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ABSTRACT

This document is the Final Report for the U.S. Department of Energy under contract No. DE-FG26-01BC15364, a three-year contract with a no-cost extension entitled: “Improving CO2 Efficiency for Recovering Oil in Heterogeneous Reservoirs.” This research improved our knowledge and understanding of CO2 flooding and included work in the areas of injectivity and mobility control. Chapter 1 summarizes a survey performed for all the CO2 injection projects in the Permian Basin. Chapter 2 covers CO2-brine-reservoir rock interactions that were studied to better understand injectivity implications. Chapter 3 summarizes work performed to determine possible injectivity and productivity reduction due to high flow rate in near-wellbore regions, and Chapter 4 summarizes work in the areas of foam stability, interfacial tension, surfactant adsorption and desorption, and mobility control. Chapter 5 lists the papers, reports, workshops, and presentations produced as a result of the research work under this contract.

The work performed under this contract and the results achieved through this research in the related fields of mobility control and injectivity will improve industry understanding of CO2 flooding mechanisms, with the ultimate goal of economically recovering more of the U.S. oil reserves. Results include:

- Identification of the extent that various properties affect foaming agent adsorption, i.e.: rock type, surfactant type, surfactant concentration, co-surfactants, sacrificial agents, brine salinity, pH, and temperature.
- Understanding of the extent of synergistic effects on adsorption and desorption in dual chemical systems for five powdered minerals and three rock types.
- Identification of parameters that change injectivity and improve sweep efficiency.
- Identification of causes of injectivity changes: fines migration, permeability changes, dissolution, precipitation, stress/pressure gradient, phase behavior, flow rate, etc.
- Development of models to predict advancing rates of individual components in mixed chemical systems with adsorption and desorption kinetic and equilibrium rates, foam behavior in heterogeneous systems, and injectivity.
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INTRODUCTION

This study, “Improving CO$_2$ Efficiency for Recovering Oil in Heterogeneous Reservoirs,” emphasized laboratory studies with related analytical models for improved oil recovery (IOR). In the United States (US), oil that is potentially producible by IOR methods amounts to approximately 32 billion cubic meters ($m^3$) (200 billion barrels) of the 56 billion $m^3$ (351 billion barrels) remaining in US oil reserves. Of the available IOR methods, carbon dioxide (CO$_2$) injection holds the greatest promise for additional oil recovery from light oil reservoirs in the US. CO$_2$ flooding is a proven IOR technology for IOR that extends the life of mature oilfields. It is almost universally a technical success when applied, and is reported to be profitable in a vast majority of projects.$^{1,2}$ Even during the 1998–1999 oil price collapse, most CO$_2$ recovery projects continued, although a number acquired new operators.

New CO$_2$ projects are being initiated and new sources of CO$_2$ are being identified every year. The Permian Basin of west Texas and southeast New Mexico is the oil province most active in CO$_2$ usage, yielding about 80% of the oil produced by CO$_2$ injection in the US—29,000 cubic meters per day ($m^3/d$) (180,000 barrels of oil per day (BOPD)). Additionally, there are at least nine other states that have active or planned CO$_2$ projects: California, Colorado, Kansas, Louisiana, Michigan, Mississippi, Oklahoma, Utah, and Wyoming. With increasing natural and manmade (waste industrial products) CO$_2$ sources and pressure to sequester anthropogenic CO$_2$, there will be continuing incentive to increase the use of CO$_2$ for economic benefits.

The use of CO$_2$ is not foolproof, as many CO$_2$ floods display inadequate injectivity and/or poor sweep efficiency. Many reservoirs have not been considered for CO$_2$ flooding because of low fracture pressure, poor injectivity, and/or extreme heterogeneity. The CO$_2$ floods that have not been economic successes are usually the results of poorly understood mechanisms of sweep and displacement efficiency in heterogeneous reservoirs. Factors that increase sweep efficiency also create resistance to flow and limit injectivity. A better understanding of these mechanisms will lead to improved project economics, or prevent implementation of an uneconomic project. This study has continued the investigation of improve sweep efficiency through examining mobility control through CO$_2$ foam and determining causes of injectivity.
changes. Although the purpose of this study was not to judge the economics of systems, the results concentrated on systems, products and methods that have a realistic potential for economic viability.

This report describes new research in CO₂ flooding that is an extension of previous work preformed at the PRRC and elsewhere for understanding and improving CO₂ and other gas injection processes for IOR in heterogeneous reservoirs. It is more crucial than ever that research organizations and the DOE work with US operators on IOR techniques for optimizing CO₂ injection, in order to maximize domestic hydrocarbon reserves. The completion of this project results in the expansion of the range of reservoirs amenable to CO₂ flooding. This research is a direct result of interaction with CO₂ operators—it focused on solving the most important ongoing technical challenges in CO₂ flooding. Thus, developments from the past, present and future projects are an asset to the economic and strategic future of the US.

Results of previous work have been described in reports to the DOE, in papers presented to the Society of Petroleum Engineers (SPE), and in other conference proceedings and refereed publications. A summary of resent accomplishments can be obtained from DOE Annual and Final Project Reports.3-6 These reports covered specific topics such as: injectivity, phase behavior and multiphase flow, pressure effects, mobility control and foam properties, selective mobility reduction, foam mechanisms, mixed surfactants and sacrificial agents, gravity drainage, imbibition, interfacial tension, field foam modeling and history matching, numerical methods, and CO₂ reservoir injection studies.

This report summaries results of this project taken from Annual Reports,7-9 published work from refereed journals and conference presentations,10-26 and yet unpublished work. Areas of interests are: 1) mobility control, 2) understanding and mitigation of reduced injectivity, and 3) modeling process mechanisms.

Despite favorable characteristics of CO₂ for IOR,27 CO₂ floods frequently experience poor sweep efficiency caused by gas fingering and gravity override, augmented by reservoir heterogeneity,28 and low productivity caused by lower-than-expected injectivity. Poor sweep efficiency results from a high mobility ratio caused by the low viscosity of even high density CO₂ compared to that of water or oil. The effectiveness of water injection alternating with gas (WAG), a common process used for mobility control during CO₂ floods, is reduced by gravity segregation between water and CO₂ and amplified by permeability differences. Foaming agents
introduced in the aqueous phase control mobility. However, costs incurred by the loss of expensive chemicals to adsorption on reservoir rock often exclude this potentially beneficial option for many well operators. This work demonstrates systems with lower concentrations of good foaming agents that will reduce cost. These systems are derived using a sacrificial agent or a cosurfactant that shows synergistic improvements when mixed with the good foaming agents.

The WAG process frequently reduces injectivity more than expected and the addition of mobility control agents inherently compounds this problem. Normally, improved mobility ratios reduce injectivity, and for this purpose it is critical that the two effects be optimized together. Improved injectivity also result from the lower chemical concentrations and through some of the synergistic improvements using the cosurfactant systems mentioned above.

Some of the beneficial results of this project are:

- Identification of the extent that various properties affect foaming agent adsorption, i.e.: rock type, surfactant type, surfactant concentration, co-surfactants, sacrificial agents, brine salinity, pH, and temperature.
- Understanding of the extent of synergistic effects on adsorption and desorption in dual chemical systems for five powdered minerals and three rock types.
- Identification of parameters that change injectivity and improve sweep efficiency.
- Identification of causes of injectivity changes: fines migration, permeability changes, dissolution, precipitation, stress/pressure gradient, phase behavior, flow rate, etc.
- Development of models to predict advancing rates of individual components in mixed chemical systems with adsorption and desorption kinetic and equilibrium rates, foam behavior in heterogeneous systems, and injectivity.

Project results have immense consequences for the future of IOR. Parameters determined will result in more efficient CO₂ flooding in heterogeneous reservoirs and include the following benefits:

- Extending the life of the petroleum reservoir, maintaining or increasing employment, and increasing oil recovery.
- Expanded range of reservoirs amenable to CO₂ flooding, and
- Reduction of chemical cost: optimizing oil saturation tolerance of foam, decreasing primary foaming agent adsorption, and decreasing required primary foaming agent concentration.
- Improved sweep efficiency using SMR foam to decreased CO₂ mobility,
• Delayed production of CO$_2$ and increased retention of CO$_2$ in the reservoir (sequestration),
• Improved injectivity of CO$_2$ and water,
• Improved CO$_2$ flooding predictions, and
• Decrease in the mobility of CO$_2$ during the alternate injection of brine and CO$_2$. 
EXECUTIVE SUMMARY

This document is the Final Report for the U.S. Department of Energy under contract No. DE-FG26-01BC15364, a three-year contract with a no-cost extension entitled: “Improving CO2 Efficiency for Recovering Oil in Heterogeneous Reservoirs.” The research improved our knowledge and understanding of CO2 flooding and includes work in the areas of injectivity and mobility control. The bulk of this work has been performed by the New Mexico Petroleum Recovery Research Center, a research division of New Mexico Institute of Mining and Technology. This report covers the reporting period of September 28, 2001 through March 31, 2005.

This report summarizes the work completed under the above-mentioned contract, except for the completion and documentation of a revised version of the U.S. Department of Energy pseudo-miscible simulator, MASTER (Miscible Applied Simulation Technique for Energy Recovery). A topical report on MASTER is forthcoming in mid-2005. This document does not attempt to detail all the work that has been completed. Much of the work from this project has been reported in the three previous annual reports7-9 and various publications,10-26 and thus will not be duplicated here, but generally only summarized for the previously published work.

Chapter 1 summarizes a survey performed for all the CO2 injection projects in the Permian Basin. Engineers working on each project for those companies that would allow it were interviewed during this project. The coverage was not as good as that hoped for, because two major players did not choose to be interviewed. These represented almost 40% of the properties. Information for these was obtained best we could from outside sources. Even excluding these, a good cross section was obtained from more than 60% of the companies ultimately surveyed. The first Annual Report contains a literature review that, with a publication, summarizes the technical state of CO2 injection in the Permian Basin as well as areas where further research is the most critical.

Chapter 2 covers CO2-brine-reservoir rock interactions. This study evolved from research designed to understand causes of greater than expected injectivity losses often occurring during water alternating with gas (WAG) in CO2 injection projects. The dissolution of carbonates near the wellbore injection and precipitation of carbonates occur as the fluid moves from the near wellbore region, with subsequent deposition as the fluid becomes supersaturated with dissolved
solids with pressure drop. This dissolution appears to occur in the field. The evidence of precipitation in the field apart from permanent reduction in injectivity in many CO$_2$ WAG projects has not been identified.

Chapter 3 summarizes the work that has been performed over the past several years to determine possible injectivity and productivity reduction due to high flow rate in the near-wellbore regions. High flow rates are evident especially in the production wells at CO$_2$ breakthrough. This causes increased pressure drop due to non-Darcy flow behavior. This reduction does not appear to be permanent, but can cause reduction in production after CO$_2$ breakthrough and related well damage. If near-wellbore conditions are at or near the critical conditions for CO$_2$, cooling can occur that further limits production and might damage the near-wellbore region. This cooling was seen both experimentally and in a CO$_2$ production well.

Chapter 4 summarizes work in the areas of foam stability, interfacial tension, surfactant adsorption and desorption, and mobility control. Parameters that were studied that affect foam stability included: pH, brine salinity, brine composition, temperature, pressure, and surfactant concentration and type. Surfactant adsorption and desorption kinetics and equilibrium were studied as a function of surfactant concentration and type, temperature, pH, brine composition and salinity, and rock and mineral type.

Chapter 5, “Technology Transfer,” summarizes the numerous papers, reports, presentations, and workshops as a result of research performed under this contract.
EXPERIMENTAL

Equipment

Corefloods. Two types of corefloods were performed. The first series were about 5 cm in diameter by at least 15 cm long, used to determine rock-brine-CO2 interactions. The second used a triaxial overburden pressure system for determining effects of overburden and high fluid flow rates. A simplified diagram of the apparatus used for the first type of corefloods is illustrated in Fig. 1. Large volumes of brine and CO₂ are supplied from high-pressure floating piston accumulators that are driven by external high-pressure syringe pumps. These pumps are late models with high accuracy digital control and may be configured by the system plumbing for continuous flow or alternating flow to simulate any desired injection scheme. Oil injection was accomplished through a metering pump connected by a valve ahead of the core. System pressure was maintained by a backpressure regulator (BPR) at the core outlet. Each accumulator pressure was maintained by an individual BPR in order to precisely control fluid density and avoid any fluid surges due to multiphase flow effects. System pressures were measured by absolute and differential pressure transducers and a computer controlled data acquisition board logged the data.

BSE imaging and compositional analysis was performed on pre-flood samples of each core and on a number of samples from along the length of each flooded core. The electron microprobe (model SX-100) utilized three wavelength-dispersive spectrometers, and an accelerating voltage of 15 kV and 20 nA beam current.

The second series of corefloods were performed in order to simulate high velocity fluid flow at the near-wellbore region, an experimental system was designed that could vary flow rate, temperature, and axial and radial pressures. Figure 2 is a schematic of the system. It has the following features:
1. Independent axial and radial stresses up to 10,000 psi; independent inlet and outlet backup pressures up to 5,000 psi;
2. Controlled heating and cooling of the injection pump, the tubing and the core up to 200°F; and
3. Pump rate from 0 to 10,000 cc/hr, and injection pressure from 10 to 3750 psi.
Tests were done on Indiana limestone, Berea sandstone, and Dakota sandstone. Samples of 1 in. diameter by 2 in. long were drilled, flushed with 5–10 pore volumes (PV) of tetrahydrofuran (THF), and oven-dried at 100°F for two days before use. The key part of this experimental system is the triaxial core holder. Figure 3 shows the structure of the core holder used in this research. The sample was sealed by the rubber sleeve in the radial direction and by the end plugs in the axial direction.

![Core Flooding System Diagram](image)

**Fig. 1.** The coreflooding apparatus is set up for alternate or co-injection of two fluids. The effluent can be sampled under ambient or system (installed for last two experiments) conditions.
Fig. 2. Experimental system.

Fig. 3. Triaxial core holder.
**IFT and Foam Stability Measurement Methods.** Interfacial tension (IFT) is a measurement of the cohesive energy present at an interface, expressed in either energy/area or force/length. The common units for surface tension are milliNewtons/meter (mN/m) or dynes/centimeter.

The drop weight method of measuring the interfacial tension of liquid with respect to air (dense CO₂ in CO₂ foam) consists of determining the number of drops falling/rising from a capillary (Fig 4). The drops are allowed to fall into a container until enough have been collected so that the weight per drop can be determined accurately. The principle of the method is that the size of the drop falling from a capillary tube depends on the surface tension of the liquid. A considerable portion of the drop (up to 40%) may remain attached to the capillary tip after the drop detaches. This effect is compensated with Harkin-Brown correction factor, \( f \),\(^{29,30}\) as described by Adamson\(^30\) (Fig 5),

\[
W = \Delta mg .......................................................1
\]

where \( W \) is the weight of the drop, \( \Delta m \) is the differential mass between the two fluids in grams; \( g \) is the gravitational force, cm/sec\(^2\); \( r \) is the needle radius, cm; \( \sigma \) is the IFT, dynes/cm. Also

\[
\Delta mg = 2\pi r \sigma f...................................................2
\]

or

\[
\frac{4}{3} \pi R^3 (\rho_{surf} - \rho_{CO₂}) g = 2\pi r \sigma f .........................3
\]

where \( R \) is the average bubble radius, cm; \( \rho \) is the fluid densities, g/cm\(^3\); and \( f \) is the Harkin-Brown correction factor.

In this work, the calculation of the IFT measurements is analogous to that of the drop weight method.\(^{29,30}\) The rate of introducing dense CO₂ is determined by the aqueous phase withdrawal rate. The number of produced bubbles per time period is recorded, from which the volume and radius of each bubble are calculated. The correction factor takes into account effects of attraction to the end of the tube and imperfections in the system, generally ranging from 0.5 to 1.0 (see Fig. 5). The correction factor in most of the experiments in this study range from 0.5 to 0.7. The drop weight method is fairly accurate and perhaps the most convenient in the laboratory for measuring both gas-liquid and liquid-liquid interfacial tensions. Design and construction of the apparatus (Fig. 6) was based on this method.

Like other types of colloidal dispersions, foams are not thermodynamically stable,. Eventually they collapse, but it is possible to make surfactant-stabilized, static bubbles and films that endure for months or even years under suitable conditions. Though foams are not
thermodynamically stable, they can exhibit kinetic stability, which is defined here as the CO₂ foam kinetic stability. Equation 4 shows how CO₂ foam stability was calculated from foam height measurements.

\[
\text{CO}_2 \text{ foam stability} = 100 - \left( \frac{H_1(t)}{H_1(0) + H_2(0)} \times 100 \right) \quad \text{........... 4}
\]

where \( t \) is time, \( H_1(t) \) is the height of the CO₂ layer with time, \( H_1(0) \) is the initial height of the CO₂ layer, and \( H_2(0) \) is the initial height of the foam layer.

![Fig. 4. Illustration of needle and drop.](image)

![Fig. 5. Harkins-Brown correction factor for drop-weight method (after Adamson).](image)
Adsorption. Two dynamic flow methods, circulation and flow-through experiments, were used to study surfactant adsorption and desorption onto three core types; these methods have been detailed in an earlier report. A static method was also used to study surfactant sorption onto five powdered minerals.

