REDUCTION OF FINE POLYDISPERSE PARTICLES IN A ONCE-THROUGH REACTOR UNDER CONDITIONS OF GAS SUSPENSION

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The article presents the theoretical and experimental results of the process of reduction of a polydisperse system of particles for the quasisteady regime in a once-through reactor.

The substantial intensification of the processes of reducing fine ores and concentrates upon interaction with a gas is connected with the increase of the reaction surface for reducing fine iron ore materials under conditions of gas suspension in a once-through reactor.

The intensity of reduction of a separate particle is determined by the ratio of the following mass exchange processes: convective mass exchange from the gas to the surface of the particles, adsorption and desorption of the reagents on the surface of the particle, the speed of the chemical reaction and of diffusion in the solid phase. In addition to that, certain difficulties are entailed in describing the process of reduction of a real iron ore concentrate which is a polydisperse material and also taking into account the mass exchange in an actual reactor along which the content of reaction products in the gas undergoes a change.

The effect of the polydispersity of the material is taken into account by the introduction of the size distribution function of the particles into the kinetic equation in accordance with [1].

The modeling of reduction of a separate particle is based on the notion of a particle with a noninteracting core. It is assumed that the particles are dense and have spherical shape. They do not crumble or become fused in the transformations of iron oxides. The layer of forming reaction products does not inhibit the process.

At any arbitrary instant the particle distribution f(r, t) over the radii of the cores obeys the equation [1]

$$\frac{\partial f(r,\ t)}{\partial t}+\frac{\partial}{\partial r}[W(r,\ t)f(r,\ t)]=0 \tag{1}$$

with the initial condition (for t = 0)

$$f(r,\ t)=f(r,\ 0)=f_0(r)=f_0(R),\quad \int\limits_0^\infty f_0(r)\,dr=1, \tag{2}$$

where $f_0(R)$ and f(r, t) are the initial and the running particle distribution over the radii of the nonreacted core; W(r, t) is the rate of change of the radius of the core.

The problem of finding f(r, t) on the basis of the kinetic equation (1) with the function W(r, t) is nonlinear. Firstly, the running radius of the core r depends on the radius R of the particle itself, and secondly, the concentration of reagents in the gas depends on the kinetics of reduction on each separate particle.

The authors of [2, 3] obtained an approximate solution of (1) for self-similar regimes of mass exchange (only the number of reacting particles in the system changes):

$$f(r,\ t)=\langle R\rangle^{-1}\exp(-r/\langle R\rangle)\exp\Big[-\langle R\rangle^{-1}\int\limits_0^t W(t)\,dt\Big]. \tag{3}$$

We write the degree of reduction of the system of particles with the aid of the distribution function (3):

$$\varphi=1-\frac{M_{0c}}{M_0}=1-\frac{\langle r^3\rangle}{\langle R^3\rangle}=1-\exp\Big[-\langle R\rangle^{-1}\int\limits_0^t W(t)\,dt\Big], \tag{4}$$

where the moments of third order are

$$\langle r^3\rangle=\int\limits_0^\infty r^3 f(r,\ t)\,dr=6\langle R\rangle^3\exp\Big[-\langle R\rangle^{-1}\int\limits_0^t W(t)\,dt\Big]; \tag{5}$$

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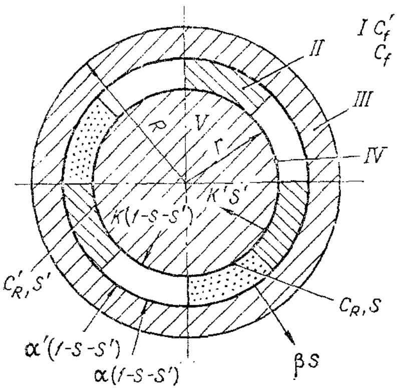

Fig. 1

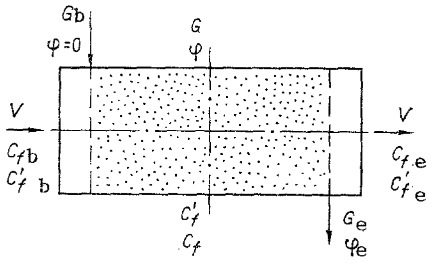

Fig. 2

Fig. 1. Mass exchange of a particle with the gaseous and the solid phase: I) gas; II) adsorbed layer; III) diffusion zone; IV) reaction front; V) initial phase (core).

