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THE CONCEPT OF SLAG DECOPPERISATION IN THE FLASH FURNACE PROCESS BY USE OF COMPLEX REAGENTS

KONCEPCJA ODMIEDZIOWANIA ŻUŻLI Z PROCESU ZAWIESINOWEGO REAGENTAMI ZŁOŻONYMI

The article presents an outline of the new technology of pyrometallurgical processing of slag in the direct-to-blister process. The analysis is based on the example of the production process of KGHM Polish Copper SA. A new way of implementing the technology of recovery of copper from the flash furnace slag by means of different feedstocks has been proposed. The method of controlling the processes is another innovation discussed in the paper. The presented concept intensify the reduction reactions, using the Carbo-N-Ox method, of copper compounds to forms of metallic phases in the slag. The processes of coagulation are accelerated and the processes crystallization of metallic phases are under control.
Keywords: slag, decopperisation, reagents, recycling

W artykule przedstawiono zarys nowej technologii pyrometalurgicznego przetwarzania żużli w procesie jednostadialnego otrzymywania miedzi. Zaproponowano nowy sposób realizacji technologii odzyskiwania miedzi z żużli z pieca zawiesinowego z zastosowaniem odmiennych materiałów wsadowych. Zaproponowano sposób sterowania procesami. Proponowana koncepcja prowadzi do intensyfikowania reakcje redukcji związków miedzi, metodą Carbo-N-Ox, do postaci faz metalicznych w żużlu. Przyspieszone też zostaną procesy koagulacji faz metalicznych. Zaproponowany został sposób analizy formowania się faz metalicznych w żużlu.

1. Introduction

In the suspension furnace, there are formed blister copper and post-process slag: suspension slag containing up to 16% of copper, the slag from the converter of the second period containing 35% of Cu and 22% of Pb, and anode slag containing about 1,6-2% of Cu. The slag is used for routed to the electric furnace, to the beginning of the manufacturing process the input materials – for a shaft furnace, or even to the stage of flotation. It is also frequently referred directly to waste. Waste materials currently stored in dumps or laid as a ballast under the roads, comprise at least 0.6% of copper, often reaching up 0.8% or even 1% of Cu.

2. Analysis of problems

Most of technological studies begin the evaluation of the so-called "slag-cleaning" (decopperisation) with a thermodynamic analysis of possible reactions. Surface phenomena occurring during extraction are also assessed. The studies take into consideration the following properties: the viscosity of the slag and metal, the electrical conductivity of the slag, kinetics of slag – metal phase, as well as, the results of structural studies in liquid mass transfer. However, the results of many experimental studies [1-4] show, that it is impossible to connect all of the above physico-chemical properties, due to the substantial deviations from the equilibrium conditions that take place during manufacturing process.

2.1. Surface phenomena

It is assumed that the wettability of copper and slag, determined by the interfacial tension of copper and slag σ_{M-S} (according to (1)), should be as small as possible:

$$\sigma_{M-WN} > \sigma_{M-S} + \sigma_{S-WN} \tag{1}$$

where:

σ_{M-WN} – the interfacial tension of the metal and the melting losses of the copper

σ_{M-S} – the interfacial tension of the metal and the slag

σ_{S-WN} – the interfacial tension of the slag and the melting losses of the copper

The analysis of the technology used in copper smelter in Głogow (Huta Głogow) for suspension furnaces leads to the conclusion, that such an approach is one of the causes of the increased amount of copper in the post-process slag. Taking

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into consideration the endeavor to limit the emulsification of copper in the slag, it is clear that one should rather try to increase the interfacial tension on the phase boundary of metal and slag, which means, to strive towards the high value of (σ_{M-S}). There is always a need for the thorough removal of slag from the surface of copper before pouring it to the ingots. To provide the optimum conditions for this type of treatment it is necessary to decrease to minimum the work of adhesion – W_{M-S} (2), required to detach the slag from the metal.

$$W_{M-S} = \sigma_S + \sigma_M - \sigma_{M-S} \tag{2}$$

where:

σ_S – the surface tension of the slag,
σ_M – the surface tension of the metal,
σ_{M-S} – the interfacial tension of the metal and the slag

The slag removal in the final stage of slag-cleaning process is an effective operation, widely used in steel plants, which foster the removal of slag from the metal surface. It means (according to the formula 2) the strive for increasing the interfacial tension between the metal and slag (σ_{M-S}). Such a conclusion contradicts the inequality (1). It is a reason for returning the system to the initial state – the increase of copper content in waste slag, in case of a very long time of shuttering slag from furnaces.

In the proposed solution the surface tension is continuously adjusted on the basis of the results of technological tests and by means of an optimization program.

