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Accelerating Dissolution Trapping by Low Saline WAG Injection Scenario

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Abstract

Sequestration of anthropogenic CO₂ into subsurface geologic formation is the most reliable methodology in stabilizing the ever increasing CO₂ concentration in atmosphere. However the sequestered buoyant CO₂ always tends to migrate back to the atmosphere through possible migration pathways. Ensuring storage safety by accelerating dissolution trapping is the only possible methodology, while dissolution is a strong function of pressure, temperature, salinity and local availability of brine. In the present paper, an attempt has been made to investigate the effect of salinity on accelerating dissolution of CO₂ in resident brine. It has been observed that low saline brine injection enormously increases the dissolution trapping mechanism of injected CO₂.

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Keywords: CO₂ storage; Saline aquifer; accelerating dissolution trapping; low saline brine injection.

1. Introduction

Fossil fuels are the prominent energy sources that have the potential to meet ever growing demand for energy, when compared with other eco-friendly energy sources. Burning of fossil fuels for energy production lead to rapid increase in atmospheric concentration of anthropogenic greenhouse gases that includes CO₂, leading to global warming and subsequent climate change issues. Sequestration of CO₂ into underground subsurface formation such

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as in saline aquifer is the only reliable mitigation techniques available [4,6,9]. The injected buoyant CO_2 is retained within the formation by overlying impermeable cap rock. Host storage formation is selected in such a way that the risk of CO_2 leakage into the overlying formations is minimal throughout the storage period. The injected CO_2 within the formation is claimed to be permanently stored, only when total mass of injected CO_2 are precipitated as minerals by mineralization process. However, the mineralization of injected CO_2 within the subsurface formation is a time consuming process, spanning in terms of hundreds of years. This time period before mineralization is presumed to be the lowest storage safety period [7,13]. Ensuring safety of CO_2 storage during this period is the active area of ongoing research.

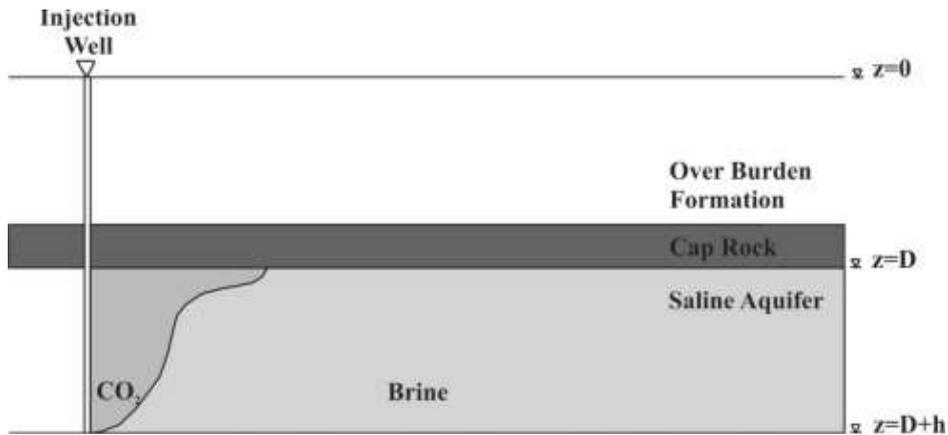


Fig. 1. Schematic diagram of CO_2 sequestration scenario in saline aquifer.

Figure 1 illustrates the pictorial representation of CO_2 storage in saline aquifer located at depth (D) from surface. Conceptually, injected CO_2 flows away from the injection well which displaces the resident brine and subsequently, an interphase is developed between them. Across the interphase, there is an instantaneous transfer of mass from CO_2 phase to brine phase which results in the dissolution of CO_2 in aqueous brine. The dissolved aqueous CO_2 fractions in the brine phase are trapped by capillarity, which makes the CO_2 immobile, and such trapping by immobilization of dissolved CO_2 is referred to as dissolution trapping. The dissolved CO_2 mole fractions undergo further chemical processes that includes formation and dissociation of carbonic acid which would ultimately initiate the mineralization process, resulting in reduction of pH of the system [5,6]. Reduction in pH of the system is a function of mole fraction of dissolved aqueous CO_2 and this will have significant effect on disintegration of rock integrity. However, dissolution trapping plays an inherent role in nurturing the intended purpose of the storage process, while time taken for dissolution is however slow ranging in terms of several decades. Hence, acceleration of this dissolution process by applying fundamental reservoir engineering concept is the primary focus of the present work. Dissolution of CO_2 is a strong function of pressure, temperature, salinity and local concentration of CO_2 in brine [4,5,6,12]. It has been emphasized that increase in reservoir pressure of the system increases solubility of CO_2 ; whereas salinity has inverse effect on solubility of CO_2 . Hence injection of low saline brine shall have positive impact on accelerating dissolution of CO_2 . On the contrast, accelerating dissolution shall have inverse effect on pH of the system, as mole fraction of aqueous CO_2 keeps increasing, while it enhances the efficiency of storage process [6,11]. The objective of the present work is to numerically study the coupled impact of low saline Water Alternating Gas (WAG) injection on accelerating dissolution of injected CO_2 in saline aquifer and to investigate its associated impact on pH of the system.

