Modeling and Simulation of Alternative Injections of CO_2 and Water into Porous Carbonate Formations

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Abstract

Water alternating gas (WAG) technique is used in the petroleum industry to inject carbon dioxide (CO_2) into underground formations either for sequestration or enhanced oil recovery (EOR) processes. CO_2 injection causes reactions with formation brine or aquifer and produces carbonic acid, the acid dissolves calcite and changes flow behavior significantly. Modeling and investigating effects of CO_2 injection into carbonate formations during WAG processes, investigating parameters related to chemical reactions between reservoir rock and injecting fluid and also better understanding of the process theory for future experiments are the most important goals of this paper. To achieve these experimental data were used. Changes of output calcium concentration from a calcite core sample during three WAG cycles have been studied in laboratory works. The sample is modeled as a medium consisting of a set of capillary pipes and two pore size distribution models are used. Plug flow model and mass conservation law are used for modeling and Darcy law and Hagen-Poiseuille equation are also used to determine characteristics of the porous model. The model is built for linear, miscible and one-dimensional flow. The results show that experimental and model data coincide well in the first and second cycles of both porous models however; they are not coincided in the third cycle. It is because of precipitation and dissolution that cause permeability alternations. Results of the two porous models are compared also.

Keywords: Water alternating gas, Carbon dioxide, Pore size distribution, Porous medium model, Reaction rate constant

Introduction

Carbon dioxide (CO_2) is injected into underground formations for sequestration and also for Enhanced Oil Recovery processes (EOR) in oil and gas reservoirs. Generally it is injected into reservoirs with more than 800 meters depth, because it is in super critical form in these depths and has an optimum density for storage [1].

CO_2 sequestration also reduces emission of greenhouse gases into the atmosphere. After injection into deep saline aquifers, CO_2 can be trapped by four mechanisms however, it is possible for it to emit from reservoir to surface and migrate to atmosphere depending on the potential of well and blemish of cap rock. (CO_2 is trapped by hydrodynamic, capillary, dissolution and mineral mechanisms) [2].

After injection CO_2 reacts with brine and produces carbonic acid; the acid then reacts with reservoir rock and cause dissolution and precipitation of ions. As a result there must be alternations in some reservoir rock properties like porosity and permeability.

In concern with great oil and gas carbonate reservoirs in Iran and recent studies of CO_2 injection both for sequestrating and EOR process, further detailed studies of chemical and physical reactions of CO_2 with reservoir rock and parameters affecting the reactions are most necessary.

Many studies have been done on reactions of CO_2 with reservoir rock. Krumhansl et al. [3] experiments showed that if the brine is saturated with calcium, continuous dissolution of calcite causes calcium sulfate precipitation. They also investigated different effects of temperature and salinity on solubility.

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Izgec et al. [4] stated that after injection changes of rock properties are depended on pore size distribution and injecting water composition. They showed that porosity and permeability alternations have similar behavior at various temperatures.

Grigg and Svec [5] investigated changes of injectivity and CO_2 sequestration in EOR and storage processes.

Mohamed et al. [6] used three synthetic types of water to investigate effects of sodium sulfate on injecting water during CO_2 storage into carbonate aquifers. They also studied effects of injection flow rate, temperature and water salinity (formation or injecting water) on calcium sulfate precipitation and final permeability. Results showed permeability enhancement by increasing flow rate. At low temperatures calcium sulfate solubility increases and causes sample permeability enhancement. It was seen that increasing temperature decreases solubility of calcium sulfate and increases formation damage.

Mohamed et al. [2, 7] also studied effects of salinity of both formation water and injecting water during WAG injection processes. They showed that anhydrite solubility increased by increasing sodium chloride concentration of formation water. They also investigated effects of water salinity on gypsum solubility.

Generally geochemical and thermodynamic models and reaction transfer simulators are used to predict long time reactions of CO_2 with formation water and reservoir rock and also alternations of rock porosity and permeability. Constructing and correcting the models is possible only with the use of experimental data.

