

## Features of Removal of Phosphorus and Sulfur from Remelting Stock during Electric Arc Melting of Steel

**Ramin I. Karimov**  
“Baku Steel Company” MMC

*The paper provides information on the application of the process of steel smelting in an electric arc furnace. The article describes the compositions of charge materials for producing steels in an electric arc furnace, which consist of the metal part, slag-forming agents, deoxidizing agents and alloying materials, carburizing components and oxidizers. Their functions in the smelting of steel in an electric arc furnace have been defined. In addition, the role of an electric arc furnace in obtaining high-quality steel for various industries has been evaluated.*

*The prospects for the development of electric melting of steel on an industrial scale are shown, including new smelting furnaces, extra-furnace treatment plants, continuous casting of liquid steel, systems for providing smelting shops and electric smelting units with raw materials, results of development and introduction of casting and rolling facilities.*

*The paper also presents chemical reactions for the removal of phosphorus and sulfur from the liquid metal during electric arc melting. A diagram of the distribution of slag separation sites containing phosphoric anhydride at various SiO<sub>2</sub> concentrations in the slag is given. The paper contains a triple diagram illustrating the effect of slag content on the distribution coefficient of phosphorus in the liquid metal. The author analyzes the course of chemical reactions to remove sulfur from the liquid metal. The diagram of the state of FeS – MnS alloys, the dependence of sulfur in these alloys on manganese concentration, and the effect of manganese concentration on sulfur dissolution are described. A nomogram has been constructed to show the dependence of the sulfur distribution coefficient between the metal and slag on the slag composition.*

**Keywords:** alloy, sulfur, phosphorus, basicity, phosphorus distribution coefficient, silicon dioxide, ferrous oxide, lime, concentration.

**1. Introduction.** In the city of Baku (the Azerbaijan Republic), the Baku Steel Company LLC has been operating since 2000, which has been producing products of various types of electric arc steel for the needs of the construction and oil industry of the republic, CIS countries and other foreign countries. The steel is smelted in a 50-ton electric-arc furnace using the technology of remelting metal waste followed by extra-furnace treatment.

It should be noted that the role of the electric furnace and other equipment for the effective high-performance implementation of the entire technological cycle from

the preparation of raw materials to the warehouse of finished products and delivery to the consumer is extremely important. The competitiveness of any technology, no less than the physical and chemical aspects, depends on the correctly chosen design of the main and auxiliary equipment, its durability and reliability, ease of maintenance, and perfect operation during the entire depreciation period. The combination of technology with the potential of equipment at the present stage is crucial when creating new and improving the existing processes for the smelting of electric arc steel and ferrous alloys [1-3].

At the same time, in the last 25-30 years, the rapid development of electrometallurgical production, especially of electric arc steel production, has taken place. A whole range of new smelting units, extra-furnace processing plants and units for continuous casting of steel, systems for providing smelting workshops and electric smelting units with raw materials and the unloading of smelting products have been created. Casting and rolling facilities are being developed and introduced in production. Factories providing finished products for the needs of construction and engineering are being used on an industrial scale. Electrometallurgical production is at the stage of equipment modernization and technical re-equipment [4 - 6].

Therefore, at present, the process of smelting steels for various purposes through the remelting of metal waste in electric furnaces is becoming more and more common.

The process of electric arc steel melting of metal waste is characterized by its own typical features. The content of phosphorus and sulfur in a similar charge is much lower compared to the fresh charge. In other words, metal waste is pre-cleaned of phosphorus and sulfur during the previous smelting. However, despite this, additional components are introduced into the charge, which leads to additional contamination. At the same time, on the border of "metal - slag", "metal - refractory lining of the furnace" and the ladle there is a possibility of repeated contamination of the metal with phosphorus and sulfur. When using metal waste, the process of melting steel from the charge materials differs in its characteristics. Therefore, in this paper, the author shows how important phosphorus and sulfur removal is during electric arc melting of steel from remelting stock.

**2. Materials and methods for conducting experiments.** When smelting steel in an electric arc furnace, a significant amount of charge materials is used. They include: metal charge (metal waste, scrap, waste from secondary processing shops, fragmented scrap, metallized pellets, cast iron, which are all subjected to further remelting); scorifiers (lime, limestone, aluminosilicate materials, quartzite, fluorspar); ferrous alloys (alloying and deoxidizing agents); carburizers (coke, electrode scrap, cast iron), and oxidizing agents [1 - 4].

The materials that are part of the metal charge provide the metal part of the bath furnace, from which, after smelting, steel of the required composition and grade is obtained.

Scorifiers and oxide materials ensure the formation of slag with the required physical and chemical characteristics and are used in the course of the corresponding technological stages of the process of electric arc smelting.

Deoxidizers and alloying materials are used mainly in the form of ferrous alloys and as pure metals. These materials are designed to purify the liquid metal from oxygen and oxide inclusions, and are also used in the partial alloying of steel. Such materials include ferrosilicon, ferrosilicomanganese, ferromanganese, ferrochrome, ferromolybdenum, ferrotitanium, ferro-tungsten, titanium, aluminum, silicocalcium, magnesium, etc.

Carburizers are designed to provide the carbon potential in the bath furnace of liquid steel and the required carbon content in the finished steel.

Oxidizers are materials that promote the oxidation of excess carbon and harmful impurities and are used in the oxidative period of smelting in the form of technical oxygen, iron ore, iron cinder, and iron ore pellets [7 - 9].

The loading of the charge material was carried out continuously, that is, started after the end of the furnace refilling. Charging was carried out from above using a loading basket (tub).

Furnace refilling was performed to maintain the melting space in working condition. To do this, after the release of the next smelting to the damaged areas of the bottom and slopes (the transitions of the furnace bottom to the walls), dry magnesite powder was added using a filling machine, and, in the case of major damage, powder with the addition of liquid glass was used.

After the end of the filling, the vault with the electrodes was installed in the furnace, graphite electrodes were lowered into the furnace space and the electric current was switched on. Under the action of the high temperature of the electric arc, the charge material was melted first under the electrodes, the liquid metal flowing down and accumulating in the central part of the bottom. Gradually, the zone melting of the charge occurred. To speed up the process of melting, pieces of the melted charge from the furnace slopes were pushed into the zone of electric arcs. A characteristic feature of the first melting period is the formation of "wells" in the charge, around the electrodes (or in our case one "well" in a 60-ton super-power furnace). During the period of melting, slag formation occurs, both due to lime additives and due to the oxidation of the elements that make up the charge from remelting metal waste. During melting, silicon is fully oxidized, as compared to the 45–55% of manganese, carbon and iron are partially oxidized, and phosphorus and sulfur are oxidized as well.

The process of melting the charge from the remelting stock can be divided into four stages.

Stage 1 - the arcs burn on the surface of the charge, which gradually melts near each of these three electrodes. During this period, a significant part of the heat is radiated to the roof and, in order to avoid its melting, a current of moderate power was applied to the electrode.

Stage 2 - as the charge is melted, the electrodes automatically descend and the arcs are immersed in the charge, while the power of the current supplied to the electrodes increases.

