

# Advanced technological solutions for developing a technology of steel production from the steel scrap with excessive copper content

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On the background of fluctuation of the steel scrap quality, steelmakers should focus attention to the metal charge chemistry to guarantee the necessary level of residuals in steel. Within the condition of up to date steelmaking technologies it is impossible to refine the iron melts from tramp elements. As a result the necessary content of such tramp elements can be ensured only by dilution of metal bath of the steelmaking unit with the “clean” charge [1]. The method of charge dilution assures the successful solution of the problem of low copper content steelmaking, but does not solve the problem of residuals accumulation in the steel scrap.

Up to date steelmakers try to remove copper mainly at the stage of steel scrap preparation via careful separation or special treatment [2, 3]. For distinct metallic copper removing the enhanced shredding process is used. Copper-containing coatings are removed by electrolytic leaching. Vacuum heating and active gas treatment are also used. However it is possible for physically distinct metallic copper only. Dissolved copper cannot be removed from the solid scrap. As for dissolved copper, numerous trials were made [3, 4], but the tested methods are not competitive at the commercial level yet. In spite of possibility remove copper into gas phase this technique apparently will not be beyond special metallurgy sphere.

The most effective method to copper removal from iron melts is sulfidizing refining [5]. Sulfide systems on the base of FeS, Na<sub>2</sub>S, Al<sub>2</sub>S<sub>3</sub> are preferable to refining.

Copper removes from the liquid metal into a sulfide phase according to the reaction



The expression for the distribution ratio of copper between metal and the sulfide phase may be written down as follows

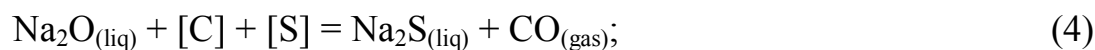
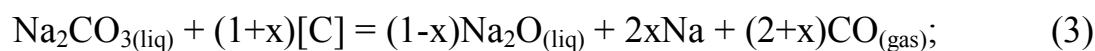
$$L_{\text{Cu}} = \frac{(\% \text{Cu})}{[\% \text{Cu}]} = K \cdot a_{(\text{FeS})}^{1/2} \left( \frac{\gamma_{[\text{Cu}]}}{\gamma_{(\text{CuS}_{0.5})}} \right), \quad (2)$$

where  $\gamma_{(\text{CuS}_{0.5})}$ ,  $\gamma_{[\text{Cu}]}$  – activity coefficients of copper sulfide in the sulfide phase and copper in the metal phase correspondingly;  
 $a_{(\text{FeS})}$  – activity of iron sulfide;  
 $K$  – constant.

The last equation illustrates a way to get the higher values of the copper distribution ratio. It is necessary to keep up the high sulfur potential in the system and try to

decrease the activity coefficient of copper sulfide in a sulfide phase. In equilibrium the copper distribution ratio amounts to 9 between the flux on the base of iron sulfide and iron melt at the equilibrium sulfur concentration about 1.9% and temperature 1400°C [6]. Adding of some alkaline or alkaline-earth sulfides to the flux increases the distribution ratio of copper up to about 30 and decreases the equilibrium sulfur concentration in the metal. Similar results are observed for aluminum sulfide additions [7].

There are different variants of the sulfidizing treatment. Thus, for example, the technological scheme intends the several stages treatment for iron melts under the coat of the sulfide flux layer at all steps was proposed [7]. However in some cases direct addition of sulfides to refine metal from copper is not obligatory. As it was reported a treatment by powders of sodium compounds ensured removing up to 10-40% of copper from high carbon iron melt at the initial sulfur concentration 0.2-1.5% [8]. Decomposition of soda ash after contact with liquid metal can form a sodium sulfide according to reactions



Laboratory investigations were made to study a technique of iron melts treatment by mixtures on the base of sulfur and soda. In laboratory experiments iron melts were treated by the reagents in a graphite crucible under argon atmosphere. The duration of treatment was up to 5-10 minutes. The copper removing level changed in the limits of 25-45% for different tests at the initial copper concentration about 1% and the final sulfur in the metal 0.3-0.6%. After treatment the lowest copper content was 0.49% at the final sulfur percentage 0.51%. Deeper refining was reached in trials with FeS-Al<sub>2</sub>S<sub>3</sub> flux. The copper percentage in metal was reduced up to 0.04% at primary copper concentration 0.3%.

The next stages of the experimental work were made with the 200 kg induction furnace. Iron melts with copper contents of about 1.0-1,5% were treated with powder mixtures on the base of sulfur and soda. The powdered reagents were injected into the iron melts via a submerged lance in the argon stream. The developed technique insures reducing in copper percentage up to 50-60% after one stage of the treatment. The sulfur concentration in the metal rose up to 0.7%-0.9% during mixture injection and high sulfide potential was kept in the system (Fig. 1). Aluminum addition into the metal after blowing was applied to increase the efficiency of treatment [9]. It allowed some increase of the copper extraction into a sulfide phase and metal yield, and a decrease of the sulfur content in metal at the same time (Figure 2).