Fig. 2. Diagram of the once-through reactor: V) flow rate of hydrogen, m^3/h; G) productivity in regard to iron ore concentrate, kg/h (G_b is the initial, G_e the final one); C_f) concentration of gaseous reagents, m^3/m^3 (with prime: hydrogen; without prime: water vapors).

$$\langle R^3 \rangle = \int_0^\infty r^3 f_0(r,\ 0)\, dr\big|_{r=R} = 6 \langle R \rangle^3; \tag{6}$$

M_{0c} is the content of oxygen in the cores of all particles at the instant t; M_0 is the initial oxygen content in the ensemble of particles.

The rate of change of the radius of the core W = dr/dt can be found from the mass velocity for a separate particle:

$$\frac{dM^{(r)}}{dt} = \frac{d}{dr} \Delta M_c = 4\pi r^2 (\rho_b - \rho_e) \frac{dr}{dt}, \tag{7}$$

where ΔM_c is the decrease of the mass of the core, or, bearing in mind that $(\rho_b - \rho_e) = \rho_b O_2'$ and going over to the specific molar flow of oxygen, we obtain

$$\frac{2}{4\pi r^2 \mu} \frac{dM^{(r)}}{dt} = \frac{2\rho_b O_2'}{\mu} \frac{dr}{dt}. \tag{8}$$

Since external mass exchange in the reduction of iron ore concentrates under conditions of gas suspension by hydrogen has no effect on the kinetics of the process [4], we can distinguish the following stages determining the speed of reduction: adsorption of the reducing agent on the surface of the particle, its diffusion in the solid phase to the reaction surface, physicochemical transformation of the oxides, diffusion of the reaction products from the solid phase to the adsorbed layer and their desorption into the gaseous phase. On the effect of diffusion in the solid phase on the kinetics of reduction of iron oxides the following has to be said: the known experimental data indicate that in the temperature range 700-900°C and with a degree of reduction below 90% solid-phase diffusion is not the limiting process because the activation energy for the migration of vacancies is ~120 kJ/mole [7, 8], and for processes of reduction of fine particles in a stream of hydrogen this magnitude is equal to 25-40 kJ/mole [5, 6]. The chemical reaction does not inhibit the process either [7]. It was experimentally established in [5, 9-11] that the desorption processes have a decisive effect on the kinetics of reduction of metal oxides. Within the framework of these notions the main cause of the lowering of the speed of reduction is the clogging of the reaction surface with water vapors which block the active surface. The mathematical model of the kinetics of filling the surface layer of a particle with reagents was dealt with in [12, 13]. However, this model does not take into account the real conditions connected with the polydispersity of the initial material and the special features of mass exchange determined by the type of reactor.

TABLE 1. Conditions of the Experiments and Their Results

Experiment No.	t, sec	φ, frac. of unity	V_{sp}, m^3/kg	K_*, sec^{-1}
7	7,6	0,59	2,82	0,0141
8	7,6	0,59	2,56	0,0155
10	7,2	0,50	2,60	0,0106

Let us examine the reduction of fine iron ore particles by hydrogen at high relative speed of particles and gas (more than 15 m/sec) and low concentration of particles in the gas (less than 10^{-4} m^3/m^3).

