The Change in Pore Size Distribution from Surface Reactions in Porous Media

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When a porous solid is penetrated by a reactive fluid which changes the pore geometry, the macroscopic properties of that porous material may be greatly changed. A model is proposed in which the matrix is visualized as being a number of short cylindrical pores dispersed randomly throughout the solid. The change in the distribution of these cylindrical pores is then represented by a integrodifferential equation which is solved for two special cases.

The evolution of the pore size distribution is determined by the particular way in which the solid-liquid boundary takes place. The case considered here is that of a surface reaction which dissolves the solid thus continuously enlarging the pores. The rate of reaction is calculated theoretically using a laminar flow diffusion model and this growth rate expression is then taken as the basis for numerical calculations relating to the action of dilute hydrochloric acid on limestone.

A comparison is made with experimental results and it is found that the model behaves in much the same way as the real system although the observed rate of pore growth was two to three times that predicted by the diffusion model. Several possible explanations for this discrepancy are being tested.

An exact solution of the integrodifferential equation for highly retarded reaction rates has been found with the change in permeability being given in terms of the change in porosity. This result will permit a prediction of the stimulation that can be achieved in acidizing oil wells with retarded acids.

There are many important phenomena arising from a change in pore structure resulting from the interaction of a penetrating fluid with a porous solid. The deactivation of catalysts owing to the loss in specific surface area during reaction and the plugging of micropore filters by the deposition of precipitates on the pore walls are both examples of a change in pore structure directly stemming from the presence of a fluid in the interstices. Many investigators (*5, 16, 27*) have recognized the importance of pore structure in catalysis, but none have attempted to follow the evolution of this structure during reaction. Kuo and Closmann (*24*) studied the effect of precipitation in porous media, but their arguments were macroscopic in nature utilizing to some extent the observations of Kennedy and Wieland (*23*). Many other systems such as clarification of suspensions (*26*) and the washing of porous materials (*13*) are related generally to the evolution of a pore structure. This problem is to be studied here with all of the processes mentioned above being more or less embodied within the basic framework developed. The principal motivation, however, for this work stems from a need to understand the mechanism whereby an acid reacting with the solid boundary of a porous medium alters the properties of that medium. A very common method of stimulating oil wells to greater production is to inject acid into an oil bearing formation with the hope of significantly increasing the permeability in some region about the wellbore. This approach has proven to be rather successful and in recent years many modifications of the method have been reported with these being primarily aimed at reducing the rate of acid attack on the porous solid or further protecting the metal parts contacted by the acid during the injection process. As the number and sophistication of the possible treatments are increased, the need for good engineering design becomes more pressing. This study is intended to provide the fundamental basis for making reliable estimates of the influence of acid on the pore structure. While our goal is to understand matrix acidization, this same approach will also yield results pertinent to the allied problems cited above. Indeed any problem which is basically concerned with the interaction of the porous solid-fluid system and its effect on pore structure should be susceptible to arguments similar to those presented here.

The process of matrix acidization consists simply of pumping an acid down the tubing or casing of a completed wellbore. The acid thus injected will flow into the formation (porous medium) displacing to some extent the resident fluids. The acid will react with the porous solid as it flows through the interstices thus continuously depleting the concentration of acid along the flow path. The rate of this reaction is determined, of course, by a number of factors such as temperature, pressure (a gas tends to be evolved in some cases), type of acid and acid concentration. The reacting acid will dissolve a portion of the porous solid thus changing the pore structure. To what extent will this dissolution of solid enhance tthe permeability of the reservoir? How far will the acid penetrate? What is the effect of flow rate? Does reaction rate influence the results? The answers to all of these questions are essential to the design of an effective acid treatment.

The change in the pore structure must be calculated to intelligently respond to the needs of the design engineer. The process is clearly a complex one, a very complex one indeed, and our approach is through the use of a mathematical model. Its behavior will hopefully represent that of the real system.

THE EVOLUTION EQUATION

In the discussion to follow a porous medium is considered to be a solid containing a matrix of randomly distributed holes or voids which are interconnected to some extent so that it is possible under the influence of a pressure gradient to cause fluid to flow through the solid. This definition then excludes packed beds of spheres which are placed in a well-defined and repeating pattern as well as matter impervious to flow. To characterize the porous system it is very convenient to discuss a pore size distribution and yet because it is not possible to distinguish a well-defined position for the boundary between pores, it has not yet been possible to define precisely what is meant by the size of a pore. To circumvent these difficulties which cannot be precisely resolved, a model will be proposed with the pore structure being represented by a large number of short cylinders distributed randomly throughout the solid. The cross-sectional area will in general vary from pore to pore, but the pores are all assumed to be geometrically similar. For the analysis to follow, it is not necessary to define in any detail the mechanism by which fluid communicates from one pore to another, but simply to note that fluid does flow from one pore to another in the direction of an imposed pressure gradient. This idealization of a porous medium is very similar to that often called capillaric models (*37*) and these have met with some success in interpreting many of the observations stemming from experiments with porous media. Important phenomena such as capillary pressure (*3, 4, 25, 29, 33*) permeabilities (*3, 4, 29*) and dispersion (*36*) and relative permeabilities (*3*) have all been interpreted using the capillaric model. While all of these analyses are subject to some criticism (*11, 37*), the use of the model in this paper is limited to the determination of ratios of the values of the relevant properties at some point in time to the initial values of those properties. This limited use of the model is possible because our interest is focused on the evolution of the pore structure given its initial structure rather than on the task of predicting all of the properties of a porous medium starting with the observation of a single property. Thus the properties at the start of the process are given. If this less demanding use of the model is adopted, then most of the criticisms commonly levelled at the use of capillaric models are dispelled.

A sketch depicting the idealized model of the pore structure is shown in Figure 1. A pore size density function is defined so that $W(A, x, L, t)dAdLw^2dx$ is the number of pores having an area between A and $A + dA$ and a length between L and $L + dL$ in the volume (see Figure 1) w^2dx about x at the time t. A pore is counted in the volume w^2dx if its center of volume is there. These pores are supposedly oriented in a direction parallel to the direction of flow with x being a distance in that direction measured from one face of the porous medium. Restricting the pores to be oriented in the direction of flow will not detract from the generality of the results since the pores are randomly distributed (no correlation between the area of a pore and its orientation) and also because all results of interest are in ratios. Therefore, geometric factors introduced by a random orientation would cancel on taking ratios.

The evolution of the pore size density function W is to be determined once the details of the fluid-solid interaction are specified. If W is known the variables of interest can be calculated. For example, the porosity is given by

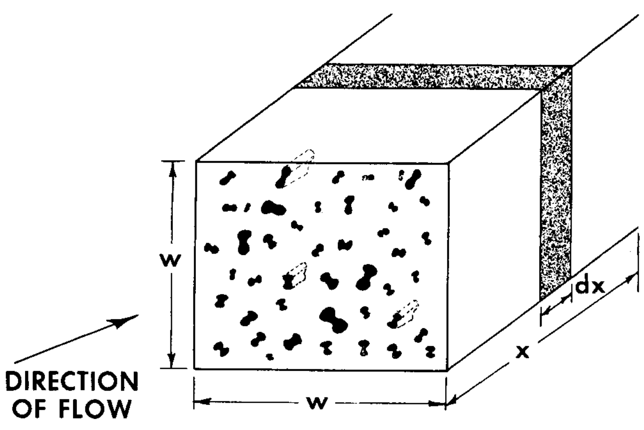

Fig. 1. Idealized model of a porous medium.

$$\phi = \int_o^\infty \int_o^\infty ALW(A, L, x, t)\,dAdL \qquad (1)$$

The permeability can be computed in the following way. Suppose that a plane is passed through the porous medium perpendicular to the x-axis at x. All of the $W(A, L, x, t)$ $dAdLw^2dx$ parallel pores contained in volume w^2dx will intersect the plane together with a number of other pores whose center of volume lies outside of the volume w^2dx if the pore lengths are much larger than dx. On the other hand, if the pore lengths are on the average much smaller than dx, only a fraction of the pores will pass through the plane. In most systems of interest, pore lengths are much less than the distance over which changes in the average pore structure take place and the latter situation will be the one considered in the arguments to follow. This being the case, the probability that certain pore contained in volume w^2dx about x will intersect the plane is L/dx since the pores are randomly distributed. Thus of the $WdAdLw^2dx$ pores $LWdAdLw^2$ of them intersect the plane.

Note that the assumption of randomness in the spatial distribution yields a void area per unit area to equal the void volume per unit volume. This can be seen by multiplying the number of pores intersecting the plane by their respective areas. If this result is summed over all possible areas, the total void area of the plane is obtained. Thus the fraction void area is shown to be

$$(\phi)_{\text{area}} = \int_o^\infty \int_o^\infty ALW(A, L, x, t)\,dAdL$$

which is identical to the fraction of volumetric voids expressed by Equation (1).

