Near-Critical Thermophysical Effects on CO_2 Dissolution Trapping: Implications for Underground Storage

Introduction

Prediction of the amount of dissolved carbon dioxide (CO_2) present in the subsurface reservoir is an important factor that must be taken into account while assessing the geological carbon storage potential. Dissolved trapping helps to provide enhanced long-term security to the stored CO_2 through reduced buoyant plume movement and the stabilization of pressure in deep reservoirs (Celia et al., 2015). In the assessment of the reservoir scale, the solubility of the gas is often assumed to be directly related to pressure and inversely related to temperature.

However, CO_2 has rapid and non-linear changes in density and compressibility near the critical region due to the transition from the gas-like state to the supercritical state. These changes in the thermophysical properties of CO_2 play an important role in the calculation of the fugacity. Therefore, the monotonic pressure and temperature relationship might not adequately represent dissolution behavior in reservoirs. Neglecting near-critical effects may therefore introduce uncertainty in dissolved CO_2 predictions and storage performance assessments.

This study investigates the nonlinear pressure–temperature response of dissolved CO_2 amount under storage-relevant conditions and evaluates its implications for underground CO_2 storage.

Compressibility Behavior of CO_2

The thermodynamic behavior of CO_2 under geological storage conditions is strongly influenced by its proximity to the critical region. In deep formations, pressure and temperature often approach or exceed the critical point of CO_2 (31.1 °C and 73.8 bar), where fluid properties exhibit strong nonlinearity (Duan & Sun, 2003). Among these properties, compressibility plays an important role in controlling density evolution and fugacity behavior.

Figure 1 presents the compressibility of CO_2 as a function of pressure at different temperatures. A nonlinearity is observed within a limited pressure interval, particularly at lower temperatures. Around the near-critical region, compressibility exhibits a distinct peak followed by a rapid decline as pressure increases. This behavior reflects significant changes in intermolecular interactions and the transition from gas-like to supercritical fluid characteristics. At higher temperatures, the compressibility curve becomes smoother, and the near-critical amplification effect is reduced.

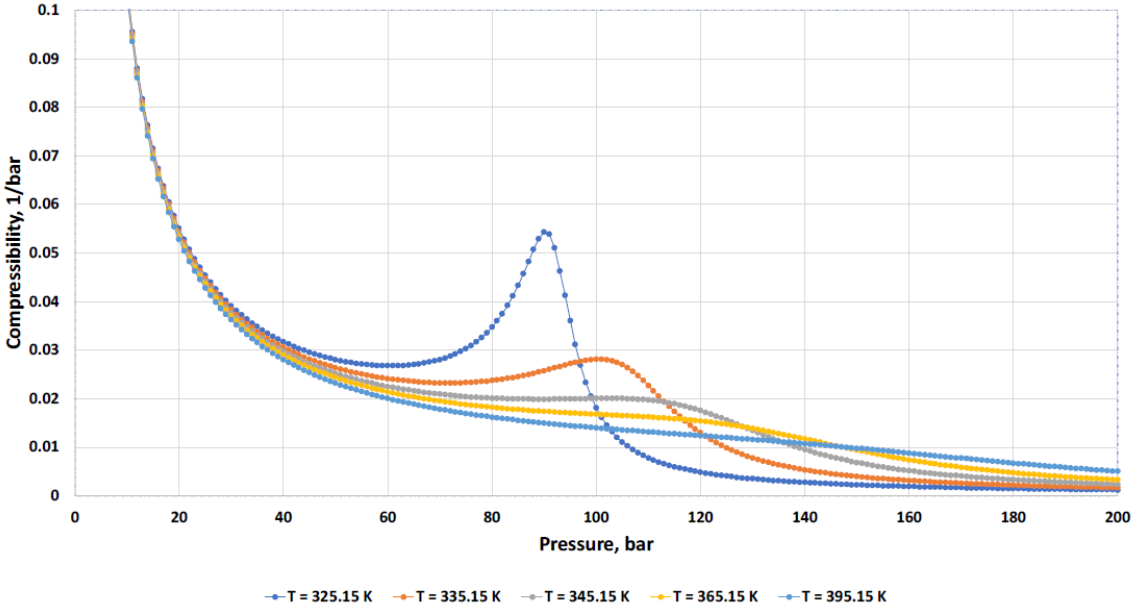

Figure 1 *Carbon dioxide compressibility at different pressure and temperature values.*

