

A Case Study of Using Aqueous Formate Solution for Carbon Sequestration and Geological Storage

**Oluwafemi Precious Oyenowo, Kai Sheng, Gayan A. Abeykoon,
Francisco J. Argüelles-Vivas, and Ryosuke Okuno**

Hildebrand Department of Petroleum and Geosystems Engineering
The University of Texas at Austin, Austin, Texas 78712

ABSTRACT

Carbon dioxide (CO₂) has been used as a carbon carrier for geological carbon storage. However, various shortcomings come from its physical properties, such as small carbon density at low to moderate pressure, low mass density, low viscosity, immiscibility with water, and corrosivity.

This paper presents the first case study of using aqueous formate solution as carbon-bearing water for carbon storage and enhanced oil recovery. Properties of formate solutions in brine were measured, such as solubilities, densities, and viscosities. Then, numerical reservoir simulations were performed for carbon storage and enhanced oil recovery by aqueous formate solution and by CO₂. The two cases exhibited different flow regimes, and the formate injection case resulted in a greater amount of oil recovery and carbon storage, primarily because of more stable fronts of oil and water displacement.

An economic analysis based on numerical reservoir simulations gave the equivalent cost of CO₂ reduction into formate for the same net present value as the CO₂ injection case, and the breakeven cost of the reaction process for the formate injection case. This is the first time formate, the simplest carboxylate, was studied as a carbon carrier to reduce the carbon emission of oil production.

INTRODUCTION

The Intergovernmental Panel on Climate Change reported in their sixth assessment report that the global warming thresholds of 1.5°C and 2°C would be exceeded before the end of the 21st century without large-scale reductions in carbon dioxide (CO₂) emissions (IPCC, 2021). Carbon capture and storage (CCS) has been identified as an important technology to keep the sustainable growth of countries (Kelemen et al., 2019).

Current CCS processes involve supercritical compression of captured CO₂ for transport, injection, and storage. The challenges involved with these processes include the substantial cost associated with the CO₂ capture, compression, transport, and recycling after CO₂ breakthrough. Also, the small viscosity and density of CO₂ and its immiscibility with formation water at the subsurface conditions result in inefficient use of pore space and buoyancy-driven flux, leading to the potential risk of CO₂ leakage from the underground storage (Al-Mamoori et al., 2017; IPCC, 2005; Shaffer, 2010).

Conversion of CO₂ into other useful products has been studied to utilize the captured CO₂. Formate/formic acid has been identified as one of the economically feasible products via the electrochemical reduction of CO₂ (Philips et al., 2020; Li et al., 2020). Formate has been used as a component in drilling fluids as presented by Downs (1993) and Howard (1995), in which properties of formate brines can be found, including the health-safety-environment profile. Recently, Baghishov et al. (2021) showed that formate can alter the wettability of carbonate rock from oil wet to water wet with a slight pH adjustment. We present a case study of using formate as a carbon carrier that makes it possible to sequester carbon in aqueous phase for efficient and reliable carbon storage.

EXPERIMENTAL METHODS and RESULTS

Experiments were performed to obtain fundamental data of aqueous formate solution. The resulting data were used to set input parameters for the numerical simulation presented later.

Sodium formate was dissolved in brine to obtain several formate solutions with varied molar concentrations. This was repeated to obtain three batches of samples at 25°C, 50°C, and 75°C. The pH values of the solutions were then adjusted to 7 by adding the volumes of formic acid calculated with the Henderson-Hasselbalch equation,

$$pH = pKa + \log_{10} \frac{[A^-]}{[HA]},$$

where Ka is the acid dissociation constant, pKa is the negative logarithm of Ka , $[HA]$ is the concentration of acid, and $[A^-]$ is the concentration of the conjugate base. The acid dissociation constants at 50°C and 75°C were adjusted based on the experimental results and model from Kim et al. (1996).

Table 1 shows the solubilities of formate in NaCl/CaCl₂ brine at 25°C, 50°C, and 75°C. The solubility increased with temperature from 30 wt% at 25°C to 35 wt% at 75°C. The table also shows the densities measured by weighing a known volume of solution and the viscosities measured by using a rheometer.

Formate can be adsorbed on rock surfaces, and surface adsorption is expected to be one of the reliable forms of carbon storage. Therefore, experiments were performed to measure the adsorption of formate by dynamic adsorption tests with Texas Cream limestone and Boise sandstone. The formate adsorption was measured to be 0.11 mg/g-rock for Texas Cream limestone and 0.10 mg/g-rock for Boise sandstone. However, the simulations to be shown later did not consider the surface adsorption of formate since most of the carbon storage was expected in the bulk aqueous phase.

CASE STUDY

This section presents a comparative case study of CCS with CO₂ and with aqueous formate solution. The electrochemical reduction of CO₂ into formate is currently rated to be a technology

readiness level of 4; hence, the costs for this reaction process are highly uncertain for large-scale CCS applications. Therefore, this case study solved for the cost for the reaction process, below which the formate case resulted in a greater net present value (NPV) than the CO₂ case. Since the analysis relied primarily on the numerical reservoir simulations of CO₂ injection and aqueous formate injection, they are presented in the first subsection below. Then, the subsequent subsection shows the economic analysis of the two cases based on simulation results.