To determine the permeability, the total volume of fluid passing through the plane perpendicular to x must be found. If the fluid in the pores is in steady laminar flow, the mean velocity, $\overline{v}$, in each pore is proportional to the area [this is the essential result necessary to develop the Kozeny equation (*37*)] and thus

$$\overline{v} = \epsilon A \qquad (2)$$

where ϵ is a factor which depends on the pressure gradient, viscosity, and pore geometry. By dimensional arguments

$$\epsilon = -\,(\text{Geometric Factor})\,\frac{1}{\mu}\,\frac{\partial p}{\partial x} \qquad (3)$$

where μ is the viscosity and the $\partial p/\partial x$ is the pressure gradient. ϵ is therefore the same for each pore since they are geometrically similar. The volumetric flow rate, q, through the plane can be found by summing the volume flowing through each of the pores which intersect the plane. Thus,

$$q = w^2 \int_o^\infty \int_o^\infty \overline{v}\,ALW(A, L, x, t)\,dAdL$$

$$= \epsilon w^2 \int_o^\infty \int_o^\infty A\overset{2}{L}W(A, L, x, t)\,dAdL \qquad (4)$$

Since Darcy's Law is

$$q = \frac{-w^2K}{\mu}\,\frac{dp}{dx} \qquad (5)$$

the permeability, K, defined by Equation (5) can be identified using Equations (3) and (4) as

$$\frac{K(x, t)}{K(x, o)} = \frac{\displaystyle\int_o^\infty LA^2W(A, t, x, t)\,dAdL}{\displaystyle\int_o^\infty LA^2W(A, L, x, o)\,dAdL} \qquad (6)$$

whereby taking ratios it is seen that the geometric factors cancel. Of course, this result is dependent on the maintenance of geometric similarity during the evolution from the initial pore structure to that at time t.

More general treatments are perhaps possible, as for example, the restriction of geometric similarity might be relaxed and other assumptions substituted; however, the simplified model used here contains more information than is generally available and it is in fact necessary in the present state of the art to make certain simplifications rather than increase the complexity of the system. A simplification can be achieved by writing

$$W(A, L, x, t)\,dA\,dL\,w^2dx = \eta(A, x, t)\,P(L)\,w^2dA\,dL\,dx \tag{7}$$

where $P(L)$ is defined to be the fraction of the pores having a length between L and $L + dL$. Equation (7) implies that any set of pores will exhibit the same distribution of pore lengths without regard for pore area. This assumption is probably false. One might expect that pores having larger areas will also on the average be longer. However, data giving both distributions of pore areas and lengths are not available.

The function $P(L)$ is restricted so that $\int_0^\infty P(L)dL = 1$ and $w^2\eta(A, x, t)\,dA\,dx$ can be correctly regarded as the number of pores in w^2dx having an area A irrespective of length. The porosity reduces to

$$\phi = \overline{L}\int_0^\infty A\ \eta(A, x, t)\,dA \tag{8}$$

where the mean pore length $\overline{L}$ is given by $\int_0^\infty LP(L)dL$.

These preliminary considerations have aimed at isolating the quantities of interest so that the model and its evolution can be now represented in mathematical terms. Progress can only be made through such a representation because of the complexity of the process. The formal definitions and idealizations have indicated that the reduced density function $\eta(A, x, t)$ is the quantity of real interest as the properties of the porous medium (at least their ratios) can be computed using η.

Before the change in η with time can be determined, the fluid-solid interaction must be defined. It is convenient at this point to leave this question open and to use the general form

$$\frac{dA}{dt} = \psi(A, x, t) \tag{9}$$

Here ψ is a function which determines the growth rate of a pore having a particular size. The function ψ is, of course, different from situation to situation, and must be derived for each individual case. The case of matrix acidization is treated in the following sections.

There are two mechanisms by which a pore can change its area. First, its area can be changed by the action of the invading fluid the rate of this change being given by Equation (9). Secondly, there is the possibility that a growing pore (ψ positive) will collide with a neighboring pore. Thus, if attention is focused on a certain group of pores, namely, those having an area between A_l and A_u at time t in volume w^2dx about x, then the number of pores in the group is given by

$$\int_{A_l}^{A_u} w^2dx\ \eta\ (A, x, t)\,dA$$

Since the areas of all of the pores change in time, then to bracket the same group of pores during a certain time interval both the smallest A_l, and the largest A_u areas must depend on time. If in fact, these two areas are forced to change in accordance with Equation (9), then the total number of pores obtained by performing the required integration at various time would remain constant except for those entering and leaving the group owing to collisions. If the number of collisions per unit of time per unit of volume resulting in the creation of a pore with area A is called $\{\Delta\eta_c\}$ and if similarly the number of collisions per unit of time per units of volume resulting in the destruction of a pore of radius A is denoted by $\{\Delta\eta\}_D$, then certainly

$$\frac{d}{dt}\int_{A_l(t)}^{A_u(t)} \eta(A, x, t)\,dA = \int_{A_l(t)}^{A_u(t)} [\{\Delta\eta\}_c - \{\Delta\eta\}_D]\,dA \tag{10}$$

that is, only by creation or destruction can a pore leave the group $A_u \leqq A \leqq A_l$ when the limits change in accordance with Equation (9). With the aid of Leibnitz's rule Equation (10) can be written as

$$\int_{A_l}^{A_u}\left[\frac{\partial\eta}{\partial t} + \frac{\partial}{\partial A}(\psi\eta) - \{\Delta\eta\}_c + \{\Delta\eta\}_D\right]dA = 0$$

Since both A_u and A_l are arbitrary, the integrand must vanish as follows:

$$\frac{\partial\eta}{\partial t} + \frac{\partial}{\partial A}(\psi\eta) - \{\Delta\eta\}_c + \{\Delta\eta\}_D = 0 \tag{11}$$

The net rate of creation is obtained from the following arguments. Consider a pore having an area A_2. After a time dt has elapsed, this pore will have an area $A_2 + \psi(A_2)dt$ and therefore, a volume $\overline{L}\ (A_2 + \psi_2\ dt)$ [with $\psi(A_2, x, t) \equiv \psi_2$]. The total change in the volume of all pores having this area is the number of such pores, $w^2\eta(A_2, x, t)dA_2dx$, multiplied by the increase in volume per member. Thus $w^2\overline{L}\eta_2\psi_2dtdA_2dx$ is the volume increase of all pores having an area between A_2 and $A_2 + dA_2$ in volume w^2dx about x during time interval dt. How many pores having an area A_1 will occupy this same volume and as a consequence collide with pores of area A_2? The pores are randomly distributed and therefore, the total number of pores having an area A_1 which are in the volume $w^2\overline{L}\eta_2\psi_2dtdA_2dx$ is the same as any other volume element of equal size in the larger volume w^2dx. Since the number of pores of A_1, per unit volume is η_1dA_1, the total number of collisions is therefore, given as $w^2\overline{L}\eta_2\eta_1\psi_2dA_2dA_1dtdx$. Not all of these collisions, however, produce a pore of area A. Indeed only those for which the sum of areas of the colliding pores is equal to A contribute to the total number of pores having that area, that is, a contribution to A occurs if

$$A = A_1 + A_2 \tag{12}$$

The total rate of creation is obtained by summing all such collisions so that

$$\{\Delta\eta\}_c = \overline{L}\int_0^A \psi(A_2, x, t)\,\eta(A - A_2, x, t)\,\eta(A_2, x, t)\,dA_2 \tag{13}$$

The upper limit on this integration is A since any collision between two pores either one of which having an area larger than A cannot yield a resulting pore with area A.

The rate of destruction per unit volume is obtained by counting the number of collisions between pores of area A in a unit volume per unit time and all other pores for each such collision represents a loss of a pore having area A. Pores of area A_2 can increase their volume during time dt and encounter pores of area A and of course, pores of A grow during the same time period and collide with A_2.

The result is the same in any case since a pore having area A is destroyed. The volume change of a pore having an area A_2 is $\overline{L}\,\psi_2 dt$ and the total volume change in w^2dx is $w^2\overline{L}\psi_2\eta_2 dA_2dxdt$. Taking this volume and multiplying by the number of pores of A per unit volume yields the number of collisions in volume w^2dx during time dt owing to the growth of A_2. This number is

$$w^2\overline{L}\psi_2\eta_2\eta \quad dA_2dAdxdt$$

Similarly, the number of collisions due to the growth of A is

$$w^2\overline{L}\psi\eta_2\eta dAdA_2dxdt$$

The total number of destructions per unit time per unit volume is

$$\{\Delta\eta\}_D = \overline{L}\int_o^\infty [\psi(A, x, t) + \psi(A_2, x, t)] \eta(A_2, x, t)\eta(A, x, t)dA_2 \qquad (14)$$

The evolution of the pore size distribution resulting from a changing pore area at a rate given by ψ is then

$$\frac{\partial\eta}{\partial t} + \frac{\partial(\psi\eta)}{\partial A} = \overline{L}\left\{\int_o^A \psi(A_2, x, t)\eta(A - A_2, x, t)\eta(A_2, x, t)dA_2 - \int_o^\infty [\psi(A, x, t) + \psi(A_2, x, t)] \eta(A, x, t)\eta(A_2, x, t)dA_2\right. \qquad (15)$$

This nonlinear integrodifferential equation is a very complex one to solve having an appearance very similar to the classical Boltzmann equation (*7*) which describes the distribution of velocities and positions of molecules in a dilute gas. The term on the right-hand side of Equation (15) then corresponds to the molecular collision term which is also second-order in the distribution function. Other evolution equations are found in the field of aerosols (*18, 19*), crystal size distribution in crystallizers (*14, 19, 30*), the distribution of ages in biological systems (*12, 39*), the area of catalyst particles in a chemical reactor (*35*), the coalescence of drops (*40*), and grinding (*31*).

