



# Modelling and computer simulation of reagents diffusion in high temperature diffusion controlled heterogeneous reactions

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## ABSTRACT

**Purpose:** In this paper a computational method which takes into account convection in the melting metal and slag phases is discussed.

**Design/methodology/approach:** A deterministic computational model of high-temperature heterogeneous reaction between metal and oxide melts has been developed.

**Findings:** Transport of reagents and products of reaction occur simultaneously both by diffusion and by laminar natural convection of the melting metal and oxide fluxes. The convection-diffusion equations have been numerically solved by a finite-differences time-implicit discretization scheme. The model was implemented by program which had been written in C# language. The computations have been performed for desulfurization reaction between liquid metal and slag phases.

**Research limitations/implications:** To verify the reliability of the model, the computed results have been compared with experimental data. The good agreement has been obtained. The numerical results agree well with the results which were found by two independent experiments.

**Originality/value:** This computational model enables to obtain results, for example sulfur concentration changes along the x axis, which is very difficult, almost impossible, to get by experiment. Using this mathematical model allows to predict the distribution of elements in the metal during the refining process and to reduce expenses in selection of optimum process' conditions, which provide the metal with required composition. This model can be used for quantitative analysis of the diffusion stage of the heterogeneous reactions.

**Keywords:** Mathematical modeling; Simulation convection; Diffusion; Desulfurization; Metal-slag interface

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## METHODS OF ANALYSIS AND MODELLING

### 1. Introduction

During the past century, the steel industry, welding and coating technologies have been transformed by major

technological changes. Coupled with the implementation of innovative production systems, there have been ever increasing demands for improved product quality.

The processes of production of steel, alloys, heavy non-ferrous metals, welding and coating occur at high temperature (1200 - 1800°C) in heterogeneous systems, where liquid (metal and slag), gaseous (evolved gases and furnace atmosphere) and some solid phases (fettle, solid additives, non-metallic inclusions etc.) take part. A system of metal-slag-gas is always multi-component and complex. Processes occurring on the metal-slag and metal-gas boundaries determine the chemical composition of a metal and, therefore, its structure and properties.

One of the most important and complicated problems in those processes is to obtain metals with required properties. An empirical solution of this problem is both expensive and time-consuming and the result may be far from the optimal solution. An effective alternative used for tackling such problems is computer modeling. Mathematical modeling has for a long time been of crucial importance for prediction properties of materials. Lately, during the last three decades, the development of the digital computers has offered new tools to the process analysis. As the number crunching capabilities of the computers expand, the limitations in penetrating the inner depth of the processes seems to be less attributed to the computer power, but rather more to the human capability to describe the physics of the phenomena involved [1]. It has become possible to mathematically model complex physicochemical processes in metallurgical systems [2-23].

Developing a mathematical model of physicochemical processes in a metal-slag system of metal production requires that thermodynamics and kinetics of the processes on the phase boundary between the metal and oxide melts be analyzed. The directions of individual chemical reactions in real technological processes and of the conditions for the achieving of equilibria have been sufficiently studied and analyzed in detail [12,15,24-26]. The kinetics of metal-slag interactions have been studied by many researchers e.g. [27,28]. Most researches come to the conclusion that the activation process is not rate determining stage in the oxidation of impurities in steel production processes [29,30]. In most cases high temperature reactions occur under diffusion control conditions. There are only a few exceptions to this, such as the oxidation of carbon in carbon-iron melts [31] or that of sulfur in copper, nickel or cobalt sulfides [32]. The results of these investigations were very useful for us.

There are numerous researches on mathematical modeling of metallurgical processes, for example [2,15,16,19,26,33-48]. However, most of them are empirical, statistical or "black box type" input-output models for instance [2,15,35,19] or models that take into consideration the processes which occur only in the metal or the oxide phase e.g. [33,34]. Interesting results were obtained from the model [48]. It considers rates of transfer of elements through the metal-oxide interface and mutual influence of the chemical reactions taking place on this interface. However, transport of elements in the bulk of the metal and oxide phases is considered without going into details.

