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COPPER DROPLETS AGGLOMERATION / COAGULATION IN THE CONDITIONS SIMILAR TO INDUSTRIAL ONES

The studied copper droplets suspension in the liquid slag came from the direct-to-blister technology developed in the KGHM – Polska Miedź S.A. plants. A treatment by the stimulators and reagents was performed in the conditions delivered / ensured by the BOLMET S.A., Wiechlice. These conditions were similar to those usually applied to the industrial process. Particularly, this treatment was similar, to some extent, to that known for the electric arc-furnace technology employed in the Smelter and Refinery Plant, Głogów. An effectiveness of the newly developed and patented complex chemical / reagent for the copper removal from slag was tested during the treatment. The effect of the liquid slag stirring on the copper droplets self-cleaning was also analysed. The performed test confirmed the effectiveness of the studied complex reagent in agglomeration, coagulation and sedimentation of the copper droplets.

Keywords: Thermo-chemical treatment, Copper droplets, Post-processing slag, Coagulation

1. Suspension of copper droplets in liquid slag

A direct-to-blister technology is an extraction process. Usually, it is performed in the smelter furnace and forms the copper droplets primary suspension of the droplets in the liquid slag. This slag is usually subjected to further treatment in the electric arc furnace, (Fig. 1a). So, it is obvious that the extraction technology plays an essential role in the subsequent process of droplets coagulation, [1]. The coagulation (preceded by the copper droplets agglomeration) is carried out during the second step of the slag treatment performed with the use of some reagents, [2]. Subsequently, sedimentation of sufficiently large droplets on the crucible / furnace bottom is expected, especially, when the application of the recently patented complex reagent, [3], would be applied, (Fig. 1b). The sedimentation / settlement is completed by the droplets solidification which leads to segregation / separation of lead and other elements incorporated into

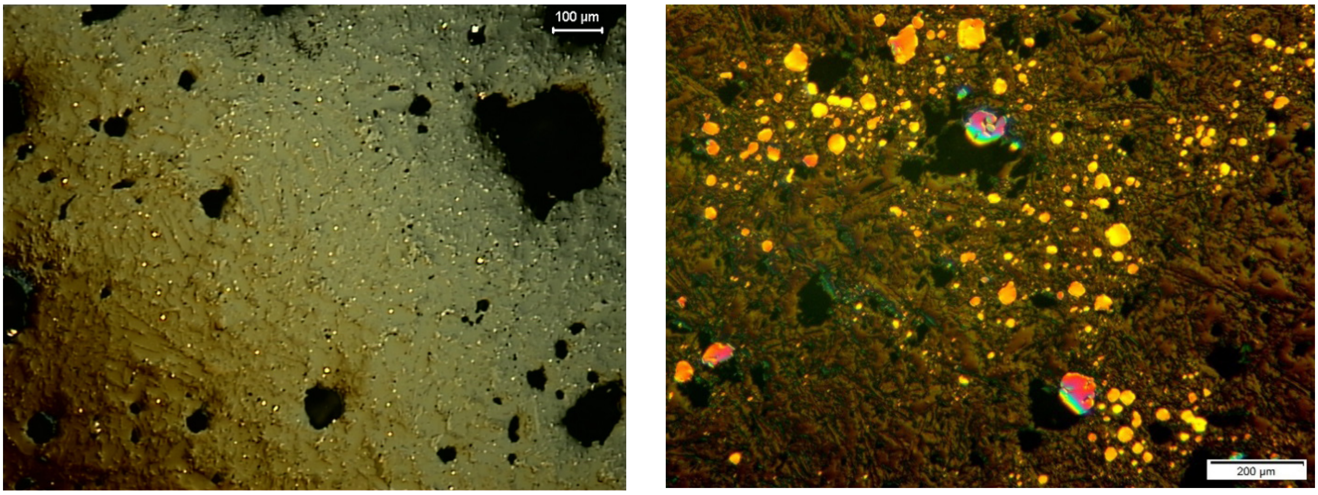

Fig. 1. Copper droplets / liquid slag suspension; a/ with the partial agglomeration of the copper droplets as caused by the addition of the CaO – chemical in the electric arc furnace in the Smelter and Refinery Plant, Głogów, b/ with an essential agglomeration and coagulation of copper droplets as caused by the addition of the NaCl, CaO, CaC_2, Na_2CO_3 – chemicals (and others, [3]).

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a given copper droplet. In many cases, the Cu-Cu_2O – eutectic precipitates accompanying copper solidification are observed in / near droplets, (Fig. 2). The appearance of some Cu(Fe) dendrites is also possible, [4]. Then, the de-oxidation with calcium carbide melts is recommended, [5].

