NATIONAL ENERGY TECHNOLOGY LABORATORY

Mobility and Conformance Control for Carbon Dioxide Enhanced Oil Recovery (CO_2-EOR) via Thickeners, Foams, and Gels – A Detailed Literature Review of 40 Years of Research

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EXECUTIVE SUMMARY

Carbon dioxide (CO_2) has been used commercially to recover oil from geologic formations by enhanced oil recovery (EOR) technologies for over 40 years. The U.S. Department of Energy Office of Fossil Energy and its predecessor organizations have supported a large number of laboratory and field projects over the past decades in an effort to improve the oil recovery process including investments to advanced reservoir characterization, mobility control, and conformance of CO_2 flooding.

Currently, CO_2 EOR provides about 280,000 barrels of oil per day, just over 5 percent of the total U.S. crude oil production. Recently CO_2 flooding has become so technically and economically attractive that CO_2 supply, rather than CO_2 price, has been the constraining developmental factor. Carbon dioxide EOR is likely to expand in the United States in upcoming years due to "high" crude oil prices, natural CO_2 source availability, and possible large anthropogenic CO_2 sources through carbon capture and storage (CCS) technology advances.

A revised national resource assessment for CO_2 EOR (July 2011) prepared by Advanced Resources International for DOE indicated:

- "Next Generation" CO_2 EOR can provide 137 billion barrels of additional technically recoverable domestic oil, with about half (67 billion barrels) economically recoverable at an oil price of $85 per barrel.
- This volume of economically recoverable oil is sufficient to support nearly 4 million barrels per day of domestic oil production (1.35 billion barrels per year for 50 years), reducing oil imports by one-third.
- Federal/state treasuries would be a large beneficiary, receiving $21.20 of the $85 per barrel oil price in the form of royalties on Federal /state lands plus severance, ad valorem and corporate income taxes. Total revenues to Federal/state treasuries would equal $1,420 billion.
- The general U.S. economy would be the largest beneficiary, receiving $25.80 of the $85 per barrel of oil price, in the form of wages and material purchases. Total revenues would equal $1,730 billion.
- Nearly 20 billion metric tons of CO_2 would need to be purchased by CO_2 EOR operators to recover the 67 billion barrels of economically recoverable oil. Of this, at least 18 billion metric tons would need to be provided by anthropogenic CO_2 captured from coal-fired power plants and other industrial sources.

"Next Generation" technologies include increasing CO_2 injection volumes by 50% or more, drilling horizontal wells for injection or production, improving mobility ratio and flood conformance, extending the conditions under which miscibility between the oil and CO_2 can be achieved, and applying advanced methods for monitoring flood performance.

Despite its well-established ability to recover oil, the CO_2 EOR process could be improved if the high mobility of CO_2 relative to reservoir oil and water can be effectively and affordably reduced. The CO_2 EOR industry continues to use water-alternating-with-gas (WAG) as the technology of choice to control CO_2 mobility and/or mechanical techniques (e.g., cement, packers, well control, infield drilling, and horizontal wells) to help control the CO_2 flood conformance. If the "next generation" CO_2 EOR target of 67 billion barrels is to be realized, new solutions are needed that can recover significantly more oil than the 10–20% of the original oil in place associated with current flooding practices.

This literature review concentrates on the history and development of CO_2 mobility control and profile modification technologies in the hope that stimulating renewed interest in these *chemical techniques* will help to catalyze new efforts to overcome the geologic and process limitations such as poor sweep efficiency, unfavorable injectivity profiles, gravity override, high ratios of CO_2 to oil produced, early breakthrough, and viscous fingering. Carbon dioxide mobility control technologies are in-depth, long-term processes that cause CO_2 to exhibit mobility comparable to oil. Profile modification and conformance control are achieved by a near-wellbore, short-term process primarily intended to greatly reduce the permeability of a thief zone.

The premise of this report is that a thorough review of the literature related to the past successes and failures of lab- and field-scale efforts to reduce CO_2 mobility using CO_2 thickeners, foams, and gels will provide a baseline understanding of the remaining challenges and the research needed to advance this technology. Solving these challenging CO_2 flooding problems will ultimately increase domestic oil production via CO_2 EOR. This review has highlighted a number of successes. For example:

There has been considerable lab-scale progress in *(direct) thickening* of CO_2, most notably with the fluoroacrylate-styrene copolymer polyFAST and silicone oil-toluene solutions. PolyFAST is capable of significantly increasing the viscosity of CO_2 (~10-fold) flowing through Berea sandstone at reservoir conditions in dilute concentrations (~1wt %).

There have been a multitude of successful lab-scale tests involving *water-soluble surfactants* capable of stabilizing *CO_2-in-brine foams.* These achievements led to 13 published reports of pilot tests conducted between 1984 and 1994, most of which were aimed at attaining conformance control. Five of these projects were considered to be successful technical efforts and favorable economic assessments were associated with most of them.

It appears that the emergence of robust *gel-based conformance techniques* (including monomer solutions that polymerize and crosslink (gel) in situ, polymer solutions that crosslink in situ, foams that gel in situ, and pre-formed particle gel dispersions) coupled with WAG for mobility control may have led to a decline in the use of foams as a conformance control technique, especially in extremely high permeability flow paths where foams are generally ineffective. These gel methods appear to be more effective and robust than CO_2 foams, as demonstrated in a series of generally successful field tests conducted beginning in the late 1970s and continuing to the present day.

A large number of lab-scale studies were directed at the design of *in-depth mobility control foams*. This led to two pilot tests aimed solely at CO_2 mobility control, one of which indicated that a 60% increase in the apparent viscosity of CO_2 occurred where the foam formed, and several pilot tests that were designed to both increase the apparent viscosity of CO_2 and block a high permeability zone, one of which clearly demonstrated that CO_2 foams could simultaneously enhance conformance control and mobility control. Although CO_2 was not used as the displacement gas, it is important to note that the biggest and most successful mobility control foam field demonstration occurred at Norsk Hydro's Snorre Field in the North Sea where analysis concluded that the alternating injection of surfactant slugs and hydrocarbon gas slugs contributed to 250,000 m^3 (1.6 million barrels) of oil recovery while consuming only approximately $1,000,000 of surfactant.

Recently, CO_2 foams generated with *CO_2-soluble nonionic surfactants* have been successfully tested in the lab and through an on-going pilot test. Further, lab-scale testing of foam stabilization with *water-dispersible nanoparticles* has been initiated in an attempt to circumvent problems often associated with surfactant solutions flowing for extending periods of time through a porous medium, such as adsorption losses and chemical instability of the surfactant.

The results of 40 years of research and field tests clearly indicate that mobility and conformance control for CO_2 EOR with thickeners, foams, and gels can be technically and economically attainable for some fields; however significantly more research needs to be conducted to improve the technology and the economics. The following Game Changer technologies are recommended as primary candidates for further research, based on this literature review.

CO_2 EOR Game Changer Candidate #1: CO_2 Viscosifiers (Direct Thickeners)

An affordable CO_2 thickener has been recognized as a Game-Changing technology for over 25 years, but has not yet been developed. The design of such a thickener is a much more challenging problem than was envisioned several decades ago primarily due to the low CO_2 solubility, or complete CO_2 insolubility, of compounds that contain the chemical groups responsible for viscosity-enhancing intermolecular associations. However, the development of a CO_2 thickener that could change the CO_2 viscosity to that of the oil being displaced would have profound effects on oil recovery and is worth pursuing.

A CO_2 thickener would be a particularly effective mobility control agent because the viscosity of the thermodynamically stable, CO_2-rich solution could be manipulated simply by varying the thickener concentration. Unlike CO_2 foams, the CO_2 viscosity change induced by a thickener would not be dependent on rock characteristics, oil and brine properties, or fluid saturations and flow rates. It has been demonstrated that CO_2 can be thickened with high molecular weight silicone oil at reservoir conditions in the presence of significant amounts of an organic co-solvent such as toluene; although this thickened CO_2 was shown to improve oil recovery from cores, the co-solvent requirement (roughly 10% co-solvent, 90% CO_2) made pilot-testing costs prohibitive. DOE-funded research has led to the identification of the only known thickener that does not require a co-solvent: a fluoroacrylate-styrene copolymer (polyFAST). Several other compounds that provide only modest increases in viscosity have also been developed, such as a fluorinated telechelic ionomer, a tri(semi-fluorinated alkyl) tin fluoride, a surfactant with two twin-tailed fluorinated tails, and a high molecular weight fluoroacrylate homopolymer. In these cases the compound is highly fluorinated, extremely expensive, and high concentration (3–6wt%) of the compound is required to achieve a modest 2–4 fold increase in CO_2 viscosity. Only polyFAST was capable of significantly increasing the viscosity of CO_2 (~10-fold) flowing through Berea sandstone at reservoir conditions in dilute concentrations (~1wt%) in the absence of a co-solvent, but the cost of the fluoroacrylate monomer makes polyFAST prohibitively expensive.

Subsequent research on potential *non-fluorous* polymeric thickeners including poly(benzoyl vinylacetate), a non-fluorous analog of polyFAST, showed that these copolymers did not dissolve in CO_2 unless pressures far in excess of the minimum miscible pressure (MMP) were applied. The on-going thickener research that is being funded by the DOE is directed at small compounds that self-assemble into viscosity-enhancing rods or helices in dense CO_2. Progress in the design of small molecular thickeners for CO_2 is impeded by their very low solubility in CO_2.

Even if a CO_2 thickener, whether a polymer or small molecule, is identified, operational constraints may face operators who would try to implement the technology in a pilot-test. First, nearly every promising CO_2 thickener is a solid at ambient temperature and a means of introducing a powder into the CO_2 stream must be therefore employed, possibly by first dissolving the thickener in an organic solvent in order to form a concentrated, viscous, pump-able solution. Second, high-pressure mixing tanks would be required if static, in-line mixers are insufficient to rapidly dissolve the thickener in the CO_2. Therefore, it will be important for researchers to begin to investigate the process engineering aspects of field operations while continuing to seek a low-cost thickener.

CO_2 EOR Game Changer Candidate #2: Near-Wellbore Conformance Control with CO_2 Foams and Gels

The improved performance of the gel technologies in blocking flow paths, enhanced gel robustness, the lack of a pressing need to reverse foam conformance control treatments, and operator's ability to apply gel treatments in formations with fractures or highly permeable open flow paths has made gels popular tools for conformance control during a CO_2 *flood. It appears that unless significant advances are made, persuading operators to consider* CO_2 *conformance control foams as a "game changing" alternative technology may be difficult given the mixed successes and disappointments during a decade of* CO_2 *conformance control foam field tests and the refinement of robust, alternative technologies based on chemical gels. However, there seems to be a consensus that the* CO_2 *conformance control foams are less expensive and more readily reversible (via water injection, if desired) than any of these gel treatments. Given the ability of foams to be designed for conformance control and/or mobility control, it may be prudent to combine the two technologies where gels are employed for conformance control and* CO_2*-in-brine foam (rather than WAG) is used for mobility control.*

Carbon dioxide-in-brine foams are generated in situ, usually via the simultaneous injection of CO_2 and an aqueous surfactant solution in lab-scale tests, and via the alternating injection of surfactant and CO_2 slugs (surfactant-after-gas or SAG) in the field. The capability of foam to form more readily and effectively in higher permeability rock layers is desirable to reduce the flow of CO_2 into previously waterflooded, or CO_2 flooded, high permeability layers, while promoting the flow of CO_2 into lower permeability oil-rich zones. Because the surfactant required to stabilize the aqueous lamellae is typically dissolved in water (which is a very strong solvent for compounds with polar or ionic groups) numerous inexpensive surfactants have been identified in the lab of which only a few (Chaser CD 1045, Alipal CD 128, and Chaser CD 1040) were used extensively in pilot tests.

Foam generation requires interactions between the porous medium and the injected fluids, thus a multitude of lab-scale studies directed at understanding the effects of temperature, pressure, surfactant type, surfactant concentration, flow rate, foam quality, brine salinity, rock type, rock wettability, matrix permeability, presence of fractures, degree of heterogeneity, presence of vugs, oil composition, and oil saturation on the performance of these foams were conducted. Laboratory foam mobility results for various porous media indicated that foams are typically most readily formed in higher permeability, water-wet to mixed wettability, fracture-free cores. Carbon dioxide foams have been found to reduce the residual oil saturation beyond that achieved by CO_2 floods when the foam flood occurred after the CO_2 flood in cores initially containing high oil and residual water saturation.

Eleven field tests using foams were conducted beginning in the mid-1980s that focused primarily on blocking thief zones and impeding gravity override. There was a good deal of variability in the degree of technical and economic success ascribed to these conformance control tests. About half of these projects were considered to be successful technical efforts, and favorable economic assessments were associated with most of them. However, about half of the field tests reported problems that rendered the technical results as either unsuccessful or inconclusive. Problems noted during these field tests included the dilution of CO_2 foam by subsequently injected water, the inability of foam to be effective in formations containing fractures or extremely high permeability open flow paths, the very short propagation of the CO_2 from the injection well, cold weather ice and hydrate formation, unacceptably large decreases in injectivity associated with co-injection, and other unspecified "operational problems." The inability to determine how much incremental oil was associated with application of the CO_2 foam was also cited as an impediment to providing an accurate assessment of the process. Specific conformance control field test results include:

- During the Unocal/Long Beach Oil Dev. Co. Wilmington Immiscible Trial at Long Beach, California in 1984, a SAG conformance control pilot successfully diverted flow into the T zone. Gas and water injection profiles indicated that the T zone received as much as 43.3% of the injected gas, a dramatic increase from the 1.3% value prior to SAG.
- Chevron initiated a CO_2 WAG flood at their Rangeley Weber Sand Unit in Colorado. The operators found the results encouraging in that the foam project—which resulted in the incremental production of roughly 50 BOPD during April and May 1989—paid out in two months.
- One of the best documented field tests of CO_2-in-brine foams occurred during 1992 in the Phillips' East Vacuum Grayburg/San Andres Unit (EVG/SAU). The operator estimated that 14,700 bbl. and 4,460 bbl. of incremental oil were produced as a result of the first and second SAG tests, respectively.
- During Amoco's Wasson ODC Unit conformance control foam test in 1994, CO_2 breakthrough was delayed from 8 to 22 days and CO_2 production was reduced from roughly 2000–2500 Mscf/d to 1000–1500 Mscf/d.

- During Mobil's Slaughter Field, East Mallet Unit, Well 31 test in 1991, injection profile logs indicated that fluids were completely diverted from the thief zone and oil production in the entire pattern increased by about 26%, or 19 BOPD.

The decline of interest in CO_2 foams may also have been due in part to the emergence of other conformance control techniques, including monomer solutions that polymerize and crosslink (gel) in situ, polymer solutions that crosslink in situ, foams that gel in situ, and pre-formed particle gel dispersions. Marked reductions in mobility have frequently been reported for these gel technologies, especially in extremely high permeability flow paths where foams are generally ineffective. These gel methods appear to be more effective and robust than CO_2 foams, as demonstrated in a series of generally successful field tests conducted beginning in the late 1970s and continuing until the present day:

- At Amoco's Wertz field ten wells were treated with gels that extended the economic life of the field by two years, enabling the production of 35,000 to 140,000 barrels of oil per pattern.
- Eighty percent of the 49 wells treated with gels at Rangely-Weber Sand Unit between 1994 and 1997 were considered successes. The $2,060,500 investment yielded 685,000 incremental barrels of oil, which resulted in a 365% rate of return and an 8-month payout period.
- Due to severe channeling of both water and solvent through a thief zone, a lignosulfonate gel conformance control project was implemented in nine injection wells at Amoco's South Swan Hills Miscible Unit located in Alberta, Canada. Thirteen producers had a significant increase in incremental oil, and the total incremental oil production from this project was estimated to be 3,300,000 barrels.
- Two problem injection wells at the Lick Creek field were treated with a low viscosity, aqueous monomer solution that contained an organic crosslinker Incremental oil production attributable to these treatments was 65 BOPD, totaling 25,000 bbl. by November 1985.

CO_2 EOR Game Changer Candidate #3: In-Depth Mobility Control CO_2 Foams

Research results have demonstrated that surfactant-induced CO_2 foams are an effective method for mobility control in CO_2 foam flooding, but have potential weaknesses. Because the foam is by nature ultimately unstable, its long-term stability during a field application is difficult to maintain. Nonetheless, one can make a convincing argument that the potential of CO_2 mobility control foams has not been fully explored in pilot tests, especially given the immense body of promising lab-scale technical knowledge that has been reported. Carbon dioxide-soluble surfactants, which are currently being tested in the field at SACROC, ensure that the surfactant appears (and the foam forms) only where the CO_2 flows. These provide a modest degree of conformance and mobility control, are easy to implement even for operators who only employ continuous CO_2 injection, and may greatly reduce the need for alternating slugs of brine. New nano-science technologies may also provide an alternative for the generation of stable CO_2 foam. Using nanoparticles instead of surfactant to stabilize CO_2 foam may overcome the long-term instability and surfactant adsorption loss issues that affect surfactant-based CO_2 EOR processes.

Although a large number of lab-scale studies were directed at the design of in-depth mobility control foams, only two field tests were specifically designed to assess the performance of in-depth mobility control foams using CO_2 as the injected gas.

- The 1990 mobility control trial at Joffre Viking was unsuccessful because the foam propagated only a few feet from the injector.
- The 1984 Rock Creek trial was somewhat inconclusive since reservoir fluids and the in situ generated foam did not flow past the observation well as anticipated, although pressure measurements indicated that a 60% increase in the apparent viscosity of CO_2 was attained in regions where the foam formed.

Several other foam trials, such as the successful Mobil pilot-test at EMU 31, recognized that CO_2 foams could be used to simultaneously improve both conformance and mobility control.

Although CO_2 was not used as the displacement gas, it is important to note that the biggest and most successful mobility control foam field demonstration occurred at Norsk Hydro's Snorre Field in the North Sea.

The injection gas at Norsk Hydro's Snorre Field in the North Sea was a hydrocarbon mixture with approximately 70% methane gas content. In-depth mobility control foams were used successfully and profitably to recover substantial amounts of oil. Modeling results indicated that the SAG contribution to oil recovery was 250,000 m^3 of oil whereas a material balance indicated that as much as 350,000 m^3 of oil could have been displaced by injected methane gas. Because the cost of the surfactant treatment was only $1,000,000, this project was considered a technical and economic success.

The very favorable results of the Snorre Field mobility control foam flood did not translate into renewed interest in CO_2 mobility control foams in the United States, however. Other successful hydrocarbon gas mobility control foam field tests include:

- At Signalta Resources' Pembina/Ostracod 'G' Pool Field in 1987, the injection of two surfactant slugs was sufficient to increase oil production from 25 m^3/d to 33 m^3/d for three months.
- Hydrocarbon miscible gas foam was injected during 1987 at Dome Petroleum's Triassic 'A' Pool Field. Baseline injectivity was later reestablished, indicative that the hydrocarbon miscible gas foams would not induce permanent changes in injectivity and that the foams could be dissipated by water injection.

There are no reports of CO_2 foam pilot tests using brine-soluble surfactants for mobility control after 1990. This may be attributable to a combination of factors including the unsuccessful Joffre Viking test; the modest to inconclusive mobility control results at Rock Creek; several literature studies that warned of the great difficulty in maintaining the integrity of a mobility control foam of specified quality deep within the formation; the North Ward-Estes pilot that lauded the reduction of compression costs associated with CO_2 cycling via conformance control over the attempts to enhance areal sweep and increase oil recovery via mobility control; the relative difficulty associated with forming weak foams of specified mobility in low perm, oil-bearing zones compared to generating strong foams in high perm, water-out zones; and demanding logistics of SAG mobility control treatments, especially for cycles of very short duration.

Given the multitude of lab-scale efforts conducted to understand and design CO_2 mobility control foams and the very small number of mobility control pilot-tests, CO_2 mobility control foams may remain a promising area for future field testing. Gels are designed for dramatic increases in viscosity, and are therefore incapable of being used for mobility control purposes, leaving SAG CO_2 mobility foams as a viable alternative to WAG. These mobility control foams could even be used in conjunction with gel-based conformance control techniques. The performance of such processes could be contrasted with the current state-of-the-art of or gel-based and mechanical techniques for conformance control combined with WAG for mobility control.

There has been a limited and very recent rekindling of interest in CO_2 foams associated with an old idea: CO_2-soluble surfactants. The objective is to dissolve the surfactant in the injected CO_2 rather than in alternating slugs of brine. Given the large amounts of brine in the pore space, the foams could still be generated in situ; thus it should be possible to reduce or possibly eliminate the need for alternating injections of brine. Further, unlike SAG, this process would ensure that the surfactant would be present where the CO_2 flows in the formation. Finally, this technique could also be employed by companies that only conduct continuous CO_2 injections rather than WAG.

Extensive surfactant studies conducted at the University of Texas at Austin have resulted in promising single-well injectivity pilot test results using a Dow Oil & Gas surfactant at SACROC in 2010, and have led to the expansion to a four-well oil recovery pilot at the same field. Results from the first phase showed a consistent increase in the cumulative CO_2 volume injected versus time at constant injection pressure indicating that (for the duration of this test) the foam propagated through the matrix for 500 hours following the introduction of surfactant. Further, injection profiles indicated that about 30% of the injected CO_2 was diverted to a lower portion of the formation while only 1% of the CO_2 flowed into the lower zone prior to the addition of the surfactant. Favorable lab-scale results from an Office of Fossil Energy– University of Pittsburgh project are leading to the identification of inexpensive, CO_2-soluble, nonionic surfactants from other chemical suppliers.

New nano-science technologies may also provide an alternative for the generation of stable CO_2 foam. Studies show that small solid particles such as fumed silica can adsorb at fluid/fluid interfaces to stabilize drops in emulsions and bubbles in foams. The nanoparticles readily disperse in water and this dispersion is capable of flowing through unconsolidated porous media. Using nanoparticles instead of surfactant to stabilize CO_2 foam may overcome the long-term instability and surfactant adsorption loss issues that affect surfactant-based CO_2 foams. Recent laboratory-scale tests show promise, but no nanoparticle-stabilized core, lab-scale oil recovery, pilot, or field tests have yet been reported because this technology is still in its infancy.

Furthering the "Next Generation" of CO_2 EOR Research

Despite industry's best efforts, previous attempts for controlling CO_2 floods have been only partially successful for conformance control (these technologies have not been widely accepted for a variety of reasons) and less successful for CO_2 mobility control.

DOE's Office of Fossil Energy through the National Energy Technology Laboratory (NETL) awarded a number of new projects in 2010 seeking to further next generation CO_2 EOR to the point of pilot (small) scale testing. Three of these research activities are related to mobility control in CO_2 flooding; two are focused on nanoparticle technologies and one on CO_2 soluble surfactants.

The University of Texas (Austin) is evaluating inexpensive alternative nanoparticle sources to provide the large volumes needed for foam stabilization in field-scale CO_2 floods. The study entails using low cost, commercially available "bare" silica nanoparticles and applying a polyethylene glycol (PEG) coating in-house to produce low-cost alternatives as well as the use of natural nanoparticles (e.g., fly ash) to develop CO_2 foam.

A New Mexico Institute of Mining and Technology research activity is conducting complementary research on the use of nanoparticles to increase CO_2 flood sweep efficiency. The effects of particle retention on core permeability and porosity will be investigated using long-term core flooding experiments and nanoparticle-stabilized CO_2 foams. Additionally, surfactant molecule effects on the stability and performance of nanoparticle-based CO_2 foams will be examined and evaluated for field application.

Another research activity (also at the University of Texas) is focusing on the development of mobility control agents using surfactants injected with carbon dioxide (CO_2) rather than with water for CO_2 enhanced oil recovery (EOR) in heterogeneous carbonate and sandstone reservoirs.

A fourth research activity is field testing gels for conformance control. The remaining awards supported projects designed to develop advanced computer simulation and visualization capabilities for CO_2 EOR, an electromagnetic (EM) monitoring effort to track the CO_2 flood front, and a field case study of an existing CO_2 flood targeting the residual oil zone. Residual (or stranded) oil exists in the transition zone below the traditional oil-water contact in many domestic oil reservoirs. This resource has not previously been included in any official domestic oil resource database but in some cases appears to be amenable to CO_2 EOR.

The DOE supported this CO_2 mobility control and conformance control literature review in the hope of stimulating renewed interest in generating new ideas to advance the technologies that would overcome the geologic and process limitations of CO_2 EOR. The report premise assumes that a thorough literature review related to past successes and failures of lab- and field-scale efforts to reduce CO_2 mobility using chemical additives will provide a better understanding of future research needed to advance this technology.

OBJECTIVE AND PREMISE OF THIS LITERATURE REVIEW

The Department of Energy is interested in the development and implementation of economical, next-generation CO_2 floods that can recover significantly more than 10%–20% OOIP associated with the WAG process. There has been great interest in chemical techniques for improving mobility and/or conformance control of CO_2 floods. *These chemical techniques for improved CO_2 mobility control are the main topic of this report.* Although there are also numerous mechanical strategies for enhancing oil production such as infill drilling, horizontal wells, etc., these techniques fall outside of the scope of this report.

The use of thickeners and foams as *mobility control* agents for the suppression of fingering or channeling will be emphasized in this report. For example, irregularities of CO_2 fronts associated with multiple-contact miscibility displacements will typically occur at locations and in directions governed by the permeability variations within the reservoir, but the rate of growth is influenced by the mobility ratio. “Fingers” of CO_2 form due to instabilities at the front, while “channels” of CO_2 form in high permeability heterogeneities that are correlated to the direction of flow. Fingers and channels that exhibit close lateral spacing are typically not problematic because transverse dispersion can mitigate the concentration differences and suppress fingers and channel growth. However, widely spaced fingers or channels can continue through the life of the displacement. In this case, CO_2 mobility must be reduced on a large-scale. Further, the depth of the flow patterns behind the front that feed into the fingers are proportional to their transverse dimension; the larger the finger, the larger the region of unfavorable flow patterns behind the front. As a result, the suppression of fingering must be accomplished on a large scale. Therefore, it should be expected that a very substantial fraction of the CO_2 will be made less mobile (whether by direct thickener or foam) [Heller, 1994]. *It is unlikely that the injection of a small pore volume (PV) slug of thickened CO_2 or foam will suppress fingering and channels throughout the life of the CO_2 flood.* In general, mobility control methods involve relatively large CO_2 slugs (e.g., 0.1 PV [Dellinger et al., 1984]) containing dilute amounts of additives that decrease the mobility of the CO_2 to a level comparable to that of the oil ($M \sim 1$), thereby suppressing fingers and channels without causing excessive pressure drop. The less mobile CO_2 will also improve conformance control by evening the flow distribution between layers.

The secondary objective of this report is to assess chemical techniques that are designed primarily to improve conformance control by selectively blocking high permeability flow paths in oil-depleted zones. This can be accomplished, in general, by the use of smaller volumes of fluids that can greatly reduce the permeability of open voids, fractures, vugs, and high permeability streaks using very low mobility foams formed with high concentrations of surfactant, foam gels, gels, or pre-formed particle gels.

Ultimately, the goal of this literature review is to stimulate the reader to generate new insight into, and propose and develop new technology that could help CO_2 EOR make the transition to ‘next generation, game changing’ technologies that may increase domestic oil production.

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LIST OF ACRONYMS

AAPG	–	American Association of Petroleum Geologists
Ac. Ft.	–	Acre-feet
AEGS	–	Alcohol ethoxy glyceryl sulfonate
AFAAI	–	Air foam-alternating-air injection
AGA	–	American Gas Association
AIME	–	American Institute of Mining and Metallurgical Engineers
Amu	–	Atomic mass units
AOS	–	Alpha olefin sulfonate
AOT	–	Aerosol OT
API	–	American Petroleum Institute
B	–	Billion 1,000,000,000 or 10^9
bbl.	–	Barrels
bbl./d	–	Barrels per day
Bcf/d	–	Billion cubic feet per day
BHP	–	Bottomhole pressure
Bscf	–	Billion cubic feet
BO	–	Butylene oxide
BOPD	–	Barrels oil per day
BOVA	–	Benzoyl - vinyl acetate
Btu	–	British thermal unit
CAPEX	–	Capital Expenditure for Construction
CBM	–	Coal Bed Methane
CC/AP	–	Cr (III)-carboxylate/acrylamide polymer gels
CCS	–	Carbon Capture and Storage
CFB	–	Central fault block
CIM	–	Canadian Institute of Mining, Metallurgy, and Petroleum
CH_4	–	Methane
CLASS	–	U.S. DOE’s Reservoir Depositional Classification System (Program)
CMU	–	Central Mallet Unit, Slaughter field
CO	–	Carbon monoxide
CO_2	–	Carbon dioxide
cP	–	Centipoise
CP	–	Crystallized copolymer
DBG	–	Dibutylglycerine-based ethoxylates
DDOA	–	2,3,bis n-decyloxybenzene
DH	–	Degree of hydrolysis
DOE	–	United States Department of Energy
DOG	–	Dioctylglycerine
DP	–	Dykstra Parsons permeability coefficient
Dv	–	Displaceable pore volume

ECBM – Enhanced coal bed methane
EGR – Enhanced gas recovery
EO – Ethylene oxide
EOR – Enhanced oil recovery
EVGSAU – East Vacuum Graysburg/San Andres Unit
FAST – Fluoroacrylate
FAWAG – Foam Assisted WAG
G – 1,000,000,000 or 10^9
Gal – Gallon
GASIS – Gas Information System (A U.S. DOE reservoir and production database)
GHG – Greenhouse gas
GOR – Gas/oil ratio
Gr – Group
GS – Geological storage
GT – Gigatonne, 1Gt = 10^9 metric tons = 10^9 tonne
HSA – Hydroxystearic acid
H_2S – Hydrogen sulfide
HCPV – Hydrocarbon pore volume
IFT – Interfacial tension
IGCC – Integrated gasification combined cycle
IGP – In-situ generated polymer
IOGCC – Interstate Oil and Gas Compact Commission
IOR – Improved Oil Recovery
JCPT – Journal Canadian Petroleum Technology of CIM
JPT – Journal of Petroleum Technology of Society of Petroleum Engineers
Kg – Kilogram
KMD – Knowledge Management Database (hosted by DOE NETL)
Ls – Limestone
LVF – Liquid volume fraction
M – Mobility ratio
M – Thousand or 1,000 or 10^3
Ma or MYP – Millions of years before present
Mar – Margin (continental)
MPa – Megapascals
mD – Milli-Darcy
MM – Million or 1,000,000 or 10^6
MMP – Minimum miscible pressure
MMBBL – Million barrels
MMscf/d – Million standard cubic feet per day
Mw – Molecular weight
N_2 – Nitrogen
NA – Not available
NAS – National Academy of Science
NATCARB – National Carbon Sequestration portal of databases
NETL – DOE’s National Energy Technology Laboratory
NOx – Nitrogen oxides

NPC – National Petroleum Council
NWE – North Ward-Estes (field Texas)
OAO – Oligo(3-acetoxy oxetane)
OCTA – Oligomers of cellulose triacetate
OIP – Oil-in-place
OOIP – Original-oil-in-place
OPEX – Cost of Operation and Maintenance
OVAc – Oligo(vinyl acetate)
Pa – Pascal (unit of force per unit area, one newton per square meter)
PACD – Per-acetylated cyclodextrin rings
PAcGIcVE – Poly((1-*O*-(vinyloxy)ethyl-2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside
PDMS – Polydimethylsiloxane
PEG – Polyethylene glycol
PEO – Polyethlene oxide
PFA – Polyfluoroacrylate
PFOA – Poly(1-,1-,dihydroperfluorooctyl acrylate)
PHPA – Hydrolyzed polyacylamide
PLA – Amorphous polylactic acid
PO – Propylene oxide
polyFAST – Poly(fluoroacrylate-styrene)
PPG – Pre-formed particle gels
PPM – Parts per million
Psi – Pounds per square inch
Psia – Pounds per square inch above atmospheric
PRRC – Petroleum Recovery Research Center (New Mexico Institute of Mining and Technology)
PV – Pore volume
PVAc – Polyvinyl acetate
PVEE – Polyvinyl ethylether
PVI – Pore volume injected
PVMME – Polyvinyl methoxy methyl ether
R&D – Research and development
ROZ – Residual oil zone
SACROC – Scurry Area Canyon Reef Operators Committee (Unit) in Texas
SAG – Surfactant-alternated-CO_2 also solution-alternating-air
SANS – Small-angle neutron scattering
SCF – Standard cubic feet
SCFD – Standard cubic feet per day
SG – Specific gravity
SI – Système International (units)
SIE – Selective injection equipment
SPE – Society of Petroleum Engineers
SPEJ – SPE Journal
SOx – Sulfur oxides
Ss or SS – Sandstone
SSH – South Swan Hills (Alberta field)

SSHMU – South Swan Hills Miscible Unit
STB – Stock tank barrels
STOOIP – Stock tank oil originally-in-place
STP – Standard pressure and temperature (0 ^{o}C and 1 atmosphere; 1.013 bar)
T – Turbidite
TBD – To be determined (not established at the time of this report)
TDS – Total dissolved solids
TMN – Trimethylnonyonal (ethoxylates)
TORIS – DOE'S Tertiary Oil Recovery Information System
TPD – Tons per day
UFS – Unconsolidated friable sandstone
U.S. – United States of America
WAG – Water-alternating-gas
WAGS – Water-alternating–gas with surfactant
WFB – Western fault block

UNIT CONVERSIONS

A common conversion that relates the volume of CO$_2$ as used in enhanced oil recovery (CO$_2$-EOR) and that used in carbon capture and sequestration (CCS) is MMcf/d of CO$_2$ can be converted to million metric tons per year by first multiplying by 365 (days per year) and then dividing by 18.9 * 10^3 (Mcf per metric ton).

acre	×	4.046 873 E+03	=	m^2
acre	×	4.046 873 E–01	=	Ha
acre	×	4.046 873 E-3	=	km^2
acre-ft.	×	1.233 489 E+03	=	m^3
°API		141.5/(131.5+°API)	=	g/cm^3
atm		1.46 E+01	=	psi
atm	×	1.013 250* E+05	=	Pa
atm	×	1.01	=	bar
bar	×	1.0* E+05	=	Pa
bar	×	14.5 E+00	=	psi
bbl. (oilfield barrel)	×	1.589 873 E–01	=	m^3
Btu	×	1.055 056 E+00	=	kJ
cm	×	0.032808399	=	ft
cm^3/g	×	32.0369	=	scf/ton
cp	×	1.0* E–03	=	Pa•s
dyne	×	1.0* E–02	=	mN
eV	×	1.602 19 E–19	=	J
ft.	×	3.048* E–01	=	m
ft.	×	30.48	=	centimeter
ft^2	×	9.290 304* E–02	=	m^2
ft^3	×	2.831 685 E–02	=	m^3
ft./day	×	3.5 E-06	=	m/s
°F		(°F – 32)/1.8	=	°C
°F		(°F + 459.67)/1.8	=	°K
g	×	2.2046 E-03	=	lbm
gal (U.S. liq)	×	3.785 412 E–03	=	m^3
hp	×	7.460 43 E–01	=	kW
hp-hr	×	2.684 520 E+00	=	MJ
in	×	2.54* E+00	=	cm
in^2	×	6.451 6* E+00	=	cm^2
in^3	×	1.638 706 E+01	=	cm^3
kg	×	2.204 6	=	lbm
km^2	×	247.1	=	acre
kPa	×	0.1450	=	psi
kW-hr	×	3.6* E+06	=	J
l	×	2.642 E-01	=	gal

lbf	×	4.448 222 E+00	=	N
lbm	×	4.535 924 E–01	=	Kg
lb./ft^3	×	1.60185 E-02	=	g/cm^3
M	×	3.2808	=	ft.
m^3	×	35.315	=	ft^3
m^3	×	6.290 E+00	=	oilfield barrel
metric ton carbon	×	3.667	=	metric ton carbon dioxide
mg/l	×	1.0* E+00	=	ppm
micrometer	×	1.0* E+00	=	μ
mL	×	1.0* E+00	=	cm^3
mile	×	1.609 344* E+00	=	Km
psi	×	6.894 757 E+00	=	kPa
psi^2	×	4.753 8 E+01	=	kPa^2
ppm TDS	×	1.00* E+00	=	mg/l TDS
sq. mile	×	2.589 988 E+00	=	km^2
stokes	×	1.0* E–04	=	m^2/s
Ton (short) 2000 lb.	×	9.071 847 E–01	=	MT
ton (metric)	×	1.0* E+00	=	MT
tonne	×	1.0* E+00	=	MT
tonne	×	1.0* E+03	=	kg
tonne (CO_2)	×	556.2	=	m^3 CO_2 at (1bar; 25^{o}C)
ton (CO_2)			=	17.23 Mcf
tonne (metric ton CO_2)	×	1	=	18.9 Mcf

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LITERATURE REVIEW

1. Introduction to CO_2 Enhanced Oil Recovery

Carbon dioxide (CO_2) enhanced oil recovery (EOR), also known as CO_2 IOR (improved oil recovery) is an evolving set of technologies for increasing oil production. The (historical) development of CO_2 EOR [Grigg and Schechter, 1997; Jarrell, et al., 2002] in the 1950s saw some of the earliest research on CO_2 and flue gas for oil recovery and continued with significant laboratory research during the 1960s that included some field pilots. Results from some of the early pilots (some successful and others not) encouraged major expansion in the 1970s with development of CO_2 pipelines to the Permian Basin. During the 1980s some projects such as flood of the Weber Sand in the Rangely Field of Colorado were implemented. There are plateaus in CO_2 EOR production (Figure 1.1) where oil prices and the availability of CO_2 have limited production [Hargrove, 2008; Taber, Martin, and Seright, screening -parts 1 and 2, 1997]. However, additional quantities of CO_2 have become available within the last few years and have permitted development of CO_2 floods in Mississippi, Alabama, and southeast Texas (Jackson Dome as CO_2 source), as well as development of additional fields in Wyoming where ExxonMobil strips CO_2 from natural gas [Moritis, 2001; Moritis, 2003; Moritis, 2008; Moritis, 2010].

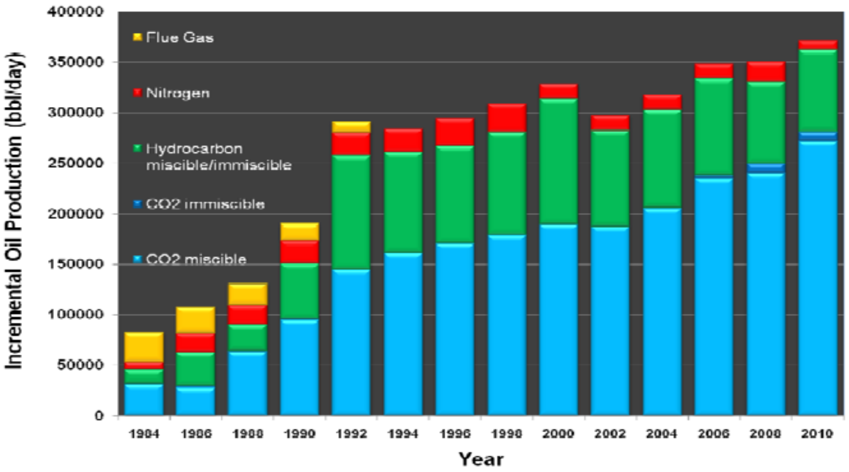


Figure 1.1. U.S. Enhanced Oil Recovery with Gases over the last decades [Koottungal, 2010].

The first commercial CO_2 EOR flood occurred in Scurry County, Texas in 1972, in what was known as the SACROC Unit (Scurry Area Canyon Reef Operators Committee). SACROC used anthropogenic CO_2 captured from Val Verde natural gas plants (South Texas) as the CO_2 source. The technical success of this project, coupled with the high oil prices (at the time) of the late 1970s and early 1980s, led to the construction of three major CO_2 pipelines connecting Permian Basin oil fields with natural underground CO_2 sources located at the Sheep Mountain and McElmo Dome sites in Colorado and Bravo Dome in northeastern New Mexico. The construction of these pipelines spurred an acceleration of CO_2 injection activity in Permian Basin clastic and carbonates fields. The process is often illustrated schematically by Figure 1.2 (Lindley, 1960s) as a CO_2 WAG (water alternating gas) flood where alternate slugs of CO_2 and water (operated as either miscible [as shown] or immiscible conditions) are used to drive oil from injector to producing well. As shown, Figure 1.2 neglects the differences in density between fluids, which cause gravity override, and in viscosity, which cause fingering of fluids, and neglects reservoir geology (including higher and lower permeability porous rock) all of which influence the sweep efficiency and recovery of oil with CO_2. This report attempts to summarize the literature that addresses some of the chemical systems used to resolve these deficiencies.

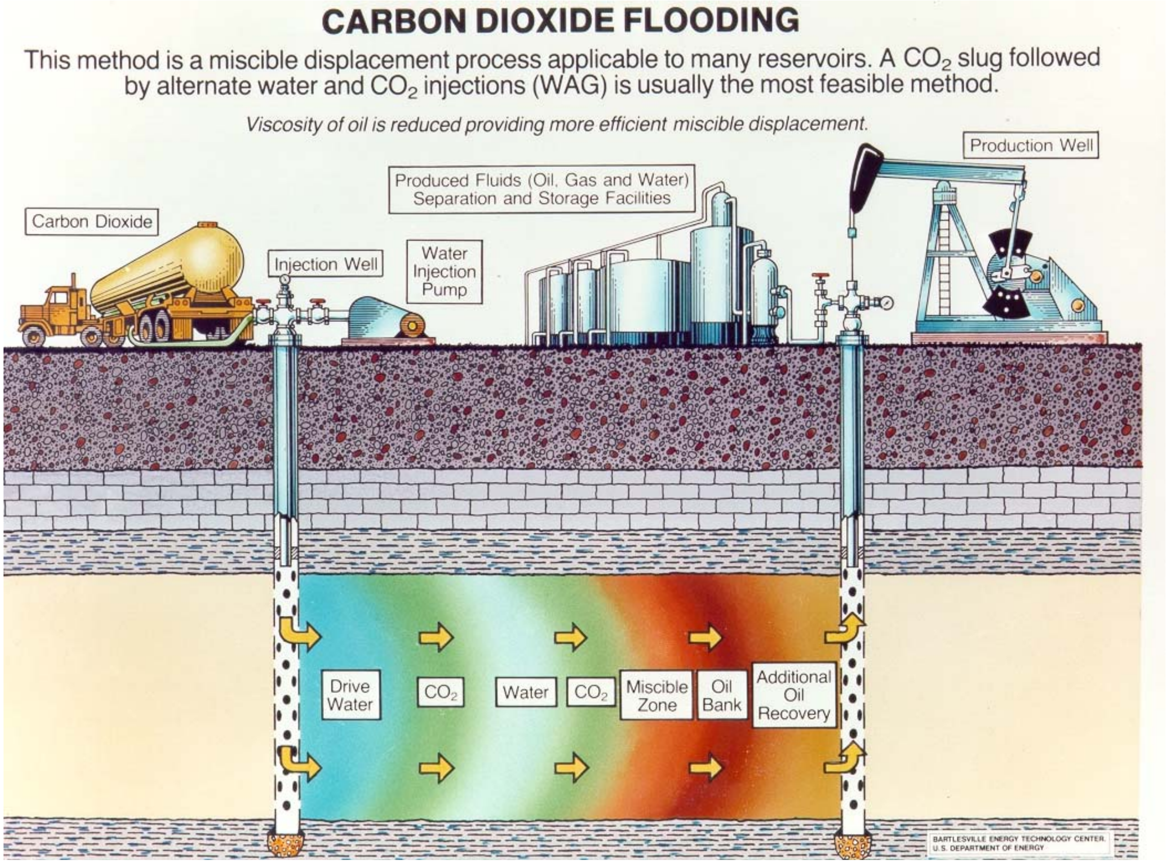


Figure 1.2 Simplified Illustration of a CO_2 Flood [Lindley, 1960s].

Injection of flue gas (N_2, CO_2) had essentially been replaced by CO_2 by 1980. Oil production by thermal EOR oil peaked in 1986 at 480,000 b/d. Chemical flooding has been declining for decades and, although practiced, is rarely reported by operators. In contrast, oil production from gas floods, especially miscible CO_2 floods, has been steadily increasing over the last two decades, as has the number of projects (shown in Figure 1.1).

Oil and Gas Journal (OGJ) published its first EOR survey on May 3, 1971, and the voluntarily contributed survey data has been published biennially since 1974. The 2010 survey [Moritis, 2010; Koottungal, 2010] shows United States (U.S.) EOR production from the preceding year (2009) accounted for 663,431 barrels of oil per day (BOPD). This accounts for 12.2% of total

U.S. crude oil production that averaged 5,451,000 barrels per day (b/d) in 2009 [EIA, 2010]. Thermally produced heavy oil contributed 291,992 b/d, chemical EOR 70 b/d, and gas injection 371,369 b/d. Carbon dioxide miscible produced 272,109 b/d from 109 projects and CO_2 immiscible produced 9,160 b/d from five projects. Combined they account for 5.1% of total U.S. oil production. U.S. EOR production has averaged about 10%–11% for nearly two decades and was in slow decline as late as 2008. Carbon dioxide EOR should experience a significant increase when it is reported in the 2012 OGJ survey, as a number of new projects in Wyoming, Texas, and Louisiana have been initiated and reservoir fill-up is underway.

Although CO_2 has been used commercially to recover oil from geologic formations for nearly 40 years, there remain some classic texts on the subject in addition to those that cover EOR. SPE Monograph 8, "Miscible Displacement" by Fred Stalkup [1983] remains a classic on miscible displacement (CO_2 and hydrocarbon). The monograph examines miscible and immiscible flooding, the concepts behind minimum miscibility pressure (MMP), and the influence of oil composition, temperature, pressure, salinity, and capillary number. The monograph examines basic principles and key laboratory and field-trial performance through the early 1980s. The monograph predicts performance of miscible processes, with an emphasis on the reservoir engineering aspects. SPE Monograph 22, "Practical Aspects of CO_2 Flooding" [Jarrell, et al., 2002] updates by 20 years the lessons learned in CO_2 flooding and serves as a logical guide to the practicing engineer focused on the "how to" and "why" of miscible and immiscible CO_2 flooding. The book outlines the entire project development sequence from conception and justification through field design and operation. The monograph provides current (2002), practical CO_2 flooding technologies and industry experiences; also, targets are described including planning, designing, and implementing CO_2 floods. Monograph 22 contains 5 appendices, including a compendium of practical, field-specific publications, and some screening models in CO_2 Prophet (results from a DOE funded project in the CLASS program that is a first pass screening tool for CO_2 EOR).