2.2. The isolation and formation of the solid phase

The segregation of ingredients during a solidification processes is an important factor influencing the formation of metallic solid phases (containing copper) in the slag. The eutectic solidification process is a decisive one. The separation of the components [5-7] determines the material properties of alloys formed in slag, such as Cu-Pb-Fe. The existence of concentration gradient causes the diffusion in the solid state during the crystallization, what fosters the elimination of segregation. Segregation and diffusion are the main causes of changes of the physico – chemical properties during the processes of slag-cleaning . Analysis of a differential equation (3) describing the phenomenon of segregation

$$\frac{dC(x;\alpha)}{dx} = \frac{(1-k)\;C(x;\alpha)}{1+\alpha\,k\,x-x}, \quad \alpha = \frac{D\,t}{L^2} \tag{3}$$

completed with a redistribution equation (4)

$$R(x;\alpha) = f\left(C(x;\alpha)\right) \tag{4}$$

where:

C – solute concentration,
x – current amount of the growing crystal (grain),
α – back-diffusion parameter,
k – partition ratio,
D – diffusion coefficient into the solid,
t – local solidification time,
L – half size of the crystal (grain),
R – solute redistribution after back-diffusion,

leads to the conclusion that both equations (3 and 4) must satisfy the following conditions:

a / for the lack of diffusion they must be fully mathematically reduced to Scheil's theory,

b / for the full diffusion they must meet the requirements of equilibrium crystallization.

In this system time t is the local time of crystallization necessary for solidification of a given phase. However, the value of the temperature T, which does not perform in the equations 3 and 4, fits within the definition of the back-diffusion parameter described by the coefficient of diffusion D. The proposed concept considers the modeling of segregation of components in the slag with regard to the instantaneous parameters obtained on the basis of technological tests.

2.3. Reagents

The discussed concept takes into consideration the impact of the non-carbon reagents, and this constitutes the next aspect of its originality. Most of the methods of pyrometallurgical recovery of copper from post-process slag, including those applied in copper smelter in Głogow, employ coal [8-10] in the form of coke or coal briquettes. It is used in conjunction with the fluxes that correct physico – chemical properties of processed slag. However, in the light of the experience of the authors and other scientists [11-15], as well as theoretical analysis, that form of carbon reagent appears to be very inefficient. Reacting only with the agents of the melting atmosphere, solid carbonaceous/carbon does not dissolve itself, and, therefore, it does not react in the slag. That is why some different reagents, such as the carbon – nitrogen – carbide ones, have been introduced.

As several studies on the conditions of melting cooper and its alloys have shown, carbon ions $\{C^{2+}\}$and $\{C^{4+}\}$are the decisive components of the reactions that take place in slag (Fig. 1).

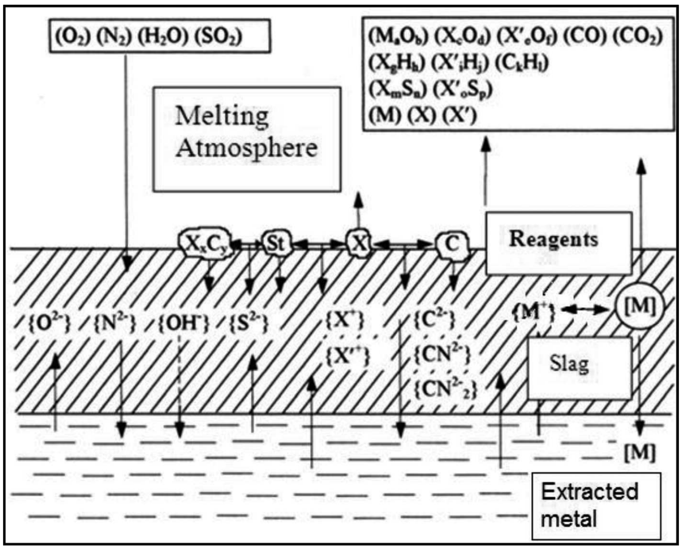

Fig. 1. A proposed scheme [11, 12] of extracted process of a liquid slag with a carbide-cyjanamide reagents – scheme of the Carbo-N-Ox method, where: ( ) – gas, M – extracted metal, X – reagent St – reaction stymulator, {}– ions in the slag, [ ] – elements in the extracted metal

They arise as a result of inserting carbide reactants or metal carbide with carbon or carbides to the slag – Carbo-N-Ox method [12-14]. Carbon – nitrogen reagents are of greater chemical activity than carbon and carbide. However, the insufficient separation of metallic phases from slag is their disadvantage. The researches based on the extraction of metallic and non-metallic inclusions from cooper by means of slag containing complex chemical reagents have shown, that it is possible to gain the state of emulsification in the slag of the metallic phase.

Then, the formation and subsequently liquid precipitates its crystallization in the form of precipitates containing 70-80% by weight copper.

The substances used for slag-cleaning proposed by the authors contain carbon reducers, as well as, metal carbide and carbide ones. They are applied in conjunction with the enhancers of ionic reactions in slag and with fluxes correcting physical – chemical properties of slag. The main physico – chemical benefits of the application of such substances rely on their interaction with a properly prepared – both in terms of composition and properties of surface -active agents – slag layer [16, 17]. Such an approach is a novelty in the pyrometallurgy of copper and currently is the object of patent application [18]. It enables the full usage of extraction reactions. The processes of reducing metals chemically bonded with a non-metallic slag phase, mainly copper, are intensified. Those summing up interactions in liquid slag result in the decrease of the content of copper deposited on the bottom of melting unit.