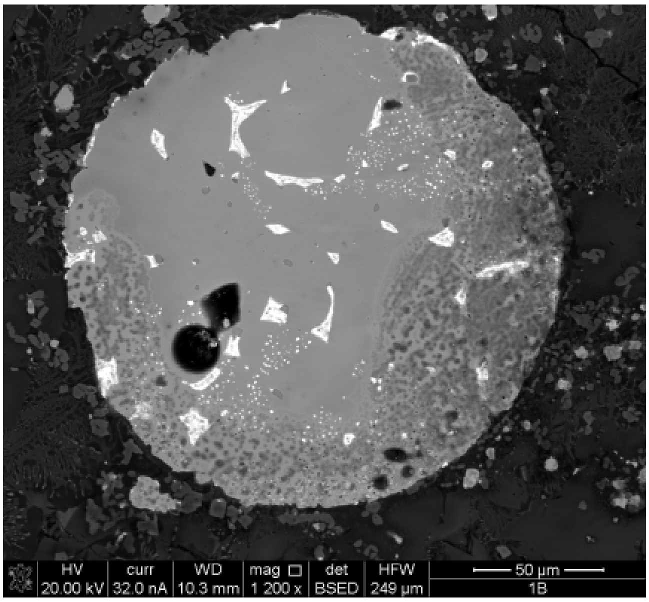

Fig. 2. Copper droplet as frozen; droplet contains lead (white areas) and Cu-Cu_2O eutectic (dark grey + grey areas) as some precipitates accompanying the droplet solidification.

2. Copper droplets agglomeration, coagulation and sedimentation

Different chemicals can be applied to succour the agglomeration and coagulation of droplets suspended in the liquid post-processing slag, [6-15]. Generally, there are stimulators and reagents which are applicable in the studied copper removal from the slag. The use of stimulators results in the decrease of the specific surface free energy of both copper droplets and liquid slag phases (particles), [16-17]. The reagents, themselves, effect directly on the droplets agglomeration / coagulation.

The study was focused on the behaviour of the copper droplets to show whether the droplets are settled on the furnace bottom due to the effect of gravity, as required. The copper droplets can also be agglomerated or partially coagulated but pushed to the liquid slag's surface when buoyancy force is winner in the competition with gravity.

The following chemicals were subjected to examination in the electric arc furnace: CaO, $CaCO_3$, Na_2CO_3, $NaCl$, and the complex stimulator with the addition of a phosphate, (and other activators, [3]).

The CaO, or sometimes $CaCO_3$ – chemicals are typical for the industrial practice. The patented complex reagent / chemical, [3], was applied to this as if industrial process of copper removal from the slag to study this chemical effectiveness and to compare it with the effectiveness of the mentioned industrial reagents.

Some observations of the copper droplets behaviour during the applied treatment show the different stages of agglomeration, and coagulation, (Fig. 3).

The mentioned analysis of the copper droplets behaviour confirm that the electric arc furnace could be modified in order to intensify the stirring of the studied suspension, as analysed previously from the technological viewpoint, [18-24]. It will allow to intensify the centrifugal force which is responsible for the self-cleaning of the copper droplets, (Fig 3d), (Fig. 3h).

The detailed studies of the different stimulators and reagents (components of the patented chemical) activity in the copper droplets + liquid slag suspension are gathered in (Fig. 4).

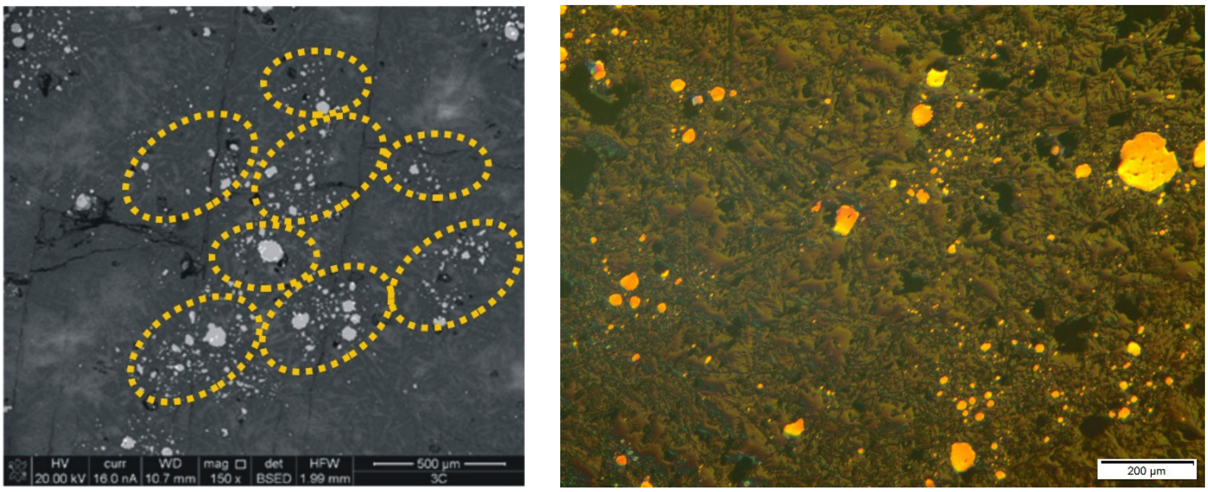

Fig. 3a. Initial coagulation of copper droplets in the liquid slag due to the CaO, and Na_2CO_3 – chemicals addition into the suspension as in the fully industrial process

