

## EFFECT OF PRESSURE ON MASS TRANSFER IN HETEROGENEOUS CHEMICAL PROCESSES IN A FLUIDIZED BED

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A heterogeneous process in a fluidized-bed reactor with continuous feed and removal of material was investigated at pressures ranging from 0 to  $196.1 \cdot 10^4 \text{ N/m}^2$ . A general relationship connecting the rate of mass transfer between the gas flow and the particles in the bed in the Re range 15-274 with the pressure from 0 to  $196.1 \cdot 10^4 \text{ N/m}^2$  is found.

Fluidized beds are now widely used in various branches of industry, particularly power engineering and chemical technology.

The success of this technique can be attributed to its advantages: good mixing of the particles, equalization of temperatures and concentrations, and the fluidity of the bed. A fluidized bed, however, has certain disadvantages in comparison with the usual fixed bed. The possibility of increasing the gas flowrate and, hence, the output of a fluidized-bed apparatus is limited by a certain maximum degree of expansion of the bed  $\lambda = H/H_0$ , where  $H$  is the height of the fluidized bed and  $H_0$  is the height of the bed at rest.

Operation of the bed under pressure is an effective way of improving the fluidized-bed technique [3]. An investigation of the hydrodynamics of a fluidized bed under a pressure  $p = 0-196.1 \cdot 10^4 \text{ N/m}^2$  (0-20 atm) showed that increase of pressure reduced the gas flowrate required to produce a given degree of expansion of the bed, reduced the entrainment of particles, improved the structure of the bed, and reduced the number of gas bubbles in the bed [3]. Since the mean gas flowrate  $w$  (referred to the free cross-sectional area of the reactor) is reduced by a factor of approximately  $\sqrt{p}$ , the weight flow of gas  $G$  or, in other words, the specific weight output of the apparatus  $G = \rho g w \text{ kg/m}^2 \cdot \text{sec}$  is increased by a factor  $\sqrt{p}$ , since the gas density  $\rho = p/gR_g T$  is increased by a factor  $p$ . Thus, the use of a fluidized bed under pressure can lead to an increase in the output of an apparatus containing particles of a particular granulometric composition if other conditions are equal. Pressure increase, which produces considerable changes in the hydrodynamic characteristics of the fluidized bed, must affect the mass transfer and the course of the chemical reactions.

In a previous paper [4] we gave an account of the results of an investigation of the mass transfer and the effect of various factors on its rate in a fluidized bed at a pressure close to atmospheric.

In this paper we give the results of investigation in the pressure range  $0-196.1 \cdot 10^4 \text{ N/m}^2$  (20 atm) on the basis of our adopted experimental method—a chemical model.

The aim of these investigations was not only to investigate mass transfer and its intensification in a fluidized bed under pressure. The increase in pressure and, hence, in the density of the gas introduced

into the bed enable us to enlarge considerably the Re range from 15 at  $p = 0$  to 274 at  $p = 196.1 \cdot 10^4 \text{ N/m}^2$  for a bed with a given granulometric composition.

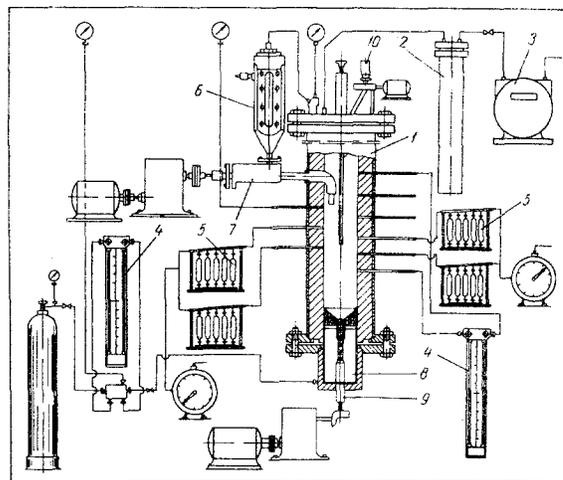


Fig. 1. Diagram of apparatus for investigation of mass transfer in a fluidized bed under pressure: 1) reactor; 2) trap; 3) GKF gas meter; 4) DT-150 differential manometer; 5) gas pipets with GSB gas meter; 6) hopper for feed of particles; 7) screw conveyor for particles; 8) hopper for removal of particles; 9) screw conveyor for removal of particles; 10) hopper for labeled particles.