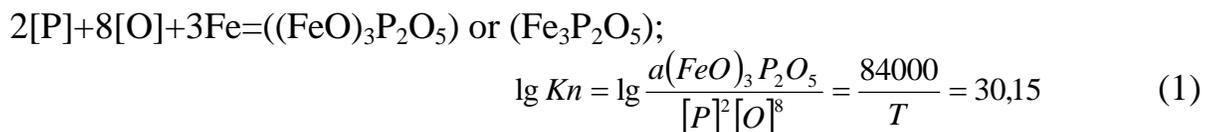
Stage 3 - the electrodes burn wells in the charge and the arcs burn between a layer of liquid metal located on the furnace bottom and the electrodes. The amount of liquid metal increases, and the lengths of the arcs decrease, the electrodes automatically rise, and the charge between the electrodes is melted.

Stage 4 - almost all of the charge is melted and the electric arcs burn openly above the surface of the slag and the liquid metal, the heat absorption of which is much less than that of the solid charge. The radiation of heat on the walls and roof of the furnace increases and, in order to avoid the melting of the refractory brick lining, the power of the current supplied to the electrode is reduced [10 - 12].

Thus, the process of melting the charge from remelting metal waste, the composition of which is described on the previous pages, is completed.

**3. Results.** When metal waste is heated in an electric arc furnace, the oxidation of iron, manganese, and silicon occurs, which proceeds with the release of a significant amount of heat, which accelerates the process of melting of the residual metal scrap. During the oxidation period of the heat, the phosphorus content decreases to 0.01–0.015%, the content of hydrogen and nitrogen in the metal significantly decreases, the metal is heated to the required temperature (120–130 °C above the melting point).

**3.1. Oxidation of phosphorus.** The possibility of complete removal of phosphorus from metal raw materials is considered one of the main problems of a steelmaker. With the exception of rare cases, phosphorus is mainly removed from a metal alloy through oxidation. This process is described by the following equation [14 - 16]:



At the last stage of melting in the temperature range of 1550-1650 °C, the oxygen concentration with respect to the equilibrium concentration of phosphorus is relatively high.

Even at phosphorus concentrations of 0.2–0.3%, the equilibrium concentration is higher than the one which is actually observed in the steel bath.

Typically, the amount of phosphorus in the charge of remelting stock is 0.015-0.03, but the oxidation of phosphorus to such low concentrations occurs not through the thickness of the metal, but on the surface layer in contact with slag and oxidizing gas (see Table 1, reactions 14 and 15).

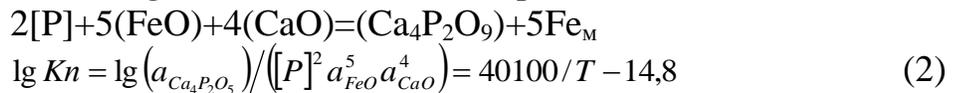
The 14th reaction (see Table 1) is an intermediate stage; at this stage, calcium is formed in the main slags during the formation of tri- or tetraphosphates:  $(P_2O_5)+3(CaO)=Ca_3P_2O_8$  or  $(P_2O_5) + 4(CaO)=(Ca_4P_2O_9)$ , or ion groups are formed ( $PO_3^{3-}$  or  $Ca^{2+}$ ).

At the beginning of melting, a small part of phosphorus, at low temperatures, forms the ionic groups  $PO_4^{3-}$  and  $Fe^{2+}$ , passing into the still unformed slag (low  $a_{CaO}$ ).

When considering the thermodynamics of the dephosphorization reaction, it can be seen that low temperature contributes to the removal of phosphorus.

Iron triphosphate is not a solid compound, it melts incoherently, therefore the removal of phosphorus from steel always leads to the formation of tri- or tetraphosphate, that is, maintaining sufficient slag mobility is based on achieving high values of  $a_{CaO}$  activity, which is possible only at high temperatures. Slag formation plays a crucial role in the removal of phosphorus. However, it is necessary to bear in mind that there must be some optimal compositions and slag temperature, which, on the one hand, ensure maximum metal dephosphorization rates (with other conditions being equal) and, on the other hand, maximum residual phosphorus concentrations. It is necessary to provide optimal slag properties both in terms of thermodynamics and in terms of the kinetics of the dephosphorization process.

The equation (15) given in the table can be presented as follows:



In accordance with the given  $K_n$  values, it might seem that the distribution of phosphorus between slag and metal, usually denoted as  $n_n = a_{Ca_4P_2O_9} / [P]$  or  $n'_\phi = (P_\Sigma) / [P]$ , should increase with increasing  $a_{FeO}$ , as well as  $a_{CaO}$ .  $P_\Sigma$  is the symbol for the concentration of phosphorus in the slag, regardless of its form. Both in pure FeO - CaO -  $P_2O_5$ , and in systems with varying concentrations of  $SiO_2$  (FeO - CaO -  $P_2O_5$ ), the slag has segregation areas.

Figure 1 shows a chart of the quasi-ternary system, [(FeO) - (Fe<sub>2</sub>O<sub>3</sub>) - (MnO)] - [(P<sub>2</sub>O<sub>5</sub>) - (CaO)] - [(SiO<sub>2</sub>)] (according to Kerber), which shows layered slag areas at various concentrations of SiO<sub>2</sub> (0.5 and 10%).

When processing phosphoric materials, this chart has practical significance. At the segregation borders of the charge, the change in the amount of CaO or FeO cannot affect the distribution coefficient of phosphorus between the metal and the charge, since the reactivity of the charge is determined in this case from the phases with a constant and immiscible composition (1550-1700 ° C).

In addition, an increase in the CaO concentration in the charge dramatically increases its viscosity ( $t = \text{const}$ ), which makes the kinetic characteristics of the dephosphorization process significantly important, therefore an experimental work was attempted to provide some optimal ratio of FeO and CaO. This is shown in Figure 2 [17].

At the last stage of melting (the distribution of phosphorus is close to equilibrium), to quantify the distribution of phosphorus between metal and slag, the Chipman and Winkler diagrams are used (Fig. 3). The disadvantage of this diagram is that the composition of the charge is calculated in mole percent, despite that the influence of all components of the charge is taken into account. When drawing the diagram, it was suggested that to calculate the activity of  $O^{2-}$  ions, the charge presents an ideal ionic solution. Only  $O^{2-}$  oxide donor of FeO is separated from the total amount.

Phosphorus removal rate is a function of certain variables in the main processes of steel melting:

$$V_n = f \left\{ [P], \frac{(CaO)_a}{(FeO)}, \frac{(CaO)_a}{(SiO)_2 + (P_2O_5)}, T_b, F \right\} \quad (3)$$

where  $(CaO)_a$  is the concentration of active CaO dissolved in the charge melt (except for the material that is in the solid phase, but not yet assimilated);  $T_b$  is the bath temperature;  $F$  - interphase spacing (charge - metal contact), which, in turn, is a function of the intensity of the mixture of metal and charge.

Of all the variables listed, the correlation dependence ( $V_p$ ) is so different for different equipments and methods that it is impossible to single out more precise patterns.

When developing the slag regime for the processing of phosphorus-containing steels, it is necessary to bear in mind that phosphoric anhydride is among the components that most intensively reduce the surface tension of slags. This leads to the fact that, in practice, the foaming of phosphorous slags during intensive oxidation of carbon is difficult to regulate both in acid - converter processes and in pool furnaces.