The governing physics has been conceptualized as immiscible two phase fluid flow with distinct capillary interphase. The hysteresis effect on relative permeability of gas during brine injection has been considered. Solubility of CO_2 into brine phase has been calculated using the developed thermodynamic EOS model. Effect of salinity on solubility of CO_2 has been incorporated. Rheological properties such as density and viscosity of both the phases were computed using experimental correlations from existing literature. The nonlinear partial differential equations in the mathematical model have been numerically solved by using Implicit Pressure Explicit Saturation (IMPES) scheme. Neumann type boundary condition has been incorporated at the left boundary and no flow

boundary condition has been implemented at the right boundary. The set of algebraic equations derived from finite difference approximation is solved using conjugate gradient solver. Time marching has been done carefully considering suitable stability criteria.

In the present study, the effect of low saline WAG injection scenario on dissolution of CO₂ has been studied. Subsequently, the sensitivity of injected brine salinity on dissolution of CO₂ has been quantitatively analyzed. Finally, the coupled effect of flow and CO₂ dissolution on pH of the system has also been numerically investigated.

Nomenclature

ϕ	Porosity of the formation in <i>fraction</i>
K	Intrinsic permeability in m^2
k_{ra}	Relative permeability in <i>fraction</i>
P_α	Phase pressure in <i>Pa</i>
S_α	Phase saturation in <i>fraction</i>
μ_α	Viscosity in <i>Pa s</i>
ρ_α	Density in kg/m^3
q_α	Darcy flux in <i>m/s</i>
Q_α	Source term in kg/m^3s
C_{co2}	Compressibility of CO ₂ gas in Pa^{-1}
P_c	Capillary pressure in <i>Pa</i>
P_b	Entry pressure in <i>Pa</i>
m	Pores size distribution parameter
m	Number of moles in <i>mol</i>
v_α	Injection flux in <i>m/s</i>
MW	Molecular weight of CO ₂ in <i>kg/mol</i>
R	Universal gas constant
x	Spatial variable in <i>m</i>
t	Temporal variable in <i>t</i>

Subscript

g	CO ₂ phase
w	brine phase

2. Physical system and Governing Equation

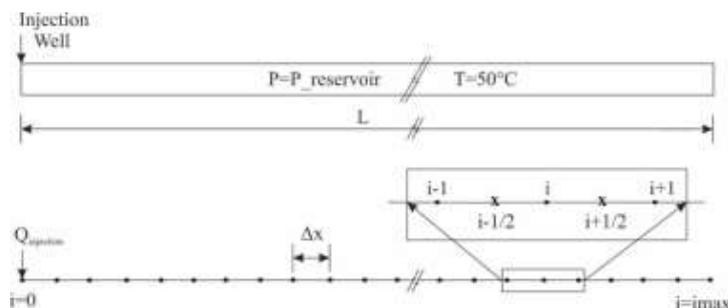


Fig. 2. Schematic diagram of the physical and computational domain considered

Schematic diagram of the physical scenario has been portrayed in figure 2. Present paper considers isothermal horizontal flow of two immiscible fluids in an isotropic homogeneous porous medium. Rock and resident brine are incompressible and injected supercritical CO₂ is slightly compressible. Fluid flow is governed by Darcy's law.

