ANALYTICAL MODEL FOR ESTIMATION OF PORE VOLUME TO BREAKTHROUGH IN CARBONATE ACIDIZING WITH ORGANIC AND MINERAL ACIDS

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ABSTRACT

Acidizing treatment is one of the most useful methods in oil well stimulations to form wormholes in carbonate formations in order to enhance reservoir fluid production. Obtaining the number of pore volumes to breakthrough is an important objective in carbonate acidizing to determine the wormhole properties such as type, shape, and size. Finding this number in experimental works requires a considerable amount of time, energy, and cost. Therefore, this study aimed to establish an analytical model in which a reasonable result would be achieved for the number of pore volumes to breakthrough. This purpose was accomplished by only using acid and formation properties without performing any experimental works. The process of wormhole modelling is simulated by developing an analytical model which uses the conservation of mass law. The carbonate core is treated as a closed system and the overall mass in the system as constant during the acid injection process. Furthermore, a constant number is added to the mathematical part of the model in order to eliminate the dimensionless Damköhler number which is supposed to be calculated experimentally. The results of the analytical procedure of the developed model are further compared to six other experimental and numerical works, which led to the computation of average accuracy and coefficient of determination of this model. Evaluation of the developed model with other experimental and numerical results gives an excellent assessment of 95.45% for the average accuracy and 0.9938 for the average coefficient of determination. This study establishes a comprehensive analytical model to estimate the number of pore volumes to breakthrough with an acceptable accuracy rate merely through implementing known acid and core properties.

ABSTRAK

Rawatan asid ialah satu daripada kaedah berguna dalam perangsangan telaga bagi membentuk lubang cecacing dalam formasi karbonat dengan tujuan untuk meningkatkan pengeluaran bendalir reservoir. Memperoleh jumlah isipadu liang untuk bulus ialah objektif penting dalam pengasidan matriks karbonat, bagi menentukan sifat-sifat lubang cecacing, misalnya jenis, bentuk, dan saiz. Memperoleh angka ini menerusi kerja ujikaji melibatkan banyak masa, tenaga dan kos. Oleh itu, kajian ini bertujuan untuk membina model analisis bagi menghasilkan dapatan munasabah bagi jumlah isipadu liang untuk bulus. Matlamat ini boleh disempurnakan dengan hanya menggunakan sifat-sifat formasi dan asid tanpa melibatkan sebarang ujikaji. Proses pemodelan lubang cecacing diselaku dengan membangunkan model analisis menerusi hukum keabadian jisim. Teras batuan karbonat dianggap sebagai suatu sistem tertutup dan keseluruhan jisim di dalam sistem sebagai malar semasa proses penyuntikan asid. Selain itu, angka malar ditambah ke dalam model matematik bagi menyingkir nombor Damköhler tanpa dimensi yang sepatutnya dikira secara ujikaji. Dapatan daripada tatacara analisis model terbabit selanjutnya dibandingkan dengan enam hasil kerja terdahulu yang dilaksana secara ujikaji dan berangka sehingga berjaya menghasilkan kejituan purata dan pekali penentuan model. Penilaian terhadap model terbabit dengan hasil kerja secara ujikaji dan berangka memberikan keputusan yang baik, iaitu 95.45% bagi kejituan purata dan juga 0.9938 untuk pekali purata penentuan. Kajian ini berjaya menghasilkan satu model analisis yang komprehensif bagi menganggar jumlah isipadu liang untuk bulus dengan kadar kejituan yang boleh diterima dengan hanya mengguna pakai sifat-sifat asid dan teras.

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LIST OF ABBREVIATIONS

CDTA	-	Cyclohexylenedinitrilotetraacetic acid ($C_{14}H_{22}N_2O_8$)
DTPA	-	Diethylenetriaminepentaacetic acid ($C_{14}H_{23}N_3O_{10}$)
EDTA	-	Ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$)
HAc	-	Acetic acid (CH_3COOH)
HCl	-	Hydrochloric acid
HF	-	Hydrofluoric acid
MAPE	-	Mean Absolute Percentage Error (*%*)
SD	-	Standard Deviation