**3.2. Sulfur removal.** One of the important processes in the production of steel is the removal of sulfur from the metal. The sulfur tendency to oxidate is relatively lower than that of carbon,  $1/2 \{ S_2 \} + \{ O_2 \} = \{ SO_2 \}$  for the reaction  $\Delta G = f(T)$  is linear,  $2Fe_{M-6} + \{ O_2 \} = 2(FeO)$  for the reaction is much higher.

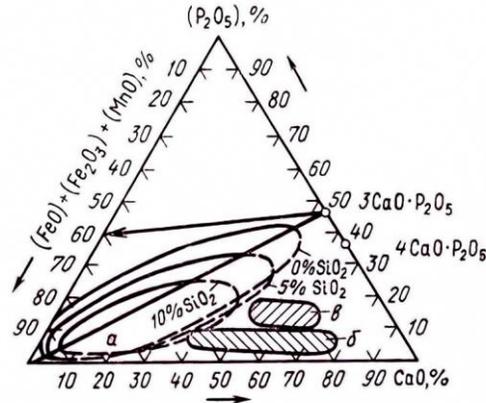


Figure 1. The location of the segregation of the charge  $\text{CaO} - \text{P}_2\text{O}_5(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MnO})$  at different concentrations of  $\text{SiO}_2$   
 a – areas of segregation;  $\bar{b}$  – normal areas of the charge;  
 B – slags of the phosphorous limit

According to reaction 16 (see Table 1), the equilibrium oxidation constants of sulfur, soluble in the metal, are practically independent of temperature and at the temperatures of the process of electric arc melting (1550-1600 ° C)  $K = P_{\text{SO}_2} / [\text{S}] [\text{O}]^2$  are close to 0.001, i.e.  $P_{\text{SO}_2} = 0.1 \text{ MPa} [\text{S}] [\text{O}]^2 \approx 100$ .

If we compare this value with  $[\text{C}] [\text{O}] = 0.0025$ , then it is clear that sulfur can be oxidized only in excess of oxygen, when the possibility of the influence of all other furnace bath components on the behavior of sulfur is almost excluded.

Indeed, due to the high surface activity of sulfur at the metal – gas border, some of its quantities in the reaction zone are oxidized by oxygen bubbles.

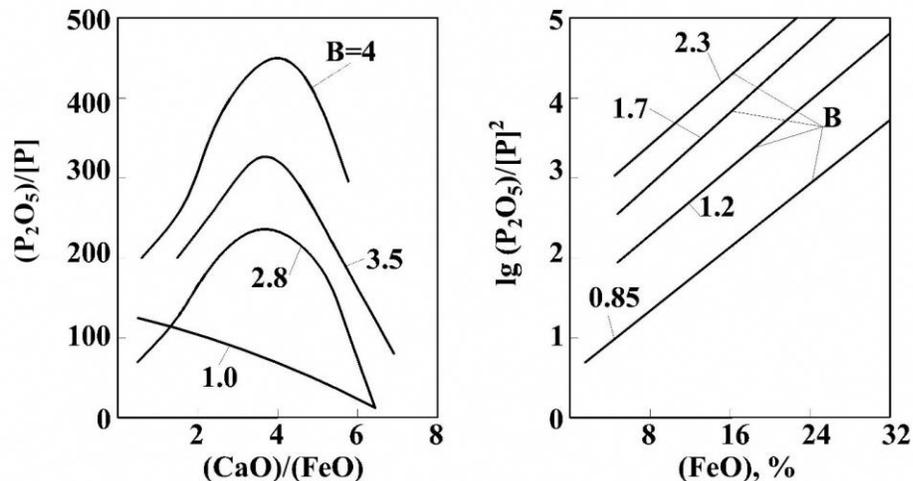


Figure 2.8. The dependence of the distribution coefficient of phosphorus between the slag and the metal at different values of basicity  $B = (\text{CaO}) / [(\text{SiO}_2) + (\text{P}_2\text{O}_5)]$  from  $(\text{CaO}) / (\text{FeO})$  (a) and  $\lg (P_2O_5) / [P]^2$  from  $(\text{FeO})$  (b)

Table 1

Thermodynamic characteristics of the oxidation reactions of the components of a metal bath during electric arc melting

No. of reaction	Reaction	Standard change in isobaric potential, kJ/mol	Temperature function of equilibrium constant
1	$1/2\{O_2\}=[O]$	$\Delta G_1^\circ = -116,94 - 0,0024T$	$\lg K_1 = \lg\left(\frac{[O]}{\rho_{O_2}^{1/2}}\right) = (6100/T) + 0,12$
2	$Fe_{ж} + 1/2 \{O_2\}=(FeO)$	$\Delta G_2^\circ = -237,95 + 0,05T$	$\lg K_2 = \lg\left(\alpha_{FeO} / \rho_{O_2}^{1/2}\right) = (12\ 420/T) - 2,61$
3	$Fe_{ж} + [O] = (FeO)$	$\Delta G_3^\circ = -121,00 + 0,052T$	$\lg K_3 = \lg\left(\alpha_{FeO} / [O]\right) = (6320/T) + 2,734$
4	$[C] + [O] = \{CO\}$	$\Delta G_4^\circ = -36,63 - 0,031T$	$\lg K_4 = \lg\left(\rho_{CO} / [C][O]f_{C'O}\right) = (1860/T) + 1,643$
5	$[C] + 1/2 \{O_2\} = \{CO\}$	$\Delta G_5^\circ = -152,57 - 0,034T$	$\lg K_5 = \lg\left(\rho_{CO} / [C]f_{C'O_2^{1/2}}\right) = (7965/T) + 1,77$
6	$[C] + \{O_2\} = \{CO_2\}$	$\Delta G_6^\circ = -431,26 + 0,051T$	$\lg K_6 = \lg\left(\rho_{CO_2} / [C]f_{C'O_2}\right) = (22510/T) - 2,64$
7	$\{CO\} + 1/2 \{O_2\} = \{CO_2\}$	$\Delta G_7^\circ = -278,69 + 0,084T$	$\lg K_7 = \lg\left(\rho_{CO_2} / \rho_{CO} \rho_{O_2}^{1/2}\right) = (14550/T) - 4,40$
8	$[Si] + 2[O] = (SiO_2)$	$\Delta G_8^\circ = -593,84 + 0,233T$	$\lg K_8 = \lg\left(\alpha_{SiO_2} / [Si][O]^2\right) = (31000/T) - 12,15$
9	$[Si] + \{O_2\} = (SiO_2)$	$\Delta G_9^\circ = -827,73 + 0,228T$	$\lg K_9 = \lg\left(\alpha_{SiO_2} / [Si]\rho_{O_2}\right) = (43200/T) - 11,90$
10	$[Si] + 2(FeO) = (SiO_2) + 2[Fe]$	$\Delta G_{10}^\circ = -351,71 + 0,127T$	$\lg K_{10} = \lg\left(\alpha_{SiO_2} / [Si]\alpha_{FeO}^2\right) = (18360/T) - 6,68$
11	$[Mn] + [O] = (MnO)$	$\Delta G_{11}^\circ = -244,53 + 0,109T$	$\lg K_{11} = \lg\left(\alpha_{MnO} / [Mn][O]\right) = (12760/T) - 5,68$
12	$[Mn] + 1/2 \{O_2\} = (MnO)$	$\Delta G_{12}^\circ = -361,56 + 0,107T$	$\lg K_{12} = \lg\left(\alpha_{MnO} / [Mn]\rho_{O_2}^{1/2}\right) = (18860/T) - 5,56$
13	$[Mn] + (FeO) = (MnO) + Fe_{ж}$	$\Delta G_{13}^\circ = -123,35 + 0,056T$	$\lg K_{13} = \lg\left(\alpha_{MnO} / [Mn]\alpha_{FeO}\right) = (6440/T) - 2,95$
14	$2[P] + 2,5\{O_2\} = (P_2O_5)$	$\Delta G_{14}^\circ = -154,68 + 0,438T$	$\lg K_{14} = \lg\left(\alpha_{P_2O_5} / [P]^2 \rho_{O_2}^{2,5}\right) = (80750/T) - 22,88$
15	$2[P] + 5[O] + 4(CaO) = (Ca_4P_2O_9)$	$\Delta G_{15}^\circ = -1372,83 + 0,55T$	$\lg K_{15} = \lg\left(\alpha_{Ca_4P_2O_9} / [P]^2 [O]^5 \alpha_{CaO}^4\right) = (71667/T) - 28,73$
16	$[S] + 2[O] = \{SO_2\}$	$\Delta G_{16}^\circ = -5,63 + 0,054T$	$\lg K_{16} = \lg\left(\rho_{SO_2} / [S][O]^2\right) = -(294/T) - 2,80$