2.4. Other impacts

Another commonly used, technological solution is a multiple (3-10 cycles) processing of post-trial slag in electric furnaces. However, it takes more time and results in energy loss, as well as significant increase of the cost of the process of slag-cleaning. There are also mechanical devices to accelerate the settling of cooper drops that were reduced by carbon reagents from slag. Such, rotating or vibrating, devices are expensive and do not lead to interactions with the copper chemically bounded to slag, though. It is caused by some metal precipitates of a submicroscopic size emulsified in the slag, that are not influenced by the laws of gravity. That also contributes to the significant percentage of copper – not less than 0.6% – in slag waste.

3. The extracting concept of recycling copper from slag

The critical attitude to the possibility of achieving optimal process conditions only on the base of the surface characteristics of materials used in the extraction coating, is the starting point for the presented concept. Therefore, there have been assumed: the necessity of considering the changes of surface properties as a function of time and temperature, as well as, the necessity of using chemically active, complex reagents. The special technological tests and a database Slag – Prop (Fig. 2 and 3) are the components of automatic adjustment cycle.

Thanks to the program for modeling the phenomenon of solidification of eutectic phase and physico- chemical phenomena, it is possible to add the precise doses of chemical reactants, catalysts and reaction promoters to the slag.

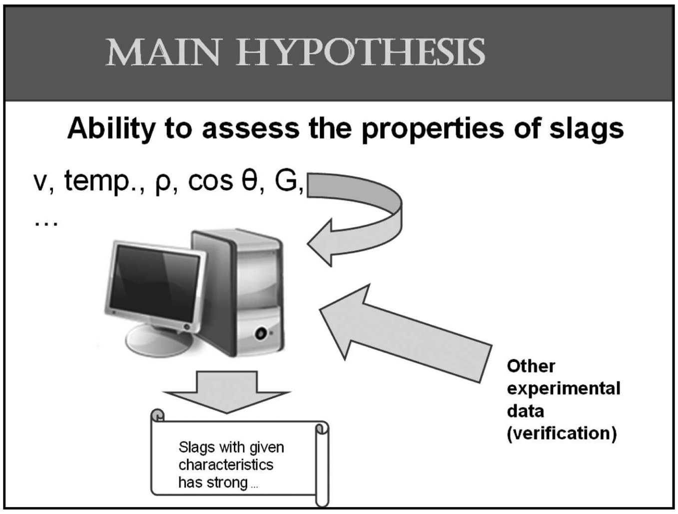

Fig. 2. The main hypothesis of the Slag – Prop

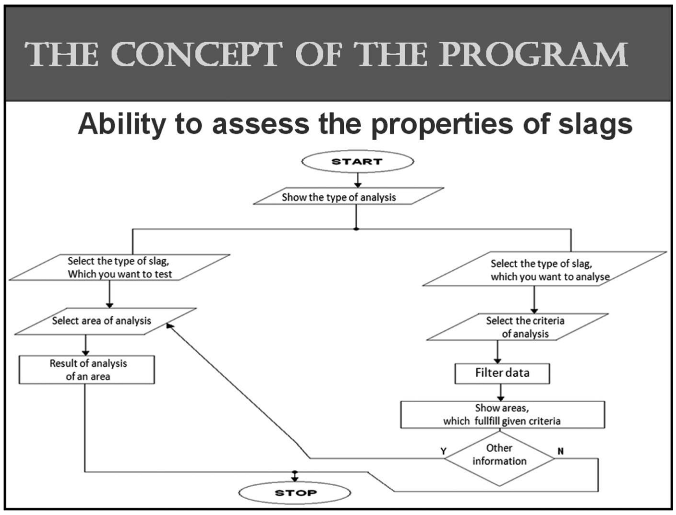

Fig. 3. The concept of numerical software Slag – Prop

The method of analyzing the refining properties of metallurgical slag by means of the proprietary computer program (material database "Slag -prop"), bases on the laboratory method of determining refining ability through DTA analysis. It allows to combine the results of the comprehensive analysis of heat effects generated during physicochemical interactions in slag, with its main thermodynamic, physical, chemical and technological properties.

The research area is defined and verified for the melting conditions of copper. The base is open for users. It takes into account the participation of additional components of slag such as (Fig. 1): stimulators response, corrective reagents and catalysts. It also considers another components such as: melting skimming counterparts, melting atmosphere (inert, oxidizing, reducing) technological and measuring conditions (eg. time, temperature, the type of measurement tools, the type of furnace and its lining).

4. Conclusion

The method of tracing changes of the physical properties of post-process slag, and the program for mathematical modeling of the phenomenon of crystallization of metallic phases in the slag, together with the simultaneous application of complex, carbide reagents, allows to reach the content of 0.3% copper in slag.

Suggested structural and organizational changes – discussed in the next article – will help to reduce operating costs by about 25%. The discussed technology allows to reduce the amount of copper in slag that is stored as waste heaps or used as a construction material. It will result in some environmental and social benefits, as well.

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