THERMODYNAMIC AND KINETIC FEATURES OF PHOSPHORUS OXIDATION DURING PHOSPHOROUS CAST IRON TREATMENT

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Results of thermodynamic and kinetic analyses of phosphorus oxidation during blowing phosphorous cast iron in heavy-duty converters are presented. In the final blowing stage phosphorus oxidation is limited by the stage of its mass transfer from the metal volume towards the slag-metal boundary.

Keywords: phosphorous cast iron, thermodynamics, kinetics, oxidation, process limitation.

Good steel mechanical and production properties are mainly governed by the concentration of harmful impurities and metal cleanliness. In view of this questions connected with studying chemical features of thorough oxidation refining of iron-carbon melt and creation based upon it of new production processes providing thorough metal dephosphorization and quite a low level of metal oxidation under phosphorus transfer conditions are an important task.

**Phosphorus Oxidation Reaction Thermodynamics and Kinetics**

In accordance with molecular theory of molten slag structure the reaction system for phosphorus removal from metal be written

$$2[P] + 5(FeO) + 4(CaO) = (4CaO \cdot P_2O_5) + 5[Fe] \tag{1}$$
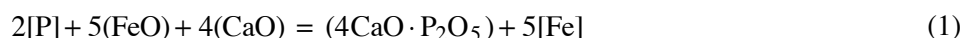
or in simpler form as a phosphorus oxidation reaction

$$2[P] + 5(FeO) = (P_2O_5) + 5[Fe]. \tag{2}$$

From the point of view if ionic representation of molten slag structure the oxidation reaction for phosphorus has the form

$$[P] + 2.5(Fe^{2+}) + 4(O^{2-}) = (PO_5^{3-}) + 2.5[Fe]. \tag{3}$$
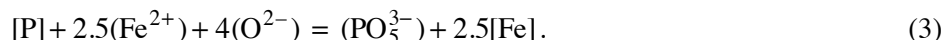
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Reaction (1)–(3) equilibrium constants are:

$$K_1 = \frac{a_{(4CaO \cdot P_2O_5)}}{[P]^2 \cdot a_{(CaO)}^4 \cdot a_{(FeO)}^5}, \tag{4}$$

where $a_{(4CaO \cdot P_2O_5)}$, $a_{(CaO)}^4$, $a_{(FeO)}^5$ are correspondingly equilibrium activities for calcium tetraphosphate, calcium oxide, and ferrous oxide in slag; [P] is phosphorus equilibrium concentration in metal.

$$K_2 = \frac{a_{(P_2O_5)}}{a_{(FeO)}^5 \cdot [P]^2} \tag{5}$$

where $a_{(P_2O_5)}$, $a_{(FeO)}$ are correspondingly equilibrium activity od phosphorus and iron oxide in slag; [P] is phosphorus equilibrium concentration in metal.

$$K_3 = \frac{x_{PO_4^{3-}}}{[P] \cdot [O]^{2/5} \cdot x_{O^{2-}}^{3/2}}, \tag{6}$$

where $x_{PO_4^{3-}}$, $x_{O^{2-}}^{3/2}$ are ionic proportions of phosphorus and oxygen anions in slag; [P], [O] are equilibrium concentration of phosphorus and oxygen in metal.

Equations (4)–(6) make it possible to express equilibrium minimal phosphorus contents in metal under slag of prescribed chemical composition with a maximum level of oxidation capacity:

$$[P]_1 = \left(\frac{a_{(4CaO \cdot P_2O_5)}}{K_1 \cdot a_{(CaO)}^4 \cdot a_{(FeO)}^5} \right)^{1/2}, \tag{7}$$

$$[P]_2 = \left(\frac{a_{(P_2O_5)}}{a_{(FeO)}^5 \cdot K_2} \right)^{1/2}, \tag{8}$$

$$[P]_3 = \frac{x_{PO_4^{3-}}}{K_3 \cdot [O]^{5/2} \cdot x_{O^{2-}}^{3/2}}. \tag{9}$$

A summary of experimental data obtained by Winkler and Shipman about equilibrium reaction (1) made it possible for the authors of [1, 2] to obtain a temperature dependence of equilibrium constants that has the following form

$$lqK_1 = \frac{40067}{T} - 15.06. \tag{10}$$

The equilibrium constant for reaction (2) calculated by V. A. Kozheurov by experimental data from a number of researchers [3] in the temperature range 1590–1610°C hardly changes and takes a value of a constant equal on average to 0.0229.