Numerical Reservoir Simulations

The reservoir model was taken from the SPE-10 case of SPE's comparative solution projects (Christie and Blunt, 2001). The original SPE 10 model has the dimensions of 1200 × 2200 × 170 ft³. The current study used a section of 400 × 400 × 70 ft³ for a quarter of a five-spot pattern. The uniform gridblock size of dimensions 20 × 10 × 2 ft³ resulted in 20 × 40 × 35 (28,000) gridblocks. **Figure 1** shows a 3-D view of the reservoir porosity distribution. The numerical simulator used was CMG GEM (Computer Modelling Group).

Table 2 contains the properties of the selected reservoir section, and the injection conditions. For both cases, oil production was initiated by 5 years of waterflooding at 1350 psia (**Figure 2**). After that, a constant rate of carbon injection, 5 t of CO₂ equivalent (114 kmol of carbon) per day, was assumed for the two cases: one with CO₂ and the other with formate as a carbon carrier. The production pressure was kept at 1000 psia. The phase behavior was modeled by the Peng-Robinson equation of state. The minimum miscibility pressure for the oil with CO₂ was calculated to be 1526 psia at the reservoir temperature, 106°F.

Figure 3 shows that the two cases resulted in different flow regimes. The CO₂ case exhibited a substantial level of channeling, resulting in rapid breakthrough within the first year of CO₂ injection (**Figure 4**). It also showed a clear gravity override by the end of the simulation. The formate case yielded more stable propagation of displacement fronts with no gravity-driven flow.

The endpoint mobility ratio for the injectant and oil was calculated to be 26 for the CO₂ case, and 0.16 for the formate case. The endpoint mobility ratio for the injectant and formation water was calculated to be 6.4 for the CO₂ case (the displacement of water by formate solution was a miscible process with a favorable viscosity ratio). Because of the difference in mobility ratio, the impact of breakthrough on carbon storage and oil recovery was much less in the formate case than in the CO₂ case as shown in **Figures 5 and 6**. This is a substantial advantage of using formate as a carbon carrier for CCS since the permeability heterogeneities and their impact on flow regime are highly uncertain. Note that it is practically possible to control the in-situ flow regime for formate (the carbon carrier) by adjusting the density and viscosity of the formate solution injected.

After two years of CO₂ injection, the recycled CO₂ accounted for 64.4% of the CO₂ injected. In the formate case, recycling only rose to 50% after 7.5 years of the formate injection at the same molar rate of injection as in the CO₂ case. Although recycling occurred for both cases (**Figure 4**), the formate case resulted in a much greater amount of carbon storage (see **Figure 5**) because the displacement of the initial reservoir water and oil by the injected formate solution was more stable than that by the injected CO₂. **Figure 7** shows the two contributions to carbon storage: water displacement and oil displacement (note that the y axes have different scales). The carbon storage

by water displacement in formate solution injection was substantially greater than that in CO₂ injection.

Economic Analysis

This section examines the economic viability of the formate injection case. The equivalent cost of the CO₂ reduction into formate is the cost below which the formate case yields a greater NPV than the CO₂ case. This section also gives the breakeven cost of the reaction process for the formate injection case as a standalone project.

The economic analysis of the CO₂ case considered the cost of CO₂, and its transport and injection costs. Both cases assumed the availability of existing wells, pipelines, separators, and water treatment facilities. The CO₂ recycling plant was included as part of the injection cost for the CO₂ injection case.

A levelized transport cost of \$0.06/tonne-mile was used for both cases. The transport distance from the CO₂ capture/processing plant to the injection site was set at 30 miles for both cases, with no booster compression. The delivery pressure of the CO₂ transport pipeline was assumed to be 1350 psia.

The injection cost included the recycling cost, fluid lifting cost, injection energy cost, and annual maintenance cost. Equations from Godec (2014) were used in calculating the injection costs for CO₂ injection. It was assumed that the recycling of formate solution could be done using existing separator and water treatment facilities. The formate solution recycle cost was estimated using water treatment costs reported in Godec (2014).

Further assumed were \$40/t-CO₂, \$60/bbl-oil, \$50/MWh for electricity, \$45/t-CO₂ for carbon tax credit, and 3% for discount rate. The tax credit was treated as part of the revenue, and the entirety of the credit was assumed.

Table 3 shows a summary of results for the 29 years of CCS/EOR without considering the 5 years of waterflooding prior to the CCS/EOR. Only a quarter of the five-spot pattern was considered for the results shown. The CO₂ case yielded an NPV of \$1.3 million, which corresponds to the NPV at Year 34 in **Figure 8**. **Figure 9** shows the equivalent and breakeven costs for the CO₂ reduction into formate calculated for the formate injection case. At Year 15 when the NPV for the CO₂ case leveled off (Figure 8), the equivalent cost was \$204/t-CO₂ and the breakeven cost was \$286/t-CO₂.