We take it that the speed of reduction of oxides is proportional to the number of hydrogen moles desorbed inside the solid particle, or to the proportion of the surface of the particle S' occupied by adsorbed hydrogen [14]. Then we obtain from (8) an equation for determining the rate of change of the core radius

$$-\frac{2\rho_b O_2'}{\mu}\frac{dr}{dt} = K_x S'. \tag{9}$$

The magnitude K_x plays the role of the speed of the process.

To find S', we use the model from [12]. We will assume that convective mass exchange with the surface layer of the particle and the chemical reaction and diffusion in the solid phase occur sufficiently rapidly so that the limiting processes are adsorption and desorption, both from the gaseous and from the solid phase.

Figure 1 shows the diagram of mass exchange of the adsorbed layer of a spherical particle with the gaseous and the solid phase. Flows of reduction agent and oxidant are directed to the surface, and they are adsorbed on the free surface not occupied by reagents. From the adsorbed layer part of the reduction agent is desorbed into the solid phase in which the reaction has already ended, and it proceeds to the reaction surface. The forming reaction products are adsorbed in the surface layer and from it they are desorbed into the gas. Assuming that adsorption is Langmuir (independent) adsorption, and neglecting the adsorption of hydrogen from the solid phase and its desorption into the gas, we write the equations of exchange of the surface layer of the particle in the form [12]

$$\begin{gathered}\frac{dS'}{dt} = \alpha C_R' (l')^3 (1 - S - S') + \frac{\delta S'}{\delta t},\quad \frac{\delta S'}{\delta t} = -K'S';\\ \frac{dS}{dt} = \alpha C_R l^3 (1 - S - S') - \beta S + \frac{\delta S}{\delta t},\quad \frac{\delta S}{\delta t} = K C_R l^3 (1 - S - S').\end{gathered} \tag{10}$$

In the reduction of iron ore concentrates in a stream of gas suspension, beginning at some (insignificant) magnitude, the partial pressure of the water vapors does not exert any influence on the kinetics of the process [5]. It may be assumed that in this case there is a quasisteady regime characterized in time by a constant surface occupied by hydrogen and water vapors:

$$\frac{dS}{dt} = \frac{dS'}{dt} = 0.$$

The stationary solution of system (12) for $\alpha \gg \alpha'$; $b \gg b'$ and $C_R b \gg 1$ has the form

$$S = 1;\ S' = \frac{b'C_R'}{bC_R};\ b' = \alpha' (l')^3/K';\ b = (\alpha + K)\, l^3/\beta. \tag{11}$$

Since convective mass exchange in a biphase stream in the field of action of a centrifugal force at a speed of the gas exceeding 20 m/sec and a particle concentration of less than 10^{-4} m^3/m^3 does not influence the kinetics of reduction [4], $C_R' = C_f'$, $C_R = C_f$ and $C_f \ll C_f'$. Taking these circumstances into account, we obtain from (11) and (9) that

$$W = \frac{dr}{dt} = -K_r \frac{b'C_f'}{bC_f},\ K_r = K_x \mu / 2\rho_b O_2'. \tag{12}$$

We use relations (4) and (12) for determining the degree of reduction of material φ in a once-through type reactor (Fig. 2).

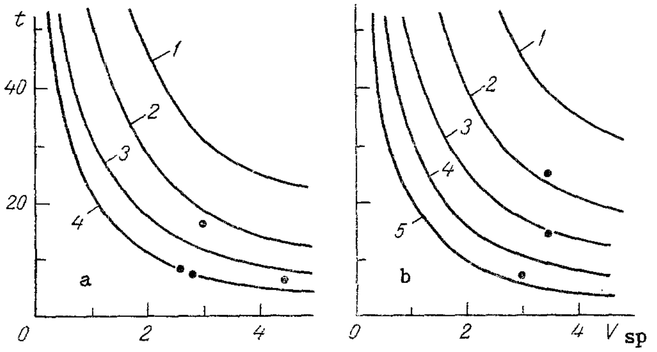

Fig. 3. Dependence of the length of reduction t, sec, of Kachkanary concentrate, T = 880°C (a), and of Kremenchug concentrate, T = 680°C (b), to different degrees of transformation φ, fractions of unity, on the specific flow rate of hydrogen V_{sp}, m^3/kg: 1) $\varphi = 0.9$; 2) 0.8; 3) 0.7; 4) 0.6; 5) 0.5.

