

ACIDIZATION—V

THE PREDICTION OF THE MOVEMENT OF ACID AND PERMEABILITY FRONTS IN SANDSTONE

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Abstract—A new model has been developed which describes the acidization of sandstone cores. The results show that the reaction of hydrofluoric acid with the dissolvable minerals occurs in a narrow zone which moves as a reaction front through the sandstone core. The width of the reaction front is related to the Damkohler Number and the velocity of the reaction front is related to the acid capacity number. The model has virtually no adjustable parameters and agrees extremely well with the experimental results.

1. INTRODUCTION

In the previous papers [1-3] we reported the kinetics of the reaction between HCl and HF/HCl acid mixtures with minerals which are commonly found in sandstone (e.g. calcite, dolomite, sodium feldspar, and potassium feldspar). Furthermore, we reported techniques used to study and identify the important parameters in the flow and reaction of acids in porous sandstone [4]. Experimental correlations were presented which described the movement of the permeability front through a linear sandstone core. In the present paper we shall present a mathematical model which predicts the movement of the permeability and acid fronts through the sandstone cores. The sandstone studied is a quartzite, whose mineralogical properties have been previously described [4].

2. A NEW MODEL

During the acidization of a sandstone core, the acid mixture flowing axially through the cylindrical core reacts with and dissolves some of the solids on the surface of the porespace. The acid mixture may not only participate in the heterogeneous dissolution reactions but also in a series of homogeneous reactions with the products from the heterogeneous reactions. Neglecting axial dispersion in the core, a differential mole balance on a solute i in the liquid phase yields:

$$\frac{\partial(\phi C_i)}{\partial t} + \frac{\partial(V C_i)}{\partial x} = (R_s + R_h)_i \quad (1)$$

where:

ϕ is the porosity, C_i is the concentration of solute i ; moles/cm³ of fluid, V is the superficial velocity; cm/min, t is the time; min, x is the distance in axial direction; cm, R_s and R_h are the heterogeneous and homogeneous reaction rates respectively of solute i ; moles/cm³ of bed volume/min. Similarly a differential mole balance (in the solid phase) on a dissolvable mineral species j in the

sandstone yields:

$$\frac{\partial[(1-\phi)W_j]}{\partial t} = r_j \quad (2)$$

where W_j is the concentration of mineral species j ; mole/cm³ of solids, r_j is the rate of reaction of mineral j ; mole/cm³ of bed volume/min. The change in porosity may be found by multiplying eqn (2) by the ratio of the molecular weight of mineral species j , M_j , to the density of the mineral species j , ρ_j , and then summing over all of the minerals present in the core and noting that:

$$\sum \frac{W_j M_j}{\rho_j} = 1$$

in which case eqn (2) becomes:

$$\frac{\partial\phi}{\partial t} = - \sum \frac{r_j M_j}{\rho_j} \quad (3)$$

The heterogeneous reaction rates of the solutes and the minerals, $(R_s)_i$ and r_j , are interconnected by a reaction stoichiometry matrix, $\{v_{ij}\}$:

$$\{(R_s)_i\} = \{v_{ij}\}\{r_j\}.$$

This expression takes into account that the solute species may be produced (or consumed) in any of the heterogeneous reactions. A similar expression may be written for the homogeneous reactions occurring in the flowing acid mixture. The homogeneous reactions are the reactions of hydrofluoric and hydrochloric acid with solution species such as the fluoride ion, carbonic acid, alumino fluorides, and silicon fluorides. Given the boundary and the initial conditions, the problem is in principle fully defined. The problem has been stated in a general form so that its complexity may be appreciated; however, we will need to simplify it considerably in order to obtain a meaningful solution.

The rate of dissolution of quartz is much slower than the rate of dissolution of the other minerals present in the sandstone, and consequently, the quartz does not react to

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any appreciable extent during the period of acid injection. Of the other minerals present in the quartzite, plagioclase and microcline are the main constituents and dissolve at essentially the same rate. The dissolution of these minerals may then be described by a single rate law. Analysis of the effluent acid showed that the concentration of HCl did not vary appreciably from its inlet value and that the stoichiometry for the reaction of hydrofluoric acid with the quartzite was reasonably constant. Assuming the homogeneous reactions are fast compared with the heterogeneous reactions we may let an overall (lumped) stoichiometric coefficient describe the reactions. The stoichiometric coefficient will then express the number of moles of HF needed to dissolve one mole (lumped) of the minerals which are being dissolved from the sandstone. Owing to the fact that the dissoluble minerals in Phacoides sandstone react virtually at the same rate[3], we can use a lumped parameter model to describe the dissolution process. With these simplifying restrictions the mole balances become (omitting the indices):

$$\frac{\partial(\phi C)}{\partial t} + \frac{\partial(V C)}{\partial x} = R_s \quad (4)$$

$$\frac{\partial[(1-\phi)W]}{\partial t} = r_A \quad (5)$$

where C , is the concentration of hydrofluoric acid; R_s , is the rate of reaction of hydrofluoric acid; W , is the lumped concentration of all minerals other than quartz in the quartzite; r_A , is the rate of reaction of the lumped minerals. Equations (4) and (5) are coupled through the reaction stoichiometry which is

$$R_s = \nu r_A \quad (6)$$

The average stoichiometric coefficient ν is expressed as moles of HF consumed per mole of lumped mineral dissolved.

The rate law for the dissolution rate of the feldspars has been previously shown[3] to have the following dependence on the concentration of HCl, $[HCl]$, and the concentration of HF, $[HF]$.

$$-r_A = k_1'(1 + K_1[HCl]^a) [HF] S_F \quad (7)$$

where k_1' , K_1 , and a are characteristic constants, S_F is the surface area of the feldspars per unit bed volume; sqcm/cm³. The dissolution rate of the feldspars will be a relatively weak function of the hydrochloric acid concentration in the concentration range of interest. Letting the specific surface area of the feldspars be given by the product of its weight fraction and the total specific surface area of the quartzite, then we may express S_F in terms of W , the average molecular weight of the feldspars, M_F , the sandgrain density, ρ_s , and S , the internal specific surface area of the sandstone.