Recently, a model for transfer of element from the metal to the slag phase by means of a heterogeneous reaction and diffusion of this element in the stationary melts based on the thermodynamics and kinetics analysis was developed [49]. Unfortunately, the computation results disagreed with the experimental data; viz. the time necessary to reach the equilibrium was significantly longer than the expected one. To overcome this difficulty, we propose in this paper a computational method which

takes into account convection in the melting metal and slag phases. The model was implemented by C# code.

## 2. The modelling method

The development of computational methods for heterogeneous reaction, taking place at the metal-slag interface, requires the study of the three steps:

1. Transport of reagents from the bulk to the interface.
2. Reaction at the interface.
3. Transport of the products of the reaction from the interface.

Let us consider each of these steps in details, the steps 1 and 3 being described together.

### Mass transfer

This process comprises two mechanisms: the molecular diffusion and the convective transport. Thus the flux of element  $j$  ( $^{12}\Lambda$ ) consists of two components, one due to diffusion  $jD$  and the second due to convective flow  $je$

$$j = j_D + j_C$$

We assume that both the data and the geometry do not depend on the variables  $y, z$ . Then the problem can be identified with an one-dimensional problem, posed in the domain  $[0, l]$  (see Fig. 1). This domain is divided into two subdomains by the metal-slag interface located on  $x = d$ , ( $0 < d < l$ ), where  $x$  denotes the space variable.

In this way, the mathematical Equations, which describe the transport of the element in the moving metal and slag melts, are

$$\frac{\partial C_{[E]}}{\partial t} = u_M \frac{\partial C_{[E]}}{\partial x} + D_{[E]} \frac{\partial^2 C_{[E]}}{\partial x^2} \quad \text{in } [0, d], \quad (1)$$

$$\frac{\partial C_{(E)}}{\partial t} = u_S \frac{\partial C_{(E)}}{\partial x} + D_{(E)} \frac{\partial^2 C_{(E)}}{\partial x^2} \quad \text{in } [d, l], \quad (2)$$

where

$C_{[E]}$  and  $C_{(E)}$  are the concentrations of the element in the metal and slag phases respectively,  $mol \cdot cm^{-3}$ ;

$t$  denotes the time variable, sec;

$u_M$  and  $u_S$  are the velocities of the movement of the liquid metal and slag phases respectively,  $cm \cdot sec^{-1}$ ;

$D_{[E]}$  and  $D_{(E)}$  are the diffusion coefficients of the element in the metal and slag phases respectively,  $cm^2 \cdot sec^{-1}$ .

### Transfer of the element across the metal-slag boundary

The element is removed by metal-slag reaction in which the element is transferred from the metal through the metal-slag interface into the slag. Since the slag is an ionic solution (25), the reactions are electrochemical by nature and can be written as follow



where  $[E] + ze = (E^{z-})$  are the element in the metal and its anion in the slag phases respectively.

In the derivation of the interface transport term, it is useful to assume that the chemical reaction is infinitely fast and that a local thermodynamic equilibrium exists at the interface between metal and slag phases [1]. The distribution coefficient  $L$  of the element between liquid metal and slag phases is determined by means of this equilibrium, namely

$$L = \frac{C_{(E)r}}{C_{[E]l}}, \quad (4)$$

where  $C_{(E)r}$  and  $C_{[E]l}$  are respectively the right and the left limit values of concentration of the element at the interface.

The system of Equations (1, 2) together with the interface condition (4) is the basis of our mathematical model.

### 3. Description of results

In order to simulate the convection, the one-dimensional domain  $[0, l]$  is divided into two layers ("upper" and "lower"). More precisely, the nodes along the x-axis are doubled with two degrees of freedom at the same coordinate. In addition, it is assumed that the velocity of the metal and slag phases in the "upper" layer is positive (+u) and the velocity of these phases in the "lower" one is negative (-u).

