

## SPE-181348-MS

# Modeling of Wormhole Propagation During Matrix Acidizing of Carbonate Reservoirs by Organic Acids and Chelating Agents

Olatokunbo O. Akanni and Hisham A. Nasr-El-Din, Texas A&M University

Copyright 2016, Society of Petroleum Engineers

This paper was prepared for presentation at the SPE Annual Technical Conference and Exhibition held in Dubai, UAE, 26-28 September 2016.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

## Abstract

Numerous carbonate matrix acidizing models have been developed to study the flow and reaction of Hydrochloric acid (HCl) in calcite, but there is a significant gap in the literature for models built to investigate wormhole propagation by alternative acidizing fluids such as organic acids and chelants. In this work, a model is developed to study wormhole propagation by these alternative fluids, using the two-scale carbonate acidizing model approach with Navier-Stokes formulation for fluid-flow description.

The reaction kinetics used for acetic acid (HAc) in the model is modified to account for the slight dissociation of the weak acid in aqueous solution and a fractional order of reaction. The output from the model is compared with available experimental data in the literature for qualitative and quantitative validation. This study extends the linear first-order reaction kinetics used for HCl in previous two-scale models for the chelating agents ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), with updated dissolution rate constants and dispersion coefficients, and the output compared with experimental data for qualitative validation.

The acid efficiency curves generated from the model for acetic acid compares qualitatively and quantitatively with reported experimental data, and the numerical simulations show that a higher amount of acid will be required to reach breakthrough for acetic acid than for HCl, as expected. The model output for the chelating agents does not match quantitatively with experimental data, but the qualitative trend can be observed from the numerical simulation results. The updated reaction kinetics for acetic acid is extendable to formic acid, which is the other commonly used organic acid in carbonate matrix acidizing, to obtain an equally dependable model output. However, a more complex reaction kinetics will be required to model the multi-step chemistry that occurs in the dissolution of carbonate by chelating agents.

The model developed in this study accurately captures the wormholing phenomena by acetic acid, and it can also be used to predict optimum injection rates for organic acids. The simulation results also show that the model, based on Navier-Stokes momentum formulation, is computationally less expensive than previous models with the Darcy-Brinkman formulation, and simulations at very high injection rates with this model require less computational time than models developed with the Darcy formulation.

## Introduction

The success of a carbonate matrix stimulation treatment depends on the acidizing fluid's ability to create dominant wormholes that propagate beyond the damaged or low-permeability region near the wellbore. Dominant wormholes are formed in an acid dissolution process during a carbonate matrix acidizing treatment if the acid is injected at an optimum rate. As the acid is thus injected, the large pores on the surface of the rock grow at a higher rate than the smaller pores. As the larger pores receive an increasing portion of the acidizing fluid during the process, their length and volume increase, eventually becoming wormholes. Wormhole patterns do not necessarily form in the dissolution of carbonate rock with an acid; the dissolution structure is mainly dependent upon the injection rate and fluid-mineral properties, which include the reaction kinetics, mass transfer rates, flow geometry, formation heterogeneity, and fluid loss rate. The dissolution patterns that can be formed during carbonate matrix acidizing are face dissolution, conical wormholes, dominant wormholes, ramified wormholes, and uniform dissolution.

At very low injection rates in laboratory coreflood tests, the acidizing fluid is consumed at the inlet flow face of the core before it can penetrate the rock, resulting in face dissolution. A high volume of the fluid is then required to reach breakthrough at the outlet. At slightly higher injection rates, a conical-shaped dissolution channel is formed as more acidizing fluid is consumed on the walls of the flow channels, and the fluid penetrates into the rock and enlarges flow channels. At an optimum injection rate, the fluid is transported to the tip of the evolving flow channel and propagates the channel, which then leads to the formation of a dominant wormhole. At injection rates higher than the optimum rate, the fluid is forced into smaller pores and the dissolution channels become more branched, resulting in ramified wormholes. At very high rates, the fluid penetrates into the medium but is not completely spent due to insufficient resident time, which leads to uniform dissolution patterns and unsuccessful treatment in field conditions.

The dissolution pattern during matrix stimulation affects the skin evolution because this pattern determines the depth of penetration of the acid into the rock. When dominant wormhole patterns are formed, the acid penetrates deepest into the formation, which leads to the highest reduction in skin after treatment. Therefore, to obtain the best results from an acid stimulation treatment, it is important to inject the acid at the optimum injection rate for the particular fluid-mineral system.

HCl is often used in carbonate matrix acidizing because it is relatively cheap, readily available, has a high dissolving power and the reaction products formed from the dissolution of carbonates is soluble. However, the use of HCl is impeded at elevated reservoir temperature conditions because the optimum injection rate for HCl to form dominant wormholes becomes higher than the maximum allowable injection rate to avoid formation fracture due to the increase in the surface dissolution rate with temperature, higher corrosivity of the acid on the well completion materials, and precipitation of acid-induced sludge or formation of rigid film emulsions from asphaltene present in the crude.

Alternative acidizing fluid systems such as organic acids, chelating agents, mixed acids, and retarded acids (foamed, emulsified, and gelled acids) have been successfully employed to stimulate carbonate reservoirs in high temperature conditions. The common factor with these fluids is a lower surface reaction rate, which means a lower injection rate will be needed to obtain the dominant wormhole patterns for an optimum treatment. Furthermore, there is easier corrosion inhibition control of the acids on the well completion materials.

To design optimal treatments, numerous theoretical and experimental studies have been conducted in the past to understand the propagation of wormholes during carbonate matrix acidizing. From these studies, mathematical models were developed to predict the dissolution structure of the acid-rock reaction, the optimum injection rate for the most efficient treatment, and/or the propagation rate of the wormholes in the rock with volume injected to monitor the skin evolution during treatment. Even though the transport and reaction of HCl in carbonate rock has been extensively studied in these models in the literature, little work has done on modeling wormhole propagation by the alternative acidizing fluid systems.

In this study, the propagation of wormholes in calcite by HCl, HAc, EDTA, and DTPA is modeled using a two-scale approach, modified with the Navier-Stokes momentum formulation to describe the fluid flow in porous media. The simple linear first-order reaction kinetics model used in the previous two-scale models for HCl cannot be applied for organic acids, because these weak acids do not dissociate completely in aqueous solution; therefore, the dissociation equilibrium has to be considered in their reaction kinetics with carbonates. A different reaction kinetics for acetic acid is used in this study, which accounts for the dissociation of weak acid and the linear first-order kinetics is used for chelating agents.

### **Literature Review**

Brief reviews of some carbonate acidizing models in literature can be found in Schechter (1992), Golfier (2002), Panga et al. (2005), and Glasbergen et al. (2009). A more extensive review and validation of carbonate acidizing models was made by Fredd and Miller (2000), in which the authors classified the mathematical models in five categories based on the approach to solution, and this was later extended to seven categories by Akanni and Nasr-El-Din (2015). These categories are the capillary tube approach, Damköhler number approach, transition pore theory, network models, Péclet number approach, semi-empirical approach, and two-scale (averaged continuum) models. Some models are based on more than one of the approaches listed with the Damköhler number theory being the most often combined one.

In the capillary tube approach, the wormhole is modeled as a cylindrical tube. The early models based on this approach simulated mass-transfer-limited dissolution based on bundles of capillary tubes (Rowan 1959) with a focus on the effect of fluid leakage and the mechanism of transport and reaction in the wormhole. Schechter and Gidley (1969) extended this theory to include the effects of pore merging surface reaction limited dissolution. Hung et al. (1989), Wang et al. (1993), Huang et al. (1997), and Buijse (2000) have also developed models based on this approach. A fundamental limitation of these models is the assumption of the initial formation of dominant wormholes, and, thus, microscopic pore distribution (number of pores and radii on rock surface where acid is injected) is required to set up the model.