From the balance of the mass between the entrance and an arbitrary section for steady-state conditions we have

$$\frac{C_f'}{C_j} = \frac{1}{2}\,\frac{V_{sp}\rho_{O_2}C_{fb}'}{O_2'\varphi} - 1, \tag{13}$$

where $V_{sp} = V/G_b$.

Bearing in mind that $C_{fb} = 0$ and $C_{fb}' \gg C_f'$, we may neglect the one in (13). Substituting (13) with a view to this into (12), we find

$$W = \frac{dr}{dt} = -K_r^*\frac{V_{sp}}{\varphi}, \tag{14}$$

$$K_r^* = \frac{K_x\alpha'\beta\mu\rho_{O_2}C_{fb}'}{4(\alpha + K)K'\rho_b O_2'}\left(\frac{l'}{l}\right)^3. \tag{15}$$

When we substitute (14) into (4) and differentiate with respect to t, we obtain the ordinary differential equation

$$\frac{d\varphi}{dt} = K_* V_{sp}\frac{1-\varphi(t)}{\varphi(t)}, \quad K_* = K_r^*/\langle R\rangle, \tag{16}$$

where K_* is the effective constant of reduction. Its solution with the initial condition $\varphi(0) = 0$ has the form

$$\varphi + \ln|1-\varphi| = -K_* V_{sp} t. \tag{17}$$

Formula (17) describes the reduction of polydisperse material in a once-through device operating in steady-state regime. In reduction in a stream of gas suspension the main technological parameter affecting the final degree of reduction is the specific gas flow rate. It should be noted that Eq. (17) is correct within the following limits concerning degrees of reduction: $\varphi \geq 0.2$, because with lower degree of reduction and specific gas flow rate $V_{sp} \geq 1.5$ m^3/kg, the quasisteady-state regime has not been attained yet; $\varphi \leq 0.9$, because when the degree of reduction is higher, the effect of solid-phase diffusion begins to manifest itself.

In accordance with Eq. (17) we processed the results of the experiments with reduction of Kachkanary and Kremenchug concentrates in a coil reactor. The reactor and the method of carrying out the experiments were repeatly described in the literature [4, 5]. In Kachkanary concentrate the total content of iron (Fe_{tot}) was 60.4%, and the mean mass particle size d_{me} was equal to $6\cdot10^{-5}$ m. In Kremenchug concentrate $Fe_{tot} \simeq 66.0\%$, and $d_{me} = 5.2\cdot10^{-5}$ m. The reduction temperature of Kachkanary concentrate was 870-890°C, of Kremenchug concentrate it was 680°C. The speed of hydrogen under operating conditions was about 30 m/sec. The mean partial water vapor pressure along the reactor was 2.5-4 kPa.

Table 1 presents the conditions and results of the reduction of Kachkanary concentrate in a coil reactor. The mean effective constant of the speed of reduction is equal to 0.0134 sec^{-1}. The accuracy of its measurement is 15-20%.

The effective constant of the speed of reduction for Kremenchug concentrate, calculated on the basis of experiments by Eq. (17), is equal to 0.0098 ± 0.0014 sec^{-1} ($P_{H_2O} > 2$ kPa).

With a view to the values of K_* found by the experiment, Fig. 3 presents the theoretical dependences of the length of reduction of two types of concentrate on the specific hydrogen flow rate. The dots in the figure indicate the results of multiple passages of the same batch of concentrate through the coil ($P_{H_2O} > 2.5$ kPa). The agreement between theoretical and experimental data is perfectly satisfactory: the difference does not exceed the accuracy of measurement of the effective constant of the speed of reduction.