SUMMARY AND CONCLUSIONS

We presented the first case study of the injection of aqueous formate solution for CCS/EOR in comparison to the conventional CO₂ injection. The main objective was to estimate the equivalent cost for the CO₂ reduction into formate that resulted in the same NPV as the CO₂ injection case. The key conclusions are as follows:

1. Properties of formate solutions in NaCl/CaCl₂ brine were measured. The solubility ranged from 30 wt% at 25°C to 35 wt% at 75°C in 102,600-ppm brine. The viscosity ranged from 12 cp at 25°C to 5 cp at 75°C.
2. The CO₂ and formate solution cases resulted in different flow regimes in the simulation model used. The former case showed a significant level of channeling and gravity-driven flux of CO₂. The latter case showed much more stable fronts of oil and water displacement. The more stable fronts yielded the oil recovery and the carbon storage that were less sensitive to the injectant breakthrough.
3. The NPV for the CO₂ injection case leveled off around Year 15 (10 years after the commencement of CO₂ injection). The equivalent cost for the CO₂ reduction into formate was calculated to be \$204/t-CO₂ at Year 15 and \$169/t-CO₂ at Year 34. The breakeven cost was \$286/t-CO₂ at Year 15 and \$240/t-CO₂ at Year 34.

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TABLES

Table 1. Properties of formate solution in NaCl/CaCl₂ brine. The brine had a total salinity of 102,646 ppm (97,897 ppm NaCl and 4,749 ppm CaCl₂).

Temperature (°C)	Solubility (wt%)	Density (g/mL)	Viscosity (cP)
25.0	29.60	1.3675	11.68
50.0	32.20	1.3795	6.05
75.0	34.75	1.4388	5.10

Table 2. Properties of the reservoir, wells, and oil for the simulation case study.

	Values
Reservoir properties	
Top depth	2200 ft
Initial pressure	1000 psia
Temperature	106°F
OOIP	328,946 bbl
Initial oil saturation	85%
Initial water saturation	15%
Porosity	0 to 0.50
Permeability	0 to 20 D
Residual water saturation	15%
Oil properties	
Viscosity	2.61 cp
API gravity	44°API
Bubble point	812 psia
Oil composition (mole percent)	
N ₂	0.5%
CO ₂	0.4%
CH ₄	12.7%
C ₂ H ₆	6.7%
C ₃ H ₈	6.9%
n-C ₄ H ₁₀	6.2%
n-C ₅ H ₁₂	5.2%
n-C ₆ H ₁₄	2.9%
C ₇₊	58.6%

Table 3. Results of economic analysis for the CO₂ case and the formate case at Year 34 without considering the initial five years of waterflooding. The latter case does not contain the cost of CO₂ reduction into formate, which was set as an unknown to be solved for in the analysis. Only a quarter of the five-spot pattern (Figure 1) was considered in the analysis.

	Amount
CO₂ injection case	
Cost of CO ₂	\$ 259,715.57
Transport cost	\$ 11,687.20
Recycle and injection cost ^{CAPEX + OPEX}	\$ 606,130.95
Maintenance cost	\$ 1,249,900.00
Fluid lifting cost	\$ 25,377.14
Tax credit	\$ 292,180.02
Oil sale revenue	\$ 3,633,839.06
NPV	\$ 1,273,438.12
Formate solution injection case	
Transport cost	\$ 33,156.13
Recycle/Water treatment and injection cost ^{OPEX}	\$ 393,764.56
Maintenance cost	\$ 1,249,900.00
Fluid lifting cost	\$ 193,674.81
Tax credit	\$ 810,343.16
Oil sale revenue	\$ 7,059,317.34
Breakeven cost (at year 34)	\$ 240.20/tonne of CO ₂ converted
Equivalent cost (at year 34)	\$ 169.49/tonne of CO ₂ converted

