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# Enhanced solubility trapping of $CO_2$ in fractured reservoirs

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**Abstract**

The dissolution of supercritical $CO_2$ in formation water is one of the main trapping mechanisms for $CO_2$ storage in saline aquifers. We develop an analytical solution for one-dimensional flow of $CO_2$ in a fracture with dissolution into the surrounding matrix. The solute in the matrix is transported perpendicular to the fracture by molecular diffusion. We show that there is a time-scale when the mass transfer from dissolution and advection in the fractures is comparable – after this, there is significant dissolution of the injected $CO_2$ and the transport through the fracture is slowed down. This time-scale is typically of order 1 day, implying that dissolution is significant for $CO_2$ injection into fractured aquifers. This analysis suggests that dissolution may be a significant long-term trapping mechanism for fractured reservoirs. Although the reservoir volumes into which the $CO_2$ must be injected will be huge, the $CO_2$ will rapidly dissolve and hence is stored safely. We conclude by discussing dissolution as a potential permanent storage mechanism in fractured aquifers and the design of $CO_2$ injection in such systems. We compare analytical and numerical solutions for a single fracture. The numerical solution also accommodates transport of the solute in the fracture plane and confirms that the analytical analysis is a very close approximation of the full three-dimensional problem for simple fracture geometries. The numerical model allows for two-phase flow and accounts for mutual dissolution of $CO_2$ and water. The solution to this problem is mathematically similar to work on single-phase tracer flow [1,2,3] and heat propagation in a fractured environment, but is new in its application to $CO_2$ storage in geological formations.

Keywords: $CO_2$ Storage; Dissolution Trapping; Fractures; Single Phase Flow; Analytical

## 1. Introduction and background

The last decade of intense research and good performance of major pilot injection sites has shown that CCS is a very promising technology to reduce human $CO_2$ emissions. Long term storage of $CO_2$ can therefore be an important part of future, less $CO_2$ emitting, energy sources.

The storage part of CCS depends on the successful trapping of injected $CO_2$ in porous rocks in the subsurface. The trapping mechanisms have been identified to be structural, capillary, dissolution, chemical, and residual trapping. They reflect the mutual influence of geological environment and physical flow processes on the overall storage process. All trapping processes happen at the same time and influence each other, but with changing strength, depending on many factors such as pressure and temperature gradients, fluid saturations, rock chemistry, and structure of the porous rock matrix. For smaller and homogenous systems, the basic characteristics are well understood. To a certain level of accuracy they could be repeated in laboratory experiments and numerically

simulated. But, the step up to lager models with a heterogeneous description of the geology that simulate coupled processes over millenniums is still a major challenge. In this paper we study the dissolution of $CO_2$ in brine in a porous rock containing fractures.

The occurrence of natural fractures in sedimentary rocks as potential storage formations is widespread. At the Weyburn, In Salah, Snøhvit and Spraberry $CO_2$ storage sites fractures have already been described [4,5]. It is likely that many future storage sites will contain fractures. This is a challenge for both characterizing efforts and $CO_2$ flow simulations. Fractures provide conductive preferential pathways for $CO_2$ flow and may therefore reduce the storage capacity of the aquifer [6]. Consequently, an operator would need to abandon an otherwise suitable storage site if there would be widespread $CO_2$ conducting faults and fracture. However, fractures also allow a large surface area between $CO_2$ and water to develop, which fosters dissolution of the $CO_2$ into the water contained in the matrix. In any situation, to what extend fractures have an impact on $CO_2$ storage and the long term behavior of such systems has been addressed sparsely and only qualitatively so far.

A number of analytical concepts have been developed to evaluate the mathematically similar problem of radioactive tracer flow between single fractures or simple fracture geometries and the bulk matrix. Bodine et al. [7,8] give an extensive review of solute transport in fractured aquifers. All models of solute transport in Bodine's review treat transport by molecular diffusion as single phase flow; two-phase flow and the role of capillary entry pressure are therefore not accounted for. Tang et al. [1] developed an analytical solution for transport along a plane single fracture and accounted for molecular diffusion from the fracture into the matrix. Sudicky and Frind [9] extended the single fracture solution for a set of parallel fractures. Graf and Simmons [10] additionally accounted for fluid density variations and developed a modified velocity term for flow in a vertical fracture. Tsang [3] extended a particle-tracking method from Yamashita and Kimura [11] from infinite matrix to finite rock matrix blocks to calculate tracer transport in fractures with molecular diffusion into the matrix. However, this work did not consider two separate fluid phases with continuous injection of one phase. On the other hand, for multi-phase flow, there is a large body of studies that document the role of molecular diffusion as part of oil recovery mechanisms in fractured reservoirs (see e.g. [12-15]).

