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ECOLOGICAL CLEAN PROCESS OF CRUDE COPPER PRODUCTION

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for the two years (November 1999 - October 2001)

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EXECUTIVE SUMMARY

The aim of this work was to complete an integrated study, which could contribute to the development of a continuous technology for direct crude copper production from sulphide raw materials, based on the autogeneous Vanyukov's process and maximum impoverishment of slags. A laboratory model of a coke filter furnace for slag impoverishment was constructed.

The work included investigation of matte and slag samples from Vanyukov's furnace, and slag samples from the coke filter furnace. The samples were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Thermodynamic calculations and determination of metal (Cu, Zn, Pb) losses in waste slags were performed. A study of the physico-chemical properties of matte and slag melts was completed. A kinetic study of sulphide oxidation and oxide reduction was accomplished. The electrical and thermal characteristics of the laboratory coke filter furnace were measured. Investigations of slag reduction in the coke filter furnace were completed. The results obtained confirm that an ecological, clean and continuous crude copper production process with impoverished waste slag is possible. The construction of an assembly for this process in a combined furnace, including the oxidation of autogeneous sulphide raw materials and simultaneous slag impoverishment using a coke filter, is proposed.

Two articles based on the results of the present project have been submitted for publication to Metallurgical and Materials Transaction and these articles are currently being modified to conform to reviewer suggestions.

A senior member of the project team, Prof. S. Vaisburd (Technion), visited the Institute of Metallurgy and Ore Benefication (IMiO, Almaty), and Prof. S.M. Kozhakhmetov was twice at the Technion (Haifa) for discussions with co-workers on this program and to see the methods of analysis used at Technion at first hand.

An IMiO doctoral candidate, E.B. Kenzhaliev spent two semesters at Technion, where he studied methods for physico-chemical melt investigation. He has also participated in a course of study for SEM/EDS and qualified as a specialist in these methods. A project for the construction of a Kazakhstan National Center for SEM/EDS in Almaty is now under consideration. The experimental unit developed at Technion for the study of physico-chemical properties of melts has been prepared for transfer to IMiO (Almaty, Kazakhstan).

As a first step to improve the continuous technology of crude copper production with maximum waste slag impoverishment, a coke filter furnace with a productivity of 2.5 t/h, slag and 0.5 kW has been proposed for pilot application in the furnace regimes used in the copper plant, as an intermediate industrial stage for full production. In addition, an industrial furnace for the continuous crude copper process with maximum slag impoverishment of 50t/h slag and 9MW combining Vanyukov's autogeneous furnace and a coke filter furnace is also proposed.

A. RESEARCH OBJECTIVES

The objective of this work is to complete an integrated investigation, to prepare the background for an ecological, clean, continuous technology of direct crude copper production from sulphide ores. The basic sources of copper ores in Kazakhstan (excluding the Geskazgan formation) are lean sulphide ores containing 0.5 to 1.0% Cu. Current flotation methods are used to obtain concentrates that are usually autogeneous smelted, ensuring the most efficient use of the exothermic heat of reaction and sulphur extraction from the exhaust gases. Such ores yield copper sulphide concentrates with copper contents no more than 17%.

Autogeneous processes are in common use by Noranda, Worcra, Mitsubishi, Outokumpu, KIVCET and others [1,2]. Some isolated attempts have been made to develop direct crude copper production by autogeneous smelting, excluding the converter process, [3-7]. However, this route resulted in rich slags, containing 2 to 11% copper, which required additional treatment by coke or gas followed by leaching of the reduced slags with copper lean sulphide melts. Flotation treatment of such cooled slags has also been applied. But all these methods are inefficientt and expensive. They do not separate the smelting furnace from the circulating materials, which reduces the productivity of the furnace. Ar present the optimal product of an autogeneous process is considered to be a rich matte (30-50% Cu) that is subsequently retreated by the conversion process.

Such a process was developed in Kazakhstan. The Institute of Metallurgy and Ore Benefication of the Kazakhstan Academy of Science has introduced a process for autogeneous smelting of sulphide copper raw materials, obtaining rich copper mattes, at Joint-stock company "Balkhashmed" [8-10]. The autogeneous process in Vanyukov's furnace was chosen as a smelting process [11]. This choice was determined by some specific features of Vanyukov's process: (1) high productivity (2.1-3.3 $ton \cdot m^{-2} \cdot h^{-1}$); (2) low dust loss (about 1% of the charge weight); (3) charge processing without complete drying (up to 6-8% moisture); (4) processing of lump materials (down to 50 mm). Vanyukov's process is an autogeneous method for sulfide concentrates of non-ferrous metals present in a liquid matte-slag emulsion. Melting is accomplished in a specially designed furnace for the continuous counter-flow of matte and slag melts. The furnace incorporates an autogeneous smelting aggregate with two separate zones of different oxidizing potential and with counter-flow of the slag [11]. Both zones can be equipped with separate tuyeres, so that the desired oxidizing potential in each zone can be controlled. This furnace has shown its effectiveness for copper sulphide materials at "Norilsk" and "Balkhashmed" [11], and at present Vanyukov's furnace is successfully used at "Balkhashmed" in Kazakhstan for copper matte production. At copper contents in the mattes of 45–50%, the waste slag contains 1% Cu and 90% direct sulphur extraction is achieved in the smelting process. However, subsequent conversion of the rich mattes is accompanied by considerable discharge of sulphur dioxide into the atmosphere (drastically reducing sulphur extraction) and by production of a great quantity of converter slag. These slags are retreated in the liquid and solid state in reverberatory furnaces, which lowers the productivity for sulphide concentrates by more than 50%.

Change in the direct crude copper production process could solve these problems, but the high copper concentration in the slag (2-11%) is a major obstacle. It could be removed by deep reduction of liquid slags using solid carbon. Such a process can be realized in a coke filter furnace. The aim of this project is to develop an ecological clean process of crude copper production by incorporating a coke filter furnace. One of the tasks

of this investigation is to construct a model of a coke filter furnace and to study its possibilities. At the same time it has to be demonstrated that the flows of liquid matte leaving Vanyukov's furnace and the flows of liquid slag into an industrial coke filter furnace can be co-ordinated. These flows of the liquid phases are connected with rates of matte oxidation and slag reduction, so these problems are also a part of this investigation.

The two components of the proposed technology (Vanyukov's process and slag reduction in a coke filter furnace) are presently at two different sites. Vanyukov's furnace is at the Balkhash copper smelting plant (Kazakhstan) and industrial samples were available from this process. The furnace with a coke filter has yet to be constructed, so samples were obtained from a laboratory assembly that included slag reduction under some regimes. Since the characteristics of sulphide oxidation and oxide reduction have been thoroughly studied, only the influence of additional factors on the oxidation of copper-iron sulphide melts and on the reduction of copper oxides by solid carbon are included in this investigation.

Some additional aspects of the problem of waste slags were addressed. To discuss the forms of metal losses in liquid slag, thermodynamic calculations for slag-matte interaction are required and measurements of the physical properties of silicate and sulphide melts (viscosity, density, surface tension) are needed. SEM/EDS and XRD characterization of the matte and slag give important information. Vanyukov's process has not been studied in as much detail as other autogeneous processes, so that these investigations are also of more general interest.

B. METHODS AND RESULTS

1. CHARACTERIZATION OF SAMPLES FROM VANYUKOV'S FURNACE AND FROM THE COKE FILTER FURNACE

Methods

Phase and elemental analysis of the specimens using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) was conducted on an XL30 (Philips, Holland) scanning electron microscope equipped with a LINK ISIS (Oxford Instruments, England) energy dispersive spectrometer. The measurements were performed at an accelerating voltage of 20 kV, a probe current of 1 nA and a working distance of 10.5 mm. Under these analytical conditions the probe diameter on the sample surface was about 100 nm. The morphology of the different phases at the sample surface was imaged using back-scattered electrons in compositional contrast mode. After imaging in scanning mode, the electron probe was positioned sequentially at specific points on the sample surface and EDS spectra were collected. The take-off angle for x-ray radiation collection was 35° and the spectra acquisition time was set at 100 s. In all cases the standard deviation of the measured intensity in a single measurement did not exceed 5%. Quantitative microanalysis was performed using the conventional ZAF correction procedure included in the LINK ISIS software. The final results were normalized to 100%. In order to analyse quantitatively small sub-micron particles directly a correction technique was used specially developed for this type of analysis [12,13].

Phase composition of samples was determined by X-ray diffraction (XRD) analysis. XRD spectra were obtained with the Bragg-Brentano focusing scheme in a Philips

Analytical PW3020 powder diffractometer operated at 40 kV and 40 mA. Diffraction patterns were acquired from polished samples in step mode with 0.02° steps (2θ) and 4 s per point over diffraction angles from 20° to 90°.

Samples of slag and matte were obtained from Vanyukov's furnace in the Balkhash copper melting plant (Kazakhstan) and from the coke filter furnace constructed in the Institute of Metallurgy and Ore Benefication - IMiO (Almaty, Kazakhstan). Chemical analysis of the samples was performed at IMiO using standard methods. The compositions are presented in Table 1. Specimens for SEM/EDS measurements were cut from the samples, polished and carbon coated. SEM/EDS sample preparation and all measurements were performed at Technion.

Results

Samples from Vanyukov's furnace

Data of samples from Vanyukov's furnace at the copper smelting plant "Balkhashmed" (Kazakhstan) were presented in the 1st year report [14-15]. The phases present in a matte sample are mainly sulphides of very diverse chemical composition: copper-iron sulphides, zinc-iron sulphides, copper-iron sulphides containing lead and also lead and zinc together. Small amounts of metal phases (copper and copper alloys) and magnetite are also present. This variety of phases is a result of liquation processes occurring during cooling of the homogeneous melt. The matte also contains a few slag inclusions.

Two samples of cooled slag show fields of meta- and orthosilicates, with magnetite as a separate phase resulting from liquation, and matte inclusions. Two types of matte inclusions are observed in the silicate continuum: regulae of 5-10 μm and regulae of about 0.2 μm (Fig 1). The chemical composition of these two types of regulae is not identical but the composition of the larger regulae is close to the matte composition while the 0.2 μm regulae consist basically of copper-iron sulphides. Comparison of the two slag samples shows that their phase and chemical composition are nearly identical, but the over-current slag contains more non-ferrous metals, especially copper (3.80% compared to 0.31% in the waste slag), and contains larger matte inclusions (regulae of 100 μm) not observed in the waste slag. It is concluded that slag formation in Vanyukov's furnace is complete before the over-current zone, but this slag contains matte inclusions, which subsequently coalescence and don't reach the waste slag.

Samples from the coke filter furnace

The initial slag

The first slag sample comprises converter slag produced by conversion of Vanyukov's process matte. This slag should model the slag, obtained by continuous crude copper production in Vanyukov's furnace. Chemical analysis of the sample at the Institute of Metallurgy and Ore Beneficiation in Almaty gave the results cited in Table 1.

SEM images obtained from the polished surface of this slag sample (back-scattered electrons, compositional contrast mode), Fig.2, show complex contrast typical of a multiphase structure. Results of quantitative EDS analysis for different phases found in the initial slag and marked by numbers in Figs 2 are presented in Table 2. The major phases contained in the initial slag are ortho- and metasilicates of iron, iron oxides and

lead enriched phase. The average composition of the large oval grains corresponds to iron oxide, FeO, whereas the majority of trapezoid and dendritic grains (points 9, 10) have a composition, which is close to that of magnetite Fe_3O_4. Particles of the lead enriched phase have dimensions of 0.1–0.2 μm and contain more than 85 wt% of Pb and about 8 wt% of O. Due to their small sizes an unambiguous interpretation of their phase composition based on EDS data alone is impossible. In addition to the major phases the initial slag contains many metal regulae (points 4, 5, 6,7, 8) mainly consisting of copper or Cu_2S. Regulae of ZnS were also present.

The initial slag after heating without coke (calcination)

Typical SEM images obtained from the polished surface of the initial slag sample after reduction at 1500^0 C are presented in Figs.3. Results of quantitative EDS analysis for different phases found in this sample are presented in Table 3. Most of the section consists of iron aluminates, iron silicates and iron oxides. Iron aluminates are the result of chemical interaction between silicates and the walls of the alumina crucible. The sample also contains many lead-enriched particles and regulae of metal copper, copper sulphide and zinc sulphide. This morphology and phase composition were found to be typical for all calcination temperatures of the initial slag.

Infiltration of the initial slag through the coke filter

1450^0 C, 30 s

SEM micrographs are presented in Fig.4 and EDS results of the different phase constituents are listed in Table 4. The surface morphology of this sample is very similar to that of the initial slag sample (compare Figs.4 and 2). This conclusion is supported by data of EDS analysis for these samples. The major phases are iron silicates and magnetite. In addition the sample contains many particles of a lead enriched phase and regulae of copper based alloy and sulphides, mainly $(Cu, Fe)_2S$.

1450^0 C, 6 min.

SEM micrographs are presented in Fig.5 and EDS results of the different phase constituents are listed in Table 5. The surface morphology of this sample differs markedly from that of the initial slag sample. The sample consists mainly of large fields of ortho- and metasilicates of iron and does not contain iron oxides. No lead enriched phase was found. The sample contains a considerable number of iron regulae and sulphides of FeS or (Fe, Cu, Zn)S. Regulae containing Pb were not present.

1600^0 C, 2 min.

SEM micrographs are presented in Fig.6 and EDS results of the different phase constituents are listed in Table 6. The sample consists mainly of large fields of ortho- and metasilicates of iron and does not contain iron oxides. Similar to the initial slag, the sample contains many particles of a lead enriched phase and regulae of a copper-based alloy, an iron-based alloy and sulphides, mainly $(Cu, Fe)_2S$ or FeS.

2. THERMODYNAMIC CALCULATIONS AND METAL LOSSES IN WASTE SLAGS

Method

The thermodynamic calculations were based on data given in [16,17]. The calculation used the first approximation of Ulich's formula [18], which is justified

provided that the value of the parameter M, defined below, is less than errors in the assumed values of ΔH^S and $T\Delta S^S$, where ΔH^S and ΔS^S are the enthalpy and the entropy change for any reaction under standard conditions. The parameter M is calculated from the relation:

$$M = \Delta c_p^S \cdot T \cdot M_o, \qquad (1)$$

where Δc_p^S is the heat capacity change for the reaction considered under standard conditions, T is the absolute temperature and $M_o = \ln(T/298) - 1 + 298/T$. The present case should meet the conditions for using the first approximation. The slag is released from the furnace at 1300°C so this temperature was used for the calculation. However, the oxides considered are solid at this temperature whereas they are liquid when dissolved in the slag. Therefore the latent heat of melting for the oxides and their heat capacity in the liquid state were included in the calculation.

