PRESSURE DROP ACROSS PACKED BEDS OF POROUS SOLIDS

by

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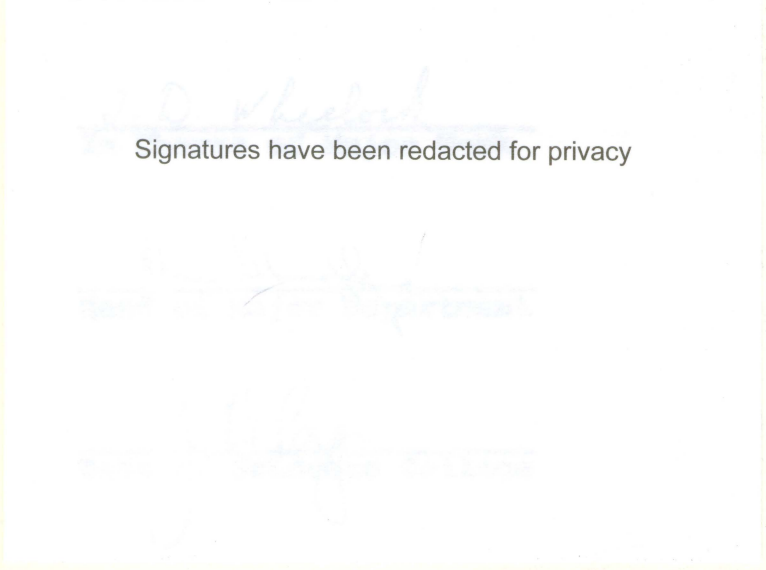

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NOMENCLATURE

Units are in the English system unless otherwise indicated.

A,B	Terms in Furnas' fluid-flow equation
A_c	Cross-sectional area of the empty column
d	Nominal particle diameter
d_e	Diameter of an equivalent capillary channel (if other than circular)
d_p	Particle diameter as determined by the arithmetic average between two successive standard screen openings, mm.
D_p	Effective particle diameter = $6/S_v$
D_s	Diameter of a sphere with the same volume as the particle
D	Column diameter, mm.
F_f	Friction-factor factor as proposed by Brown (2, p. 211)
F_m	Mean volumetric flow rate, evaluated at average column conditions
F_{Re}	Reynolds number factor as proposed by Brown (2, p. 211)
g_c	Conversion factor = 32 (lb. mass)(ft.)/(lb. force)(sec.)(sec.)
G	Mass velocity = $\rho_G U$
k	= 5. A constant in the Kozeny-type flow equations

k_1 = 150. A constant in the Ergun equation

k_2 = 1.75. A constant in the Ergun equation

K Permeability, (cu. ft.)(sec.)/(lb. mass)

K' Specific permeability = $K\mu$, sq. ft.

L Height to which bed is packed

L_e Actual length of flow path

M Packing factor = $\frac{g_c d_p^2 U_m \Delta P}{150 \mu L}$

n The ratio of the specific surface area of a particle to the specific surface area of a sphere with the same diameter as the particle

P Pressure

P_o Outlet pressure

P_i Inlet pressure

$\bar{P}$ Average column pressure, computed by method of Keulmans (22, p. 144). See Appendix B.

R Multiple correlation coefficient

S Substrate level, gm. substrate per 100 gm. uncoated brick

S_v Specific surface, surface of solids per unit volume of solids. (This does not include the void space between individual particles)

T Tortuosity = L_e/L

U Superficial linear velocity based on cross-sectional area of empty column

U_m Mean superficial linear velocity evaluated at average column temperature and pressure, based on cross-sectional area of empty column

V_o Volume of gas emerging from outlet per unit time

W Wall effect factor

Δp Pressure drop

ϵ Fractional void volume

μ Fluid viscosity

ρ_B Bulk density of bed, based on uncoated particles, (gm.)/(cu. cm.)

ρ_G Fluid density

ρ_p Particle density

ϕ Particle shape factor. The ratio of the surface area of a sphere having the same volume as the particle to the surface area of the particle

ABSTRACT

The pressure drop resulting from the flow of gas through columns packed with particles of porous insulating firebrick, coated with dibutyl phthalate was measured in the laminar flow range. When tested with helium, nitrogen, hydrogen, and n-butane, Ergun's fluid flow equation was found to correlate adequately the gas density, viscosity and flow rate.

A packing factor M was defined to account for the bed properties such as porosity, particle shape, and amount of dibutyl phthalate. This factor was found to be a function of the column diameter, particle diameter, bulk density of the packing, and the mass ratio of dibutyl phthalate to dry brick. The following empirical equation was fitted to the data:

$$M = -24.74 + 65.44\,\rho_B - 14.76\,d_p + 0.5188\,D - 0.001093\,S^2 + 346.9\,\frac{d_p^2}{D} + 328.3\,\frac{\rho_B d_p}{D} - 1480\,\frac{d_p^2}{D^2} + 1.141\,\frac{S d_p}{D}\,.$$

By means of this equation it is possible to predict M, which in turn can be used with the following modification of Ergun's equation to predict the pressure drop in packed beds:

$$\frac{\Delta P}{L}\,g_c = \frac{150\,\mu U_m M}{d_p^2}\,.$$

INTRODUCTION

The purpose of this project was to determine the gas flow and pressure drop characteristics for the laminar flow range of packed beds of porous solids which are coated with a liquid substrate. Beds of this nature are commonly found in gas chromatography columns where the liquid substrate serves as a partitioning agent. The information obtained in this investigation should find application in the analysis of such devices. A discussion of gas chromatography and some of its applications, including those in the nuclear field, is given in Appendix A.

Fluid flow through porous beds has been well studied. In spite of the abundance of written material on the subject, there are apparently no two investigators that agree completely on what formulas or plots should be used to predict the value of the energy loss or pressure drop.

Variables that affect the pressure drop across packed beds may be classed into two categories:

I. Variables related to the fluid passing through the bed
    1. Velocity
    2. Density
    3. Viscosity

II. Variables related to the bed
    1. Bed voidage

2. Particle orientation
3. Particle shape
4. Particle size
5. Column diameter
6. Particle surface roughness

In this investigation, an additional variable, the liquid substrate level, was also considered.

A search of the literature yielded a flow equation that seemed to give consistent and reliable results. This was the Kozeny-type flow equation enunciated by Ergun (15), who tested it with beds of spheres, cylinders, tablets, nodules, round sand and crushed material such as glass, coal, coke, etc., and found the equation to be valid. The equation is as follows:

$$\frac{\Delta P}{L} g_c = 150 \frac{(1-\epsilon)^2}{\epsilon^3} \frac{\mu U_m}{D_p^2} + 1.75 \frac{1-\epsilon}{\epsilon^3} \frac{G U_m}{D_p}$$

The first term on the right hand of the Ergun equation accounts for the viscous energy losses and the second term accounts for the kinetic energy losses. Since this investigation was restricted to the laminar range, only the first term was considered. After omitting the second term, making several substitutions and rearranging (see Appendix B), the Ergun equation takes the following form:

$$\frac{g_c d_p^2 A_c \Delta P}{150 \mu F_m L} = \frac{(1-\epsilon)^2 n^2}{\epsilon^3}$$

The left hand side of this equation is composed of parameters which can be measured easily while the right hand side contains parameters which are difficult to measure accurately. Moreover, since relatively large powers of specific surface ratio and porosity are involved, small inaccuracies in these parameters can produce large errors in the prediction of pressure drop. In view of this difficulty it was decided to replace the right hand side of the above expression with a single parameter M which will be called the packing factor in this report. The packing factor could not be measured directly but was computed from the values of the parameters which appeared in the left hand side of the equation. The packing factor is thus defined as

$$M = \frac{g_c\, d_p^2\, A_c\, \Delta P}{150\, \mu\, F_m\, L} = \frac{g_c\, d_p^2\, \Delta P}{150\, \mu\, U_m\, L}$$

If it can be assumed that the right hand side of the rearranged Ergun equation will account for the effect of liquid substrate as well as bed porosity, particle shape, surface roughness, etc., then M will also be related to the porosity and specific surface ratio as follows:

$$M = \frac{(1-\epsilon)^2 n^2}{\epsilon^3}$$

Confirmation of this assumption was considered beyond the scope of this study.

This investigation was conducted in two phases. Phase

one consisted of testing the Ergun equation to determine whether or not it correlated the properties of the fluid, and phase two was undertaken to relate M to readily measured packing parameters. In connection with phase two, the following variables were investigated:

1. Column diameter
2. Particle size
3. Bulk density of the packing
4. Liquid substrate level

LITERATURE REVIEW

The theory of laminar flow through porous beds was based on a set of experiments by D'Arcy (11) in 1856. He found that the rate of flow through a sand bed was proportional to the pressure gradient across it. The equation was of the form

$$U = K \frac{\Delta P}{L}$$

An excellent modern-day discussion of D'Arcy's law may be found in an article by Hubbert (21).

The empirical equation of D'Arcy is closely analogous to one derived by Poiseuille (37) for the flow of a viscous liquid through a circular capillary. If Poiseuille's law is written in comparable form, one may see that it is the equivalent of D'Arcy's law for capillaries, modified to include viscosity. Poiseuille's equation is

$$U = \left(\frac{d_e^2}{32\mu}\right)\left(\frac{g_c \Delta P}{L}\right)$$

Although Poiseuille's law was originally empirical, it was eventually derived from the definition of viscosity. D'Arcy's law, on the other hand, does not lend itself to derivation from first principles.

The first extension of D'Arcy's law was proposed by Dupuit (13). He realized that the apparent velocity must be less than the actual or interstitial velocity within the pores

of the bed. By assuming that the fractional free area of a bed is constant for any given cross section normal to the flow, the fractional free area becomes equal to the fractional free volume. Following this line of reasoning, D'Arcy's equation could be written in the following manner:

$$\frac{U}{\epsilon} = K \left(\frac{d_e^2}{\mu}\right)\left(\frac{\Delta P}{L}\right)$$

Blake (1) was the first to use the dimensional analysis approach on packed beds. He obtained dimensionless groups that were analogous to those commonly used in fluid flow through conduits. His first attempt was to plot

$$\frac{d_p \rho_G \Delta P}{L G^2} \quad \text{versus} \quad \frac{d_p G}{\mu}$$

For particles of different diameter, however, the points fell on different lines. Realizing that the diameter was not an adequate parameter with which to describe the particles, he used the assumptions of Dupuit to arrive at different functions of the velocity and the particle diameter. He assumed that the velocity in the pore space was inversely proportional to the porosity of the bed, and that the effective path diameter was proportional to the void volume per unit surface area. After substituting G/ϵ for G and ϵ/S_v for d_p, his points were drawn sufficiently close together to support a generalization. His plot of

$$\frac{\rho_G \Delta P \epsilon^3}{LG^2 S_v} \text{ versus } \frac{G}{S_v \mu}$$

was the first attempt at a friction factor versus Reynolds-number type plot for packed beds. For viscous flow, following the form of the D'Arcy equation, Blake presented the equation,

$$k = \frac{\Delta P g_c \epsilon^3}{LU\mu S_v}$$

where k is generally known as Kozeny's constant. It is a constant in the general law of streamline motion through granular beds. This equation was developed independently and almost simultaneously by Kozeny (26) and Fair and Hatch (16).

By using the same assumptions as Blake and adding a shape factor, Kozeny (26) derived an equation similar to that of Blake. Permeability or specific surface determinations based on fluid flow measurements owe their widespread use to the Kozeny-type equation.

Since the Kozeny equation was derived from D'Arcy's law, it is subject to the limitations of D'Arcy's law. The most important limitation is that it is invalid for

$$\frac{\rho_G U}{\mu S_v} > 2.$$

In this flow region the pressure drop increases more quickly than the flow rate.

Burke and Plummer (4) tried to lend theoretical credence

to the equation of Blake by an entirely different approach. Instead of assuming that the bed was composed of a group of parallel channels, they regarded the total resistance of the bed to fluid flow as the sum of the separate resistances of the particles as measured from their rate of free fall. They proposed a variable which was a function of porosity. This variable was $(1-\epsilon)^a/\epsilon^b$, which represents the simplest exponential function which would fulfill the requirement that the pressure drop approach infinity for a void fraction of zero and the pressure drop goes to zero for a void fraction of one. The viscous energy loss was found to be proportional to $(1-\epsilon)/\epsilon^2$ and the kinetic loss proportional to $(1-\epsilon)/\epsilon^3$. The equation they developed for the laminar flow range was

$$\frac{\Delta P}{L} = k \left[\frac{\rho_G U^2 S_V}{\epsilon^3}\right] \left[\frac{\mu S_V \epsilon}{\rho_G U(1-\epsilon)}\right]$$

Burke and Plummer suggested that the uncertainty in the literature data might be caused by the uncertainty in the determination of ϵ. Since ϵ enters into the factor to the third power, even small errors in ϵ will lead to disproportionately large errors in the dependent factors.

Although Furnas (17) contributed important information to the field of fluid flow, his method of correlation has been questioned by several later workers (4, 7). His equation was

$$\frac{\rho_G \Delta P}{L} = A G^B$$

where A and B are complex functions of particle size, temperature, void fraction, density, viscosity, and molecular weight. Chilton and Colburn (7) pointed out that Furnas' data was partly in the viscous region and partly in the turbulent region. This means that his equation applied only to the particular conditions under which his experiments were run and complexity of the functions of A and B was caused by the changing state of flow.