$$S_F = \frac{M_F S}{\rho_s} W \quad (8)$$

During acidization the bulk of the acid mixture flows through the larger pores of the core and it is primarily the feldspars and clays in these pores that will be dissolved by the acid. This was clearly shown by the aluminum petrologs of the quartzite cores which had undergone acidization[4]. Only the surface area of the minerals significantly accessible to the acid mixture should be used in the rate expression, and we may modify eqn (8) to take this into account:

$$S_F = \frac{M_F S}{\rho_s} (W - W_1) \quad (9)$$

where W_1 is the irreducible content of minerals other than quartz. The dissolution rate, $-r_A$, is only a weak function of the hydrochloric acid concentration, and since this concentration does not vary appreciably in the core during the acidization, the rate expression may be simplified to:

$$-r_A = k_1 C (W - W_1) \quad (10)$$

where the constant, k_1 , is given by:

$$k_1 = k_1' \frac{M_F S}{\rho_s} (1 + K_1 [HCl]^a) \quad (11)$$

Furthermore, the change in the porosity of the quartzite may be considered to be small and slow as compared to the change in the concentration of hydrofluoric acid. Introduction of these simplifications into the mole balances yields:

$$\phi_0 \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} + k_1 C (W - W_1) = 0 \quad (12)$$

$$\nu(1 - \phi_0) \frac{\partial (W - W_1)}{\partial t} = -k_1 C (W - W_1) \quad (13)$$

where ϕ_0 is the initial value of the porosity.

The initial and boundary conditions for this set of coupled first order non-linear partial differential equations are:

$$\begin{aligned} C(x, t) &= C_0 \quad \text{for } x = 0 \\ W(x, t) &= W_0 \quad \text{for } \phi x / V \geq t. \end{aligned} \quad (14)$$

If we define the following parameters:

$$\psi = C / C_0; \quad \eta = (W - W_1) / (W_0 - W_1), \quad \tau = \frac{\phi_0 L}{V}$$

$$\theta = V t / (\phi_0 L) = t / \tau; \quad \epsilon = x / L$$

in which τ is the space time of the core, and θ the number of pore volumes of fluid injected, then the HF acid mole balance becomes:

$$\frac{\partial \psi}{\partial \theta} + \frac{\partial \psi}{\partial \epsilon} + Da \psi \eta = 0 \quad (15)$$

and the dissoluble mineral (i.e. feldspar) mole balance becomes:

$$\frac{\partial \eta}{\partial \theta} = -DaAc\eta\psi. \quad (16) \quad \text{or}$$

Two important parameters which have been introduced into eqns (15) and (16) are the Damkohler number, Da , and the acid capacity number, Ac .

The Damkohler number, Da

$$Da = \frac{k_1(W_0 - W_1)L}{V} \quad (17)$$

is a measure of the rate at which the acid reacts as compared with the rate the acid is transported by convection.

The acid capacity number, Ac

$$Ac = \frac{\phi C_0}{v(1 - \phi_0)(W_0 - W_1)} \quad (18)$$

is the molar ratio of the acid present in the pore space to the acid needed to dissolve all the dissoluble minerals in the corresponding solid space.

The initial and boundary conditions for these equations are:

$$\begin{aligned} \psi &= 1 & \text{for } \epsilon &= 0 \\ \eta &= 1 & \text{for } \theta &\leq \epsilon. \end{aligned} \quad (19)$$

The system of first order non-linear partial differential equations, which describe the acidization of sandstone cores are analogous in type to those describing fixed-bed operations such as adsorption and ion-exchange [5, 6]. If the rate process is described by a simple rate law then an analytical solution may be possible; otherwise for more complex rate laws the problem may be attached successfully by the method of characteristics [6, 7] combined with a numerical solution. An analytical solution [8-10] exists for the system of partial differential equations [eqns (15), (16) and (19)] which describes the acidization of quartzite and this solution is given in terms of:

$$\begin{aligned} 1/\psi &= 1 + \exp \{DaAc[(1 + 1/Ac)\epsilon - \theta]\} \\ &\quad - \exp \{DaAc(\epsilon - \theta)\} \end{aligned} \quad (20)$$

$$\begin{aligned} 1/\eta &= 1 + \exp \{-DaAc[(1 + 1/Ac)\epsilon - \theta]\} \\ &\quad - \exp \{-Da\epsilon\}. \end{aligned} \quad (21)$$

In eqns (20) and (21) we can recognize two different fronts, each of which move with their own characteristic velocities through the core. A front in a property (such as concentration or permeability) may be defined as a zone in the core where the value of the derivative of a property with respect to the axial distance is very large when compared with values at other positions in the core.

The location of the first of these fronts is given by:

$$\epsilon = \theta$$

$$X = Vt/\phi_0.$$

This front is the interface between the distilled water (which was present in the core before the acidization started) and the injected acid mixture. The velocity, V_s , of the interface is simply the interstitial velocity of the acid:

$$V_s = V/\phi_0.$$

The reaction front is the second of these fronts, and its mean position may be found from the expression:

$$(1 + 1/Ac)\epsilon = \theta$$

or

$$X = \frac{VC_0 t}{\phi_0 C_0 + v(1 - \phi_0)(W_0 - W_1)}. \quad (22)$$

The velocity V_f of the reaction front is given by:

$$V_f = \frac{Ac}{1 + Ac} V_s$$

or

$$V_f = \frac{VC_0}{\phi_0 C_0 + v(1 - \phi_0)(W_0 - W_1)}.$$

The reaction front will be fully developed in the core when the last term in eqns (20) and (21) becomes insignificant. This occurs when the spacetime is large and the velocity of the reaction front is much less than the interstitial acid velocity. Once the front is fully developed its shape will stay constant.

The porosity at any time and position is given by:

$$\phi = \phi_0 + (1 - \phi_0)(W_0 - W)M_F/\rho_s. \quad (23)$$

The change in the porosity may also be expressed in dimensionless form if we note that the maximum possible change in the porosity is given by:

$$(\Delta\phi)_{\max} = \phi_{\max} - \phi_0 = (1 - \phi_0)(W_0 - W_1)M_F/\rho_s$$

then substituting this into eqn (23) yields:

$$\Delta\phi = (1 - \eta)(\Delta\phi)_{\max}. \quad (24)$$

The change in porosity at any point and time in the core may be determined from eqns (21) and (24):

$$\frac{\Delta\phi}{(\Delta\phi)_{\max}} = \frac{\exp \{-DaAc[(1 + 1/Ac)\epsilon - \theta]\} - \exp \{-Da\epsilon\}}{1 + \exp \{-DaAc[(1 + 1/Ac)\epsilon - \theta]\} - \exp \{-Da\epsilon\}}. \quad (25)$$