The circulation method (Fig. 8) was used: (1) to study the kinetics of surfactant adsorption onto reservoir core; (2) to establish the adsorption/desorption isotherm; and (3) to study the effects of salt type and concentration and temperature on surfactant equilibrium adsorption density. The apparatus consists of a flask with a solution of known weight and concentration; a core of known PV, bulk volume and weight; and a metering pump and some tube lines connecting each part. A known initial concentration of surfactant solution was circulated through the core at constant temperature and injection rate. For adsorption kinetic
experiments, two samples were taken from the flask to analyze surfactant concentration at predetermined intervals. For adsorption/desorption isotherm experiments, two samples were taken out for the analysis of concentration and were replaced by equal volumes of surfactant solution (adsorption process) or were replaced by equal volumes of brine (desorption process) at predetermined intervals. For the experiments of salt type and concentration effect, surfactant solution prepared by distilled water was first circulated through the core for 48 hours, then two solution samples were taken for analysis and a specific amount of salt was added to the solution in the flask. This was repeated several times until reaching the predetermined maximum salt concentration.

The flow-through method (Fig. 9) was used to determine desorption kinetics and to study the effect of postflush rate and interruption on the desorption process. Brine was directly injected through the core and the effluent was kept in a series of test tubes for later determination of the effluent solution. The amount of surfactant adsorbed onto the core during desorption process was determined using the equations described in earlier reports paper.7-9

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**Fig. 8. Circulation schematic for sorption tests.**

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Static experiments were performed to study surfactant adsorption onto pure powdered minerals. A specific volume of solution with a desired surfactant concentration was pipetted into a bottle. The bottle and a mineral were kept in a thermostatic bath to allow the solution to achieve thermal equilibrium. Then a weighed amount of mineral was put into the bottle and vigorously agitated for about a minute. This was then placed into a mechanical shaker and agitated continuously for 24 hrs and then left undisturbed for another 48 hrs. A sample was removed and centrifuged at 2000 rpm for 20 min, and then the supernatant solutions were separated by decantation from the solids after gravity sedimentation. The concentration difference between the stock and the sample were used to evaluate the adsorption density. Figure 10 is the schematic diagram of the static experiment.
Materials

Chemicals. The calcium lignosulfonate (CLS) used in this study was Lignosite® 100, which was obtained from the Georgia-Pacific Corporation. The product provided is a powder produced by sulfonation of softwood lignin. Chaser CD1045 (CD), the good foaming agent, is Chaser CD1045™, which was identified as one of the best foaming agents in several earlier studies3-6 and was supplied by Chaser International as 46.7 wt% active aqueous solution. Dimidium Bromide-Disulphine Blue Indicator, used for anionic surfactant determination, supplied by BDH Laboratory Supplies, was used to detect CD. HPLC grade chloroform containing approximately 0.75% ethanol as a preservative was used as part of the CD process. A 2% synthetic brine (1.5 wt% NaCl and 0.5 wt% CaCl₂) was prepared and used in all solutions. Sodium chloride (NaCl) and calcium chloride dehydrate (CaCl₂·2H₂O) are both A.C.S. reagent grade (98+%), the nitric acid (HNO₃) is 70% nitric acid and the sodium hydroxide (NaOH) is A.C.S. reagent grade (98.6%).

Adsorbents. Five minerals common in oil reservoirs were used as adsorbents: silica, kaolinite, montmorillonite, calcite, and dolomite. All minerals are non-porous. Silicates are oxides of silicon with traces of other elements constructed of SiO₄ tetrahedra that share all four corners with other SiO₄ tetrahedra. Kaolinite is 2Al₂Si₂O₅(OH)₄ or 2SiO₄·Al₂O₃·2H₂O per unit cell, with no isomorphous substitutions. The montmorillonite is a Wyoming bentonite composed primarily of sodium montmorillonite. It is a hydrous aluminum silicate approximately represented by the formula: 4SiO₂·Al₂O₃·2H₂O+water; but with some of the aluminum cations, Al³⁺, being displaced by magnesium cations, Mg²⁺. The name sodium montmorillonite refers to clay minerals in which the loosely held cation is the Na⁺ ion. Calcite and dolomite are carbonate minerals with similar structures. Calcite is formed by alternate layers of calcium ions and carbonate ion groups. Dolomite is composed of alternate layers of calcium ions, magnesium ions, and carbonate ions. Both solids are salt type minerals; therefore, their solubility in water is higher than oxides and silicates. Three types of porous media were applied: Berea sandstone, Lockport sandstone and Indian limestone. There were no visual fractures in these cores.
**Analytical Method to Detect Surfactant Concentration.** CD is a multi-component formulation, colorless in solution. One analytical method suggested by the manufacturer and used in this study is a colorimetric method. Since CD is colorless, an indicator solution of dimidium bromide-disulphine blue is used. The procedure is described in more detail in an earlier publication.\(^3\)\(^-\)\(^6\) The absorbance of CD solution has an excellent absorbance peak at 523 nm that has minimal interference with co-surfactant CLS.

*Calcium lignosulfonate (CLS) calibration curve.* A spectrophotometer was used to determine the concentration of CLS. The 283 nm wavelength was used in all measurements to analyze the CLS concentration. CLS had earlier been determined to have the maximum absorbance in the neighborhood of 283 nm. To calculate CLS concentration, a standard calibration curve of CLS in 2 wt% brine was established, shown in Fig. 11. CLS was diluted to less than 400 mg/l before its concentration was measured because concentration versus absorbance is linear at concentrations below 400 mg/l.

![CLS standard curve at 283 nm (2% brine).](image)

The absorbance of CLS prepared by different salt types and concentrations was measured using a spectrophotometer. Figure 12 shows the effect of salt type and concentration on CLS absorbance at the wavelength of 283 nm. Both the type and concentration of salt have influence on CLS absorbance. Table 1 lists the fit equations of CLS standard curve at different salt types and concentrations. The absorbance of 200 mg/l of CLS solution was measured at different pH
conditions, shown in Fig. 13. Under these conditions, solution pH has negligible effect on the absorbance of CLS.

Fig. 12. Effect of salt on CLS absorbance at 283 nm.

Table 1. Equations of CLS Standard Curves with Different Salts

<table>
<thead>
<tr>
<th>Salt</th>
<th>Equations of standard curves</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>( {ABS} = 0.0084 \cdot {Conc.} + 0.0075 )</td>
<td>0.9985</td>
</tr>
<tr>
<td>5% NaCl</td>
<td>( {ABS} = 0.0082 \cdot {Conc.} + 0.019 )</td>
<td>0.9982</td>
</tr>
<tr>
<td>10% NaCl</td>
<td>( {ABS} = 0.0086 \cdot {Conc.} + 0.0202 )</td>
<td>0.9964</td>
</tr>
<tr>
<td>5% CaCl₂</td>
<td>( {ABS} = 0.0084 \cdot {Conc.} + 0.0184 )</td>
<td>0.9977</td>
</tr>
<tr>
<td>10% CaCl₂</td>
<td>( {ABS} = 0.0087 \cdot {Conc.} + 0.0113 )</td>
<td>0.9985</td>
</tr>
</tbody>
</table>

Fig. 13. Effect of pH on CLS absorbance at the wavelength of 283 nm.
CD solution is colorless, so an indicator solution must be used to treat it before measurement the colorimetric method using a spectrophotometer can be employed. It is suggested by the supplier that dimidium bromide-disulphine blue stock solution be used as an indicator. The indicator solution used to measure CD concentration states that it is a solution for anionic surfactant determination. Therefore, it is assumed that CD is an anionic surfactant. The procedure to determine CD concentration have been discussed in earlier publications.3-9

The absorbance of CD solution prepared with 2 wt% brine was measured by a spectrophotometer, which was set to scan through a set range of wavelength from 0 to 700 nm. CD solution has three peaks in the measured range of wavelength: 295 nm, 406 nm and 520 nm. Table 2 gives a series of absorbance measurement results of CD solution with different concentration.

<table>
<thead>
<tr>
<th>Conc.</th>
<th>Absorbance at Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>295 nm</td>
</tr>
<tr>
<td>10</td>
<td>0.1017</td>
</tr>
<tr>
<td>50</td>
<td>0.2405</td>
</tr>
<tr>
<td>100</td>
<td>0.4135</td>
</tr>
<tr>
<td>150</td>
<td>0.5970</td>
</tr>
<tr>
<td>200</td>
<td>0.8120</td>
</tr>
<tr>
<td>250</td>
<td>0.8750</td>
</tr>
<tr>
<td>300</td>
<td>1.0380</td>
</tr>
<tr>
<td>400</td>
<td>1.5090</td>
</tr>
<tr>
<td>500</td>
<td>1.7400</td>
</tr>
<tr>
<td>600</td>
<td>2.1560</td>
</tr>
</tbody>
</table>

For the peak of 406 nm, the absorbance is very small and is not linear with CD concentration. For the 295 nm and 523 nm peaks, the absorbance is linear with CD concentration if the concentration is below 600 mg/l, as shown in Figs. 14 and 15. The standard equations are:
At 295 nm: \[ \text{Conc.} = 299.83 \cdot \text{ABS} - 27.41 \quad R^2 = 0.9938 \]

At 523 nm: \[ \text{Conc.} = 2493.77 \cdot \text{ABS} + 61.10 \quad R^2 = 0.9964 \]

where \( \text{Conc.} \) refers to CD concentration and \( \text{ABS} \) refers to the absorbance value of CD solution at 295 nm or 523 nm.

Fig. 14. Standard curve of CD at 295 nm.

Fig. 15. Standard curve of CD at 523 nm.
The absorbance of CD solution at the peak of 523 nm was selected as an evaluation standard for the CD concentration because CLS is mixed with CD as a sacrificial agent for some tests in this study and it has an absorbance peak at the wavelength of 283 nm, which interferes with the peak of CD at 295 nm.

**Effect of salt and pH on the absorbance of CD solution.** Increasing the concentration of CaCl$_2$ and NaCl will decrease absorbance of CD at 520 nm with CaCl$_2$ having a greater impact, shown in Figs. 16 and 17. Figure 18 shows the influence of pH on the absorbance of CD. Within the range of tested pH and concentration, pH has negligible effect.

![Fig. 16. Absorbance of 100mg/l CD prepared with different brine.](image1)

![Fig. 17. Absorbance of 200 mg/l CD prepared with different brine.](image2)
Fig. 18. Effect of pH on CD absorbance at wavelength of 520 nm.

**Mixture of CD and CLS.** CLS was tested as a sacrificial agent or a co-surfactant of CD in earlier research.\(^{14,23}\) This study further investigated the effect of CLS on CD adsorption. Thus, it was necessary to know whether one agent (CD or CLS) would influence the measurement of another agent. Figure 19 shows the influence of CD on CLS absorbance at the wavelength of 283 nm. The solution was prepared with 2% brine. CD has negligible effect on CLS absorbance at the wavelength of 283 nm when CD concentration is 200 mg/l. In this study, the influence of CD on CLS was ignored if the CD concentration was below 200 mg/l in the measured solution.

Figure 20 presents the influence of CLS on CD absorbance at the wavelength of 520 nm. The solution was prepared with brine. The colorimetric method was used to determine CD concentration. It was found that precipitate was produced if CLS was too high. Increasing CLS concentration decreased the absorbance of CD.

Although CLS in CD solution influences the absorbance of CD, CD concentration has a linear relationship with its absorbance at the wavelength of 520 nm for a constant concentration of CLS. Table 3 shows the fit equations of CD standard curves at different CLS concentration s and R square values. These results show that using the standard equation of CD without CLS to calculate CD concentration in their hybrid system will overestimate the CD concentration.
Fig. 19. Effect of CD on CLS absorbance at 283 nm.

Fig. 20. CD standard curve at different concentration of CLS.

Table 3. Equations of CD Standard Curves at Different Concentrations of CLS

<table>
<thead>
<tr>
<th>No.</th>
<th>CLS Conc. (mg/l)</th>
<th>Equations of standard curves</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>Conc. = 2057.61 · ABS + 56.17</td>
<td>0.9991</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>Conc. = 2136.49 · ABS + 51.80</td>
<td>0.9987</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>Conc. = 2145.46 · ABS + 60.16</td>
<td>0.9996</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>Conc. = 2406.74 · ABS + 57.67</td>
<td>0.9974</td>
</tr>
<tr>
<td>5</td>
<td>5000</td>
<td>Conc. = 3610.11 · ABS + 92.99</td>
<td>0.9979</td>
</tr>
</tbody>
</table>

Notes: ABS refers to the absorbance value measured at 520 nm from a spectrophotometer and CONC. refers to CD concentration.
Based on the results shown in Figs. 21 and 22, a method was developed to calculate CD concentration when it is mixed with CLS. Figure 21 shows that the line slope and CLS concentration from equations listed in Table 4 have a good linear relationship. The fit equation is:

\[ \text{Slope} = 0.3096 \cdot \text{Conc.} + 2062.6 \quad (R^2 = 0.9951) \]

Figure 21. The relationship between CLS concentration and slope of fit equations.

Figure 22 shows that the intercept and CLS concentration are also linear. The fit equation is:

\[ \text{Intercept} = 0.0078 \cdot \text{Conc.} + 53.4467 \quad R^2 = 0.9690 \]

For many experiments in this study, CD concentration was measured from the mixture of CD and CLS. Because CD has negligible effect on CLS absorbance (shown Fig. 20), the CLS standard calibration curve without CD was used directly to calculate CLS concentration. For CD concentration calculations, new calibration equations were calculated from Eqs. 7 and 8. For example, if the CLS concentration is 2000 mg/l, the corresponding standard curve should be obtained according to the following steps:

1. Use Eq. 7 to calculate slope: \( y = 0.3096 \times 2000 + 2062.6 = 2681.8 \);
2. Use Eq. 8 to calculate intercept: \( y = 0.0078 \times 2000 + 53.4467 = 69.0467 \); Therefore
3. The standard calibration equation is: \( \text{Conc.} = 2681.8 \times \text{Abs.} + 69.0467 \)

Figure 23 shows the standard curves of CD solution at different concentration of CLS. The solution was prepared with distilled water. Table 4 lists the fit equations of these standard curves.
Table 4. CD Standard Curves at Different Concentrations of CLS (Distilled Water)

<table>
<thead>
<tr>
<th>CLS Conc. (mg/l)</th>
<th>Equations of standard curves</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Conc. = 1791.8 · ABS + 45.514</td>
<td>0.9988</td>
</tr>
<tr>
<td>100</td>
<td>Conc. = 1838.2 · ABS + 44.46</td>
<td>0.9971</td>
</tr>
<tr>
<td>500</td>
<td>Conc. = 2013.3 · ABS + 39.477</td>
<td>0.999</td>
</tr>
<tr>
<td>1000</td>
<td>Conc. = 2159.7 · ABS + 40.676</td>
<td>0.9944</td>
</tr>
<tr>
<td>2500</td>
<td>Conc. = 2601 · ABS + 41.231</td>
<td>0.9451</td>
</tr>
<tr>
<td>5000</td>
<td>Conc. = 4481.8 · ABS + 96.534</td>
<td>0.9909</td>
</tr>
</tbody>
</table>

The same method as the hybrid system prepared with brine can be used to determine CLS and CD concentration when they are mixed. Figure 24 shows the relationship of slope/intercept with CLS concentration.

The following equations can be used to calculate standard curve of CD at different CLS concentrations.

\[
\text{Slope} = 8 \times 10^{-5} \cdot \text{Conc}^2 + 0.1378 \text{Conc} + 1855.3 \quad R^2 = 0.9953 \quad \text{..................9}
\]

\[
\text{Intercept} = 5 \times 10^{-6} \text{Conc}^2 - 0.0127 \text{Conc} + 45.87 \quad R^2 = 0.9951 \quad \text{...... 10}
\]
Fig. 24. Calculation of slope and intercept at different CLS.

Slope = 8E-05x^2 + 0.1378x + 1855.3

Intercept = 5E-06x^2 - 0.0127x + 45.87
RESULTS AND DISCUSSION

Chapter 1: State of the Industry in CO₂ Injection

Chapter 1 summarizes a survey performed for all the CO₂ injection projects for improved oil recovery (IOR) in the Permian Basin. Engineers working on each project for those companies that would allow it were interviewed during this project. The coverage was not as complete as had been targeted because two major players chose not to be interviewed. These represented almost 40% of the properties. Information for these was obtained from outside sources and thus not as complete and up to date as the others. Even excluding these, a good cross-section was obtained from surveyed units, which represented more than 60% of the projects. The First Annual Report contains a literature review summarizing the technical state of CO₂ injection in the Permian Basin and pointing out areas where further research is the most critical. The literature review is also summarized in a publication, “Long-term CO₂ Storage: Using Petroleum Industry Experience,” in: Carbon Dioxide Capture for Storage in Deep Geologic Formations, Volume 2, R.B. Grigg, Thomas, D.C. and Benson, S.M. (Eds.), 2005 Elsevier Ltd.

There is significant experience and knowledge in the oil and gas industry to separate, compress, transport, inject, and process the quantities of CO₂ that are envisioned for CO₂ storage, Improvements will occur as incentives, time and fluid volumes increase.

