Modeling Reservoir Rock and Formation Fluid Geochemical Interactions: Implications for CO\textsubscript{2} Sequestration from Citronelle Oil Field, Alabama*

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Abstract

The Citronelle field in southwest Alabama is the site of a U.S. Department of Energy pilot project on long-term geologic storage of CO\textsubscript{2} and the efficacy of CO\textsubscript{2}-EOR. The target for injection is the Donovan Sand, an assemblage of arkosic fluvial sandstones intercalated with mudstones within the Lower Cretaceous Rodessa Formation. Following injection in November, 2009, production from updip well Permit 706 increased 20\% to 493 bbl/month in 3 months. However, after February, 2010, monthly production decreased by 50\% to 250 bbl/month, and it has not been >300 bbl/month, as of March 2012, despite water-flooding beginning March, 2010. Reservoir rock samples from 6 cored wells were analyzed via thin-section petrography, bulk geochemistry, and SEM-EDS to model reservoir rock composition. Sand mineralogy is uniform, but authigenic mineralogy and porosity are heterogeneous. Porosity averages \~2-5\%, but locally is up to \~13\%. A total of 47 SP well logs were used to estimate bulk density, from which an estimated porosity curve and porosity distribution map were generated. Paragenesis indicates early calcite cementation and later calcite cement dissolution, combined with feldspar alteration, generated secondary porosity. In contrast, authigenic clay is rare, suggesting an open diagenetic system during feldspar alteration. A later generation of anhydrite and calcite concretions and pyrobitumen occludes both primary and secondary pores. Formation fluids collected during late CO\textsubscript{2} injection and the subsequent water-flood show increases in the concentrations of Br, Ca, and Fe, along with pH decreases for most wells. Saturation indices for minerals in the reservoir rock do not indicate that mineral-dissolution reactions could cause the observed element-concentration trends. Instead, ion exchange reactions between H\textsuperscript{+}, sourced from carbonic acid generated by injected CO\textsubscript{2}, and cations on the surfaces of reservoir minerals is likely to be occurring. A simplified TOUGHREACT model of fluid flow was unable to simulate the observed breakthrough times for CO\textsubscript{2} in any of the observation wells, suggesting the primary fluid transport pathway may be fracture-controlled; thus, fluids may interact with minerals of non-porous lithologies or may generate redistributional porosity/mineral trapping in calcite-cemented zones. Iron fouling or possibly interactions between calcite and acidic formation fluid may have caused observed lowered injectivity during water-flooding.
References Cited


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Our study is focused on the Donovan sand of the Rodessa Formation shown here. It is a subsurface unit of the AL coastal plain succession that formed in a Cretaceous marginal marine environment. The Rodessa Formation is the major reservoir unit of the Citronelle field located on the crest of the Citronelle dome, a giant salt-cored anticline with 4-way closure. There the Rodessa Formation has produced nearly 170 million barrels from ~524 wells and recovered about one-third of the oil in place. The reservoir is sealed by the regionally extensive and thick Ferry Lake Anhydrite. Donovan pay interval, ~200 feet thick, contains 10’s of productive sand bodies.
Presenter’s notes: Citronelle Field has been in water flood since 1961. 63% of oil production was produced prior to 1973.
- 7500 tons of CO₂ injected into well
  Permit 3232/B-10-10 beginning late November 2009
- Continuous injection achieved from 1/27-9/25/10
- Average injection rate = 31 tons/day
  (35 tons/day anticipated by reservoir simulations)

Presenter’s notes: DOE-sponsored project has been testing CO₂-EOR and potential storage in the Citronelle field.
• Loss in production from Permit 1209/B-19-11
• Loss of injectivity to Permit 3232/B-19-10
  • Injectivity to water decreased from ~140 to 20 bbl/day in the upper sand but remained approximately the same at 31-39 bbl water/day in the lower sand