With respect to $CO_2$ storage, the contribution of molecular diffusion to $CO_2$ transport has been evaluated mainly for convection due to density differences between the fluid phases. $CO_2$ dissolves in brine and changes the bulk brine density over time in such a way that $CO_2$ saturated brine becomes heavier than the untainted brine. The heavier $CO_2$-brine solution triggers a downwards directed movement leading to the onset of convection. These analyses assume unfractured homogeneous media [16,17].

To summarize we can say that existing analytical solutions for single-phase solute tracer flow cannot be simply applied to our problem. We consider in our investigation advective two-phase flow of water and $CO_2$ through a single fractures, accounting simultaneously for molecular diffusion of $CO_2$ from the fracture to the matrix where it dissolves. To evaluate the impact of this process on solubility trapping of supercritical $CO_2$ we formulate an analytical solution for a case with an infinite matrix. To support our concept we performed conceptual numerical simulations with a finite difference simulator using a fine gridded mesh that is populated with reservoir parameters qualitatively similar to properties from the In Salah $CO_2$ storage site in Algeria. Finally we discuss further implications of our work and how we plan to extend our conceptual model to more complicated systems.

## 2. Model geometry

In this work, we study the injection of incompressible $CO_2$ into a porous matrix that contains a single horizontal fracture. The problem is sketched in Figure 1. Injected $CO_2$ flows through a single horizontal fracture. The supercritical $CO_2$ flows in its own phase and fully saturates the initially brine-saturated fracture. Where $CO_2$ is present in the fracture, we assume a constant saturation of $S_g=1$ for the $CO_2$ phase. The high capillary entry pressure prevents $CO_2$ from entering the matrix in its own phase. It is only the concentration gradient that allows $CO_2$ to move from the fracture into the matrix by the process of molecular diffusion. $CO_2$ dissolves instantaneously in the brine saturated matrix. For our analytical solution we consider molecular diffusion acting perpendicular to the fracture only. To address this problem, we present in chapter 3 an analytical solution for an assumed infinite matrix block.
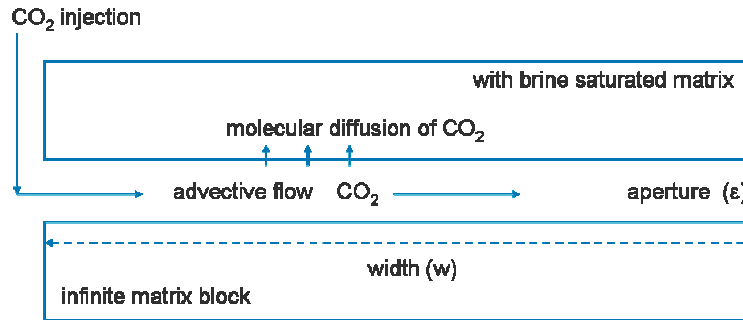
Figure 1: Sketch of $CO_2$ flowing through a single horizontal fracture that is embedded in an infinite matrix. The molecular diffusion of $CO_2$ takes place perpendicular to the horizontal fracture plane.

### 3. The analytical solution

We present a shortened mathematical derivation of the analytical solution. First, we invoke conservation of mass in and express the volumetric flow rate Q [$m^3 s^{-1}$] for the flowing $CO_2$ at the inlet of the fracture as sum of advective flow through the fracture space and molecular diffusive flow from the fracture into the matrix,

$$\rho_0 Q = \rho_0 A v(t) + F \tag{1}$$

$\rho_0$ [$kgm^{-3}$] is the $CO_2$ density in its own phase, $A$ the cross sectional area of the fracture, $v(t)$ the velocity at time $t$, and $F$ [$mol\ m^{-2}s^{-1}$] the term for total diffusive flux. We introduce $q=Q/A$ and an auxiliary variable $b=a/A\rho_0$, and obtain an expression for the volumetric flux [$m\ s^{-1}$],