The following equation for the equilibrium constant temperature dependence is quite well known [3]:

$$lqK_3 = 7x_{Ca^{2+}} + \frac{14660}{T} - 7.44 .$$ (11)

There is quite extensive use of slag activity constant calculation developed by Kozheurov [3]. Slags are considered as a regular ionic solution consisting of simple ions and not containing complexes. In calculation of ion activity Kozheurov only considered thermal effects of mixing components and by using statistical thermodynamic methods gave an expression for ion activity coefficients in slags, in particular for the system FeO–MnO–CaO–MgO–SiO$_2$–P$_2$O$_5$ being of most interest for steel smelters. An equation has been obtained by a semi-empirical method for ferrous oxide activity coefficients

$$lq\gamma_{FeO} = \frac{1000}{T} \Big[2.18 \cdot x_{MnO} \cdot x_{SiO_2} + 5.90(x_{CaO} + x_{MgO}) \cdot x_{SiO_2} + 10.50 \cdot x_{CaO} \cdot x_{P_2O_5} \Big]$$ (12)

and phosphorus pentoxide

$$lq\gamma_{P_2O_5} = lq\gamma_{FeO} - \frac{1000}{T} \cdot x_{CaO} .$$ (13)

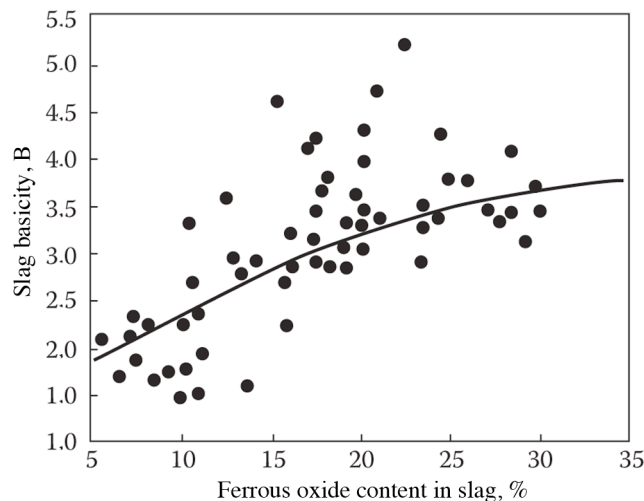## Calculation of Equilibrium Phosphorus Content in Metal and Evaluation of Model Adequacy

By summarising the equations provided above, obtained on the basis of experimental data and molecular and ionic theories for molten slag, an algorithm has been developed for calculating the phosphorus equilibrium content in metal beneath slag of prescribed chemical composition that was put into Basic language and implemented in a computer. For calculation Winkler, Shipman [4, 5] data were used obtained by them during a study of the equilibrium distribution of phosphorus between slag and metal. Slag chemical composition varied in a wide concentration range (FeO = 2.55–51.76%, MnO = 0–12.18%, CaO = 10.89–58.8%, SiO$_2$ = 2.36–27.72%, P$_2$O$_5$ = 1.67–26.9%), and metal temperature was within the limits 1590–1610°C.

The reliability of the calculation models used for the equilibrium phosphorus content was evaluated by the deviations of actual phosphorus concentrations [P]$_{act}$ on calculated [P]$_{equ}$ by Eqs. (7)–(9). A histogram for deviations is given in Fig. 1.

Therefore, from the procedures considered within the volume of work calculation of the equilibrium phosphorus content in metal over a wide range of slag chemical composition, the lowest absolute error is exhibited by a model based on regular ionic solution theory.

This is mainly due to the fact that the Kozheurov model proposed, in spite of considerable simplification of molten slag structure, in contrast to complete ionic solution theory and moreover molecular theories, the main feature is the different nature of bonds between structural elements of a solution and as a consequence the non-ideal nature of energy.

Completeness for occurrence of the reaction is assessed from the value of deviation of the metal-slag system from equilibrium during oxidation refining. Deviation from equilibrium in the slag-metal system has been studied using a model for calculating the metal equilibrium phosphorus content based on regular ionic solution theory. Calculations for the phosphorus equilibrium content in metal beneath slag with a different iron oxide content (13.0–33.0%) showed that thermodynamically highly basic slag exhibits adequate phosphorus absorption capacity even with a low level of system oxidation capacity (Table 1).

**Fig. 1.** Effect of slag oxidation capacity on its basicity.

Table 1
Phosphorus Equilibrium Content and Change in Slag Composition

Slag chemical composition, %						Slag basicity	Phosphorus content, %
CaO	SiO$_2$	P$_2$O$_5$	MnO	MgO	FeO		
39	8	5	3	5	31	3	0.012
42	9	5	3	5	27	3	0.011
45	10	5	3	5	23	3	0.01
40	5	5	3	5	33	4	0.01
44	6	5	3	5	28	4	0.008
48	7	5	3	5	23	4	0.008

However the actual phosphorus content in metal achieved in test melts beneath a slag with basicity modulus 3.0–4.0 and oxidation level 14.5–27.7% considerably exceeds the equilibrium concentration (Fig. 2). Presence of a super-equilibrium phosphorus content in metal beneath slag of prescribed chemical composition points to presence of difficulties in the occurrence of the phosphorus oxidation reaction during refining of an iron-carbon melt, i.e., it points to existence of a limiting link holding back occurrence of this process.

