CCUS: 4177285

FAG: Alternating Injection of CO_2 and Aqueous Formate Solution for Maximizing Carbon Storage and Oil Recovery

Abouzar Mirzaei-Paiaman*[1], Ryosuke Okuno[2], Lorena Moscardelli[1]
1. Bureau of Economic Geology, Jackson School of Geosciences, The University of Texas at Austin, 2. Department of Petroleum and Geosystems Engineering, The University of Texas at Austin.

This paper was prepared for presentation at the Carbon Capture, Utilization, and Storage conference held in Houston, TX, 03-05 March.

Abstract

In the context of carbon capture, utilization, and storage (CCUS) integrated with enhanced oil recovery (EOR), achieving both high oil recovery and substantial carbon storage is a critical challenge. Conventional injection methods often entail trade-offs between these objectives. Continuous CO_2 injection typically favors CO_2 storage but limits oil recovery because of its inefficient volumetric sweep, while water-alternating-gas (WAG) injection tends to enhance oil recovery at the cost of reduced CO_2 storage. This study introduces a novel injection strategy, formate-alternating-gas (FAG), which alternates between CO_2 and an aqueous formate solution. Formate, a carbon carrier produced via CO_2 reduction reactions, is leveraged to achieve simultaneous enhancements in oil recovery and carbon storage compared to traditional methods. A compositional simulation model of a San Andres oil reservoir in the Permian Basin was developed to compare continuous CO_2 injection, WAG injection, and FAG injection. The performance of these methods was evaluated in terms of oil recovery, carbon storage, and storage security.

The results demonstrated that FAG injection increased oil recovery by 22.4% compared to continuous CO_2 injection and by 4.1% compared to WAG injection. Moreover, FAG injection achieved 2.9% higher carbon storage than continuous CO_2 injection and 17.4% higher carbon storage than WAG injection. The alternating slugs of CO_2 and formate in the FAG process enhanced sweep efficiency, boosting oil production while optimizing the use of pore space for carbon storage. The formate solution, being more viscous than brine, contributed to improved sweep efficiency, even when compared to WAG injection. Additionally, FAG injection provided the highest level of storage security, with the greatest amount of carbon stored in more secure forms of storage (i.e., dissolution in brine and oil), and the lowest amount of carbon stored as less secure, mobile supercritical CO_2.

Introduction

Carbon capture, utilization, and storage (CCUS) through the injection of anthropogenic CO_2 into oil reservoirs provides a dual benefit: reducing atmospheric CO_2 emissions to support climate change mitigation, while simultaneously enhancing oil recovery and strengthening energy security. Oil produced through anthropogenic CO_2 injection results in lower net emissions compared to other recovery methods due to the concurrent CO_2 storage (Cooney, 2015; Azzolina et al., 2017; Abuov et al., 2022). Under certain conditions, such as project lifespan and net produced water (Núñez-López and Moskal, 2019; Mirzaei-Paiaman et al., 2024a,b,c; Bryant, 2024), the CO_2 stored can outweigh emissions, leading to net-negative emissions or carbon-negative oil.

When reservoir pressures exceed the minimum miscibility pressure (MMP), CO_2 injection effectively mobilizes residual oil and enhances production. This is driven by multicontact miscibility between CO_2 and oil, facilitated by convection-dominated flow and mass transfer. Additional mechanisms, such as oil dilution and swelling from CO_2 dissolution, further improve recovery. CO_2 is stored underground in various forms—mobile fluid (often supercritical), capillary-trapped, and dissolved in brine and oil—with proportions changing over time.

CO_2 injection faces technical challenges, including significant mobility and density contrasts between CO_2 and reservoir fluids. These contrasts, combined with reservoir rock heterogeneities, result in early CO_2 breakthrough, inefficient CO_2 utilization, higher costs of CO_2 recycling and injection, inefficient volumetric sweep and low oil recovery factors. To address this challenge, water-alternating-gas (WAG) injection is employed, where alternating slugs of CO_2 and water reduce CO_2 mobility. A key drawback of WAG is reduced CO_2 storage, as water occupies pore space that could otherwise store CO_2.