Furnas' most important contribution was the introduction of the wall effect factor. From photographs of bed cross sections, he noticed that the porosity next to the container wall was higher than for the rest of the bed. He reasoned that this should result in a higher flow rate near the wall and thus, a lower over-all pressure drop than would be obtained from an unbounded bed of the same packing material. For this reason, the wall effect factor is a function of the ratio of the column diameter to the particle diameter. His mathematical treatment of the wall effect factor was from geometrical considerations and from imagining a cylinder being pressed into an infinite bed of particles with the simultaneous removal of the particles intercepted by the downward movement of the wall. Furnas observed that for ratios of D/d_p of more than 50, the correction needed for the wall effect was insignificant.

Saunders and Ford (41) verified Furnas' idea of a higher

porosity next to the container wall by using a pitot tube to investigate the velocity profile across the exit surface of a packed bed. They found the velocity constant except for a ring of about one particle diameter from the wall. The velocity in this region was approximately 50% higher than for the rest of the bed.

Chilton and Colburn (7) carried out their experiments on a variety of pellets. Their resultant equation for laminar flow was:

$$\frac{\Delta P}{L} = 53 \frac{\mu U W}{D_s^2 g_c}$$

Because of the difficulty in evaluating some of the factors, they correlated their data and the data of some earlier investigators with a friction factor versus Reynolds number curve. The curve obtained was similar in shape to the familiar friction factor versus Reynolds number plots for fluid flow in pipes.

Fair and Hatch (16) developed an equation similar to that of Kozeny and Blake. Their equation was:

$$U = \left(\frac{k\epsilon^3}{T\mu\ S_v^2}\right)\left(\frac{\partial P}{\partial L}\right)$$

Once again difficulty arose in determining the parameters. In general, equations of this type where the permeability is related to the inverse square of the surface are called Kozeny equations.

Carman (6) provided another substantiation of Kozeny's equation. He noticed that at low flow rates the method of Blake led to Kozeny's equation and at high flow rates, the method of Burke and Plummer led to Kozeny's equation. For the laminar flow range he obtained

$$\frac{\Delta P}{L} g_c = k_1 \left[\frac{(1-\epsilon)^2}{\epsilon^3}\right]\left[\frac{\mu U}{D_p^2}\right]$$

and for the turbulent flow range

$$\frac{\Delta P}{L} g_c = k_2 \left[\frac{(1-\epsilon)}{\epsilon^3}\right]\left[\frac{\rho_G U^2}{D_p^2}\right]$$

Finding trouble with the evaluation of the surface area, Carman used particle diameter in connection with a shape factor that was defined to equal one for spheres. His final equation was

$$\frac{\Delta P}{L} g_c = 180 \left[\frac{\mu(1-\epsilon)^2 U}{\epsilon^3 \phi^2 D_p^2}\right]$$

Later, Carman (5) developed a method for the determination of particle surface area. He did not test his method for particles smaller than 1 mm. This equation was

$$S_v = 14\sqrt{\left[\frac{1}{k\mu}\right]\left[\frac{\epsilon^3}{(1-\epsilon)^2}\right]}$$

Lea and Nurse (27) used the method of Carman to find the specific surface of cement. They used gases rather than liquids. In doing this, they assumed that the Kozeny constant

was constant. Later they concluded that k actually varied with porosity (28).

Oman and Watson (34) made an attempt at standardizing methods of packing in order to achieve reproducible porosity. They also refined the equation of Blake by solving for a different exponent of porosity in the friction factor term. Their work was conducted mostly in the turbulent range.

Rose (38, 39, 40) in a series of papers published in 1945 thought that most of the data of previous workers could be correlated by various extensions of Carman's equation in the form:

$$S_v = \sqrt{\left[\frac{g}{5kU}\right]\left[\frac{\epsilon^3}{(1-\epsilon)^2}\right]}$$

He also derived a wall effect factor that was somewhat different from that of Furnas.

Martin, et al. (31), studied the orientation effects of ten different geometrical arrangements of steel balls. They concluded that orientation has a very definite effect and probably accounts for some of the discrepancies in the results of different investigators. In other words, the variation in pressure drop when the particle size, shape factor, and porosity are constant, may be attributable to differences in particle orientation.

Coulson (9) thought that the preponderance of data on spherical particles had tended to obscure the importance of

the shape factor. Consequently, he used beds packed with plastic blocks and prisms. Coulson included a plot of Kozeny's constant as a function of the voids for different values of shape.

The correlations of Brown, et al. (2), depend upon a number of charts which describe Reynolds-number factors and friction-factor factors as functions of porosity, shape, and particle size. Depending on charts rather than the appropriate formulas could lead to considerable inaccuracy.

The work of Ergun (14, 15) represented a considerable advance in the field of fluid flow through porous media. Until this time, most of the investigators proposed two equations. One of the equations was to be used for the viscous range and another equation was to be used for the turbulent range. Ergun suggested that the resistance to fluid flow was the sum of the viscous and kinetic energy losses. Therefore, an equation of the form

$$\frac{\Delta P}{L U_m} = a + bG$$

where

a = viscous coefficient = $k_1 \mu S_v^2 (1-\epsilon)^2/\epsilon^3$

b = kinetic coefficient = $k_2 S_v (1-\epsilon)/\epsilon^3$

would apply to both the laminar and turbulent flow ranges. The equation was examined from the point of view of its dependency on the fluid properties and the bed properties such

as void volume, orientation, surface roughness, etc. So far as was possible, conditions were chosen so the effect of one variable at a time could be considered. Ergun (14) used this correlation along with

$$\epsilon = 1 - \frac{\rho_B}{\rho_p}$$

to determine experimentally particle density and surface area. The particle density and surface area so determined would be the parameters of most interest in fluid flow equations. The determination is particularly valuable when dealing with internally porous material because particle density and particle surface are difficult to define.

Leva (29, 30) proposed the following equation:

$$\frac{\Delta P}{L} g_c = 200\left[\frac{G_L}{D_p^2 \rho_G \phi^2}\right]\left[\frac{(1-\epsilon)^2}{\epsilon^3}\right]$$

He included no term for wall effect in his equation because he felt that it was taken into consideration in the porosity function as the average porosity.

Wagstaff and Nirmaier (44) studied the correlations of Carman, Chilton and Colburn, Leva, Ergun and Brown. They found that the best proposals were those of Leva and Ergun. Of these two, Ergun's work was found to be the most consistently reliable. They noticed that the k_1 and k_2 of the Ergun equation varied slightly with bulk density.

Using data of previous investigators on beds packed with nickel saddles and lead shot, Schriver (42) found that the constant, k_1 increased with increasing porosity. For very high porosities, on the order of 0.8, he found that the constant should be around 600 rather than 150.

Summary

The flow of a fluid through a bed of porous material has been investigated by a large number of workers. In general, the trend has been to reduce the variables down to a friction factor. This friction factor is then related to Reynolds number by means of a plot. The friction factor and the Reynolds number are both modified to include terms for bed porosity and particle shape.

Most of the work in the field has been of an empirical or semi-empirical nature. The reason for this is that the actual structure of the pores is a complicated, intertwining network of passageways of continually varying cross section and is practically impossible to describe rigorously in a mathematical form.

The physical model most commonly used has been one of a bundle of capillaries of constant radius. Usually, the particle diameter is considered an estimate of the capillary diameter. If the particle deviates from a sphere, a shape factor is usually incorporated.

The major difficulty has been in accurately determining

the parameters of particle size, particle shape, porosity, orientation, and surface roughness. A study of the experimentally determined relationships indicates considerable discrepancies among the results of different experimenters. This problem of the ill-defined shape, orientation and void fraction parameters could possibly account for these discrepancies.

The Kozeny-type equation as presented by Ergun seems to be the most reliable and consistent. This is particularly true if the bed packing is composed of internally porous material. The largest source of error encountered in the use of the Ergun equation is the variation of k_1 with porosity.

EXPERIMENTAL INVESTIGATION

Apparatus and Materials

A flowsheet of the apparatus is shown in Figure 1. The gas from the storage cylinder passed through two flow regulating valves and through a drying column containing "Drierite". The gas then passed through the pressure drop measuring column and through a soap-film meter flow-measuring device and was then vented to the atmosphere. The three mercury manometers were arranged in such a manner that the inlet pressure, outlet pressure, and pressure drop across the column could be measured simultaneously.

Columns for measuring pressure drop

The columns were fabricated from borosilicate glass tubing and were approximately 135 cm. long. The four columns primarily used were of the following inside diameters: 3.39 mm., 5.1 mm., 8.33 mm., and 10.14 mm. Two additional columns were used in connection with the factorial design experiment. They had inside diameters of 4.88 mm. and 11.79 mm. Since the inside diameter of a column was not entirely uniform, an average diameter based on the average cross-sectional area obtained by filling the columns to a known height with a known volume of water was used in correlating the results.

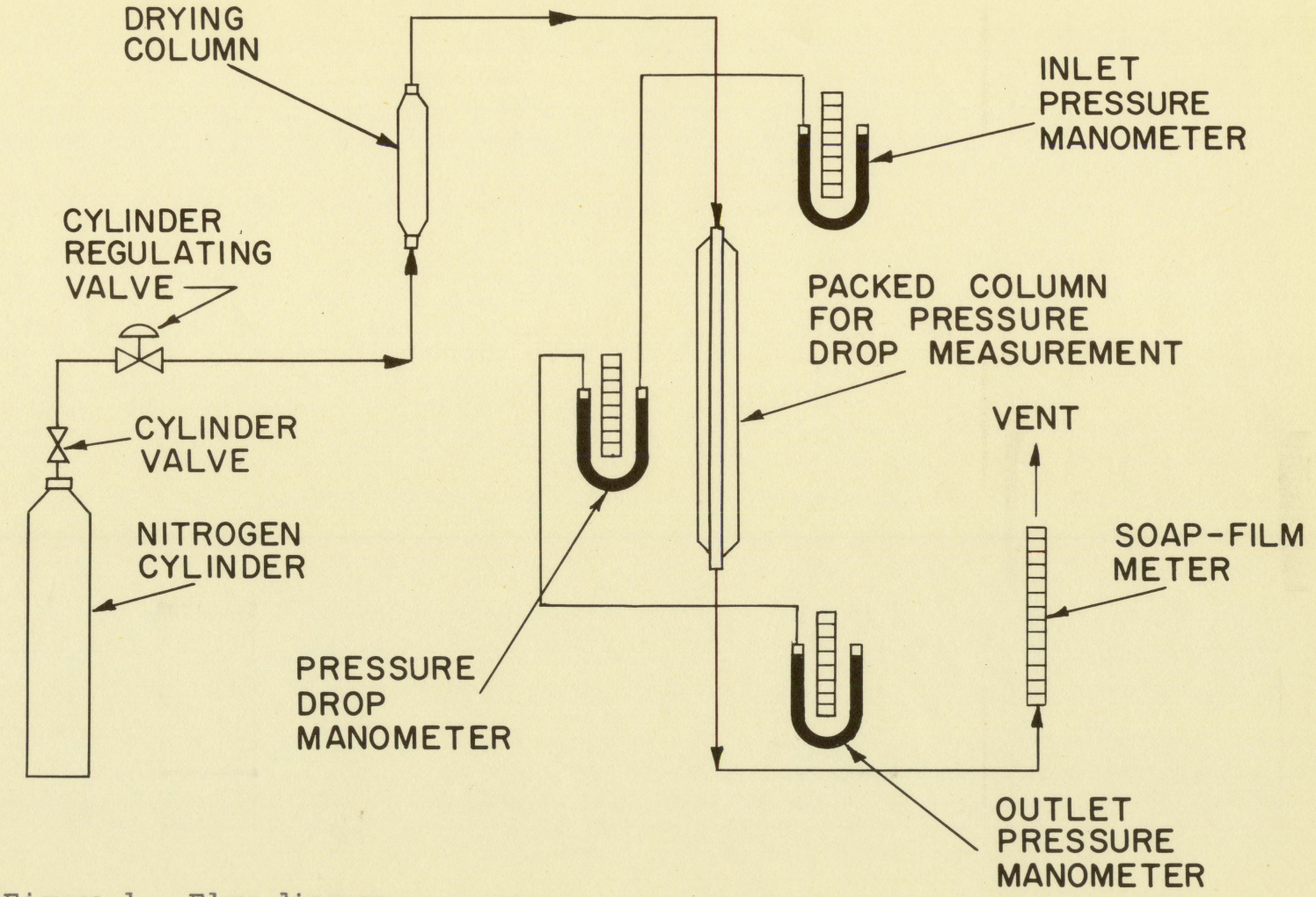


Figure 1. Flow diagram

Packing

The packing was crushed and sized Johns-Manville Type C-22 firebrick coated with varying amounts of dibutyl phthalate. The firebrick was crushed and screened to the proper size and washed with dilute hydrochloric acid to remove any metallic impurities and fines that might be present. It was then washed with water to remove the acid and dried in an oven for ten hours at 130°C.

The liquid substrate was dissolved in diethyl ether and added slowly to the proper amount of firebrick with complete mixing. The wet packing was then spread in a thin layer and allowed to air dry. The evaporation of the diethyl ether left each particle coated with a thin layer of the partitioning agent. Additional screening was then required to remove the fines that were produced during the mixing process. The levels of substrate used varied from 0 to 50.0 grams of dibutyl phthalate per 100 grams of dry brick.

Since the columns were packed on the basis of grams of dry brick per cubic centimeter of bed volume, it was necessary to determine exactly how much substrate was present. This was done by firing a sample of the coated brick in an oven at 685°C. for two hours. During this time the dibutyl phthalate was completely oxidized. By weighing the sample before and after firing, the exact amount of substrate could be determined.