Smirnov et al. [8] presented two models to determine the optimum conditions of the well bottom zone treatment in a carbonate formation. A mathematical model taking account for fluid flow and the chemical reaction between the acid and the rock matrix was also presented.

Lagneau et al. [9] tried to investigate the possible benefits of reactive transport modeling in the context of CO_2 sequestration. They chose two deep saline aquifers to test the performance and limitations of the codes. The simulations highlighted the performance of the reactive transport codes, particularly the possibility to represent in detail a source (or sink) term with the dissolution of the CO_2 bubble (the precipitation of carbonated minerals), coupled to the transport of the dissolved CO_2. Furthermore, flux assessment at various points of the system illustrated the storage capacity of the systems

Ngheim et al. [10], Settari and Mourits [11] used coincidence and alternative porous media simulators and also geochemical simulators to inspect geochemical effects in flowing simulators.

Modeling and investigating changes of output calcium extraction from porous carbonate formations during WAG processes, investigating parameters related to chemical reactions between reservoir rock and injecting fluid and also better understanding of the process theory for future experiments are the most important goals of this paper. To achieve these targets, the experimental data of Mohamed et al. [2] were used. They tried to study changes of output calcium concentration from a calcite core sample during three WAG injections.

Porous core sample is considered as a medium consisting of a set of capillary pipes. Two pore size distribution models are used. First the medium is considered as a set of pipes with same sizes (radius). Then it is considered as two sets of pipes with two different radius sizes.

CO_2 Reactions with water and reservoir rock

Injection of CO_2 into underground reservoir causes reactions with formation brine or aquifer and produces a weak acid named carbonic acid:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad (1)$$

Carbonic acid dissolves calcite and produces calcium bicarbonate:

$$H_2CO_3 + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (2)$$

Dissolution of calcite in limestone makes some channels in the formation rock and changes flow behavior significantly. Carbonic acid also reacts with dolomite [9, 10]:

$$2H_2CO_3 + CaMg(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \qquad (3)$$

Experimental data

Mohamed et al. [2] used a pump with 2cm^3/min flow rate and two piston accumulator sat 1300 psi pressure and 200 ^{0}F temperatures to investigate changes of calcium concentration from the outlet of a 15.24 cm length and 1.9 cm radius calcite core sample during three WAG injections.

In the experiments injecting volumes of CO$_2$ and water during the process were the same.

Modeling

The process of modeling WAG injections into the core sample is shown in this part. Plug flow model and mass conservation law are used to model the process. Hagen-Poiseuille equation and Darcy law are also used to determine characteristics of the model.

Plug flow model is used for describing and predicting behavior of chemical reactions in continues flow systems. Results of this model are acceptable for many liquids and gases. Basic assumptions of the model are plug flow, steady state flow regime, constant fluid density and single reaction. Figure 1 shows the scheme of plug flow model.