2.1 Governing equations

The general mass conservation equations for the individual phases are given by Eq. [1a & 1b].

$$\frac{\partial(\rho_w \phi S_w)}{\partial t} = \frac{\partial(\rho_w q_w)}{\partial x} + Q_w \quad (1a)$$

$$\frac{\partial(\rho_g \phi S_g)}{\partial t} = \frac{\partial(\rho_g q_g)}{\partial x} + Q_g \quad (1b)$$

The horizontal fluid flow for α phase is governed by pressure gradient only, neglecting gravity effect. The Darcy flux for α phase is presented by Eq. (2).

$$q_\alpha = - \frac{k k_{r\alpha}(S_\alpha)}{\mu_\alpha} \frac{\partial P_\alpha}{\partial x} \quad (2)$$

The associated auxiliary equations for determining fluid saturation and fluid pressure are given by Eqs. (3 & 4)

$$S_w + S_g = 1 \quad (3)$$

$$P_c = P_g - P_w \quad (4)$$

\bar{Q}_g is the interphase mass transfer function and shall be computed from real gas equation.

$$\bar{Q}_g = - \frac{\partial \rho}{\partial t} = - \left(\frac{MW}{ZRT} \right) \frac{\partial P_g}{\partial t} \quad (5)$$

Isothermal compressibility of the injected SC-CO₂ is computed using the expression given below

$$C_g = - \frac{1}{V} \left(\frac{\partial V}{\partial P_g} \right) \quad (6)$$

2.1.1. Capillary pressure model

Various capillary pressure models relating phase pressure and phase saturation are available in literature. Brooks-Corey capillary pressure model has been incorporated in current paper, which can be expressed as,

$$P_c = -P_0 S_e^{-1/2} \quad (7)$$

$$S_e = \frac{S_w - S_{rw}}{(1 - S_{rw} - S_{rg})} \quad (8)$$

The relative permeability of wetting and non-wetting phases was expressed as:

$$K_{rw} = S^{* \frac{2+3\lambda}{\lambda}} \quad (9)$$

$$K_{rg} = (1 - S^*)^2 \left(1 - S^{* \frac{(2+\lambda)}{\lambda}} \right) \quad (10)$$

Taking derivative of equation (7) with respect to S_w ,

$$P_c' = \frac{dP_c}{dS_w} = -\frac{1}{\lambda} P_o S^{* \left(\frac{1+\lambda}{\lambda} \right)} \frac{1}{(1 - S_{rw} - S_{rg})} \quad (11)$$

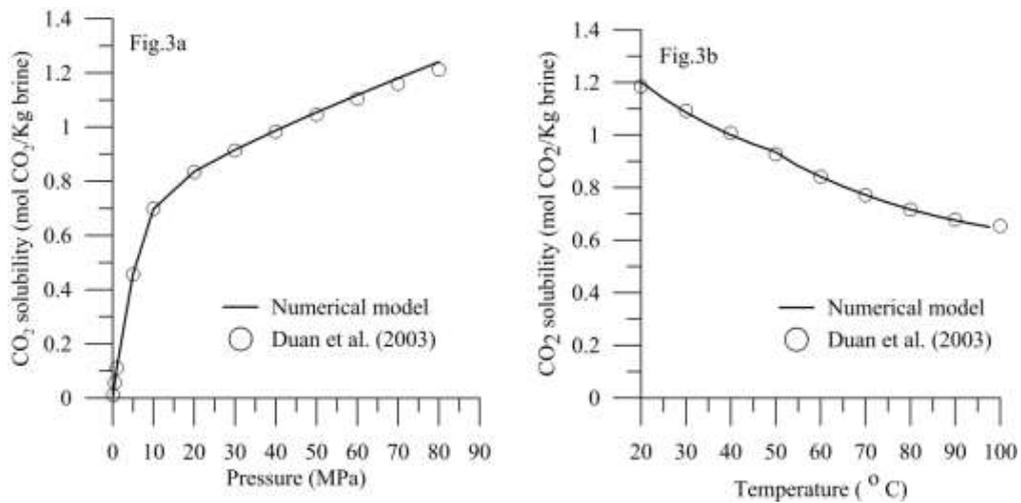


Fig. 3. Verification of developed EOS model with respect to (a) pressure and (b) temperature with Duan et al. (2003)

2.1.2 Thermodynamic EOS model

The thermodynamic model has been developed following the numerical procedure presented in [4] for computation of solubility of CO₂ in brine. Figures 3a and 3b show the verification of developed solubility model with [4] following [6]. Salinity of brine is taken as 1 mol NaCl/Kg brine. Temperature is kept constant as 50 degree Celsius for figure 3a; whereas, pressure is kept constant as 10 MPa for figure 3b. It can be observed from the figure 3 that the present model shows good agreement with the data gathered from [4]. It can also be observed from figure 3a that, solubility increases rapidly for pressure increase up to 10 MPa and later stabilizes linearly for pressure greater than 10 MPa. It can also be observed from figure 3b that temperature has inverse effect on solubility.

