

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.

TABLE OF CONTENTS

	TITLE	PAGE
	DECLARATION	iii
	DEDICATION	iv
	ACKNOWLEDGEMENT	v
	ABSTRACT	vi
	ABSTRAK	vii
	TABLE OF CONTENTS	viii
	LIST OF TABLES	xi
	LIST OF ABBREVIATIONS	xviii
	LIST OF SYMBOLS	xix
	LIST OF APPENDICES	xxi
CHAPTER 1	INTRODUCTION	1
	1.1 Background of the Study	1
	1.2 Statement of the Problem	3
	1.3 Objectives of the Study	3
	1.4 Scope of the Study	4
	1.5 Significance of the Study	4
	1.6 Layout of the Thesis	5
CHAPTER 2	LITERATURE REVIEW	7
	2.1 Introduction	7
	2.2 History of Matrix Acidizing	7
	2.3 Damköhler Number	9
	2.3.1 Optimum Injection Rate in Carbonate Acidizing	17
	2.4 Semi Experimental Model for Pore Volumes to Breakthrough	17
	2.4.1 The Wormhole Process	21
	2.4.2 A Semi Experimental Wormhole Model	25

2.5	Experimental Models for Pore Volumes to Breakthrough	27
2.5.1	Wormhole Transport and Reaction in Carbonates	28
2.5.2	Linear Core Injection Experiments	31
2.5.3	Experimental Models for Vuggy Carbonates	32
2.6	Other Models for Carbonate Acidizing	34
2.7	Pore Porosity Classification	42
2.8	Summary	44
CHAPTER 3	RESEARCH METHODOLOGY	45
3.1	Introduction	45
3.2	Data Collection	47
3.2.1	Data Gathering from Experimental Works	49
3.2.2	Data Gathering from Numerical Works	55
3.3	Modeling Methodology	57
3.3.1	Mathematical Methodology	57
3.3.2	Chemical Methodology	59
3.4	Model Verification Method	60
3.5	Specifications of the Acids	62
3.5.1	Hydrochloric Acid	62
3.5.2	Acetic Acid	63
3.5.3	Ethylenediaminetetraacetic Acid	63
3.5.4	Cyclohexylenedinitrilotetraacetic Acid	64
3.5.5	Diethylenetriaminepentaacetic Acid	64
3.6	Specifications of the Cores	65
3.6.1	Limestone Core	65
3.6.2	Dolomite Core	66
3.7	Hypotheses of Acidizing Modeling	66
3.8	Instruments of the Research	67
3.9	Summary	67
CHAPTER 4	MODEL DEVELOPMENT AND ANALYSIS	69
4.1	Introduction	69

4.2	Development of the Model	69
4.3	Dissolution Rate Equation	74
4.3.1	Reaction of Limestone and Hydrochloric Acid	75
4.3.2	Reaction of Limestone and Acetic Acid	77
4.3.3	Reaction of Limestone and <i>EDTA</i>	79
4.4	Coefficient Number for Model Calibration	80
4.5	Evaluation of the Developed Model	84
4.5.1	Evaluation of the Developed Model with Experimental Works	85
4.5.2	Evaluation of the Developed Model with Numerical Models	104
4.6	Verification of the Developed Model	110
4.7	Summary	113
CHAPTER 5	CONCLUSIONS AND RECOMMENDATION	115
5.1	Conclusions	115
5.2	Recommendations	116
	REFERENCES	118
	LIST OF PUBLICATIONS	145