In some cases, certain phenomena that have been noted during waterflood were not included in simulating CO₂ processes—an omission that can prove, and has proven in some cases, to be detrimental to the success of the project. When the reservoir is well understood, CO₂ has performed as expected. Also, the thermodynamic phase behavior of CO₂ must be honored in predictive models. High-pressure CO₂ performs as expected: it mobilizes oil, dissolves into brine, and promotes dissolution of carbonates. Brine can become supersaturated with dissolved solids; when pressure drops as it advances through the reservoir, precipitants can form. However, the kinetics of dissolution and precipitation under many reservoir conditions requires further study.

In the time frame wherein CO₂ has been actively injected into geological formations, seals appear to have maintained their integrity and retained CO₂. Monitoring and verification of
CO₂ flow in geological formations is critical to verification of storage, but additional research and monitoring demonstration are needed.

Summary
Listed below are major lessons learned from CO₂ injection into geological formations for IOR and that are most applicable to CO₂ storage.

1. Significant experience and knowledge in the industry exists to separate, compress, transport, inject, and process the quantities of CO₂ that are envisioned for CO₂ injection into geological formations for IOR or hydrocarbon storage. As the volume of injected CO₂ increases, significant technological improvements are expected.

2. Monitoring and verification of CO₂ flow in geological formations is in the infancy of its development.

3. Experience has shown that CO₂ goes where expected. The challenge is developing detailed reservoir characterizations and honoring them. In some cases, phenomena have been noted during waterflood, but not included when simulating the CO₂ oil recovery process, resulting in surprises during the project that could have been avoided. The phase behavior of CO₂ must be honored as well.

4. CO₂ does what is expected: mobilizes oil, dissolves in brine, and promotes dissolution of carbonates. Through dissolution of reservoir rock as brine flows away from the injector, brine will become supersaturated, the pressure will drop and precipitation will result. The kinetics of these processes under a wide range of reservoir conditions requires further studies.

5. In the short geological timeframe that CO₂ has been actively injected into geological formations for IOR, seals generally are retaining the CO₂ subsurface. Oil reservoir seals, to date are generally performing as expected, but it must be remembered that a maximum of several decades is short compared to the longer time periods required for effective CO₂ storage.
Chapter 2: CO$_2$/Brine/Rock Interaction

Chapter 2 covers CO$_2$-brine-reservoir rock interactions. This research developed out of previous attempts at trying to understand the causes of greater-than-expected injectivity losses that often occur during water alternating with gas (WAG) in CO$_2$ injection projects. The dissolution of carbonates near the wellbore injection and precipitation of carbonates occur as the fluid moves from the near-wellbore region, with subsequent deposition as the fluid becomes supersaturated with dissolved solids with pressure drop. This dissolution appears to occur in the field, but the evidence of precipitation in the field apart from permanent reduction in injectivity in many CO$_2$ WAG projections has not been identified.

2.1 Physical Effects of WAG Fluids on Carbonate Core Plugs

It is a given that carbonate mineral dissolution and deposition occur in a formation in geologic time; these are expected, to some degree, in carbon dioxide (CO$_2$) floods. Water-alternating-gas (WAG) core flood experiments conducted on limestone and dolomite core plugs confirm that these processes can occur over relatively short time periods (hours to days) and in close proximity to each other.

Summary
1. Dissolution features were observed in both the dolomite and limestone cores. In the dolomite core anhydrite dissolution occurred during brine flood and dolomite dissolution occurring during the WAG cycles. In the limestone core the calcite dissolved during the WAG process.
2. In the shorter dolomite core no carbonate deposition was detected, while in the longer limestone core significant carbonate was deposited downstream, indicated by decreased permeability. But in neither case was significant impurity or compositional difference detected with respect to either pre- and postflooding samples or position along the core.
3. In the limestone core both permeability increases and decreases were noted. The permeability increases were caused by dissolution of calcite grains and cement and channel formation. The permeability decreases appear to be caused by precipitation of calcite in the downstream area of the core once a calcium carbonate saturated condition is reached in the WAG fluid.
4. Oil contamination tests performed in both core types showed no evidence that oil contamination would cause permanent permeability reduction. In each case the system returned to pre-oil conditions after CO$_2$ was injected into the system. However an injectivity reduction effect was noted if the oil slug was followed by a brine half-cycle.

**Implications for field injectivity.** What implications do these laboratory tests have for CO$_2$ flooding field projects? Since the cores were only 5 to 20 in. long, they most closely simulate near-wellbore conditions. Dissolution of carbonate or other soluble minerals occurring near-wellbore would increase porosity, permeability, and injectivity. Both dissolution and deposition of carbonate could occur as fluid advances a short distance into the reservoir. As fluid flows away from the wellbore, the carbonate solubility decreases with the rapid pressure drop. If the fluid is at or near saturation then solid mineral phases will precipitate, changing formation porosity, permeability, and/or injectivity. Thus, injectivity can be increasing and decreasing locally and whichever process dominates will be measured at the surface. Though these tests indicate that oil contamination effects should only be temporary near-wellbore, they might have implications deeper into the reservoir.

**2.2 Evaluation of CO$_2$-Brine-Reservoir Rock Interaction with Laboratory Flow Tests and Reactive Transport Modeling**

Injection of carbon dioxide (CO$_2$) into geological formations, already used in IOR, is one method proposed for isolating anthropogenic CO$_2$ from the atmosphere. Determining the viability, risks, and optimal locations for CO$_2$ injection into the subsurface requires detailed knowledge of the complex interactions among CO$_2$, rock matrix, and pore fluids under appropriate in-situ pressure and temperature conditions. Many physical and chemical processes are known to occur both during and after geologic CO$_2$ injection, including diagenetic chemical reactions and associated permeability changes. Although it is commonly assumed that CO$_2$ injected into a reservoir, given enough time, will ultimately become mineralized, the rates of these changes, including CO$_2$ hydration in brines, are known to be relatively slow. Together with hydrated CO$_2$, cations from produced brines may form solid-state carbonate minerals, ostensibly providing permanent sequestration.
We used results of earlier laboratory CO₂-brine flow experiments performed in rock core to calibrate a reactive transport simulator. We are using the calibrated model to estimate in situ effects of a range of possible sequestration options in depleted oil/gas reservoirs. The code applied in this study is a combination of the well known TOUGH2 simulator, for coupled groundwater/brine and heat flow, with the chemistry code TRANS for chemically reactive transport.

Variability in response among rock types suggests that CO₂ injection will induce ranges of transient and spatially dependent changes in intrinsic rock permeability and porosity. Determining the effect of matrix changes on CO₂ mobility is crucial in evaluating the efficacy and potential environmental implications of storing CO₂ in the subsurface.

Summary

Although the TRANSTOUGH model remains in the developmental stages, simulated results compared favorably to experimental results, suggesting that the model accurately simulates CO₂ sequestration under deep reservoir conditions, at least for small spatial scales.

Additional TRANSTOUGH simulations were performed employing a range of geologic media, solution pH, and brine alkalinities. The results indicate that under equivalent volumetric fluid injection of CO₂ and brine, little difference in the magnitude of dissolution occurs with variation in brine pH and alkalinity. The results of the laboratory experiments and the corresponding bench scale numerical simulations suggest that chemical reactivity with the geologic media can be extreme, depending on mineral kinetic reaction rates and the volume of brine fluid present.

Bench scale simulations and laboratory experiments are a necessary first step to better characterization of CO₂-brine-media interactions. Reservoir scale simulations are critical in gaining an understanding of the more applicable large scale effects of heterogeneities that may be incurred from CO₂ injection.

Other Tests

Simulations of a calcite reservoir cross-section model were performed as a basic examination of larger scale processes, paving the way for future reservoir studies. Contrary to the calcite bench scale model, little dissolution occurred in the comparable calcite reservoir scale model. A close
examination near the injection well revealed that as CO$_2$ was injected, the brine solution was forced outward, away from the injection well, causing the saturation of separate phase CO$_2$ to increase locally. As the saturation of separate phase CO$_2$ increased, the mobility of the residual brine solution decreased as a result of decreasing relative permeability and capillary effects. Therefore, simultaneous flushing of several pore volumes of CO$_2$ and brine through the same rock volume did not occur. As a result, little dissolution was predicted in the reservoir as compared to the constant injection bench scale laboratory experiments, suggesting the possibility that matrix changes to the media induced by CO$_2$ injection at the reservoir scale may be minor.

2.3 Laboratory and Model Tests at Reservoir Conditions for CO$_2$-Brine-Carbonate Rock Systems Interactions

Determining the viability of, risks in, and optimal locations for injecting CO$_2$ into the subsurface requires detailed knowledge of the complex interactions among CO$_2$, rock matrix, and pore fluids under appropriate in-situ pressure and temperature conditions. Many physical and chemical processes are known to occur both during and after geologic CO$_2$ injection, including diagenetic chemical reactions and associated permeability changes. Although it is commonly assumed that CO$_2$ sequestered in this way will ultimately become mineralized, the rates of these changes, including CO$_2$ hydration in brines, are known to be relatively slow. Together with hydrated CO$_2$, cations from brines may form solid-state carbonate minerals, ostensibly providing permanent sequestration.

Results of a series of laboratory CO$_2$-brine flow tests in rock core were used to calibrate a recently coupled reactive transport simulator, TRANSTOUGH. TRANSTOUGH is a combination of the TOUGH2 simulator, for coupled groundwater/brine and heat flow, with the LANL chemistry code TRANS for chemically reactive transport. This paper presents laboratory test results and compares these to the model predictions. Variability in response among rock types suggests that CO$_2$ injection will induce ranges of transient and spatially dependent changes in intrinsic rock permeability and porosity. Determining the effect of matrix changes on CO$_2$ mobility is crucial in evaluating the efficacy and potential environmental implications of storing CO$_2$ in the subsurface.
Summary
The TRANSTOUGH model was shown to quantitatively replicate the outcome of the dolomite-anhydrite and the limestone, CO₂ and brine injection experiments. The major controlling influence was found to be lithology type, while in the case of the quartz-evaporite media, dissolution may be time-dependent. A secondary influence was the magnitude of fluid flushed through the media in relation to the reactive surface area. Although the TRANSTOUGH model remains in the developmental stages, simulated results compared favorably to experimental results, suggesting that the model could accurately simulate CO₂ sequestration under known conditions. As bench scale simulations and laboratory experiments are a necessary first step to better characterization of CO₂-brine-media interactions, reservoir-scale simulations are critical in gaining an understanding of the more applicable large scale effects of heterogeneities that may be incurred from CO₂ injection.

Laboratory tests show that dissolution does occur and that at least some carbonates can precipitate in a relatively short distance. Dissolution and precipitation can be detected from porosity, permeability, and compositional changes in the reservoir rock. The introduction of tracers that will form carbonates into the brine was successfully tested. Both in the laboratory tests and the simulation model, deposition of dissolved carbonates in a saturated solution seem to create a deposition bank at the leading edge of the wormhole.

2.4 Co-Injected CO₂-Brine Interactions with Indiana Limestone
Limestone was coreflooded with co-injected carbon dioxide (CO₂) and brine at reservoir pressure and temperature. Metal chlorides were added as tracer components to the injection brine and appeared in quantities well above natural levels in deposited carbonates. Core segment porosity and permeability are reported to indicate dissolution and deposition. Finally, the core was sectioned and analyzed by chemical and back-scattered electron imaging (BSEI) and chemical titration for compositional changes.

Porosity and permeability increased and decreased corresponding to suspected dissolution and precipitation. Qualitative and quantitative analyses confirmed the deposition of trace metals within deposited carbonate material, providing direct evidence of deposition. These phenomena can occur during CO₂ injection into carbonate geological formations, whether for
improved oil recovery (IOR) or greenhouse gas sequestration. With IOR the concern is for injectivity changes, while the issues for sequestration are long-term storage capacity and seal integrity.

Summary
1. Dissolution of carbonates at reservoir conditions during co-injection of CO$_2$ and brine was confirmed visually, and by porosity and permeability increases.
2. Deposition of carbonates was indicated by porosity and permeability reduction.
3. Deposition was determined by BSEI identification of high Z areas and reached a maximum near the end of the solution channel.
4. The composition of deposits was strongly influenced by the tracer brine composition.
5. Deposition and dissolution were found to occur in close proximity.

2.5 CO$_2$/Brine/Carbonate Rock Interactions: Dissolution and Precipitation

Five large-core flooding experimental series were performed on quarried and reservoir carbonates (limestone and dolomite) with co-injected or alternating injections of CO$_2$ and brine at reservoir conditions. Metal chlorides were added as tracer components in injection brines for three tests, appearing in quantities well above natural levels in deposited carbonates in one test. Core segment porosity and permeability are reported to indicate dissolution and deposition. Cores were sectioned and analyzed by chemical and back-scattered electron imaging (BSEI) and chemical titration for compositional changes. In two tests fluid samples taken at reservoir conditions and neutron computed tomography (CT) were used to monitor changes in in-situ fluid compositions and the development of the 3-D porosity structure of the flooded cores, respectively.

Dissolution of carbonates at reservoir conditions during co-injection of CO$_2$ and brine was confirmed by porosity and permeability increases, neutron CT, and brine compositional analysis performed on effluent brine samples obtained at reservoir conditions. When deposition occurred it was indicated by porosity and permeability reductions in downstream core, BSEI identification, and modeling. The composition and extent of deposits was strongly influenced by the brine composition. Deposition and dissolution were found to occur in close proximity. The
results are being used to calibrate a CO$_2$ model coupling multiphase flow to chemical reactions that will be used to predict in situ dissolution and deposition related to CO$_2$ geologic sequestration.

### Table 5. Brine Compositions Used in the Series of Five Large-Core Floods

<table>
<thead>
<tr>
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<th>Reservoir Brine #2</th>
<th>Brine #3 Tracer #1</th>
<th>Brine #4 Tracer #2</th>
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**COREFLOOD A – INDIANA LIMESTONE**

The first coreflood was on quarried Indiana limestone at 2000 psig and 100°F using Reservoir Brine #1 (Table 5). Brine was injected alternating with CO$_2$ (WAG). After injecting several hundred pore volumes (PV) a 25-cm long solution channel had formed while the permeability of the whole core was essentially the same as the fresh core (Figs. 25 and 27). There was no evidence of plugging, though the permeability of the second core half was reduced by about half, which is an indication of deposition (Fig. 26). Using BSEI and compositional analyses, all possible deposition had the same composition as the fresh core; thus in Coreflood C metal tracers were added to aid in identifying deposition.

![Fig. 25. Post-WAG Indiana limestone dissolution channel extends from inlet face into first half of core length (~ 25 cm).](image)
Fig. 26. Second half of the core did not have a solution channel (last ~ 25 cm). Final permeability of unchannelled core, $k=19.5$ mD. Initial perm in this same region before WAG ~ 36 mD.

Coreflood B – San Andres Dolomite

The second coreflood was on San Andres core from the Seminole field in west Texas (Fig. 28). The primary component of the San Andres is dolomite. A significant increase in porosity occurred during the brine flood (Fig. 29) due to anhydrite dissolution. Brine #2 composition was patterned after Seminole produced water (Table 5). Extensive porosity and permeability increases occurred during the WAG portion of the flood with dissolution of dolomite and further dissolution of anhydrites (Figs. 30 and 31).
Fig. 28. Pre-flood dolomite, Seminole San Andres, Gaines County TX. Vuggy anhydritic, very fine grain dominated packstone, anhydrite nodules, and stylolites.

Fig. 29. Post waterflood sectioned core after brine flood showing anhydrite dissolution.
Fig. 30. Post-WAG Seminole San Andres core showing dolomite dissolution with additional anhydrite dissolution.

Fig. 31. Measured and calculated porosity and permeability during the flooding of San Andres dolomite.

COREFLOOD C – INDIANA LIMESTONE WITH BRINE #3 TRACER #1
The third coreflood was on quarried Indiana limestone core (Fig. 32) with a co-injection of brine having high levels of metal tracers manganese and strontium added to the brine as chlorides,
which are naturally found at very low levels in this limestone. The limestone is over 98% calcite (Figs. 37 and 38) in the non-reacted areas. A solution channel formed in the first 15 cm of Segment A (Figs. 33 and 34) while overall permeability and porosity stayed about the same or decreased (Fig. 35). Significant deposits of manganese and strontium occurred as carbonates throughout the core shown in the plot in Fig. 36 and BSE images and quantitative analysis shown Figs. 37 and 38. It was suspected that the system was oversaturated with the tracer carbonates and that in a new system the tracer quantities would be reduced significantly.

<table>
<thead>
<tr>
<th></th>
<th>Diameter [cm]</th>
<th>Length [cm]</th>
<th>Porosity [%]</th>
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<td>17.15</td>
<td>16.91</td>
</tr>
<tr>
<td>Segment B</td>
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<td>39.37</td>
<td>17.54</td>
</tr>
<tr>
<td>Entire Core</td>
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<td>56.52</td>
<td>17.35</td>
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Fig. 32 Pre-flood limestone core.
Fig. 33. Post-flood limestone core sectioned.

Fig. 34. End view of Segment A inlet.