Results

The first stage in pyrometallurgy is always to form two liquid phases, matte and slag, so as to concentrate the impurities of the ore in the slag. The process is controlled by the interaction between the phases in this heterogeneous system. The slag in non-ferrous metallurgy always contains iron oxide, and the behaviour of different metal compounds dissolved in the slag is determined by the chemical equilibria of the following reactions:

$$(FeO) + (MeS) = (FeS) + (MeO), \qquad (2)$$
$$(FeO) + [MeS] = [FeS] + (MeO), \qquad (3)$$
$$[MeS] = (MeS), \qquad (4)$$

where Me is a non-ferrous metal, the round brackets denote the homogeneous liquid slag and the square brackets denote the homogeneous liquid matte. Since the equilibrium in this complicated system is always conjugated, any shift of the equilibrium in reaction (2) to the right will also lead to a shift of the equilibrium of the heterogeneous reaction (3) to the right. Consequently, when the (MeS) concentration is low, dissolution of the sulfide in the slag, reaction (4) practically does not proceed, sp the metal is dissolved in the slag mainly in oxide form. By contrast, if reaction (2) is shifted to the left, then sulfide is dissolved in the slag, and the equilibrium of reaction (4) is then shifted to the right. It follows that the chemical state of non-ferrous metals dissolved in liquid slag is determined by the conjugated equilibrium of all three reactions (2), (3) and (4). The same conclusion should be true for systems where sulfur is substituted by other metalloids such as selenides, tellurides, arsenides or silicides [24].

The calculated values of the equilibrium constants K are given in table 2 which also lists the ratio of the equilibrium contents of sulfide and oxide derived from equation (2) for various non-ferrous metals $C_{(MeS)}/C_{(MeO)}$:

$$\frac{C_{(MeS)}}{C_{(MeO)}} = \frac{K_\gamma}{K} \cdot \frac{C_{(FeS)}}{C_{(FeO)}}, \qquad (5)$$

where $K_\gamma = \prod_i \gamma_i$ and γ_i is the activity coefficient of the component i (Me = Cu, Pb, Zn). The value of $K_\gamma C_{(FeS)} / C_{(FeO)}$ was estimated to be about 0.01 [20]. For comparison, table 2 also lists data calculated for cobalt, whose partition between slag and matte is well known [19,21]: Cobalt dissolves in the slag mainly in the oxide form. Zinc is similar to cobalt in its behaviour and the value of $C_{(ZnS)}/C_{(ZnO)}$ should be close to that of $C_{(CoS)}/C_{(CoO)}$. As can be seen from table 2 the ratio values are 0.12 for cobalt and 0.11 for zinc, which tends to confirm the validity of the calculation. Lead dissolved in the slag is present

mainly in the oxide form (with only 20% in the sulfide form). By contrast, copper is dissolved in the slag only in the sulfide form, as is known [19,21].

These conclusions are confirmed by the present SEM/EDS results. Comparison of the total zinc content in the liquid slag with that in the silicate portion of the slag shows clearly that zinc, similar to cobalt, exists in the liquid slag mainly as oxide. Lead shows the same behaviour. Small regulae, educed by liquation from the slag, are sulfide, mainly of copper and iron; with zinc and lead present in very small quantities according to the data of Table X. The sub-micron sulfide inclusions of oval shape differ widely in composition from the average matte composition and are evidence for sulphides dissolved in slag. Thus, the SEM/EDS data confirm the prediction of the thermodynamic calculations. The combined SEM/EDS and thermodynamic results corroborates the three different forms of metal losses in liquid slag: mechanical (matte regulae), physical (dissolved sulfides), and chemical (dissolved oxides). The data show that physical losses of zinc and lead are very small, and these elements are mainly dissolved in the slag in the form of chemical losses, while copper gives only physical losses in parallel with mechanical losses.

3. PHYSICO-CHEMICAL PROPERTIES OF MELTS FROM VANYUKOV'S FURNACE

Method

The density and surface tension of liquid slag and matte were measured by the maximum bubble pressure method, slag viscosity was measured by the rotational method. All measurements were made using the experimental unit developed at the Faculty of Materials Engineering (Technion, Haifa) [22]. The high temperature viscometer was newly calibrated [23] and the calibration results compared accurately with data obtained some years ago, confirming the reliability of measurements on this experimental unit. Matte and slag samples were the same as for part 1 of this report, taken from the Vanyukov's furnace in the Balkhash copper melting plant (table 1). The industrial slag-containing matte inclusions should behave as a Newtonian liquid for the viscosity measurements. Preliminary melting of the slag allowed flotation by SO_2 gas and removal of matte regulae. The same procedure removed slag inclusions from industrial matte samples.

Results

Measurements were performed in the temperature range 1350 – 1550 °C and extrapolated to 1300 °C. Fig. 7 gives an example of the data obtained. The influence of temperature on the dynamic viscosity shows classical exponential dependence; the density and surface tension data also demonstrate a classical temperature dependence [29]. The matte viscosity cannot be measured by the rotational method applied for slag measurements because of the high fluidity of the matte; so for matte and metal melts the torsion oscillation method should be used [19]. In the present work the kinematical viscosity values for the liquid matte were calculated from reference data [19]. All the data for this part of the work are summarized in tables 3 – 6.

The matte and slag melts studied here are complex liquids, and the measured data cannot be compared exactly with known reference data for either matte [19] or slag [25]. However, the measured properties are of the same order of magnitude as data for liquid slags and mattes observed for traditional metallurgical processes [11,21,26]. The analysis

of our data leads to the conclusion that the melt properties are compatible with the metallurgical process. Indeed, the viscosity of both the slag and the matte is sufficiently low to ensure that the melts flow easily off the furnace. In addition to the low slag viscosity, the slag density is sufficiently lower than the matte density to ensure effective sedimentation of matte regulae in the slag, as is confirmed by the results of SEM/EDS measurements. The surface properties of the two melts also favour efficient coalescence of matte regulae in the slag.

4. INFLUENCE OF SEVERAL FACTORS ON THE MATTE OXIDATION AND SLAG REDUCTION PROCESSES

4.1. MATTE OXIDATION

Method

This work was performed at the Institute of Metallurgy and Ore Benefication (Almaty, Kazakhstan). The factors investigated include the degree of matte metallization, the effect of additions of metallic copper and iron, silica and magnetite, the presence of CO_2 and water vapour as inhibitors for the oxidation reaction, In addition the effect of carbon on the velocity and mechanism of liquid copper-rich matte oxidation was studied both by the method of continuous SO_2 analysis in the gaseous phase and by continuous conductometry as wekk as by chemical and physico-chemical analysis of the oxidized products [14]. Experimental data in the temperature range 1200-1400 ^{0}C were processed by a complete three-phase experiment. The experiments were performed with synthetic copper matte with various ratios of copper and iron in the melt. The melt was prepared from a composition of stoichiometric sulphides, Cu_2S and FeS.

Results

Results on the influence of matte and gas composition correlated well with earlier investigations in the Institute of Metallurgy and Ore Benefication [27,28]. The new experiments concentrated on the oxidation of melt compositions FeS - Cu_2S in the presence of carbon since under the conditions of Vanyukov's furnace a quantity of coal is added to the sulphide burden. As was expected, the degree of oxidation increases with the iron content in the melt and decreases when carbon is added. Addition to FeS - Cu_2S melts of 20wt% carbon (of the melt mass) decreases the degree of oxidation by a factor of two.

The study of the copper enrichment of liquid-phase oxidation of Cu_2S - FeS melts, demonstrated the possibility of oxy-sulphide formation, whose physico-chemical properties and structure have been investigated in detail [29,30]. During cooling these oxy sulphides reject magnetite, which is distributed between slag and matte, increasing the losses of copper and other metals in the slag. Under the conditions of Vanyukov's process, especially during production of copper rich mattes and white matte, the gaseous phase is characterized by a high oxidizing potential. At the same time, the matte-slag emulsion, especially in the region of the tuyeres, is at a high temperature (1400-1500 ^{0}C). These peculiarities of Vanyukov's process together with the high rate of mass-exchange during active gas bubbling in the liquid bath of matte-slag melt above the tuyeres, all suggest that this stage of oxidation will not limit the overall productivity of the melting installation. The results of kinetic investigation and the mechanism of liquid-phase oxidation, both of mono sulphides of iron and copper and also of their melt compositions, confirm this proposition, which is also confirmed by the industrial exploitation of Vanyukov's furnace at the Balkhash copper-melting plant in Kazakhstan. Based on these considerations, further

studies of matte melts oxidation, planned for the second year, was considered unnecessary, and most attention was given to oxide reduction.

4.2. OXIDE REDUCTION

Method

These investigations were performed at IMiO (Almaty). Some experiments used the equipment «Setaram» to determine the mechanism of copper (II) oxide reduction. An experimental circulation unit [1] was used to study the influence of various factors on the reduction of liquid slag containing copper (I) oxide [14]. Solid copper oxides CuO and Cu_2O were used. Liquid samples were prepared by dissolving Cu_2O in synthetic slag. The compositions of these slags are listed in table 12. All slag samples for measurements contained 10% of copper oxide Cu_2O.

Results

Typical experimental results are shown in figs. 8 and 9. The experimental variable is the pressure of the gas phase. Although the final value of the degree of copper oxide reduction after three hours exposure is the same for vacuum and at one atmosphere pressure of helium, the initial degree of reduction (from 15 minutes to 1 hour) in vacuum is considerably higher, especially at 800 ^{0}C. This influence of a rare gas atmosphere can be explained by a decrease of diffusion hampering the possible reduction reactions:

$$CuO + CO \rightarrow Cu + CO_2 \quad (1)$$

$$CO_2 + C \rightarrow 2\,CO \quad (2)$$

$$2CuO \rightarrow 2\,Cu + O_2 \quad (3)$$

$$O_2 + 2\,C \rightarrow 2\,CO \quad (4)$$

Reactions (1) and (2) reflect an adsorption mechanism, while reactions (3) and (4) correspond to a dissociation mechanism. At 800 ^{0}C reaction (2) does not develop appreciably so that at this temperature the adsorption mechanism is barely possible. At this temperature, 800 ^{0}C, especially in vacuum, reactions (3) and (4) can proceed quite fast, because diffusion of the gaseous product and oxygen in the gas phase from the oxide to solid carbon is facilitated.

Possibilities for the adsorption mechanism appear at higher temperaturem between 900 and 1100 ^{0}Cm because reaction (2) at these temperatures is faster and all four reactions occur, especially in vacuum. The possibility of reaction (4) is reduced at atmospheric pressure and in a gaseous medium containing up to 90% CO, because in this regime oxygen formed during copper oxide dissociation will first react with CO molecules in the gas phase near the surface of the oxide or with adsorbed molecules of carbon monoxide on the surface copper oxide. Thus, at these temperatures it is possible to combine the two schemes of reduction discussed earlier into one integrated adsorption-dissociation mechanism for copper oxide reduction. Results from the «Setaram» equipment complement these data. Two peaks are present on the DTG-curve for continuously increasing temperature. The first peak at 800 ^{0}C corresponds to the maximum rate of reaction

$$CuO + \text{reducer} \rightarrow Cu_2O + \text{reduced oxide.} \quad (5)$$

As Cu_2O is formed, the rate of this reaction falls, and the partial pressure of oxygen is reduced because of its interaction with reducing agent. The second peak then appears at 900 ^{0}C, corresponding to the reaction

$$Cu_2O + \text{reducer} \rightarrow Cu + \text{reduced oxide.} \quad (6)$$

A similar picture was observed when metallic titanium was used as the reducing agent, as well as when copper oxide was reduced by carbon at one atmosphere pressure of a neutral gas and at low partial pressures of carbon monoxide (10^{-2} Pa). Thus, these results demonstrate the reduction of CuO by a dissociation mechanism using solid carbon (coke fines) as the reducing agent.

A third group of reduction experiments was made with liquid silicate samples containing 10% Cu_2O (table 12). The aim was to study the influence of some: slag-forming components, such as low-melting oxides, Na_2O and B_2O_3, on Cu_2O reduction from the liquid silicate phase. However, the complexity of the systems prevented any significant findings and it was decided to continue the investigation of the reduction process under the conditions in a coke filter furnace by building a laboratory model of a furnace with coke filter that would allow the reduction of real slag on direct contact with solid carbon. The experiments described are a further development of investigations continuing in the Institute Metallurgy and Ore Benefication (Kazakhstan) and concerning the principles of metal oxide reduction.

5. THE COKE FILTER FURNACE

5.1. THE LABORATORY MODEL

The laboratory model of a coke filter furnace is designed for the study of processes of deep impoverishment of slag and metal reduction from oxide melts (fig. 10). The assembly consists of a vertical high-temperature furnace (1) and a low temperature furnace fitted with a coke filter (3). The construction is mounted on a frame, with the vertical high-temperature furnace placed on guide cylinders which permit vertical movement for loading and unloading of coke from the coke filter. The crucible (2) is equipped with a needle valve, from which furnace melted slag is poured into the lower p art of the assembly. The furnace shaft cross-section is 100×100 mm and has a height of 300 mm. Opposing walls of the furnace shaft are prepared from graphite blocks that also conduct the electric current. Two other side-walls and the furnace floor are lined by firebrick. Asbestos lining is placed between the brick lining and the steel body, and the shaft of the furnace is filled with coke fines. The steel water-cooling supply is isolated from the furnace body by stoppers and asbestos. Electrical current is supplied to the coke from a transformer TDFG-2000, and temperature is measured by a Pt-PtRh thermocouple.

5.2. TEMPERATURE DEPENDENCE IN THE COKE LAYER

In selecting the appropriate electrical parameters for the coke filter furnace and it's transformer, the value of the specific electrical conductivity of the coke layer ρ in the temperature range of interest is very important. The value ρ was determined in the coke filter furnace in the absence of liquid slag by determining the volt-ampere characteristics and

determining the electrical resistance of the coke layer **R** at any given temperature and using the equation"

$$\rho = \frac{R * S}{\ell},$$

where **S** is the electrode cross section and ℓ is the distance between electrodes.

At temperatures up to 1000^0C the electrical resistance is unstable and depends on the conditions of contact between individual coke pieces. As the coke is heated the specific electrical resistance gradually decreases (fig. 11) and at temperatures above 1200^0C reaches 0.02Ohm*m. On further heating to 1400^0C the resistance change is insignificant. Fig. 12 shows the dependence of the specific resistance of the coke layer on the size of the coke pieces at several temperatures. In the range of temperatures of interest (above 1400^0C) the influence of coke dimensions on coke layer resistance decreases.

5.3. SLAG REDUCTION IN THE COKE FILTER FURNACE

Method

Industrial converter slag was used to study slag reduction in the coke filter furnace, since this slag models that from Vanyukov's furnace producing crude copper. The composition of the slags, which were obtained from "Balkhashmed" plant, are given in table 1. The samples taken for experiments were 600 to 2000g. Preliminary melting of slag was made in silit crucibles (silicon carbide heaters) at 1250-1300^0C. The experimental temperature range in the coke filter furnace was 1450 to 1600^0C and was regulated by controlling the furnace electrode voltage from 30 to 40V. The current was 700 to 800 ampere. The slag in the coke filter furnace is exposed for from 10 sec to 6 min. To improve the physico-chemical properties of the slag and for more complete separation of the metal alloy from the slag, 8% CaO and 3%B_2O_3 were added in some experiments. A total of 10 experiments were made. Molten slag from the silit furnace was put in the coke filter furnace pre-heated to the desired temperature. Products of the experiment were collected in a crucible receiver. Initial charges and final products (slag and metal) were weighed. The composition of the slag after melting in the silit furnace, and of the final slag and metal alloy after slag reduction was controlled by SEM/EDS analyses. These data are presented in table 1.