LIST OF SYMBOLS

ΔC	-	Fluid concentration changes (gr/cm^3)
ΔP	-	Pressure difference (psi)
a	-	Cross section of the wormhole (cm^2)
A	-	Cross section of core (cm^2)
B	-	Constant
C	-	Acid concentration (mol/lit)
C_0	-	Acid initial concentration (mol/lit)
C_1	-	Acid concentration before injection (gr/cm^3)
C_2	-	Product fluid concentration after reaction (gr/cm^3)
$CaCO_3$	-	Limestone (Calcium Carbonate)
$CaMg(CO_3)_2$	-	Dolomite (Calcium Magnesium Carbonate)
$Co.$	-	Coefficient number
d	-	Wormhole diameter (cm)
D	-	Core diameter (cm)
D_e	-	Effective diffusion coefficient (cm^2/s)
D_R	-	Dissolution rate constant (cm^3/min)
f_d	-	Fraction of total flow
k	-	Permeability (mD)
$\hat{k}$	-	Overall dissolution rate (cm/min)
K_1	-	Mass transfer coefficient for reactant (cm/s)
K_3	-	Mass transfer coefficient for product (cm/s)
K_{eq}	-	Effective equilibrium constant
K_{mt}	-	Mass transfer coefficient (cm/s)
K_r	-	Surface reaction rate constant
l	-	Wormhole length (cm)
L	-	Core length (cm)
M	-	Molarity (mol/lit)
m_a	-	Mass of acid (gr)
n	-	Number of samples
η	-	Pump efficiency

N_{Da}	-	Damköhler number (*Dimensionless*)
n_{wh}	-	Number of dominant dissolution channels
$\emptyset$	-	Porosity
P	-	Pressure (*psi*)
$\mathcal{P}$	-	Pump power
PV_1	-	Pore volume of core before acid injection (cm^3)
PV_2	-	Pore volume of core after acid injection (cm^3)
PV_{BT}	-	Pore volume to breakthrough
q	-	Injection rate (cm^3/min)
R^2	-	Coefficient of determination
r_f	-	Radius of reservoir (*ft*)
r_w	-	Radius of wellbore (*in*)
T	-	Processing time (*min*)
t	-	Time (*min*)
U_i	-	Acid interstitial velocity (*cm/min*)
v	-	Stoichiometric ratio of reactants
V_c	-	Core volume (cm^3)
V_i	-	Volume of injected fluid (cm^3)
$V_{i\text{-}opt}$	-	Optimum acid interstitial velocity (*cm/min*)
V_w	-	Wormhole volume (cm^3)
V_{wh}	-	Wormhole volume growth rate (*cm/min*)
W_B	-	Constant in wormhole model ($(m/s)^{-2}$)
W_{eff}	-	Constant in wormhole model ($(m/s)^{1/3}$)
X	-	Length of core (*cm*)
$\bar{X}$	-	Data average
Z	-	Confident interval level
Γ	-	Kinetic parameter
μ	-	Viscosity (*cp*)
π	-	Pi number (*3.14*)
ξ	-	Dimensionless fluid loss term

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

There are various methods in increasing the efficiency of oil well production. One of the common ways for this enhancement is acidizing. According to glossary of Schlumberger, in the acidizing process the intended acid is pumped into the wellbore to eliminate the damaged zone due to drilling process around well formation. This technique generally enhances reservoir fluid production by increasing the effective well radius and matrix acidizing is a useful treatment for carbonate formations with a stimulation fluid or acid (Schlumberger, 2019).

In the carbonate formations, injected acid dissolves the carbonate formation during penetration and this matrix acidizing treatment creates wormholes to enhanced production of reservoir fluids. In this method, acid injected in oil well creates wormholes around the well and expands porosity and permeability and leads to improve oil flow rate (Dong et al., 2016; Mahrous et al., 2017). Selecting a proper acid depends on various factors such as type of reservoir rock, mineralogy, ionic composition, temperature, pressure, and depth. Acidizing will usually be used when the bottom hole is damaged because of cementing, penetration of mud drilling, well perforation, etc.

Matrix acidizing is a stimulation method mostly used for carbonates and sandstones formations. There are various differences between these two kinds of reservoirs concerning acidification of them, although both of them are based on the same principle of chemical dissolution in the mineral formations. In carbonate formations, the effects of acid reaction rate and acid concentration lead to several dissolution patterns. These patterns are known as wormholes (Schwalbert et al., 2019).

According to Shokry and Keshtta (2010), the acid reaction and transport rate in the carbonate reservoirs creates high conductive flow channels or wormholes. These wormholes increase the reservoir fluid flow significantly because they have a higher conductivity compared with the original porous medium of reservoir formation. Therefore, this stimulation technique has a very high success result in carbonate formations which depends on wormhole shape. A good shape wormhole is capable to bypass the damaged zone around the wellbore. On the other hand, a bad shape wormhole leads to fluid leak off and decreases the depth of acid penetration. The structure of the wormhole channels, which varies significantly with acid flow conditions and formation properties, ultimately control the shape of wormhole and effectiveness of stimulation treatments (Walle and Papamichos, 2015).

