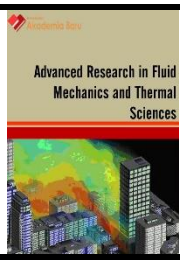
Penerbit Akademia Baru

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



An Analytical Derivation Method to Estimate Pore Volumes to Breakthrough in Carbonate Acidizing with Complex Acids

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ARTICLE INFO

Article history:
Received 7 June 2019
Received in revised form 10 July 2019
Accepted 2 August 2019
Available online 19 September 2019

ABSTRACT

Acidizing stimulation is a common and useful method within the oil well treatment to create wormholes channels in carbonate formations to increase the reservoir oil and gas production. Finding the amount of pore volumes to breakthrough number is a critical target in carbonate acidizing. Finding this number by experimental works needs a substantial amount of energy, price and time. For that reason, this study expected to determine an analytical technique to estimate the pore volumes to breakthrough number with high accuracy. This method is accomplished by exclusively applying formation and acid properties without using any experimental works. Pore volumes to breakthrough calculation are done through developing an analytical method based on the conservation of mass law in which the carbonate core is considered as a closed system and the overall mass in the system as a constant throughout the process of acid. Moreover, a constant number is added to the mathematical part of the model with the aim of removing the dimensionless Damköhler number which is supposed to be calculated experimentally. This method results are compared to four other experimental works, which led to calculating the average accuracy of this model that is shown to be 81.36%. This study puts forward an inclusive analytical method to estimate the number of pore volumes to breakthrough with an acceptable accuracy rate just through known core and acid and properties.

Keywords:
Analytical method; carbonate acidizing; pore volumes to breakthrough; complex acids

1. Introduction

The technique of modeling in the study includes scaling the acid injection rate to the carbonate core to create wormhole channels by using the conservation of mass law [1]. According to this method, the overall mass in the system is constant throughout the injection acid process and carbonate core is considered to be a closed system also the wormhole shape is assumed cylindrical. Therefore, the volume of created wormhole is shown through the injected mass of acid at the surface of carbonate core minus output mass of injected acid at the end of wormhole after reaction time. To

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establish the mathematical part of the model the Damköhler number is used [2-7]. The Damköhler number is named after the German chemist Gerhard Damköhler. It is a dimensionless number and is described as the ratio of flow time scale to the chemical time scale [8]. To eliminate the dimensionless Damköhler number which is supposed to be calculated experimentally, the dissolution rate constant number is added to the mathematical part of the model. This constant number has a direct relation with Damköhler number. The number of dissolution rate constant indicates the rate of wormhole growing by chemical reaction time [9]. This is a specific constant number equation, which is linear, for each acid and rock [10, 11]. Acid and core properties and temperature determine the optimum injection rate. Among them, core and acid properties are the most significant factors. In slow reactions in carbonate cores, acid mass needs to increase significantly and on the other hand, injection rate must decrease meaningfully. Moreover, by increasing temperature, the reaction rate between acid and core will be increased. Many studies have been carried out regarding the optimum injection rate in carbonate acidizing [12-19]. Besides, variety and effect of fluid flow for incompressible fluids have been approved in several types of research [20-22].

Concentration changes of injected acid that is reacted with carbonate core are accounted to calculate the chemical part of the model. To calculate the concentration changes, chemical equation balance rule is used. The equation contains of the chemical formulas of the products and the reactants. Because injected acid amount is not as much as carbonate core volume and cannot dissolve the whole core, limiting reagent method is used for molar mass and weight of chemical reaction products. The limiting reagent or limiting reactant in a chemical reaction is the substance that is entirely consumed when the chemical reaction is done [23]. A constant equation for Ethylenediaminetetraacetic acid (EDTA) has been utilized to develop the model. And the model is compared with two other complex acids (Cyclohexylenedinitrilotetraacetic acid (CDTA) and Diethylenetriaminepentaacetic acid (DTPA)). Porosity is another parameter that is applied in the mathematical part of this method and the average porosity of the core is used in this study. To calculates the number of pore volumes to breakthrough only known properties of carbonate core and injected acid are used in the final equation.

2. Model Development

Consider a horizontal model of porous media, that is in a stable condition with injected fluid rate of q and concentration of C to one side of this porous media as a solvent fluid flow to create a wormhole channels in the core and the acid has a preferential flow path in the capillary tube during acidizing. The wormhole volume is calculated assuming to have a tube shape with area of a, and length of l. The system is depicted in Figure 1.