3. APPLICATION OF MODEL

An approximate value of the average stoichiometric coefficient, ν , may be determined by the methods previously outlined [3]. The stoichiometric coefficient is dependent on the concentration of HF in the effluent acid but for our purposes we shall choose to evaluate it at a HF concentration of 0.01 mole/l. For the acid mixtures used in this investigation calculations show that the stoichiometric coefficient is fairly constant as long as the HF concentration is greater than 0.01 mole/l. For example, for an initial acid mixture of 1.0 N HCl and 1.0 N HF the stoichiometric coefficient only varies 20% in the HF concentration range 0.01–1.0 moles HF/l. As the HF (or HCl) concentration becomes much smaller than 0.01 mole/l, the stoichiometry of the dissolution reaction may change drastically but the effect of this on the acidization process will be rather insignificant. A lumped stoichiometric coefficient, ν , describing the acidization of quartzite was calculated as a weighted mean [10].

$$\nu = 15.0 \text{ mole HF/mole feldspar.}$$

The derived model for the acidization of quartzite predicts the change in porosity at any point and time in the core but it does not directly predict the change in the permeability. An experimental correlation between the permeability and the porosity has been determined independently for quartzite [11] by flowing mixtures of hydrofluoric and hydrochloric acid through quarter inch disks of quartzite. The permeability was measured during the experiment and the change in porosity was calculated from the analysis of the effluent acid. The following correlation giving the local permeability as a function of local porosity was found to fit the reported data quite well [11].

$$k/k_0 = \exp(95 \Delta\phi) \quad (26)$$

where k_0 is the initial value of the permeability. Porosity measurements of cores which have undergone acidization show that $(\Delta\phi)_{\max}$ is approximately 0.08 for quartzite and eqn (26) becomes:

$$k/k_0 = \exp\left(\beta \frac{\Delta\phi}{(\Delta\phi)_{\max}}\right) \quad (27)$$

where $\beta = 7.5$. The permeability does not necessarily reach as high a value as eqn (27) predicts and therefore we may simply limit the maximum value attainable by eqn (27) to a value suggested by the individual experiment (i.e. $k \leq k_{\max}$). The maximum value of the permeability will be a function of the actual number of larger pores and the degree of collapse in the core. The overall permeability of the core, K , may then be determined by performing the integration on the local permeability over the length of the core.

$$K = L \int_0^L \frac{dx}{k} \quad (28)$$

Since the integration is performed on the reciprocal of the permeability, the sections with low permeability will be dominating, and k_{\max} will have little effect on the average

permeability. Given values for the Damkohler and the acid capacity numbers, the permeability of the core undergoing acidization may now be calculated at any time.

The permeability [as predicted by eqns (25), (27) and (28)] is a monotonically increasing function of time, and we know this is not necessarily true for the experimentally measured permeability because of possible damage in the core. This damage is caused by interactions between the flowing fluid and the interstitial clays in the porespace of the core. The core will show the least effect of any damage when the permeability ratio has increased substantially. Our model was therefore matched to the permeability data of each acidization experiment (by making a proper choice of the values of Da and Ac) at as high a value of the permeability ratio as possible without the latter showing signs of approaching a maximum. Many of the acidization experiments showed little or no damage of the cores and in these cases the calculated permeability profile matches very well with the experimentally determined profile. In the Figs. 1 and 2 the measured and calculated permeability of a core undergoing acidization are compared for two different experiments: R435, and R346. The experimental error in these measurements is within 10%. In Run R435 the core was initially damaged by the acid treatment whereas this is not the case in R346. As expected the present form of the model does not accurately predict those stages of the acidization process where damage is the controlling phenomena. However, we shall soon see that when the core is undamaged or slightly damaged, the model does give an excellent representation of the acidization.

From eqns (17) and (18) we note that we can form the two ratios (Da/τ) and (Acv/C_0) , whose values depend only on the initial properties of the particular sandstone under investigation, i.e.

$$Da/\tau = k_i(W_0 - W_1)/\phi_0; \quad \text{min}^{-1} \quad (29)$$

$$Acv/C_0 = \phi_0/(1 - \phi_0)(W_0 - W_1); \quad \text{cm}^3/\text{mole.} \quad (30)$$

The actual fitting of the model to the permeability data from each experiment was performed numerically by choosing a value for (Da/τ) and then using a root finding technique to determine the value of (Acv/C_0) which would make the experimental and computed permeability curves match at a specified value of the permeability ratio. A best estimate of (Da/τ) was found by choosing a value which makes the variance of the calculated (Acv/C_0) value from all the experiments small and at the same time gives a good match between the calculated and measured concentration of the effluent acid. Furthermore, we will see in Section 5 that the model, the experimental data from the permeameter, and the rate studies on the pure minerals may be tied together in a fundamental manner so that (Da/τ) and (Acv/C_0) could be calculated from first principles.

4. DISCUSSION AND RESULTS

The proposed model for the acidization of quartzite [eqns (21), (22) and (25)] describes the change of the mineral concentration, porosity, and acid concentration in

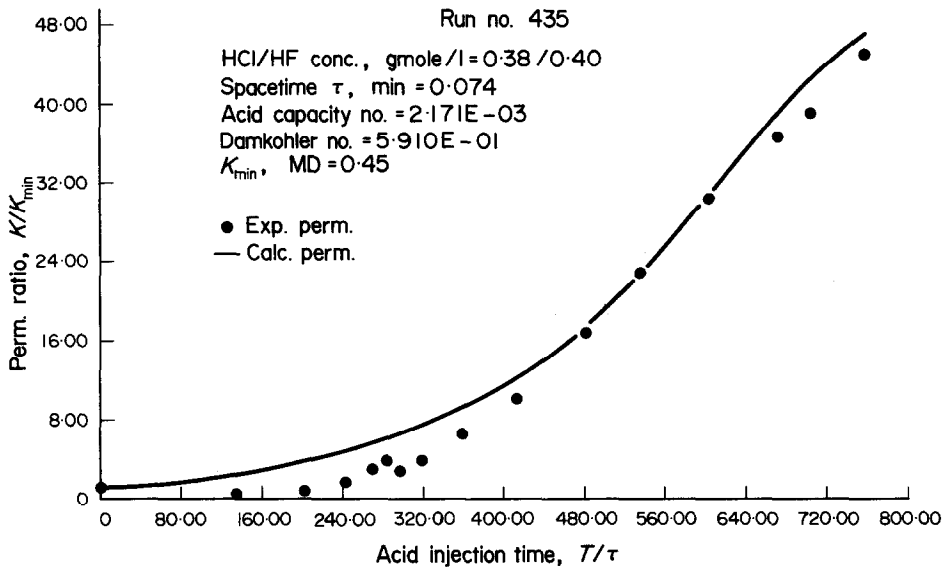


Fig. 1. Permeability of a core during acidization vs dimensionless time for R435.