Fig. 35. Permeability results limestone (Coreflood C).
Fig. 36. Cross-section composition for manganese and strontium along the length of both core segments in Coreflood C.

<table>
<thead>
<tr>
<th></th>
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<th>Mg</th>
<th>Mn</th>
<th>Sr</th>
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<tr>
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<td>0.20</td>
</tr>
<tr>
<td>3.</td>
<td>19.4</td>
<td>0.30</td>
<td>79.7</td>
<td>0.28</td>
</tr>
</tbody>
</table>

@ 35 cm zonation

Fig. 37. BSE Quantitative analysis [% as carbonate] for calcium, magnesium, manganese, and strontium.
COREFLOOD D – INDIANA LIMESTONE & COREFLOOD E – LOCKPORT DOLOMITE (both with Brine #4 Tracer #2)

The fourth (D) coreflood was on quarried Indiana limestone, and the fifth (E) on quarried Lockport dolomite. Each was performed at 2000 psig and 100°F with co-injected CO₂ and Brine #4. Brine #4, compared to Brine #3, contained no strontium, less than 4% as much manganese and magnesium, similar calcium concentration, and increased sodium to make up to a similar level of dissolved solids. The intent was to have levels of tracer high enough to detect but not high enough to saturate the system with manganese. In addition to the tests performed during the earlier test series, three CT scans were performed on each core segment: one on the fresh core, one at an interval during the flood, and the final after the last flood period; a bromide tracer diffusivity test was performed for each system (Figs. 43–46 and 52–55), and in situ fluid samples were taken for compositional analysis to compare with ambient samples.

Figure 39 is a view of all three limestone sections after the first flood period. The flood had to be stopped because the core sleeve failed due to dissolution, creating a cavity near the inlet. In the limestone test injection was interrupted twice due to sleeve failure. After each flood
period the core was trimmed. Figure 40 compares the ends after the three flooding periods. Figures 41 and 42 are color-enhanced CT images on the fresh core (I), after the first flooding period (II), and following the last flooding period (III) as a cross section at about 6 cm deep (Fig. 41) and 90° longitudinal sections (Fig. 42) for each of the three times with the location of the cross section indicated. Figures 43–46 are plots of produced compositions taken during the diffusivity test for limestone. Figure 43 shows the produced bromide concentration versus PV injected. The first part is with the bromide spiked Brine #4 displacing unspiked Brine #4. The later stage is a displacement with a coinjection of CO₂ and Brine #4. CO₃ as calcite in solution is also plotted, showing an increase of dissolved carbonate with the presence of CO₂. Figures 47–55 are similar figures for dolomite.

In each system there was an increase in porosity and permeability for the three core segments (Figure 51). Most of the increase was in the first core segment, but there were small increases in porosity and permeability in the two downstream segments. There was not sufficient data in the limestone for a definitive value, but the dolomite had 14% porosity increase in Segment A and 0.8 and 0.4% porosity increases in Segments B and C, respectively, or a system increase of 5% (9.9 cm³). The mass loss calculated using effluent compositions is over 23 g or over 8.0 cm³. Neither BSEI or chemical analysis detected any tracer precipitation in either core type.

Some observations in comparing the limestone and dolomite results are:
1. A comparison of Figs 43 and 52 shows that the flow behavior of the limestone indicates a less homogeneous flow distribution than that of dolomite.
2. Figures 44 and 53 compare the production of manganese, which, in both cases, experiences a reduction after a soaking period early in the test. There is a spike in produced manganese concentration corresponding to CO₂ breakthrough. There appears to be some manganese precipitation early on in the core that is produced after CO₂ breakthrough. At ambient conditions most of the manganese precipitates.
3. Figures 45 and 54 compare the effluent calcium concentrations. In both systems solution calcium increases after CO₂ breakthrough, with significant concentrations precipitating at ambient conditions. The higher concentration of calcium is in the limestone that has little magnesium in the solution.
4. Figures 46 and 55 compare magnesium concentration in the effluent. There was little change in either system until CO$_2$ breakthrough. As might be expected, the increase in effluent concentration is small in limestone (~30%), which contains less than 1% magnesium, while increases of about eightfold appear in dolomite, which contains about equal mole concentrations of magnesium and calcium. Most of the magnesium stays in solution at ambient conditions with little precipitation in either system.

5. Figures 56–58 compare the manganese, calcium, and magnesium concentrations in the effluent with time through the entire tests series for the dolomite core. The first 8 PV are shown in Figs. 53–55. Samples of the effluent were taken both in front of and behind the back pressure regulator (see Fig. 1). The samples taken at ambient conditions compare well with those taken under pressure (Figs. 56–58).

6. Figure 59 shows some photos of carbonate reservoir rock (dolomite) taken about 100 feet from a CO$_2$ injection well several years after WAG had started. These were from a high flow zone that had experienced significant increases in flow rate. These samples appear much like some of the samples shown in Figs. 25, 30, 34, 39, 40, 47, and 48. Note the grainy texture.

**Summary**

Dissolution occurred in all samples with CO$_2$ saturated brine. There was evidence of precipitation detected in corefloods A-C, but none in D and E. The primary difference that was noted with earlier floods was a significant change in brine composition. Each of the first three brines (including the reservoir brines) had much high levels of magnesium and the first tracer brine had high levels of manganese and strontium as well as magnesium.
Fig. 39. Three limestone core segments after the first flooding period.

Fig. 40. First segment inlet after each flooding period (limestone Coreflood D).

Fig. 41. CT cross section images at ~6 cm from the end of the original limestone Segment A inlet. Pre-flood (I_L), after the first flooding period (II_L), and post-flood (III_L) (limestone Coreflood D).
Fig. 42. CT longitudinal sections of core after first flooding period with the corresponding cross sections (Fig. 18 marked (limestone Coreflood D)).

Fig. 43. Bromide diffusivity and alkalinity results (limestone Coreflood D).
Fig. 44. Manganese concentration in the effluent (limestone Coreflood D).

Fig. 45. Calcium concentration in the effluent (limestone Coreflood D).

Fig. 46. Magnesium concentration in the effluent (limestone Coreflood D).
Fig. 47. Three dolomite core segments after the first flooding period (Coreflood E).

Fig. 48. Inlet of first segment after each flooding period (dolomite Coreflood E).

Fig. 49. CT cross section images at ~6 cm from the end of the original dolomite Segment A inlet. Pre-flood (I_D), after the first flooding period (II_D), and post-flood (III_D) (Coreflood E).

Fig. 50. Dolomite core segment porosity and permeability trends (dolomite Coreflood E).
Fig. 51. CT longitudinal sections of core after first flooding period with the corresponding cross section (Fig. 26) marked (dolomite Coreflood E).

Fig. 52. Bromide diffusivity and alkalinity results (dolomite Coreflood E).
Fig. 53. Manganese concentration in the effluent (dolomite Coreflood E).

Fig. 54. Calcium concentration in the effluent (dolomite Coreflood E).

Fig. 55. Magnesium concentration in the effluent (dolomite Coreflood E).
Fig. 56. Fluid Mn production versus PV injected brine for dolomite.

Fig. 57. Fluid Ca production versus PV injected brine for dolomite.
Fig. 58. Fluid Mg production versus PV injected brine for dolomite.

Fig. 59. Example of dolomite core samples from a high permeability zone about 100 feet from the injection well after several years of WAG.
Chapter 3. Flow Rate and Injectivity

Flow rates increase approaching the wellbore for both injection and production wells. Assuming a constant fluid density, as the wellbore is approached the flow rate increases inversely proportional to the distance from the wellbore; the closer the proximity, the higher the rate. Moving away from the injector, the fluid expands, decreasing the rate at which the fluid velocity decreases due to an increase in volume corresponding to a decrease in density. Near the production well the pressure decreases as one approaches the wellbore. This decrease in pressure results in a decrease in density of the produced fluid. This decrease results in an increase in volume and subsequently in the flow rate. With the increase in pressure gradient due to non-Darcy flow behavior and the expanding fluid compounding the flow rate near wellbore, the pressure drop can become extremely large; with possible liquid dropout the productivity of the reservoir can be significantly reduced. In our work an Indiana limestone, Berea sandstone, and Dakota sandstone were tested for flow rates over three orders of magnitude, pore pressures from 1000 to 10,000 psi and overburden pressure in both the axial and radial directions form 1000 to 10,000 psi.

3.1 Experimental Study of Overburden and Stress Influence on Non-Darcy Gas Flow in Dakota Sandstone

A series of laboratory experiments were conducted to investigate the influence of overburden and in-situ stresses on non-Darcy gas flow behavior in Dakota sandstone. Nitrogen was flooded through cylindrical core in a triaxial core holder under specific condition of temperature at 100°F, with core outlet pore pressure at 500 psi, axial and radial stress from 2,000 to 10,000 psi, and nitrogen reservoir pump pressure at 2,000 psi with pump flow rates from 25 to 10,000 cc/hr at 80°F. Permeability and non-Darcy coefficient were determined using Forchheimer’s method. It was found that with the increase of overburden and in-situ stresses, permeability decreases while non-Darcy flow coefficient increases. Average effective normal stress and shear stress were used to quantitatively express the influence of overburden and in-situ stresses. It was found that average effective normal stress has a good linear relationship with both permeability and non-
Darcy flow coefficient. In contrast, average shear stress did not appear to influence the permeability and non-Darcy coefficient.

Summary
From this study, the following conclusions are arrived on the non-Darcy nitrogen flow behavior through Dakota sandstone:

1. Non-Darcy flow behavior is influenced by overburden/in-situ stresses. The higher the overburden and in-situ stress level, the lower the permeability and the higher the non-Darcy flow coefficient.
2. Linear correlations were determined between permeability, non-Darcy flow coefficient and overburden/in-situ stresses in terms of average effective normal stress. Results also show that average shear stress does not correlate to permeability and non-Darcy flow coefficient, indicating that pore deformation is a less important factor in comparing to compaction.
3. This work confirms previous studies, which indicated that though the Forchheimer equation is useful in describing high velocity flow in porous media, that in many cases it is not sufficient.

3.2 Laboratory Investigation of Stress-Sensitivity of Non-Darcy Gas Flow Parameters
Non-Darcy flow parameters were investigated in 159 series of high pressure/high temperature/high velocity gas flooding experiments on five different rock samples under field reservoir conditions. The results of these experiments reconfirm and extend to new conditions that permeability increases, while non-Darcy flow coefficient decreases with effective stresses; both are independent of shear stresses. General formulas have been developed to quantify the stress sensitivity in terms of nominal non-Darcy parameters. General equations have been proposed to predict the change of permeability and non-Darcy flow coefficient with given effective stresses and nominal non-Darcy flow parameters.
Summary
In summary, 159 series of high temperature, high pressure and high velocity gas flooding experiments have been conducted in five rocks to investigate the stress sensitivity of non-Darcy flow parameters. The tested rocks have petrophysical properties that represent many reservoir formations. The test conditions cover the majority of field in-situ stress fields, temperatures and gas production/injection flow rates. All the experiments gave consistent results which confirmed and extended previous conclusions observed in one single rock at a single temperature. Based on these experiments in this study, the following conclusions are derived:

1. Permeability, $k$, decreases while non-Darcy flow coefficient, $\beta$, increases linearly with effective stresses.
2. Stress sensitivity of non-Darcy flow parameters, $s_k$ and $s_\beta$, is proportional to the nominal permeability, $k_0$, and nominal non-Darcy flow coefficient, $\beta_0$, regardless of rock properties, in-situ stress fields, and temperatures. General stress sensitivity functions have been developed and can be used to estimate the stress sensitivity of non-Darcy flow parameters.
3. General functions, $k(\sigma_{\text{eff}})$ and $\beta(\sigma_{\text{eff}})$ were derived in terms of stress sensitivity, $s_k$ and $s_\beta$, and nominal non-Darcy flow parameters, $k_0$ and $\beta_0$. Influence of reservoir pressure change on $k$ and $\beta$ can be predicted using these functions.
4. Under the same effective stress, permeability increases with reservoir pressures and decreases with reservoir temperatures; non-Darcy flow coefficient changes in an opposite manner under these two factors.
5. Shear stress does not have significant correlation with permeability and non-Darcy flow coefficient, indicating that $k$ and $\beta$ are not sensitive to the change of shear stresses.

3.3 Comparison of Non-Darcy Flow of CO$_2$ and N$_2$ in a Carbonate Rock
In this part of the project, 85 series of high-velocity gas flooding experiments under high-pressure and high-temperature conditions were used to investigate the non-Darcy behavior results of CO$_2$ compared to the previous studies using N$_2$. It was found that pore pressure has more influence on permeability in CO$_2$ flooding than it does in N$_2$ flooding. In contrast, temperature has definite and consistent influence on both permeability and non-Darcy flow coefficient in N$_2$ flooding, but the same influence in CO$_2$ flooding was not observed. Mechanism
behind these differences is attributed to physical property differences of the two gases. Much of the work was near the CO₂ critical point or liquid regions. Other anomalies are attributed to thermal effects caused by expansion cooling of the CO₂. Field data indicates that this phenomenon could be responsible for productivity loses in high flow rate CO₂ wells. Accordingly, attention should be paid to avoid flowing CO₂ at conditions near its critical point.

Summary
Based on 85 series of laboratory experiments, comparisons between the non-Darcy flow behaviors of N₂ and CO₂, flooding under high-pressure/high temperature revealed that non-Darcy flow parameters in CO₂ flooding are different from those in N₂ flooding. Mechanisms for the differences have been analyzed, and significance to field operations discussed. In summary, the following conclusions were obtained.

1. Non-Darcy flow parameters measured in CO₂ flooding are different from those in N₂ flooding while the non-Darcy flow coefficient in CO₂ flooding is slightly higher than that in N₂ flooding.
2. Pore pressure has an obvious influence on permeability in CO₂ flooding; a similar influence on permeability in N₂ flooding is less obvious.
3. Temperature shows clear and consistent influence on non-Darcy flow parameters in N₂ flooding, but its influence in CO₂ flooding is less pronounced.
4. Some difference in non-Darcy flow behavior between CO₂ and N₂ is attributed to a cooling effect in CO₂ flooding. As temperature and pressure within the core approaches critical point conditions of CO₂, the cooling effect enhances. Multiphase flow may occur within the core.
5. This cooling effect and the resulting multiphase flow could be responsible for the loss of injectivity and productivity in some CO₂ wells. Care should be paid to avoid flowing CO₂ at conditions close to the critical point.

3.4 A Criterion for Non-Darcy Flow in Porous Media
Non-Darcy behavior is important for describing fluid flow in porous media in situations where high velocity occurs. A criterion to identify the beginning of non-Darcy flow is needed. Two types of criteria, the Reynolds number and the Forchheimer number, have been used in the past for identifying the beginning of non-Darcy flow. Because each of these criteria has different
versions of definitions, consistent results cannot be achieved. Based on a review of previous work, the Forchheimer number is revised and recommended here as a criterion for identifying non-Darcy flow in porous media. Physically, this revised Forchheimer number has the advantage of clear meaning and wide applicability. It equals the ratio of pressure drop caused by liquid-solid interactions to that by viscous resistance. It is directly related to the non-Darcy effect. Forchheimer numbers are experimentally determined for nitrogen flow in Dakota sandstone, Indiana limestone and Berea sandstone at flowrates varying by four orders of magnitude. These results indicate that superficial velocity in the rocks increases nonlinearly with the Forchheimer number. The critical Forchheimer number for non-Darcy flow is expressed in terms of the critical non-Darcy effect. Considering a 10% non-Darcy effect, the critical Forchheimer number would be 0.11.

Summary
1. The two types of non-Darcy criteria, the Reynolds number and the Forchheimer number, for fluid flow in porous media have been reviewed. A revised Forchheimer number is recommended due to the clear meaning of variables involved.
2. The Forchheimer number represents the ratio of pressure drop consumed by liquid-solid interactions to that by viscous resistance. It has a direct relation to non-Darcy effect.
3. Forchheimer numbers for nitrogen flow at varied flowrates in Dakota sandstone, Indiana limestone and Berea sandstone are determined using experimentally measured permeability and non-Darcy coefficient. The results add considerably to the array of Forchheimer numbers for characterizing fluid flow in consolidated rocks.
4. An expression for the critical Forchheimer number is given in terms of non-Darcy effect limit. This non-Darcy effect-based expression allows the user to define the critical Forchheimer number according to the features of the problem, and should be scientifically more reasonable in comparing to a fixed critical value. A good reference for the critical Forchheimer number is 0.11, which corresponds to a 10% non-Darcy effect.
Chapter 4. Surfactant Sorption, Stability, and Mobility

Chapter 4 summarizes research results in studies on foam stability, interfacial tension, surfactant adsorption and desorption, and mobility control. During this period of the project, foam stability as a function of pH, brine salinity, brine composition, temperature, pressure, and surfactant concentration and type were explored. Surfactant adsorption and desorption kinetics and equilibrium versus surfactant concentration and type, temperature, pH, brine composition and salinity, and rock and mineral type were studied.