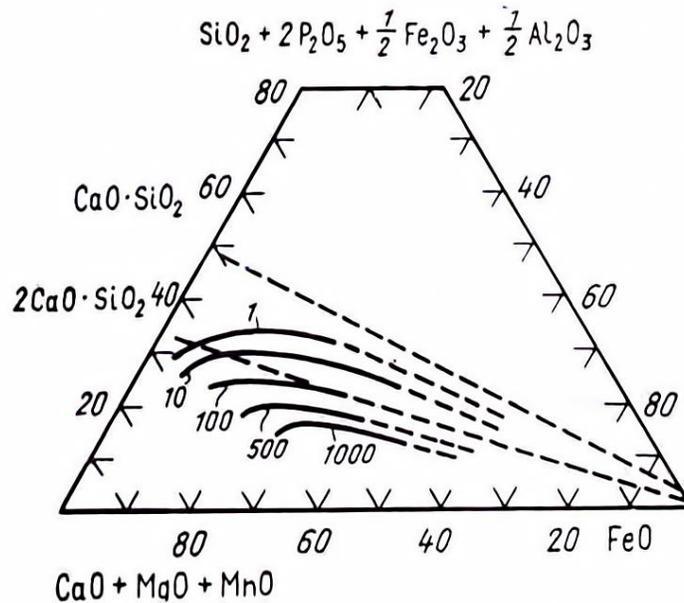


Figure 3. The influence of the charge composition on the distribution coefficient of phosphorus  $N_{(CaO)_4P_2O_5} / [P]^2$  (figures at the curves show the values of the dephosphorization coefficient at 1600 °C)

According to production data, the amount of sulfur passing through the gas phase ( $SO_2$  in the figure) does not exceed 10-20% of the total sulfur content removed from the charge.

Sulfur removal processes are associated with the ability to form sulfides that are not soluble in the metal bath.

For any of the following types of reaction:



With relatively low concentrations of sulfur (0.03-0.07% [S]), it is important to achieve higher values of  $a_S$ . This provides a low sulfur concentration and a high rate of sulfur recovery.

In accordance with the diagram of the influence of some elements of the sulfur activity coefficient in iron [3] from ordinary iron impurities, carbon and silicon have a particularly strong influence on the sulfur activity coefficient. Theoretically, it is more expedient to desulfurize cast iron (a component of a metal charge) to redistribute it in steel than a low-carbon and brittle metal in the process of electric arc melting of steel; this is confirmed by the practice of all industrialized countries.

The following elements having a higher sulfur-containing agent (greater negative  $\Delta G$  of sulphide-formation reaction) than iron can be used to desulfurize the cast iron component of the charge: Mn, Na, Mg, Ca, and Ce. With a high content in

the iron component of the charge, manganese can be considered as the main desulfurizer. In the production of electric steel, manganese does not form a pure MnS sulfide phase; it forms a continuous series of solid and liquid solutions with FeS (Fig.4). The system Fe - Mn - S at a given temperature is monovariant, so the composition of complex sulfides is determined entirely by the manganese content at  $t=\text{const}$  (Fig.5).

It is natural [18] that carbon and silicon have a particularly strong influence on the coefficient of sulfur activity. During steel production, manganese almost does not form a purely sulfide MnS phase; together with the FeS system, it creates a sequence of solid and liquid solutions (Fig. 4). Therefore, the Fe – Mn – S system is monovariant at this temperature, and therefore the content of complex sulfides at  $t=\text{const}$  is determined by the total value of manganese (Fig. 5). The composition of sulphides can change only with a change in temperature or even with the cooling of the liquid metal of a solid.

The solubility of sulfur in liquid iron is not limited, but when the concentration of MnS in the Fe – Mn – S complex groups increases (as their melting temperature increases (Fig. 6)) their solubility in the metal decreases (increasing the distribution coefficient of sulfur content between the metal and slag). All this makes the essence of the desulfurization process.

Figure 7 shows the concentration of manganese in iron and steel on a logarithmic scale along the coordinate axes. Figure 7 shows that the desulfurizing ability of manganese, especially at high temperatures, is very low compared to steelmaking processes.

In most industrialized countries, it is considered necessary to have  $\leq 0.02\%$  of cast iron in electric furnaces when molding ordinary steel. However, if manganese would be an rare element, it would be impractical to use it as a desulfurizer, since it is impossible to provide a high degree of desulfurization with manganese.

However, it is impossible to ensure the sulfur concentration from 0.06 to 0.08% or less using sulfur-containing coke grades in blast furnaces. The main process that determines the behavior of sulfur in an electric furnace is its distribution between the metal and slag, as well as its transfer to the slag.

