i = pertaining to i^{th} class of droplets
in = at initial conditions
o = at nozzle exit
p = of the product
x = at a vertical distance x below the nozzle
w = at wet bulb temperature of the air

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Manuscript received October 9, 1975; revision received April 6 and accepted April 7, 1976.

A Method of Moments for Measuring Diffusivities of Gases in Polymers

A method of moments has been formulated for the determination of the diffusivity of a gas in a polymer from a step response in a continuous permeation chamber. Contributions of system components other than the polymer are easily factored out to determine the contribution of the polymer alone, and this contribution is then analyzed to calculate the diffusivity. The method has been applied to the measurement of the diffusivities of sulfur dioxide in PTFE (Teflon) and fluorosilicone rubber tubes over a wide temperature range.

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SCOPE

Traditional methods for measuring the diffusivity of a gas in a polymer involve either passage of the gas through a membrane into a closed chamber in which the pressure is monitored or sorption of the gas in a small polymer sample suspended from a spring whose elongation is monitored. In either experiment, a substantial driving

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force is needed to achieve measurable penetration fluxes, thereby limiting the penetrant concentrations for which data may be obtained.

An approach in which a gas permeates through a membrane into a flowing stream overcomes many of the experimental problems associated with closed volume systems and allows accurate measurements of gas transport properties for penetrant concentrations as low as tens of parts per million (Pasternak et al., 1970; Ziegel et al., 1969). This technique is not without its drawbacks, however. The complete solution of the time dependent diffusion equation is at best an infinite series, and curve fitting methods for estimating the diffusivity generally utilize either short or long time asymptotic solutions. When deviations from the anticipated straight line behavior occur, it is difficult to determine whether they are due to experimental error, to a violation of the assumptions of the diffusion model, or simply to the invalidity of the asymptotic solution in the range of response times where the deviations occur.

Felder, Spence, and Ferrell (1975*a*) recently formulated a method for estimating the diffusivity of a gas in a polymer from a moment of a step response in a continuous permeation chamber. The method requires only numerical integration, rather than curve fitting, and does not depend on the existence of a short- or long-time asymptotic solution of the diffusion equation.

A problem associated with this technique (and with any other dynamic response technique) is that what is measured is the response of the entire system (connecting lines, chamber, permeable membrane, and gas analyzer) to a step concentration change upstream of the chamber, while what is needed to evaluate the desired diffusivity is the step response of the membrane alone. This paper develops an extension of the moment technique which provides a simple but accurate resolution of this problem.

CONCLUSIONS AND SIGNIFICANCE

The method of moments for determining the diffusivity of a gas in a permeable material has been found to provide several advantages over traditional closed volume and continuous measurement techniques.

1. The use of a continuous permeation chamber rather than the closed volume chamber of the standard time lag experiment permits the attainment of a true steady state and yields data which are less susceptible to cumulative errors. The data obtained in a single experiment may be analyzed to determine the diffusivity, the permeability, and the solubility of the penetrant in the polymer.
2. Maintaining equal pressures on both sides of the membrane (which cannot be done in a closed volume chamber) minimizes the requirements for membrane support and sealing and allows accurate measurements with very low penetrant concentrations.
3. The complete response to a step change in penetrant concentration is utilized, rather than a portion of the response which falls within the region of validity of a short or long time asymptotic solution of the diffusion equation.
4. Simple numerical integration of response data rather than curve fitting is required.
5. The method is applicable to cylindrical tubes as well as flat membranes.
6. The contributions of system components other than the membrane may be factored out of the measured response by simple subtraction of moments to obtain the contribution of the membrane alone.

The method has been applied to the measurement of the diffusivity of sulfur dioxide in fluorosilicone rubber and PTFE (Teflon) tubes at temperatures from 21° to 227°C. Calculated diffusivities have in several cases been substituted into the analytical solution of the diffusion equation to regenerate the response curves from which the diffusivities were estimated. The close agreement between the measured and calculated responses validates both the estimation technique and the diffusion model upon which it is based.

THEORETICAL

Measurement of Transport Properties in a Continuous Flow Permeation Chamber

In a continuous permeation experiment, a penetrant is introduced at a partial pressure p_1 (cm Hg) on one side of a flat membrane or on the outside of a hollow cylindrical tube and permeates through the polymer into a gas stream flowing past the membrane or through the inside of the tube. The concentration of the penetrant in the exiting gas is monitored continuously until a steady state is attained.