4.1 Cost Reduction and Injectivity Improvements for CO₂ Foams for Mobility Control

The results of a series of tests on CO₂ foams identified chemical cost reduction derived from the synergistic effects of co-surfactant systems using a good foaming agent and a less expensive, poor foaming agent. The required good foaming agent was reduced by at least 75%. Also the effect on injectivity was reduced by as much as 50% using the co-surfactant system, compared to a previously used surfactant system. Test results demonstrate that mobility control of injected CO₂ for improved oil recovery can be achieved with significant reduction in the chemical cost of SAG (injection of surfaction solution alternating with gas), improved injectivity of SAG, and improved economics of CO₂ injection project when compared to reported systems.

Summary

Several concepts were inferred from the laboratory tests that are recommended for field tests:
1. The concentration of CD with CLS can be lowered well below the concentration required without CLS and still have significant foaming/diversion capability, thus oil production.
2. The co-surfactant system had significant oil production with much less effect on injectivity (lower pressure drop).
3. The co-surfactant system foaming properties seemed to be less sensitive to oil saturation. Fluid diversion caused by foam started before oil saturation in the high permeability region was reduced to miscible residual saturation.
4. The co-surfactant system appears to have the possibility of varying concentrations of the two surfactants in such a way as to tailor a system to optimize the competing effects of sweep injectivity.
5. The analysis of the EVGSAU (East Vacuum Grayburg San Andres Unit) results using the results of the co-surfactant system suggests that the new technology can be profitable.

4.2 Salinity, pH, and Surfactant Concentration Effects on CO₂-Foam

The influence of a number of parameters on CO₂-fume stability and surfactant adsorption at reservoir conditions were determined in a series of tests. Changes of pH from 1 to 12, salinity from 0 to 25 wt%, and surfactant concentration from 0 to 1 wt % were tested for foam stability in a bubble chamber and for adsorption in a static adsorption apparatus using pure kaolinite powder. The mechanisms by which pH and salinity influence CO₂-fume behavior were also elucidated.

Stability of CO₂-fume is surfactant concentration-dependent. The foam was stable under all tested pH and salinities at concentrations both below and above the critical micelle concentration (CMC) except at the lowest concentration tested (0.005 wt%). The adsorption of surfactant onto kaolinite increased with salinity for both NaCl and CaCl₂ with the divalent salt system inducing a higher adsorption onto the kaolinite.

Summary

1. CO₂ foam stability is surfactant concentration-dependent. Only at CD concentration of 0.005 wt%, well below the CMC, can coalescence of bubbles be observed.
2. Adsorption onto kaolinite increases with surfactant concentration.
3. Foam stability is insensitive to a wide range of surfactant (CD) concentrations in synthetic 2 wt% brine (NaCl:CaCl₂ weight ratio of 3:1).
4. Adsorption increases with salinity for both NaCl and CaCl₂, with the divalent salt system inducing a higher adsorption on the kaolinite.
5. Foam stability is insensitive to salinity when CD concentrations are 0.025 wt% and high, but is sensitive to salinity when CD concentration is 0.005 wt%.
6. Adsorption decreases with pH due to the electrostatic repulsion between bubbles and the grains of rock.
7. Foam stability is insensitive to pH when CD concentrations are 0.05 wt% and high but decreases with pH decreases when CD concentration is 0.005 wt%.
4.3 CO₂ Foam Behavior: Influence of Temperature, Pressure, and Concentration of Surfactant

In these tests, a high-pressure, high-temperature (HPHT) bubble chamber apparatus was used to determine CO₂ foam stability, interfacial tension (IFT) between HPHT CO₂ and surfactant solutions and critical micelle concentration (CMC). CD was used for this study. Changes of temperature from 25 to 75ºC, pressure from 800 to 2000 psig, and surfactant concentration from 0.005 wt% to 1 wt% were tested for foam stability, IFT and CMC. The relationship of foam stability to IFT was also addressed.

IFT decreased with surfactant concentration below the CMC and was essentially constant above the CMC, increasing with the increase of temperature and the decrease of pressure. Stability of CO₂-foam is surfactant concentration-dependent. The foam was stable under all tested temperatures at surfactant concentrations of 0.1 wt% and above, and decreased with increase of temperature at surfactant concentrations of 0.05 wt%. The foam was stable under all tested pressure at surfactant concentrations of 0.025 wt% and above, and decreased with increase of temperature at surfactant concentration of 0.005 wt%.

Summary

1. IFT was determined to decrease with surfactant concentration below the CMC and to be essentially constant above the CMC, to increase with the increase of temperature and decrease of pressure, to remain essentially constant over the initial pH range from 1 to 12, and to be insensitive to brine concentration over a wide range with a minimum around 10%.
2. Foam is stable at 60ºC and below, at all tested temperatures and CD concentrations, except at the lowest CD concentration (0.005 wt%) tested. However, foam stability increases with CD concentration at 75ºC.
3. Foam is stable under all tested pressures at surfactant concentrations of 0.025 wt% and above, and foam stability decreases with increasing temperature at the surfactant CD concentration of 0.005 wt%.
4. Interfacial tension (IFT) does not directly correlate to foam stability and foam stability cannot be predicted solely by the value of IFT.
4.4 Parameters Effecting and Magnitude of Adsorption of Calcium Lignosulfonate onto Five Minerals

Lignosulfonate (LS), a paper waste product, has been used as a sacrificial agent and proposed as a co-surfactant for improved oil recovery (IOR). Its effectiveness mainly depends on its adsorption properties onto mineral sites. This series of experiments investigated calcium lignosulfonate (CLS) adsorption onto minerals common to oil reservoirs: silica, kaolinite, bentonite, calcite, and dolomite. Comparing CLS adsorption density onto different minerals will be an aid in estimating relative adsorption mass in a well-characterized reservoir.

A number of series of batch static adsorption experiments were carried out to study the effects of CLS concentration, pH, salinity, brine hardness, and temperature on CLS adsorption density onto five minerals. For silica adsorbent, CLS adsorption density was near zero at all tested conditions. For the other four, adsorption density increased with the increase of CLS concentration, salinity and valence, and decreased with increasing temperature. At pH above 7, adsorption was neutral for the four systems; but at pH below 7, adsorption density increased with increased pH for bentonite and kaolin clay, and decreased with increasing pH for calcite and dolomite.

This study also elucidated adsorption mechanisms that operate under the various conditions. The results of this research will aid in designing surfactant systems for specific reservoir types and conditions.

Summary

To develop transport and sorption models and to better predict chemical requirement, the adsorption density of pure components for five common reservoir rock minerals with varied parameters was determined in this task. This information can be used for qualitative assessment of chemical requirements in reservoir flooding processes.

Based on a series of batch static adsorption experiments of calcium lignosulfonate onto five minerals common to reservoirs: silica, montmorillonite, kaolinite, dolomite and calcite, the following conclusions were drawn:
1. For silica, CLS adsorption density was essentially zero at all tested conditions,
2. For the other four, adsorption increased with increasing concentration, salinity and valence, and decreased with increasing temperature.
3. At pH below 7—neutral for all systems; above 7—increased with increased pH for montmorillonite and kaolinite, and decreased for increasing pH for calcite and dolomite.

4. The order of CLS adsorption density onto the five minerals is:
   montmorillonite > kaolinite > dolomite > calcite > silica.

### 4.6 Calcium Lignosulfonate Adsorption and Desorption on Berea Sandstone

Adsorption and desorption studies were carried out with calcium lignosulfonate (CLS) on Berea sandstone. Circulation experiments were performed to determine CLS adsorption isotherms and the effects of CLS concentration, temperature, salinity, brine hardness, and injection rate on adsorption density. Flow-through experiments were performed to assess the reversibility of CLS adsorption and the influence of postflush rate, brine concentration, brine hardness, brine pH, and temperature on the desorption process. Results indicated that CLS adsorption isotherms on Berea sandstone follow the Freundlich Isotherm law. The results of this research on the effects of CLS adsorption and desorption on Berea sandstone show that: (1) increasing CLS concentration and salinity increases CLS adsorption density; (2) increasing temperature will decrease adsorption density; (3) increasing injection rate of CLS solution will slightly decrease CLS adsorption density, (4) post-flush rate and salinity of brine have a large impact on the CLS desorption process; (5) the adsorption and desorption process are not completely reversible; and (5) temperature and pH of the postflush brine have little effect on desorption.

### Summary

In a chemical process in a reservoir, it is not uncommon to have over 90% of a component required to satisfy adsorption onto the rock. Thus, understanding adsorption and desorption processes is critical in assessing transport of chemicals and in accurately assessing the volume of chemicals required for a successful operation. In this study, CLS was used to look at the effects on sorption of a number of parameters for a single rock type, Berea sandstone.

Based on the results of CLS adsorption and desorption experiments using Berea sandstone, the following conclusions can be drawn:

1. The CLS adsorption density on Berea sandstone was influenced by CLS solution concentration, temperature, salinity, and injection rate. The results show that:
a. Increasing CLS concentration (to at least 25,000 mg/L) increases adsorption density.
b. The adsorption isotherm can be fit using Langmiur and Freundlich adsorption models.
c. Increasing temperature will decrease adsorption density. This is an indication that physical adsorption is a principal mechanism controlling CLS adsorption.
d. Increasing brine and divalent concentration will increase CLS adsorption density.
e. Increasing the flow rate results in a slight decrease in adsorption density.

2. Postflush brine concentration, temperature, pH and injection rate have the following effects on CLS desorption on Berea sandstone:
   a. Two Freundlich adsorption isotherm equations with different slopes fit the desorption isotherm curves well, indicating different adsorption/desorption mechanisms.
   b. Temperature and pH have little effect on CLS desorption.
   c. Increasing brine concentration reduces CLS desorption mass and may stop desorption.
   d. Changing postflush flow rates changed the effluent concentration of CLS, indicating that equilibrium was not reached and that the kinetics and/or diffusion are slow relative to the flow rates.

3. Adsorption and desorption are not completely reversible in the time frame of the experiments and desorption rates lag well behind adsorption rates in solution concentrations below 2600 mg/L CLS.

4. Core conditions before commencement of desorption experiments are the principal factors influencing the recovery of CLS from Berea sandstone.

4.6 Calcium Lignosulfonate Transport through Berea Sandstone

Another series of experiments looked at CLS transport mechanisms through Berea sandstone by combining the experiment results of calcium lignosulfonate (CLS) adsorption onto Berea sandstone and five powdered pure minerals that are found on sandstone. SEM and tracer breakthrough experiments were carried out to describe sandstone cores and to address on analyzing the transport mechanisms of CLS.

The equilibrium time of CLS adsorption onto porous Berea sandstone and powdered minerals were compared. Results show that the equilibrium time for the former is much longer than that for any of the latter, indicating that diffusion is the main mechanism controlling CLS transport time through Berea sandstone. Effects of flow interruption or changing postflush rate
on effluent concentrations were investigated during desorption. Results show that in a coreflood CLS desorption is not an equilibrium process under normal reservoir flow rate.

CLS adsorption densities onto five common reservoir minerals were compared. Results show that silica, which constitutes more than 80% of Berea sandstone and is the bone structure of sandstone, adsorbs little CLS, and that other minerals found in sandstone contribute most of the adsorption of CLS onto Berea sandstone.

A dual porosity model is suggested to simulate CLS transport through Berea sandstone, even though sandstone is generally regarded as a homogeneous porous medium.

Summary
1. The equilibrium time of CLS adsorption on porous Berea sandstone is much longer than any of five powered pure minerals.
2. Diffusion is the principle mechanism to control equilibrium time of CLS adsorption onto Berea sandstone.
3. CLS desorption onto Berea sandstone is a non-equilibrium process under normal reservoir flow rate.
4. The adsorption of CLS onto silica, the primary component of Berea sandstone, is essentially zero, and other minerals (minor components) contribute essentially all the adsorption of CLS on Berea sandstone.
5. A dual porosity model is suggested to simulate CLS transport through Berea sandstone, though sandstone is generally regarded as a homogeneous porous medium.

4.7 Kinetics and Equilibria of Calcium Lignosulfonate Adsorption and Desorption onto Limestone

Equilibria and kinetics are two basic properties needed to adequately understand the adsorption and desorption processes between surfactants and rocks. The adsorption and desorption of calcium lignosulfonate (CLS), commonly used as a sacrificial agent in surfactant-based EOR processes, was examined in a series of dynamic depletion experiments.

Kinetics results show that adsorption and desorption are both time-dependent—not instantaneous. Both adsorption and desorption were characterized by a biphasic pattern, a fast
step followed by a slow step. Apparent adsorption and desorption rate coefficients were
determined by a one-site second-order kinetic model. Desorption is a much slower process than
adsorption. Desorption is an unequilibrium process under normal reservoir flow rate condition.

Equilibrium results showed that CLS adsorption and desorption onto limestone can well
be described by Langmuir isotherm in our tested CLS concentration range, and increasing
concentration increases adsorption density. Both CLS adsorption and desorption are subject to
hysteresis. Increasing flow rate slightly decreased CLS equilibrium adsorption. Increasing both
NaCl and CaCl$_2$ concentrations increased adsorption density; however, CaCl$_2$ has a much greater
impact on the adsorption. Increasing pH decreased CLS adsorption onto limestone. The reasons
for different factors’ effect were elucidated through further investigation.

Summary
1. CLS adsorption and desorption onto limestone are both time-dependent, not instant. Both
adsorption and desorption were characterized by a biphasic pattern, a fast step followed by a
slow step.
2. CLS adsorption onto limestone follows the pseudo-second-order kinetic model for the whole
process, and it also follows diffusion equation at the later stage.
3. The pseudo-first-order and pseudo-second-order kinetic models were derived. CLS
desorption from limestone follows the pseudo-first-order kinetic model, the pseudo-second-
order kinetic model, and the diffusion model, except for the first two points.
4. Desorption is a much slower process than adsorption. A higher temperature has a higher
pseudo-adsorption rate.
5. CLS desorption from limestone is an unequilibrium process under normal reservoir flow rate
conditions.
6. CLS adsorption and desorption onto limestone can well be described by the Langmuir
isotherm in our tested CLS concentration range, and increasing concentration increases
adsorption density. CLS adsorption and desorption are subject to hysteresis.
7. Increasing NaCl and CaCl$_2$ concentrations both increases adsorption density; CaCl$_2$ has a
much greater impact on the adsorption.
8. CLS equilibrium adsorption increases with the increase of pH and the decrease of flow rate.
4.8 Kinetics and Equilibrium of Calcium Lignosulfonate Adsorption and Desorption onto Dolomite

This section reports the results of studies on the adsorption and desorption of calcium lignosulfonate (CLS) onto dolomite. Kinetic results have shown that adsorption and desorption are both time-dependent, not instantaneous. Both adsorption and desorption were characterized by a biphasic pattern: a fast step followed by a slow step. Apparent adsorption rate coefficients were determined by a second-order kinetic model. Desorption did not reach equilibrium in the rested core under normal reservoir flow rates. Equilibrium results show that CLS adsorption and desorption onto dolomite are well-described by the Langmuir isotherm over the tested CLS concentration range, and that increasing concentration increases adsorption density. There is significant hysteresis between CLS adsorption and desorption isotherms. Increasing both NaCl and CaCl₂ concentrations increased adsorption density; however, CaCl₂ had a much greater impact on the adsorption. The reasons for the effects of the different factors are elucidated in this chapter.

**Equilibrium and kinetics.** Equilibrium and kinetics are basic to the proper understanding of adsorption and desorption processes between surfactants and rocks. Equilibrium data provide information about the final state of a system, and kinetic data are concerned especially with rates of change. Equilibrium adsorption of lignosulfonate onto certain rocks has been studied. Little, however, has appeared in literatures concerning lignosulfonate adsorption kinetics. Knowledge of the adsorption and desorption rates aids in discerning the mechanisms controlling surfactant transport through reservoirs and predicting the fate of surfactant to provide cost-effective injection strategies. As Section 4.4 summarized the study of kinetics and equilibrium of CLS adsorption onto limestone, so this chapter focuses on the kinetics and equilibrium of CLS adsorption and desorption onto dolomite.