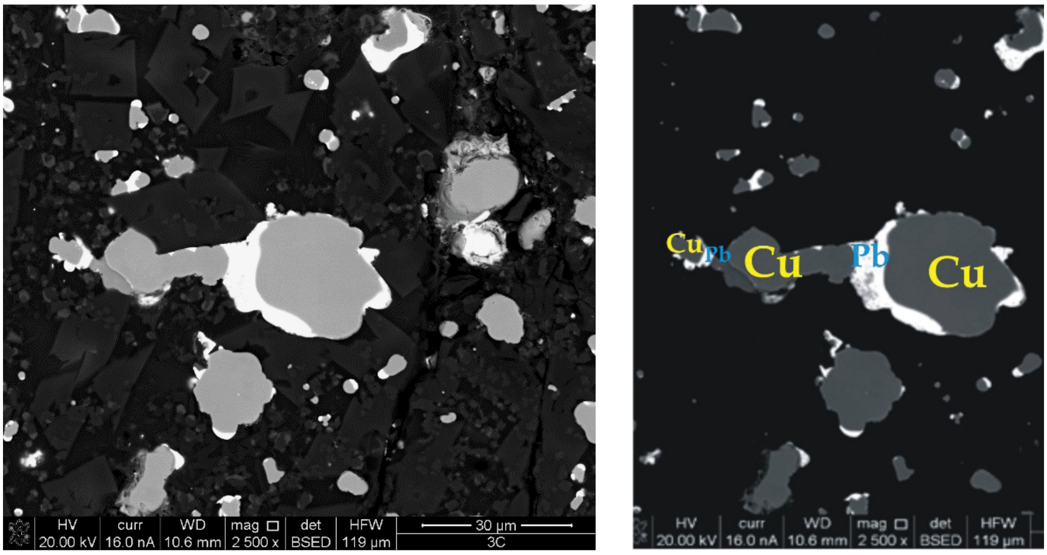

Fig. 3b. Formation of the Cu/Pb/Cu or Cu/Pb(Fe)/Cu – joints as a first step to coagulation; treatment by some components of the patented chemical; mainly by the Na_2CO_3, CaO, and K_3PO_4 – reagents

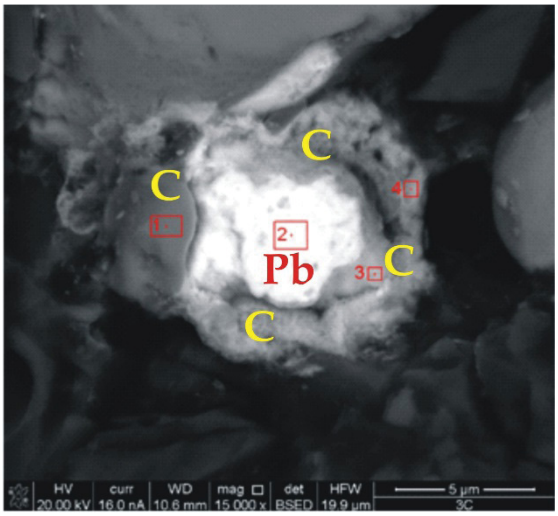

Fig. 3c. Separation of the lead droplet by carbon's envelope

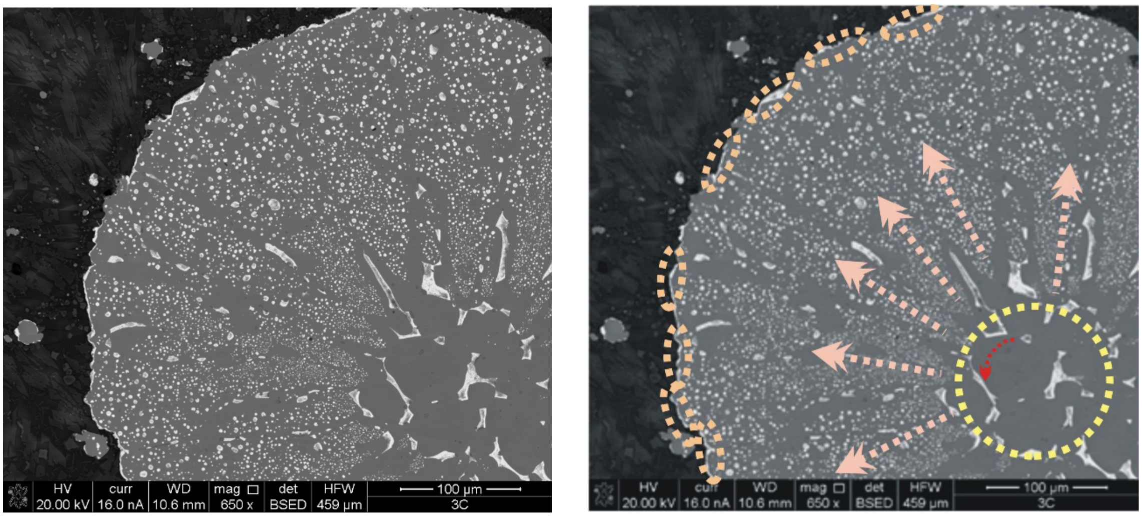

Fig. 3d. Rotating copper droplet; a/ containing small particles (droplets) of lead, b/ arrows show the tendency / motion of lead droplets to the periphery of the copper droplet (dotted lines) due to centrifugal force connected with the copper droplet rotation (red arrow); application of the patented chemical