For obtaining the wormhole shape and type, the number of pore volumes to breakthrough (PV_{BT}) is required. This number is a dimensionless number for determining the ratio of injected acid and pore volume in the core (Fredd, 2000). The dynamic model of wormhole formation also was described in other studies (Schwalbert et al., 2019). Also, the wormhole type and structure are related through another dimensionless parameter known as Damköhler number (N_{Da}) (Fredd and Fogler, 1999). This number presents the ratio of flow time scale to the chemical time scale. Both of these numbers required experimental work.

Finding the pore volumes to breakthrough number is one of the most important parameters in the matrix acidizing. Experimental processes are vital to find this number (Davudov et al., 2018). On the other hand, in most numerical models, the concentration of fluid flow was considered as a constant. A model that can estimate the pore volume number has not yet been developed for different types of acids and formations with the effect of concentration of fluid flow changes without the need for an experimental work.

1.2 Statement of the Problem

In the past, mineral acids and mostly hydrochloric acid (*HCl*) as an inexpensive acid or hydrofluoric acid (*HF*) were used in carbonates reservoirs acidizing. With development in petroleum industry, organic acids such as acetic acid (CH_3COOH) and complex acids such as ethylenediaminetetraacetic acid (*EDTA*) or ($C_{10}H_{16}N_2O_8$) are also used to create more effective wormholes based on the type of the formations (Kankaria et al., 2017; Sokhanvarian et al., 2016).

Chemical reactions of these different types of acids by various concentrations with different types of formations create many different types of wormholes. To measure these wormholes, finding the pore volume to breakthrough number is so important. Experimental works were basically needed to find this number, which require lots of energy, time and cost (Nino-Penaloza and Gomaa, 2016).

Due to the numerous chemical reactions between different types of acids and carbonate formations, developing a fully numerical model is essential. This model is capable of estimating the pore volume to breakthrough number based on the properties of acids and carbonate formations without any experimental work.

1.3 Objectives of the Study

The main objectives of this research are as follow:

i. To develop an analytical model for different types of acid such as organic, mineral or complex with different concentrations to be used in carbonate formations.

ii. To determine the number of pore volume to breakthrough in carbonate matrix acidizing by the developed model.

iii. To validate the results of the developed model by calculating the deviation, determination and accuracy through comparing them to the results of former experimental works and models.

1.4 Scope of the Study

The scope of this work consists of the following actions:

i. Developing an analytical model for different types of organic, mineral, or complex acids in different concentrations with full mathematical methods and chemical properties of acids and formations with real data from experimental works.

ii. The formation in this study is focused on two types of carbonate rocks; limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Also the acids include organic, mineral, and complex acids with different molar concentrations.

iii. The model will be validated by measuring the deviation and determination through comparing the results to different experimental works and numerical model developed previously that are done formerly in other studies. The accuracy of the model will also be assessed.

1.5 Significance of the Study

Acidizing is an important and inevitable process in the oil well stimulations to create wormhole in the formation. The number of pore volumes to breakthrough is the main index for knowing wormhole type, shape and size. Therefore, finding the number of pore volumes to breakthrough is one of the main goals in the matrix acidizing. Obtaining this number always requires experimental works. In this study, a model is developed to determine an acceptable result for the number of pore volumes to the breakthrough without using experimental works with solely using

acid and formation properties. As a matter of fact, increasing the efficiency of oil production is one of the important goals for petroleum companies. Depending on the types of problems in oil wells, different solutions are generated. Acidizing is one of the useful solutions for the damages happening around well bore in order to increase oil production. In the past, most carbonate formations were acidized with *HCl* but currently various acids are used in industry to create wormholes in carbonate formations.

This study aims to create a model capable of finding the number of pore volumes to breakthrough for carbonate formations with any type of acids such as organic, mineral and complex with any concentration in carbonate formations. Therefore, the originality of this study is to develop a new numerical model to estimate the pore volumes to breakthrough number with high accuracy merely using specified properties of acid and core. Consequently, this study can contribute to studies in finding pore volumes to breakthrough number in carbonate matrix acidizing.

1.6 Layout of the Thesis

The presented thesis contains five main chapters. Chapter One presents the introduction of the thesis including the research background, objectives, scopes and significance of the study. Followed by the introduction chapter, literature review is presented in Chapter Two. The literature review chapter provides an overview of other experimental and numerical models and studies for pore volumes to breakthrough number.

In Chapter Three, the research methodology and the selected data for developing the acidizing model in carbonate formations are presented. Mathematical and chemical methods and tools are further presented in this chapter.

In Chapter Four, the model is developed based on the conservation of mass law and chemical equation balance between acids and carbonate rock by using

experimental results that are carried out previously by other scholars. Subsequently, the model is tested through comparing to other experimental works that are previously done using different acids and carbonate formations. The comparison is made in order to assess the accuracy of the developed model.

Lastly, the discussions, conclusions and recommendations for the possible future works are presented in Chapter Five.

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