FIGURES

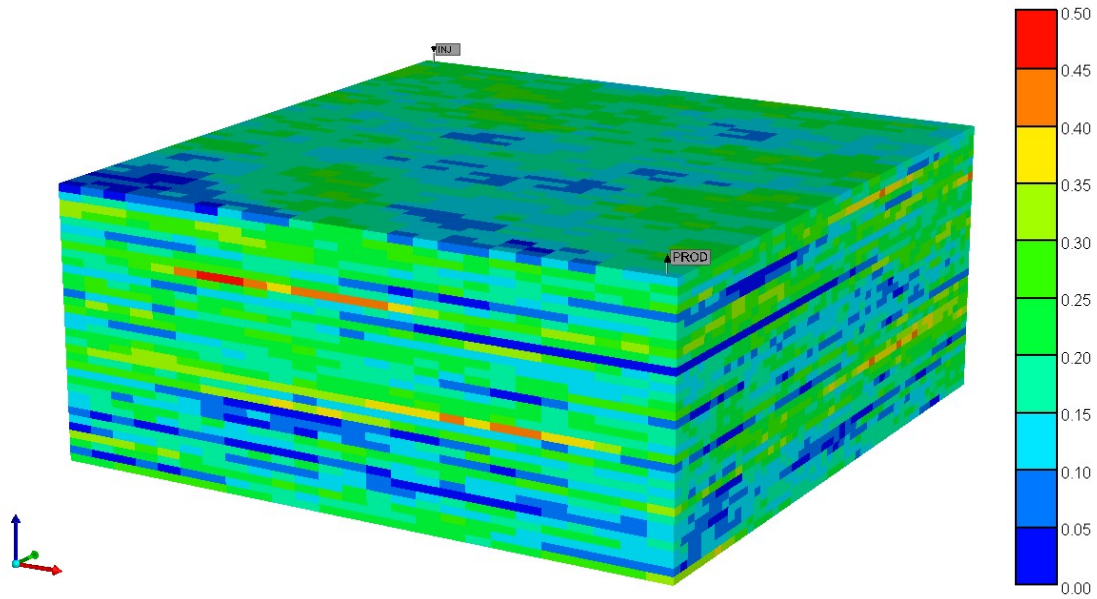


Figure 1. 3-D view of the reservoir porosity distribution taken from the SPE-10 case. This was used for a quarter of a five-spot pattern.

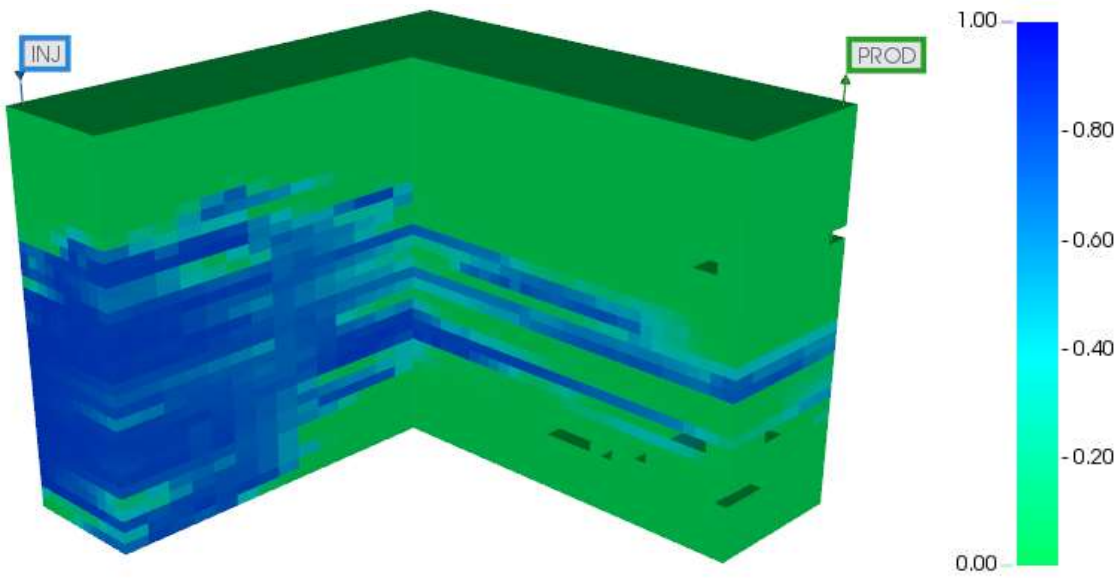
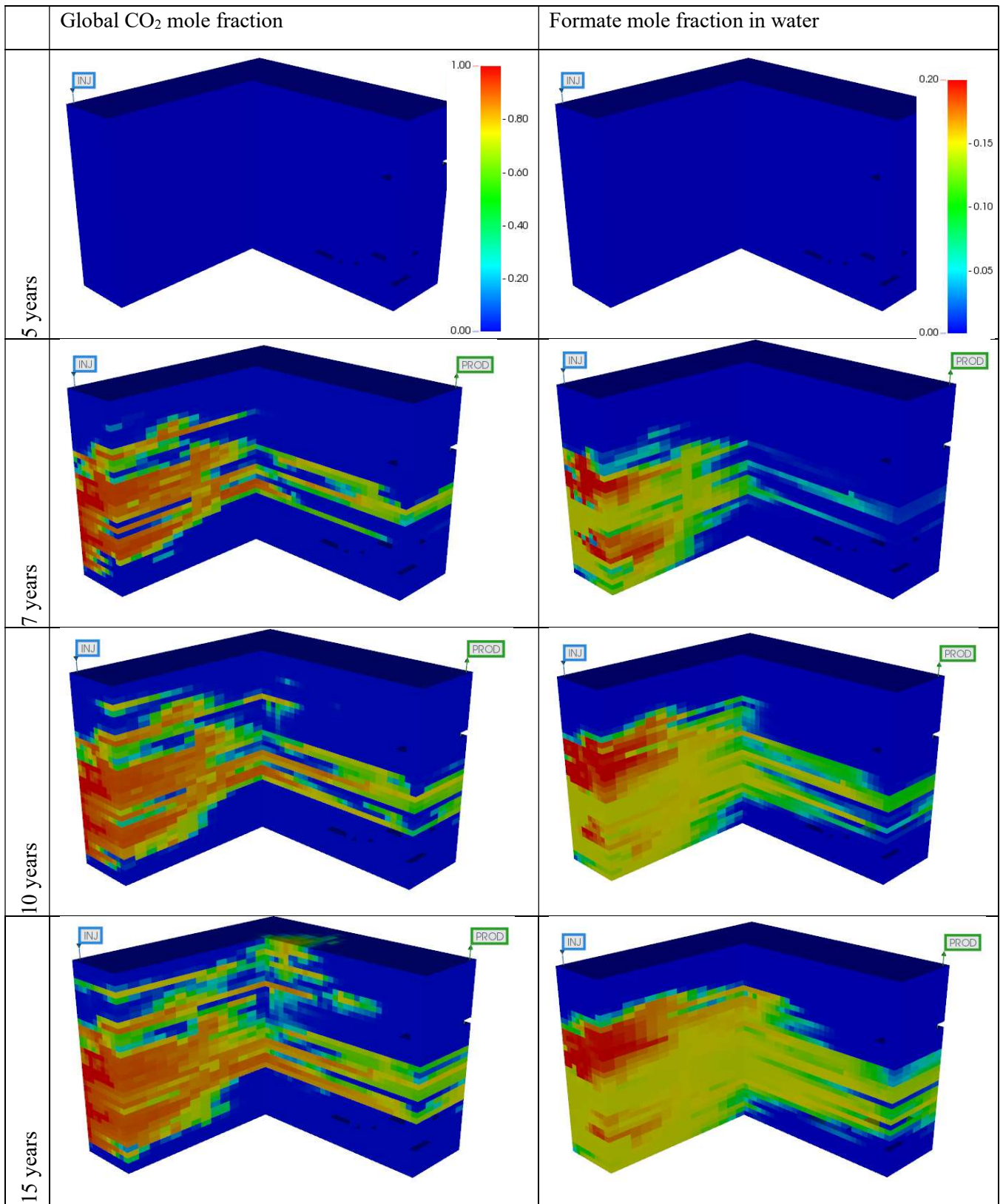