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 2.1	Pore porosity classification in carbonate cores	43
Table 3.1	Chemical formula, symbols, and species of cores and acids	48
Table 3.2	Overview of the others works	49
Table 3.3	Overview of collected data from Wang et al. (1993)	50
Table 3.4	Wang et al. (1993) results for 1 M <i>HCl</i> , 25 °C and dolomite core properties	50
Table 3.5	Wang et al. (1993) results for 1 M <i>HCl</i> , 50 °C and dolomite core properties	50
Table 3.6	Wang et al. (1993) results for 1 M <i>HCl</i> , 75 °C and dolomite core properties	50
Table 3.7	Wang et al. (1993) results for 4.4 M and 1 M <i>HCl</i> and limestone core properties	50
Table 3.8	Overview of collected data from Fredd and Fogler (1998b)	51
Table 3.9	Fredd and Fogler (1998b) results for 0.5 M <i>HCl</i> and limestone core properties	51
Table 3.10	Fredd and Fogler (1998b) results for 0.5 M <i>HAc</i> and limestone core properties	51
Table 3.11	Fredd and Fogler (1998b) results for 0.25 M <i>EDTA</i> and limestone core properties	52
Table 3.12	Fredd and Fogler (1998b) results for 0.25 M <i>CDTA</i> and limestone core properties	52
Table 3.13	Fredd and Fogler (1998b) results for 0.25 M <i>DTPA</i> and limestone core properties	52
Table 3.14	Overview of collected data from Izgec et al. (2009)	53
Table 3.15	Izgec et al. (2009) results for 4.4 M <i>HCl</i> and limestone core properties	53
Table 3.16	Overview of collected data from Etten (2015)	53
Table 3.17	Etten (2015) results for 4.4 M <i>HCl</i> and limestone core properties ($\phi=11\%$)	54

Table 3.18	Etten (2015) results for 4.4 M <i>HCl</i> and limestone core properties ($\emptyset=15\%$)	54
Table 3.19	Etten (2015) results for 4.4 M <i>HCl</i> and limestone core properties ($\emptyset=16\%$)	54
Table 3.20	Etten (2015) results for 4.4 M <i>HCl</i> and limestone core properties ($\emptyset=25\%$)	55
Table 3.21	Overview of collected data from Buijse and Glasbergen (2005)	55
Table 3.22	Buijse and Glasbergen (2005) results for 1.5 M <i>HCl</i> , 25 °C and limestone core properties	56
Table 3.23	Buijse and Glasbergen (2005) results for 1.5 M <i>HCl</i> , 60 °C and limestone core properties	56
Table 3.24	Overview of collected data from Maheshwari and Balakotaiah (2013)	57
Table 3.25	Maheshwari and Balakotaiah (2013) results for 0.5 M <i>HCl</i> and limestone core properties	57
Table 3.26	<i>HCl</i> concentration	63
Table 3.27	<i>HAc</i> concentration	63
Table 3.28	<i>EDTA</i> concentration	64
Table 3.29	<i>CDTA</i> concentration	64
Table 3.30	<i>DTPA</i> concentration	65
Table 4.1	Mass concentration for chemical balance of 0.5 M <i>HCl</i> with limestone	76
Table 4.2	Equation 4.21 results for 0.5 M <i>HCl</i> and limestone core	76
Table 4.3	Mass concentration for chemical balance of 0.5 M <i>HAc</i> with limestone	78
Table 4.4	Equation 4.21 results for 0.5 M <i>HAc</i> and limestone core	78
Table 4.5	Mass concentration for chemical balance of 0.25 M <i>EDTA</i> with limestone	79
Table 4.6	Equation 4.21 results for 0.25 M <i>EDTA</i> with limestone core	79
Table 4.7	Deviation between Equation 4.21 and Fredd and Fogler (1998b)	81
Table 4.8	Calculated coefficient numbers by Equation 4.28	81
Table 4.9	Injected and product fluid concentrations	84