Therefore, the thermodynamic calculations completed for metal phosphorus content beneath slag, corresponding with respect to chemical composition to the concluding blowing stage, have confirmed the fundamental possibility for occurrence of thorough dephosphorization during oxidation refining of iron-carbon melt with a low slag oxidation potential.

Macrokinetics of actual metallurgical processes are mainly determined by transfer processes. In this connection it is important to determine characteristics of heterogeneous reaction in order to reveal the limiting link and to describe individual stages quantitatively. A considerable amount of work [6–12] has been devoted to

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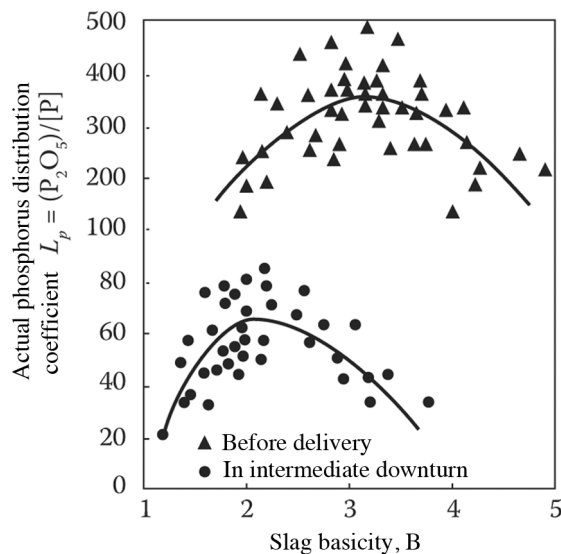
Fig. 2. Effect of slag basicity on actual phosphorus distribution coefficient between metal and slag.

studying the mechanism and kinetics of oxidation processes occurring within a steel melting bath [6–12], although until now there is no single point of view on the question of the limiting link of phosphorus oxidation reaction during oxidation refining of an iron carbon melt.

Individual authors [1, 13] confirm that phosphorus oxidation is controlled by the chemical reaction rate occurring at an interphase surface. Research conducted using radioactive isotopes [13] has shown that the phosphorus oxidation chemical reaction proceeds instantaneously, and the process is determined by phase mixing conditions.

A number of authors [14–17] consider that oxidation may be limited by stages of internal mass transfer, especially with low component concentrations in a melt. This contradiction of existing ideas about a limiting link of the phosphorus oxidation reaction is due mainly to scale and concentration factors. Quantitative characteristics of individual stages of the process depend essentially on controlling substance concentration, and size and form of the reaction surface. Therefore, within the volume of existing work an attempt has been made to clarify kinetic features of the phosphorus oxidation component proceeding during oxidation refining of the Fe–1.0%C–0.3%P system in heavily loaded converters.

Research has been conducted in the AO ArselorMittal Temirtau converter workshop in 300-ton converters operating by a system for gas extraction with partial combustion. Phosphorus behavior has been studied during blowing of the second melting period. Test melts were conducted by existing production instructions. The slag forming materials used were lump limestone and dolomite. During performance of an experiment temperature measurement was accomplished and metal and slag samples were selected in the intermediate downturn of the converter and on completion of the main second blowing period. The content of carbon, manganese, phosphorus and sulfur was determined within metal samples, and the concentration of individual slag components was determined by chemical analysis.

Verification of the assumption of limiting phosphorus oxidation process in an iron-carbon melt for the stage of the adsorption chemical link was conducted according to values of the apparent activation energy calculated by an Arrhenius logarithmic equation:

$$E = 2.303R \cdot \frac{Lg(K_2/K_1)}{(1/T_1 - 1/T_2)}, \qquad (14)$$

where R is universal gas constant; K_2, K_1 are reaction constants; $1/T_1$, $1/T_2$ are phosphorus oxidation rate ratios at T_1 and T_2.

It is well known [3] that if the apparent activation energy exceeds 400–420 kJ/mole then the process is limited by a chemical or adsorption link. With values of apparent activation energy less than 150–170 kJ/mole the process is limited by the diffusion component.

It has been established by experiment that with an average metal phosphorus concentration for the second melting period of 0.07% the oxidation rate with temperature in the system of 1545°C corresponds to 0.0146%/min, and at 1580°C it corresponds to 0.0176%/min. With stable uniform conditions it may be assumed that $K_1/K_2 = V_1/V_2$ and by using Eq. (14) to calculate the apparent activation energy. Values of apparent activation energy obtained $E = 115$kJ/mole) indicate that the phosphorus oxidation process under the specific conditions considered cannot be limited by the chemical reaction stage, but it is probably determined by the diffusion component.