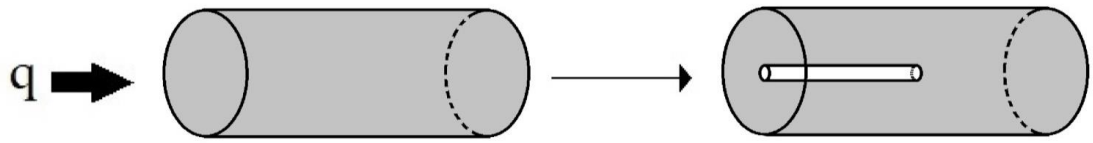

Fig. 1. Horizontal model of wormhole created in core

The starting point of the model is writing the mass conservation equation for mixture acid concentration rate of fluid injected. The overall equation for this model is

$$\begin{Bmatrix} mass\ of\ acid \\ into\ the\ core \end{Bmatrix} - \begin{Bmatrix} mass\ of\ acid \\ out\ of\ the\ core \end{Bmatrix} = \begin{Bmatrix} rate\ of\ chages\ of\ mass \\ inside\ the\ core \end{Bmatrix} \quad (1)$$

$$\{q_1C_1\}_{in} - \{q_2C_2\}_{out} = \frac{\Delta}{\Delta t}\{laC\} \quad (2)$$

where q_1 and q_2 are fluid injection rate and rate of fluid coming out of the core respectively, C_1 and C_2 are injected fluid concentration and product fluid concentration respectively, a is capillary tube area, C is fluid concentration, l is length of core and t is time.

Dividing by concentration changes, the conservation of mass or continuity equation defined as below

$$\frac{q_1C_1 - q_2C_2}{\Delta C} = \frac{al}{\Delta t} \quad (3)$$

Eq. (1) is further expanded using the following equations in order to determine the number of pore volume to breakthrough.

$$C_1 = \frac{m_a}{V_i} \quad (4)$$

where m_a is mass of injected acid, V_i is the volume of injected fluid acid and q is fluid injection rate. Put forward by Fredd and Fogler [3], the acid injection rate and pore volume to breakthrough by definition are calculated by Eq. (5) and (6).

$$q = \frac{\pi dl\text{ƙ}}{N_{Da}} \quad (5)$$

$$PV_{BT} = \frac{V_i}{XA\emptyset} \quad (6)$$

where π is equal to 3.14, d is the wormhole diameter, l is the wormhole length, ƙ is overall dissolution rate constant of acid and rock, N_{Da} is Damköhler number, PV_{BT} is pore volume to breakthrough and Ø is porosity of core. The pore volumes space of rock that acid penetrate in it is calculated by Eq. (7).

$$V_w = \frac{\pi d^2 l}{4} \quad (7)$$

where V_w is volume of wormhole, the differential of time equals the acid reaction time with the rock. The wormhole is created in the formation at this time. So, the total processing time in this model is shown by T. Therefore Eq. (1) is developed as below.

$$\Delta t = T \quad (8)$$

$$\frac{q_1C_1 - q_2C_2}{\Delta C} = \frac{\pi d^2 l}{4T} \quad (9)$$

The assumption is, acid is injected in the core with the flow rate of q and due to being a single shot injection with a certain amount of acid to create wormhole in the core and there is no flow rate at the other side of the core and q_2 is equals zero. Therefore the Eq. (9) is drive as

$$qC_1 = \frac{\pi d^2 l\Delta C}{4T} \quad (10)$$

The concentration of acid before the injection is shown as C_1. The acid concentration is inconsistent and it changes during reaction with the rock. Therefore, the injected acid is assumed to be the only fluid that flows in the rock and the acid has a reaction with the rock to make a wormhole. Thus, the acid concentration changes during the T time. The changes in fluid flow concentration are accounted as ΔC.

According to definition of pore volumes to breakthrough, the number of pore volumes to break through (PV_{BT}) as the ratio of the volume of fluid injected to achieve channel breakthrough to the volume of the pore space in the core as shown in Eq. (6). The XA part of this equation is the whole core volume that is presented by V_c. Also, the injected acid concentration is defined as mass of acid (ma) divided by volume of fluid injected to the core (V_i).

$$PV_{BT} = \frac{V_i}{V_c \emptyset} \tag{11}$$

$$C_1 = \frac{m_a}{V_i} \tag{12}$$

The following changes are done to Eq. (10) to create an equation for pore volume to breakthrough.

$$q \frac{m_a}{V_i} = \frac{\pi d^2 l \Delta C}{4T} \tag{13}$$

The term $V_c\emptyset$ is further multiplied by both side of Eq. (13) and the q_{ma} part is shifted to the other side of the equation.