Equation (15) is, as has been noted, complex and difficult to integrate by other than numerical means and even this approach may be difficult. Several solutions for special cases are, however, possible and the two such solutions of interest here are developed.

If collisions can be ignored or possibly do not exist because ψ is negative, then the right-hand side of Equation (15) vanishes and the solution of the resulting equation is

$$\eta(A, x, t) = \frac{\eta(\beta, x, o)\psi(\beta, x)}{\psi(A, x)} \qquad (16)$$

where β is defined so that

$$t = \int_\beta^A \frac{d\lambda}{\psi(\lambda, x)} \qquad (17)$$

The solution is subject to the further restriction that ψ not depend explicitly on time. This result will be of particular value in the evolution under the influence of infinite reactivity where matrix acidization with a fast acting acid is considered.

The second solution which has application in this paper is found in the special case

$$\psi = f(x, t)A \qquad (18)$$

that is, when the rate of pore growth is proportional to the area. In this case the evolution equation takes the form

$$\frac{\partial\eta}{\partial\tau} + \frac{\partial}{\partial A}(A\eta) = \overline{L}\left\{\int_o^A A_2\eta(A - A_2, \tau)\eta(A_2, \tau)dA_2 - \int_o^\infty [A + A_2]\eta(A, \tau)\eta(A_2, \tau)dA_2\right\} \qquad (19)$$

where

$$\tau = \int_o^t f(x, t)dt \qquad (20)$$

This equation still appears complex being a nonlinear integrodifferential equation, however, it is susceptible to a rather simple solution if approached by solving for the moments rather than the distribution function. Moreover, a knowledge of all of the moments of a distribution function is essentially equivalent to complete knowledge of the function itself since the mean value of any property can be determined using the moments (*9*). Define as the jth moment

$$M_j(\tau) = \int_o^\infty A^j\eta(A, \tau)dA \qquad (21)$$

for $j = 0, 1, \ldots.$

A moment equation can be developed by multiplying Equation (19) by A^j and integrating the resultant equation between the limits of zero and infinity. The moment equation found by this procedure is

$$\frac{\partial M_j}{\partial\tau} - jM_j = \overline{L}\left\{\sum_{s=0}^{j} \frac{j!}{j - s!s!} M_sM_{j-s+1} - M_oM_{j+1} - M_1M_j\right\} \qquad (22)$$

for $j = 0, 1, \ldots.$

These equations interrelate the moments of the pore size distribution within the framework of a hierarchy of coupled differential equations. The task of solving these equations is not as formidable as it might appear on first inspection. The best approach is to first solve this equation for $j = 1$ as it is then uncoupled from the remaining equations. The solution for M_1 is

$$\frac{M_1}{M_1^{(o)}} = e^\tau \qquad (23)$$

where $M_1^{(o)}$ is the known initial first moment. Since this is a study in evolution, the initial state must be specified. Solving the moment equation with $j = 0$ gives

$$\frac{M_o}{M_o^{(o)}} = \exp - [\overline{L}M_1^{(o)}\ (e^\tau - 1)] \qquad (24)$$

Integrating for $j = 2$

$$\frac{M_2}{M_2^{(o)}} = \exp 2\,[\tau + \overline{L}\,M_1^{(o)}\ (e^\tau - 1)] \qquad (25)$$

and in general (for $j > 2$)

$$M_j = M_j^o \left[\frac{M_2}{M_2^{(o)}}\right]^{\frac{j}{2}} + \overline{L}\left[\frac{M_2}{M_2^{(o)}}\right]^{\frac{j}{2}} \int_o^t \left[\frac{M_2(\epsilon)}{M_2^{(o)}}\right]^{\frac{-j}{2}} \left.\sum_{s=2}^{j-1} \frac{j!}{j - s!\,s!} M_s(\epsilon)M_{j-s+1}(\epsilon)\right\} d\epsilon \qquad (26)$$

Equation (26) may be used to generate the moments sequentially starting with $j = 3$. In this way the right-hand side depends only on those moments which have already been computed. Thus by a process involving multiple integration all of the moments can be generated and the solution of the evolution equation for the special case of the growth rate being proportional to the area has been accomplished. If the growth rate is independent of the area, this approach of solving the moment equation is also fruitful; however, if the growth rate depends on the area taken to powers greater than unity this approach is not successful without introducing some further assumptions. The hierarchy of equations in the case of $\psi = fA^l$ with $l > 1$ cannot be solved sequentially. This situation is similar to that encountered in the molecular theory of liquids (*10*).

The model has been utilized to its fullest extent without detailing the mechanism of the fluid solid interaction. This aspect is studied next with the special case of reactions at the solid surface being considered.

SURFACE REACTIONS WITHIN THE PORE STRUCTURE

To find the growth rate of a pore having an area A the details of the interaction between the fluid and the solid must be investigated. The particular situation of interest in this work is that which exists when the fluid flowing in the pore is reactive and the reagent concentration is therefore depleted as the fluid progresses along the pore. This situation is depicted in Figure 2 where it is shown that the concentration of the reactant at the axial position z and the point $\{x_1, x_2\}$ in the cross section is $C_p(z, x_1, x_2, t)$. A mass balance on the reacting substance may, neglecting diffusion in one direction, be written as

$$\frac{\partial C_p}{\partial t} + v(x_1, x_2)\frac{\partial C_p}{\partial z} = D\left\{\frac{\partial^2 C_p}{\partial x_2^2} + \frac{\partial^2 C_p}{\partial x_1^2}\right\}$$

where C_p is the reactant concentration in the pore, v is the axial velocity, D is the diffusion coefficient, z is the axial position measured from the pore entrance, and x_1 and x_2 are position vectors defining a point in A. The particular pore being considered can be located arbitrarily in the matrix so that the concentration of reactant at the pore entrance will depend on both time and the pore position relative to the point of injection, x. Thus,

$$C_p = C(x, t) \quad \text{at} \quad z = 0 \tag{28}$$

A second boundary condition to be satisfied is

$$-D\left\{\frac{\partial C_p}{\partial x_1}n_1 + \frac{\partial C_p}{\partial x_2}n_2\right\} = k\ C_p \quad \text{on } \Gamma \tag{29}$$

This particular equation merits some discussion for it is at this point that the rate of reaction is introduced into the problem. The term on the left-hand side represents the diffusion to the wall with n_1 and n_2 being the x_1 and x_2 components of the outward drawn normal. As the reactant diffuses to the wall, it reacts and the rate is expressed by the right-hand side of Equation (29). Here k is a kinetic constant for the reaction at the wall which is assumed first-order with respect to concentration. [A first-order relationship has been found experimentally by Hendrickson, et al. (*17*) for the case of acid-limestone reactions which is the system of prime interest here.]

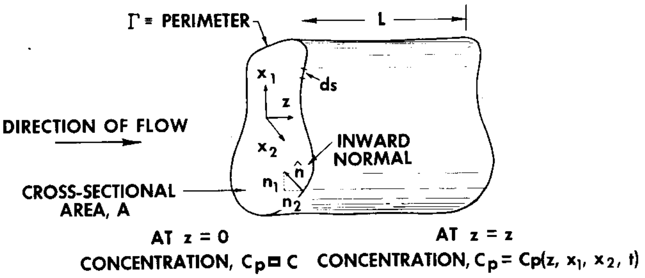

Fig. 2. Coordinate system associated with a single pore.

Initially, there is no reactant present in the pore, that is,

$$C_p = 0 \quad \text{for} \quad t = 0 \tag{30}$$

Define an average concentration at each axial position as

$$\overline{C_p} = \frac{1}{A}\int_A C_p\, dx_1\, dx_2$$

Equation (27) can be written as

$$\frac{\partial \overline{C_p}}{\partial t} + \frac{1}{A}\int_A v\frac{\partial C_p}{\partial z}dx_1\, dx_2 = \frac{D}{A}\int_\Gamma \left\{\frac{\partial C_p}{\partial x_1}n_1 + \frac{\partial C_p}{\partial x_2}n_2\right\}ds \tag{31}$$

after using Green's theorem, where ds is an element of arc along the curve Γ.