The particle diameters were based on an arithmetic average of the openings of two successive Tyler standard mesh screens. The Tyler screen fractions and average particle diameters used were -28+48 (0.442 mm.), -48+65 (0.2515 mm.), -65+100 (0.1775 mm.), -100+150 (0.1255 mm.) and -150+200 (0.089 mm.). The columns were packed by introducing a weighed amount of packing into the column and vibrating it down to a predetermined height. The packing was supported in the column by glass wool plugs.

Flow measurement

A soap-film meter was employed to measure the gas flow. The principal component of this device was a burette in which the rate of travel of a soap film was timed as it proceeded up the tube. This type of flow meter was used because of its accuracy in the low flow range. Keulmans (22, p. 59) states that the errors in flow measurements by this method are less than 1% over a wide range of flow rates. The flow rates measured in this manner were for outlet conditions and had to be corrected for the temperature and average pressure prevailing in the column. Since saturation in the soap-film meter was almost complete, a correction for the vapor pressure of water also had to be applied.

Gases used

Nitrogen, having a minimum purity of 99.7 mole per cent (Air Reduction Co., Inc., New York, N.Y.) was employed as the

fluid flowing through the column for the majority of the measurements. Earlier in the investigation, three additional gases were used. They were hydrogen with a minimum purity of 99.8 mole per cent (The Matheson Company, Joliet, Ill.), helium with a minimum purity of 99.99 mole per cent (The Matheson Company), and normal butane with a minimum purity of 99.5 per cent (The Matheson Company).

Procedure

A column was packed to a height of 50.0 inches with particles of known size and substrate content to a predetermined bulk density using an electric vibrator.

After the column was connected into the system and the gas flow established, approximately five minutes were allowed for the system to come to equilibrium and for the manometers to settle out. Then, the pressure drop at two different flow rates was measured. The packing factor reported for a particular run was the average of the packing factors calculated from the Ergun equation at these two different flow rates. It was previously determined that pressure drop across the system, exclusive of the packing, was negligible for the flow rates used; therefore, no blank run was needed for a correction.

The parameters recorded for each run were: pressure drop, flow rate, bulk density, particle size, column diameter, substrate level and temperature. All of the experimental runs were made at room temperature which varied approximately

between 26°C and 32°C.

Results

This investigation was conducted in two phases. The first phase was to test the Ergun equation to see whether or not it adequately accounted for changes in the gas density, gas viscosity and gas flow rate. The second phase was to determine the effects of column diameter, particle size, bulk packing density and liquid substrate level on the packing factor.

Phase two of the experimental work could not be carried out by the classical method of varying one of the parameters while holding the remainder constant because of the strong interactions between the variables. This problem of interactions was circumvented by making a multiple regression analysis on the data with the aid of an IBM 650 digital computer. This analysis led to a prediction equation.

A completely randomized 2x2x2x3 factorial experiment was used as a guide in selecting the terms to be included in the mathematical model of the prediction equation.

Testing the Ergun equation

The 5.1 mm. column was packed with -48+65 standard Tyler mesh size particles coated with 0.35 parts of dibutyl phthalate to firebrick to a bulk density, based on uncoated firebrick, of 0.425 gm./cc. The height of the packing was

50.0 inches. Hydrogen, helium, nitrogen and n-butane were passed through the bed in succession. The pressure drop was measured at several different flow rates. When the pressure drop was plotted versus 150 $L\mu F_m/g_c\, d_p^2\, A_c$, a straight line intersecting the origin was obtained (Figure 2). The slope of this line, which is identically equal to M, was essentially constant for all four gases (Table 1). The measured

Table 1. Effect of gas density and viscosity

Gas	Gas density[a] (gm./cc.) x10^4	Gas viscosity[a] (centipoise)	M
He	1.60	0.01995	12.02
H_2	0.824	0.00891	11.92
N_2	11.58	0.01768	12.12
n-C_4	23.9	0.01109	12.17

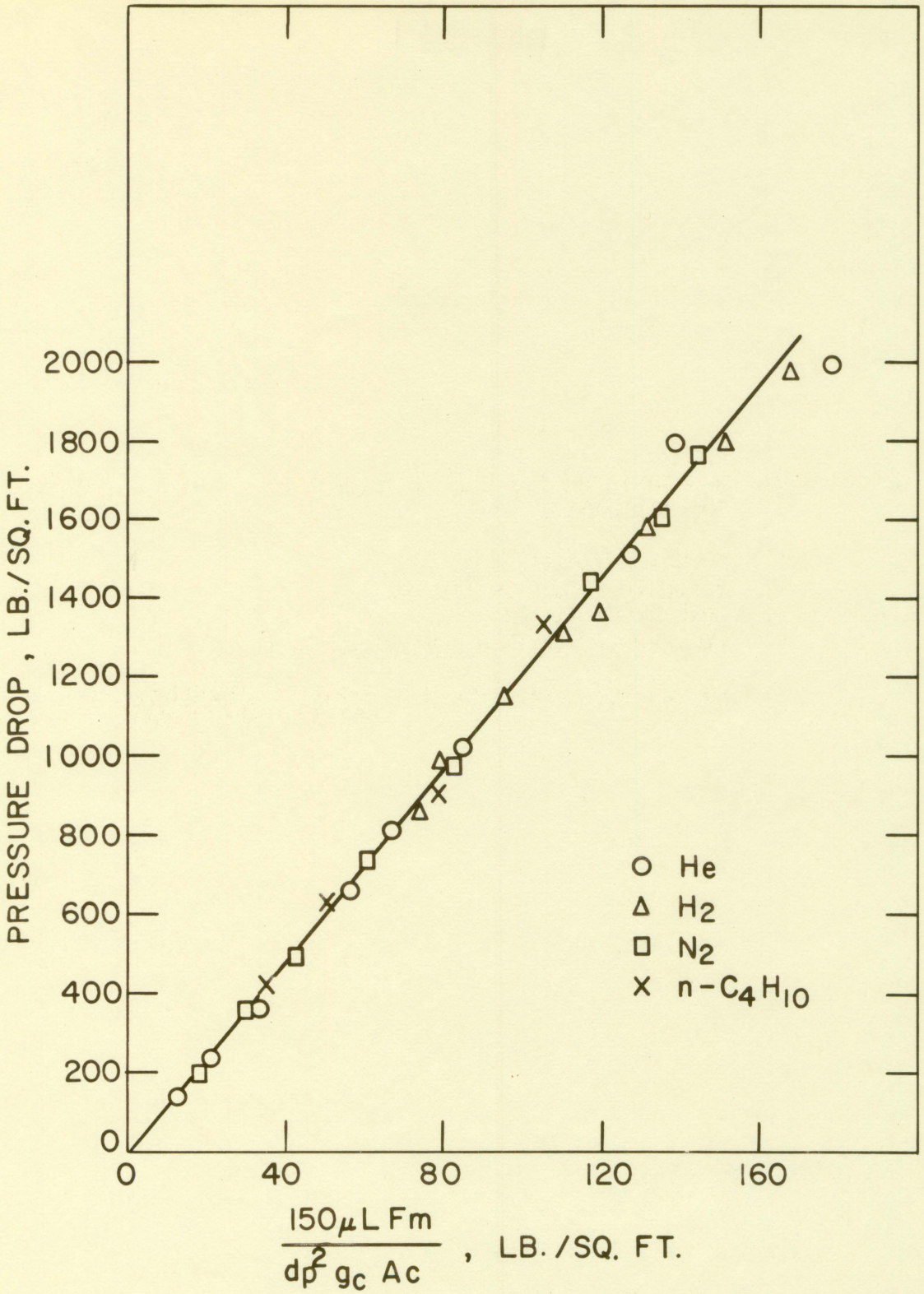
[a]At average column temperature and pressure for run.

packing factors for hydrogen and n-butane differed only by 2% while the other values of M differed even less. If the Ergun equation correctly correlates the fluid viscosity, density and flow rate with the pressure drop, then the value of the packing factor, which is a function of the bed properties alone, should remain constant. Since the observed packing factors appeared to be independent of gas properties and flow rate,

Figure 2. Pressure drop as a function of flow rate for various gases

height of bed = 50 in.
particle size = 0.2515 mm.
column diameter = 5.1 mm.
bulk density = 0.425 gm./cc.

substrate level = 35 $\frac{\text{gm. substrate}}{\text{100 gm. dry brick}}$


PRESSURE DROP, LB./SQ.FT.
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
40
80
120
160
$\frac{150\mu L\,Fm}{dp^2 g_c\,Ac}$, LB./SQ. FT.
O He
Δ H_2
□ N_2
X $n-C_4H_{10}$

the Ergun equation seems satisfactory for correlating the fluid parameters.

Factorial experiment

The decision to use a completely randomized factorial experiment was based on some preliminary data that indicated strong interactions between several of the variables. For example, in Figure 3 it may be seen that the response of the packing factor to varying particle size is different for different column diameters. In the words of Ostle (35, p. 345),

> "Interaction is the differential response to one factor in combination with varying levels of a second factor applied simultaneously; that is, the two factors combine to produce an added effect not due to one of them alone."

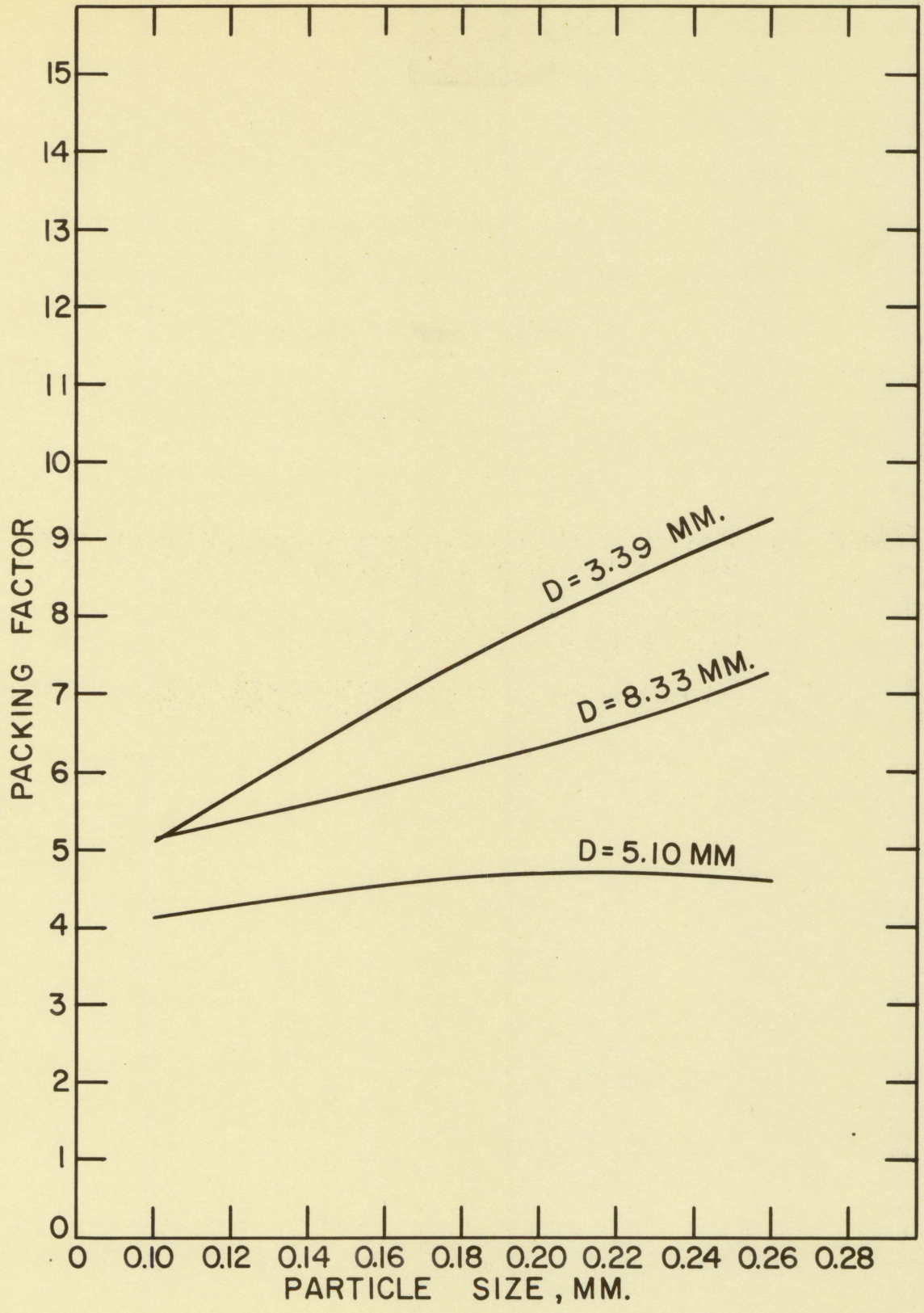
The treatments in a factorial experiment include all possible combinations of predetermined levels of the different variables to be tested. By means of an analysis of variance the results of a factorial experiment may be analyzed in such a manner as to reveal both the individual effects and the interactions among the parameters.