Results

Table 13 shows the metal balance for experiment № 7 (the temperature of the coke layer was 1600^0C, time 2min). Analysis of the metal composition shows that copper, lead and zinc were all quite effectively extracted:: 78.4% for copper (in the metal alloy), 95% for lead and 86.4% for zinc (in the fume). At the same time about 40% of the iron was reduced and constituted the alloy matrix. Extraction of Cu, Pb and Zn from the oxidized forms was much greater than from sulphide forms. Analysis of the content of slag forming oxides (SiO_2, CaO, Al_2O_3) after reduction showed that the silica content in slag remained practically unchanged, the alumina content increased due to partial dissolution of the lining. Fig. 2-6 demonstrate typical results of SEM/EDS investigation of slag samples before and after reduction. Not only the composition, but also the morphology of slag were significantly changed. Iron oxide phases disappeared completely, partially reduced and transformed into the metal phase, the remainder forming a separate spinel phase, with oxides of Cr, Mg, and Al also a result of interaction between slag and lining. Changes were also observed in the sulphide inclusions. The distribution and size of the sulphide regulae are far higher in the slag before reduction. In the reduced slag, regulae of size more than

5μm were not detected, while in the initial slag regulae up to 200μm were common. Characteristic phases in the reduced slag are metal alloy regulae. The alloys contain copper, iron and small quantities of lead. Sulphides are founded primarily at the periphery of the regulae.

Comparison of SEM/EDS results from three samples of slag shows that exposure for 20 sec at 1450^{0}C is not enough to start reduction, but increasing exposure at the same temperature to 6min causes significant reduction. However, sufficiently fast reduction is only achieved at 1600^{0}C: when a two-minute exposure causes deep exhaustion of the slag.

6. SUMMARY: THE CONTINUOUS PRODUCTION OF CRUDE COPPER.

Experiments on the production of crude copper using autogeneous technology have been reported by Noranda, Workra, Mitsubishi, KIVCET and others [ ], But the problem of slag impoverishment is still unsolved: Such slags contain up to 11% copper. Therefore primary attention in this work was given to the exhaustion of the slag, not only of copper, but also of lead and zinc. The investigation leads to the following conclusions for the successful design of an industrial coke filter furnace to be combined with an autogeneous process:

1. For intensive slag reduction and liquid phase (slag and metal) separation and also to achieve high electro-conductivity in the coke layer, the temperature in the furnace must be no less than 1600^{0}C.
2. The high temperature zone between the electrodes should not contact the lining to avoid dissolution of the lining components in the liquid slag. The width of the high temperature zone is not much greater than the electrode diameter, so the position of the flank walls of the furnace at a distance of 2-3 electrode diameters should exclude influence lining attack in the high temperature zone.
3. A satisfactory degree of non-ferrous metals extraction from the slag is attained only when partial reduction of iron oxides forms an alloy, which is an extracting phase for copper, zinc and lead sulfides and metallic copper.
4. The sulphide form of non-ferrous metals is the most difficult to extract from the slag. Therefore the sulphide content in the slag has to be minimized by increasing the degree of oxidation and using conditions that decrease the presence of matte regulae in slag (melt temperature, bubbling inert gas, optimal slag composition promoting coalescence and sedimentation, increased: interphase interface tension, reduced viscosity and density control).
5. In joining a coke filter furnace with a melting furnace a common furnace floor can be used to exclude seapage of the separating metallic phase as it becomes occluded in the matte phase.
6. It is necessary to combine the heat release zone and the heat absorption zone (the region of contact between coke pieces and the slag melt). This is achieved by the inclined position of the electrodes and forcing coke into the liquid slag by use of a 2-2.5 m high coke post in the coke lock-feeder.
7. The specific resistance of the coke layer at the work temperature (above than 1600^{0}C) is critical: 0.02 Ohm*m
8. The specific expenditure of electrode power should be not less than 200 kW-h/t of slag.

Fig. 13 shows sketch of a coke filter furnace for pilot investigation of scale-up for liquid slags. The above conclusions take account of the results of the present experiments with a laboratory coke filter furnace, which will now be used to develop the basic parts and

technology of a future industrial furnace. The capacity of the furnace is 475 kW at the slag productivity 2-2.5 t/h. For the industrial unit to be combined with Vanyukov's furnace a coke filter furnace is proposed to replace the present slag siphon (Fig. 14). Combining the melting process of copper sulfide ore concentrates with a continuous impoverishment of slag melts requires a productivity balance of the two parts of the assembly. The proposed scheme for joining the two furnaces fulfills such a balanced scheme. At the "Balkhashmed" plant the productivity of Vanyukov's furnace equals 80-100 t. fusion mixture per hour with a slag outlet of about 50% of the electrical power of the coke filter furnace. The power required to work 40-50 t. of liquid slag should then be not less than 9MWt. Assuming constant flow of liquid slag from the melting furnace, the control of temperature and degree of slag reduction could be realized by controlling the voltage between the electrodes and by changing the inter-electrode distance. To ensure continuous slag extraction from the furnace granulation is proposed.

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C. IMPACT RELEVANCE AND TECHNOLOGY TRANSFER

The project has proved useful in several respects:

- The exchange of scientific and technical experience. The Kazakhstan collaborator Prof. S.M.Kozhakhmetov visited the Technion twice (in April 2000 and in April 2001) where he became acquainted with the physical methods used in the Faculty of Materials Engineering. He also took part in the discussion of the results obtained and has participated in the preparation of the two management reports. Professor S.E.Vaisburd (Israel) visited IMiO, Almaty, Kazakhstan three times (in November 1999, in October 2000 and in September 2001), where he coordinated the initial joint work plan, discussed the results obtained during the investigation and, together with colleagues from Kazakhstan, prepared the annual and final reports.

- A post-graduate doctoral candidate from ImiO, E.B.Kenzhaliev, was at Technion for two extended visits of 5 months (from February till July 2000 and from March till July

2001), where he took part in the SEM/EDS and melt viscosity investigations. Previously he studied the measurement of physico-chemical properties of melts and has participated in a course of Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) given at Technion. E.B.Kenzhaliev has now returned to Kazakhstan as a specialist in both these fields.

-The experimental unit constructed at Technion for the measurement of physico-chemical properties of melts (viscosity, density, surface tension) has been prepared for transfer to the Institute of Metallurgy and Ore Benefication (Kazakhstan).

- A project to establish a SEM/EDS Center in Almaty is being discussed. This Center is proposed to be a national scientific center for Kazakhstan.

- As a result of this work IMiO has developed a laboratory model of a coke filter furnace for metallurgical investigation.

- The completed project of an industrial coke filter furnace is a logical next step to realize the technology of a direct process for crude copper production in the Republic Kazakhstan. The direct technology, excluding converter production of crude copper, will greatly improve the ecological situation in the Balkhash region of Kazakhstan.

In addition to the above achievements, we would claim that the most important result of this work is the professional contact developed between Israel and Kazakhstan, which straddles both the exact sciences and technology. And this contact was so successful that the Kazakhstan colleagues have expressed the wish for continued collaboration with Israel in other scientific and technological endeavors.

D. PROJECT ACTIVITIES.

All visits of Prof. Kozhakhmetov to the Technion (Haifa, Israel) and of Prof. Vaisburd to IMiO (Almaty, Kazakhstan) were accompanied by meetings with collaborators to discuss the research results and to plan future experiments. In addition, Rrof. Vaisburd during his visits to Kazakhstan gave lecturesfor scientific workers at IMiO and for collaboraters and students of the Kazakhstan Polytechnical University on three themes: physico-chemical principles of metallurgical processes, properties and structure of metallurgical melts, physical methods of study for metallurgical processes.

The post-graduate student (now completing a doctorate at IMiO) has participated in a course of Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) in Technion. E.B.Kenzhaliev obtained a certificate of competence in these methods. He also studied the measurement of properties of slag and matte: viscosity, density and surface tension , while at Technion.

Two articles describing the results of this investigation ("Slags and mattes in Vanyukov's process for the extraction of copper" and "Physico-chemical properties of matte – slag melts from Vanyukov's furnace for copper extraction") have been submitted to "Metallurgical and Materials Transactions" (USA). At present the authors are working to correct the articles to comply with comments received from the reviewers..

E. PROJECT PRODUCTIVITY.

The present investigation provides a scientific base for a direct process of crude copper production, in accordance with the basic objective of this work. So the project has met the proposed goals.

F. FUTURE WORK.

As a first step to develop a continuous technology of crude copper production with improved waste slag, a coke filter furnace with a productivity of 2.5t/h, slag operating at 0.5kW is proposed for installation in furnace regimes employed at the copper plant as an intermediate stage leading to an industrial furnace. In addition an industrial furnace for a continuous crude copper process with deep slag exhaustion of 50t/h slag and 9MW is proposed which combines Vanyukov's autogeneous furnace and a coke filter furnace.

Table 1. Results of chemical analyses of samples from Vanykov's furnace and coke filter furnace

Samples		Cu	Fe	FeO	Zn	Pb	CaO	SiO_2	Fe_3O_4	Al_2O_3	S
Vanyukov's furnace	N1, matte	48.9	16.5	-	3.6	2.5	0.12	1.3	-	1.35	22.1
	N2, slag from over current	3.8	-	39,8	6.5	1.26	2.5	31.7	2.4	5.4	1.8
	N3, waste slag	0.31	-	41,8	6.3	1.2	2.9	33.8	3.2	5.1	1.9
Coke filter furnace	initial slag	6.0	-	61,5	7.6	4.5	0.54	13.3	-	1.0	1.4
	initial slag calcinated at 1500^0C	3.8	-	74,4	6.8	2.7	0.5	10.5	-	9.5	0.6
	1450^0C 30s	1.8	-	45,8	8.6	3.9	9.7	18.1	-	1.5	0.73
	1450^0C 6min	0.4	-	33,6	1.6	0.2	9.9	26.7	-	7.7	0.66
	1600^0C 2 min	0.6	-	40,2	1.5	0.17	8.8	27.1	-	5.9	0.66

Table 2. Results of EDS analysis of the initial slag sample

N of point	Content, % atomic													Possible phases
	Cu	Fe	Zn	Pb	Al	Mg	K	Ca	As	Sb	Si	S	O	
1	-	24.6	5	-	0.30	0.14	-	-	-	-	13.8	-	56.2	Silicate Fe_2SiO_4
2	-	7.6	5.9	0.34	4.0	-	3.7	2.5	-	-	17.5	-	58.7	Silicate $FeSiO_3$
3	-	41.3	5.7	0.03	1.1	-	-	-	-	-	0.50	-	51.5	FeO
4	4.4	4.4	1.1	39.4	5.1	-	-	-	0.3	0.11	-	1.4	44.0	Pb or PbO
5	54.6	4.9	0.71	1.9	0.6	0.01	0.04	0.03	-	-	0.74	26.8	9.7	Cu_2S
6	80.2	4.0	0.43	0.44	1.1	0.11	0.12	0.01	4.6	1.6	0.42	0.24	7.0	Cu
7	61.0	1.8	0.46	0.51	0.66	0.12	0.01	0.06	-	0.07	0.31	29.3	5.8	Cu_2S
8	7.2	2.8	40.1	0.28	0.43	1.0	0.08	0.02	0.64	0.02	0.28	44.3	5.5	ZnS
9	-	36.4	3.1	0.10	1.1	-	-	-	-	-	1.3	-	56.1	Magnetite, Fe_3O_4
10	0.16	40.0	3.0	-	1.3	0.05	0.05	-	0.06	-	0.41	0.03	55.3	Magnetite, Fe_3O_4

Table.3. Results of EDS analysis of the initial slag sample after reduction at 1500^{0}C without coke addition

N of point	Content, % atomic										Possible phases
	Cu	Fe	Zn	Pb	Al	K	Ca	Si	S	O	
1	-	20.4	5.0	-	17.5	-	-	0.31	-	56.7	Iron aluminate
2	-	21.0	5.0	-	16.8	-	-	0.23	-	57.0	Iron aluminate
3	-	8.6	2.9	0.29	5.5	2.9	3.2	14.6	1.0	60.9	Iron silicate $FeSiO_3$
4	-	8.4	2.6	0.27	5.4	3.3	3.3	15.7	1.1	59.7	Iron silicate $FeSiO_3$
5	-	43.5	3.0	-	0.65	-	-	0.43	-	52.4	FeO or Fe_3O_4
6	-	34.8	3.2	-	1.9	-	-	4.8	-	55.3	FeO or Fe_3O_4
7	-	43.8	3.0	-	0.57	-	-	0.40	-	52.2	FeO or Fe_3O_4
8	-	43.4	3.3	-	0.56	-	-	0.45	-	52.3	FeO or Fe_3O_4
9	-	43.9	3.2	-	0.67	-	-	0.42	-	51.9	FeO or Fe_3O_4
10	86.6	4.7	0.76	-	0.76	-	-	-	-	7.0	Cu
11	77.9	8.5	0.97	2.9	0.51	-	-	0.60	-	8.7	Cu
12	83.7	3.9	0.90	-	1.8	-	-	-	-	9.3	Cu
13	51.6	6.0	0.74	-	1.2	-	-	0.53	26.2	13.7	Cu_2S
14	49.7	6.6	0.37	0.30	1.9	-	-	0.34	28.2	12.6	Cu_2S
15	2.0	3.8	0.87	35.3	6.5	-	-	-	1.0	50.8	Pb or PbO

Table.3. Continuation

N of points	Content % atomic										Possible phases
	Cu	Fe	Zn	Pb	Al	K	Ca	Si	S	O	
16	81.8	1.6	0.61	0.52	2.0	-	-	-	-	13.0	Cu
17	79.4	1.5	0.79	4.9	1.0	-	-	-	-	11.7	Cu
18	3.7	1.9	-	37.3	4.3	-	-	-	-	51.7	Pb or PbO
19	57.2	2.2	-	-	0.87	-	-	-	29.9	9.6	Cu_2S
20	2.4	2.5	43.1	-	0.40	-	-	0.31	45.9	5.1	ZnS
21	10.5	4.0	0.11	27.8	4.9	-	-	-	5.7	47.2	Pb or PbO
22	-	22.3	4.8	-	15.1	-	-	0.29	-	57.5	Iron aluminate
23	-	9.8	1.8	0.15	4.5	3.1	4.1	15.8	0.74	59.6	Iron silicate $FeSiO_3$
24	-	42.2	3.4	-	0.72	-	-	0.62	0.15	52.9	FeO or Fe_3O_4
25	-	42.0	3.2	-	0.65	-	-	0.29	0.15	53.7	FeO or Fe_3O_4
26	-	25.1	3.1	-	0.28	0.09	0.18	13.5		57.8	Iron silicate Fe_2SiO_4

Table.4. Results of EDS analysis of the initial slag sample after infiltration through the coke filter at 1450^0 C during 30 s