In 2005–06, U.S. DOE published a series of reports based on Advanced Resources International's (ARI) analysis of CO_2 EOR in ten U.S. geologic basins [ARI, 2005–2006]. They applied streamline simulation to cover 22 basins in oil producing states plus offshore Louisiana and included 1,581 large (>50 MMbbl OOIP) oil reservoirs (accounting for about two-thirds of U.S. oil production). Since that time, ARI has expanded their analysis to look at what 'game changer' improvements in CO_2 EOR recovery efficiency and 'next generation' technology may potentially accomplish [Kuuskraa and Koperna, 2006]. Their projections were impressive, indicating billions of barrels of additional oil being technically producible. The reports indicated that "the wide-scale implementation of 'next generation' CO_2 EOR technology advances have the potential to increase domestic oil recovery efficiency from about one-third to over 60 percent," doubling the technically recoverable resources in six domestic oil basins/areas studied to date. Application of next generation CO_2 EOR technologies extrapolated to other U.S. oil basins and regions could bring about truly 'game changing' advances in oil recovery and domestic oil production. The technologies, which have been described in general, include:

- Use of much larger volumes of CO_2 [Merchant, 2010]
- Gravity-stable CO_2 floods (top-down floods)
- Flooding of the residual oil zone (ROZ) [Melzer, 2006]. (Currently in 2011, there are 11 ROZ projects in the Permian Basin.)

- Innovative flood design and well placement [Taber and Seright, 1992; Laieb and Tiab, 2001]
- Use of technology for diagnostics and control
- Viscosity and miscibility enhancement of the CO_2

The ARI basin report [Kuuskraa, 2006] did not specifically identify details of these new technologies, and thus the challenge remains to find economic 'game changing' technologies and then use these advances in the field. A now outdated "State-of-the-Industry in CO_2 Flooding" was written by Grigg and Schechter [1997]. Today's CO_2 flooding projects inject much higher pore volumes of CO_2 and many have reduced well spacing, Vertical and areal pattern expansions have occurred and new fields have been brought online, especially in Wyoming, Mississippi, Alabama, and southeast Texas. However, many of the comments in the 1997 review are as true today as when written. The mature CO_2 EOR flooding industry is making only small incremental advances in technology to improve oil recovery efficiency. DOE has recently published a primer on "Carbon Dioxide Enhanced Oil Recovery" that summarizes this technology [NETL, 2009].

Although ARI's reports on CO_2 EOR offer some insight into potential recoverable oil resources, the details of how to effectively recover these resources are elusive. There are many potential R&D areas that could improve oil recovery, but this literature review, as it applies to CO_2 EOR, has two major parts that address chemical rather than mechanical control of CO_2:

- Mobility control
- Conformance control/profile modification

While there are other ways to address sweep and areal conformance (such as infill drilling, horizontal wells, and various completion practices and use of cement or packers for isolation, etc.) these are outside the scope of this review.

Mobility control of CO_2 attempts to overcome some of the density and viscosity differences between CO_2 and reservoir fluids. Despite more than 20 years of R&D, only a single direct CO_2 viscosifier (soluble at conditions where most CO_2 EOR floods operate) has been designed that is capable of providing a significant increase in viscosity (~10-fold) at dilute concentration, but it is not cost-effective and is environmentally persistent. Several other CO_2 thickeners have been designed, but their effect on viscosity is modest and they typically require pressures much greater than MMP to attain even dilute levels of solubility. The CO_2 EOR industry continues to use water alternating with gas (WAG) as the technology of choice or mechanical means such as packers, well control, cement, infield drilling, and horizontal wells [Taber and Seright, 1992] to control CO_2 floods.

Conformance control/profile modification is a much broader technology set in that it tries to address reservoir heterogeneity (both naturally/geologically controlled and man-made) as a result of drilling, completion, and production operations, including injection of CO_2 and water. Profile modification is applied in primary production, waterflooding, steam floods, gas floods (including hydrocarbon), CO_2, sour gas (i.e., H_2S and CO_2), flue gas (CO_2, CO, N_2, NO_x), and N_2 in an attempt to control fluid fronts and unwanted production of water and injected fluids [Smith and Ott, 2006 a,b,c; Seright et al., 2003; Reyes et al., 2010]. Industry and DOE have funded a tremendous volume of R&D. Recently, SPE published a book by Sydansk and Romero-Zeron [2011] entitled *Reservoir Conformance Improvement* wherein technologies, including those specifically for CO_2 conformance, were reviewed.

There have been a wide variety of successfully demonstrated conformance control/profile modification technologies, both mechanical and chemical. Despite there being many successful chemical profile modification technologies (even with reported good economics, as demonstrated in pilots documented in the literature) there are far fewer papers detailing where a specific technology was widely adopted and applied field-wide. This scarcity of literature could have multiple causes. For example, companies often only publish when it is in their self-interest to do so, and there are many impediments to successfully transitioning from a successful pilot to much broader application either within the same field or company or to other companies and fields. Numerous practitioners and developers of the chemical profile technology that produced good pilot performance encountered similar challenges (independent of company or technology) in advancing it. Nonetheless, failure to transition from successful pilot to widespread application is a significant challenge that many practitioners view as an obstacle to the development of the technology. There are exceptions, mostly within a few major companies or national oil companies. One example of widespread implementation (within a company and a field) was highlighted in a paper by Soliman et al., [2000] where more than 900 wells in CO_2 floods in the Permian Basin were treated. Similar but not widely published CO_2 conformance has occurred in the Weber Sandstone Unit, Rangely, Colorado and the Salt Creek field of Wyoming.

Carbon dioxide flooding of domestic oilfields, most of which have been previously waterflooded, is a commercial success. Every day more than 110 domestic field projects, 60% of which are in the Permian Basin, inject 3.1 Bscf of CO_2 into sandstone and carbonate formations to recover more than 280,000 bbl. of oil. This corresponds to roughly 5% of the ~5 MM bbl. / (MM BOPD) of domestic oil production. The number of CO_2 flooding projects has increased steadily in recent years—in contrast to other EOR methods—and CO_2 flooding is poised to become an even more popular oil recovery technique in the foreseeable future. It appears that the limiting factor for the expansion of CO_2 flooding is in transitioning from a low oil price to the availability of large volumes of high-pressure CO_2 because most current CO_2 suppliers are operating at full capacity. For example, new CO_2 flooding projects in the Permian Basin are being constrained by the need for an additional 0.3–0.4 Bscf/d of CO_2 in the region. Conversely, the rapid growth of CO_2 EOR in Mississippi reflects the growth of CO_2 supplies in this region [Hargrove et al., 2010].

About 74.4% of the CO_2 used for EOR is provided by gas treating and processing facilities associated with the production of CO_2-rich natural gas from formations, while 19.4% originates in natural gas plants, 4.8% from a coal synfuel plant, and the remainder from various chemical and petroleum facilities. For example, the Permian Basin projects draw much of their CO_2 from McElmo Dome, Sheep Mountain, Bravo Dome, West Bravo, and the Century Plant. The most significant sources of CO_2 outside of the Permian Basin include LaBarge in Wyoming, Jackson Dome in Mississippi, and the Great Plains Coal Plant in North Dakota [Hargrove et al., 2010]. The dehydrated, high-pressure CO_2 from these sources is transported to oilfields where it is compressed to the desired injection pressure, combined with recycled CO_2, and injected into the reservoir.

Implementation of any of the above technologies requires significantly better knowledge of reservoir characterization. It was this lack of knowledge of fluid flow in reservoirs and in understanding reservoir internal architecture that caused the problems encountered in many of the EOR floods (including chemical and gas floods) that prompted the creation the DOE/industry funded program on Reservoir Depositional Classification—the 'CLASS' Program. The results of that program and copies of all the archive reports are available from DOE NETL library as CD collections or online (www.netl.doe.gov) as individual reports within the DOE NETL Knowledge Management Database (KMD) hosted by DOE NETL [Olsen, Schatzinger, and Koons, 2008]. Better understanding of the reservoirs also required better diagnostics and imaging, downhole tools for logging and drilling /completion—an R&D program whose efforts also have been archived [Olsen, et al., September 2008].

Sandstone and limestone reservoirs best suited for miscible CO_2 floods contain oil with a viscosity as high as ~10 cP, but averaging about 1.5 cp. Immiscible CO_2 floods can be conducted with reservoir oils of 100–1,000 cP viscosity. The API gravity for miscible floods is typically greater than 30^o and averages $\sim36^o$, which corresponds to a CO_2 density value of 0.876 g/ml or less, and an average density of 0.845 g/ml. Immiscible floods can have API gravity values as low as 22^o API or density values as high as 0.922 g/ml. Oil saturation should exceed 20% and typically has a value of ~55%. The pressure required to attain miscibility is a function of CO_2 purity, the amount and identity of gases (such as CH_4 and N_2) in the CO_2, reservoir temperature, and the oil composition as measured by the ($C_5 – C_{30}$) content [Enick, Holder et al., 1988]. The MMP increases from roughly 1,400 to 1,600 psia at 25 ^oC and to 3,000 to 4,000 psia at 100 ^oC. A more accurate estimate of the MMP can be obtained by first determining the CO_2 density required for effective oil displacement. This density value increases from ~0.4 g/ml to ~0.8 g/ml as the (C_5–C_{30}) content of the oil decreases from 100% to 50% [Holm and Josendal, 1982]. One then estimates the MMP as the pressure required to attain this density at reservoir temperature. Formations must be deep enough to have fracturing pressures greater than the MMP; therefore, reservoirs in which CO_2 miscible floods are conducted are typically 3,000 – 7,000 ft. in depth.

The introduction of dense CO_2 into these sandstone or carbonate formations pressurizes the reservoir, simultaneously swells and reduces the viscosity of oil, and (for miscible floods) can develop multiple-contact miscibility with lighter oils. These multiple mechanisms result in the very efficient displacement of residual oil (95%–100%) in the portions of the reservoir that are swept by CO_2 at pressures at or above the MMP. The efficacy of oil recovery by CO_2 combined with the availability of large amounts of natural CO_2, a growing network of CO_2 pipelines feeding new projects, the lack of any residue associated with CO_2 upon its depressurization, and the ease of CO_2 separation from produced fluids and recycle to injection wells have resulted in CO_2 flooding becoming a vibrant, proven, improved oil recovery (IOR) technology.

Despite its longstanding success as an IOR technique, CO_2 flooding does not recover all of the oil in the formation regardless of whether the reservoir has been previously waterflooded. Typically, primary recovery results in the production of ~5%–15% OOIP, while secondary recovery is responsible for an additional 20%–40% OOIP. Although CO_2 is capable of displacing nearly all of the oil from the portion of the porous media through which it flows, miscible CO_2

floods typically recover 10%–20% of the OOIP via the injection of a volume of dense CO_2 equivalent to ~80% of the hydrocarbon (oil) pore volume (HCPV). Not surprisingly, immiscible CO_2 floods recover only 5%–10% OOIP because of the interfacial tension between the CO_2 and viscous oil. As a result, 35%–65% of the OOIP remains unrecovered after CO_2 flooding. Further, based on the domestic totals of three billion scf/d CO_2 consumed for the production of 280,000 BOPD, the average domestic CO_2 utilization ratio is 10,700 scf of CO_2 /barrel of oil. At typical reservoir conditions, this corresponds to ~6 bbl. of dense CO_2 per barrel of oil recovered; a much larger than desired ratio of solvent to oil.

The fundamental causes of this disappointingly low oil recovery can be traced to the density and viscosity of dense CO_2 (Figures 1.4 and 1.5). First, the low density of high-pressure CO_2 relative to oil promotes gravity override of the CO_2, reducing oil recovery in the lower portions of the formation. Second, the low viscosity of dense liquid or supercritical carbon dioxide at typical CO_2 flooding conditions is ~ 0.05–0.10 cP, a value so much lower than typical oil and brine viscosity values that it results in an unfavorable mobility ratio. This leads to viscous fingering, which in turn leads to early CO_2 breakthrough, high CO_2 utilization ratios, delayed CO_2 production, depressed oil production rates, and low percent OOIP recovery. These problems can be exacerbated when the injection well is completed in two or more producing zones; the low viscosity of CO_2 promotes its flow into the more permeable layers that have been effectively waterflooded, while disappointingly small amounts of CO_2 enter the lower permeability zones that contain more recoverable oil.

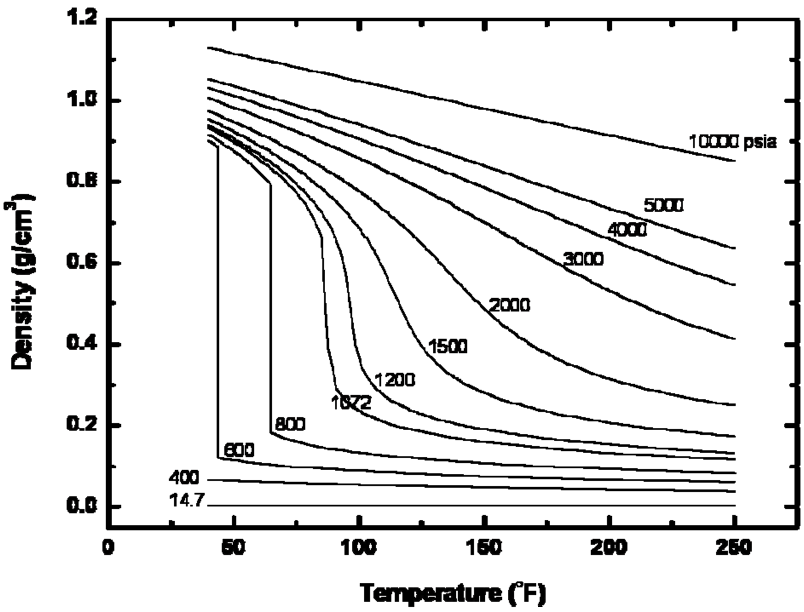


Figure 1.3. CO_2 density as a function of temperature and pressure [data from NIST web book]

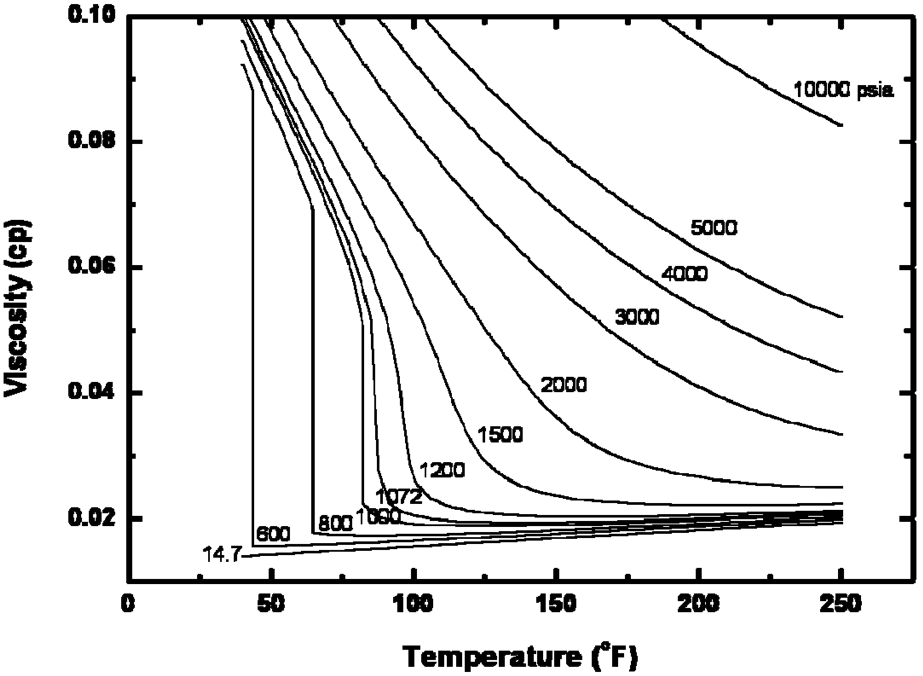


Figure 1.4. Viscosity of CO_2 as a function of temperature and pressure [data from the NIST web book]

Mobility and conformance issues are generally acknowledged to be the most serious concerns associated with CO_2 flooding, and chemical means of addressing these problems are the focus of this report. It should be noted, however, that there are other problems that may diminish the effectiveness of a CO_2 flood. For example, it may not be feasible to attain the minimum miscibility pressure within the formation, resulting in the recovery of CO_2 via an immiscible process that leaves behind undesirably high residual oil saturations. Additionally, during the development of miscibility with crude oil in the formation, asphaltene precipitation may occur within the porous media, possibly hindering the flow of CO_2 into oil-rich zones of the formation or leading to asphaltene deposition on the surfaces of the production and processing equipment. Further, when high-pressure CO_2 and water or brine come into contact, a small amount of CO_2 dissolves in the aqueous phase, and a portion of that dissolved CO_2 dissociates and forms carbonic acid. The pH of the water will drop to values less than 3, and the acidic brine can react with and dissolve carbonate media, forming high permeability flow paths for CO_2 that exacerbate conformance control issues. (The reader is encouraged to review Appendix A, which details the properties and attributes of CO_2.)

There have been previous basin-wide evaluations of CO_2 floodable reservoirs (studies from the 1960s through 1980s). Many of reports can be found in the DOE's archives of research funded on basin analysis [Olsen et al, Nov 2009], CO_2 EOR [Jackson et al., 2008; Olsen et al., September 2008], and EOR [Olsen et al., March 2009]. The ARI ten "basin studies" were the first to address CO_2 storage capacity from combining CO_2 sequestration and CO_2 EOR [ARI, 2008]. ARI determined that with state-of-the-art best practices, CO_2 EOR has the potential to recover more than 47 B bbl. of domestic oil (from the basins evaluated) and application of "Next Generation" technologies could recover more than an additional 30 B bbl. from U.S. oil fields [ARI, 2006; Dittrick, 2010]. The U.S. has an estimated 596 B barrels OOIP. We have produced 175 B barrels with 21 B barrels carried on company books as proven reserves (at end of 2006) with 400 B barrels oil representing the future challenge for recovery [Kuuskraa and Ferguson, 2008]. The paper "Storing CO_2 with Enhanced Oil Recovery," presents updated projections of technically recoverable resources (as shown in Table 1.1) based on analyses of 2,012 oil reservoirs accounting for nearly three-quarters of the U.S. oil resource base in 27 states, including oil reservoirs in the Appalachian Basin. The paper has an expanded set of oil price and oil price/CO_2 cost scenarios incorporated into the economic analyses. The report concludes that application of CO_2 EOR could add 84.8 B bbl. (half of what the U.S. has produced over the entire life of the industry) of incremental domestic oil supplies; 2.3B bbl. have previously been produced by CO_2 EOR). The report highlights storing of CO_2 through CO_2 EOR but also reiterates the potential for widespread domestic oil production, and provides details of modeling the volume of CO_2 from these anthropogenic sources, the impact of the learning curve, and the cost of electricity generated.

ARI has recently completed for DOE [Kuuskraa et al., 2011] an expanded review of the potential of CO_2 EOR in the U.S. based on an aggressive carbon capture from mostly coal-fired electrical generation units. With active use of "Next Generation" CO_2-EOR technology, technically recoverable oil from CO_2-EOR (Table 1.2) could more than double (from 64 to 136.6 billion barrels) the original "state-of-the-art" production estimated by Kruskraa and Ferguson in 2008. Of the technically recoverable oil from CO_2-EOR, 67.2 billon barrels are potentially economically recoverable. Similar volumes of CO_2 could be sequestered in domestic oil fields.

The potential to acquire significantly larger volumes of CO_2 from carbon capture and sequestration (CCS) activities may prompt significant expansion of CO_2 EOR and simultaneously sequester some CO_2. ARI estimated that carbon capture from proposed U.S. climate legislation could increase U.S. oil production by 3 to 3.6 million b/d by 2030 if all the captured CO_2 were used for EOR. Anthropogenic CO_2 sources in the U.S. currently provide 17% of the CO_2 used in CO_2 EOR [Hargrove, 2008]. The promise of significantly larger volumes of CO_2 captured from coal-fired or other hydrocarbon-fired electrical generation units (and other sources and industries such as ethanol plants, refineries, cement manufacturing, and natural gas processing) may reduce CO_2 availability constraints. However, cost is always the controlling factor. Large stationary exhaust or flue gas (a mixture of N_2, NO_X, SO_X, CO, and CO_2) is available but at much higher cost than the current price of CO_2 [SNC-Lavalin, 2004]. Significant amounts CO_2 may become available contingent on future legislation and the market. CO_2 EOR is but one option for managing anthropogenic CO_2 emissions; there are other disposal options, including geologic sequestration, as shown in Figure 1.3 [Olsen, Rawn-Schatzinger, Felber, and Carr, 2009; Dressel, 2010]. However, only CO_2 EOR or use of CO_2 to extract additional natural gas, as in enhanced coal bed methane (ECBM), has the potential to economically generate a marketable energy resource. There are arguments for and against CO_2 sequestration and for and against development of CO_2 EOR as a stepping-stone to widespread geologic sequestration of CO_2 [Dooley, 2010; Meyer, 2007], but the fact remains that CO_2 EOR is a major method for recovering the nation's remaining petroleum reserves.

Table 1.1. Technically Recoverable Resources from Applying “State-of-the-Art” CO_2-EOR: Database and National Totals [Kuuskraa and Ferguson, 2008].

	DATABASE			NATIONAL	
Basin/Area	OOIP (Billion Barrels)	OOIP Favorable for CO_2-EOR (Billion Barrels)	Technically Recoverable (Billion Barrels)	OOIP (Billion Barrels)	Technically Recoverable (Billion Barrels)
1. Alaska	65.4	64.5	12.0	67.3	12.4
2. California	75.2	31.6	5.7	83.3	6.3
3. Gulf Coast (AL, FL, MS, LA)	26.4	20.2	4.2	44.4	7.0
4. Mid-Continent (OK, AR, KS, NE)	53.1	28	6.4	89.6	10.7
5. Illinois/Michigan	12.0	4.6	0.8	17.8	1.2
6. Permian (W TX, NM)	72.4	63.1	13.5	95.4	17.8
7. Rockies (CO,UT,WY)	23.7	18.0	2.9	33.6	4.2
8. Texas, East/Central	67.4	52.4	10.9	109.0	17.6
9. Williston (MT, ND, SD)	9.4	7.2	1.8	13.2	2.5
10. Louisiana Offshore	22.2	22.1	4.6	28.1	5.8
11. Appalachia (WV, OH, KY, PA)	10.6	7.4	1.2	14.0	1.6
Total	437.8	319.1	64	595.7	87.1

Table 1.2. Oil Recovery and CO_2 Storage from “Next Generation” CO_2-EOR Technology [Kuuskraa, et al., 2011]

Reservoir Setting	**Oil Recovery*** (Billion Barrels)		**CO_2 Demand/Storage** (Million Metric Tons)	
	Technical	**Economic****	**Technical**	**Economic****
1. Miscible CO_2-EOR				
Lower-48 Onshore	104.4	60.3	32,250	17,230
Alaska	8.8	5.7	4,110	2,330
Offshore	6.0	0.9	1,770	260
Sub-Total	**119.1**	**67.0**	**38,130**	**19,820**
2. Near Miscible CO_2-EOR	**1.2**	**0.2**	**800**	**110**
3. Residual Oil Zone***	16.3	n/a	6,500	n/a
TOTAL	**136.6**	**67.2**	**45,430**	**19,930**

* Includes 2.6 billion barrels already produced or being developed with miscible CO_2-EOR and 2,300 million metric tons of CO_2 from natural sources and gas processing plants

** At $85 per barrel oil price and $40 per metric ton of CO_2 market price with ROR of 20% (before tax)

*** ROZ resources below existing oil fields in three basins; economics of ROZ resources were beyond study scope

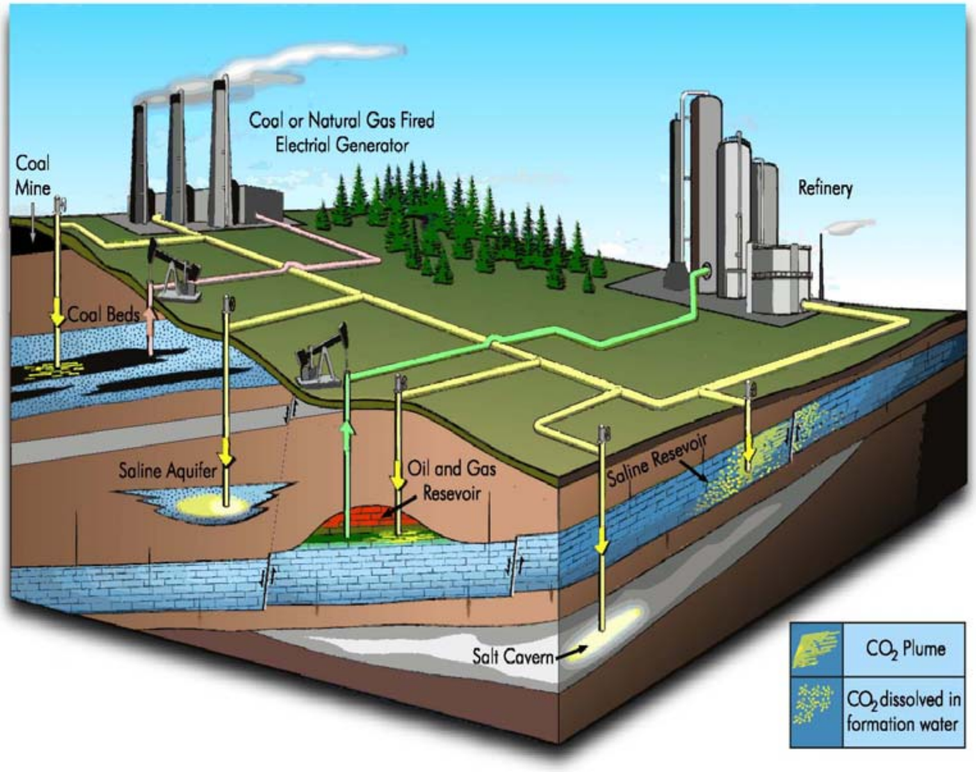


Figure 1.5. Schematic of CO_2 from a Thermoelectric Power Plant and Refinery Being Sequestered in Various Geologic Formations [(Adapted from original figure, courtesy of Dan Magee, Alberta Energy Utilities Board, Alberta Geologic Survey, 2008; Olsen, Rawn-Schatzinger, Felber and Carr, 2009].

Each of the technology areas previously listed is currently being pursued by industry and DOE, some more vigorously than others. The role that CCS can play in expanding CO_2 EOR has been extensively documented based on an MIT and Texas Bureau of Economic Geology sponsored symposium held on June 23, 2010, covering the "Role of Enhanced Oil Recovery in Accelerating the Deployment of Carbon Capture and Sequestration," [MIT-BEG, 2010]. If legislation is passed requiring the disposal of CO_2 captured from existing coal-fired power plants and new integrated gasification combined cycle (IGCC) plants, initial attempts to sequester the anthropogenic CO_2 are very likely to be associated with supplementing the current sources of CO_2 for enhanced oil recovery [Merchant, 2010]. This will enable the simultaneous geologic sequestration of CO_2 in the same formation from which oil is recovered. Further, the sequestration and monitoring of CO_2 during EOR would build a knowledge base that would enhance the design of facilities to sequester massive amounts of anthropogenic CO_2 in deep saline aquifers.

The objective of this report is to review chemical means for addressing CO_2 flooding mobility control and conformance control problems that stem from the low density and viscosity of CO_2 at reservoir conditions. Unfortunately, one cannot alter the density of the CO_2 entering the formation significantly via the addition of a CO_2-soluble additive or the implementation of an injection strategy. The density of CO_2 is essentially a function solely of temperature and pressure, and the mitigation of gravity override must be accomplished by mobility or conformance control. It is possible, however, to alter the mobility of dense CO_2 by reducing its relative permeability via water-alternating-gas injection strategies, increasing its viscosity via the addition of direct CO_2 thickeners, or decreasing its mobility by generating CO_2-in-brine foams. It is also possible to favorably alter the distribution of the injected CO_2 into a layered formation, especially if the injected fluids are diverted from high permeability, watered out thief zones into lower permeability, oil-rich zones. Although conformance control is achieved to some extent by each of the mobility control strategies, there are also techniques—such as gels, foam gels, or dispersions of swellable, pre-formed particle gels (PPG)—designed specifically to effectively block high permeability zones.

2. Potential Recovery Benefits of Mobility Control

The primary advantage of improving the mobility ratio is the reduction of viscous fingering. Over 50 years ago, elegant low-pressure miscible displacement experiments were conducted by Habermann that quantified the effect of mobility ratio on solvent breakthrough and oil recovery as a function of pore volumes of solvent injected [Habermann, 1960]. Although these experiments were conducted with miscible liquid solvents in a homogeneous, unconsolidated porous medium, the results accurately reflect how unfavorable mobility ratios, such as those that occur during CO_2 floods, impede efficient oil recovery. Further, the results illustrate how an improvement in the mobility ratio will improve the efficiency of the displacement. For example, Figure 2.1 [Habermann, 1960] can be used to estimate the amount of solvent injected at breakthrough during a miscible flood.

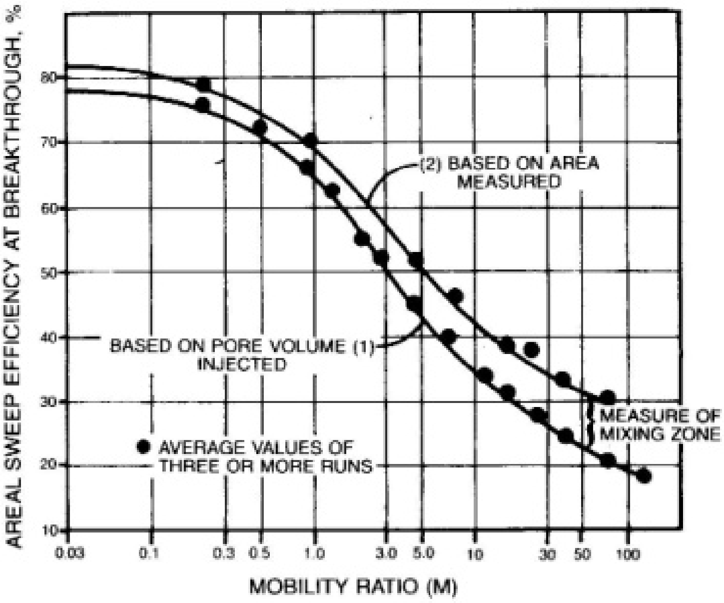


Figure 2.1. Sweep efficiency at breakthrough for miscible displacement based on physical model [Habermann, 1960]

For example, at a mobility ratio of 30, breakthrough of the solvent occurs after 26% PV solvent is injected.

Figure 2.2 represents a similar plot, but it also includes oil recovery after breakthrough as a function of mobility ratio and miscible solvent PVI [Claridge, 1972; Dyes 1954; Koval, 1963].

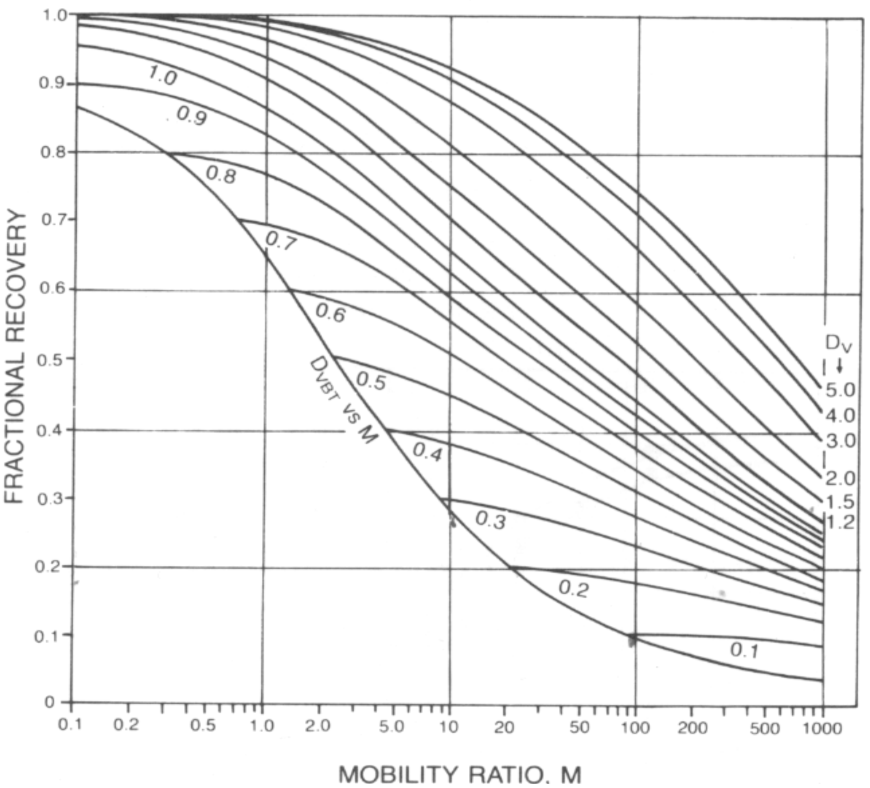


Figure 2.2. Smoothed results for the effect of mobility ratio on solvent breakthrough and post-breakthrough oil recovery as a function of solvent injected [Claridge, 1972]

Consider a miscible displacement example where the mobility ratio of solvent to oil is 20.0, meaning that the low viscosity solvent is 20 times more mobile than the oil. At the beginning of the flood, a unit of oil is produced for each unit of solvent injected. This continues until just under 0.20 displaceable pore volumes (Dv) of solvent have been injected. When 0.20 Dv have been injected, however, the solvent breaks through. This is the first time at which both solvent and oil appear in the product. After breakthrough, less than one unit of oil is produced per unit of solvent injected because an ever-increasing fraction of solvent is being produced with the oil. For example, after 0.50 Dv of solvent have been injected, only 0.42 units of oil are produced; the 0.30 Dv solvent injected after breakthrough has yielded 0.22 units of oil and 0.08 units of solvent. After 0.80 Dv solvent have been injected, only 0.56 units of oil are produced along with 0.24 Dv of solvent; the 0.60 Dv solvent injected after breakthrough has yielded 0.36 units of oil and 0.24 Dv of solvent.

Now let us assume that we have developed a means to reduce the mobility ratio to unity in an attempt to inhibit the effects of viscous fingering. In this case, solvent breakthrough does not occur until 0.65 Dv of solvent has been injected. After the injection of 0.80 Dv solvent, the oil recovery is 0.75 Dv; the 0.15 Dv solvent injected after breakthrough has yielded 0.10 Dv oil and 0.05 Dv solvent.

There are numerous other techniques based on scaled physical models [Lewis et al., 2008] and reservoir simulations that have been used to quantify the effect of improved mobility ratio on oil recovery. These correlative and predictive tools may also include the effects of pressure, solvent composition, oil composition, core- or field-scale heterogeneities, viscous-to-gravity ratio, transverse Peclet number, and well configuration. Modeling of laboratory- and field-scale displacements is not the main topic of this report. There is a general consensus, however, that significant reductions in the mobility ratio will improve the areal sweep efficiency as illustrated by this simple example and Figures 2.3 and 2.4.

A notable decrease in the mobility of CO_2 should also improve vertical sweep efficiency during the multiple-contact miscible displacement of oil by CO_2. Gravity override is driven by a density difference between the injected solvent and the oil and brine in the formation. Unfavorable mobility ratios can exacerbate the low vertical displacement efficiency of solvent tongues, however. Consider the simple case of a secondary oil recovery solvent displacing oil from a single, homogeneous layer with equal horizontal and vertical permeability with flow rates corresponding to flow regimes where only a single gravity tongue forms. The results obtained with a physical model of such a system are illustrated in Figure 5 [Craig, 1971; Craig et al., 1957]. At any given value of the x-axis, which represents the ratio of viscous to gravity forces, increased solvent mobility (i.e., increasing values of the mobility ratio M) decreases vertical sweep efficiency at breakthrough. For example, when ($\Delta P_h/\Delta P_v$) equals 10, vertical sweep at breakthrough increases from ~9% to ~75% as the mobility ratio decreases from 50 to unity.

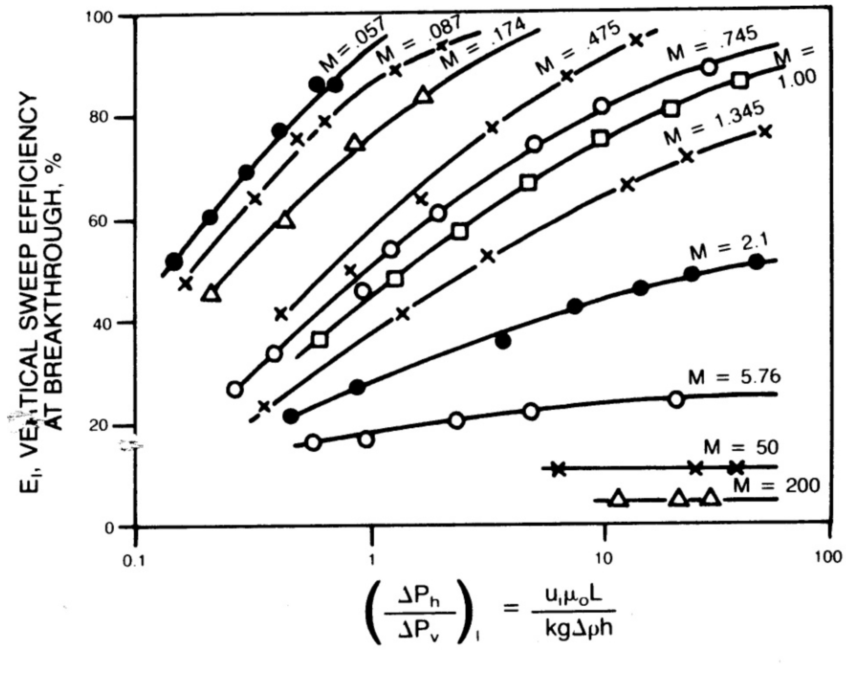


Figure 2.3. Vertical sweep efficiency as a function of the viscous:gravity force ratio and the mobility ratio in single layer, uniform, isotropic porous medium [Craig, 1971]

Vertical sweep efficiency is also diminished during secondary and tertiary oil recovery in stratified formations, especially when the mobility ratio is unfavorable. For example, consider the immiscible, piston-like displacement of oil by water as described by the continuous, realtime, Dykstra-Parsons equation in a formation with log-normal permeability distribution coefficient of 0.6. As shown in Figure 2.4 [Enick, Reznik and Miller, 1988], vertical coverage or sweep drops dramatically with increasing mobility ratio for a 50-layer formation characterized by a 0.8 coefficient of permeability variation, indicative of a very wide distribution of permeability values.

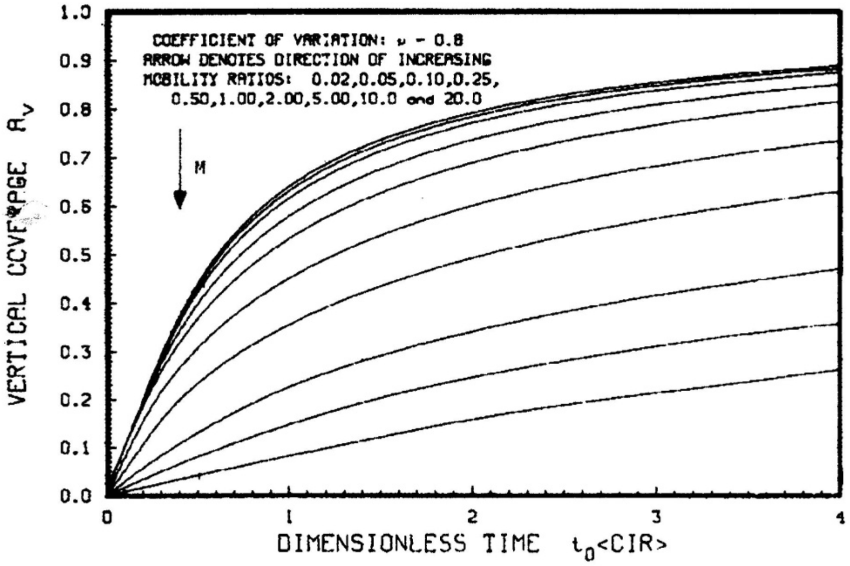


Figure 2.4. Effect of mobility ratio on vertical sweep as a function of dimensionless time for the piston-like displacement of oil by water [Enick, Reznik and Miller, 1988]

For example, at a dimensionless time of 2.0 (the time required to inject two displaceable PVs of water) the vertical sweep increases from 18% to 63% as the mobility ratio decreases from 20 to 1. When the Buckley-Leverett displacement model is employed to provide a more accurate description of the saturations behind the front, the detrimental impact of high mobility ratios on vertical sweep becomes enhanced [El-Khatib, 2001].

Further, unlike secondary flooding processes that involve immiscible liquids such as water displacing oil, the introduction of miscible or multiple-contact miscible solvents can also be affected by transverse and longitudinal dispersion of the solvent into the oil.

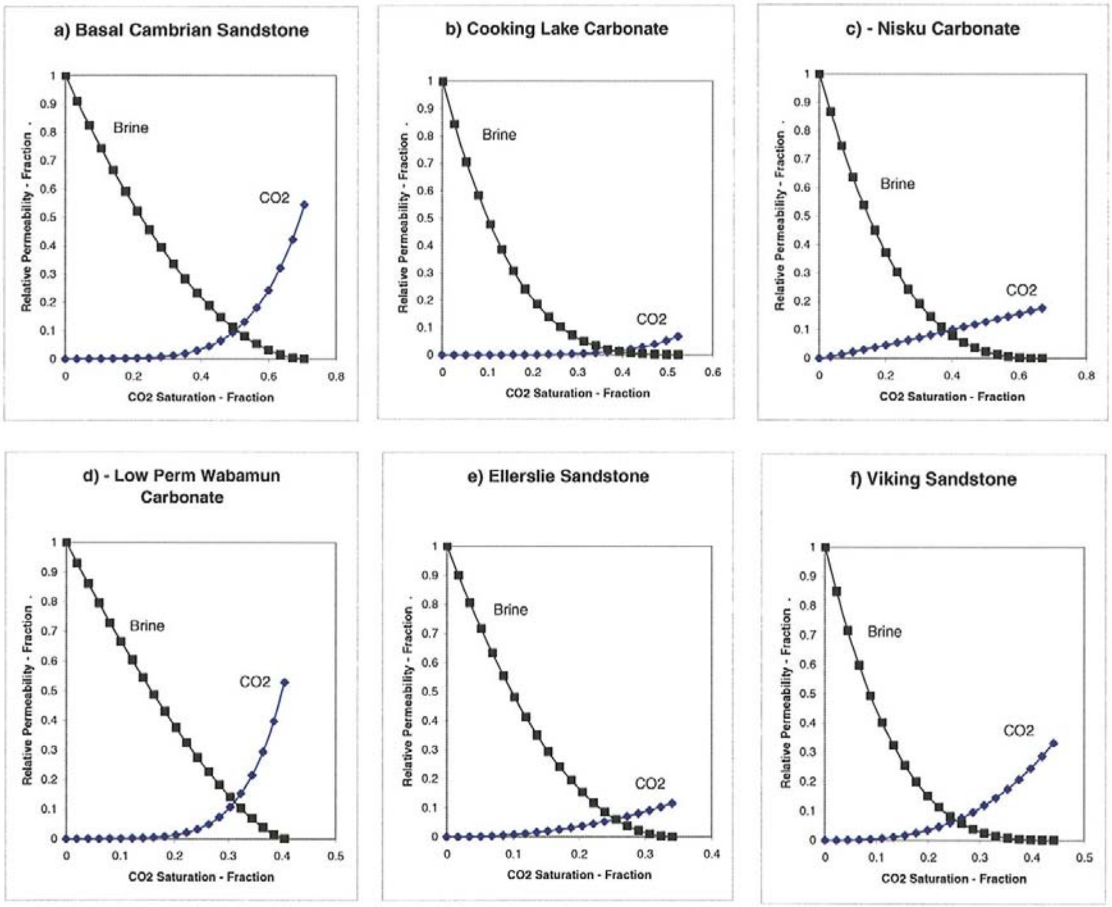
3. Current State-of-the-Art; WAG and Continuous CO_2 Injection

The mobility ratio is a fraction that compares the ability of a solvent to flow through porous media relative to the fluid that it is intended to displace. Darcy's law enables the mobility ratio for CO_2 and oil to be expressed as follows:

$$M_{CO2/oil} = \frac{k_{r,CO2}/\mu_{CO2}}{k_{r,oil}/\mu_{oil}}$$

Because the viscosity of dense CO_2 is typically significantly less than that of the oil, the mobility ratio for a CO_2 flood is greater than unity. This unfavorable ratio results in viscous fingering of the CO_2 and the associated problems. Mobility control refers to a technique that reduces the mobility ratio in an attempt to reduce or suppress fingering by changing the relative permeability or viscosity values such that $M \leq 1$.

Mobility control has been most readily accomplished with the injection of both CO_2 and water into the formation, usually in an alternating sequence that promotes near-wellbore injectivity and diminishes mobility away from the wellbore. The alternating injection of brine and CO_2 does not make the CO_2 more viscous; rather it increases the water saturation and thereby decreases the CO_2 saturation within the pores. Many studies, including several recent investigations [Bennion and Bachu, 2005 and 2007], have demonstrated that the reduction of CO_2 saturation causes a reduction in the relative permeability of CO_2, as shown in Figure 3.1. This in turn lowers the mobility ratio and inhibits the formation of viscous fingers.



a) Basal Cambrian Sandstone

b) Cooking Lake Carbonate

c) - Nisku Carbonate

d) - Low Perm Wabamun Carbonate

e) Ellerslie Sandstone

f) Viking Sandstone

Figure 3.1. The relationship between CO_2 saturation and the relative permeability of CO_2 and brine in porous media [Bennion and Bachu, 2005]

Consider the Basal Cambrian Sandstone in Figure 3.1. At a CO_2 saturation of 0.7 and an irreducible brine saturation of 0.3, the relative permeability of CO_2 is 0.52. If the CO_2 saturation is only 0.4, however, the relative permeability of CO_2 is only ~0.04 and the relative permeability of the brine is ~0.22.

This process of injecting water (brine) and CO_2 into an injection well is referred to as Water-Alternating-Gas (WAG), and it remains the state-of-the-art technique for reducing the mobility of CO_2 flowing through porous media. Typical cycle times range from months to a year, and the volumetric ratio of water to dense CO_2 is commonly 1:1 to 2:1.