$$q = v(t) + \int_0^t \frac{bv(t')}{\sqrt{t-t'}} dt' \tag{2}$$

$t'$ is the time at which $CO_2$ first arrives and $a$ is another auxiliary variable. We will derive the auxiliary variables $a$ and $b$ later in this section. The second term on the right hand side of Equation 2 describes the total molecular diffusive flux from start of the injection at time $0$ to the location of the $CO_2$ front after time $t$. As next step, we evaluate the location of the front at early time when the front speed corresponds to the volumetric flux $q$ and late time when the front speed is approaching a value of zero. To achieve this, we perform a Laplace transformation, use the convolution theorem, the complementary error function (details will be published in an upcoming publication), and solve for $v(t)$.

For the early time situation with $v(t) \approx q$, the front speed of $CO_2$ can be estimated to be similar to the injection rate. The late time behaviour with $v(t) \rightarrow 0$ can be expressed:

$$v(t) \approx \frac{q}{b\pi\sqrt{t}} \tag{3}$$

Next, we will derive the auxiliary variables $a$ and $b$. We calculate the change in $CO_2$ concentration by molecular diffusive mass transport with Fick's First Law,

$$\frac{dc}{dt} = D \frac{\partial^2 c}{\partial y^2} \tag{4}$$

$c$ [$mol\ m^{-3}$] is the concentration of $CO_2$, $D$ [$m^2 s^{-1}$] is the molecular diffusion coefficient in the matrix and $y$ the position of the $CO_2$ front. The flux per unit length of fracture then yields to,

$$F = -Dw \frac{\partial c}{\partial y}\Big|_{y=0}$$

(5)

$w$ is the fracture width. After a series of algebraic transformations and introducing boundary conditions (7a,b) we obtain for the concentration $c$:

$$c = c_0 \left(1 - erf\left(\frac{y}{\sqrt{4Dt}}\right)\right)$$

(6)

The initial boundary conditions for this solution are,

$$c(y = 0, t) = c_0 \text{ and } c(y = \infty, t) = 0$$

(7a,b)

where $c_0$ is the source concentration. Next, we insert Equation (6) in (5) and get the flux $F$ per unit length $y$,

$$F = -Dw \frac{\partial c}{\partial y}\Big|_{y=0} = \dots = c_0 w \frac{\sqrt{D}}{\sqrt{\pi t}}$$

(8)

The diffusive flux becomes,

$$f = \frac{a}{\sqrt{t}}$$

(9)

The auxiliary variables $a$ and $b$ become,

$$a = c_0 w \sqrt{\frac{D}{\pi}} \quad \text{and} \quad b = \frac{c_0 w}{A \rho_0} \sqrt{\frac{D}{\pi}}$$

(10,11)

With the contact area $A$ between the fracture and matrix domain area, $A = \varepsilon w$ (aperture x width), we find:

$$b = \frac{c_0}{\rho_0 \varepsilon} \sqrt{\frac{D}{\pi}} \Rightarrow \pi b^2 = \left(\frac{c_0}{\rho_0}\right)^2 \frac{D}{\varepsilon^2}$$

(12)

Now we are in the position to look at a first estimate of implications from the above derived solution in Equation (12). Let us therefore consider molecular diffusion that is significant for a time

$$b\sqrt{t\pi} \approx 1$$

(13)

To do this, we insert equation (12) and obtain the expression,

$$\frac{c_0^2}{\rho_0^2 \varepsilon^2} \frac{D}{\pi} t\pi \approx 1$$

(14)

As the final expression in this chapter and estimate for the time t, we derive Equation (15) after rearranging,

$$t \approx \frac{\rho_0}{2c_0} \frac{\varepsilon^2}{D}$$

(15)

This expression for time is independent of rate. This in itself is a rather interesting derivation.

