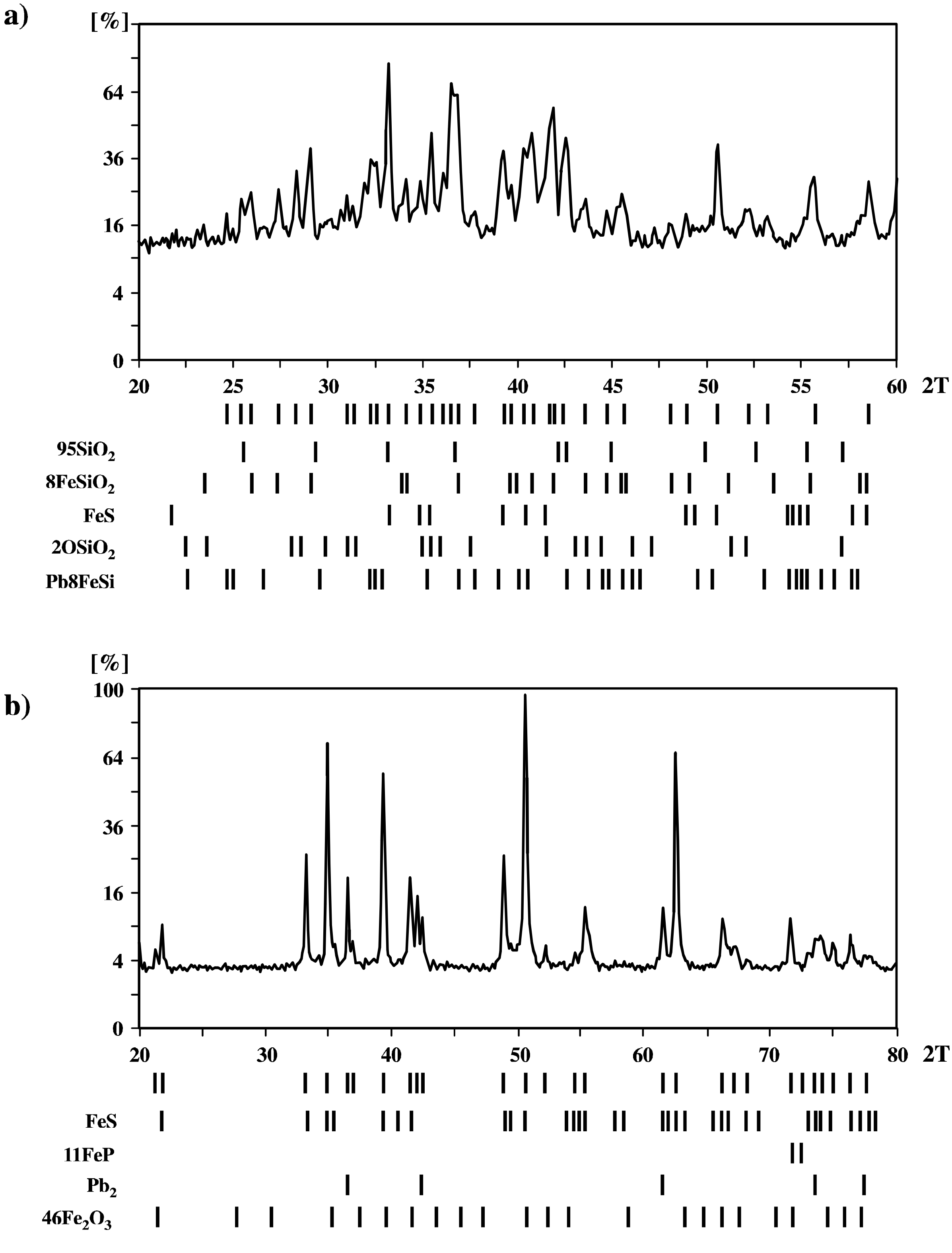


Fig 4 Diffraction patterns of rotary-and rocking furnace slags

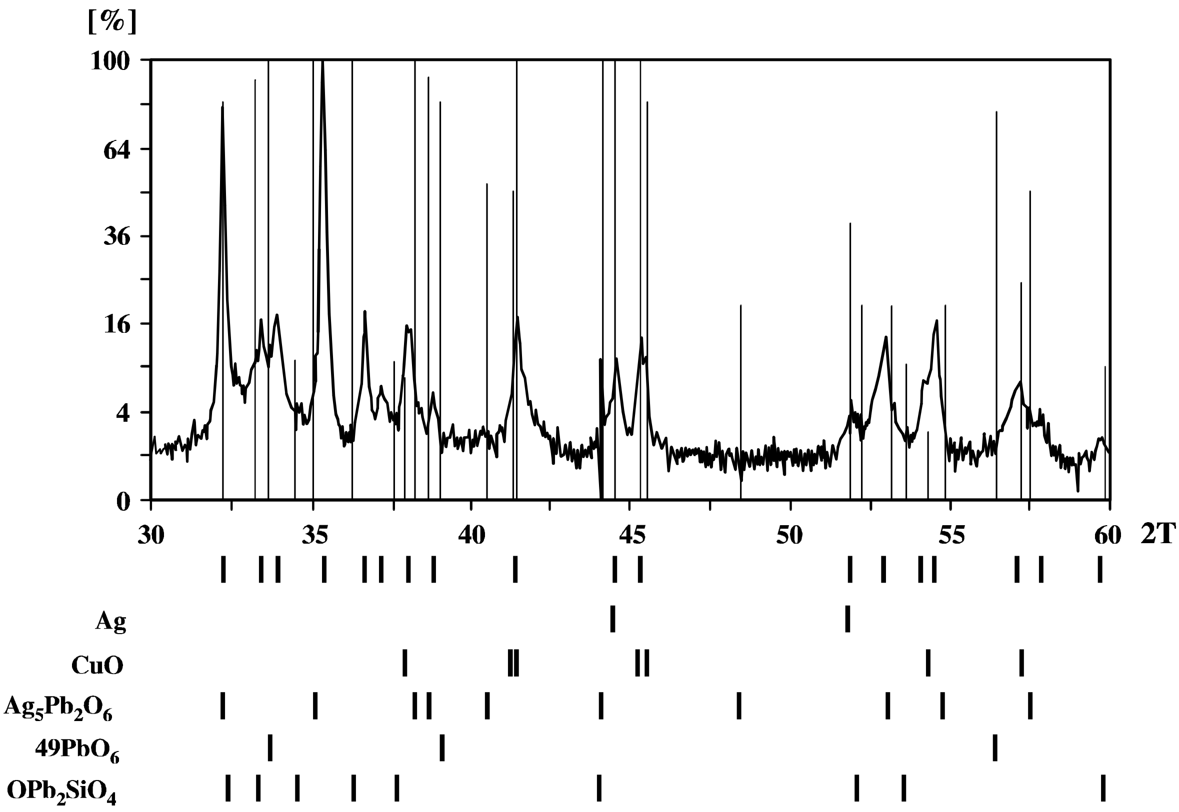