A high-pressure five-spot physical model, shown in Figure 3.2, was developed [Lewis et al., 2008] that provided a clear example of the sweep efficiency benefits of WAG.

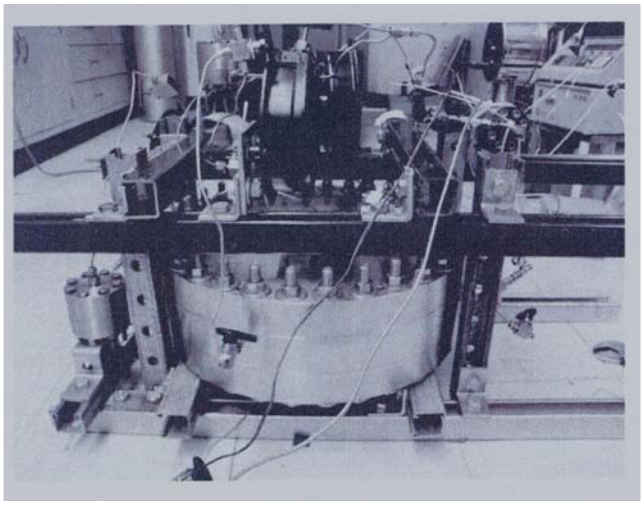


Figure 3.2. High-pressure, three-dimensional physical model for studying volumetric sweep efficiency [Lewis et al., 2008]

Ethane was selected as the first-contact miscible solvent for the recovery of a dead crude oil from unconsolidated sand porous medium. Like CO_2, ethane is also capable of reducing the viscosity of the dead crude oil as it diffuses into the oil. The following figure illustrates results when ethane was injected into a quarter five-spot physical model with an initial water saturation of 9% and an oil saturation of 91%. During the gas flood at a pressure greater than the MMP, 0.50 PV of ethane was injected followed by 1.50 PV of water. During the WAG experiments, 0.50 PV of solvent was injected as fifty 0.01 PV solvent slugs. The first slug was the gas (primary WAG), and the volumetric WAG ratios studied were 0.5, 1.0 and 2.0. A secondary waterflood was also conducted to demonstrate the importance of utilizing a first contact-miscible, oil viscosity-reducing fluid as a displacing agent when high oil recovery is desired. The results are shown in Figure 3.3.

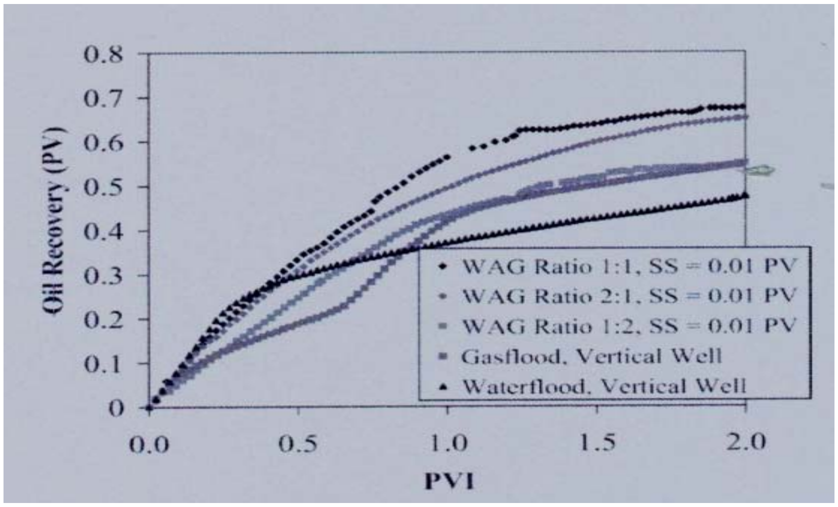


Figure 3.3. The effect of WAG ratio on oil recovery in a quarter-five-spot miscible displacement of dead crude oil from unconsolidated sand by ethane in a high-pressure physical model with vertical wells [Lewis et al., 2008]

Note that the lowest oil recovery after 2 PV of fluid injected is the 48% value corresponding to the immiscible waterflood. The remaining curves correspond to the cumulative injection of 0.5 PV of ethane. The gas flood exhibited breakthrough at 0.07 pore volumes injected (PVI), water broke through at 0.87 PVI (these breakthrough points are not shown on the plot), and the oil recovery after 2.0 PV fluid injection was 55%. The WAG result for a low ratio of water to gas, WAG = 0.5, was comparable to the gas flood result throughout the process, including an oil recovery of 55% at 2.0 PVI. The oil recovery vs. PVI results were best for a WAG ratio of unity, with an oil recovery of 68% at 2.0 PVI, gas breakthrough at 0.12 PVI, and water breakthrough at 0.52 PVI. The amount of oil recovered at any value of PVI was greater for the WAG = 1 case than for any other case shown in this figure. When the WAG ratio was increased to 2.0, the oil recovery at 2.0 PVI dropped slightly to 65%; gas broke through at 0.08 PVI and water broke through at 0.40 PVI. In this particular experiment, the best WAG ratio for the recovery of oil was ~1:1.

The WAG process has been used in the field for several decades. In a recent review of CO_2 WAG recovery for field projects in which up to 80% hydrocarbon PV (HCPV) CO_2 has been injected and an assessment of WAG projects for HCPVI values above 0.80 [Merchant, 2010], it was noted that 90% of domestic tertiary CO_2 field projects employed WAG, with the remainder utilizing gravity drainage, double displacement, gas cycling, and huff-and-puff processes. WAG is also not suitable for tight reservoirs or water-sensitive reservoirs; continuous CO_2 injection is more appropriate in these cases. CO_2 floods that were conducted in the 1980s employed a WAG ratio that was invariant throughout the entire CO_2 flood; typical WAG values fell in the 1–2 range with CO_2 slug sizes being on the order of 1% HCPV. In 1989, Amoco implemented a "tapered" WAG in the Slaughter and Wasson fields, and this variable-WAG process has since been implemented by most operators. In these fields, a relatively large slug of "dry" CO_2 is initially introduced, followed by a tapered WAG in which the WAG ratio is incrementally increased from values less than unity to values greater than unity, a process referred to as "wetting the WAG". For example, an 85% HCPV slug (note that CO_2 and brine density values used to determine HCPV and WAG are assessed at reservoir conditions) of CO_2 could be injected in the following manner: 20% HCPV continuous CO_2, 5% HCPV at a WAG of 0.10, 10% HCPV at a WAG of 0.50, 20% HCPV at WAG of 1.0, 30% HCPV at a WAG of 2.0 (CO_2 slug size of ~1% HC during the tapered WAG), followed by chase water [Merchant, 2010].

Although WAG usually yields better results than continuously injecting CO_2, WAG floods still leave behind approximately one-third to two-thirds of the oil left behind by waterflooding. Further, the WAG process requires the installation of water injection, production, collection, and separation facilities; delays the injection of a specified volume of CO_2; and may inhibit the intimate contact of CO_2 and oil within the pores of the reservoir rock. The large volumes of brine injected along with the CO_2 can prolong the life of the project, delay the injection of the CO_2, inhibit the contact of CO_2 and oil, and result in the production of large amounts of water. Nonetheless, WAG remains the state-of-the-art technique for reducing the mobility of CO_2 in porous media despite leaving 35%–65% OOIP.

4. Direct Thickeners for CO_2 Mobility Control

The most obvious solution for decreasing the mobility of CO_2 is to identify a CO_2 thickener (an additive that could increase the viscosity of CO_2 such that a favorable mobility ratio is realized). Such a compound would enable the CO_2 to be viscosified in a carefully controlled manner simply by changing the thickener concentration. Ideally, the CO_2-soluble thickener would be brine- and crude oil-insoluble, which would inhibit its partitioning into these other fluid phases and its adsorption onto the reservoir rock. Most thickened solutions exhibit shear-thinning behavior, allowing for low viscosity and high mobility near the wellbore that promotes injectivity, while yielding more viscous solutions in the bulk of the reservoir where improved sweep efficiency is desired. Thickened CO_2 would also flow more uniformly into multiple layers, providing a measure of improved conformance control.

A thickener can be composed of an ultra-high molecular weight (Mw) polymer (Mw>10,000,000). The dissolution of relatively small amounts of such ultra-high molecular weight polymers can induce substantial increases in the fluid viscosity.

Alternatively, a fluid thickener may be a small, associating compound composed of a solvent-philic segment that promotes dissolution and a solvent-phobic group that promotes attractive interactions with the neighboring thickener molecules. These intermolecular interactions of the solvent-phobic groups enable the formation of large, associating, macromolecule structures of incredibly high apparent molecular weight that thicken the fluid. Consequently, small molecule thickener design must strike a careful balance: the stronger the interactions of the solvent-phobic group, the more likely that a viscosity-enhancing macromolecular network can form, but it is also more likely that the thickener will not be able to dissolve in CO_2 or remain dissolved in CO_2 if the solution had to be heated to dissolve the thickener. If, however, the interactions of the CO_2-phobic associating groups are too weak, the thickener may readily dissolve, but its impact on viscosity may be marginal.

Thickeners are typically solids at ambient temperature and are inherently difficult to dissolve. This is not surprising because the very same interactions that hinder dissolution also promote intermolecular viscosity-enhancing interactions once the thickener molecules are dissolved. In other words, if a "thickener" dissolves instantly, it is quite unlikely to be effective because the intermolecular associations are so weak that the solvent disrupts them almost instantly. The attractive interactions of the associating groups (e.g., hydrogen bonding, electronegative/positive interactions, and ionic interactions) are typically strong enough at ambient temperature that the thickener may never dissolve in the liquid, or the fluid-thickener mixture will need to be stirred vigorously for extended periods of time for dissolution to occur. Stirring alone may be insufficient to achieve dissolution and the mixture may also need to be heated to diminish the intermolecular interactions (e.g., hydrogen bonding) that inhibit dissolution. When the solution is cooled, the interactions will be re-established and the viscosity-enhancing networks may form. Even if this occurs the resultant "thickened" liquid or "gel" may be inappropriate for flow through porous media. For example, the thickener may indeed dissolve in a solvent at elevated temperature and pressure, but upon cooling the thickener may fall out of solution in the form of solid micro-fibers dispersed in a low viscosity liquid. Although such a dispersion may gel the liquid in a small vial, such a gel would have difficulty flowing through micron-scale pore throats of porous media. Therefore, CO_2 thickeners for oil recovery should form transparent, single-phase, viscous solutions rather than opaque, two-phase dispersions of solid fibers dispersed in dense CO_2.

Prior to the attempts to thicken CO_2, many thickeners for other solvents had been identified. For example, it is easy to design water thickeners, such as the very high molecular weight polyacrylamide, because water is a strong polar solvent capable of dissolving extremely high molecular weight polymers with polar functional groups. There are also many hydrocarbon thickeners, such as the lithium soaps, that are used to transform oils into grease because the soaps contain hydrocarbon tails that enhance dissolution in oil and ionic head groups that interact with other ionic head groups of nearby soaps. Hydrodroxyaluminum bis(2-ethyl hexanoate) is a water-insoluble surfactant that dissolves in gasoline and thickens it (Napalm) as the gasoline-phobic hydroxyaluminum head groups associate in the core of the micelle and the 2-ethylhexanoate tails promote dissolution in gasoline and the formation of viscosity-enhancing helical micelles. Tributyltin fluoride is a remarkably effective thickener for light alkanes such as liquid propane, butane, pentane, or hexane. The electropositive central tin atom is attracted to the electronegative fluorine atom of the adjacent molecule, while the three butyl groups interact with the solvent to promote dissolution and the formation of a linear macromolecule in solution. This results in the formation of a long, linear, associating polymer in which every tributyltin fluoride molecule can be thought of as an associating "monomer".

Polymeric CO_2 thickeners

It has proven to be extraordinarily difficult to thicken CO_2 using polymers. CO_2 is a feeble solvent for extremely high molecular weight polymers (Mw > 1,000,000). Although a handful of polymers with lower molecular weight values (Mw 1,000–1,000,000) have been designed or identified that can dissolve in liquid or supercritical CO_2, the pressure required for dissolution of dilute concentrations is typically in the 10,000–40,000 psia range. These pressure values are significantly greater than the typical minimum miscibility pressure values associated with CO_2 floods (1,200–4,000 psia). There has also been little success in using small, associating molecules to thicken CO_2, primarily because CO_2 is an extremely poor solvent for the polar and ionic associating groups that are commonly incorporated into small molecule thickeners. The remainder of this section highlights specific achievements in the quest to identify a CO_2 thickener. Highlights from a DOE literature survey on this topic up to 1998 [Enick, 1998] will be included, along with developments that have been reported between 1998 and 2010.

The initial attempts to thicken CO_2 were primarily associated with assessments of compounds used to thicken oils because CO_2 is miscible with many light oil components but only slightly miscible with water. Therefore, it was anticipated that non-polar organic polymers that were oil-soluble would be more likely to dissolve in CO_2 than water-soluble polymers. Heller and co-workers investigated numerous hydrocarbon polymers [Heller, Dandge et al., 1985] and identified 18 polymers that exhibited solubility values of 0.22–10 g/liter (0.24–1.1wt%) at temperatures of 20–58 ^{o}C and pressures of 1,700–3,100 psia—conditions that yielded CO_2 density values of ~ 0.7–0.9 g/ml. None of the polymers were capable of inducing significant viscosity increases, although several of the polymers caused slight viscosity increases. For example, a ~1% solution of low molecular weight (Mw 409) atactic poly(methyl oxirane) increased the viscosity of CO_2 by ~25% at 28–33 °C and pressures of ~2,000–2,600 psia. Subsequent attempts by Heller and co-workers to maximize the entropy of mixing, and thereby the polymer solubility in CO_2, focused on the synthesis [Dandge and Heller, 1987] of poly α-olefins, such as poly α-hexenes. Although some of these polymers were slightly soluble in CO_2, none were effective thickeners. In general, in order to realize even a small measure of CO_2 solubility, the molecular weight of the polymers had to be quite low (Mw~1,000 or less), far below the ultra-high molecular weights that characterize thickeners. An attempt was also made by researchers at the University of Wyoming to circumvent the low solubility of polymers in CO_2 by polymerizing CO_2-soluble monomers, including ethylene, octene, and decene, in dense CO_2 [Terry et al. 1987]. However, the polymers that formed in CO_2 precipitated.

In an attempt to identify very high molecular weight polymeric thickener candidates, Chevron researchers [Harris et al., 1990; Bae and Irani, 1990] selected candidates that exhibited solubility parameters less than ~7 $(cal/cc)^{0.5}$ in an apparent attempt to match the temperature- and pressure-dependent solubility parameter of CO_2 [Williams et al., 2004] at reservoir conditions, which is roughly 6 $(cal/cc)^{0.5}$. Further, it was desired that the polymer exhibit multiple electron donor sites associated with oxygen, nitrogen, or sulfur atoms that could interact favorably with the electron acceptor site of the CO_2 molecule, which is the carbon atom. Polymer electron donor functional groups included siloxane, ether, thioether, sulfone, carbonyl, ester, tertiary amine, dialkylamide, and silylether. It was determined that very high molecular weight silicone oil (polydimethylsiloxane (PDMS))—Mw = 197,000, kinematic viscosity = 600,000 centistokes, 7.3 $(cal/cc)^{0.5}$—could effectively thicken CO_2, but only if a significant amount of a co-solvent such as toluene (solubility parameter = 8.9 $(cal/cc)^{0.5}$) was added. For example, a 4wt% PDMS, 20wt% toluene, 76% CO_2 mixture had a viscosity of 1.2 cP, while pure CO_2 at the same condition exhibits a viscosity of only 0.04 cP [Bae and Irani, 1990]. This solution was remarkably less mobile during Berea and SACROC core floods than pure CO_2, resulting in delayed CO_2 breakthrough and increased oil recovery. This result demonstrated that viscosified CO_2 could indeed be expected to exhibit diminished mobility in porous media, but the level of co-solvent required was not practical for field application. Further, it demonstrated that selecting or designing polymers that had favorable electron donor–electron acceptor interactions with CO_2 was a promising route. Specifically, the finding that 4wt% of high molecular weight PDMS (Mw = 197,000) could dissolve in CO_2 when an organic co-solvent was employed was consistent with the finding of Heller and co-workers that ~0.03wt% PDMS (Mw = 135,000) could dissolve in CO_2 at 25 °C and 2750 psia [Heller, Dandge et al., 1985]. In other words, high molecular weight silicone oils were found by both groups to be CO_2-philic, although not to the extent that PDMS could thicken CO_2 without the use of prohibitive amounts of a co-solvent.

The finding that PDMS was indeed more CO_2-philic than hydrocarbon-based polymers [Shen et al., 2003] was further confirmed by PDMS solubility data reported by several other research groups [Bayraktar and Kiran, 2000; O'Neill et al., 1998].

Many studies of polymer solubility were presented soon thereafter due to interest in both petroleum engineering (CO_2 flooding and CO_2 fracturing) and chemical engineering processes (supercritical CO_2 fluid processing) that would benefit from novel CO_2-soluble additives. The first breakthrough concerning the design of high molecular weight polymers capable of dissolving in CO_2 at moderate pressures without the need for a co-solvent was reported by DeSimone and co-workers [McClain et al., 1996]. These researchers found that poly(1-,1-,dihydroperfluorooctyl acrylate), PFOA, Mw = 1,400,000 (Figure 4.1) could dissolve in CO_2 and induce a significant increase in viscosity as measured with a falling object viscometer,(Figure 4.2). PFOA is also referred to as a polyfluoroacrylate, PFA.

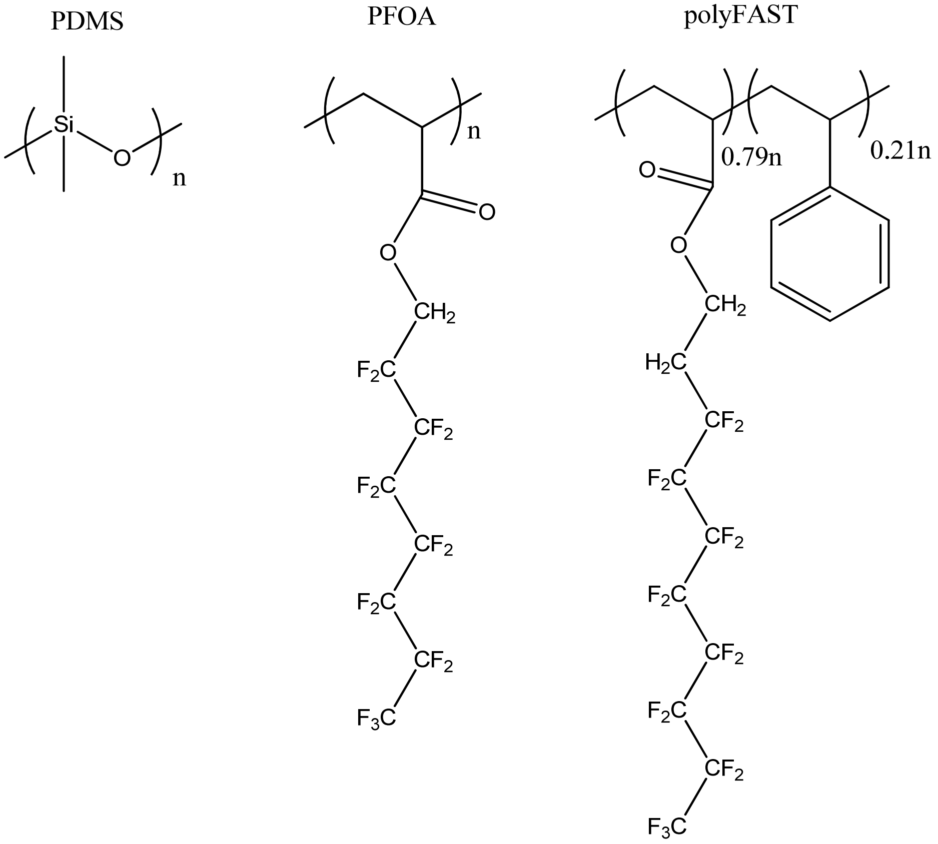


Figure 4.1. Structures of PDMS [Harris et al., 1990; Bae and Irani, 1990]; PFOA homopolymer [McClain et al., 1996] and the polyFAST random copolymer CO_2 thickener [Huang et al., 2000; Xu and Enick, 2001; Xu et al., 2003]

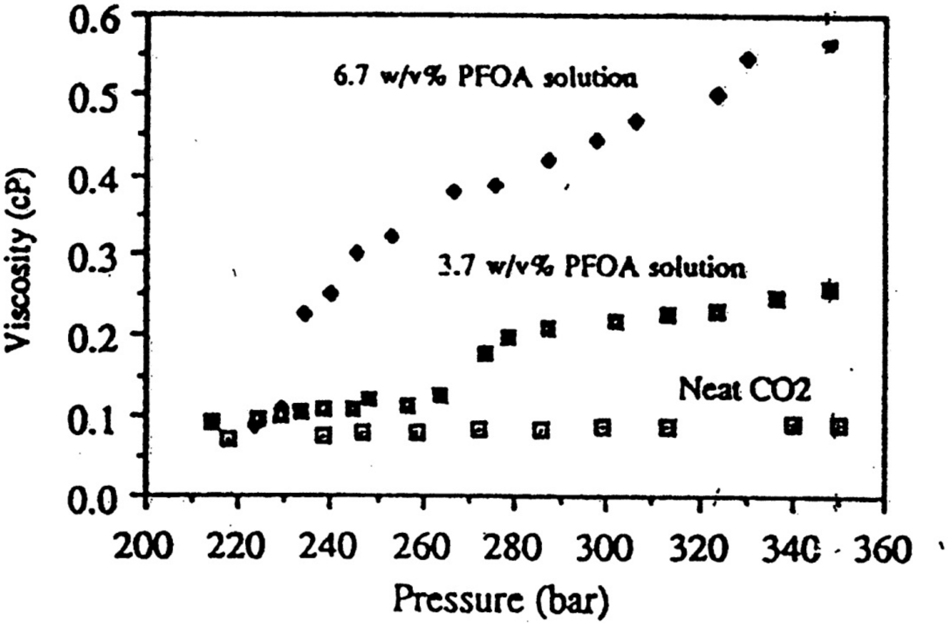


Figure 4.2. Viscosity increase caused by dissolution of high molecular weight polyfluoroacrylate in CO_2 [McClain et al., 1996]

For example, at 50 °C and 3.4 wt./vol% PFOA in CO_2, the solution viscosity was ~0.25 cP at ~300 bar (~4,500 psia), about 2.5 times greater than the viscosity of pure CO_2 at the same condition. At 6.7 wt./vol%, the solution viscosity at the same temperature and pressure was 0.45 cP, about six times greater than the viscosity of CO_2. DeSimone's work [McClain et al., 1996] was the first to demonstrate that high molecular weight polymers could dissolve in CO_2 at conditions commensurate with CO_2 EOR reservoir conditions and significantly thicken CO_2. Further, polyfluoroacrylate is still the most CO_2-soluble polymer that has been identified. Nonetheless, the concentration of the PFOA was too high to be practical for CO_2 flooding.

Enick, Beckman, and co-workers then developed an associative co-polymeric thickener based on a perfluoropolyacrylate in the hope of reducing the amount of thickener needed to attain a specified viscosity [Xu and Enick, 2001; Xu et al., 2003; Huang et al., 2000]. The most effective thickener was a random co-polymer composed of ~79 mol% of a CO_2-philic fluoroacrylate monomer (1-,1-,2-,2-tetrahydro heptadecafluorodecylacrylate) and 21mol% of a mildly CO_2-phobic monomer with a pendant associating group—styrene. Although not as common as other types of polar or ionic associating groups, aromatic rings are known to attract one another via a mechanism referred to as "π-π stacking" that results from a different electron density along the periphery of the aromatic ring than in the core of the ring. Further, this copolymer is reasonably soluble in CO_2 at temperature and pressure conditions similar to CO_2 EOR conditions [Xu et al., 2003]. For example, at 25 °C polyFAST is 1.5 wt.% soluble in CO_2 at 15 MPa (2,175 psia) and 1.0 wt.% soluble at 13 MPa (1,885 psia). This fluoroacrylate-styrene copolymeric thickener, referred to as polyFAST and illustrated in Figure 4.3, was capable of thickening CO_2 in both falling cylinder viscometry and mobility measurements using Berea sandstone cores (Figure 4.4). In both cases the solution was found to be shear-thinning.

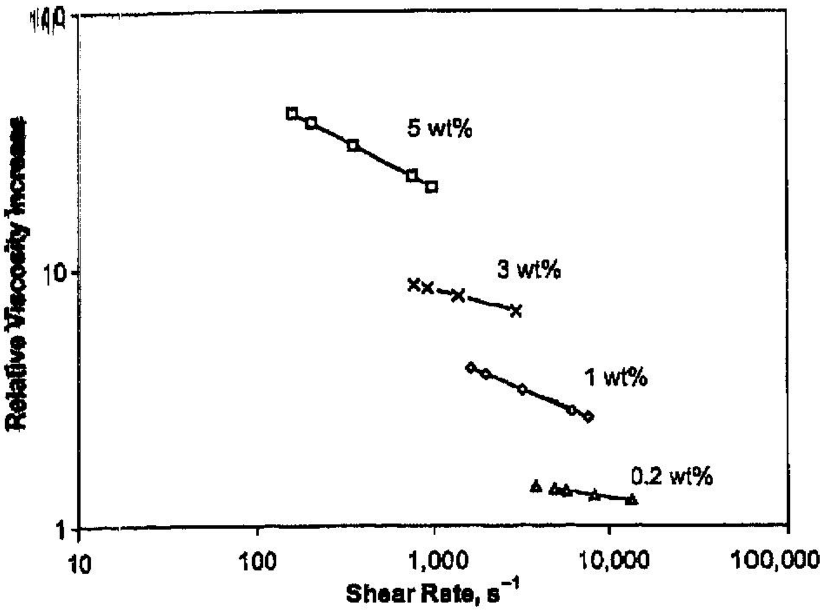


Figure 4.3. Falling cylinder viscometer results for the effect CO_2 viscosity as a function of polyFAST concentration and shear rate; relative viscosity is solution viscosity/pure CO_2 viscosity at same conditions [Xu et al., 2003]

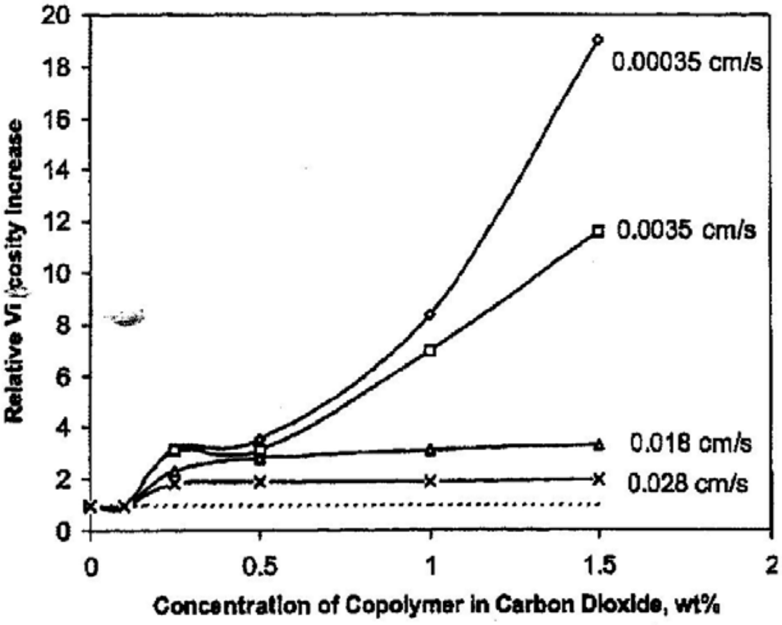


Figure 4.4. Viscosity of thickened CO2 relative to pure CO_2 as a function of superficial velocity and polyFAST concentration [Xu et al., 2003]

For example, at a concentration of 1.5wt% in CO_2, polyFAST was able to increase the viscosity of CO_2 flowing through Berea sandstone by a factor of 19 (an 1800% increase) at a superficial velocity of 1 ft./day (0.00035 cm/s), a factor of 12 at 10 ft./day (0.0035 cm/s), and a factor of 3 at

50 ft./day (0.018 cm/s). PolyFAST remains the only CO_2 thickener capable of dissolving in CO_2 in dilute concentrations (<1wt%) at typical CO_2 flooding reservoir conditions and significantly increasing (~10 times) the viscosity of CO_2 at low superficial velocities (1–10 ft./day).

Another strategy for enhancing the thickening capability of a polymer is to put associating groups at each end of the polymer. These linear, difunctional, telechelic ionomers are effective thickeners for non-polar solvents because the terminal ionic groups can aggregate into pairs, multiplets of a few ion pairs, or clusters of up to 100 ion pairs. Researchers at the New Mexico Petroleum Recovery Research Center (PRRC) synthesized a relatively low molecular weight sulfonated polyisobutylene as a CO_2 thickening candidate [Martin and Heller, 1990]. Although the non-functionalized polyisobutylene polymer is about 0.4wt% soluble in CO_2 [Heller, Dandge et al., 1987], the sulfonated ionomer was only sparingly soluble in CO_2 because CO_2 is such a poor solvent for ionic groups. Therefore, Enick and co-workers synthesized a fluorinated polyurethane telechelic ionomer based on more CO_2-soluble polymers—a relatively low molecular weight perfluoropolyether diol that was reacted with a fluorinated diisocyanate to yield a fluorinated polyurethane diol [Enick, Beckman et al., 1998]. This diol was then transformed into a fluorinated polyurethane disulfate. This fluorinated telechelic ionomer (Mw = 30,000) dissolved in CO_2 without the need for a co-solvent, increasing the viscosity of CO_2 at 25 ^oC and 25 MPa by a factor of 2.7 at a concentration of 4wt%. Given the expense of the fluoroether oil and the high concentration of the ionomer required to thicken CO_2, this was not considered a viable thickener.

Enick and co-workers then began the design of a non-fluorinated version of polyFAST in the hope of identifying a thickener that works at low concentration. Given the great expense and environmental persistence of the fluoroacrylate materials, the strategy was to either identify or design the most CO_2-philic non-fluorous polymer and to co-polymerize its corresponding monomer with styrene. There was a great interest in non-fluorinated CO_2-philic compounds for chemical engineering applications at that time; therefore, a great number of hydrocarbon-based polymers were investigated. Rather than simply testing a wide array of polymers as had already been done in the 1980s, polymers were designed and selected to contain one or more sites for favorable thermodynamic interactions with CO_2, or to exhibit other properties that would tend to favor dissolution in CO_2. In general, small compounds, oligomers, and polymers that were rich in oxygen atoms found in ether, carbonyl, acetate, sugar acetate, or vinyl groups were found to be CO_2-philic [Enick, Karanikas et al., 2003; Enick, Hong et al., 2005; Kilic et al., 2009; Potluri et al., 2002], but hydroxyl groups (-OH) were CO_2-phobic. These oxygen atoms are somewhat electropositive, while the carbon of CO_2 is electronegative, allowing Lewis acid–Lewis base interactions to occur. Further, the electronegative oxygen atoms of the CO_2 were found to exhibit Lewis acid–Lewis base interactions with the hydrogen atoms (protons) on the backbone or side chain of the polymer. With regard to alkyl chains, relatively small, highly branched alkyl chains were found to be more CO_2-philic than longer, linear alkyl groups [Eastoe et al., 2003].

The most CO_2-philic high molecular weight oxygenated hydrocarbon polymers were found to be polyvinyl acetate (PVAc), followed by poly [(1-*O*-(vinyloxy)ethyl-2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside)] (PAcGIcVE) (a polymer with pendant sugar acetate groups), and amorphous polylactic acid [Tapriyal and Enick, 2008]. Even though a new monomer (3-acetoxy oxetane) was designed with molecular modeling tools to exhibit the greatest number of favorable Lewis acid–Lewis base interactions with CO_2, the oligo(3-acetoxy oxetane) (OAO) was less CO_2-philic than PVAc [Wang et al., 2009]. Other CO_2-soluble compounds include polyvinyl ethylether (PVEE) [Kilic et al., 2007]; polyvinyl methoxy methylether (PVMME) [Wang et al., 2009]; polymethyl acrylate (PMA) [Shen et al., 2003], and oligomers of cellulose triacetate (OCTA) [Hong et al., 2008]. The structures of these oxygenated hydrocarbon-based CO_2-philic polymers are shown in Figure 4.5. Although not shown in Figure 4.5, per-acetylated cyclodextrin rings (PACD) can be considered as oligomers that contain 6–8 sugar acetates in a closed ring structure and are also CO_2-soluble [Potluri et al., 2003].

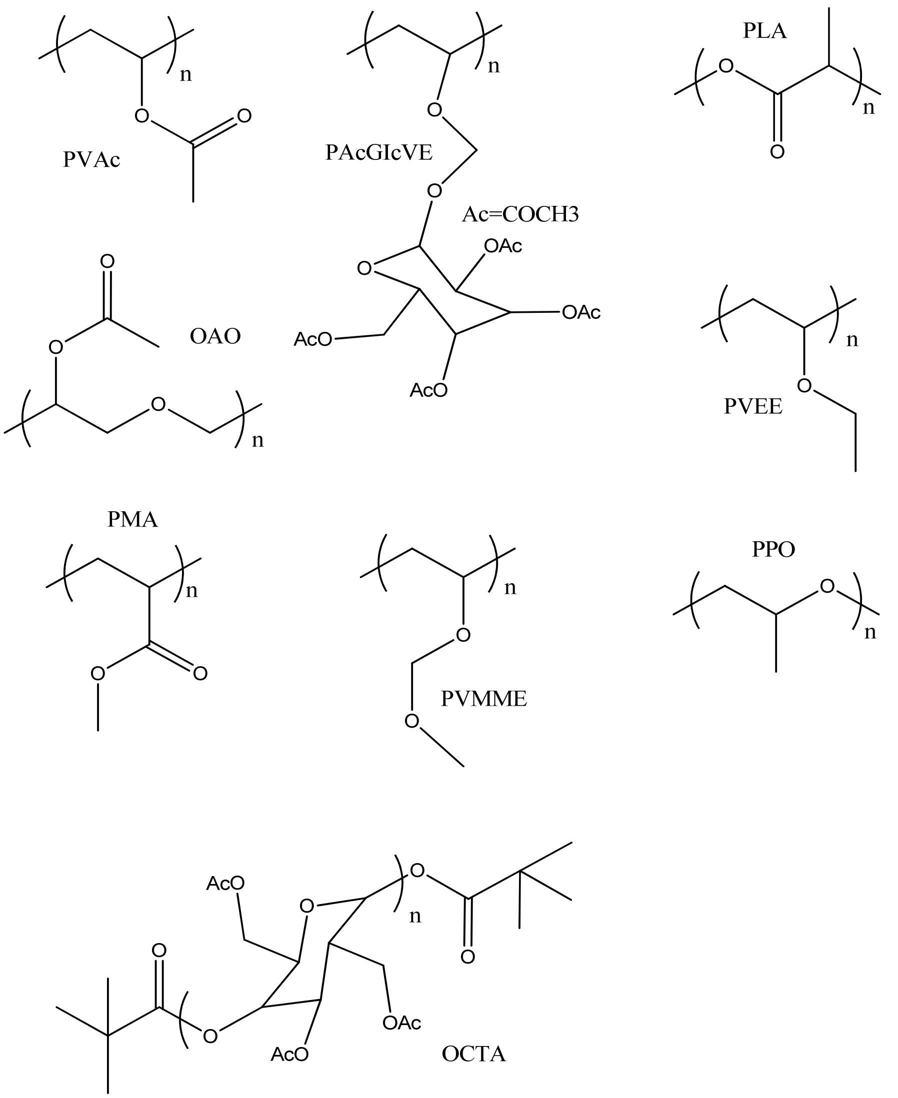


Figure 4.5. Structures of oxygenated hydrocarbon CO_2-soluble polymers; poloyvinyl acetate (PVAc); poly((1-*O*-(vinyloxy)ethyl-2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside) (PAcGIcVE); amorphous polylactic acid (PLA); oligomers of (3-acetoxy oxetane) (OAO); polyvinylethylether (PVEE); oligomers of cellulose triacetate (OCTA); not shown: per-acetylated cyclodextrins (PACD) [Potluri et al., 2003].

In order to attain a quantitative comparison of how CO_2-philic these polymers are, it is common to determine the pressure required to dissolve 5wt% of the polymer in CO_2 at ~25 ^{o}C over a range of polymer molecular weights or number of repeat units. The results for the polymers discussed in this report are provided in Figure 4.6 [Wang et al., 2009]. The lower the curve for the polymer, the more CO_2-soluble or CO_2-philic it is. The most CO_2-soluble high molecular weight polymer is PFA, followed by PDMS, followed by PVAc. All other oxygenated hydrocarbon-based polymers are less CO_2-soluble than PVAc.

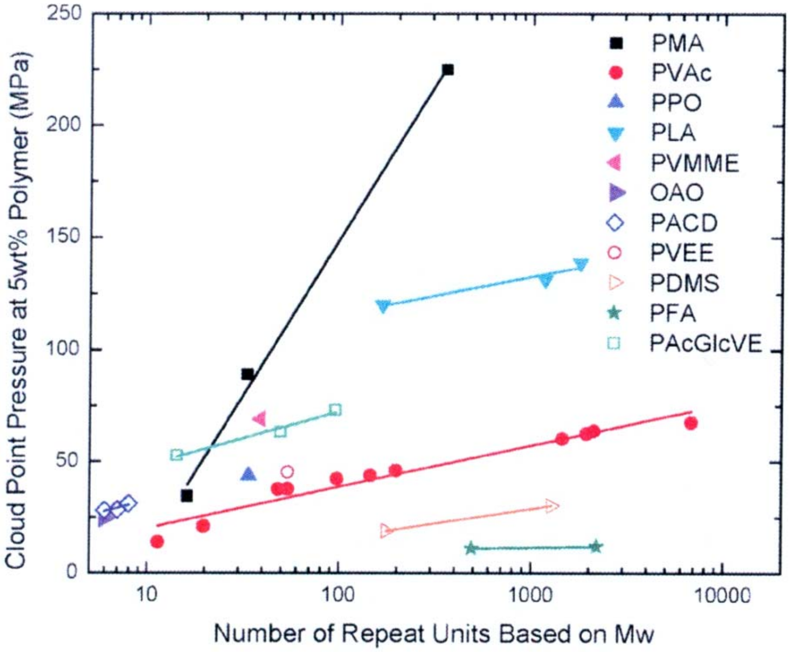


Figure 4.6. A comparison of the pressure required to dissolve 5wt% of the polymers and oligomers shown in Figures 9 and 12 in CO_2 at 25 ^{o}C as a function of composition and number of repeat units in the polymer or oligomer [Wang et al., 2009]; data for polyFAST and oligomers of cellulose triacetate are not shown on this plot.

The solubility of these oxygenated hydrocarbon-based polymers was dramatically less than that of polyfluoroacrylate or polydimethyl siloxane, however. For example, the dissolution of 5wt% PVAc in CO_2 at 25 ^{o}C requires ~6,300–10,000 psia as the PVAc molecular weight increases from Mw 12,500 to 585,000 [Shen et al., 2003], and the pressure required to dissolve PAcGIcVE and amorphous polylactic acid (PLA) is substantially greater [Tapriyal and Enick, 2008; Shen et al., 2003].

Because PVAc was shown to be the most CO_2-philic oxygenated hydrocarbon thickener, an attempt was made to copolymerize vinyl acetate with a monomer containing a pendant aromatic ring, thereby making a non-fluorous analog of polyFAST. This resulted in the successful synthesis of polyBOVA, a benzoyl-vinyl acetate copolymer.

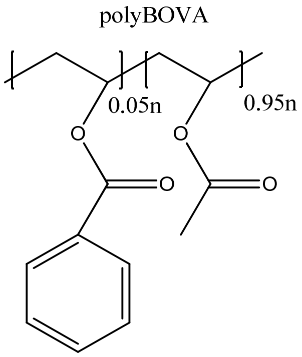


Figure 4.7. PolyBOVA [Tapriyal, 2009]; Mw = 12,000; this copolymer was slightly soluble in CO_2 at pressures far above MMP and induced a 40% increase in CO2 viscosity at 1wt%, 25 ^{o}C, 10,000 psia

Although ~40% and ~80% increases in viscosity were realized at 1 and 2wt% concentrations of polyBOVA, the pressure required to dissolve only 0.5wt% of a vinyl acetate-styrene random polymer (Mw = 12,000) in CO_2 was 64 MPa (~ 10,000 psia) at 25^{o}C [Tapriyal, 2009].

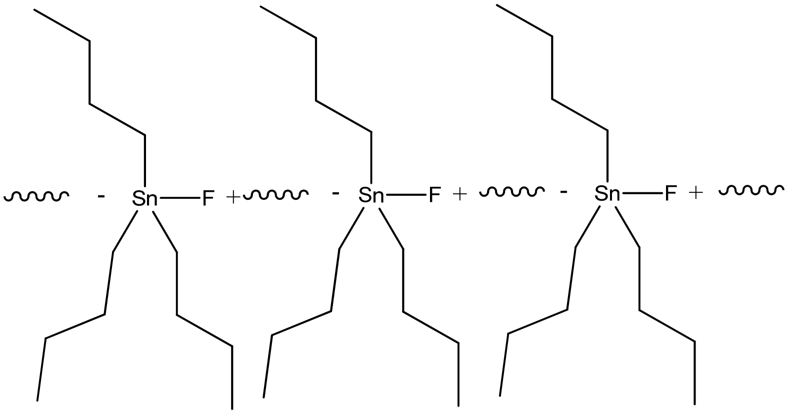
In conclusion, several polymer-based thickeners have been identified. These include a fluorinated polyurethane disulfate telechelic ionomer and a homopolymer of fluoroacrylate. In both of these cases the compound is highly fluorinated and roughly 3%–5wt% of the compound is required to achieve a two-to four fold increase in CO_2 viscosity. An effective CO_2 thickener, polyFAST, has been identified that can significantly increase the viscosity of CO_2 (~10-fold) at reservoir conditions in dilute concentrations (~1wt%), but the cost of the fluoroacrylate monomer is prohibitive. A non-fluorous analog of polyFAST, referred to as polyBOVA, was only slightly CO_2 soluble at a pressure far beyond the MMP and induced small changes in CO_2 viscosity. Therefore, at the time of this report, an affordable, non-fluorous, polymeric or co-polymer or associative polymeric CO_2 thickener capable of dissolving in CO_2 in dilute concentrations (0.1 – 1.0 wt.%) at typical EOR conditions and increasing the CO_2 viscosity by a factor of 2–20 at low superficial velocities has yet to be identified.

Small molecule CO_2 thickeners

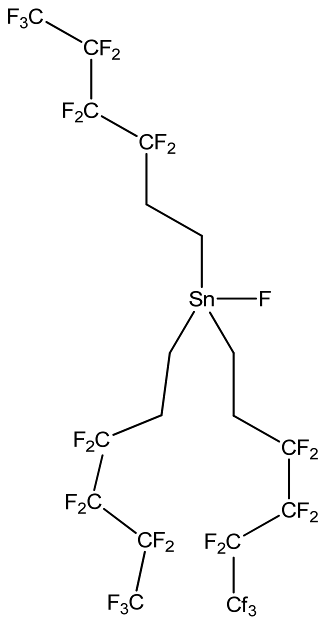
The second strategy that has been explored for CO_2 thickeners has been the design of small molecules that have the capability to associate and form viscosity-enhancing macromolecular structures. Therefore, in each case, the molecule contains a segment that is CO_2-philic enough to promote dissolution of the compound in CO_2. The compound also contains one or more CO_2-phobic moieties that are intended to be attracted to/associate with the CO_2-phobic moieties of neighboring molecules, thereby establishing a viscosity-enhancing, associating, non-covalently bound, macromolecular network.

Trialkyltin fluorides and semi-fluorinated trialkyltin fluorides

Heller and co-workers recognized the remarkable ability of tributyltin fluoride (Figure 4.8) to induce incredibly large viscosity increases in light alkanes at dilute concentration (e.g., ~ three orders of magnitude at 1wt%). The tin atom is slightly electropositive and the fluorine atom is slightly electronegative, while the three butyl arms extending from the tin atom enhance the solubility of the molecule in alkanes. These molecules apparently form linear, transient, associating polymers in solution as the tin atom of one molecule is attracted to the fluorine atom of the neighboring molecule. The butyl arms do not interfere with these associations and help to stabilize the linear macromolecule. Unfortunately, neither tributyltin fluoride nor any other trialkyltin fluoride synthesized by Heller was CO_2-soluble enough to serve as a CO_2 thickener, although some success was realized in thickening propane and butane [Heller, Kovarik, Taber, 1986 and 1987; Heller and Kovarik, 1988]. The addition of pentane as a co-solvent did not enhance the solubility of the compounds in CO_2 [Iezzi, Enick et al., 1987]. After it had been established that fluorination of alkyl groups could enhance CO_2 solubility, Enick and co-workers synthesized tri(2-perfluorobutyl ethyl)tin fluoride, $(F(CF_2)_4(CH_2)_2)_3SnF$ [Shi et al., 2001] (Figure 4.8). Although this compound was soluble in CO_2 without the need for a co-solvent the viscosity increase was far less than expected. For example, when 3wt% of this semi-fluorinated troalkyltin fluoride compound was dissolved in CO_2 at 25 ^oC and 16.5 MPa (~2,400 psia), the viscosity of CO_2 tripled. Apparently, the fluorine atoms at the ends of the C_6 arms of the compounds competed with the fluorine atom bound to the tin, thereby disrupting the formation of extraordinarily long associating polymers.