Table 4.10	Mass concentration for chemical balance of 1 M <i>HCl</i> with dolomite	85
Table 4.11	Model results for 1 M <i>HCl</i> , 25 °C with dolomite core	85
Table 4.12	Model results for 1 M <i>HCl</i> , 50 °C with dolomite core	86
Table 4.13	Model results for 1 M <i>HCl</i> , 75 °C with dolomite core	87
Table 4.14	Model results for 4.4 M and 1 M <i>HCl</i> with limestone core	89
Table 4.15	Model results for 0.5 M <i>HCl</i> , with limestone core	90
Table 4.16	Model results for 0.5 M <i>HAc</i> with limestone core	91
Table 4.17	Model results for 0.25 M <i>EDTA</i> with limestone core	92
Table 4.18	Mass concentration for chemical balance of 0.25 M <i>CDTA</i> with limestone	93
Table 4.19	Model results for 0.25 M <i>CDTA</i> with limestone core	94
Table 4.20	Mass concentration for chemical balance of 0.25 M <i>DTPA</i> with limestone	95
Table 4.21	Model results for 0.25 M <i>DTPA</i> with limestone core	95
Table 4.22	Mass concentration for chemical balance of 4.4 M <i>HCl</i> with limestone	98
Table 4.23	Model results for 4.4 M <i>HCl</i> , with limestone core	98
Table 4.24	Model results for 4.4 M <i>HCl</i> , with limestone core ($\emptyset = 11\%$)	99
Table 4.25	Model results for 4.4 M <i>HCl</i> , with limestone core ($\emptyset = 15\%$)	100
Table 4.26	Model results for 4.4 M <i>HCl</i> , with limestone core ($\emptyset = 16\%$)	101
Table 4.27	Model results for 4.4 M <i>HCl</i> , with limestone core ($\emptyset = 25\%$)	102
Table 4.28	Mass concentration for chemical balance of 1.5 M <i>HCl</i> with limestone	105
Table 4.29	Model results for 1.5 M <i>HCl</i> , with limestone core in 25 °C	105
Table 4.30	Model results for 1.5 M <i>HCl</i> , with limestone core in 60 °C	107
Table 4.31	Model results for 0.5 M <i>HCl</i> , with limestone core	109
Table 4.32	Evaluation of the developed model	111
Table 4.33	Confidence and data range for limestone and dolomite	112

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
Figure 2.1	Wide ranges of wormholes observed in experiments (Fredd, 2000)	15
Figure 2.2	Schematic of different types of wormholes (Fredd, 2000)	16
Figure 2.3	Pore volumes to breakthrough by acid injection velocity (Buijse and Glasbergen, 2005)	22
Figure 2.4	Wormhole growth rate (Buijse and Glasbergen, 2005)	23
Figure 2.5	Wormhole types by 0.25 M <i>EDTA</i> (Fredd and Fogler, 1998a)	29
Figure 2.6	Pore volumes to breakthrough results for different acids and limestone core by Fredd and Fogler (1998b)	32
Figure 2.7	Vuggy and non vuggy carbonate by Izgec et al. (2009)	34
Figure 2.8	Pore volumes to breakthrough by Kalia and Glasbergen (2010)	35
Figure 2.9	Pore volumes to breakthrough results by Wang (2011)	36
Figure 2.10	Comparison of Newtonian with gelling acids by Ratnakar et al. (2012)	37
Figure 2.11	3D simulation results by Maheshwari and Balakotaiah (2013)	38
Figure 2.12	Wormhole types in 3D by Maheshwari et al. (2013)	39
Figure 2.13	Comparison of pore volumes to breakthrough for fresh and spent acids by Qiu et al. (2013)	41
Figure 2.14	Pore volumes to breakthrough at different temperatures (Xue et al., 2018)	42
Figure 2.15	Three groups of carbonate cores	43
Figure 3.1	Flowchart of the research design	46
Figure 3.2	Data gathering preview	48
Figure 4.1	Horizontal model of wormhole created in a porous media	70
Figure 4.2	Comparison of the results obtained by Equation 4.21 and experimental results given by Fredd and Fogler (1998b) for 0.5 M <i>HCl</i> with limestone core	77