Studies by Hoefner and Fogler (1988) show that the wormhole formation process is controlled by the Damköhler number. The effect of the Damköhler number on the wormhole structure was investigated and confirmed by their experimental work. The Damköhler number is defined as the ratio of the net rate of acid dissolution to the rate of transport of acid by convection. Fredd and Fogler (1998, 1999) conducted further studies on the effects of transport and reaction on the formation of wormholes for a wide range of fluid systems, including strong acids, weak acids, and chelating agents. They showed that these fluid systems are influenced by transport and reaction processes, and when both processes are taken into account, a common dependence on the Damköhler number is observed. A Damköhler number of approximately 0.29 is reported as optimal for all the fluid/mineral systems they investigated. The models based on the Damköhler number theory need to be combined with other models to predict skin evolution because they do not independently predict wormhole growth. Wormhole density and dimensions are required because the Damköhler number only applies to a single wormhole for a linear coreflood test, and the results do not translate directly to field scale.

The transition pore theory was originally developed by Wang et al. (1993) to calculate the optimum flux to generate dominant wormholes during a matrix acid treatment. They postulated that there exists a critical pore cross-sectional area on the face of the rock for the formation of wormholes. An expression was obtained from the growth rate functions, based on previous work by Schechter and Gidley (1969), which relates the optimum acid flux with the Damköhler number and emphasizes the effects of rock mineralogy, reaction temperature, and acid concentration. This method requires microscopic pore description for implementation. It cannot be applied for monitoring skin evolution during treatment, and it incorrectly predicts that an increase in acid concentration will decrease the optimal acid flux. Huang et al. (1997) included a fluid loss

model with the transition pore theory to translate the results from laboratory core scale to field scale, but the model exhibits the same basic limitations also observed in the Wang et al. (1993) model.

The network approach has been used by various investigators to describe processes in porous media where the important structural property of pore interconnectedness must be included. It was first introduced by Fatt (1956) and, according to Hoefner and Fogler (1988), has been employed successfully to include fluid displacement (Simon and Kesley 1972), relative permeability (Rose 1957), and dispersion in porous media (Sahimi et al. 1990). Hoefner and Fogler (1988) carried out a theoretical study on the dissolution of porous media by flowing acid using this approach, and also combined their work with experimental observations. They extended the works of Bryant et al. (1993) and Thompson and Fogler (1997) of a 3D physically representative network (PRN) model to simulate the effects of transport and reaction on the formation of wormholes. The network models require enormous computational power to translate to field or laboratory scale, making them unavailable for practical application.

The Péclet number theory model was first presented by Daccord et al. (1989) as a model which quantifies wormholes by their equivalent hydraulic length. This method is based on correlations at the scale of the core sample itself. The physical parameters involved in the problem are introduced in the form of dimensionless numbers. The model postulates that the propagation of wormholes is a function of the Péclet number, injection volume, and a fractal dimension. In developing the growth-rate equation for the radial case, it is assumed that the effect of a finite wellbore radius is equivalent to pumping an extra volume of fluid equal to that necessary to get a penetration equal to the wellbore radius. Frick et al. (1994) extended the work of Daccord et al. (1989) by also considering wormholes as fractals. The influences of acid volume, injection rate, fractal dimension, porosity, and the ratio of undamaged to damaged permeability on well performance are factored in. The results of their study incorrectly suggest that the injection rate has no major effect on the dissolution patterns.

Buijse and Glasbergen (2005) developed a semi-empirical approach to capture the essential physics and chemistry of wormhole propagation in carbonates, in which the growth rate of the wormhole front was modeled as a function of the interstitial velocity of the acid. Parameters such as permeability, mineralogy, temperature, and acid concentration are not modeled explicitly, but they are incorporated in the model in the form of two constants calculated from the optimum acid velocity and pore volume to breakthrough at this velocity. These constants are obtained from coreflood tests for the fluid/mineral system being investigated. In developing a radial analogue of the linear wormhole model, it is assumed that the functional relationship between the interstitial velocity and the growth rate increase of the wormhole front as observed in coreflood tests holds for radial geometry.

Furui et al. (2012) extended this semi-empirical model and combined it with the earlier described capillary tube model (Hung et al. 1989), which is based on acid transport and fluid loss from a single wormhole. This model improves on the original one by accounting for the effect of core dimensions used in the coreflood test, from which the parameters used in the model are obtained. Wormhole growth is related to the in-situ injection velocity at the tip of the dominant wormhole, and at sufficiently high injection velocity, the acid concentration at the wormhole tip is assumed to be equal to the acid concentration at the injection point. The effective surface area available for the acid reaction is assumed to be proportional to the wormhole penetration length. The results of this model depend on the efficiency of the coreflood experiments, from which the main parameters used in the equations are obtained.

In the two-scale (averaged-continuum) approach, the transport and reaction of the acidizing fluid is modeled as an interaction between the Darcy scale and the pore scale. Liu et al. (1997) developed a Darcy-scale coupled fluid flow simulator for sandstones, which was extended for the dissolution of carbonates by Golfier et al. (2002). The modified model uses a mass transfer coefficient that is calculated from a pore scale simulation at each stage in the model simulation, thereby coupling the pore-scale phenomena to the Darcy scale. The model assumes a complete mass transfer controlled reaction and is shown to capture qualitative and quantitative features of dissolution in the mass transfer controlled regime. Panga et

5

al. (2004, 2005) later developed a two-scale continuum model, which captures the reaction and transport mechanisms for describing wormhole formation in carbonates. Kalia and Balakotaiah (2007) built on the work by Panga et al. (2005) to simulate radial flow in the model. Kalia and Balakotaiah (2009) studied the effect of heterogeneities of the porous medium on the dissolution patterns formed during a carbonate acidizing process using the two-scale model.

For quantitative comparison with experimental data, Maheshwari et al. (2012) extended the two-scale model for 3D simulation. This model was further extended to be made applicable for gelled acids by Ratnakar et al. (2012), in which the two-scale model is combined with a semi-empirical rheological model that accounts for viscosity as a function of pH, shear rate, and temperature. This was also employed for emulsified acids by Maheshwari et al. (2014). These authors were able to match the numerical simulation output with quantitative trends from previous experimental results. Other applications of the two-scale approach have been made by various investigators. De Oliveira et al. (2012) used the model to investigate the effect of mineralogical heterogeneity on the amount of acid injected as a function of injection rates. Liu et al. (2012) examined the effect of normally distributed porosities on wormholing patterns, and Zhang et al. (2014) studied wormhole propagation behavior and its effect of acid leakoff in acid fracturing with the two-scale model.

The two-scale models give a good prediction of the dissolution pattern for the HCl-based systems as mentioned. They can also provide an estimation of the optimum injection rate for laboratory scale experiments but will require enormous computational power to be directly applicable for field scale simulation. For emulsified acid, the Maheshwari et al. (2014) model does not account for emulsion droplet size distribution, and it is assumed that the droplets are very fine and will be unchanged as the acid propagates through the rock. For gelled acid, the Ratnakar et al. (2012) and Maheshwari et al. (2014) models do not account for polymer adsorption at the pore walls. First order irreversible reactions are assumed for the kinetics in these models, which makes them inapplicable for acidizing fluids with more complex reaction kinetics with carbonates. There is no carbonate acidizing model for wormhole propagation by chelants and organic acids in the literature at the time of writing.

## **Model Description**

Reaction and transport of the acidizing fluid in calcite is modeled with the two-scale approach. The model is briefly presented here; a detailed explanation of the development of the approach is given in Panga et al. (2002, 2005). The flow field is given by Darcy's law in their model, but in this study the flow field is described by the Navier-Stokes momentum formulation. The equations for the Darcy and pore scale models are presented below.