The diffusion component of a heterogeneous phosphorus oxidation reaction includes several stages: supply of oxidizing agent to the phase interface, phosphorus diffusion within metal, and removal of reaction products into the slag phase. A limiting link of this process may be determined from the ratio of the rates for each stage [14]:

$$\alpha \approx \frac{(C)}{[C]} \cdot \left(\frac{D_C^{sl}}{D_C^{met}} \right)^{0.5}, \tag{15}$$

where

   (C), $[C]$ are component content in slag and metal, %;

   D_C^{sl}, D_C^{met} are diffusion coefficients for components in slag and metal, m^2/sec.

With $\alpha < 1$ the process is limited by component diffusion within slag and with $\alpha > 1$ by the diffusion of components within metal. If $\alpha = 1$ then the process is limited simultaneously in both phases.

We determine the ratio of rates for possible individual stages of the phosphorus oxidation reaction in the system Fe–1.0%C–0.3%P by using an expression [15]:

$$\alpha_{(P_2O_5/P)} \approx \frac{(P_2O_5)}{[P]} \cdot \left\{ \frac{D_{(P_2O_5)}}{D_{[P]}} \right\}^{0.5}, \tag{16}$$

$$\alpha_{(FeO/P)} \approx \frac{(FeO)}{[P]} \cdot \left\{ \frac{D_{(FeO)}}{D_{[P]}} \right\}^{0.5}, \tag{17}$$

$$\alpha_{(FeO/P_2O_5)} \approx \frac{(FeO)}{(P_2O_5)} \cdot \left\{ \frac{D_{(FeO)}}{D_{(P_2O_5)}} \right\}^{0.5}. \tag{18}$$

Diffusion coefficients were adopted from data of authors in [3, 6-9]. Calculations of the rate ratios for the possibilities of individual components of the dephosphorization process, fulfilled according to Eqs. (16)–(18), showed that within the limits of reliability adopted for calculating diffusion coefficients the phosphorus oxidation rate cannot be limited by oxidizing agent supply to the reaction front (Table 2). The value of $\alpha_{(FeO/P)}$ significantly exceeds one.

Table 2
Relationship of Rate Possibilities for Dephosphorization Process

Test number	Slag chemical composition, %		Metal phosphorus content [P], %	Temperature, °C	Ratio		
	(FeO)	(P_2O_5)			$(P_2O_5)/[P]$	(FeO)/[P]	$(P_2O_5)/(FeO)$
1	10	10	0.3	1500			
2	15	7	0.1	1550	6.4	55	0.12
3	25	5	0.01	1600	44.7	10.1	0.04

Ratios of rate possibilities for the process obtained within the limits of reliability adopted for calculating diffusion coefficients for the value of rate possibility ratios indicate that the phosphorus oxidation rate cannot be limited by supply of oxidizing agent to the reaction front. The value of $\alpha_{(FeO/P)}$ significantly exceeds one.

These data are in good agreement with results provided in Fig. 2. In fact, theoretically in order to provide thorough dephosphorization it is sufficient to have a level of slag oxidation capacity of 12–15%, and this is lower by a factor of 1.5–2 than the actual ferrous oxide concentrations in slags in the concluding stage of blowing.

As is seen from Table 2, the phosphorus oxidation process cannot be limited by removal of reaction products since $L(P_2O_5)/[P]$ significantly exceeds one and varies from 3.3 at the start of blowing of the first period to 44.7 at the end of blowing.

The most probable retarding factor in the phosphorus oxidation case in question in the Fe–1.0%C–0.3%P system is internal mass transfer, i.e., phosphorous transport from the volume of metal towards the reaction front. In this case the phosphorus oxidation rate should be described by a differential equation [3]:

$$\frac{d[P]}{d\tau} = \beta \left(\frac{S}{V} \right) ([P]_0 - [P]_n),\qquad(19)$$

where

β is phosphorus mass transfer coefficient in metal, m/min;

S is surface area in which the reaction proceeds, m^2;

V is metal volume, m^3;

$[P]_0$, $[P]_n$ are correspondingly phosphorus concentration within the volume of metal and at the slag boundary, %.

Since the phosphorus oxidation reaction proceeds at the metal-slag surface, then its surface concentration as a rule approaches equilibrium, whose value is low compared with the phosphorus content within the volume of metal. This is confirmed by research performed in the KarMK workshop converter [14–17]. The phosphorus content in metal samples collected beneath slag is less by a factor of 1.2–1.8 than the phosphorus content within the volume of metal. Therefore, taking account of Eq. (19) the oxidation rate maybe described in the following form;