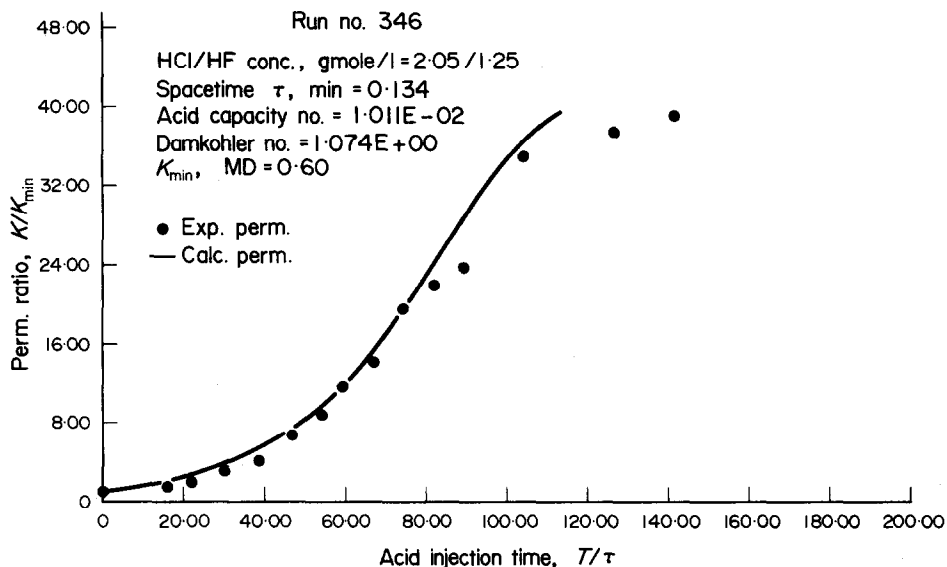


Fig. 2. Permeability of a core during acidization vs dimensionless time for R346.

the sandstone core as a function of time and axial position. Only two parameters, the acid capacity number Ac and the Damkohler number Da , need to be specified for the problem solution to be fully defined. In the actual implementation of the model an estimate of the permeability at any time and position in the sandstone is often desired. This necessitates an added relationship giving the permeability as a function of the porosity and added parameters may thereby be introduced. For the case of quartzite two parameters, β and k_{\max} , were introduced.

The parameter, β , determines the sensitivity of the permeability to changes in the porosity and thereby the location of the permeability front relative to the reaction front. An independent experimental investigation[11] showed that $\beta = 7.5$ describes the response of quartzite to acidization. Other values of β such as $\beta = 5.0$ and 10.0 were tried in the matching of the model to the

experimental permeability vs time curves but they did not affect the calculated value of the break-through time significantly. When no limitations are placed on the permeability that the sandstone may attain, the permeability of a core undergoing acidization will always have an increasing slope with respect to time (i.e. positive curvature). Introduction of a maximum value in the local permeability allows the model to reproduce the characteristic shape of the break-through curve of a core with its inflection point and negative curvature at higher values of the permeability ratio. Since the average permeability of the core is found by integrating the reciprocal of the permeability, this maximum value in the permeability will have little effect on the overall permeability at lower values of the permeability ratio of the core.

The presence of a damage zone in the core during the acidization camouflages to some extent the true response

of the core and it does not appear fruitful at the present time to investigate in detail the effect of the two parameters, β and k_{\max} , on the permeability curve. The model does not depend on our ability to represent the permeability profile in the core undergoing acidization exactly since the experimental permeability vs time curve is used in an indirect manner to indicate the condition of the core during the acidization.

During the acidization, the traveling fronts of the hydrofluoric acid concentration, the feldspar concentration, the porosity, and the permeability will be established in the core. Our model allows us to calculate the shape of these fronts for each experiment and typical results (computed for R421) are given in Figs 3-5. The maximum value of the permeability ratio was limited to 7.6 in R421. We note that after an initial time period, the shape of the fronts becomes constant and that they then travel through the core with a constant velocity. The concentration and porosity fronts attain a sigmoidal shape whereas the permeability front always has a positive curvature. The

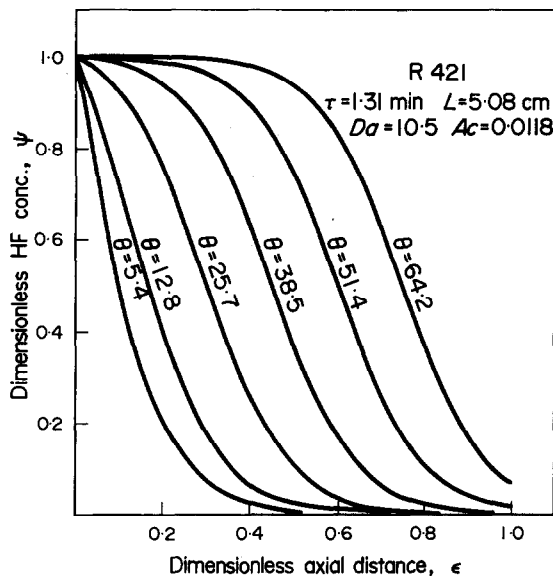


Fig. 3. Concentration profile of HF in a core during acidization.

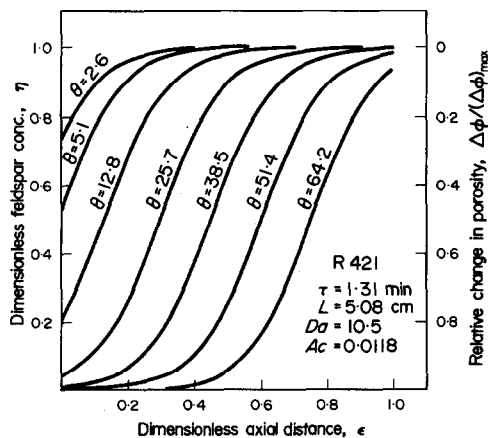


Fig. 4. Concentration profile of feldspars in a core during acidization.