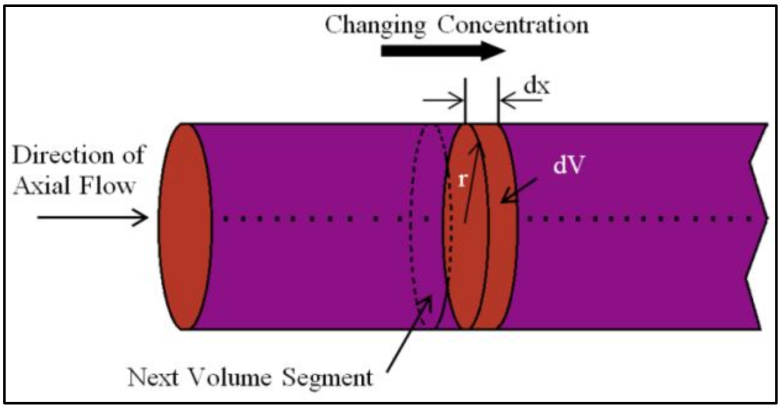

Figure 1: Scheme of plug flow model

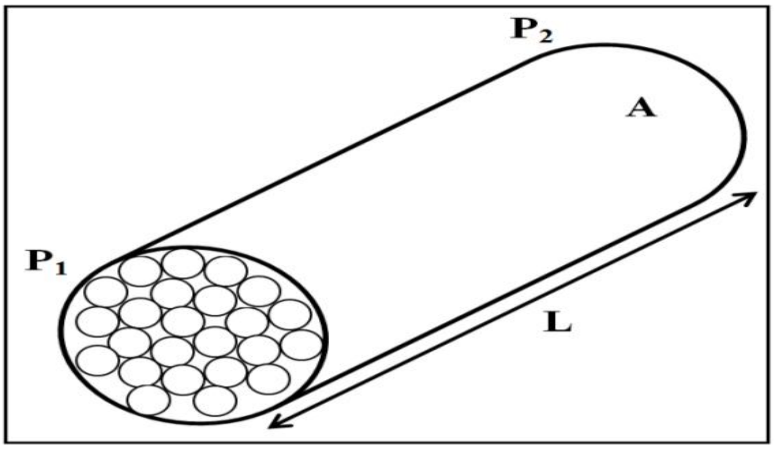

Figure 2: Scheme of same pipe set model

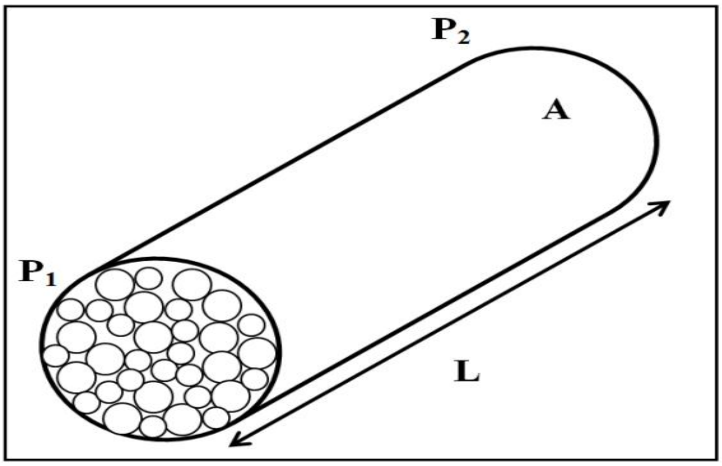

Figure 3: Scheme of two pipe sets model

Reaction rate is expressed as the number of any consuming moles or the number of any producing moles per time unit. Consider the following reaction:

$$aA + bB \rightarrow cC \tag{4}$$

Reaction rate law for the reaction is:

$$R = k.[C]^n \tag{5}$$

Where k is an experimental quantity, named *reaction rate constant*, and n is order of reaction related to the substance C.

If pore volumes are considered as a set of capillary pipes, plug flow model can be used to model WAG process. *Volumetric reaction rate constant* for the capillary pipes is expressed as:

Volumetric reaction rate constant= (velocity/unit area)(inner area/inner volume)*

$$k_v = k_s \times \left(\frac{2\pi.r.h}{\pi.r^2.h}\right) \tag{6}$$

$$k_v = k_s \times \left(\frac{2}{r}\right) \tag{7}$$

In equation 6, k_v is volumetric reaction rate constant and k_s is called surface reaction rate constant. Equation 6 indicates that volumetric reaction rate constant is greater in smaller pipes. [12, 13]

Material balance equation for one-dimensional and linear flow of calcium through the pipes is also as follows.

$$Q.C - Q.(C + dC) + R.A.dz = \frac{d(C.A.dz)}{dt} \tag{8}$$

$$\frac{\partial C}{\partial t} + \frac{Q}{A}\frac{\partial C}{\partial z} = R \tag{9}$$

Where Q is volumetric flow rate, C is calcium concentration and R is reaction rate constant. [14, 15]

Porous medium modeling

Porous mediums consist of disordered pore figures with extremely complicated pore size distribution that make the modeling difficult.

