Kinetics of Phase Interaction During Secondary Cast Iron Melting

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ABSTRACT

The article deals with the kinetics of phase interaction during secondary cast iron melting in cupolas and electric furnaces. The calculation of mass transfer according to the equations of electrochemical kinetics is possible only for individual cases. As the task of secondary melting of cast iron is to achieve a certain composition of cast iron, it is advisable to program complex mass transfer processes in the form of a generalized function, including the transport coefficients and the driving force of mass transfer. It is proposed to introduce the notion of the visible mass transfer coefficient (k^v), which is the density of the mass flow of an element related to one percent of the element's concentration in cast iron. The interaction of phases in devices for secondary cast iron melting is analyzed according to the laws and periods of melting. A mathematical model of mass transfer during secondary cast iron melting has been developed. Studies were conducted using a laboratory gas cupola and a 700 kg/h gas cupola, and quantitative characteristics of mass transfer have been established.

Keywords: *Secondary cast iron melting, Kinetics of phase interaction, Mass transfer during melting, Mathematical model of mass transfer.*

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1. INTRODUCTION

1.1. Theoretical Background

The kinetics of heterogeneous reactions between metal, slag and gas in devices of secondary cast iron melting has not been studied sufficiently and is rather complicated (Grachev, 2016). Mass transfer is interpreted by analogy with the theory of heat transfer. In this case, the mass flux density of the *i*-th component (m_i) in molecular diffusion is treated by analogy with the Fourier law in the form of the following formulation of Fick's law:

$$m_i = -\mathrm{D}_i grad\, \rho_i \ \mathrm{kg}/s \cdot \mathrm{m}^2, \qquad (1)$$

where D_i is the diffusion coefficient; ρ_i is partial density of the *i*-th component, kg/m^3.

For stationary diffusion conditions: $m_i = \mathrm{D}_i \frac{\rho_0 - \rho_s}{h} = \beta(\rho_0 - \rho_s)$ kg/s, where ρ_0 and ρ_s are partial density at the beginning (h) and density on the surface at the end of the diffusion; $\beta = \frac{\mathrm{D}_i}{h}$ is the mass transfer coefficient, cm/s. Mass transfer by diffusion is considered as the sum of two processes: molecular and convective diffusion.

The differential equation of convective diffusion is written as: $\frac{\partial C}{\partial \tau} + v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} + v_z \frac{\partial C}{\partial z} = \mathrm{D}\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right)$, where v_x, v_y, v_z are components of the flow velocity along the corresponding axes.

The rate of convective and molecular diffusion and mass transfer in the boundary layer does not usually coincide with the speed of the chemical act itself and the adsorption phenomena accompanying it. The analogy with heat transfer is only partial, but there is a tendency to bring the analogy to the full expression of the mass transfer coefficient. Thus, the total mass transfer coefficient for stationary diffusion in two layers is expressed by the formula: $\frac{1}{\beta} = \frac{1}{\beta_I} + \frac{1}{\beta_{II}}$.

In this case, we are only dealing with diffusion and it is more correctly to call β the coefficient of mass conductivity by analogy with the theory of heat transfer (D/n).

The mass transfer coefficient (k) is proposed (Wagner, 1936) to be interpreted as follows: $\mathrm{k} = \frac{1}{\frac{1}{\beta_1} + \frac{1}{\alpha_1} + \frac{1}{\alpha_x} + \frac{1}{\alpha_2} + \frac{1}{\beta_2}}$, where β is the coefficient of mass transfer by convection $\frac{1}{\beta} = \frac{1}{\beta_{md}} + \frac{1}{\beta_{cd}}$ (β_{md} is the coefficient of mass conductivity or mass transfer of molecular diffusion; β_{cd} is the coefficient of mass transfer by convective diffusion); α is the mass transfer coefficient in the boundary layer $\alpha = -\frac{D}{\Delta C}\left(\frac{\partial C}{\partial n}\right)_{n=0}$, α_x is the coefficient of interphase mass transfer, for example, in a chemical reaction, during dissolution, etc. $\frac{1}{\alpha_x} = \frac{1}{\alpha_a} + \frac{1}{\alpha_x'} + \frac{1}{\alpha_D}$; α_a and α_D are the coefficients characterizing adsorption and desorption; α_x' is the mass transfer coefficient itself in a chemical reaction or in another process of transport across the phase interface.

Equations of electrochemical kinetics for the oxidation of elements in various regimes as $(FeO) + \left[\frac{n}{m} \cdot Me\right] = [Fe] + \left(\frac{1}{m} Me_n O_m\right)$ are known (Grachev, 2016). Experimentally determined oxidation rates are commonly used for practical calculations (g·at/cm^2·s) (Grachev, 2016)

for carbon:

$$j_C = 2.2 \cdot 10^{-2} \exp(-16{,}200/T)(\% \cdot FeO)^{0.4} \cdot [C]^{0.65}, \qquad (2)$$

for silicon:

$$j_{Si} = 0.9 \cdot 10^7 \exp(-\frac{43{,}500}{T}) \cdot a_{Si}^{0.84} \cdot a_{SiO_2}^{0.16} \cdot (\frac{a_{FeO}}{a_{FeO}^{eq}})^{0.1}, \qquad (3)$$

for manganese:

$$j_{Mn} = 6.5 \cdot 10^7 \exp(-50{,}500/T) a_{Mn}^{0.5} \cdot a_{FeO}^{0.5} \cdot (K_P^{Mn})^{0.3}. \qquad (4)$$

Studies of mass transfer in various metallurgical processes continue to this day (Bechetti *et al.*, 2014). They rely on the fundamental works of Rostovtsev (1969); Karabasov and Chizhikova (1986); Yesin and Toporishchev (1971), Thonstad and Hove (1964); Kronenberg (1969); Swalin (1959); Morse (1929); Nagasaka *et al.* (1985) etc.

These days they are presented in the proceedings of the 5th and 6th International Congress on Advances in Materials Technology (Sarver and Tanzosh, 2008; Blum and Bugge, 2011) of the European Symposium on Superalloys and Their Applications (Speicher *et al.*, 2010) the 33rd and 34th International Technical Conference (Gagliano *et al.*, 2008;2009). There are works on kinetics in alloys (Lippold *et al.*, 2011) etc.

The calculation of mass transfer according to electrochemical kinetic equations is possible only for the simplest cases, because the determination of surface concentrations, as well as other quantities included in the formulas, is very difficult.

1.2. Relevance

The kinetics of phase interaction processes is of great practical importance, since the composition of the resulting alloy is the result of mass exchange and, if it is impossible to predict, then there are certain difficulties in obtaining an alloy of the required composition.

Since the task of cast iron melting is to achieve a certain composition of cast iron, it is advisable to program complex mass transfer processes in the form of a generalized function that includes the transport coefficients and the driving force of mass transfer. Such a task for melting casting alloys has not been solved yet and is topical.

Cast iron melting in the foundry is performed in cupola and electric furnaces, and it is necessary to develop a mathematical model of mass transfer for these methods of melting, that is, for the so-called secondary cast iron smelting.

1.3. Purpose and Objectives of the Study

The purpose of the work is to develop a methodology for calculating the processes of mass transfer during cast iron melting.

1.4. Objectives of the Study

1. To propose a universal quantitative criterion or coefficient describing mass transfer over zones and periods of cast iron melting in various melting units.
2. To propose a mathematical model of mass transfer in secondary cast iron melting units.
3. To investigate mass transfer in gas-fired melting units – gas cupolas.

2. RESEARCH METHODOLOGY

The creation of a mathematical model of mass transfer with the proposed generalized criterion was carried out for specific zones and periods of melting (Figure 1). The zones and periods of melting for coke cupola, gas cupola and electric furnace were considered separately. Each melting unit and each zone is characterized by its own mass transfer modes: periodicity or continuity, a combination of reactive phases, etc.