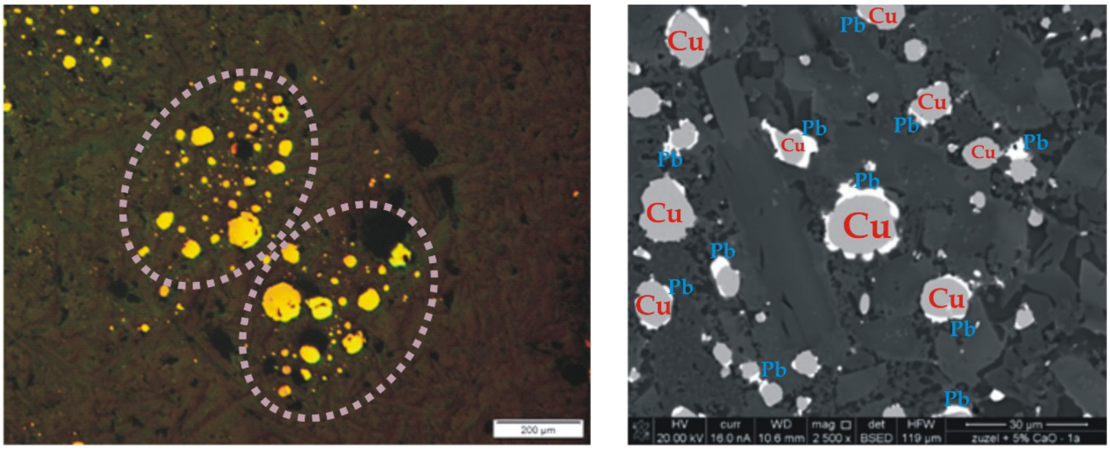

Fig. 3e. Copper droplets agglomeration together with the lead situation at their peripheries due to the positive effect of the centrifugal force to which the droplets are subjected in the process of copper removal similar to the fully industrial process

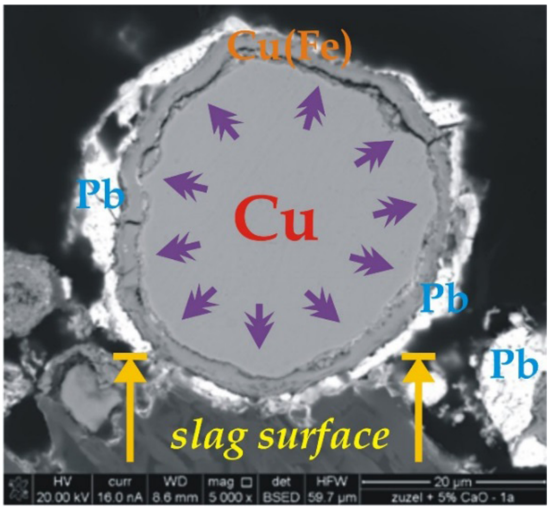

Fig. 3f. Self-cleaning of the copper droplets due to centrifugal force which appears as a result of the droplets rotation in the liquid slag; however, the fully cleaned copper droplet is surrounded by: Cu(Fe), and Pb – envelopes which block the further coagulation of the droplet; buoyancy force pushed the droplet to the liquid slag surface (no sedimentation is possible)

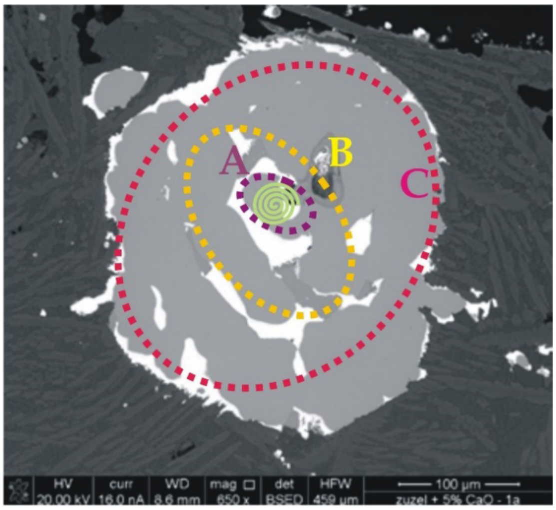

Fig. 3g. Triple droplet; every componential droplet: A, B, and C, is accompanied by its individual lead envelope, just before formation of the final / general lead envelope; three copper droplets are in course of the rotation (green spiral) and coagulation; unfortunately, the final / general lead envelope will block further coagulation