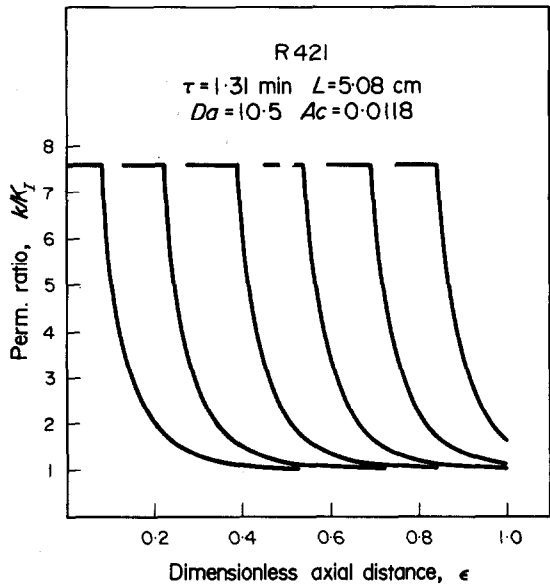


Fig. 5. Permeability profile in a core during acidization.

shape of the latter does not match exactly the experimentally measured permeability fronts (Fig. 5), as these curves all had a negative curvature in the undamaged part of the core. This is not surprising since the existence of damage in the core changes the response of the core to the acidization and therefore will also modify the shape of the permeability front drastically. The permeability of the whole core is determined as an integral of the local permeability, and consequently errors in estimating the actual shape of the local permeability will cancel out to some degree. A strong point of the proposed model of the acidization of sandstone is that its application does not depend on our ability to describe the permeability front in the core in an accurate manner. This is because the evaluation of the parameters of the model is primarily based on the time it takes the permeability front to pass through the core and not the shape of the front.

The Damkohler number, Da , is a measure of the rate at which the acid reacts as compared with the rate the acid is transported by convection. For larger values of the Damkohler number, the reaction between the dissolvable solids in the quartzite and the acid progresses to a higher degree of completion at any point in the core and therefore we could expect the internal fronts to become sharper. For a low value of Da the concentration of acid and feldspar are nearly uniform throughout the core and the core behaves like a differential reactor. The shape of the permeability vs time curve for the entire core is also strongly affected by the value of the Damkohler number (Fig. 6). The larger the value of the Damkohler number the steeper the breakthrough curve becomes. For the two larger values of Da shown, the breakthrough time is approximately the same, whereas this is not the case for $(Da/\tau) = 1 \text{ min}^{-1}$. Here the reaction rate is slow compared to the rate of convection and most of the acid is transported out of the core before it has had time to react.

The acid capacity number expresses the ratio of the acid present in the void fraction to the amount of acid

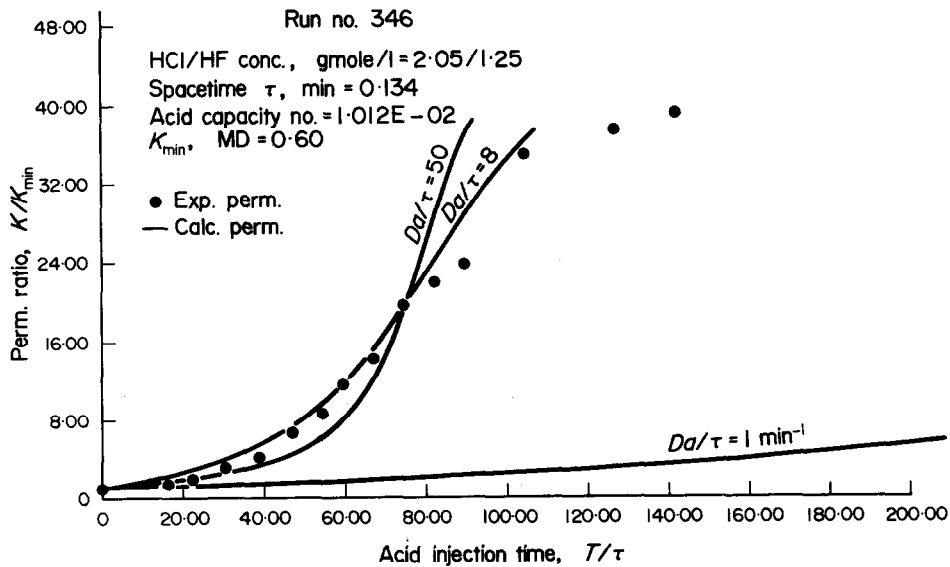


Fig. 6. Permeability of a core during acidization for various values of the Damkohler number.

necessary to consume the dissoluble minerals in the corresponding solid structure. The larger the acid capacity number, the faster we can expect the reaction and permeability fronts to traverse the core. This is illustrated in Fig. 7 where the calculated overall permeability of a core is given as a function of the acid injection time for different values of the acid capacity number.

The effect of the Damkohler and the acid capacity numbers may also be viewed in a slightly different manner. When the length of the reaction front is smaller than the length of the core, then the break-through curve will primarily be a function of the value of the product $Da \cdot Ac$. On the other hand, when the reaction front is larger than the core length no simple relationships exist. Both Da and Ac will affect both the shape of the break-through curve and the time for break-through in a complex manner. For cores longer than the reaction front,

Eqn (22) will describe the location of the front and thereby the approximate time of the break-through. Comparison of eqn (22) with the experimentally determined break-through correlation, eqn (14) of Ref. [4].

$$R = qC_0t_b/L \tag{31}$$

shows the two equations to be identical when R is given by:

$$R = \phi_0 C_0 + v(1 - \phi_0)(W_0 - W_1)$$

or in terms of the acid capacity number:

$$R = \phi_0 C_0(1 + 1/Ac). \tag{32}$$

As we would expect from analysis of the model in the

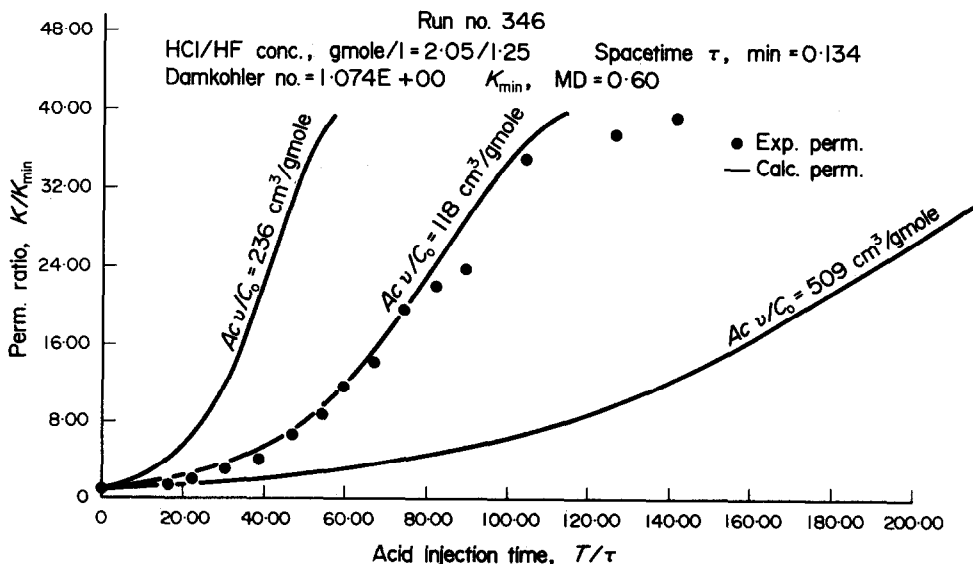


Fig. 7. Permeability of a core during acidization for various values of the acid capacity number.

present paper, the correlation should break down under the experimental conditions of high acid velocity through short cores. Under these conditions the time of breakthrough is a function of both the Damkohler and the acid capacity number and not only the latter.