Figure 2. Water saturation after 5-years of water injection.



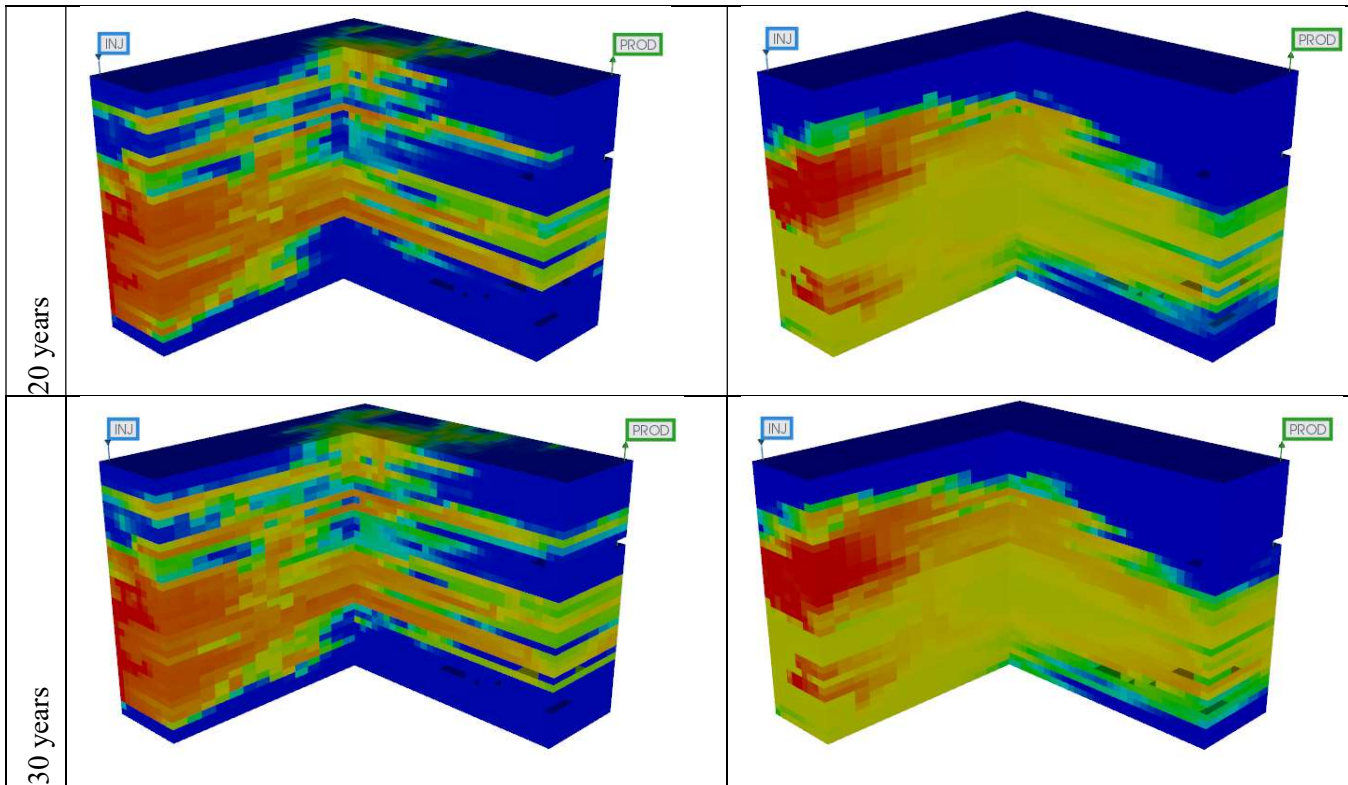


Figure 3. Vertical cross section for the CO₂ and formate solution cases. Left: CO₂ molar concentration on the water-free basis. Right: formate molar concentration in aqueous phase.