Figure 4.3	Comparison of the results obtained by Equation 4.21 and experimental results given by Fredd and Fogler (1998b) for 0.5 M <i>HAc</i> with limestone core	78
Figure 4.4	Comparison of the results obtained by Equation 4.21 and experimental results given by Fredd and Fogler (1998b) for 0.25 M <i>EDTA</i> with limestone core	80
Figure 4.5	Coefficient number and Damköhler number relation for <i>HCl</i>	82
Figure 4.6	Coefficient number and Damköhler number relation for <i>HAc</i>	82
Figure 4.7	Coefficient number and Damköhler number relation for <i>EDTA</i>	83
Figure 4.8	Coefficient number for <i>HCl</i> , <i>HAc</i> and <i>EDTA</i>	83
Figure 4.9	Model results evaluation for 1 M <i>HCl</i> , 25 °C with dolomite core	86
Figure 4.10	Coefficient of determination of PV_{BT} for 1 M <i>HCl</i> , 25 °C with dolomite core	86
Figure 4.11	Model results evaluation for 1 M <i>HCl</i> , 50 °C with dolomite core	87
Figure 4.12	Coefficient of determination of PV_{BT} for 1 M <i>HCl</i> , 50 °C with dolomite core	87
Figure 4.13	Model results evaluation for 1 M <i>HCl</i> , 75 °C with dolomite core	88
Figure 4.14	Coefficient of determination of PV_{BT} for 1 M <i>HCl</i> , 75 °C with dolomite core	88
Figure 4.15	Evaluation of the developed model with Wang et al. (1993) experimental results for dolomite core	89
Figure 4.16	Model results evaluation for 0.5 M <i>HCl</i> with limestone core	90
Figure 4.17	Coefficient of determination of PV_{BT} for 0.5 M <i>HCl</i> with limestone core	91
Figure 4.18	Model results evaluation for 0.5 M <i>HAc</i> with limestone core	91
Figure 4.19	Coefficient of determination of PV_{BT} for 0.5 M <i>HAc</i> with limestone core	92
Figure 4.20	Model results evaluation for 0.25 M <i>EDTA</i> with limestone core	92

Figure 4.21	Coefficient of determination of PV_{BT} for 0.25 M <i>EDTA</i> with limestone core	93
Figure 4.22	Model results evaluation for 0.25 M <i>CDTA</i> with limestone core	94
Figure 4.23	Coefficient of determination of PV_{BT} for 0.25 M <i>CDTA</i> with limestone core	95
Figure 4.24	Model results evaluation for 0.25 M <i>DTPA</i> with limestone core	96
Figure 4.25	Coefficient of determination of PV_{BT} for 0.25 M <i>DTPA</i> with limestone core	96
Figure 4.26	Evaluation of the developed model results with Fredd and Fogler (1998b) experimental work	97
Figure 4.27	Coefficient of determination of PV_{BT} for 4.4 M <i>HCl</i> with limestone	98
Figure 4.28	Model results evaluation for 4.4 M <i>HCl</i> with limestone core ($\emptyset=11\%$)	99
Figure 4.29	Coefficient of determination of PV_{BT} for 4.4 M <i>HCl</i> with limestone core ($\emptyset=11\%$)	100
Figure 4.30	Model results evaluation for 4.4 M <i>HCl</i> with limestone core ($\emptyset=15\%$)	101
Figure 4.31	Coefficient of determination of PV_{BT} for 4.4 M <i>HCl</i> with limestone core ($\emptyset=15\%$)	101
Figure 4.32	Model results evaluation for 4.4 M <i>HCl</i> with limestone core ($\emptyset=16\%$)	102
Figure 4.33	Coefficient of determination of PV_{BT} for 4.4 M <i>HCl</i> with limestone core ($\emptyset=16\%$)	102
Figure 4.34	Model results evaluation for 4.4 M <i>HCl</i> with limestone core ($\emptyset=25\%$)	103
Figure 4.35	Coefficient of determination of PV_{BT} for 4.4 M <i>HCl</i> with limestone core ($\emptyset=25\%$)	103
Figure 4.36	Evaluation of the developed model with Etten (2015) experimental work	104
Figure 4.37	Model results evaluation for 1.5 M <i>HCl</i> , 25 °C with limestone core	106
Figure 4.38	Coefficient of determination of PV_{BT} for 1.5 M <i>HCl</i> , 25 °C with limestone core	106