Presenter’s notes: Less-than-hoped-for, but still considered moderately successful as production decline appears to be flattening and holding steady after post-CO₂ waterflood.
Presenter’s notes: The goal of our project is to identify potential for interaction between pore fluids and reservoir rock. Injection of supercritical (sc) CO₂ forms a plume and CO₂ of that plume will not directly interact with rock-matrix minerals. However, lab studies of CO₂ injection show that connate fluids will be largely flushed from the pore network, but thin films and droplets of water can remain, and CO₂ could dissolve in that water and drive down pH of pore fluids.
Donovan Sandstone Lithofacies:

Upward-fining facies succession:
1. Rudstone conglomerate
2. Cross-bedded fine sandstone
3. Massive to horizontally laminated fine sandstone
4. Ripple-laminated siltstone
5. Massive to horizontally laminated siltstone
6. Gray-green-red bioturbated siltstone
7. Horizontally laminated dark shale
8. Calcareous mudstone
Donovan Sandstone Lithofacies

*red indicates hydrocarbon stain observed*

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Homogeneous sandstone composition; Heterogeneous porosity development
Early calcite cement:

- Open grain packing preserved
Feldspar stability in compacted sandstone:
Feldspar dissolution

- *In situ* grain dissolution in moderately compacted sandstone
  - No early calcite cementation
- Creates secondary porosity
  - Meso-, micro-, & nano-scale
Feldspar dissolution

- Lack of clay precipitation:
  - Organic complexing of Al\(^{3+}\) ions
  - Acidic formation fluids
  - High fluid flux
  - Fluid pressure driven by hydrocarbon charge
Rutile after Ilmenite: evidence for acidic pore water
Rutile after Ilmenite:

Fractures induced by 40% volume reduction through ilmenite to rutile transition

Janssen et al. (2010)  
Mineralogical Magazine
Late-stage concretions

Anhydrite and calcite:
Late-stage Concretions: Calcite

- Dissolution of feldspar arrested
- Concretions locally fill secondary and primary pores
Late-stage Concretions:
Anhydrite

- Sulfur sourced from early-charge fluids induces switch to anhydrite precipitation.
- Localized concretion development: Pore space preserved away from concretions.
Hydrocarbon Charge:

- Early-charge fluids may have facilitated dissolution of grains and early cement
- Later hydrocarbons infilled secondary and primary pores
Hydrocarbon charging:

- Degraded oil/pyrobitumen now occludes some of the original-charged porosity & isolates reactive mineral surfaces
  - Prevented further cementation
SUMMARY: Heterogeneity

• Rodessa Fm. consists of upward-fining sandstone units of mixed reservoir and non-reservoir facies
  – Laterally discontinuous = variable horizontal porosity

• Heterogeneous vertical porosity distribution controlled by interbedded porous and non-porous lithologies
SUMMARY: Pore system

- Keys to porosity development:
  - Fairly uniform arkosic sandstone composition
  - Early calcite cement created non-porous facies
  - Lack of early calcite cement allowed interaction with acidic pore water

![Diagram showing the timeline of geological processes with a note on compaction](image-url)
SUMMARY: paleo-fluid composition

- Later development of secondary porosity likely due to high flux of acidic pore water driven by early-charge-generated fluids
  - Feldspar dissolution
  - Lack of clay cement
  - Conversion of ilmenite to rutile

![Diagram showing time and depth with various processes]

- Calcite cementation
- Feldspar alteration
- Feldspar dissolution
- Rutile after ilmenite
- Calcite precipitation/concretions
- Anhydrite concretions
- Hydrocarbon charging
- Pyrobitumen accumulation
- Dolomitization
SUMMARY: implications

- Acidification of thin water films and “bubbles” left on grains could replay diagenetic processes in reverse during (sc)CO₂–EOR or carbon sequestration
  - Pore throats and micro/nano-pores susceptible to precipitation of carbonate dissolved by acidic water films and bubbles
  - Pyrobitumen coats could impede this
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