# DEVELOPING MODEL OF MASS-EXCHANGE PROCESSES IN POROUS BODIES ON EXAMPLE OF IRON-ORE PELLETS OXIDATION PROCESS

There is developed a model of magnetite oxidation in agglomeration of iron-ore pellets. Unlike the oxidation models proposed before, this model considers the porous structure of a pellet: the surface and the distribution of pores by sizes. The process of magnetite oxidation is considered as three-unit: diffusion by pores, diffusion through products of oxidation and proper chemical reaction. The model considers various limiting steps at different stages of the process. There were carried out pilot studies on the basis of SSMCC pellets for confirming the correctness of the proposed model. This model can be used in a broader aspect: for the description of the process of chemical reaction in polyporous bodies.

*Key words:* Iron-ore pellets porous body, pores distribution by sizes, magnetite oxidation, diffusion efficient coefficient, chemical reaction

## INTRODUCTION

Iron ore pellets as a furnace charge components, represent porous bodies with well-developed system of different type pores. The type and the surface of pores, their distribution, determine the course of such defining quality processes as oxidation and restoration during agglomeration and subsequent metallization of the product [1-4].

The majority of real technological processes (restoration, secondary oxidation and others) are defined by the diffusion of gas–reagent in a porous body and the chemical reaction of interaction itself. The equation of gas diffusion in the volume of a porous body taking into account chemical reaction can be written down as follows [5]:

$$[\mathrm{D}]\frac{d^2C}{dx^2} = k\rho SC^n,\tag{1}$$

where [D] is diffusion effective coefficient;

C is gas concentration;

k is speed constant;

$\rho$ is porous matter density;

S is pores surface;

n is reaction order/

The integration of equation (1) leads to the equation for the process speed [6]:

$$f = 4\pi\, r^2 (\frac{2}{n+1} k\rho S[\mathrm{D}]^{\frac{1}{2}}C^{\frac{n+1}{2}} \times$$
$$\times \left[\frac{1}{tn3\varPhi} - \frac{1}{3\varPhi}\right]\tag{2}$$

where $\varPhi$ is Tile-Zeldovich parameter;

r - is pore radius;

Sv. S. Kvon, T. S. Fillippova, H. I. Malashkevichute, Karaganda State Technical University, Karaganda, Kazakhstan

*th* - hyperbolic tangent.

It should be noted that the given equations well describe such processes as filtration of gas and liquids or diffusion through rather porous films, but are inapplicable in the description of such processes, as, for example, oxidation, especially at the final stages. As a result of this process there is formed a rather dense film and it is necessary to speak not of diffusion through the porous environment any more, but through a solid body of certain porosity.

## EXPERIMENTAL STUDIES

The process of oxidation consists of three stages: diffusion on the pellet pores, diffusion through the formed layer of products and proper chemical magnetite oxidation reactions. The speed of magnetite oxidation at rather high temperatures is high [7], therefore the speed of the process will be defined by two factors in general: either transfer of oxygen in the pores, or diffusion through the hematite layer. I.e. at different stages of oxidation the speed of diffusion is to be described by various equations.

The process of oxidation at the first stage is considered as two-unit: diffusion in a porous body and a chemical reaction.

The total speed of the process can be presented in the form:

$$\mathrm{f}_n = \sqrt{\frac{2}{n+1} k[\mathrm{D}]C_0^{n+1}}\tag{3}$$

where $\mathrm{f}_n$ is the amount of oxygen reacted for a unit of time per a pellet area unit / $g/cm^3$;

n is the reaction order by oxygen;

$C_0$ is oxygen concentration on the pellet surface / g / cm³;

k is the reaction effective speed constant for a unit of the porous body volume / c⁻¹.

Thus, in equation (3) all values are known, except for the effective coefficient of diffusion [D].

Studying the porous structure of pellets showed that they are characterized by a wide range of pores. The effective coefficient of diffusion [D] for polyporous bodies, is, according to [8], described by the model of Cunningham - Jeancoplis [9].