#### **Darcy-Scale Equations**

The fluid flow field is given by the Navier-Stokes formulation:

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \nabla \cdot \boldsymbol{\tau} - \frac{\mu}{\mathbf{K}} \mathbf{u} \quad , \tag{1}$$

where **u** is the superficial velocity vector,  $\rho$  is the fluid density, **K** is the permeability tensor, *p* is pressure, and  $\tau$  is the stress tensor. The continuity equation, Eq. 2, derived from the mass balance of fluids, accounts for the effect of local volume change during dissolution on the flow field:

$$\frac{\partial \varepsilon}{\partial t} + \nabla \cdot \mathbf{u} = 0 \quad . \tag{2}$$

The Darcy-scale description of the transport of acid species, from fluid phase balance of reacting species, is given by:

$$\frac{\partial(\varepsilon C_f)}{\partial t} + \mathbf{u} \cdot \nabla C_f = \nabla \cdot \left(\varepsilon \mathbf{D}_{\boldsymbol{e}} \cdot \nabla C_f\right) - k_c a_v (C_f - C_s) \quad , \tag{3}$$

where  $\varepsilon$  is the porosity of the medium,  $C_f$  is the concentration of the acid in the fluid phase,  $C_s$  is the concentration of the acid at the fluid-solid interface,  $D_e$  is the effective dispersion tensor,  $k_c$  is the local mass-transfer coefficient, and  $a_v$  is the interfacial area available for reaction per unit volume of the medium. The reaction kinetics in Eq. 4 balances the amount of acid transferred from the fluid phase to the surface to the amount reacted at the surface:

$$k_c(C_f - C_s) = R(C_s) \quad . \tag{4}$$

The porosity evolution equation, derived from the balance between the solid dissolved and fluid consumed, is given by:

$$\frac{\partial \varepsilon}{\partial t} = \frac{R(C_s)a_v\alpha}{\rho_s} \quad , \tag{5}$$

where  $R(C_s)$  represents the reaction kinetics,  $\rho_s$  is the density of the rock, and  $\alpha$  is the dissolving power of the acid. Equations 1 through 5 are the Darcy scale model equations, as described by Panga et al. (2005).

*Reaction kinetics for HCl.* The kinetics equation for HCl can be written as:

$$R(C_s) = k_s C_s \quad , \tag{6}$$

where  $k_s$  is the surface dissolution rate constant. Substituting this kinetics equation into Eq. 4 gives a direct relation between the acid concentration in the fluid phase and at the fluid-solid interface (as a function of the local mass transfer coefficient and surface dissolution rate) as given below:

$$C_s = \frac{C_f}{\left(1 + \frac{k_s}{k_c}\right)} \quad . \tag{7}$$

*Reaction kinetics for Acetic acid.* The linear first-order reaction kinetics used for HCl cannot be applied for organic acids because weak acids such as organic acids do not dissociate completely in aqueous solution. Therefore, the dissociation equilibrium has to be considered in their reaction kinetics with carbonates. The dissociation of an acid in aqueous solution can be represented by the reaction in Eq. (8) below:

$$HA \rightleftharpoons H^+ + A^- \quad . \tag{8}$$

The dissociation (equilibrium) constant,  $K_d$ , is expressed by:

$$K_d = \frac{a_{\rm H} + a_{\rm A}}{a_{\rm HA}} \quad , \tag{9}$$

where  $a_{H}^{+}$  and  $a_{A}^{-}$  denote the activities of the H<sup>+</sup> and A<sup>-</sup> ions, respectively.

The kinetics equation for organic acid-carbonate reaction in Eq. 10 is given by Schechter (1992), and this is used for acetic acid-limestone in the model in this study:

$$R(C_{HAc}) = k_s K_d^{n/2} C_{HAc}^{n/2} \quad , \tag{10}$$

where  $C_{HAc}$  is the concentration of acetic acid at the solid-fluid interface, equivalent to  $C_s$  in Eq. 6. The dissociation constant, a function of temperature (T in °K), is obtained from Eq. (11):

$$-\log_{10}K_d = \frac{A_1}{T} - A_2 + A_3T \quad . \tag{11}$$

The values of the constants  $A_1$ ,  $A_2$ , and  $A_3$  are given as 1170.48, 3.1649, and 0.013399, respectively (Schechter 1992). In addition to replacing Eq. 6 in the two-scale model for HCl-limestone with Eq. 10 for acetic acid-limestone reaction, the model is updated with the values of dissolution rate constant, acid diffusivity, density, and viscosity for acetic acid at pH values of 2.5 and 4.6.

#### **Pore-Scale Equations**

The porosity of the rock increases as the acid propagates and dissolves part of the solid phase. This results in changes of pore-scale properties such as permeability, pore-radius ( $r_p$ ), and interfacial surface area per unit volume. The relationship between these rock properties and porosity are adapted from the Carman-Kozeny correlation and are given by the following pore scale equations (Panga et al. 2005):

$$\frac{K}{K_o} = \frac{\varepsilon}{\varepsilon_o} \left( \frac{\varepsilon(1 - \varepsilon_o)}{\varepsilon_o(1 - \varepsilon)} \right)^{2\beta} \quad , \tag{12}$$

$$\frac{r_p}{r_o} = \left(\frac{\varepsilon(1-\varepsilon_o)}{\varepsilon_o(1-\varepsilon)}\right)^{\beta} \quad , \tag{13}$$

and

$$\frac{a_{\nu}}{a_{o}} = \left(\frac{\varepsilon}{\varepsilon_{o}}\right) \left(\frac{\varepsilon(1-\varepsilon_{o})}{\varepsilon_{o}(1-\varepsilon)}\right)^{-\beta} \quad , \tag{14}$$

where  $\beta$  is the pore structure relation constant. The local mass transfer and effective dispersion coefficients are obtained using correlations (Gupta and Balakotaiah 2001; Balakotaiah and West 2002):

$$Sh = \frac{2k_c r}{D_m} = Sh_{\infty} + 0.7Re_p^{1/2}Sc^{1/3} \quad , \tag{15}$$

$$\boldsymbol{D}_{\boldsymbol{eX}} = \alpha_{os} D_m + \frac{2\lambda_X \|\mathbf{u}\|r}{\varepsilon} \quad , \tag{16}$$

and

$$\boldsymbol{D}_{\boldsymbol{e}T} = \alpha_{os} D_m + \frac{2\lambda_T \|\mathbf{u}\|_T}{\varepsilon} \quad . \tag{17}$$

Sh is the Sherwood number or dimensionless mass-transfer coefficient;  $Sh_{\infty}$  is the asymptotic Sherwood number;  $Re_p$  is the Reynolds number defined by  $\operatorname{Re}_p = \frac{2\|\mathbf{u}\|r}{v}$ , and Sc is the Schmidt number given by  $Sc = \frac{v}{D_m}$ ; v is the kinematic viscosity;  $\alpha_{os}$  is a constant that depends on the structure of the porous medium (pore connectivity);  $D_{eX}$  is the longitudinal dispersion coefficient;  $D_{eT}$  is the transverse dispersion coefficient in the y- and z- directions;  $\lambda_X$  and  $\lambda_T$  are constants that depend on the structure of the medium ( $\lambda_X \approx 0.5$  and  $\lambda_T \approx 0.1$  for a packed bed of spheres). These correlations account for both diffusive and convective contributions in fluid transport (Maheshwari and Balakotaiah 2013).

### Model Implementation

To run the simulations of the described two-scale model with Navier-Stokes formulation, a commercial Computational Fluid Dynamics (CFD) software is employed to solve the momentum, mass continuity, and transport equations in the Darcy scale. This is combined with functions and routines written in the C programming language to solve the porosity evolution equation, update the pore scale parameters at every

time step, and couple the pore scale with the Darcy scale. Fig. 1 gives the workflow of the simulation showing the sequence of equations solved in the model.



Figure 1—The simulation workflow showing the sequence of solutions and properties updates.

The simulations are run on Texas A&M University (TAMU) High Performance Research Computing (HPRC) systems to facilitate parallel processing. The computational time to reach breakthrough in the dominant wormholing regime is nearly three to four hours, but the time taken to reach breakthrough in the ramified and uniform dissolution regimes (high injection rates) is lower than that. At very low injection rates (face dissolution regime), the computational time is in days.

### **Base Case**

The base case is modeled to simulate the acidizing coreflood tests of 0.5 M HCl on calcite core samples, based on the experimental work by Fredd and Fogler (1998). In the simulation study for the 3D model, the numerical mesh domain is a 4 in. long cylindrical shape with a 1.5 in. diameter. The grid cells are made of 400,000 hexahedral and quadrilateral cells. For the 2D case, the numerical mesh domain is rectangular with a dimension of  $1.5 \times 4$  in. and made up of 110,000 quadrilateral grid cells.