At this point introduce the approximation

$$\frac{1}{A}\int_A v\frac{\partial C_p}{\partial z}dA = \overline{v}\frac{\partial \overline{C_p}}{\partial z} \tag{32}$$

and Equation (31) reduces to

$$\frac{\partial \overline{C_p}}{\partial t} + \overline{v}\frac{\partial \overline{C_p}}{\partial z} \cong -\frac{1}{A}\int_\Gamma kC_p ds \tag{33}$$

To solve this differential equation the value of C_p on Γ must be related to $\overline{C_p}$. One approximation has already been made, that being expressed by Equation (32), and a second is required.

A quantity α is defined by

$$\alpha = \frac{\frac{1}{\Gamma}\int_\Gamma C_p ds}{\overline{C_p}} \tag{34}$$

where α is the ratio of the mean surface concentration to the mean bulk concentration. It is asserted that α is dependent on the pore geometry, the diffusion coefficient and the reaction velocity constant; but is independent of time and axial position along the pore. This is the second approximation.

Equation (33) can be integrated to give

$$\overline{C_p} = C\left(x, t - \frac{z}{\overline{v}}\right)\exp\left\{-\frac{\alpha k\Gamma}{A\overline{v}}z\right\} \text{ for } t > \frac{z}{\overline{v}} \tag{35a}$$

and

$$\overline{C_p} = 0 \text{ or } t \leq \frac{z}{\overline{v}} \tag{35b}$$

$C(x, t)$ is the reactant concentration at the pore entrance.

Consider now the rate of change of pore cross section with time. Suppose that during the time interval dt an amount $kdt \int_\Gamma C_p ds$ reacts per unit length of pore. Therefore, $\gamma kdt \int_\Gamma C_p ds$ g. of solid will dissolve if γ is defined as the grams of solid dissolved per gram of reactant. This action will result in an increase in the pore area from A to $A + dA$. If ρ_s is the density of the solid, then

$$\rho_s dA = \gamma kdt \int_\Gamma C_p ds$$

or

$$\frac{dA}{dt} = \frac{\gamma\alpha k}{\rho_s} \Gamma \, \overline{C}_p \tag{36}$$

Equation (36) is too detailed for the applications considered in this paper. It shows the local change in area of the pore along its axis. It is sufficient here to know the average rate of change of area for a given pore. Define

$$\left(\frac{dA}{dt}\right)_{\text{avg.}} = \frac{1}{L}\int_o^L \frac{dA}{dt}\, dL \tag{37}$$

Substituting Equations (35) and (36) into (37) gives

$$\left(\frac{dA}{dt}\right)_{\text{avg.}} = \frac{\alpha\gamma k\Gamma}{\rho_s L}\int_o^L C\left(x, t, -\frac{z}{\overline{v}}\right) \exp\left\{-\frac{\alpha k\Gamma z}{A\,\overline{v}}\right\} dz \tag{38}$$

The time scale over which the concentration varies at a particular point is most often much greater than $L/\overline{v}$ since the average pore lengths are normally very small compared to the dimensions of the porous medium being studied.

$C(x, t)$ will not vary significantly during time $L/\overline{v}$ and Equation (38) can be simplified to the form

$$\left(\frac{dA}{dt}\right)_{\text{avg.}} = \frac{\alpha\gamma k C(x,t)\Gamma}{\rho_s L}\int_o^L \exp\left\{-\frac{\alpha k\Gamma z}{A\,\overline{v}}\right\} dz \tag{39}$$

Giving the growth rate as

$$\psi = C(x, t)\,\frac{\gamma A\overline{v}}{\rho_s L}\left[\,1 - \exp\left\{-\frac{\alpha k\Gamma L}{A\,\overline{v}}\right\}\right] \tag{40}$$

The quantities A and Γ are now interpreted as averages and owing to insufficient knowledge of the distribution function $P(L)$, L is now set equal to $\overline{L}$ in all applications of Equation (40).

Equation (40) shows that the rate of increase in area is linear in the concentration of the reactant and also depends on a knowledge of the pore geometry (A, Γ, L), the surface dissolution rate (k, γ), the matrix density (ρ_s), the mean pore velocity ($\overline{v}$), and the ratio of the mean surface concentration to the mean bulk concentration (α). All of these parameters are well-defined except α. To determine α, one must specify the shape of the pore. However, subsequent analysis will show that this important ratio is not particularly sensitive to the configuration of the pore. The demonstration of this fact consists of solving for α in several special cases, namely for circular, square and rectangular cylinders all without flow and comparing the variation in α among these cases. As an example consider the pore to be a circular cylinder. For no flow, the concentration of reactant in the pore is defined by

$$\frac{\partial C_p}{\partial t} = D\frac{1}{\theta}\,\frac{\partial}{\partial\theta}\left(\theta\frac{\partial C_p}{\partial\theta}\right) \tag{41}$$

with the boundary condition at the wall

$$-D\frac{\partial C_p}{\partial\theta} = k\ C_p \quad \text{at} \quad \theta = r \tag{42}$$

where θ is the position vector denoting distance measured from the center of a cylinder having a radius r. This system of equations has the solution

$$C_p(\theta, t) = \sum_{i=1}^{\infty}\ e^{-\lambda_i^2\frac{Dt}{r^2}} A_i J_0\left(\lambda_i\frac{\theta}{r}\right) \tag{43}$$

where J_0 is the Bessel function of zero order and the first kind. The eigenvalues, λ_i, satisfy the equation

$$\lambda_i\, J_1(\lambda_i) = \frac{kr}{D}\, J_0(\lambda_i) \tag{44}$$

where J_1 is the Bessel function of order one. This expression determines a series of discrete values of λ_i which depend on kr/D. Representative values of the smallest of the discrete values, λ_i, are given in Table 1. Since λ_1 is the smallest eigenvalue [with $\lambda_i \cong (i-1)\,\pi + \lambda_1$], after a sufficient time has elapsed ($Dt/r^2 > 1$) only the first term in the series defined by Equation (43) will survive and one finds

$$\alpha = \frac{(C_p)_{\theta=r}}{\overline{C_p}} = \frac{D}{2kr}\,\lambda_1^2 \tag{45}$$

The value of λ_1 is tabulated as a function of the dimensionless parameter kr/D in Table 1.

TABLE 1. SMALLEST EIGENVALUES FOR VARIOUS SHAPES

	Square of side length, *a*	Rectangle where side *a* is half side *b*	Rectangle where side *a* is ¼th side *b*	Circle of radius *r*
r_ϵ/a	1	4/3	8/5	1
kr_ϵ/D	λ^2* 1	λ^2 1	λ^2 1	λ^2† 1
0.002	0.004	0.0039	0.0039	0.004
0.02	0.04	0.0386	0.0386	0.04
0.2	0.375	0.369	0.368	0.38
1.0	1.53	1.48	1.52	1.59
2.0	2.32	2.36	2.46	2.54
10.0	4.08	4.4	5.07	4.75
20.0	4.50	4.90	5.79	5.25
∞	4.94	5.48	6.71	5.76

* Appendix IV, (*6*).
† Appendix IV, (*6*).

A similar analysis to that shown for circular cylinders is also possible for rectangular cylinders with the result being precisely the same as that given by Equation (45) provided the radius r appearing in this equation is interpreted as being twice the hydraulic radius (hydraulic radius equals the area normal to flow divided by the wetted perimeter, that is (A/Γ). Of course, the smallest eigenvalue, λ_1, differs from shape to shape, but this difference is in fact not large. These eigenvalues are given in Table 1 and it is seen that λ_1 is practically independent of geometry. Thus Equation (45) defines the value of α and this value is independent of geometry for our purposes. This is an essential result for at this point the growth rate of the pore is defined in terms of such basic quantities as the reaction rate, coefficient of diffusion, hydraulic radius of the pore and the fluid velocity within the pore. This is the detail needed to explore the evolution of a pore structure resulting from the reaction of the flowing fluid with the solid boundary.

The validity of our arguments hinge essentially on two assumptions namely those represented by Equations (32) and (34). It is possible to compare our solution with more general ones for certain special cases thereby gaining some insight into the reliability of our result.