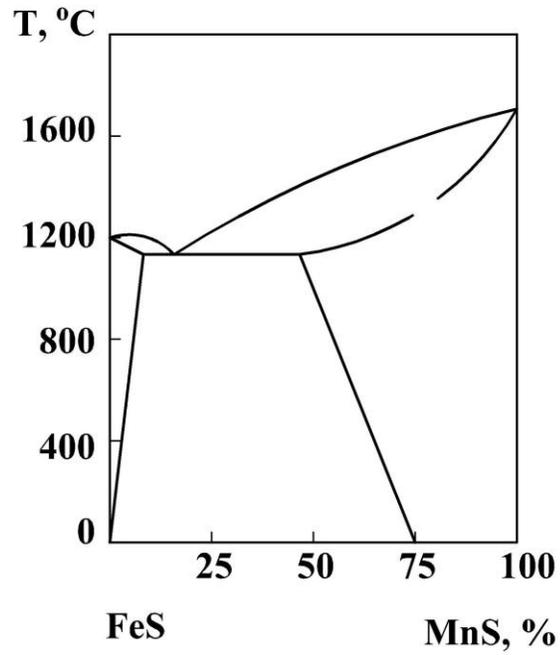


Figure 4. Diagram of FeS – MnS state

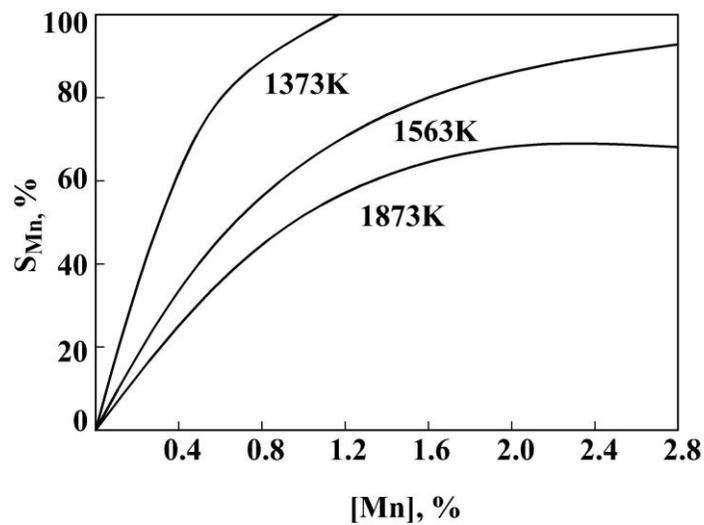


Figure 5. Dependence of the proportion of sulfur bound to manganese in FeS-MnS alloys from the concentration of manganese at various temperatures

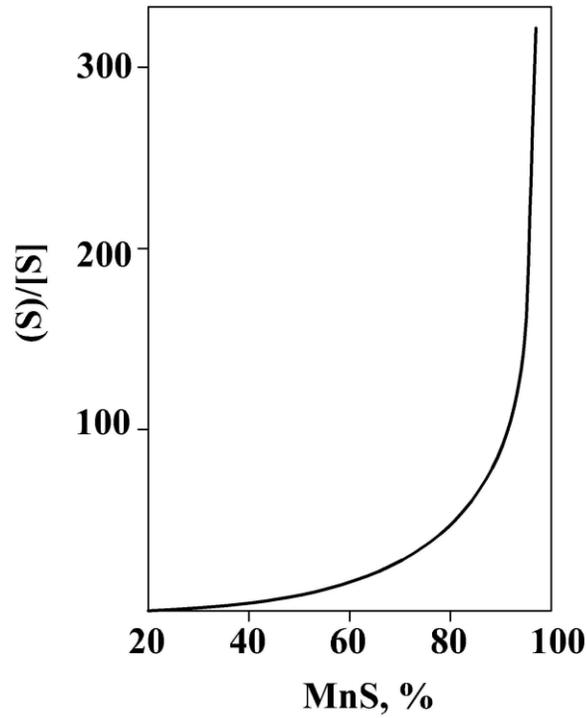


Figure 6. The relationship between the containment of MnSi in FeS-MnS alloys and the coefficient of distribution of sulfur by metal and sulfide phase at 1600 ° C

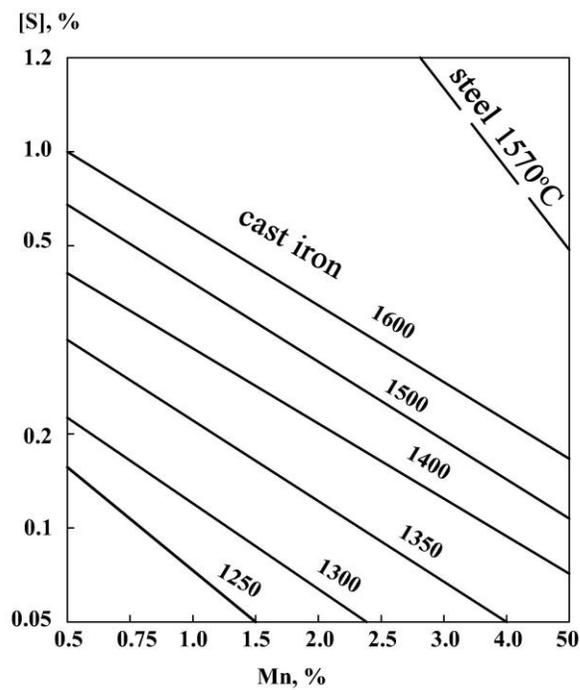
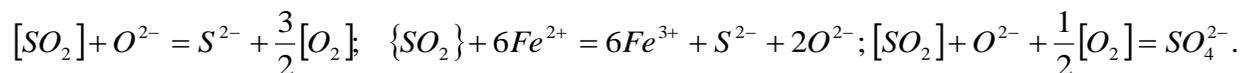


Figure7. The effect of manganese concentration on the solubility of sulfur in molten iron and steel

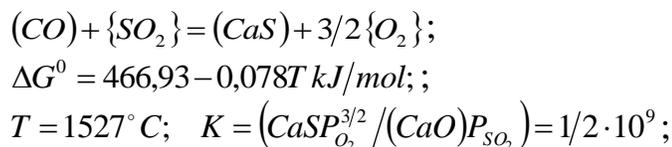
When smelting steel in a Siemens-Martin furnace and, to a much lesser extent, in tandem furnaces, the source of sulfur in finished steel is not limited only the charge, it can also be the gas phase occurring when using sulfur fuel. In the gas phase of a Siemens-Martin furnace, sulfur can be present only in the form of sulfurous anhydride. During the melting of the charge, direct contact of metal and sulfur-containing gases is possible. In this case, the occurrence of the process is most likely.

$$(SO_2) = [S] + 2[O]; \quad \lg k = \lg[S] \cdot [O]^2 / P_{SO_2} = 4280/T - 0,05$$

At  $T = 1527^\circ\text{C}$ ,  $k = 4 \cdot 10^2$ , i.e. during the direct contact of sulfur dioxide and melting iron, the transition of sulfur into the metal is thermodynamically possible. After the formation of the slag cover, the process of transferring sulfur to the metal from the gas phase through the slag does not stop completely. The following processes are possible:



Then there is a mass transfer of  $S^{2-}$  and  $SO_4^{2-}$  ions and from the slag-gas contact surface to the slag-metal interphase surface. The presence of the slag cover and convective transfer of sulfur in it reduce the rate of transition of sulfur from the gas to the metallic phase. The above process in molecular form is represented by the following equation:



Obviously, the transition of sulfur to slag and from slag to metal can be significantly suppressed when working with excess air and ensuring that the fuel fed in the furnace is quickly and completely burned.

According to the ionic theory of the slag structure, which characterizes the nature of the process, the distribution of sulfur between the metal and the relatively low-base slag is accompanied by the following reaction:  $Fe_{\text{ж}} + [S] = Fe^{2+} + S^{2-}$ . Under these conditions  $n_c = (S^{2-})/[S] = K_c / (Fe^{2+})$ , that is, in the case of other conditions being equal, the coefficient of sulfur distribution between metal and slag decreases with the increase of the iron content.

In the highly basic slags, sulfur is removed from the metal mainly by the ion exchange reaction:  $[S]+O^{2-}=S^{2-}+[O]$ . In this case, the distribution coefficient of sulfur is  $n_c'' = (S^{2-})/[S] = K_c''(O^{2-})/[O]$ , i.e. the volume of slag in relation to sulfur is characterized by basicity,  $(O^{2-})$ , but with an increase in metal oxidation, the distribution coefficient of sulfur decreases.

The experiment provides reliable confirmation of the interpretation of the process of sulfur removal from slag. In this case, we present only the generalized Chipman diagram (Fig. 8).