N of point	Content, % atomic														Possible phases
	Cu	Fe	Zn	Pb	Al	Mg	K	Ca	Ni	As	Sb	Si	S	O	
1	-	11.2	3.5	-	2.2	0.32	0.59	8.0	-	-	-	15.3	0.42	58.3	Silicate $FeSiO_3$
2	-	40.7	2.6	-	0.51	0.35	-	0.40	-	-	-	0.45	-	54.8	Magnetite, Fe_3O_4
3	-	41.7	2.8	-	0.48	0.31	-	0.26	-	-	-	0.53	-	54.0	Magnetite, Fe_3O_4
4	3.0	3.5	0.79	39.1	0.58	-	-	0.34	-	-	-	-	-	52.1	Pb or PbO
5	81.5	3.2	0.63	-	-	-	--	-	1.1	2.5	2.2	0.36	-	8.8	Cu
6	51.1	8.5	0.60	-	-	-	-	0.27	-	-	-	0.68	27.6	10.8	$(Cu, Fe)_2S$
7	52.9	5.7	0.43	-	0.40	-	-	0.59	-	--	-	1.1	28.3	10.2	$(Cu, Fe)_2S$
8	81.1	2.3	0.49	-	-	-	-	-	0.92	2.3	2.1	-	-	10.3	Cu

Table.5. Results of EDS analysis of the initial slag sample after infiltration through the coke filter at 1450^0 C during 6 min

N of point	Content, % atomic													Possible phases
	Cu	Fe	Zn	Pb	Al	Mg	K	Ca	Ti	Co	Si	S	O	
1	-	10.6	0.97	-	4.9	0.35	0.60	8.2	0.13	-	11.4	0.69	62.2	Silicate $FeSiO_3$
2	-	17.0	0.47	-	0.17	8.3	-	1.3	-	-	12.8	-	60.0	Silicate Fe_2SiO_4
3	7.8	34.6	6.7	0.53	0.34	-	-	0.41	-	-	0.37	36.0	13.2	(Fe, Cu, Zn)S
4	7.7	38.3	1.6	-	-	-	0.11	0.35	-	-	0.27	34.8	16.8	(Fe, Cu, Zn)S
5	12.0	25.4	8.5	-	0.96	-	0.20	2.9	-	-	2.7	32.3	14.6	(Fe, Cu, Zn)S
6	3.0	84.0	-	-	-	-	-	-	-	0.50	0.28	0.28	11.9	Fe
7	-	12.7	0.38	-	3.7	4.	0.30	5.0	0.11	-	12.5	0.42	60.5	Silicate $FeSiO_3$
8	1.1	49.6	-	-	-	-	-	-	-	-	0.23	41.5	7.7	FeS
9	0.79	48.6	-	-	0.20	-	-	-	-	-	0.33	41.6	8.5	FeS
10	3.3	84.9	-	-	-	-	-	-	-	0.72	0.27	0.29	10.2	Fe
11	0.65	48.9	-	-	-	-	-	--	-	-	0.29	46.2	3.9	FeS
12	45.2	14.7	-	-	-	-	-	-	-	-	0.31	35.6	4.2	$(Cu, Fe)_2S$

Table.6. Results of EDS analysis of the initial slag sample after infiltration through the coke filter at 1600^0 C during 2 min

N of point	Content, % atomic											Possible phases
	Cu	Fe	Zn	Pb	Al	Mg	Ca	Sb	Si	S	O	
1	-	11.7	0.63	-	4.3	0.83	8.0	-	11.9	0.65	61.3	Silicate $FeSiO_3$
2	-	18.1	0.35	-	0.20	7.3	1.5	-	12.4	-	59.8	Silicate Fe_2SiO_4
3	83.0	4.5	1.2	-	0.30	-	-	0.29	0.36	-	9.6	Cu
4	6.1	80.4	-	-	-	-	-	-	0.38	-	10.7	Fe
5	6.8	79.7	-	-	-	-	-	-	0.38	0.21	10.3	Fe
6	1.8	4.3	-	37.8	3.7	-	-	-	-	1.8	49.7	Pb or PbO
7	41.7	13.7	0.37	0.75	-	-	-	-	0.42	34.5	8.2	(Cu, Fe)S
8	41.9	14.0	-	0.77	0.51	-	-	-	0.34	33.4	9.1	(Cu, Fe)S
9	10.7	34.5	0.56	2.9	0.23	-	-	-	0.22	36.6	13.7	(Fe, Cu)S
10	6.2	79.0	0.48	-	-	-	-	-	0.34	-	11.1	Fe
11	81.2	4.7	0.91	-	0.62	-	-	0.50	0.45	-	10.3	Cu
12	83.2	4.1	0.89	1.6	-	-	0.33	0.89	0.26	-	8.0	Cu
13	35.0	14.0	0.56	2.4	1.2	-	1.4	-	1.8	30.0	13.5	(Cu, Fe)S
14	1.3	3.3	-	36.9	3.3	-	0.40	-	-	1.0	53.4	Pb or PbO

Table 6. Continuation

N of point	Content, % atomic											Possible phases
	Cu	Fe	Zn	Pb	Al	Mg	Ca	Sb	Si	S	O	
15	3.8	83.7	-	-	0.32	-	0.14	-	0.33	-	11.3	Fe
16	2.8	84.4	-	-	0.37	-	-	-	0.30	0.70	10.	Fe
17	4.4	83.3	-	-	0.27	-	0.17	-	0.22	-	10.70	Fe
18	1.0	31.6	16.9	-	-	-	0.14	-	0.28	44.8	5.6	(Fe, Zn)S
19	1.1	46.6	-	-	-	-	0.15	-	0.38	45.8	5.7	FeS

Table 7. Equilibrium parameters for the matte conversion reactions at 1300°C.

Reaction	*K*	$C_{(MeS)}/C_{(MeO)}$
(FeO) + (CoS) = (FeS) + (CoO)	$8.2 \cdot 10^{-2}$	0.12
(FeO) + (ZnS) = (FeS) + (ZnO)	$9.3 \cdot 10^{-2}$	0.11
(FeO) + (PbS) = (FeS) + (PbO)	$4.8 \cdot 10^{-2}$	0.21
(FeO) + (Cu_2S) = (FeS) + (Cu_2O)	$2.0 \cdot 10^{-5}$	$0.5 \cdot 10^{3}$

Table 8. Viscosity of the waste slag.

t (°C)	T (°K)	1000/T	[RD].10^{-3}	η (Pa.s)	log η
1300	1573	0.636		0.31*	-0.509*
1350	1623	0.616	4.06	0.26	-0.585
1400	1673	0.598	3.47	0.22	-0.658
1450	1723	0.580	3.02	0.19	-0.721
1500	1773	0.564	2.56	0.16	-0.796
1550	1823	0.549	2.18	0.14	-0.853

[RD] – readings of the digital
* - extrapolated data

Table 9. Kinematic viscosity of matte.

t (°C)	T (°K)	1000/T	ν (m^2/s)	log ν
1300	1573	0.636	6.3	0.800
1350	1623	0.616	6.1	0.782
1400	1673	0.598	5.8	0.764
1450	1723	0.580	5.6	0.746
1500	1773	0.564	5.3	0.729

Table 10. Surface tension of the waste slag and matte.

t (^{0}C)	T (^{0}K)	slag			matte		
		n	P_m (mm H_2O)	σ (mN/m)	n	P_m (mm H_2O)	σ (mN/m)
1300	1573			359*			340*
1350	1623	3	145.6±1.7	364	3	136.8±1.2	342
1400	1673	4	148.0±1.3	370	3	138.0±1.5	345
1450	1723	4	150.0±1.8	375	4	138.8±1.8	347
1500	1773	5	152.8±1.9	382	4	139.6±1.7	349
1550	1823	5	154.8±1.8	387			

Table 11. Density of the waste slag and matte.

t, ^0C	T, ^0K	h, mm	slag				matte			
			n	P_m, mm H_2O	ΔP_m, mm H_2O	$\rho \cdot 10^{-3}$, kg/m^3	n	P_m, mm H_2O	ΔP_m, mm H_2O	$\rho \cdot 10^{-3}$, kg/m^3
1300	1573					3.34*				4.74*
1350	1623	3.0	4	155.4 ± 0.6	9.80	3.27	3	150.9 ± 0.5	14.13	4.71
		6.0	3	165.3 ± 0.6			3	165.1 ± 0.7		
		9.0	3	175.0 ± 0.6			3	179.2 ± 0.6		
1400	1673	3.0	4	157.6 ± 0.5	9.63	3.21	4	152.0 ± 0.6	14.03	4.68
		6.0	3	167.2 ± 0.5			3	166.1 ± 0.6		
		9.0	3	176.9 ± 0.6			3	180.1 ± 0.7		
1450	1723	3.0	4	159.4 ± 0.7	9.43	3.14	4	152.8 ± 0.6	13.97	4.66
		6.0	4	168.9 ± 0.6			3	166.7 ± 0.8		
		9.0	3	178.3 ± 0.8			3	180.7 ± 0.8		
1500	1773	3.0	4	162.1 ± 0.5	9.23	3.08	4	153.5 ± 0.7	13.90	4.63
		6.0	4	171.5 ± 0.4			4	167.5 ± 0.8		
		9.0	3	180.8 ± 0.6			3	181.3 ± 0.7		
1550	1823	3.0	4	163.8 ± 0.6	9.05	3.02				
		6.0	4	172.9 ± 0.5						

Table 12. Composition of synthetic slags*.

Type of slags	Contents, %				Ratio	
	FeO	SiO_2	CaO	Al_2O_3	SiO_2/CaO	FeO/SiO_2
I	54,77	33,10	5,80	6,00	5,71	1,65
II	33,17	42,10	15,00	9,10	2,81	0,79
III	13,63	50,30	24,20	11,30	2,08	0,27

* All samples for the measurememnts have contained 10% of copper oxide Cu_2O.

Table 13. Metal balance of the coke filter furnace smelting

	Mass,g	Distrib,%	Cu			Cuoxide			Cusulphide			Fe		
			cont,%	Mass,g	Distrib,%	cont,%	Mass,g	Distrib,%	cont,%	Mass,g	Distrib,%	cont,%	Mass,g	Distrib,%
Charge														
Initial Slag	1332	100	1,8	24,0	100,0	0,6	8,0	100	1,2	16,0	100	36,3	483,5	100
Obtain														
Reduced Slag	865,8	65	0,6	5,2	21,8	0,08	0,69		0,53	4,6		31,2	270,1	55,9
Alloy	266,4	20	7,0	18,6	78,2	0,00						80,1	213,4	44,1
Sublimates	133,2	10	0,0	0,0	0,0	0,00								
Discrepancy	66,6	5	0,0	0,0	0,0	0,00								

	Mass,g	Distrib,%	Zn			Znoxide			Znsulphide		
			cont,%	Mass,g	Distrib,%	cont,%	Mass,g	Distrib,%	cont,%	Mass,g	Distrib,%
Charge											
Initial Slag	1332	100	7,8	103,3	100,0	4,1	54,6	100	3,7	49,3	100
Obtain											
Reduced Slag	865,8	65	1,5	12,9	12,5	0,10	0,90	1,65	1,4	12,1	24,59
Alloy	266,4	20	0,4	1,1	1,1						
Sublimates	133,2	10	67,0	89,3	86,4						
Discrepancy	66,6	5									

	Mass,g	Distrib,%	Pb			Pboxide			Pbsulphide		
			cont,%	Mass,g	Distrib,%	cont,%	Mass,g	Distrib,%	cont,%	Mass,g	Distrib,%
Charge											
Initial Slag	1332	100	3,9	51,95	100,0	3,1	41,29	100	0,8	10,66	100
Obtain											
Reduced Slag	865,8	65	0,2	1,47	2,83	0,05	0,43	1,04	0,12	1,04	9,76
Alloy	266,4	20	0,4	1,07	2,06						
Sublimates	133,2	10	37,1	49,40	95,10						
Discrepancy	66,6	5									