Table 1 gives the values of the parameters used in the base case of this simulation study. These values are obtained from the aforementioned experimental work of Fredd and Fogler (1998) and simulation study by Maheshwari and Balakotaiah (2013). The experiments were conducted at temperature of 23°C. Table 2 lists the fluid properties of the chelates used in this model (from the same experimental studies).

#### Table 1—Parameters used in numerical simulations (from Fredd and Fogler 1998; Maheshwari and Balakotaiah 2013).

Parameter	Value
Acid diffusivity ( <i>D<sub>m</sub></i> )	3.6e-09 m <sup>2</sup> /s
Acid dissolving power $(\alpha)$	50 kg/kmol
Acid viscosity ( $\mu$ )	0.001 kg/m-s
Asymptotic Sherwood number $(sh_{\infty})$	3.66
Average porosity $(\varepsilon_{\theta})$	0.2
Constant in dispersion correlations ( $\alpha_{os}$ )	0.5
Constant in axial dispersion correlation $(\lambda_x)$	0.5
Constant in transverse dispersion correlation ( $\lambda_T$ )	0.1
Initial average permeability $(K_o)$	1e-15 m <sup>2</sup>
Initial interfacial area per unit volume $(a_o)$	5000 m <sup>-1</sup>
Initial mean pore size $(r_o)$	1 μm
Pore structure relation constant $(\beta)$	1
Porosity heterogeneity magnitude $(\varDelta \varepsilon_0)$	± 0.1
Rock density $(\rho_s)$	2710 kg/m <sup>3</sup>
Surface dissolution reaction-rate constant $(k_s)$	0.002 m/s

#### Table 2—Fluid properties of chelants updated in the model (from Fredd and Fogler 1999).

Acidizing fluid	Acid diffusivity (m <sup>2</sup> /s)	Reaction rate constant (m/s)	Inlet acid concentration (mass fraction)
0.25 M EDTA (pH 4)	6e-10	1.4e-06	0.0848
0.25 M DTPA (pH 4.3)	4e-10	4.8e-07	0.0655

For simulation of very low injection rates (which leads to face dissolution regime), the number of grid cells has to be increased to effectively capture the dissolution at these regimes. According to simulation studies by Maheshwari and Balakotaiah (2013), approximately 160 million grid cells will be required to effectively capture face dissolution for the mesh domain size of a  $1.5 \times 1.5 \times 4$  in. rectangular parallelepiped domain, which is similar to the cylindrical domain of 1.5 in. diameter by 4 in. length used in this work.

As expected, more computational time will be required to complete the simulation at very low injection rates because the dissolution takes place at a slower rate and more of the rock will be dissolved in the facedissolution regime. In addition, since a high number of grid cells are required to accurately capture the dissolution pattern at these regimes, the simulation runs at a much slower rate in real time, which means more computational time will be needed. Unfortunately, there are limited high performance computing licenses available for parallel computing with the CFD software at the TAMU HPRC facility to practically run simulations at face dissolution regimes for this large computational mesh domain and high number of grid cells.

The current solution to this limitation is to use a smaller mesh domain to capture and demonstrate the dissolution patterns at the conical and face dissolution regimes. The domain is reduced by a factor of five for the 3D and 2D linear cases with the number of grid cells kept the same. The pore volumes to breakthrough  $(PV_{BT})$  results for the larger domain compare qualitatively with that of the smaller domain at and above the optimum injected rates, and this is extended for rates below the optimum injection rate. Information on other domain sizes used in this work to study the radial flow and the effect of medium dimensions on the acid efficiency curve will be provided in the discussion of results.

## **Numerical Solution Scheme**

A control-volume-based technique is used to solve the momentum conservation and transport equations in the Darcy scale of the two-scale model. The equations are converted to algebraic equations which are then solved numerically with the finite volume method.

A Pressure-Implicit with Splitting of Operators (PISO) pressure-velocity coupling scheme is employed, with neighbor and skewness correction to improve efficiency. A least squares cell-based spatial discretization method is used for constructing the fluid concentration values at the cell faces with a second order upwind scheme, and a Quadratic Upstream Interpolation for Convective Kinematics (QUICK) scheme is used for the momentum term.

The time-step size for the numerical simulation is varied between 0.1s and 0.01s, depending on the dissolution regime. The lower time-step size is used at the conical and face dissolution regimes. The maximum number of iterations per time step is set at 20.

## **Initial and Boundary Conditions**

For wormholes to be initiated in the carbonate rock, there must be some heterogeneity in the porous medium. This is introduced in this model in the form of porosity heterogeneity. The average porosity of the base case is 0.2 with a heterogeneity of 50%, which means the values in the porosity distribution profile range from 0.1 to 0.3. A least squares interpolation method is then used to assign the porosity values from the generated profile to individual grid cells in the numerical domain. Fig. 2 shows the initial porosity distribution for the different domain cases used in this study. Other initial conditions are zero velocity field in the medium and zero acid concentration.



Figure 2—The initial porosity profiles of domain cases used in this study.

The boundary condition at the core inlet is a constant injection velocity, based on the input for the particular simulation run, and a concentration of 0.5 M HCl. The acid flux and average pressure at the outlet of the core is kept at zero. There is no flow and zero acid flux across the boundary at the walls of the domain.

## **Results and Discussion**

The results of sensitivity test simulations carried out in this study are presented mainly in the form of acid efficiency curves. This is a plot (log or semilog) of the  $PV_{BT}$  versus the injection rate or velocity. From

these curves, the optimum injection rate and the minimum  $PV_{BT}$  values for the conditions being investigated can be observed. The breakthrough time of acid at the outlet of the core in the numerical simulation is determined to occur when the pressure drop across the porous medium drops to 1/100th of its initial value (Kalia and Balakotaiah 2009).

#### 2D and 3D Linear Flow Model

The results from the 2D and 3D flow models are presented here. The dissolution patterns from a 2D simulation model with linear flow are displayed in Fig. 3 by the porosity contour of the numerical simulation of the coreflood acidizing process. The output shows that the model effectively captures the dissolution patterns in carbonate acidizing and also shows the effect of injection rate (and Damköhler number) on the type of dissolution pattern formed.



Figure 3—Porosity contour showing the dissolution patterns obtained from injection rates ranging from a minimum of 3.23e-06 m/s to a maximum of 0.323 m/s (to capture all possible dissolution patterns) from the 2D linear flow model.

Fig. 4 presentes the acid efficiency curve from the 2D linear flow model. The semilog plot shows that at low injection rates, a large amount of acid is required to reach breakthrough at the outlet of the porous medium. This is because face dissolution occurs at these rates and the acid will have to completely dissolve the solid phase before fluid breakthrough is observed at the exit of the core. The amount of acid to breakthrough decreases as the injection rate increases until it reaches an optimum injection rate at which minimum  $PV_{BT}$  occurs. The amount of acid required to breakthrough gradually increases at rates above the optimum injection rate. The  $PV_{BT}$  is observed to increase with the acid injection rate (Q) as  $Q^{1/3}$ , which is similar to the experimental results reported by Frick et al. (1994) and Bazin (2001). At very high injection rates (in the uniform dissolution regime), the slope of the plot is observed to change from one-third to unity. Maheshwari and Balakotaiah (2013) also reported this trend of the proportionality of the acid injection rate and  $PV_{BT}$  values above optimum injection rate from simulation studies.



Figure 4—The acid efficiency curve of the 2D numerical simulation with linear flow showing the effect of the injection rate on the volume of acid required to reach breakthrough.

The output from the numerical simulation of the 3D linear flow model showing the various dissolution regimes are presented in Fig. 5 and the patterns are similar to experimentally observed dissolution images reported in previous studies (Hoefner and Fogler 1988; Fredd and Fogler 1998; Fredd and Miller 2000). The dissolution process and the effect of injection rate on wormhole formation in the 3D model are similar to those in the 2D model, as explained in the previous section.



Figure 5—Dissolution patterns from the numerical simulation of the 3D linear flow model.