In experiments at atmospheric pressure the Re range was greatly restricted by the small possible limits of increase in the blowing rate to ensure the maximum degree of expansion of the fluidized bed ( $\lambda \approx 2$ ). Pressure increase removed this limitation. This method of increasing the Re range is used in aerodynamic tests.

The investigation of mass transfer at high pressures in our experiments with a chemical model had yet another significant advantage. With pressure increase the diffusion coefficient  $D$  decreases in inverse proportion to the pressure increase:

$$D = D_0 \frac{p_0}{p} \quad (1)$$

(the zero subscript denotes  $p = 0$ ).

The rate of a heterogeneous chemical reaction as pressure increases very rapidly becomes determined by the diffusion rate, and the over-all constant  $k$ , which can be determined experimentally, is equal in this case to the mass transfer coefficient.

As in our previous investigation [4] the reacting gas and solid particles chosen for the fluidized bed were:

a mixture of carbon dioxide and nitrogen (initial  $\text{CO}_2$  concentration 2.5–10%) and granulated soda lime [84%  $\text{Ca}(\text{OH})_2 + 4\% \text{NaOH} + 12\% \text{H}_2\text{O}$ ]. The advantage of this chemical model is that the reaction proceeds at low temperature and in almost isothermic conditions. This method has been used successfully to investigate the laws of heterogeneous chemical processes [6, 7].

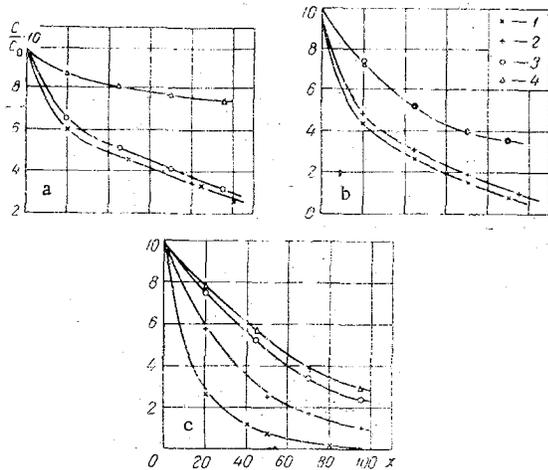


Fig. 2. Distribution of relative concentration  $c/c_0$  over reactor height  $x$ , mm for a degree of expansion 1.5 and different pressures: 1)  $p = 0$ ; 2)  $49 \cdot 10^4$ ; 3)  $98 \cdot 10^4$ ; 4)  $196.1 \cdot 10^4$   $\text{N/m}^2$  at distances from the reactor axis of  $y_r = 0$  mm (a), 10 mm (b) and 15 mm (c).

The experimental apparatus for the investigation of mass transfer in a fluidized bed under pressure (Fig. 1) consisted of a clear plastic reactor with an internal diameter  $\Phi = 40$  mm and height 500 mm, mounted in a metal case with windows. The reactor could withstand a pressure of  $490 \cdot 10^4$   $\text{N/m}^2$  (50 atm).

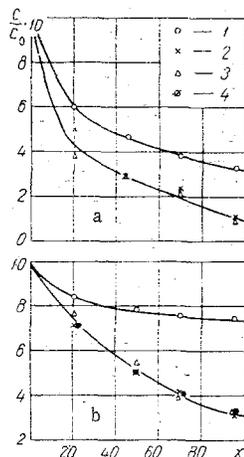


Fig. 3. Distribution of relative concentration  $c/c_0$  over reactor height  $x$ , mm for degree of expansion 1.5 and distances from the axis of  $y_r = 0$  (1), 10 (2), 15 (3), and 5 mm (4) for pressures  $49 \cdot 10^4$  (a) and  $196.1 \cdot 10^4$  (b)  $\text{N/m}^2$ .