**Experimental Materials.** In each test 2 wt% (1.5 wt% NaCl and 0.5 wt% CaCl₂) synthetic brine was used unless otherwise stated. The lignosulfonate used in this study is Lignosite®100 calcium lignosulfonate (CLS), obtained from the Georgia-Pacific Corporation. The product provided is a powder produced by sulfonation of softwood lignin. A spectrophotometer was used to determine
the concentration of CLS in solutions. CLS has a maximum absorbance in the neighborhood of 283 nm. Detailed information on CLS solution preparation and concentration determination is described in the literature.\textsuperscript{23}

### Table 6. Parameters of Dolomite Core

<table>
<thead>
<tr>
<th>Code</th>
<th>Length, cm</th>
<th>Diameter, cm</th>
<th>Volume, cm(^3)</th>
<th>Mass, g</th>
<th>PV, cm(^3)</th>
<th>Porosity, %</th>
<th>Permeability, md</th>
</tr>
</thead>
<tbody>
<tr>
<td>D01</td>
<td>5.70</td>
<td>3.81</td>
<td>64.99</td>
<td>150.47</td>
<td>10.36</td>
<td>15.94</td>
<td>24.72</td>
</tr>
</tbody>
</table>

### Table 7. Experiment Schedule of CLS Adsorption/Desorption onto Dolomite

<table>
<thead>
<tr>
<th>Series No</th>
<th>Experiment Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>D01-A</td>
<td>Adsorption: Establish CLS adsorption isotherm; Desorption: Establish CLS desorption isotherm; Desorption: Interruption effect on desorption process(Inject 2% brine to flush the core at 15 cm(^3)/hr, direct flow).</td>
</tr>
<tr>
<td>D01-B</td>
<td>Adsorption: NaCl concentration effect on equilibrium concentration. Desorption: Injection rate effect on desorption process. (Inject 5% NaCl brine to flush the core, direct flow)</td>
</tr>
<tr>
<td>D01-C</td>
<td>Adsorption: CaCl(_2) concentration effect on equilibrium concentration. Desorption: Injection rate effect on desorption process.</td>
</tr>
<tr>
<td>D01-D</td>
<td>Adsorption kinetics: circulate 4,794 mg/L CLS solution at 23 °C (core was saturated by distilled water before circulation); Desorption: Inject 2% brine to flush the core at 15 cm(^3)/hr(direct flow)</td>
</tr>
<tr>
<td>D01-E</td>
<td>Adsorption kinetics: circulate 4,833 mg/L CLS solution at 45 °C (core was saturated by 2% brine before circulation); Adsorption: temperature effect on CLS equilibrium adsorption Desorption: Inject 2% brine to flush the core at 15 cm(^3)/hr(direct flow)</td>
</tr>
<tr>
<td>D01-F</td>
<td>Adsorption kinetics: circulate 4,830 mg/L CLS solution at 23 °C (core was saturated by 2% brine before circulation); Desorption: Inject 2% brine to flush the core at 15 cm(^3)/hr(direct flow)</td>
</tr>
</tbody>
</table>

Note: D01-D and D01-F were carried out at 23°C; other experiments were carried out at 45 °C unless specifically mentioned.

The core material used in this study was dolomite, composed mainly of CaMg(CO\(_3\))\(_2\).\textsuperscript{36}

The properties and parameters of the core used in this study are found in Table 6. Six series of adsorption/desorption experiments were run in this core; the schedules for all the experiment series are found in Table 7. Between every two series of experiments, the core was flushed with 400 cm\(^3\) (~38 pore volumes (PV)) of tetrahydrofuran (THF), dried using nitrogen gas flow, and evacuated before being resaturated with 2 wt% brine or distilled water (distilled water was used to resaturate the core before experiments D01-B, D01-C and D01-D and brine for the other three).

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**Experimental methods.** Two dynamic flow methods, circulation and flow-through experiments, were used to study CLS adsorption and desorption onto dolomite core; these methods have been detailed in an earlier annual report.$^{34,35}$

**Results: Kinetics of CLS Adsorption onto Dolomite.** Circulation experiments were carried out to investigate the effect of contact time versus adsorption of CLS onto dolomite at the initial CLS concentration of about 4,800 mg/L and a circulation rate of 15 cm$^3$/hr (Step 1 of D01-D, D01-E and D01-F). The difference between D01-D and D01-F is that the core was saturated by different fluid before CLS solution was circulated. The core for D01-D experiment was saturated with distilled water before CLS solution was circulated. The core for D01-F experiment was saturated with 2% brine before CLS solution was circulated. The adsorption densities as a function of circulation time for the three adsorption kinetics are plotted in Fig. 60.

The adsorption density increases with the elapsed time within our measured time range for both temperatures. As shown in Fig. 60, triple curves were characterized by a short period of rapid adsorption, followed by a long period of slower adsorption. During the tests the CSL concentration of the circulating solution decreased. This is caused by dilution with brine from the core and tube line and CLS adsorption onto the pore surface of the dolomite. During the initial few hours, the CLS solution that flowed through the core displaced brine out of core pores and line tube to dilute the CLS solution in the flask and partial CLS was adsorbed onto the surface as the surfactant flowed through the core. In general, the pores that CLS flowed through during the initial few hours were the main fluid flow path and the surface area contributed most of the surface area of the dolomite core. Thus rapid adsorption occurred within the initial few hours. This stage was controlled by solution advection and dispersion. After circulating a number of PVs of CLS solution, the concentration between the main flow path of the core and the flask was not affected by concentration gradients due to dilution.$^{37}$ The CLS concentration loss was principally caused by diffusion between macropores (main path) and micropores (stagnant areas or low permeability paths) due to concentration differences.
Comparing CLS adsorption for which core was saturated with brine shows that the adsorption density was greater at the lower temperature. This is an indication that CLS adsorption onto dolomite is physical. Comparing CLS adsorption densities at the same temperature with the core saturated by different solution (one was prepared by distilled water and another one was prepared with brine) shows that CLS adsorption with distilled water is much lower than that with brine, indicating salinity increase CLS adsorption and preflush core using low salinity brine before surfactant injection will decrease surfactant loss in the rock incurred by adsorption.

Modeling CLS adsorption kinetics onto dolomite. CLS adsorption onto dolomite did not reach equilibrium during the test time. The equilibrium adsorption data is thus not available, so the pseudo-first-order cannot be used directly to fit our results. Figure 61 shows the result using the pseudo-second-order model to fit CLS adsorption kinetics onto dolomite.

The plot of $t/q_t$ versus $t$ is a straight line for each experiment and CLS adsorption kinetics are well-described by the pseudo-second-order equation. Table 8 lists the fitting
equations, correlation factors and the calculated equilibrium density and pseudo-second-order rate constants.

Fig. 61. CLS adsorption kinetics model on dolomite using a pseudo-second-order equation.

Table 8. Results of Modeling CLS Adsorption onto Dolomite Using a Pseudo-Second-Order Equation

<table>
<thead>
<tr>
<th>Series No.</th>
<th>Fitting Equation</th>
<th>$R^2$</th>
<th>$q_e$ (mg/g)</th>
<th>$K_a$ (mg/g/hr)</th>
<th>Temp, (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1 of D01-E</td>
<td>( \frac{t}{q_t} = 2.5831t + 31.436 )</td>
<td>0.9943</td>
<td>0.387</td>
<td>0.212</td>
<td>45</td>
</tr>
<tr>
<td>Step 1 of D01-F</td>
<td>( \frac{t}{q_t} = 2.1948t + 25.013 )</td>
<td>0.9982</td>
<td>0.456</td>
<td>0.193</td>
<td>23</td>
</tr>
<tr>
<td>Step 1 of D01-D</td>
<td>( \frac{t}{q_t} = 2.8728t + 46.049 )</td>
<td>0.9861</td>
<td>0.348</td>
<td>0.179</td>
<td>23</td>
</tr>
</tbody>
</table>

The calculated equilibrium adsorption densities listed in Table 8 are 0.387 and 0.456 and 0.348 mg/g, respectively, which are higher (20-25%) than the adsorption densities (0.307, 0.365 and 0.263 mg/g) determined after 48 hours, which indicated CLS adsorption onto dolomite takes a longer time to reach equilibrium than it does onto limestone. The rate constants of D01-E and D01-F are 0.193 and 0.212 at 23°C and 45°C, respectively, which indicates an increasing
reaction rate between CLS and dolomite with increasing temperature. Thus, the required time to reach adsorption equilibrium should be shorter at the higher temperature.

Rearranging equations listed in Table 8, the following equations can then be used to calculate CLS adsorption rate:

At 23 ºC (core was saturated with brine):

\[
\frac{q_t}{t} = \frac{1}{2.1948t + 25.013} \\
\]

At 45 ºC (core was saturated with brine):

\[
\frac{q_t}{t} = \frac{1}{2.5831t + 31.436} \\
\]

At 23 ºC (core was saturated with distilled water):

\[
\frac{q_t}{t} = \frac{1}{2.8728t + 46.049} \\
\]

If the calculated equilibrium adsorption densities are applied to the pseudo-first-order equation, it can be used to fit the CLS adsorption kinetics onto dolomite. The plot of \( \frac{q_t}{q_e - q_t} \) versus \( t \) has a fair linear relationship as shown in Fig. 62, and the fit equations are:

At 23 ºC (core was saturated with brine):

\[
\frac{q_e}{q_e - q_t} = 1.4078e^{0.0288t} \quad R^2 = 0.9629 \\
\]

At 45 ºC (core was saturated with brine):

\[
\frac{q_e}{q_e - q_t} = 1.352e^{0.0293t} \quad R^2 = 0.9606 \\
\]

At 23 ºC (core was saturated with distilled water):

\[
\frac{q_e}{q_e - q_t} = 1.3217e^{0.0245t} \quad R^2 = 0.9118 \\
\]

Figure 62 shows that the y-intercept is not 1; thus, CLS adsorption onto dolomite does not follow the pseudo-first-order equation.
Fig. 62. Modeling CLS adsorption onto dolomite using a pseudo-first-order equation.

The plot of \( \log\left(\frac{1}{q_e - q_t}\right) \) versus \( t \) also shows a straight line, shown in Fig. 63 with the results shown in Table 9.

### Table 9. Results of Modeling CLS Adsorption Kinetics Using A Pseudo-First-Order Equation

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Fitting Equations</th>
<th>( R^2 )</th>
<th>( K_a )</th>
<th>( q_e )</th>
<th>Temp, (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D01-D</td>
<td>( \log\left(\frac{1}{q_e - q_t}\right) = 0.0107t + 0.5795 )</td>
<td>0.9118</td>
<td>0.0246</td>
<td>3.7975</td>
<td>23</td>
</tr>
<tr>
<td>D01-E</td>
<td>( \log\left(\frac{1}{q_e - q_t}\right) = 0.0127t + 0.5434 )</td>
<td>0.9606</td>
<td>0.0292</td>
<td>3.4946</td>
<td>45</td>
</tr>
<tr>
<td>D01-F</td>
<td>( \log\left(\frac{1}{q_e - q_t}\right) = 0.0125t + 0.4896 )</td>
<td>0.9629</td>
<td>0.0288</td>
<td>3.0875</td>
<td>23</td>
</tr>
</tbody>
</table>
The calculated equilibrium adsorption densities shown in Table 9 are much higher than those calculated from the pseudo-second-order equation; however, these are not reasonable. Therefore, CLS adsorption onto dolomite does not follow the pseudo-first-order equation.

![Graph showing 1/(q-e) vs. time for different brine concentrations.](image)

**Fig. 63.** Dolomite results of CLS adsorption kinetics fit to pseudo-first-order equations.\(^{18}\)

Figure 64 shows the relationship between \(q_t\) and \(t^{0.5}\), used to determine whether the diffusion model fits the adsorption kinetics. The curve is not linear for the first few points but it is almost linear for the last few points. This result indicates that diffusion is not a controlling mechanism, at least not initially.

![Graph showing adsorption vs. (Time)^0.5 for different brine concentrations.](image)

**Fig. 64.** The fit result of CLS adsorption kinetics onto dolomite using a diffusion model.
**Equilibrium of CLS adsorption onto dolomite: experimental results of adsorption and desorption isotherm.** CLS adsorption and desorption isotherms onto dolomite were established at 45°C, (see Fig. 65) for Steps 1 and 2 of experiment D01-A. For both isotherms, surfactant adsorption increased with increased CLS solution concentration. When the two isotherms are compared, the adsorption density for the desorption isotherm is higher than the adsorption isotherm at the same equilibrium concentration, indicating adsorption hysteresis. This may be caused by the attraction forces between pore surfaces of dolomite and CLS above the displacing force and other repulsion forces.

![Fig. 65. CLS adsorption and desorption isotherm onto dolomite at 45 °C.](image)

Figure 66 compares CLS initial and equilibrium concentrations and relative loss due to CLS adsorption onto dolomite. The CLS concentration decrease is from 6.09% to 13.56%; the percentage lost decreased with increasing solution concentration over the measured range while total adsorption increased.
Fig. 66. Concentration change and loss due to adsorption.

Modelling CLS Adsorption and Desorption Isotherms. Figure 67 shows the fit of the experimental adsorption data to the Langmuir equation and Table 10 summarizes the results. The CLS adsorption isotherm onto dolomite can be described by the Langmuir equation with a correlation factor of 0.9642. Correspondingly, the maximum adsorption density is 0.534 mg/g and the Langmuir adsorption constant is $2.3 \times 10^{-4}$ l/mg. In contrast, the desorption isotherm does not fit the Langmuir model.

Fig. 67. Modeling CLS adsorption and desorption isotherms onto dolomite using the Langmuir equation.
Table 10. Parameters from Modeling the CLS Adsorption and Desorption Isotherm Using the Langmuir Isotherm Equation

<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
<th>$R^2$</th>
<th>$q_{\text{max}}$ (mg/g)</th>
<th>$K_L$ (l/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ads.</td>
<td>$\frac{1}{q_e} = 8144.5 \cdot \frac{1}{C_e} + 1.8658$</td>
<td>0.9642</td>
<td>0.534</td>
<td>0.00023</td>
</tr>
<tr>
<td>Des.</td>
<td>$\frac{1}{q_e} = 151.29 \cdot \frac{1}{C_e} + 3.1548$</td>
<td>0.7632</td>
<td>0.317</td>
<td>0.02085</td>
</tr>
</tbody>
</table>

Figure 68 shows the fit of the adsorption and desorption isotherm using the Freundlich equation. Table 11 summarizes the fit to the Freundlich equation and corresponding parameters. The CLS adsorption isotherm for dolomite can be described by a Freundlich equation with a correlation factor of 0.9929 and a Freundlich constant and heterogeneity factor of 0.0010 and 1.5017, respectively. The CLS desorption isotherm also was fit by a Freundlich equation with a relative low correlation factor of 0.9405; the corresponding Freundlich constant and heterogeneity factor are 0.0941 and 6.2972, respectively.

Fig. 68. Modeling CLS adsorption and desorption isotherms using the Freundlich equation.
Table 11. Parameters from Modeling CLS Adsorption and Desorption Isotherms onto Dolomite Using the Freundlich Equation

<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
<th>R²</th>
<th>KF</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>q_e = 0.001C_e^{0.6659}</td>
<td>0.9929</td>
<td>0.0010</td>
<td>1.5017</td>
</tr>
<tr>
<td>Desorption</td>
<td>q_e = 0.0941C_e^{0.1588}</td>
<td>0.9405</td>
<td>0.0941</td>
<td>6.2972</td>
</tr>
</tbody>
</table>

**Effect of Temperature on Equilibrium Adsorption.** A temperature gradient can exist near-wellbore and from reservoir to reservoir. Thus, CLS equilibrium adsorption densities at different temperatures were measured by the circulation method at Step 2 of D01-E at a circulation rate of 15 cm³/hr. The experiment started from the end of the adsorption kinetics experiment at 45°C. The temperature was decreased to 40°, 34°, and 23°C, and then returned to 45°C. Figure 69 shows CLS adsorption density change for each temperature. CLS adsorption density increased as temperature decreased and returned to near the initial adsorption when the temperature was returned to 45°C. These results are an indication that physical adsorption is one of the main mechanisms controlling CLS adsorption onto dolomite.

![Figure 69](image.png)

**Fig. 69. Effect of temperature on CLS adsorption onto dolomite.**

**Effect of Salt Type and Concentration on Equilibrium Adsorption.** Two series of experiments were run to study the influence of NaCl and CaCl₂ on CLS adsorption onto dolomite (D01-B and D01-C). For each experiment, About 4,700 mg/L CLS solution was circulated until
adsorption equilibrium was achieved. Then salt (NaCl or CaCl₂) was added incrementally to the circulation solution in flask until the salt concentration reached the desired maximum. The highest concentrations were 5 wt% brine for both NaCl and CaCl₂. Figure 70 shows CLS adsorption densities onto dolomite at different NaCl and CaCl₂ concentrations. For both NaCl and CaCl₂, increasing concentration increased CLS adsorption, with the divalent CaCl₂ having the stronger effect. The adsorption of CLS prepared by distilled water is about 0.240 mg/g. Adding 0.01 M (Molar) or 0.058 wt% NaCl increased CLS adsorption density to 0.276 mg/g, and adding 0.01 M (0.11 wt%) CaCl₂ increased CLS adsorption density to 0.491 mg/g.

![Figure 70: Effect of salt type and concentration on CLS adsorption onto dolomite.](image-url)

Although there is no universal agreement regarding the isoelectric condition of dolomite,³⁸,³⁹ much research indicates that dolomite has a negative charge in aqueous solutions with a pH near neutral.⁴⁰ The measured equilibrium pH of a CLS solution circulated through dolomite is close to neutral. The effect of NaCl and CaCl₂ on adsorption can be explained as follows: CLS is an anionic surfactant having a functional group with a negative charge in aqueous medium. Adding NaCl or CaCl₂ decreases the functional group-group electrostatic repulsion in the adsorbed layer. Increasing salt concentration can compress the electric double layer and thus CLS adsorption will increase with an increase of salt concentration. Ca²⁺ may adsorb onto the dolomite surface, which may be the reason that CaCl₂ has a stronger effect than
NaCl. The adsorbed Ca\(^{2+}\) can make the surface more positive, thus attracting more CLS by electrostatic interaction.