The paper presents two models to model real porous core sample. The sample will be considered as a model consisting of a set of same capillary pipes and also as a model consists of two different sets of capillary pipes with different sizes. They will be described in details in the following sections.

Same pipe set model

It is possible to consider porous core sample as a medium consisting of a set of same pipes as it is shown in Figure 2.

With the same pipe set model, radius of all capillary pipes will be the equal and total injection flow rate will be distributed between them equally.

$$n.v = V_{tot} \tag{10}$$

$$n.q = Q_{tot} \tag{11}$$

n is number of pipes and v, q, V_{tot} and Q_{tot} are volume, flow rate, total volume and total flow rate respectively.

Total volume (V_{tot}) is 29.52 cm^3 and total flow rate (Q_{tot}) is 2 cm^3/min. It is possible to rewrite equations 10 and 11 in *SI* units:

$$n.\pi r^2 h = \pi R^2 h \tag{12}$$

$$n.q = 0.033\times 10^{-6} \tag{13}$$

Where R is the total radius of the pipes and is equal to 1.9 cm.

In equations 12 and 13*n*, *r and q* are unknown parameters which must be determined. As it is obvious we need three independent equations to determine the three unknown parameters. Equations 12, and 13 and *Hagen- Poiseuille equ*ation can help us.

Hagen- Poiseuille equation is used for calculating fluid flow pressure drop in cylindrical pipes. Assumptions of the equation are flow of viscous and incompressible fluid and laminar flow through a constant circular cross-section pipe that its length is greatly longer than its diameter. [16, 17]

The equation is as follows:

$$\Delta p = \frac{8\mu Lq}{\pi r^4} \tag{14}$$

Replacing $r^2$with R^2/n and n. *q with* Q_{tot} in Hagen- Poiseuille equation results:

$$r^2 = \frac{8\mu L Q_{tot}}{\pi R^2 \Delta p} \tag{15}$$

In equation 15 $\Delta p/\mu$ is calculated using Darcy equation for the case that there is only water which is as follows:

$$Q_{tot} = \frac{kA}{\mu}\frac{\Delta p}{L} \tag{16}$$

Where k is permeability. Assumptions of Darcy equation are steady state flow regime, laminar flow, isothermal condition and homogenous porous medium.

Parameters *r*, *n* and *q* are determined by equations 12, 13 and 15. Values of these parameters are shown in Table 1.

Table 1: Characteristics of same pipe set model

Parameter	Value	Unit
n	213×10^6	-
$r\times10^4$	1.7	cm
$q\times10^8$	9.45	cm^3/min
$A\times10^8$	9.07	cm^2
q/A	1.038	cm/min

Two pipe sets model

Porous core sample can be considered as a medium consisting of two different sets of capillary pipes.

There are smaller and larger pipes and depending on the total pore volume allocated to each set, number of capillary pipes and their flow rate will be different. The model scheme is shown in Figure 3.

Allocating 12.34 cm^3 volume and 1 cm^3/min rate to a pipe set, and 17.18 cm^3 and 1 cm^3/min to another one, characteristics of the model are shown in Table 2.