Fig. 6 shows the comparison of the acid efficiency curves from the 2D and 3D models. This compared output follows the expected theoretical trend presented in a previous study (Panga et al. 2005). The plot shows that the amount of acid required to breakthrough in the wormhole regimes and the optimum injection rate are higher in the 2D than in the 3D model. The difference in  $PV_{BT}$  values occurs because in 2D, the wormhole volume is the wormhole surface in two discretized directions multiplied by the depth of the domain in the third undiscretized direction, and this volume is greater than the wormhole volume in the 3D model (Cohen et al. 2008). The  $PV_{BT}$  values at the face and uniform dissolution regimes are independent of the dimension of the model because spatial gradients do not appear in the asymptotic limits (Panga et al. 2005).



Figure 6—Comparison of the acid efficiency curves from the numerical simulation of 2D and 3D models.

#### **Effect of Flow Geometry**

To investigate the effect of flow geometry on the acid efficiency curve, a 2D radial flow model is developed for comparison with the 2D linear flow model with the same aspect ratio. The 2D domain is a circular mesh with an external radius of 0.79 inches and an internal radius of 0.079 inches. The mesh is made up of 110,000 quadrilateral grid cells. The injection inlet is at the internal radius, and the fluid propagates radially towards the external radius until breakthrough at the boundary. The dissolution patterns from radial flow are similar to the patterns from the linear flow model (Fig. 7).



Figure 7—Porosity contour showing the dissolution patterns obtained from injection rates ranging from a minimum of 3.23e-06 m/s to a maximum of 0.323 m/s (to capture all possible dissolution patterns) from the 2D radial flow model.

Fig. 8 shows the comparison of the acid efficiency curves from the radial and linear flow models. It can be seen that the optimum injection rate in the radial flow model is higher than that of linear flow. The optimum injection rate in the radial flow model is higher because the injection velocity decreases with the increasing domain radius as the wormholes propagate in the medium (Kalia and Glasbergen 2009). The radial flow model exhibits enhanced branching of wormholes that are thinner than those in the linear flow model. Thus, the  $PV_{BT}$  at the optimum injection rate in the radial flow model is lower than that of the linear model. These results are consistent with observations from previous studies (Frick et al. 1994; Cohen et al. 2008).



Figure 8—The comparison of the acid efficiency curve of the linear and radial flow 2D cases show that the optimum injection rate is higher for the radial case with a lower volume of acid required to reach breakthrough.

#### **Effect of Initial Average Porosity**

To study the effect of initial average porosity on wormhole propagation, three 2D linear flow cases of initial average porosity values of 0.1, 0.2, and 0.3 with the same porosity heterogeneity range of 50%, are simulated. Fig. 9 shows the dissolution patterns at the optimum injection rate. It can be seen that the higher the initial average porosity of the medium, the larger the wormhole diameter due to more fluid loss along the walls of the wormhole. Fig. 10 gives the acid efficiency curves highlighting the amount of acid injected to breakthrough for the three cases.



Figure 9—Effect of initial average porosity on wormhole patterns (formed at an injection rate of 1.5 cm<sup>3</sup>/min).



Figure 10—Acid efficiency curves showing the effect of initial average porosity on the amount of acid injected to reach breakthrough.

In the face dissolution regime, a higher amount of acid is required to reach breakthrough for cases with lower initial average porosity values. This is because complete dissolution of the rock occurs in this regime, and the lowest porosity case will require the most amount of acid to reach breakthrough due to the highest percentage of solid phase in the medium. In the intermediate regime, the acid injected to breakthrough is higher for cases with higher initial average porosity because of the formation of wider wormholes, as previously explained. At high injection rates, the medium exhibits increased fluid loss for cases with high initial porosity, requiring more acid to achieve a certain factor of increase in permeability than for low initial porosity cases.

#### **Effect of Porosity Heterogeneity**

The influence of medium heterogeneity on wormholing and  $PV_{BT}$  is examined here. Cases with porosity heterogeneity ranging from 0.5 to 0.95% of average porosity are simulated. The wormholes become thinner and more branched as the heterogeneity of the medium increases (Fig. 11). Fig. 12 presents the acid efficiency curves of the various cases simulated with different heterogeneity magnitude values and Fig. 13 shows the effect of heterogeneity magnitude on  $PV_{BT}$  at the optimum injection rate.



Figure 11—Dissolution structures showing the effect of porosity heterogeneity magnitude on the wormhole patterns.



Figure 12—Acid efficiency curves showing the effect of porosity heterogeneity magnitude on the pore volumes of acid required to reach breakthrough.



Figure 13—Effect of porosity heterogeneity on pore volumes to breakthrough at the optimum injection rate.

The difference in the  $PV_{BT}$  values for the various heterogeneity cases is pronounced in the wormholing regime, but not as much as in the face and uniform dissolution regime (Fig. 12). In the uniform dissolution regime, the  $PV_{BT}$  slowly decreases as the porosity heterogeneity magnitude increases. This is because at a high heterogeneity magnitude, ramified wormholes tend to form (instead of uniform dissolution) more than they would at a lower heterogeneity magnitude with the same injection rate, which leads to a reduced amount of acid required for breakthrough.

At the optimum injection rate, Fig. 13 shows that the  $PV_{BT}$  will be high for cases with very low heterogeneity magnitude. For a rock with very low heterogeneity, the dissolution process resembles that of face dissolution at the initial stage before branching occurs, and an additional amount of acid will be consumed in the dissolution of the face of the rock (Fig. 11a). Another reason for high  $PV_{BT}$  values for cases with low heterogeneity magnitude is that the diameter of the wormholes is thicker and less branched, also requiring more acid for propagation.

Results show that  $PV_{BT}$  decreases with an increase in porosity heterogeneity magnitude (Fig. 13) until a critical value ( $\Delta \varepsilon_c = \pm 0.05$ ) is reached, after which higher heterogeneity values has no significant effect on the  $PV_{BT}$  at this optimum injection rate.

#### **Effect of Presence of Vugs (Large-Scale Heterogeneities)**

To examine the effect of vugs on wormholing in carbonates, the initial porosity profile is modified according to vuggy carbonate characterization results from the Nuclear Magnetic Resonance (NMR) study conducted by Vik et al. (2007). A case with total initial average porosity of 0.3 is designed with random vugs in the medium that accounts for 65% of the total porosity. The vugs are assigned porosity values of 0.9 and the matrix porosity values vary between 0.15 and 0.45. Fig. 14a shows the initial porosity profile with random distribution of vugs in the 2D domain, and Fig. 14b presents the wormhole patterns in form of the porosity contour profile after simulation of coreflood injection at an optimum rate.



Figure 14—Porosity contour profile showing (a) initial porosity profile of vuggy carbonate core and (b) wormhole patterns formed with acid injected at a flowrate of 1.55 cm<sup>3</sup>/min in the vuggy carbonate core.

The velocity field at various time intervals during the coreflood injection simulation is illustrated in Fig. 15. The images show the effect of vugs on the branching of the flow field during injection, and also how their sizes and distribution determine the flowpath of the acid (Figs. 15a and 15b). After breakthrough is achieved at the outlet of the core, the fluid flows through the singular path of least resistance, which is the dominant wormhole created in the dissolution process (Fig. 15c).



Figure 15—Contours of velocity magnitude as acid propagates in the vuggy carbonate rock at different time (t) intervals during injection at a flowrate of 1.55 cm<sup>3</sup>/min: (a) t = 40 s (b) t = 80 s (c) t = 140 s.

The numerical simulation shows that acid propagates faster in the vuggy medium than in the uniform heterogeneous porosity medium. This is evident in the plot given in Fig. 16, which compares the acid

efficiency curves of both carbonate mediums with different heterogeneity scales. The diameter of the vugs in the path of the wormhole determines its diameter. The amount of acid required to reach breakthrough in the vuggy carbonate core is lower than that of a non-vuggy carbonate, which is agreement with experimental results reported by Izgec et al. (2010). Their experimental and numerical work also showed that the wormhole flow path is determined by the local pressure drops created by vugs. The  $PV_{BT}$  value in the vuggy medium is dependent on the positions, amount and connectivity of vugs.