**Kinetics of CLS Desorption from Dolomite.** Most of the previous work reported has focused on adsorption kinetics\(^ {40-46}\) with little attention devoted to desorption kinetics. Desorption kinetics models were derived by referring to the definitions of adsorption kinetics described earlier.\(^ {24}\)

**Modeling CLS desorption from dolomite.** The core was flushed with 2% brine to displace the solution left in the pore space and tube line and to desorb the adsorbed CLS at the constant flow rate of 15 cm\(^3\)/hr at 45°C (D01-D, D01-E, D01-F). Figure 71 shows adsorption density as a function of time during desorption. The adsorption density during desorption is characterized by a short, rapid desorption period followed by a longer, slow desorption period.

![Fig. 71. Adsorption change with time during the desorption process.](image)

The plot of \(1/q_t\) versus \(t\) shown in Fig. 72 indicates that CLS desorption can be well fit by the pseudo-second-order desorption kinetic model. Table 12 lists the fitting equations, correlation factors, and the calculated desorption rate constant and residual adsorption density. The residual adsorption is close to zero, indicating the CLS can almost completely desorb from dolomite.
Fig. 72. The pseudo-second-order model to fit CLS desorption from dolomite.

Table 12. Results of Modeling CLS Desorption from Dolomite Using Pseudo-Second-Order Equation

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Equation</th>
<th>$R^2$</th>
<th>$K_d$</th>
<th>$q_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D01-D</td>
<td>$\frac{1}{q_t} = 0.1075t + 4.0008$</td>
<td>0.9593</td>
<td>0.1075</td>
<td>0.0249</td>
</tr>
<tr>
<td>D01-E</td>
<td>$\frac{1}{q_t} = 0.0598t + 2.7996$</td>
<td>0.9752</td>
<td>0.0598</td>
<td>0.01361</td>
</tr>
<tr>
<td>D01-F</td>
<td>$\frac{1}{q_t} = 0.6176t + 4.1379$</td>
<td>0.9883</td>
<td>0.6176</td>
<td>-0.0229</td>
</tr>
</tbody>
</table>

If $q_r$ is assumed to be zero, the pseudo-first-order kinetic model can be used to fit CLS desorption from dolomite, as shown in Fig. 73. Each series of data was fit by one line in the semilog plot of $q_t$ versus $t$. Table 13 lists the fitting equations, correlation factors, and the calculated desorption rate constant and initial adsorption density.

If a diffusion equation is used to fit CLS desorption from dolomite, one line is a fair fit to the desorption process of D01-D and D01-E but two lines are better especially to fit the desorption process of D01-F (Fig. 74).
Table 13. Pseudo-First-Order Equation used to model CLS Desorption from Dolomite.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Equation</th>
<th>$R^2$</th>
<th>$K_{dl}$</th>
<th>$q_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D01-D</td>
<td>$q_t = 0.2462e^{-0.019t}$</td>
<td>0.9103</td>
<td>0.0190</td>
<td>0.2462</td>
</tr>
<tr>
<td>D01-E</td>
<td>$q_t = 0.3510e^{-0.0157t}$</td>
<td>0.9425</td>
<td>0.0157</td>
<td>0.3510</td>
</tr>
<tr>
<td>D01-F</td>
<td>$q_t = 0.1776e^{-0.0428t}$</td>
<td>0.9503</td>
<td>0.0428</td>
<td>0.1776</td>
</tr>
</tbody>
</table>

Fig. 73. Pseudo-first-order model to fit CLS desorption from dolomite.

Fig. 74. Diffusion model to fit CLS desorption from dolomite.
**Effect of interruption and flow rate on CLS desorption.** Interrupting or changing the flow rate during the desorption experiment aids in determining if the flow stream is equilibrating with the core during its resonance time. Interrupting (stopping) the flow during the tests allows additional time to equilibrate. Interruption experiments were performed at Step 3 of D01-E during flow-through experiments at a flow rate of 15 cm$^3$/hr. Flow was stopped at 5.50 PV (Fig. 75). After flow resumed, the effluent concentration was increased to above the effluent concentration immediately before the interruption and then returned to a decreasing CLS concentration curve similar to that before the interruption. The results indicate that CD desorption does not reach equilibrium in the core at a flow rate of 15 cm$^3$/hr.

![Graph showing interruption effect on CLS desorption](image.png)

**Fig. 75. Interruption effect on CLS desorption from dolomite.**

Varied flow rates and flow interruptions were performed in Step 2 of D01-C at 45°C. The desorption experiment was run at 15 cm$^3$/hr for 4.80 PV, then at 3 cm$^3$/hr for 19.80 PV (from 4.80 PV to 24.62 PV) with a 24 hr interruption at 8.34 PV. Finally, flow was returned to 15 cm$^3$/hr for the remainder of the test, shown in Fig. 76. When the flow rate was decreased from 15 to 3 cm$^3$/hr, effluent CLS concentration increased. When the flow rate was increased from 3 to 15 cm$^3$/hr, effluent CLS concentration decreased. After the interruption, the effluent CLS concentration was higher than the effluent concentration before the interruption. Results from both interruption and flow rate changes indicate that CLS desorption equilibrium is not achieved.
at the flow rates and core lengths tested. The two rates (15 and 3 cm³/hr), translating to interstitial flow rates of 14 and 2.8 ft/day, which cover a range frequently encountered at reservoir conditions.

![Graph](image-url)

**Fig. 76. Interruption and flow rate effect on CLS desorption.**

**Summary**

1. CLS adsorption and desorption onto dolomite core are both time-dependent. Both adsorption and desorption are characterized by a two-phase pattern, a rapid sorption period followed by a slower period.

2. CLS adsorption onto dolomite is best fit by a pseudo-second-order kinetic model, but can also be fit to a diffusion equation during the second period. Even though the plot of \( \log \left( \frac{1}{q_e - q_t} \right) \) versus \( t \) is linear, CLS adsorption does not follow a pseudo-first-order kinetic adsorption model due to the inconsistent match between measured and calculated equilibrium adsorption density.

3. A higher temperature gives a higher pseudo-adsorption rate, but lower absolute adsorption.

4. Equilibrated CLS adsorption and desorption isotherm onto dolomite can be described by a Langmuir equation in the tested CLS concentration range; increasing concentration increases adsorption density. Desorption isotherm better fits using the Freundlich model.
5. Increasing both NaCl and CaCl$_2$ concentrations increases adsorption density with a greater impact of CaCl$_2$.
6. CLS desorption from dolomite can be fit using either pseudo-first-order kinetic model or pseudo-second-order kinetic models.

4.9 Sorption of Surfactant Used in CO$_2$ Flooding onto Five Minerals and Three Porous Media$^{25}$

This series of experiments involved adsorption and desorption tests performed for five powdered mineral and three rock types using a carbon dioxide–aqueous phase foaming agent, surfactant CD. These experiments were performed in order to better understand surfactant adoption behaviors and transport mechanisms through three different porous media. Batch experiments were run to determine the kinetics of the surfactant adsorption onto five powdered minerals common to the selected three porous media. Dynamic experiments were performed to determine the kinetics and equilibria of surfactant adsorption onto three porous media. Characterizations of the three porous media were performed by SEM (Scanning Electron Microscopy) to aid in discerning the mechanisms controlling the retention and release reaction rates of the surfactant through the three different rock types.

Results showed that CD adsorption and desorption onto powered minerals could be established in one hour. The decreasing order of the surfactant adsorption density onto the five minerals is: montmorillonite, dolomite, kaolinite, silica and calcite. Surfactant adsorption onto the three core systems took at least one order of magnitude longer than that onto the five powdered minerals, and the surfactant adsorption onto Berea sandstone required a longer time than either Indiana limestone or Lockport dolomite. Desorption of the surfactant from the three porous media followed exponent decline equations.

Summary
The decreasing order of the surfactant CD adsorption density (mg/g) onto the five powdered minerals is: montmorillonite, dolomite, kaolinite, silica and calcite.

1. Surfactant adsorption onto the three core systems took much longer than that onto the five powdered minerals, and the surfactant adsorption Berea sandstone required a longer time than
either Indianan limestone or Lockport dolomite due to its multicomponent and complex porous structure.

2. Increasing CD concentration increased CD adsorption density onto the three tested porous media. No plateau was found even when surfactant concentration was above its CMC.

3. Exponent decline equations can be used to describe surfactant desorption process from the three porous media.

4. CD desorption from Berea sandstone does not reach equilibrium in a short core unless it is circulated over several days.

4.10 Competitive Adsorption of a Hybrid Surfactant System onto Five Minerals, Berea Sandstone, and Limestone

This series of experiments examined adsorption/desorption with two surfactant systems and with a mixture of the two onto five minerals and two porous media. The systems were composed of CD and CLS. Two series of experiments were carried out: (1) static adsorption of CLS, CD, and CLS/CD mixtures onto five pure minerals (silica, montmorillonite, kaolinite, dolomite, and calcite); (2) dynamic adsorption of CLS, CD, and CLS/CD mixtures onto core samples of Berea sandstone and Indian limestone. All experiments were performed at 40°C using a 2.0% brine solution with concentrations of 500 mg/l of CD and 5,000 mg/l of CLS. Static adsorption experiment results showed that: (1) CLS adsorption density onto silica is less than background noise (zero); on the other four minerals, adsorption density ranged from 0.5 to 10 mg CLS per g of mineral; (2) CD adsorption density onto the five minerals ranged from 0.4 to 1.2 mg CD per g of mineral; (3) CD adsorption density onto the five minerals decreased by 20 to 70% when mixed with CLS. Dynamic adsorption experiment results showed that: (1) The times required to reach adsorption equilibrium for both CD and CLS were longer for Berea sandstone than for Indiana limestone and for both porous media, were much longer than those for the non-porous minerals; (2) Competitive adsorption generally took several days to reach equilibrium. Stability and interfacial tension tests on both injected and effluent samples were performed. Results correlated well with the adsorption/desorption tests; for example, foaming capability was lost in some systems due to adsorption.
Summary

1. Static adsorption experiment results showed that:
   a. CLS with an initial concentration of 5000 mg/l adsorption density onto silica is essentially zero; CLS adsorption density for the other four minerals ranges from 0.5 to 10 mg/g on calcite, dolomite, kaolinite, and montmorillonite, respectively.
   b. CD with an initial concentration of 500 mg/l adsorption density onto the five minerals ranged from 0.4 to 1.2 mg/g for calcite, silica, kaolinite, dolomite, and montmorillonite, respectively.
   c. CD adsorption density onto five minerals decreased from 20 to 70% when CD was mixed with CLS. The reduction of CD adsorption onto clay was higher than that onto the other minerals.

2. Dynamic adsorption experiment results showed that:
   a. CD adsorption can be greatly reduced by pre-adsorbing CLS onto sandstone or limestone or by injecting a mixture of CD and CLS;
   b. Adsorption equilibrium time of CD and CLS onto Berea sandstone is much longer than that onto Indiana limestone;
   c. Competitive adsorption of CD and CLS generally took several days.

3. Foam stability and IFT show a decrease in foaming capability similar to that expected due to adsorption.

4. The results from this work are being used to develop optimum solution concentrations of CD and CLS for specific reservoir rock, which are anticipated to optimize foaming ability, production cost economy, and adsorption.

4.12 Foam Stability and Surfactant Solution Stability

Effect of gases on IFT and CMC. The IFT between N₂ and CD aqueous solutions was greater than the IFT between CO₂ and CD aqueous solutions at 1500 psig and 25°C. Also, the critical micelle concentration (CMC) was greater for N₂ than for CO₂. Since CO₂ is a liquid under the temperature and pressure conditions tested while N₂ is a gas, the significant density difference and the difference in molecular structure are probably the cause of these differences in interfacial behavior.
Co-surfactant CLS and CD. For a mixture of CLS and CD, the IFT increased with increasing concentrations of lignosulfonate at constant CD concentration. IFT decreased with CD concentrations at constant lignosulfonate concentration (Figs. 78–80). CMC for a mixture of CLS and CD with 2500 mg/L CLS is much higher than the CMC for CD brine solution (Fig. 78). But when the concentration of CLS was equal to or more than 5000 mg/L, the CMC for a mixture of CLS and CD was greater than the measured values, 10,000 mg/L (Figs. 79 and 80). Additionally, IFTs among a mixture of CLS, CD, and CO₂ were much higher than the CD brine solution’s IFT (Figs. 79 - 80).
Fig. 78. 2500 mg/L lignosulfonate effect on IFT and CMC.

Fig. 79. 5000 mg/L lignosulfonate effect on IFT and CMC.
Effect of gases on foam stability. The CO$_2$ foam stability of CD was insensitive to surfactant concentration over a wide range of concentrations (from 0.01wt% CD to 1 wt CD). Coalescence of bubbles was observed only at 0.005 wt% CD concentration (Fig. 81). A similar trend was observed for N$_2$ foam stability with CD (Fig. 82).
Effect of CLS on foam stability. For a mixture of CLS and CD, the IFT increased with increasing concentrations of CLS at a constant CD concentration (Figs. 78–80). Correspondingly, adding CLS destabilized CO$_2$ foam (Fig. 83).
**Lignosulfonate solution stability.** Non-aqueous materials have been observed in both CLS and sodium lignosulfonate (SLS) solutions. This is a concern especially if injecting these solutions into low permeability reservoirs, causing reduced permeability and thus reduced injectivity. There is also the inconvenience of filtering when required to remove precipitates before using the lignosulfonates solutions. The possibility that the chemical structure or composition is changing, and the effect these might have on the absorbance of the lignosulfonates is another concern.

Two types of material have been observed. The first are fine particles that settle to the bottom, usually in small quantities and occurring in the first couple of days after mixing. These are a concern because they could cause problems in the near-wellbore region. These particles appear to be inorganic and are expected to be insoluble material in the lignosulfonates. The second material does not settle, but remains suspended and has the appearance of a gel. Microbial experiments were performed on samples of SLS and CLS that had been prepared for a long period of time and had developed the gel. The gels were observed under an optical microscope and found to be bacteria, fungi and a certain amount of dirt.

Two batches of solutions were prepared with each batch containing pairs of 2% brine and 5000 ppm lignosulfonate solutions. A pair was made up of a SLS and a CLS set. Table 14 summarizes the different treatment types. Table 15 summarizes each of the treatments left in the light over a period of 65 days. For the last 40 days there were little or no changes. Table 16 summarizes the changes in the same set of treatments as listed in Table 15, except each vial was kept in the dark for 192 days.

**Summary**

1. Formaldehyde prevents formation of a suspended material (gel) or a precipitate when the applied formaldehyde concentration is equal to or greater than 500 mg/L.
2. Sodium azide prevents a suspended solid (gel) and a minimum of precipitate forming in CLS solution in concentrations at least as low as 50 mg/L. Gel decreased in SLS with sodium azide concentration increase.
3. SLS solution had precipitate no matter what treatment was applied. If no treatment is applied both SLS and CLS solutions will form gel with time, but CLS solution will not have precipitate.
4. Sodium hypochlorite will bleach the solution to a very light yellow and will have white precipitate for both SLS and CLS. This occurred the first day with no change thereafter.

5. In tests conducted and reported earlier ultrasonic and boiling tests were run. The ultrasonic test had no effect and the boiling test, once filtered, had no further effect.

