

# A numerical simulation study of rock matrix dissolution in different tight carbonate gas reservoirs during CO<sub>2</sub> injection and sequestration process

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## 1. Summary

In light of the burgeoning interest in mitigating anthropogenic CO<sub>2</sub> emissions, carbonate reservoirs have emerged as promising sequestration sites due to their substantial storage potentials [1,2]. However, the complexity of CO<sub>2</sub> storage in carbonate reservoirs supersedes that in conventional sandstone reservoirs, predominantly due to the rapid interactions occurring between the injected CO<sub>2</sub>, brine, and the carbonate rock matrix [3]. Carbonate reservoir varies greatly in lithology and pore structures. The impacts of these interactions on the pore structure and macroscopic flow properties of different types of carbonate reservoirs are poorly understood [4,5].

In this study, a numerical model was developed to scrutinize the carbonate rock dissolution process and the physical property variations of different carbonate gas reservoirs during CO<sub>2</sub> injection and sequestration process. In particular, a chemical CO<sub>2</sub>-brine-rock interaction module was incorporated in the numerical simulation, which enables a comprehensive analysis of the entire physical and chemical processes such as CO<sub>2</sub> injection, CO<sub>2</sub> dissolution in brine, carbonate rock dissolution, and enlargement of pore space during a continuous CO<sub>2</sub> injection process. More specifically, a total of twenty distinct scenarios were simulated to examine the effects of lithology, pore size, pore-throat structures, and CO<sub>2</sub> injection rate on the modification of carbonate gas reservoirs due to the presence of the injected CO<sub>2</sub>. It was found that the calcite is significantly easier and quicker to react with CO<sub>2</sub> diluted brine than the dolomite. As a result, limestones exhibited an expedited rock dissolution and pore volume increment, alongside a slower pressure buildup in comparison to dolostones. Also, the carbonate reservoir with a smaller pore size presents a higher rock dissolution rate than that with a larger pore size. What's more, the fracture-dominated carbonate reservoir possesses a higher CO<sub>2</sub> injectivity than the pore-dominated reservoir. However, on the other hand, the simulation results show that the injected CO<sub>2</sub> can modify the pore-dominated carbonate reservoir to a more pronounced extent than the fracture-dominated carbonate reservoir. Lastly, the rate of carbonate-rock dissolution increases with the decrease of CO<sub>2</sub> injection rate since a lower CO<sub>2</sub> injection rate means a longer reaction time. The insights derived from this research provide pivotal information to assess the variations in physical properties of different types of carbonate reservoirs before and after CO<sub>2</sub> injection, aiding evaluations related to CO<sub>2</sub> injectivity, storage capacity, and reservoir integrity, thereby paving the way for environmentally and structurally sound carbon sequestration strategies.

## 2. Method

In this study, twenty scenarios were numerically simulated to analyze the effects of lithology, pore size, pore-structure type and CO<sub>2</sub> injection rate on the carbonate rock dissolution during CO<sub>2</sub>

injection and sequestration process. The simulator involves four major parts: CO<sub>2</sub> injection, CO<sub>2</sub> dissolution in residual water, carbonate rock dissolution, reservoir property variation.

In each simulation step, CO<sub>2</sub> is injected into the depleted gas reservoir at a constant injection rate. After CO<sub>2</sub> is injected into the depleted gas reservoir, the reservoir pressure will build up. It is assumed that the injected CO<sub>2</sub> can instantaneously and evenly diffuse into and fill the pore space. As a result, the reservoir pressure can instantaneously reach balance once CO<sub>2</sub> is injected into the reservoir. The reservoir pressure is calculated using the Peng–Robinson equation of state (P-R EOS) [6]. Since the gas pressure in the carbonate pore space is built up, the injected CO<sub>2</sub> will start to dissolve in the residual brine, which will lead to a decreased amount of CO<sub>2</sub> in pore space and an increased amount of CO<sub>2</sub> in residual brine. This will result in a CO<sub>2</sub> partial pressure in pore space and an increase of CO<sub>2</sub> partial pressure in brine. An equilibrium will be reached until CO<sub>2</sub> partial pressure in the pore space is equal to that in the residual brine. CO<sub>2</sub> partial pressure in the pore space is calculated by using the P-R EOS [3]. Meanwhile, CO<sub>2</sub> partial pressure in the residual brine is calculated by using the Henry's law [7].

$$C = k * P$$

Once the injected CO<sub>2</sub> is dissolved in the residual brine in the pore space, the residual brine will be acidic and able to dissolve the carbonate rock matrix and enlarge the pore space. The kinetics of CO<sub>2</sub>-brine-carbonate interaction is illustrated by the following kinetic rate law, which is given by TOUGHREACT [8].