#### **Effect of Medium Dimension**

Various mesh domains for the 2D model are developed to study the effect of the aspect ratio (core dimensions) on the acid efficiency curve. The aspect ratio is defined as the ratio of the height of the domain to its length. Fig. 17 shows the dimensions of the domains and corresponding aspect ratio values used in this study. The maximum core length investigated is 1.574 in. due to computational limitations. An extremely high number of grid cells will be required to simulate conical and face dissolution in core lengths of 6 in. and 20 in., used in experimental work by Furui et al. (2012) to study the effect of core dimensions on wormhole propagation.



Figure 17—Wormhole patterns for cores with various dimensions with the following aspect ratios (AR): (a) AR = 0.4, (b) AR = 2, (c) AR = 4, (d) AR = 0.2.

The first set of results presented in Fig. 18a show that the value of the optimum injection rate is higher for the long core. The longer the acid propagates in the domain before breakthrough at the outlet, the more the acid is consumed at the walls of the wormhole, so a higher optimum injection rate will be required to transport the acid to the tip of dominant wormhole for longer domains. This trend is in agreement with experimental studies by Bazin (2001) on the effect of core length on the acid efficiency curve.



Figure 18a—Numerical model results showing the effect of core length on the acid efficiency curve (short core length = 0.787 in. and long core length = 1.574 in.).

Fig. 18b shows the results of the effect of the domain height (core diameter) on the acid efficiency curve. The plot shows that  $PV_{BT}$  in the wormhole regimes is inversely proportional to the domain height. It can be seen from Fig. 17 that the number of wormholes initiated at the injection inlet increases with the height of the domain, but only one dominant wormhole reaches the outlet. This means that the fractional amount of solid phase to be dissolved for the acid to reach breakthrough is reduced with an increase in the domain height. At very high injection rates, the  $PV_{BT}$  does not depend on the height of the domain because the amount of acid required to reach breakthrough increases proportionally with domain height due to the uniform dissolution of the solid phase. These results are consistent with experimental studies by Furui et al. (2012) on the effect of core diameter on amount of acid injected to breakthrough.



Figure 18b—Simulation results showing the effect of the core aspect ratio on the acid efficiency curve [length of core is fixed at 0.787 in.; diameters of the three cases are 0.314 in. (AR = 0.4), 1.574 in. (AR = 2), and 3.149 in. (AR = 4)].

#### **Effect of Reaction Kinetics**

The effect of the reaction rate constant and the order of reaction on the optimum injection rate and  $PV_{BT}$  values are examined.

**Reaction Rate Constant.** Three cases with different reaction rate constants are simulated, and Fig. 19 presents the resulting acid efficiency curves. To reach the dominant wormhole regime, the faster reacting acid will have to be injected at a higher rate than a slower reacting acid in order for most of the acid to be transported to the tips of the wormholes and not be totally consumed along the walls of the wormholes. Previous experimental studies have shown that wormholes created by highly reactive acid are thinner and more branched than those created by slow-reacting acid. This leads to lower  $PV_{BT}$  values and higher optimum injection rates at the wormhole regimes for acids with higher reaction rate constants. This trend in Fig. 19 is similar to that observed in the experimental study by Bazin (2001) and Furui et al. (2012) on the effect of acid concentration (which determines acid reactivity) on the acid efficiency curve.



Figure 19-Numerical model results showing the effect of reaction rate constant on the acid efficiency curve.

**Order of Reaction.** In the cases presented so far for this simulation study, linear first-order kinetics is assumed, and the output has been shown to agree qualitatively with experimental results. Here, a nonlinear reaction kinetics model is used in which,  $R(C) = k_s C_s^n$ , where n is the order of reaction. The simulation results showing the effect of the order of reaction are presented in Fig. 20. The higher the order of reaction, the lower the optimum injection rate and amount of acid required to reach breakthrough. As noted by Maheshwari et al. (2012), there is no agreement in the literature about the magnitude of reaction rate constant and order of reaction, but these simulation results show that the order of reaction significantly influences  $PV_{BT}$  values.



Figure 20-Numerical model results showing the effect of order of reaction on the acid efficiency curve.

#### Alternative acidizing fluids

The reaction kinetics are modified to model the alternative acidizing fluids. For acetic acid, Eq. 6 used for HCl is replaced by a non-linear relation (Eq. 10), which accounts for the weak dissociation of the organic acid as explained in the Model Description section. For the chelating agents, the values of the reaction kinetics parameters of Eq. 6 are updated accordingly.

### **Acetic Acid**

The  $PV_{BT}$  values from the 2D numerical simulations for acetic acid, at pH 2.5 and 4.6, are normalized with HCl  $PV_{BT}$  values, and the acid efficiency curves are plotted alongside experimental results from Fredd and Fogler (1999) for comparison (Fig. 21). The simulation results are represented by the solid lines and experimental data by marker points.



of HCI and acetic acid with experimental work from Fredd and Fogler (1999).

The experimental and simulation results for HCl give a good match, as has been demonstrated in the previous results shown. For acetic acid, the model output also matches well with the experimental results, except at the extreme values of injection rates. This slight mismatch could be due to how the  $PV_{BT}$  values are obtained from the model, which is when the pressure drop across the numerical domain drops to  $1/100^{\text{th}}$  of its initial value. This gives  $PV_{BT}$  values lower than experimentally obtained ones, because of the additional time in the experiment in which acid physically breaks through at the outlet of the core.

#### **Chelating Agents**

The multi-step chemistry at the solid-fluid interface that occurs during the dissolution of limestone by chelants is complicated and not representable by any available kinetics equation in the literature. In this study, the linear first-order reaction kinetics equation for HCl is used to simulate calcite acidizing with EDTA and DTPA. The fluid properties in the model are changed to those of EDTA and DTPA (values obtained from Fredd and Fogler 1999), as given in Table 2.

Fig. 22 shows that acid efficiency curves from the numerical simulation of EDTA and DTPA as acidizing fluids do not quantitatively match with experimental results from Fredd and Fogler (1998) as well as that

of HCl. This trend is expected because the first order kinetics equation used is more representative of the reaction of HCl-calcite than that of chelant-calcite. A more complex multi-step chemistry, beyond the scope of this paper, is involved in the dissolution by chelants.



Figure 22—Normalized model results comparing the acid efficiency curves of HCI and chelating agents (EDTA and DTPA) with experimental results from Fredd and Fogler (1998).

# Conclusions

In this study, a modified two-scale model has been used to study wormhole propagation during carbonate acidizing. The reaction kinetics is modified to extend the model for acetic acid, EDTA, and DTPA. The results from this model are compared with reported experimental data and previous models in the literature. The following conclusions are made from the numerical simulations conducted in this study:

- 1. The Navier-Stokes momentum formulation can be used to effectively describe fluid flow in the twoscale model, and the modified model in this work captures all the dissolution patterns that occur during carbonate matrix acidizing.
- 2. Sensitivity tests conducted on the model for various factors that affect wormhole propagation by HCl provided results consistent with experimental observations and previous two-scale models with flow field given by Darcy's law.
- 3. At dissolution regimes above the optimum injection rate, the computational time using the Navier-Stokes formulation is significantly lower than the reported computational time by the models based on Darcy's law and the Darcy-Brinkman formulation.
- 4. Simulation results showed that higher  $PV_{BT}$  values are obtained when lower fractional values of the order of reaction are used in the reaction kinetics equation of the model. This is because the fractional order of reaction in the model reduces the concentration of acid available for dissolution of calcite (to increase porosity); therefore, more acid will be required to be injected to achieve breakthrough than would be for a first-order kinetics equation.
- 5. To apply the two-scale model for acetic acid, the use of the Schechter (1992) reaction kinetics equation of organic acids and calcite produces normalized simulation output that are in agreement with experimental results.

6. The complex multi-step chemistry in the dissolution of calcite by the chelating agents is not easily modeled in the two-scale approach, and the normalized simulation results from the application of first order kinetics in the model does not match perfectly with experimental results.

This work has shown that the fluid flow in the two-scale model can be effectively described by the Navier-Stokes momentum formulation and the simulation results compare favorably with experimental and theoretically expected results. The output from the modified model for acetic acid matches reported experimental data, confirming the model can be effectively used for alternative acidizing fluids.

## Acknowledgements

The authors also acknowledge Gia Alexander for help in proofreading the manuscript.