$$\frac{V_c \emptyset}{V_i} = \frac{\pi d^2 l \Delta C \, V_c \, \emptyset}{4 \, q \, m_a \, T} \tag{14}$$

Therefore,

$$PV_{BT} = \frac{4 \, q \, m_a \, T}{\pi \, d^2 \, l \, \Delta C \, V_c \, \emptyset} \tag{15}$$

In Eq. (5), the term ƙ indicates the dissolution rate constant reaction between core and acid with dimension of $[L.T^{-1}]$ and πdlƙ in Eq. (5) shows the rate of wormhole creation in core with dimension of $[L^3.T^{-1}]$ that is always calculated by experimental work for every acid and rock type. The wormhole creation rate in the rock is as follows.

$$\pi d l \text{ƙ} = \frac{V_w}{T} \tag{16}$$

So, Eq. (5) changes into

$$q = \frac{V_w/_T}{N_{Da}} \tag{17}$$

and Eq. (15) becomes

$$PV_{BT} = \frac{q\, m_a\, T}{V_w\, V_c\, \Delta C\, \emptyset} \tag{18}$$

To make the analysis less complicated, the dissolution rate constant (D_R) is shown as follows

$$D_R = \frac{V_W}{T} \tag{19}$$

and Eq. (19) is transformed into

$$D_R = N_{Da}\, q \tag{20}$$

So, the main equation to calculate the number of pore volume to breakthrough is presented in Eq. (21).

$$PV_{BT} = \frac{m_a}{N_{Da}\, V_c\, \Delta C\, \emptyset} \tag{21}$$

3. Dissolution Rate Equation

In order to calculate the concentration of acid before injection, the molarity of acid with the dimension of [mol.L^{-3}] is multiplied by the molar mass of acid with the dimension of [m.mol^{-1}]. For example, the concentration of acid before injection is 0.25M EDTA (0.25 mol/lit) multiplied by the molar mass of EDTA (292.24264 g/mol) that is equal to C_1 (0.0731 g/cm^3). The chemical balance equation of the reaction between hydrochloric acid and limestone is:

$$C_{10}H_{16}N_2O_8 + CaCO_3 \rightarrow CaC_{10}H_{16}N_2O_8 + CO_3 \tag{22}$$

To determine the mass of other compounds, the amount of acid mass is accounted as shown in Eq. (22). Table 1 presents the example of primary mass amounts. Furthermore, the mass of limestone ($CaCO_3$) core is 259 gram and is calculated by size, probity and density of the core [3]. The post-reaction injected fluid flow concentration is calculated by Eq. (23) with mass and volume of chemical equation products.

$$C_2 = \frac{\sum m}{V_i} \tag{23}$$

Table 1
Mass concentration for chemical balance of 0.25M EDTA with limestone

	Compound	Constant	Molar mass (g/mol)	Molar concentration (mol/lit)	Weight in 1 litre (g)	Mass Concentration (g/cm^3)
Injected fluid	$C_{10}H_{16}N_2O_8$	1	292.242264	0.25	73.06066	0.0731
Product fluid	$CaC_{10}H_{16}N_2O_8$	1	332.32064	0.25	83.08016	0.0831
	CO_3	1	60.0089	0.25	15.00223	0.0150

The amount of product fluid concentration will not change for each amount of acid mass after the reaction. The reason is the limiting reagent, which is the substance that is totally consumed when the chemical reaction is fully done. This reagent limits the amount of created product because the

reaction is unable to continue without it. Injected acid is always the limiting reagent compound in carbonate acidizing. Similar process is accomplished on the reaction of limestone with Cyclohexylenedinitrilotetraacetic acid ($C_{14}H_{22}N_2O_8$) (CDTA) and Diethylenetriaminepentaacetic acid ($C_{14}H_{23}N_3O_{10}$) (DTPA) to calculate C_1 and C_2 for each reaction.

$$C_{14}H_{22}N_2O_8 + CaCO_3 \rightarrow CaC_{14}H_{22}N_2O_8 + CO_3 \quad (24)$$

$$C_{14}H_{23}N_3O_{10} + CaCO_3 \rightarrow CaC_{14}H_{23}N_3O_{10} + CO_3 \quad (25)$$

Table 2 shows the concentration amounts of injected acid and product fluid for each acid and core that used in this study.

