ABSORPTIVE CAPACITY OF POWDERS

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The change in pressure during gas desorption from the clayey material of the skeleton of a porous medium is examined. It is shown that absorptive capacity of the powder can be determined from pressure measurements.

Appreciable adsorption occurs (especially of heavy components) when a gas at high pressure comes in contact with the surface of the sandy-argillaceous skeleton of a porous medium. For single-component gases, the degree of coverage θ is given by the Langmuir equation [1-3]

$$\theta = \frac{1}{1 + p^*/p}, \qquad (1)$$

where p^* is the characteristic pressure. According to the kinetic theory of adsorption [2], equilibrium is established almost instantaneously at all points of the surface, in accordance with (1). Adsorption–desorption processes which occur during changes in external conditions such as gas pressure take place rather slowly. This is because local pressures resulting from transient processes vary from point to point in the medium, and the time required for stabilization is determined by the velocity of the currents which equalize the pressures. The most typical case of this kind is a large-grained adsorbent with a system of micropores which are much smaller than the grains. Many synthetic adsorbents have this structure, which is like that of the sandy-argillaceous skeleton of a natural porous medium. The clayey particles (grains) of the latter consist of a very large number of platelets, with very high adsorptive capacity. Because of the small size of the intragranular channels (dimensions are of molecular size), the grains may be considered impenetrable to filtration flow, but their adsorptive capacity and its related volume flow must be considered.

It is not difficult to see the similarity between a medium with this structure* and the "dual" porous medium proposed by Barenblatt and Zheltov [4-6] in describing filtration in a fissured porous medium. Using this analogy, it is easy to write the flow equations for a gas in a hindered-flow sorbent.

We introduce two gas pressures, p in the macropores between grains and p_1 in the grain micropores; two quantities of desorbed gas per unit volume, a and a_1; and the bulk gas flow q per unit volume, from the grains into the macropores between grains. The equations are

$$\begin{gathered} \frac{\partial M}{\partial t} + \operatorname{div} \rho \mathbf{w} = q; \quad \frac{\partial M_1}{\partial t} + q = 0; \\ \mathbf{w} = -\frac{k}{\mu} \operatorname{grad} p; \quad \rho = \rho(p); \qquad (2) \\ M = M(p) = mp \frac{\rho_{\text{at}}}{p_{\text{at}}} + a(p); \quad M_1 = m_1 p_1 \frac{\rho_{\text{at}}}{p_{\text{at}}} + a_1. \end{gathered}$$

The gas flow q is determined by the pressure difference $p_1 - p$ and may be described either as a microfiltration flow

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*Structures of this kind have long been studied in adsorption theory [1]. The dynamics of adsorption in a more complex "three-stage" medium are examined in [7].

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$$q \simeq \frac{\alpha k_1 s}{\mu}\cdot\frac{p_1-p}{d^4}\cdot\frac{p\rho_{at}}{p_{at}}, \qquad (3)$$

or diffusion flow, which is more accurate because of the ultramicroscopic structure of the clayey material. This results in an expression similar to (3),

$$q \approx \beta\,\frac{D_1}{d^2}\cdot\frac{\rho_{at}}{p_{at}}(p_1-p), \qquad (4)$$

where the diffusion coefficient will be assumed to be of the same order as that for the diffusion of a gas in a solid ($D_1 \simeq 10^{-7}$ cm^2/sec).

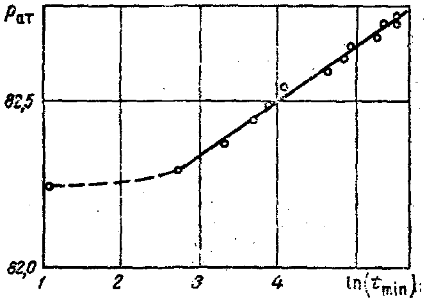

Fig. 1. Pressure rise. Medium: 50% sand, 50% clay, 2% (wt.) residual water. Initial pressure decrease 112.63-82.25 atm.

In the usual procedure for determining the adsorptive capacity of the micropores of an adsorbent, the pressure decreases from its initial value p_0 to some value p_1, and the amount of gas desorbed is then measured as a function of time. However, the amount of gas adsorbed may be determined more simply in the case of a dual-structure medium, in which the bulk of the free gas is in the macropores, while most of the adsorbed gas is in the micropores of the clayey grains. We first release a certain portion of the gas from the macropores, which results in a pressure decrease. Immediately after decreaseing the pressure, the release of gas is halted, and the change in pressure in the sample (or at several points in the sample) is observed over a long period of time. It can be easily seen that the pressure will first equalize over the length of the sample (in time $l^2/\varkappa$, i.e., of the order of a fraction of a second to one second). A uniform pressure $p_1 < p_0$ will then exist in all the macropores, while the former (higher) pressure p_0 persists in the micropores, if the gas has been released rapidly. The subsequent slow transfer of gas from the particles into the macropores will cause the pressure to rise gradually from p_1 to $p_2 > p_1$. The amount of gas desorbed can be determined in principle from p_0, p_1, and p_2, and q can be determined from the rate of pressure increase. A series of experiments has recently been performed by Z. A. Nurmamedova at the M. Azizbekov Azerbaidzhan Institute of Petroleum and Chemistry; the results confirm the above qualitative picture.