The following assumptions are made:

1. Gas phase resistance to mass transfer is negligible.
2. Absorption of the penetrant at the polymer surface is an instantaneous process.
3. The concentration of the dissolved gas at the downstream membrane surface is negligible compared to that on the side where the penetrant was introduced.
4. The solubility of the penetrant in the polymer is independent of the penetrant concentration in the gas phase.
5. Diffusion in the polymer is Fickian with a constant diffusivity D (square centimeters per second).

The diffusion equation may be solved for the rate of permeation of the gas through the polymer (see Appendix A),* and the solutions may in turn be used to derive expressions for the diffusivity D. Let $\phi(t)$ (mole per second) be the measured permeation rate, ϕ_s the asymptotic (steady state) value of this rate, and define

$$M_0 = \int_0^\infty \left[1 - \frac{\phi(t)}{\phi_s} \right] dt \qquad (1)$$

Felder et al. (1975*a*) have shown that for a flat membrane with a surface area A (square centimeters) and thickness h (centimeters)

$$D = h^2/6M_0 \qquad (2)$$

and for a cylinder with inner radius a and outer radius b

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* Supplementary material has been deposited as Document No. 02838 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N.Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

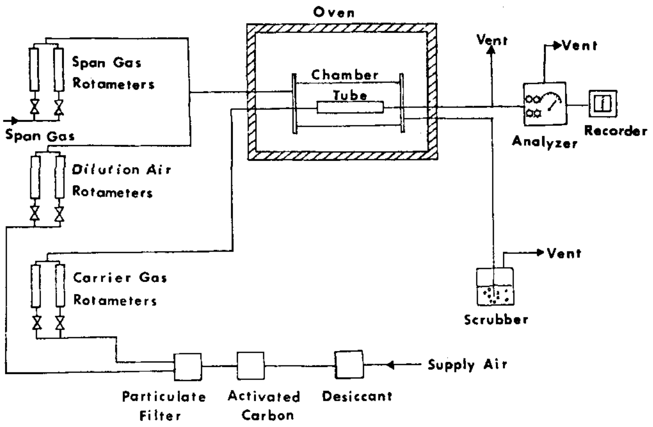

Fig. 1. Schematic of experimental apparatus.

$$D = \frac{a^2 - b^2 + (a^2 + b^2)\ln(b/a)}{4M_0 \ln(b/a)} \qquad (3)$$

If diffusivities are measured at several temperatures, an Arrhenius plot of ln D vs. $1/T$ yields the activation energy for diffusion of the penetrant in the polymer (Stannett, 1968).

The analytical solution for the permeation rate $\phi(t)$ through the wall of a hollow cylindrical tube is given in Appendix A,* along with a numerical technique for evaluating the infinite series which is a part of the solution.

Deconvolution of the Polymer Tube Response from the Total System Response

A difficulty associated with dynamic response measurements of the type just described is that what is measured is the response of the entire system (connecting lines, chamber, polymer, and gas analyzer) to a step concentration change upstream of the chamber, while what is needed to evaluate the diffusivity from Equations (1) and (2) or (3) is the response of the polymer alone.

In the experiments described by Felder et al. (1975*a*), this problem was solved by assuming that the connecting lines, the chamber, and the analyzer each acted as pure time delays, and the measured response was accordingly shifted horizontally by the total of these delays. The values of the delays for the lines and the chamber were taken to be the nominal mean residence times (volume/volumetric flow rate) of the gases flowing through these units, and the time delay attributed to the analyzer was arbitrarily set equal to the time required for the analyzer reading to reach 90% of its final value in calibration runs.

In previous diffusivity measurements, the time lag due to the polymer accounted for most of the total system response time, so that the particular method used to correct for the other contributions to the response was immaterial. However, if, for example, the diffusivity of a gas in a thin membrane at a high temperature is to be measured, the response times of the other system components may be equal to or even greater than that of the polymer. In such cases, representing all the time lags as pure delays would be a serious error; the analyzer, in particular, is unlikely to be a pure delay, or for that matter a pure first-order process or anything else that can easily be modeled.