Thus, Equations (1, 2) can be rewritten

$$\frac{\partial C_{[E]U}}{\partial t} = \mathbf{u}_M \frac{\partial C_{[E]U}}{\partial x} + D_{[E]} \frac{\partial^2 C_{[E]U}}{\partial t^2} \quad \text{in } [0, d], \quad (5)$$

$$\frac{\partial C_{[E]L}}{\partial t} = -\mathbf{u}_M \frac{\partial C_{[E]L}}{\partial x} + D_{[E]} \frac{\partial^2 C_{[E]L}}{\partial t^2} \quad \text{in } [0, d], \quad (6)$$

$$\frac{\partial C_{(E)U}}{\partial t} = \mathbf{u}_S \frac{\partial C_{(E)U}}{\partial x} + D_{(E)} \frac{\partial^2 C_{(E)U}}{\partial t^2} \quad \text{in } [d, l], \quad (7)$$

$$\frac{\partial C_{(E)L}}{\partial t} = -\mathbf{u}_S \frac{\partial C_{(E)L}}{\partial x} + D_{(E)} \frac{\partial^2 C_{(E)L}}{\partial t^2} \quad \text{in } [d, l]. \quad (8)$$

where  $C_{[E]u}$  and  $C_{[E]l}$  are the concentrations of the element in the "upper" and "lower" layers respectively in the metal phase;  $C_{(E)u}$  and  $C_{(E)l}$  are the concentrations of the element in the "upper" and "lower" layers respectively in the slag phase.

To solve these Equations, reference frames which move with the velocity  $\pm u$  were chosen. For this purpose, we introduce the following notations. Let us denote by  $\eta_M$  and  $\mu_M$  (respectively  $\eta_S$  and  $\mu_S$ ) the moving reference frames in the corresponding "upper" and "lower" layers in the metal phase (respectively in the slag phase). We also introduce  $u_M t$  and  $u_S t$  the metal and slag phases travel distances, namely the distance traveled by the metal and by the slag phases respectively at time  $t$ .

Hence, in the new reference frames

$$\eta_M = x + u_M t, \quad \eta_S = x + u_S t, \quad \mu_M = x - u_M t, \quad \mu_S = x - u_S t,$$

the concentration of the element can be transformed into

$$C_{[E]U}(x, t) = \psi(\eta_M, t), \quad (9)$$

$$C_{[E]L}(x, t) = \phi(\mu_M, t), \quad (10)$$

$$C_{(E)U}(x, t) = \psi(\eta_S, t), \quad (11)$$

$$C_{(E)L}(x, t) = \phi(\mu_S, t). \quad (12)$$

Substituting Equations (9 - 12) into (5 - 8) respectively leads to

$$\frac{\partial \psi}{\partial t} = D_{[E]} \frac{\partial^2 \psi}{\partial \eta_M^2}, \quad (13)$$

$$\frac{\partial \phi}{\partial t} = D_{[E]} \frac{\partial^2 \phi}{\partial \mu_M^2}, \quad (14)$$

$$\frac{\partial \psi}{\partial t} = D_{(E)} \frac{\partial^2 \psi}{\partial \eta_S^2}, \quad (15)$$

$$\frac{\partial \phi}{\partial t} = D_{(E)} \frac{\partial^2 \phi}{\partial \mu_S^2}. \quad (16)$$

We have used the following initial, boundary and interface conditions:

**The initial conditions** (see Fig. 1).

$$\begin{cases} C_{[E]}(x, 0) = C_{[E]1}, & 0 \leq x < h, \\ C_{(E)}(x, 0) = C_{(E)2}, & h < x \leq l. \end{cases} \quad (17)$$