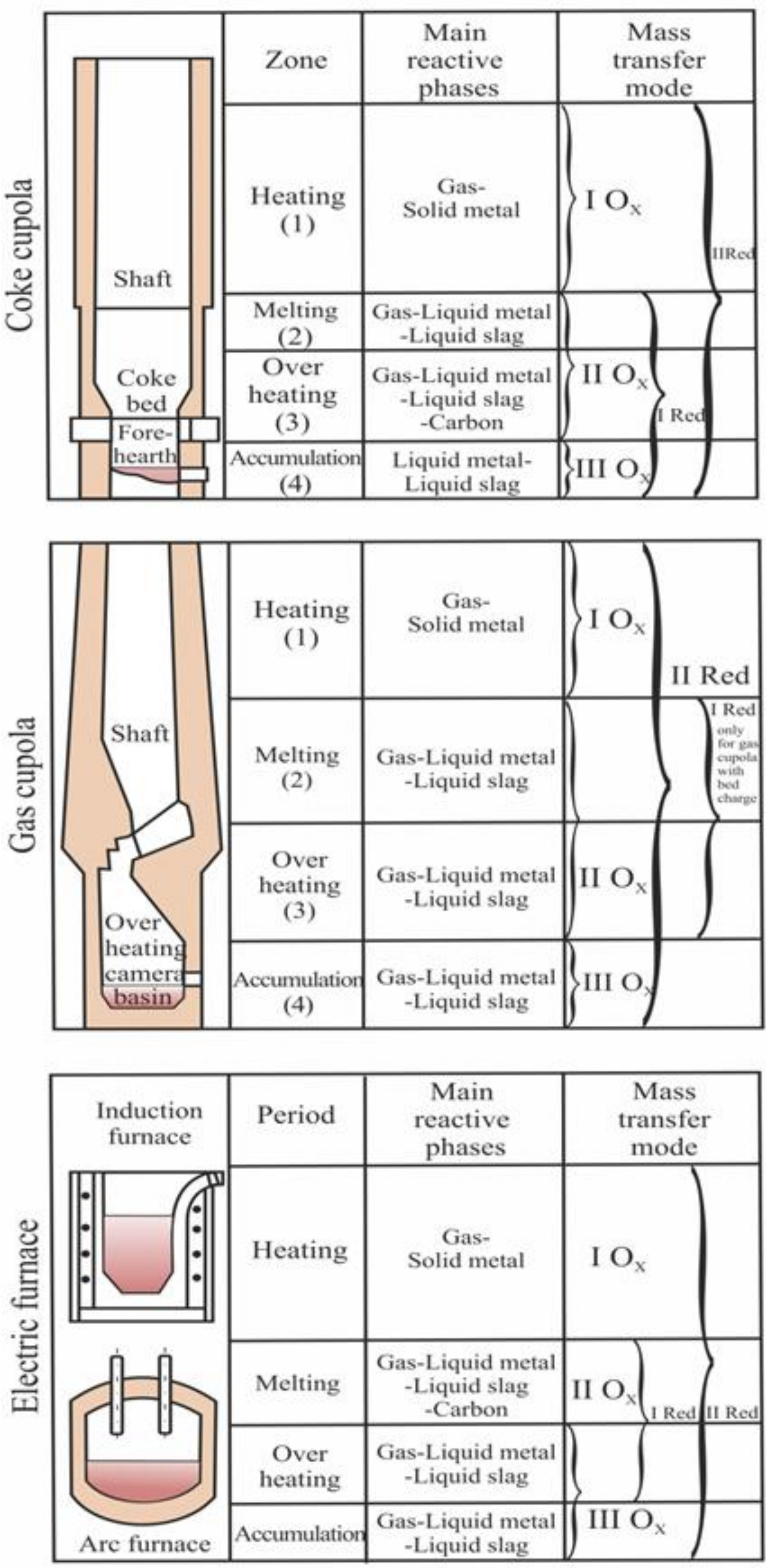

Figure-1. Analysis of mass transfer by zones and periods of melting
Source: Grachev (2016)

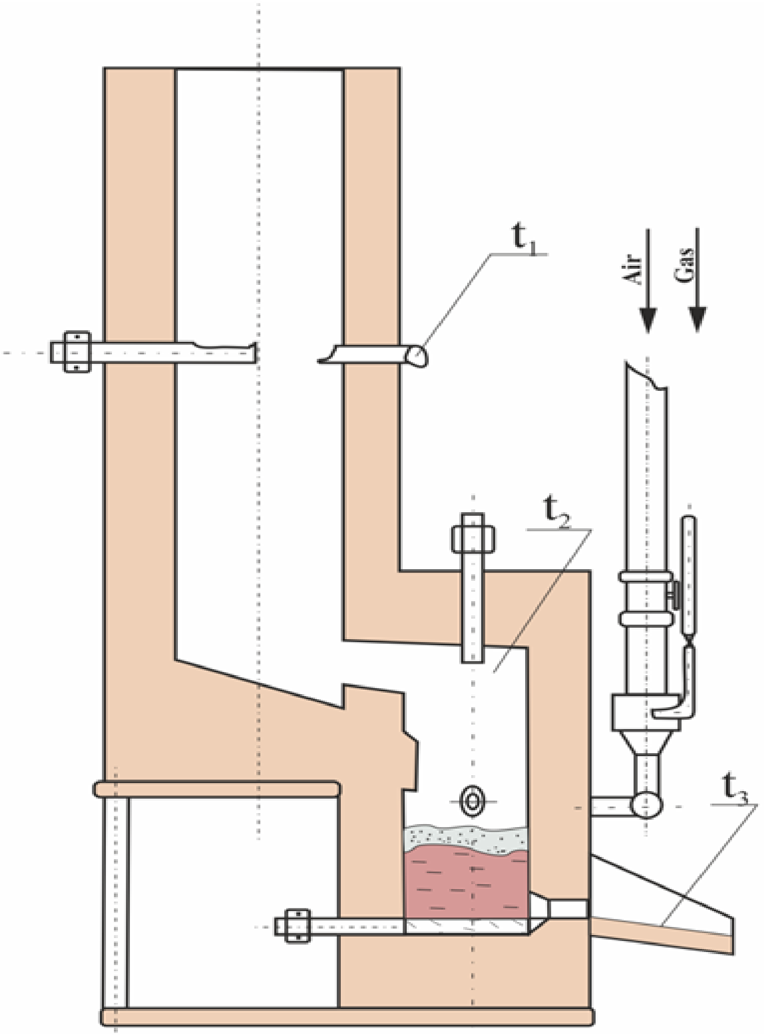

Figure-2. Laboratory gas cupola with a capacity of 20 kg/h
Source: Grachev (2016)

The mass transfer was studied in experimental gas cupola shown in Figure 2, and in experimental gas cupola with a refractory nozzle with a capacity of 700 kg/h. The temperature was measured using platinum/rhodium to platinum thermocouples (t_1, t_2, t_3).

700 kg/h capacity gas cupola has a similar construction. It is installed in the melting department of the Core Laboratory of the plant in Penza, Russia.

In the laboratory gas cupola, a special hole was made in the lower part of the shaft for metal sampling. Thus, it was possible to "separate" the loss in the heating and melting zone from the loss in the overheating zone. Constructionally, it is difficult to ensure sampling clearly after each zone, so the experimental material is supplemented with the calculated data.

At the gas cupola with a heterogeneous nozzle, sampling was also carried out from the shaft and fore-hearth.

3. RESULTS AND DISCUSSION

To describe the processes of mass transfer in melting furnaces, the author has proposed to introduce the notion of the visible mass transfer coefficient (k^v); it is the density of the mass flow of an element attributed to one percent of the element's concentration in cast iron. The coefficient is measured as kg/m²·s·pc (pc is percentage of concentration, introduced in the mass transfer coefficient k^v due to the fact that in practical calculations this value is used to characterize the composition of cast iron).

In accordance with the definition, $k^v = \frac{dM_i}{d\Omega \cdot d\tau \cdot K}$, $dM_i = k^v \cdot K_i \cdot d\Omega \cdot d\tau$, where K_i is the concentration of the i-th element in mass per cent.

It is assumed that in the general case $k^v = K\frac{d\mu}{dn}$; in diffusion $k^v = \frac{\beta(C-C^n)}{K}$. The dimension of k^v is determined from the definition, in the physical sense assuming the presence of a driving force in k^v itself:

$$dM_i = M_{\sum} \cdot dK \cdot 10^{-2}, \qquad (5)$$

$$M_i = \frac{M_{\sum} \cdot K_i}{100}, \qquad (6)$$

$$dK_i = 10^2 \cdot k^v \frac{K_i}{M_{\sum}} \cdot d\Omega \cdot d\tau. \qquad (7)$$

It is advisable to enter 10^2 "inside" k^v, $k^{v'} = k^v \cdot 10^2$, that is:

$$k^{v\prime} = k^v \cdot 10^2 (\mathrm{kg/m^2 \cdot s}). \qquad (8)$$

Then

$$dK_i = k^{v\prime} \cdot K_i \frac{d\Omega}{M_{\sum}} \cdot d\tau \text{ or } \frac{dK_i}{K_i} = k^{v\prime} \frac{d\Omega}{M_{\sum}} \cdot d\tau. \qquad (9)$$

Integrating this equation over the area Ω, from K^0 to K and from O to τ (mass transfer time), and introducing the notion of the specific surface of the charge materials $\omega = \frac{\Omega}{M_{\Sigma}}$ (m^2/kg), we obtain:

$$K = K^0 \cdot \exp(k^{v\prime} \cdot \omega \cdot \tau). \qquad (10)$$

Eq. (10) is the basic equation for determining the concentration of the element during secondary cast iron melting. The sign in front of $k^{v\prime}$ is determined by the direction of mass transfer: in case of melting loss of the element, it is the minus sign. The mathematical model should be built on the basis of the equation of mass conservation:

$$\frac{\partial M}{\partial \tau} + \mathrm{div}_{\vec{\mathrm{J}}} = 0, \qquad (11)$$

where J is the mass flow, kg/s (the change in mass within the system is equal to the flow of this mass $\frac{\partial M}{\partial \tau} = \mathrm{div\,J}$), and proceeding from the real conditions of mass transfer over the zones and periods of melting.

