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Investigation of pore structure by a non-steady-state gas diffusion technique

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Experimental details are given of a technique for investigating the internal geometry of a porous material, with particular reference to dead-end pores, especially those of the "ink-bottle" geometry (restricted-access pores). The pores of the sample are initially filled with a tracer gas (e.g. methane), and the transient diffusion of the tracer into a carrier gas (e.g. nitrogen) is measured (e.g. by flame ionization detection). Typical results are given, which indicate the potential of the method for studying a key aspect of the pore structure of technologically important materials. Current approaches to the theoretical modelling of the relevant structures are also indicated.

1. Introduction

Porous materials are extremely common, and the detailed structure of their pore systems is of paramount importance in many areas of technology, e.g. concrete and other constructional materials, oil-bearing sandstones and shales, industrial carbons and nuclear reactor graphites, sintered metal electrodes in batteries and fuel cells, and industrial catalysts for petroleum reforming, ammonia synthesis, etc. Despite the large volume of literature which exists on the study of pore geometries [1–3], there are several aspects which have been surprisingly neglected, and which are demonstrably of considerable significance in some uses of porous materials.

Some of the experimental measurements have simple interpretations; e.g. by measuring the crystal density of the solid and comparing it with the bulk density of the material, the total pore volume can be found. Another technique measures the open pore volume accessible to helium gas (OPV) and the difference between these two will give the closed pore volume (CPV). Although the CPV is not immediately involved in the flow and diffusion properties of the solid, it can be important if the solid is to be used in a corrosive environment which might open paths to the CPV. Other techniques give results which are related in a much more complex way to the pore geometry. For example, mercury porosimetry provides information on pore radius by forcing mercury into the pores against the reverse capillary pressure; the results can be processed to give effective pore entrance diameters, but these are not readily interpreted in terms of actual pore geometry. They do however demonstrate, particularly when combined with porosimetry hysteresis and with gas-adsorption surface-area measurements, that a substantial part of many pore systems consists of relatively large volumes behind relatively small necks. Such pores are known as "ink-bottle" or restricted access pores (RAPs), and may play a vital role in determining the rates of chemical or physical processes taking place in the material. A knowledge of their geometry is thus very necessary, but unfortunately is not easily obtained.

Pore geometry has a very strong influence on the transport properties of fluids through the medium. In the usual measurements, either a pressure difference is applied across a sample and the gas flow through it is measured to give viscous and slip flow coefficients (B_0 and K_0), or alternatively, using a concentration difference, the diffusion through the sample is measured and the ratio of the measured diffusion coefficient to the free-gas value for the gas pair used gives the diffusivity (λ). These two transport techniques are steady-state methods, and the results are determined by the geometry of the transport pores (TPs), which may be defined as comprising all pores in which

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pressure or concentration gradients exist during steady-state transport. By contrast, steady-state flow is completely unaffected by the geometry, or even the existence, of dead-end pores which are connected to the transport pore system by single openings only. These contain concentration gradients only during transients, and are likely to be of RAP geometry, and are of crucial importance in many uses of porous materials.

Information on the geometry of the very important dead-end pore volume can be obtained by measuring non-steady-state flow phenomena [4]; other workers have monitored the establishment of steady-state bulk flow [5, 6] or injected a pulse of methane into a gas flow on one side of a specimen and measured the changes of concentration on the other [7]. In the present work we have developed a relatively straightforward technique in which the sample is sealed except for one face, through which it is evacuated and then filled with a tracer gas. An inert carrier gas is then allowed to flow over the surface of the sample and the rate of diffusion of tracer into the carrier is measured as a function of time. The purpose of this paper is to describe the technique and to indicate some areas of current application, together with an outline of theoretical approaches to modelling transport phenomena in terms of pore geometry.

2. Experimental details

The essential features of the apparatus are shown diagrammatically in Fig. 1. The specimen holder S is connected to valve SV, a low dead-volume two-position gas sampling valve. Schrader 43003MS was originally used but has been replaced by Loenco L-208-8 or Carl 5521. In one position of SV the carrier gas from cylinder N and flow meter F is directed straight to the detector D, and the sample is connected to the vacuum line via V1 and the tracer gas cylinder T via V2 and V3. In the second position the carrier gas flows through the sample holder to the detector. To carry out a run, the sample is evacuated and flushed with the tracer from T, then filled and left to equilibrate. Meanwhile the carrier flow and detector response has been stabilized. The pressures in the sample holder and carrier stream are carefully equalized using M1 and M2, then the elution of the tracer is initiated by switching SV, and the output of the detector is monitored on a chart recorder, typically over a period of ½ to 2 h. Results may be taken from the chart recorder and punched on cards for computer processing, and a current development involves on-line digitization and real-time data acquisition and processing.