The compressibility coefficient is determined using the following equation (Craft, Hawkins, & Terry, 1991):

$$c = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right) = \frac{1}{p} - \frac{1}{z}\left(\frac{\partial z}{\partial p}\right)$$

where ρ is fluid density, p is pressure, and z is the compressibility factor. The term $\partial z/\partial p$ is evaluated numerically. This equation demonstrates that compressibility is directly governed by the pressure-dependent variation of z-factor. Rapid changes in z-factor near the critical region therefore result in amplified compressibility behavior.

Since the fugacity and density of CO_2 are a function of pressure and the compressibility factor, the non-linear variation in the z-factor will influence the thermodynamic driving force in the dissolution process. Thus, the dissolution process of CO_2 in brine solution does not linearly vary with pressure. Moreover, the near-critical compressibility effect in Figure 1 shows that there are certain pressure ranges in which the dissolution process is more sensitive.

These thermophysical characteristics indicate that accurate prediction of dissolved CO_2 under storage conditions requires explicit consideration of compressibility behavior.

Methodology

Numerical simulations were conducted using the CMG-GEM (Computer Modelling Group Ltd., 2025) compositional reservoir simulator. A homogeneous 50 × 50 × 10 Cartesian grid model was constructed to isolate thermodynamic effects from geological heterogeneity. A conceptual homogeneous reservoir model with idealized properties was developed to isolate thermodynamic influences from geological heterogeneity. Reservoir properties and simulation parameters are summarized in Table 1.

Table 1 *Model parameters*

Parameter	Value
Grid System	50 × 50 × 10
Bulk Volume	3.125×10^9 m³
Porosity	0.20
Horizontal Permeability	1000 mD
Vertical Permeability (z)	100 mD
Initial Water Saturation	100%
Boundary Condition	Closed
Temperature Range	35–70 °C
Initial Reservoir Pressure Range	5000–15000 kPa
Injection Rate	1,000,000 m^3/day (std)
Injection Duration	6 months
Incubation Period	6 months
Perforated Grid Block	25, 25, 5

The reservoir was initially 100% water-saturated and bounded by closed outer boundaries. Absolute permeability was defined as 1000 mD in the horizontal directions and 100 mD in the vertical direction. The injection well was perforated at grid block (25, 25, 5), corresponding to the central region of the model.

Reservoir temperature was varied between 35–70 °C, and initial reservoir pressure ranged from 5000–15000 kPa to capture subcritical and near-critical CO_2 behavior. CO_2 was injected at a constant rate of

1,000,000 m^3/day (standard conditions) for six months, followed by a six-month incubation period without injection to allow continued dissolution and equilibration. The total dissolved CO_2 mass at the end of the one-year simulation period was used to evaluate pressure–temperature sensitivity.

Results and Discussion

The pressure–temperature dependence of dissolved CO_2 obtained from the CMG-GEM simulations is presented in Figure 2. The results demonstrate that the dissolved CO_2 mass does not follow a simple linear increase with pressure nor a strictly monotonic decrease with temperature. Instead, a distinct nonlinear region is observed within the evaluated pressure–temperature domain.

As shown in Figure 2, higher dissolved CO_2 values generally occur at elevated pressures; however, the magnitude of increase is not uniform across the temperature range. At moderate temperatures, the dissolved CO_2 mass increases more sharply with pressure compared to higher temperature cases. In particular, a pressure interval can be identified where dissolution sensitivity is significantly amplified.