Tributyltin fluorides

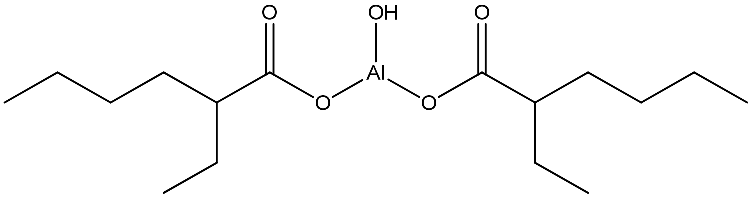


Tri(semi-fluorinated alkyltin)fluoride

Figure 4.8. Tributyltin fluoride, an excellent light hydrocarbon thickener that is CO_2-insoluble; tri (semi-fluorinated hexyl tin fluoride), a modest CO_2-thickener [Shi et al., 2001]

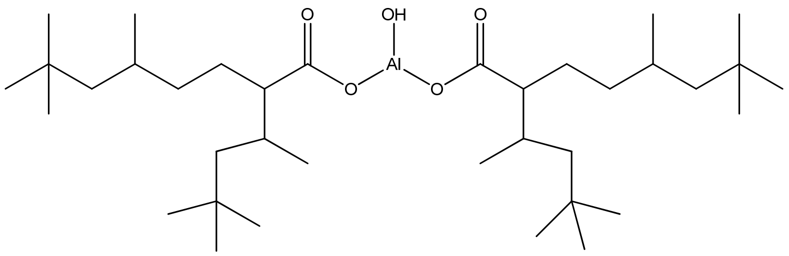
Hydroxyaluminum disoaps and fluorinated hydroxyaluminum disoaps

Perhaps one of the most famous hydrocarbon thickeners was developed for the purpose of weaponizing gasoline. Dilute concentrations of a hydroxyaluminum disoap transformed low-viscosity gasoline into a sticky, extremely high viscosity fluid referred to as Napalm. The thickener is composed primarily of the water-insoluble surfactant hydroxyaluminum bis(2-ethyl hexanoate) (Figure 4.9) or hydroxyaluminum bis(mixed iso-octanoates). In a manner analogous to tributyltin fluoride, this aluminum disoap dissolves in light alkanes and self-assembles into long, cylindrical, viscosity-enhancing, dry micelles. The core of this macromolecular structure is composed of the hydroxyaluminum head groups (electropositive aluminum, electronegative oxygen atoms in the hydroxyl group). The branched , 2-ethyl hexanoate chains not only enable the disoap to dissolve in the oil, but also provide the precise steric hindrance required for the micelles to form cylindrical, rather than spherical, micelles. A modest change in the structure, such as the use of linear, rather than branched C_8 chains, causes the surfactant to lose its ability to thicken the oil. Enick and co-workers synthesized a series of hydroxyaluminum disoaps in the hope of identifying a CO_2 soluble version capable of thickening CO_2. Although some of these disoaps can thicken propane, none of the hydroxyaluminum disoaps were CO_2 soluble [Enick, 1991]. Recent unpublished results from Enick's lab have shown that even when the alkyl arms of the disoap are fluorinated, or when they are replaced with highly branched alkyl chains that have been shown to enhance CO_2 solubility of some small compounds [Eastoe et al., 2003], the resultant hydroxyaluminum disoaps remained CO_2 insoluble (Figure 4.10).

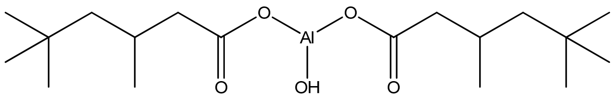


Hydroxyaluminum bis(2-ethyl hexanoate)

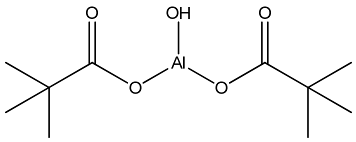
Figure 4.9. Hydroxyaluminum bis(2-ethyl hexanoate), an excellent thickener for light alkanes and gasoline that is CO_2-insoluble.



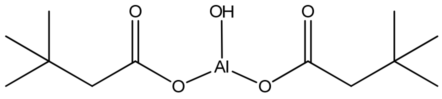
hydroxyaluminium di-isostearate-N soap



hydroxyaluminium di-AOT4 tail soap



hydroxyaluminium di-trimethyl acetate tail soap



hydroxyaluminium di-TC14 tail soap

Figure 4.10. Various highly branched hydroxyaluminum disoaps, all are CO_2-insoluble. Fluorinated and semi-fluorinated versions (not shown) are also CO_2 insoluble.

Metallic stearates

Attempts to thicken CO_2 by heating a mixture of CO_2 and metallic stearate powders were also unsuccessful. When this mixture is heated in hydrocarbon oils, the attractive forces between these compounds are weakened, enabling the compound to dissolve in the oil and form viscosity-enhancing metallic stearates as the solution cools. Even at high temperature and pressure conditions, however, the metallic stearates could not dissolve in CO_2 [Lewis, 1990].

Semi-fluorinated alkanes

Attempts to thicken CO_2 with semi-fluorinated alkanes were also made [Iezzi, Bendale et al., 1989]. These linear diblock compounds—$F(CF_2)_n(CH_2)_mH$, which can be considered as two immiscible segments forced to join one another through a covalent C-C bond—can gel organic liquids if they are heated in the solvent, allowed to dissolve, and then permitted to cool. As the solution cools, the semi-fluorinated compounds form high porosity, interdigitated, micro-fibrillar networks that can gel bulk fluids. The fibers form as the fluorinated segments stack with neighboring fluorinated segments, as do the hydrocarbon segments. These semi-fluorinated alkanes were able to gel dense CO_2. The resultant "gel" was not suitable for EOR, however. Rather than being a transparent, single-phase, viscous solution that could flow through a porous medium, it was actually a dispersion of an interlocking network of micron-scale diameter fibers in dense CO_2. These fibers would be retained at the surface of sandstone or limestone.

12-hydroxystearic acid

Heller and co-workers also studied a small organic compound, 12-hydroxystearic acid (HSA), known to gel hydrocarbon and chlorinated solvents [Gullipalli et al., 1995]. This compound, $H_3C(CH_2)_5$ $CHOH(CH_2)_{10}COOH$, is terminated at one end with a –COOH carboxylic acid group. In solution, the electropositive –OH group of one HSA molecule associates with the electronegative carbonyl (=O) atom of the HSA molecule that it faces. The –OH hydroxyl group on the 12th carbon in the alkyl chain helps to align the tails of the HSA molecules above/below it. HSA was essentially insoluble in CO_2 unless 10%–15% co-solvent (ethanol) was added. For example, a solution of 3% HAS/15% ethanol/ 82% CO_2 exhibited a slight viscosity increase at 34 ^oC and 1,800 psia. Capillary viscosity measurements indicated that at a slightly lower temperature of 27–28 ^oC a 100-fold increase in viscosity was detected. The occurrence of microfibers in the CO_2-rich gels indicated that such solutions would probably not be capable of flowing through porous media during EOR.

Co-solvents

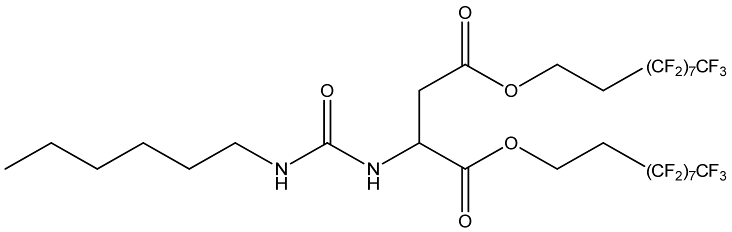
Investigators at NIPER considered the use of entrainers, or co-solvents, as CO_2-thickeners [Llave et al., 1990]. It was also desired to increase the CO_2 density and CO_2-rich phase solvent strength. Although the researchers were successful in these respects, substantial improvements required very high concentrations of co-solvent. For example, at 122 ^oF and 1,800 psia, 13 mol% isooctane increased the CO_2 viscosity by 243%. When 34.3 mol% of 2-ethyl hexanol was added to CO_2 at 40 ^oC and 2,000 psig, the solution viscosity increased by 943%. Although these are impressive increases, the amount of co-solvent required is extremely high.

Diesel fuel thickeners

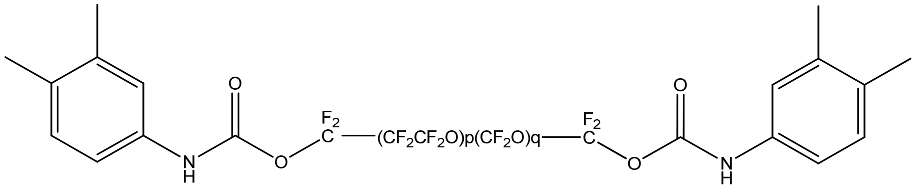
Canadian Fracmaster postulated that compounds known to gel organic liquids such as diesel fuel might be effective CO_2 thickeners. Their interest was in increasing the viscosity of CO_2 as a fracturing fluid flowing through a fracture, rather than as an EOR solvent flowing through porous media [Lancaster, et al. 1987]. Therefore, relative to CO_2 EOR, they considered low temperatures to account for refrigerated tankers of CO_2 being delivered to the well site, and higher pressures that are required to fracture a formation. Further, the occurrence of micron-scale dispersed fibers would not be problematic because of the large scale of the wellbore and open fracture width compared to the fibers. Caprolactone-based polymers were CO_2-insoluble. Hydrophilic and hydrophobic fumed silica particles could not be dispersed in CO_2 even when co-solvents were added to the mixture. The reaction resulting from addition of CO_2-soluble tetraisopropoxy titanate with functionalized organic substrates (e.g., –OH or –COOH) in the presence of a co-solvent yielded a CO_2-insoluble macromolecule that precipitated, causing no viscosity increase. The reaction between amine-terminated organics and CO_2 yielded CO_2-insoluble ammonium carbamates that simply precipitated in the solution instead of gelling it.

Fluorinated and non-fluorous bisureas

Researchers at the University of Pittsburgh and Yale University designed small compounds with either one or two urea groups. Urea groups can interact via hydrogen bonding with urea groups in neighboring molecules and “stack” in solution, thereby providing a mechanism for the formation of long, viscosity enhancing, associating macromolecules in CO_2-rich solutions [Shi et al., 1999]. In four of the twelve compounds studied, the bis-urea was capable of dissolving in CO_2 without being heated and increasing the viscosity of CO_2 by factors of about 3–5 at concentrations of ~5wt% at 25 ^{o}C and 4,500 psia. Two of the four fluorinated bisureas that exhibited this behavior are shown in Figure 4.11.



Semi-fluorinated urea



Semi-flourinated bisurea

Figure 4.11. An example of a semi-fluorinated urea (top) and a semi-fluorinated bis-urea (bottom); both are capable of modestly thickening CO_2.

In an attempt to design a non-fluorous analog of these fluorous bis-ureas, CO_2-philic hydrocarbon groups and CO_2-philic carbonyl and ether groups were incorporated into the structure as illustrated in Figure 4.12 [Paik et al., 2007].

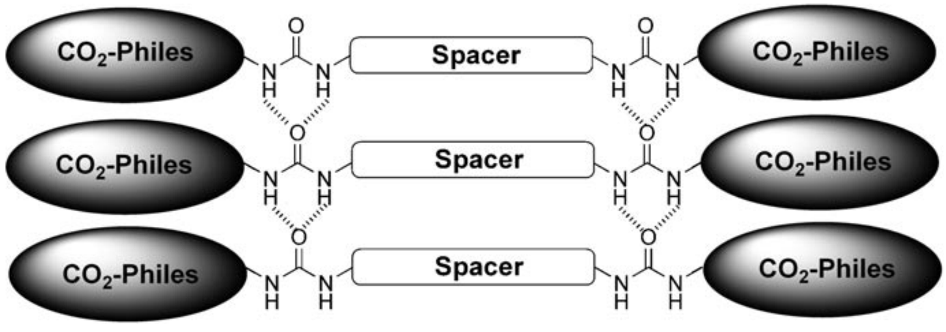
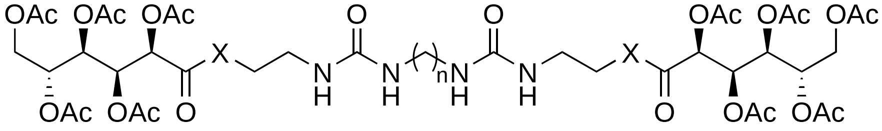


Figure 4.12. The general structure of the non-fluorous, CO_2-soluble bisureas [Paik et al., 2007]

It was hoped that these compounds might also dissolve in CO_2, self-assemble into long cylinders (as shown in Figure 4.13), remain in solution, and thicken CO_2. The actual structures of the non-fluorous bis-ureas are shown in Figure 4.13.



2a: X = NH, n = 4
2b: X = O, n = 4
2c: X = O, n = 6

Figure 4.13. The non-fluorous bis-ureas with CO_2-philic, acetate-rich arms [Paik, et al. 2007]

Compounds 2b and 2c were CO_2 soluble at 25 °C to ~1wt% at elevated pressures of 62 and 65 MPa, respectively. This single-phase, transparent solution slowly turned into a dispersion of interlocking white fibers at a constant temperature and pressure, however. Apparently, as the molecules began to self-assemble, they came out of solution and formed fibers rather than staying in solution and thickening CO_2.

Fluorinated, dual, twin-tailed surfactants with divalent metal cations

Researchers at Bristol University and the University of Pittsburgh designed surfactants that were not only CO_2-soluble, but also capable of forming viscosity-enhancing rod-like micelles with the addition of small amounts of water [Trickett et al., 2010]. The design of the surfactant was based on previous observations for normal AOT-stabilized microemulsions, such as cyclohexane, in organic solvents. In such systems the exchange of Na^+ with Co^{2+} or Ni^{2+} is known to drive a sphere-to-rod transition, promoting viscosity enhancements up to 40-fold at 10 wt. % inorganic solvents [Eastoe et al., 1992, 1993, 1994]. Modeling of small-angle neutron scattering (SANS) data is consistent with occurrence of rigid, rather than flexible, micellar rods. Eastoe and co-workers at Bristol University synthesized the following semi-fluorinated, CO_2-soluble surfactants (Figure 4.14) using dense CO_2 as the solvent and the addition of small amounts of water to stabilize the micelles in an attempt to demonstrate this principle.

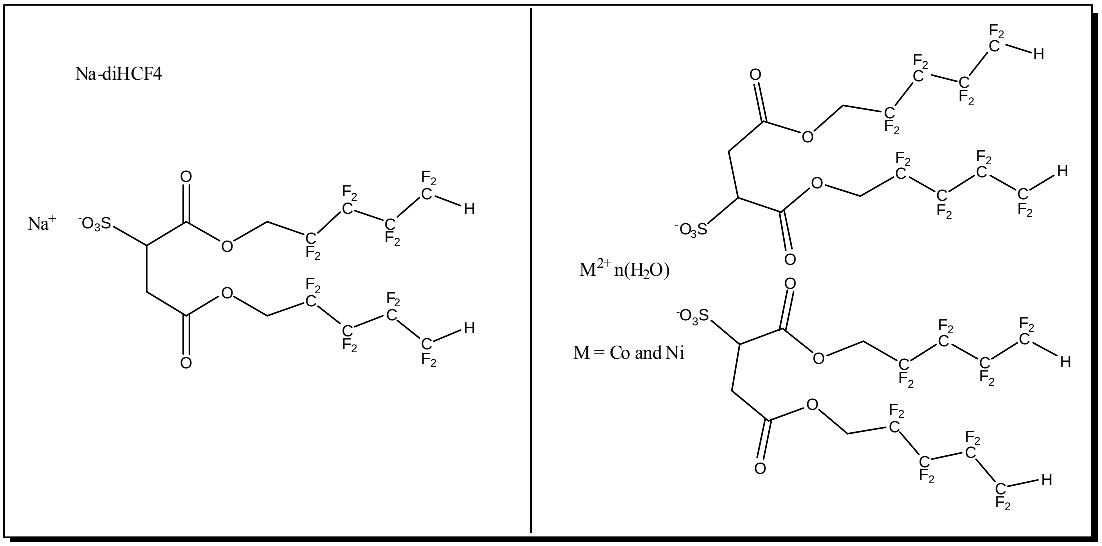


Figure 4.14. The structure of fluorinated AOT surfactants with the monovalent Na+ cation for spherical micelles, and divalent Ni^{+2} or Co^{+2} cation for viscosity-enhancing rod-like micelles [Trickett et al., 2009].

The surfactants were soluble in CO_2 at 25 °C, although the requisite pressure was greater than typical MMP values. Further, both high-pressure SANS and high-pressure falling cylinder viscometry confirmed that rod-like micelles did indeed form. Figure 4.15 shows that at a concentration of ~6wt% surfactant at 25 °C and 350 bar, with 10 moles of water present for each mole of surfactant, a ~50% increase in viscosity occurred. This is a modest degree of viscosity enhancement at a relatively high concentration of an expensive surfactant, however. These researchers are currently engaged in the design of more effective, non-fluorinated analogs of these compounds.

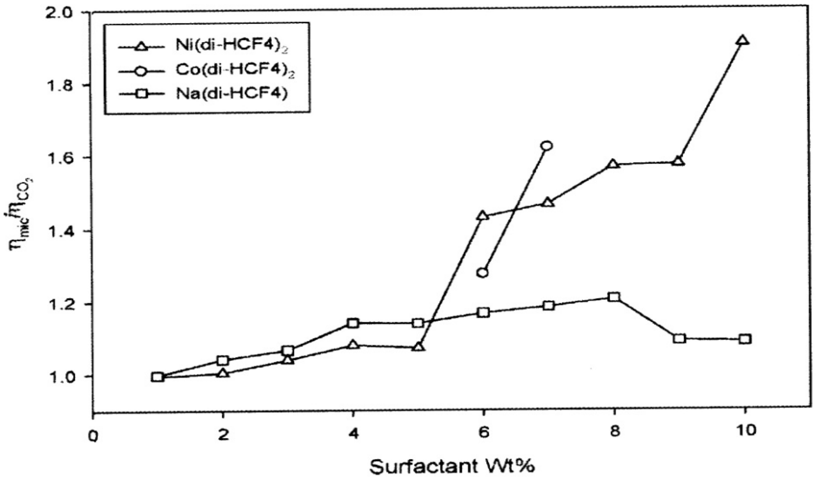


Figure 4.15. The thickening of CO_2 via the addition of surfactants that form rod-like micelles when small amounts of water are introduced to the CO_2-surfactant solution [Trickett et al., 2009].

Recently, Eastoe, Enick, and co-workers designed and assessed the viability of surfactants designated as F7H4 (Figure 4.16) that are less fluorinated, dissolve in CO_2, and form rod-like micelles in the presence of small amounts of water that stabilize the micelles. The F7H4 designation refers to the fluorinated tail C7 and a hydrocarbon C4 tail.

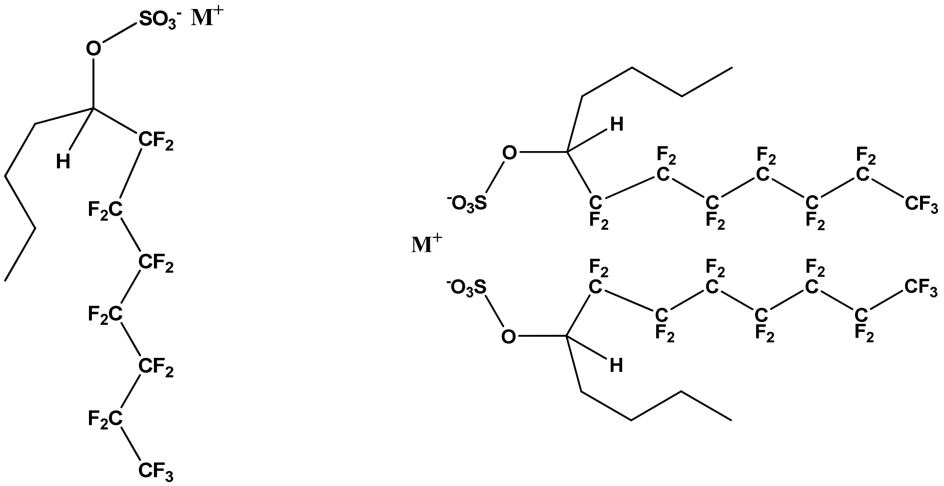


Figure 4.16. Monovalent (left, $M^+ = Na^+$) and divalent (right $M^+ = Co^{+2}$) versions of the F7H4 surfactants.

Na^+ $F7H4^-$ was capable of inducing a 50 to 80% increase in CO_2 viscosity at a concentration of 4.5 wt.% at 25 °C and 400 bar (Figure 4.17) in the presence of 5 to 12.5 moles of water per mole of surfactant.

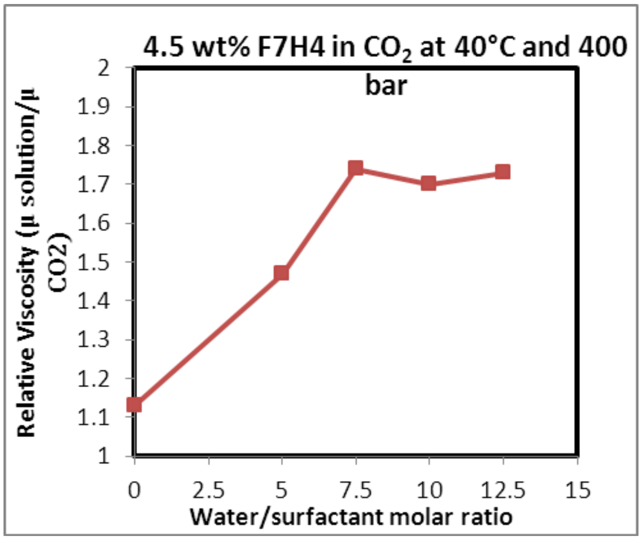


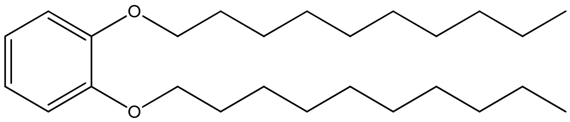
Figure 4.17. The increase in CO_2 viscosity resulting from the addition of 4.5 wt.% F7H4 at 40°C and 400 bar, ranging from 0 to 12.5 water/surfactant mole ratio [Xing and Enick, 2011].

Simple aromatic-dialkyl hydrocarbon gelling agents

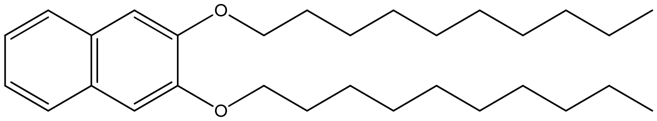
As shown in a recent review [George et al., 2006], the simplest organic compounds that have been shown to form various types of gels in organic solvents are composed of one, two, or three aromatic groups and two alkoxy tails [Brotin et al., 1991; Clavier et al., 1998; Clavier et al., 1999; Placin et al., 2000] (Figure 4.18). The aromatic groups are attracted to each other through the π-π stacking mechanism, while the alkyl tails both promote dissolution in the solvent and help to stabilize the formation of linear, associating macromolecules via London interactions. A simple organogelator, 2,3,bis n-decyloxybenzene (di-n-decyloxybenzene) (Figure 4.18 top) has been shown to gel acetonitrile, propylene carbonate, dimethylformamide, and dimethylacrylamide [Clavier et al., 1999]. DDOA (Figure 4.18 middle) has been shown to gel aliphatic alcohols and amines [Brotin et al., 1991]. 2-3-n-alkoxyanthraquinoine (Figure 4.18 bottom) can gel methanol, ethanol, and n-heptane [Clavier et al., 1998]. In all cases, gelation occurs via the formation of fine, fibrous networks of interlocking gelator strands.

These molecules may be viable CO_2 thickeners because they lack the polar, ionic, hydrogen-bonding, or metallic functionalities that tend to make thickeners insoluble in CO_2. The goal would be the formation of a network of viscosity-enhancing, linear macromolecules that would remain in solution rather than forming fibers. However, the molecular weight of these hydrocarbons, particularly those with three aromatic rings, may render the compounds sparingly soluble in CO_2. A group of researchers [Placin et al., 2000] combined a small amount of DDOA (20 mg) in a 20 ml vessel that was subsequently filled with dense CO_2. The mixture was then taken to 25 MPa and 90 ^oC, just above the 87 ^oC melting point of DDOA. The system was then cooled to 40 ^oC prior to the slow release of the CO_2. The researchers were successful in their attempt to form a dry organic aerogel. (They had no interest in viscosity-enhancement; therefore, no viscosity data was taken when the DDOA was in solution.) Upon removal of the CO_2 via depressurization, they obtained a brittle, low-density aerogel (0.002 g/ml) composed of fibers with diameters of 100–200 nm.

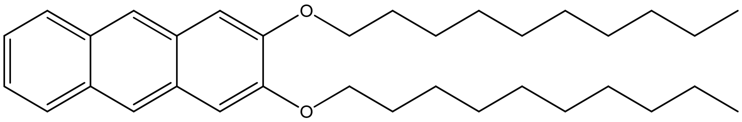
With regard to CO_2 thickening, this result shows that DDOA (Mw = 490) is CO_2-soluble to only 0.47 mmol DDOA/liter of solution (0.03wt %) at 90 ^oC and 25MPa (CO_2 density = 0.72 g/ml), conditions that are typical of CO_2 miscible displacement at high temperature. No single-phase viscosity measurements were made, however. It was also demonstrated that as the CO_2 is cooled to temperatures below the melting point of DDOA, this compound came out of solution and self-assembled in the form of fibers that are roughly micron-scale in thickness. It is possible to tailor the organogelator structure, and thereby its melting point, by altering the number of aromatic rings (1, 2, or 3) or the length of the alkoxy chains, or by the inclusion of carbonyl oxygen in the ring structure. Therefore, it may be possible to design a similar organogelator that can dissolve in CO_2, remain in solution, self-assemble, and enhance the viscosity of CO_2 over a broad temperature range. However, it may prove that when the aromatic head group provides enough π-π stacking for self-assembly to occur, the macromolecule may fall out of solution and/or be so sparingly soluble in CO_2 that no thickening results.



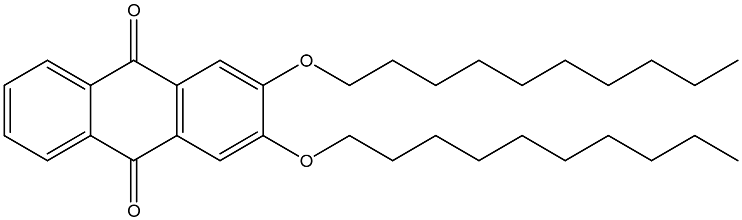
2,3-n-decyloxy-benzene



2,3-n-decyloxy-naphthalene



2,3-n-decyloxy-anthracene; DDOA



2,3-n-decyloxy-anthroquinone

Figure 4.18. Examples of simple hydrocarbon-based compounds with no metallic, polar, or ionic groups: In these examples, the tails contain 10 carbons. These compounds can gel various organic liquids: 2,3,-n-decyloxy benzene (di-n-decyloxy benzene) [Clavier, et al., 1999]; 2,3-bis-n-decyloxy naphthalene [Terech, et al., 2006]; 2,3-n-decyloxy anthracene (DDOA) [Brotin, et al., 1991]; 2,3-n-decyloxy anthroquinone [Clavier, et al., 1998].

In summary, several small molecule CO_2 thickeners have been identified, including a tri(semi-fluorinated alkyl)tin fluoride, several fluorinated urea and bisurea compounds, a dual, fluorinated, twin-tailed surfactant with a divalent metal cation, and a surfactant with a hydrocarbon tail and a fluorinated tail. All of these compounds are fluorinated and capable of inducing 50%–500% increases in CO_2 viscosity only at relatively high concentrations of ~2–10 wt.%. Therefore, the quest continues for an effective, affordable, small molecule thickener that can dissolve in CO_2 at typical reservoir conditions in dilute concentrations and increase the CO_2 viscosity to a level comparable to oil. To date, no field tests of a CO_2 thickener have been attempted because non-fluorous thickeners have not been successfully identified in the lab.

Researchers must remember that even if a CO_2 thickener—whether a polymer or small molecule—is identified, numerous operational hurdles face operators who would try to implement the technology in a pilot-test. First, every oil thickener and every promising CO_2 thickener is a solid at ambient temperature, thus a means of introducing a powder into the CO_2 stream must be employed. If the thickener is first dissolved in an organic solvent in order to form a concentrated, viscous, pumpable solution, the solvent cost may interfere with the self-assembly. Second, it must be verified that the thickened CO_2 is a transparent single phase capable of flowing through porous media, rather than a dispersion of micron- or sub-micron-scale fibers in the liquid CO_2 that would be retained by the face of the porous media near the injection well. Third, enormous high-pressure mixing tanks would be required if prolonged mixing is required. Also, if the thickener needs to be mixed with CO_2 at elevated temperature, extensive energy requirements and extremely high pressures may be required of the surface mixing equipment.

5. Carbon Dioxide Foams

Given the longstanding difficulty in identifying a viable CO_2 thickening agent, other means of using chemical additives to reduce the mobility of CO_2 have been considered. Perhaps the most promising of these techniques has been the use of CO_2 foams. Although the term "foam" is used generically in petroleum engineering, the term "emulsion" or "macroemulsion" is also appropriate, especially when the CO_2 is in the liquid phase at sub-critical (88 ^oF) temperatures. These foams or emulsions are *not* thermodynamically stable, transparent, single-phase microemulsions of CO_2. Rather, they are unstable, two-phase foam systems that will collapse with time.

Foams are familiar materials that are formed by mixing air, water, and a surfactant in kitchen sinks and bathtubs. A low pressure, air-in-water foam stabilized by a dishwashing detergent can appear as a frothy white material. The tiny pockets of air can become so crowded at high gas volume fractions (i.e., high quality) that they form polyhedral (rather than spherical) cells separated by thin, aqueous, flat films of surfactant-stabilized water referred to as lamellae. Similar foams can be formed with high-pressure gases such as CO_2 (Figure 5.1).

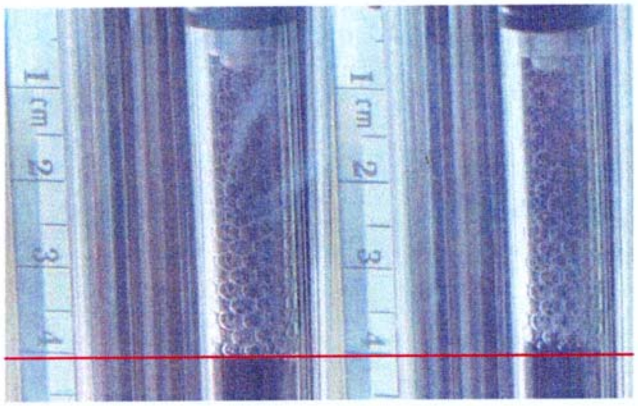


Figure 5.1. The polyhedral geometry of high pressure CO_2 "bubbles" observed in a high-pressure phase behavior cell [Liu, Grigg, and Bai, 2005]

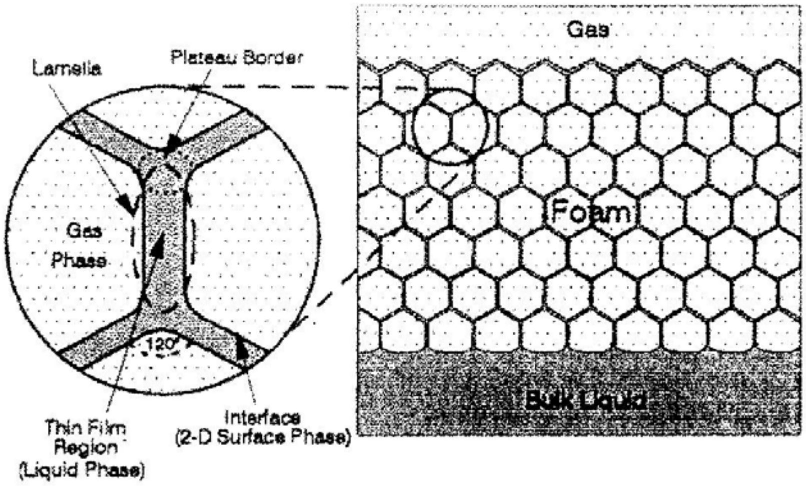


Figure 5.2. A cartoon of the CO_2-in-brine foam [Liu, Grigg, and Bai, 2005; Schramm, 1994]

These bubbles of gas are typically much smaller than the container in which they reside or flow. Finally, if the foam is left undisturbed, it will gradually collapse, leaving a clear, aqueous surfactant solution behind. The foam can be regenerated only if air is once again mixed with the soap solution. Although the transport of foams through pipes is an important engineering design consideration in the chemical and petroleum engineering industry [Bonilla and Shah, 2000], the primary topic of interest in this report is mobility reduction in porous media resulting from foam.

The foams used to reduce the mobility of high-pressure CO_2 share some of the characteristics of bulk foams. The foam must be stabilized by the addition of effective surfactants that contain a hydrophilic segment and a hydrophobic segment. In accordance with Bancroft's rule, the surfactant is typically more soluble in the continuous phase (brine, in this example) than the discontinuous CO_2 phase. Therefore, the mixture must be agitated to form the foam and a water-soluble surfactant is typically needed to stabilize it.

While this report provides an overview of the basic characteristics of foams and their application in field trials, an excellent review of experimental studies of foams in porous media that sheds light on the key microscopic mechanisms for reduced mobility—and foam models based on these mechanisms—is presented by Nguyen and colleagues [Nguyen et al., 2000].

IFT reduction between water and CO_2

Surfactants lower the interfacial tension between two phases, and the surfactants used to generate CO_2-in-brine foams are no different. Because it is relatively easy to measure surface tension of a liquid in contact with air, measurements of surface tension as a function of surfactant concentration are commonly used to estimate the critical micelle concentration (CMC) of a specific surfactant, which is the lowest concentration at which the dissolved surfactant molecules self-assemble to form micelles. The plot of IFT vs. surfactant concentration decreases with increasing surfactant concentration and then exhibits a discontinuity at the CMC, as shown in Figure 5.3.

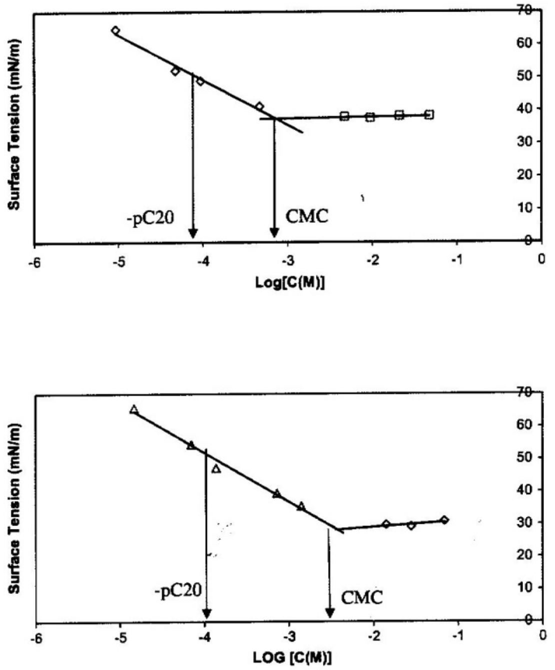


Figure 5.3. Determination of the CMC of an aqueous surfactant solution in contact with air for the surfactants 15-S-20 and LA-EO$_{12}$ [Adkins, Chen, Nguyen et al., 2010]

It is possible to also measure the interfacial tension between liquid CO_2 and water, γ_o; the interfacial tension between liquid CO_2 and water when surfactant is present, γ; and the surface pressure, $\pi = \gamma_o - \gamma$, and pC20, which is the surfactant concentration required to achieve a 20 mN/m reduction in interfacial tension [Adkins, Chen, Nguyen, et al., 2010]. Such data are reported less frequently because only a few experimental groups are currently capable of providing such measurements. The greatest level of IFT reduction in this example is exhibited by a twin-tailed, glycerol-based, non-ionic ethoxylate, DOG-12 (structures of the surfactants in Table 5.1 are provided in the "CO_2-soluble surfactants" section of this report).

Table 5.1.Critical micelle concentration, interfacial tension, interfacial tension – interfacial tension of the CO_2-water system, area per surfactant molecule, and the concentration of surfactant required to produce a 20 mN/m reduction in interfacial tension [Adkins, Chen, Nguyen, et al., 2010].

Surfactants	CMC at A-W (% w/w)	γ (mN/m)	π (mN/m)	A_m (A^2/molecule)	pC20 24 °C	pC20 40 °C	pC20 60 °C
2EH-PO_5-EO_9	0.28	7.5	20.2	219	3.9	4.2	4.5
2EH-PO_5-EO_{15}	0.28	5.6	22.1	233	4.4	5.2	5.2
1Hex-PO_5-EO_{15}	1.47	8.5	19.2	339	3.7	4.4	5.5
DOG-EO_{12}	0.015	4.1	23.6	-	5.1	5.7	-
LA-EO_{12}	0.21	7.9	19.8	-	3.8[a]	–	–
2EH-$EO_{11.8}$	0.99	12.8	14.9	-	–	-	-
2EH-PO_5-EO_{11}	0.42	7.6	20.1	-	4.0[a]	-	-

[a] Indicates the pC20 are estimated from the 0.01% w/w γ data.

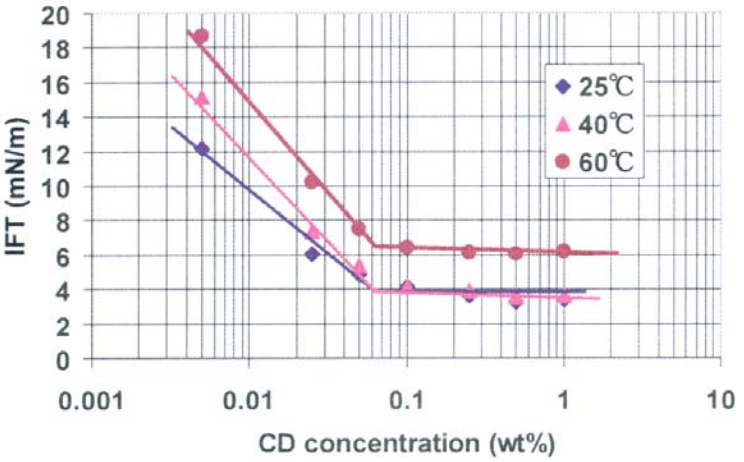


Figure 5.4. IFT between aqueous solutions of Chaser CD 1045 and CO_2 at 1500 psia [Liu, Grigg, and Svec, 2005]

Trapped Gas in CO_2 Foam Floods and Wettability

The reduced mobility of CO_2 foams is attributable to the flow of dispersed high-pressure CO_2 droplets separated by surfactant-stabilized lamellae within the pores of the formation. Although mathematical models of foam flow will not be reviewed in this report, some of the simple models and basic assumptions found in models provide a useful frame of reference for understanding foam formation in porous media. For example, consider Figure 5.5 [Chen, Gerritsen et al., 2008; Kovscek and Radke, 1994].

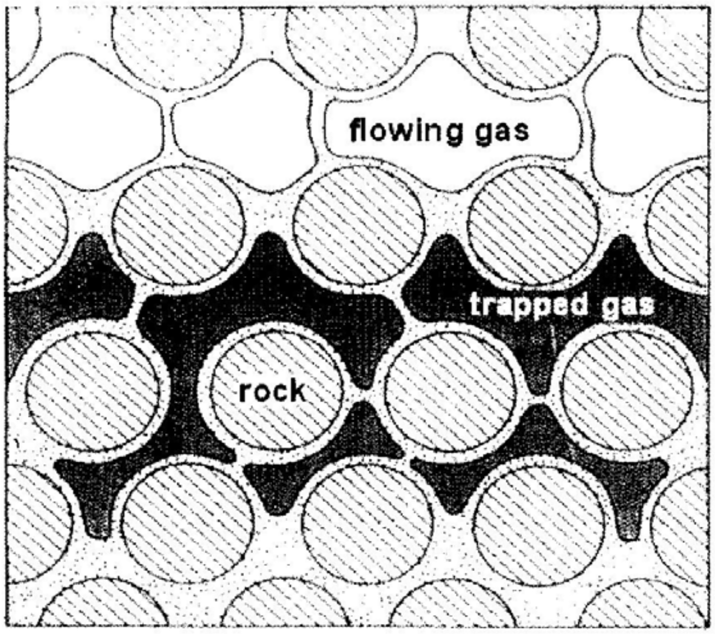


Figure 5.5. Foam flow in 2-dimensional porous media; crosshatched regions = water-wet sand grains shown as uncemented for clarity; dotted regions = surfactant solution; dark regions = trapped CO_2 with small pore constrictions and channels; white regions = flowing CO_2 cells in larger pore channels separated by surfactant-stabilized lamellae [Radke and Gillis, 1990].

Visual two-dimensional micromodels have also been constructed to provide direct views of lamellae formation and movement within porous media. In the Figure 5.6 image [Kuhlman, 1990] the “immobile foam” is composed of stationary bubbles that are much smaller than the pores in this 2-D micromodel, while the mobile lamella is shown as a thin film that bridges across the entire pore and is able to move.

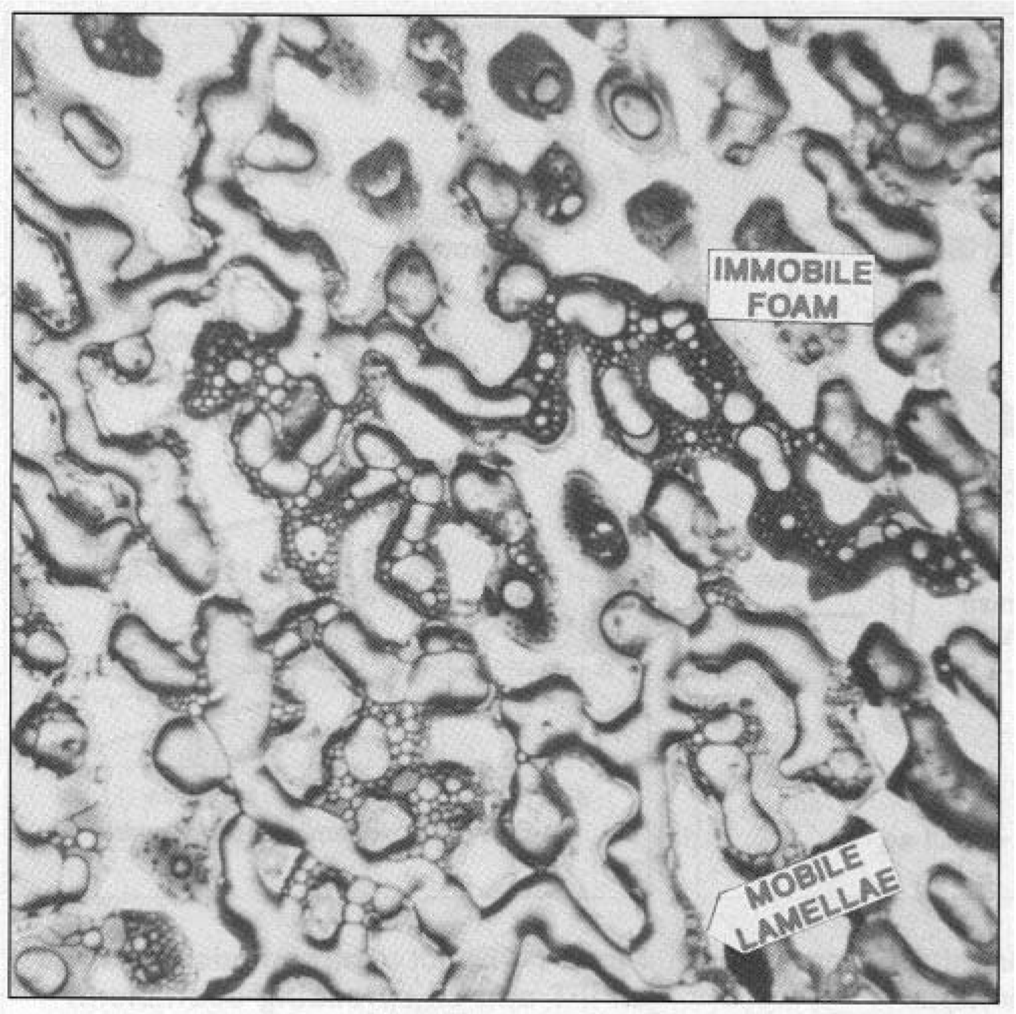


Figure 5.6. Immobile foam composed of small bubbles that formed late in the experiment when the oil did not spread have a viscosity of ~100 cP; bubbles that grow to 1-2 pore diameters have a viscosity of ~5-10 cP; bubbles that grow to ~2.5 pore diameters have a viscosity of ~1 cP. Mobile lamellae separated by ~ pore diameters [Kuhlman, 1990].

It is also possible to analyze photographic images of foams formed by the shear forces within the porous medium as they emanate from the porous medium, as shown in Figure 5.7 [Adkins et al., 2010], of the ~10 micron-scale CO_2 bubbles of a 90% quality CO_2 foam leaving a sand pack.

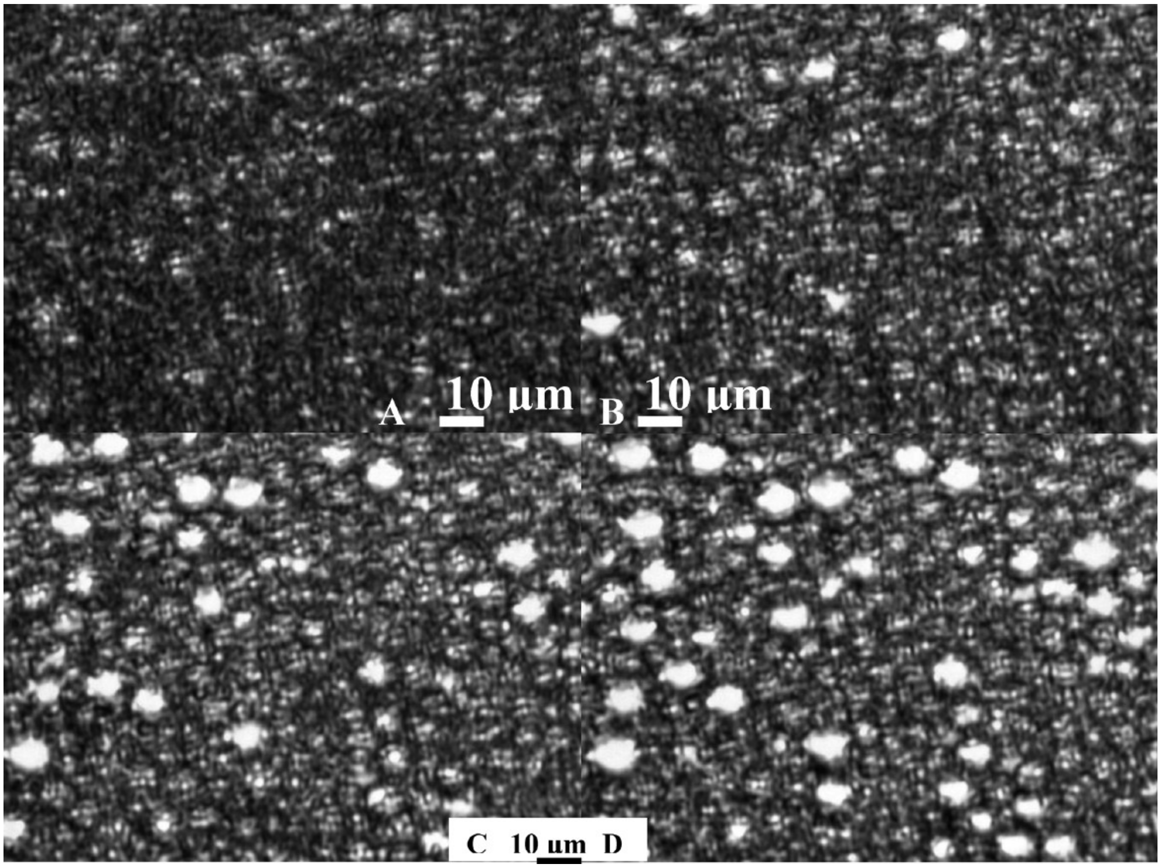


Figure 5.7. Micrographs of a 90%v/vCO$_2$ foam stabilized with1% v/v DOG-EO12 highly sheared in a 10 μm pore sand pack at 24 ^{o}C and 2,000 psia as a function of time at (A) 0, (B) 30, (C) 80, and (D) 20 s. Scale bars are located in the micrographs [Adkins et al., 2010].