Table 2: Characteristics of two pipe sets model

Parameter	Value		Unit
	Small Pipes	Big Pipes	
n	143×10^5	744×10^5	-
$r\times10^4$	1.58	1.86	cm
$q\times10^8$	7.03	13.5	cm^3/min
$A\times10^8$	7.48	8010	cm^2
q/A	0.896	1.24	cm/min

Determination of changes of output calcium concentration

In the modeling section a model was presented for WAG injections into the porous core sample:

$$\frac{\partial C}{\partial t} + \frac{Q}{A}\frac{\partial C}{\partial z} = R$$

Because of small changes in pH, n is considered zero and equation 9 can be written as follows:

$$\frac{\partial C}{\partial t} + \frac{Q}{A}\frac{\partial C}{\partial z} = k \tag{17}$$

The partial differential equation (PDE) 17 must be solved to determine the output of calcium concentration from the sample. It can be solved both by analytical and numerical methods. The equation was solved with finite difference method in explicit form (forward in time and backward in space) using *MATLAB* software.

Stability condition is as follows:

$$\Delta t \leq \frac{A.\Delta x}{Q} \tag{18}$$

In order to solve the PDE, the sample length is divided into ten segments (ten grids, $\Delta x = 1.524 cm$) and obviously an initial condition and a boundary condition for each pipe segment are needed.

Boundary conditions is considered zero for all segments at different injection cycles of both porous medium models. Values of initial conditions of both models are shown in Table 3.

Results and discussion

Figure 4 compares experimental and model data of output calcium concentrations in different injection cycles of same pipe set model.

Volumetric reaction rate constant, k_v is calculated using the following equation:

$$k_v = \frac{Q\Delta C}{V} \tag{19}$$

In equation 19, ΔC is changes in concentration and V is pore volume. Surface reaction rate constant, k_s, depends on the acid and rock. For example it is 6×10^{-6} mol.cm^{-2}.min^{-1} for carbonic acid and dolomite.

In all injection cycles of both the models the acid and rock are unchanged so; k_s was assumed constant [7].

Table 3: Values of initial conditions for both porous models

Space (segment), cm	First Cycle	Second Cycle	Third Cycle
1.524	0.400	0.400	0.400
3.048	0.400	0.473	0.479
4.572	0.400	0.546	0.558
6.096	0.400	0.620	0.673
7.620	0.400	0.693	0.717
9.144	0.400	0.767	0.796
10.688	0.400	0.840	0.875
12.192	0.400	0.913	0.954
13.716	0.400	0.987	1.034
15.240	0.400	1.060	1.113