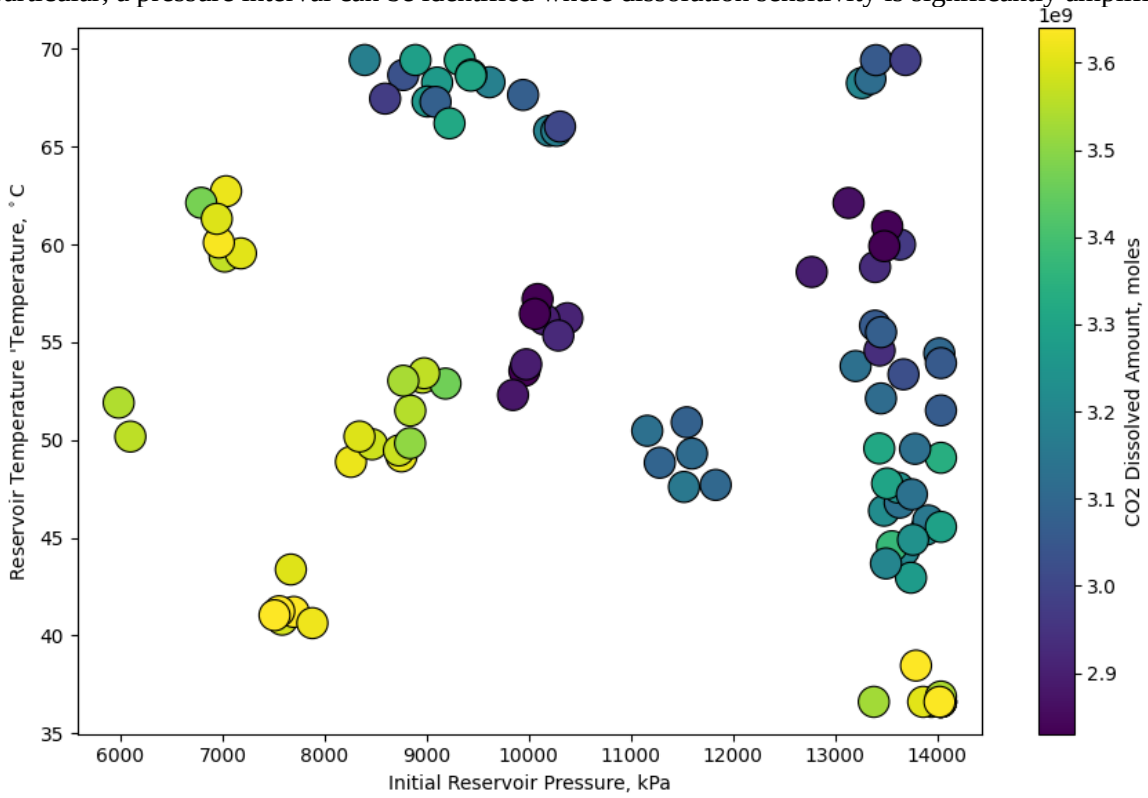

Figure 2 *Pressure–temperature dependence of dissolved CO_2 mass after one year of simulation (6 months injection + 6 months incubation)*

This behavior can be directly related to the thermophysical properties discussed earlier. As illustrated in Figure 1, compressibility undergoes pronounced nonlinearity in the same pressure interval, indicating strong changes in intermolecular interactions and fugacity behavior.

The combined effect of density amplification and compressibility variation leads to a nonlinear dissolution response. Rather than following a simple “higher pressure–lower temperature” trend, dissolved CO_2 exhibits region-dependent sensitivity governed by near-critical thermodynamic transitions. At higher temperatures, the density transition becomes smoother and compressibility variations are less pronounced, resulting in a reduced dissolution response compared to lower temperature cases at similar pressures.

These findings demonstrate that dissolution trapping under geological storage conditions cannot be accurately predicted using simplified solubility assumptions alone. Instead, explicit consideration of

near-critical CO_2 thermophysical behavior is required for reliable estimation of dissolved amount and storage capacity. Ignoring these nonlinear transitions may lead to under-estimation or over-estimation of dissolution trapping efficiency, particularly in reservoirs operating within pressure ranges close to the critical transition zone.

Conclusions

This study aimed to evaluate the pressure-temperature sensitivity of dissolved carbon dioxide in geological storage using compositional reservoir simulations. From the results, it was seen that the dissolution capacity of carbon dioxide does not behave in a linearly increasing pattern in relation to pressure or a monotonically decreasing pattern in relation to temperature. However, the nonlinear thermodynamic effects in the critical region can affect the dissolution capacity.

The variations in the compressibility of CO_2 show that the near-critical effects can influence the pressure-dependent dissolution capacity. It is therefore important to incorporate the thermophysical properties of near-critical carbon dioxide in operations in order to accurately estimate the dissolution capacity in the subsurface formations.

Acknowledgements

We would like to thank Computer Modeling Group Ltd. (CMG) for providing simulation package.

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