The experiment was designed to contain two levels of particle size, two levels of bulk density, three levels of liquid substrate, and two levels of the ratio of column to particle diameter. The ratio of column to particle diameter was used as a variable rather than the column diameter because

Figure 3. Variation of packing factor with particle size for various column diameters

height of bed = 50 in.
bulk density = 0.400 gm./cc.

substrate level = 35 $\frac{\text{gm. substrate}}{\text{100 gm. dry brick}}$


PACKING FACTOR
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
D = 3.39 MM.
D = 8.33 MM.
D = 5.10 MM
0
0.10
0.12
0.14
0.16
0.18
0.20
0.22
0.24
0.26
0.28
PARTICLE SIZE, MM.

it was felt that the column diameter by itself would not affect the value of M. There may be some question as to the use of the diameter ratio because it is not independent of particle diameter; however, there is precedent in the literature for the inclusion of such a factor. The wall-effect factors of Furnas (17), Carman (5), and Rose (38) are functions of this ratio. In order to achieve a factorial design with respect to this variable, four different column diameters were actually employed. (Later it was shown that column diameter exerts an independent effect upon M so the factorial experiment was not completely valid.)

The inclusion of all possible combinations of the above described levels of the four variables, required twenty-four runs. Two observations were made on each of the treatment combinations, bringing the total number of runs to forty-eight. The forty-eight experimental runs were completely randomized by the use of a table of random numbers.

The treatment combinations and the value of M (average of two observations) are given in Table 2. Table 3 shows the levels at which the experiment was run. The coding system used is interpreted as follows:

-1 Low level of variable

0 Medium level of variable

+1 High level of variable

The results of the analysis of variance, made as outlined

Table 2. Treatment combinations and average values of M in the factorial experiment

ρ	$\frac{d_p}{D}$	d_p	S	M avg.
+1	+1	+1	-1	8.18
+1	+1	+1	0	9.90
+1	+1	+1	+1	8.96
+1	+1	-1	-1	6.86
+1	+1	-1	0	8.12
+1	+1	-1	+1	6.74
+1	-1	+1	-1	7.39
+1	-1	+1	0	7.68
+1	-1	+1	+1	7.26
+1	-1	-1	-1	6.70
+1	-1	-1	0	7.68
+1	-1	-1	+1	6.68
-1	+1	+1	-1	6.24
-1	+1	+1	0	6.38
-1	+1	+1	+1	5.48
-1	+1	-1	-1	4.36
-1	+1	-1	0	4.08
-1	+1	-1	+1	5.03
-1	-1	+1	-1	5.40
-1	-1	+1	0	5.30
-1	-1	+1	+1	5.13
-1	-1	-1	-1	4.54

Table 3. Levels of variables used in the factorial experiment

Code	ρ (gm./cc.)	$\frac{d_p}{D}$	d_p mm.	S gm. substrate / 100 gm. dry brick
-1	0.375	0.02132	0.1775	0
0				20
+1	0.400	0.05238	0.2515	35

in Ostle (35, Chapts. 9 and 11), are given in Table 4. The mean square for each category, which is the corresponding sum of squares divided by the appropriate degrees of freedom, is an estimate of the variance. The F test is a statistical method for comparing the means of several samples. The F ratio is formed by dividing the mean square of a particular category by the error mean square. To invoke an F test, one begins with the hypothesis that there is no significant difference between the means to be compared. It is used to determine whether or not the variance due to a particular classification exists; that is, whether the means are significantly different from those that could be expected from chance alone. If the F, calculated from the data, exceeds the value given in a table of the F distribution (35, p. 454) at the 0.01 level, the hypothesis of no significant difference between the means is rejected and it may be concluded that the variances are significantly different. This conclusion will be wrong only 1.0% of the time.

To make this explanation clearer, perhaps an example would be in order. The sum of squares of the bulk packing density is 75.60 (Table 4). Dividing this figure by one degree of freedom gives a mean square of 75.60. To form the F ratio, the mean square for this category (75.60) is divided by the error mean square (0.044). This operation yields an F ratio of 1718. This number is compared with the F distribution

Table 4. Analysis of variance for the factorial experiment

Source of variance	Degrees of freedom	Sum of squares	Mean square	Calculated F
ρ_B	1	75.60	75.60	1718[a]
$\frac{d_p}{D}$	1	4.58	4.58	103[a]
d_p	1	12.67	12.67	291[a]
S	2	3.51	1.76	39.4[a]
$\frac{\rho_B d_p}{D}$	1	0.73	0.78	17.52[a]
$\rho_B d_p$	1	0.028	0.023	0.63
$\rho_B S$	2	1.95	0.98	21.4[a]
$\frac{d_p^2}{D}$	1	3.40	3.40	75.5[a]
$\frac{Sd_p}{D}$	2	0.45	0.22	5.06
Sd_p	2	0.13	0.065	1.46
$\frac{\rho_B d_p^2}{D}$	1	0.22	0.22	4.95
$\frac{\rho_B d_p S}{D}$	2	0.31	0.16	3.48
$\frac{d_p^2 S}{D}$	2	nil	nil	nil
$\rho_B d_p S$	2	1.17	0.57	12.79[a]

[a]Significant at the 0.01 level

Table 4. (Continued)

Source of variance	Degrees of freedom	Sum of squares	Mean square	Calculated F
$\frac{\rho_B d_p^2 S}{D}$	2	1.73	0.86	19.39[a]
Error	24	1.41	0.044	
Total	47	106.98		

(35, p. 454) for one degree of freedom for the greater mean square and 24 degrees of freedom for the lesser mean square. The tabular value at the 0.01 confidence level is 7.82. Since the F formed from the data exceeds the tabular entry it may be concluded that the bulk packing density makes a very significant contribution to the value of the packing factor.

The categories marked with an "a" in Table 4 exceed the value of F in the F table and are significant. In other words, any change in the variables or combination of variables so marked would cause a significant change in the packing factor. It may be concluded the, that some function of the following terms contributes to the variation in the packing factor:

$$\rho_B,\ \frac{d_p}{D},\ d_p,\ S,\ \frac{\rho_B d_p}{D},\ \rho_B S,\ \frac{d_p^2}{D},\ \rho_B d_p S \text{ and } \frac{\rho_B d_p^2 S}{D}.$$

Multiple regression analysis

In multiple regression analysis, a mathematical model is proposed and the data are fitted to it. A polynomial of the

form

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_K X_K$$

which describes a multi-dimensional response surface is most commonly used. The true functional form of the data is unknown, but if the proposed polynomial includes the proper terms, it will serve as an adequate empirical prediction equation. The method of least squares is used to determine the unknown coefficients, β_0, β_1, β_2 . . . β_K. If the equation contains over three independent variables, the number of calculations is so large that an automatic computer is essential. In the present investigation, the data were fitted to the model with the aid of an IBM 650 digital computer.

The preliminary mathematical model contained eleven terms and was of the form

$$M = \beta_0 + \beta_1 \rho_B + \beta_2 d_p + \beta_3 \frac{d_p}{D} + \beta_4 S + \beta_5 \frac{d_p^2}{D} + \beta_6 \rho_B S + \beta_7 \frac{\rho_B d_p}{D} + \beta_8 \frac{d_p^2}{D^2} + \beta_9 S^2 + \beta_{10} D + \beta_{11} \frac{S d_p}{D} .$$

These eleven terms were chosen mainly on the basis of the factorial experiment. All of the main effects and the second order interactions that were significant were included as terms in the model. In addition to these terms, the substrate squared and diameter ratio squared were added, because earlier data had indicated that these were of a quadratic nature. The column diameter and $\frac{S d_p}{D}$ were added just to be on the safe

side.

In order to determine which of these terms should be in the equation, the program for the IBM 650 digital computer was arranged in such a manner that on the first pass through the computer, the model contained all eleven terms of the preliminary model. On the second pass through the computer, the first term was eliminated from the model. On the third pass, the second term was eliminated and the first term replaced, etc. until the data had been programmed eleven times, each time with one of the terms missing from the original model. The square of the multiple correlation coefficient, which is a measure of how well the proposed model fits the data, is given in the fourth column of Table 5 for each of these passes through the computer. From this it may be seen that the terms, $\frac{d_p}{D}$, S and $\rho_B S$, do not contribute much to the "goodness of fit" of the preliminary model; that is, the equation is approximately the same whether these three terms are included or not.

Another method of determining which terms should be eliminated is the "t" test. Column 3 of Table 5 gives the calculated "t" for each of the unknown coefficients. The "t" test was used to test the hypothesis that $\beta_i = 0$. If the calculated "t" exceeds the tabulated value of the "t" distribution (35, p. 451) for the appropriate degrees of freedom, then the hypothesis is rejected and it may be concluded that

Table 5. "t" test on preliminary model

Variable	Coefficient	Calculated t	R^2 when variable omitted[a]
ρ_B	67.03	8.994[b]	0.8985
d_p	11.22	2.276[b]	0.9269
$\frac{d_p}{D}$	47.72	1.141	0.9283
s	0.1002	1.212	0.9282
$\frac{d_p^2}{D}$	317.96	5.741[b]	0.9165
$\rho_B s$	0.2096	0.960	0.9285
$\frac{\rho_B d_p}{D}$	406.32	4.050[b]	0.9227
$\frac{d_p^2}{D^2}$	1369.3	6.134[b]	0.9147
s^2	0.001595	3.687[b]	0.9237
D	0.4432	4.541[b]	0.9211
$\frac{sd_p}{D}$	1.1839	7.691[b]	0.9067

[a] The R^2 for equation containing all eleven terms was 0.9288.

[b] Significant at the 0.05 level.

the unknown coefficient is not equal to zero. The calculated values of "t" marked with an "b" in Table 5 exceed the values of the tabular "t" on the 0.05 level. Then it may be said with 95% assurance that the coefficients so indicated are not equal to zero. It was found that three of the unknown coefficients were not significantly different from zero. These terms were $\frac{d_p}{D}$, S and $\rho_B S$, the same three terms that appeared to be superfluous from an examination of the square of the multiple correlation coefficients. Upon eliminating these three terms, the data were reprogrammed and the final prediction equation, including the values of the new coefficients, then became

$$M = -24.74 + 65.44\,\rho_B - 14.76\,d_p + 0.5188\,D - 0.001093\,S^2 + 346.9\,\frac{d_p^2}{D} + 328.3\,\frac{\rho_B d_p}{D} - 1480\,\frac{d_p^2}{D^2} + 1.141\,\frac{S d_p}{D}$$

Table 6 gives the confidence limits and "t" values for the coefficients in the final prediction equation. With 95% assurance it may be said that the values of the coefficients fall within the range of confidence limits given in column three of Table 6.

This final prediction equation had a multiple R^2 of 0.9274 where R is the coefficient of multiple correlation. This means that the proposed equation accounts for 92.74% of

Table 6. Confidence limits for the coefficients in the final prediction equation

Variable	Coefficient	95% Confidence Limits	Calculated t
ρ	65.44	± 7.24	17.82[a]
d_p	- 14.76	± 8.74	3.33[a]
$\frac{d_p^2}{D}$	346.9	± 104.58	6.54[a]
$\frac{\rho d_p}{D}$	328.3	± 112.74	5.74[a]
$\frac{d_p^2}{D^2}$	-1480	± 423.0	6.90[a]
s^2	- 0.001093	± 0.00033	6.44[a]
D	0.5188	± 0.168	6.09[a]
$\frac{Sd_p}{D}$	1.141	± 0.237	9.48[a]

[a]Significant at the 0.05 level.

the variation in the packing factor as measured by the sum of squares. The other 7.26% of the variation may be attributed to experimental error of the effects of some unconsidered variables. Another way of looking at R^2 is to consider it the square of the coefficient of multiple correlation. This coefficient is a measure of the degree of linear association between the estimated and observed values of the dependent variable.

Discussion of Results

The figures referred to in this section are drawn from the final prediction equation rather than the actual data. No attempt will be made to offer conclusive reasons for the shapes of the curves since it is considered beyond the scope of the present investigation. However, a few comments will be made in passing in hopes that they will serve as indications of areas needing further investigation.

Effect of bulk density

Figures 4 and 5 show that the packing factor varies directly with the bulk density. This is an expected result since the bulk density varies inversely with porosity and since it can be shown that $(1-\epsilon)^2/\epsilon^3$ also varies inversely with porosity.