Fortunately, the true dynamic characteristics of the system components may be taken into account in correcting the measured response, with little more effort than was required for the oversimplified method used previously. The procedure is to calculate as before the mean residence times of the gas in the line leading to the chamber (τ_1) and in the chamber itself (τ_2), and the mean residence time of the carrier gas in the line leading from the chamber to the analyzer (τ_3). Next, if $R_a(t)$ is the transient response of the analyzer to a step change in the penetrant concentration at its inlet (that is, the response measured when the analyzer is calibrated), and R_{as} is the steady state value of this response, then the time lag due to the analyzer may be determined by numerical integration as

$$\tau_a = \int_0^\infty \left[1 - \frac{R_a(t)}{R_{as}}\right] dt \qquad (4)$$

Finally, if $R(t)$ is the measured response of the entire system to a step concentration change (R is presumed to be proportional to the penetrant flux), R_s is the steady state value of this response, and

$$M_0' = \int_0^\infty \left[1 - \frac{R(t)}{R_s}\right] dt \qquad (5)$$

then the correct value of M_0 to use in the diffusivity formulas [Equations (2) and (3)] is

$$M_0 = M_0' - (\tau_1 + \tau_2 + \tau_3 + \tau_a) \qquad (6)$$

The theoretical justification for this procedure is given in Appendix B.

EXPERIMENTAL

Apparatus

A permeation chamber was constructed by clamping two 6 in.^{2} square stainless steel end plates with Teflon gaskets to ends of a 3 in. I.D., 24 in. long stainless steel chamber. Each end plate was drilled and tapped to accept a 0.125 in. thermocouple bulkhead fitting, a 0.125 in. pipe fitting, and a 0.375 in. pipe fitting. All fittings were stainless steel. Each of the 0.375 in. fittings was drilled internally to allow a length of 0.375 in. O.D. stainless steel tubing to pass through the end plate to the interior of the chamber. The polymer tube was connected between these internal fittings and supported by a stainless steel rod inserted inside the tube. The chamber assembly was then placed inside a thermostatically controlled oven.

A schematic diagram of the flow apparatus is shown in Figure 1. The feed to the chamber is a mixture of a cylinder gas containing roughly 1.5% sulfur dioxide in air and air containing less than 0.03 p.p.m. sulfur dioxide. The precise concentration of sulfur dioxide in the cylinder gas is determined by using EPA method 6 [absorption of the sulfur dioxide in an isopropanol-hydrogen peroxide solution and titration with a standardized barium perchlorate solution (Environmental Protection Agency, 1971)]. The dilution air is obtained by passing room air through a calcium chloride drying column, an activated charcoal column, and a particulate filter. The cylinder gas and dilution air are fed through rotameters into a tee, and the combined stream passes into the chamber on the outside of the polymer tube. A second stream of clean air (the carrier gas) is metered and fed into the inside of the tube; the sulfur dioxide permeating through the tube wall is picked up by this stream, which passes out of the chamber to a Meloy Laboratories model SA-160 flame photometric sulfur detector. The rate of permeation of sulfur dioxide is calculated as the product of the concentration read by the detector and the known volumetric flow rate of the carrier gas.

Copper-constantan thermocouples are used to monitor the temperature at two locations near the outside surface of the polymer tube, and the pressures of the chamber and carrier gases are measured with manometers. Strip chart recorders are used to obtain continuous records of the signals from the sulfur dioxide analyzer and from one of the thermocouples. The analyzer is calibrated before and after each run with a gas obtained by passing purified air at a measured rate over a calibrated sulfur dioxide permeation tube.

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* See footnote on p. 725.