For the elementary volume of the melting unit dV = ($d_x \cdot d_y \cdot d_z$), which has a heterogeneous interaction inside the surface dΩ, Eq. (11) is valid for the mass. However, for each component it is advisable to enter the following subdivision:

$$\frac{\partial M_i}{\partial \tau} = \frac{\partial_i M_i}{\partial \tau} + \frac{\partial_c M_i}{\partial \tau}, \qquad (12)$$

where $\partial_i M_i$ is "appearance" of the mass of the i-th element in the volume dV during the interaction of the phases; $\partial_e M_i$ is the mass flow of the i-th element, $\frac{\partial_e M_i}{\partial \tau} = \mathrm{div\,J}$.

Of course, for n elements forming dV, $\sum_{i=1}^{n} \frac{\partial_i M_i}{\partial \tau} = 0$.

So,

$$\frac{\partial M_i}{\partial \tau} = \frac{\partial_i M_i}{\partial \tau} + \operatorname{div}_{\vec{\mathrm{J}}^i}, \tag{13}$$

where $\frac{\partial_i M_i}{\partial \tau}$ is melting loss of this element in the volume dV: $\frac{\partial_i M_i}{\partial \tau} = k^v \cdot K_i \cdot d\Omega$, or

$$\frac{dK_i}{d\tau} = k^{v\prime} \cdot K_i \frac{d\Omega}{M_\Sigma} + \frac{10^2}{M_\Sigma} \cdot \operatorname{div}_{\vec{\mathrm{J}}^i}, \tag{14}$$

$\operatorname{div}_{\vec{\mathrm{J}}^i} = \frac{\partial J_i}{\partial x} + \frac{\partial J_i}{\partial y} + \frac{\partial J_i}{\partial z}$ has a simple physical meaning of the scalar mass difference, which has entered the elementary volume and left it.

The calculation of Eq. (14) for each element, for each of the zones or periods of melting will create a mathematical model of mass transfer in secondary cast iron melting.

Phases interaction at iron melting units is usually analyzed by dressing zones, named after the physical processes occurring in them: heating, melting, reduction and oxygen zones of the bed charge, fore-hearth (for cupola).

Mass transfer processes define the formation of pig iron of a certain composition and properties. Mass transfer mode can be different within the same zone and identical in different zones. Therefore, it is advisable to consider mass transfer regimes for zones and periods (for periodically operating furnaces) of melting.

There is the analysis of mass transfer processes by zones and periods of melting for the main types melting units in Figure 1. Continuous melting units are divided into zones: heating, melting, overheating and accumulation. The same processes are realized at periodically operating units in the form of melting periods.

Mass transfer in the melting unit is determined by the process that makes the highest contribution to the formation of cast iron composition in a particular zone. Thus, heating is characterized by surface oxidation of the batch. After that, droplets and trickles of metal are already exposed during the melting of oxidation from the gas phase; liquid slag is already involved in the process. In the next overheating zone, the oxidation mechanism remains the same, but a new process appears: the direct reduction of oxides by the carbon in the coke bed. Finally, in the hearth or in the fore-hearth the metal is under the slag; the main thing is their interaction at the interface.

Obviously, it is advisable to analyze the mass transfer in the main characteristic mode, while counter mass flow of recovery should be taken into account separately. Thus, we can distinguish the main modes of mass transfer:
I *Ox* – oxidative, characterizing the oxidation batch pieces during heating;
II *Ox* – oxidative, characterizing the oxidation of metal in droplets when the liquid metal reacts with gas;
III *Ox* – oxidizing in the metal-slag system;
I *R* – mode of dissolution of elements (C, for example);
I *Red* – a reduction mode characterizing the direct reduction of oxides by carbon from the slag;
II *Red* – recovery mode, characterizing the recovery due to other phases involved in the process.

The latter mode is characteristic of cast iron, since the oxidation and reduction of its elements are closely related. Thus, the oxidation of silicon is at the same time the reduction of iron, etc. The same mode determines the reduction of elements according to the "crucible" reaction.

The boundaries of the implementation of mass transfer modes do not coincide with the boundaries of physical zones, but such delineation is more convenient than for zone division. Some processes, for example, carbon reduction or heating in the range of 0-1,100 °C, have been studied to a certain extent. The final result of mass transfer is formed by the algebraic sum of the substances fluxes in all modes of mass transfer.

For example, for the *i*-th element:

$$J_i = j_i \Omega\tau = -J_i^{IOx} - J_i^{IIOx} - J_i^{IIIOx} + J_i^{IR} - J_i^{IRed} + J_i^{IIRed} \quad (15)$$

or

$$M_i = m\Omega\tau = -M_i^{IOx} - M_i^{IIOx} - M_i^{IIIOx} + M_i^{IR} + M_i^{IRed} + M_i^{IIRed}. \quad (16)$$

The task is to determine the individual components of the mass flows.

3.1. Oxidation of Solid Batch (Mode IOx)

Oxidation of a solid metal by the gas phase is a complex process, since the resulting solid condensed phase – the oxide layer – limits the diffusion transfer of the components.

Wagner (1936) obtained a general kinetic equation for the rate of growth of the oxide layer:

$$\frac{dm}{d\tau} = \frac{g}{x}\left[\frac{300}{96{,}500}\frac{1}{Ne}\int_{\mu AB}^{\mu CD}(n_1 + n_2)n_3 x_{z_2}^{d\mu}\right], \quad (17)$$

where m is the mass of the forming oxide; τ is the time; g is the cross-section of a metal plate; x is the thickness for a dross layer; *CD* and *AB* are the external and internal boundaries; n_1, n_2, and n_3 are the number of transfer of components, anions, electrons; x is the total electrical conductivity; z_2 is the anionic charge.

Obviously, Eq. (17) cannot be used for real calculations.

In area of high-temperature heating of steel feed, a lot of research has been done; there are empirical formulas for calculating the thickness of a scale dross. So, the surface loss of steel is determined by the Eq. (18):

$$a = 8.13\sqrt{\tau_1}\exp(-900/T) \text{ kg/m}^2, \quad (18)$$

where τ_1 is the heating time; T is the heating temperature.

Calculations according to this Eq. (18), made by V.N. Morgunov for cupola melting, showed significant discrepancies with the experimental data.

Oxides layer on a cast iron batch, according to the data of L.M. Marienbakh (Kuznetsov *et al.*, 2014) has a thickness of 0.25 mm and contains about 1% of SiO_2, 1% of MnO and more than 95% of iron oxides. That is, melting loss of C, Si, Mn in this zone is insignificant, but iron loss depends practically only on time and heating surface. Thus, it is recommended to use a simple equation for the determination of iron loss:

$$M_{Fe}^{IOx} = k_{Fe}^{vIOx} K_{Fe} \Omega\tau \text{(kg)}, \quad (19)$$

where k_{Fe}^{vIOx} is the visible mass transfer coefficient, kg/pc·m²·s; K_{Fe} is the concentration of iron in the component (concentration percentage); Ω is the batch surface, m²; τ is the time, s.

Specific surfaces for different types of batch materials have the following limits:

1) Pig iron 0.0074-0.0013 m²/kg;
2) Cast iron scrap – frame 0.02-0.03 m²/kg;
   scrap of mould 0.004-0.005 m²/kg.
3) Steel scrap sheet 0.03-0.04 m²/kg;
   rolled metal 0.005-0.015 m²/kg;
4) Shaving 0.14-0.16 m²/kg.

The surface of shaving is taken from the data of Puzyrkov-Uvarov O.V. Thus, the research task in the IOx mode is to determine k^v for various types of batch materials. Eq. (19) is applicable for any element of cast iron:

$$M_i^{IOx} = k_i^{vIOx} \cdot K_i \cdot \Omega \cdot \tau \text{(kg)} \quad (20)$$

However, K_i is not a constant value, therefore, Eq. (20) can be taken with K_i^{av} – the average concentration of the period or zone – only for average calculations. For a more accurate solution, it is necessary to use the ratio (21):

$$K_i^{(1)} = K_i^0 \exp(k_i^{v'IOx} \cdot \omega_1\tau_1), \quad (21)$$

where $K_i^{(1)}$ is the concentration of the i-th component at the outlet from the zone (1).

3.2. Oxidation in Droplets (IIOx Mode)

Droplets of molten metal are formed in the melting zone; during the passage of the melting zone (τ_2) and the zones of the bed charge (τ_3), droplets are exposed to the oxidative action of the gas phase. The speediness of processes in the droplets mode and the impossibility of practical determination of the passage time of droplet surface zones make it possible to use Eq. (19) and (21) for the calculation of mass transfer:

for iron

$$M_{Fe}^{IIOx} = k_{Fe}^{vIIOx} K_{Fe}.\Omega \cdot \tau, \qquad (22)$$

for the *i*-th element

$$K_i^{(3)} = K_i^{(1)} \exp\left(k_i^{v'IIOx} \omega_{(2)+(3)} \cdot \tau_{(2)+(3)}\right), \qquad (23)$$

The droplet diameter can be determined from the studies of G.P. Dolotov (Boronenkov, 1974):

$$d_i = d_0 + 0.121 \exp(0.111 \cdot h_D) \quad , \qquad (24)$$

where d_0 is the diameter of the droplet without a counter-flow of gases (for cast iron d_0 = 4.815 mm); h_D is the dynamic head of gases.