The bulk density in this investigation was taken as the grams of uncoated firebrick per cubic centimeter of the bed volume. The packing factor was found to vary linearly with bulk density within the range investigated which was roughly between 0.350 gm./cc. and 0.430 gm./cc. This represented the range of densities physically attainable with the packings and columns used. The rate of change of M with respect to the bulk density was practically constant with all possible combinations of particle size and column diameter except for the smallest column (3.39 mm.) packed with the largest particle

Figure 4. Variation of packing factor with bulk density for various levels of particle size and substrate ratios for the 3.39 mm. column

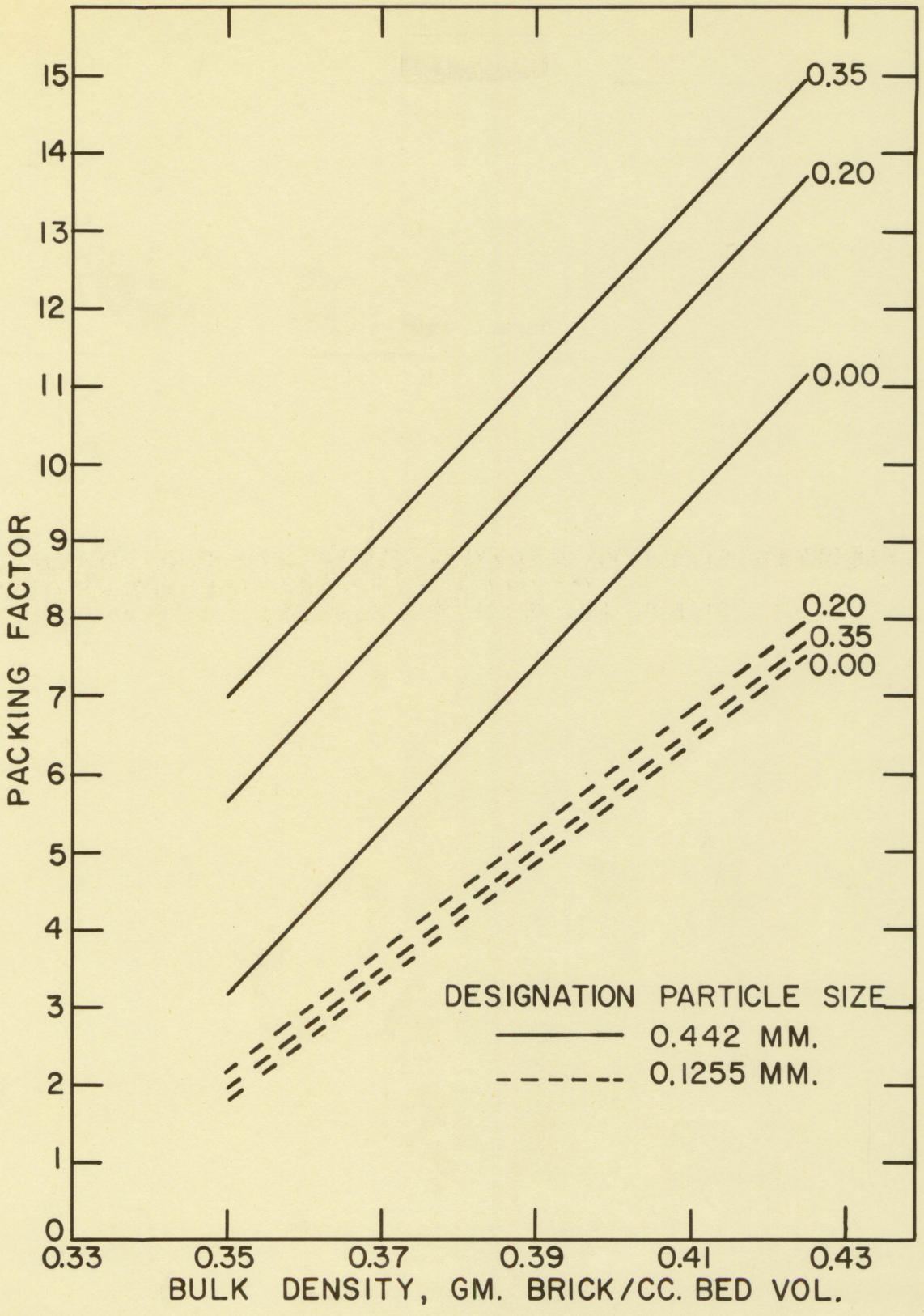
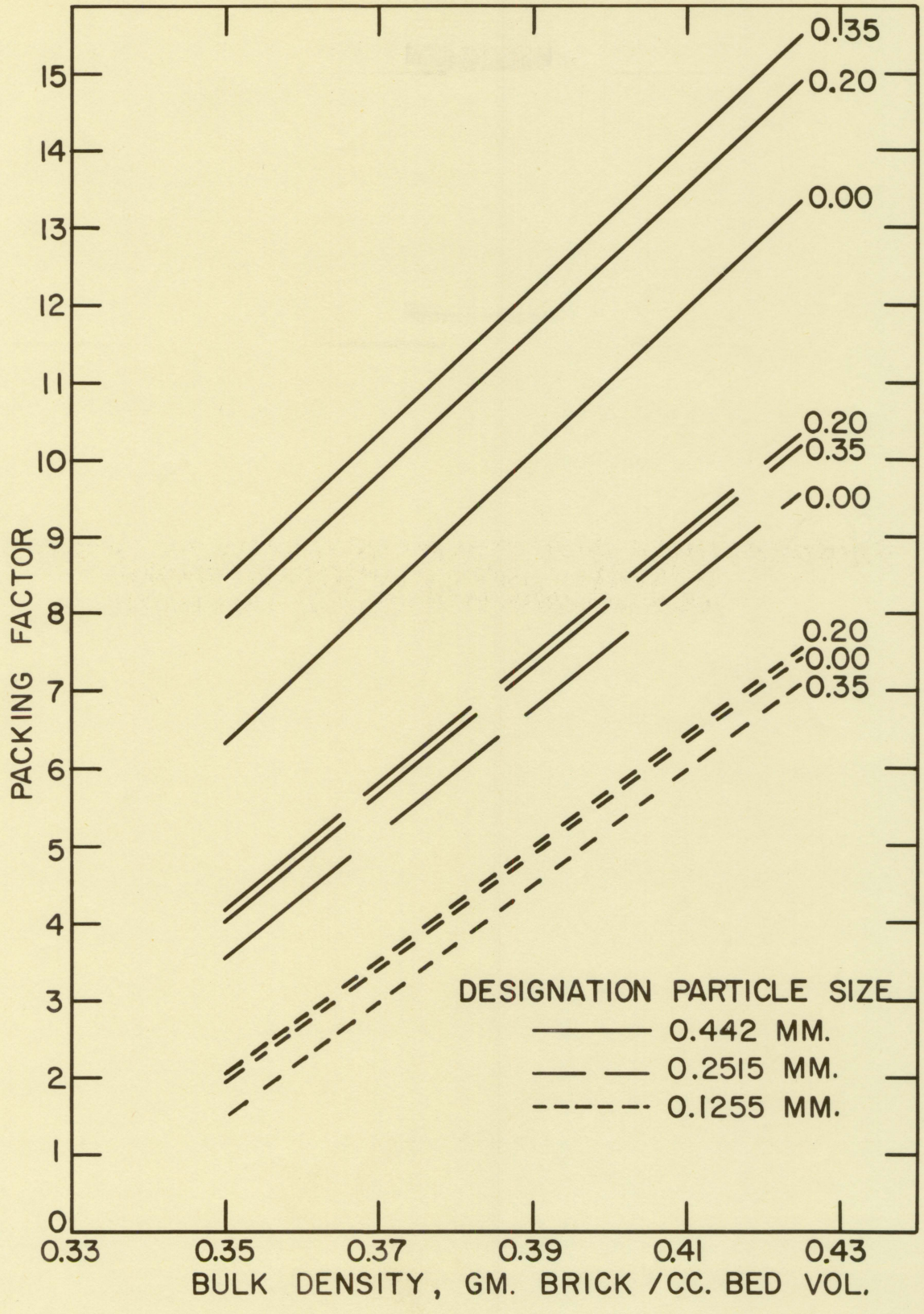

PACKING FACTOR
BULK DENSITY, GM. BRICK/CC. BED VOL.
0.33
0.35
0.37
0.39
0.41
0.43
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0.35
0.20
0.00
0.20
0.35
0.00
DESIGNATION PARTICLE SIZE
0.442 MM.
0.1255 MM.

Figure 5. Variation of packing factor with bulk density for various levels of particle size and substrate ratios for the 5.1 mm. column


0.35
0.20
0.00
0.20
0.35
0.00
0.20
0.00
0.35
DESIGNATION PARTICLE SIZE
0.442 MM.
0.2515 MM.
0.1255 MM.
PACKING FACTOR
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0.33
0.35
0.37
0.39
0.41
0.43
BULK DENSITY, GM. BRICK /CC. BED VOL.

(0.442 mm.). (See Figure 4.) The ratio of column to particle diameter, in this case, was 7.67 which was the lowest attainable ratio in the present investigation.

Effect of particle size and column diameter

Inspection of the prediction equation shows that d_p and D appear in several terms. In one term particle size appears by itself. In another term column diameter appears by itself. In four of the terms the ratio of particle diameter to column diameter appears. The effect of varying D while holding d_p constant is shown in Figure 6. In the ranges of particle size and column diameters tested, M increases with particle size and decreases with column diameter. For small column diameters the prediction equation suggests that the packing factor increases with D but this has not been tested experimentally. Perhaps in this range of column diameters, the wall effect becomes a parameter of prime consideration. More probably, this increase is due to the inadequacy of the model to predict the packing factor outside the range of parameters actually investigated.

In several terms the reciprocal ratio of D to d_p appears. In Figure 7 M is plotted against the ratio of D/d_p for two cases. In one case, d_p is held constant and D varied and in the other case, D is held constant and d_p varied. Varying this ratio by varying the column diameter results in a dif-

Figure 6. Variation of packing factor with column diameter for various particle sizes

height of bed = 50 in.
bulk density = 0.400 gm./cc.

substrate level = 35 $\frac{\text{gm. substrate}}{\text{100 gm. dry brick}}$

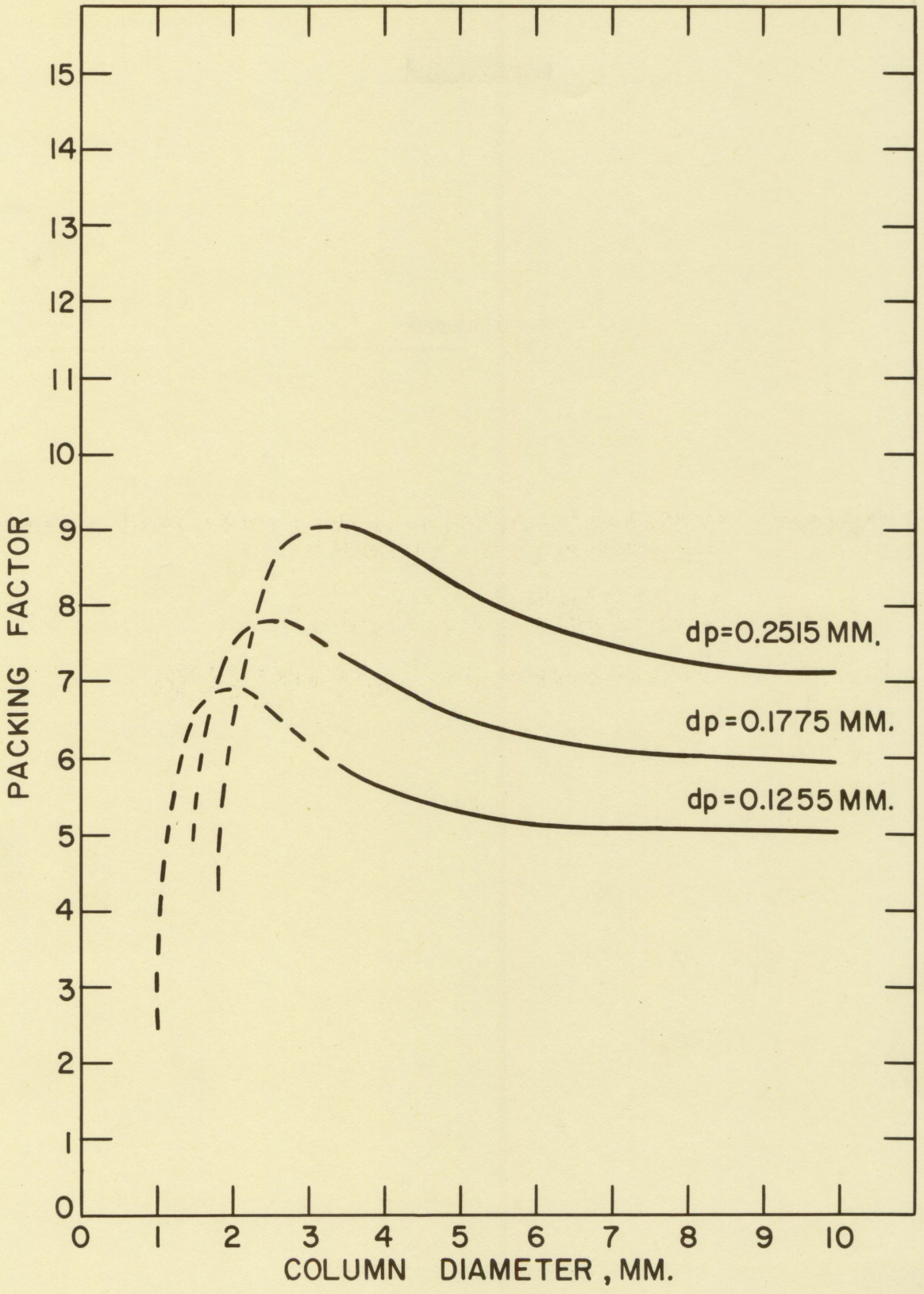
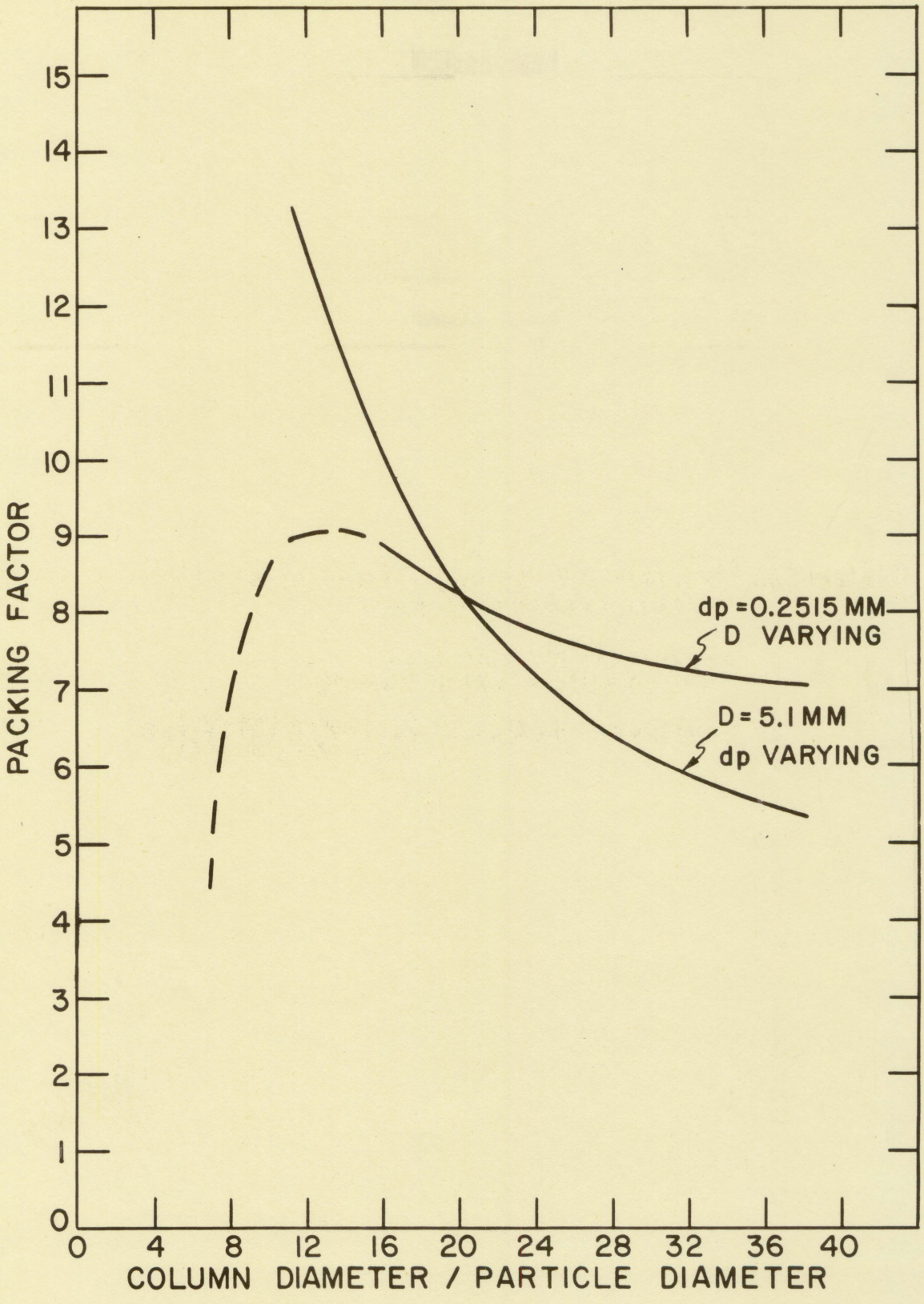