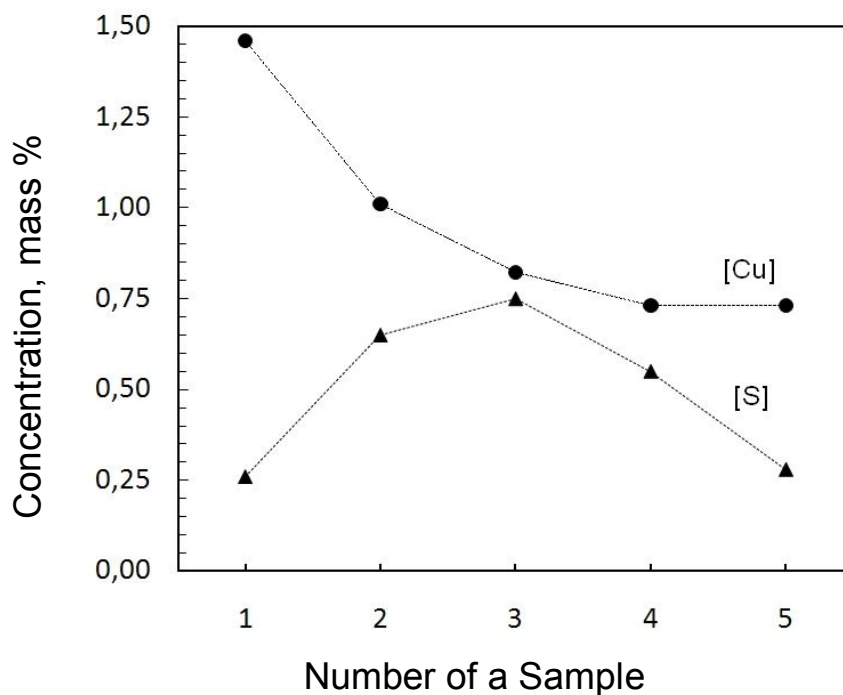


Figure 1 – Change in copper and sulfur concentration in the liquid metal during a treatment (Characteristic of sampling moment: 1 – before treatment; 2 – the middle of blowing; 3 – at the end of blowing; 4, 5 – after aluminum addition into the metal)

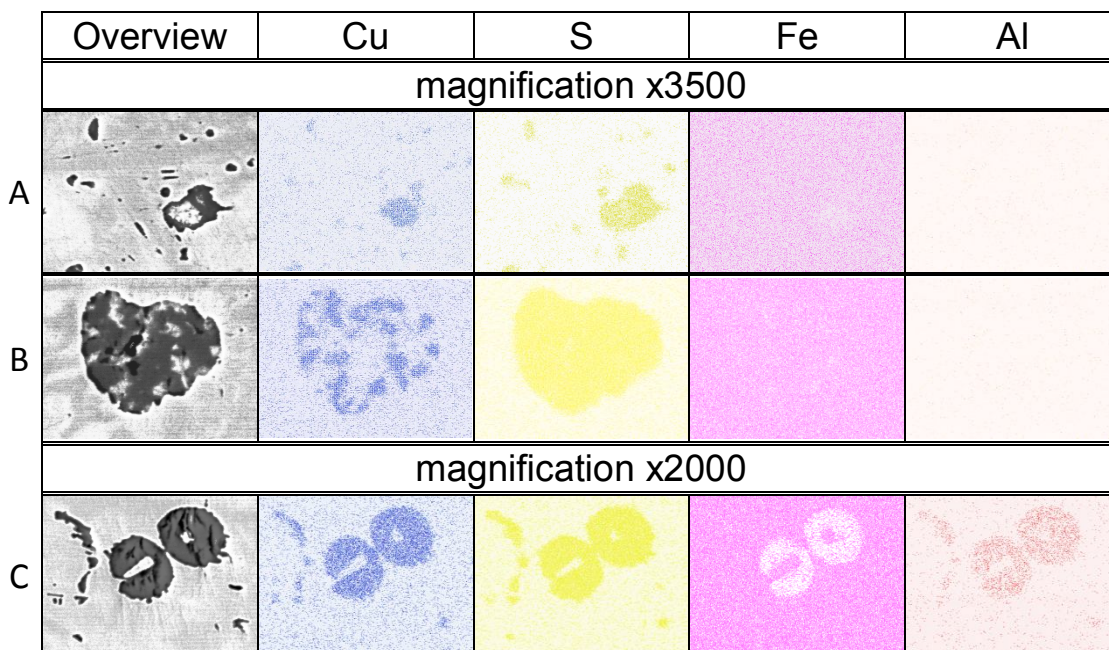


Figure 2 – Images of sulfide inclusions in the metal at the different stages of treatment, achieved with the help of electron microscope (row A – inclusion from a sample which was taken at the middle of blowing; row B – inclusion from a sample which was taken immediately at the end of blowing; row C – inclusion from a sample which was taken after aluminum addition)

Tests with forming and maintaining a sulfide flux layer on the metal surface without blowing or mixing showed low effectiveness of the treatment. Technique with reagents injection is considered to be more effective. Injection of powdered or granulated materials in the inert gas stream makes favorable conditions for a quick saturation of the melt with sulfur due to intensive agitation, good recovering of the reagents and conduces to formation and enlargement of sulfide inclusions in the liquid metal volume. In addition, inert gas constrains oxidative effect of atmosphere air on the sulfide phase.