The time of the drop in flight is determined by the formula: $\tau_2 + \tau_3 = \sqrt{\frac{2(0.5H_2 + H_3)}{g}}$; where H_2 and H_3 are the heights of melting and overheating zones.

The mechanism and kinetics of the liquid metal oxidation by gas phase are very complex and there is still no consensus on the limiting stage of the process.

In the study of the oxidation of a liquid metal by the gas phase, a limiting stage in the oxidation, for example, of carbon (Rundman, 2014) is considered to be the diffusion of oxygen in the gaseous phase, the adsorption-chemical act, the diffusion of carbon in the metal. There are other points of view.

The oxidation of Si and Mn is complicated by the formation of an iron oxides layer and its reduction by these elements; that is, the oxidation mechanism itself is complex.

The processes of carbon oxidation from the melt can be limited by the supply rate of the oxidizing gas (Rundman, 2014).

In the secondary cast iron melting, an analogous factor is the exact surface of the reaction that is unknown. Therefore, it is expedient to calculate the oxidation of iron in this mode using Eq. (19) with the corresponding values of k_{Fe}^{vIOx}, Ω and τ. For other elements, it is expedient to use the oxidation mechanism through ferrous oxide and calculate using Eq. (23).

In this case:

$$j_C^{IIOx} = j_{Fe(C)}^{IIRed};\ j_{Si}^{IIOx} = 2 j_{Fe(Si)}^{IIRed} \text{ and } j_{Mn}^{IIOx} = j_{Fe(Mn)}^{II\,Red}, \qquad (25)$$

where $j_{Fe(C)}^{IIRed}$ is the flux of iron reduction due to the oxidation of the *i*-th element.

The process of metal oxidation in a drop containing on its surface oxides layer (consisting of 90 to 95% of iron oxides) can be expressed by Eq. (2)-(4), which will obviously have a slightly different form:

$$j_C^{IIOx} = 2.2 \cdot 10^{-2} \cdot e^{-\frac{16,200}{T}} \cdot [\%C]^{0.65}, \qquad (26)$$

$$j_{Si}^{IIOx} = 0.9 \cdot 10^{7} \cdot e^{-\frac{43,500}{T}} \cdot a_{Si}^{0.84} \left(\frac{1}{a_{FeO}^{eq}}\right)^{0.1}, \qquad (27)$$

$$j_{Mn}^{IIOx} = 6.5 \cdot 10^{7} \cdot e^{-\frac{50,500}{T}} \cdot a_{Mn}^{0.5} (K_p^{Mn})^{0.3}. \qquad (28)$$

It means that the iron oxides layer has $a_{FeO} = 1$ and the activity of SiO_2 in the oxides layer is so small that it can be ignored.

Eq. (26)–(28) can be used to determine k^v:

$$k_i^v = \frac{j_i \cdot A \cdot 10^3}{10^4 \cdot K_i}, \qquad (29)$$

where j_i is the mass flow of the *i*-th element, g at/cm^2 s; A is the mass of one atom of the substance, g/ton-at; 10^3 and 10^4 are the conversion factors (g in kg and cm^2 in m^2).

3.3. Oxidation of Metal by Slag (Mode IIIOx)

In this mode, the metal under the slag is oxidized. The interface in this case is fairly well known and it is possible to calculate the loss of elements by the formula:

$$K_i^{(4)} = K_i^3 \exp(k_i^{v\prime IIIOx} \omega_4 \cdot \tau_4), \qquad (30)$$

For the smelting of cast iron in the cupola (interaction on the interface in the hearth and in the fore-hearth) and for the periodic processes in electric furnaces, it is necessary to perform calculations using Eq. (26)–(29). It should be borne in mind that when melting in an induction furnace, the diffusion difficulties on the metal side are removed by electromagnetic mixing of the metal.

The problem of the area of secondary cast iron melting is to establish the values of the visible mass transfer coefficients based on the experimental and calculated data.

3.4. Reduction of Oxides by Carbon (IRed Mode)

Reducing processes due to solid carbon are most typical for a coke cupola, because there the metal and slag flow down the coke and react with it. In this case, the reacting surface should be determined by analogy with the II*Ox* mode.

There are two types of reacting in I*Red* mode: slag-carbon and metal-carbon. As a result of the first process, C + MeO = Me + CO.

As a result of the second process (let us call it I*R* mode), carbon dissolves in the metal due to molecular and convective diffusion.

The kinetics of the metal oxides reduction by solid carbon has been studied by many authors. An analysis of the work on this issue is given in the dissertation of Boronenkov (1974). From the analysis, it was concluded that there is a significant discrepancy in the experimental data on the rates of the processes of carbon-thermal reduction, depending on the concentrations, temperature, and other conditions. There is no consensus on the limiting stages of the process, etc. In this case, the problem is to use the literary data on the kinetics of direct reduction of iron and silicon to find acceptable values for the secondary cast iron melting. For the I*R* mode, it is necessary to use the data of L.M. Marienbach (Kuznetsov *et al.*, 2014) and other authors studying the dissolution of carbon in cast iron at cupola melting, and the data of V.S. Shumikhin (Kuznetsov *et al.*, 2009) on the dissolution of carbon in induction melting. The allowance for reducing flows and dissolution fluxes for the overheating period or the zone is made by introducing into Eq. (23) of a member including k_i^{vIRed}, k_i^{vIR}.

3.5. Reduction of Oxides By Cast Iron Elements (IIRed Mode)

The reduction of oxides is possible due to carbon and other elements dissolved in the metal. The source of the reduction element in this case may be the slag or lining of the furnace.

To restore iron under conditions close to the conditions of secondary cast iron melting, it was found (Kronenberg, 1969): $j_{Fe(C)}^{IIRed} = 2.2 \cdot 10^{-2} (FeO)^{0.4} [C]^{0.65} e^{-\frac{16,200}{T}}$.

There are other literature data on the speed of this process. It is also necessary to take into account the reduction of iron due to Mn and Si, i.e. $j_{Fe[Si]}^{II\,Red}, j_{Fe[Mn]}^{II\,Red}$.

For manganese in conditions close to cast iron melting (slag: 35% SiO_2, 45% CaO, 10% Al_2O_3, 0.15-5% MnO, 10% MgO), it was found:

$$I_{Mn(C)}^{IIRed} = Ka_{MnO} = 1.28 \cdot 10^{-5}\, a_{MnO}\text{mole/cm}^2\text{min}). \qquad (31)$$

For the rate of silicon reduction by carbon:

$$j_{Si(C)}^{IIRed} = (0.1 - 3.5) \cdot 10^{-6}\ \text{g·at·Si/cm}^2\text{·s}. \qquad (32)$$

In the conditions of cast iron melting, it is necessary to go over to the values $k_i^{v'IIRed}$ by Eq. (29).

The reduction of silicon is possible not only from slag, but also from the furnace lining, that is, it is necessary to take into account $j_{Fe<Si>}^{IIRed}$.

The presence of the 2 *Red* mode requires the introduction into the under-exponential expressions of the members with $k_{Fe[C]}^{v'IIRed}, k_{Fe[Si]}^{v'IIRed}, k_{Fe[Mn]}^{v'IIRed}, k_{Si[C]}^{v'IIRed}$, etc.

3.6. Mathematical Model of Mass Transfer in Secondary Cast Iron Melting

On the basis of the above regularities, for example, for carbon, we can write:

$$\left.\begin{aligned} \mathrm{K}_{\mathrm{C}}^{(1)} &= \mathrm{K}_{\mathrm{C}}^{0} \exp\{-k_{\mathrm{C}}^{v'IO_{\mathrm{x}}} \cdot w_{(1)} \cdot \tau_{(1)}\} \\ K_C^{(3)} &= K_C^{(1)} \exp\{-k_{\mathrm{C}}^{v'\mathrm{IIO_x}} \cdot w_{(2,3)} \cdot \tau_{(2+3)} + k_{\mathrm{C}}^{\mathrm{v}'IR} \cdot w_{(3)} \cdot \tau_{(3)}\} \\ \mathrm{K}_{\mathrm{C}}^{(4)} &= \mathrm{K}_{\mathrm{C}}^{3} \exp\{-k_{\mathrm{C}}^{\mathrm{v}'IIIO_{\mathrm{x}}} \cdot w_{(4)} \cdot \tau_{(4)}\} \end{aligned}\right\} \qquad (33)$$

For the zone or accumulation period, a flow can be received without an outflow. Therefore, the system of Eq. (33), compiled for each of the elements by zones and periods, is only an approximate mathematical model of mass transfer during the cast iron melting.