Fig 5 Diffraction pattern of the cupellation process slag

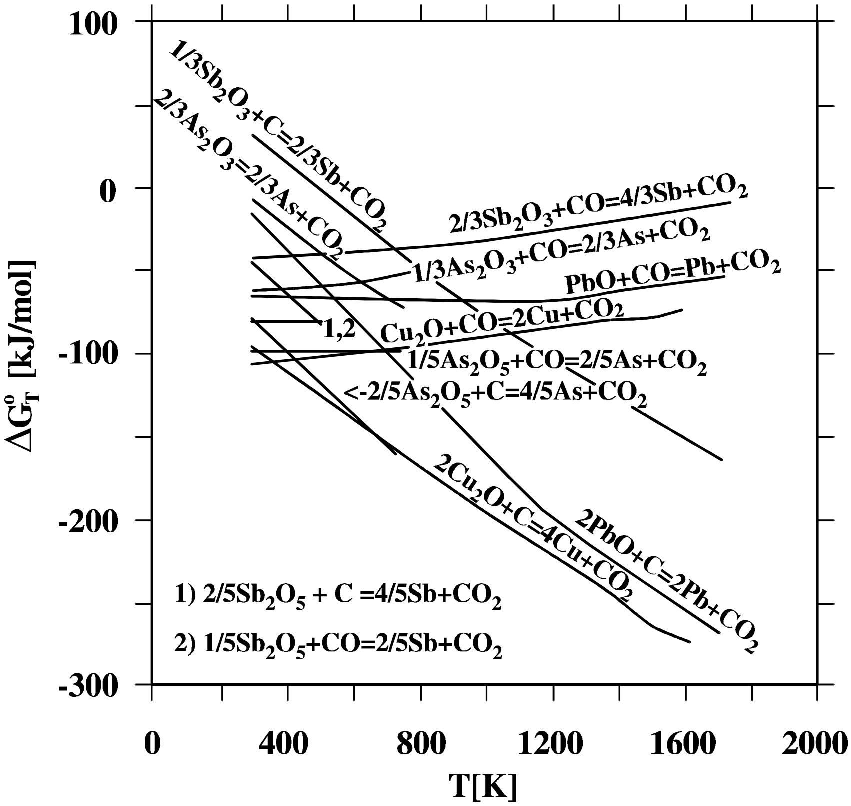
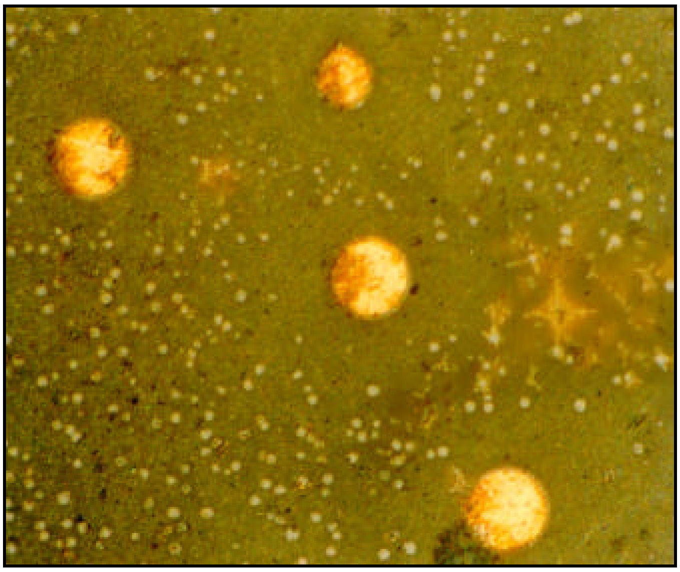
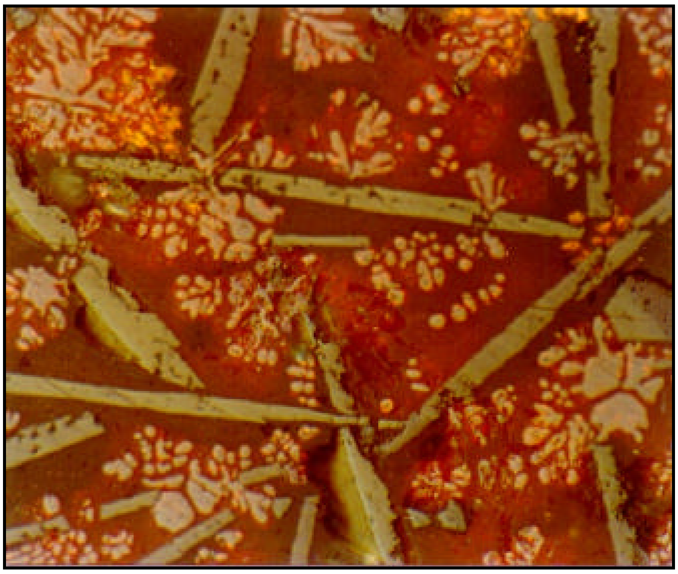


Fig 8 Graphical presentation of changes in free enthalpy (ΔG_T^o) of the reaction of reduction of metal oxides with carbon and carbon monoxide

a)



b)



c)