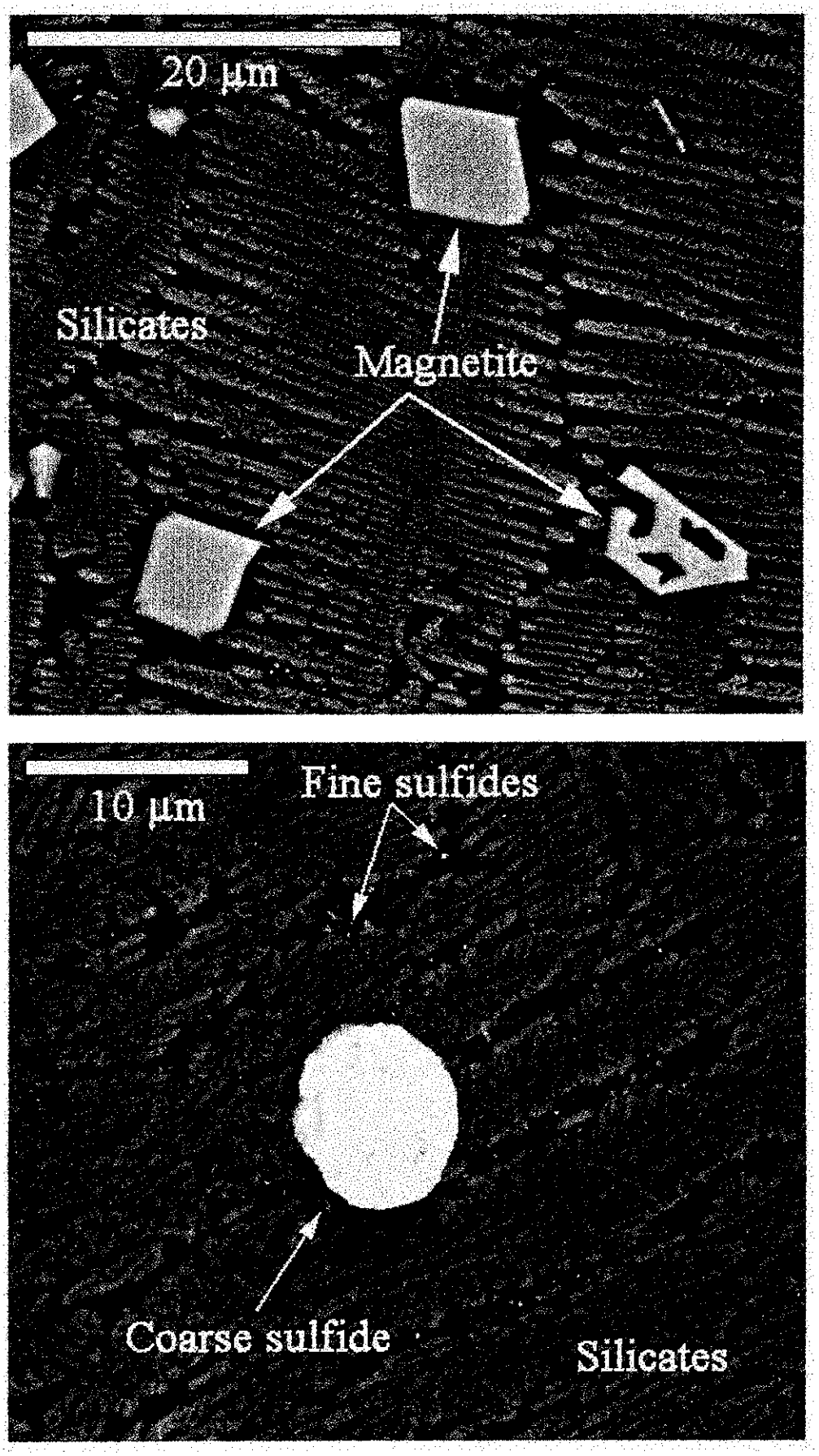
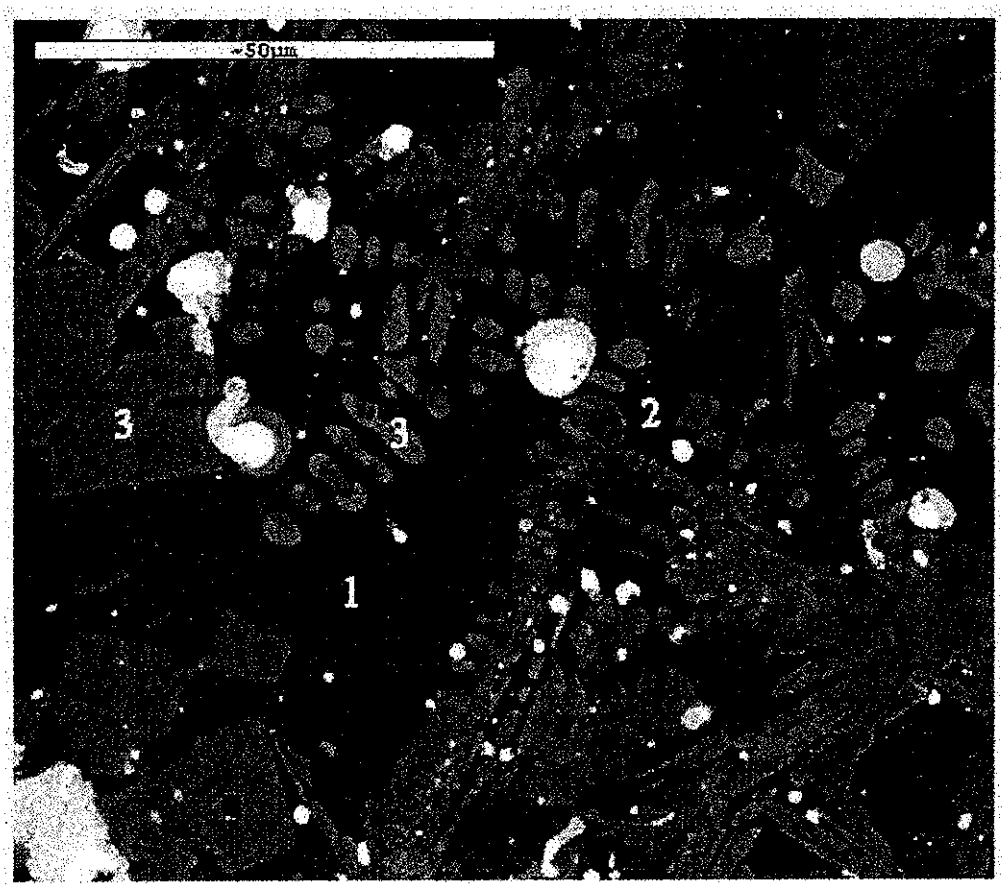


Fig.1. Typical SEM micrographs obtained from the waste slag with back scattered electrons in compositional contrast mode.



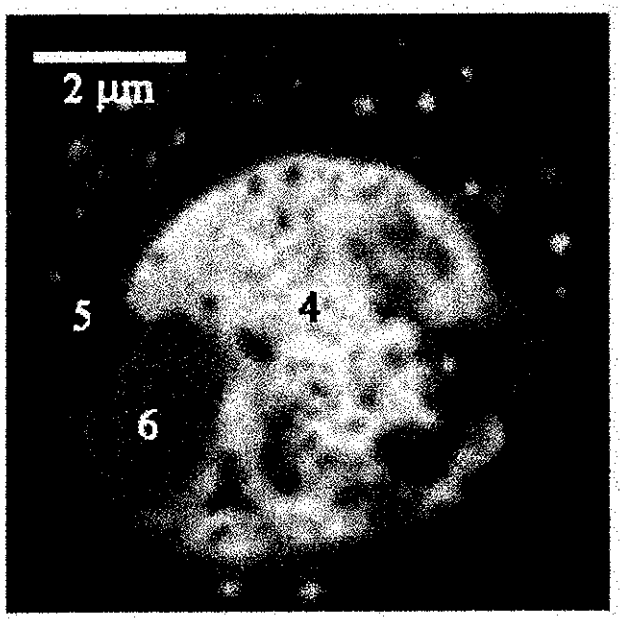


Fig.2a. SEM micrographs from the initial slag sample:
1, 2 - silicates, 3 - FeO, 4 - Pb enriched phase,
5 - Cu_2S, 6 - Cu regular.

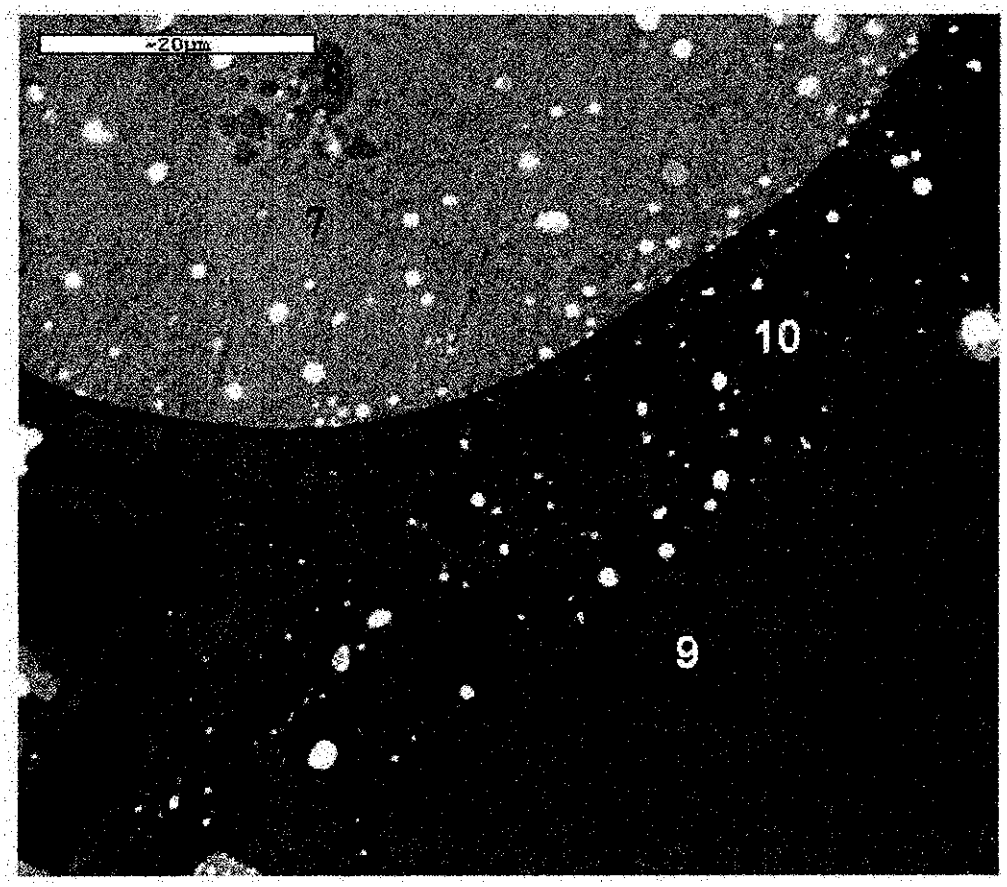


Fig.2b. SEM micrograph from the initial slag sample:
7 - Cu_2S, 8 - ZnS, 9, 10 - magnetite Fe_3O_4.

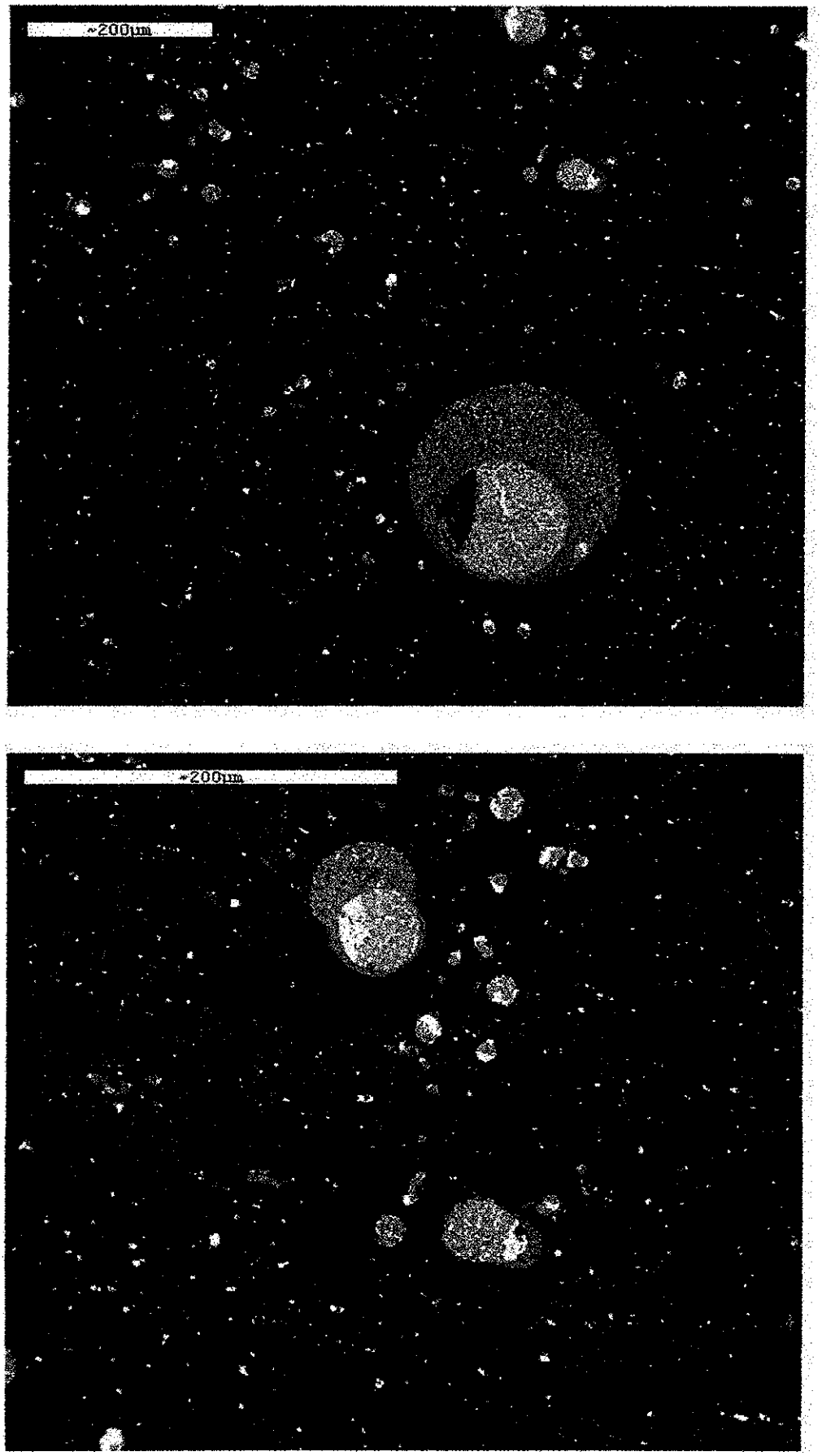


Fig.3a. SEM micrographs from the initial slag after reduction at 1500°C without coke addition. Overview.

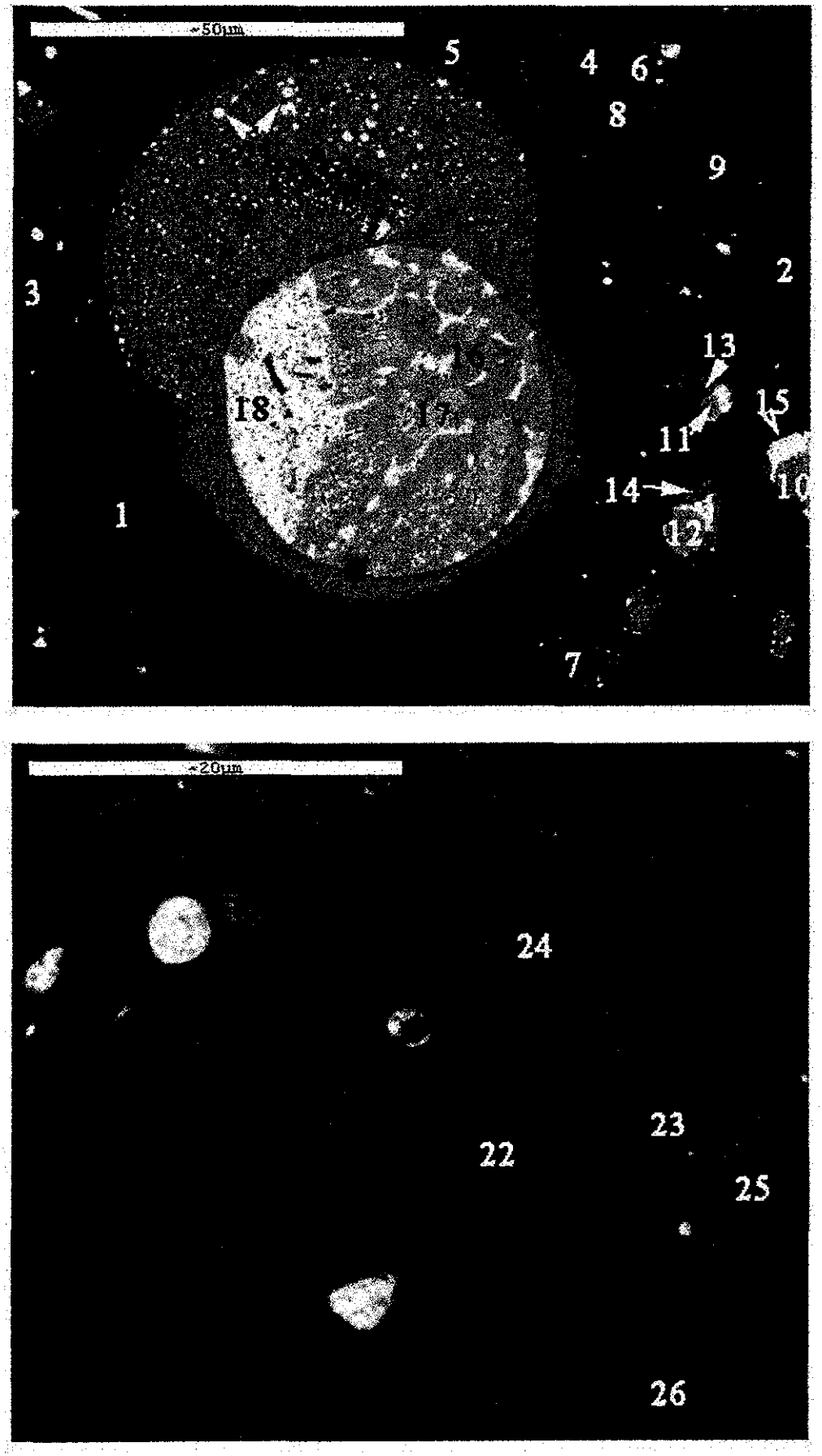


Fig.3b. SEM micrographs from the initial slag after reduction at 1500°C without coke addition: 1-2, 22 - iron aluminates, 3-4, 23, 26 - iron silicates, 5-9, 24-25- iron oxides,10-12, 16-17 - Cu, 13-14, 19 - Cu_2S, 20 - ZnS, 15, 18, 21 - Pb enriched phase.