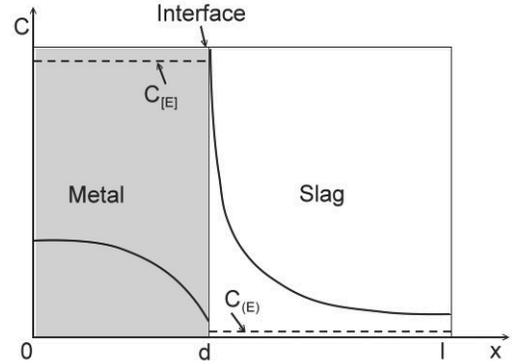


Fig. 1. Concentration profile of the element in the metal and slag phases

**The boundary conditions (for  $t > 0$ )**

$$\left( \frac{\partial \psi(\eta_M, t)}{\partial \eta_M} \right)_{0, d_l} = 0, \quad (18)$$

$$\left( \frac{\partial \phi(\mu_M, t)}{\partial \mu_M} \right)_{0, d_l} = 0, \quad (19)$$

$$\left( \frac{\partial \psi(\eta_S, t)}{\partial \eta_S} \right)_{d_r, l} = 0, \quad (20)$$

$$\left( \frac{\partial \phi(\mu_S, t)}{\partial \mu_S} \right)_{d_r, l} = 0. \quad (21)$$

where  $d_l$  and  $d_r$  are the left and right limit value of  $x$  at the interface. In addition to the above boundary conditions, the following ones, which helped to describe the bottom-up and top-down movements of the melts, were chosen:

$$\psi(\eta_M, t)_0 = \phi(\mu_M, t)_0 \quad x = 0, \quad (22)$$

$$\phi(\mu_M, t)_{d_l} = \psi(\eta_M, t)_{d_l} \quad x = d_l, \quad (23)$$

$$\phi(\mu_S, t)_{d_r} = \psi(\eta_S, t)_{d_r} \quad x = d_r, \quad (24)$$

$$\psi(\eta_S, t)_l = \phi(\mu_S, t)_{d_l} \quad x = l. \quad (25)$$

**The interface conditions (metal-slag interface)** (see Fig. 2)

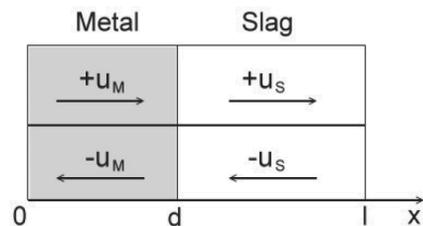


Fig. 2. Metal-slag interface

Since the heterogeneous reaction (3) occurs at the metal-slag interface, it provides new flux boundary condition. The concentration of sulfur at the metal-slag boundary ( $x = d$ ) is calculated from condition (4) and the mass conservation. Let us denote by  $m_{(E)}$  and  $m_{[E]}$  the right and left limit values of the element mass at the interface correspondingly. Then, introduce  $\Delta m$ , the mass of the element transferred from the metal to the slag. Finally, let  $MS_r$  (respectively  $Mm_l$ ) be the right limit value of the slag mass (respectively the left limit values of the metal mass) at the interface.

Then Equation (4) can be rewritten as follow

$$L = \frac{m_{(E)r} + \Delta m}{MS_r} \cdot \frac{M_{Ml}}{m_{[E]l} - \Delta m}, \quad (26)$$

from which we deduce that

$$\Delta m = \frac{LM_{S_r}m_{[E]l} - M_{Ml}m_{(E)r}}{M_{Ml} + MS_rL}, \quad (27)$$

and consequently

$$C_{[E]l} = \frac{m_{[E]l} - \Delta m}{M_{Ml}} \quad x = d_l, \quad (28)$$

and

$$C_{(E)r} = \frac{m_{(E)r} + \Delta m}{MS_r} \quad x = d_r. \quad (29)$$

### 3.1. Discretization of the equations

Equations (13 - 16) have been numerically solved by a finite-differences approach. We denote by  $\Delta t$  the constant time step. For the space variable  $x$ , the mesh size  $\Delta x_M$  in the metal phase, and  $\Delta x_S$  for the slag phase are chosen following

$$\Delta x_M = u_M \Delta t, \quad \Delta x_S = u_S \Delta t, \quad (30)$$

and for any function  $f(x,t)$ , the quantity  $f(i\Delta x, n\Delta t)$  is denoted by  $f_i^n$ .