$$V = \frac{dP}{d\tau} = \beta \cdot \frac{S}{V} \cdot [P]_{sp},\qquad(20)$$
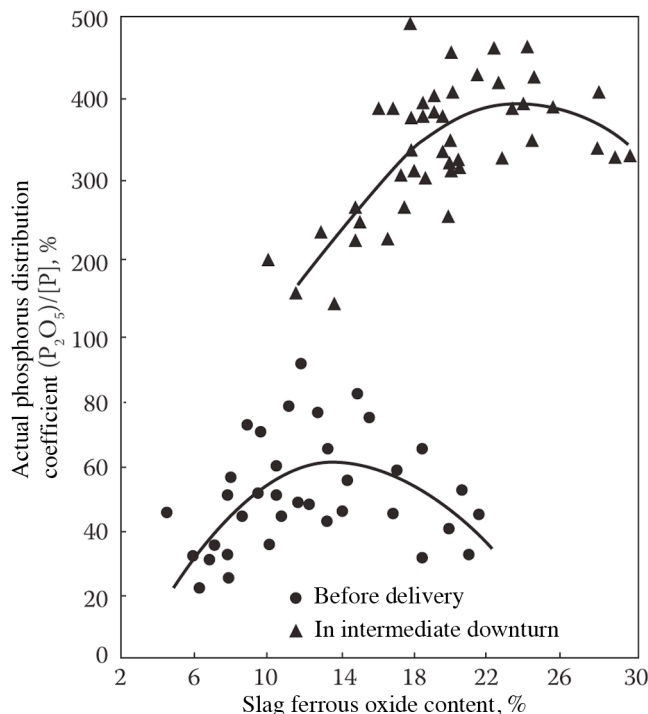
Fig. 3. Dependence of actual phosphorus distribution on slag ferrous oxide content.

from which it follows that the rate of heterogeneous reaction for phosphorus oxidation in the Fe–1.0%C–0.3%P system is determined to a first approximation by the phosphorus concentration the volume of metal.

Experimental data provided in Fig; 3 almost confirm the assumption made above about the limiting role of phosphorus internal mass transfer from the volume of metal towards the reaction front. In fact, dephosphorization develops in two regimes separated by the critical phosphorus concentration equal to 0.25%. With a phosphorus concentration less than 0.25% the process occurs by an intradiffusion regime and it is most clearly defined by the intradiffusion region for occurrence of the process with metal phosphorus content less than 0.06–0.10%. A further increase in phosphorus concentration up to 0.25% is accompanied by an increase experimental data scatter, although the tendency towards an increase in phosphorus oxidation rate with an increase in its concentration is maintained. The scatter in experimental data obtained with a high metal phosphorus concentration is apparently due to combined occurrence of dephosphorization from the intradiffusion region in a mixed diffusion-kinetic region, where the phosphorus oxidation rate is not determined by its diffusion in metal $[P]_O^{cr} >$ 0.25%, but is limited by diffusion in slag and the fact of chemical interaction.

Therefore, the heterogeneous phosphorus oxidation rate in the Fe–1.0%C –0.3%P system with a metal phosphorus content of mot less than 0.25% is limited by the intradiffusion link, i.e., phosphorus transfer from the volume of metal towards the reaction front occurrence and with a reduction in phosphorus concentration its oxidation rate decreases sharply. This due primarily to deterioration of mass exchange conditions.

The mass transfer rate as already noted is determined by the component concentration, phase surface, and mass transfer coefficient (equation 20). The main parameter governing mass transfer conditions in a liquid bath is the intensity of gas liberation within it, and in particular the carbon oxidation rate [14–17]. With an increase in gas liberation intensity there is an increase in slag emulsification and an increase in slag-metal contact surface. This undoubtedly facilitates acceleration of oxidation processes at the metal boundary with slag. However, carbon oxidation changes strongly in the course of blowing and correspondingly there is a significant change

in the overall specific capacity for bath stirring, as a rule achieving a minimum value at the end of blowing when the power of bath mixing due to CO bubbles decreases sharply due to a reduction in carbon oxidation rate, and the oxygen stream energy appears to be inadequate for intensification of mass transfer processes. This is the main reason for significant slag over-oxidation since with slow phosphorus oxidation rates at the end of blowing in order to provide thorough metal dephosphorization it is necessary to increase the blowing duration and as a consequence overall oxygen consumption.

Melting low-carbon steel especially of high quality for producing thin-sheet cold-rolled product under phosphorus limit conditions is connected with certain production difficulties connected with a requirement for preparing metal with a low final phosphorus and sulfur content, and a relatively constant level of metal and slag oxidation before discharge into a ladle

On the other hand, considering questions connected with oxidation capacity of oxygen-converter metal it is necessary to emphasize the following: during melting of low-carbon rimmed steel an extremely important index is not only achievement of a certain average level of metal oxidation, but also provision of the maximum possible stabilization of metal oxidation during discharge, i.e., provision of low limits for the change in oxygen concentration in individual melts, which with a fixed deoxidation regime and prevention of slag entering into a ladle provides preparation of a high quality rimmed steel ingot.