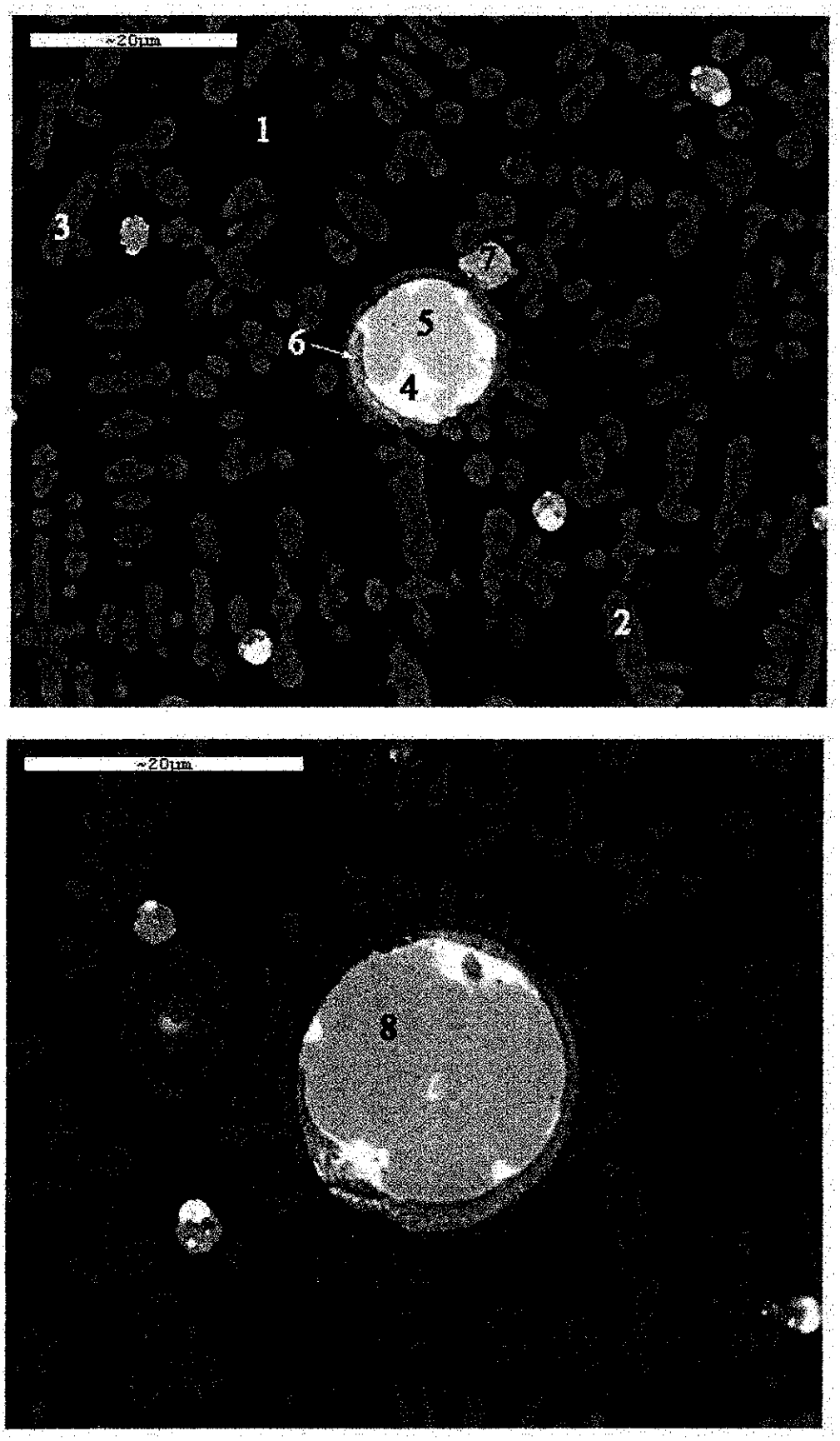
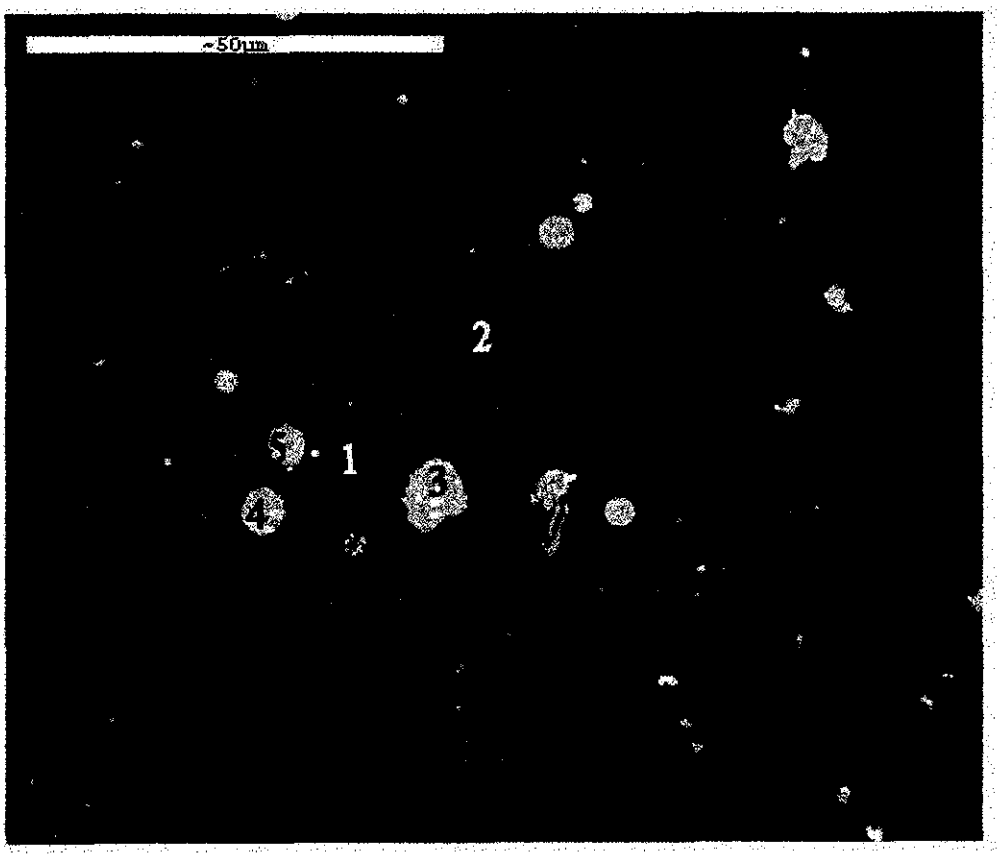


Fig.4. SEM micrographs from the initial slag sample after infiltration through the coke filter at 1450° C during 30 s: 1 - iron silicate, 2, 3 - magnetite, 4 - lead enriched phase, 5, 8 - copper reguli, 6, 7 - $(Cu, Fe)_2S$.



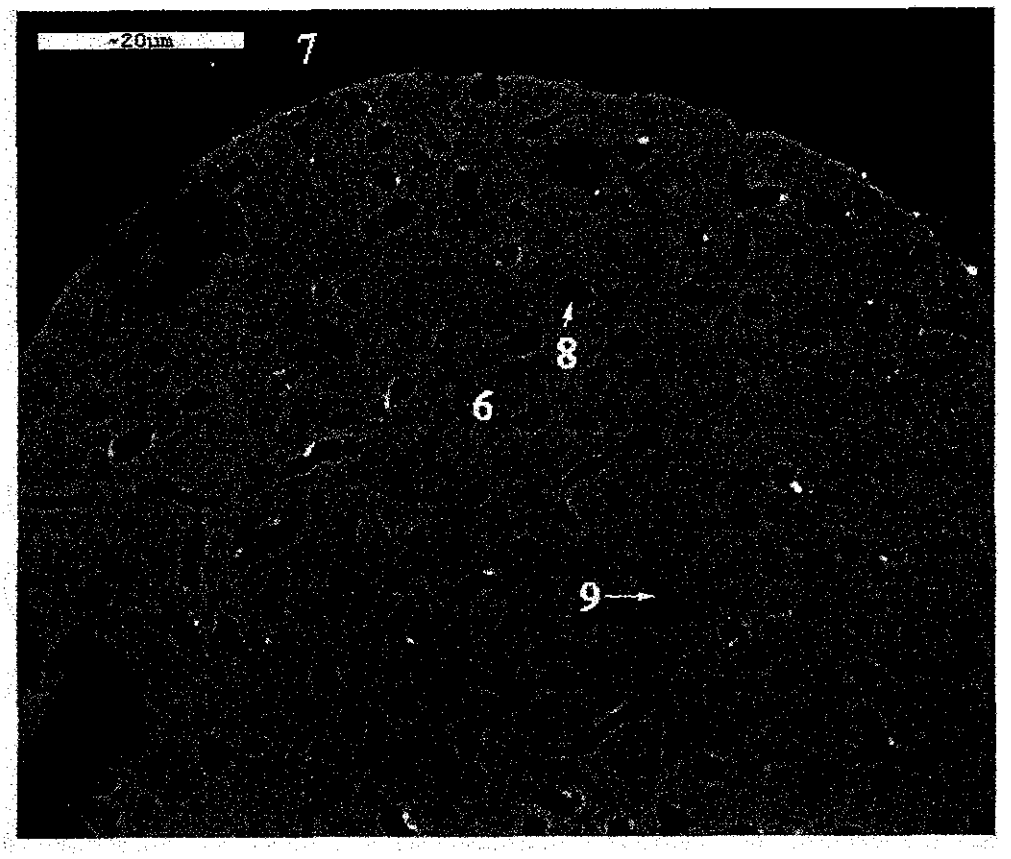


Fig.5a. SEM micrographs from the initial slag sample after infiltration through the coke filter at 1450° C during 6 min: 1, 2, 7 - iron silicates, 3-5 - (Fe, Cu, Zn)S, 6 - iron regulus, 8, 9 - FeS.

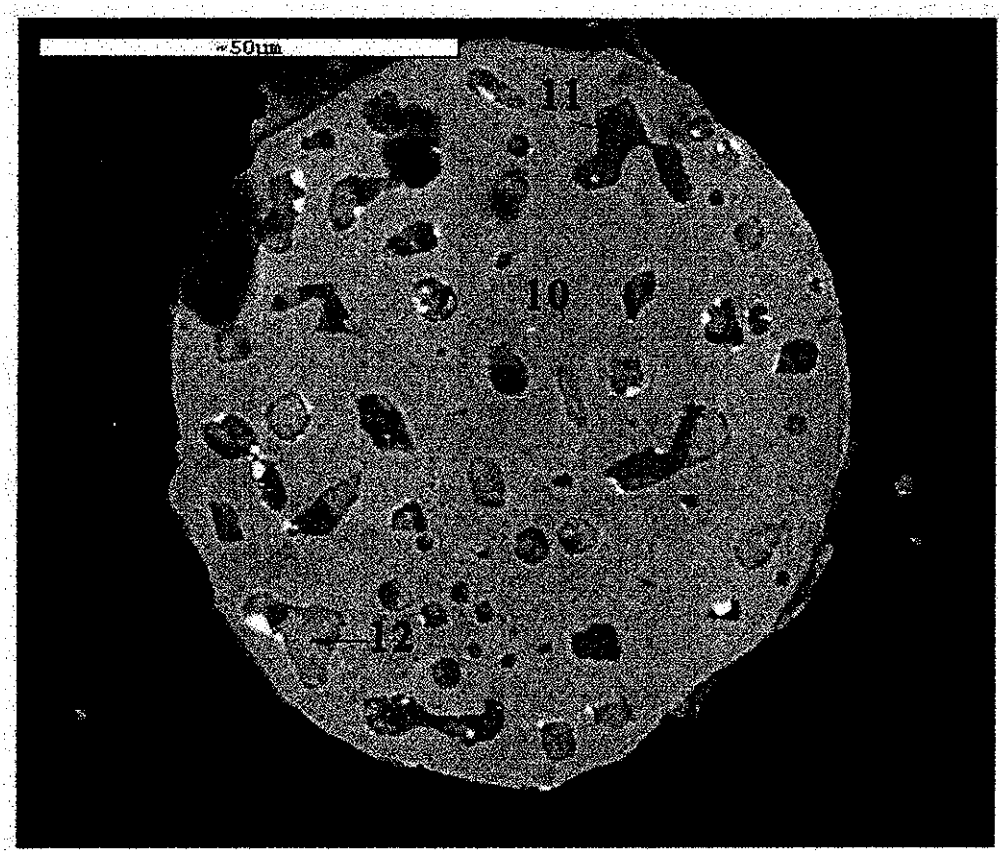


Fig.5b. 10 - iron regulus, 11 - FeS, 12 - $(Cu, Fe)_2S$.