Good results showed a technique with vigorous agitating of flux and metal by their pouring from the furnace into a ladle and back (table 1). A mixture of sulfur, soda and graphite was used in order to formation of a slag. But such technique demands on special measures to minimize harmful influence on ambience from one hand and oxidizing influence of atmospheric oxygen on the system from other hand.

*Table 1 Changes in chemical composition of metal during treatment by pouring from the furnace into a ladle and back*

Trial	The moment of sampling	C, %	Mn, %	Cu, %	S, %
Number 1	Before treatment	3.37	0.81	1.12	0.046
	After treatment by the first portion of flux	3.57	0.19	0.62	>0.50
	After treatment by the second portion of flux	3.98	0.15	0.23	>0.50
Number 2	Before treatment	3.51	0.74	0.56	0.014
	After treatment by the first portion of flux	3.67	0.15	0.29	>0.50

But vigorous agitation is not enough for intensive sulfide inclusions formation in the melt. A separation between sulfide and iron phase is observed only in the certain range of concentrations in Fe-C-S ternary system [10]. The content of sulfur in iron melt equilibrated with molten FeS becomes the lowest at carbon saturation, and increases with decreasing carbon content until the critical composition where immiscibility disappear to a single homogeneous liquid phase. Additionally increased carbon raises the activity coefficient of copper in the metal and lowers oxidizing level in the system. Thereby it promotes the copper accumulation in the sulfide phase. Thus a sulfidizing treatment for copper removal is effective for high carbon iron melts only. An aluminum addition to the liquid metal ensures fuller separation of sulfide and iron phases and raises the distribution ratio of copper.

The investigations have uncovered some troubles inherent to work with sulfide fluxes. The main problem is concerned with sulfide flux removing from the metal surface after treatment. Thus it is rather difficult to separate the sulfide phase from metal properly by hand. Moreover it is practically impossible to restrict interaction of

sulfide phase with atmospheric air at the moment of flux removing by hand. Thus it was proposed to do it by means of addition of granular material on the surface of metal to absorb sulfide flux. After the absorption of liquid sulfides it can be easily and rather simply removed away from the surface of metal. As a sorptive material was tested some crushed refractory materials on the base of alumina, silica and lime.

Refining of metal from the precipitated sulfide inclusions and effective removing of the sulfide flux away from the liquid metal surface is important because it allows thoroughly separate the copper containing sulfide phase from metal after blowing and improves results. Filtration technique can be employed to achieve this purpose. But the serious drawback of the direct filtration technique is the limited resource of a separate filter, which results in the impossibility of effective treatment of big volumes of liquid metal. Therefore a modified variant of filtration technique is of some interest, when granules of filtering material are introduced directly into liquid metal to absorb sulfides saturated with copper and give a substrate for arising new ones. Such approach allows treating whatever volumes of liquid metal.

The idea of combination of different refining methods has great potential and may be used as a base for industrial technology. The refinement can be done during a preliminary refining heat to make an intermediate product with allowable copper concentration for subsequent charging into electric arc furnaces which working according to the traditional technology. But it is possible to realize other technological scheme comprises such consequent steps as: scrap melting and carburization; sulfidizing treatment; separation metal and sulfide phases; desulfurizing treatment; decarburization and finishing. Naturally sulfur content in iron melt after sulfide refinement far exceeds the indices characteristic of the steelmaking process. Therefore it needs the working out of special technological decisions to ensure the acceptable economic indices of technology. In whole the questions as for hot iron desulfurization were thoroughly investigated by steelmakers and strategy of desulfuration can arrive at a solution. Thus we can talk about the real possibility of the creation of this technology industrial variant, which will make the steelmaking from the scrap with the excessive copper content possible.

## **Conclusions**

It was shown, that it is possible to raise effectiveness of the sulfide treatment with the help of special organization of the process: intensive saturation of the iron melt with sulfur in the process of its blowing with powders based on sulfur and sulfur-containing compounds; the creation of favorable conditions for sulfide inclusions formations and following extension of them, as well as further thorough separation of sulfide and iron phases. Applying to modified filtration technique to separate these phases allows considerably increase the total copper removal from metal after sulfidizing treatment and decrease contamination by sulfides. The worked out and tried in the investigations technical solutions make promising the realization of copper removal from iron-carbon melts at industrial conditions.

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