## 4. Numerical simulations

We built a 2D model that is discretised into 200 x 1 x 90 blocks, see Figure 2. The matrix grid blocks have a size of 0.1m in each direction (x, y, and z) and a porosity of 20%. The horizontal fracture is represented by a single row of grid blocks, placed in the middle of the model. The fracture blocks have an aperture of 1mm and a porosity of 100%. These properties give the model a surface area of $1.8m^2$ between the fracture and matrix domain. The resulting pore volume of the entire model is $3.6m^3$. The matrix grid blocks have a permeability of $10 \times 10^{-14}$ $m^2$ (10mD) while the fracture has a permeability of $4 \times 10^{-12}$ $m^2$ (4 Darcy). Initially the simulation model is completely filled with brine. Supercritical $CO_2$ is injected through a vertical well located in the twentieth row on the left hand side. For reasons of

pressure and mass balance we placed a water producer in the last row on the right hand side. We used a depth of 1000m for the top layer of the model and an initial pressure of 100 bars to ensure a supercritical pressure- and temperature regime for the $CO_2$ throughout the numerical experiment. The $CO_2$-injector is rate controlled and operates with a bottom hole pressures limit of 30MPa (300 bar). The water producer is controlled by a reservoir fluid volume rate target of maximum 10 m$^3$ per day. Both wells are completed over the interval from layer 30 to layer 60. The mutual dissolution of $CO_2$ and water is calculated according to Spycher and Pruess [18]. The relative permeability curves for water-$CO_2$ and capillary pressure data are taken from experiments with sandstone cores from the In Salah storage site in Algeria. From the same experiments we applied capillary pressure data for the matrix blocks. The relative permeability curve for the fracture is of X-shape. The molecular diffusion is driven by the concentration gradient as expressed in Fick's law. We used a value of $10^{-10}$ m$^2$s$^{-1}$ which is a common value and similar to the value used in the analytical calculation. In our case we deal with cross phase molecular diffusion as $CO_2$ molecules migrate from the pure $CO_2$ phase into the water phase.
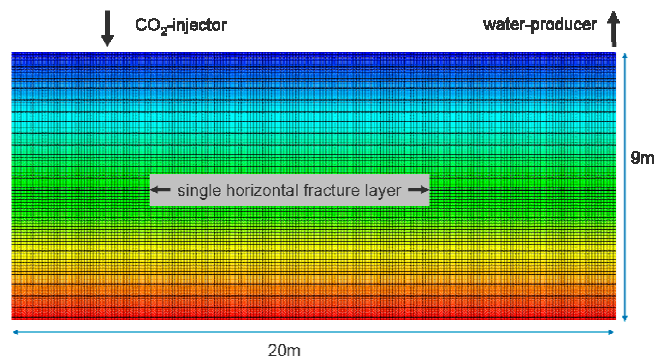


Figure 2: 2-dimensional simulation grid of 20 x 9 m$^2$ with one $CO_2$ injector and one water producer. The model is initially filled with brine.

## 5. Results

When we use the above derived Equation (15) and insert typical values as summarised in Table 1, we are able to calculate a time $t$ after which the diffusion and dissolution of $CO_2$ is significant. In this case it is approximately one day. It means that dissolution of $CO_2$ in the presence of a fracture takes place rather quickly.

Table 1: Standard $CO_2$ and fracture parameters used to evaluate Equation (15).

| $CO_2$ density (own phase) $\rho_0$ | concentration $c_0$ | aperture $\varepsilon$ | diffusion coefficient D |
|---|---|---|---|
| 700 kgm$^{-3}$ | 20 kgm$^{-3}$ | $10^{-4}$ m (100μm) | $10^{-10}$ m$^2$s$^{-1}$ |

To confirm the effect of enhanced dissolution of $CO_2$ in brine in the presence of fractures we ran a number of simulations with the above described numerical model. Table 2 gives the simulated percentage of $CO_2$ dissolved in water, trapped as immobile gas, and mobile phase for three simulation cases. For the simplest case with no fracture, 16.9 % of the injected $CO_2$ will be dissolved in water after 20 days. 3.5 % are immobile due to residual trapping and 79.6 % remain mobile. When we introduce a single fracture the amount of dissolved $CO_2$ is increased to 21.6%. A simulation with 4 fractures gives a further enhancement of dissolved $CO_2$ to 26.9%. Immobile gas trapped is slightly increased to 4.1% (1 fracture) and 4.8% (4 fractures). The fraction of mobile $CO_2$ gas is reduced accordingly, see Table 2. Figure 3 shows the spreading of dissolved $CO_2$ in the matrix for no fracture (left), single fracture (middle) and four fractures (right) after 20 days. In figure 4 we show the similar situation, but this time for the free $CO_2$ gas saturation.