Formate (HCOO−) can be synthesized through, for example, the electrochemical reduction of CO_2 (Hisatomi et al., 2024). Recently, formate has gained attention as a promising alternative carbon carrier, offering solutions to challenges associated with CO_2 utilization in carbon management (Oyenowo et al., 2021; Okuno, 2022; Baghishov et al., 2022; Oyenowo et al., 2023, 2024; Wang et al., 2023; Breunig et al., 2023; Mirzaei-Paiaman et al., 2024c). Wettability alteration and enhanced viscosity synergistically improve sweep and displacement efficiencies. Aqueous formate solutions show significant potential as dual-purpose fluids for enhancing oil recovery and facilitating carbon storage (Oyenowo et al., 2023; Mirzaei-Paiaman et al., 2024c). Building on these insights, we propose a novel approach utilizing alternating injection of CO_2 and aqueous formate solution (FAG). This method aims to achieve simultaneous enhancements in oil recovery and carbon storage, surpassing the performance of conventional techniques of continuous CO_2 injection and WAG injection (Figure 1).

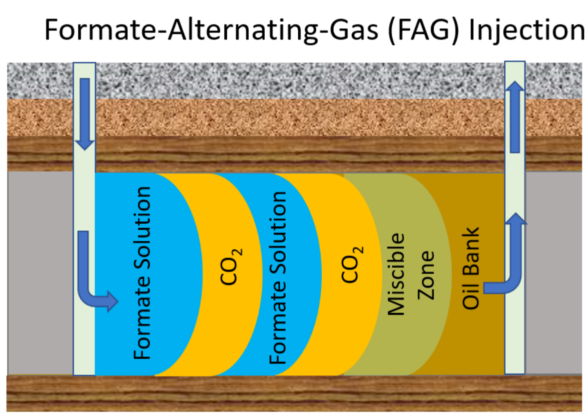


Figure 1. Schematic representation of FAG (formate solution alternating with CO_2) injection to maximize oil recovery and carbon storage.

Reservoir Model

A reservoir model representative of the San Andres carbonate formation in the Permian Basin, West Texas, was developed using the CMG-GEM compositional simulator (Computer Modelling Group, 2024). The model incorporates fluid and petrophysical data from multiple sources, including well-specific and regional datasets (Wang et al., 1998; Honarpour et al., 2010), ensuring general applicability. The model spans 660 × 660 × 80 ft^3 and is divided into 15 × 15 × 20 grid blocks, representing one-quarter of a 5-spot well pattern. Each grid block measures 44 × 44 × 4 ft^3. Vertical production and injection wells are positioned at opposite corners, with initial hydrostatic pressure and a reservoir temperature of 104°F. The reservoir model features porosity values ranging from 0.07 to 0.15, with a mean and median of 0.11. Horizontal permeability varies between 0.96 mD and 19.46 mD, with an average of 7.55 mD and a median of 5.92 mD. Vertical permeability ranges from 0.02 mD to 11.92 mD, with a mean of 1.43 mD and a median of 0.30 mD. The connate water saturation is 0.23, and the residual oil saturation to water flooding is 0.32. Wettability was assessed using oil-water relative permeability, with Lak and modified Lak indices calculated as -0.43 and -0.17, indicating oil-wet conditions (Mirzaei-Paiaman, 2021; Mirzaei-Paiaman et al., 2022).

A calibrated fluid model based on the Peng-Robinson EOS (Peng and Robinson, 1976, 1978) with seven components was used. The MMP for CO_2 and reservoir oil was estimated at 1350 psia at reservoir temperature of 104°F, and Henry's law was applied to simulate CO_2 solubility in reservoir brine. Given low temperature, low permeability, and high producer bottomhole pressure (slightly above MMP), highly concentrated sodium formate solutions were unsuitable. Therefore, a 15% sodium formate solution was used, with viscosity estimated at 2.03 cp at reservoir conditions, compared to 0.80 cp for 70,000 ppm brine (Oyenowo et al., 2023). Potential wettability alteration by formate was excluded from simulations as FAG displacement efficiency is primarily CO_2-driven. For continuous CO_2 and WAG injections, the model includes CO_2 storage as mobile CO_2, CO_2 dissolved in brine, and CO_2 dissolved in residual oil. For FAG injection, formate in brine is also considered an additional carbon storage mechanism.

Injection Strategies

Continuous CO_2 injection, WAG injection, and FAG injection were simulated over a 25-year period, following primary and secondary recovery phases. An equal amount of CO_2 was injected in all three scenarios, as displacement efficiency was governed by the injected CO_2 volume. For the WAG and FAG injection cases, the CO_2 slug size for one half-cycle was 2.6% of the reservoir pore volume. Each half-cycle lasted 90 days. The WAG (or FAG) ratio, defined as the water (or formate solution) volume divided by the CO_2 volume at reservoir conditions, was 0.47. Injection constraints included a maximum allowable bottomhole pressure of 4000 psia at the injection well, safely below the formation's fracturing pressure. At the production well, the bottomhole pressure was maintained at 1400 psia, slightly above the MMP. For WAG and FAG cases, brine and aqueous formate solution injection rates were set at 100 STB/day.