As can be seen from Figure 8, the best conditions for desulfurization are observed in the blast furnace process (although they do not always really occur), while melting in an electric arc furnace occupies an intermediate position. The least favorable conditions arise in a converter and open-hearth processes. Figure 8 shows sulfur distribution curves obtained under laboratory conditions at various high values of excess basicity (EB):

$$EB = n_{CaO} + n_{MgO} + n_{MnO} - 2n_{SiO_2} - 4n_{P_2O_5} - 2n_{Al_2O_3} - n_{Fe_2O_3},$$

where  $n$  is the molar quantity of each component forming the slag.

The data presented in Figure 8 can only be considered as semi-qualitative. It is known that  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Mn^{2+}$  ions are not equally valuable in the desulfurization process, but the theory of heterogeneous microscopocity of slag alloys might be poorly developed and cannot quantify the equilibrium of the desulfurization process.

However, it is also known that the previously adopted descriptions of the desulfurization process using the equations  $Fe_M + [S] + (CaO) = (CaS) + (FeO)$ ;  $Fe_M + [S] + (MnO) = (MnS) + (FeO)$  do not reflect the nature of the desulfuration process and do not even provide reliable quantitative data for describing the process.

For sufficiently basic slags ( $(CaO)/(SiO_2) > 2$ ), the following equation can be applied:  $(O^{2-}) + [S] = [O] + (S^{2-})$ ;  $\Delta G^0 = -124,57 + 0,050T \text{ kC/mol}$ ;

$$\lg K_c''' = \lg \left( \frac{[S]N_{O^{2-}}}{[O]N_{S^{2-}}} \right) = (6500/T) - 2,625, \quad (4)$$

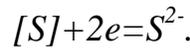
where  $[S]$  and  $[O]$  are expressed as percentages by weight;  $N_{O^{2-}}$ ;  $N_{S^{2-}}$  is the ionic fraction of the share of oxygen and sulfur, calculated from the total number of ions (anions and cations). Given the relatively low enthalpy of the process, the distribution coefficient of the sulfur content between the metal and slag can be set at 1500-1650 °C in the diagram (see Figure 9), depending on the composition of the latter.

According to Schenck, the following process takes place at high concentrations of carbon in the bath:

$$[S] + (O^{2-}) + [C] = (S^{2-}) + \{CO\}$$

$$\lg K^{IV} = \lg((S^{2-}) / (O^{2-})) (P_{CO} / [C][S]) = - (3800/T) + 3,71 \quad (5)$$

This process, apparently, has some development, for example, in the smelting of high carbon steel in open-hearth and arc furnaces. Most researchers believe that the removal of sulfur at high temperatures and in a sufficient amount of moving slag can be described by the following reaction:



At the same time, in order to preserve electroneutrality at the phase border, the  $Fe_{ж} - 2e = Fe^{2+}$  process (in slags with low basicity) or the opposite transition of oxygen from slag to metal  $O^{2-} = [O] - 2e$  (with high slag basicity) should take place.

$$\sum a = (SiO_2) + 0,634(P_2O_5) + 0,9(Al_2O_3)$$

However, according to some data (Esinin, Skalin, Travin, and others), not only the rate of removal, but also the order of the sulfur removal reaction varies with temperature, the intensity of mixing of metal and slag.

According to the information provided by the authors [18 - 21]:

$$d[S]/d\tau = K[S]^{(1+B)}, \quad (6)$$

where  $d[S]/d\tau$  is the desulfurization rate; K is the speed constant, B is the factor of turbulence: the rate increases from zero to one with the increase of temperature.

Numerous data from studies [19–21] allow us to conclude that the determination of the rate of sulfur removal in the metal can be both adsorption-kinetic (process  $[S] + 2e = S^{2-}$ ) and diffusion-solid (mass transfer in the slag layer from the metal slag in slag thickness) link.

This situation is not uncommon in metallurgy, but in most cases it is a prerequisite for determining the “diffusion-kinetic limitation”. First, it is difficult to distinguish the limitation of one or another link in most cases with the help of research tools, and secondly, in certain circumstances, it is possible to change the limiting links.

The fractional order of the desulfurization reaction observed by a number of authors indicates some complex chemical processes. An increase in temperature increases the chemical units and the rate of mass transfer in the metal and slag. Gas flushing of the bath with oxygen or CO bubbles increases the surface of the metal and slag contact equally, and mass transfer increases in both phases.

Electromagnetic mixing of a liquid metal not only increases the mass transfer in its volume, but also intensifies the flow of sulfur atoms to the metal and slag boundary, which is equivalent to an increase in the phase boundary. A constant electric field (anode to slag and cathode to metal) increases the rate of sulfur desulfurization as a result of accelerating the passage of sulfur through the metal-slag phase boundary.

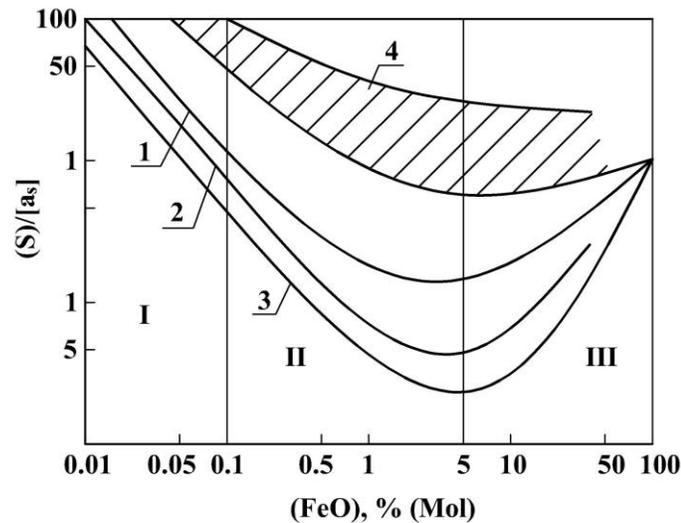


Figure 8. The dependence of the coefficient of sulfur distribution between the slag and the metal in various high concentrations of slag basicity at different concentrations of (FeO):

- I – blast furnace process; II – process in an electric arc furnace; III – process in the converter and open-hearth furnace;
  - 1. Excess basicity (EB)=0.22 of laboratory alloy;
  - 2. 2 – HB =0.15; 3 – HB =0.10; 4 – in different furnaces in real alloys
- (S)/[a<sub>s</sub>] area with values

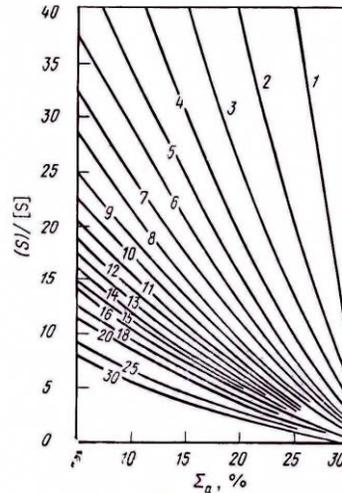


Figure 9. Dependence of the sulfur distribution coefficient on the composition of the slag at metal-slag border: the curves give the values of FeO, in%;

When the temperature increases, the viscosity of the slag decreases; above all, the fixation of the fluorspar significantly increases the desulfurization rate and plays a significant role in the diffusion process.