The concentration of reaction products in the effluent acid (and thereby indirectly the concentration of hydrofluoric acid) from a core undergoing acidization were measured in several experiments and it is of great interest to compare the experimental HF concentration profiles with those we computed from our model. From the chemical analysis of the effluent acid the hydrofluoric acid concentration was calculated with previously stated simplifying assumptions [3, 4], and there may exist some bias in the absolute value of the calculated HF concentrations. To lessen effect of this uncertainty we may just compare the slopes of the HF concentration-

time curves. The concentration of the effluent acid may be found by evaluating eqn (20) at the end of the core, i.e. $\epsilon = 1$:

$$\psi = (1 + \exp \{DaAc[(1 + 1/Ac) - \theta]\} - \exp \{DaAc(1 - \theta)\})^{-1} \quad (33)$$

The derivative of this expression with respect to dimensionless time is simply:

$$\left(\frac{\partial \psi}{\partial \theta}\right)_{\epsilon=1} = DaAc(\psi - \psi^2)^2. \quad (34)$$

This expression is fairly insensitive to variations in ψ ; for example, in the range $0.25 < \psi < 0.75$ the slope varies less than 25%.

In Figs. 8 and 9 the concentration of HF in the effluent

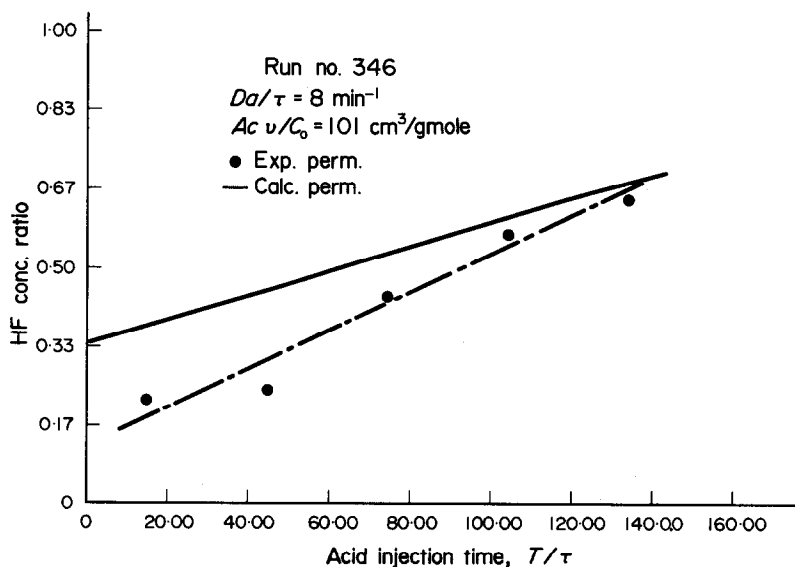


Fig. 8. Concentration of HF in effluent acid vs dimensionless injection time for R346.

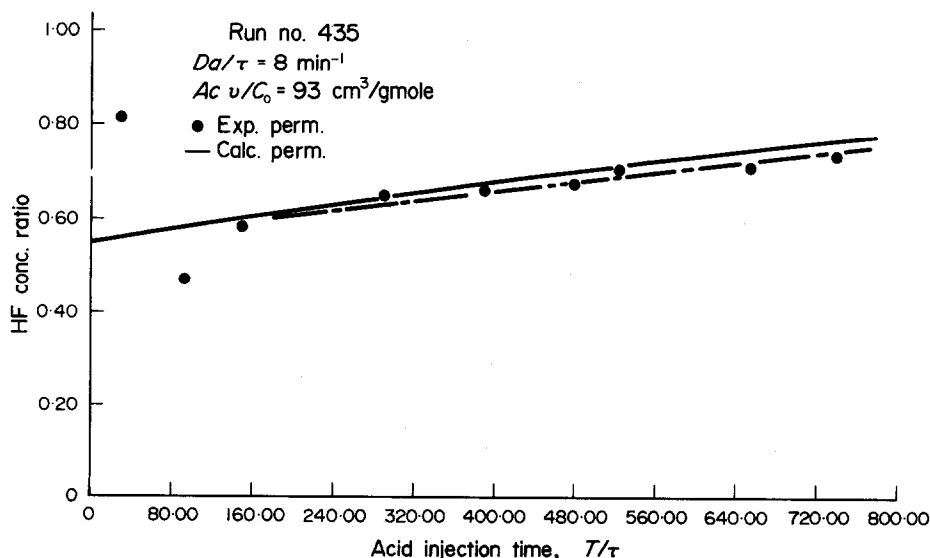


Fig. 9. Concentration of HF in effluent acid vs dimensionless injection time for R435.

acid is shown as a function of the dimensionless time for two acidization experiments respectively. The dashed line represents the average slope as indicated by the experimental points whereas the solid curve represents the concentration of the effluent acid calculated from the model. The same values of (Da/τ) and (Acv/C_0) that were evaluated from the matching of the permeability curves were used in computing the concentration profiles. The comparison between the hydrofluoric acid concentration profiles from theory and experiment allows therefore an independent check on the model; the agreement between the two is very good.