Table 2
Concentration of injected acid and product fluid

Acid type	Core type	Acid concentration (g/cm^3)	Product fluid concentration (g/cm^3)
0.25 M EDTA	Limestone	0.0731	0.0981
0.25 M CDTA	Limestone	0.0866	0.1116
0.25 M DTPA	Limestone	0.0983	0.1234

4. Model Calibration by Coefficient Number

In order to develop the model a dimensionless coefficient number (Co.) is added to Eq. (21). The coefficient number is created by equalizing the number of pore volumes in the model with the actual number of pore volume to the breakthrough calculated by Fredd and Fogler [3] for EDTA.

$$PV_{BT} = \frac{Co.m_a}{N_{Da}\, V_c\, \Delta C\, \emptyset} \quad (26)$$

Table 3 shows the coefficient number that is calculated through Eq. (26) for 0.25M EDTA whose Damköhler number had been provided by Fredd and Fogler [3].

Table 3
Calculated coefficient numbers by Eq. (26)

0.25 M EDTA		
q (cm^3/min)	N_{Da}	Co.
0.01	8.7	3.0027
0.025	3.5	1.2066
0.06	1.5	0.5056
0.15	0.6	0.2031
1	0.09	0.0308
3	0.03	0.0103

The relation between Damköhler numbers and acid injection rates with the coefficient number is analyzed so this number as an experimental factor can be excluded in the model. The outcome indicates that these coefficient numbers have a direct relation with Damköhler numbers as shown in Figure 2.

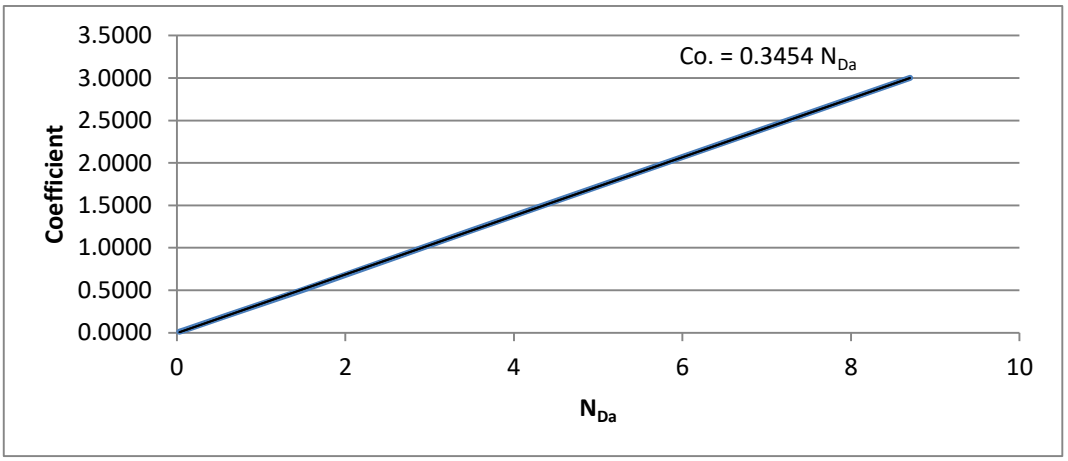

Fig. 2. Coefficient number and Damköhler number relation for 0.25 M EDTA

The following equations are calculated for EDTA acid to represent the numerical relation between Damköhler number and the coefficient number.

For $EDTA \rightarrow Co. = 0.3454 N_{Da}$ (27)

To find the final equation usable for complex acids with any concentration and limestone cores, Eq. (28) is the concluding equation in which the final coefficient number is discovered to be 0.3454.

$$PV_{BT} = \frac{0.3454 m_a}{V_c \, \Delta C \, \emptyset} \quad (28)$$

5. Evaluation of The Model

The final results are compared to the pore volume to breakthrough results provided by Fredd and Fogler [4] (as listed in Table 4) on different complex acids and limestone cores for the deviation and accuracy evaluation of the model. Figures 3, 4, and 5 compare the results.

Table 4
Overview of the others works

	Acid type	Core type	Core porosity (%)	Core diameter (cm)	Core length (cm)
Fredd and Fogler [4]	0.25 M EDTA	Limestone	20	3.81	10.16
	0.25 M CDTA	Limestone	20	3.81	10.16
	0.25 M DTPA	Limestone	20	3.81	10.16

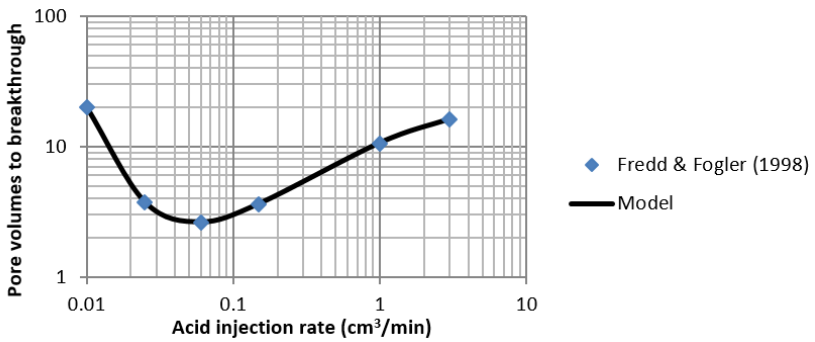

Fig. 3. Comparison of the model with Fredd and Fogler [4] results for EDTA and limestone