$$R_m = -S_m k_m e^{-\frac{E_m}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right)} \left( 1 - \frac{Q_m}{K_m^{eq}} \right)$$

### 3. Results, Observations, Conclusions

#### 3.1 Effects of Lithology

In this study, CO<sub>2</sub>-brine-rock matrix interactions in two different lithological reservoirs, i.e. dolostone reservoir and limestone reservoir. It is assumed that limestone consists solely of calcite and dolostone solely of dolomite. The simulation results reveal that limestone reacts more swiftly with CO<sub>2</sub>-saturated brine compared to dolostone. More specifically, it was observed that the pore volume in a pore-dominant limestone reservoir can increase by nearly 9% after 72 hours of CO<sub>2</sub> injection at an injection rate of 0.1 mol/min, whereas dolostone reservoirs exhibit a mere 0.16% increase under identical conditions. Consequently, dolostone reservoirs demonstrate a faster pressure buildup than limestone reservoirs. This suggests that dolostone reservoirs have superior initial injectivity, likely due to their more developed natural fractures. However, the limestone reservoirs may hold greater potential for CO<sub>2</sub> sequestration in the long run, attributable to their higher reactivity with CO<sub>2</sub>-saturated brine.

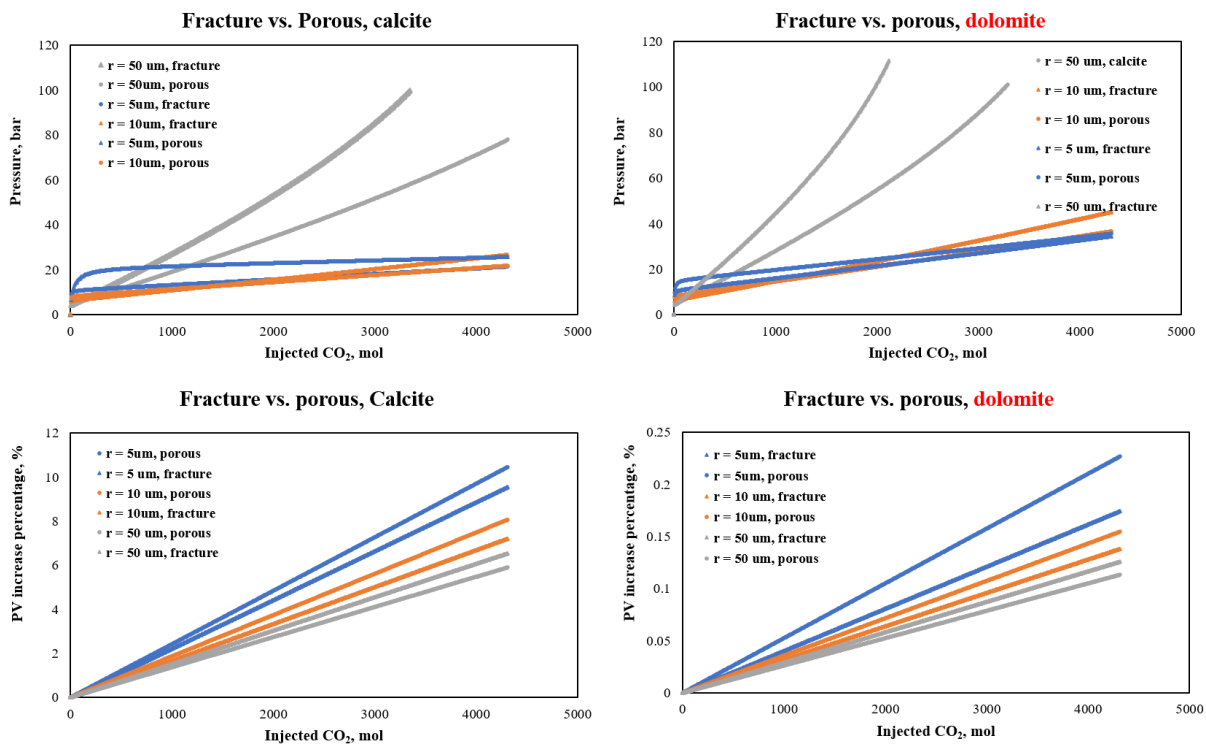
#### 3.2 Effects of Pore-throat structures