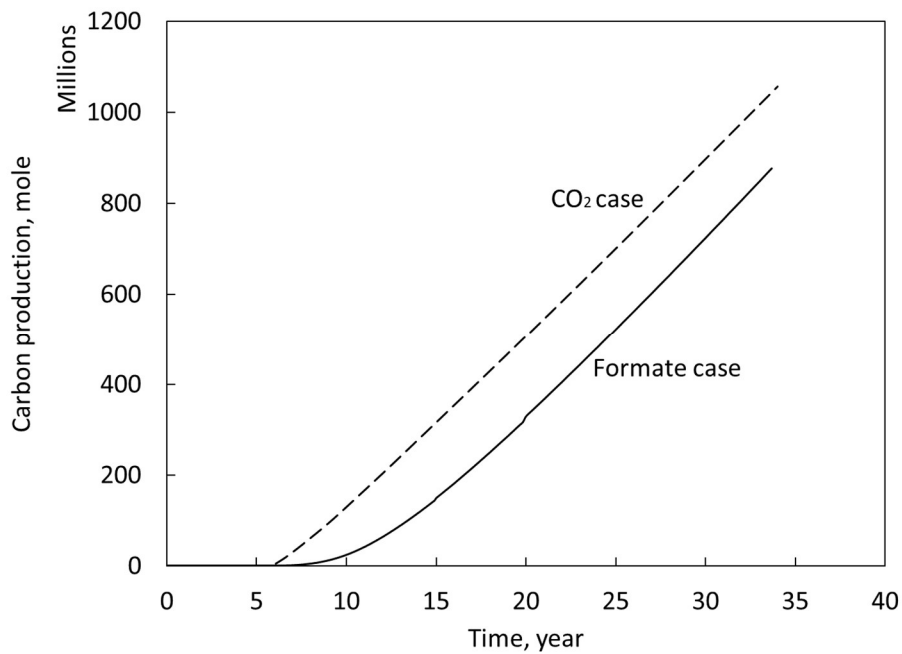


Figure 4. Production histories of the injectants, CO₂ and formate solution, in carbon mole number.

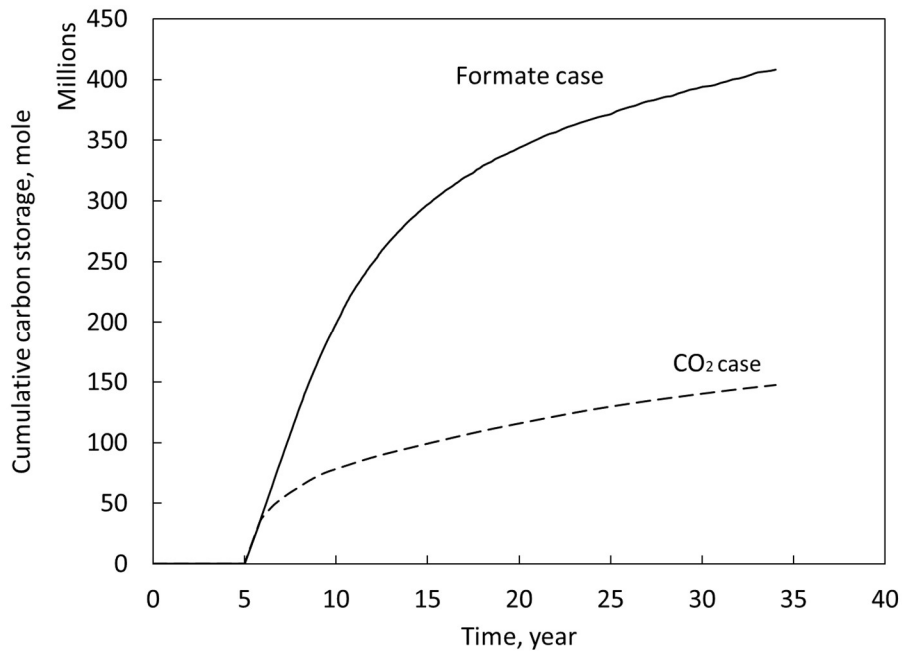


Figure 5. Cumulative carbon storage in carbon mole.