The convection-diffusion Equation can be discretized by an explicit time-scheme. Despite its simplicity such an implementation requires to ensure a stability condition that is written in that case

$$\frac{D\Delta t}{(\Delta x)^2} \leq \frac{1}{2}. \quad (31)$$

This means that the time to propagate through a distance  $\Delta x$  is proportional to  $\Delta x^2$ . Moreover, from (30) and (31) we get

$$\Delta t = \frac{\Delta x}{u}, \quad (32)$$

$$\Delta t \leq \frac{(\Delta x)^2}{2D}. \quad (33)$$

As we intend to apply the model for low values of  $u$ , it appears a contradiction. Indeed, as  $u$  tends to zero,  $\Delta t$  tends to infinity and has to remain lower than  $\frac{(\Delta x)^2}{2D}$ .

For these reasons, we rather use a time-implicit discretization scheme, which does not require any stability condition. Remark however that implicit schemes are stable for larger time step, but tend to damp the smaller scales. Hence,  $\Delta t$  can be chosen greater than for an explicit time-scheme, but not too large, in order to preserve the accuracy of the modelisation. Approximating the second derivatives  $\left(\frac{\partial^2}{\partial n^2}, \frac{\partial^2}{\partial \mu^2}\right)$  by a second order centered scheme, the discrete versions of Equations (13 - 16) are given below

$$\frac{\psi_i^{n+1} - \psi_i^n}{\Delta t} = \frac{D_{[E]}}{(\Delta x_M)^2} (\psi_{i-1}^{n+1} - 2\psi_i^{n+1} + \psi_{i+1}^{n+1}), \quad 1 \leq i \leq k, \quad (34)$$

$$\frac{\psi_i^{n+1} - \psi_i^n}{\Delta t} = \frac{D_{(E)}}{(\Delta x_S)^2} (\psi_{i-1}^{n+1} - 2\psi_i^{n+1} + \psi_{i+1}^{n+1}), \quad k+1 \leq i \leq p, \quad (35)$$

$$\frac{\phi_i^{n+1} - \phi_i^n}{\Delta t} = \frac{D_{[E]}}{(\Delta x_M)^2} (\phi_{i-1}^{n+1} - 2\phi_i^{n+1} + \phi_{i+1}^{n+1}), \quad 1 \leq i \leq k, \quad (36)$$

$$\frac{\phi_i^{n+1} - \phi_i^n}{\Delta t} = \frac{D_{(E)}}{(\Delta x_S)^2} (\phi_{i-1}^{n+1} - 2\phi_i^{n+1} + \phi_{i+1}^{n+1}), \quad k+1 \leq i \leq p, \quad (37)$$

where  $k$  and  $p - k$  are the number of nodes along the  $x$ -axis in the metal and slag phase respectively.

Let us consider the solution of Equations (34 - 37), for example Equation (34). Defining

$$r = \frac{D_{[E]}}{(\Delta x_M)^2}, \quad (38)$$

Equation (34) can be rewritten for a given  $i$  in the following form:

$$\psi_i^n = r\psi_{i-1}^{n+1} + (1 + 2r)\psi_i^{n+1} + r\psi_{i+1}^{n+1}. \quad (39)$$

In these conditions, the system of  $k$  Equations (34) can be expressed as

$$\begin{aligned} \psi_0^n &= (1+r)\psi_0^{n+1} + r\psi_1^{n+1} \\ \psi_1^n &= r\psi_0^{n+1} + (1+2r)\psi_1^{n+1} + r\psi_2^{n+1} \\ \psi_2^n &= r\psi_1^{n+1} + (1+2r)\psi_2^{n+1} + r\psi_3^{n+1} \\ &\vdots \\ \psi_{k-1}^n &= r\psi_{k-2}^{n+1} + (1+2r)\psi_{k-1}^{n+1} + r\psi_k^{n+1} \\ \psi_k^n &= r\psi_{k-1}^{n+1} + (1+r)\psi_k^{n+1} \end{aligned} \quad (40)$$