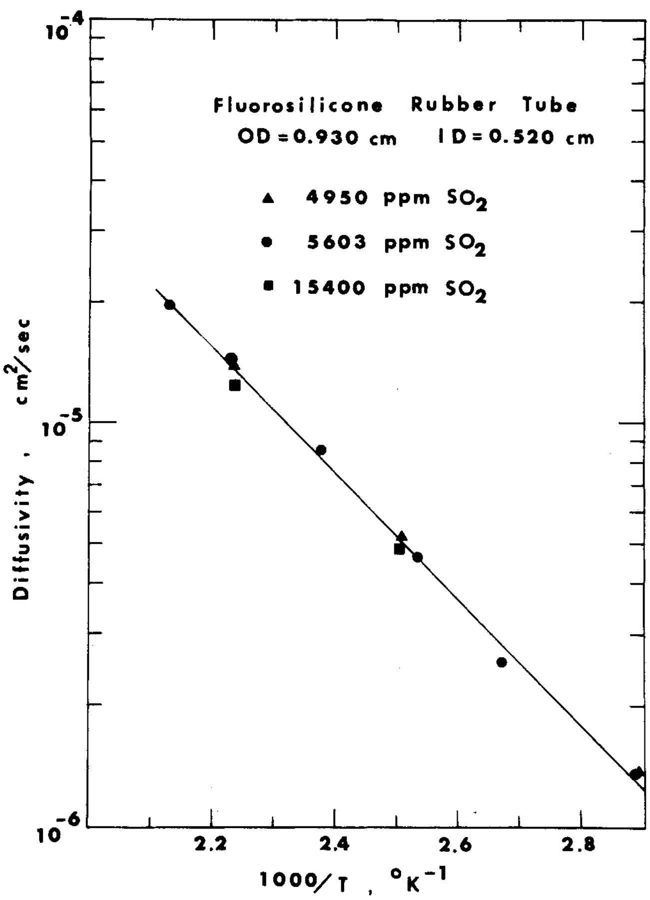

Fig. 2. Diffusivities of sulfur dioxide in a fluorosilicone rubber tube.

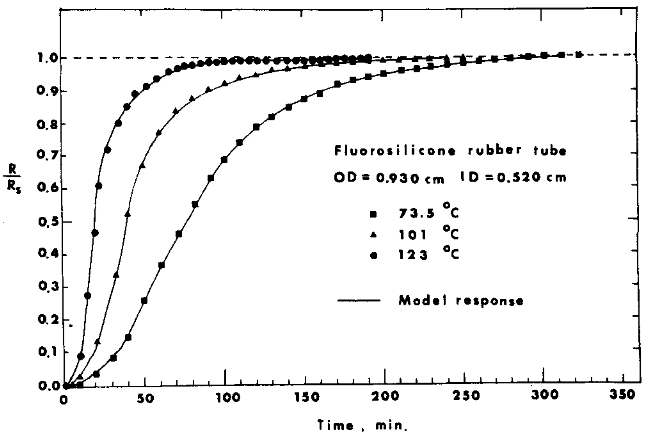

Fig. 3. Theoretical and experimental transient response isotherms.

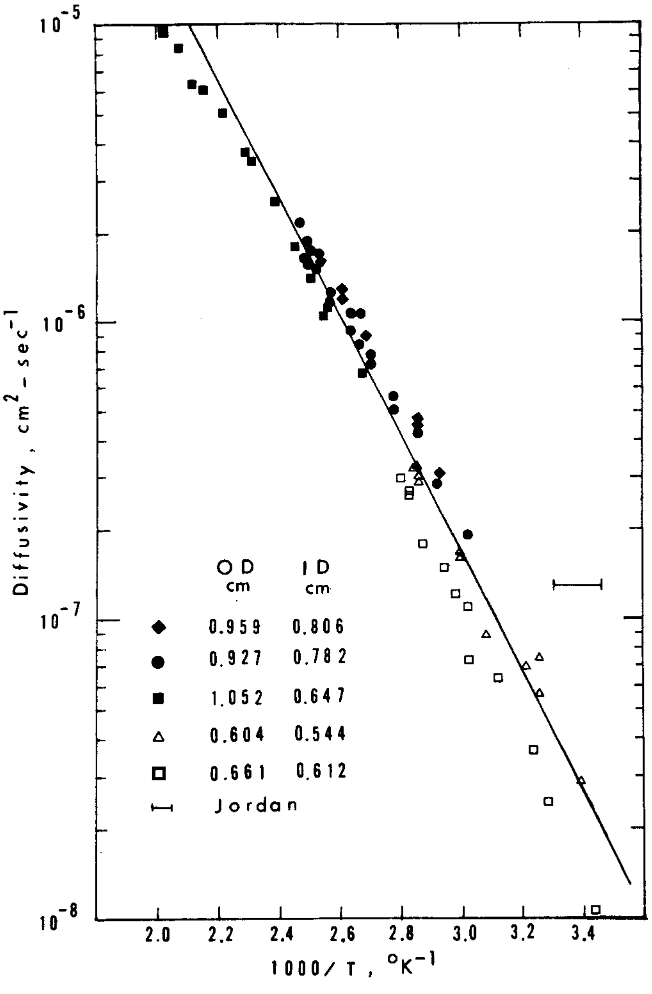

Fig. 4. Diffusivities of sulfur dioxide in PTFE tubes.