In view of the thermodynamic and kinetic features revealed for the behavior of phosphorus and oxygen within metal in the concluding stage of blowing it is noted that in order to obtain a lower concentration of sulfur, phosphorus and oxygen there are kinetic difficulties connected with worsening of mass transfer processes in a converter bath with a low carbon concentration. However, an increase observed in actual iron oxide concentration in slag requires clarification of the slag melting regime, noting substantiated limits for a changes.

Treatment of the results for industrial melts in AO ArselorMittal Temirtau300-ton converters in the ferrous oxide range in slag within limits of 5.0–30.0%, metal temperature 1520–1640°C it has been established that an increase in ferrous oxide in slag facilitates an increase in slag basicity and more complete assimilation of limestone is achieved (see Fig. 1) that is described by the following equation:

$$B = 1.181 + 0.131(FeO) - 0.00167(FeO)^2, \tag{21}$$

$$r = 0.607, \quad \mu = 12.78.$$

A characteristic of the dephosphorization process is the ratio:

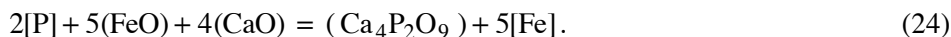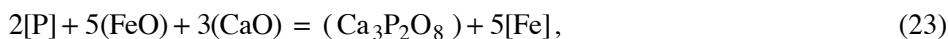$$L_d = \frac{(P)}{[P]}, \tag{22}$$

where

L_d phosphorus distribution coefficient;

(P), [P] are phosphorus content within volumes of slag and metal respectively.

The levels required for phosphorus oxidation are determined with consideration of equilibrium constants for the overall reaction [3, 6]:

$$2[P] + 5(FeO) + 3(CaO) = (Ca_3P_2O_8) + 5[Fe], \tag{23}$$

$$2[P] + 5(FeO) + 4(CaO) = (Ca_4P_2O_9) + 5[Fe]. \tag{24}$$

The most stable phosphorus in the $CaO–P_2O_5$ system is the grouping $(Ca_4P_2O_9)$ [1], and from an equilibrium reaction equation (24):

$$K_d = \frac{(P_2O_5) \cdot f_{(CaO)_4 P_2O_5}}{[P]^2 \cdot (FeO)^5 \cdot f_{FeO}^5 \cdot (CaO)^4 \cdot f_{CaO}^4} \qquad (25)$$

we find the value of the phosphorus distribution coefficient:

$$L_d = \frac{P_2O_5}{[P]^2} = K_d \cdot (FeO)^5 \cdot (CaO)^4 \cdot f_{11}, \qquad (26)$$

where

$$f_{11} = f_{FeO}^5 \cdot f_{CaO}^4 / f_{Ca_4P_2O_9}. \qquad (27)$$

The value of f_{11} (ratio of component activity coefficients at the corresponding levels) is a complex function of slag composition. Phosphorus under equilibrium conditions is transferred from slag into metal more completely the greater the activity values for ferrous oxide and calcium oxide and the lower the metal temperature.

An optimum ratio is evident from Eq. (26) between the ferrous oxide and calcium oxide contents in slag providing a maximum dephosphorization effect (see Figs. 2, 3).

The extreme nature of the change in the dependence of L_d on slag ferrous oxide content may be explained by a reduction in a_{CaO} with an increase in ferrous oxide in view of a reduction in a_{FeO} as a result of forming calcium ferrite (Fig. 3). More precisely this limitation also applies for a_{FeO} with fixed values of calcium oxide content in slag, i.e., with a certain level of a_{FeO} there is a sharp reduction in the value of a_{CaO} (as a result of forming calcium ferrite) (see Fig. 3).

Results of treating test melt data show that the maximum phosphorus distribution coefficient between slag and metal for each of the periods corresponds to a diffract value of slag basicity. In this sense production studies confirm the previously established extreme relationship between values of ferrous oxide, slag, and basicity established in studies in 1946 [5]. On the other hand, results of studying research results make it possible to establish that for each converter slag composition (intermediate and final) there are optimum temperatures providing the most complete bath dephosphorization (see Figs. 2, 3). Equation (25) and (26) obtained from the results of production studies point to the fact that:

  – he concentration of residual phosphorus content in metal depends on the combined effect of iron oxide and calcium oxide in slag at a given temperature, and also on P_2O_5 content in slag;

  – the phosphorus distribution between slag and metal (distribution coefficient $(P_2O_5)/[P]$ or dephosphorization coefficient) depends on (Fe)) concentration in slag and its basicity.