PACKING FACTOR
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
1
2
3
4
5
6
7
8
9
10
COLUMN DIAMETER, MM.
dp=0.2515 MM.
dp=0.1775 MM.
dp=0.1255 MM.

Figure 7. Variation of packing factor with column to particle diameter ratio

height of bed = 50 in.
bulk density = 0.400 gm./cc.

substrate level = 35 $\frac{\text{gm. substrate}}{\text{100 gm. dry brick}}$


PACKING FACTOR
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
4
8
12
16
20
24
28
32
36
40
COLUMN DIAMETER / PARTICLE DIAMETER
dp = 0.2515 MM
D VARYING
D = 5.1 MM
dp VARYING

ferent curve than would be obtained from varying the ratio by varying the particle size; thus, indicating that the ratio was not an independent variable as was assumed in the factorial experiment.

Figure 3 shows that the packing factor increases with increasing particle size. Dallavalle (10, p. viii) states that there is evidence of an indirect nature in the field of adsorption phenomena which sustains the belief that particles tend to become more spherical as they become smaller. If this is true, then the increase of the packing factor with increasing particle size could be attributed to a change in the shape factor, n. The author agrees with Coulson (9) that the preponderance of data on spherical particles has obscured the importance of the shape factor. This constitutes an area of fluid flow through beds of porous solid where further investigation should prove interesting. The two effects of particle size may be seen in Figure 8. The change in M involved in going from the bottom line to the top line is caused by the interactive effect of the particle size; whereas, the change in M caused by going from one end of the curve to the other, at a constant column to particle diameter ratio, is caused by the direct effect of the particle size and column diameter.

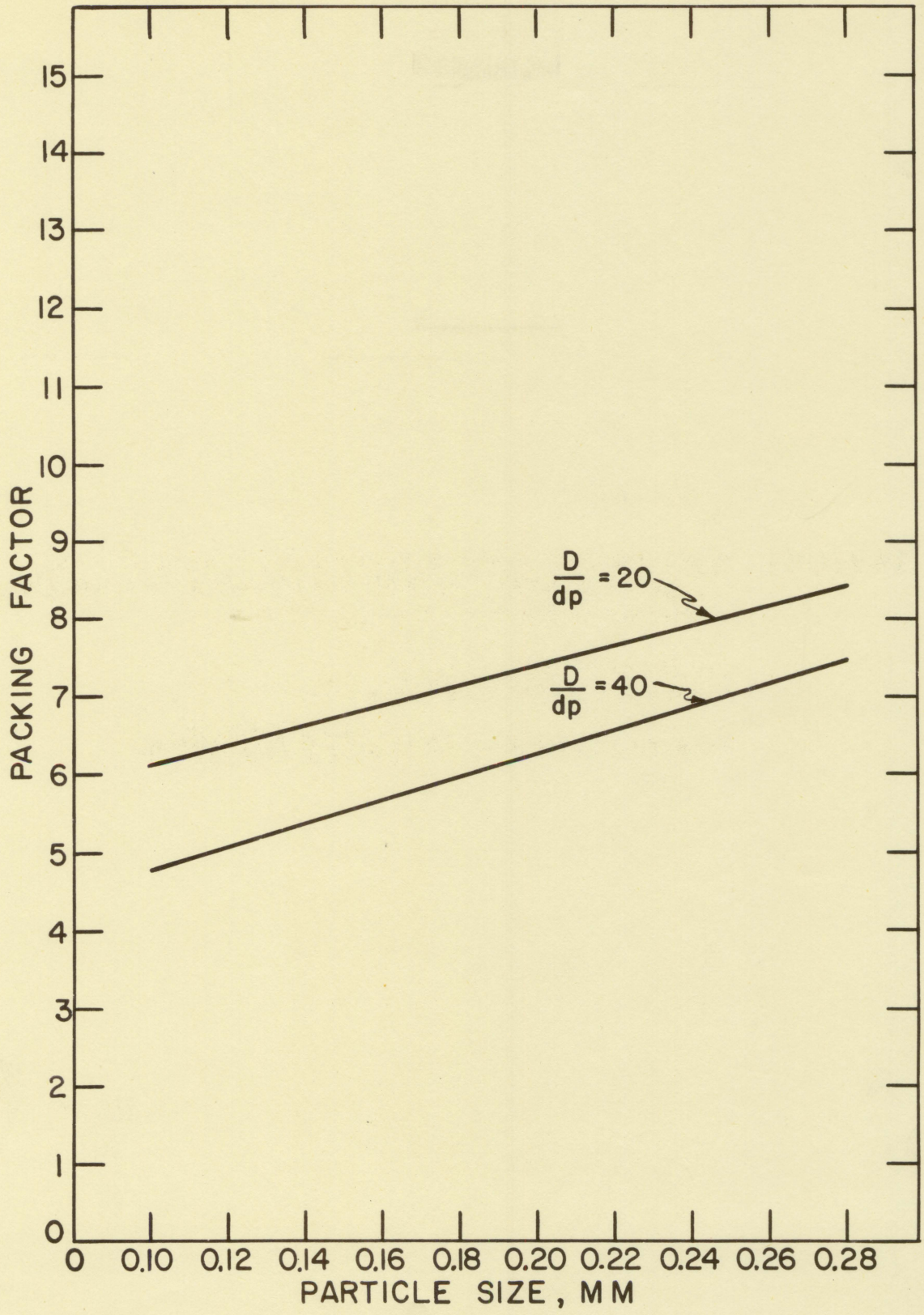
Effect of liquid substrate level

The flat curves of Figures 9 and 10 show that substrate has very little effect on the value of the packing factor. It

Figure 8. Variation of packing factor with particle and column diameter for different column to particle diameter ratios

height of bed = 50 in.
bulk density = 0.400 gm./cc.

substrate level = 35 $\frac{\text{gm. substrate}}{\text{100 gm. dry brick}}$


PACKING FACTOR
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
D/dp = 20
D/dp = 40
0
0.10
0.12
0.14
0.16
0.18
0.20
0.22
0.24
0.26
0.28
PARTICLE SIZE, MM

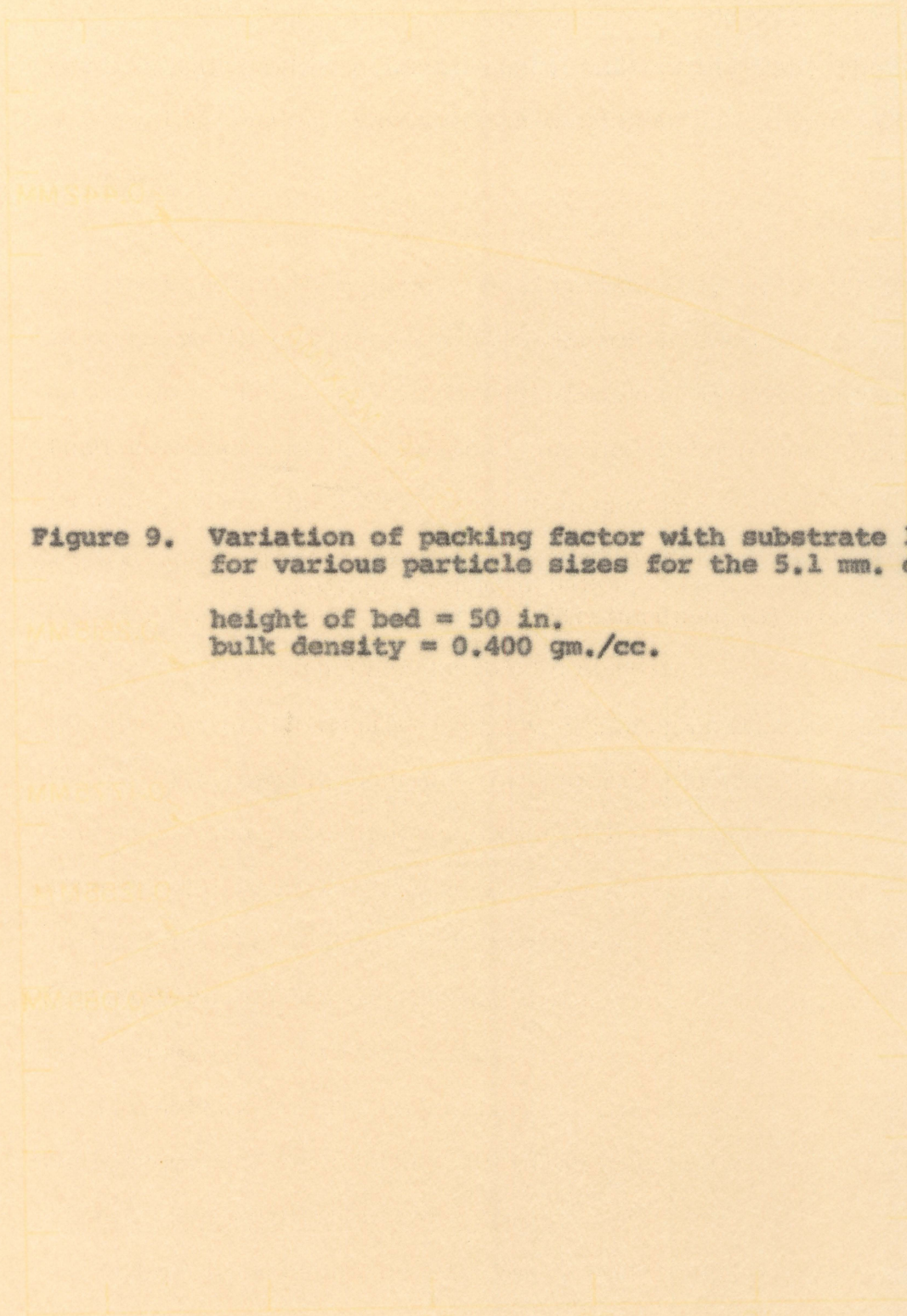


Figure 9. Variation of packing factor with substrate level for various particle sizes for the 5.1 mm. column

height of bed = 50 in.
bulk density = 0.400 gm./cc.