Simplified mass transfer models can also be compiled on the basis of average periods and concentration zones. In this case, it is possible to draw up a system of equations for the direct determination of the mass of the loss and burn-on of each of the elements. For example, for Fe this is more convenient, since it is not customary to express it in percent (Fe is the basis):

$$M_{\mathrm{Fe}}^{\Sigma} = M_{\mathrm{Fe}}^{\mathrm{IO_x}} + M_{\mathrm{Fe}}^{\mathrm{IIO_x}} + M_{\mathrm{Fe<C>}}^{\mathrm{IRed}} + M_{\mathrm{Fe[C]}}^{\mathrm{IIRed}} + M_{\mathrm{Fe[Si]}}^{\mathrm{IIRed}} + M_{\mathrm{Fe[Mn]}}^{\mathrm{IIRed}}, \quad (34)$$

where $M_{\mathrm{Fe<C>}}^{\mathrm{IRed}}$ is the mass of Fe reduced by the carbon of coke or another carburizer; $M_{\mathrm{Fe[Si]}}^{\mathrm{IIRed}}$ is Fe reduction by the cast iron elements (C, Si, Mn) according to the general reaction: FeO+Me=Fe+MeO.

Writing out (34) for the zone and periods and taking $\mathrm{K_{Fe}}$ = const, we obtain:

$$M_{\mathrm{Fe}}^{\Sigma} = K_{\mathrm{Fe}} \cdot \left[k_{\mathrm{Fe}}^{v\mathrm{IO_x}}\Omega_{(1)} \cdot \tau_{(1)} + k_{\mathrm{Fe}}^{v\mathrm{IIO_x}}\Omega_{(2,3)} \cdot \tau_{(2+3)} + k_{\mathrm{Fe<C>}}^{v\mathrm{IRed}}\Omega_{(3)} \cdot \tau_{(3)} + \Omega_{(2+3+4)} \cdot \tau_{(2+3+4)} (k_{\mathrm{Fe[C]}}^{v\mathrm{IIRed}} + k_{\mathrm{Fe[Si]}}^{v\mathrm{IIRed}} + k_{\mathrm{Fe[Mn]}}^{v\mathrm{IIRed}}\right]. \qquad (35)$$

The resulting mass flows of other elements can be determined from other equations:

$$M_{\mathrm{C}}^{\Sigma} = M_{\mathrm{Fe}}^{\mathrm{IIO_x}} + M_{\mathrm{C}}^{\mathrm{IR}} + M_{\mathrm{Fe}}^{\mathrm{IIIO_x}}, \qquad (36)$$

$$M_{\mathrm{C}}^{\Sigma} = -k_{\mathrm{C}}^{v\mathrm{IIO_x}} K_C^{(2+3)} \Omega_{(2)} \cdot \tau_{(2)} + \Omega_{(3)} \cdot \tau_{(3)} + k_{\mathrm{C}}^{v\mathrm{IR}} K_C^{(3)} \Omega_{(3)} \cdot \tau_{(3)} - k_{\mathrm{C}}^{v\mathrm{IIIO_x}} K_C^{(4)} \Omega_{(4)} \cdot \tau_{(4)}, \quad (37)$$

$$\mathrm{M}_{\mathrm{Si}}^{\Sigma} = -M_{\mathrm{Si}}^{\mathrm{IIO_x}} + M_{\mathrm{Si}}^{\mathrm{IRed}} + M_{\mathrm{(Si)[C]}}^{\mathrm{IIRed}} - M_{\mathrm{Si}}^{\mathrm{IIIO_x}}, \qquad (38)$$

$$M_{\mathrm{Si}}^{\Sigma} = \mathrm{k}_{\mathrm{Si}}^{(2+3)} \cdot (\Omega_{(2)} \cdot \tau_{(2)} + \Omega_{(3)} \cdot \tau_{(3)})(k_{\mathrm{Si}}^{v\mathrm{IIO_x}} + k_{\mathrm{Fe(Si)[C]}}^{v\mathrm{IIRed}} + k_{\mathrm{Fe<Si>[C]}}^{v\mathrm{IIRed}}) - k_{\mathrm{Si}}^{v\mathrm{IIIO_x}} \cdot \mathrm{K}_{\mathrm{Si}}^{(4)} \Omega_{(4)} \cdot \tau_{(4)} + k_{\mathrm{Si}}^{v\mathrm{IIIO_x}} \cdot k_{\mathrm{Si}}^{v\mathrm{IRed}} \mathrm{K}_{\mathrm{Si}}^{(3)} \Omega_{(3)} \cdot \tau_{(3)}, \qquad (39)$$

$$M_{\mathrm{Mn}}^{\Sigma} = -M_{\mathrm{Mn}}^{\mathrm{IIO_x}} + M_{\mathrm{Mn}}^{\mathrm{IIIO_x}} + M_{\mathrm{Mn}}^{\mathrm{IRed}}, \qquad (40)$$

$$M_{\mathrm{Mn}}^{\Sigma} = k_{\mathrm{Mn}}^{v\mathrm{IIO_x}} K_{Mn}^{(2+3)} (\Omega_{(2)} \cdot \tau_{(2)} + \Omega_{(3)} \cdot \tau_{(3)}) + k_{\mathrm{Mn}}^{v\mathrm{IIIO_x}} K_{Mn}^{(4)} (\Omega_{(4)} \cdot \tau_{(4)} + k_{\mathrm{Mn}}^{v\mathrm{IRed}} K_{Mn}^{(3)} \Omega_{(3)} \cdot \tau_{(3)}. \quad (41)$$

It must be taken into account when summing the mass flows that the terms of the modes IO_x, IIO_x, $IIIO_x$ have a minus sign, that is, k^{vOx} is negative.

A more exact mathematical model must take into account the divergence of the element's streams:

$$\frac{\partial M_i}{\partial \tau} = k_i^v \cdot K_i \cdot d\Omega + div_i^m. \qquad (42)$$

The flow of metal into the accumulation zone can be characterized by the difference between the incoming flux m^{in} and the outgoing flux m^{out}. For example, for carbon in the fourth zone without carburizers entering:

$$\frac{\partial M_C^{(4)}}{\partial \tau} = k_{\mathrm{C}}^{\mathrm{IIIO_x}} \cdot K_C \cdot d\Omega + m_C^{in} - m_C^{out}, \qquad (43)$$

m_C^{in} is the incoming carbon flow, kg/s, $m_C^{in} = \frac{\partial M_\Sigma^{in} \cdot K_C}{\partial \tau \cdot 100}$; m_C^{out} is the outgoing carbon flow, kg/s, $m_C^{out} = \frac{\partial M_\Sigma^{out} \cdot K_C}{\partial \tau \cdot 100}$.

Then:

$$\frac{\partial M_C^{(4)}}{\partial \tau} = k_{\mathrm{C}}^{\mathrm{IIO_x}} \cdot K_C \cdot d\Omega + \frac{\partial M_\Sigma^{in} \cdot K_C^3}{\partial \tau \cdot 100} - \frac{\partial M_\Sigma^{out} \cdot K_C}{\partial \tau \cdot 100}. \qquad (44)$$

In the steady-state mode of receipt and release of metal $\frac{\partial M_\Sigma^{in}}{\partial \tau} = \frac{\partial M_\Sigma^{out}}{\partial \tau}$, where $\frac{\partial M_\Sigma^{in}}{\partial \tau}$ (kg/s) is the mass second capacity of melting, $\frac{\partial M_\Sigma^{out}}{\partial \tau} = g^{in} = \frac{G \cdot 100}{3{,}600} = \frac{G}{3.6} = g^{out}$, G being the cupola capacity, t/h.

If $\frac{\partial M_\Sigma^{out}}{\partial \tau}$ (kg/s) = g^{out} is the rate of release of cast iron (from the taphole), then:

$$\frac{\partial K_C}{\partial \tau} = \mathrm{k}_{\mathrm{C}}^{\mathrm{IIIO_x}} \cdot K_C \cdot d\Omega \frac{10^2}{M_\Sigma} + \frac{g^{in} \cdot K_C^{(3)}}{M_\Sigma} - \frac{g^{out} \cdot K_C}{M_\Sigma}. \qquad (45)$$

By integrating this equation from 0 till $\tau_{(4)}$ and from $K_C^{(3)}$ till $K_C^{(4)}$, we obtain:

$$K_C^4 = K_C^3 \Bigg\{ \Bigg(1 + \frac{g^{in}}{k_C^{v'IIIOx} \cdot \Omega_4 - g^{out}} \Bigg) \exp \Bigg[\tau_4 (k_{\mathrm{C}}^{v'\mathrm{IIIO_x}} X\, w_{(4)} - \frac{g^{out}}{M_\Sigma^{(4)}} \Bigg] - \frac{g^{in}}{k_{\mathrm{C}}^{v'\mathrm{IIIO_x}} \Omega_{(4)} - g^{out}} \Bigg\}. \qquad (46)$$