This model considers simultaneously some parameters of the structure (function of pores distribution on radiuses, general porosity, etc.).

Having divided all pores into groups characterized by the equivalent radius $\rho_i$ and porosity $\varepsilon_i$, having allocated micropores which equivalent radius $\rho_1 \ll \rho_i$ (for all i>1), [D] can be presented in the form:

$$[D] = 2\sum_{k\rangle 1}\varepsilon_k \sum_{j\rangle 1}\varepsilon_j \left[D^{-1}(\rho_k) + D^{-1}(\rho_j)\right]^{-1} + \frac{\varepsilon_1^2(1 + 3\sum_{k\rangle 1}\varepsilon_k}{1 - \sum_{k\rangle 1}\varepsilon_k}\, D^{\infty}(\rho_1) \tag{4}$$

The equivalent radius of the i-th group pores entering equation (4) can be presented as:

$$\rho_i = (\int_0^\infty \frac{1}{\rho} y(\rho)d\rho)^{-1} \tag{5}$$

where $y(\rho)$ is the volume function of pores distribution on radiuses.

The value $y(\rho)$ can be calculated either from experimental data of mercury porosimetry, or from parameters of the accepted model of a porous body.

Thus, having defined by equation (4) the effective coefficient of diffusion [D] and accepting the order of oxidation reaction by oxygen equal to 1, it is possible to calculate the macroscopic speed of the oxidation process for this sample:

$$W_n = S_{ok} \times f_n = S_{ok} \times C_o \times \sqrt{k[D]} \tag{6}$$

where $S_{ok}$ is the sample external surface / cm²;

$f_n$ - is the amount of oxygen reacted for a unit of time per a pellet area unit / g/cm³

Equation (6) is fair for the process consisting of two components: the process of diffusion on pores and the proper chemical reaction on the pores surface. Such conditions are met only at the first stages of the process when magnetite oxidation happens directly on the internal surface of pores, at this the concentration in pores $C_n$ reduces practically to zero.

At later stages of the process on the pores surface there forms a dense integumentary bed of hematite which interferes with the process of transferring oxygen to the interaction zone, i.e. the oxidation process now consists of three stages: diffusion on pores, diffusion through the layer of the formed hematite and chemical reaction of oxidation on the hematite – magnetite interfaces. The

limiting stage of the process there becomes diffusion through the hematite layer, therefore in pores there is established some, other than zero, concentration of $C_\kappa$.

Thus, the process of oxidation of a porous body can be described by two equations:

At $|\tau| < |\tau_k|$

$$W_n = S_{ok} \times C_0 \times \sqrt{\kappa[D]}$$

$$|\tau_k| = \left|\frac{S_{ok} \times r \times \sqrt{\kappa[D]}}{S_c[D]}\right|, \tag{7}$$

where $|\tau|$ - time of the process / sec;

$|\tau_k|$ - time, within which the process of oxidation will directly happen on the pores surface / sec.

The process is limited by diffusion through the pores.

At $|\tau| < |\tau_k + \tau_n|$

$$W_T = S_n \sqrt{\frac{Da \times C_0}{2k_1 \times \tau}}$$

$$\tau_n = \frac{m \times r}{[D] \times S_c \times (C_0 - C_k)}, \tag{8}$$

where $W_T$ - the speed of process;

$|\tau_n|$ - the time of process limited by diffusion.

The process is limited by diffusion through the hematite layer.

As an experimental object for confirmation of the correctness of the developed model there were selected the pellets made of the concentrate of the Sokolovsko-Sarbaysky field (Kazakhstan).

For studying the porous structure of samples there was used the method of mercury porosimetry. By means of this method it is possible to determine the size and number of pores, absolute density of materials, specific surface and distribution of pores by sizes. Besides, knowing a hysteresis loop form, it is possible to judge the pores form qualitatively.

Experimentally the method of mercury porosimetry is reduced to scoping the pressed mercury depending on pressure.