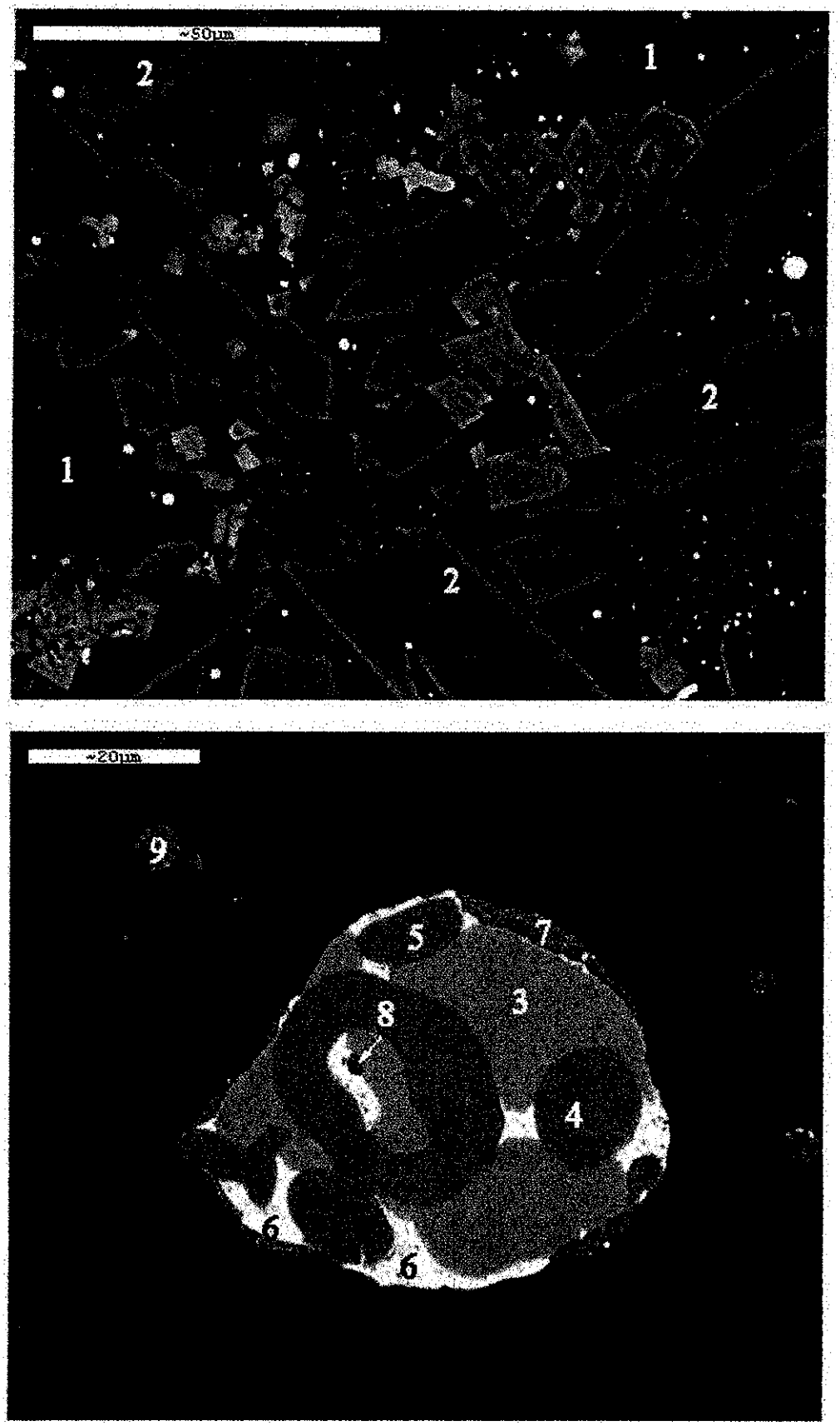
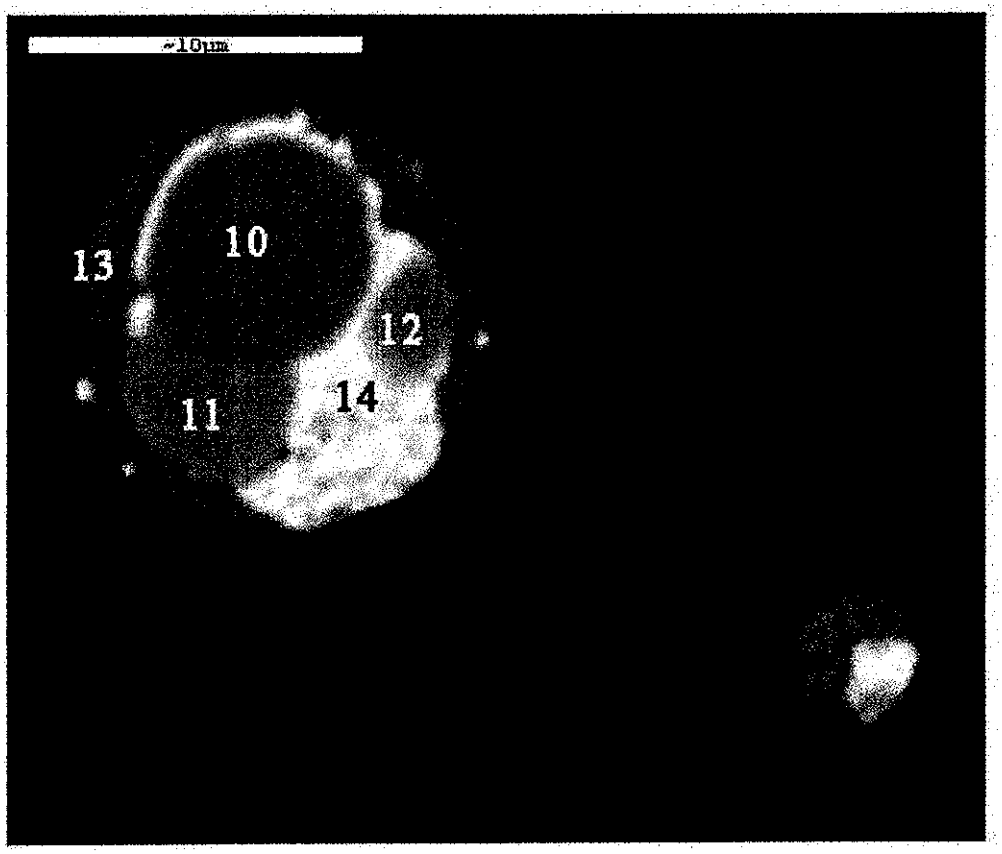


Fig.6a. SEM micrographs from the initial slag sample after infiltration through the coke filter at 1600° C during 2 min.: 1, 2 - iron silicates, 3 - copper regulus, 4, 5 - iron reguli, 6 - lead enriched phase, 7, 8 - (Cu, Fe)S, 9 - (Fe, Cu)S.



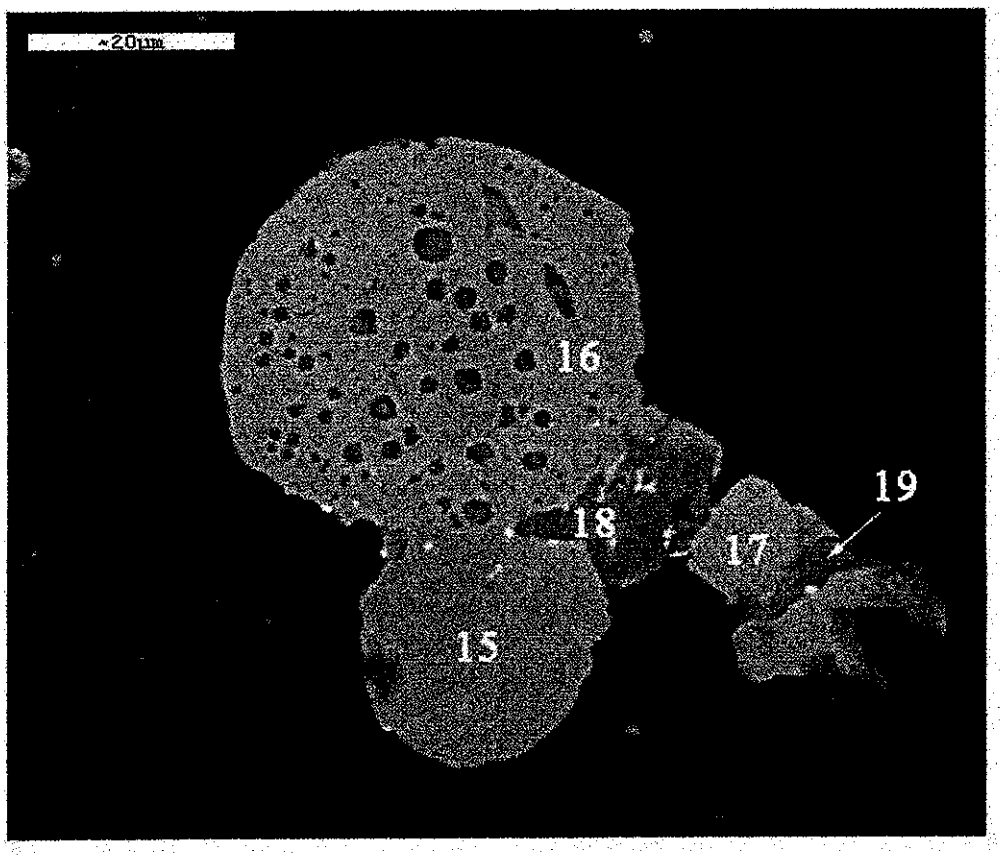


Fig.6b. 10, 15-17 - iron reguli, 11, 12 - copper reguli, 13 - (Cu, Fe)S, 14 - lead enriched phase, 18 - (Fe, Zn)S, 19 - FeS

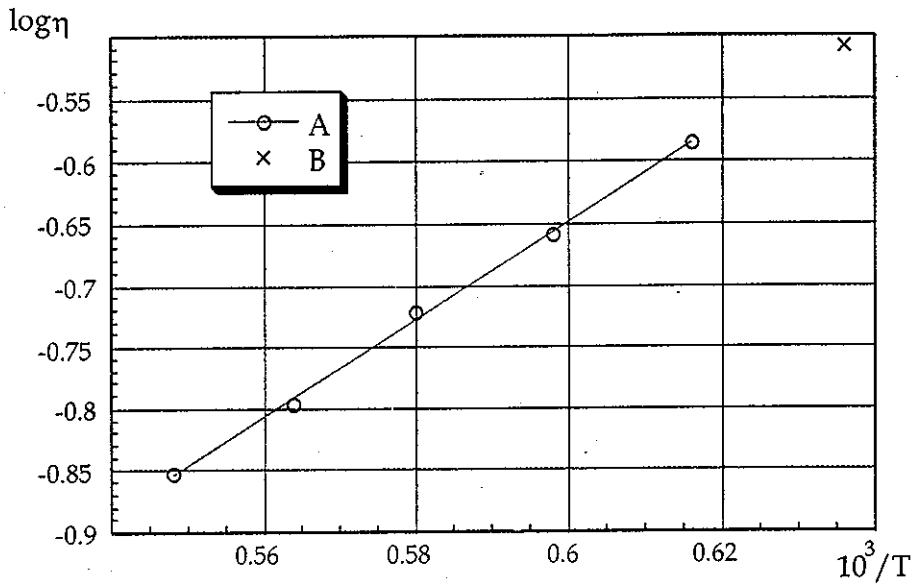


Fig.7.
Viscosity (η) of the waste slag.
A – experimental data, B – data extrapolated to 1300 °C.

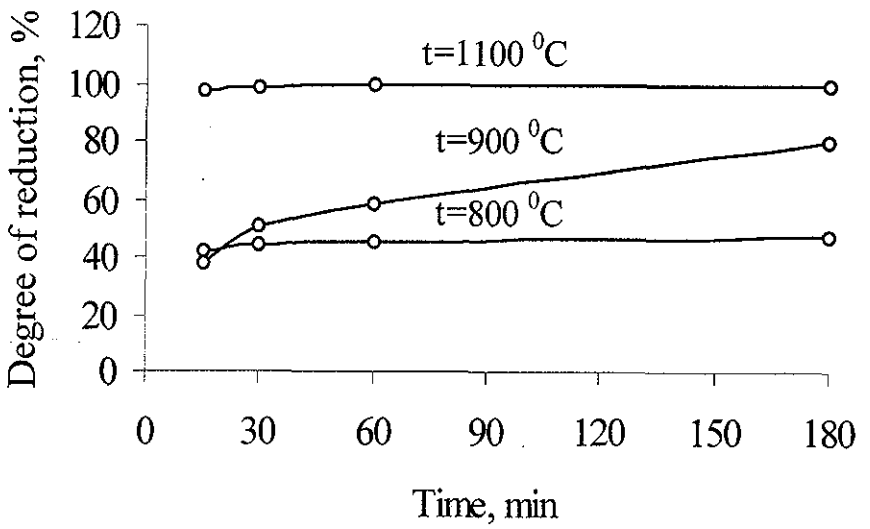


Fig. 8.
Degree of CuO reduction by charcoal at vacuum of 10^{-3} Pa.

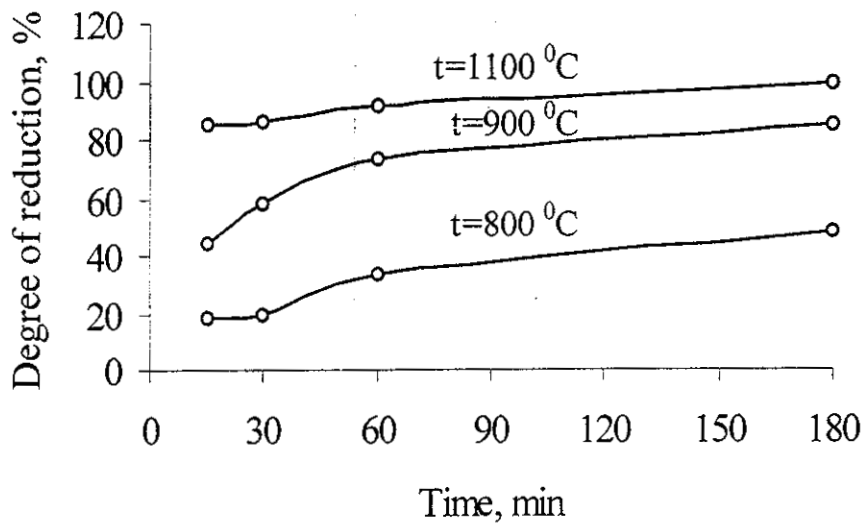


Fig. 9.
Degree of CuO reduction at atmospheric pressure of gaseous phase.

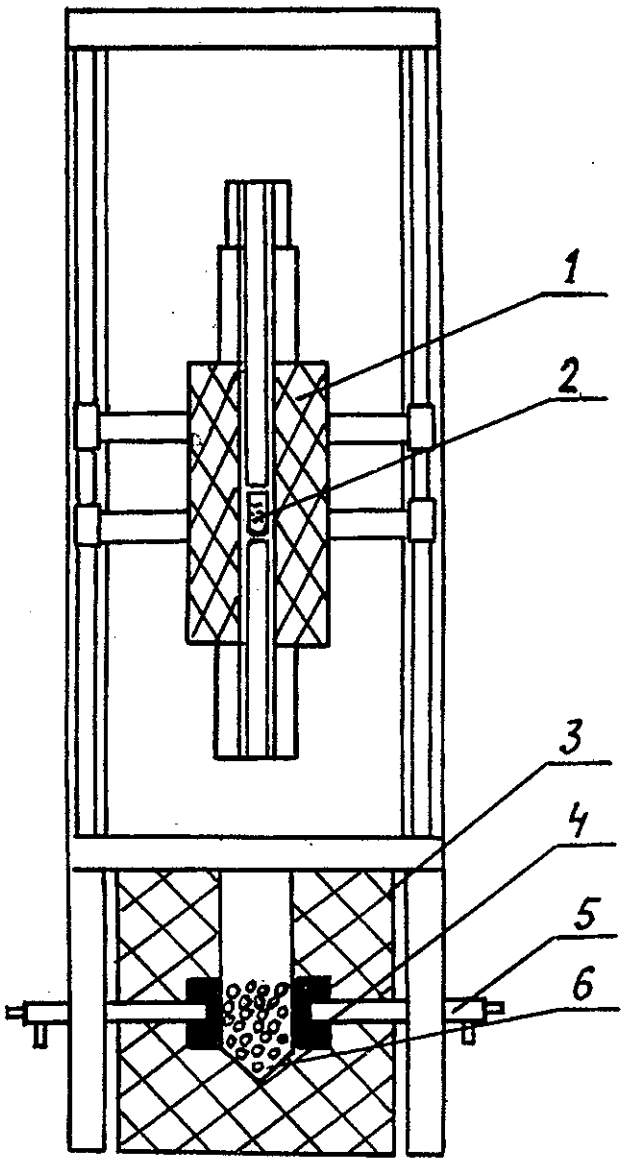


Fig. 10. Scheme of laboratory model of furnace with coke filter
1 – high-temperature vertical furnace; 2 – crucible; 3 – lower furnace with coke filter; 4 – graphites; 5 – current suppliers; 6 – pouring opening.