2.1.2 pH model

Peng et al. (2013) conducted experimental study on pH of CO₂-H₂O system and developed empirical relation of pH as function of mole fraction of CO₂ in brine; whereas, mole fraction of CO₂ is function of pressure, temperature and salinity of brine.

$$pH = A(px_m) + B \quad (12)$$

Where, $px = -\log_{10}(x_m)$ and x_m is the mole fraction of CO_2 in aqueous phase. A and B are computed using correlation presented in [11]. This empirical relation showed good correlation with CO_2 – H_2O mixture and is valid for pressure and temperature range of up to 15 MPa and $308 \text{ K} < T < 423 \text{ K}$ respectively.

Mole fraction of CO_2 is computed using thermodynamics EOS model developed for pH calculations. Computed pH value is compared with experimental results published by [2,10] as in figure 4. [10] presented pH reduction for CO_2 in pure water with respect to pressure at 315.15K. [2] presented experimental results of pH reduction of saline water due to CO_2 . The computed pH values follow the trend followed by experimental results. Deviation of about $\Delta\text{pH} = 0.2$ was observed. It was observed that pH drops at slower rate on further increase in pressure.

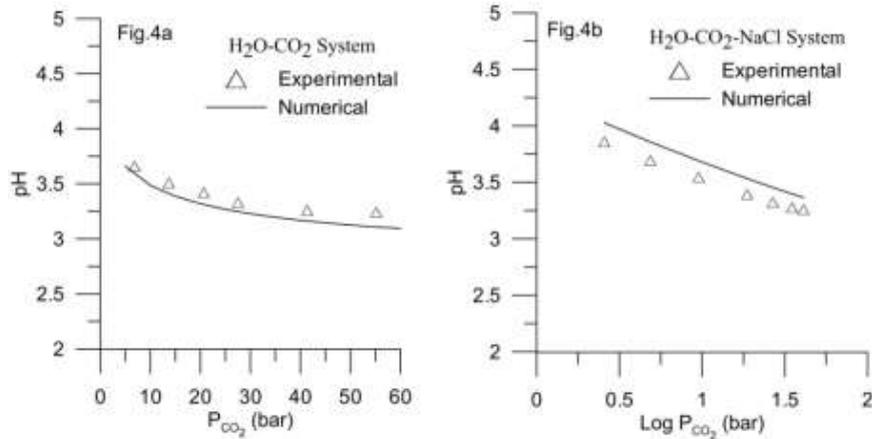


Fig. 4. Verification present pH model with published experimental results for (a) CO_2 in pure water and (b) CO_2 in saline water

2.1.3 Initial Conditions:

The governing equations are formulated using pressure of gas and saturation of water formulation. The initial and boundary conditions approximating physical scenario are presented below. The aquifer is considered to be at reservoir condition initially.

$$P_g(x, t = 0) = P_{\text{reservoir}} \quad (13)$$

$$S_w(x, t = 0) = 1 - S_{rg} \quad (14)$$

2.1.4 Boundary Conditions:

Present model assumes flux type boundary condition at left boundary and no flow boundary condition at right boundary.

$$q_{w,x=0} + q_{g,x=0} = v_w + v_g \quad (15)$$

Pressure and saturation boundary conditions were calculated from equation (15) by substituting Darcy's law (equation 2).

$$q_{w,x=0} + q_{g,x=0} = 0 \quad (16)$$

2.1.5 Numerical Scheme implemented

The governing equations are approximated using Finite Difference schemes. The system of nonlinear partial differential equations is sequentially coupled using IMPES scheme.