In electric arc steel melting, the following functional dependence has become important:

$$V_S = f(1/[O]; \Delta(CaO)/(SiO_2); (CaO)/(SiO_2); (CaO)/(SiO_2), T, F_n; 1/\eta_{sl}), (7)$$

where  $\Delta(CaO)/(SiO_2)$  –slag basicity increase rate during smelting;  $(CaO)/(SiO_2)$  – basicity; T – temperature;  $F_n$  – metal slag inter-phase surface;  $\eta_{sl}$  – slag viscosity.

Increasing each of the listed variables adequately increases the desulfurization rate  $V_S$ .

**4. Discussion.** All processes of producing liquid metal in electric arc steel-smelting furnaces is associated with the formation of slag. Slags consist of oxides and a small amount of sulphides. Chemical analysis allows us to establish the composition of the slag, but cannot provide information about the mineralogical structure of it, especially in the liquid state.

In this paper, the oxidation and deoxidization of iron in an electric bath are not considered. These processes are the subjects of separate works.

The quality of any steel, as a rule, is determined by the content of harmful impurities in it, such as phosphorus and sulfur.

Many authors [22 - 24] believe that the process of dephosphorization of steel is necessary when the charge for steelmaking consists mainly of cast iron and ferrous alloys. Phosphorus is introduced into the bath by these components in relatively large

quantities as compared to the charge consisting of remelted metal waste. Such a charge before secondary remelting has already undergone the processes of dephosphorization and desulfurization.

In this case, the distribution of phosphorus between the metal and slag depends on the total iron content in the slag, its basicity and temperature. The melting was carried out in the main electric arc furnace. Phosphorus is well removed from the metal as compared with the acid refractory lining of the furnace. This is well illustrated by the location of the  $\text{CaO} - \text{P}_2\text{O}_3$  ( $\text{FeO} + \text{Fe}_2\text{O} + \text{MnO}$ ) charge sections at different  $\text{SiO}_2$  concentrations (Fig. 1). Therefore, with a relatively large amount of  $\text{SiO}_2$  in the slag (up to about 10%), the segregation areas of the charge predominate, the oxidation of phosphorus becomes more difficult. When the concentration of  $\text{SiO}_2$  is up to 5%, the usual charge areas and the oxidation of phosphorus are present and the period of pure boiling is accelerated, that is, in this case, the so-called hot dephosphorization is observed. In the absence of  $\text{SiO}_2$  concentration in the slag, the oxidation of phosphorus is in full swing. Naturally, the following factors affect the degree of dephosphorization:

1. The amount of slag (the more the amount of slag, the more completely phosphorus is removed from the metal).
2. The content of ferrous oxide in the slag (direct relationship).
3. Slag basicity (direct relationship).
4. The concentration of phosphorus in the initial charge (inverse relationship).
5.  $\text{P}_2\text{O}_5$  content in the slag (inverse relationship).

When using steel waste melting stock, the fourth point loses its significance, since phosphorus is already removed to the maximum extent at the first steel smeltings. However, in view of the fact that cast iron and ferrous alloys for carburizing, boiling and deoxidation are additionally introduced into the charge consisting of metal waste, then high-quality phosphorus removal still remains relevant in this case. Especially during the deoxidation period, the recovery of phosphorus from slag can be observed. Already with the preliminary deoxidation of metal in an electric arc furnace, the deoxidation of phosphorus begins. Mixing the metal with the slag during the release intensifies this process. Even during steel casting, due to a reduction in the basicity of the slag in the ladle, phosphorus continues to recover from the slag.

After the release of the metal from the electric arc furnace, phosphorus was additionally removed by extra-furnace deformation consisting in the processing of steel with synthetic powders made of lime and feldspar. After this treatment, the

phosphorus content in the finished electric steel produced from metal waste melting stock does not exceed 0.03%.

It is also important to desulphurize electrical steel when it is produced from metal waste, since sulfur in steel is a harmful impurity, forming sulfide compounds. Conventionally, sulfur in liquid steel is designated as an anion. Sulfur can be dissolved indefinitely in liquid iron, while in solid iron the alpha solubility is insignificant. Therefore, when the electric steel is cooled to an ordinary temperature, sulfur is released in the form of sulphides and the formation of an eutecticum is possible with a melting point of 985 °C [3].

In addition, sulfur, together with the oxygen released from the solution during the solidification of steel, forms a low-melting FeO-FeS compound with a melting point of 940°C. The formation of a low melting point oxysulfide eutecticum is also possible, which makes steel brittle. Manganese, introduced into steel as a ferromanganese during deoxidation, changes the conditions of formation and release of sulfur inclusions in the direction of weakening or eliminating hot-brittleness when processing reinforcing steel with pressure.

As mentioned above, the solubility of sulfur in solid steel is negligibly low, therefore, excess sulfur carried to the charge by its cast-iron component during the crystallization of electric steel is released and in the form of sulphides or oxysulfides is dispersed at the grain boundaries, weakening their attraction, which negatively affects the mechanical properties of the steel.

The distribution coefficient of sulfur between the slag and the electric metal depends mainly on the basicity of the slag. Excess basicity of the slag at the level of  $EB = 0.22$  (laboratory alloy) leads to a significant decrease in sulfur concentration in the finished steel. However, in the ladle during the casting of electric steel, despite the reduction of the basicity of the slag, no recovery of sulfur from the slag is observed.

Consequently, part of the sulfur can be removed from the electric steel during the extra-furnace desulfurization. The extra-furnace desulfurization of electric steel by alumina-lime slag in the ladle can contribute to the removal of up to 50% of sulfur.

When calculating the charge from metal waste, it is necessary to check the possible concentration of sulfur in the metal under the main slag of this composition at the end of the smelting using the formula of Mower and Bischoff[25]:

$$\frac{(S):S}{(S):S_0} = 1 + 5Mn, \quad (8)$$

where  $Mn$  – the final content of manganese in the metal after deoxidation, %;  
 $S$  – sulfur content in metal, %;

( $S$ ) – sulfur content in slag, %;

( $S$ ): $S_0$  – the distribution of sulfur between the slag and the metal, provided that the manganese content in the metal is zero.

The ( $S$ ): $S_0$  value is determined by the nomogram depending on the content in the final slag of  $CaO$  and  $SiO_2$ . The obtained value must be substituted into the formula. The found value of sulfur distribution should be corrected taking into account the content of  $P_2O_5$  in the slag. Then, based on the distribution of sulfur between the metal and slag, by substituting the sulfur content in the slag, it is possible to determine the sulfur content in the metal. It should correspond to the specified sulfur content in steel according to the calculation of the metal waste charge. Otherwise, it is necessary to change the basicity of the slag.

In electric steel melting, the quality of the final product largely depends on the quality of the charge loaded into the furnace. When using metal waste, the regulation of the quality of steel for harmful impurities, such as phosphorus and sulfur, is hampered due to the large difference in the metal waste feedstock from batch to batch. At the same time, in melting by the method of remelting, there is almost no oxidation period. With the correct calculation of the charge after smelting, the recovery period immediately begins, the metal is deoxidized, some alloying additives are added and then the metal is cast. Consequently, the electric smelting by remelting metal waste is significantly shorter compared to conventional electric smelting.

With electric steel melting, the recovery period is aimed not only at deoxidation of the metal, but also at removing sulfur, adjusting the chemical composition of the steel from the waste to the required composition, and controlling the process temperature.