## Nomenclature

- $A_1$  = constant used in calculating dissociation constant, T, °K
- $A_2$  = constant used in calculating dissociation constant
- $A_3$  = constant used in calculating dissociation constant, 1/T, 1/°K
- AR =aspect ratio
- $a_o$  = initial interfacial area per unit volume of the medium, 1/L, m<sup>-1</sup>
- $a_v$  = interfacial area per unit volume of the medium, 1/L, m<sup>-1</sup>
- $a_{H^+}$  = activity coefficient of hydrogen ion
- $a_{A-}$  = activity coefficient of conjugate base of acid
- $C_f$  = original concentration of acid in the fluid phase, n/L<sup>3</sup>, mol/L
- $C_{HAc}$  = concentration of acetic acid at the solid-fluid interface, n/L<sup>3</sup>, mol/L
  - $C_s$  = concentration of acid at the solid-fluid interface, n/L<sup>3</sup>, mol/L
  - $D_e$  = effective dispersion tensor, L<sup>2</sup>/t, m<sup>2</sup>/s
- $D_{eX}$  = effective longitudinal dispersion coefficient, L<sup>2</sup>/t, m<sup>2</sup>/s
- $D_{eT}$  = effective transverse dispersion coefficient, L<sup>2</sup>/t, m<sup>2</sup>/s
- $D_m$  = acid diffusivity, L<sup>2</sup>/t, m<sup>2</sup>/s
- K = permeability tensor, L<sup>2</sup>, m<sup>2</sup>
- $k_c$  = local mass transfer coefficient, L/t, m/s
- $K_d$  = dissociation constant
- $K_o$  = initial permeability tensor, L<sup>2</sup>, m<sup>2</sup>
- $k_s$  = surface dissolution reaction-rate constant, L/t, m/s
- n =order of reaction
- $p = \text{pressure, m/L}^2 t^2$ , MPa
- $PV_{BT}$  = pore volumes of acid injection to reach breakthrough
  - Q = acid injection rate, L<sup>3</sup>/t, m<sup>3</sup>/s
- R(C) = reaction kinetics, n/t/L<sup>2</sup>, mol/s/m<sup>2</sup>
  - $Re_p$  = Reynolds number number in fluid flow to predict velocity at which turbulence will occur
    - $r_o$  = initial pore radius, L, m
    - $r_p$  = pore radius, L, m
  - Sc = Schmidt number ratio of momentum diffusivity (viscosity) and mass diffusivity
  - Sh = Sherwood number ratio of the rate of mass transfer to the rate of diffusive mass transport

 $Sh_{\infty}$  = asymptotic Sherwood number

T = temperature, T, °C [°K]

- u = superficial velocity vector, L/t, m/s
- $\alpha$  = dissolving power of acid, m/n, g/mol
- $\alpha_{os}$  = constant in dispersion correlations
- $\beta$  = pore structure relation constant
- $\Delta \varepsilon$  = porosity heterogeneity magnitude
- $\Delta \varepsilon_c$  = critical porosity heterogeneity magnitude
  - $\varepsilon$  = porosity of the porous medium
  - $\varepsilon_o$  = initial porosity
  - $\rho$  = fluid density, m/L<sup>3</sup>, kg/m<sup>3</sup>
- $\rho_s = \text{rock density, m/L}^3, \text{ kg/m}^3$
- $\lambda_X$  = constant in axial dispersion correlation
- $\lambda_T$  = constant in transverse dispersion correlation
- $\mu$  = fluid viscosity, m/Lt, mPa.s
- v = kinematic viscosity, L<sup>2</sup>/t, m<sup>2</sup>/s
- $\tau$  = stress tensor, m/L<sup>2</sup>t<sup>2</sup>, psi [MPa]

## References

- Akanni, O. O. and Nasr-El-Din, H. A. 2015. The Accuracy of Carbonate Matrix-Acidizing Models in Predicting Optimum Injection and Wormhole Propagation Rates. Presented at the SPE Middle East Oil and Gas Show and Conference. Manama, Bahrain, 8-11 March. SPE 172575-MS. http://dx.doi.org/10.2118/172575-ms.
- Balakotaiah, V. and West, D. H. 2002 Shape Normalization and Analysis of Mass Transfer Controlled Regime in Catalytic Monoliths. *Chem Eng Sc* 57 (8): 1269–1286. http://dx.doi.org/10.1016/s0009-2509(02)00059-3.
- Bazin, B. 2001. From Matrix Acidizing to Acid Fracturing: A Laboratory Evaluation of Acid/Rock Interactions. *SPE Prod* & *Fac* **16** (01): 22–29. SPE-66566-PA. http://dx.doi.org/10.2118/66566-pa.
- Bryant, S. L., Mellor, D. W., and Cade, C. A. 1993. Physically Representative Network Models of Transport in Porous Media. AIChE Journal 39 (3): 387–396. http://dx.doi.org/10.1002/aic.690390303.
- Buijse, M. A. 2000. Understanding Wormholing Mechanisms Can Improve Acid Treatments in Carbonate Formations. SPE Prod & Oper 15 (3): 168–175. SPE-38166-MS. http://dx.doi.org/10.2118/38166-ms.
- Buijse, M. A. and Glasbergen, G. 2005. A Semiempirical Model to Calculate Wormhole Growth in Carbonate Acidizing. Presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas, 9-10 October. SPE 96892-MS. http://dx.doi.org/10.2118/96892-ms.
- Cohen, C. E., Ding, D., Quintard, M. et al. 2008. From Pore Scale to Wellbore Scale: Impact of Geometry on Wormhole Growth in Carbonate Acidization. *Chem. Eng. Sc.* 63 (12) 3088. http://dx.doi.org/10.1016/j.ces.2008.03.021.
- Daccord, G., Touboul, E., and Lenormand, R. 1989. Carbonate Acidizing: Toward a Quantitative Model of the Wormholing Phenomenon. *SPE Prod Eng* **4** (1): 63–68. SPE-16887-PA. http://dx.doi.org/10.2118/16887-pa.
- De Oliveira, T. J. L., De Melo, A. R., Oliveira, J. A. et al. 2012. Numerical Simulation of the Acidizing Process and PVBT Extraction Methodology Including Porosity/Permeability and Mineralogy Heterogeneity. Presented at the SPE International Symposium and Exhibition on Formation Damage Control. Lafayette, Louisiana. 15-17 January. SPE 151823-MS. http://dx.doi.org/10.2118/151823-ms.
- Fatt, I. 1956. The Network Model of Porous Media. I, II, III. Pet. Trans. AIME 207: 144.
- Fredd, C. N. and Fogler, H. S. 1999. Optimum Conditions for Wormhole Formation in Carbonate Porous Media: Influence of Transport and Reaction. SPE J. 4 (3): 196–205. SPE-56995-PA. http://dx.doi.org/10.2118/56995-pa.
- Fredd, C. N. and Fogler, H. S. 1998. Influence of Transport and Reaction on Wormhole Formation in Porous Media. AIChE Journal 44 (9): 1933. http://dx.doi.org/10.1002/aic.690440902.
- Fredd, C. N. and Miller, M. J. 2000. Validation of Carbonate Matrix Stimulation Models. Presented at the International Symposium on Formation Damage Control, Lafayette, Louisiana, 23-24 February. SPE 58713-MS. http:// dx.doi.org/10.2118/58713-ms.
- Frick, T. P., Kurmayr, M., and Economides, M. J. 1994. Modeling of Fractal Patterns in Matrix Acidizing and Their Impact on Well Performance. SPE Prod & Oper 9 (1): 61–68. SPE-23789-PA. http://dx.doi.org/10.2118/23789-pa.