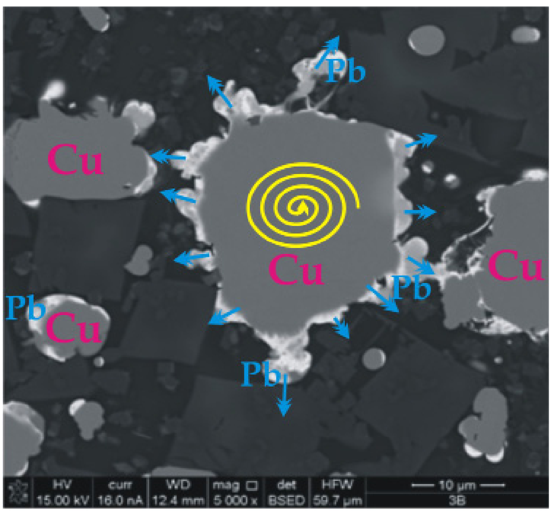

Fig. 3h. Sufficiently intensive centrifugal force (yellow spiral indicates the droplet rotation) leading to formation of broken lead envelope and even to the separation of some parts of the lead envelope (blue arrows); application of all components of the patented chemical

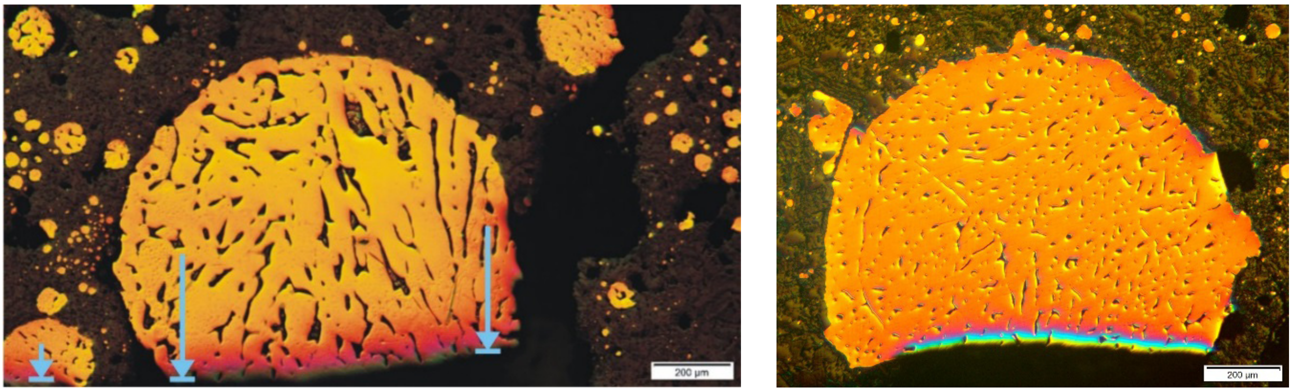

Fig. 3i. Copper droplets sedimentation (after agglomeration and coagulation) on the bottom of furnace / crucible due to the victory of gravity over buoyancy force (due to the incessant competition between these two forces); the critical diameter of the copper droplets was exceeded; application of all components of the patented chemical

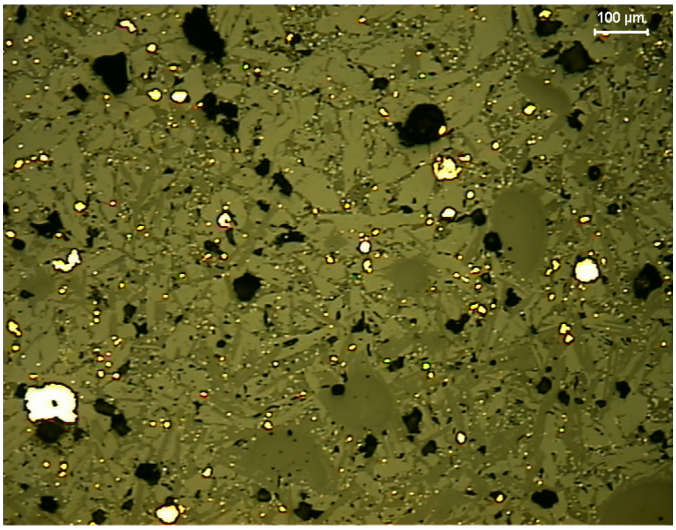

Fig. 4a. Post-processing slag containing the copper droplets; as treated by the CaO – chemical in the electric arc furnace installed in the Smelter and Refinery Plant, Głogów