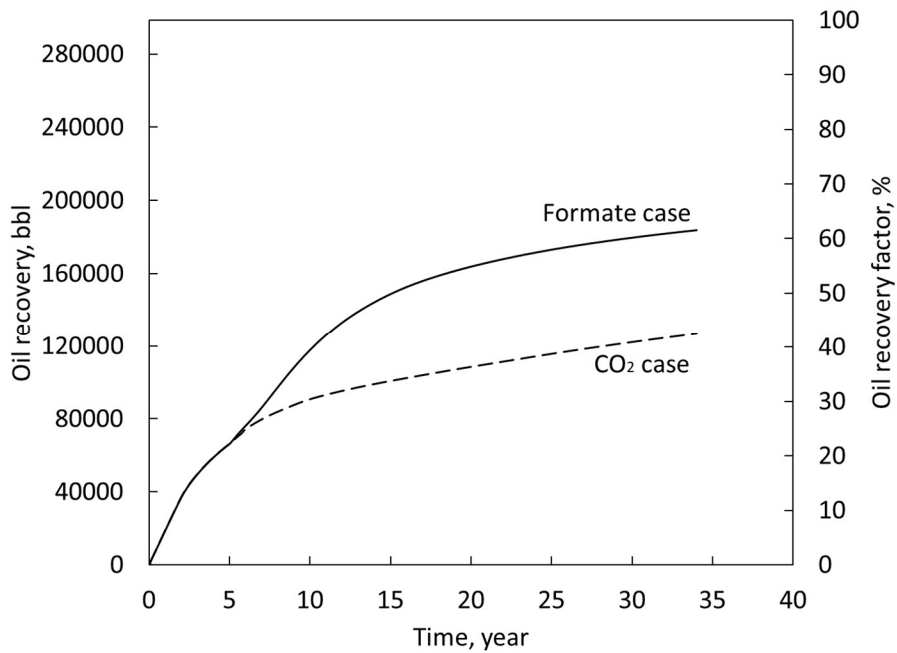
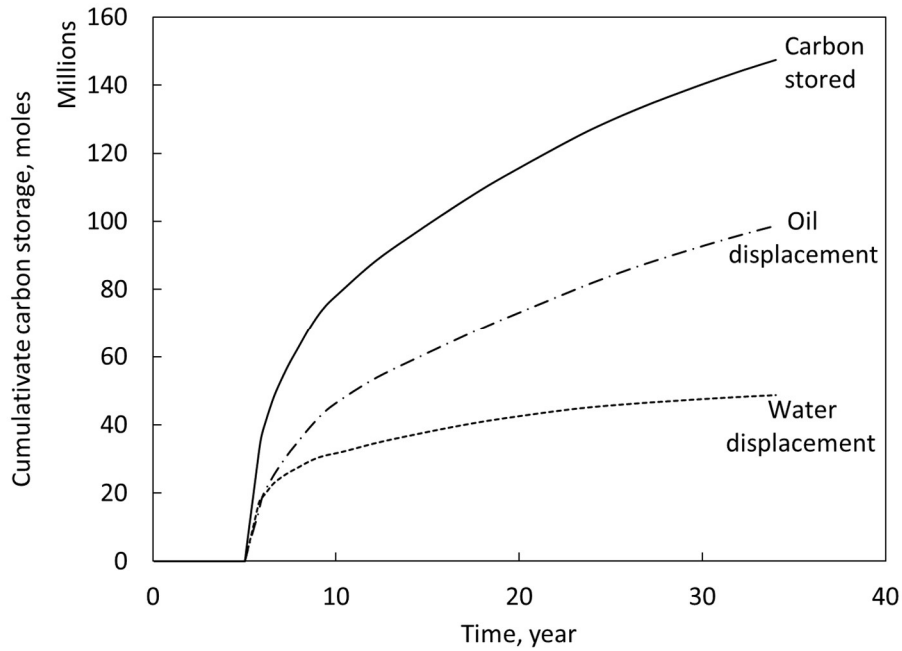
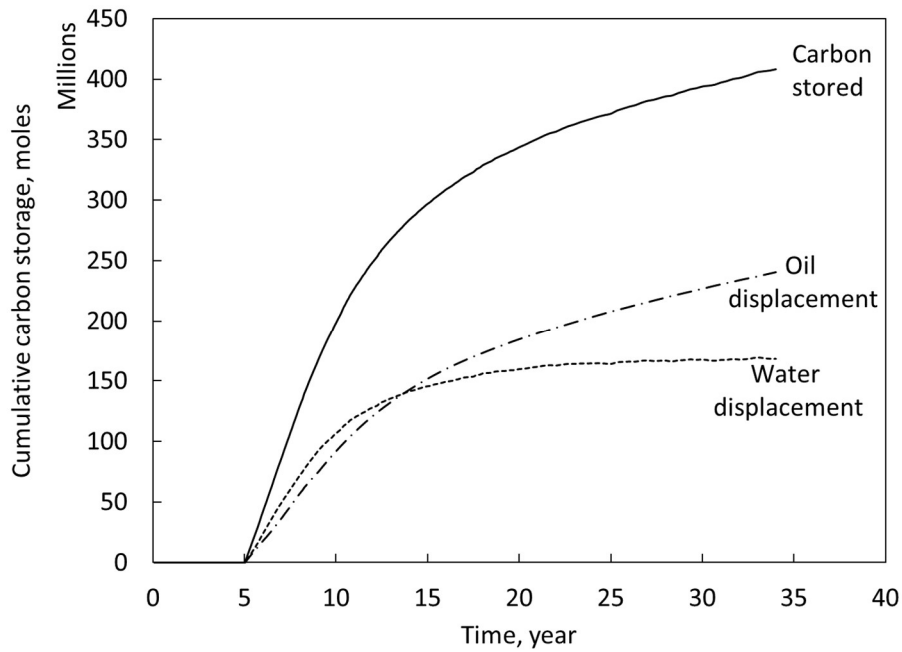