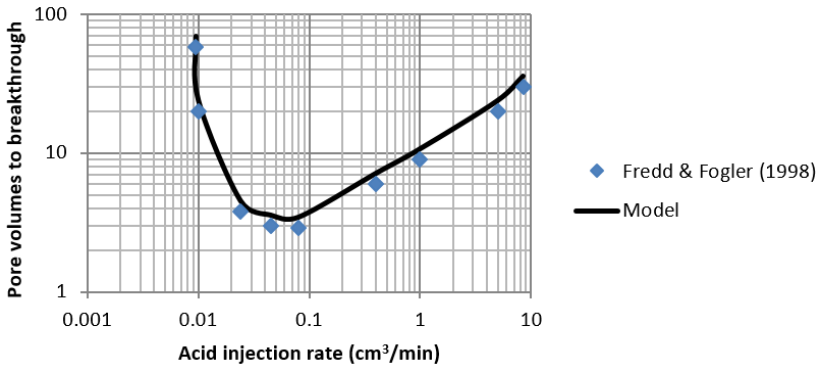

Fig. 4. Comparison of the model with Fredd and Fogler [4] results for CDTA and limestone

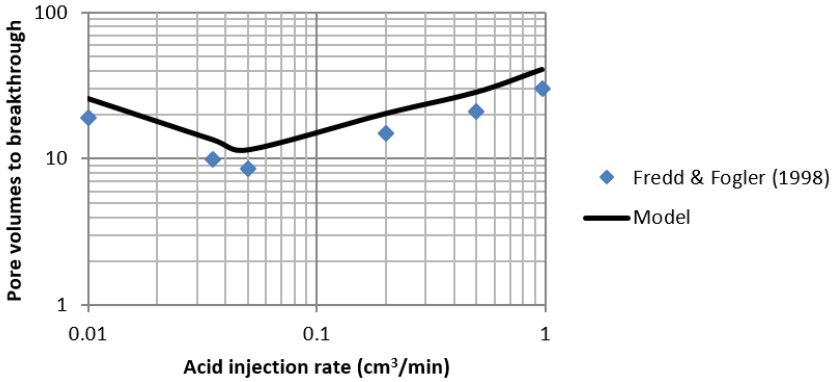

Fig. 5. Comparison of the model with Fredd and Fogler [4] results for DTPA and limestone

6. Evaluation of The Model by Deviation and Accuracy

The accuracy of the model is measures using the standard deviation formula as presented in Eq. (29)-(31). Error, deviation and accuracy are shown in Table 5.

$$SD = \sqrt{\frac{\sum_{i=1}^{N}(PV_{actual}-PV_{model})^2}{N}} \tag{29}$$

$$\%MAPE = \frac{1}{N}\frac{\sum_{i=1}^{N}|PV_{actual}-PV_{model}|}{PV_{actual}} \times 100 \tag{30}$$

$$\%\ Accuracy = 100 - \%MAPE \tag{31}$$

where SD is the standard deviation, MAPE is the mean absolute percentage error, PV_{actual} is the number of pore volumes to the breakthrough that was calculated experimentally; PV_{model} is the number of pore volumes to the breakthrough that is calculated by this model and N is the number of observations.

Table 5
Evaluation of the model

	Acid type	Core type, Porosity (%)	SD	MAPE (%)	Accuracy (%)
Fredd and Fogler [4]	0.25 M EDTA	Limestone, 20	0.1155	0.99	99.01
	0.25 M CDTA	Limestone, 20	2.8159	19.65	80.35
	0.25 M DTPA	Limestone, 20	6.5972	35.27	64.73
			Average	18.64	81.36

7. Conclusions

By comparing the results with 21 samples from three experimental works, the average accuracy of the model has been measured as shown to be 81.36% for complex acids and limestone. Comparing the results of the model to these experimental results indicates that the accuracy of the model decreased when the concentration of acid increased. This study puts forward an inclusive analytical method to estimate the number of pore volumes to breakthrough with an acceptable accuracy rate just through known acid and core properties.

Acknowledgments
The authors would like to thank the Department of Petroleum Engineering, School of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM) for providing support.

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