This experimental system has been used to determine steady state permeabilities of sulfur dioxide and water in a number of polymers (Rodes et al., 1973; Felder, Ferrell, and Spivey, 1974; Felder, Spence, and Ferrell, 1975*b*). Additional details about its design are given in these references.

Procedures for Diffusivity Measurements

The sample tube dimensions are measured before the tube is connected to the fitting in the chamber. The outer diameter of the tube is measured with a micrometer at several points around a circumference well away from an end, and an average value is calculated. A small length of the tube is then cut axially, and the wall thicknesses at several points are measured with the micrometer and averaged. The inner diameter is determined from the mean outer diameter and wall thickness.

The tube is mounted in the chamber, and the chamber in turn is mounted in the oven. The oven thermostat is set, and the chamber temperature is monitored until it reaches a constant value. The flow rates of the cylinder gas and dilution air are adjusted to produce a chamber gas with a known sulfur dioxide concentration, and the flow rate of the carrier gas is adjusted to provide a sample gas with a sulfur dioxide concentration within the range of the flame photometric detector (ideally 0.1 to 1 p.p.m.). The total pressure on both sides of the tube is maintained at approximately 1 atm.

The flow of the cylinder gas commences at a time $t = 0$, and the run continues until the measured concentration of sulfur dioxide in the sample gas levels off and remains level for at least 15 min. The sample gas sulfur dioxide concentration is multiplied by the volumetric flow rate of the sample gas to calculate the flow rate of sulfur dioxide leaving the tube, and the relatively small flow rate of sulfur dioxide in the entering air is subtracted to determine the sulfur dioxide permeation rate $\phi(t)$. The time lags τ_1, τ_2, and τ_3 attributable to the connecting lines and the chamber are calculated from the known volumes of these components and volumetric flow rates of the chamber and carrier gases, and the analyzer time lag τ_a is determined from calibration data by using Equation (4). The total system time lag M_0' is obtained from $\phi(t)$ $[\equiv R(t)]$ by using Equation (5), and the lag due to the polymer alone is determined from Equation (6). Finally, the diffusivity of sulfur dioxide in the polymer is calculated from Equation (3).

RESULTS AND DISCUSSION

Fluorosilicone Rubber Tubes

Diffusivities of sulfur dioxide in a fluorosilicone rubber tube (Dow Corning: SILASTIC LS-63U®) were measured at temperatures between 74° and 198°C by use of three different chamber gas sulfur dioxide concentrations. The results are shown on an Arrhenius plot in Figure 2. The near coincidence of the data points obtained for the different concentrations at a fixed temperature suggests the constancy of D at the sulfur dioxide partial pressures of 10 mm Hg and less used in these measurements. The activation energy for diffusion obtained from Figure 2 is $E_d = 30.6 \pm 0.9$ kJ/mole.

As a test of the validity of the diffusivity estimation technique, the theoretical expression given in Appendix A* for the permeation rate $\phi(t)$ was evaluated by means of diffusivities calculated at three different temperatures. Figure 3 shows plots of the resulting curves of R/R_s $(\equiv \phi/\phi_s)$ vs. t, along with the experimental data. The close correspondence between the experimental and theoretical responses at each temperature provides evidence for the validity of both the diffusivity estimation technique and the diffusion model on which the technique is based.

PTFE Tubes

Diffusivities of sulfur dioxide in PTFE (Teflon) tubes have been measured at temperatures from 21° to 227°C. Figure 4 shows an Arrhenius plot of the results obtained to date, along with a diffusivity measured by Jordan (1973) at a temperature presumed to be in the range 20° to 30°C. Straight lines can be fit quite well to the data for each individual tube, but noticeable variations occur from one tube to another. The diffusivity reported by Jordan is comparable to but higher than those measured in the present work, a result probably attributable to the substantially higher sulfur dioxide concentrations used in Jordan's study.