Gas sampling tubes with  $\Phi_{\text{int}} = 1$  mm were mounted over the height of the reactor and could move freely in

a horizontal direction. The design of the apparatus allowed visual observations of the behavior of the bed. The constancy of the height of the fluidized bed in time was secured by the synchronous feed and removal of particles by screw conveyers.

The apparatus was equipped with the necessary inspection and control devices, which allowed measurement of the pressure and flow of gas on the low and high sides.

The operating conditions in the experiments were as follows: Gas composition 2.5%  $\text{CO}_2 + 97.5\% \text{N}_2$ , 5.0%  $\text{CO}_2 + 95.0\% \text{N}_2$ , 10.0%  $\text{CO}_2 + 90.0\% \text{N}_2$ ; particle diameter  $d_{\text{av}} = 0.82$  mm; ratio of diameter of apparatus to particle diameter  $\Phi/d = 49$ .

For a degree of expansion	1.3	1.5	2.0
of the bed $\lambda$			
the gas velocity $w$ , m/sec			
for $p = 4.9 \cdot 10^4$ $\text{N/m}^2$	0.25	0.35–0.40	0.52
$p = 49 \cdot 10^4$	0.22	0.28–0.29	0.40
$p = 98 \cdot 10^4$	0.19	0.23	0.32
$p = 196.1 \cdot 10^4$	0.14	0.19	0.23
the feed rate of the lime particles $\mu$ , cm/sec			
for $p = 4.9 \cdot 10^4$		0.04–0.08	
$p = 49 \cdot 10^4$		0.05–0.10	
$p = 98 \cdot 10^4$		0.10–0.12	
$p = 196.1 \cdot 10^4$		0.13–0.16	

At a specified pressure the degree of expansion  $\lambda$  of the bed varied from 1.3 to 2, since the fluidization of the bed was stable in this range and the least number of gas bubbles was formed [3]. In this case the gas flow was progressive, and only a small part of it was trapped and circulated along with the particles.

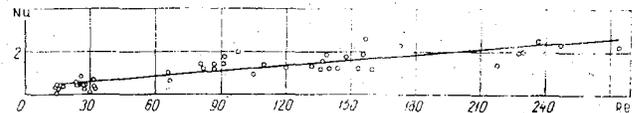


Fig. 4. Relationship  $\text{Nu} = f(\text{Re})$ .

Figure 2 shows that the curves  $c/c_0 = f(x)$  ( $c$  is the local concentration and  $c_0$  the initial concentration) have a smaller gradient at the high pressures  $p = 98 \cdot 10^4$  and  $196.1 \cdot 10^4$   $\text{N/m}^2$  (10 and 20 atm). This means that the concentration of reacting gas falls more slowly with pressure increase than at the low pressures  $p = 9.8 \cdot 10^4$  and  $49 \cdot 10^4$ . Thus, with pressure increase the apparent rate of mass transfer per unit volume of the reactor falls. It should be noted that the rate of feed of processed soda lime increased from 0.05 to 0.01, 0.12, and 0.16 cm/sec with pressure increase to  $49 \cdot 10^4$ ,  $98 \cdot 10^4$ , and  $196.1 \cdot 10^4$   $\text{N/m}^2$ , respectively. Figure 3 shows the marked difference in the distribution curves of  $\text{CO}_2$  concentration sampled over the axis of the reactor. They generally have a smaller gradient than the other curves which were obtained on approach to the wall. The observed reduction in the rate of  $\text{CO}_2$  absorption in the center of the reactor can be attributed to two causes: 1) the more rapid removal of spent particles and the formation of a less

dense bed than in the surrounding region; 2) the higher gas flow rate.