The slope of the concentration-time curves may be estimated most accurately from experiments with small spacetimes, and the particulars of the calculations are given in Table 1. The average value of (Acv/C_0) for these five experiments was estimated from the permeability data to be $105/\text{cm}^3$ mole. From the data given in Table 1 the average value of (Da/τ) was found to be 9.0 min^{-1} , which is in very good agreement with the estimate from the permeability data. Some variation in the computed value of the product

$$(Da/\tau) \cdot (Acv/C_0) = \frac{k_1}{1-\phi_0} \quad (35)$$

is apparent and it is of interest to see if this variation is due to the different concentration of hydrochloric acid in the acid mixture. The rate of reaction of the feldspars is a weak function of the hydrochloric acid concentration [eqn (7)], and consequently the Damkohler number should then also be a weak function of the hydrochloric acid concentration:

$$Da = k_1(W_0 - W_1)L/V \quad (19)$$

where

$$k_1 = \frac{k'_1 M_{FS}}{\rho_s} (1 + K_1 [\text{HCl}]^a) = \frac{k_1 M_{FS}}{\rho_s} f.$$

If we divide eqn (35) by the dependence of HCl on the reaction rate, $f = (1 + k_1 [\text{HCl}]^a)$, then the ratio $[k'_1 M_{FS}/\rho_s (1 - \phi_0)]$ should be a constant dependent only on the sandstone selected. For each acidization experiment an average estimate of this dependence on HCl may be calculated from the rate laws for the two feldspars [3] and the computed values of $\{k'_1 M_{FS}/[\rho_s (1 - \phi_0)]\}$ are given in Table 1. The agreement between the model and the experimental data is amazingly good. The correction

for the effect of hydrochloric acid is relatively minor and it was not attempted in the analysis of the other acidization experiments.

The best average estimate (within 15%) of the two parameters (Da/τ) and (Acv/C_0) for all the quartzite acidization experiment were determined from the available data to be:

$$(Da/\tau) = 8 \text{ min}^{-1} \quad \text{and} \quad (Acv/C_0) = 159 \text{ cm}^3/\text{mole}.$$

It will be of interest to see how well the model is able to predict the break-through time. Originally, for each experiment the value of $(Ac \cdot v/C_0)$ was determined for a certain choice of (Da/τ) by matching the experimental and computed permeability vs time curves at a specified (but somewhat arbitrary and different from experiment to experiment) value of the permeability ratio, $(k/k_0)_{\text{test}}$. The time necessary to reach this value of the permeability ratio may be called the break-through time for the core. [Note. This definition of the break-through time is only slightly different from the one used in Ref. [4].] A good way of testing the validity of the model (using the above average values of $Da/\tau = 8.0 \text{ min}^{-1}$ and $(Acv/C_0) = 159 \text{ cm}^3/\text{mole}$ will then be to calculate from eqns (25), (27) and (28) the time necessary to reach the permeability ratio $(K/k_0)_{\text{test}}$ and compare it with the time the experimental permeability takes to reach this value of the ratio. This is done in Fig. 10. When we consider the range of experimental conditions covered, the relative simplicity of the model, and the complexity of the porous media, then the agreement is very good.

In the previous paper [4] we presented a purely experimental break-through correlation:

$$qC_0 t_b / L = R \quad (31)$$

where R was equal to 0.0046 mole/cm^3 . If the reaction front can be assumed to be fully developed in the core then eqn (32) allows the direct calculation of R using the determined value of the ratio (Acv/C_0) :

$$\begin{aligned} R &= \phi_0 C_0 (1 + 1/Ac) = \phi_0 C_0 + \phi_0 v \frac{C_0}{Acv} \\ &= 0.0103 \text{ mole/cm}^3. \end{aligned}$$

As expected the agreement between the two values of R is only approximate owing to the differences in the definitions of the breakthrough times. The term t_b in the correlation (eqn 31) is the time necessary for the permeability to move sufficiently into the core so as to

Table 1. Calculations on the concentration of the effluent acid

Run	HF conc. gmole/l	HCl conc. gmole/l	space time τ , min.	slope $\frac{d\psi}{d\theta}$	Da	Ac	$\frac{k_1}{1-\phi_0}$	$1+K(\text{HCl})^a$	$\frac{k'_1 M_{FS}}{\rho_s (1-\phi_0)}$
R346	1.25	2.05	0.134	4.0×10^{-3}	1.60×10^{-2}		1.40	2.1	0.67
R435	0.40	0.38	0.074	3.0×10^{-4}	1.08×10^{-3}		0.59	1.42	0.42
R439	1.0	1.0	0.129	1.82×10^{-3}	7.3×10^{-3}		0.84	1.70	0.49
R440	1.0	1.0	0.059	7.8×10^{-4}	3.1×10^{-3}		0.78	1.70	0.46
R445	2.5	2.88	0.144	6.9×10^{-3}	2.8×10^{-2}		1.06	2.4	0.45

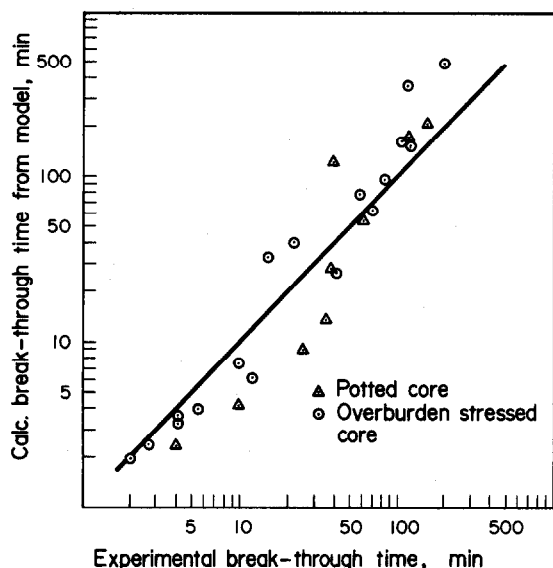


Fig. 10. Calculated break-through time from model vs experimental break-through time.

start to bring about a significant increase in the overall permeability of the core. On the other hand the breakthrough time calculated from the acid capacity number is the time necessary for the front to move completely through the core. In addition, the breakthrough time based on the correlation will depend on the Damkohler number. When the experiment and theory are compared on the same basis, the agreement between the model and the experimental results, as can be seen in Fig. 10, is extremely good.

5. CALCULATION OF THE PERMEAMETER PARAMETERS FROM FUNDAMENTAL PRINCIPLES

From the average values of (Da/τ) and (Acv/C_0) at 125°F, we may calculate independent estimates of the concentration of the dissoluble minerals, $(W_0 - W_1)$, and the rate at which they react, k'_1 . To achieve this we first recall that

$$(Acv/C_0) = \phi_0/[1 - \phi_0](W_0 - W_1) \quad (30)$$

$$= 159 \text{ cm}^3/\text{mole}.$$

The average porosity of the quartzite is 11% and the concentration of dissoluble solids (expressed as feldspars) can be calculated from eqn (30):

$$(W_0 - W_1) = 0.78 \times 10^{-3} \text{ mole/cm}^3 = 0.78 \text{ mole/l.}$$

The aluminum petrologs of the unacidized quartzite allow us to calculate the approximate concentration of the dissoluble minerals:

Table 2.