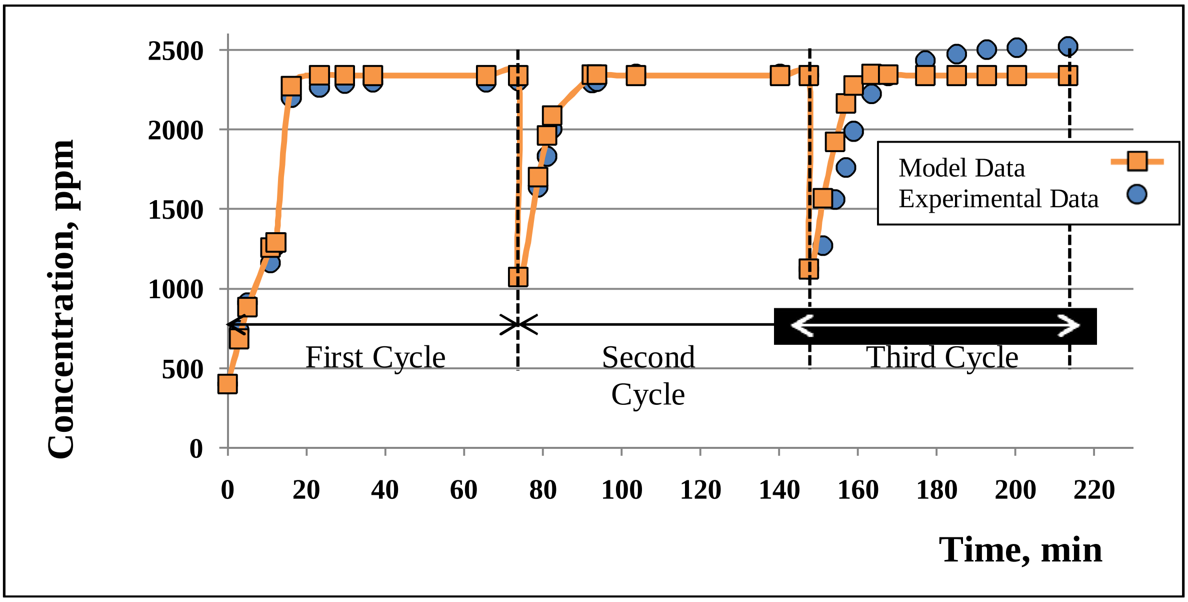

Figure 4: Experimental and model data of output calcium concentration of same pipe set model

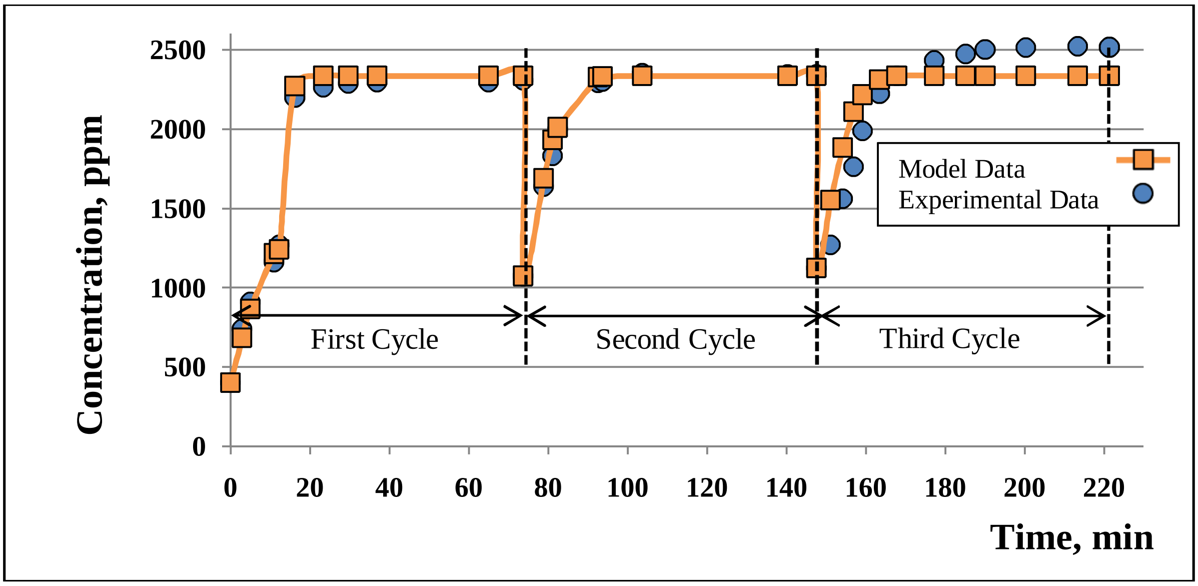

Figure 5: Experimental and model data of output calcium concentration of two pipe sets model