Table 14. Tests Identifications

<table>
<thead>
<tr>
<th>Treatment Type</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment (Standard)</td>
<td>5000ppm Ligno + Brine*</td>
</tr>
<tr>
<td>Bleach (sodium hypochlorite)</td>
<td>1% bleach + 5000ppm Ligno + Brine</td>
</tr>
<tr>
<td>Sodium azide (Sodium Trinitride)</td>
<td>0.1% sodium azide + 5000ppm Ligno + Brine</td>
</tr>
<tr>
<td></td>
<td>0.05% sodium azide + 5000ppm Ligno + Brine</td>
</tr>
<tr>
<td></td>
<td>0.01% sodium azide + 5000ppm Ligno + Brine</td>
</tr>
<tr>
<td></td>
<td>0.005% sodium azide + 5000ppm Ligno + Brine</td>
</tr>
<tr>
<td>Formaldehyde (HCHO)</td>
<td>0.1% HCHO + 5000ppm Ligno + Brine</td>
</tr>
<tr>
<td></td>
<td>0.05% HCHO + 5000ppm Ligno + Brine</td>
</tr>
<tr>
<td></td>
<td>0.01% HCHO + 5000ppm Ligno + Brine</td>
</tr>
<tr>
<td></td>
<td>0.005% HCHO + 5000ppm Ligno + Brine</td>
</tr>
</tbody>
</table>

* All brine was the same composition (1.5wt% NaCl + 0.5wt% CaCl₂)
Table 15. The Results of Tests Exposed to the Light

<table>
<thead>
<tr>
<th>TREATMENT TYPE</th>
<th>SAMPLE TYPE</th>
<th>DAY 1</th>
<th>DAY 2</th>
<th>DAY 3</th>
<th>DAY 4</th>
<th>DAY 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard (No treatment)</td>
<td>Calcium</td>
<td>None</td>
<td>Few strands</td>
<td>Strands increase</td>
<td>Increase</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>None</td>
<td>Gel and precipitate visible at bottom of test tube</td>
<td>Gel increases. Precipitate stays the same</td>
<td>Increase (precipitate and gel)</td>
<td>Increase</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Calcium</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
<td>Small Precipitate</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>None</td>
<td>precipitate</td>
<td>Precipitate increase</td>
<td>Precipitate increase</td>
<td>No Change</td>
</tr>
<tr>
<td></td>
<td>Calcium</td>
<td>None</td>
<td>Precipitate</td>
<td>Precipitate increase</td>
<td>Precipitate increase</td>
<td>Precipitate increases</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>None</td>
<td>Precipitate &amp; gel</td>
<td>Precipitate and gel increase.</td>
<td>Precipitate and gel increase.</td>
<td>Increases</td>
</tr>
<tr>
<td></td>
<td>Calcium</td>
<td>None</td>
<td>Precipitate, Few Strands</td>
<td>Precipitate increase. Gel formed</td>
<td>Precipitate and gel increase</td>
<td>Increase</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>None</td>
<td>Precipitate</td>
<td>Precipitate increase</td>
<td>Precipitate increase</td>
<td>Increase</td>
</tr>
<tr>
<td>Sodium Azide</td>
<td>Calcium</td>
<td>None</td>
<td>Few strands</td>
<td>Small precipitate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>None</td>
<td>Precipitate</td>
<td>Precipitate increase</td>
<td>Precipitate increases</td>
<td>Increase</td>
</tr>
<tr>
<td></td>
<td>Calcium</td>
<td>None</td>
<td>Few Strands</td>
<td>Small precipitate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>None</td>
<td>Precipitate</td>
<td>Precipitate increase</td>
<td>Precipitate increases</td>
<td>Increase</td>
</tr>
<tr>
<td></td>
<td>Calcium</td>
<td>None</td>
<td>Few strands</td>
<td>Small precipitate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>None</td>
<td>Precipitate &amp; gel</td>
<td>Slight increase in precipitate</td>
<td>Precipitate increases</td>
<td>Increase</td>
</tr>
<tr>
<td></td>
<td>Calcium</td>
<td>None</td>
<td>Few Strands</td>
<td>Small precipitate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>None</td>
<td>Precipitate &amp; gel</td>
<td>Slight increase in precipitate</td>
<td>Precipitate increases</td>
<td>Increase</td>
</tr>
<tr>
<td>Bleach (sodium hypochlorite)</td>
<td>Calcium</td>
<td>Color intensity was reduced and white precipitate formed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No Change after 1st Day</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TREATMENT TYPE</td>
<td>SAMPLE TYPE</td>
<td>DAY 6</td>
<td>( \text{DAY 8} )</td>
<td>DAY 10</td>
<td>DAY 11</td>
<td>DAY 15</td>
</tr>
<tr>
<td>----------------</td>
<td>------------</td>
<td>-------</td>
<td>----------------</td>
<td>--------</td>
<td>--------</td>
<td>-------</td>
</tr>
<tr>
<td><strong>Calcium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard (No treatment)</td>
<td>Calcium</td>
<td>Precipitate and gel continue to increase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Precipitate stays the same. Gel increase</td>
<td>Gel increase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sodium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calcium</td>
<td>No change in precipitate after Day 5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No Change</td>
<td>Precipitate increase</td>
<td>Increase (precipitate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Formaldehyde</strong></td>
<td>Calcium</td>
<td>Slight increase</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td>Precipitate increase</td>
<td>Increase (precipitate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.01%</strong></td>
<td>Calcium</td>
<td>Small precipitate</td>
<td>Precipitate stays the same and gel increases</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Increase (precipitate and gel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.005%</strong></td>
<td>Calcium</td>
<td>Precipitate and gel</td>
<td>Gel increase</td>
<td>Precipitate and gel increase</td>
<td>Increase</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Increase (precipitate and gel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sodium Azide</strong></td>
<td>Calcium</td>
<td>Small increase precipitate</td>
<td>No change in precipitate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td>Increase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.05%</strong></td>
<td>Calcium</td>
<td>No change in precipitate</td>
<td></td>
<td></td>
<td></td>
<td>Small precipitate</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td>Increase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.01%</strong></td>
<td>Calcium</td>
<td>Increase</td>
<td>No change</td>
<td>Increase</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td>Increase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.005%</strong></td>
<td>Calcium</td>
<td>Increase</td>
<td>No change</td>
<td>Increase</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td>Increase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleach (sodium hypochlorite)</td>
<td>Calcium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No Change after first day</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TREATMENT TYPE</td>
<td>SAMPLE TYPE</td>
<td>DAY 17</td>
<td>DAY 23</td>
<td>DAY 25</td>
<td>DAY 26</td>
<td>DAYS 30/43/65</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Standard (No treatment)</td>
<td>Calcium</td>
<td>Precipitate and gel continue to Increase</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td>Increases</td>
<td>No change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Calcium</td>
<td>No change</td>
<td>after day 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1% Sodium</td>
<td>Calcium</td>
<td>No change</td>
<td>after day 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td>after day 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05% Sodium</td>
<td>Calcium</td>
<td>No change</td>
<td>after day 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td>Precipitate increase</td>
<td>No Change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01% Sodium</td>
<td>Calcium</td>
<td>Gel increase</td>
<td>Gel increases (Mesh), Mold-like substance appears on mesh</td>
<td>Mesh increase</td>
<td>No change</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Increase (precipitate and gel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005% Sodium</td>
<td>Calcium</td>
<td>Gel increase</td>
<td></td>
<td>No Change</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Increase (precipitate and gel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Azide</td>
<td>Calcium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1% Sodium</td>
<td>Calcium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05% Sodium</td>
<td>Calcium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01% Sodium</td>
<td>Calcium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005% Sodium</td>
<td>Calcium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleach (sodium hypochlorite)</td>
<td>Calcium</td>
<td>No change after first day</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 16. The Results of Tests in the Dark

<table>
<thead>
<tr>
<th>TREATMENT TYPE</th>
<th>SAMPLE TYPE</th>
<th>Observed after 192 days</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard (No treatment)</strong></td>
<td>Calcium</td>
<td>Gel present (amount less that the samples exposed to light)</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Gel present (floating on liquid surface), precipitate at bottom of test tube. ** less gel than the sample exposed to light</td>
</tr>
<tr>
<td><strong>Formaldehyde</strong></td>
<td>Calcium</td>
<td>No precipitate or gel noted</td>
</tr>
<tr>
<td>0.1%</td>
<td>Sodium</td>
<td>Small amount of precipitate but no gel</td>
</tr>
<tr>
<td><strong>0.05%</strong></td>
<td>Calcium</td>
<td>Few particles are visible</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Precipitate (brown) at bottom of test tube</td>
</tr>
<tr>
<td><strong>0.01%</strong></td>
<td>Calcium</td>
<td>Gel present</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Gel present.</td>
</tr>
<tr>
<td><strong>0.005%</strong></td>
<td>Calcium</td>
<td>Gel present</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Gel &amp; Precipitate</td>
</tr>
<tr>
<td><strong>Sodium Azide</strong></td>
<td>Calcium</td>
<td>No change</td>
</tr>
<tr>
<td>0.1%</td>
<td>Sodium</td>
<td>Precipitate. No gel</td>
</tr>
<tr>
<td><strong>0.05%</strong></td>
<td>Calcium</td>
<td>No change</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Precipitate present. About two gel strands are visible</td>
</tr>
<tr>
<td><strong>0.01%</strong></td>
<td>calcium</td>
<td>No change</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Precipitate 2-3 gel strands</td>
</tr>
<tr>
<td><strong>0.005%</strong></td>
<td>Calcium</td>
<td>No change</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Precipitate 4 strands of gel</td>
</tr>
<tr>
<td><strong>Bleach (sodium hypochlorite)</strong></td>
<td>Calcium</td>
<td>Solution decolorized</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>White precipitate</td>
</tr>
</tbody>
</table>
Chapter 5. Technology Transfer

A considerable number of papers and presentations were generated in the pursuit of this research project. These include:


The following are presentations that did not include a published paper.
AUG Chapman Conference: San Diego – January 2005
US/Norway Summer School: Research Experience in Carbon Sequestration: Santa Fe – August 2004
DOE/NPTO Project Review: Tulsa – August 2003
Project review with producers: Midland – March 2003
Presentation at the Regional American Chemical Society Meeting: Oklahoma City – June 2002
Project review with producers: Midland – November 2001
Project review with producers: Houston – November 2001
Thesis – D.B. Gupta
Thesis – Sakish Ganda
Thesis – Tristan Wellman
Thesis – L.V. Bethapudi
CONCLUSIONS

A number of conclusions are drawn in the work comprising this Final Report. They are summarized by chapter.

Chapter 1: Industry Survey

Results of this survey showed that:

- Significant experience and knowledge in the industry exist to enable the successful management of CO2 injection into geological formations for IOR or hydrocarbon storage.
- Monitoring and verification of CO2 flow in geological formations is in the infancy of its development.
- Experience has shown that CO2 goes where expected. The challenge is developing detailed reservoir characterizations and honoring them and the phase behavior of CO2 as well.
- CO2 does what is expected: mobilizes oil, dissolves in brine, and promotes dissolution of carbonates. The kinetics of these processes under a wide range of reservoir conditions requires further studies.
- In the short geological timeframe that CO2 has been actively injected into geological formations for IOR, seals generally are retaining the CO2 subsurface.

Chapter 2: CO2/Brine/Rock Interaction

- Water-alternating-gas (WAG) core flood experiments conducted on limestone and dolomite core plugs confirmed that carbonate mineral dissolution and deposition can occur over relatively short time periods (hours to days) and in close proximity to each other.
- Results of earlier laboratory CO2-brine flow experiments performed in rock core were used to calibrate a reactive transport simulator. The calibrated model was used to estimate in situ effects of a range of possible sequestration options in depleted oil/gas reservoirs. The code applied in this study, TRANSTOUGH, was a combination of the well known TOUGH2 simulator, for coupled groundwater/brine and heat flow, with the chemistry code TRANS for chemically reactive transport. Although the TRANSTOUGH model remains in the developmental stages, simulated results compared favorably to experimental results, suggesting that the model accurately simulates CO2 sequestration under deep reservoir conditions, at least for small spatial scales.
Limestone was coreflooded with co-injected CO\textsubscript{2} and brine at reservoir pressure and temperature. Analysis confirmed the deposition of trace metals within deposited carbonate material, providing direct evidence of deposition. These phenomena can occur during CO\textsubscript{2} injection into carbonate geological formations: in IOR the concern is for injectivity changes, while the issues for sequestration are long-term storage capacity and seal integrity.

Five large-core flooding experimental series were performed on quarried and reservoir carbonates (limestone and dolomite) with co-injected or alternating injections of CO\textsubscript{2} and brine at reservoir conditions. The results are being used to calibrate a CO\textsubscript{2} model coupling multiphase flow to chemical reactions that will be used to predict in situ dissolution and deposition that can result in significant reservoir injectivity.

Chapter 3: Flow Rate and Injectivity

A series of core experiments with nitrogen flowed through cylindrical core confirmed previous studies, which indicated that though the Forchheimer equation is useful in describing high velocity flow in porous media, that in many cases it is not sufficient.

Non-Darcy flow parameters were investigated in 159 series of high pressure/high temperature/high velocity gas flooding experiments on five different rock samples under field reservoir conditions. The results of these experiments reconfirm and extend to new conditions that permeability increases, while non-Darcy flow coefficient decreases with effective stresses; both are independent of shear stresses.

The non-Darcy behavior results of CO\textsubscript{2} (compared to the previous studies using N\textsubscript{2}) were investigated in 85 series of high-velocity gas flooding experiments under high pressure and high temperature. It was found that pore pressure has more influence on permeability in CO\textsubscript{2} flooding than it does in N\textsubscript{2} flooding. In contrast, though temperature has definite and consistent influence on both permeability and non-Darcy flow coefficient in N\textsubscript{2} flooding, the same influence in CO\textsubscript{2} flooding was not observed. Field data indicates that this phenomenon could be responsible for productivity loses in high flow rate CO\textsubscript{2} wells. Accordingly, attention should be paid to avoid flowing CO\textsubscript{2} at conditions near its critical point.
• The two types of non-Darcy criteria, the Reynolds number and the Forchheimer number, for fluid flow in porous media were reviewed. A revised Forchheimer number is recommended due to the clear meaning of variables involved.

Chapter 4: Surfactant Sorption, Stability, and Mobility

• The results of a series of tests on CO₂ foams identified chemical cost reduction derived from the synergistic effects of co-surfactant systems using a good foaming agent and a less expensive poor foaming agent. The required good foaming agent was reduced by at least 75%. Additionally, the deleterious effect on injectivity was reduced by as much as 50% using the co-surfactant system, compared to a previously used surfactant system.

• The influence of a number of parameters on CO₂-foam stability and surfactant adsorption at reservoir conditions were determined in a series of tests. The stability of CO₂-foam was found to be surfactant concentration-dependent. Another series of tests demonstrated that interfacial tension (IFT) does not directly correlate to foam stability and foam stability cannot be predicted solely by the value of IFT.

• A series of experiments investigated calcium lignosulfonate (CLS) adsorption onto minerals common to oil reservoirs: silica, kaolinite, bentonite, calcite, and dolomite. Comparing CLS adsorption density onto different minerals was undertaken to develop transport and sorption models to better predict chemical requirements in reservoir flooding processes. The order of CLS adsorption density onto the five minerals was found to be: montmorillonite > kaolinite > dolomite > calcite > silica.

• Adsorption and desorption studies were carried out with CLS on Berea sandstone. The results of this research show that: increasing CLS concentration and salinity increases CLS adsorption density; increasing temperature will decrease adsorption density; increasing injection rate of CLS solution will slightly decrease CLS adsorption density, post-flush rate and salinity of brine have a large impact on the CLS desorption process; the adsorption and desorption process are not completely reversible; and temperature and pH of the postflush brine have little effect on desorption.

• Another series of experiments looked at CLS transport mechanisms through Berea sandstone by combining the experiment results of calcium lignosulfonate (CLS) adsorption onto Berea sandstone and five powdered pure minerals that are found on sandstone. Results showed that the Berea sandstone required a much longer equilibrium
time for CLS adsorption than did any of the other substances, indicating that diffusion is the main mechanism controlling CLS transport time through Berea sandstone. When

- CLS adsorption densities onto five common reservoir minerals were compared, results showed that silica, which constitutes more than 80% of Berea sandstone and is the bone structure of sandstone, adsorbed little CLS, and that other minerals found in sandstone contributed most of the adsorption of CLS onto Berea sandstone. Thus, a dual porosity model is suggested to simulate CLS transport through Berea sandstone, though sandstone is generally regarded as a homogeneous porous medium.

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- Studies on the adsorption and desorption of calcium lignosulfonate (CLS) were performed with limestone and dolomite. Kinetic results have shown that adsorption and desorption are both time-dependent, not instant. Both adsorption and desorption were characterized by a biphasic pattern: a fast step followed by a slow step. Apparent adsorption rate coefficients were determined by a second-order kinetic model. Desorption did not reach equilibrium in the rested core under normal reservoir flow rates. Equilibrium results show that CLS adsorption and desorption onto limestone or dolomite can be described well by the Langmuir isotherm over the tested CLS concentration range, and that increasing concentration increases adsorption density. There is significant hysteresis between CLS adsorption and desorption isotherms. Increasing both NaCl and
CaCl$_2$ concentrations increased adsorption density; however, CaCl$_2$ had a much greater impact on the adsorption.

- A series of experiments comprising adsorption and desorption tests was performed for five powdered minerals and three rock types using a CO$_2$–aqueous phase foaming agent, surfactant CD. Results showed that CD adsorption and desorption onto powered minerals could be established in one hour. The decreasing order of the surfactant adsorption density onto the five minerals is: montmorillonite, dolomite, kaolinite, silica and calcite. Surfactant adsorption onto the three core systems took at least one order of magnitude longer than that onto the five powdered minerals, and the surfactant adsorption onto Berea sandstone required a longer time than either Indiana limestone or Lockport dolomite. These results led to a better understanding of surfactant adoption behaviors and transport mechanisms through different porous media.

- Another series of experiments examined adsorption/desorption with two surfactant systems (CD and CLS) and with a mixture of the two onto five minerals and two porous media. The results from this work are being used to develop optimum solution concentrations of CD and CLS for specific reservoir rock, which are anticipated to optimize foaming ability, production cost economy, and adsorption.

- A number of foam stability and surfactant solution stability tests were carried out. The results showed that:
  - Formaldehyde prevents formation of a suspended material (gel) or a precipitate when the applied formaldehyde concentration is equal to or greater than 500 mg/L.
  - Sodium azide prevents a suspended solid (gel) and a minimum of precipitate forming in CLS solution to concentrations at least as low as 50 mg/L. Gel decreased in SLS with sodium azide concentration increase.
  - SLS solution had precipitate no matter what treatment was applied. If no treatment is applied both SLS and CLS solutions will form gel with time, but CLS solution will not have precipitate.
  - Sodium hypochlorite will bleach the solution to a very light yellow and will have white precipitate for both SLS and CLS. This occurred the first day with no change thereafter.
  - Previously conducted ultrasonic and boiling tests were found to have no effect
In addition to these experimental results, a substantial technology transfer effort, detailed in Chapter 5, was accomplished.

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Devon                               Transpetco
Denbury

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