Figure 4.39	Model results evaluation for 1.5 M <i>HCl</i> , 60 °C with limestone core	107
Figure 4.40	Coefficient of determination of PV_{BT} for 1.5 M <i>HCl</i> , 60 °C with limestone core	108
Figure 4.41	Evaluation of the developed model with Buijse and Glasbergen (2005) numerical results	108
Figure 4.42	Model results evaluation for 0.5 M <i>HCl</i> with limestone core	109
Figure 4.43	Coefficient of determination of PV_{BT} for 0.5 M <i>HCl</i> with limestone core	110
Figure 4.44	Overall coefficient of determination of PV_{BT}	111
Figure 4.45	Frequency and distribution of model and actual results for limestone	112
Figure 4.46	Frequency and distribution of model and actual results for dolomite	113

LIST OF ABBREVIATIONS

<i>CDTA</i>	-	Cyclohexylenedinitrilotetraacetic acid ($C_{14}H_{22}N_2O_8$)
<i>DTPA</i>	-	Diethylenetriaminepentaacetic acid ($C_{14}H_{23}N_3O_{10}$)
<i>EDTA</i>	-	Ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$)
<i>HAc</i>	-	Acetic acid (CH_3COOH)
<i>HCl</i>	-	Hydrochloric acid
<i>HF</i>	-	Hydrofluoric acid
<i>MAPE</i>	-	Mean Absolute Percentage Error (%)
<i>SD</i>	-	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 (<i>Dimensionless</i>)
n_{wh}	-	Number of dominant dissolution channels
\emptyset	-	Porosity
P	-	Pressure (<i>psi</i>)
\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 (<i>ft</i>)
r_w	-	Radius of wellbore (<i>in</i>)
T	-	Processing time (<i>min</i>)
t	-	Time (<i>min</i>)
U_i	-	Acid interstitial velocity (cm/min)
ν	-	Stoichiometric ratio of reactants
V_c	-	Core volume (cm^3)
V_i	-	Volume of injected fluid (cm^3)
V_{i-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 (<i>cm</i>)
\bar{X}	-	Data average
Z	-	Confident interval level
Γ	-	Kinetic parameter
μ	-	Viscosity (<i>cp</i>)
π	-	Pi number (<i>3.14</i>)
ξ	-	Dimensionless fluid loss term

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
Appendix A	Hydrochloric acid (<i>HCl</i>)	127
Appendix B	Acetic acid (<i>CH₃COOH</i>) or (<i>HAc</i>)	129
Appendix C	Ethylenediaminetetraacetic acid (<i>C₁₀H₁₆N₂O₈</i>) or (<i>EDTA</i>)	131
Appendix D	Cyclohexylenedinitrilotetraacetic acid (<i>C₁₄H₂₂N₂O₈</i>) or (<i>CDTA</i>)	133
Appendix E	Diethylenetriaminepentaacetic acid (<i>C₁₄H₂₃N₃O₁₀</i>) or (<i>DTPA</i>)	135
Appendix F	Limestone (Calcium carbonate) or (<i>CaCO₃</i>)	137
Appendix G	Dolomite (Calcium magnesium carbonate) or (<i>CaMg(CO₃)₂</i>)	139
Appendix H	Abstract of publication in Petroleum Journal	141
Appendix I	Abstract of publication in Journal of Advanced Research in Fluid Mechanics and Thermal Sciences	142
Appendix J	Abstract for publication in Journal	143
Appendix K	Abstract for publication in Journal	144

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 (*CH₃COOH*) and complex acids such as ethylenediaminetetraacetic acid (*EDTA*) or (*C₁₀H₁₆N₂O₈*) 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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