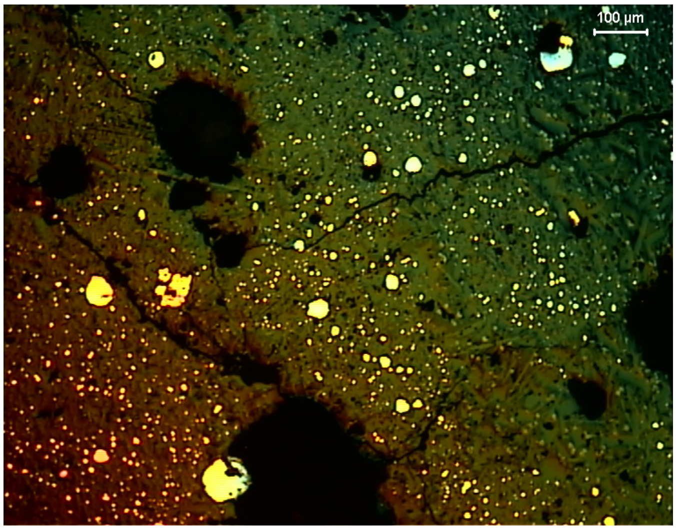

Fig. 4b. Post-processing slag containing the copper droplets; as treated by the CaO, and Na_2CO_3 – chemicals in the conditions similar to those usually applied to the industrial practice

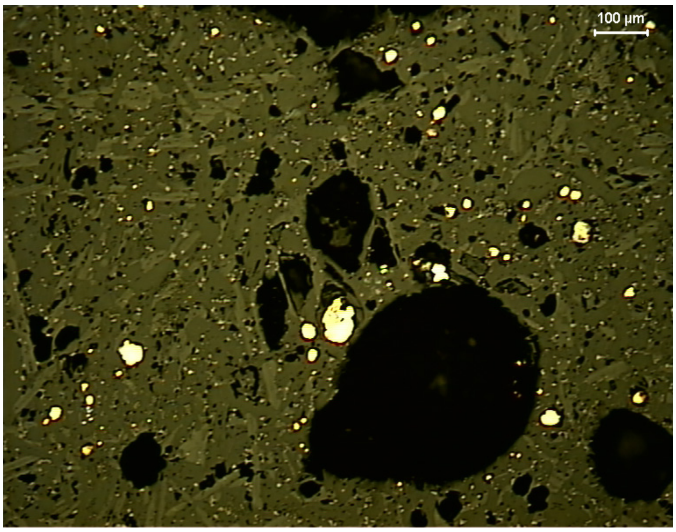

Fig. 4c. Post-processing slag containing the copper droplets; as treated by the CaO, and NaCl – chemicals in the conditions similar to those usually applied to the industrial practice

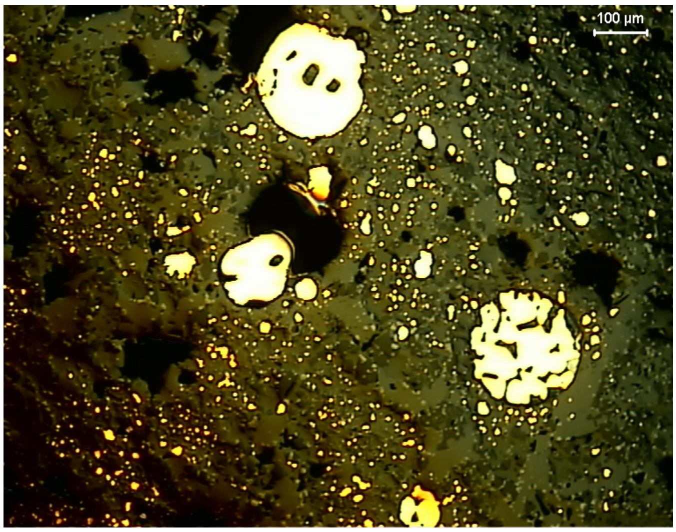

Fig. 4d. Post-processing slag containing the copper droplets; as treated by the CaC_2, CaO, and Na_2CO_3 – chemicals in the conditions similar to those usually applied to the industrial practice

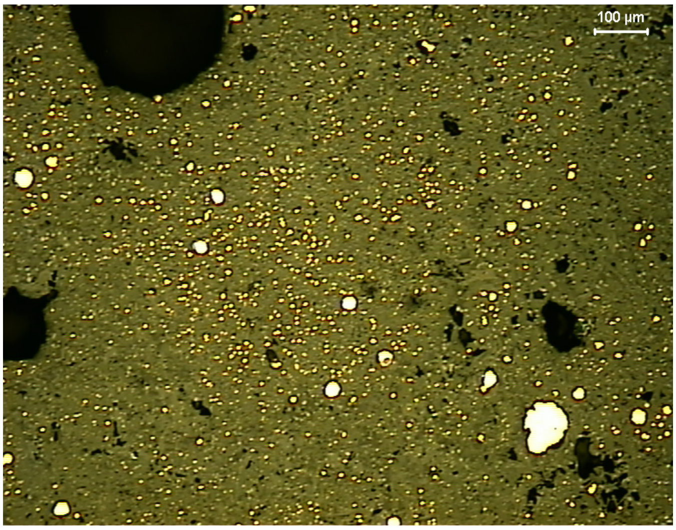

Fig. 4e. Post-processing slag containing the copper droplets; as treated by the CaO, NaCl, and Na_2CO_3 – chemicals in the conditions similar to those usually applied to the industrial practice