The choice of tracer and carrier is to some extent arbitrary; we have used mainly methane and nitrogen, with detection by a Pye 104 Flame Ionization Detector (FID), which has a very high dynamic range ($10^5:1$) and could measure methane concentrations down to about 0.5 ppm in nitrogen with reasonable accuracy. For large specimens, the tracer can advantangeously be a mixture of (e.g.) 1% methane in nitrogen, and methane in carbon dioxide has also been used. The FID is calibrated each day by flowing methane at a known rate into the carrier stream through the restrictor R, the flow rate having been previously calibrated against pressure drop measured on the water manometers M3 and M2. The FID calibration was found to be

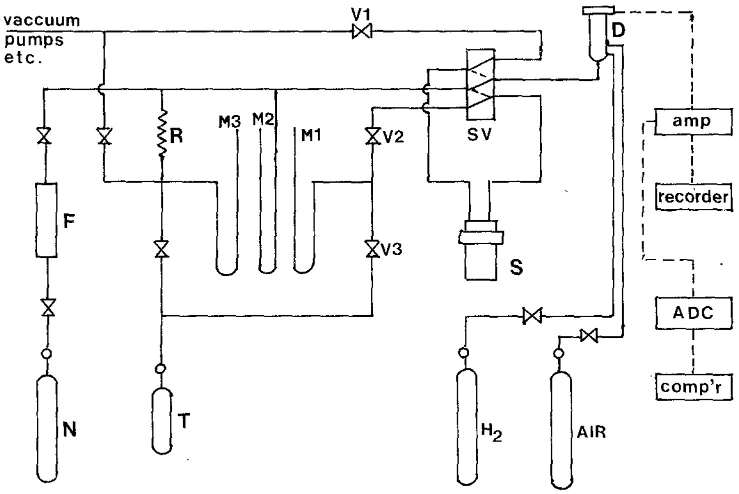

Figure 1 Apparatus: S = specimen holder (Fig. 2), SV = switching valve, D = detector (FID), V = valves, F = flowmeter, M = manometers, R = restrictor.

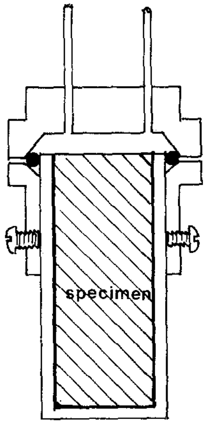

Figure 2 Specimen holder.

linear at all but the highest concentrations of methane.

Although any shape of sample could be used in principle, it simplifies the theoretical analysis to use specimens with a uniform cross-section, and cylinders are experimentally convenient. The samples were mounted in brass cylinders with epoxy resin or Picein and fitted into the apparatus with an O-ring coupling (Fig. 2). Sample sizes have ranged from 12 mm diameter x 15 mm long to 25 mm diameter x 75 mm long.

3. Typical results and discussion

3.1. Artificial RAPs

As a check on the validity of the results obtained, measurements were made on artificial pores machined from brass and having a simple cylindrical pore structure whose diffusional properties could be calculated *a priori*. This structure (Fig. 3) consisted of a large volume V with a narrow neck to the face of the sample. The neck was packed with straight copper wires to produce a set of fine uniform capillaries, so that turbulent mixing caused by the carrier flow past the neck would not propagate far down the neck. The geometries were chosen to give time-constants similar to those obtained for nuclear reactor graphite and were such as to justify the assumptions that:

(a) diffusion from the specimen was sufficiently slow that concentration gradients down the neck were effectively constant (i.e. nearly steady-state), and

(b) the concentration in the large volume was effectively homogeneous.

