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Dynamics of Admixture Consumption from a Gaseous Flow in Reaction with a Solid Reactant: An Analytical Solution to the Problem

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Abstract—Dynamics of admixture consumption from gaseous flow during a reaction with a solid reactant is expressed in terms of a set of two partial differential equations. The analytical solution to the problem is found. The solution is illustrated by the plots of admixture distribution in the gas and absorbent.

The problem of dynamics of admixture consumption from a gaseous or liquid flow has a variety of technical applications, including environmental safety. The dynamics of catalyst poisoning by an admixture in a gaseous flow belongs to the same class of problems.

The two most general technical solutions for the removal of an admixture from a gaseous flow are reduced to admixture consumption by an absorbent or a chemical reaction with a solid reactant.

The problem of admixture consumption at a linear rate ω by absorption was considered by Tikhonov and Samarskii [1] based on the solution proposed in [2]. These authors formulated the problem as set (1) of two partial differential equations with respect to the unknowns $c(l, t)$ and $a(l, t)$, which are the concentrations of absorbed substances in the gas and absorbent, respectively:

$$\begin{cases} -\omega\dfrac{\partial c}{\partial l} = \dfrac{\partial c}{\partial t} + \dfrac{\partial a}{\partial t} \\ \dfrac{\partial a}{\partial t} = k(c - c_{\mathrm{eq}}), \end{cases} \tag{1}$$

with the initial conditions $c(l, t = 0) = 0$ and $a(l, t = 0) = 0$ and the boundary condition $c(l = 0, t) = C$, where l is the coordinate along the axis of the gaseous flow, t is time, and w is the linear gaseous flow rate.

In the case of the Henry isotherm $c_{\mathrm{eq}} = \gamma a$ (where γ is the Henry coefficient), the authors suggest an analytical solution. In the case of the Langmuir isotherm, the solution to the problem can be obtained by the finite-difference method.

This paper is devoted to the problem of admixture consumption from a gaseous or liquid flow by the reaction with a solid reactant (absorbent).

A mathematical description for admixture consumption from the flow is determined by the fact that the concentration of an absorbed substance affects the rate of consumption, and this concentration changes along the absorbent bed. The properties of an absorbent change along the bed and with time. Let us briefly consider the physical model of the process.

Suppose a gaseous flow containing an admixture reacts with an absorbent in a cylindrical flow-type plug-flow reactor and the reacted absorbent loses its reactivity and becomes inert. The proper rate of consumption depends on the absorbent properties and concentrations of absorbed admixture in the gas. The dependence of the rate of consumption W on the admixture concentration in the gaseous flow can in most cases be described by the second-order equation. If we neglect the diffusion control, the dependence of the consumption rate on the absorbent concentration (or, to be more exact, the residual absorbent capacity) can be described in an analogous way. We can assume that the rate of consumption is proportional to the concentration of the admixture in the gas, and the current absorbent capacity is $W = kc(1 - x)$, where k is the rate constant of the interaction of the absorbent with the admixture; x is the absorbent conversion $x = \frac{a}{A}$ expressed as the amount of reacted absorbent a divided by the total absorbent capacity A. For the absorbent bed in a flow reactor, this equation characterizes the situation in an arbitrary section of the absorbent at a certain distance l from the edge of the bed, and $x(l, t)$ is determined as a fraction of the reacted absorbent in this section at the time t.

Then, for the rate of reacted absorbent accumulation in the section l, we can write the equation

$$\frac{\partial a}{\partial t} = kc\left(1 - \frac{a}{A}\right). \tag{2}$$

This equation is linear with respect to unknown functions, which makes it different from the second equation of set (1).

To describe a change in the concentration of the admixture in the gaseous flow due to its consumption, we can use an equation that is analogous to the first equation in set (1) proposed by Tikhonov and Samarskii.

Thus, we have the following set of equations:

$$\begin{cases} -\omega\dfrac{\partial c}{\partial l} = \dfrac{\partial c}{\partial t} + \dfrac{\partial a}{\partial t} \\[2mm] \dfrac{\partial a}{\partial t} = kc\left(1 - \dfrac{a}{A}\right) \end{cases} \qquad (3)$$

with the initial conditions $c(l, t = 0) = 0$ and $a(l, t = 0) = 0$ and the boundary condition $c(l = 0, t) = C$ (where a has the concentration units as in set (1)).

