

## CO<sub>2</sub> solubility and diffusivity in brines: insights from laboratory tests and implications for geological CO<sub>2</sub> storages

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### Summary

Geological sequestration of CO<sub>2</sub> in saline aquifers occurs through various mechanisms: stratigraphic structural trapping of mobile CO<sub>2</sub>, capillary trapping of residual immobile CO<sub>2</sub>, solubility storage in water and carbonation through CO<sub>2</sub>-water-rock interactions with mineral dissolution and precipitation. Solubility trapping plays an important role in secure CO<sub>2</sub> storage in near and long terms as CO<sub>2</sub>-saturated water has higher density and tends to move downward driven by buoyancy force whereas the CO<sub>2</sub>-rich phase migrates upward with potential leaking through cap rocks. Studies (e.g. Leslie et al. 2021) have suggested that solubility trapped CO<sub>2</sub> can be up to 30% of the injected CO<sub>2</sub> at the end of injection period (20-30 years), 40% in 100 years, and 60% in 1000 years (**Figure 1**). However, the fraction of solubility-trapped CO<sub>2</sub> can vary significantly among different storage sites or aquifers due to variable rock properties and their heterogeneities, water salinity, and pressure and temperature of reservoirs or aquifers. CO<sub>2</sub> solubility in water or brine is a strong function of pressure, temperature, and salinity or water chemistry; but how fast the injected CO<sub>2</sub> is dissolved into water and thus relatively securely sequestered in a storage site depends on the dissolution kinetics controlled by CO<sub>2</sub> diffusivity in brine in contact with the CO<sub>2</sub> plume, and the convection dynamics to transport the dissolved CO<sub>2</sub> away from the contact and into deeper parts of a storage site. Solubility and diffusivity of dissolved CO<sub>2</sub> in water and associated changes in water densities are critical parameters to quantify the reactive transport and sequestration process.

CO<sub>2</sub> solubility in water or brines has been extensively studied. But most studies only considered pure water or brines with simplified water chemistry or composition (e.g. consisting of mainly one or two salts such as NaCl, KCl, and CaCl<sub>2</sub>). CO<sub>2</sub> diffusivity in bulk brines under reservoir conditions is not yet well understood, especially in brines with complex compositions. In this study, CO<sub>2</sub> solubility and diffusivity in water in literature is reviewed and analyzed with commonly-used simulation models. Laboratory measurements of CO<sub>2</sub> solubility and diffusivity in simulated brines of the Basal Cambrian saline aquifer are conducted under reservoir conditions. Laboratory studies are also being carried out to understand the dynamics of CO<sub>2</sub>-brine-rock interactions and their consequential effects on petrophysical properties of host rocks through batch-mixing tests and core flooding under reservoir conditions.

The laboratory CO<sub>2</sub> solubility and diffusivity results of a simulated basal Cambrian saline aquifer are in general consistent with models constrained with literature data but discrepancies remain and different models have different predictability of CO<sub>2</sub> solubility in brine. Overall, the data show that, under the prevalent pressure and temperature conditions for CO<sub>2</sub> storage in saline aquifers, CO<sub>2</sub> solubility in water can be reduced by up to 40% with increasing salinity from 0% to 10%, and another 40% reduction in solubility with salinity increasing from 10% to 20% (**Figure 2**). Increasing temperature from 45 °C to 100 °C reduces CO<sub>2</sub> solubility by 20% - 30%, with stronger effects on lower-salinity brines. At lower pressure (e.g., <10 MPa), CO<sub>2</sub> solubility increases linearly with pressure up to 1.2 mole/kgw for fresh water and 0.6 mole/kgw for brine of 20% salinity at 45 °C; at pressure higher than ~10 MPa, CO<sub>2</sub> solubility increases slowly with

increasing pressure (e.g., less than 20% increase in solubility with 200% increase in pressure from ~10 MPa to ~30MPa), and smaller increase in CO<sub>2</sub> solubility for higher salinity brine.

Literature data show that CO<sub>2</sub> diffusivity in bulk water or brine range approximately between  $1 \times 10^{-9}$  m<sup>2</sup>/s and  $200 \times 10^{-9}$  m<sup>2</sup>/s while majority studies suggest CO<sub>2</sub> diffusivity is around  $10 \times 10^{-9}$  m<sup>2</sup>/s or lower, suggesting CO<sub>2</sub> diffusivity in water is poorly constrained, or varies markedly in brines with different salinities under different temperature and pressure conditions. CO<sub>2</sub> diffusivity through aquifers / porous rocks is further retarded by tortuous pore networks, which is rarely studied; Experimental tests of CO<sub>2</sub> diffusion through basal Cambrian sandstone have planned for a future study to obtain better understanding of the reactive transport processes.