One comparison in the time independent case is with the work of Brown (2), who has presented a very accurate solution to the Graetz-Nusselt (*20*) problem in heat transfer. If the reaction rate becomes very large, then Brown's heat transfer results should apply directly to the problem considered here. A comparison of the two solutions is a severe test of the validity of replacing the distribution of

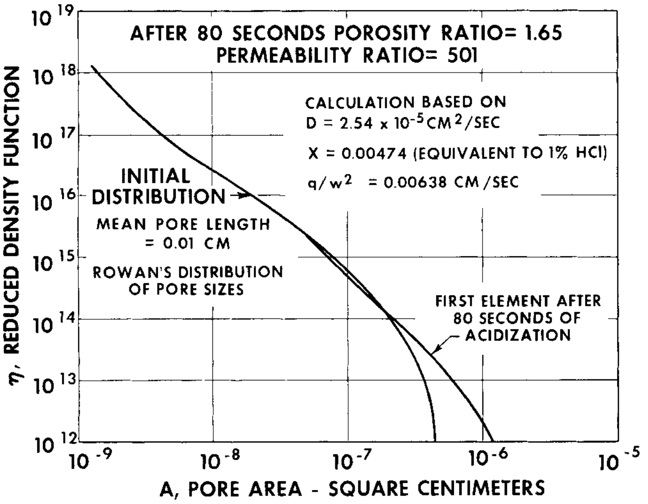

Fig. 3. Change in pore size distribution on acidization.

velocities by an average since Brown does not simplify the velocity distribution as is done here and also since the error incurred by ignoring the velocity variations is likely to be largest at the larger reaction rates. Comparing the ratio of the inlet to outlet reactant concentrations as given by Equation (35) (in the steady state) with the results of Brown; for $E = Dz/2r^2\overline{v} = 0.1$, our result is $\overline{C}_p/C = 0.561$ compared to Brown's more accurate value of 0.579 and for $E = 0.3$ our result is 0.176 whereas Brown finds 0.273. The percentage deviation continues to increase as E increases so that for large E the percentage error becomes extremely large, however, the acid has been depleted for all practical purposes and large errors here will not lead to any significant differences in the pore structure. The approximation is, however, about 30% in error when 25% of the reactant remains and there is, therefore, the possibility of improving the approximation by making a more sophisticated calculation repeating the Graetz-Nusselt problem for various levels of surface reactivity. This task has not been undertaken. Actually Katz (*22*) has considered the problem of surface reactions attending laminar flow of reactant in a circular tube, but his results being in the form of integral equations are too complex for our purposes. The approximation given here is in fact very similar to that used by Alwitt and Kapner (*1*).

EVOLUTION UNDER THE INFLUENCE OF INFINITE REACTIVITY

The particular application which has motivated this work is the matrix acidization of oil bearing porous rock. The practice of pumping acids into the porous formations containing oil is very wide spread and time honored, although little design of these operations has heretofore been possible due primarily to the lack of a reasonable model with which to correlate the experimental data. The primary information used to estimate the type, amount and addition rate of acid required for a given treatment is gleaned from core studies. A core is usually a cylindrical piece of porous rock mounted in such a way that fluid introduced at one end of the cylinder is constrained to flow parallel to the axis of the cylinder. No lateral leakage is permitted. The typical sizes of such cores range from ¼ to 2 in. in diameter and from 1 to 6 in. in length. A number of core experiments have been reported in which acid is pumped into the rock matrix at one face and collected at the other (*17, 21, 38*).

The effluent is sometimes analyzed as is the permeability increase. Such experiments cannot be used to quantitatively design the most effective methods of operations without further analysis; they do, however, provide a crude guide eliminating certain practices.

The early work of Rowan (*34*) has provided much of the conceptual framework upon which this mathematical treatment is based. Rowan properly considered matrix acidization as a process in which the pore structure is modified with pores of different areas being altered differently. There are two serious defects in Rowan's analysis which have tended to minimize the practical importance of his work. First of all the rate of acid attack does not enter into his calculations so that neither the diffusivity nor the surface reactivity play any role at all. These parameters are important and indeed provide the basis for understanding the experimental observations. The second defect in the Rowan calculation is that spatial and temporal changes in the pore size distribution are not considered. In the process of matrix acidization pores located near the point of acid injection will react with an acid having the inlet concentration. This reaction will deplete the acid to some extent and pores further removed from the point of injection will react with an acid which is less reactive. The progressive decay in the acid concentration along the flow path thus introduces a spatial and temporal dependence which must be understood to effectively model the process.

As an example of his method, Rowan computed the effect of acidization on a limestone having a pore size distribution very nearly that shown in Figure 3. Rowan supposed that each pore received a share of the acid proportional to the square of its area and that all of the entering acid is spent. Thus those pores having the larger areas receive the bulk of the acid thus becoming even larger than the others and gaining an even larger share of the input acid. This process which envisions continued preferential growth of the larger pores is in fact in some agreement with the experimental observations which indicate that a few pores grow to be rather sizeable, but in contradiction with Rowan's predictions, these larger pores reach a terminal size with growth proceeding, but at a greatly reduced rate. A typical example of the growth of these larger pores or wormholes is shown in Figure 4.

These photographs are of the face of an Indiana limestone core (7.68 cm. long and 2.50 cm. in diameter)

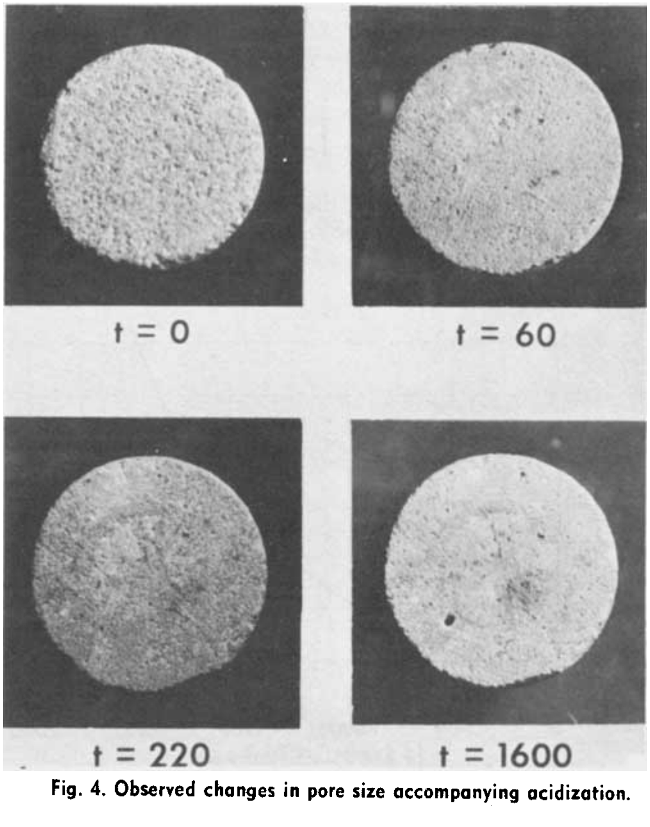

Fig. 4. Observed changes in pore size accompanying acidization.

through which acid (1% hydrochloric acid) at room temperature and 900 lb./sq.in. gauge pressure is being pumped at the rate of 0.0355 cc./sec. or equivalently at a superficial velocity of 0.00638 cm./sec. Periodically injection of acid was halted, a 3 wt. % brine solution used to flush the acid from the core and the face of the core photographed. The change of the pore sizes is seen as the larger pores grow. In this particular experiment as in most of the acidizing experiments performed in the laboratory, a few holes begin to conduct all of the fluid thus suppressing the growth of the others. Here a single hole has at the end achieved a dominate position. This hole has grown from an area approximately 0.0014 sq.cm. at the onset to a size of 0.036 sq.cm. after 1,600 sec. of contact with the acid. The growth of this pore is shown as a function of time in Figure 5 with the area being estimated by the use of a microscope.

The permeability of the core was also measured during the course of the experiment and these data are presented in Figure 6.

These observations cannot be predicted with calculations based on the capillaric model unless the acid reactivity is included in the analysis. If on the other hand the reactivity is properly considered in formulating the growth rate expression, wormholing can be understood. The calculations presented in this section are intended to show that the idealized capillaric model does in fact predict the result observed when a highly reactive acid is introduced into a rock matrix. To make these calculations, collisions are neglected. This is not a necessary assumption as the complete evolution equation including the collision terms can in principle be solved. The calculations are rather complex and hardly seem justified especially in view of the fact that a partial correction for the contribution of collisions is possible using the results of the following section.

The essential idea is to study the evolution of a particular system, namely the one whose pore size distribution is represented in Figure 3, under the influence of a very reactive acid with the hope of finding wormholes. These calculations form the basis of a possible design scheme for the engineering of acid treatments in practical systems.

If the surface reaction rate is large ($k \to \infty$), then for circular pores $\alpha \to (2.40)^2/2(D/kr)$ (see Table 1). For any other geometry the value of α is very nearly the same. Equation (40) reduces to the form

$$\psi = C(x,t)\,\frac{\gamma A\overline{v}}{\rho_s\overline{L}}\left\{1-\exp\left[-\frac{18.1\ D\overline{L}}{A\,\overline{v}}\right]\right\} \qquad (46)$$

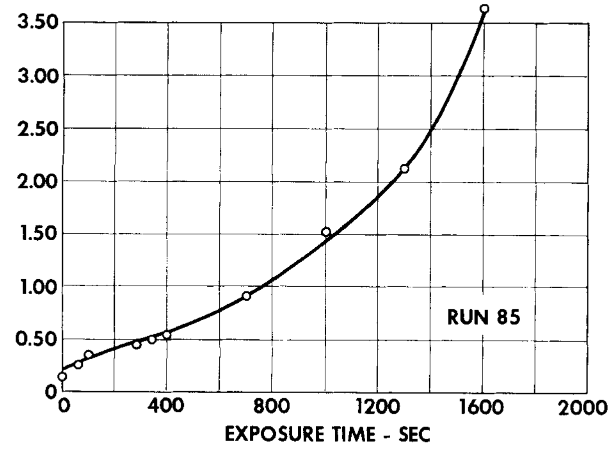

Fig. 5. Observed areal growth rate of the largest pore.