Because $g^{in} = g^{out} = g = \frac{G}{3.6}$,

$$K_C^4 = K_C^3 \Bigg\{ \Bigg(1 + \frac{g^{in}}{k_C^{v'IIIOx} \cdot \Omega_{(4)} - g^{out}} \Bigg) \exp \Bigg[\tau_{(4)} (k_{\mathrm{C}}^{v'\mathrm{IIIO_x}} X\, w_{(4)} - \frac{G}{3.6 \cdot M_\Sigma^{(4)}} \Bigg] - \frac{g^{in}}{k_{\mathrm{C}}^{v'\mathrm{IIIO_x}} \Omega_{(4)} - g^{out}} \Bigg\}. \qquad (47)$$

Proceeding from the foregoing, the general mathematical model of mass transfer in secondary cast iron melting can be represented in the form:

$$K_i^{(1)} = K_i^{(1)} \Bigg\{ \Bigg(1 + \frac{G}{3.6\, k_i^{v'IOx} \cdot \Omega_{(1)} - G} \Bigg) \exp \Bigg[\tau_{(1)} \Bigg(k_{\mathrm{i}}^{\mathrm{v'IO_x}} \cdot\ w_{(1)} - \frac{G}{3.6 M_\Sigma^{(1)}} \Bigg) \Bigg] - \frac{G}{k_i^{v'IOx} \cdot \Omega_{(1)} - G} \Bigg\}; \qquad (48)$$

$$K_i^{(2)} + K_i^{(1)} \Bigg\{ \Bigg(1 + \frac{G}{3.6\, k_i^{v'\Sigma(2)} \cdot \Omega_{(2)} - G} \Bigg) \exp \Bigg[\tau_{(2)} \Bigg(k_{\mathrm{i}}^{v'\Sigma(2)} \cdot\ w_{(21)} - \frac{G}{3.6 M_\Sigma^{(2)}} \Bigg) \Bigg] - \frac{G}{3.6\, k_i^{v'\Sigma(2)} \cdot \Omega_{(2)} - G} \Bigg\}, \qquad (49)$$

$$\text{where } k_{\mathrm{i}}^{v'\Sigma(2)} = k_{\mathrm{i}}^{v'\mathrm{IIO_x}} + k_{\mathrm{i}}^{v'\mathrm{IIRed}};$$

$$K_i^{(3)} = K_i^{(2)} \Bigg\{ \Bigg(1 + \frac{G}{3.6\, k_i^{v'\Sigma(3)} \cdot \Omega_{(3)} - G} \Bigg) \exp \Bigg[\tau_{(3)} \Bigg(k_{\mathrm{i}}^{\mathrm{v}'\Sigma(3)} \cdot\ w_{(3)} - \frac{G}{3.6 M_\Sigma^{(3)}} \Bigg) \Bigg] - \frac{G}{k_i^{v'\Sigma(3)} \cdot \Omega_{(3)} - G} \Bigg\}, \qquad (50)$$

$$\text{where } k_i^{v'\Sigma(3)} = k_i^{v'IIOx} + k_i^{v'IRed} + k_i^{v'IIRed} + k_i^{v'IR};$$

$$K_i^{(4)} = K_i^{(3)} \Bigg\{ \Bigg(1 + \frac{G}{3.6\, k_i^{v'\Sigma(4)} \cdot \Omega_{(4)} - G} \Bigg) \exp \Bigg[\tau_{(4)} \Bigg(k_{\mathrm{i}}^{v'\Sigma(4)} \cdot\ \omega_{(4)} - \frac{G}{3.6 M_\Sigma^{(4)}} \Bigg) \Bigg] - \frac{G}{k_i^{v'\Sigma(4)} \cdot \Omega_{(4)} - G} \Bigg\}, \qquad (51)$$

$$\text{where } k_i^{v'\Sigma(4)} = k_i^{v'IIIOx} + k_i^{v'IRed} + k_i^{v'IIRed} + k_i^{v'IR}.$$

The successive solution of Eq. (48)–(51) allows calculating the concentration of the *i*-th element in cast iron for any variants of K_i^0, w, τ, G, M_Σ, k_i^v.

For Si in the conditions of cupola continuous melting, by linking the parameters M_Σ, τ and Ω, we obtain for the first zone $\left(\tau_1 = \frac{M_\Sigma \cdot 3.6}{G}\right)$:

$$K_{Si}^{(1)} = K_{Si}^{(0)}\left\{\left(1 + \frac{G}{3.6\, k_{Si}^{v'IOx} \cdot \omega_{(1)} \cdot \mathrm{M}_\Sigma^{(1)} - G}\right)\exp\left[\frac{\mathrm{M}_\Sigma^{(1)} \cdot 3.6}{G} \mathrm{x}\left(k_{Si}^{v'IOx} \cdot \omega_{(1)} - \frac{G}{3.6\mathrm{M}_\Sigma^{(1)}}\right)\right] - \frac{G}{3.6 k_{Si}^{v'\Sigma(4)} \cdot \omega_{(1)} \cdot \mathrm{M}_\Sigma^{(1)} - G}\right\}. \qquad (52)$$

It is similar for the second zone:

$$K_{Si}^{(2)} = K_{Si}^{(1)}\left\{\left(1 + \frac{G}{3.6\, k_{Si}^{v'IOx} \cdot \omega_{(2)} \cdot \mathrm{M}_\Sigma^{(2)} - G}\right)\exp\left[\frac{\mathrm{M}_\Sigma^{(2)} \cdot 3.6}{G} \mathrm{x}\left(k_{Si}^{v'IOx} \cdot \omega_{(2)} - \frac{G}{3.6\mathrm{M}_\Sigma^{(2)}}\right)\right] - \frac{G}{3.6 k_{Si}^{v'\Sigma(2)} \cdot \omega_{(2)} \cdot \mathrm{M}_\Sigma^{(2)} - G}\right\}. \qquad (53)$$

For the third zone, a more convenient parameter for calculating is $\tau_{(3)} = \frac{3.6\mathrm{M}_\Sigma^{(3)}}{G}$ or $M_\Sigma^{(3)} = \frac{\tau_{(3)} \cdot G}{3.6}$:

$$\mathrm{K}_{Si}^{(3)} = \mathrm{K}_{Si}^{(2)}\left\{\left(1 + \frac{1}{k_{Si}^{v'\Sigma(3)} \cdot \omega_{(3)} \cdot \tau_{(3)} - 1}\right)\exp\left(k_{Si}^{v'\Sigma(3)} \cdot \omega_{(3)} \mathrm{X}\, \tau_{(3)} - 1\right) - \frac{1}{k_{Si}^{v'\Sigma(3)} \cdot \omega_{(3)} \cdot \tau_{(3)} - 1}\right.. \qquad (54)$$

For the fourth zone:

$$K_{Si}^{(3)} = K_{Si}^{(2)}\left\{\left(1 + \frac{G}{3.6\, k_{Si}^{v'\Sigma(4)} \cdot \Omega_{(4)} - G}\right)\right.. \qquad (55)$$

$k_{Si}^{v'\Sigma(2)}$ is the visible mass transfer coefficient of silicon (total) for the second zone, $k_{\mathrm{Si}}^{v'\Sigma(2)} = k_{\mathrm{Si}}^{v'\mathrm{IO_x}} + k_{\mathrm{Si}}^{v'\mathrm{IIO_x}} + k_{\mathrm{Si}}^{v'\mathrm{IIRed}}$; $k_{Si}^{v'\Sigma(3)}$ is the same for the third zone $k_{\mathrm{Si}}^{v'\Sigma(3)} = k_{\mathrm{Si}}^{v'\mathrm{IIO_x}} + k_{\mathrm{Si}}^{v'\mathrm{IRed}} + k_{\mathrm{Si}}^{v'\mathrm{IIRed}}$; $k_{Si}^{v'\Sigma(4)}$ is the same for the fourth zone, $k_{\mathrm{Si}}^{v'\Sigma(4)} = k_{\mathrm{Si}}^{v'\mathrm{IIIO_x}} + k_{\mathrm{Si}}^{v'\mathrm{IRed}} + k_{\mathrm{Si}}^{v'\mathrm{IIRed}} + k_{\mathrm{Si}}^{v'\mathrm{IR}}$; $k_{\mathrm{Si}}^{v'\mathrm{IR}}$ is the visible mass transfer coefficient for dissolving Si from ferrosilicon introduced into the accumulation.

For C, Si, Mn, under the concrete conditions of various melting aggregates, on the basis of Eq. (48) and (55), it is possible to compile working mathematical models.