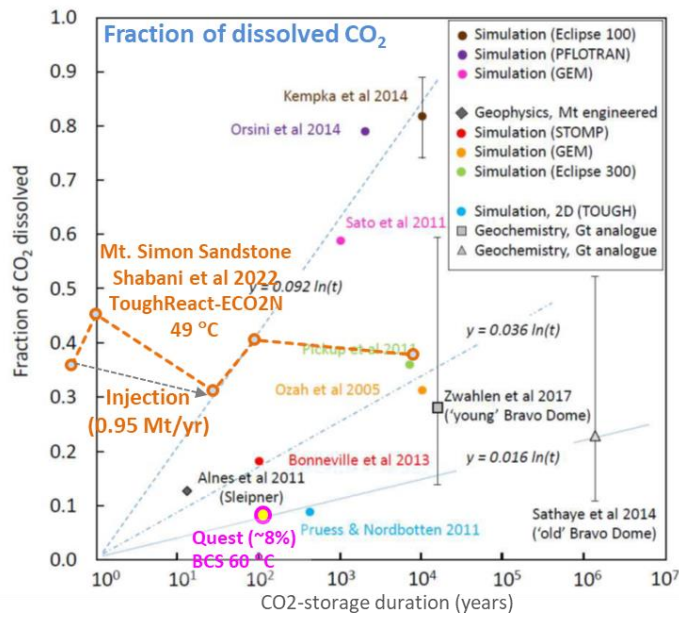
The remarkable variability in CO<sub>2</sub> solubility in brines and associated changes in water properties can have significant impacts on long-term CO<sub>2</sub> storage and pressure evolution in aquifers. The uncertainties in diffusivity of CO<sub>2</sub> in bulk water / brine and porous rocks also influence the predictability of near and long-term CO<sub>2</sub> sequestration, which is essential for MMV planning. Furthermore, the CO<sub>2</sub>-dissolved brine reacts with host-rocks along its path, which may enhance or retard the transport of CO<sub>2</sub> from CO<sub>2</sub>-plume-water contact into deeper aquifers. These effects are further investigated with reactive transport modeling using the basal Cambrian sandstone aquifer and overly cap rocks as an example based on public data and our laboratory tests results of CO<sub>2</sub>-brine-rock interactions; and the implications of near- and long-term geological CO<sub>2</sub> storages are also discussed.

## Acknowledgements

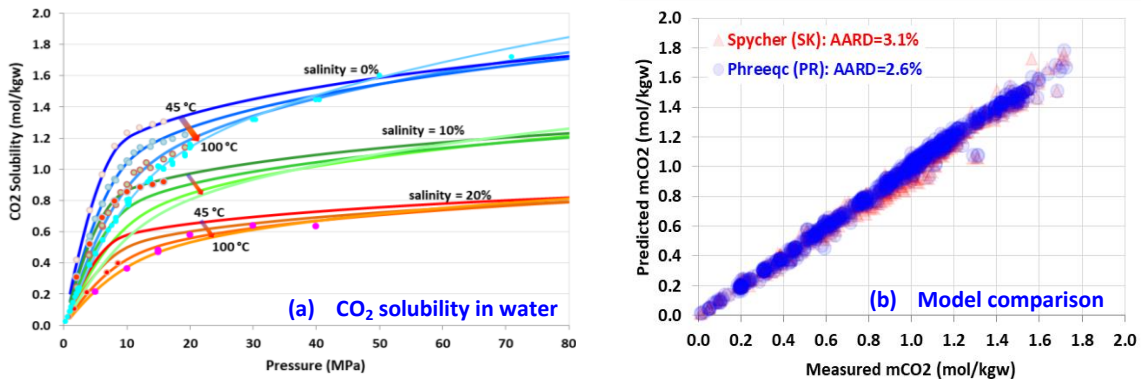
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## References

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**Figure 1.** Fraction of CO<sub>2</sub> solubility trapping of injected CO<sub>2</sub> in various storage sites and studies (modified from Leslie et al. 2021)



**Figure 2.** Solubility of CO<sub>2</sub> in water and brines (a) and model comparison (b). Dots in (a) represent experimental data from literature and solid lines are modeled CO<sub>2</sub> solubility using Phreeqc with modified Peng-Robison EOS to model the CO<sub>2</sub>-rich vapor phase.