A least-squares line has been fitted to the data shown in Figure 4 to obtain the following estimation formula for the diffusivity of sulfur dioxide in PTFE:

$$D(\text{cm}^2/\text{s}) = 0.238 \exp(-4\,760/T) \qquad (7)$$

The activation energy for diffusion should not be deduced from Equation (7), since differences between the diffusivities of the thick walled tubes used at the higher temperatures and those of the thin walled tubes used at the lower temperatures introduce a bias in the slope of a line fit to all the data points. This point is the subject of continuing study.

ACKNOWLEDGMENT

This work was supported by Environmental Protection Agency Grant #801578. The authors acknowledge with thanks assistance provided by Dr. Roger Spence. A paper based on this work was presented at the 80th National Meeting of the American Institute of Chemical Engineers, Boston, Massachusetts, September, 1975.

NOTATION

a = inner cylinder radius, cm
b = outer cylinder radius, cm
C = dissolved penetrant concentration, mole/cm^3
C_1, C_2 = penetrant concentrations at the upstream and downstream membrane surfaces, mole/cm^3
D = diffusivity, cm^2/s
E_D = activation energy for diffusion, kJ/mole
$F(t), F_s$ = transient step response of total system and its steady state limit
$F_i(t), F_{is}$ = transient step response of i_{th} system component and its steady state limit
$G(s)$ = Laplace transform of $g(t)$
$G_i(s)$ = Laplace transform of $g_i(t)$
$g(t)$ = unit impulse response of total system
$g_i(t)$ = unit impulse response of i^{th} system component
h = thickness of flat membrane, cm
J_n = n^{th}-order Bessel function of the first kind
k_n = $\alpha_n a$
L = length of cylinder, cm
M_0 = zeroth moment of negative normalized step response of polymer, s
M_0' = zeroth moment of negative normalized step response of total system, s
$R(t), R_s$ = transient response to a step change in penetrant concentration and its steady state limit
$R_a(t), R_{as}$ = transient response of the analyzer alone to a step change at its inlet and its steady state limit
r = radial coordinate, cm
s = Laplace transform variable, s^{-1}
T = temperature, °K
t = time, s
U_0 = function defined by Equation (A6)*
x = b/a
$x_i(t)$ = signal at outlet of i^{th} system component
Y_n = n^{th}-order Bessel function of the second kind

Greek Letters

α_n = root of $U_0(\alpha_n a) = 0$
$\delta(t)$ = Dirac delta function, s^{-1}
μ_i = variable defined by Equation (B1), s
τ = total system time lag, s
τ_i = time lag of i^{th} system component, s
$\phi(t), \phi_s$ = transient permeation rate and its steady state limit, mole/s

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APPENDIX B: DECONVOLUTION OF THE STEP RESPONSE OF A POLYMER IN A CONTINUOUS FLOW PERMEATION CHAMBER

In the experiments described in this paper, the input signal to the system is imposed by opening a valve which commences the flow of a gas containing the penetrant. The gas flows through a connecting line and enters the chamber on one side

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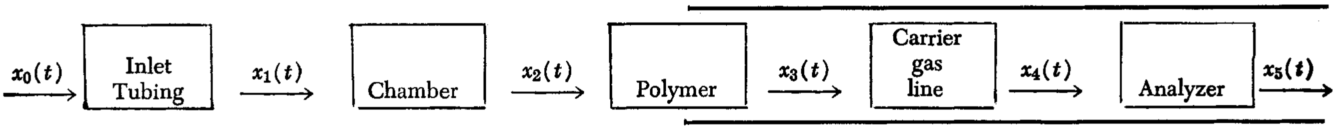
* See footnote on p. 725.

of the polymer; a portion of the penetrant dissolves in and diffuses through the polymer into a carrier gas, which passes to an analyzer where the penetrant concentration (the output signal) is measured.

Schematically, the system may be viewed as a series of process units, each with its own dynamic characteristics.



What is measured is the response $x_5(t)$ to a step input $x_0(t)$, whereas what is desired is related to the response of the polymer alone (x_3) to a step change in the chamber gas concentration (x_2). Standard process dynamics procedures are applicable to this problem, if it is assumed that each component behaves linearly. This assumption is valid for the polymer if the penetrant diffusivity and solubility are both independent of the penetrant concentration, and may or may not be valid for the analyzer. Most of the theoretical foundations for the development that follows may be found in the work of Douglas (1972).