To solve set (3) of equations, let us change variables $\begin{cases} \lambda = l \\ \tau = t - \frac{l}{\omega} \end{cases}$. After expressing $\frac{\partial}{\partial l}$ and $\frac{\partial}{\partial t}$ in terms of new variables, $\frac{\partial}{\partial l} = \frac{\partial}{\partial \lambda} - \frac{1}{\omega}\frac{\partial}{\partial \tau}$, $\frac{\partial}{\partial t} = \frac{\partial}{\partial \tau}$ we obtain a new set of equations

$$\begin{cases} -\omega\dfrac{\partial c}{\partial \lambda} = \dfrac{\partial a}{\partial \tau} \\[2mm] \dfrac{\partial a}{\partial \tau} = kc\left(1 - \dfrac{a}{A}\right) \end{cases}$$

or because $\lambda = l$,

$$\begin{cases} -\omega\dfrac{\partial c}{\partial l} = \dfrac{\partial a}{\partial \tau} \\[2mm] \dfrac{\partial a}{\partial \tau} = kc\left(1 - \dfrac{a}{A}\right). \end{cases} \qquad (4)$$

Let us consider how the initial and boundary conditions change. At $\tau = 0$ $l = \omega t$. By this time, the gas reached the section l, and then $a(l, \tau = 0) = 0$. At $l = 0$ $\tau = t$, and the boundary condition does not change: $c(l = 0, \tau) = C$. If we fix the parameter $l = 0$, the set of differential equations is reduced to an ordinary differential equation with respect to $a(l = 0, \tau) = a(\tau)$ and the initial condition $a(\tau = 0) = 0$. Then we obtain the equation $\frac{A}{kC}\frac{\mathrm{d}a}{\mathrm{d}\tau} + a = A$ whose solution $a(l = 0, \tau) = A(1 - \mathrm{e}^{-\frac{C}{A}k\tau})$ is the boundary and initial condition for $a(l, \tau)$.

If we fix the parameter $\tau = 0$, we obtain an analogous condition for $c(l, \tau)$, and solve equation $c(l, \tau = 0) = c(l)$ for $-\omega\frac{\mathrm{d}c}{\mathrm{d}l} = kc$ with the initial condition $c(l = 0) = C$. Then, we arrive at $c(l, \tau = 0) = C\mathrm{e}^{-\frac{k}{\omega}l}$.

Thus, the initial set (3) is transformed into

$$\begin{cases} -\omega\dfrac{\partial c}{\partial l} = \dfrac{\partial a}{\partial \tau} \\[2mm] \dfrac{\partial a}{\partial \tau} = kc\left(1 - \dfrac{a}{A}\right) \end{cases} \text{ with conditions } \begin{aligned} a(l = 0, \tau) &= A\left(1 - \mathrm{e}^{-\frac{C}{A}k\tau}\right) \\ c(l, \tau = 0) &= C\mathrm{e}^{-\frac{k}{\omega}l}. \end{aligned} \qquad (5)$$

Let us express $c(l, \tau)$ using the second equation: $c = \frac{1}{k}\frac{\partial a}{\partial \tau}\frac{A}{A - a}$ and denote $f(l, \tau)$ by $A - a$ $\left(\text{when } \frac{\partial a}{\partial \tau} = -\frac{\partial f}{\partial \tau}\right.$ and $\left. c = -\frac{A}{k}\frac{1}{f}\frac{\partial f}{\partial \tau}\right)$. Then, the set is simplified:

$$\begin{cases} \omega\dfrac{\partial c}{\partial l} = \dfrac{\partial f}{\partial \tau}, \quad f(l = 0, \tau) = A\mathrm{e}^{-\frac{C}{A}k\tau} \\[2mm] c = -\dfrac{A}{k}\dfrac{1}{f}\dfrac{\partial f}{\partial \tau}, \quad c(l, \tau = 0) = C\mathrm{e}^{-\frac{k}{\omega}l}. \end{cases} \qquad (6)$$

Let us differentiate the second equation of set (6) with respect to l and equate it to $\frac{\partial c}{\partial l}$ from the first equation: $-\frac{A}{k}\frac{\partial}{\partial l}\left(\frac{1}{f}\frac{\partial f}{\partial \tau}\right) = \frac{1}{\omega}\frac{\partial f}{\partial \tau}$. The latter expression can be rearranged as follows: $\frac{\partial}{\partial l}\left(\frac{1}{f}\frac{\partial f}{\partial \tau}\right) + \frac{k}{A\omega}\frac{\partial f}{\partial \tau}$. Let us then use the identity $\frac{\partial}{\partial l}\left(\frac{1}{f}\frac{\partial f}{\partial \tau}\right) \equiv \frac{\partial}{\partial \tau}\left(\frac{1}{f}\frac{\partial f}{\partial l}\right)$:

$$\frac{\partial}{\partial \tau}\left(\frac{1}{f}\frac{\partial f}{\partial l}\right) + \frac{k}{A\omega}\frac{\partial f}{\partial \tau} = 0 \text{ or } \frac{\partial}{\partial \tau}\left(\frac{1}{f}\frac{\partial f}{\partial l} + \frac{k}{A\omega}f\right) = 0.$$

The last expression means that the term inside the brackets is independent of τ and equals some function $h(l)$: $\frac{1}{f}\frac{\partial f}{\partial l} + \frac{k}{A\omega}f = h(l)$. This allows us to obtain the solution to our problem.