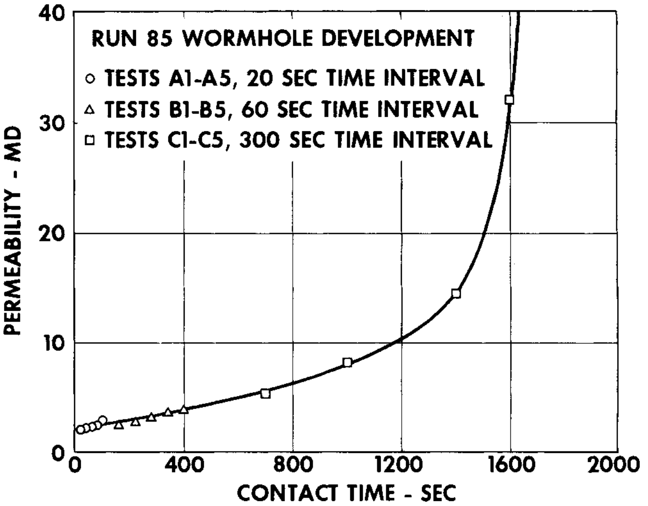

Fig. 6. Observed permeability.

As given by Equation (2), the velocity in a given pore is proportional to the area, that is, $\overline{v} = \epsilon A$, and since the sum of the volumetric flows in each pore must equal the total, then

$$q = w^2\int_0^\infty A\,\overline{v}\,\overline{L}\ \eta\ dA = \epsilon\ w^2\int_0^\infty \overline{L}\ A^2\ \eta\ dA = \epsilon K w^2 \qquad (47)^*$$

or $\overline{v} = q\ A/Kw^2$. Using this expression for the velocity, the growth rate becomes

$$\psi = FXA^2\left\{1-\exp\left[-\frac{18.1D}{FA^2}\right]\right\} \qquad (48)$$

where $F = q/K\overline{L}w^2$ and X is the dissolving power of the acid (volume of solid dissolved/volume of acid spent) The dissolving power [$X = C(x,t)\gamma/\rho_s$] depends of course, on the acid concentration and is therefore a function of both time and position.

Before describing the method of calculation and the results, it is possible to gain some insight into the mechanism of wormhole formation by examining Equation (48) more closely. If a pore becomes very large ($A^2F/18.1D > 1$), then $\psi \to 18.1\ DX$ or for a given dissolving power the growth rate approaches a constant. Thus regardless of the size it achieves a pore will continue to grow, but certainly not at a rate proportional to the area squared as postulated by Rowan and indeed for the larger pores, the percentage change over a given time interval becomes very small, a quasi-equilibrium is established and wormholing occurs. The growth in this latter circumstance has become diffusion limited. Wormholing is, therefore, a result of a preferential flow through large pores and a growth rate that is a diffusion limited process.

The calculation of the change in pore structure as a function of time and position is essentially a finite difference calculation wherein the concentration of acid at a particular position, x, within the porous medium is assumed to be constant over a small interval of time ranging from t to $t + \Delta t$. If the pore structure is assumed to be such that all of the pores have a length $\overline{L}$ (equivalent to taking a difference in x direction), then the evolution of the pore structure between the time t and $t + \Delta t$ is determined by Equations (16), (17), and (48) provided the concentration of acid can be fixed as a function of position. Equation (16) which was developed for growth rates which do not depend on time can be applied to determine the $\eta(A, x, t + \Delta t)$ given $\eta(A, x, t)$ since the growth rate does not change over this small time increment.

The remaining problem in determining the reduced density function at the new time is to devise a scheme for evaluating the acid concentration as a function of time. This can be accomplished by noting that Equation (35)

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[*] Here $K = \overline{L}M_2$ which is proportional to, but not equal to, the permeability. As noted in the second section of this paper, the true permeability is determined by using ratios as in Equation (6).

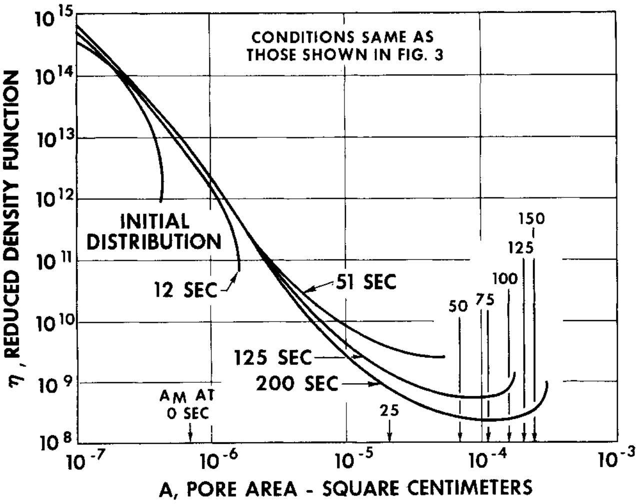

Fig. 7. Time change in pore structure of the first element.

together with the assumption that the residence of time of the acid within a single pore is small compared to the time over which macroscopic changes occur gives the ratio of outlet acid concentration from the pore to the inlet concentration as

$$\frac{C_{\text{out}}}{C_{\text{in}}} = \exp\left\{-\frac{\alpha k\Gamma}{A\,\bar{v}}\bar{L}\right\} = \exp\left(-\frac{18.1\ D}{FA^2}\right) \tag{49}$$

for fast reactions.

Equation (49) indicates that the acid concentration leaving a pore depends on the area of that pore. Since the model does not provide any information as to the dispensation of the acid leaving a particular pore, that is, no way of computing the particular pore area at the position $x + \bar{L}$ which will receive the acid entering a pore of area A at x, it is therefore, reasonable to assume that the acid is mixed after reacting in a group of pores. Thus if $C(x, t)$ is the concentration of acid at the position x and if $C(x + \bar{L}, t)$ is the concentration at $x + \bar{L}$, then

$$\frac{C(x+\bar{L}, t)}{C(x, t)} = \frac{\bar{L}\int_0^\infty A^2 \exp -\left(\frac{18.1\ D}{FA^2}\right)\ \eta(A, x, t)\,dA}{K(x, t)} \tag{50}$$

The method of computation can now be summarized. The particular core to be simulated is imagined divided into segments each being of length $\bar{L}$ and the time scale is likewise divided into increments of Δt. The change of the reduced density function in the first segment during time Δt is computed using Equations (16), (17), and (48) with the acid concentration being that of fresh acid and the permeability the initial one. The acid feed to the second segment is the outlet of the first as determined by Equation (50). Using therefore, the same calculations as for the first segment excepting that the inlet acid concentration is that leaving the first, the change in pore distribution of the second segment during the first time interval can be computed. This process is repeated for each successive segment until the acid is depleted.

The distribution of pore sizes is now known at the new time step. To continue new permeabilities are computed for each segment and precisely the same calculations are repeated.

After 80 sec. of contact with 1% hydrochloric acid the pore size distribution shown in Figure 3 is established and can be compared with the initial distribution. Since the calculation is based on the assumption that the collision term vanishes, the area under the reduced density function curve must remain constant with there being a corresponding decrease in the density of pores having a smaller area to compensate for any increase in the density of larger pores.

Figure 3 provides one very important and basic fact, that is, the smaller pores do not participate in the action because the volume of acid pumped into each pore is proportional to the square of its area. To characterize the response of a particular core, the distribution of the larger pores is critical. The change in the distribution of the larger pores is shown in Figure 7. Because the growth of the larger pores becomes diffusion limited, they seem to gather within a small range of pore area causing the density of pores in that range to increase markedly as seen in Figure 7 while the density of slightly smaller pores is reduced significantly. It should be remembered that the plot is a logarithmic one and while it might appear that smaller pores actually attain the same size as pores which were larger at an earlier time, such is not the case and a pore which is initially larger will always remain larger. The percentage difference between the areas of two pores may, however, become much smaller as is in fact indicated by the results shown in Figure 7.