Ferromanganese, ferrosilicon, and aluminum were used as steel deoxidizers. In addition, alloying additives were added for the production of AT500 reinforcement steel to introduce the necessary alloying elements into the metal. After that, the metal was released from the furnace into a steel-pouring ladle installed under the chute, for which the furnace was automatically tilted in the direction of the steel outlet. After that, additional deoxidation and alloying of electric steel were carried out in the ladle. Thus, the two-slag process of steel smelting from metal waste was carried out.

As noted above, the melting of such a charge of alloyed metal waste is based on remelting without oxidation. The charge for such smelting was composed in such a

way that the carbon content in the metal was 0.05-0.1% lower than the required steel grade. Due to the fact that during alloying and deoxidation the carbon content increases, the charge was composed only of the waste of alloyed steels, which are both produced directly at BakuSteelCompany LLC, and supplied from different engineering, shipbuilding and ship repair enterprises. In the preparation of the charge the goal was to use the maximum amount of waste of this steel grade or other brands close to it. Such a rational use of waste at BakuSteelCompany LLC provides great savings of alloying elements, electric power and increases the performance of the electric furnace.

As a result of the application of such a “precision” technology to the electric steel smelting, high-quality reinforcing steel of the AT500 grade with increased mechanical properties was obtained. The content of harmful impurities of phosphorus and sulfur in such steel is not exceeding the following values: for phosphorus - no more than 0.03, and for sulfur - no more than 0.025%.

## **5. Conclusion.**

1. Phosphorus removal reactions were carried out in a bath with liquid metal and their equilibrium ratios were evaluated. It is noted that during the formation of phosphorus anhydride in the slag, depending on the concentration of  $\text{SiO}_2$ , slag segregation can occur. For this purpose, a special chart has been drawn with areas of slag segregation at different  $\text{SiO}_2$  concentrations. The distribution coefficient of phosphorus at the metal – slag boundary was determined depending on the basicity of the slag. This coefficient was estimated by the composition of the slag.

2. The process of removing sulfur from the liquid bath was analyzed, and the provisions and reasoning existing in this area were expanded. The dependence of sulfur content on manganese concentration in FeS - MnS alloys at different temperatures has been established. The dependence of the distribution coefficient of sulfur diffusion on the slag-metal interface on the basicity of the slag (at different concentrations of FeO) has been established. The graphs of the distribution of sulfur depending on the composition of the slag at the metal-slag interface are presented. For the process of electric steel melting, the formula for the functional dependence of the desulfurization rate on the technology parameters is presented.

To ensure substantial savings of alloying elements, electricity and to increase the performance of the electric furnace, a charge of alloy steel waste was used. The charge was fed to the electric furnace continuously, in order to save electricity. Proper preparation of the charge allowed the use of the maximum amount of steel waste and to ensure the minimum amount of harmful impurities in the reinforcing steel. The amount of sulfur in the finished steel in this case amounted to 0.025%, and that of

phosphorus to 0.03%. Such purity of steel ensures the production of high-quality AT500 reinforcing steel with very high mechanical properties.

Currently, the reinforcing steel manufactured by BakuSteelCompany LLC is successfully used in the construction industry of Azerbaijan, Iran and the countries of the CIS. Since the start-up of the BakuSteelCompany LLC, that is, from 2000 to the present, no complaints have been received regarding the quality of these products.

### References

1. Процессы и машины электрометаллургического производства. Монография / С.Р.Рахманов, В.Л.Тополов, М.И.Гасик, А.Т.Мамедов, А.А.Азимов. Баку – Днепр: «Системные технологии» - Издательство «Сабах», 2017 – 568с.
2. Проектирование и оборудование электросталеплавильных и ферросплавных цехов: учебник / В.А.Гладких, М.И.Гасик, А.Н.Обчарук, Ю.С.Пройдак – Днепропетровк. ГНПП «Системные технологии», 2004, 736с.
3. Горобец В.Г., Гаврилова М.Н. Производство стали в дуговой печи. – М.: Metallurgia, 2006, 208с.
4. Кудрин В.А. Теория и технология производства стали: Учебник для вузов, М.: «Мир» ООО «Издательство АСТ», 2003, 528с.
5. Малиновский В.С., Малиновский В.Д., Ярных Л.В., Мошков В.А. Сравнительные плавки алюминиевых сплавов в дуговой печах постоянного тока нового поколения (ДППТНП) с другим более широко используемым плавильным оборудованием // ИТБ «Литье Украины», 2004, №2, (42).
6. Малиновский В.С., Малиновский В.Д., Ярных Л.В., Мошков В.А. Дуговые печи постоянного тока нового поколения (ДППТНП) ООП «НТФ» «ЭТКА» - новый путь повышения эффективности литейных и металлургических предприятий, улучшения качества выпускаемой продукции // ИТБ «Литье Украины», 2003, №11 (39).
7. Berg V. The Scaninject Journal of Metallurgy, 2003, V/3, P. 146 – 149.
8. Dunn E., Paridaens S., Freibuth A. Fachberichte Hüttenpraxis Metallweiterverarbeitung, 2003, V.21, №10, p.776-779.
9. Haissing M., Fuchs G., Auer W. EAF technology beyond the year, 2000, MPT International, №1, 1999, p.56-63.
10. Wusche E., Sinko R. EAF Steelmaking With quasisubmerged arcs and foamy slags // Iron and Steel Engineer, April, 2004, P. 35 – 40.
11. Wager F. Reality check for mini steel plant. Отчет компании Technometal для завода US Steel Duisburg, 1995, p.82.

12. Di Donato A., Volponi V., de Miranda U. Development of flexible operating practices to produce steel with Consteel EAF process in ORI Martin plant. Публикация компании Techint Technologies, Vennewbz, Май, 2002, p. 353 – 360.
13. Argenta P. The process and environmental benefits of Consteel, 2012, p.82-89.
14. Krouchinin A.M., Sawicri A.A. Theory of Electrical Arc Heating. The publishing office of Technical University of Constance, 2003, 174p.
15. Krouchinin A.M., Sawicki A. Piece 1 urzadzenialukowe. Wydawnictwo politechniki Czeskiej, Constance, 2000, 196R.
16. Бугеев А.М. Металлургия стали. М.: Металлургия, 1997, 439с.
17. Кочов С., Ершеников В.А. Физико-химическая и теплофизические особенности современного мартеновского процесса, М.: Металлургия, 2001, 488с.
18. Металлургия стали. В.И. Явойский, С.Л. Бантисманской и др. М.: Металлургия, 1983, 816с.
19. Поволский Д.Я. Раскисленные стали. М.: Металлургия, 2002, 207с.
20. Явойский В.И. Теория процессов производства стали. М.: Металлургия, 1987, 790с.
21. Явойский В.И. Дорофеев Г.А., Повх И.Л. Теория продувки сталеплавильной ванны. М.: Металлургия, 1984, 435с.
22. Крамаров А. Д. Производство стали в электропечах. М.: Металлургия, 2008, 455с.
23. Ойкс Г.Н., Иофоре Х.М. Производство стали. М.: Металлургия, 2009, 520ч.
24. Ойкс Г.Н., Иофоре Х.М. Производство стали М.: Металлургия, 2004, 625с.
25. Bason N. Iron and steel, 2005, April, V, v. 18, N4, 124p.