The rate f_t of tracer flow out of the neck at time t is then given by

$$f_t = f_0 \exp(-D_{12}at/Vl)$$

where V is the volume of the main pore, l is the length, a is the cross-sectional area of the neck pores, and D_{12} is the diffusion coefficient for the gas pair used. Since the FID output signal is directly proportional to the tracer flow, a plot of log (signal) against time should be linear. Experimentally (e.g. Fig. 4), there was a very sharp initial drop for a few seconds, which can be attributed to the dead-volume of the sample holder (since a solid block sample gives the same initial curve) and following this initial disturbance, the elution was linear for over 200 min and several decades of concentration, in exact agreement with the prediction. Use of the estimated geometry gave $D_{12} = 0.186\,\text{cm}^2\,\text{sec}^{-1}$ for methane/nitrogen and

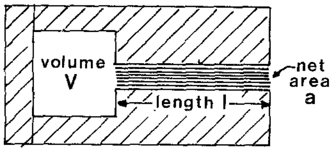

Figure 3 Artificial restricted-access pore (RAP); typically $V = 4.8\,\text{cm}^3$, $l = 2.5$ cm and a (net) $= 0.047\,\text{cm}^2$.

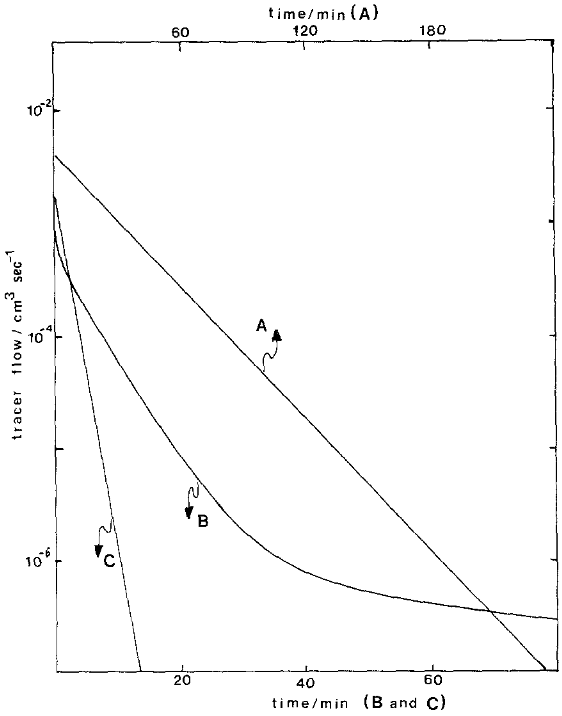

Figure 4 Typical experimental results for (A) an artificial RAP, and (B) a nuclear reactor graphite, and (C) theoretical curve for uniform capillary pores having same λ as the graphite.

0.146 cm^2 sec^{-1} for methane/carbon dioxide at 293 K, compared with the accepted values of 0.208 cm^2 sec^{-1} [8], and 0.167 cm^2 sec^{-1} [9], respectively. These results are in extremely good agreement considering the uncertainty in estimating the neck area a, and could well be used to "calibrate" the system as a means of determining unknown diffusion coefficients.

A more sophisticated theoretical treatment of the diffusion is currently under consideration. This uses finite element methods, and avoids assumptions (a) and (b) above. Preliminary results indicate that the diffusion flow is still exponential, after a short initial deviation, but that the geometric factor in the time-constant is slightly different from that of the simple theory above.

3.2. Nuclear reactor graphites

Fig. 4 also shows a typical elution curve for a nuclear reactor moderator graphite. As before, the dead volume of the sample holder is emptied in an initial burst, then diffusion of the tracer from the graphite continues over an extended period. To interpret this sort of curve fully it is necessary to have a theory of the diffusion in the material, and work is currently proceeding on the development of such an interpretation. However, some qualitative conclusions can be drawn. The transient diffusion equation for uniform capillaries can be solved analytically [10], and hence the elution curve can be predicted for a material having the known diffusivity of the graphite in question. Such a curve is shown in Fig. 4, and it is immediately evident that the graphite has a considerable restricted-access pore volume giving rise to the long tail of the elution curve. This feature occurs with all the graphites we have measured, and since the tail is approximately linear on the log plot it can be described approximately by an exponential function. The relevant time-constant is typically of the order of 50 min, and this implies a dead-end pore space of markedly RAP geometry.

Theoretical modelling of systems of RAPs connected to a TP network is being investigated by means of:

(a) infinite series solution of the differential equations for a system with one RAP size, based on Goodknight and co-workers [5, 6];

(b) finite difference integration for a system with more than one RAP size;

(c) finite element solutions for systems of more complex geometry.

Experimental work with a variety of virgin and oxidized reactor graphites will be reported elsewhere, and the technique is currently being applied to a range of other porous materials.

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