For cupola melting, it is difficult to separate the loss from some zones. In particular, it is advisable to combine the melting zone with the heating zone or the overheating zone, more exactly, in part with the heating zone (oxidation of the batch pieces), in part with the overheating zone (oxidation in droplets – IIOx mode). In this case, for Fe, Eq. (35) will have the following form:

$$M_{\mathrm{Fe}}^{\Sigma} = K_{Fe}(k_{\mathrm{Fe}}^{v\mathrm{IO_x}} \cdot \left(\Omega_{(1)} \cdot \tau_{(1)} + \Omega_{(2)}^{sol} \cdot \tau_{(2)}\right) + k_{\mathrm{Fe}}^{v\mathrm{IIO_x}}\left(\Omega_{(2)}^{liq} \cdot \tau_{(2)} + \Omega_{(3)} \cdot \tau_{(3)}\right) + \left(k_{Fe[C]}^{vIIRed} + k_{Fe[Si]}^{vIIRed} + k_{Fe[Mn]}^{vIIRed}\right)\left(\Omega_{(2)}^{liq} \cdot \tau_{(2)} + \Omega_{(3)} \cdot \tau_{(3)} + \Omega_{(4)} \cdot \tau_{(4)}\right), \qquad (56)$$

where $\Omega_{(2)}^{sol} is$ the surface area of solid batch in the melting zone; $\Omega_{(2)}^{liq}$ is the surface area of liquid metal droplets in the melting zone.

Similar refinements can be made for each element in Eq. (48)–(55).

To determine the visible mass transfer coefficients, the actual possibilities of dividing them by the zones and types of mass transfer processes should be taken into account. In most cases, the visible mass transfer coefficients must be determined empirically.

One such case is the mass transfer to the electric furnace in the mixing mode. The reaction surface is equal to the metal-slag interface; the time can be tightly fixed. The process of mass transfer is complicated only by the multicomponent nature of the melt.

The basic equation of mass transfer

$$\frac{\mathrm{dM_i}}{\mathrm{d\tau}} = k_{\mathrm{i}}^{v'} \cdot \mathrm{K_i} \cdot \Omega \qquad (57)$$

is true in the case when cast iron is not added to the furnace and no cast iron is added and is not taken for casting the molds. Integrating this equation from 0 to τ (mix time) and from K_i^0 till K_i^{out} (final concentration), we obtain

$$K_i^{out} = K_i^0 \exp\left(k_{\mathrm{i}}^{v'} \cdot w \cdot \tau\right). \qquad (58)$$

However, in most cases, the mixing is carried out in such a way that there is always metal in the furnace; metal is taken from it and added into it in certain portions.

The weight of the metal in the furnace is given by:

$$M_\Sigma = M_0 + M^{in} \cdot n^{in} - \ M^{out} \cdot n^{out}, \qquad (59)$$

where M_0 – the metal mass in the furnace at the initial instant of counting, $\tau = 0$; M^{in} and M^{out} – mass of one portion of incoming and outgoing metal; N^{in} and n^{out} – the number of portions of the incoming and outgoing metal, respectively, over a period of τ.

The mass of the *i*-th element in cast iron at the time τ will be equal:

$$M_i = M_\Sigma \frac{K_i}{100} = \left(M_0 + M^{in} \cdot n^{in} - M^{out} \cdot n^{out}\right) \frac{K_i}{100}. \qquad (60)$$

The basic equation of mass transfer is:

$$\frac{dM_i}{d\tau} = \frac{d(M_\Sigma \cdot K_i)}{d\tau \cdot 100} = \ k_{\mathrm{i}}^{v'} \cdot \frac{K_i}{100} \cdot \Omega + \frac{M^{in} \cdot n^{in} \cdot K_i^{in}}{\tau \cdot 100} - \frac{M^{out} \cdot n^{out} \cdot K_i^{out}}{\tau \cdot 100}, \qquad (61)$$

$$\frac{dK_i}{d\tau} = k_{\mathrm{i}}^{v'} \cdot K_i \frac{\Omega}{(M_0 + M^{in} \cdot n^{in} - M^{out} \cdot n^{out})} + \frac{M^{in} \cdot n^{in} \cdot K_i^{in}}{(M_0 + M^{in} \cdot n^{in} - M^{out} \cdot n^{out})\tau} - \frac{M^{out} \cdot n^{out}}{(M_0 + M^{in} \cdot n^{in} - M^{out} \cdot n^{out})\tau}. \qquad (62)$$

Denote by $K_i = y$, $\tau = x$, $\frac{k_{\mathrm{i}}^{v'} \cdot \Omega}{(M_0 + M^{in} \cdot n^{in} - M^{out} \cdot n^{out})\tau} = A$, $\frac{M^{in} \cdot n^{in} \cdot \mathrm{K}_{\mathrm{i}}^{in}}{(M_0 + M^{in} \cdot n^{in} - M^{out} \cdot n^{out})} = B$, $\frac{M^{out} \cdot n^{out}}{(M_0 + M^{in} \cdot n^{in} - M^{out} \cdot n^{out})} = C$.

Then:

$$\frac{dy}{dx} = Ay + \frac{B}{x} + C \frac{y}{x}. \qquad (63)$$

The solution of this differential equation can be realized with the aid of a computer for specific numerical values.

If we admit a number of assumptions, then a simpler mathematical model can be obtained. We divide (conditionally) the processes of concentration change as a result of the mass change and as a result of the selection of the metal and its receipt. The concentration of the *i*-th element at the initial instant is K_i^0 (in the mass M_0). If we add $M^{in} \cdot n^{in}$ and take away the $M^{out} \cdot n^{out}$ mass of metal, then:

$$\frac{K_i \cdot M_\Sigma}{100} = \frac{K_i^0 \cdot M_0}{100} + \frac{K_i^{in} \cdot M^{in} \cdot n^{in}}{100} - \frac{K_i^{out} \cdot M^{out} \cdot n^{out}}{100} \text{ or } K_i = K_i^0 \frac{M_0}{M_\Sigma} + K_i^{in} \frac{M^{in} \cdot n^{in}}{M_\Sigma} - K_i^{out} \frac{M^{out} \cdot n^{out}}{M_\Sigma} \ .(64)$$

On the other hand, during this time the concentration will change by the mass of the oxidized metal:

$$K_i = K_i^0 \exp\left(k^{v\prime} \ \frac{\Omega}{M_\Sigma} \tau\right) \text{ or } K_i^{out} = K_i^0 - K_i^0 \exp\left(k^{v\prime} \ \frac{\Omega}{M_\Sigma} \tau\right).(65)$$

Assume that the mass $M_\Sigma = \text{const}$, transform (64) and combine with (65):

$$K_i^{out} = \frac{\frac{K_i^o M_0}{M_\Sigma} + \frac{K_i^{in} M^{in} n^{in}}{M_\Sigma}}{1 + \frac{M^{out} n^{out}}{M_\Sigma}} - K_i^o \exp\left(k_i^{v'} \frac{\Omega}{M_\Sigma} \tau\right), \qquad (66)$$

where K_i^{out} – the desired concentration of the *i*-th element in the produced metal; K_i^0– concentration in the furnace at the time $\tau = 0$; K_i^{in} – the concentration of each portion of the added metal; n^{in} and n^{out} – the number of incoming and outgoing portions in the time τ; M_Σ – the average total mass of the metal processed in the furnace in the time τ.

The mathematical model of the melting process in electric furnaces on solid filling is a system of equations covering all modes of mass transfer. In this case, it is possible to combine the periods of heating and melting (their duration τ_{mel}), and overheating and accumulation (their duration τ_{oh}).

$$K_i^{mel} = K_i^0\, exp\left\{\left(k_i^{v'IOx} + k_i^{v'IIRed} + k_i^{v'IRed}\right)\frac{\Omega_{mel}}{M_\Sigma}\,\tau_{mel}\right\}, \qquad (67)$$

$$K_i^{out} = K_i^{mel} exp\left\{\left(k_i^{v'IRed} + k_i^{v'IIRed} + k_i^{v'IRed} + k_i^{v'IR}\right)\frac{\Omega_{oh}}{M_\Sigma}\,\tau_{oh}\right\}. \quad (68)$$

Eq. (67) and (68) are valid if the charge portion is loaded and melted, and there is neither release nor addition of metal or batch during the whole process. If the metal is discharged or the batch is added, then Eq. (67) and (68) are replaced by Eq. (62) or (66). It should be taken in account that at the beginning of the melting period, the oxidation surface is ωM_z, and by the end of the period, it decreases to Ω_{oh}, and Ω_{mel} can be taken equal to $\frac{\omega M_z}{2}$. The visible mass transfer coefficients of the overheating period are advisable to be attributed to the area of the metal mirror in the furnace, since the mass transfer processes occur mainly along this surface. Only the "crucible" reaction occurs over the surface of the crucible, which is in a certain relation to the surface of the metal mirror in the furnace, and therefore the assumption can be considered quite acceptable.

For iron melting in an electric furnace, it is advisable to apply a mathematical model on the basis of Eq. (56):

$$M_{Fe}^{\Sigma} = K_{Fe}\left[k_{Fe}^{vIOx}\frac{\omega M_\Sigma}{2}\tau_{mel} + \left(k_{Fe<C>}^{v'Red} + k_{Fe<C>}^{vIIRed} + k_{Fe<Si>}^{vIIRed} + k_{Fe<Mn>}^{vIIRed}\right)\Omega_{oh}\,\tau_{oh}\right]. \qquad (69)$$

The most difficult problem is the solution of the mass transfer equations in the case when $g^{out} = g^{in}$, and the process is continuous.