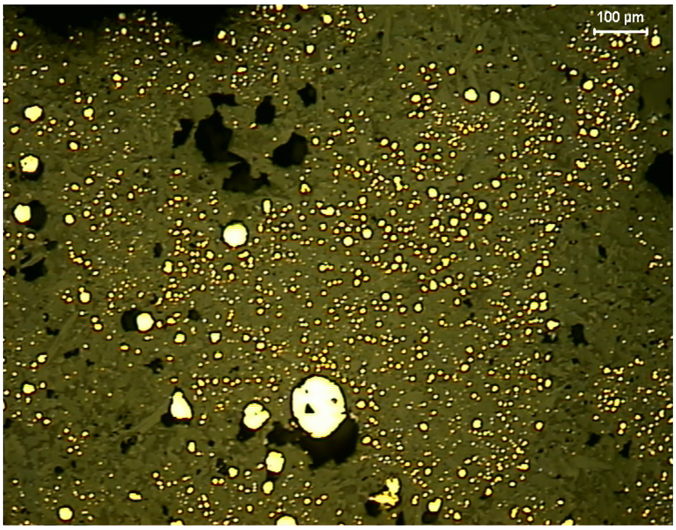

Fig. 4f. Post-processing slag containing the copper droplets; as treated by the CaO, CaC_2, NaCl, and Na_2CO_3 – chemicals in the conditions similar to those usually applied to the industrial practice

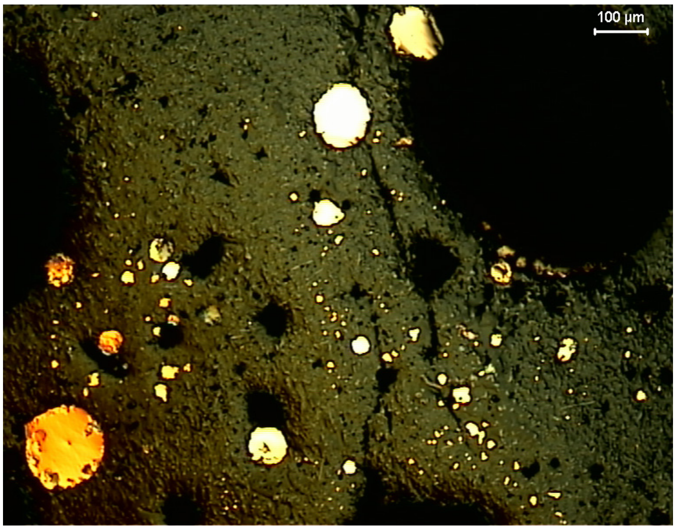

Fig. 4g. Post-processing slag containing the copper droplets; as treated by the CaO, CaC_2, NaCl, K_3PO_4, and Na_2CO_3 – chemicals (and others, [3]) in the conditions similar to those usually applied to the industrial practice

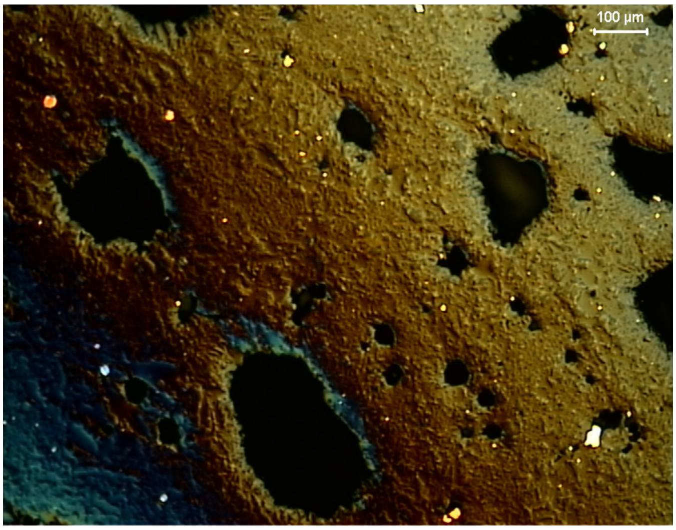

Fig. 4h. Post-processing slag containing the copper droplets; sample taken directly from the industrial process (from the smelter furnace in the Smelter and Refinery Plant, Głogów)

3. Concluding remarks

Generally, a weak, partial agglomeration of the copper droplets, is possible when the real industrial treatment for copper removing is applied to the copper droplets + liquid slag suspension and performed in the electric arc furnace, (Fig. 1a). A lead separation from copper can also be expected. The subsequent coagulation and sedimentation are usually, completed at the 0.9 – 1.0 wt.% content of copper in the remaining slag. Unfortunately, the remaining slag is assigned to locate in waste dumps.

The agglomeration and coagulation is significantly sustained when some components of the recently patented complex chemical, [3], are applied, (Fig. 1b).

The more regular in shape is the spherical droplet the highest content of copper it presents. Some micro-irregularities in the droplet shape, at its periphery, result from the local mechanical equilibria sustained by the neighboring both a part of the copper droplet and adequate phase (particle) of the slag, (Fig. 2). The copper droplet can contain not only some lead particles but the Cu-Cu_2O eutectic areas.