Statistical treatment of results of these studies make it possible to establish that the highest phosphorous distribution coefficient in the first period with a comparatively narrow temperature range (1520–1560°C) is observed with basicity of 1.8–2.5 units (equation (23)) and in the concluding blowing stage at 1590–1620°C it is 3.0–3.5 units (equation (24)) (see Fig. 2):

$$L_d^{act} = -149.11 + 199.12 \cdot B - 44.25 \cdot B^2, \tag{28}$$

$$r = 0.785, \quad \mu = 11.95;$$

$$L_d^{act} = -1250 + 1075 \cdot B - 175 \cdot B^2, \tag{29}$$

$$r = 0.735, \quad \mu = 11.75.$$

Considering the expediency of increasing slag basicity it should be remembered that operation with slags of increased basicity is correct in the case when complete assimilation of limestone is achieved and not due to the high iron oxide content in slag. Then it is important how the calcium oxide content achieves prescribed slag basicity.

The phosphorus distribution coefficient in relation to slag ferrous oxide content is described by the following regression equations (30) and (31) (see Fig. 3):

– for the first period:

$$L_d^{act} = -51.88 + 17.67 \cdot (FeO) - 0.67 \cdot (FeO)^2, \tag{30}$$

$$r = 0.654, \quad \mu = 12.99;$$

– for final slag:

$$L_d^{act} = -517.94 + 77.81 \cdot (FeO) - 1.64 \cdot (FeO)^2, \tag{31}$$

$$r = 0.696, \quad \mu = 13.45.$$

During blowing cast iron with a different phosphorus content a requirement arises for obtaining a certain slag oxidation capacity in order to provide the minimum steel phosphorus content (see Fig. 3). The greatest degree of phosphorus removal is provided with a certain ratio of (FeO) and (CaO) concentrations. During evaluation of the role of (FeO) and CaO) during phosphorus oxidation it is necessary to find whether occurrence of reaction (24) is impossible with absence of iron oxide (Fe^{2+} cations) capable of providing oxygen transfer from slag into metal. As far as component CaO (Ca^+) is concerned then it is capable not only of moving equilibrium of reaction in the iron direction with formation of calcium phosphates $(CaO)_3 P_2O_5$ or $(CaO)_4 P_2O_5$ (Ca^{2+}, PO_4^{3+} ions), although in the absence of iron oxide in slag this is impossible.

An important conclusion of studying phosphorus cast iron in large converters is provision of the optimum ratio of decarbonizing and dephosphorization rates and avoidance of a period metal over-blowing. If at the instant of achieving the final carbon content there is no provision of prescribed phosphorus content then subsequent metal blowing with the aim of more complete phosphorus oxidation is retarded due to kinetic limitations established above and only leads to slag over-oxidation of slag and metal and a reduction in output.

The phosphorus removal rate from metal on the course of flushing proceeding at a metal-slag interphase boundary is determined by the rate of change in equilibrium value of its concentration due to slag composition and temperature:
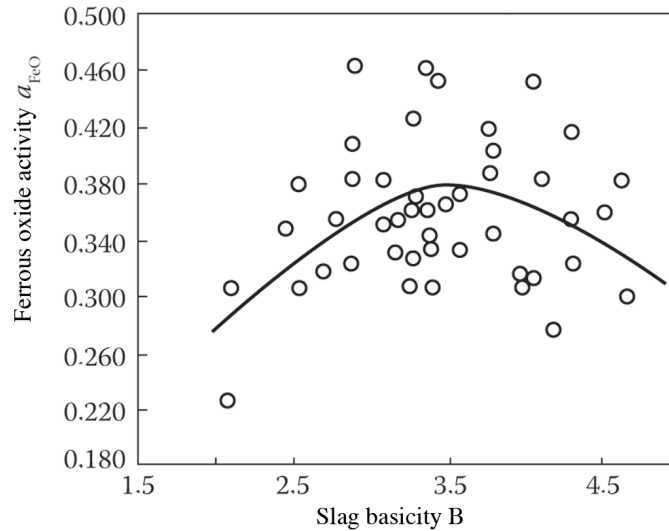
Fig. 4. Effect of slag basicity on ferrous oxide activity.

$$[P] = A_{0.5}/[O]_s^{2.5} K_d^{0.5}, \tag{32}$$

where $A = a_{Ca_4P_2O_9}/a_{CaO}^4$; $[O]_s$ slag oxygen concentration in metal in equilibrium with slag %.

Phosphorus is oxidized more rapidly the faster there is an increase in slag basicity, the lower P_2O_5 in slag (since in this case there is a more rapid reduction in the value of $A = a_{Ca_4P_2O_9}/a_{CaO}^4$) and the higher the ferrous oxide content in slag governing the equilibrium value $[O]_s$.

Dephosphorization in the course of melting should be accomplished not only in the direction of obtaining the least phosphorous content in metal, but also in the direction of continuous reduction on the P_2O_5 content.