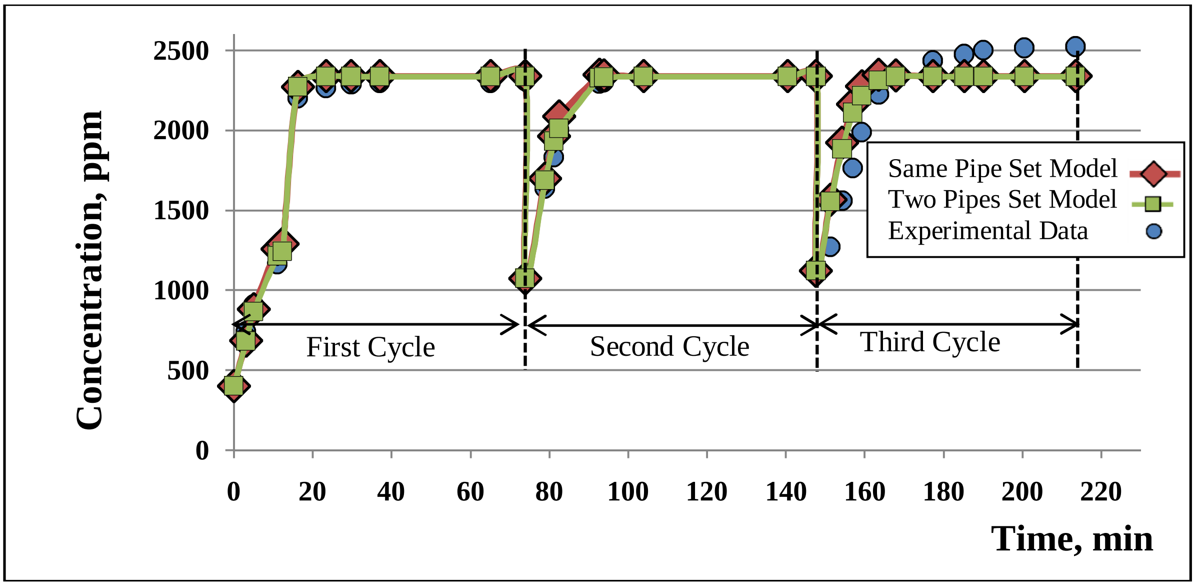

Figure 6: Comparison of experimental and model data

Having k_v form equation 19, k_s can be calculated using equation 7.

$$k_v = k_s \times (\frac{2}{r}) \qquad (7)$$

It is 0.15×10^{-7}gr.cm^{-2}.min^{-1}. It must be mentioned that the value is considered constant for all cycles of both models. Radius of all capillary pipes in same pipe set model is equal so we have just a value for k_v. Using equation 7, it is 0.177gr.litr^{-1}.min^{-1}.

In the first cycle calcium extraction rate increases after elapsing 12.34 min. due to CO_2 accumulation in the sample. It should be noted that k_s was considered as 0.8×10^{-8}gr.cm^{-2}.min^{-1}for the first 12.34 min. because it is assumed that the acid did not reach its optimum concentration until the time. When k_v is also 0.095 gr.min^{-1}.litr^{-1} for it.

In the second cycle, k_v is equal to that of steady state part of the first cycle (0.177 gr.litr^{-1}.min^{-1}).

Coincidence of experimental and model data in this cycle shows accuracy of k_v values.

Small differences between model and experimental data in the first and second cycles are due to basic assumptions of the model that affect k_v (such as pore size distribution, constant permeability and etc.). In the third cycle k_v is the same as steady state part of first cycle. As it is seen experimental and model data are not coincided well in this cycle. Model data are greater than experimental data before first 20 min. of the cycle but, they are smaller after that.

Mohamed et al. [2] showed that at the end of second water injection cycle increasing permeability causes pressure drop decrease. But, after 20 min. elapsing of the third cycle precipitation and dissolution decreases pore sizes and permeability which increases pressure drop. Values of k_v and output calcium concentration will also increase after the time.

The model assumed constant pore sizes so differences between experimental and model data are expectable.

Figure 5 compares experimental and model data of output calcium concentrations in different injection cycles of the two pipe sets model.

Average output calcium concentrations in the Figures are calculated using equation 20:

$$C_{Ave.} = \frac{1}{Q_{tot}} \sum_{i=1}^{2} C_i . Q_i \tag{20}$$

It must be noted that determination of k_v for the model has been done using the same procedure as same pipe set model, however it is obvious that because of two different pipe sizes there are two different k_v values (equation 7).

In the first cycle model data are a bit greater than experimental data. As it is seen calcium concentration increases significantly at 12.34 min. The point is considered as accumulation time for a set of pipes, and 17.18 min. is also considered as accumulation time for another set. Values of k_v for the time intervals are shown in Table 3.