At all other distances from the reactor axis, from  $y_r = 5$  mm to  $y_r = 15$  mm, the  $CO_2$  distribution curves are the same in the pressure range  $49 \cdot 10^4$  to  $196 \cdot 1 \cdot 10^4$  N/m<sup>2</sup>. Hence, we used these curves as a basis for the analysis of the experimental data.

A comparison of the  $CO_2$  concentration distributions at higher pressures with the same curves at atmospheric pressure and other conditions equal showed a considerable reduction in the scatter of the points and a convergence of the curves representing different distances from the axis. This can be attributed to the improved structure of the fluidized bed at increased pressure, to equalization of the gas flow rate distribution, and to reduction in the linear velocity of the gas.

All these qualitative conclusions derived from the results of the experiments were confirmed by an analysis of the experimental data on the basis of a theoretical consideration of the reaction of particles in a fluidized bed. To explain the effect of different factors on the mass transfer coefficient in a fluidized bed we compile the system of mass-transfer differential equations describing a steady-state heterogeneous process. By  $c$  (kg/m<sup>3</sup>) we mean the average concentration of gas in a given cross section  $x$ :

$$\begin{aligned} c &= f(x), \\ \frac{\partial c}{\partial \tau} &= 0. \end{aligned} \quad (2)$$

The reacted amount of gas  $y$  (kg/m<sup>3</sup>) absorbed by the solid particles in the same unit of volume can be expressed by the equation

$$y = \gamma(S_0 - S) \delta M, \quad (3)$$

where  $y$  is the density of the particle material, kg/m<sup>3</sup>;  $\delta$  is the depth of processing after the reaction, m;  $S$  is the effective reaction surface of the particles in unit volume of the bed at a distance  $x$  from the entrance section, m<sup>2</sup>/m<sup>3</sup>;  $S_0$  is the initial reaction surface of the fresh particles entering the bed at  $x = 0$ , m<sup>2</sup>/m<sup>3</sup>;  $M$  is the stoichiometric coefficient of the reaction.

We introduce an absorption coefficient  $\beta = 1/\gamma\delta M$  and we will not separate the quantities contained in it.

Hence, we obtain the simple linear relationship between  $S$  and  $y$ :

$$S = S_0 - \beta y. \quad (4)$$

The differential equation for the reacting gas is

$$-w \frac{d(cw)}{dx} - kSc = 0, \quad (5)$$

and for the absorbed gas which has reacted with the solids,

$$-u \frac{dy}{dx} + kSc = 0, \quad (6)$$

where  $u$  is the particle feed rate, m/sec.

Neglecting the change in the gas flow rate over the height of the bed, which is permissible in view of the small change in gas volume as a result of the reaction,

we write Eq. (5) in the following form:

$$-w \frac{dc}{dx} - kSc = 0.$$

In Eq. (5) the first term expresses the convective transfer of the concentration of reacting gas, and the second term expresses the rate of a first-order reaction. The diffusive transfer through the reaction zone in comparison with the convective transfer is small at high Re numbers, and we can neglect it.

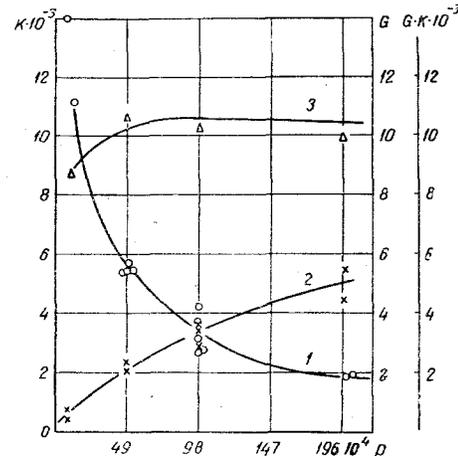


Fig. 5. Mass transfer coefficient  $k$ , m/sec (1), and weight flow of gas  $G$ , nl/sec (2), and output  $Gk$ , nl · m/sec<sup>2</sup> (3) as functions of pressure  $p$ , N/m<sup>2</sup>.