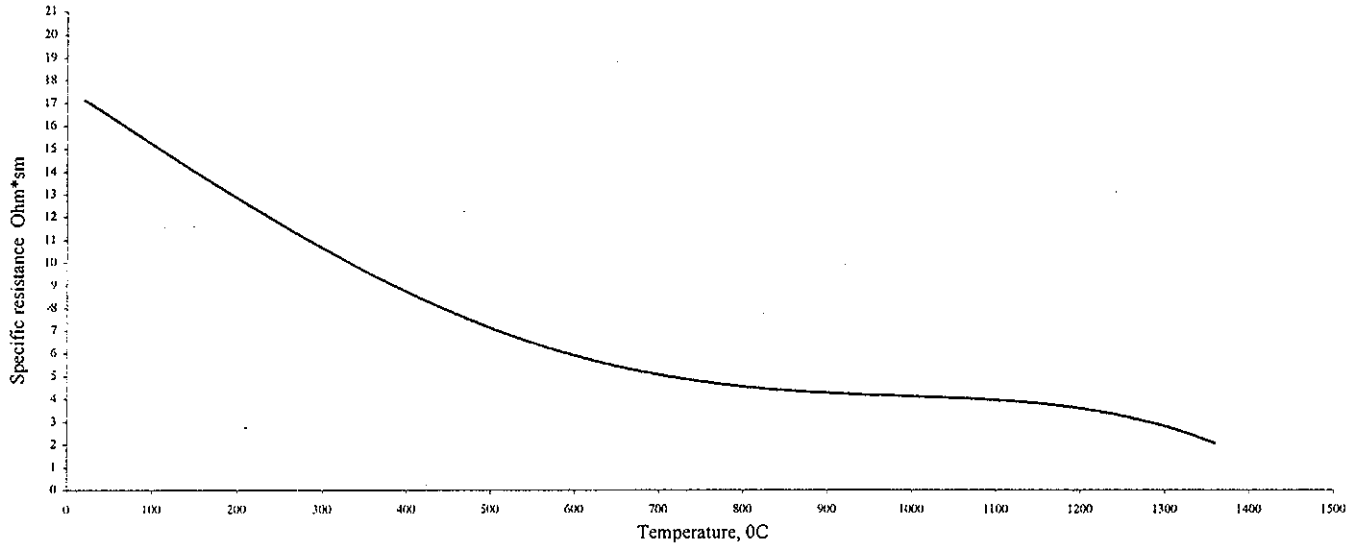


Fig.11. Dependence of the specific resistance of the coke layer from temperature

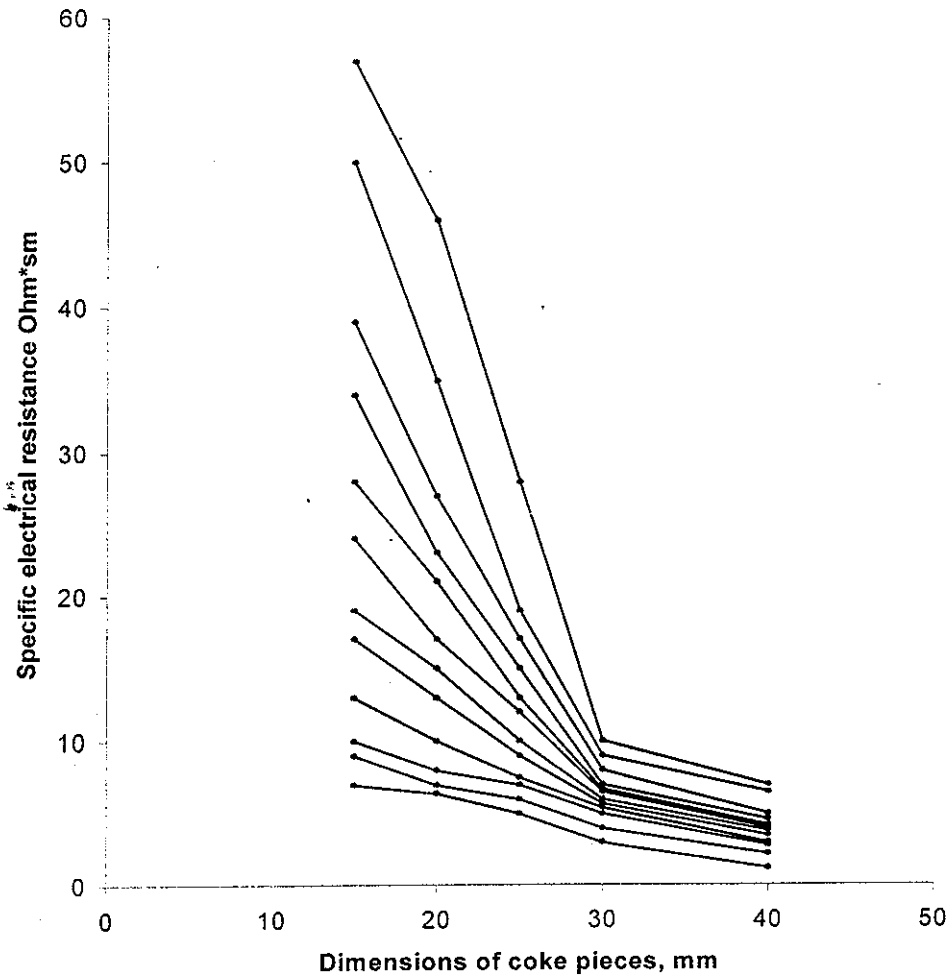


Fig.12. Dependence of the specific resistance of the coke layer from dimensions of coke pieces

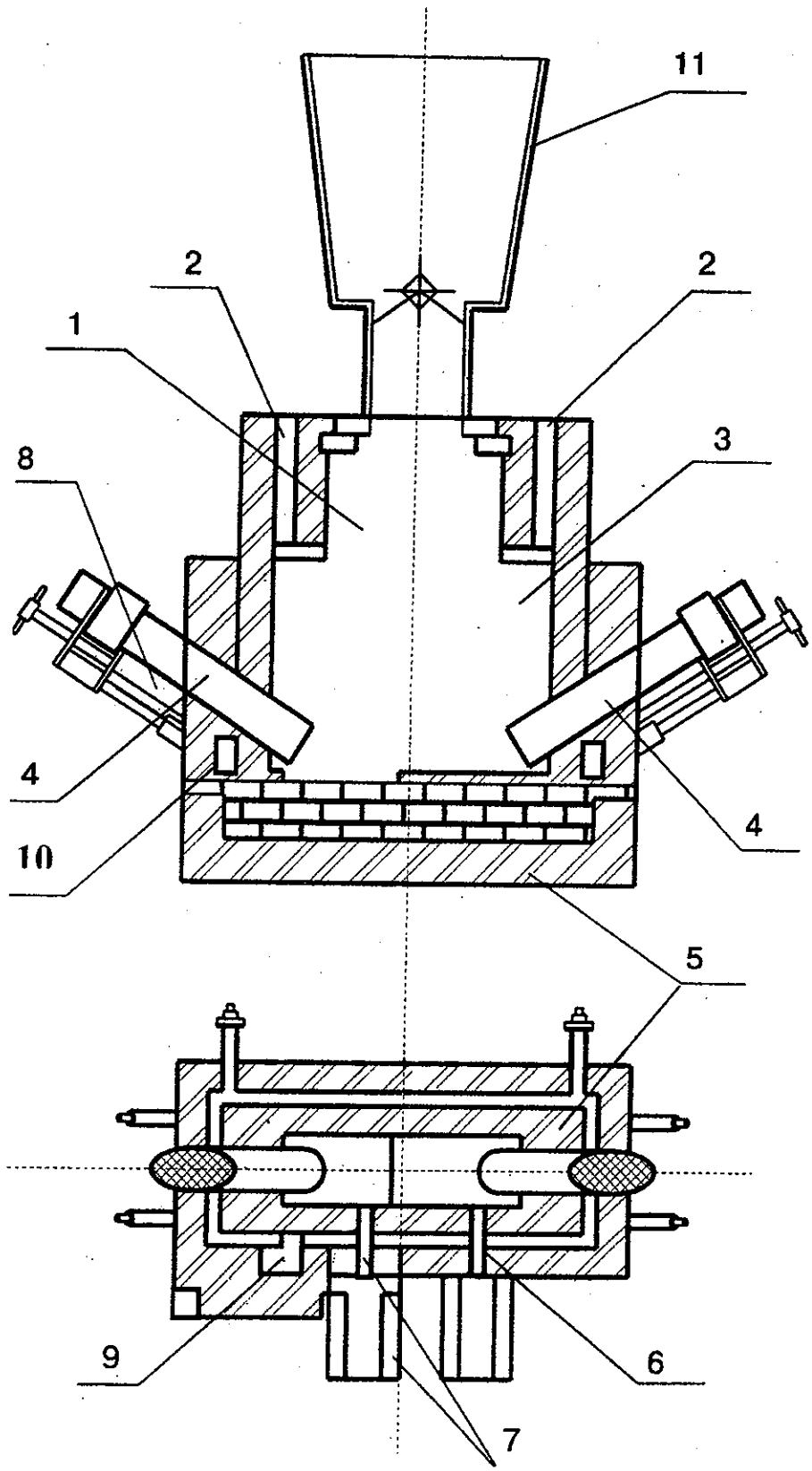


Fig.13. Coke filter furnace for enlarged experiments

1 - Coke chamber; 2 - Flues; 3 - Reduction area; 4 - Electrodes; 5 - Fire brick lining; 6 - Opening for slag pouring; 7 - Opening for alloy pouring; 8 - Electrode holders; 9 - Opening for the charge; 10 – Water cooled part of the lining; 11 – Equipment for the coke charge.

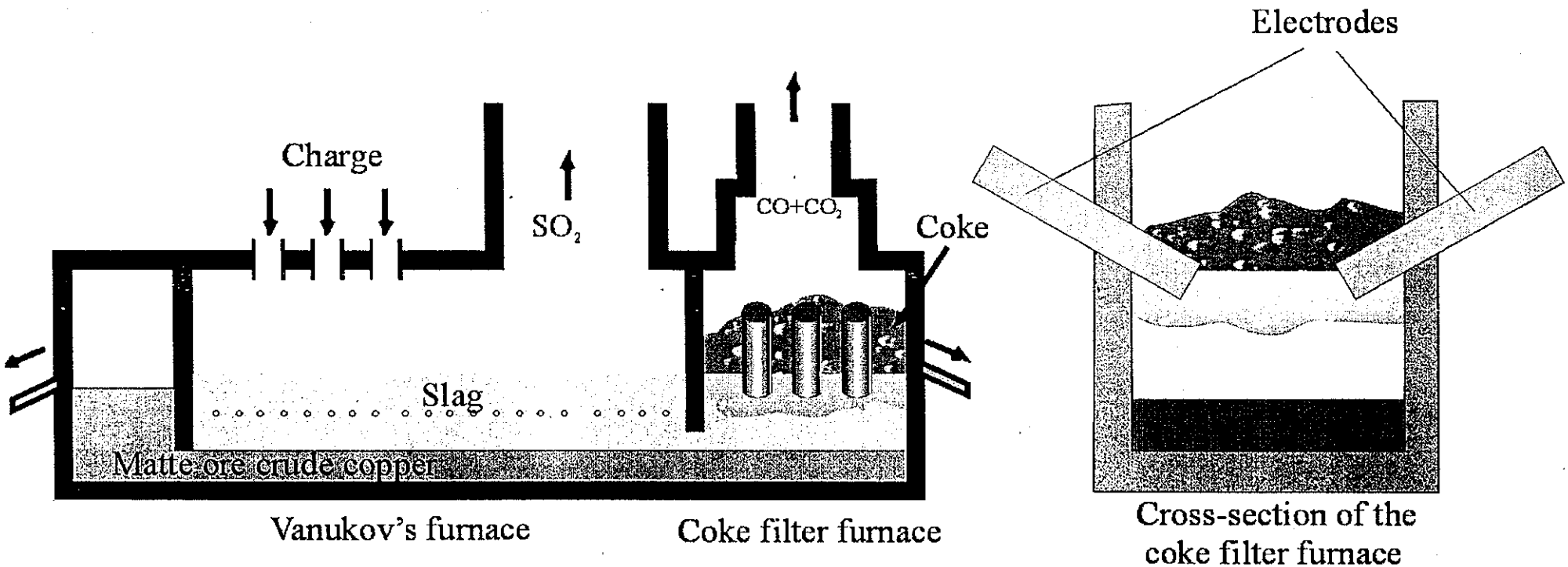


Fig.14. Aggregate for the continuous production of crude copper

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14 June 2001

Prof. David G. Brandon
Technion – Israel Institute of Technology
Faculty of Materials Engineering
Technion City, Haifa 32 000 Israel

Subject: Paper (01-201-B) "Slags & Mattes in Vanyukov's Process for the Extraction of Copper" By: Vaisburd, Berner, Brandon, Kozhakhmetov, Kenzhaliyev and Zhalelev

Dear Prof. Brandon:

Our review committee has advised us that the material in your manuscript is essentially suitable for publication as a Technical Publication in *Metallurgical and Materials Transactions.* However, a considerable revision appears to be mandatory before final acceptance and publication, and I trust that you will be willing to undertake such a revision. This revision is described by the enclosed comments of the review committee.

Please note that your revised manuscript will be returned to the review committee for reappraisal. Your letter of transmittal should indicate explicitly how you have responded to the reviewer comments. Two copies of your letter as well as two copies of your revised manuscript are required. A marked manuscript is also being returned to you for your assistance in revision; please return it along with your revised manuscript.

Sincerely yours,

R. J. Fruehan

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14 June 2001

Prof. David G. Brandon
Technion - Israel Institute of Technology
Faculty of Materials Engineering
Technion City, Haifa 32 000 Israel

Subject: Paper (01-202-B) "Physico-Chemical Properties of Matte - Slag Melts Taken from Vanyukov's Furnace for Copper Extraction" By: Vaisburd, Brandon, Kozhakhmetov, and Kenzhaliev

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Sincerely yours,

R.J. Fruehan/dm

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