Table 2: The state of injected $CO_2$ after 20 days in numerical simulations models with 0, 1, and 4 fractures.

| simulation case | dissolved $CO_2$ [%] | $CO_2$ trapped gas, immobile [%] | $CO_2$ mobile gas [%] |
|---|---|---|---|
| 0 fracture | 16.9 | 3.5 | 79.6 |
| single fracture | 21.6 | 4.1 | 74.3 |
| 4 fractures | 26.9 | 4.8 | 68.3 |
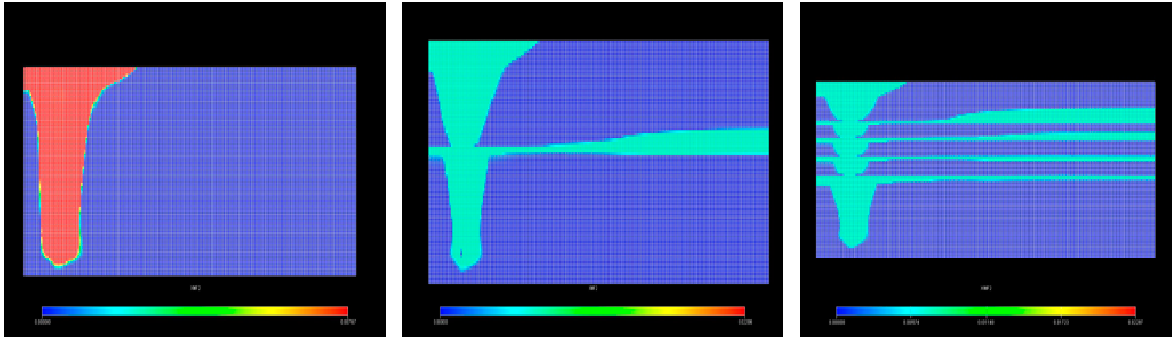


Figure 3: Concentration of dissolved $CO_2$ for a model with 0 (left),1 (middle), and 4 (right) fracture(s) after 20 days. Models containing fractures show enhanced dissolution around the fracture location.
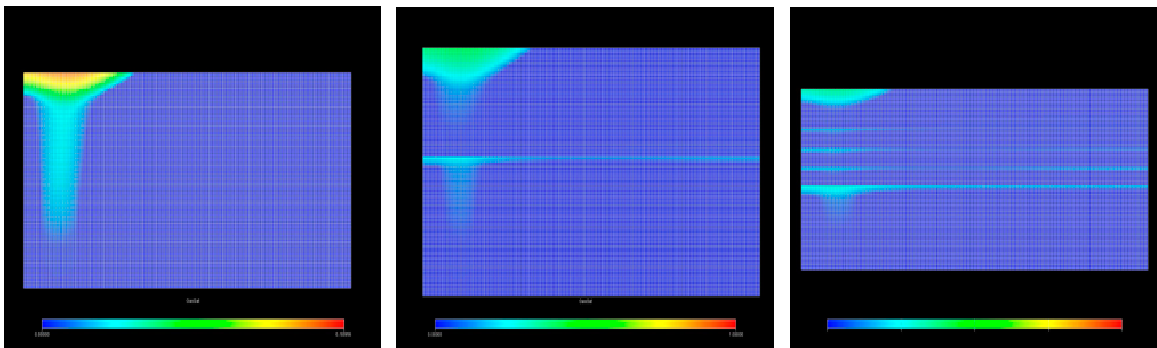


Figure 4: Concentration of $CO_2$ as free gas phase for a model with 0 (left), 1 (middle), and 4 (right) fracture(s) after 20 days. The two models containing fractures show some degree of free $CO_2$ gas phase migration around the fracture location.