Mineral	Concentration
Plagioclase	0.49 mole/l
K-Feldspar	1.04 mole/l
Kaolinite	0.10 mole/l

Expressed as total feldspar equivalents: $W_0 = 1.68$ mole/l. Al-petrologs performed on the cores after acidization showed [4] that approx. 30–40% of these dissoluble minerals were consumed, i.e.

$$(W_0 - W_1) = 0.50 \text{ to } 0.67 \text{ mole/l.}$$

These values are in excellent agreement with the values calculated from eqn (30). Similarly, the ratio of (Da/τ) is given by:

$$(Da/\tau) = k_1(W_0 - W_1)/\phi_0 = 8 \quad (29)$$

where the rate constant k_1 is:

$$k = k'_1 \frac{M_F S}{\rho_s} (1 + K[\text{HCl}]^a) = k'_1 \frac{M_F S}{\rho_s} f. \quad (35)$$

The mercury pore size distribution measurement allows an approximate calculation of the internal surface area of the pores and typically the results fall in the range:

total internal surface area $1.2 \times 10^4 - 2.0 \times 10^4$ sqcm/cm³
surface area of macro pores 500–700 sqcm/cm³.

The macropores are pores of a diameter greater than 1.0 microns. Since primarily the larger pores are important in the acidization process it makes more sense to use the surface area of these pores in the calculations (but it is of course somewhat arbitrary where the break between the macro and micro pores is placed). However, this value of 1.0 μ was chosen by comparing the pore size distributions of the acidized and unacidized sandstones. One observes that below 1 μ there is little difference between the acidized pore size distribution and the unacidized distribution; while above 1 μ there is a significant difference between the two [10]. Since the average molecular weight of the feldspars is $M_F = 278$ g/mole; the sand-grain density is $\rho_s = 2.62$ g/cm³; and the average effect of the hydrochloric acid is $f = 1.7$; we have after combining eqns (29) and (35)

$$k'_1 = \frac{8\phi_0}{(W_0 - W_1)} \times \frac{\rho_s}{M_F S f} \text{ cm}^3/\text{sqcm}/\text{min}$$

and evaluating the parameters

$$k'_1 = 1.03 \times 10^{-2} \text{ cm}^3/\text{sqcm}/\text{min} = 1.7 \times 10^{-7} \text{ l}/\text{sqcm}/\text{sec}.$$

This value of the specific reaction rate compares well with the value of $k'_1 = 1.4 \times 10^{-7}$ l/sqcm/sec obtained for the two feldspars in the rotating disk apparatus [3]. This close agreement may be somewhat fortuitous since only engineering estimates are available for some of the variables in the above equation for the rate constant.

SUMMARY

The acidization of quartzite cores may be described mathematically in terms of differential mass balances on the lumped, dissoluble minerals and the hydrofluoric acid. If the rate of reaction between the hydrofluoric acid and

the lumped minerals is given by the first order (average) rate law determined experimentally for the two feldspars, then the differential equations describing the acidization may be solved analytically.

Experimental and theoretical analysis show that the acid-mineral reactions take place in a narrow zone that moves through the sandstone core as a reaction front.

Two dimensionless groups, the Damkohler number and the acid capacity number, characterize the acidization. The Damkohler number is a measure of the rate of the acid-dissolution reaction as compared to the rate of convection of the acid, whereas the acid capacity number is a measure of the amount of acid needed to dissolve the lumped minerals in the larger pores. The larger the Damkohler number the steeper the reaction and the permeability fronts are in the cores. The larger the acid capacity number the faster the reaction and permeability fronts will travel through the core and the sooner break-through will occur.

The agreement of the model with the measured experimental data such as the concentration of hydrofluoric acid in the effluent acid and the time for break-through of the cores is excellent. Matching of the experimental data and the model allows the determination of average values of the two dimensionless groups (i.e. the Damkohler number and the acid capacity number). These values agree remarkably well with estimates computed directly from the physical properties of the sandstone in an independent manner.

The effect of acidization on another sandstone may readily be evaluated if either it is a feldspathic quartzite or the dissolution rate of the minerals being dissolved is first order in the hydrofluoric acid concentration. The results of only two acidization experiments are needed for the evaluation of the Damkohler and the acid capacity numbers. One experiment performed at a low flowrate allows the calculation of the acid capacity number from the break-through time. The second experiment should be carried out at a high rate of acid injection and the concentration of hydrofluoric acid in the effluent acid should be measured. The slope of the concentration vs time curve allows the determination of the product of the Damkohler and the acid capacity numbers. The latter experiment also allows the determination of the permeability of the sandstone as a function of the porosity.

NOTATION

a	constant
Ac	acid capacity number
C	concentration of hydrofluoric acid
C_i	concentration of solute i
Da	Damkohler number
E_a	activation energy
f	dependence of dissolution rate on the concentration of hydrochloric acid
[HF]	indicates the concentration of HF; similar for the other solutes
k	local permeability
k_0	initial value of the permeability of the core
k_1	specific reaction rate defined by eqn (7)

k'_1	specific reaction rate defined by eqn (11)
k_{\max}	maximum value of the local permeability
K	overall permeability
K_1	a constant
L	length of core
M_F	average molecular weight of the feldspars
M_j	molecular weight of mineral species j
r_A	rate of reaction of lumped minerals
r_j	rate of reaction of mineral j
R	characteristic constant of the porous media
R_s	heterogeneous rate of reaction of hydrofluoric acid
$(R_s)_i$	heterogeneous rate of reaction of solute i
$(R_h)_i$	homogeneous rate of reaction of solute i
S	specific internal surface area
S_F	specific internal surface area of the feldspars
t	time
t_b	break-through time
V	superficial velocity
V_s	velocity of interface between acid and deionized water
V_f	velocity of reaction front
W	concentration of lumped minerals in solid phase
W_j	concentration of mineral species j in solid phase
W_1	irreducible concentration of lumped minerals in solid phase
x	distance in axial direction
X	location of front

Greek symbols

β	characteristic constant
$\Delta\phi$	change in porosity
$(\Delta\phi)_{\max}$	maximum change in porosity
ϵ	dimensionless distance in axial direction
η	dimensionless concentration of lumped minerals
θ	dimensionless time
ν	lumped stoichiometric coefficient
ν_{ij}	stoichiometric coefficient
ρ_j	density of mineral species j
ρ_s	sand grain density
τ	space time
ϕ	porosity
ψ	dimensionless concentration of hydrofluoric acid

Subscripts

0	indicates initial value of property
i, j, n	indices
test	indicates value of permeability ratio at which the break-through time is computed

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