A recent study has provided SEM images of surfactant-stabilized lamellae bridging pore throats [Kutay and Schramm, 2004]. In Figure 5.8 (the SEM images of a sectioned portion of a porous medium in which a foam had been generated [Schramm et al., 1999]) a lamellae appears as a thin sheet covering the entrance to several pores.

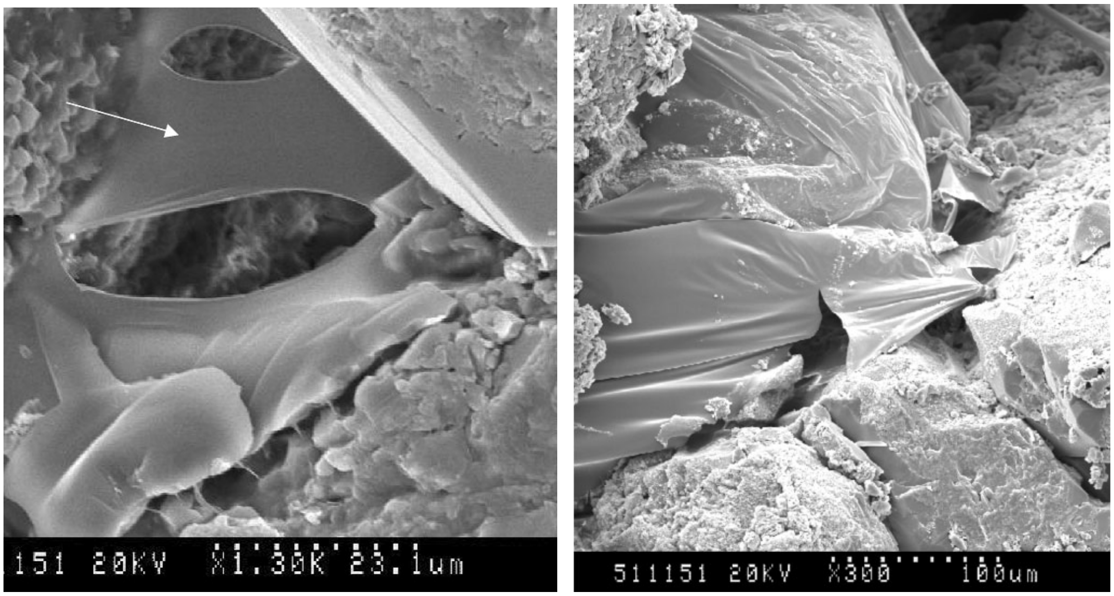


Figure 5.8. Left: Low-energy SEM image of perforated sheet-like foam lamellae spanning the pore space (Rewoteric and polyacrylamide). The arrow indicates foam film. View is looking into the pore. Right: A low-energy SEM image of a broad undulating sheet-like foam lamella that is covering the entrances to a number of pores (Rewoteric and polyacrylamide) [Kutay and Schramm, 2004].

Because the lamellae are thought to bridge across pore throats, they would be expected to form most readily in water-wet porous media. There have been reports, however, of foam formation in oil-wet models [Lescure and Claridge, 1986; Romero and Kantzas, 2004] or dolomite cores [Kuehne et al., 1992]. Although conventional surfactants did impart a modest degree of mobility reduction in the oil-wet dolomites, surfactants that both reversed the wettability of the oil-wet surfaces (making them hydrophilic) and stabilized the emulsions were capable of generating less mobile foams [Sanchez and Hazlett, 1992]. Further, the lower levels of surfactant adsorption on oil-wet media (relative to water-wet media) were thought to promote foam formation in oil-wet systems [Lescure and Claridge, 1986; Romero-Zeron and Kantzas, 2003; Romero-Zeron and Kantzas, 2005; Romero-Zeron and Kantzas, 2006].

Capillary forces cause the smallest pores to be filled with the wetting phase (water), which also coats the rock surfaces through the medium. This enhances the continuity of the aqueous phase making its relative permeability relatively insensitive to the presence of foam (Figure 5.9). The largest pores are occupied by cells/droplets of the non-wetting CO_2 phase, which enables the gas to be transported through the pores along with the lamellae that separate them. These “trains” of flowing CO_2 bubbles encounter drag forces related to the pore surfaces and constrictions and lead to alteration of the gas-liquid interface by viscous and capillary forces. Further, the transport of surfactant from the front to the rear of moving bubbles establishes a surface-tension gradient that impedes bubble flow [Tang and Kovscek, 2004]. These phenomena give the flowing foam a non-Newtonian character and an apparently high viscosity, or low mobility, compared to pure CO_2 and water flowing through the pores in the absence of surfactant and lamellae. The following figure provides a representative illustration of the effects of foam on the gas and water relative permeability curves. Note that the relative permeability of the aqueous phase does not depend on surfactant concentration, while the gas permeability decreases substantially as the surfactant concentration increases.

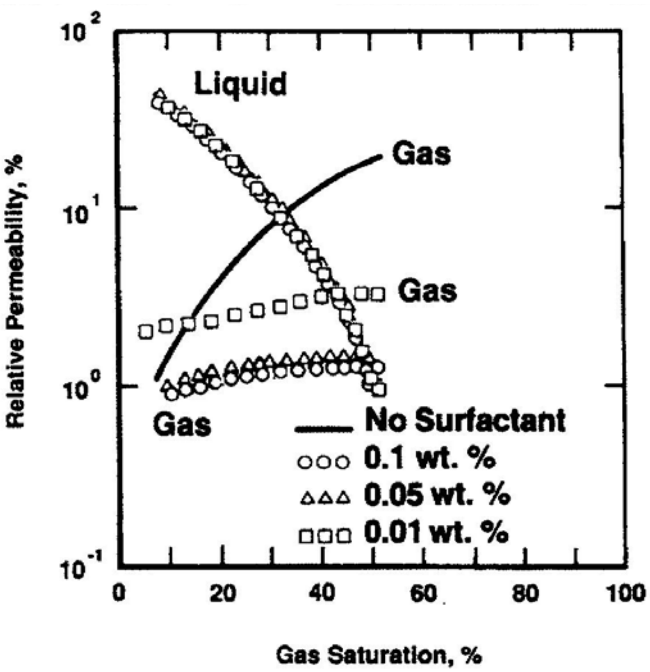


Figure 5.9. The effect of an anionic surfactant on the relative permeability of gas and liquid in a Berea core [Friedmann, Chen, and Gauglitz, 1991]

The intermediate size pores can become filled with immobile, trapped bubbles of the gas phase, which reduces the pore volume available for the flow of CO_2 foam through the rock. The majority of the gas within foam in sandstone at steady state can be trapped in these intermediate size pores [Chen, Gerritsen et al., 2008]. The gas trapping leads to gas blocking which, in turn, reduces the gas mobility even further.

An assessment of the level of gas trapping by foams [Tang and Kovscek, 2004] during steady-state flow in sandstone indicated that for superficial gas velocities between 0.4 and 30 m/day, the trapped gas fraction varied between 0.88 and 0.56 (mobile gas saturation varied between 0.12 and 0.44). At a constant liquid velocity, increasing gas velocity increased the mobile gas fraction. At a constant gas velocity, increasing liquid velocity reduced the fraction of mobile gas. Increases in surfactant concentration also reduced the fraction of mobile gas.

A high-temperature (150 ^{o}C) foam study used a tracer gas to determine trapped gas saturation in Berea sandstone cores of ~0.9 – 2.6 um^2 permeability [Friedman et al., 1991]. A 95% nitrogen – 5% brine mixture was injected into a core until steady state was achieved, and then the gas was switched to krypton. The effluent composition of krypton was then measured as a function of pore volumes of gas injected. The experiment was then repeated with 1wt% Chaser SD 1000 surfactant in the brine in order to generate foam in the core. The results from a typical run are shown in Figure 5.10.

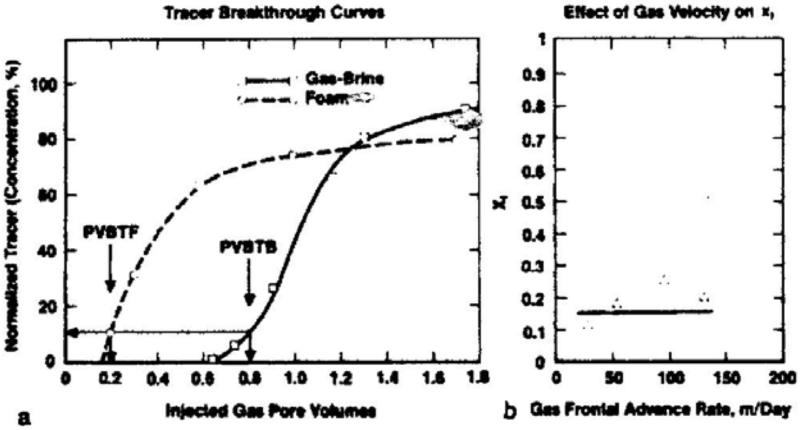


Figure 5.10. High temperature tracer study results indicting a ~15% mobile gas saturation when foam is generated, and that this fraction increases slightly with gas frontal advance rate (solid line at ~15% indicates that in a model an average value was used) [Friedman et al. 1991].

In the absence of foam, krypton breakthrough occurred after ~65% pore volume was injected. When surfactant was present and foam was generated, less cross-sectional area was available due to the presence of trapped gas and breakthrough occurred after 10%–20% pore volumes were injected, with the value increasing slightly with gas frontal velocity. The mobile and trapped gas saturation values in this study were therefore about 15% and 85%, respectively [Friedman, 1991].

A similar study of trapped gas fractions was conducted with a 2.3 μm^2 fired Berea sandstone core at ambient temperature and pressure conditions. Efforts were made to account for mass transfer of the tracer gas into the trapped gas. Dilute concentrations of methane and sulfur hexafluoride were used as gas tracers in the nitrogen. Aqueous solutions containing $C_{14\text{-}16}$ α-olefin sulfonate surfactant were used to generate foams. Gas fractional flows were varied between 0.80 and ~1, and superficial velocities varied between 0.4 and 4.0 m/day. The trapped gas saturations were quite high in this study, ranging from 79% to nearly 100% [Radke and Gillis, 1990].

In 2009, a study was conducted using X-ray computed tomography and effluent analysis [Nguyen et al., 2009]. For the first time, CT images of in situ gas tracer fractions in foam flowing through a core were presented. This study indicated that the realistic assessment of gas trapping was more complex than that associated with numerical studies of gas phase tracers in one-dimensional systems. For example, the tracer concentration was not uniform in either the trapped or flowing gas, tracer diffusion from the injection face into the core was significant over the duration of the experiments, and the foam flow fluctuated over long time and length scales. It was found that for the 1-D transport models, fitting the experimental breakthrough portion of the effluent data gave a lower value of the trapped gas fraction than when the entire effluent curve was fit. Reasonable fits of the data were obtained with estimates of the flowing gas fraction varying by as much as 0.2. For example, global optimum and manual fit estimates of the trapped gas fractions in five floods were estimated to be 0.39/0.60, 0.48/0.66, 0.47/0.36, 0.58/0.50, and 0.65/0.70. The trapped gas fraction was found to decrease slightly with increasing gas injection rate and increase slightly with increasing liquid injection rate, trends that were the same as those observed by Tang and Kovscek [Tang and Kovscek, 2004] but different from the earlier conjectures concerning these trends [Rossen and Wang, 1999].

In a subsequent study by Nguyen and colleagues [Kil et al., 2009], it was found that when a 3-D Taylor-Aris dispersion model was employed to estimate the trapped gas fraction, the flowing gas fraction decreased by 1–2 orders of magnitude compared to the results obtained with 1-D capacitance models [Nguyen et al., 2009]. For example, the flowing gas fraction was estimated to be only ~1% or less, with the gas flowing through paths only 1 or 2 pores in width. Therefore, the trapped gas fractions were close to 100%, and the investigators urged caution when applying a one-dimensional capacitance model to interpret the results of three-dimensional flow experiments.

6. CO_2 Foam Formation and Propagation

There are several important distinctions between the household foams that we are familiar with and mobility control foams that form in porous media [Heller, 1994]. Dense liquid or supercritical CO_2, rather than air, is the high-volume discontinuous phase. The flow of the fluids through the tortuous, interconnected pores of the sandstone or limestone provides the requisite shear for foam generation and the stretching and movement of the bubbles. Even if a CO_2-in-brine foam is generated at the injection wellhead by the simultaneous injection of CO_2 and surfactant solution, the foam will be re-formed as it leaves the wellbore and enters the micron-scale pores of the formation. Further, unlike foams that flow through wells or pipes or are formed in high-pressure vessels, the cells of CO_2 foam in rock are not significantly smaller than the pores that contain them. CO_2 mobility control foams do not consist of multitudes of extraordinarily small CO_2 bubbles or polyhedra within the pores; the "foam" is actually a population of lamellae that stretch across pores, compartmentalizing the dense CO_2 in packets that are slightly smaller than the pores. The individual lamellae are not transported intact from the injection well to the production well by the pressure gradient in the formation. Neither does a specific bubble of CO_2 remain intact as it flows throughout the formation. Rather, the lamellae are generated, maintain their integrity for a while, and then collapse. Because there is a mechanism for the generation of these lamellae within the porous medium, new lamellae can be formed throughout the course of the mobility control flood. However, there are also mechanisms responsible for the on-going decay of the lamellae. In order for a mobility control foam to be effective, the rate of lamellae generation should be about the same as, or greater than, the rate of decay.

Lamellae generation within a given formation depends on pore geometry and is roughly proportional to the flow rate of the fluids through this interconnected network [Heller, 1994]. Lamellae decay depends upon several factors, including the type and concentration of surfactant. Low concentrations of a surfactant that does not have foam-stabilizing properties will lead to rapid drainage of water from lamellae and coalescence of neighboring bubbles, while high concentrations of surfactants known to stabilize foams will stabilize lamellae or delay the coalescence. Further, the rupture of lamellae will occur only when the CO_2 bubbles on each side of the lamellae approach one another, an event influenced by the foam quality, flow rate, and pore geometry. Finally, the ability of lamellae to form may be inhibited by the presence of oil, pore geometry, or rock wettability. Although it may be challenging to model or predict these effects, it is apparent that several significant design parameters that can be designed to optimize foam performance include the type and concentration of surfactant, the foam quality as influenced by the relative volumes of surfactant solution and CO_2, and injection rates of the CO_2 and surfactant solution.

There are three mechanisms responsible for the formation of lamellae [Chen et al., 2004]: the leave-behind mechanism, lamella division, and snap-off. A thorough review of foams completed in 2000 [Nguyen et al., 2000]; a study by Chen, Yortos, and Rossen [Chen et al., 2004]; and a report on foams by Chambers and Radke [Chambers and Radke, 1990] provide an excellent summary of these mechanisms.

The leave-behind mechanism is the stabilization of thin liquid films, or lenses, that occur in pore throats as gas invades adjacent pores and, as shown in Figure 6.1, results in lamellae that are oriented parallel to the direction of the flowing gas that forms them.

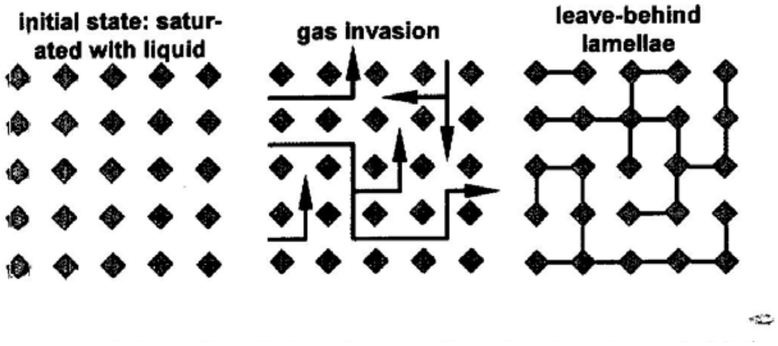


Figure 6.1. Lamella formation via the leave-behind mechanism [Chen. Yortsos and Rossen, 2004]

Consider the top left corner of the porous medium that is initially saturated with water (left image). Gas invades from the left and flows through two pore throats before exiting the medium as it exits the top of the medium (middle image). As a result (right image), films have been left behind that in essence demarcate the flow path made by the invading gas. Foams generated by this mechanism alone may tend to be considered as weak in that while they would block many flow paths to gas, they would also provide some proportion of continuous flow paths for gas.

The remaining mechanisms of lamellae formation, snap-off, and lamella division provide more pronounced decreases in gas mobility because both methods push lamellae through constrictions, thus generating films that are perpendicular to the direction of gas flow. Figure 6.2 illustrates lamella division as a lamella enters a branching point.

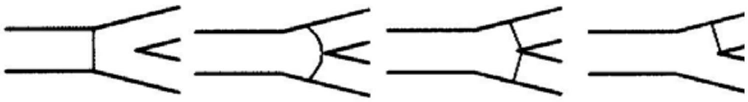


Figure 6.2. A single lamella division at a pore throat forming two lamellae from one [Chen, Yortsos, and Rossen, 2004].

When a single, mobile lamella passes by a pore throat that does not contain a liquid phase or another lamella, the mobile lamella must either break or span the throats. Figure 6.3 demonstrates how a few mobile lamalla (three in this figure) can fill a region with numerous lamallae. Typically, a local capillary pressure fluctuation must occur as the parent bubble stretches at the branch point, thereby preventing the lamella from rupturing before dividing because of liquid drainage.

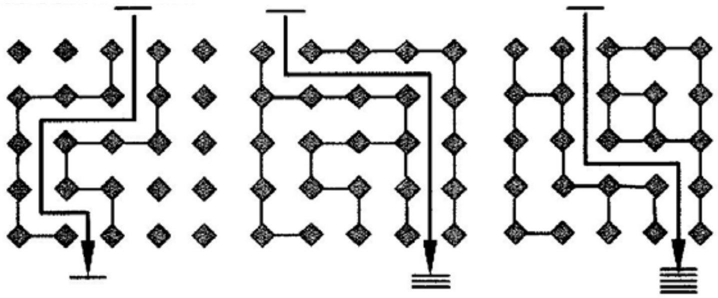


Figure 6.3. Lamella formation via lamella division at the pore network scale [Chen, Yortsos, and Rossen, 2004]

Finally, lamellae can form via the snap-off mechanism. Several types of snap-off have been identified [Chambers and Radke, 1990]. '*Pre-neck*' snap-off has only been observed when a surfactant solution was injected into a micromodel after a foam flood. In this case, the liquid pressure gradient drives the accumulation of the liquid slightly upstream of the throat to pinch-off a smaller bubble from the initial bubble that was blocking the pore throat. A similar event is snap-off. Lamellae are formed by snap-off, as shown in Figure 6.4, when the local capillary pressure falls to about half of the capillary entry pressure for the throat. There are seven mechanisms that may cause such a reduction in capillary pressure [Chen et al., 2004].

Figure 6.4. Lamella formation via snap-off in a pore throat [Chen, Yortsos, and Rossen, 2004]

In a similar process, when gas invades a large liquid-filled pore through a narrow pore throat, the liquid can drain from the walls of the pore body back into the pore throat region, forming a lamella via roof snap-off, as shown in Figure 6.5.

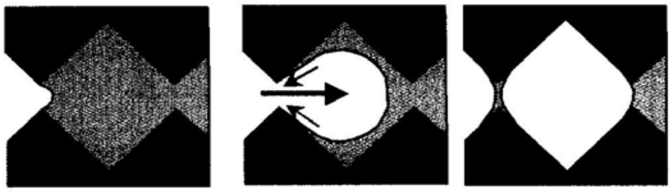


Figure 6.5. Lamella formation via snap-off and roof snap-off mechanisms [Chen, Yortsos, Rossen, 2004]

When snap-off occurs in long, straight pores, it is referred to as *'rectilinear snap-off'* [Chambers and Radke, 1990].

Some of the events that occur during foam flow, including snap-off generation of a bubble and lamella, the coalescence of two smaller bubbles into a larger one as the film between them drains, and the movement of a group or train of bubbles through pores, are illustrated in Figure 6.6.

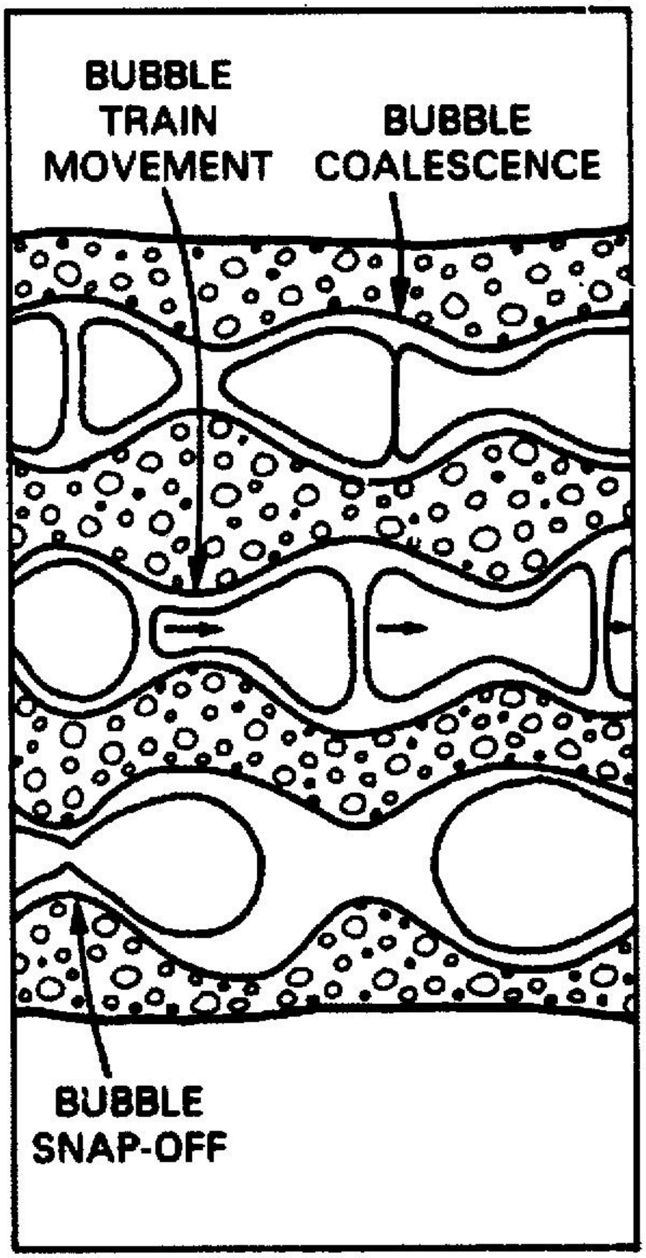


Figure 6.6. Pore-level events occurring during foam propagation [Yang and Reed, 1989]

7. Foams for Mobility Control, Conformance Control, and Production Well Treatments

Low mobility CO_2 foams in porous media have been exploited in several ways during enhanced oil recovery processes.

A *mobility control foam* is one in which the mobility of the foam is reduced approximately to a level that is comparable to the oil being displaced in an attempt to suppress fingering and channeling. A substantial portion (if not all) of the injected CO_2 will be introduced to the formation as a foam, typically via the alternating injection of surfactant solution slugs and CO_2 slugs. (It is also possible that the surfactant could be dissolved only in the CO_2, or could be introduced in both the injected brine and the injected CO_2.) The foam is intended to propagate throughout the entire formation, improving sweep efficiency through the CO_2 flood. For this reason, the foams are referred to as in-depth mobility control foams. The surfactant concentration in mobility control foam is typically dilute because it is not desired to establish an extremely low mobility, strong foam through the formation; the pressure drops would be prohibitive. Rather, one attempts to establish relatively weak foam that can be injected for a very long time, as if one was “thickening” the CO_2 enough for a mobility ratio of roughly unity to be achieved. Because the CO_2 foam is less mobile than CO_2, these mobility control foams will also improve vertical conformance. Although this results in these foams occasionally being referred to as conformance control foams, it is more appropriate to refer to them as mobility control foams because they are designed primarily to suppress fingering throughout the formation during the entire CO_2 flood.

C*onformance control foam* is primarily intended to selectively generate strong, very low mobility foams in highly permeable, watered-out thief zones. These foams are also referred to as blocking/diverting foams, or injection profile improvement foams. Typically, this is achieved by employing higher concentrations of surfactant in an aqueous solution that is injected alternately with CO_2. A surfactant known to generate strong foams more readily in high permeability sandstone or carbonate cores rather than low permeability porous media is preferred, while surfactants known to generate foams more effectively in low permeability media should be avoided. The conformance control foam is typically a short-term, near wellbore treatment that is intended to divert fluids to lower permeability, oil rich zones into which little if any CO_2 has previously flowed. A conformance control foam can also improve mobility control in the lower permeability zones if a modest or weak foam forms in these oil-rich zones; nonetheless, it is appropriate to refer to these short-term, high surfactant concentration, near-wellbore treatments as conformance control foams because their main function is to divert fluids from a high permeability thief zone.

A *production well treatment foam* is intended to reduce the gas-oil-ratio (GOR) in production wells, and is therefore referred to as a gas-oil ratio control foam. Unlike the mobility and conformance control foams that are introduced to injection wells, these foams are introduced at production wells in an attempt to provide a very low mobility impediment to gas exiting a high permeability layer. Therefore, the foams are analogous to a conformance control foam in that they are intended to selectively generate a very strong, very low mobility foam in the high permeability zone in near well-bore regions using a relatively high concentration of surfactant. Although reviews of production well treatments [Zhdanov et al., 1996; Turta and Singhal, 1998; Hanssen et al., 1994] and specific examples of production well treatments [Aarra and Skauge, 1994; Aarra et al., 1996; Blaker et al., 1999] and lab studies [Dall and Hanssen, 1996] are found in the literature, this topic is beyond the scope of the present report.

8. Water Soluble Surfactants for Foam

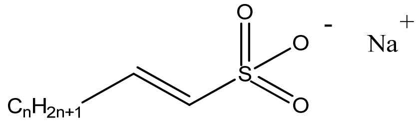
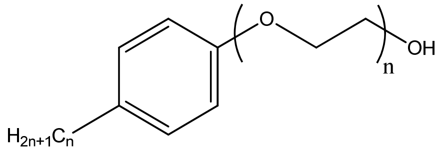
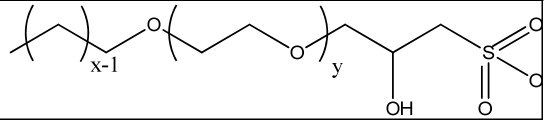
A critical component of CO_2 foam flooding is the design of the surfactant. The surfactant should be soluble in brine in order to have the surfactant stabilize CO_2-in-brine emulsions. This is in agreement with Bancroft's rule, which states that the phase in which a surfactant is more soluble will constitute the continuous phase. Although there are exceptions to this rule, it is usually accurate for CO_2-in-brine foam formation. Most of the promising CO_2 foaming surfactants are indeed very water soluble, with examples including anionics and nonionics with a relatively high number of hydrophilic ethylene oxide groups [Borchardt et al., 1988]. Most surfactants become less soluble in brines as the temperature increases and the concentration of total dissolved ions increases; therefore, it is imperative to assess CO_2 foams being considered for field tests at reservoir temperature and pressure using reservoir fluids and formation core samples [Kuehne and Frazier, 1992].

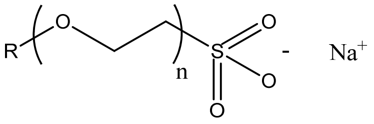
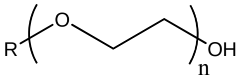
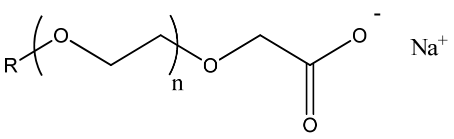
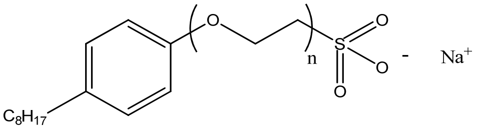
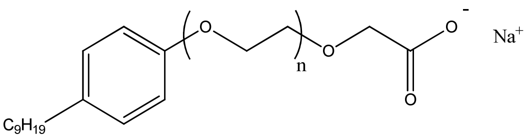
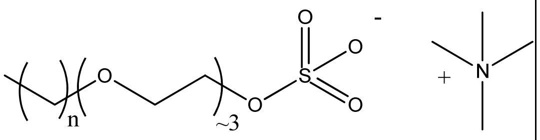
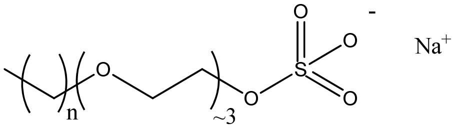
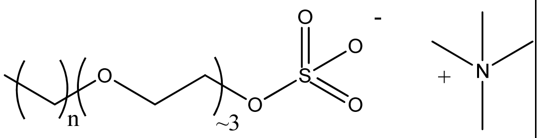
The surfactant should *not* be cationic (a surfactant with a positively charged head group and negatively charged counterion) in order to reduce adsorption losses to the negatively charged surface of sandstone formations. Therefore anionic, nonionic, and amphoteric surfactants have been more commonly assessed for CO_2 foam flooding of sandstone reservoirs. In carbonate formations, however, the surfaces can have a positive charge; therefore, anionic surfactants are not acceptable in these cases and cationic surfactants can give better results. Amphoteric surfactants, i.e., those surfactants which include both a positive and negative charge in the molecule, may also suffer from high adsorption losses.

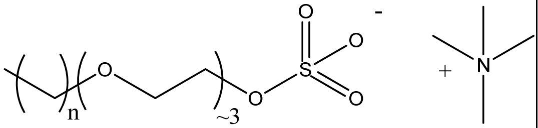
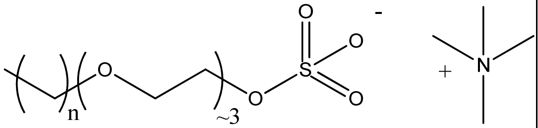
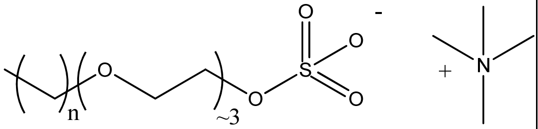
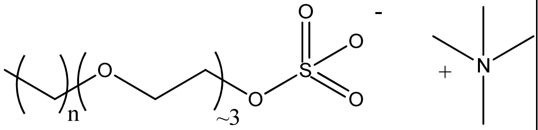
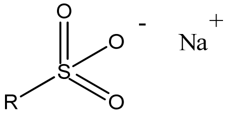
Many commercial surfactants have been identified in lab tests as viable candidates for CO_2 foam generation. Chaser CD 1045 (~45% active solution in water) has frequently been cited as an excellent foamer for the surfactant solution-alternate-gas CO_2 (SAG) process, in which the surfactant is dissolved in the brine that is injected alternately with slugs of CO_2. Although the composition of this surfactant is proprietary, it appears that this light brown liquid surfactant is a water-based proprietary blend of anionic α-olefins sulfonates, non-ionic alkyl phenol ethoxylates, and amphoterics. Chaser CD 1045 has been described by many investigators as a very good or excellent foaming surfactant [Heller, 1994; Chang and Grigg, 1999; Yaghoobi and Heller, 1994; Khalil and Asghari, 2006; Yaghoobi, Tsau and Grigg, 1998; Bai et al., 2005; Bai et al., 2010; Tsau and Heller, 1992] along with Alipal CD 128 [Casteel and Djabbara, 1988; Alkan et al., 1991; Holm and Garrison, 1988; Dellinger et al., 1984]. As will be shown in a subsequent section of this report, the vast majority of pilot tests were conducted with Chaser CD 1045 and/or Alipal CD 128.

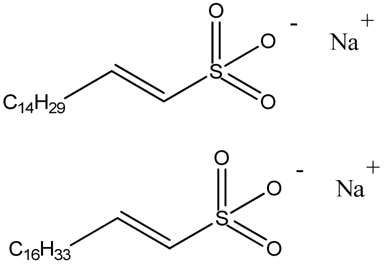
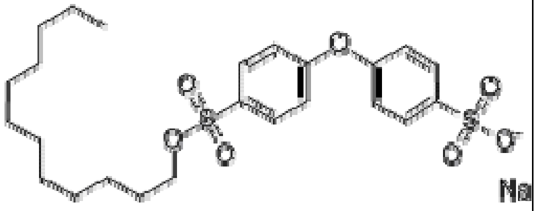
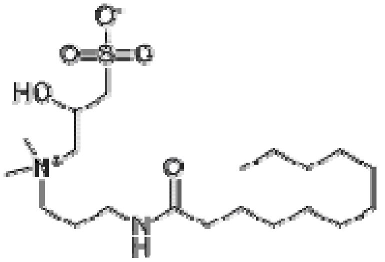
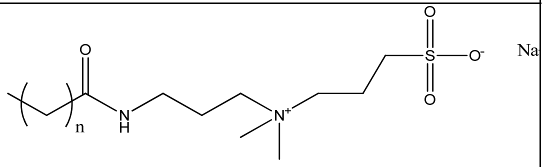
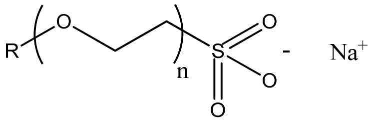
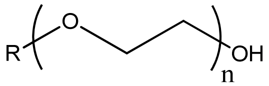
Other examples include Chaser CD 1040 [Yaghoobi and Heller, 1994], Chaser CD1050 [Yaghoobi and Heller, 1994; Tsau and Heller, 1992], NES-25 [Tsau and Heller, 1992], Avanel S30 [Tsau and Heller, 1992], Shell Enordet X2001 [Yaghoobi and Heller, 1994; Lee and Heller, 1990; Lee, Heller and Hoefer, 1991; Kuhlman et al., 2000], Sherex Varion CAS [Lee and Heller, 1988; Lee and Heller, 1990], Alipal CD 128 and an ethanolamide additive [Dellinger et al., 1984], Plurafoam NO-2N [Casteel and Djabbara, 1988], Witcolate 1247-H [Casteel and Djabbara, 1988], S-50 [Alkan et al., 1991], PAI [Alkan et al., 1991], a blend of Witco petroleum sulfonates—TRS 18 and TRS 40—with an average equivalent weight of 430 (the equivalent weight ranged from 250 to 650, with about 80% ranging from 350 to 550) and isopropyl alcohol co-solvent 1/10 of the sulfonate concentration [Bae and Petrick, 1977], alpha-olefin C_{14}-C_{16} sulfonate Shell AOS 1416 [Bertin and Apaydin, 1999], Chevron's proprietary CRSO 85/66 [Di Julio and Emanuel, 1989], DOWFAX unethoxylated alkyl biphenyl disulfonates [Kuhlman et al., 2000], Triton X 200 octylphenol ethoxylate, Neodol 25-9, NEGS 25-12 [Kuhlman 1990], Witcolate 1247H and 1276, Witconate 3203 and AOS12, Stepanflo 10, Pluronic F-68 EO-PO copolymer, Dowfax 8390, Dow XSS-84321.05 and XSS 84321.12, Ethoquad C/12 [Prieditis and Paulett, 1992], and a series of 40 surfactants described by Borchardt [Borchardt, 1985] in a study with air-based foams, including alcohol ethoxylates (AE), alcohol ether sulfates (AES), alcohol ethoxy ethyl sulfonates (AESo), alcohol ethoxy glyceryl sulfonates (AEGS), alcohol ethoxy acetates (AEA), octylphenol ethoxy ethyl sulfonates (OPES), and nonylphenol ethoxy acetates (NPEA). Borchardt concluded that the AEGS and AESo surfactants were particularly promising and both were assessed with CO_2 foam.

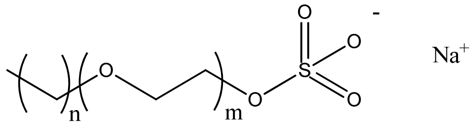
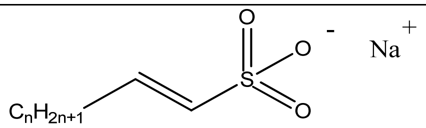
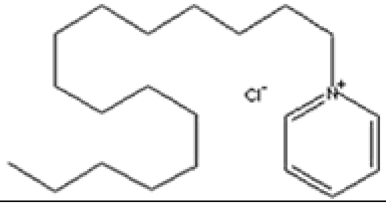
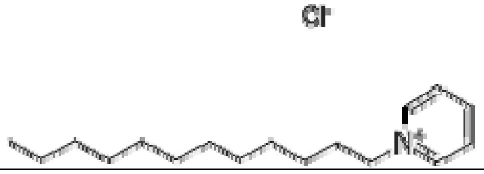
TABLE 8.1. EXAMPLES OF WATER-SOLUBLE SURFACTANTS USED IN LABORATORY STUDIES OF CO2-IN-BRINE FOAMS.

Surfactant Name	Type	% Active	Description	Structure
Chaser CD 1040	A	40%	Proprietary; some describe it to be an α-olefin sulfonates (counterion unspecified, Na+ used in example at right)	
Chaser CD 1045	M	47%	α-olefin sulfonates, non-ionic alkyl phenol ethoxylates, amphoterics	Mixture of surfactants
Chaser CD 1050	N	70%	Proprietary; Some describe it to be a alkylphenol ethoxylate	
Shell Enordet 2001	A	25%	alcohol ethoxy glyceryl	

			sulfonate (e.g., x=9, y=9) AEGS	
Shell Enordet AESo	A		Alcohol ethoxyethyl sulfonate AESo R = alkyl group	
Shell Enordet AE	N		Alcohol ethoxylate	
Shell Enordet AEA	A		Alcohol ethoxy acetate AEA	
Rohm and Haas or Diamond Shamrock OPES			Octylphenol ethoxyethyl sulfonate OPES Branched C8 chain	
Sandoz Sandopan NPEA			Nonylphenol ethoxyacetate NPEA Branched C9 chain	
Shell Enordet AES			Alcohol ether sulfate AES General structure; Ammonium or sodium counterion	 or 
Alipal CD 128	A	58%	ammonium salt of ethoxylated, sulfated linear alcohol; aliphatic sulfate esters;	

			alcohol ether sulfate; alcohol ethoxy sulfate AES	
Plurafoam NO-2N	A		ammonium salt of ethoxylated, sulfated alcohol	
Witcolate 1247-H	A		ammonium salt of ethoxylated, sulfated alcohol	
Stepanflo S 50	A		Like Alipal CD 128 ethoxylated agents with low ether oxide (EO) ratio (2.5-3.5	
Sulfotex PAI	A		Like Alipal CD 128 ethoxylated agents with low ether oxide (EO) ratio (2.5-3.5	
Witco TRS18 + TRS40	A		Petroleum sulfonate, MW 430; mixtures of sulfonated alkyl-aryl(benzene) petroleum products and free mineral oils	 R = hydrocarbon with alkyl and aryl components

Shell AOS 1416	A		alpha-olefin C14-C16 sulfonate	
DPEDS	A		C16 diphenylether disulfonate Dow Dowfax 8390; C16 chain	
Sherex Varion CAS	Z		Cocoamido-2-hydroxy propyl sulfo betaine	
Witco Rewoteric AM CAS U	Z		alkylamido sulfobetaine	
Henkel NES 25	A	40%	C9-C11 alcohol ethoxy sulfonate	
PPG/Mazer Avanel S 30	A	37%		
GAF Emulphogene BC 720	N			
Chembetaine BC3	Z			
Alcohol ethoxylate AE	N		Alcohol ethoxylate AE R = alkyl chain n = 6.5 – 100	

Triton X 200	N			
Siponate DS 10				
NEGS 25 - 12			Sulfonate of Neodol ethoxylate	
Neodol 25 - 9				
Witco Wicolate 1247H Witco Witoclate 1276	A		Alcohol ethoxy sulfate (Na+ counterion used in example)	
Stepan Stepanflo 10 Witconate 3203; C10 Witconate AOS12; C12	A		α-olefin sulfonates (counterion unspecified, Na+ used in example	
Hexel CPC	C		Cetyl pyridnium chloride	
Pfaltz & Bauer DPC	C		Dodecyl pyridnium chloride	

A = Anionic; C = Cationic; N = Nonionic; Z = Zwitterionic/Amphoteric; M = Mixed

Given the strong solvent strength of water, it is not surprising that various types of surfactants and numerous specific commercial products have been assessed for foam generation when the surfactant is dissolved in brine that is co-injected or alternately injected with the CO_2.

9. CO_2-Soluble Surfactants

It is natural to assume that the surfactant used to generate mobility control or conformance control foams in situ should be dissolved in an aqueous phase, given the strong solvency of water or brine for the dissolution of large concentrations of various types of ionic, zwitterionic, and non-ionic surfactants. Therefore, nearly every CO_2 foam pilot test that has been conducted has used alternating or simultaneous injections of CO_2 and aqueous soap solutions. In this portion of the report, the concept of employing CO_2-soluble surfactants will be addressed. Because CO_2 is a far weaker solvent for surfactants than water, there are inherently fewer types of surfactants that can be considered, and a far more careful molecular design is required to identify surfactants that can both dissolve in CO_2 and stabilize CO_2-in-brine foam.

The notion of dissolving surfactants in CO_2, rather than water, has occasionally been considered for decades. For example, the dissolution of a surfactant into CO_2 during an enhanced oil recovery process for the purpose of generating CO_2-in-brine mobility control foam or conformance control foam was suggested by Bernard and Holm in the late 1960s [Bernard and Holm, 1967]. In particular, they suggested the use of a branched octylphenol ethoxylate, Triton X-100, at a concentration of 1wt% in CO_2 at 80 ^oF (26.7 ^oC) and 1,000 psia (~6.9 MPa). Triton X-100 is not nearly this soluble in CO_2 at those conditions, however. The difficulty in dissolving surfactants in CO_2 did not escape the attention of Irani, who in 1989 suggested that a co-solvent be added to the CO_2 in an attempt to dissolve siloxane-based surfactants, which—like CO_2—have very low solubility parameters [Irani, 1989]. In 1991, Schievelbein suggested the use of hydrocarbon-based surfactants without the use of a co-solvent. In his summary, Schievelbein recommended using at least 0.2wt% (2,000 ppm) of ethoxylated alkyl or ethoxylated alkyl aryl (i.e., alkyl phenol) hydrocarbons that contain an alkyl chain with an average of 7 to 15 carbons and an average of between 1 to 7 ethoxide (i.e., ethylene oxide or EO) units [Schievelbein, 1991]. Typically, surfactants with such short EO tails are likely to be water-insoluble or water-dispersible, making them unlikely to stabilize CO_2-in-water or CO_2-in-brine emulsions. Bancroft's rule states that the surfactant should be more soluble in the continuous phase (aqueous films) than the high-volume discontinuous phase (dense CO_2) for an emulsion or foam to be stabilized. Therefore, it is highly likely that the CO_2-soluble surfactants must also be water-soluble to ensure the in situ formation of CO_2-in-brine foams.

There was a great deal of interest in the identification and design of CO_2-soluble surfactants for chemical engineering applications during the last two decades. Although most of this work was directed at the identification of CO_2-soluble surfactants that could stabilize water-in-CO_2 microemulsions for chemical engineering applications, a portion of the research was aimed at the stabilization of CO_2-in-water/brine foams at supercritical CO_2 conditions and emulsions at liquid CO_2 conditions. For example, Johnston and coworkers [Dhanuka et al., 2006] noted that Dow Tergitol TMN 6 (Mw = 552) poly(ethylene glycol)$_{8.33}$ 2,6,8-trimethyl-4-nonyl ether (90% active, 10%water) was an effective foaming agent. This surfactant, like all of the ethoxylates described in this section, has a polydisperse EO tail, with the average number of EO groups typically being presented (8.33 in this example) as shown in Figure 9.1.

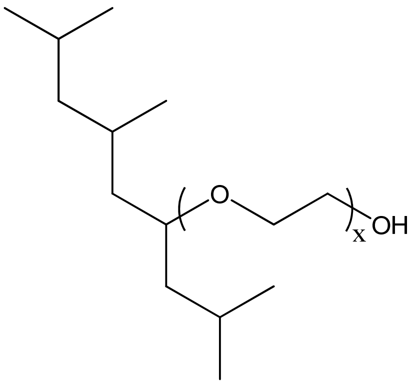


Figure 9.1. A branched alkyl ethoxylate; Dow's TMN 6 (x ~ 8.33)

Tergitol TMN-6 was added at a concentration of 5wt% of the water mass to a mixture of 90 vol% CO_2 and 10vol% water; roughly 0.5wt% Tergitol TMN-6 based on the CO_2 mass. (The ability of the surfactant to dissolve in CO_2 to this extent was not demonstrated.) After being agitated by a stirrer and a recirculation pump, very stable (more than two days) white, opaque foams formed at 25 ^oC and pressures of 20.7 MPa and 34.5 MPa. The polyhedral bubbles were roughly 10 microns in size. An excess water phase slowly formed at the bottom of the cell as the water of the lamellae slowly drained by gravity. Excess CO_2 appearing above the foam at the top of the windowed cell (which would have been formed by bubble coalescence) was not observed. In an earlier paper [Ryoo et al., 2003], Johnston and coworkers determined the solubility of several TMN surfactants of varying ethylene oxide chain length, TMN 3, 6, 10 (3, 8.33, 12 EO groups respectively); they were all soluble at 1wt% at temperatures between 25 and 75 ^oC at pressures of ~8.0–30.0 MPa, with increasing pressure required for increasing EO length and increasing temperature. Haruki and co-workers studied the phase behavior of TMN3 (with 5 EO groups) at temperatures between 308 and 343K and concentrations between ~0.5 and 3.0 wt.% [Haruki et al., 2007]. These results indicated that Johnston's experiments were conducted at conditions where the surfactant could have been completely dissolved in the CO_2 phase; therefore, Tergitol TMN-6 is a viable candidate for dissolution into the CO_2 being used for miscible flooding. Johnston and co-workers [Ryoo et al., 2003] also established that at 40 ^oC the linear alkyl ethoxylates with the same number of carbon atoms (i.e., the Nikko linear alkyl isomers of the Dow branched TMN surfactants) were less CO_2 soluble than branched analogs; although this difference was significant for concentrations between 5 and 45wt% surfactant, the difference became very small at concentrations less than 5wt%. This finding is in agreement with the well documented conclusions of Eastoe and coworkers that branching of an alkyl tail (e.g., incorporation of multiple methyl groups along the alkyl chain, incorporation of t-butyl tips) can significantly enhance the CO_2 solubility of hydrocarbon-based surfactants [Eastoe et al. 2003; Tabor et al., 2006; Eastoe et al., 2006].