## 6. Discussion and outlook

Introducing a single fracture into our simulation model does increase the amount of dissolved $CO_2$ from 16.9% to 21.6%. Accounting for the relatively short time period we regard this as being substantial and large. For reasons of comparison we performed simulations with four fractures. In such a case the amount of dissolved $CO_2$ is even more enhanced, but not in proportion to the number of fractures. The process of dissolution gets quickly complex with mutual influence of the fractures that rules out a linear interrelation. Injected $CO_2$ dissolves just around the injector and does only move slowly into the reservoir in its own phase due to the low permeable matrix. Shortly after start of injection the dissolved $CO_2$ develops the typical pattern of funnel shaped areas that are constrained by the position of

the fractures. It is the result of the interplay of upward flowing pure $CO_2$ with downward moving dissolved $CO_2$. We do observe a similar pattern at Sleipner where shale layers act as interfering barriers [19]. In Figure 3, we clearly can observe how dissolved $CO_2$ could enter the matrix space along the fracture planes, migrates into the matrix, and ultimately increases the amount of dissolved and trapped $CO_2$. As the mixture of dissolved $CO_2$ and brine is heavier as pure brine, we observe in some regions a tendency for the dissolved $CO_2$ to be below the fracture plan. This non symmetrical pattern along the fracture plane has an impact of the application of our analytical solution. It suggests that our analytical solution does overestimate the rate and volume of dissolution of $CO_2$. Figure 4 shows the typical upwards movement of free gas phase $CO_2$. When hitting a fracture layer, the upwards movement is hindered and $CO_2$ is being feed into the fracture layer and transport away from the well horizontally. The amount of residually trapped $CO_2$ was kept low by using a low value for the irreducible gas-saturation ($S_{gr}$) of 0.1. To indicate the large effect the existence of fractures on the dissolution of $CO_2$ may have, we increased the number of fractures in our simulation model to four. We showed for a simplified case analytically and numerically that the existence of fractures does have a positive effect on the amount of $CO_2$ trapped by dissolution in formation water. For the 2D case, in which a single horizontal fracture is placed in the middle of a matrix, the amount of $CO_2$ trapped by dissolution in brine is enhanced by 5.3 percentage points. Both the analytical and the numerical approaches show that the dissolution of $CO_2$ is faster than previously assumed.

Fracture flow of $CO_2$ combined with molecular diffusion into the porous matrix in a heterogeneous geological environment is a complex physical process. The numerical simulation of such a situation imposes additional uncertainties to the quantitative results as boundary conditions of the model, grid discretisation effects, and the heterogeneity of input data need to be accounted for. To what extent our 2D considerations can be extrapolated to 3D models needs to be investigated further. Mutual influence of neighbouring fractures may reduce the effect of increased dissolution. Another issue is the value of effective diffusion coefficients that should be applied in preliminary calculations or more detailed numerical simulations. Here we applied a standard value, but it has been shown that effective diffusion coefficients vary with the progress of dissolution process, early versus late stage of injection. The number of fractures accessible to the flowing $CO_2$ and consequently the contact area between fracture surface and matrix is important data to get. But, somehow similar to the importance of reaction surface area in geochemical considerations, it is very difficult to quantify real values for a particular geological storage unit.

Ideally, we would wish to exploit a potential storage site that contains a large number of conductive fractures within a well bounded geological container. Such a container would be needed to be encapsulated by non-faulted and non-fractured units, particular in the overlaying layers. Another aspect is the concentration of $CO_2$ in the brine before the $CO_2$ injection starts. The larger the amount of background $CO_2$ in the pore water, the more our here discussed effect of enhanced $CO_2$ dissolution would be reduced. It is therefore important to have a good knowledge of pre-injection $CO_2$ concentration in the brine. The onshore $CO_2$ storage site at In Salah, Algeria, is for a number of reasons of particular interest here. The fracture field is the best mapped and investigated of all present CCS pilots. At this location, fractures occur in the storage formation and the lower part of the cap rock, but there are no major faults around the storage container that would the $CO_2$ allow to escape from the target location. A fracture zone is needed to explain some key observations, but to what extent the fractures are conductive still remains the objective of ongoing research. So indeed, In Salah could maybe represent such a described 'fracture-container'. It is clear that the here proposed concept requires much research to clarify the aspects we mentioned above.

In summary, we believe that our concept has high potential for enhanced trapping of $CO_2$ in fractured formations. It is important to note the uncertainties inherent in this modeling. However, the results of the simulations provide some insight into the processes occurring during injection. There are many aspects that deserve to be studied in detail as they may have a strong influence on the quantitative evaluation of trapping.

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