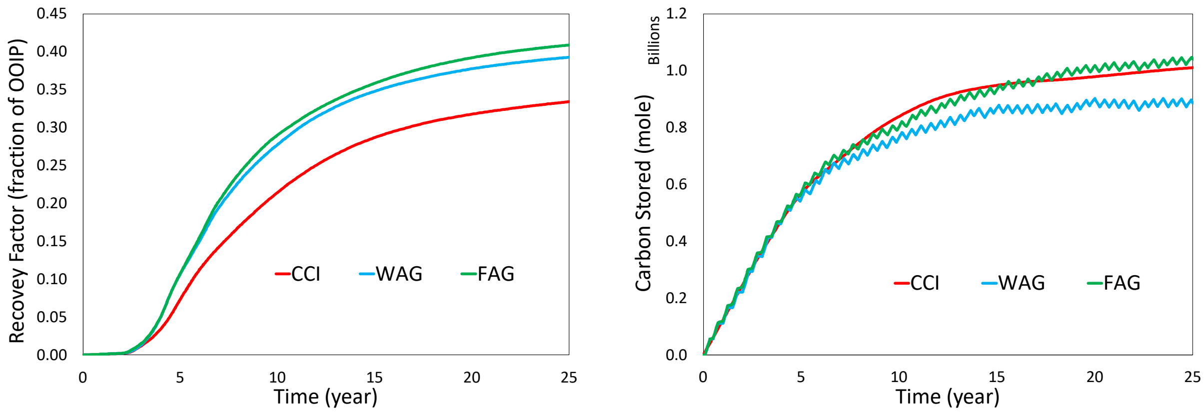
Results and Discussion

At the end of the project, FAG injection increased oil recovery by 22.4% compared to continuous CO_2 injection and by 4.1% compared to WAG injection (Figure 2a). Moreover, FAG injection achieved 2.9% higher carbon storage than continuous CO_2 injection and 17.4% higher carbon storage than WAG injection (Figure 2b). The alternating slugs of CO_2 and viscous formate solution in the FAG process enhanced sweep efficiency, boosting oil production while optimizing the use of pore space for carbon storage.

The stored carbon is categorized into various forms: mobile supercritical CO_2, CO_2 dissolved in oil, CO_2 dissolved in brine, and formate species in the aqueous phase. Figure 3a shows that FAG injection resulted in the lowest amount of carbon stored as mobile supercritical CO_2, emphasizing its advantage in reducing the risks associated with mobile CO_2 migration. FAG injection also achieved the highest absolute amount of carbon stored in brine, enhancing storage security. This was further supported by the unique contribution of formate species in the aqueous phase, exclusive to FAG injection. In contrast, all three injection methods stored similar amounts of CO_2 dissolved in oil.

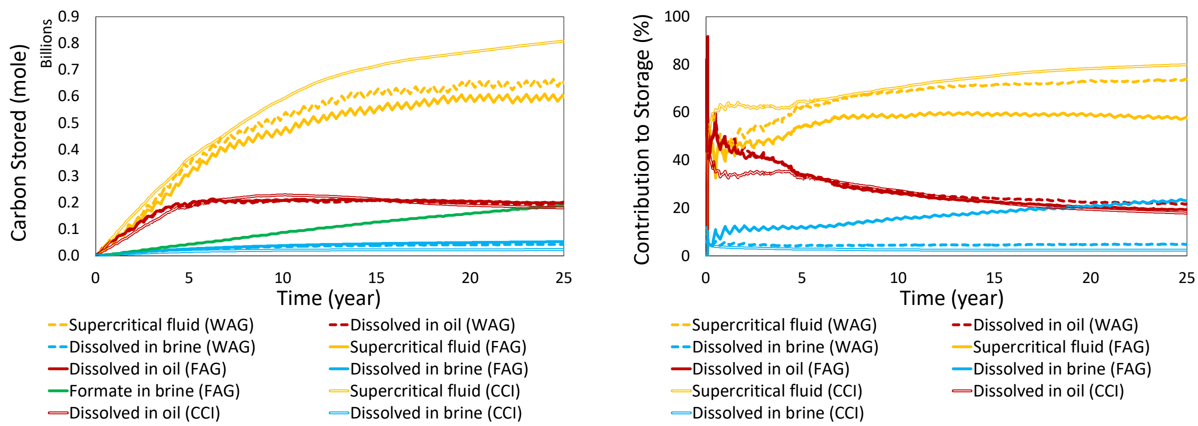
Figure 3b illustrates the relative contribution of each storage mechanism to the total carbon stored. FAG injection showed the highest proportional contribution from carbon species in brine (including CO_2