The time derivative is approximated using first order accurate forward Euler scheme.

$$\frac{\partial P_i}{\partial t} = \frac{P_i^{n+1} - P_i^n}{\Delta t} + O(\Delta t) \quad (17)$$

The spatial derivative is approximated using second order accurate central differencing scheme.

$$\frac{\partial^2 P_i}{\partial x^2} = \frac{P_{i-1} - 2P_i + P_{i+1}}{\Delta x^2} + O(\Delta x^2) \quad (18)$$

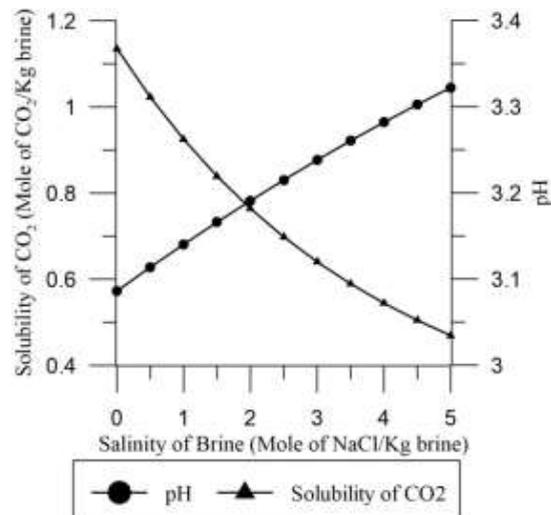


Fig.5 Impact of salinity of brine on solubility of CO₂ and pH.

Table 1: Parametric values considered for the present study

Parameters	Values
Intrinsic Permeability	1E-13
Porosity	0.15
Capillary pressure	$P_b = 1.33E4$ $\lambda=2$
Relative permeability values	$S_{wr} = 0.3$ $S_{gr} = 0.01$
Initial reservoir pressure	9 MPa
Reservoir temperature	50°C
Reservoir brine salinity	2 mol/kg
CO ₂ injection rate	0.5E5 m/s
Brine injection rate	0.5E-5 m/s

3. Results and discussion

Numerical simulation has been performed using above developed model. Input parameters were organized in table 1. Initial pH of resident brine is assumed to be 7. SC-CO₂ is injected at left boundary at constant injection rate. As injected SC-CO₂ propagates displacing resident brine, saturation of CO₂ at near well bore region increases. As

soon as SC-CO₂ propagates, transfer of mass take place from CO₂ phase to brine phase. Dissolution of brine to CO₂ phase is considered insignificant as per [5]. Dissolved mole fraction of CO₂ reduces the pH of the CO₂ enriched brine. Though pH reduction is a function of CO₂ mole fraction in brine, the mole fraction, in turn, is a function of pressure, temperature and salinity. It can be inferred from figure 3a&4a that as pressure increases solubility of CO₂ increases and CO₂ enriched brine becomes more acidic. It can also be hypothesized that increase in salinity of brine (increase in NaCl concentration) shall have direct impact on acidity of brine solution. Contradicting to this hypothesis, acidic nature of brine solution reduces as salinity of brine increases; as in figure 5. In figure 5, distribution of solubility of CO₂ and pH of brine solution were plotted for various brine salinity. It can be observed that, as salinity of brine increases at constant pressure (10MPa) and temperature (50°C), solubility of CO₂ in brine decreases; subsequently, mole fraction of CO₂ in brine decreases and pH of brine solution increases. Hence, it can be summarized that as pressure increases, solubility increases and solution becomes more acidic. Whereas, as temperature increases, solubility of CO₂ decreases and acidic nature of solution reduces; and, as salinity of brine increases, CO₂ solubility decreases and acidic nature of solution reduces. However, the above investigation is based on the developed thermodynamics model, while the coupled impact of CO₂ injection based pressure buildup in the porous medium and associated impact on mass of dissolved CO₂ and subsequent alterations in pH of the CO₂ enriched brine need to be addressed clearly.

In this section, the coupled complex nature of flow and dissolution of CO₂ on pH of brine solution pertained to continuous injection of CO₂ has been numerically investigated. Numerical simulations have been performed using above validated model for continuous injection of CO₂ in porous medium for 24 hours. Injection rate of CO₂ is kept constant and infinite boundary condition is implemented at right boundary. The observed results have been graphically represented in figure 6. Figure 6a summarizes the distribution of CO₂ along porous media at different time intervals. It can be observed from figure 6a that propagating front of CO₂ plume is approximately at 8 m from left boundary after 6 hours of injection and at 37 m from left boundary after 24 hours of injection. It can be observed that, injected SC-CO₂ starts propagating the porous medium displacing the resident brine. The near well bore pressure increases to meet constant injection rate. Such buildup of pressure essentially important, for injected CO₂ to flood every small pores; rather than, sweeping through preferential pathways.