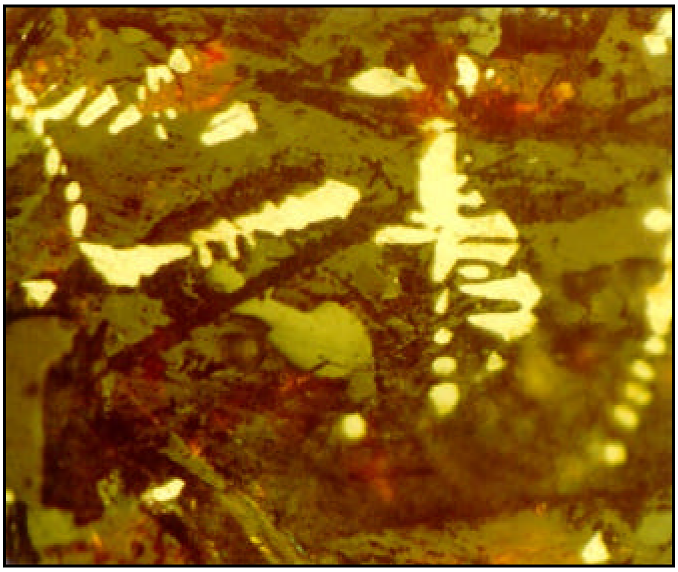


Fig. 6 Coloured microphotography of slags from a) the Outokumpu flash smelting process, b) the Cu-Pb-Fe alloy converting process (visible are copper inclusions), c) the cuppelation process

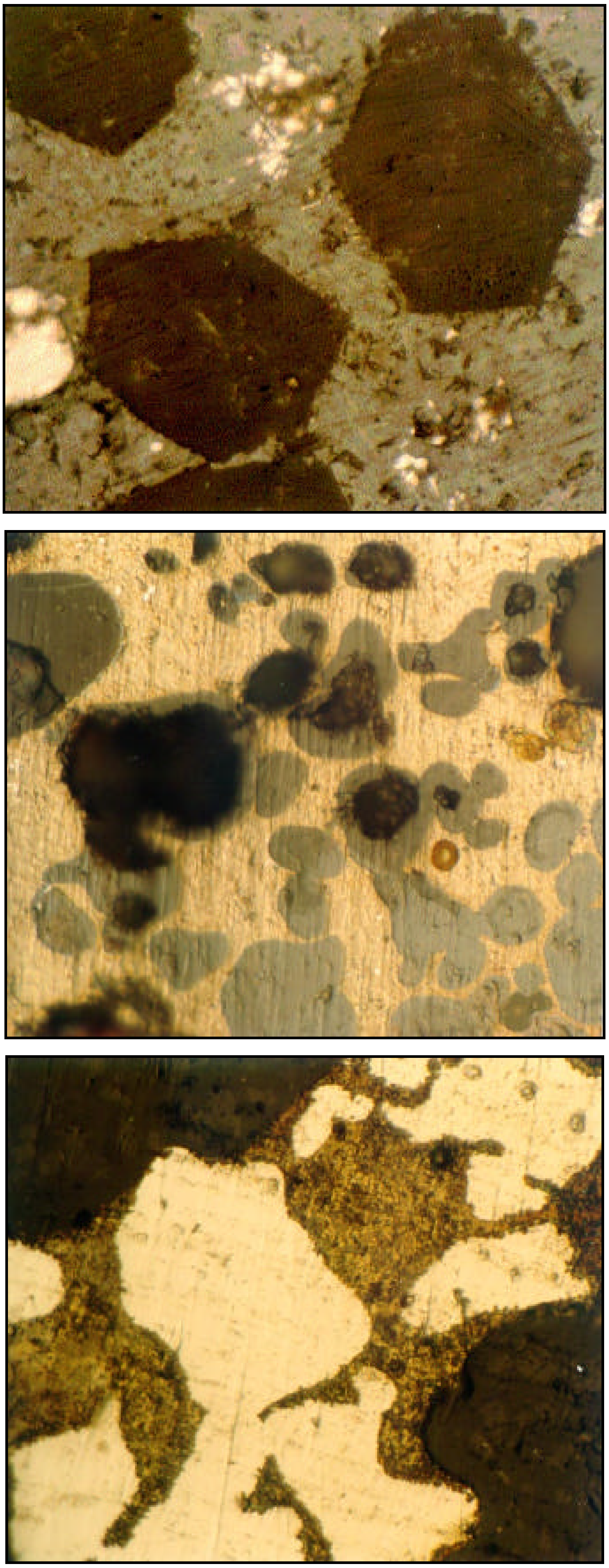

a) b) c)