In conclusion it should be noted that, regardless of the complexity of the process of reduction of a system of polydisperse particles in a stream of gas suspension, the kinetics of reduction is described by a fairly simple equation. The good agreement of the theoretical solution with the experiments confirms the correctness of the adopted assumptions, in particular that the regime of reduction is quasisteady and that external mass exchange does not affect the kinetics of the process. The effective constant of the speed of reduction is a physical magnitude depending on the conditions of the process. The investigation of the influence of each of the stipulated stages on the effective constant of the speed of reduction is a separate problem whose solution makes it possible to determine ways of intensifying the process of reduction.

NOTATION

R, particle radius, m; r, core radius, m; t, time, sec; M, mass, kg; φ, degree of reduction, fractions of unity; ρ, density, kg/m^3; O_2', oxygen content in the initial material, fractions of unity; μ, molecular mass of atomic oxygen, kg/mole; K_X, speed of the chemical reaction, sec^{-1}; S, fraction of the surface area filled with reagents, fractions of unity; α and β, constants of the speed of adsorption from and desorption into the gaseous phase, respectively, sec^{-1}; C, concentration, m^{-3} and m^3/m^3; l, linear dimension of the area occupied by one molecule, m; K, K′, coefficients of adsorption and desorption of reagents into and from the solid phase, respectively, sec^{-1}; $\delta S/\delta t$, overall speed of filling the surface layer with reagents by exchange with the solid phase, sec^{-1}; G′, G, productivity in regard to the initial concentrate and in an arbitrary section of the reactor, respectively, kg/h; V, flow rate of the gas, m^3/h; d_{me}, mean weighted particle size, m; Fe_{tot}, total iron content, %. Subscripts and superscripts: ′, magnitudes relating to reduction; without prime, to oxidation; f, gas; R, surface; b, 0, initial; max, maximal; e, final; c, core; O_2, oxygen; sp, specific.

LITERATURE CITED

1. Yu. A. Buevich, Prikl. Mekh. Tekh. Fiz., No. 1, 50-57 (1966).
2. Yu. A. Buevich and G. P. Yasnikov, Teor. Osn. Khim. Tekhnol., 16, No. 5, 597-603 (1982).
3. Yu. M. Goldobin, Inzh.-Fiz. Zh., 45, No. 3, 452-457 (1983).
4. B. A. Bokovikov, L. G. Yasnikova, Yu. F. Gogolev, and O. G. Alekseev, in: Direct Production of Iron and Powder Metallurgy: Thematic Branch Collection of Scientific Papers, Issue 4, Moscow (1978), pp. 35-39.
5. L. G. Yasnikova and Yu. F. Gogolev, in: Theory and Practice of Directly Obtaining Iron, Moscow (1986), pp. 220-223.
6. S. Y. M. Ezz and R. Wild, J. Iron Steel Inst., 194, Part 2, 211-221 (1960).
7. L. F. Bogdandi and G. Yu. Éngel's, Reduction of Iron Ores [in Russian], Moscow (1971).
8. Ya. E. Geguzin, The Diffusion Zone [in Russian], Moscow (1979).
9. E. P. Tatievskaya and G. I. Chufarov, Zh. Fiz. Khim., 10, No. 5, 747-753 (1937).
10. G. I. Chufarov, B. D. Averbukh, E. P. Tatievskaya, and V. K. Antonov, Zh. Fiz. Khim., 28, No. 3, 490-497 (1954).
11. E. N. Vasil'ev, in: Powder Metallurgy: Thematic Branch Collection of Scientific Papers, Issue 72, Moscow (1970), pp. 68-74.
12. Yu. A. Buevich, Inzh.-Fiz. Zh., 46, No. 2, 233-240 (1984).
13. Yu. A. Buevich and A. V. Kamennykh, Inzh.-Fiz. Zh., 48, No. 5, 796-803 (1985).