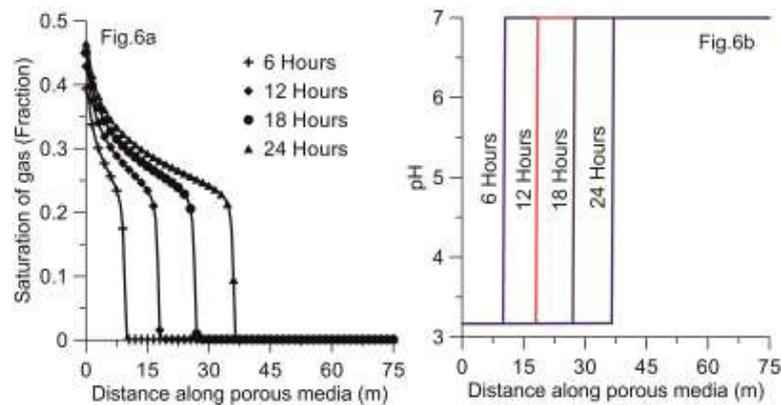


Fig 6. Distribution of saturation of CO₂ and pH of the CO₂ saturated brine along the length of the porous media

Figure 6b summarizes the associated variations in pH of the brine solution. Though pressure buildup has significant impact on dissolution of CO₂ into brine, the pH of the CO₂ enriched reduces. It can be observed that pH of brine solution suddenly drops approximately to 3.15 at the injection point. Due to CO₂ injection, solubility of CO₂ increases rapidly and stabilizes on further increase in pressure. Subsequent to rapid increase in solubility of CO₂, sudden reduction of pH (to about 3.15) shall be observed at left boundary. Acidic nature of brine solution propagates along with the propagating CO₂ front in figure 6. Further reduction in pH at left boundary due to continuous pressure buildup is inferred; but, it is very insignificant. The reduction in pH is primarily because of the formation and dissociation of carbonic acid which shall be advantageous in initiating further mineralization process. Hence dissolution of CO₂ plays indigenous role in the storage process. The numerical investigation by [13] emphasized the

importance of pressure on accelerating dissolution process. However the effect of salinity of injected brine on dissolution has not been addressed. Present paper would like to emphasize the importance of salinity on enhancing dissolution trapping.

Figure 7 summarizes the effect of salinity of injected brine on mass of CO₂ dissolved compared with the continuous injection scenario. During low saline injection scenario, brine is injected alternating CO₂ gas injection period. Injection takes place for 3 cycles, each cycle of brine alternating gas injection spanning 8 days. Effective CO₂ injection period for low saline injection scenario is spanning 12 days and the total simulation time is 24 days. The observed results have been compared with the results observed from continuous injection scenario. In case of continuous injection case injection of CO₂ take place for 12 days. The observed results at the end of total simulation time have been presented in fig 7. In case of continuous injection of CO₂, the mass of CO₂ dissolved into the resident brine phase increases linearly at slower rate. While during low saline brine injection scenario, the accelerated CO₂ dissolution has been observed. This could be because of the coupled impact of pressure buildup, salinity of the alternatively injected brine. For instance, at the end of injection of about 4 tons of CO₂ injection, about 600 Kg of injected CO₂ has been immobilized by dissolution trapping, while major fraction of injected CO₂ remains as free phase triggering the question of safety of storage. While during low saline brine injection scenario about 1200 kg of injected CO₂ has been immobilized and it is significantly higher when compared with continuous injection case. Hence it can be emphasized that low saline brine injection plays imperative role in accelerating dissolution trapping of injected CO₂.