Figure 6. Cumulative oil recovery for the CO₂ and formate solution cases.



a) CO₂ case



b) Formate solution case

Figure 7. Cumulative amount of carbon stored and the two contributions from the oil displacement and the water displacement: a) CO₂ case and b) formate solution case.

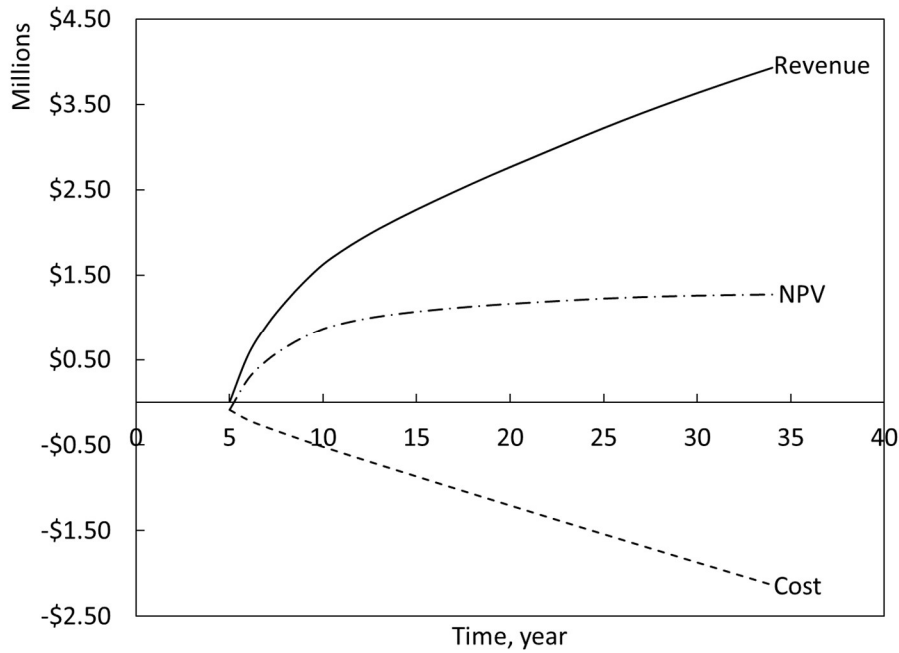


Figure 8. Revenue, cost, and NPV after the waterflooding period for the CO₂ case.

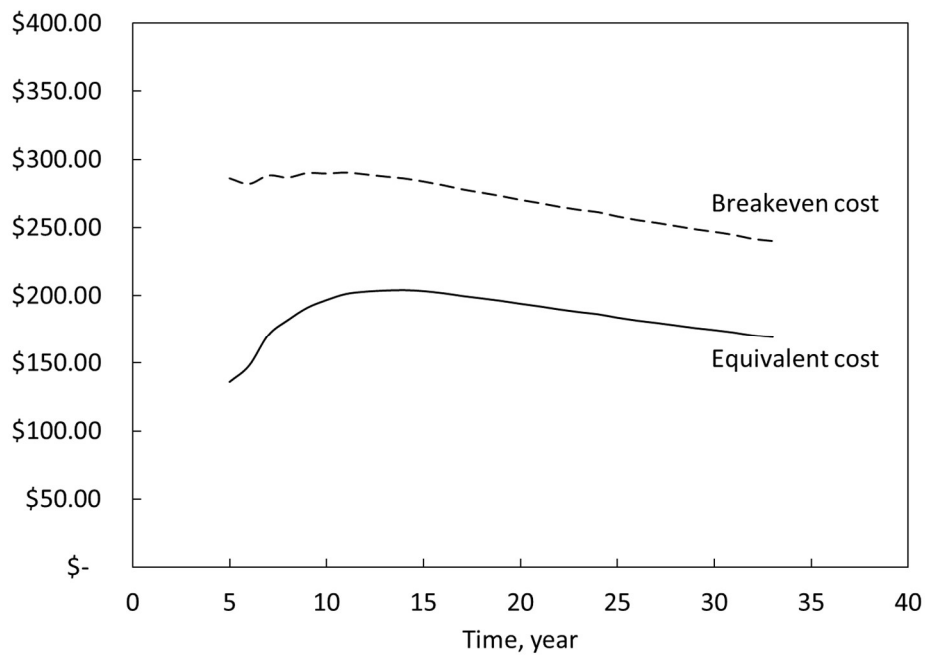


Figure 9. Equivalent and breakeven costs for the CO₂ reduction into formate.