Fig. 7 Coloured microphotography of slags from a) the KALDO converter process (visible are silver inklusions), b) the rotary –and rocking furnace, c) the Pb melting shaft furnace

Table 1

Results obtained from the determination of softening and melting points

No	Material	Temperature			
		$T_{soft.}$		$T_{melt.}$	
		[°C]	[°K]	[°C]	[°K]
1	shaft furnace slag (copper matte melting)	1065	1338	1120	1393
2	electric furnace slag	1040	1313	1105	1378
3	flash smelting furnace slag	1015	1288	1055	1328
4	slag from Cu-Pb-Fe alloy refining	960	1233	1035	1308
5	synthetic slag	505	778	680	953
6	synthetic slag	620	893	700	973
7	rotary-and rocking furnace slag	1180	1453	1320	1593

Table 2

Results from slags density determination

No	Material	Temperature		Density
		[°C]	[°K]	[g/cm³]
1	shaft furnace slag (copper matte melting)	1250	1523	2,82
		1301	1574	2,81
		1364	1637	2,80
2	electric furnace slag	1250	1523	2,73
		1300	1573	2,71
		1370	1643	2,68
3	flash smelting furnace slag	1272	1545	3,38
		1341	1614	3,35
		1372	1645	3,34
4	slag from converting Cu-Pb-Fe alloy	1250	1523	4,41
		1298	1571	4,38
		1336	1609	4,36
5	slag $PbO.SiO_2$	830	1103	5,60
		1025	1298	5,60
		1208	1481	5,58
6	slag $4PbO.SiO_2$	940	1213	7,09
		1028	1301	7,08
		1105	1378	7,08

Table 3

Results from the determination of slags viscosity

Slag	Temperature		Viscosity
	[^{o}C]	[^{o}K]	[P]
shaft furnace slag (copper matte melting)	1357	1630	37
	1319	1592	49
	1286	1559	69
	1257	1530	95
	1232	1505	130
	1212	1485	168
	1197	1470	199
	1183	1456	236
	1171	1444	288
	1159	1432	374
	1148	1421	600
electric furnace slag	1355	1628	12,5
	1318	1591	18,6
	1287	1560	24,6
	1259	1532	34
	1233	1506	47
	1210	1483	63
	1190	1463	84
	1178	1451	101
	1168	1441	119
	1159	1432	600
lead silicate $4PbO \cdot SiO_2$	923	1196	1,6
	901	1174	1,75
	879	1152	1,95
	858	1131	2,15
	818	1091	2,50
	791	1064	2,85
	769	1042	3,3
	746	1019	3,9
lead silicate $PbO \cdot SiO_2$	1207	1480	3,4
	1188	1461	4,2
	1157	1430	5,8
	1126	1399	8,5
	1094	1367	1,08
	1063	1336	13,5
	1033	1306	18,8
	1002	1275	26
	969	1242	37
	927	1200	62
	893	1166	98
	862	1135	164
	829	1102	271

Slag	Temperature		Viscosity
	[^{o}C]	[^{o}K]	[P]
flash smelting slag	1356	1629	3,7
	1318	1591	5,0
	1284	1557	6,2
	1253	1526	8,1
	1223	1496	10,6
	1194	1467	14,9
	1165	1438	22,0
	1144	1417	30
	1133	1406	40
	1121	1394	48
	1108	1381	60
	1198	1471	261
from converting Cu-Pb-Fe alloy	1113	1386	0,3
	1090	1363	0,8
	1072	1345	0,8
	1055	1328	0,9
	1040	1313	1,2
	1028	1301	1,35
	1019	1292	1,8
	1007	1280	2,8
	994	1267	3,6
	980	1253	12,1
	969	1242	25
	961	1234	600
from rotary-and-rocking furnace	1347	1620	3,1
	1307	1580	6,5
	1277	1550	11,8
	1250	1523	15,5
	1223	1496	18,3
	1203	1476	26
	1190	1463	36
	1177	1450	52
	1165	1438	202