The terms defined below will be used to obtain the desired result:

$g_i(t)$ = the unit impulse response of the i^{th} component ($i = 1 - 5$); that is, if $x_{i-1} = \delta(t)$, then $x_i(t) = g_i(t)$

$g(t)$ = the unit impulse response of the overall system: if $x_0(t) = \delta(t)$, then $x_5(t) = g(t)$

μ_i = the zero$^{\text{th}}$ moment of $g_i(t)$

$$\mu_i = \int_0^\infty g_i(t)dt \qquad \text{(B1)}$$

τ_i = the mean of g_i, which is also the mean residence time for the flow-through components ($i = 1$, 2, and 4). τ has the same significance for $g(t)$

$$\tau_i = \frac{\int_0^\infty tg_i(t)dt}{\int_0^\infty g_i(t)dt}; \quad \tau = \frac{\int_0^\infty tg(t)dt}{\int_0^\infty g(t)dt} \qquad \text{(B2)}$$

$G_i(s)$ = the Laplace transform of $g_i(t)$, or the transfer function of the i^{th} component

$$G_i(s) = \int_0^\infty e^{-st} g_i(t)dt; \quad G(s) = \int_0^\infty e^{-st} g(t)dt \qquad \text{(B3)}$$

$F_i(t), F_{is}$ = the response of the i^{th} component to a step input, and the asymptotic value of this response as $t \to \infty$

$F(t), F_s$ = the step response of the overall system and the asymptotic value of this response

$$M_0' = \int_0^\infty \left[1 - \frac{F(t)}{F_s}\right] dt \qquad \text{(B4)}$$

$$M_0 = \int_0^\infty \left[1 - \frac{F_3(t)}{F_{3s}}\right] dt \qquad \text{(B5)}$$

$$\tau_a = \int_0^\infty \left[1 - \frac{F_5(t)}{F_{5s}}\right] dt \qquad \text{(B6)}$$

The preceding notation follows that used in the main body of the paper: M_0' is calculated from the measured system response, M_0 is the quantity needed to determine the diffusivity of the penetrant in the polymer, and τ_a is determined from analyzer calibration data. The result to be proved is that

$$M_0 = M_0' - (\tau_1 + \tau_2 + \tau_4 + \tau_a) \qquad \text{(B7)}$$

According to Duhamel's principle, the input and output for the i^{th} component satisfy the relationship

$$x_i(t) = \int_0^t x_{i-1}(t - t')\, g_i(t')dt' \qquad \text{(B8)}$$

If $x_{i-1}(t)$ is a unit step function ($x_{i-1} \equiv 1$ for $t \geqq 0$), then from Equation (B8)

$$F_i(t) = \int_0^t g_i(t')dt' \qquad \text{(B9)}$$

If $t \to \infty$ in Equation (B9) and Equation (B1) is noted,

$$F_{is} = F_i(\infty) = \mu_i \qquad \text{(B10)}$$

and differentiating Equation (B9) with respect to t yields $g_i = dF_i/dt$, which for convenience in a future calculation may be rewritten as

$$g_i(t) = -\frac{d}{dt}[F_{is} - F_i(t)] \qquad \text{(B11)}$$

The quantity τ_i of Equation (B2) may be rewritten with the aid of Equations (B1) and (B10) as

$$\tau_i = \frac{1}{F_{is}} \int_0^\infty tg_i(t)dt \qquad \text{(B12)}$$

Integrating by parts with $u = t$, $dv = g_i dt$, $du = dt$, and from Equation (B11) $v = -(F_{is} - F_i)$ yields

$$\tau_i = (1/F_{is}) \left\{- t[F_{is} - F_i(t)]_0^\infty + \int_0^\infty [F_{is} - F_i(t)]dt\right\} \qquad \text{(B13)}$$

Provided that

$$\lim_{t \to \infty} t[F_{is} - F_i(t)] = 0 \qquad \text{(B14)}$$

(which must be satisfied for any real process component), Equation (B13) becomes

$$\tau_i = \int_0^\infty \left[1 - \frac{F_i(t)}{F_{is}}\right] dt \qquad \text{(B15)}$$