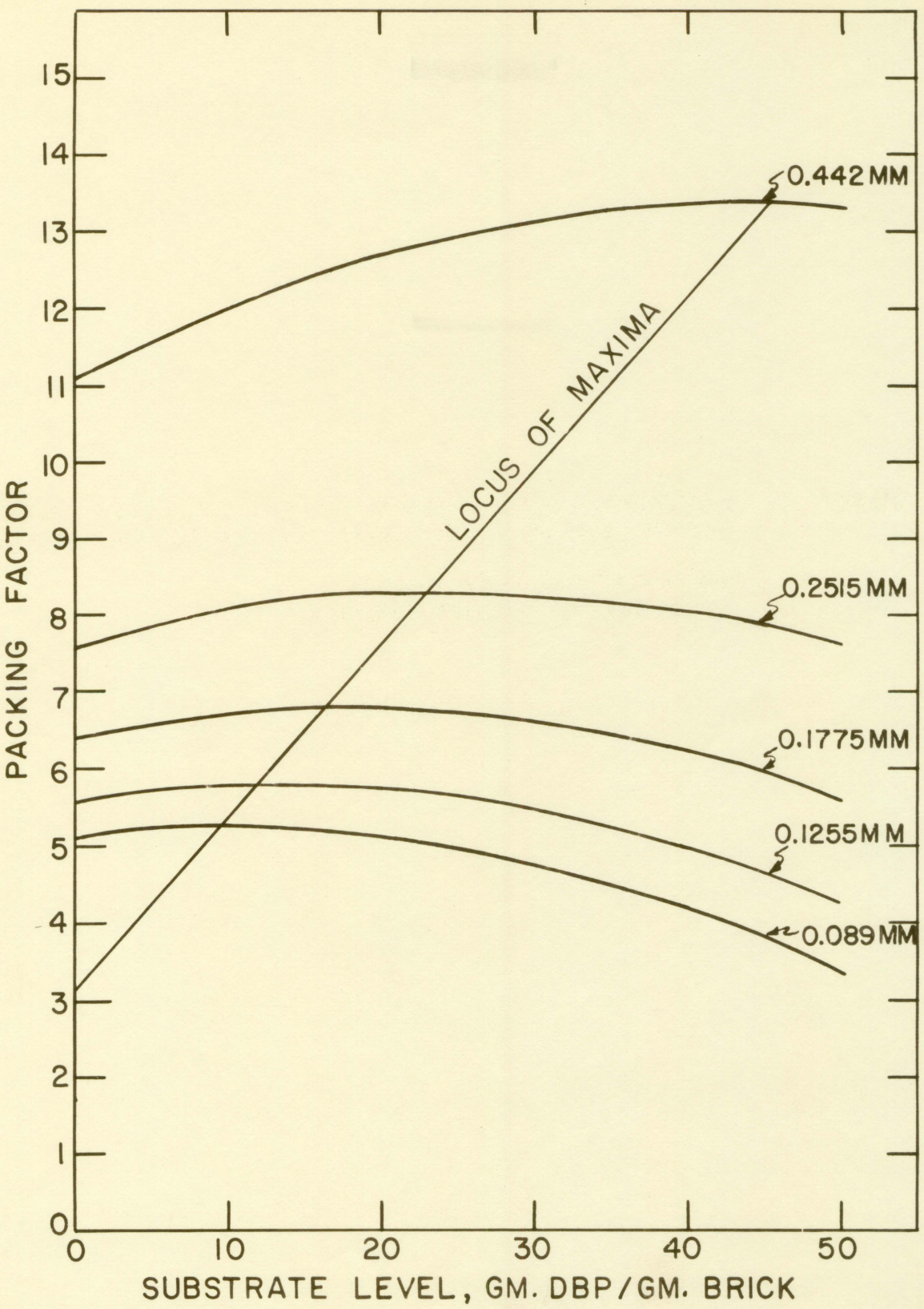
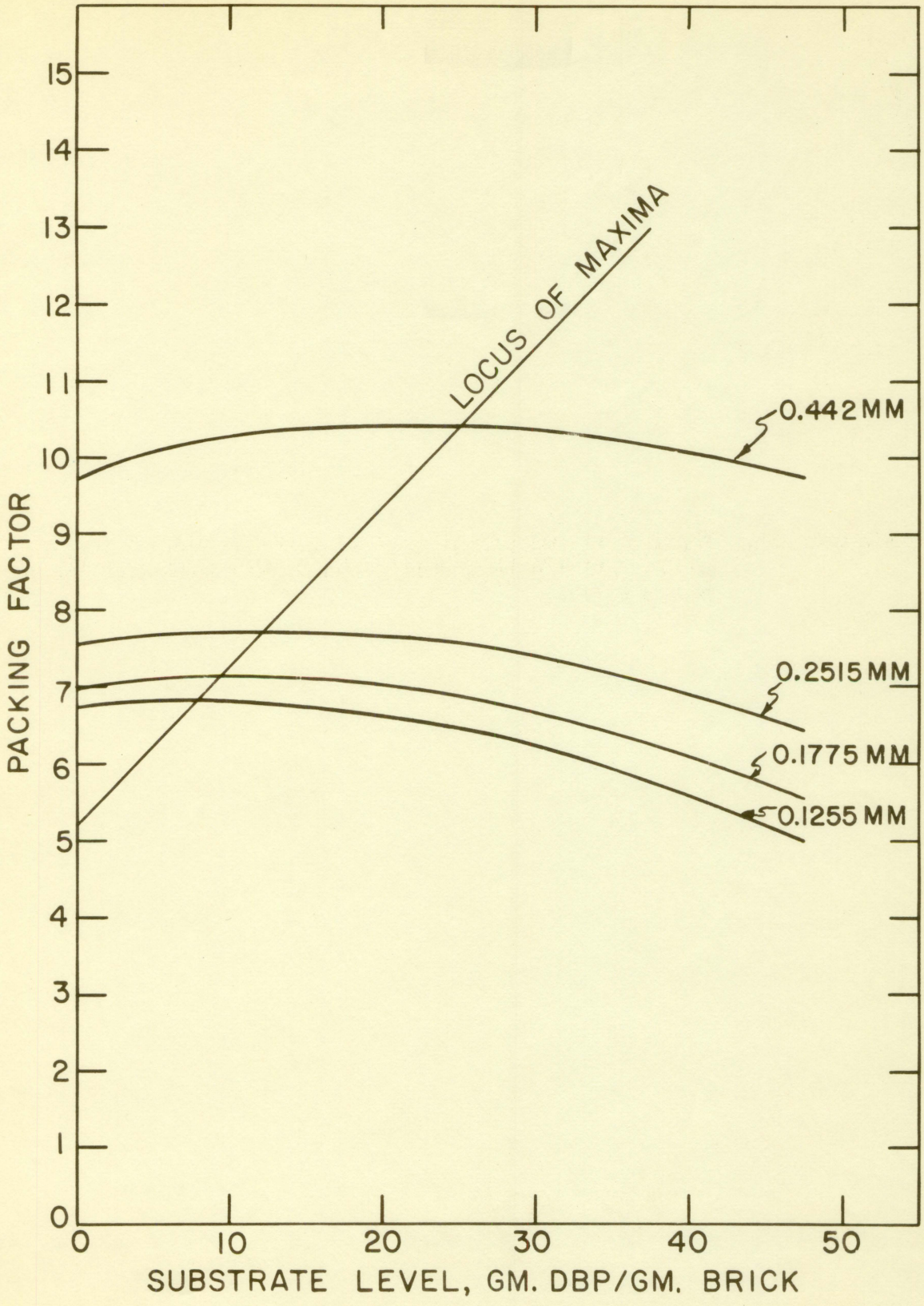

PACKING FACTOR
SUBSTRATE LEVEL, GM. DBP/GM. BRICK
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
10
20
30
40
50
0.442 MM
0.2515 MM
0.1775 MM
0.1255 MM
0.089 MM
LOCUS OF MAXIMA

Figure 10. Variation of packing factor with substrate level for various particle sizes for the 10.14 mm. column


PACKING FACTOR
SUBSTRATE LEVEL, GM. DBP/GM. BRICK
LOCUS OF MAXIMA
0.442 MM
0.2515 MM
0.1775 MM
0.1255 MM
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
10
20
30
40
50

was noticed that at substrate levels as high as 50 parts per hundred the packing was still free-flowing. This would indicate that the substrate was concentrated in the internal pores of the particles rather than on the surface. Experimental work by Duffield and Rogers (12) also indicates that the substrate enters the internal pores. Since the packing factor is relatively unaffected by the reduction in porosity due to filling or sealing off the pores, it follows that very little of the gas flows through these internal pores but rather through the interstices between the particles. The slight increase of M with increasing substrate (Figures 9 and 10) could be attributed to the reduction in porosity caused by the blocking of these pores to the small amount of gas that did pass through them originally. The subsequent decrease of these curves might be attributed to changing the shape factor by filling in some of the surface irregularities.

Limitations of the present study

The 7% of the variation in the packing factor that remains unaccounted for may be attributed to three effects:

1. Lack of fit of the proposed model
2. Experimental error
3. Unconsidered variables

The error caused by the lack of fit of the proposed model can be reduced only by adding more terms or combinations of

terms to the hypothetical equation. Adding the terms $\rho_B d_p S$ and $\rho_B D_p^2 S/D$ should improve the fit.

Besides the unavoidable errors inherent in the measuring devices, an error in the particle size determination was discovered. The average particle diameter of the -100+150 Standard Tyler screen fraction was erroneously computed to be 0.1225 mm. while the correct value of this screen fraction was 0.1255 mm. This error was not discovered until after the data had been programmed on the IBM 650 digital computer. Another of the particle size determinations may be open to some question. The largest particle size used was not as closely sized as the others; that is, it was not the average of the openings of two successive standard screens. This diameter was computed by taking the average of the openings in the 28 Tyler mesh screen and the 48 Tyler mesh screen.

Temperature may be one of the unconsidered variables affecting this investigation. Certainly, temperature affects the pressure drop by its action of the gas viscosity and gas density, but the question arises as to whether it affects the bed properties as well. Greenberg and Weger (20) investigated the effects of temperature on the specific permeability of sintered metal powders and found it to be significant.

The effect of pressure on the packing factor was not considered. However, compressible beds of solids whose permeability is a function of pressure are frequently encountered

in filtering operations (2).

Only a single substrate, dibutyl phthalate, was used in this investigation. In gas chromatography many different substrates are used. Hence, it would be desirable to extend this study to include some of the substrate properties such as surface tension which may affect the packing factor.

CONCLUSIONS AND RECOMMENDATIONS

The conclusions resulting from this study were:

1. The Ergun equation adequately correlated the effects of the fluid density, viscosity and flow rate for flow of gases in the laminar range through packed beds of porous solids coated with a liquid substrate.
2. The following terms and combinations of terms contribute significantly to the variation in the packing factor:

   ρ_B, d_p/D, d_p, S, $\rho_B d_p/D$, $\rho_B S$, d_p^2/D, $\rho_B d_p S$ and $\rho_B d_p^2 S/D$.
3. The packing factor is related to more readily measurable parameters by the following empirical equation:

$$M = -24.74 + 65.44\,\rho_B - 14.76\,d_p + 0.5188\,D - 0.001093\,S^2 + 346.9\,\frac{d_p^2}{D} + 328.3\,\frac{\rho_B d_p}{D} - 1480\,\frac{d_p^2}{D^2} + 1.141\,\frac{S d_p}{D}$$

4. Values of the packing factor predicted by the above equation can be used in the following modification of the Ergun equation to predict the pressure drop across packed beds in the laminar flow range:

$$\frac{\Delta P}{L} g_c = \frac{150 \mu U_m M}{d_p^2}$$

Recommendations for future study are

1. The data should be reprogrammed on the digital computer using a mathematical model which includes the terms $\rho_B d_p S$ and $\rho_B d_p^2 S/D$ and using the correct particle diameter for the -100+150 screen fraction to see if a better fitting response surface can be obtained.
2. An investigation similar to the present one should be made to determine the effects of different types of substrates.
3. A study to determine if temperature and pressure have an effect on the bed properties should be undertaken.
4. A more intensive study of the effect of shape factor in particles that are internally porous should be made.

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APPENDIX A

Some Applications of Gas Chromatography in the Nuclear Field

Gas chromatography is valuable both as an analytical tool and a preparative tool. Basically it is a method whereby a mixture of volatile compounds is separated by passing a slug of the mixture through a packed column where the packing is such that the components of the mixture are absorbed to varying degrees depending upon the individual component absorption isotherms. The component which is least absorbed will pass through a chromatography column in the shortest time. Each component of a mixture will have a unique column retention time for a particular packing and set of operating conditions. To increase the fractionating power of the column the packing is frequently coated with an appropriate liquid partitioning agent. The most current and comprehensive bibliography in the field of gas chromatography is found in Pecsok (36).

The applications of gas chromatography to the nuclear field include the separation and enrichment of isotopes, monitoring reactor coolant gas, identification of carbon-14 labeled compounds, and the retention of fission products in charcoal traps.

Gas chromatography was used by Glueckauf and Kitt (19) to recover deuterium from a mixture of H_2, HD, and D_2 in what they termed "unprecedented purity". They used a 44 cm. long,

8 mm. internal diameter column, packed with a mixture of palladium black and asbestos. Pure hydrogen was used as a displacing gas.

Chemical inertness and physical-property similarity between xenon-133 and krypton-85 make their separation by classical means a tedious, if not impossible, task. Koch and Grandy (25) in a recently published paper, reported that the separation of xenon and krypton by gas chromatography was relatively easy.

Gaseous fission products from nuclear processes must be reduced in activity before being vented to the atmosphere. Koch and Grandy (23, 24) and Browning and Bolton (3) made studies of the retention properties of charcoal traps. The traps, functioning on the same principals as gas chromatography, were found to be capable of retaining some gaseous fission products long enough for them to decay to a safe level.

The separation and enrichment of isotopes has also been accomplished by gas chromatography (18).

Wolfgang and Rowland (45) used a proportional counter in a series with a gas chromatography apparatus to obtain a simultaneous radioassay and mass assay of carbon and tritium labeled compounds. This method saves time in that a laborious laboratory procedure is bypassed. By comparing the shape of the thermal conductivity peak with the shape of the radio-

activity peak, activity and specific activity can be determined without having to convert to a standard form for counting.