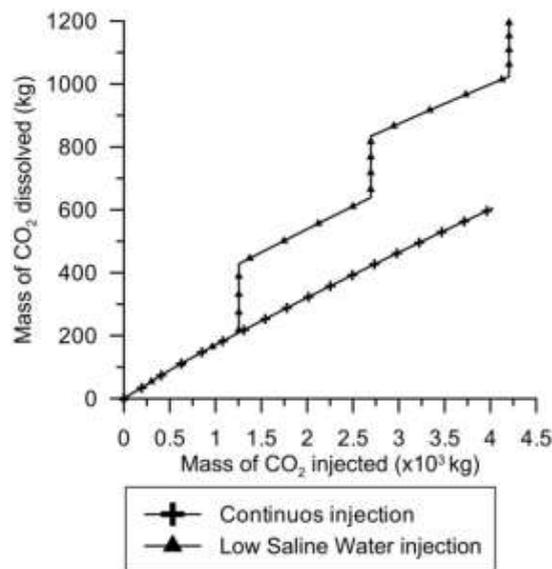


Fig 7. Effect of low salinity water injection on dissolution compared with continuous injection scenario

4. Conclusion

In this present paper, the effect of CO₂ solubility on pressure and salinity of brine and associated effect on dissolution of CO₂ and associated impact of dissolution on pH were investigated. The coupled effect of the above phenomenon on multiphase fluid flow system has been investigated. The above illustrations can be summarized as,

- As pressure increases, solubility increases and solution becomes more acidic. While, as temperature increases, solubility of CO₂ decreases and acidic nature of solution reduces; and as salinity of brine decreases, CO₂ solubility increases and again acidic nature of solution increases.
- As CO₂ is injected continuously, buildup of pressure takes place at left boundary; resulting in rapid increase in solubility, reducing pH of brine. pH of CO₂ enriched brine reaches up to 3.15.

c) Low saline brine injection plays imperative role in accelerating dissolution trapping of injected CO₂ in saline aquifer.

(d) For efficient CO₂ sequestration, the present study proposes a novel injection strategy of CO₂ injection at a pressure greater than the reservoir pressure and by alternating the CO₂ injection with the low saline water.

References

- [1] Bear J, Cheng AD. Modeling groundwater flow and contaminant transport. Vol. 23. Springer Science & Business Media; 2010.
- [2] Crolet JL, Bonis MR. pH Measurements in Aqueous CO₂ Solutions under High Pressure and Temperature. CORROSION 1983; 39, p.39-46.
- [3] Duan Z, Sun R. An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. Chem Geol 2003; 193(3), 257-271.
- [4] Gasda SE. Numerical models for evaluating carbon dioxide storage in deep, saline aquifers: Leaky wells and large-scale geological features. Ph.D., Princeton University 2008.
- [5] Hassanzadeh H, Pooladi-Darvish M, Elsharkawy AM, Keith DW, Leonenko Y. Predicting PVT data for CO₂-brine mixtures for black-oil simulation of CO₂ geological storage. Int J Greenh Gas Con 2008; 2(1),p. 65-77.
- [6] Iglauer, S. Dissolution trapping of carbon dioxide in reservoir formation brine-a carbon storage mechanism. INTECH Open Access Publisher; 2011.
- [7] Juanes R, Spiteri E, Orr F, Blunt M. Impact of relative permeability hysteresis on geological CO₂ storage. Water Resour Res 2006; 42.
- [8] Keeling CD, Whorf TP, Wahlen M, Plicht Jvd. Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980. Nature 1995; 375: p. 666-670.
- [9] Nordbotten JM, Celia MA. Geological storage of CO₂: modeling approaches for large-scale simulation. John Wiley & Sons; 2011.
- [10] Meysami B, Balaban MO, Teixeira AA. Prediction of pH in model systems pressurized with carbon-dioxide. Biotechnol Progr 1992; 8 (2), p. 149-154.
- [11] Peng C, Crawshaw JP, Maitland GC, Trusler JM, Vega-Maza D. The pH of CO₂-saturated water at temperatures between 308K and 423K at pressures up to 15MPa. J Supercrit Fluid 2013; 82, p. 129-137.
- [12] Spycher N, Pruess K, Ennis-King J. CO₂-H₂O mixtures in the geological sequestration of CO₂. I. Assessment and calculation of mutual solubilities from 12 to 100 C and up to 600 bar. Geochim Et Cosmochim Ac 2003; 67: p. 3015-3031.
- [13] Vivek R, Kumar GS. Numerical investigation on effect of varying injection scenario and relative permeability hysteresis on CO₂ dissolution in saline aquifer. Environmental Earth Sciences 2016; 75:1192.