Johnston and co-workers investigated the ability of di-block and tri-block surfactants with siloxane-based, fluorocarbon-based, and polyalkyloxide-based CO_2-philic segments to stabilize CO_2-in-water emulsions [da Rocha et al., 2001]. A (butylene oxide)$_{12}$-b-(ethylene oxide)$_{15}$, BO_{12}-EO_{15} diblock copolymeric surfactant was particularly effective at forming emulsions that were stable for over 48 hours at temperatures between 25 and 65 ^oC at very high pressures (e.g., 34.5 MPa) and a concentration of 1wt% relative to equal masses of CO_2 and water (2 wt.%

based on CO_2 alone). When water was used as the aqueous phase, CO_2-in-water emulsions were formed in accordance with Bancroft's rule, which states that the surfactant will be more soluble in the continuous lamellar phase than the discontinuous phase. In this example, the surfactant is more soluble in water (1.2 wt.%) than CO_2 (~0.1wt%) at these conditions. However, upon the addition of salt to the aqueous phase, CO_2-in-water emulsions continued to form even though the solubility of the surfactant in water became *less* than the solubility of the surfactant in CO_2. Although this result is *not* in accordance with Bancroft's generalized rule, the CO_2-in-water emulsion is desirable for the proposed EOR application. Both connate and injected aqueous phases are brine, and the ability of a surfactant to stabilize CO_2-in-water foams in the presence of substantial amounts of dissolved solids in the brine is critical to the success of the proposed technology. Therefore, (butylene oxide)$_x$-b-(ethylene oxide)$_y$ diblock surfactants may be viable candidates for stabilizing CO_2-in-brine foams or emulsions if it can be demonstrated that they are sufficiently soluble in CO_2 at injection and reservoir conditions and if they can stabilize the foams at reservoir conditions. However, there are no current suppliers of these surfactants for large-scale oilfield applications.

It has also been established that segments of oligo(vinyl acetate), OVAC, are extremely CO_2-philic and suitable for incorporation into CO_2 soluble surfactants. This functional group is so CO_2-philic that even ionic surfactants based on OVAC tails (Figures 9.2 and 9.3) and conventional ionic head groups can dissolve in CO_2 at concentrations of several weight percent [Fan et al., 2005].

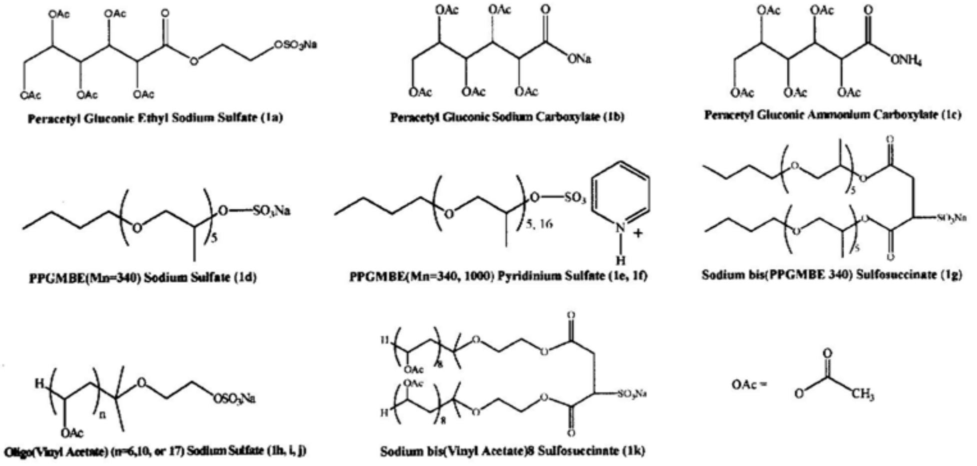

Peracetyl Gluconic Ethyl Sodium Sulfate (1a)
Peracetyl Gluconic Sodium Carboxylate (1b)
Peracetyl Gluconic Ammonium Carboxylate (1c)
PPGMBE(Mn=340) Sodium Sulfate (1d)
PPGMBE(Mn=340, 1000) Pyridinium Sulfate (1e, 1f)
Sodium bis(PPGMBE 340) Sulfosuccinate (1g)
Oligo(Vinyl Acetate) (n=6,10, or 17) Sodium Sulfate (1h, i, j)
Sodium bis(Vinyl Acetate)8 Sulfosuccinate (1k)

Figure 9.2 Ionic surfactants with oxygenated hydrocarbon tails.

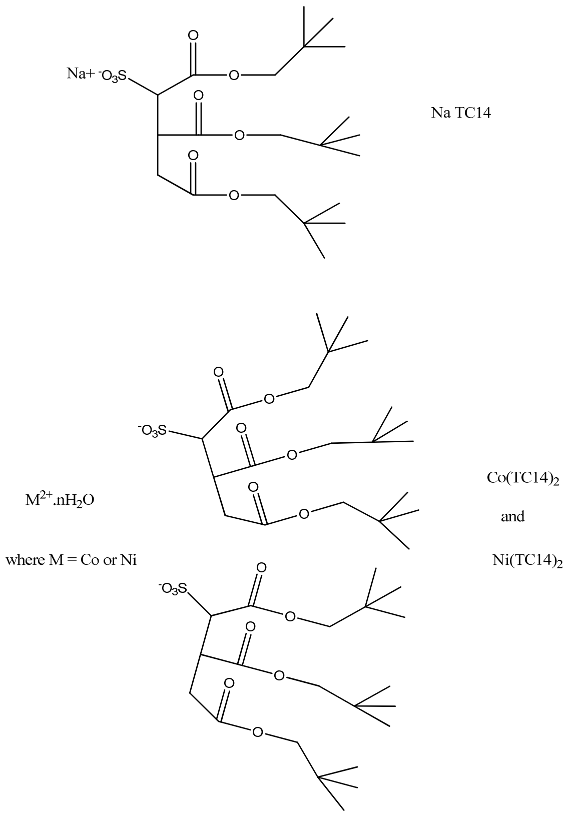


Figure 9.3. Highly acetylated, CO_2-soluble ionic surfactants: Top – although some of the sugar-acetate and oligo(vinyl acetate) are soluble to several weight percent, the pressures required for dissolution are quite high relative to MMP values [Fan et al., 2005]. Bottom – the TC14 ionic surfactants exhibit CO_2-solubility at much lower pressures that are comparable to MMP [Hollamby et al., 2009; Mohamed et al., 2010].

The pressure required for the dissolution of the sugar acetate-based and oligo(vinyl acetate) surfactants is, however, far beyond the pressures associated with CO_2 EOR.

In an attempt to design CO_2-soluble, hydrocarbon-based, ionic surfactants that are much more soluble in CO_2, Eastoe and co-workers developed a tri-chain, branched alkyl chain surfactant, sodium1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate [Hollamby et al., 2009; Mohamed et al., 2010]. This surfactant, which is referred to as TC14, is illustrated at the bottom of Figure 9.3, along with the TC14 analog that has a divalent cation such as Co^{+2} or Ni^{+2}. The sodium-based TC14, $Na^+(TC14)^-$ is 2wt% soluble in CO_2 at 25 ^oC and 2,320 psia [Mohamed et al. 2010], while the divalent versions of the TC14 surfactant, $Co^{+2}(TC14^-)_2$ and $Ni^{+2}(TC14^-)_2$, are soluble to 1% at 25 ^oC and 2,900 psia and 2wt% soluble at about 4,000 psia based on recent data from the Enick lab. These surfactants have yet to be assessed as foam-formers, however, and are expected to cost roughly 10 times as much as the commercially available surfactant AOT [Hollamby et al., 2009].

Tan and Cooper (Figure 9.4) designed non-ionic diblock OVAC-b-EO and triblock OVAc-b-EO-b-OVAc surfactants capable of stabilizing CO_2 foams; the two OVAc segments were CO_2-philic while the central PEG segment was hydrophilic. In particular, an $OVAc_{30}$-PEO_{60}-$OVAc_{30}$

surfactant at a concentration of 1.6wt% based on the total mass of the system was able to form a stable emulsion (at least 48 hours) of CO_2-in-water at 20 ^{o}C and 20.0 MPa [Tan and Cooper, 2005].

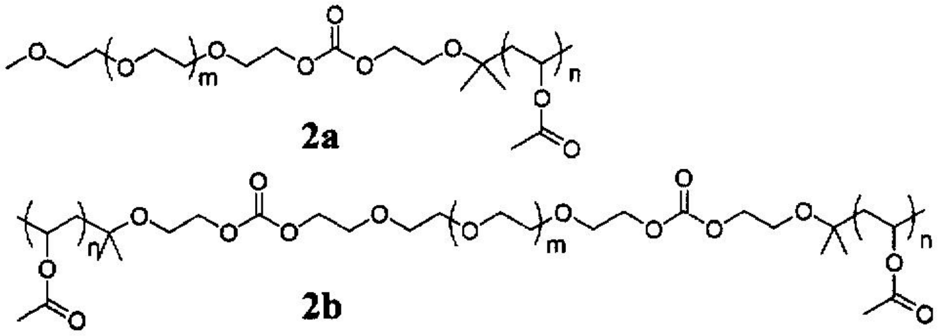


Figure 9.4. Nonionic OVAc-EO type CO_2 soluble surfactants [Tan and Cooper, 2005]

These emulsions contained as much as 97vol% CO_2; therefore, the concentration of the surfactant on a CO_2 basis was ~1.5wt%. This same research group also generated twin OVAC-tailed ionic surfactants with a quaternary ammonium cation and iodide anion that were 0.6wt% soluble in CO_2 at 25 °C and 4,200 psia [Tan et al., 2006]; the synthesis is shown in Figure 9.5.

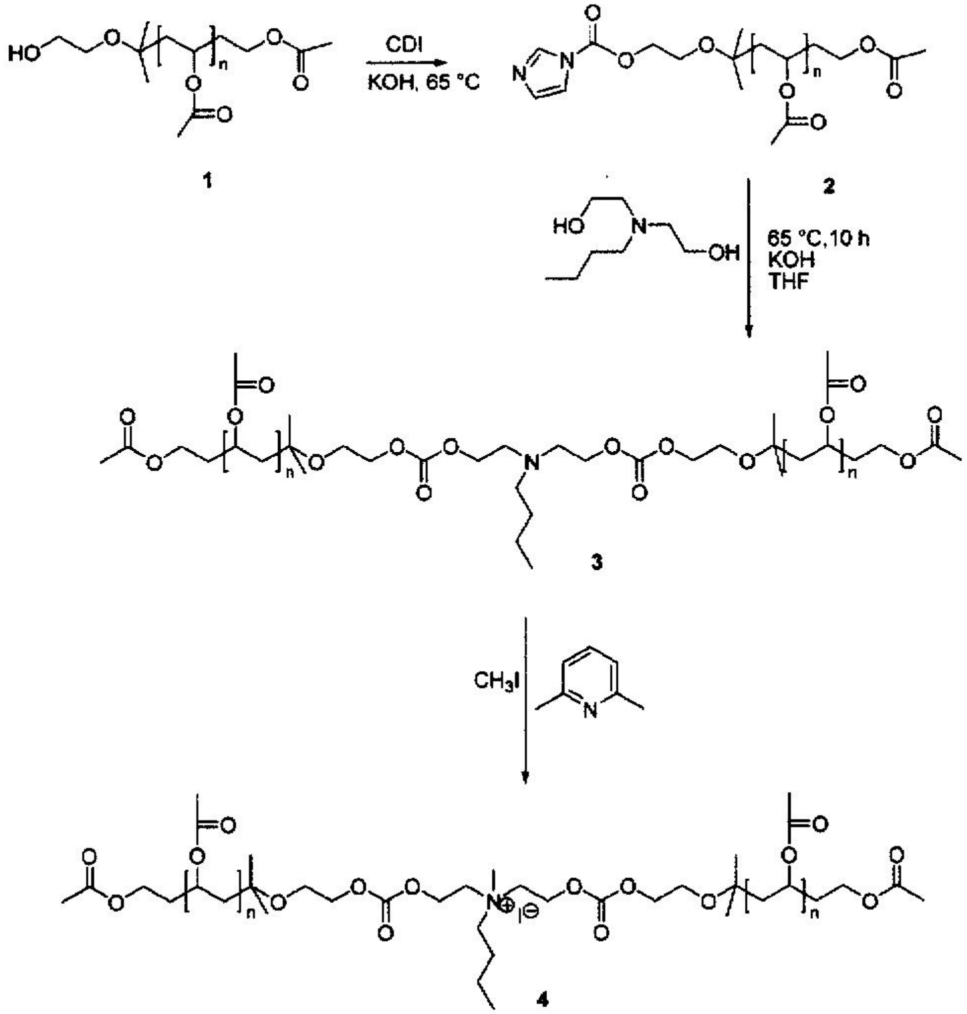


Figure 9.5. Ionic CO_2 soluble surfactants with OVAc CO_2-philic segments [Tan et al., 2006]

Although the high molecular weight polyvinyl acetate homopolymer is an inexpensive commodity chemical, it is currently somewhat difficult and expensive to generate OVAc-based surfactants. Therefore, it is very unlikely that these research surfactants will become commercially available in the immediate future.

There has been recent interest in identifying surfactants that are already commercially available, or that could be readily commercialized, based on existing products from major chemical producers. Although these surfactants do not contain extraordinarily CO_2-philic functionalities such as sugar acetates or OVAc, they do contain CO_2-philic branched hydrocarbons, ether linkages, and polypropylene glycol segments that may provide enough solubility in CO_2 to enable them to dissolve in appreciable amounts (~0.1wt%) at CO_2 EOR conditions. Further, these surfactants may, upon dissolution, have the capacity to stabilize CO_2-in-water or CO_2-in-brine emulsions suitable for mobility control. For example, the University of Texas at Austin and Dow Oil & Gas presented a study of the morphologies, stabilities, and viscosities of high-pressure carbon dioxide-in-water foams formed with water-soluble, branched, nonionic hydrocarbon surfactants that did not contain an aromatic or cyclic functionality [Adkins, Chen, Chan et al., 2010]. In each case, the hydrophile was an ethoxylate group, designated as EO_n or EO_m where n or m represented the number of repeat units in the PEG chain. Some surfactants contained a propylene oxide segment, designated as PO_n, between the hydrocarbon-based tail and the hydrophilic EO_n head group. PO_n is more CO_2-philic and less hydrophilic than the EO_n hydrophile. Specific surfactant examples, shown in Figure 9.6, include EO_n-PO_n-EO_n triblock copolymer, lauric acid-EO_{12}, 1-hexanol-PO_n-EO_m, 1-octanol-PO_n-EO_m, 2-octanol-PO_n-EO_m, 2-ethylhexanol-PO_n-EO_m, 2-ethylhexanol-$(EO_7PO_{5.5})_{random}$-EO, dodecyl/tetradecyl secondary-EO_n, TMN6 trimethylnonanol-EO_8, 1-nonanol-$PO_{3.5}$-EO_8, $C_{12\text{-}14}EO_7$ Brij surfactants, $H_3C(CH_2)_{x-1}$ PO_nEO_m, and dioctylglycerine-EO_n.

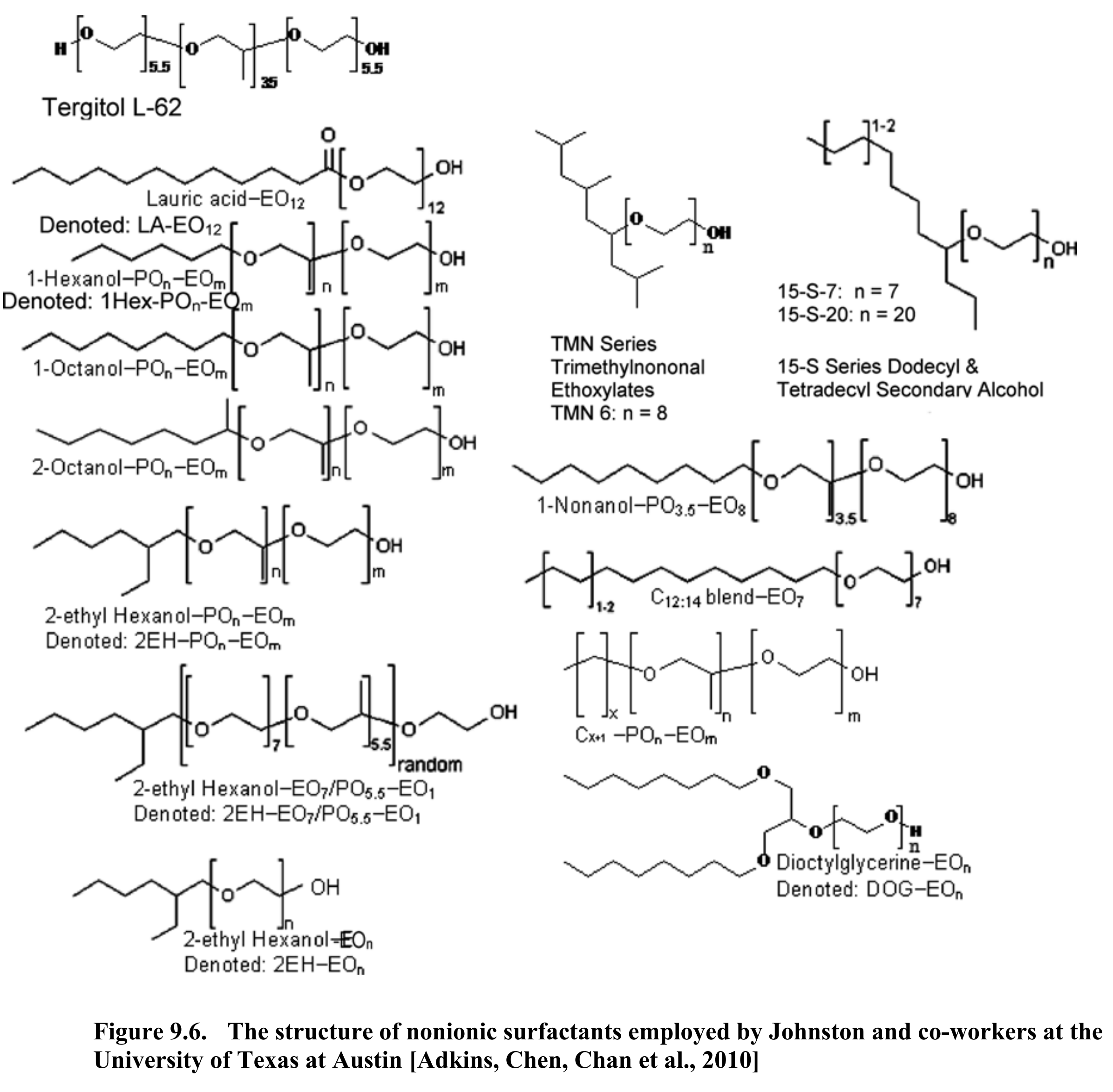


Figure 9.6. The structure of nonionic surfactants employed by Johnston and co-workers at the University of Texas at Austin [Adkins, Chen, Chan et al., 2010]

The pressure was maintained at 13.8 MPa (2,000 psia) and temperatures of 24, 40, 60 and 70 ^oC were considered. The synthetic brine was composed of 2% NaCl, 1% $CaCl_2$, and 0.5% $MgCl_2$ by weight. The volumetric ratio of the injected phases was 90% CO_2:10% surfactant solution. Because the concentration of the surfactant was 1wt% of the aqueous phase, the concentration of the surfactant relative to the CO_2 was about 0.13–0.25wt% over the 24–70°C temperature range. The surfactant solubility in dense CO_2 was not presented, however. Foams were formed by dissolving the surfactant in the brine and then co-injecting this aqueous surfactant solution along with high-pressure CO_2 into a sand pack with hydrophilic pores. Most of the surfactants did form foams at 24°C, and the surfactants with the highest cloud point temperatures (the highest temperature at which a mixture of 1wt% surfactant in the aqueous phase remains a single phase) yielded foams at the highest temperatures. For example the dodecyl/tetradecyl secondary-$EO_{20,}$ 1-hexanol-PO_5-EO_{15}, 2-ethylhexanol-PO_5-EO_{15}, and 2-ethylhexanol- $EO_{11.5}$ surfactants all had cloud point values of greater than 80 °C.

These researchers presented another study [Adkins, Chen, Nguyen et al., 2010] of the effect of surfactant branching on the interfacial properties at the CO_2-water interface (and air-water interface) using many of the same surfactants in their prior study [Adkins, Chen, Chan et al., 2010].

Recently, a team of Dow Oil & Gas and University of Texas at Austin researchers described a new, non-ionic, glycerin-based, twin-tailed, water-soluble, ethoxylated surfactant for stabilizing CO_2-in-water emulsions used for CO_2 flooding sweep improvement [Sanders, Nguyen, Nguyen et al., 2010]. These surfactants, such as the dioctylglycerine based surfactants with 9 or 12 EO units, DOG 9 and DOG 12, shown in Figure 29, were more effective at reducing the CO_2-water interfacial tension to ~27 mN/m, a value lower than other water-soluble surfactants such as the secondary alcohol based surfactants 15-S-7 and 15-S-12, which are also shown in Figure 9.7.

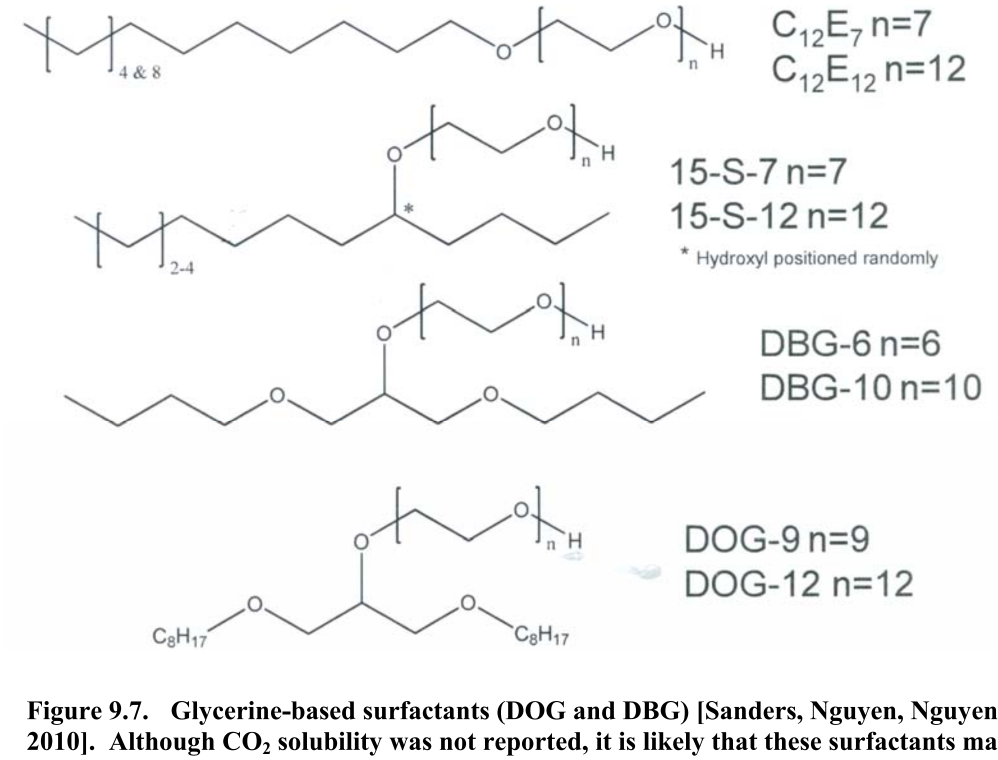


Figure 9.7. Glycerine-based surfactants (DOG and DBG) [Sanders, Nguyen, Nguyen, et al., 2010]. Although CO_2 solubility was not reported, it is likely that these surfactants may be somewhat soluble in CO_2

Because CO_2 soluble surfactants—such as those in Fig. 9.7—used for foam generation are slightly CO_2- and water-soluble, researchers at the University of Texas at Austin [Ren et al., 2011] have recently investigated the effect of this partitioning on mobility control for CD 1045 and three proprietary non-ionic CO_2-soluble surfactants designated S, 4S, and 15S. With respect to the CO_2 soluble compounds, they noted low adsorption, stronger partitioning sensitivity with respect to surfactant structure than temperature or pressure, and an optimal partition coefficient for fastest foam propagation. These investigators hope to exploit these trends in optimizing the surfactant design for CO_2 floods.

DOG 9 and DOG 12 were also more effective at reducing the IFT than similar glycerine-based surfactants with shorter alkyl chains (such as the dibutylglycerine-based ethoxylates DBG 6 and DBG 10) and Brij surfactants $C_{12}E_7$ and $C_{12}E_{12}$. Although the solubility of these surfactants in CO_2 was not determined, and although these surfactants were subsequently dissolved in water and co-injected with pure CO_2 into cores, the general features of these novel surfactants make them likely candidates for dissolution in CO_2 or brine. The likelihood that these surfactants are CO_2-soluble was also implied by the coreflooding apparatus used in this study having the capacity to inject a surfactant-in-CO_2 solution into the core. Coreflooding tests were reported for a 2” diameter, 1’ long carbonate core of ~ 80 mD permeability at 45 ^oC initially saturated with 1% NaCl brine. Pure CO_2 was co-injected with a 0.2wt% brine solution at a 90:10 ratio at a superficial velocity of 1’/day with the core effluent pressure maintained at 1,500 psig. Pressure drops realized during the experiments with DOG 9 were several times greater than those detected with an aqueous solution of 15-S-7. This was indicative of lower mobility foams being generated with the novel dioctylglycerine ethoxylate than with the secondary ethoxylated alcohol.

Johnston and co-workers also studied the use of a biocompatible, water-soluble, nonionic, ethoxylated surfactant, polyoxyethylene (20) sorbitan monooleate or polysorbate 80 or Tween 80 (Figure 9.8) for stabilizing CO_2-in-water and water-in-CO_2 emulsions and double-emulsions [Torino et al., 2010].

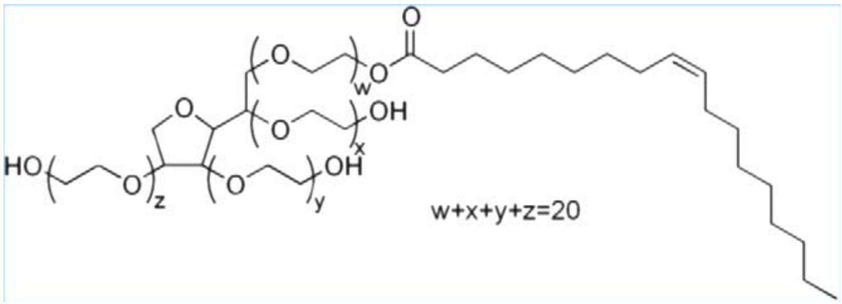
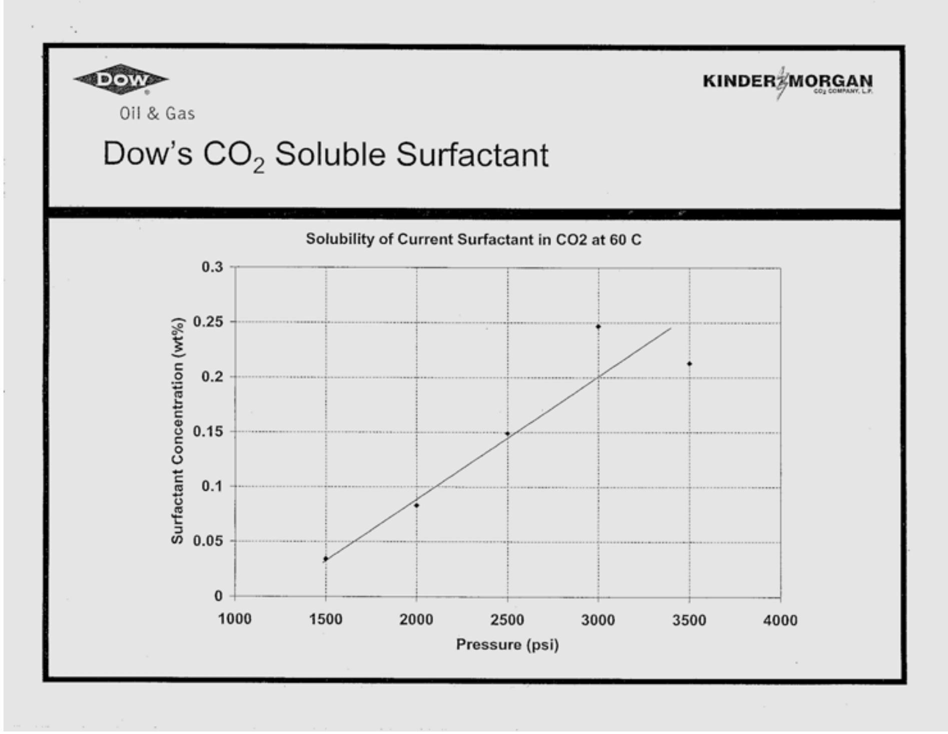


Figure 9.8. Tween 80, a CO_2-soluble, biocompatible, water-soluble surfactant [Torino et al., 2010]

This surfactant, shown in Figure 9.8, was CO_2 soluble to ~0.5–1.0wt% at pressures that are commensurate with MMP values of typical CO_2 EOR projects being conducted. The Tween 80 surfactant was also capable of stabilizing emulsions containing micron-scale CO_2 bubbles generated by co-injecting aqueous surfactant solutions and CO_2 into sand packs.

In 2008, researchers from the University of Texas at Austin and Dow Oil & Gas used a proprietary, slightly CO_2-soluble, water-soluble, nonionic surfactant dissolved at a concentration of 0.1wt% in CO_2 at ambient temperature in a mixing vessel at 1,800 psi (~12.4 MPa)—Figure 9.9 [Sanders, Jones, et al., 2010]—to recover oil from a core with an effluent back-pressure regulator set at 1,500 psi (~10 MPa) [Le et al., 2008]. The investigators assessed various modes of surfactant injection including WAGS (water-alternating-gas with surfactant dissolved in the CO_2), SAG (surfactant-alternated-CO_2 with surfactant dissolved in the water) and continuous CO_2-dissolved-surfactant injection (no alternate injection of water used) and found that the injection of the CO_2-surfactant solution into the waterflooded core without the use of alternating water slugs yielded higher oil recovery than the other injection modes.



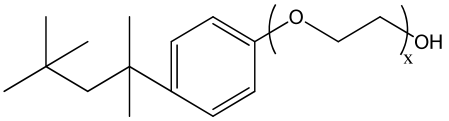
DOW Oil & Gas

KINDER MORGAN

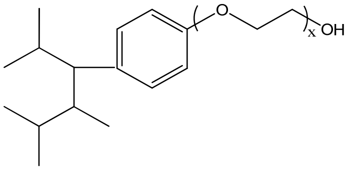
Dow's CO_2 Soluble Surfactant

Figure 9.9. Solubility of a typical Dow CO_2 soluble surfactant in CO_2 at 60 °C [Sanders, Jones, et al., 2010]

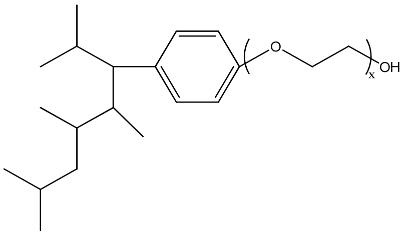
Researchers at the University of Pittsburgh and NETL are also actively attempting to identify commercially available, CO_2 soluble, water soluble, nonionic surfactants that are capable of dissolving in CO_2 at conditions commensurate with CO_2 EOR at a concentration great enough to stabilize a foam. Foams were then generated in a windowed vessel by mixing CO_2, brine, and an amount of surfactant corresponding to that which could dissolve in the CO_2 at test conditions. Foams were also generated in situ in a mobility apparatus in which a high-pressure CO_2 surfactant solution was injected into a brine saturated core. Some of the surfactants selected for this study are illustrated in Figure 9.10. There are two general classes of surfactants considered in this study: those with a phenol group (benzene ring) in the middle of the surfactant and those without the phenol group. In the foam stability tests, the alkylphenol ethoxylates were capable of stabilizing the CO_2-in-5% NaCl brine emulsions more effectively than the surfactants lacking the aromatic ring, but the surfactants without the aromatic group may be advantageous in that alkylphenol ethxylates have already been banned in Europe and Canada due to environmental concerns. Although these compounds can still be used in the U.S., it appears to be prudent to pursue the best alkylethoxylates in the event that alkylphenol ethoxylates are banned in the U.S.



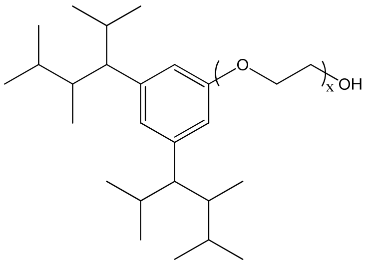
Huntsman Surfonic OP, Triton X, BASF OP, Branched octylphenol ethoxylate, x = 10



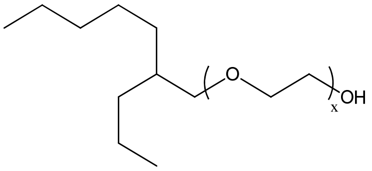
Huntsman Surfonic NP, Branched nonylphenol ethoxylate (one alkyl isomer example) x = 8.5 - 40



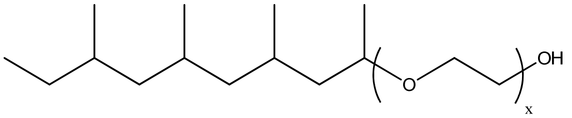
Huntsman Surfonic DDP, Branched dodecylphenol ethoxylate (one alkyl isomer example) x = 10, 12



Huntsman Surfonic DNP, Branched di nonylphenol ethoxylates (one alkyl isomer example shown) x = 15, 18



BASF XP, C_{10} Guerbet alcohol based ethoxylate; proprietary structure, qualitative example shown, x = 8, 9



Hustman TDA branched C_{13} ethoxylated alcohol, x = 8, 9

Figure 9.10. Examples of commercially available nonionic, slightly CO_2 soluble, water-soluble surfactants

Many of the surfactants shown in Figure 9.10 were soluble to ~0.03–0.15 wt.% in CO_2 at ~2,000 psig and 25 °C. For example, the solubility of Huntsman Surfonic N 150 in CO_2 at 25 °C and 58 °C is shown in Figure 9.11.

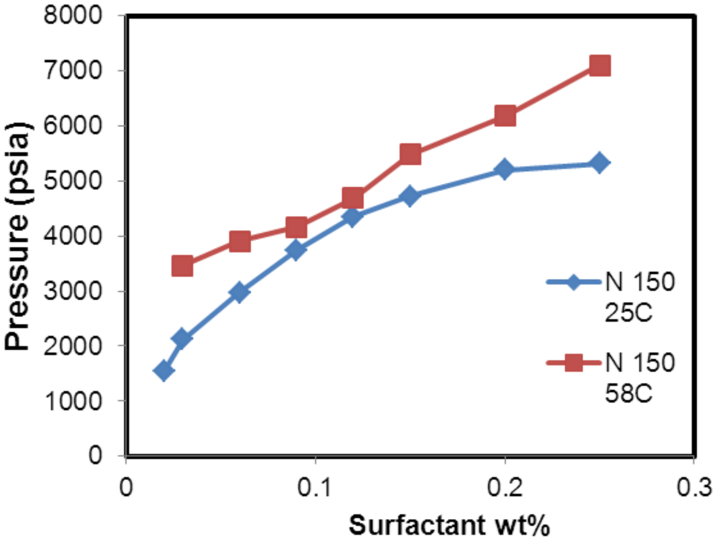


Figure 9.11. Solubility of non-ionic, water-soluble, Huntsman Surfonic N 150 in CO_2 at 25 °C and 58 °C [Xing and Enick, 2011]

An example of the technique used to assess the foam stability in the high pressure windowed cell is provided in Figure 9.12.

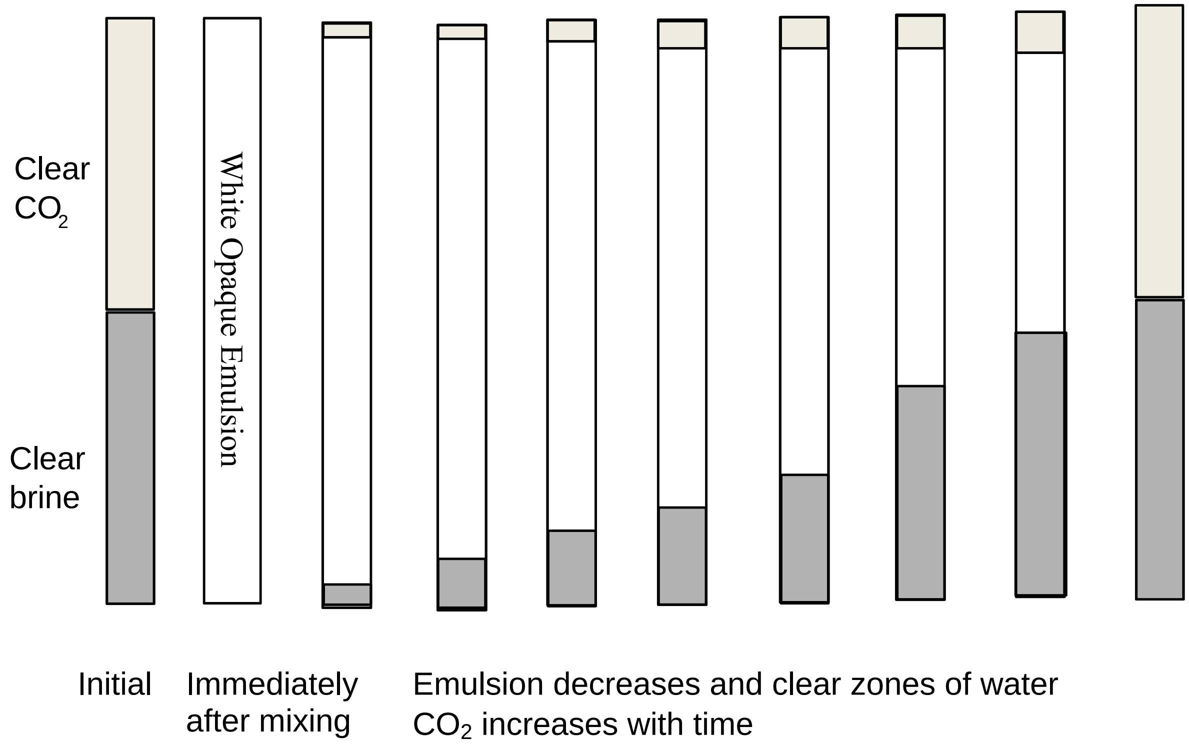


Figure 9.12. The foam stability test; foam generated by mixing equal volumes of brine and CO_2 using only as much surfactant as could dissolve in the CO_2 at the test conditions of 2,500 ^oC, ~1300–1500 psig [Xing et al., 2010].

Foam stability results for some of the Huntsman Surfonic N series surfactants are shown in Figure 9.13. Consider the Huntsman Surfonic N 150 (x=15 in Figure 32) result. Immediately after mixing ceases, the entire cell is filled with a white opaque macroemulsion. After 60 minutes, about 34% of the 5wt% NaCl brine phase remains in the emulsion along with 100% of the CO_2. Sixty-six percent of the brine resides in a clear, excess brine phase below the emulsion, while there is no clear excess CO_2 phase above the emulsion. After 210 minutes, 15% of the brine and 100% of the CO_2 remain in the emulsion, while 85% of the brine has drained from the lamellae into the excess brine phase. At this point in time, the CO_2-in-brine emulsion has a quality of about 87% CO_2.

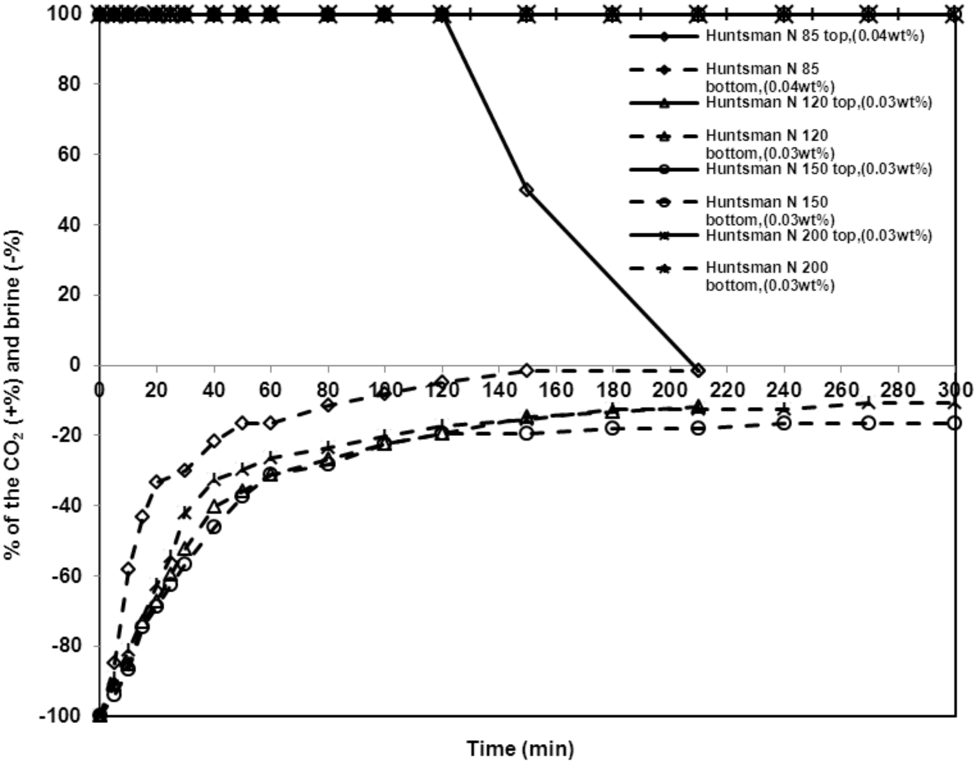


Figure 9.13. The stability of emulsions formed when equal volumes of brine and liquid CO_2 are mixed at 25 °C and 1,300 psig along with a Huntsman Surfonic N surfactant. The amount of surfactant corresponds roughly to the amount of surfactant that can be dissolved in the CO_2 at these conditions. [Xing et al., 2010].

In summary, there has been a great deal of recent interest in the design or identification of CO_2-soluble surfactants capable of dissolving in CO_2 at typical reservoir conditions. In general, these surfactants are hydrocarbon-based, single-tailed or twin-tailed ethoxylates that are slightly CO_2 soluble (~0.01–0.5wt%) and water-soluble. Branching of the alkyl tails appears to provide improved performance. The tails may also contain CO_2-philic oxygenated functionalities such as ethers, carbonyls, and/or acetates. Some surfactants have either a small PPG segment or an aromatic ring between the PEG hydrophile and the alkyl CO_2-phile. If the concentration of the surfactant is great enough at reservoir conditions, and if the surfactant is found to stabilize CO_2-in-brine emulsions, the surfactant may be a useful mobility or conformance control additive to the CO_2 being injected into a sandstone or limestone formation. Such a technology could reduce or eliminate the need for alternate injections of brine because the CO_2-rich surfactant solution could generate foams in situ as it mixes with the reservoir brine. It would also be possible to design mobility or conformance control strategies in which surfactant could be introduced to both the CO_2 and the brine slugs.

10. Common Lab Tests for Assessing Surfactants and Foams

There are numerous common laboratory tests required for the design of CO_2 floods that do not employ surfactants [Orr, et al., 1982]. Therefore, researchers have employed numerous screening tests to reduce the additional amount of tedious, high-pressure tests required to assess the viability of a foam-enhanced CO_2 flood. This is complicated by the preponderance of commercially available, water-soluble surfactants. This section contains an overview of the relatively simple, quick, inexpensive screening tests used to identify the more promising surfactants to be assessed in more difficult, time-consuming, expensive experiments conducted with consolidated porous media. Surfactants that yield excellent results in these simplistic low-pressure tests commonly yield promising results in the high pressure reservoir core flooding tests that employ reservoir fluids and high-pressure CO_2 [Borchardt et al., 1988]. Nonetheless, screening should ultimately be conducted with high-pressure systems involving CO_2 rather than air.

Low Pressure Screening Tests

There are many simple screening tests that employ studies of air or nitrogen rather than high-pressure CO_2 as the gas phase, and water, synthetic brine or formation brine as the aqueous phase. Because a small amount of the CO_2 that is dissolved in the aqueous phase dissociates and forms carbonic acid, thereby lowering the pH to ~2.8–3.6 [Schaef and McGrail, 2003], it is not uncommon in low pressure screening tests to simulate the presence of carbonic acid at reservoir conditions in water via the addition of an acid.

The solubility of the surfactant in brine is important to the success of a CO_2-in-brine foam because the surfactant is typically dissolved in brine when it is introduced to the formation. Even in the case where the surfactant is dissolved in the CO_2 rather than brine, one should determine if the surfactant is water-soluble, because surfactant should partition into the in situ brine in order to stabilize the lamellae. The surfactant solubility in brine should therefore be assessed at both surface and reservoir conditions.

One can measure the surface tension of aqueous surfactant solutions as a function of surfactant concentration in an attempt to determine the CMC and to assess which surfactant most effectively reduces the surface tension of the aqueous phase [Casteel and Djabbarah, 1988], as shown in Figure 10.1.