In using Rowan's distribution function a maximum area of the pores was assumed to be 4.8×10^{-6} sq.cm. the largest pores indicated by Rowan had a radius of roughly 4μ which is 5×10^{-7} sq.cm., and it did not seem unreasonable that a very few pores would be ten times the area of the largest detectable with mercury injection techniques. The growth of the pore having the maximum area is also indicated in Figure 7. This area rapidly increases and then begins to climb steadily. To better illustrate the growth character of this maximum area, an equivalent diameter has been computed assuming that the pores are circular. The ratio of this diameter to its initial value is plotted in Figure 8. The first element grows more rapidly than the successive elements because the acid concentration is highest at the face of that element. At some instant of time the pores in the first element become sufficiently enlarged so that acid penetrates into the second. (Here after about 60 sec.) Sometime later the acid penetrates into the third and in this way progressive acidization takes place down the length of the core. Note that the percentage growth of the largest pore decreases continuously.

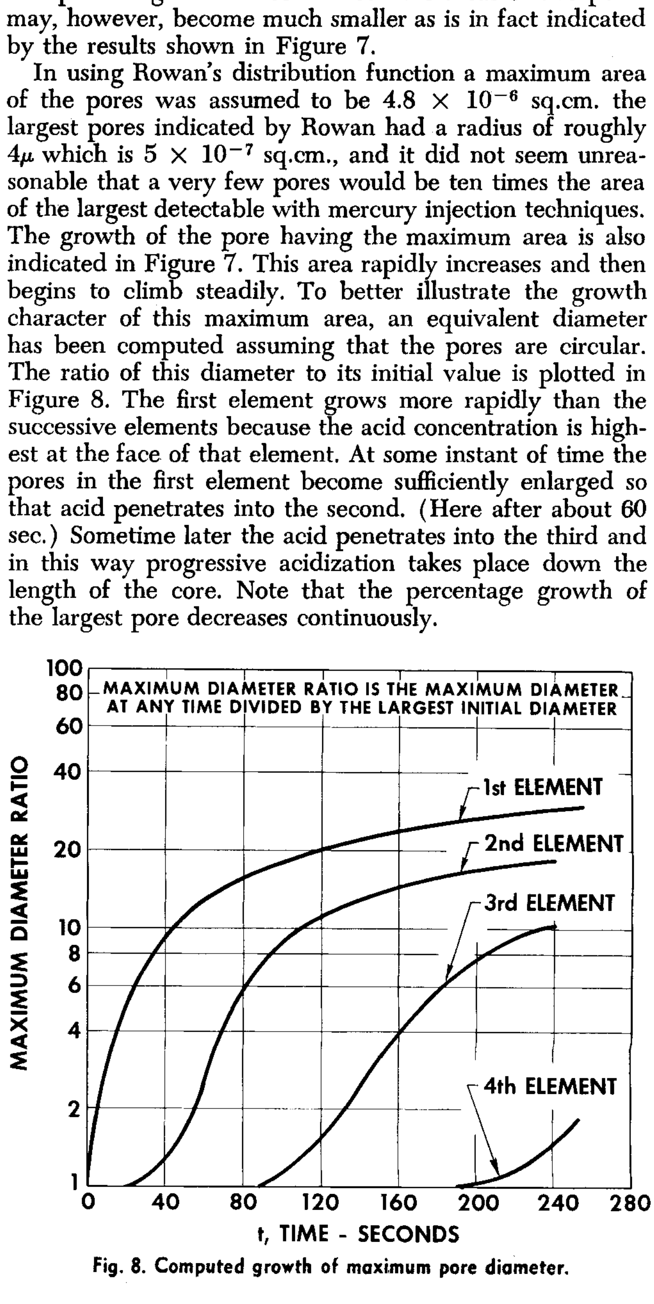

Fig. 8. Computed growth of maximum pore diameter.

The acid concentration is given in Figure 9 both as a function of time and position. The most significant feature of this graph is the approach of the outlet acid concentration from each element to a limiting level which is indeed surprising since the largest pores are continuously being enlarged and at first thought one might suspect that the concentration should therefore continue to increase. To understand these results, it must be remembered that the volumetric injection rate of acid is constant so that as the pores become larger the residence time of the fluid in the pores increases while the reaction rate decreases. These two compensating factors lead to a quasistationary state.

The concentration of acid leaving the first element relative to that at the inlet is approximately 0.56 at the quasistationary state (see Figure 9) while leaving the second element it is 0.31. Thus the same fraction of acid reacts in the first element as it does in the second ($0.31 \cong 0.56^2$). Moreover, the fraction of the acid expended in each element depends on the initial pore size distribution as will be seen in subsequent calculations.

The permeability change for each element is seen in Figure 10 to increase rapidly as acid contacts the particular element.

All of the calculations presented in this paper have been based on the pore size distribution given by Rowan and would therefore not be expected to apply to the results obtained experimentally by acidization of the Indiana limestone core. Nevertheless, some very interesting comparisons can be made.

The diffusion model suggests that the growth rate (dA/dt) of the larger pores should be given as 18.1 DX which for 1% hydrochloric acid is 0.22×10^{-5} sq.cm./sec. The area of a number of pores was measured using a microscope to observe the photographs and the rate of growth calculated. The average growth rate of these pores was found to be 0.6×10^{-5} sq.cm./sec. during the first 220 sec. of operation with the two pores which become very large in the late stages of acidization (see Figure 4) growing at the rate of about 1×10^{-5} sq.cm./sec. While the observed growth rate is somewhat higher than that calculated, this fact is not too surprising because of the laminar flow assumption made at the outset. The wormholes observed experimentally have highly tortuous paths and secondary flow induced by this path tortuosity must certainly increase the mass transfer rate. Further improvement in this approximation may be necessary. Nevertheless, the rates of growth are predicted to within the correct order of magnitude by this model.

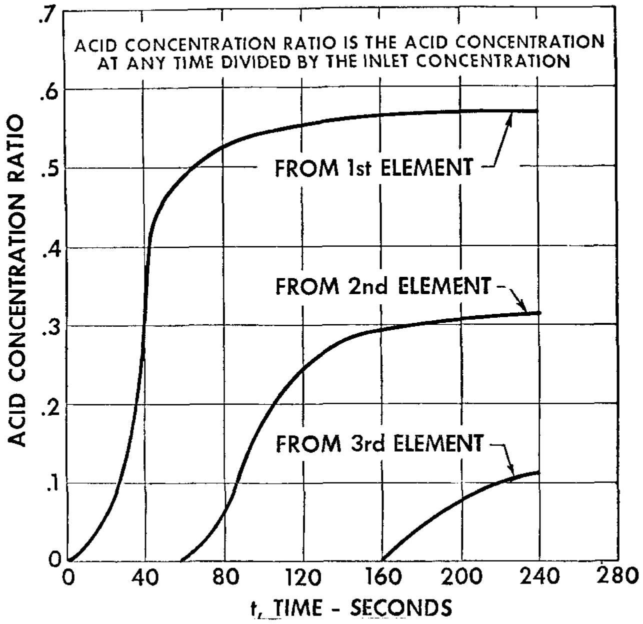

Fig. 9. Variation of concentration during acidization.

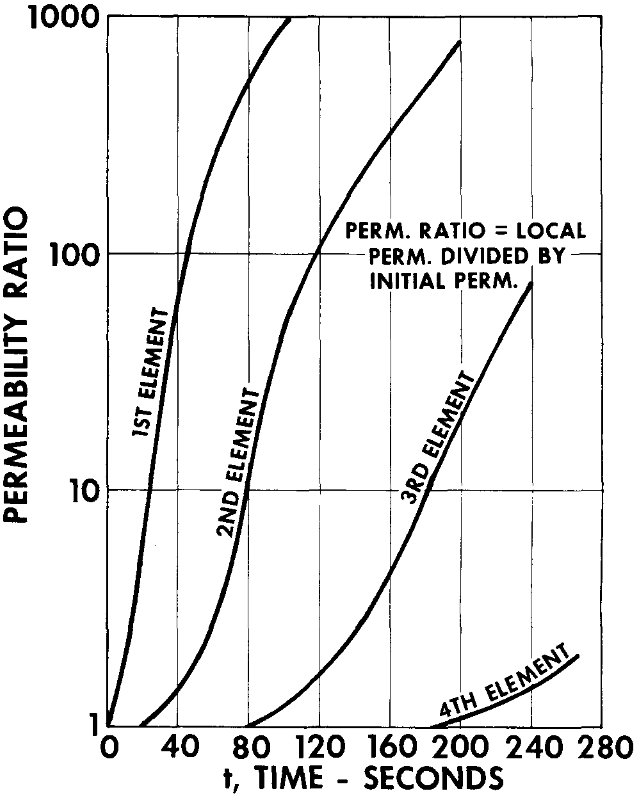

Fig. 10. Permeability increase with time.