- Furui, K., Burton, R., Burkhead, D. et al. 2012. A Comprehensive Model of High-Rate Matrix-Acid Stimulation for Long Horizontal Wells in Carbonate Reservoirs: Part I--Scaling Up Core-Level Acid Wormholing to Field Treatments. SPE J. 17 (1), 271–279. http://dx.doi.org/10.2118/134265-pa.
- Glasbergen, G., Kalia, N., and Talbot, M. S. 2009. The Optimum Injection Rate for Wormhole Propagation: Myth or Reality? Presented at the 8th European Formation Damage Conference, Scheveningen, 27-29 May. SPE 121464-MS. http://dx.doi.org/10.2118/121464-ms.
- Golfier, F., Zarcone, C., Bazin, B. et al. 2002. On The Ability of a Darcy-Scale Method Model to Capture Wormhole Formation During the Dissolution of a Porous Medium. J. Fluid Mech. 457: 213–254. http://dx.doi.org/10.1017/ s0022112002007735.
- Gupta, N. and Balakotaiah, V. 2001. Heat and Mass Transfer Coefficients in Catalytic Monoliths. *Chem. Eng. Sc.* 56 (16): 4771–4786. http://dx.doi.org/10.1016/s0009-2509(01)00134-8.
- Hoefner, M. L. and Fogler, H. S. 1988. Pore Evolution and Channel Formation During Flow and Reaction in Porous Media. AIChE Journal 34 (1): 45–54. http://dx.doi.org/10.1002/aic.690340107.
- Huang, T., Hill, A. D., and Schechter, R. S. 1997. Reaction Rate and Fluid Loss: The Keys to Wormhole Initiation and Propagation in Carbonate Acidizing. Presented at the SPE International Symposium on Oilfield Chemistry, Houston, Texas, 18-21 February. SPE 37312-MS. http://dx.doi.org/10.1016/10.2118/37312-ms.
- Hung, K. M., Hill, A. D., and Sepehrnoori, K. 1989. A Mechanistic Model of Wormhole Growth in Carbonate Matrix Acidizing and Acid Fracturing. J Pet Technol 41 (1): 59–66. SPE-16886-PA. http://dx.doi.org/2118/16886-pa.
- Izgec, O., Zhu, D., & Hill, A. D. 2010. Numerical and Experimental Investigation of Acid Wormholing during Acidization of Vuggy Carbonate Rocks. J Pet Sci Eng, 74 (1): 51–66. http://dx.doi.org/10.1016/j.petrol.2010.08.006
- Kalia, N. and Balakotaiah, V. 2009. Effect of Medium Heterogeneities on Reactive Dissolution of Carbonates. *Chem. Eng. Sc.* 64 (2): 376–390. http://dx.doi.org/10.1016/j.ces.2008.10.026.
- Kalia, N. and Balakotaiah, V. 2007. Modeling and Analysis of Wormhole Formation in Reactive Dissolution of Carbonate Rocks. Chem. Eng. Sc. 62 (4): 919–928. http://dx.doi.org/10.1016/j.ces.2006.10.021.
- Kalia, N. and Glasbergen, G. 2009. Wormhole Formation in Carbonates under Varying Temperature Conditions. Presented at the 8th European Formation Damage Conference. Scheveningen, The Netherlands, 27-29 May. SPE 121803-MS. http://dx.doi.org/10.2118/121803-ms.
- Liu, M., Zhang, S., and Mou, J. 2012. Effect of Normally Distributed Porosities on Dissolution Pattern in Carbonate Acidizing. J Pet Sci Eng 94-95 (0): 28–39. http://dx.doi.org/10.1016/j.petrol.2012.06.021.
- Liu, X., Ormond, A., Bartko, K. et al. 1997. A Geochemical Reaction-Transport Simulator for Matrix Acidizing Analysis and Design. J Pet Sci Eng 17 (12): 181–196. http://dx.doi.org/10.1016/s0920-4105(96)00064-2.
- Maheshwari, P. and Balakotaiah, V. 2013. Comparison of Carbonate HCl Acidizing Experiments with 3D Simulations. SPE Prod & Oper 28 (04): 402–413. SPE-164517-PA http://dx.doi.org/10.2118/164517-pa.
- Maheshwari, P., Maxey, J., and Balakotaiah, V. 2014. Simulation and Analysis of Carbonate Acidization with Gelled and Emulsified Acids. Presented at the SPE Abu Dhabi International Petroleum Exhibition and Conference. Abu Dhabi, UAE, 10-13 November. SPE 171731-MS. http://dx.doi.org/10.2118/171731-ms.
- Maheshwari, P., Ratnakar, R. R., Kalia, N. et al. 2012. 3-D Simulation and Analysis of Reactive Dissolution and Wormhole Formation in Carbonate Rocks. *Chem. Eng. Sc.* 90 (0): 258–274. http://dx.doi.org/10.1016/j.ces.2012.12.032.
- Panga, M. K. R., Ziauddin, M., and Balakotaiah, V. 2005. Two-Scale Continuum Model for Simulation of Wormholes in Carbonate Acidization. AIChE J 51 (12): 3231–3248. http://dx.doi.org/10.1002/aic.10574.
- Panga, M., Ziauddin, M., Gandikota, R., and Balakotaiah, V. 2004. A New model for Predicting Wormhole Structure and Formation in Acid Stimulation of Carbonates. Presented at the SPE International Symposium and Exhibition on Formation Damage Control. Lafayette, Louisiana, 18-20 February. SPE 86517-MS. http://dx.doi.org/10.2118/86517ms.
- Panga, M. K. R., Balakotaiah, V., and Ziauddin, M. 2002.Modeling, Simulation and Comparison of Models for Wormhole Formation during Matrix Stimulation of Carbonates. Presented at the SPE Annual Technical Conference and Exhibition. San Antonio, Texas. 29 September - 2 October. SPE 77369-MS http://dx.doi.org/10.2118/77369-ms.
- Ratnakar, R. R., Kalia, N., and Balakotaiah, V. 2012. Carbonate Matrix Acidizing with Gelled Acids: An Experiment-Based Modeling Study. Presented at the SPE International Production and Operations Conference and Exhibition. Doha, Qatar, 14-16 February. SPE 154936-MS. http://dx.doi.org/10.2118/154936-ms.

Rose, W. 1957. Studies of Waterflood Performance. Use of Network Models Illinois State Geology Survey, 3.

- Rowan, G. 1959. Theory of Acid Treatment of calcite formations. J. Inst. Petrol 45 (431).
- Sahimi, M., Gavalas, G. R., and Tsotsis, T. T. 1990. Statistical and Continuum Models of Fluid-Solid Reactions in Porous Media. Chem. Eng. Sc. 45 (6): 1443–1502. http://dx.doi.org/10.1016/0009-2509(90)80001-u.
- Schechter, R. S. 1992. Oil Well Stimulation. New York. Prentice Hall. Chap. 17: 512-517.
- Schechter, R. S. and Gidley, J. L. 1969. The Change in Pore Size Distribution from Surface Reactions in Porous Media. AIChE Journal 15 (3): 339–350. http://dx.doi.org/10.1002/aic.690150309.

- Simon, R. and Kelsey, F. J. 1972. The Use of Capillary Tube Networks in Reservoir Performance Studies: II. Effect of Heterogeneity and Mobility on Miscible Displacement Efficiency. Soc. Pet. Eng. J. 12 (04): 345–351. SPE-3482-PA. http://dx.doi.org/10.2118/3482-pa.
- Thompson, K. E. and Fogler, H. S. 1997. Modeling Flow in Disordered Packed Beds from Pore-Scale Fluid Mechanics. *AIChE Journal* **43** (6): 1377–1389. http://dx.doi.org/10.1002/aic.690430602.
- Vik, B., Djurhuus, K., Spildo, K., and Skauge, A. 2007. Characterisation of Vuggy Carbonates. Presented at the SPE/ EAGE Reservoir Characterization and Simulation Conference, Abu Dhabi, UAE, 28-31 October. SPE-111434-MS. http://dx.doi.org/10.2118/111434-ms.
- Wang, Y., Hill, A. D., and Schechter, R. S. 1993. The Optimum Injection Rate for Matrix Acidizing of Carbonate Formations. Presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, 3-6 October. SPE 26578-MS. http://dx.doi.org/10.2118/26578-ms.
- Zhang, Y., Yang, S., Zhang, S. et al. 2014. Wormhole Propagation Behavior and Its Effect on Acid Leakoff under In Situ Conditions in Acid Fracturing. *Transport in Porous Media* 101 (1): 99–114. http://dx.doi.org/10.1007/ s11242-013-0233-z.