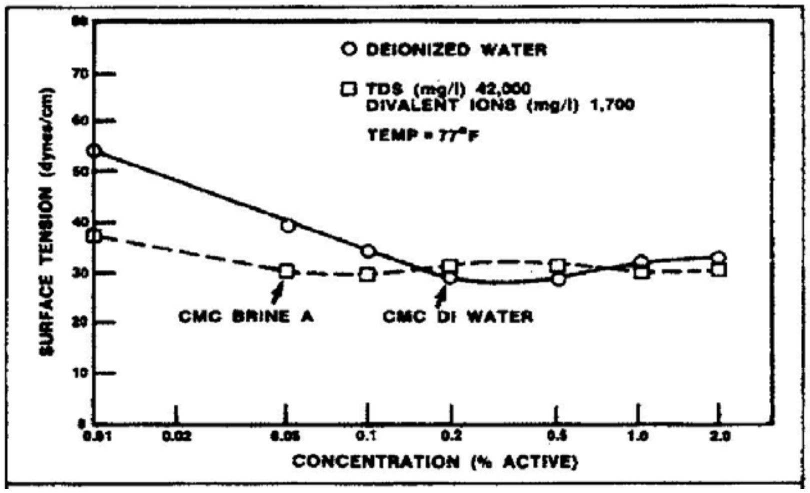


Figure 10.1. Effect of surfactant concentration on surface tension of Alipal CD 128 solutions [Casteel and Djabbarah, 1988]

A specified amount of the surfactant solution can be shaken together with a specified volume of air or iso-octane (or another alkane chosen to emulate dense CO_2) and the initial quality of the resulting foam measured. Figure 10.2 shows a surfactant solution mixed with air; the quality of the foam was determined when the mixing stopped.

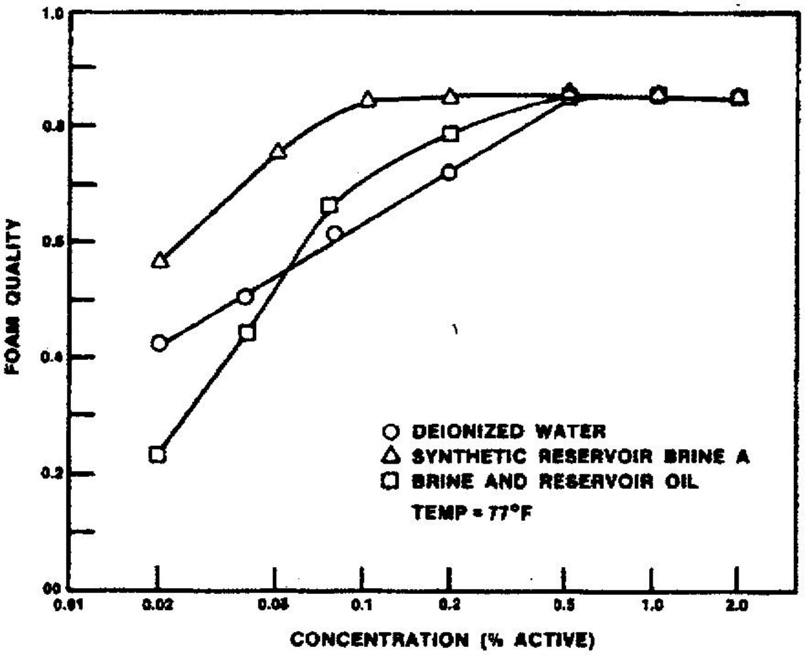
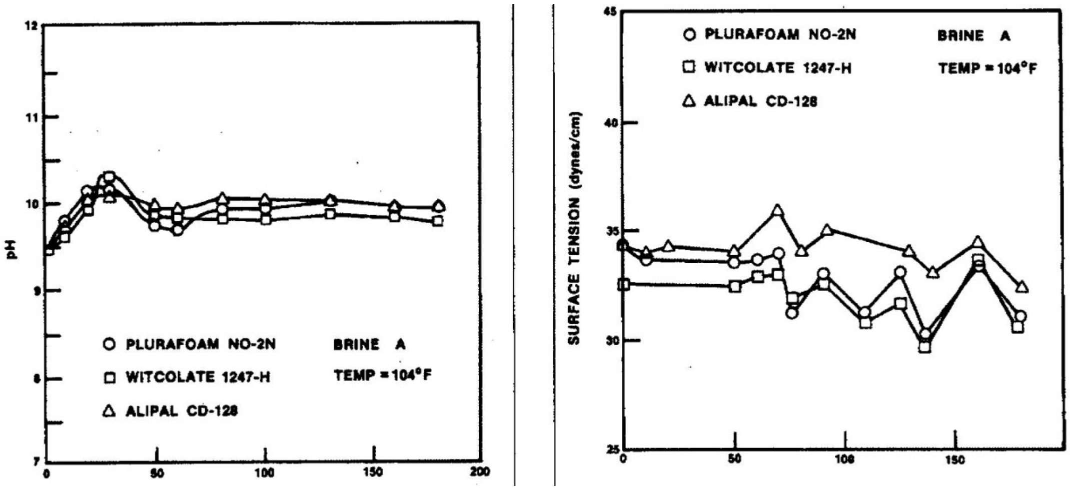


Figure 10.2. Initial air foam quality of surfactant solutions [Casteel and Djabbarah, 1988]

Similar tests have been conducted to assess the effects of surfactant type and structure, brine salinity, and the presence of an oil phase [Borchardt et al., 1987] on foam quality.

Long-term surfactant stability is typically measured during low pressure screening tests in an attempt to assess the viability of the surfactant during the extended period of time it is employed in EOR field projects [Casteel and Djabbarah, 1988]. For example, one can monitor the pH, surface tension, and surfactant concentration of the aqueous solution as a function of time for many months, as shown in Figure 10.3, in the hope that these changes will be relatively small for surfactant employed in the field.



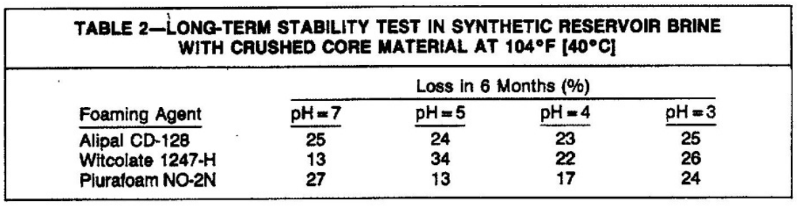


TABLE 2—LONG-TERM STABILITY TEST IN SYNTHETIC RESERVOIR BRINE WITH CRUSHED CORE MATERIAL AT 104°F [40°C]

	Loss in 6 Months (%)			
Foaming Agent	pH = 7	pH = 5	pH = 4	pH = 3
Alipal CD-128	25	24	23	25
Witcolate 1247-H	13	34	22	26
Plurafoam NO-2N	27	13	17	24

Figure 10.3. Changes in pH, surface tension, and surfactant concentration as a function of time during long-term stability tests [Casteel and Djabbarah, 1988]

Care must be taken when employing low-pressure screening tests for CO_2 soluble surfactants because it is not possible to dissolve any surfactant in air, which emulates the non-aqueous phase in low-pressure tests. Neither do conventional liquids such as octane, acetone, methyl acetate perfluorohexane, or high-pressure compressed liquids such as ethane and propane, serve as adequate screening tools for CO_2 [Fulton and Smith, 1985]. One can assume that the water-soluble alkyl ethoxylates that have been used by the research groups of Johnston and co-workers and Enick and co-workers are roughly 0.02 – 0.2wt% soluble in CO_2 at reservoir conditions; and because they can partition into the brine, low pressure screening tests should employ only ~0.02 – 0.2wt% of these types of surfactants.

Measures of Foam Mobility Reduction

The assessment of the effect of foam on CO_2 mobility is more complicated for foams than thickeners. At reservoir conditions, the type and concentration of a thickener are the primary influences on CO_2 viscosity. The mobility of a CO_2-in-brine foam at reservoir temperature and pressure is influenced by the foam quality, type and concentration of surfactant, composition of the brine, presence of oil, flow rate of the fluids, and the nature of the porous media. The mobility of the foam is therefore typically expressed relative to the same fluids moving through the same porous medium at the same conditions, but in the absence of surfactant. Consider the Darcy equation

$$\lambda = \frac{QA}{\Delta P/L} = \frac{k}{\mu}$$

where λ is the mobility and can be in units of $cm^2/(atm\ s)$, darcy/cP, or $m^2Pa\ s$. Q represents the volumetric flow rate, A is the cross-sectional area normal to flow, and $(\Delta P/L)$ is the pressure drop. When two fluid phases, namely CO_2 and water, are flowing in the absence of a surfactant, it is possible to express the mobility of these flowing phases in the following manner [Heller, 1994].

$$\lambda = \left[\frac{k_{e,co2}}{\mu_{co2}} + \frac{k_{e,brine}}{\mu_{brine}}\right]$$

When bubbles of CO_2 come into contact the interface does not offer significant resistance and the bubbles rapidly coalesce. In this case it is possible to determine the effective permeability of each of the phases flowing through the medium as a function of the saturation of the phases, and the viscosity of each phase flowing through the rock is equivalent to the bulk viscosity of the fluid.

This type of differentiation of mobility into CO_2 and aqueous components cannot be readily accomplished when a surfactant capable of stabilizing lamellae is present in the system. In this case, when bubbles of CO_2 come into close proximity, the lamellae can prevent them from coalescing. The great number of lamellae that can be generated in this case can offer resistance to flow, trap gas, and dramatically alter the pathways available for gas flow. There are at least five terms than can be used to describe the ability of a foam to flow through porous media.

It is common to measure the *mobility* of a foam of specified quality (e.g., 80vol% CO_2 and 20vol% water flowing into the core) and flow conditions as a whole rather than as the sum of aqueous and CO_2 components.

$$\lambda_{foam} = \frac{QA}{\Delta P\ L}$$

Consider the concept of *relative mobility*, λ_r, which is the foam mobility divided by the absolute permeability of the rock.

$$\Lambda_{r,foam} = \frac{\lambda_{foam}}{k} = \frac{QA}{\Delta PLk}$$

The relative mobility λ_r has units of inverse viscosity (e.g., inverse cP or cP^{-1}); therefore, the "*effective viscosity*" of the foam can be expressed as the inverse of the relative mobility.

Effective viscosity is a simple and useful tool for quantifying the reduction of foam mobility using Darcy's law.

$$\mu_{eff,foam} = \frac{1}{\lambda_f}$$

Another measure of the ability of a surfactant-stabilized foam to reduce the mobility of CO_2 is the dimensionless *mobility reduction factor*. This quantity compares a foam of specified quality to the mobility of water and brine flowing at the exact same conditions except that no surfactant is present.

$$m_{rf} = \frac{\lambda_{foam}}{\lambda_{CO2} + \lambda_{brine}}$$

Yet another expression of the lower mobility of a surfactant-stabilized foam is the *resistance factor* (R_f), which is the ratio of the mobility of CO_2 (flowing along with brine) in a surfactant-free system compared to the mobility of CO_2 flowing at the exact same conditions but in the presence of a surfactant.

$$R_f = \frac{\lambda_{CO2}}{\lambda_{foam}}$$

The flowing experimental results provide an indication of the degree of foam mobility reduction that has been observed in the laboratory. Typically, the experiments entail the simultaneous flow of a brine surfactant solution and high-pressure CO_2 into a core of known size and permeability. It is not uncommon for the fluids to be mixed in a "foam generator" prior to entering the core of interest for mobility measurements. This foam generator usually consists of a short, high permeability core retained in a separate vessel preceding the core of interest. Alternately, the short foam generator core can be retained along with the adjacent core of interest in a single core holder.

Mobility reduction as a function of surfactant type, surfactant concentration, foam quality, superficial velocity, and permeability

The ability of CO_2 foam to reduce CO_2 mobility is well illustrated by CT images of the high-pressure process in sandstone or carbonate cores [Farajzadeh et al., 2009; Farajzadeh, Andrianov and Zitha 2009; Wellington and Vinegar, 1985, 1987]; CT studies of low-pressure foams in cores [Du et al., 2007; Du et al., 2008]; and CT imaging studies of heterogeneous, co-axial systems (i.e., a core within a core) with crossflow between the media permitted [Bertin and Apydin, 1999].

CT studies of CO_2 mobility usually involve the compilation of numerous images associated with this transient process, starting with the brine saturated core, followed by images of the CO_2 flowing into the core, and ending with images following injection of several PV of CO_2.

These experiments in the following example involve the CO_2 invasion of a vertical, brine-saturated Berea sandstone core (1,010 mD, 22% porosity, 40 mm x 170 mm, 20–30 micron pore throat diameters) [Farajzadeh , Andrianov, Bruining and Zitha, 2009]. In the "base case" of the following example, there is no surfactant in the brine, thus fingering and early gas breakthrough would be expected. This is shown in the top series of CT images in Figure 10.4, where there is not a distinct CO_2 front displacing the brine and breakthrough occurs after injection of ~0.18 PV of CO_2 due to fingering. The lower series of CT images illustrates the effect of saturating the core with a surfactant solution; a sharp CO_2 front forms, fingering is inhibited, and CO_2 breakthrough does not occur until ~0.45 PV of CO_2 are injected.

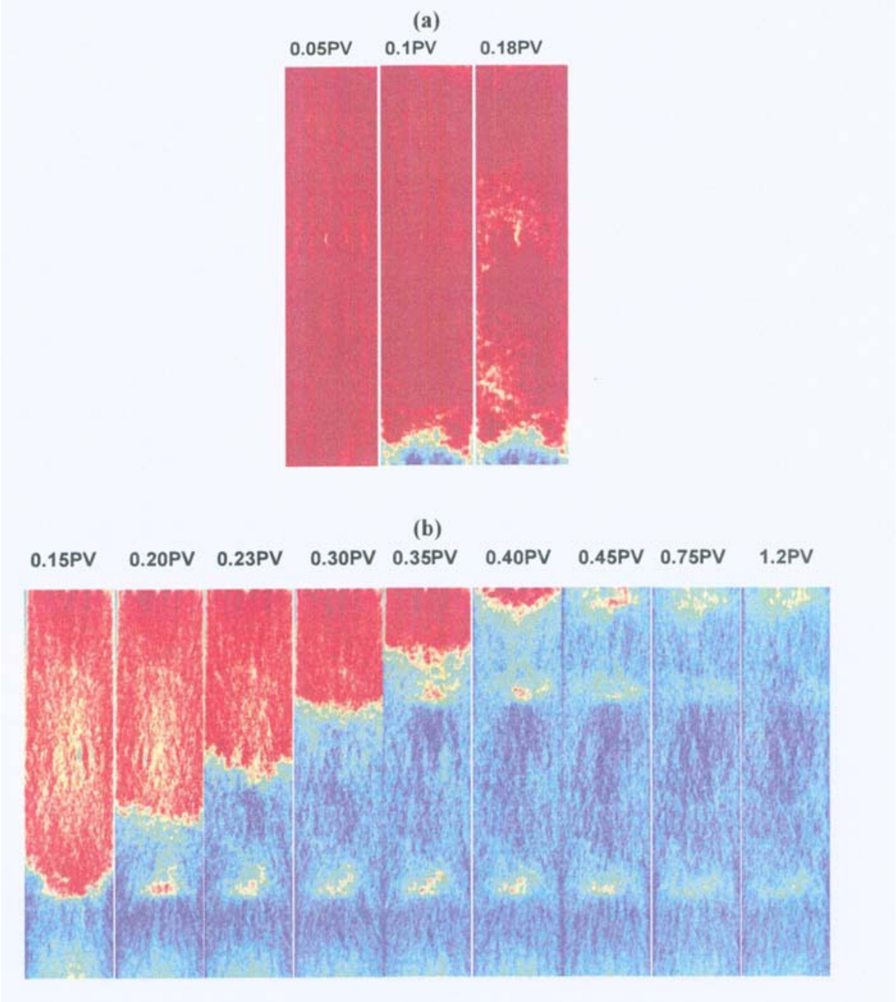


Figure 10.4. CT images of the transient process of CO_2 injected into a core initially saturated with (a) 3 wt.% NaCl brine, and (b) a 0.5 wt.% AOS surfactant brine solution; 50 ^{o}C, 90 bar [Farajzadeh, Andrianov, Bruining and Zitha, 2009]

If differential pressure data are collected (as shown in Figure 10.5) across the core during constant volumetric flow rate displacements with and without surfactant, the increase in pressure drop associated with the formation of a foam can provide additional evidence of a foam.

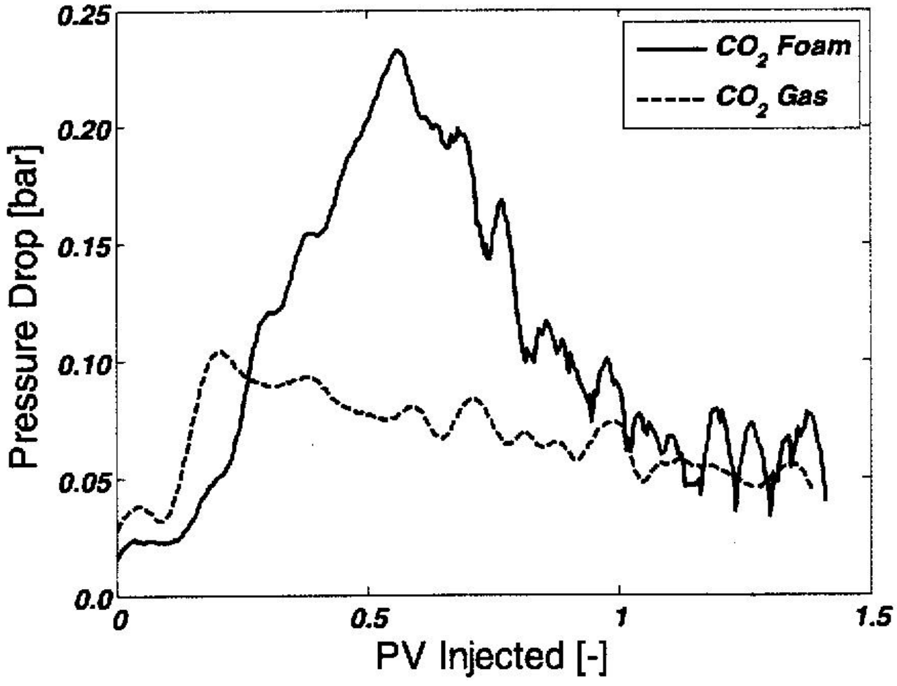


Figure 10.5. The formation of a foam leads to an increase in pressure drop if the core is initially saturated with a 0.5wt% AOS-in-brine surfactant solution rather than brine, 1 ml/min, 50°C, 90 bar [Farajzadeh, Andrianov, Bruining and Zitha, 2009].

Another excellent tool for understanding the advantages of mobility control attainable with foams is 2-D, low-pressure, visual displacements of brine (or brine and oil) from packed transparent tubes or sandpacks in which two layers with very different permeabilities are in contact with one another. For example, in the recent study [Li et al., 2008], the vertical sweep of a two-layer system is dramatically enhanced (same coverage achieved with a much smaller PV injection) when a foam was generated. In Figure10.6 it is evident that during the SAG process the sweep of green water from the high perm layer (top, dark green) and low perm layer (bottom, light green) by the clear gas occurs with much less PV injection than the WAG or a waterflood.

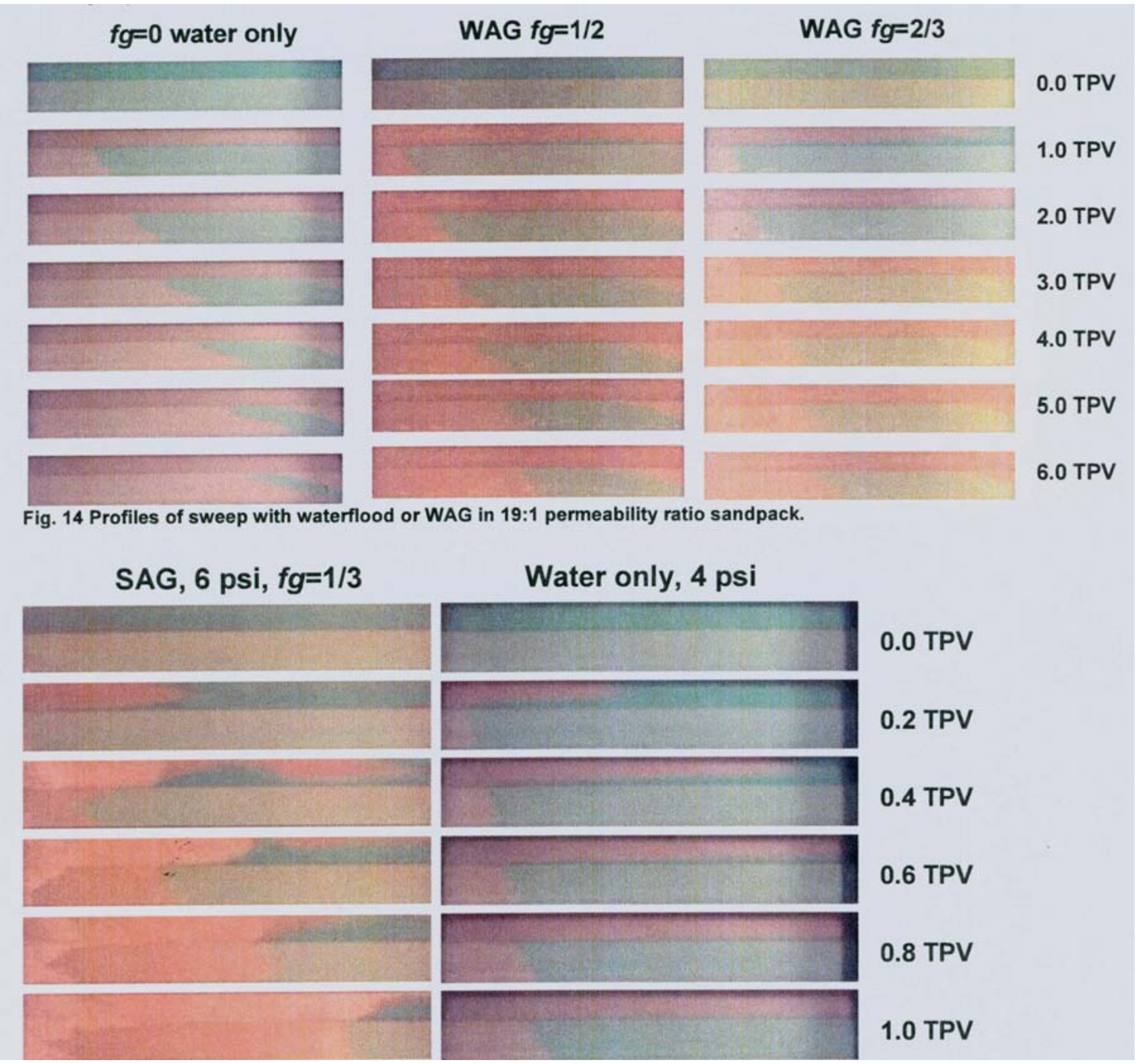


Figure 10.6. Displacement of green water from a two-communicating-layer visual sandpack experiment by waterflood WAG and SAG [Li et al., 2008]

Further, crossflow of fluid occurs in these communicating layers from the high perm layer to the low perm layer behind the foam front in the high perm layer, along with crossflow from the low perm layer into the high perm zone ahead of the foam front.

Steady-state foam mobility is usually obtained in the lab via the simultaneous injection of CO_2 into the core at fixed volumetric flow rates. Figure 10.7 presents the mobility of an 80% quality CO_2-in-brine foam generated with various concentrations of Varion CAS (denoted as ZS) and an alcohol ethoxy glyceryl sulfonate (AEGS). In the 305 mD Berea sandstone results, at ~0.001wt% ZS and less, the surfactant concentration is not high enough to stabilize lamellae, and the mobility corresponds to the 40 mD/cP combined mobility of CO_2 and water flowing through the core. At 0.01wt%, the lamellae population is great enough to reduce the mobility 75% to about 10 mD/cP. At 0.03–0.04 wt.% the mobility drops significantly to 1 mD/cP, and there is not a significant reduction in mobility as the surfactant concentration increases from 0.1wt% to

0.5 wt.%. Therefore, in this single example, a 40-fold reduction in mobility was realized for an 80% quality CO_2 foam.

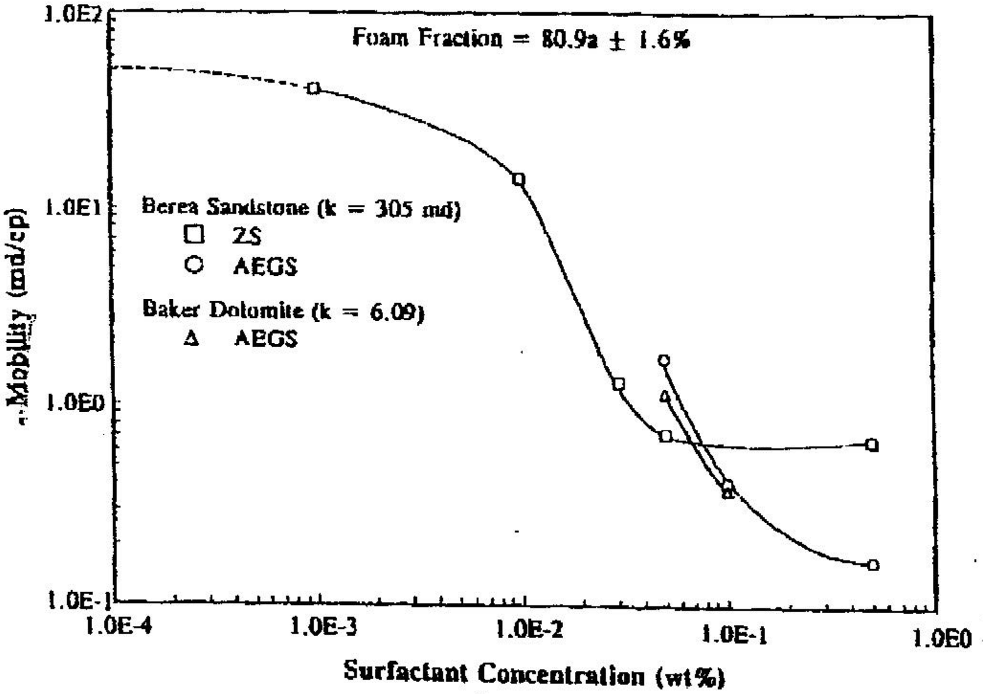


Figure 10.7. Effect of surfactant concentration on foam mobility (dashed line represents surfactant concentrations so low that a foam is not formed) for ~80% quality foams flowing at superficial velocities of 3-10 ft./day [Lee and Heller, 1990; Heller, 1994].

One of the most common characteristic measurements associated with surfactant solutions is the critical micelle concentration (CMC), the lowest concentration at which dissolved surfactant molecules aggregate into micelles. Interestingly, it has been found that CO_2 foams can be generated at concentrations below the CMC, although these foams would be relatively weak. Kuhlman and co-workers suggested that when a surfactant with a relatively high CMC is used at concentrations below the CMC, adsorption will be very low, dilute concentrations will propagate through the porous media, and a weak foam for in-depth, reservoir-wide mobility control can form. Alternately, a surfactant with a low CMC used at a concentration well above the CMC will form a strong foam that is more appropriate for near-wellbore conformance control. In this case mobility reduction can be very significant, recoverable oil may be lost to emulsification (rather than being displaced in an oil-rich phase), and the portion of the surfactant above its CMC will propagate slowly unless very high concentrations of surfactant are used [Kuhlman, et al., 1992]. The following result (shown in Figure 10.8) also indicates that foam mobility increases with surfactant concentration in the 0.1 – 0.25 wt.% concentration range. The CMC of this solution is 0.11wt%; therefore, all of the data in this figure correspond to concentrations at or above the CMC. Insignificant mobility increases are realized at concentrations greater than ~0.3wt%.

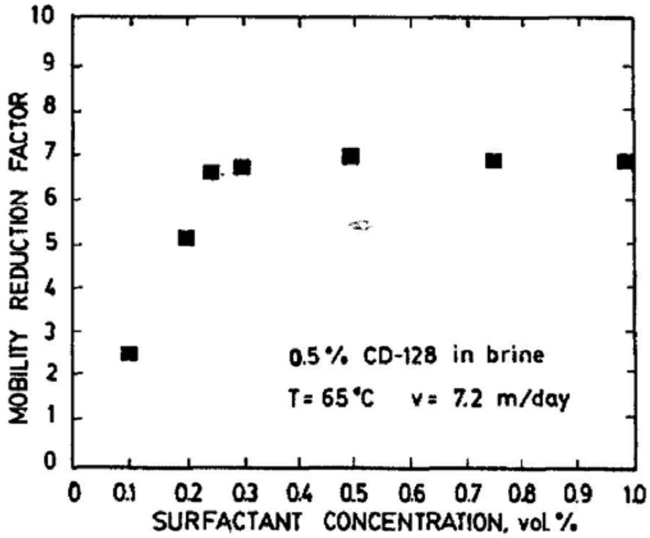


Figure 10.8. Effect of concentration on foam mobility; cmc ~ 0.11wt% [Alkan, et al., 1991]

The preceding plot indicates that CO_2-in-brine foams typically require a surfactant concentration that is greater than the critical micelle concentration (CMC), 0.11wt% in this case, to attain the maximum reduction in mobility. It is possible, and even advantageous in the right circumstances, to generate foams with surfactant concentrations below the CMC value [Kuhlman et al., 2000]. For example, it has been suggested that the use of large PV mobility control treatments that provide a moderate amount of mobility with little adsorption should be conducted with a surfactant that has a high CMC value, low adsorption at the CMC, and weak foaming capability. Conversely, the use of surfactants at high concentrations that are well above their low CMC value are characterized by higher adsorption, more significant mobility reductions, and emulsification of oil, making them more appropriate for relatively small PV treatments aimed at near-wellbore conformance control [Kuhlman et al., 2000].

An example of the effect of foam quality on mobility is shown in Figure 10.9 where Enordet X2001 is used at a concentration of 0.1wt%. Foam mobility in this Berea sandstone is shown to exhibit no dependence on shear for the lowest quality foam at 60%, slight shear thinning for foam quality values of 60–80%, and distinct shear thinning for the driest foam of 90% quality; the foam is clearly more mobile at higher velocity values.

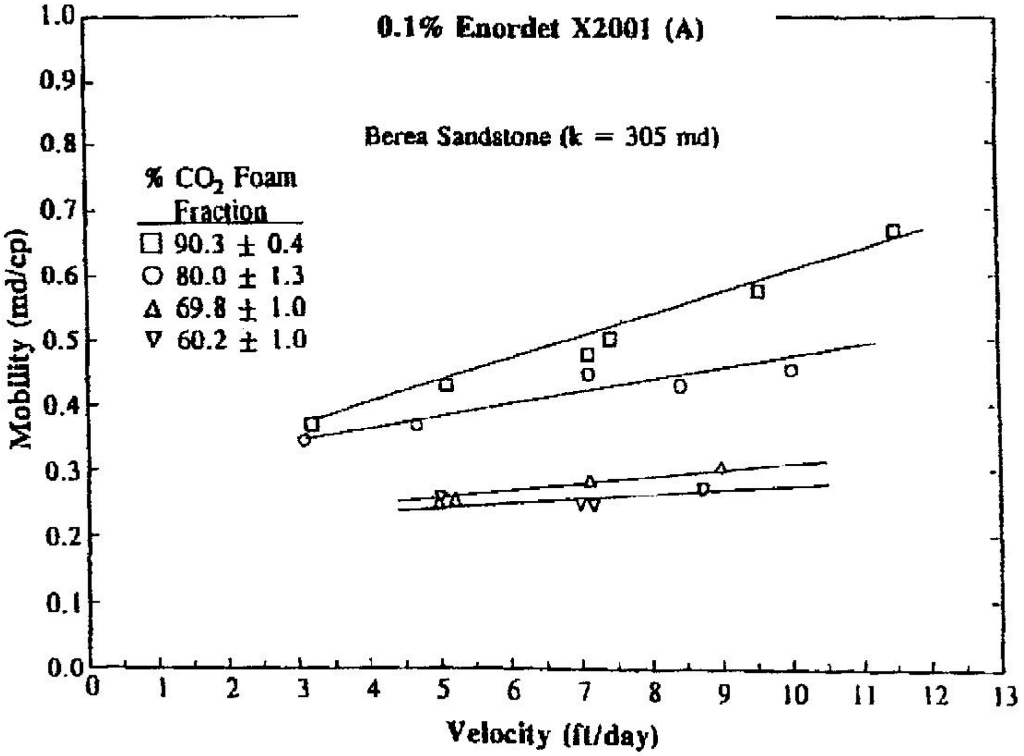


Figure 10.9. Effect of foam quality and fluid velocity on foam mobility in Berea sandstone using a 0.1wt% solution of Enordet X2001[Lee and Heller, 1990; Heller, 1994]

The preceding figure also illustrates that the foam mobility is lowest at 60%–70% quality and increases at foam quality values of 80 to 90%.

In a study of foam quality on mobility in Berea cores (shown in Figure 10.10), it was shown that mobility decreased roughly by a factor of two as foam quality increased from 20% to 80% [Chang and Grigg, 1999].

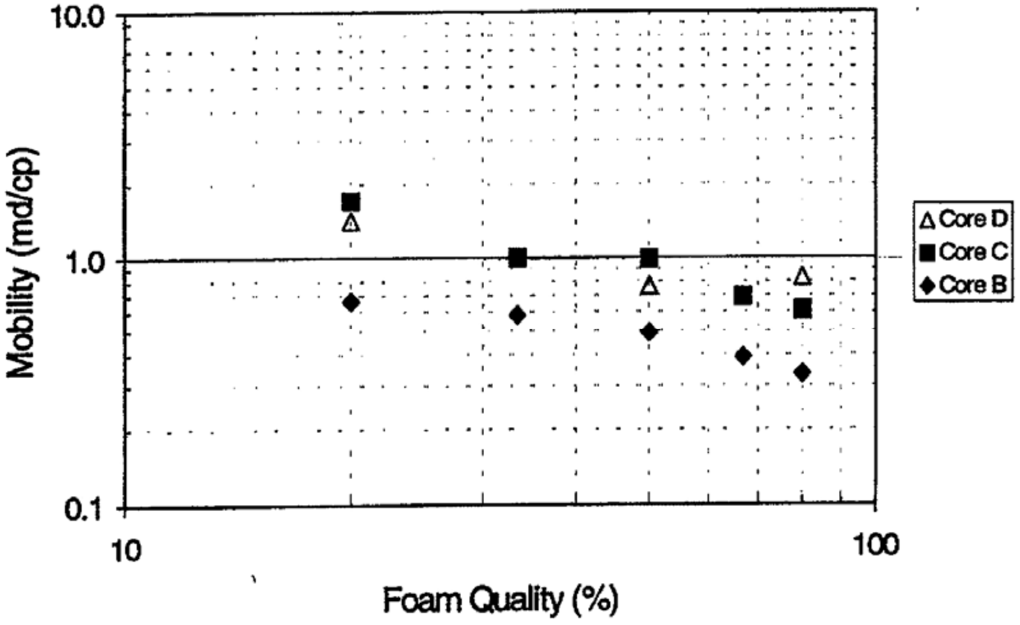


Figure 10.10. The mobility of CO_2 foams in three Berea sandstone cores as a function of foam quality (B, C, D permeability values of 196, 139, and 62 mD, respectively) [Chang and Grigg, 1999].

Moradi-Araghi and co-workers [Moradi-Araghi et al., 1997] also found that the greatest mobility reduction, or highest resistance factor, occurred with foams of 50%–70% quality as shown in Figures 10.11 to 10.13.

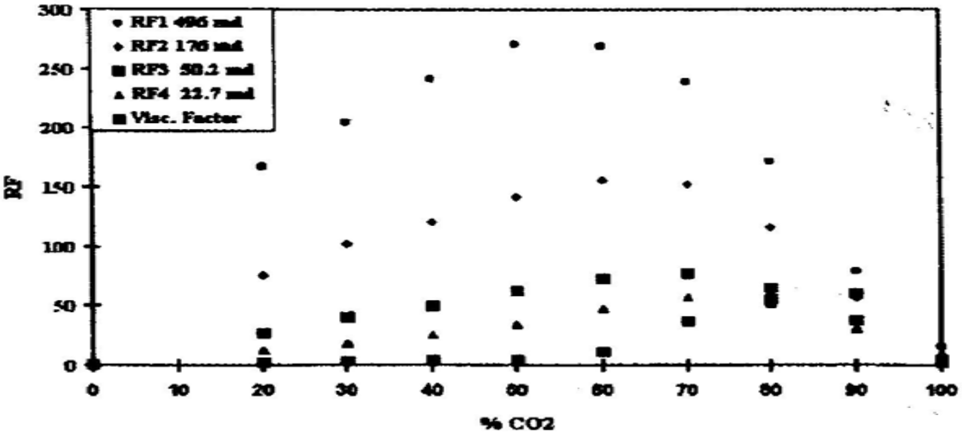


Figure 10.11. Resistance factor vs. foam quality in various South Cowden reservoir cores at reservoir conditions of 98°F and 2,000 psi using the NES 25 surfactant [Moradi-Araghi et al., 1997]

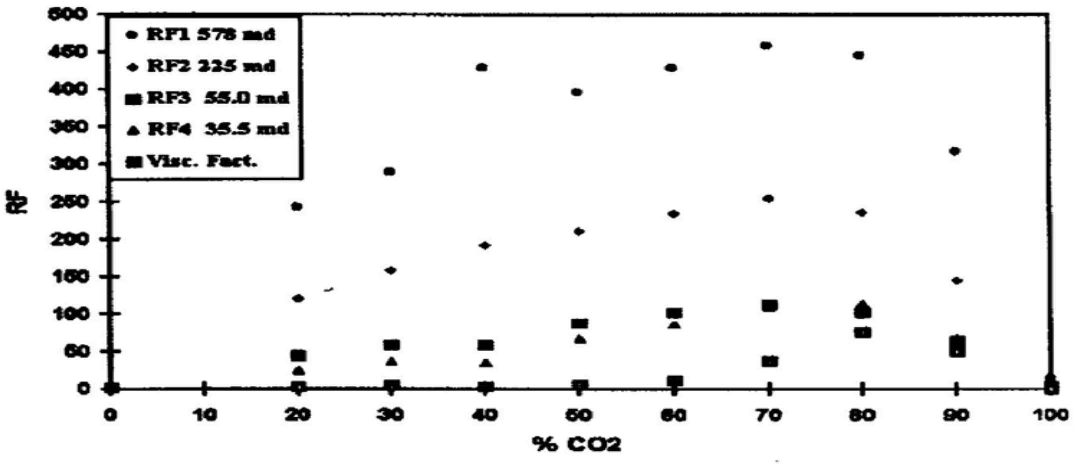


Figure 10.12.Resistance factor vs. foam quality in various South Cowden reservoir cores at reservoir conditions of 98 °F and 2,000 psi using the Rhodapex CD 128 surfactant [Moradi-Araghi et al., 1997].

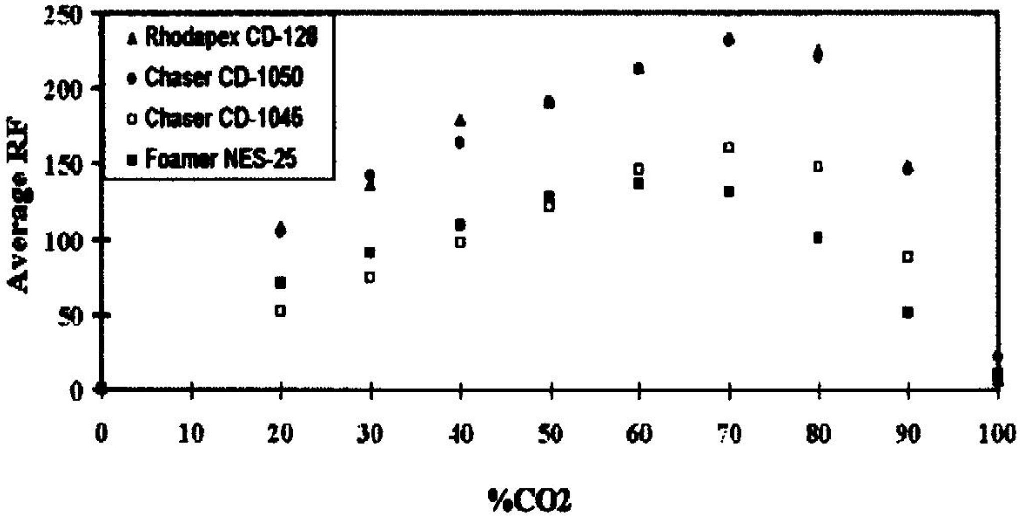


Figure 10.13.Resistance factor vs. foam quality in various South Cowden reservoir cores at reservoir conditions of 98°F and 2,000 psi using the Chaser CD 1045, Chaser CD 1050, Rhodapex CD 128, and NES 25 surfactants [Moradi-Araghi et al., 1997]

In general, it appears that when foam mobility reaches a minimum value roughly in the 50%–80% quality range, and further increases in quality to 90% or higher, it usually results in an increase in mobility, as shown in the previous examples [Moradi-Araghi et al., 1997] and in the following example shown as Figure 10.14 [Heller, Lien, and Kuntamukkula 1985].

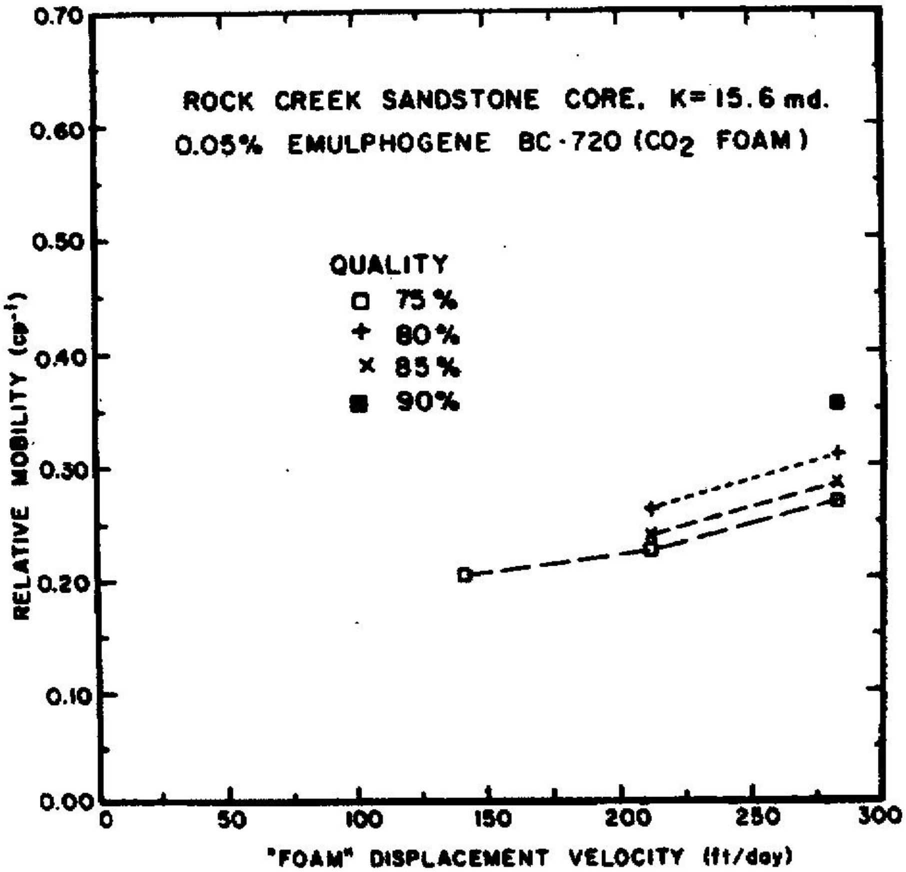


Figure 10.14. Relative mobility of foam as a function of displacement velocity and foam quality [Heller, Lien and Kuntamukkula, 1985]

The shear-thinning nature of 80% quality foams in the ~1–10 ft./day superficial velocity range is also evident in the results shown in Figure 10.15 for cores obtained from five different formations.

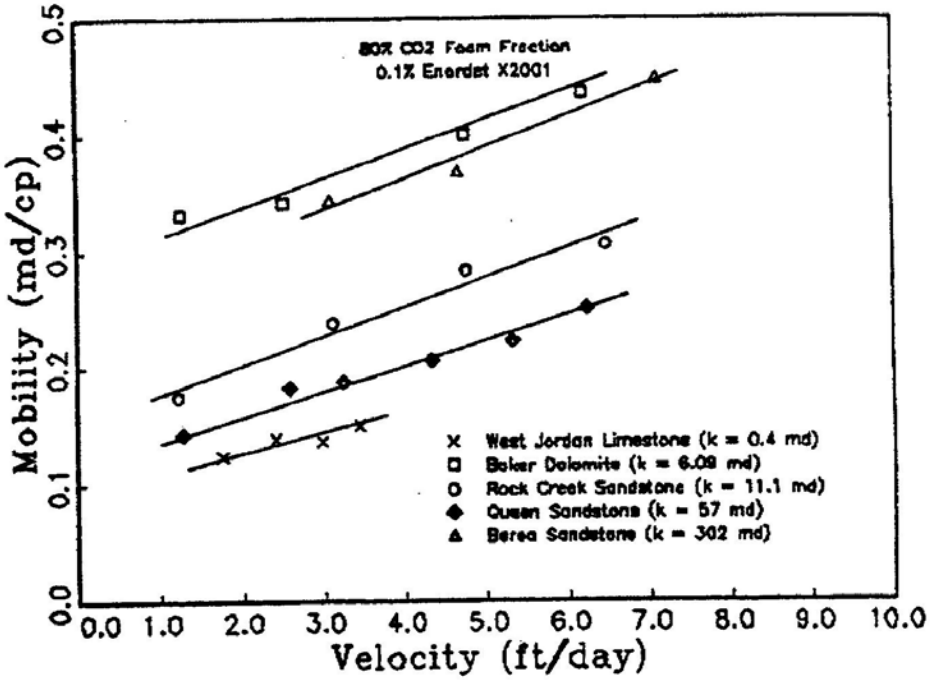


Figure 10.15. Effect of fluid velocity on 80% quality foam mobility in field cores using a 0.1wt% solution of Enordet X2001[Lee, Heller, and Hoefer, 1991]

Alkan showed that in some flow regimes some foaming surfactants exhibit relatively constant mobility, as shown in Figure 10.16 [Alkan et al., 1991].