After switching to complete derivatives, the latter expression is a Bernoullian ordinary differential equation with respect to $f(l)$, which is solvable by the standard substitution $z = \frac{1}{f}$. With the initial condition $f(l =$

0) $= Ae^{-\frac{C}{A}k\tau}$, it has the solution: $f(l, \tau) = A\frac{e^{\int_0^l h(\lambda)d\lambda}}{e^{\frac{C}{A}k\tau} + \frac{k}{\omega}\int_0^l e^{\int_0^l h(\lambda)d\lambda}dl}$. Using the second equation of the set, we find $c(l, \tau) = C\frac{e^{\frac{C}{A}k\tau}}{e^{\frac{C}{A}k\tau} + \frac{k}{\omega}\int_0^l e^{\int_0^l h(\lambda)d\lambda}dl}$. Let us apply the condition $c(l, \tau = 0) = Ce^{-\frac{k}{\omega}l}$; then, we have $\int_0^l e^{\int_0^l h(\lambda)d\lambda}dl = \frac{\omega}{k}(e^{\frac{k}{\omega}l} - 1)$, and the derivative in l is $e^{\int_0^l h(\lambda)d\lambda} = e^{\frac{k}{\omega}l}$.

After substituting the last expression and $\tau = t - \frac{l}{\omega}$ into formulas for $f(l, \tau)$ and $c(l, \tau)$, we find the final expression (7).

$$a(l, t) = A\frac{e^{\frac{C}{A}k\left(t - \frac{l}{\omega}\right)} - 1}{e^{\frac{C}{A}k\left(t - \frac{l}{\omega}\right)} + e^{\frac{k}{\omega}l} - 1},$$
$$c(l, t) = C\frac{e^{\frac{C}{A}k\left(t - \frac{l}{\omega}\right)}}{e^{\frac{C}{A}k\left(t - \frac{l}{\omega}\right)} + e^{\frac{k}{\omega}l} - 1}. \qquad (7)$$

By dividing (7) by $a(l, t)$ and $c(l, t)$, we arrive at a rather simple expression:

$$\frac{a}{c} = \frac{A}{C}\left(1 - e^{-\frac{C}{A}k\left(t - \frac{l}{\omega}\right)}\right). \qquad (8)$$

Another important property of the above solution is associated with the equality

$$\int[a(l, t) + c(l, t)]dl = \frac{A\omega}{k}\ln\left(\frac{e^{\frac{k}{\omega}l}}{e^{\frac{C}{A}k\left(t - \frac{l}{\omega}\right)} + e^{\frac{k}{\omega}l} - 1}\right), \qquad (9)$$

from which we have $S\int_0^{\omega t}[a(l, t) + c(l, t)]dl = CS\omega t$ equal to the amount of admixture supplied to the reactor by the time t.

For the illustration, we constructed the plots for $c(l, t)$ and $a(l, t)$ for sequential time intervals using the following set of rate parameters $k = 1.0$, $\omega = 1.0$, $C = 1.0$, and $A = 1.0$ (Figs. 1 and 2). As can be seen from these figures, the distribution of concentrations in the gaseous flow for this set of parameters is close to frontal. It is also seen that the concentration profiles of the admixture in the gas and absorbent become more similar with time. This follows from formula (8), because $\frac{a}{c} = \frac{A}{C} =$ const at $\tau \longrightarrow \infty$.

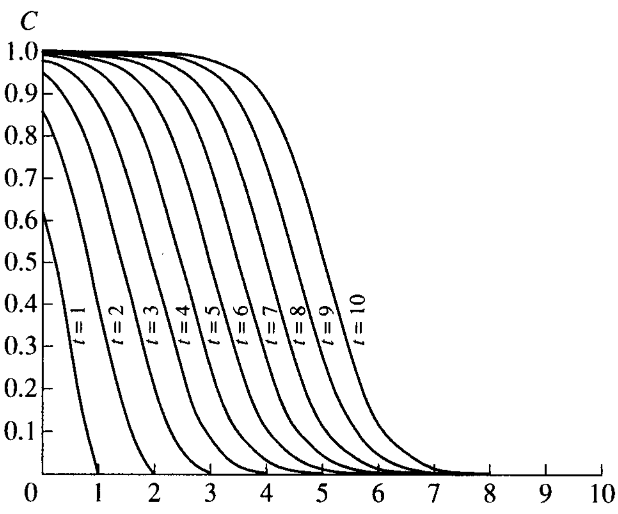

Fig. 1. Admixture concentration profiles in the absorbent along the reactor axis.