dissolved in brine and formate species), highlighting its effectiveness in prioritizing secure storage forms. In contrast, the contribution of mobile supercritical CO_2 was significantly lower in FAG injection compared to WAG and continuous CO_2 injection, which relied more heavily on this less secure mechanism. The proportion of CO_2 dissolved in oil was nearly identical across all methods.



(a) (b)

Figure 2. (a) Recovery factor and (b) carbon storage for different injection methods. FAG injection achieved higher levels of both oil recovery and carbon storage compared to WAG injection and continuous CO_2 injection. CCI stands for continuous CO_2 injection.



(a) (b)

Figure 3. (a) Different forms of carbon storage and (b) relative contribution of each storage mechanism to total carbon storage for each injection method. FAG injection achieved the highest level of storage security by maximizing secure storage forms and minimizing reliance on less secure mechanisms.

Conclusion

The FAG injection strategy offers a promising solution for maximizing oil recovery and carbon storage. Compared to continuous CO_2 injection and WAG injection, FAG injection demonstrated superior performance, achieving higher oil recovery, greater total carbon storage, and enhanced storage security. These results highlight FAG injection as an effective and innovative approach for integrating CCUS with enhanced oil recovery.

Acknowledgement

This work was funded by the State of Texas Advanced Resource Recovery (STARR) program. Publication of this work was authorized by the Director of the Bureau of Economic Geology, The University of Texas at Austin.

References

Abuov, Y., Serik, G., and Lee, W. 2022. Techno-Economic Assessment and Life Cycle Assessment of CO_2-EOR. *Environ Sci Technol* **56** (12): 8571–8580. https://doi.org/10.1021/acs.est.1c06834

Azzolina, N. A., Hamling, J. A., Peck, W. D., Gorecki, C. D., Nakles, D. V., and Melzer, L. S. 2017. A Life Cycle Analysis of Incremental Oil Produced via CO_2 EOR. *Energy Procedia* **114**: 6588 – 6596.

Baghishov, I., Abeykoon, G. A., Wang, M., Oyenowo, O. P., Argüelles-Vivas, F. J., and Okuno, R. 2022. A Mechanistic Comparison of Formate, Acetate, and Glycine as Wettability Modifiers for Carbonate and Shale Formations. *Colloids Surf A: Physicochem Eng Asp* **652**: 129849. https://doi.org/10.1016/j.colsurfa.2022.129849

Breunig, H. M., Rosner, F., Lim, T.-H., and Peng, P. 2023. Emerging Concepts in Intermediate Carbon Dioxide Emplacement to Support Carbon Dioxide Removal. *Energy Environ Sci* **16** (5), 1821–1837. https://doi.org/10.1039/D2EE03623A

Bryant, S. 2024. Carbon-Negative Crude Oil. In: Walker, T., Barabanov, S., Michaeli, M., Kelly, V. (eds) Sustainability in the Oil and Gas Sector. Palgrave Macmillan, Cham. https://doi.org/10.1007/978-3-031-51586-6_7

Computer Modelling Group Ltd., 2024. CMG GEM reservoir simulator (Version 2024.10). https://www.cmgl.ca/solutions/software/gem/

Cooney, G., Littlefield, J., Marriott, J., and Skone, T. J. 2015. Evaluating the Climate Benefits of CO_2-Enhanced Oil Recovery Using Life Cycle Analysis. *Environ Sci Technol* **49**: 7491−7500. https://doi.org/10.1021/acs.est.5b00700

Hisatomi, T., Wang, Q., Zhang, F., Ardo, S., Reisner, E., Nishiyama, H., Kudo, A., Yamada, T., and Domen, K. 2024. Photocatalytic Water Splitting for Large-Scale Solar-To-Chemical Energy Conversion and Storage. *Front Sci* **2**:1411644. https://doi.org/10.3389/fsci.2024.1411644

Honarpour, M. M., Nagarajan, N. R., Grijalba, A. C., Valle, M., and Adesoye, K. 2010. Rock-Fluid Characterization for Miscible CO_2 Injection: Residual Oil Zone, Seminole Field, Permian Basin. Presented at the SPE Annual Technical Conference and Exhibition, Florence, Italy, 19-22 September. SPE-133089-MS. https://doi.org/10.2118/133089-MS