In this work there was used a mercury porosimeter of "Microporosimeter 910" (USA) that permitted to consider pores with radius from 2 μm and above. The sample before test was exposed to drying at t = 70 °C in a vacuum case for removal of the adsorbed gases. All studies of the porous structure were carried out with 3 doubles, the convergence of separate points of the curve of pores volume distribution didn't exceed ± 3 %.

For studying the oxidation process kinetics there were used dry laboratory pellets. The studies were carried out on the installation of continuous weighing. Dry pellets placed in the furnace and maintained at t = 900 °C fore stabilization of weight in the neutral environment. For developing the non-oxidizing atmosphere the furnace was blown with argon, the expense made 2l / min. At achievement of constant weight gave air to the furnace (flow rate 2l / min) and fixed the change of the

Table 1 **Data of the porous structure of pellets of the Sokolovsko-Sarbaysky field**

| No | Effective rdius / x10³ A | | | | | | $\frac{\Sigma V}{\Sigma S}$ | Pores S, ≤ 200 A / m²/g |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | | |
| | 17 600 - 50 | 50 - 20 | 20 - 5 | 5 - 1 | 1 - 0,5 | 0,5 - 0,05 | | |
| SSMCC concentrate | 0,0018 0,0007 | 0,0535 0,0347 | 0,0273 0,1003 | 0,0283 0,3925 | 0,0029 0,0945 | 0,0034 0,7560 | 0,1172 1,3787 | 0,3287 |

**Note:** numerator – pores volume / m³/g; denominator – pores surface / m²/g.

Table 2 **Speed of magnetite oxidation of SSMCC pellets in the course of agglomeration**

| No | Pores surface S / m²/g | Pore average radius r / A | Average oxidation speed within 30 minutes / %/min (exper) | Average oxidation speed within 30 minutes / %/min (calc) | Oxidation degree within 30 minutes / % | Divergence / % |
|---|---|---|---|---|---|---|
| SSMCC | 1,3787 | 1700 | 3,1 | 2,75 | 93 | 12,7 |

pellets mass within during 30 min. The oxidation level of pellets was calculated by the formula:

$$\alpha = \frac{\Delta P}{1/9 FeO \times 0,995 \times P_s}, \qquad (9)$$

where α is the oxidation degree / %;

ΔP is mass changing / g;

FeO is FeO content in the concentrate / ppm;

$P_s$ is the oxidized pellets mass.

Besides, FeO content in the oxidized pellets was controlled by the chemical analysis. The degree of oxidation was calculated by the formula:

$$\alpha = (1 - \frac{FeO_{ок}}{FeO_{кон}}), \qquad (10)$$

where $FeO_{ок}$ is FeO content in the pellets / ppm
$FeO_{к}$ –in concentrate / ppm.

The divergence in the α values calculated by formulas (9) and (10) did not exceed ± 3 %.

## RESULTS AND DISCUSSION

As a result of the carried out pilot studies for determining parameters of the porous structure there were obtained the data of the nature of pores distribution and pores surface, Table 1.

On the basis of the obtained experimental data of the pellets porosity there was calculated the effective coefficient of diffusion. Taking into account the obtained coefficient of diffusion and the proposed model of oxidation the speed of the pellets oxidation process in the course of agglomeration, Table 2.

The analysis was carried out on 10 samples. The average data are provided in the Table.

As it is seen from the table data, the divergence of the calculated and experimental data makes 12,7 % that is quite satisfactory for the model of such complicated mass-exchange process as magnetite oxidation in iron ore pellets.

## CONCLUSIONS

The proposed model establishes the dependence of oxidation speed of a porous body with its sizes, parameters of the structure (distribution of pores on radiuses, pores surface and volume), temperature (as ) and concentration of oxygen. Unlike before proposed models, the developed model permits to calculate oxidation speed depending on temperature, partial pressure of oxygen, the size and parameters of the pellet structure in the changing conditions of forming a granule.

This model can be used in a broader aspect: in the description of chemical reactions in the gas–porous body system.

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**Note:** The responsibile for English language is Nataliya Drak, Karaganda,Kazakhstan