It is necessary to determine the dependence of the concentration of the element on time for the accumulation zone (zone 4) in the general case, that is, $g^{out} = g^{in}$.

Suppose that at the initial time the iron mass in the fore-hearth was M_0 and contained K_i^o % of the *i*-th element. At the time τ, the mass of the pig iron in the fore-hearth is determined by the time: $M_\Sigma = M_0 + (g^{in} - g^{out})\,\tau$; where g^{in} – incoming flow rate equal to the capacity of the cupola, kg/s; g^{out} – cast iron tapping speed, kg/s.

The mass of the *i*-th element in cast iron at the time τ is equal to: $M_i = \frac{M_\Sigma K_i}{100} = [M_0 + (g^{in} - g^{out})\,\tau]\frac{K_i}{100}$.

The rate of change in mass M_i:

$$\frac{dM_i}{d\tau} = \frac{d(M_\Sigma K_i)}{d\tau 100} = [M_0 + (g^{in} - g^{out})\,\tau]\frac{dK_i}{100\, d\tau} + \frac{k_i}{100}(g^{in} - g^{out}), \quad (70)$$

on the other hand,

$$\frac{dM_i}{d\tau} = k_i^{v'}\frac{K_i}{100}\Omega + \frac{g_i^{in}}{100}K_i^{(3)} - \frac{g^{out}}{100}\,K_{i,} \qquad (71)$$

where $K_i^{(3)}$ – the concentration of the *i*-th element in the overheating zone.

If equating (70) and (71), we obtain:

$$[M_0 + (g^{in} - g^{out})\,\tau]\frac{dK_i}{d\tau} + K_i(g^{in} - g^{out}) = k^{v'}K_i\omega[M_0 + (g^{in} - g^{out})\,\tau] + g^{in}K_i^{(3)} - g^{out}K_{i,}(72)$$

where $w = \frac{\Omega}{M_\Sigma}$ is the specific surface area of batch materials.

We will use the following notation: $A = g^{in} - g^{out}$; $B = -k_i^{v'}\omega M_0 + g^{in}$; $G = -k_i^{v'}\omega(g^{in} - g^{out})$; $D = g^{in}K_i^{(3)}$; $E = M_0, x = \tau, y = K_i$.

Substituting the adopted notation into Eq. (72), we obtain the differential equation:

$$\frac{dy}{dx} + \frac{B_y + G_{xy} - D}{A_x + E} = 0; \frac{dy}{dx} + \frac{B + Gx}{Ax + E} - y = \frac{D}{Ax + E}, \qquad (73)$$

which is a linear equation of the first order with respect to the unknown function and its derivative. Eq. (73) can be recorded in the following form:

$$\frac{dy}{dx} + P(x)y = Q(x). \tag{74}$$

Eq. (74) has the following solution:

$$y = e^{-\int pdx}\left[e^{\int pdx}Qdx + C\right]. \tag{75}$$

Let us calculate: $\int Pdx = \int \frac{B+Gx}{Ax+E}dx = \frac{G}{A}x + \frac{AB-GE}{A^2}ln[Ax+E]$.

The integral in square brackets in Eq. (75) in a finite form could not be obtained via elementary functions, and was calculated on a computer.

Table-1. Distribution of element's loss by zones

Indicators of the melting process	**Gas cupola with a remote chamber (20 kg/h)**		**Gas cupola with heterogeneous bed charge (700 kg/h)**		
	Melt				
	28.3	27.5	24.3	21.3	16.4
Batch composition:					
C	3.3	3.4	3.5	3.4	3.35
Si	1.86	1.76	1.74	1.392	1.42
Mn	0.48	0.61	0.54	0.49	0.52
Content in samples from the shaft:					
C	3.25	3.3	1.9	3.4	3.4
Si	1.78	1.645	1.74	1.53	1.52
Mn	0.43	0.575	0.36	0.45	0.48
Content in samples from the fore-hearth:					
C	3.05	3.05	2.0	3.3	3.35
Si	1.72	1.57	1.74	1.53	1.492
Mn	0.41	0.52	0.35	0.43	0.47
Melting loss in the camera (% of the initial composition in the batch):					
C	1.52	2.94	45.7	0	+0.7
Si	4.3	6.53	0	+9.9	+7.04
Mn	10.4	5.74	33.3	8.16	7.69
Melting loss in the overheating camera (% of the initial composition in the batch):					
C	6.06	7.36	+2.9	2.94	-0.7
Si	3.2	4.27	-1.72	0	1.94
Mn	4.18	9.01	1.9	4.04	1.93
Share of melting loss $\frac{\textit{in the shaft}}{\textit{in the overheating camera}}$ **(% ratio):**					
C	$\frac{20}{80}$	$\frac{28.5}{71.5}$	$\frac{93}{+7}$	$\frac{0}{100}$	$\frac{0}{0}$
Si	$\frac{57.2}{42.8}$	$\frac{60.5}{39.5}$	$\frac{0}{100}$	$\frac{0}{0}$	$\frac{0}{0}$
Mn	$\frac{71.3}{28.7}$	$\frac{39.5}{60.5}$	$\frac{94.6}{5.4}$	$\frac{66.9}{33.1}$	$\frac{79.9}{20.1}$

Source: Grachev (2016)

The mass transfer was calculated for cast iron melting on the basis of the mathematical model. In order to calculate the mass transfer over the cupola zones, it is necessary to determine the fraction of element loss for zones of heating, melting, and overheating. For this purpose, experimental melting was carried out in a laboratory gas cupola with a capacity of 20 kg/h and an experimental gas cupola with a heterogeneous bed charge (refractory charge) with a productivity of 0.7 t/h as described in the Research Methodology. Experiments in the laboratory cupola showed that 20-30% of carbon (from the total loss), about 60% of Si and, on average, 70% of Mn (the data on manganese vary considerably) are lost in the shaft during heating and melting. In the gas cupola with a heterogeneous nozzle, melting loss of carbon is completely formed in the shaft, and in the fore-hearth, even a certain "burn-on" was obtained. This is established by the analysis of six samples taken in parallel from each zone. Silicon, on the contrary, was not lost in the shaft at all. A big carbon loss in the charge free from carbon and a small Si loss are extreme cases, since the interphase surface there is larger than in case of melting in gas cupolas without refractory bed charge. The introduction of carbonaceous materials into the bed charge allows avoiding significant carbon loss in the presence of insignificant loss of Si and Mn. The results of mass transfer calculations are presented in Table 1.

When carrying out experimental melting in the laboratory cupola, it was established that in case of using frame-type castings as charge, it is impossible to determine the Fe loss and the total loss by weighing the batch and liquid metal due to the sand burn-on on return and other hindrances. It is also difficult to establish loss of other charge materials due to the difficulty of weighing liquid metal. More accurate is the calculation of iron loss by the amount and composition of the slag. This method can be applied in two ways: first – by weighing the slag and analyzing it, and, secondly, by drawing up a balance of manganese, which is supplied to slag as a result of the Mn loss from the cast iron. It is convenient to use this method when it is difficult to take into account the amount of slag, for example, when sampling slag from various zones of the melting unit or at considerable masses of the smelted metal.

From the data given in Table 1, it can be seen that calculation using the introduced concept of visible mass transfer coefficients allows analyzing mass transfer by zones, as a result of which the composition and properties of cast iron are formed.

When calculating the loss in IOx, it was assumed that the elements, except iron, are lost only within the layer of the lost iron. The determination of iron loss by zones is a significant difficulty; therefore, only $k_{\mathrm{Fe}}^{v\mathrm{IOx}}$ was determined. For C, Si, Mn, the values of k^{vIOx} were set, and for the gas cupola with external overheating chamber – k^{v} in the melting and overheating zones, that is, in the latter case, two modes IIOx and IIIOx were covered. For the gas cupola with a heterogeneous nozzle, it was possible to clearly calculate the values of k^{v} by zones. It was established that in the gas cupola with a bed charge, with no carbon in the composition of the charge, a significant amount of its loss was observed. 38.03 kg of Fe was recovered (pre-oxidized) due to carbon. And at the same time, the final composition of the slag reveals a significant iron loss. Upon introduction of carbon into the composition of the refractory bed charge, a mass flow appears in the II*Red* mode.

In the cupola with the heterogeneous bed charge, melting was carried out with sampling of the slag above the refractory bed charge in the melting zone from the shaft, after the refractory bed charge and from the fore-hearth (Table 2). The data of Table 2 confirm the previously stated assumptions about the nature of elements' loss in the gas cupola.

Table-2. Slags compositions from various zones of the gas cupola with a heterogeneous refractory charge

Place of sampling	**Content of components, %**					
	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	the rest
From the shaft above the refractory bed charge	53.7	26.2	15.7	1.3	1.7	1.4
After the refractory bed charge	54.0	27.5	11.0	0.8	2.6	4.1
From the fore-hearth	51.5	20.0	6.22	0.9	3.04	18.34

Source: Grachev (2016)

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