Mirzaei-Paiaman, A. 2021. New Methods for Qualitative and Quantitative Determination of Wettability from Relative Permeability Curves: Revisiting Craig's Rules of Thumb and Introducing Lak Wettability Index. *Fuel* **288**: 119623. https://doi.org/10.1016/j.fuel.2020.119623

Mirzaei-Paiaman, A., Carrasco-Jaim, O. A., and Okuno, R. 2024c. Techno-economic-environmental Study of CO_2 and Aqueous Formate Solution Injection for Geologic Carbon Storage and Enhanced Oil Recovery. *Int J Greenhouse Gas Control* **138**: 104257. https://doi.org/10.1016/j.ijggc.2024.104257

Mirzaei-Paiaman, A., Djezzar, S., Faramarzi-Palangar, M., and Kord, S. 2022. A New Approach to Measure Wettability by Relative Permeability Measurements. *J Pet Sci Eng* **208**: 109191. https://doi.org/10.1016/j.petrol.2021.109191

Mirzaei-Paiaman, A., Lake, L., and Moscardelli, L., 2024a. Maximizing Economic and Environmental Profits of Oil Recovery and CO_2 Storage in the CCUS Context: The Impact of Operator Social Responsibility and Carbon Storage Incentives. Presented at AGU24 (American Geophysical Union), Washington DC, USA, 8-13 December.

Mirzaei-Paiaman, A., Okuno, R., Lawal, T., Sheng, K., Chen, C, Lai, I., Chen, S., and Hu, L. 2024b. Techno-Economic-Environmental Analysis of CO_2 Storage and EOR in an Underdeveloped Field. Presented at the SPE Improved Oil Recovery Conference, Tulsa, Oklahoma, USA, 22-25 April. SPE-218254-MS. https://doi.org/10.2118/218254-MS

Núñez-López, V., Gil-Egui, R., and Hosseini, S. A. 2019. Environmental and Operational Performance of CO_2-EOR as a CCUS Technology: A Cranfield Example with Dynamic LCA Considerations. *Energies* **12**: 448.

Okuno, R. 2022. Aqueous Formate Solution as A Novel Carbon Carrier for Geological Carbon Storage. Presented at EAGE Asia Pacific Workshop on CO_2 Geological Storage, August, Volume 2022, p.1 – 3. https://doi.org/10.3997/2214-4609.202275012

Oyenowo, O. P., Sheng, K., and Okuno, R. 2023. Simulation Case Studies of Aqueous Formate Solution for Geological Carbon Storage. *Fuel* **334**: 126643. https://doi.org/10.1016/j.fuel.2022.126643

Oyenowo, O. P., Wang, H., Mirzaei-Paiaman, A., Carrasco-Jaim, O. A., Sheng, K., and Okuno, R. 2024. Geochemical Impact of High-Concentration Formate Solution Injection on Rock Wettability for Enhanced Oil Recovery and Geologic Carbon Storage. *Energy & Fuels* **38**(7): 6138–6155. https://doi.org/10.1021/acs.energyfuels.3c05081

Oyenowo, O.P., Sheng, K., Abeykoon, G.A., and Okuno, R. 2021. A Case Study of Using Aqueous Formate Solution for Carbon Sequestration and Geological Storage. Presented at The GEOGULF Conference, Austin, Texas, USA, 27-29 October, GCAGS Transactions, Volume 71, pp. 203 – 215.

Peng, D. Y., and Robinson, D. B. 1976. A New Two-Constant Equation of State. *Ind Eng Chem Fund* **15** (1): 59-64. https://doi.org/10.1021/i160057a011

Peng, D. Y., and Robinson, D. B. 1978. The Characterization of The Heptanes and Heavier Fractions for The GPA Peng-Robinson Programs. GPA Research Report RR-28.

Wang, F.P., Lucia, F. J., and Kerans, C. 1998. Integrated Reservoir Characterization Study of a Carbonate Ramp Reservoir: Seminole San Andres Unit, Gaines County, Texas. *SPE Res Eval & Eng* **1** (02): 105–113. https://doi.org/10.2118/36515-PA

Wang, H., Oyenowo, O. P., Okuno, R. 2023. Aqueous Formate Solution for Enhanced Water Imbibition in Oil Recovery and Carbon Storage in Carbonate Reservoirs. *Fuel* **345**: 128198. https://doi.org/10.1016/j.fuel.2023.128198