An apparent break-down in the concentration profile in the gas is stipulated by the fact that, at short contact times, the layers closer to the end of the bed do not contact with the gas, containing the admixture, in the plug-flow reactor. In a real system, such breakdowns should not be observed because of longitudinal mixing.

The sharpness of a concentration profile is determined in the general case by the ratio between the linear rate ω of the flow and the rate constant k of the reaction between the admixture and absorbent. Figure 3 shows the profiles $a(l, t)$ at variable k and fixed ω.

As the curves in Fig. 3 show, when we vary the ratio $\frac{k}{\omega}$ (which is equivalent to choosing different absorbents) or at different ratios between the rate of absorption and the rate of the gaseous flow, different distributions can be observed: from a slow decrease in the concentration in the bed to the frontal distribution.

To end this article, we consider possible deviations from the distributions due to the possible influence of longitudinal mixing. A complete description of such a nonstationary system is very difficult. However, if we consider the bed of granular absorbent, the expected effect of longitudinal mixing is insignificant. Nevertheless, we can make some estimates. Let us assume that convection is negligible for a rather long bed whose characteristic length is substantially greater than the

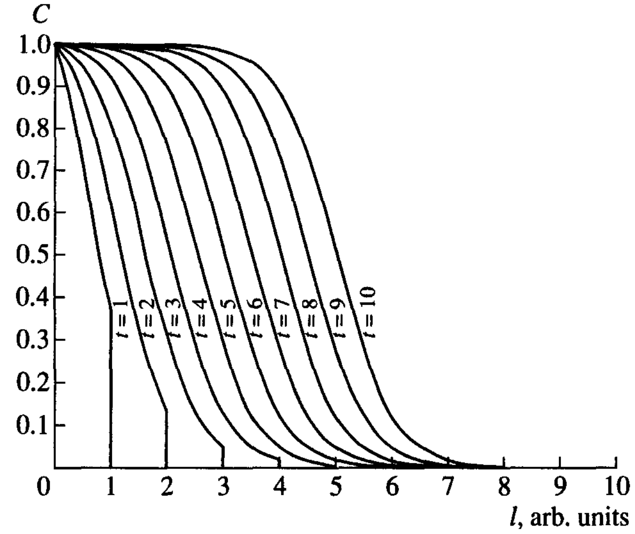

Fig. 2. Admixture concentration profiles in the gaseous flow along the reactor axis.

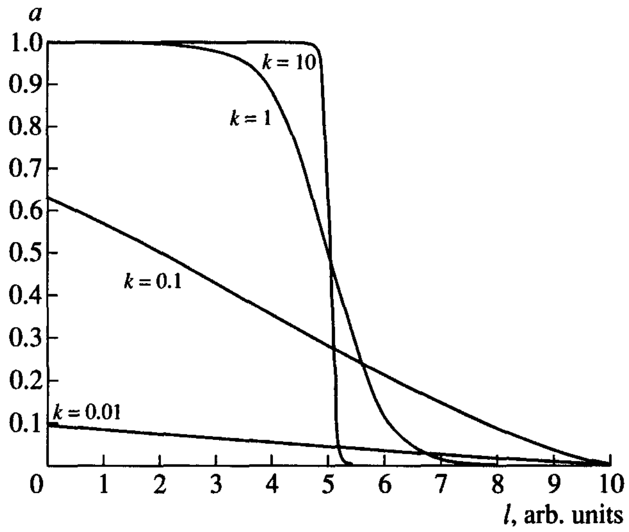

Fig. 3. Admixture concentration profiles in the absorbent along the reactor axis at different k ($\omega = 1.0$).

diameter of particles. Then, longitudinal mixing only occurs due to molecular diffusion.

In this case, the initial set of equations takes the following form.

$$\begin{cases} -\omega\dfrac{\partial c}{\partial l} + D\dfrac{\partial^2 c}{\partial l^2} = \dfrac{\partial c}{\partial t} + \dfrac{\partial a}{\partial t} \\ \dfrac{\partial a}{\partial t} = kc\left(1 - \dfrac{a}{A}\right). \end{cases}$$

Obviously, the effect of longitudinal transfer can be neglected if the strong inequality is fulfilled:

$$\left|D\frac{\partial^2 c}{\partial l^2}\right| \ll \left|\omega\frac{\partial c}{\partial l}\right|,$$

which is a necessary and sufficient condition.

Let l_1 be the distance along the reactor axis at which the concentration changes by an order of magnitude for the time t. Then, the derivatives can be approximated by the ratios of the corresponding values: $D\frac{c}{l_1^2} \ll \omega\frac{c}{l_1}$ or $1 \ll \frac{\omega}{D}l_1$. The last expression is equivalent to the inequality $Pe \gg 1$, which is a necessary and sufficient condition for the applicability of the above solution to the problem of admixture absorption from a gaseous flow.

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