Equation (6) is valid in the case of parallel motion of the material and gas.

The boundary conditions are

$$x = 0; \quad c = c_0; \quad S = S_0 \quad (y = 0).$$

In the case of parallel motion of the gas and particles we have the solution

$$-\ln \left[ \left( 1 - \frac{v}{u} \right) \frac{c_0}{c} + \frac{v}{u} \right] = - \left( 1 - \frac{v}{u} \right) k S_0 x / w. \quad (7)$$

In the case of countercurrent motion of the gas and material the system of equations will take the form

$$-w \frac{dc}{dx} - kSc = 0, \quad (8)$$

$$u \frac{dy}{dx} + kSc = 0. \quad (9)$$

This system is solved with the following boundary conditions:

$$x = 0, \quad c = c_0; \quad x = H, \quad S = S_0 \quad (y = 0).$$

If the bed is high, the solution can be simplified, since the height will have no effect in this case and we can assume that

$$x \rightarrow \infty; \quad c = 0; \quad y = 0.$$

In this case the solution will be

$$\ln \left[ \frac{c}{c_0} \left( 1 - \frac{v}{u} \right) / \left( 1 - \frac{v}{u} \frac{c}{c_0} \right) \right] = -k \frac{S_0 x}{w}. \quad (10)$$

According to our adopted experimental method, the motions of the gas and material are countercurrent

and, hence, we use only Eq. (10), which shows that the mean gas concentration in a given cross section of the reactor depends on the mass transfer coefficient  $k$ , the initial reaction surface  $S_0$  per unit volume of bed, the gas flow rate  $w$ , and the distance  $x$  from the entrance section.

The particles in the fluidized bed complete an ordered progressive motion in a vertical direction. Besides this, however, the particles also have a chaotic motion. Hence, in addition to the progressive transfer of reacting material we will have to take into account the rate of transfer due to the chaotic motion in the form of some diffusion term  $D \frac{d^2 y}{dx^2}$  [8].

But the introduction of this term imparts a nonlinear character to the system of Eqs. (8) and (9), and it can then only be solved numerically on an electronic computer.

We take into account the effect of the degree of mixing of the solids for different  $\lambda$  by the sorption wave velocity  $v$  and the particle feed rate  $u$ .

We put  $v/u = \alpha$ . The number  $\alpha$  was determined experimentally for each degree of expansion  $\lambda$  and particles of the same diameter, but at rest. In this case the reaction in the bed is unsteady, and the concentration curve spreads over the height of the bed at some mean velocity  $v$ , which can be called the sorption wave velocity.

In an unsteady fluidized bed the balance of reacting gas and solids is

$$HS_0 \gamma \delta M = \omega c_0 \tau, \quad (11)$$

and the sorption wave velocity (rate of processing of bed) is

$$v = H/\tau = \omega c_0 \beta / S_0. \quad (12)$$

Then the coefficient  $\alpha$ , introduced above, can be represented by the formula

$$\alpha = \omega c_0 \beta / S_0 u. \quad (13)$$

Formula (13) shows that the coefficient  $\alpha$  depends on the gas feed rate, the reaction surface, the initial concentration, and the particle feed rate.

Formula (12) shows that the sorption wave velocity  $v$  in the bed is directly proportional to the gas flow rate  $w$ , the initial concentration  $c_0$ , and is inversely proportional to the reaction surface  $S_0$  per unit volume of bed, which is confirmed by previous experimental investigations [6, 9]. In addition,  $S_0$  depends on the bed voidage  $\epsilon$ . Hence, the sorption wave velocity  $v$ , as well as the coefficient  $\alpha$ , depends on the degree of expansion  $\lambda$  and the blowing rate.

As we mentioned earlier, the transfer of reacting material and the associated concentration  $y$  in a fluidized bed involves not only progressive convective transfer, but also mixing of the solid particles. Hence,  $\alpha$  determines the effect of chaotic mixing, which indirectly depends on the gas flow rate.

