SCIENTIFIC ASPECTS OF THE DESULFURIZATION OF METAL

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Practical experience and numerous studies have shown that both the pig iron and the steel must be desulfurized at each stage of refining in order to produce clean, high-quality steel as the finished product. An important aspect here is determining the desulfurization method that is most efficient and most expedient from an energy standpoint.

At a certain point in the evolution of steelmaking technology, the preliminary treatment of pig iron before its addition to the steelmaking furnace became an essential step in the production of steel with low contents of sulfur and phosphorus. It was subsequently determined that removing several operations from blast furnaces and steelmaking furnaces and performing them in independent units would be expedient on both technological and economic grounds.

In steel production, energy is one of the most important cost factors. The charge component with the highest energy content is pig iron, the production of which requires a large amount of coke. The characteristics of the steelmaking process are significantly affected by the silicon content of the pig, and it is this very factor (assuming normal contents of sulfur and phosphorus) that determines the silica content of the slag and, thus, the quantity of slag-forming materials that must be added to the furnace, slag volume, and usable output.

Making pig iron with a reduced silicon content makes the steelmaking operation considerably more efficient — it decreases the consumption of coke and slag-forming materials and raises productivity. However, changing the silicon content in blast-furnace smelting also has a marked effect on the pig's content of sulfur: for each 0.1% reduction of [Si] in the melt, sulfur content increases by 0.003%. This is apparent from the following regression equation: \( [S] = 0.058 - 0.033 [Si] \).

The sulfur content of pig iron tapped from the blast furnace often reaches 0.05%. To obtain a consistently low value (below 0.025%), it is necessary to employ a well-conceived technology, have charge materials with the lowest possible sulfur content, use high-basicity slag mixtures, and significantly increase slag volume. However, according to data supplied by the Danish firm "Dofasko" [1], a reduction in the sulfur content of pig iron leads to a decrease in furnace productivity by 13% and an increase in coke consumption by 9%. Thus, it is economically more expedient to smelt conversion pig with a low silicon content and a high sulfur content.

According to studies [2], the production cost of converter steel depends linearly on the sulfur content of the pig iron. A 0.01% increase in the latter raises the cost of producing 1 ton of steel by 0.8-2%. Costs increase more dramatically with the conversion of high-silicon pig iron. Here, the savings realized in the blast-furnace shop by making pig iron with a low silicon content and a high sulfur content do not offset the additional costs incurred in desulfurizing the metal in the converter shop. In addition to the higher costs, it turns out to be nearly impossible to produce steel with the required sulfur content. Desulfurization of the metal outside the furnace is necessary in order to preserve the economic benefits realized in the blast-furnace shop by making low-silicon, high-sulfur pig iron.

The scientific aspects of the desulfurization of metal consist of the following. In a liquid iron-carbon melt, sulfur is present in the form of sulfides of iron distributed between the iron and slag in contact with the iron: \([Fe] \rightleftharpoons \begin{pmatrix} S \end{pmatrix}\). The process of sulfur transfer is accompanied by the redistribution of oxygen: \((O) \rightleftharpoons [O]\).

The coefficient expressing the distribution of sulfur between the slag and the metal depends on their composition and is related to the oxygen distribution coefficient. In the theory of ideal ionic solutions, the ratio \(L_S / L_O\) (\(L_S = [S] / [S]; L_O = (O) / [O]\)) can be represented as the ratio of the equilibrium constants in the reactions \([S] \rightleftharpoons (S)\) and \([O] \rightleftharpoons (O)\):

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\frac{n_S [O]}{n_O [S]} = \frac{K_S}{K_O}.
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Fig. 1. Effect of the state of oxidation of the slag on the sulfur distribution coefficient (○, •, □ — calculated, laboratory, and factory data, respectively).

Fig. 2. Dependence of the activity coefficient of sulfur on the carbon content of the pig iron.

where \( n_S = (S) \) is the number of sulfur ions in the slag; \( n_O = n_{CaO} + n_{MgO} + n_{FeO} + 3n_{Fe_2O_3} - 2n_{SiO_2} - 3n_{Al_2O_3} \) is the number of oxygen ions in the slag; \( [O], [S] \) are the contents of oxygen and sulfur in the metal, %.

Available values of the equilibrium constants of sulfur and oxygen allowed us to determine the equilibrium concentrations of sulfur in the metal and values of coefficients expressing the distributions of these elements for actual slags. Figure 1 shows equilibrium sulfur distribution coefficients calculated on the basis of the ionic theory of slags and obtained under laboratory conditions by the method of sequential saturation.

Melts of the ternary system \( \text{Fe}--\text{C}--\text{S} \) are far from ideal. Figure 2 shows the dependence of the activity coefficient of sulfur on the carbon content of the melt. The presence of the deviations, which have the effect of increasing the thermodynamic activity of sulfur dissolved in iron, is one of the main reasons that pig iron can be desulfurized more efficiently than steel. Thus, the sulfur distribution coefficient for pig iron is 10-15 times greater than the same coefficient for steel. Commercial trials have shown the advantages of pig iron desulfurization (compared to the desulfurization of steel) to be even greater than predicted on the basis of thermodynamic calculations: the removal of 0.01% sulfur from pig iron requires about 1 kg of a slag-forming mixture of the \( \text{CaC}_2--\text{CaO} \) type per ton of pig, while 2 kg of this mixture is needed to remove just 0.001% S from a ton of steel [3]. This result is probably related to the effect of oxygen dissolved in the steel.