Timms et al. (43) suggested that a gas chromatography unit be used to monitor the gas from gas-cooled reactors. Their experimentation showed that a complete analysis could be run in eight minutes with enough sensitivity to detect hydrogen, argon, oxygen, nitrogen, or methane at levels as low as 5 to 20 parts impurities per million parts of carbon dioxide. Gas chromatography could well replace the mass spectrometer now in use for this purpose. The chromatography unit would be both simplier and cheaper to operate.

APPENDIX B

Transformations of the Ergun Equation

For the laminar flow range the Ergun equation reduces to

$$\frac{\Delta P}{L} g_c = 150 \frac{(1-\epsilon)^2}{\epsilon^3} \frac{\mu U_m}{D_p^2}$$

where the effective particle diameter D_p is defined as follows:

$$D_p = \frac{6}{S_v} = \frac{6}{A_p/V_p}$$

Brown (2, p. 77) defines the ratio of specific surfaces n as

$$n = \frac{\text{Specific surface of particle}}{\text{Specific surface of sphere of same diameter}}$$

$$= \frac{A_p/\rho_p V_p}{6/\rho_p d_p}$$

From this it can be seen that

$$\frac{A_p}{V_p} = n \frac{6}{d_p}$$

Substituting for A_p/V_p in the expression defining D_p, the following is obtained:

$$D_p = \frac{6}{n\ 6/d_p} = \frac{d_p}{n}$$

Substituting for D_p in the Ergun equation results in

$$\frac{\Delta P}{L} g_c = 150 \frac{(1-\epsilon)^2\ n^2}{\epsilon^3\ d_p^2} \mu\ U_m$$

The mean superficial linear velocity U_m is related to the mean volumetric flow rate F_m as follows:

$$U_m = \frac{F_m}{A_c}$$

Substituting for U_m in the Ergun equation results in the following expression:

$$\frac{\Delta P}{L} g_c = 150 \frac{(1-\epsilon)^2 n^2}{\epsilon^3 d_p^2} \frac{\mu F_m}{A_c}$$

This can be rearranged to give

$$\frac{g_c d_p^2 A_c \Delta P}{150 \mu F_m L} = \frac{(1-\epsilon)^2 n^2}{\epsilon^3}$$

F_m may be evaluated in the following manner:

$$F_m = \frac{F_0 (P_0-p)}{P_0} \frac{P_0}{\overline{P}}$$

where: F_0 = Volumetric flow rate at outlet conditions measured with a soap-film meter

$\frac{P_0-p}{P_0}$ = correction factor for saturation with water from soap-film meter

P_0 = outlet pressure

p = vapor pressure of water at temperature, T.

$\overline{P}$ = average column pressure.

The average column pressure is calculated using the method given in Keulmans (22, p. 144).

$$\bar{P} = \frac{\int P \, dx}{\int dx}$$

$$U = -\frac{K'}{\mu} \frac{dP}{dx}$$

Assuming isothermal flow

$$U = \frac{P_0 V_0}{P A_c}$$

$$dx = \frac{A_c K'}{V_0 P_0 \mu} P \, dP$$

$$\bar{P} = \frac{\int_{P_0}^{P_i} -\frac{A_c K'}{V_0 P_0 \mu} P^2 \, dP}{\int_{P_0}^{P_i} -\frac{A_c K'}{V_0 P_0 \mu} P \, dP}$$

$$\bar{P} = \frac{2}{3} P_0 \frac{(P_i/P_0)^3 - 1}{(P_i/P_0)^2 - 1}$$

where: K' = specific permeability

P_0 = outlet pressure

P_i = inlet pressure

V_0 = volume of gas emerging from the outlet per unit time.

APPENDIX C

Similarity of Packing Factor to Variables Used by Other Investigators

An attempt will be made to relate M to two similar parameters used by other investigators. The parameters are

1. The permeability as used by D'Arcy (11)
2. F_g/F_{Re} as used by Brown et al. (2, p. 211)

Before relating the packing factor to permeability, a better understanding of permeability is desirable. As originally used by D'Arcy, it was the linear velocity per unit pressure gradient, $\frac{U}{\Delta P/L}$, and had the units of $L^3\ T^1\ M^{-1}$ or $L^4\ F^{-1}\ T^{-1}$; where T = time, L = length, M = mass, and F = force. The difficulty encountered here was that the permeability K pertained to a particular fluid percolating through a particular bed. In order to separate the bed effects from the fluid effects, Nutting (33) introduced specific permeability, $K' = K\mu$, which has the units of L^2. In the petroleum industry, specific permeability is measured in darcy's. One darcy = 9.87×10^{-9} sq. cm.

Permeability should not be confused with porosity even though both are related to particle size and shape. Permeability is a measure of the ease with which a fluid flows through the bed, while porosity is the fractional void volume of the bed. In fact, according to Cloud (8), a general

correlation between porosity and permeability cannot exist. It is possible for two different media to have the same porosity with entirely different permeabilities.

By making use of the above definitions of permeability and specific permeability:

$$K = \frac{g_c d_p^2}{150\ M\mu} \quad , \quad \frac{(\text{cu. ft.})(\text{ft.})}{(\text{lb. force})(\text{sec.})}$$

$$K' = \frac{g_c d_p^2}{150\ M} \quad , \quad \frac{(\text{sq. ft.})(\text{ft.})(\text{lb. mass})}{(\text{lb. force})(\text{sec.})(\text{sec.})}$$

Brown, et al. (2, p. 211), uses a variable in his fluid flow equations that is the ratio of a friction-factor factor to a Reynolds number factor, F_f/F_{Re}. It is a function of porosity, particle diameter, particle shape, orientation and surface. Brown's equation is

$$\frac{\Delta P}{L} g_c = \frac{32\ U_m \mu}{d_p^2} \quad \frac{F_f}{F_{Re}} \ .$$

From this it can be seen that

$$\frac{F_f}{F_{Re}} = \frac{150}{32} M.$$

APPENDIX D

Data for Multiple Regression

Table 7. Data for multiple regression

D	d_p	ρ_B	S	M
3.39	0.442	0.414	0	9.63
"	"	0.423	"	11.08
"	"	0.423	"	10.09
"	"	0.431	"	12.44
"	"	0.431	"	11.20
"	"	0.447	"	15.06
"	"	0.400	35	11.55
"	"	0.410	"	13.19
"	"	0.418	"	14.82
"	"	0.420	"	15.31
"	0.2515	0.390	0	6.90
"	"	0.410	"	7.80
"	"	0.390	20	7.27
"	"	0.400	"	8.54
"	"	0.410	"	9.93
"	"	0.420	"	11.50
"	"	0.390	25	7.24
"	"	0.400	"	8.29
"	"	0.410	"	9.45
"	"	0.420	"	11.61
"	"	0.390	30	8.49
"	"	0.400	"	9.55
"	"	0.410	"	10.00
"	"	0.390	35	9.05
"	"	0.400	"	9.86
"	"	0.410	"	10.85
"	"	0.420	"	12.30
"	0.1775	0.375	0	4.38
"	"	0.375	"	4.35
"	"	0.390	"	5.21

Table 7. (Continued)

D	d_p	ρ_B	S	M
3.39	0.1775	0.400	0	7.21
"	"	0.400	"	6.50
"	"	0.390	10	5.00
"	"	0.400	"	5.72
"	"	0.375	20	4.69
"	"	0.375	"	4.47
"	"	0.400	"	6.54
"	"	0.400	"	6.94
"	"	0.375	35	4.95
"	"	0.375	"	5.11
"	"	0.380	"	4.99
"	"	0.390	"	5.67
"	"	0.400	"	6.54
"	"	0.400	"	6.94
"	"	0.400	"	6.48
"	"	0.410	"	7.35
"	0.1225	0.413	"	8.87
"	"	0.418	"	9.04
"	0.089	0.428	"	4.86
"	"	0.428	"	5.78
4.88	0.2515	0.375	0	6.25
"	"	0.375	"	6.24
"	"	0.400	"	8.35
"	"	0.400	"	7.92
"	"	0.375	20	6.39
"	"	0.375	"	6.36
"	"	0.400	"	9.90
"	"	0.400	"	9.81
"	"	0.375	35	5.45
"	"	0.375	"	5.52
"	"	0.400	"	8.98
"	"	0.400	"	8.94
5.1	0.442	0.370	20	10.07
"	"	0.380	"	11.64
"	"	0.390	"	13.42

Table 7. (Continued)

D	d_p	ρ_B	S	M
5.1	0.442	0.370	25	8.68
"	"	0.380	"	10.03
"	"	0.390	"	11.54
"	"	0.400	"	13.32
"	"	0.370	30	10.51
"	"	0.380	"	12.10
"	"	0.390	"	13.91
"	"	0.390	"	13.68
"	"	0.400	"	16.28
"	"	0.390	35	10.33
"	"	0.400	"	12.00
"	"	0.410	"	13.79
"	0.2515	0.346	0	2.59
"	"	0.380	"	5.90
"	"	0.390	"	6.82
"	"	0.400	"	7.84
"	"	0.400	"	7.27
"	"	0.400	"	7.44
"	"	0.403	"	8.62
"	"	0.415	"	8.78
"	"	0.380	35	6.26
"	"	0.390	"	7.15
"	"	0.390	"	7.16
"	"	0.395	"	7.06
"	"	0.395	"	6.44
"	"	0.400	"	8.31
"	"	0.400	"	8.24
"	"	0.410	"	9.39
"	"	0.415	"	9.52
"	0.1775	0.390	0	5.80
"	"	0.400	"	6.71
"	"	0.410	"	7.63
"	"	0.400	10	6.72
"	"	0.390	20	6.18
"	"	0.400	"	7.20

Table 7. (Continued)

D	d_p	ρ_B	S	M
5.1	0.1775	0.410	20	8.34
"	"	0.390	35	6.27
"	"	0.400	"	7.09
"	"	0.410	"	8.09
"	"	0.390	50	4.93
"	"	0.400	"	5.60
"	0.1225	0.390	0	4.97
"	"	0.400	"	5.73
"	"	0.400	"	5.90
"	"	0.400	"	5.35
"	"	0.410	"	6.57
"	"	0.415	"	7.08
"	"	0.415	"	6.86
"	"	0.390	20	5.26
"	"	0.400	"	6.17
"	"	0.410	"	6.76
"	"	0.390	35	4.95
"	"	0.400	"	5.21
"	"	0.415	"	6.40
"	"	0.415	"	6.85
"	0.089	0.370	"	2.39
"	"	0.380	"	2.77
"	"	0.390	"	3.11
"	"	0.395	"	3.60
"	"	0.395	"	3.68
"	"	0.400	"	3.41
8.33	0.442	0.380	"	7.71
"	"	0.390	"	8.90
"	"	0.400	"	10.31
"	"	0.410	"	11.11
"	0.2515	0.346	0	3.48
"	"	0.346	"	3.56
"	"	0.360	"	4.33
"	"	0.342	35	2.90
"	"	0.351	"	3.32

Table 7. (Continued)

D	d_p	ρ_B	S	M
8.33	0.2515	0.356	35	3.64
"	"	0.356	"	3.53
"	"	0.360	"	4.33
"	"	0.383	"	6.60
"	"	0.390	"	6.74
"	"	0.400	"	7.67
"	"	0.410	"	8.70
"	0.1775	0.375	0	4.52
"	"	0.375	"	4.57
"	"	0.400	"	6.96
"	"	0.400	"	6.51
"	"	0.375	20	5.33
"	"	0.375	"	4.29
"	"	0.400	"	7.55
"	"	0.400	"	7.82
"	"	0.348	35	4.14
"	"	0.375	"	4.73
"	"	0.375	"	4.72
"	"	0.390	"	5.54
"	"	0.400	"	6.72
"	"	0.400	"	6.65
"	"	0.400	"	7.19
"	0.1225	0.345	0	2.57
"	"	0.360	"	3.28
"	"	0.360	"	3.30
"	"	0.345	20	2.50
"	"	0.400	"	6.34
"	"	0.345	35	2.48
"	"	0.345	"	2.38
"	"	0.345	"	2.90
"	"	0.354	"	3.18
"	"	0.354	"	3.15
"	"	0.358	"	2.82
"	"	0.358	"	3.02
"	"	0.370	"	3.18

Table 7. (Continued)

D	d_p	ρ_B	S	M
8.33	0.1225	0.385	35	5.00
"	"	0.390	"	4.26
"	0.089	0.362	35	2.69
"	"	0.362	"	2.41
"	"	0.370	"	2.39
"	"	0.380	"	2.71
"	"	0.390	"	3.05
"	"	0.400	"	3.49
10.14	0.2515	0.392	"	6.42
"	"	0.392	"	6.42
"	0.1775	0.348	"	4.14
"	"	0.360	"	3.57
"	"	0.370	"	4.24
"	"	0.380	"	4.91
"	"	0.390	"	5.75
"	"	0.390	"	5.64
"	"	0.390	"	5.54
"	"	0.400	"	7.19
"	"	0.400	"	6.41
"	0.089	0.403	"	4.08
11.80	0.2515	0.375	0	5.38
"	"	0.375	"	5.41
"	"	0.400	"	7.55
"	"	0.400	"	7.23
"	"	0.375	20	5.41
"	"	0.375	"	5.19
"	"	0.400	"	7.81
"	"	0.400	"	7.56
"	"	0.375	35	5.25
"	"	0.375	"	5.01
"	"	0.400	"	7.35
"	"	0.400	"	7.16