It follows from Equations (B15) and (B4) to (B6) that

$$\tau = M_0' \qquad \text{(B16)}$$

$$\tau_3 = M_0 \qquad \text{(B17)}$$

$$\tau_5 = \tau_a \qquad \text{(B18)}$$

Next, a Taylor expansion of the exponential in Equation (B3) for the transfer function $G_i(s)$ yields

$$G_i(s) = \int_0^\infty g_i(t)dt - s\int_0^\infty tg_i(t)dt + 0(s^2) \qquad \text{(B19)}$$

from which

$$\lim_{s \to 0} G_i(s) = \int_0^\infty g_i(t)dt \qquad \text{(B20)}$$

$$\lim_{s \to 0} -\frac{dG_i}{ds} = \int_0^\infty tg_i(t)dt \qquad \text{(B21)}$$

and hence

$$\tau_i = \frac{\int_0^\infty tg_i(t)dt}{\int_0^\infty g_i(t)dt} = \lim_{s \to 0} \left\{ \frac{1}{G_i(s)} \frac{dG_i(s)}{ds} \right\} \qquad \text{(B22)}$$

The subscripts may be dropped to obtain the analogous result for the overall system. The condition for the validity of (B22) is simply that the integrals exist, which they must for any real process.

Finally, if $G(s)$ is the overall system transfer function, then

$G(s) = G_1(s)G_2(s) \ldots G_5(s)$. Taking logs of both sides of this equation, differentiating with respect to s, and multiplying by -1, we get

$$-\frac{1}{G(s)}\frac{dG(s)}{ds} = -\sum_{i=1}^{5}\frac{1}{G_i(s)}\frac{dG_i(s)}{ds} \qquad \text{(B23)}$$

or from Equation (B22)

$$\tau = \tau_1 + \tau_2 + \tau_3 + \tau_4 + \tau_5 \qquad \text{(B24)}$$

Substituting for τ, τ_3, and τ_5 from Equations (B16) to (B18) and solving the resulting equation for M_0 yield

$$M_0 = M_0' - (\tau_1 + \tau_2 + \tau_4 + \tau_a) \qquad \text{(B7)}$$

which is the desired result. [The time lag τ_4 has been relabeled τ_3 in Equation (6) to avoid an unexplained omission in the sequence of subscripts shown in this equation.]

Manuscript received March 8, 1976; revision received April 26 and accepted April 30, 1976.

Improving Efficiency of Electrostatic Precipitation by Physicochemical Modification of the Electrical Resistivity of Flyash

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Theory and experiment show that lowered resistivity of fly ash, frequently caused by adding conditioning agents to flue gas to improve efficiency of electrostatic precipitation, is caused by capillary condensation of liquid at the contact points of ash particles, thereby providing additional pathways for flow of electrical current.

SCOPE

The efficiency of electrostatic precipitation is adversely affected by high electrical resistivity of the layer of fly ash or dust situated on the collecting electrode. Such deleterious effects are associated with high voltage which builds up in the ash layer and causes dielectric breakdown by ionization of the gas within the interstices of the particle layer (so called sparking or back corona). It has been known (White, 1970) for some time that the electrical conductivity of the ash layer is sensitive to the composition of the flue gas, and such phenomena have been used to improve ash collection during electrostatic precipitation by increasing the moisture content of the flue gas and also by adding small quantities of so-called conditioning agents, such as sulfur trioxide, sulfamic acid, and ammonia, thereby simultaneously improving the performance of the precipitator and increasing the electrical conductivity of the fly ash. In spite of the widespread use (White, 1970) of such conditioning agents, especially in electric power plants burning low sulfur coal, which produces fly ash of lower electrical conductivity (vis a vis higher sulfur coal), the phenomenon and mechanism of such conditioning remain poorly understood beyond the general rationale that they are associated with gas sorption phenomena and attendant ionic conduction either within the ash particles, at their surfaces, or at both locations. The present paper reports experiments relating the electrical resistivity of fly ash to gas sorption phenomena. In particular, a simple model has been developed which, for the first time, explains the rather extraordinary influence of temperature, gas moisture content, and concentration of conditioning agent upon the electrical resistivity of the fly ash. In this approach, the fly ash layer is represented by a well-ordered cubic array of monodisperse, spherical particles, wherein capillary condensation of water and conditioning agent occurs in the narrow crevices at the points of contact between the particles. Increased conductivity results from the added conduction path provided by the capillary condensed liquid. The conditioning agent actually enhances the extent of capillary condensation and thus the conductivity.

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