A high P_2O_5 content (more than 15–20%) in slag retards the reduction in value of A, and in order to provide more rapid dephosphorization it is necessary to create those conditions with which there would be a more rapid increase in slag basicity with retention of a corresponding quite high ferrous oxide content in slag, required both from the point of view of accelerating calcium oxide dissolution and also in order to obtain an adequate value of $[O]_s$. This leads to formation in a converter bath of an excess amount of slag that complicates conducting melting due to the unstable course of flushing with discharge of slag-metal emulsion through the mouth of the converter and leads to metal loss with discharged slag.

With stable uniform conditions the slag composition and mainly its basicity have a significant effect on metal and slag oxidation capacity. The iron content in slag and basicity affect each other reciprocally. An increase in slag oxidation capacity facilitates dissolution of added limestone and preparation of a highly basic fluid slag, and an increase in slag basicity leads to an increase in iron oxide activity is slag (Fig. 4). An increase in slag basicity facilitates an increase in oxygen ion activity in molten oxide that in accordance with the distribution rule causes an increase in oxygen ion flow from slag into metal. An increase in slag basicity above certain limits (for our conditions above 3.5) reduces iron oxide activity in t slag, which leads to retardation of the oxygen ion transfer process from slag into metal and reduces the oxygen concentration in metal (see Fig. 4).

Therefore, metal oxidation capacity only increases with an increase slag basicity to a certain value and with a subsequent increase in basicity the metal oxidation capacity is reduced. The effect of blast regime on converter bath oxidation capacity is clearly illustrated with final blowing.
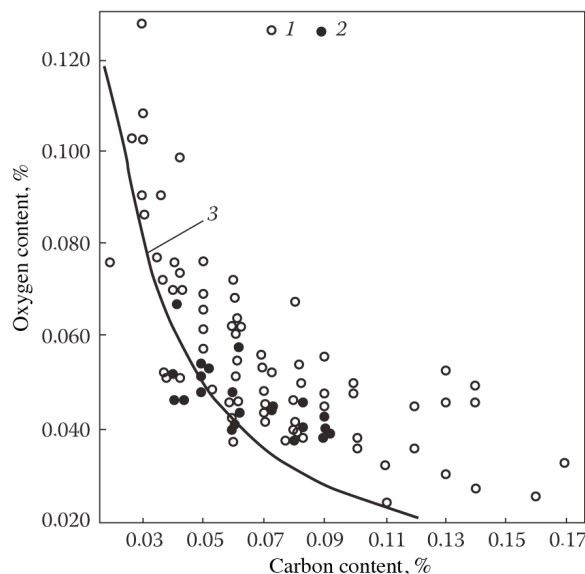
Fig. 5. Effect of thickening addition (coke and limestone) to a converter on metal oxidation capacity before discharge: *1* – melting without final slag thickening; *2* – melting with final slag thickening; *3* – equilibrium curve [C] = [O] = 0.0025.

Drawing attention to the fact that the oxygen content decreases with an increase in slag basicity above 3.5 test melts have been conducted with oxygen consumption increased to 2.100–1100 nm^3/min and lowering of the lance position to 1.2–1.4 m for 1–2 min before the end of blowing with deposit in a bath of 2–3 tons of limestone and 1.0–1.5 tons of coke. Data for melts of the test and comparative versions are provided in Fig. 5.

Adding coke and limestone to a converter during blowing leads not only to metal and slag acidification, but also to an increase in calcium oxide content and slag neutralization that as has been demonstrated above leads to a reduction in oxygen content and its approach towards equilibrium (see Fig. 5). At the instant of adding a mixture there intense bath boiling that in turn leads to additional mixing and an increase in metal-slag interface (S_{m-s}) and the degree of the phosphorus oxidation reaction with low carbon concentration is due to approach of the actual phosphorus concentration towards equilibrium for slag of the flushing concluding stage. Moreover, due to appearance of new centers (nuclei) for formation of CO bubbles the carbon oxidation process accelerates both dissolved in metal, and also coke carbon, there is an increase in metal-gas interface (S_{m-g}) and reduces metal a slag over-oxidation capacity (see Fig. 5).

Therefore, on the basis of these studies the following have been established:

1. An ultra-equilibrium phosphorus concentration at the end of oxidation refining of phosphorus cast iron is connected with limiting the process of supply of phosphorus from the volume of the bath to the front for occurrence of reaction connected with deterioration of mass exchange processes in the concluding blowing stage due to a reduction in carbon oxidation rate and the intensity of gas liberation. Metal and slag over-oxidation in the concluding stage of blowing is explained by limitation of the process for decarbonizing with a low carbon content for the stage of CO bubble generation.

2. An increase in mixing power with an oxygen stream and an increase in metal-slag interface and metal-gas with additions of slag-forming and neutralizing materials makes it possible to conduct more thorough dephosphorization, to reduce metal and slag over-oxidation, to reduce and stabilize metal degree of oxidation within narrow limits, and in addition to perform slag neutralization and thickening.

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