Calculations with the diffusion model reveal that the acid front had advanced only 0.05 cm. into the core after 220 sec. had elapsed which would indicate this front would not break through a 7.68 cm. core until times much longer than the measured 1,600 sec. had elapsed. This rate of advance is, however, very dependent on the initial pore size distribution and the reduced density function used in the calculations had as its largest pore one having an area of 4.8×10^{-6} sq.cm. whereas an examination of photographs such as those of Figure 4 revealed a number of pores in the Indiana limestone with areas in excess of 1×10^{-3} sq.cm. To show the effect of the larger pores the reduced density function shown in Figure 3 was modified so as to add a few larger pores. The magnitude of the modifications is best seen by examining the moments given in Table 2. Two modifications were made, one of which was rather small changing the second moment by about 25% while leaving the first two moments unaffected (modification no. 1). The second change significantly altered the second moment as well as the first moment to some extent. The difference in behavior was dramatic. The second modification gave acid instantly penetrating through 0.1 cm. of core whereas the first modification showed a penetration of 0.06 cm. only after 96 sec., thus giving dramatically different results depending on the distribution of large pores in the system.

The model of the acidization process proposed here is

TABLE 2. INITIAL MOMENTS OF PORE SIZE DISTRIBUTION FUNCTION

Model	Moments M_0(cm.$^{-3}$)	M_1(cm.$^{-1}$)	M_2(cm.)
Rowan	7.3418×10^9	26.052	0.15×10^{-5}
Modification #1	7.3418×10^9	26.054	0.19×10^{-5}
Modification #2	7.3418×10^9	26.272	4.15×10^{-5}

Note: M_0, M_1 and M_2 are proportional to the number of pores per unit volume, the porosity and the permeability, respectively.

able to yield the essential features of the experimental observations and progress is now being made in a program to test the model further by determining pore size distributions for cores which are to be acidized subsequently.

In revealing the growth of wormholes, this model provides the first prediction of a fact long observed experimentally, but heretofore lacking a quantitative mechanistic explanation.

RETARDED ACIDS

Some energy has been devoted to the task of reducing the rate at which hydrochloric acid solutions react with limestone (*15, 36, 37*) so that greater depth of penetration can be attained. Commonly used acids provide a more than adequate increase in permeability in the region invaded by nondepleted acid. Thus, if acid strength could be conserved so that a greater region could be affected, a greater improvement in the conductivity of the system might be achieved. The effect of very highly retarded acid can be understood within the framework of the capillaric model.

A very highly retarded acid would be so inert that during the time of pumping it into the oil reservoir (porous medium) no reaction would take place. After a long time has elapsed, the acid will finally become expended. The changes in the pore structure of that portion of the total porous medium which has been invaded by acid is to be calculated with particular attention devoted to the conditions existing at the termination of the reaction.

On injecting the highly retarded acid each pore in the invaded region will contain a mass of acid $A\bar{L}C_o$ where C_o is the initial acid concentration. As the reaction proceeds this mass is depleted and the area of the pore increases as follows:

$$\rho_s \bar{L}\frac{dA}{dt} = -\gamma\,\bar{L}\,\frac{d}{dt}(AC)$$

where C is the acid content in the pore at time t.

Solving for dA/dt gives

$$\frac{dA}{dt} = -A\,\frac{\dfrac{\gamma}{\rho_s}\dfrac{dC}{dt}}{1+\dfrac{\gamma}{\rho_s}C} = -A\frac{d}{dt}\ln\left(1+\frac{\gamma}{\rho_s}C\right) = A\,f(t) \qquad (51)$$

The growth rate is thus seen to be linear in the area and the solution previously obtained through the use of moments is applicable (see the third section) with the important quantity τ defined by Equation (20) being given for this case by

$$\tau = \ln\frac{1+\dfrac{\gamma}{\rho_s}C_o}{1+\dfrac{\gamma}{\rho_s}C(t)} \qquad (52)$$

The final conditions are of prime interest and since the process ceases when

$$C(t) = 0, \quad \tau_f = \ln\left(1+\frac{\gamma}{\rho_s}C_o\right)$$

with the subscript f being appended to denote a final state property.

The number of pores destroyed by collisions is determined by Equation (23) which is

$$\frac{M_o^{(f)}}{M_o^{(o)}} = \exp-\left(\bar{L}\,M_1^{(o)}\frac{\gamma}{\rho_s}C_o\right) = \exp-(\phi_o X) \qquad (53)$$

where ϕ_o is the initial porosity $[\phi_o = \bar{L}\,M_1^{(o)}]$ and X is the dissolving power of the acid used (volume of rock dissolved per volume of acid expended). This equation shows that the number of pores decreases as would be expected since the result of a collision is to replace the two colliding pores by a single one.

The change in porosity is simply related to the volume of rock dissolved as is given by Equation (24)

$$\frac{\phi_f}{\phi_o} = 1 + X \qquad (54)$$

The change in permeability expressed generally by Equation (25) is given here by

$$\frac{K_f}{K_o} = \frac{M_2^{(f)}}{M_2^{(o)}} = \left(\frac{\phi_f}{\phi_o}\right)^2 e^{2(\phi_f-\phi_o)} \qquad (55)$$

This is a result of some importance. The new permeability, K_f, in the invaded region can be computed thus permitting a quantitative determination of enhancement due to acidization with a highly retarded acid. This expression can be used together with an integrated form of Darcy's law to provide an estimate of the new oil production rate to be expected after acidization thus giving a monetary value to a particular treatment. This aspect will be considered in more depth in forthcoming publications. The aim here is to provide the basis for acid treatment design.

The second application of Equation (55) stems from the fact that the increase in permeability owing to collisions is found as a multiplicative factor onto the increase owing to growth. To make this matter clearer, the solution of the evolution equations neglecting collisions can be seen to give

$$\frac{K_f}{K_o} = \left(\frac{\phi_f}{\phi_o}\right)^2 \qquad (56)$$

for the retarded acid case. Therefore, the factor exp $2(\phi_f - \phi_o)$ in Equation (55) is due to collisions. Collisions increase the permeability because larger pores result and even though a pore is destroyed, a single pore having the combined area of two pores has a larger permeability than the two acting in parallel. Since the factor exp $(2\phi_f - 2\phi_o)$ does allow for collisions, it is seen that they only become important for the retarded acid case when there is a significant increase in the porosity. Therefore, confidence can be placed in the results obtained by neglecting collisions as long as the change in porosity is small. With larger changes in porosity, the permeability is underestimated by neglecting collisions.

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this work has been to develop a model which represents the effect of surface reactions in a porous medium on its properties with the principal motivation stemming from a need to understand matrix acidization. The process is modeled by focusing attention on the pore size distribution and the evolution of this pore size distribution resulting from the surface reaction. An equation has been developed which describes the changing pore structure and one of the important factors in this equation is a growth rate factor ψ which defines the way a particular pore grows in time. For matrix acidization our model thus far assumes that ψ can be determined based on a laminar flow calculation, but preliminary results have indicated that perhaps some improvement in this approximation may be required. A change in ψ will not of course, change the evolution equation nor the solutions of it given here. The numerical work is, however, sensitive to adjustments in ψ.

Given the pore size distribution the quantities of interest can be computed. The main conclusions resulting from the preliminary calculations are that it is the larger pores which determine the response of the system to acid, this response is sensitive to the distribution of these larger pores, and that a quasisteady state in acid concentration is quickly established along the core after acid breakthrough. It is this latter feature which may provide a handle for designing acid treatments in oilfields.

The formation of wormholes is understood as a result of diffusion limited surface reactions and the preliminary results have shown the model to respond in a manner consistent with experimental observations. These preliminary results, while encouraging are being tested further.

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NOTATION

A = pore area
C = concentration of acid in reservoir
$\overline{C_p}$ = mean concentration of reactant in a pore
D = molecular diffusivity
K = factor proportional to permeability of porous medium
M_j = jth moment of distribution
$M_j^{(o)}$ = initial value of jth moment
n_1, n_2 = components of unit normal vector
p = pressure
$P(L)$ = distribution of pore lengths
q = volumetric flow rate
r = radius of a circular pore
t = time
v = local velocity in pore
$\bar{v}$ = mean velocity in pore
$W(A, L, x, t)$ = pore size density function
w^2 = area normal to flow
x = position in porous medium measured from face at which fluid is injected
X = dissolving power of the acid expressed as volume of rock dissolved per volume of acid expended
x_1, x_2 = coordinate in cross section of pore
z = axial position in pore measured from inlet

Greek Letters

α = a dimensionless ratio of the mean reactant concentration in the pore to the mean surface concentration
γ = mass of solid dissolved per mass of acid expended
Γ = perimeter of pore
ϵ = geometric factor which is constant for similar geometries
η = reduced density function defining pore size distribution
$\Delta\eta_c dA$ = rate of creation of pores per unit volume having an area between A and $A + dA$
$\Delta\eta_D dA$ = rate of destruction per unit volume of pores having an area between A and $A + dA$
θ = coordinate fixing radial position in circular pore
λ_1 = smallest eigenvalue
μ = fluid viscosity
ρ_s = density of solid in porous medium
ϕ = porosity
$\psi(A, x, t)$ = pore growth rate factor expressed in area per unit of time

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