The mass transfer coefficient  $k$  was calculated from Eq. (10), which holds for conditions

$$0 < \alpha < 1.$$

Equation (10) provides a good representation of our investigated heterogeneous process in a fluidized bed.

The experimental points in all the experiments lay on the theoretical lines with little scatter. The mass transfer coefficient  $k$  (m/sec) found from Eq. (10) enabled us to determine the diffusion Nu number in the Re range 15–274 for pressures of  $4.9 \cdot 10^4$ – $196.1 \cdot 10^4$  N/m<sup>2</sup>. The relationship  $Nu = f(Re)$  can be expressed by the linear function (Fig. 4):

$$Nu = a + b Re. \quad (14)$$

It follows from formula (14) that the mass transfer coefficient

$$k = \frac{Nu D}{d} = \frac{a D}{d} + \frac{b Re D}{d}. \quad (15)$$

Equation (14) shows that in a fluidized-bed reactor operating at a particular pressure ( $p = \text{const}$ ,  $\rho = \text{const}$ ) Re number and the mass transfer coefficient increase with increase in the blowing rate  $w$ .

Formula (10), however, shows that with increase in the gas flow rate the length  $x$  of the reaction zone is extended not only by increase in the gas flow rate  $w$ , but also by reduction of the reaction surface  $S_0$ . Hence, despite some increase in the mass transfer coefficient, the intensity of the reaction zone, which is equal to the specific output  $G$  (kg/m<sup>2</sup>·sec) referred to unit volume of bed, decreases with increase in the weight flow.

We will now consider how increased pressure affects the mass transfer, output, and intensity of a fluidized bed apparatus. When other conditions are equal ( $\lambda$ ,  $d_{av}$ ,  $\rho_T = \text{const}$ ), the gas flow rate in a fluidized bed apparatus operating at increased pressure is reduced in inverse proportion to  $\sqrt{p/p_0}$ , and the Re number increases in direct proportion to  $\sqrt{p/p_0}$ . In view of these relationships we can write formula (15) in the form

$$k = \frac{D_0 p_0}{d} \left( \frac{a}{p} + \frac{b Re_0}{\sqrt{p/p_0}} \right), \quad (16)$$

where the subscript 0 denotes the value at atmospheric pressure:  $a \approx 0.28$  and  $b \approx 0.009$  are values determined experimentally from (14).

At high Re ( $> 50$ ) the numerical value of the first term is much less than that of the second when  $p > 49 \cdot 10^4$  N/m<sup>2</sup> and the first term can be neglected. Hence, the mass transfer coefficient decreases with increase in pressure by a factor  $\sqrt{p}$ .

It follows from formula (16) that with pressure increase the mass transfer coefficient decreases owing to the reduction of molecular diffusion, but the increase in Re reduces the effect of the high pressure.

Figure 5 shows the actual change in the mass transfer coefficient  $k$  with pressure increase in relation to the specific output  $G$ . As the general relationship (16) indicates, the mass transfer coefficient decreases with pressure increase, while the output  $kG$  in the pressure range  $49 \cdot 10^4$ – $196.1 \cdot 10^4$  N/m<sup>2</sup> and with bed expansion constant is practically constant. The length  $x$  of the reaction zone, as formula (10) indicates, is directly proportional to  $w$  and inversely proportional to the coefficient  $k$ .

Since  $kG = \text{const}$ ,  $w \sim 1/p$ ,  $G \sim \sqrt{p}$ , it follows that the length of the reaction zone remains practically

constant with pressure increase. The value of  $S_0$  is constant for a constant degree of expansion  $\lambda$  and does not affect the length of the zone  $x$ .

Hence, it follows that the intensity of the reaction zone per unit volume  $G/x$  of fluidized bed increases in direct proportion to  $\sqrt{p}$ .

Relationship (16) can be used for the design of fluidized reactors and to obtain conclusions regarding the effect of pressure, blowing rate, and other factors on the rate of mass transfer and the intensity of operation of the apparatus, particularly at high pressures.

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