This is a tridiagonal system of coupled implicit Equations. Due to the particular structure of this matrix (tridiagonal), special algorithms have been developed that take advantage of the tridiagonal structure, typically by not storing and using the zero elements outside the band. In our case, the system (40) was solved using LU-like matrix inversion algorithm (see (51)). This gives the solution very fast from a computational point of view.

Note that the boundary conditions (18 - 21) are taken into account in these Equations.

The final concentration of the element is given by

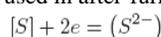
$$C_E(i\Delta x, n\Delta t) = \frac{\phi_i^n + \psi_i^n}{2} \quad (41)$$

## 4. Computer program implementation

A computer program based on the model was written on C# language. Fig. 3 shows a general flowchart of this program. More details can be found in [51]. Note that the computations do not require a lot of computational resources and were carried out on a usual PC.

## 5. Numerical results

The computations were performed on desulfurization reaction (42) using metal and slag with compositions approaching those used in after-furnace treatment.



In order to calculate sulfur distribution in the metal and slag phases, the following data were used:

- Metal composition: Fe - C - S melts containing 0.5,1, 2 and 3 wt% C, 0.02 -0.25 wt%S;
- Slag composition: 51wt%Al<sub>2</sub>O<sub>3</sub>, 43wt%CaO, 6wt%MgO;
- Temperature: 1773K;
- Diffusion coefficient in the metal phase:  $D_{[S]} = 6.2 \cdot 10^{-5}[\text{cm}^2/\text{s}]$  [52];
- Diffusion coefficient in the slag phase:  $D_{(S)} = 10^{-5}[\text{cm}^2/\text{s}]$  [53];
- Metal mass: 50 gr.;
- Slag mass: 50 gr.;
- Length of the metal phase along x-axis: 0.94 cm;
- Length of the slag phase along x-axis: 2.19 cm.

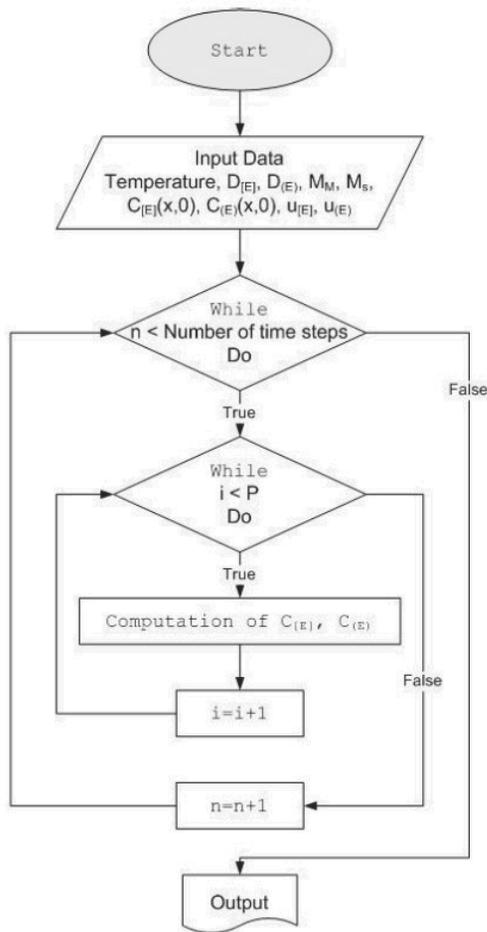


Fig. 3. General flowchart of the program

The following results have been depicted:

1. Sulfur concentration (wt%) changes in the metal and slag phases along coordinate  $x$  at the given time Fig. 4.
2. Sulfur concentration (wt%) changes in the bulk of the slag and metal phases with respect to the time Fig. 5.