The eutectic is the low melting phase and significantly controls the mechanical equilibrium in this area. Some eutectic particles (small droplets) surrounding the dominant copper droplet are also visible. They form satellites for this dominant droplet, (Fig. 2). Their influence on the liquid slag viscosity is positive.

The addition of the CaO, and Na_2CO_3 – chemical into the liquid slag suspension during the as if fully industrial process improves agglomeration and resultant coagulation, (Fig. 3a).

Formation of the Cu/Pb/Cu or Cu/Pb(Fe)/Cu – joints precedes coagulation when the treatment by some components of the patented complex chemical; mainly by the Na_2CO_3, CaO, and K_3PO_4 reagents / stimulators is applied, (Fig. 3b).

The activity of carbon seems to be positive in a separation of the lead droplet by carbon's envelope, (Fig. 3c).

A copper droplets rotation resulting from the incessant competition between buoyancy force and gravity leads to the self-cleaning of the copper droplets, (Fig. 3d). The self-cleaning is the result of the appearance of a centrifugal force which pushes small lead particle from the copper droplets to their peripheries, (Fig. 3e). Unfortunately, it appears that the copper droplets surrounded by the lead (and also iron solution in copper) are blocked in their coagulation. In this case, they are pushed towards the liquid slag surface and are not able to be subjected to sedimentation, (Fig. 3f). The analogous situation occurs when multi-droplets configuration appear and lead cannot be pushed to the droplet periphery since the centrifugal force is too weak to do it, (Fig. 3g).

However, when the centrifugal force is sufficiently great and the complex reagent is applied, they both lead to the total separation of the lead envelope from the droplet (preceded by the envelope's fragmentation), (Fig. 3h). Then the spherical copper droplet can continue its coagulation to obtain / exceed a critical diameter required by the droplet sedimentation, (Fig. 3i).

The discussed behaviour of the copper droplets leading to their sedimentation could be intensified by some improvement of the electric arc furnace design. The suggested improvement should ensure more rapid stirring of the studied suspension. Therefore, it is postulated to apply two sets of electrodes:

a) greater number of the upper electrodes which are supplied by the alternating current during the first step of the copper recovering; the electrodes should be hollowed (with the empty space inside) and equipped with the stimulators / reagents in these hollows.
b) lower electrodes set (situated at the furnace bottom) supplied by the direct current with the pulsation mode of their work; this set of electrodes should be employed during the second period of time with the work temperature equal to 1200-1350°C; these electrodes would be designed to attract the remaining small copper droplets which were not able to exceed their critical diameter necessary for sedimentation during the first step of the copper removal from the slag.

The postulated improvement of the electric furnace design should ensure the reduction of copper content in the slag from 0.8÷0.9 wt.% even up to 0.3 wt.%.

This goal was reached during the detailed study of the copper removal from the slag, Fig. 4. Therefore, the degree of the copper removal is as follows: $(0.9 - 0.3) / 0.9 \rightarrow 0.67$. This result could be confirmed in the real industrial procedure in the Smelter and Refinery Plant, Głogów.

The standard slag after copper removal in the real industrial procedure is shown in (Fig. 1a) and (Fig. 4a). Mainly, a partial coagulation is ensured only and final content of copper in the slag is equal to about 0.8÷1.0 wt.%. However, even an addition of the Na_2CO_3 – chemical essentially improves both agglomeration and coagulation of droplets, (Fig. 4b).

When the addition of the NaCl, and CaO (sometimes substituted by the $CaCO_3$)– chemicals is applied then some well coagulated dominant droplets appear. These droplets are ready to be settled on the crucible / furnace bottom as expected / desired, (Fig. 4c).

When the additions of the CaC_2, CaO, and Na_2CO_3 are introduced into the liquid slag then a partial agglomeration and significant coagulation of the dominant droplets appear. However, some dominant droplets still require to be self-cleaned, (Fig. 4d).

When the additions the CaO, NaCl, and Na_2CO_3 – chemicals are applied then a hardly visible both agglomeration and coagulation are observed with the presence of some dominant copper droplets, (Fig. 4e). This result is essentially improved with the CaO, CaC_2, NaCl, and Na_2CO_3 – chemicals treatment of the slag, (Fig. 4f).

The best result in the removal of copper from the slag is reached with the treatment ensured by the tested, recently patented, [3] chemical which contains the CaO, CaC_2, NaCl, K_3PO_4, Na_2CO_3 – chemicals (and others). The very essential agglomeration and coagulation are achieved and droplets diameter is near its critical value. The droplets are ready to be settled at the furnace bottom, as expected, (Fig. 4g). Additionally, the morphology (other standard sample) of the slag taken from the smelter furnace (from the direct-to-blister technology working in the Smelter and Refinery Plant, Głogów) is presented, (Fig. 4h), to compare it with the morphology of the slag treated by the tested chemical, (Fig. 4g).

The patented, complex reagent is recommended for the fully industrial practice. The reagent is effective not only in coagulation but in the desired sedimentation of droplets as well.

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