The impact of CO<sub>2</sub> injection on two distinct types of pore-throat structure reservoirs, namely pore-dominant and fracture-dominant reservoirs, was thoroughly simulated in this study. The dynamics of pore volume and reservoir pressure during CO<sub>2</sub> injection were analyzed for both reservoir types. A notable distinction in behavior between the two types of reservoirs was found. The pore space in the pore-dominant reservoir expands more significantly compared to fracture-dominant

ones, irrespective of whether the lithology is dolostone or limestone. Specifically, in limestone lithology, the pore volume of pore-dominant reservoirs increased by 8.5% following CO<sub>2</sub> injection at a rate of 0.1 mol/min after a period of 72-hours' continuous injection. In contrast, the fracture-dominant reservoir exhibits a smaller increase of 7.2% under identical conditions, marking a difference of 1.3% less than the counterpart of the pore-dominant reservoir. This trend was also observed in the dolostone lithology. However, the discrepancy in pore volume increment after CO<sub>2</sub> injection between the two reservoir types was marginal (0.02%), suggesting a lesser influence of pore-throat structure on dolostone reservoirs. These findings suggest that while fracture-dominant carbonate reservoirs may offer an initial advantage for CO<sub>2</sub> storage and sequestration due to the ease of injection, pore-dominant carbonate reservoirs ultimately demonstrate superior CO<sub>2</sub> storage capacity over time, attributed to a more pronounced and rapid increase in pore space.

### 3.3 Effects of Pore/fracture size

In this study, the effects of CO<sub>2</sub> injection on pore space enlargement and reservoir pressure buildups in limestone and dolostone reservoirs were simulated and analyzed, with a focus on pore sizes of 5, 10, and 50 μm. It was observed from the simulation results that the largest increase in pore space occurred in the reservoir with the smallest initial pore or fracture size of 5 μm. Conversely, the smallest increase in pore space was noted in the reservoir with the largest pore or fracture size of 50 μm. This is attributed to the larger reaction surface area in reservoirs with smaller pores or fractures, given equal pore or fracture volumes, which leads to more rapid rock matrix dissolution and a greater increase in pore or fracture volume. Additionally, a slower pressure buildup was observed in reservoirs with smaller pore or fracture sizes, a phenomenon associated with the fact of faster rock matrix dissolution in the ones with smaller pore or fracture sizes.



### 3.4 Effects of CO<sub>2</sub> injection rate



The effects of different CO<sub>2</sub> injection rates, which are 0.1, 0.5 and 1 mol.%, on CO<sub>2</sub> storage in different carbonate reservoirs with different lithologies and pore-throat structures are simulated and analyzed in this study. The simulation results indicate a significant impact of the CO<sub>2</sub> injection rate on pore volume expansion in these reservoirs. Notably, a lower injection rate resulted in a greater expansion of pore volume across all studied reservoir types. For instance, in a pore-dominant limestone reservoir, the pore volume increased by 9% when the CO<sub>2</sub> was injected at a rate of 0.1 mol/min, compared to only a 0.6% increase at a rate of 1 mol/min. This phenomenon can be attributed to the prolonged interaction time between CO<sub>2</sub>, brine, and the rock matrix at lower injection rates, leading to more extensive rock matrix dissolution and consequently, larger pore volume expansion. Furthermore, our findings suggest the existence of an optimal CO<sub>2</sub> injection rate for carbonate reservoirs. While a rapid injection rate may expedite reaching CO<sub>2</sub> storage targets and reduce costs, it could potentially compromise the long-term CO<sub>2</sub> storage capacity of the reservoirs, indicating a trade-off between immediate efficiency and future storage potential.

## Novel Information

The potential of carbonate reservoirs for CO<sub>2</sub> storage and sequestration is immense, yet research in this domain remains in its early stage, particularly when compared to the more advanced studies on sandstone reservoirs. This study marks a pioneering effort in examining the dissolution dynamics of the rock matrix in various carbonate reservoirs during CO<sub>2</sub> injection, integrating a comprehensive module of CO<sub>2</sub>-brine-rock matrix interactions. Our findings reveal that these interactions significantly alter the properties of carbonate reservoirs upon CO<sub>2</sub> injection. Intriguingly, certain carbonate reservoirs, previously deemed less suitable for CO<sub>2</sub> injection, such as pore-dominant limestone, exhibit a faster reaction rate with the injected CO<sub>2</sub>, increased pore volume expansion, and reduced pressure build-up, in contrast to the more traditionally favored fracture-dominant dolostone reservoirs. This counterintuitive result underscores the necessity of reevaluating carbonate reservoirs based on their modified characteristics post CO<sub>2</sub> injection. Effective selection of a CO<sub>2</sub> storage site in carbonate formations should therefore involve a careful consideration of the balance between the technical challenges of CO<sub>2</sub> injection and the long-term potential for CO<sub>2</sub> storage and reservoir integrity.

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