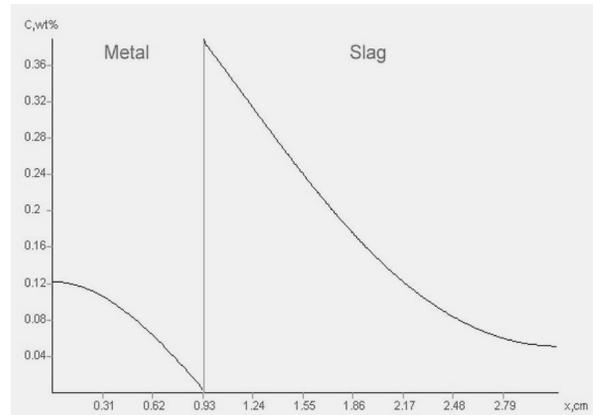


Fig. 4. Screen shot of the sulfur concentration changes at 5th min from the beginning of the desulfurization process

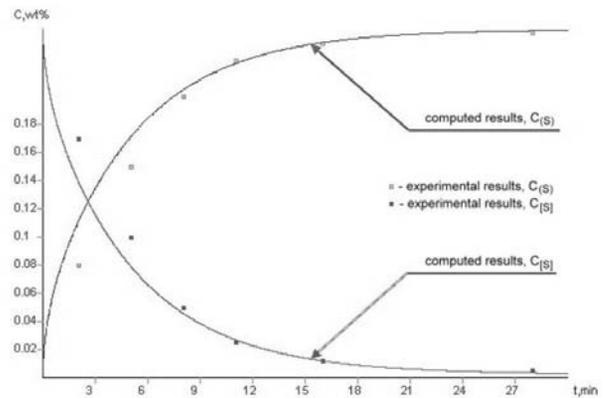


Figure 5. Sulfur concentration changes with respect to the time

## 6. Experimental verification

To verify the reliability of the computed sulfur distributions in the metal and slag phases, we have compared them with experimental data.

The changes of sulfur concentration were controlled by chemical analysis. The contents of liquid metal and slag phases were similar to those which were used in calculation. To ensure the fast achieving of equilibrium the metal and the oxide samples were grounded and mixed. Thus prepared mixtures were held in alumina crucibles at 1773K. Duration of the experiments was 15-30 minutes and small samples of the metal and the slag were taken each 5 minutes. The experimental results are marked on Fig. 5 by dots.

As it was expected, the amount of sulfur decreased in the metal phase and in parallel increased in the slag. In addition the sulfur concentration at the interface fell below and rose above the bulk concentration in the metal and slag phases respectively (see Fig. 4).

Both of these phenomena occurred due to the reaction between these phases. As the result of the reaction, a concentration gradient

of sulfur set up and sulfur diffused toward and from the metal - slag interface in the metal and slag phases correspondingly. The shapes of curves on Fig. 4 correspond to classical convective-diffusional process.

The concentration of sulfur in the metal phase was decreasing during the process until the system reached a thermodynamic equilibrium. It happened after about 30 min from the beginning of the process. The same result was obtained by experiment (see Fig. 5).

## 7. Conclusions and perspectives

A deterministic kinetic mathematical model of transfer of element from the liquid metal to the slag phase has been developed. To implement this model a program in C# language has been written. The computations have been performed for desulfurization process. The distribution of sulfur in the metal and slag phases along the  $x$  axis at a given time and the sulfur concentration changes in the volume of these phases with respect to the time have been computed.

The numerical results agree well with the results which were found by two independent experiments.

This computational model enables to obtain results, for example sulfur concentration changes along the  $x$  axis, which is very difficult, almost impossible, to get by experiment.

Using this mathematical model allows us to predict the distribution of elements in the metal during the refining process and to reduce expenses in selection of optimum process' conditions, which provide the metal with required composition.

This model can be used for quantitative analysis of the diffusion stage of the heterogeneous reactions.

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