Table 3: Volumetric reaction rate constant for first cycle of two pipe sets model

Time, min	k_v, gr.litr^{-1}.min^{-1}	
	Small Pipes	**Large Pipes**
0-12.34	0.102	0.086
12.34-73.8	0.189	0.161

Average radius of small and large pipes is 1.7×10^{-4}cm. For the average radius k_s is 0.74×10^{-8} mol.cm^{-2}.sec^{-1} for 0-12.34 min and 0.14×10^{-7} mol.cm^{-2}.sec^{-1}for 12.34-73.8 min.

k_v is 0.176 gr.litr^{-1}.min^{-1} for average radius. Experimental and model data have a good coincidence in second cycle that shows accuracy of k_v values. Model data are a bit greater than experimental data until elapsing 28 min. of the cycle. After which, they become slightly smaller. Differences are related to the model basic assumptions.

In the third cycle, k_v is the same as steady state part of first cycle. As it is seen experimental and model data are not coincided well in the cycle. The reason was explained in the third cycle of same pipe set model.

Figure 6 compares results of the two porous models with experimental data. Average absolute relative error percent of the models in comparison with experimental data are shown in Table 4. Correlation coefficients are also shown in Table 5.

Table 4: Average absolute relative error percent of the two porous medium models

Injection cycle	Error percent $\left\lvert \frac{C_{\text{Model}} - C_{\text{Exp.}}}{C_{\text{Exp.}}} \right\rvert \times 100$	
	Same pipe set model	**Two pipe sets model**
First	3.130	2.976
Second	2.276	1.448
Third	9.994	8.925

Table 5: Correlation coefficient of the two porous medium models

Injection cycle	Correlation coefficient	
	Same pipe set model	**Two pipe sets model**
First	0.9979	0.9985
Second	0.9875	0.9939
Third	0.8271	0.8643

Conclusions

- A linear, miscible and one-dimensional model was developed to model alternative injections of CO_2 and water into porous carbonate formations. The model was solved for three WAG injections to determine output calcium concentration. Results show that in both the porous medium models experimental and model data coincide well in the first and second cycles however; they do not coincide well in the third cycle.
- Two porous medium models were developed to model real porous core sample. The models use different pore size distributions.
- Model errors in the third injection cycle are because of model basic assumptions such as constant pore size and constant permeability. While it is due to precipitation and dissolution in the laboratory core permeability changes.
- Two pipe sets model can present better results in comparison with same pipe set model.
- Larger pores transfer the injecting fluid to the end of sample quickly so output calcium concentration rises as injection starts.
- Volumetric reaction rate constant is greater in smaller pores because of slower movement of fluid which allows more reactions.
- Output calcium concentration from the sample increases after a while in all cycles. It is because of lower fluid velocity in small pores which provides long time reactions. The reaction products will also appear at the end of sample after a short time.
- Model can be improved by employing experimental results of relative permeability and fluid viscosity data (for the case of immiscible injection), determining pore size distribution, and results of experiments at different temperatures and injection flow rates.

Nomenclatures

A	Cross sectional area, ft^2
C	Calcium concentration, ppm
$C_{Ave.}$	Average model calcium concentration, ppm
C_{Exp}	Experimental calcium concentration, ppm
C_{Model}	Model calcium concentration, ppm
h	Capillary pipes height, ft
k	Permeability, md
k_v	Volumetric reaction rate constant, $gr.litr^{-1}.min^{-1}$
k_s	Surface reaction rate constant, $gr. cm^{-2}.min^{-1}$.
L	Capillary pipes length, Length element, ft
n	Number of capillary pipes, dimensionless
Q	Volumetric flow rate, $m^3.sec^{-1}$
R	Reaction rate
r	Radius of capillary pipes, cm
t	Time, min
Δp	Pressure difference, psi
μ	Viscosity,cp

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