A typical experiment was the following: Natural gas (94.3% CH_4, 3.06% C_2H_6, 1.26% C_3H_8, and 1.68% C_4 and above) was introduced into a high-pressure bomb, which was connected to a column filled with a porous medium consisting of a 50-50 clay — sand mixture. After the column was filled and the pressure stabilized, a portion of the gas was released. The column outlet was then closed and the pressure monitored with gauges located at inlet and outlet. After a brief period of pressure equalization (minutes), during which the pressure decreased at the inlet and increased at the outlet, a slow pressure rise occurred, over a period of several hours. This varied from a fraction of an atmosphere to 1.5-2 kg/cm^2, and was greater for more rapid initial gas release (Fig. 1).

The amount of gas desorbed from the micropores can be determined from the data. Assuming that the secondary pressure rise δp is small compared with the bomb pressure, and neglecting effects related to change in temperature on release of the gas, we have

$$\Delta M_1 \approx \frac{\delta p\,\rho_{at}}{p_{at}}\,m; \quad \frac{\Delta M_1}{\Delta p_1} \approx \frac{\delta p}{\Delta p}\cdot\frac{\rho_{at}}{p_{at}}\,m. \qquad (5)$$

For the experimental conditions of Fig. 1, $\delta p = 0.51$ kg/cm^2, $\Delta p = 30.4$ kg/cm^2, and $m = 0.2$, so that

$$\Gamma = \Delta M_1/\Delta p_1 \approx 0.26\cdot 10^{-5}\ \text{g/cm}^3\cdot\text{atm}. \qquad (6)$$

Assuming that Γ is independent of pressure, we obtain for the total amount of gas adsorbed at 100 kg/cm^2

$$\Delta M_1 \approx 100\cdot 0.26\cdot 10^{-5} = 0.26\cdot 10^{-3}\ \text{g/cm}^3,$$

corresponding to

$$N_1 = \Delta M_1/m_0 = 0.26\cdot 10^{-3}/16\cdot 1.6\cdot 10^{-24} \approx 10^{19} \qquad (7)$$

gas molecules (methane) per cm^3 of medium. Since one adsorbed molecule occupies 10 Å^2 = 10^{-15} cm^2 of surface, the area covered by adsorbed gas is 10^4 cm^2/cm^3 at 100 kg/cm^2. This value is considerably higher than the specific surface area of a coarse-grained porous medium, although substantially less than that of clayey material. This confirms the assumption of significant adsorption within the clayey grains.

It also confirms the fact that the degree of micropore surface coverage is small and the linear portion of the Langmuir isotherm may be used. Finally, we have for the equilibrium time constant

$$T \sim \frac{\Delta M_1}{q} \sim \frac{\Gamma p_{\text{at}} d^2}{\rho_{\text{at}} \beta D_1} \sim \frac{\delta p}{\Delta p} \cdot \frac{m d^2}{\beta D_1}. \tag{8}$$

From this relationship, knowing T, d^2/D_1 can be evaluated. Assuming that T $\sim 10^3$ sec, we obtain $d^2/D_1 \sim 3 \cdot 10^5$ sec, which for $D_1 \sim 10^{-7}$ cm²/sec gives $d \sim 0.1$ cm. This agrees with the possible size range of the clayey grains of the skeleton.

We note that very small values of permeability k_1 are obtained in the filtration picture of gas transfer [Eq. (3)].

NOTATION

a, amount of gas adsorbed in macropores (per cm³ of medium); a_1, amount of gas adsorbed in micropores (per cm³ of medium); D_1, diffusion coefficient of gas in clayey grains; d, size of clayey grains of skeleton: k, permeability of clayey grains; l, sample length; M, total amount of gas in macropores (per cm³ of medium); m, sample porosity (macropores); m_1, sample porosity (micropores); p, macropore gas pressure; p_{at}, atmospheric pressure; p_1, micropore gas pressure; q, gas flow rate from clayey grains to macropores; T, equilibrium time constant; μ, gas viscosity; ρ, gas density; ρ_{at}, gas density at atmospheric pressure; $\varkappa$, piezoconductivity; θ, degree of surface coverage by adsorbed layer.

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