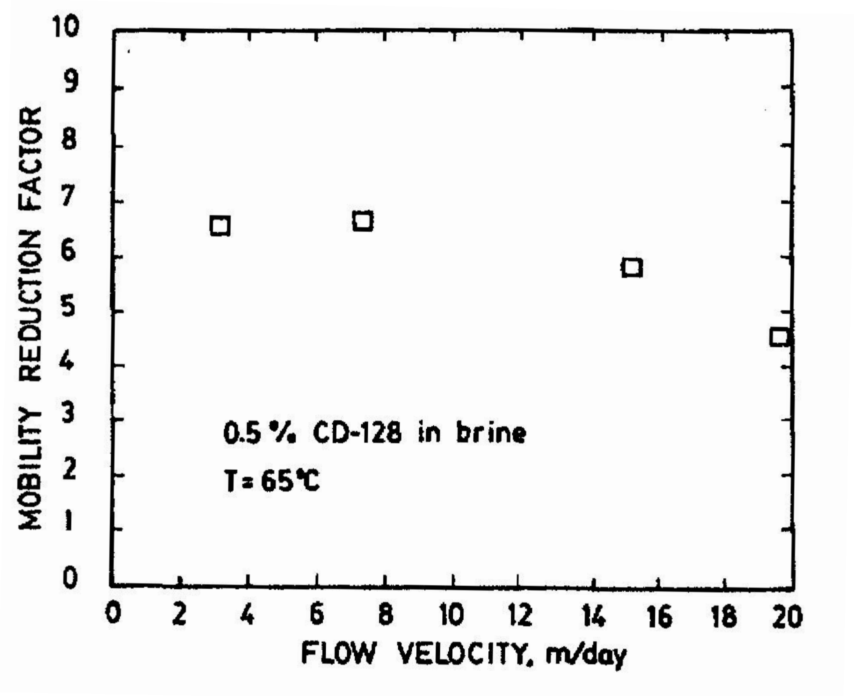


Figure 10.16. Relatively constant – slight decrease in mobility reduction (i.e., increasing mobility) over the 2-20 m/day velocity range [Alkan et al., 1991]

It appears that as velocity increases from extremely low values, the relative mobility of the foam decreases, reaches a minimum, and then increases as the flow rate approaches very high values commensurate with near wellbore conditions, as shown in Figure 10.17 [Heller, Lien and Kuntamukkula, 1985].

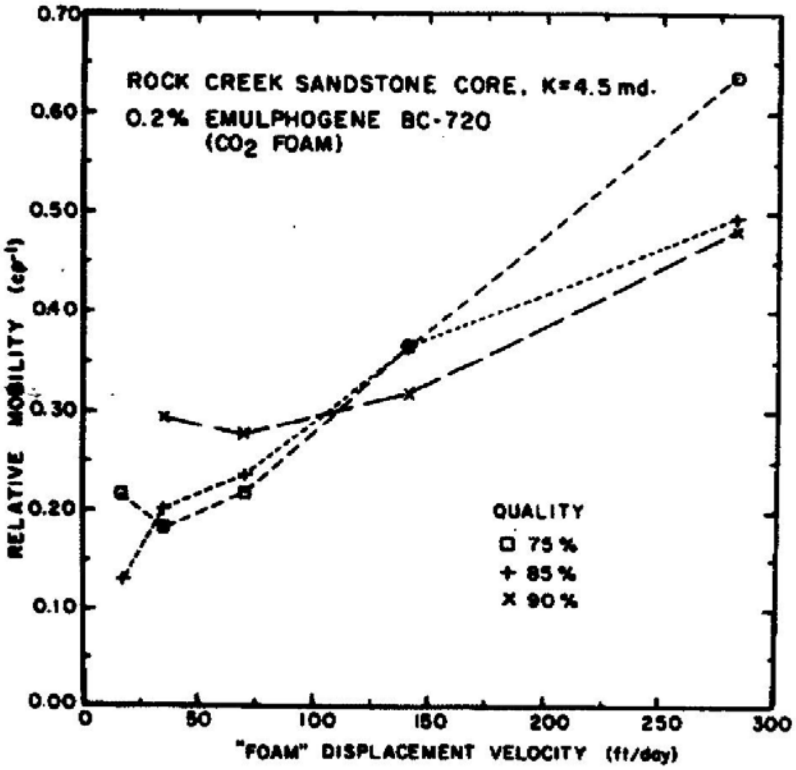


Figure 10.17.Foam mobility exhibits an apparent minimum value at low flow rates (< 2 ft./day) and increases with increasing flow rate. The mobility of pure CO_2 is about 20 cP $^{-1}$[Heller, Lien and Kuntamukkula, 1985].

If injectivity is considered, shear-thinning behavior at high flow rates is desirable if prohibitive injectivity losses are to be avoided in the near-wellbore, high fluid velocity region. If conformance control is considered, one would desire shear-thickening behavior in the near-wellbore region in order to reduce the mobility of CO_2 most significantly in highly permeable, watered-out zones. At high fluid velocity, it appears that CO_2-in-brine foams will exhibit shear-thinning.

In one study [Yang and Reed, 1989] a transition from shear thickening to shear independence to shear thinning was reported, as shown in Figure 10.18. Shear thickening was observed only at extremely low velocity values that were much less than 1 ft./day.

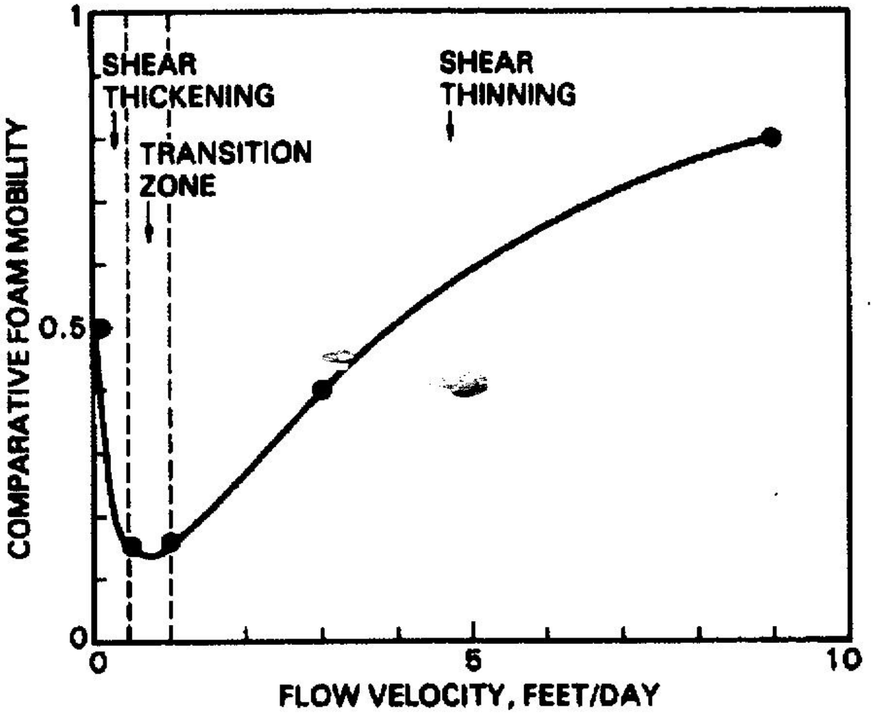
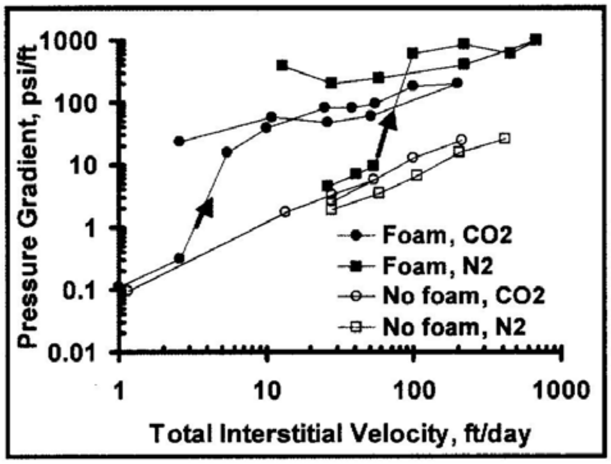


Figure 10.18. Rheology of a 0.1wt% C16 diphenylether disulfonate foam (DPEDS) as a function of superficial velocity in a 400 mD Berea sandstone core [Yang and Reed, 1989].

Because mixing—whether it is provided by an impeller in a high pressure windowed cell or by the flow of fluids through the tortuous pores of sandstone—is required to form a CO_2 foam, it is not surprising that at very low flow rates CO_2 foams may not form at all in a porous medium. Therefore, at extremely low superficial or interstitial velocities, there can be insufficient force to form a foam and mobility would be expected to increase to values comparable to the mobility of neat CO_2 (i.e., a relative foam mobility or a comparable relative mobility of unity). Likewise, it would be expected that there would be a minimum pressure drop required for the establishment of a foam in a porous medium. Experiments conducted at these conditions (Figure 10.19) affirm this to be the case for nitrogen and CO_2 foams formed in sandpacks, beadpacks, and sandstone [Gauglitz, Friedman, Kam and Rossen, 2002]. For the CO_2 foams, a 0.5wt% Chaser CD 1040 alkyl sulfonate surfactant solution was co-injected with CO_2 at constant flow rates to generate an 80% quality foam. The back-pressure regulator at the exit of the 950 mD Boise sandstone core was set at 1,500 psig. The pressure gradient and resistance factor results are provided in the following figures. At interstitial velocities of 1 and 3 ft./day (superficial velocities of ~ 0.2 and 0.6 ft./day) there was no difference in the mobility of the CO_2 whether the surfactant was used or not. Foams were generated only when the interstitial velocity was about 6 ft./day (superficial velocity of ~1.2 ft./day) or greater (up to 200 ft./day). Interestingly, when the interstitial velocity was reduced to values too low to generate a foam (3 ft./day), it was possible to maintain the movement of the foam in the porous medium.



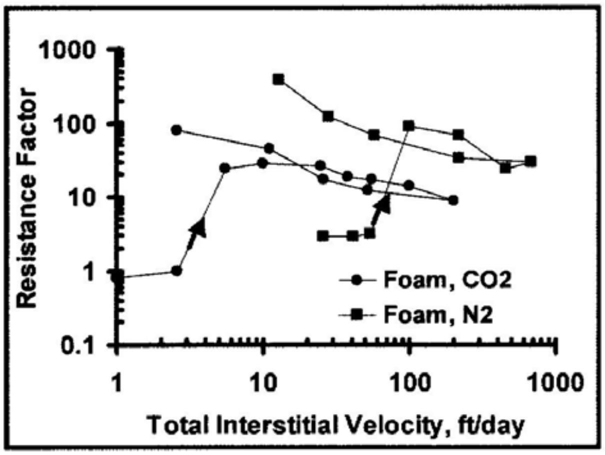


Figure 10.19. The effect of total interstitial velocity on the pressure gradient (top) and resistance factor (bottom) of CO_2 (no surfactant) and CO_2 foams in a 950 mD Boise sandstone (porosity estimated to be ~20%) at ambient temperature and a BPR setting of 1,500 psig [Gauglitz, Friedman, Kam and Rossen, 2002]

Similar tests were conducted with other Boise sandstone cores with permeability values of 950 to 7,100 mD. The results, shown in Figure 10.20, indicate that the interstitial velocity needed to generate the foam increased with permeability, but the minimum pressure gradient required to establish foam in these relatively high permeability sandstone cores was relatively constant at a value of ~1 psi/ft. Further, in each case it was possible to maintain a foam formed at a high velocity in the core at a flow rate less than that needed to generate a foam.

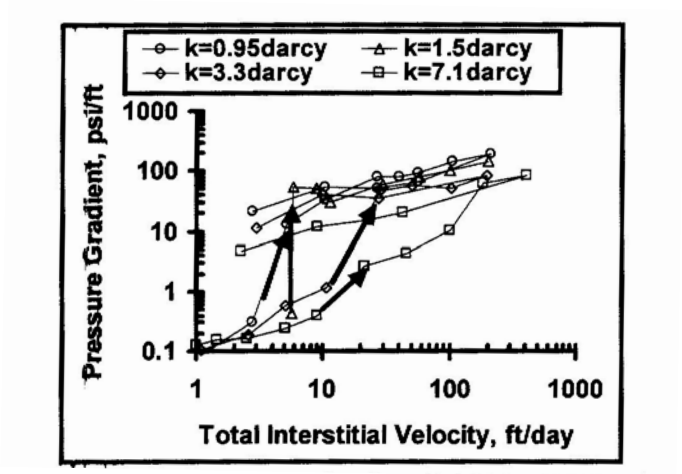


Figure 10.20.Foam flow in different permeability sandstone over various flow rates [Gauglitz, Friedman, Kam and Rossen, 2002]

Only a few cases of shear thickening have been reported for flow rates of 1–100 ft./day in very high permeability systems. For example, this behavior has been observed in sandpack [Bernard and Holm, 1964] and micromodel [Huh et al., 1989] systems.

In a study aimed at assessing the effect of flow rate on foam mobility in porous media that were 1.27 cm in diameter (1.266cm^2 cross section), as the flow rate increased from 4.2 to 8.4 to 16.8 cm^3/hr. (2.61, 5.22, 10.44 ft./day superficial velocity) the foam mobility generally increased by a factor of roughly 2–3 in Berea sandstone cores, as shown in Figure 10.21 [Chang and Grigg, 1999].

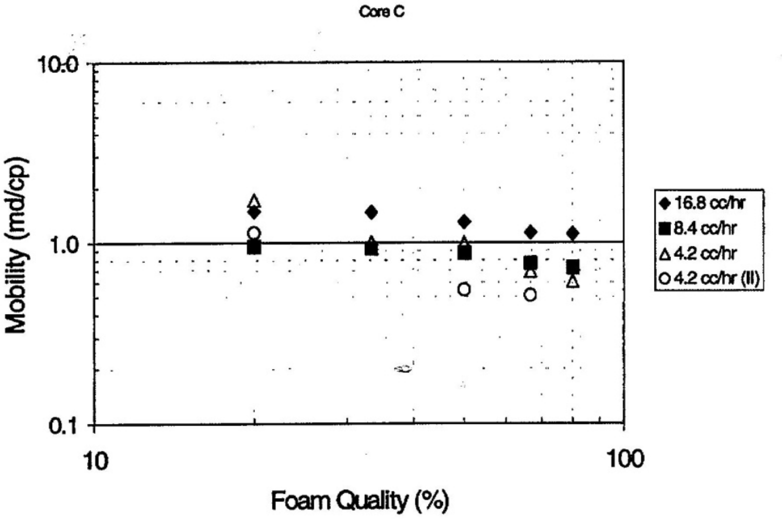


Figure 10.21. Mobility of foam as a function of quality in a 139 mD Berea sandstone core [Chang and Grigg, 1999]

and consistently increased by a factor of 2–4 in a fritted glass core as shown in Figure 10.21 [Chang and Grigg, 1998].

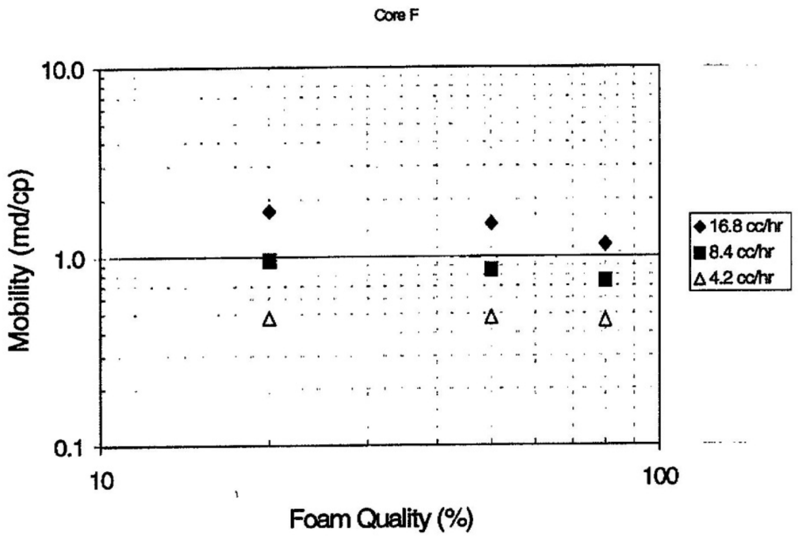


Figure 10.22. Mobility of foam as a function of quality in a 184 mD glass bead fritted core [Chang and Grigg, 1998]

A study employing Chaser 1045 demonstrated that the foams were shear thinning over the 2–70 ft. /day range [Moradi-Araghi et al., 1997]. An example of their results for the Chaser CD 1045 surfactant is shown in Figure 10.22.

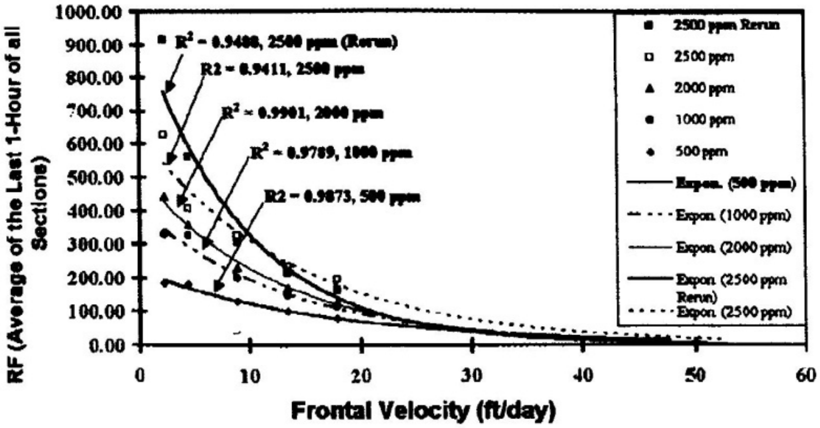


Figure 10.23. The resistance factor of CO_2 foam as a function of frontal velocity for surfactant solution made with the Chaser CD 1045 surfactant [Moradi-Araghi et al., 1997]

In core tests where CO_2 was injected into brine saturated carbonate core (15% porosity, ~150 mD), a 1.0wt% solution of Alipal CD 128 was able to delay gas breakthrough; the CO_2 saturation at breakthrough increased from 27% in the absence of surfactant to 40% with the 1.0wt% Alipal CD 128 solution. Further, the surfactant was able to reduce the mobility of the CO_2 by at least 85% at high gas saturations as shown in Figure 10.23 [Bernard et al., 1980].

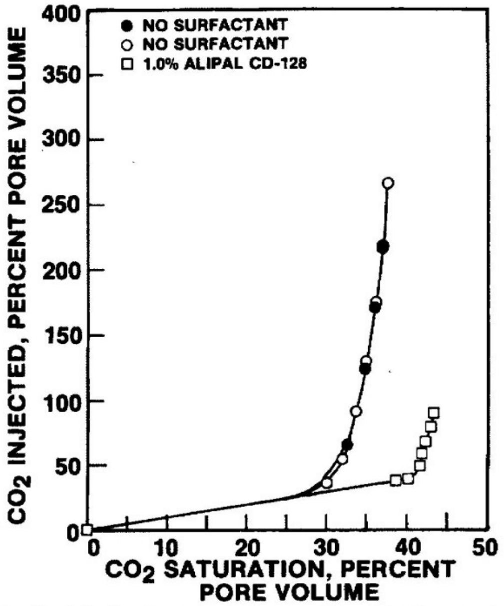


Fig. 3 – Effect of surfactant on CO_2 injection and saturation in carbonate Core A.

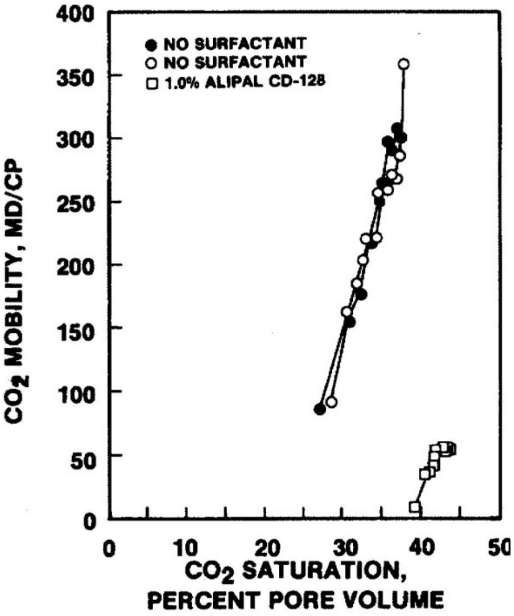


Figure 10.24. The effect of Alipal CD 128 on gas saturation and CO_2 mobility in a carbonate core initially filled with brine or surfactant solution [Bernard et al., 1980]

The efficacy of the surfactant solution was also documented for a sandstone core (19% porosity, ~560 mD) as shown in Figure 10.24 [Bernard et al., 1980].

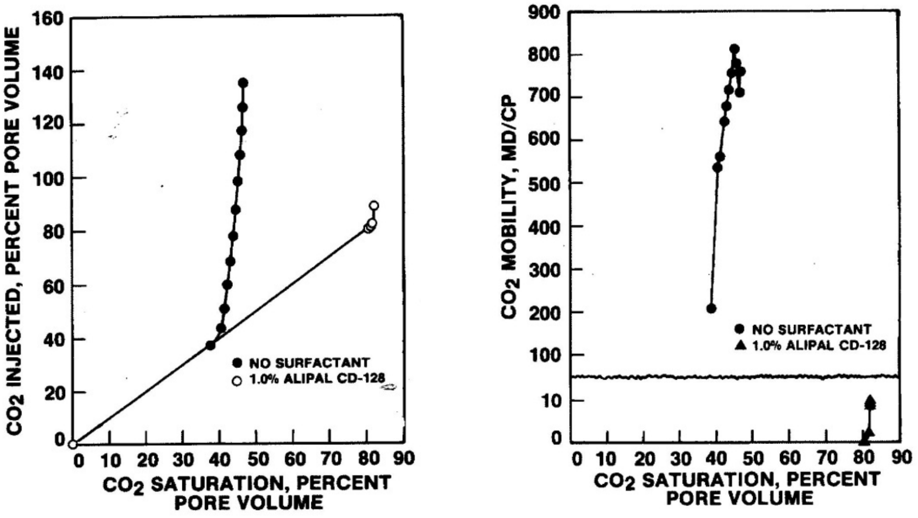


Figure 10.25.The effect of Alipal CD 128 on gas saturation and CO_2 mobility in a sandstone core initially filled with brine or surfactant solution [Bernard et al., 1980]

The ability of foams to form more readily and effectively in higher permeability rock layers is a desirable trait because one would hope to reduce the flow of CO_2 into high perm layers that have been extensively waterflooded, CO_2 flooded, and depleted of mobile oil while promoting the flow of CO_2 into lower permeability oil-rich zones. This attribute has been referred to as a "smart foam" or "selective foam". As shown in Figure 10.25, which presents foam mobility results for various porous media over a wide range of permeabilities, the apparent viscosity of CO_2 is two or three orders of magnitude greater in the highest permeability (~70 mD to ~300 mD) porous media than in the low perm cores (0.5 md to ~6 mD) over the 0.05 to 1.0wt% Enordet X2001 concentration range.

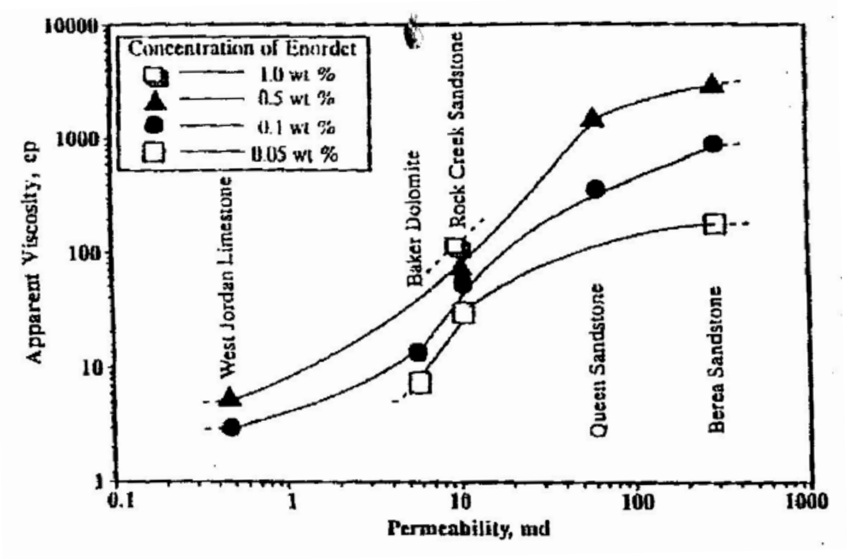


Figure 10.26.The effect of the concentration of Enordet X2001 on the apparent viscosity of 80% quality foams as a function of core permeability for flow of roughly 3 ft./day [Lee, Heller and Hoefer 1991; Heller, 1994]

This desirable effect is also apparent in the following plot (Figure 10.26) for the nonionic CD 1050 surfactant, in which the foam mobility reduction is more substantial in the higher permeability rock than in the low permeability rock. Such foams may be referred to as "smart" or "selective" because they will act as a conformance control foam to the extent that they will reduce the mobility of CO_2 more significantly in the higher perm zones, which are typically watered out thief zones, and thereby divert more of the CO_2 to the oil-rich, lower permeability zones.

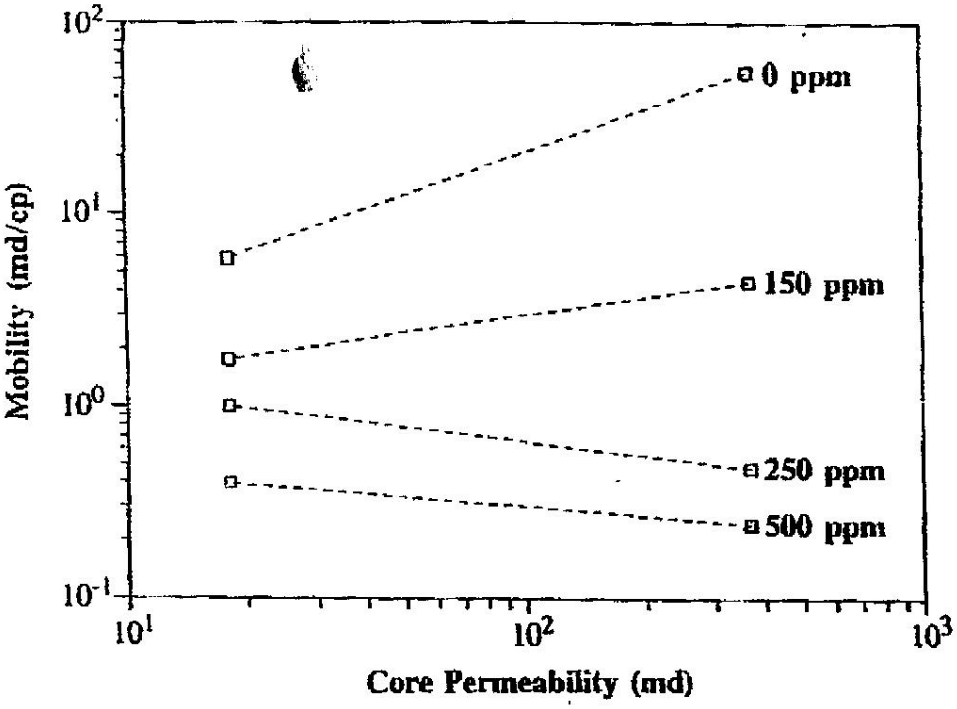


Figure 10.27.The effect of nonionic CD 1050 on the apparent viscosity of 80% quality foams as a function of core permeability [Tsua and Heller, 1992]

This is not always the case, however. In Figure 10.27 the mobility of the foam in the porous media was reduced by a comparable factor for the 25 mD and 600 mD cores when CD 1045 was used as the surfactant.

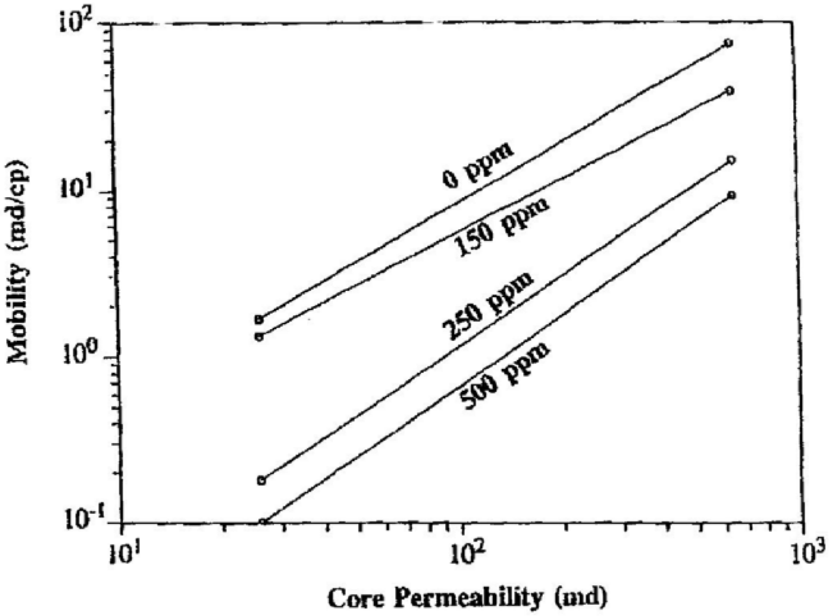


Figure 10.28.The effect of CD 1045 on mobility of 80% quality foam as a function of surfactant concentration and core permeability [Tsau and Heller, 1992]

In Figure 10.28, the mobility of the foam was actually reduced to a greater extent in the lower permeability core for the NES 25 surfactant.

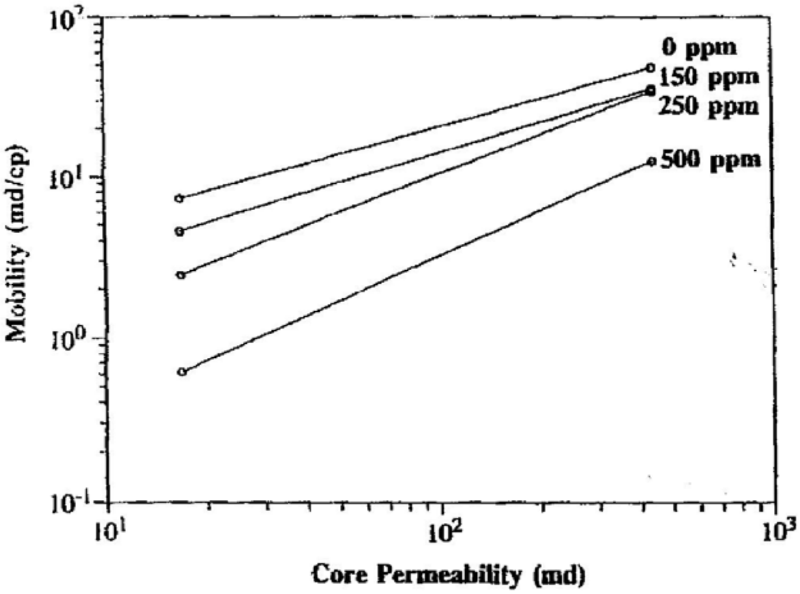


Figure 10.29. An example of NES 25 surfactant solutions reducing the mobility of CO_2 most significantly in lower permeability cores [Tsau and Heller 1992; Heller, 1994]

There are many other examples of foam mobility in the literature that illustrate how difficult it may be to assess whether a surfactant will exhibit selective mobility reduction. For example, Yahooghi and Heller assessed four surfactants, Chaser CD 1040, 1045, and 1050, and Enordet

X2001, used in the generation of 80% quality foams. At surfactant concentrations of 500 ppm and Darcy velocities of 0.4 ft./day, CD 1045 and Enordet X2001 were more effective in reducing mobility in higher perm cores, but CD 1040 and CD 1050 generated more effective foams in lower perm cores. At surfactant concentrations of 500 ppm and a Darcy velocity of 0.4 ft. /day, only Enordet X2001 exhibited the desired selective mobility reduction with increasing permeability, while CD 1045 and CD 1050 showed modest increases in mobility with increasing permeability, and CD 1040 exhibited markedly lower mobility values in the lower permeability cores. At 2,500 ppm and 0.04 ft. /day, Enordet X2201 and CD 1050 exhibited mobility values that remained relatively constant as permeability increased, while CD 1040 and CD 1045 exhibited undesirable mobility reduction trends of increased mobility at higher permeability values. At 2,500 ppm and 8.5 ft./day, all four surfactants exhibited mildly unfavorable selective mobility reduction [Yahoogbi and Heller, 1996].

Consider the performance of Sulfotex PAI, an ammonium alkyl ether sulfate (Figure 10.29), in generating foams in 3,000 mD sandstone cores, 58 mD Bati Raman limestone cores, and a 1,500 mD Bati Raman fractured core (mD prior to fracturing) [Alkan et al., 1991]. Mobility reduction was greatest in the high permeability sandstone cores, with a smaller mobility reduction occurring in the lower perm Bati Raman cores. The levels of mobility reduction—a factor of ~6–8 for the sandstone and 3–4 for the bati Raman cores—were lower than observed in many other reports. The foams were ineffective in reducing the CO_2 mobility in the fractured cores; an important observation when considering the applicability of CO_2-in-brine foams as mobility-reducing or conformance control agents.

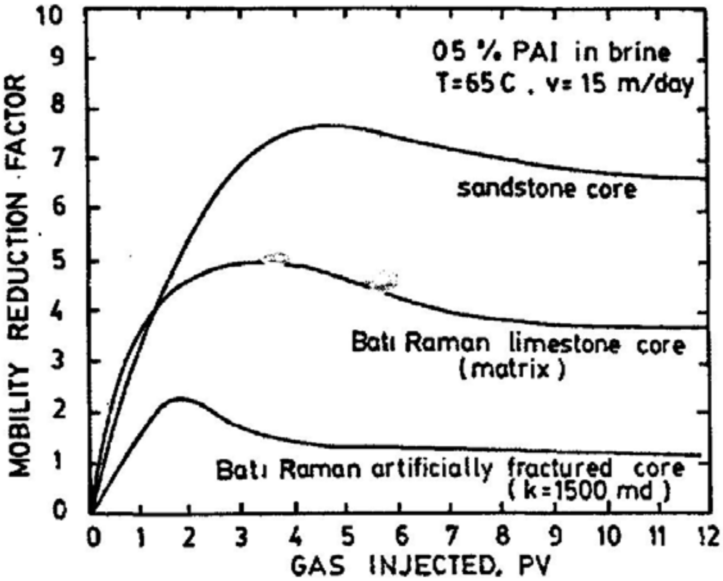


Figure 10.30. Mobility reduction of foams generated with 0.5wt% PAI in brine in 3000 mD sandstone, 58 mD Bati Raman cores, and 1500 mD fractured Bati Raman cores [Alkan et al., 1991]

There are several types of flow paths that are not suitable for mobility reduction using foams because they lack the architecture required for the generation of lamellae. These include fractures and vugs.

In summary, the surfactant concentrations for CO_2 mobility foams typically range from ~0.01wt% to 1.0 wt.%, the range over which a dramatic decrease in CO_2 mobility is observed. Concentrations less than 0.05wt% may not be great enough to cause lamellae to form, while concentrations greater than 0.5wt% may add significant cost while not imparting significant improvements in mobility reduction. Given the sensitivity of foam mobility to concentration, foam quality, rock type, permeability (and numerous other parameters), there simply is no substitute in foam design for assessing the foam mobility in reservoir cores at reservoir conditions and using reservoir fluids and commercial surfactants.

11. Effects of Process Variables on CO_2 Foam Mobility Reduction

Temperature

Because reservoir temperature is a factor that cannot be altered during a CO_2 flood, there are relatively few core flooding studies in which temperature is varied systematically. Nonetheless it is apparent that CO_2 foam flooding at temperatures above 80^oC may require more careful design than low temperature floods. There is at least one aspect of high temperature that is favorable: decreased surfactant adsorption with increasing temperature [Ziegler and Handy, 1979]. However, the primary obstacles for the application of foams in deep, hot formations include the decrease of surfactant solubility in brine that typically occurs with increasing temperature, the thermal degradation of the surfactant that is enhanced with increasing temperature [Handy et al., 1982], the slight increase in the interfacial tension between the CO_2 and the brine [Liu et al., 2005], and diminished foam stability [Wang, 1984] especially at temperatures above 60^oC that must be compensated for by higher concentrations of surfactant [Liu et al., 2005].

Pressure

In general, higher pressure favors CO_2 foam stability. CO_2 becomes a more dense solvent at higher pressure, which enhances the intermolecular associations between the CO_2 and the hydrophobic tails of the surfactant molecules. In a micromodel study, it was found that sweep efficiencies associated with CO_2 foams flowing at a pressure just below the MMP were just as high as the efficiencies measured at pressures well above the MMP. Therefore, it was concluded that the high sweep efficiencies can be accomplished using the least CO_2 if the foam flood is conducted at ~MMP rather than much higher pressures [Chang et al., 1994].

Brine Composition

In general, for a given surfactant, increased salinity (increased TDS) may tend to destabilize foam or, depending on the surfactant, have little effect. In general, a decrease in foam stability may be attributable to the increased salinity breaking the foam by decreasing the electrostatic double layer forces, or by diminishing the surfactant solubility in brine [Alkan et al., 1991].

For example, in Figure 11.1, the volume of an air-in-brine foam, in which the "base" brine (1X) contained 10.58% NaCl and 0.76% $CaCl_2$, tends to decrease with increasing salinity.

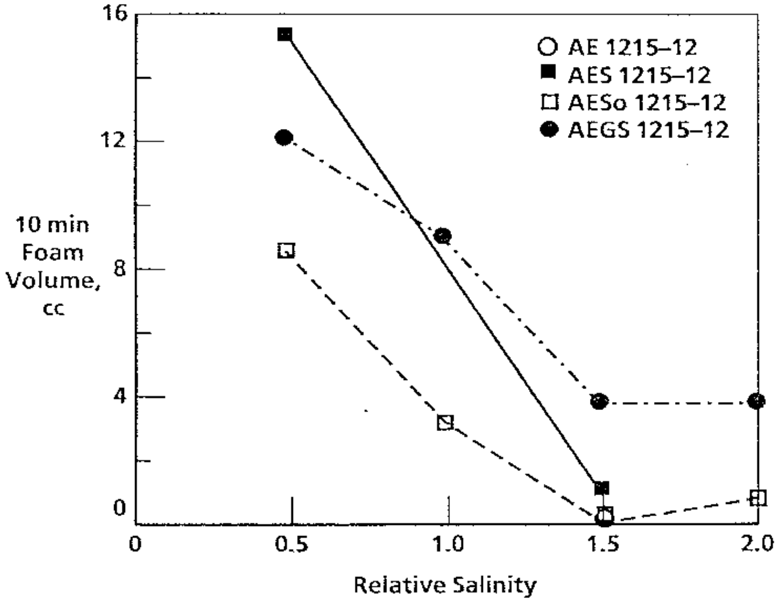


Figure 11.1. Effect of increasing salinity on foam volume in a screening test that employs air as the gas phase [Borchardt et al., 1988]

Some ionic surfactants that have excellent foaming properties, such as Chaser CD 1045, are not significantly influenced by the TDS of the brine, as shown in the Figure 11.2 images and accompanying figure [Liu et al., 2005] for aqueous solutions containing at least 0.025wt% CD 1045.

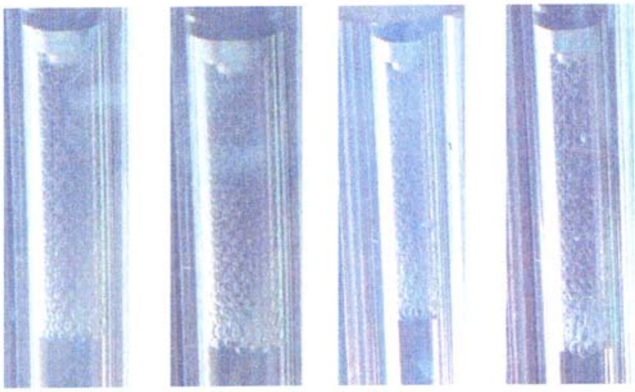


Fig. 14 Salinity versus CO_2 foam stability at different CD concentration.

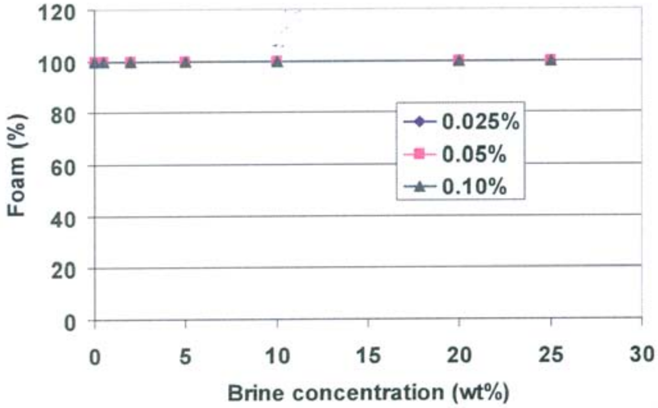


Figure 11.2. The effect on salinity on aqueous solutions containing 0.025% or more of CD 1045 [Liu et al., 2005]

At a very low concentration of 0.005wt%, however, the salinity did impact the foam performance, as shown in Figure 11.3.

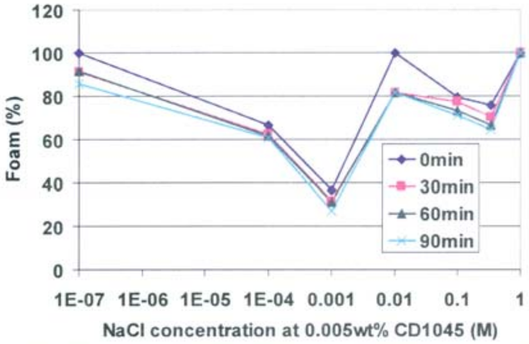


Fig. 17 Salinity effect on foam stability at CD conc. of 0.005 wt% in NaCl solution.

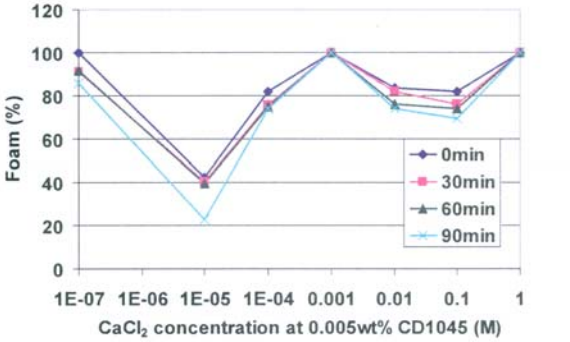


Figure 11.3. Stability of foam generated from CD1045 at a low concentration (0.005 wt.%) in different brine compositions [Liu et al., 2005]

The effect of salinity on surfactants may be more pronounced when the surfactant is dissolved in the CO_2 rather than the brine. Such systems are based on low concentrations of non-ionic surfactants, and the presence of dissolved solids in the brine can diminish the solubility of the surfactant in the brine and drive it toward the CO_2 [Torino et al., 2010]. The lower solubility of non-ionic surfactants in CO_2 is also evidenced by the decrease in cloud point temperature (the temperature at which a 1 wt. % solution of surfactant in an aqueous phase exhibits two-phase liquid-liquid behavior) when brine solutions are compared to water solutions [Adkins et al., 2010].

Oil and Oil Composition

One of the most important parameters to be considered with respect to the viability of CO_2 foams for mobility control is the effect of oil. It would be desirable for a foam to retain its reduced mobility when contacting oil in the formation. If the foam mobility is reduced by contact with oil, however, this could be exploited as a means of selective mobility reduction [Bernard et al., 1980]. The strongest foams would be generated in higher permeability, watered-out, oil-depleted layers, thereby diverting more CO_2 in the form of a weaker (but still advantageous) mobility control foam in the lower permeability oil-rich zones. It is certainly undesirable that the oil be emulsified, however, because it could be difficult to break the emulsion and recover the oil.

Simple screening tests were used to assess the effect of oil on foams, including adding refined hydrocarbons or crude oil to low-pressure air-in-brine or nitrogen-in-brine foams [Dellinger et al., 1994], or high-pressure CO_2-in-brine foams [Mannhardt et al., 2000]. Usually, the presence of oil tends to reduce the ability of surfactants to generate stable foams, as shown in Figure 11.4 describing low pressure foams [Borchardt et al., 1988].

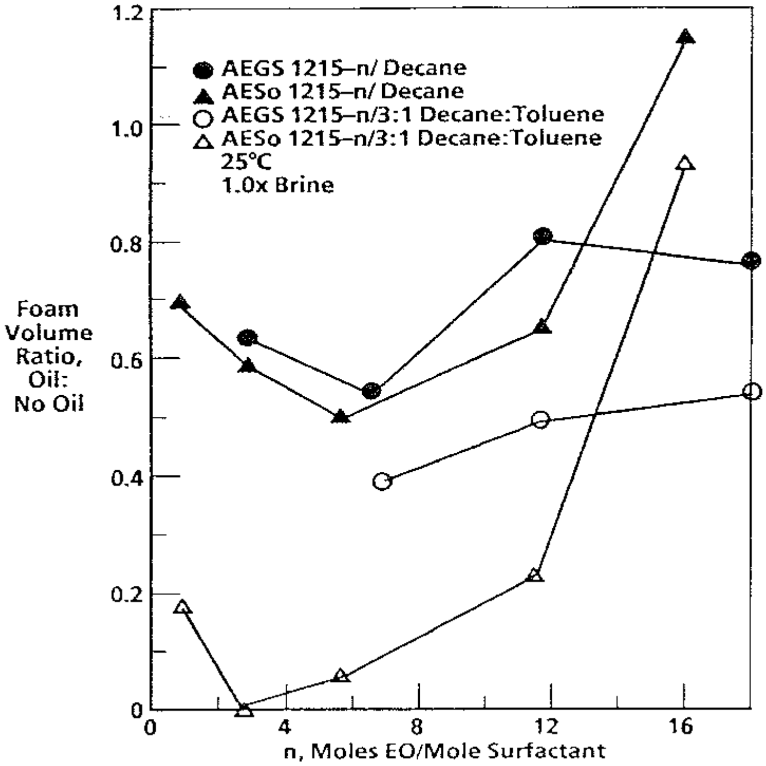


Figure 11.4. The deleterious effect of adding oil to an air-in-water foam [Borchardt et al., 1988].

In the following example (Figure 11.5), high-pressure methane-in-brine foams were generated by co-injecting CO_2 (90%) and a surfactant solution (10%) into a windowed cell. The tests were then repeated with a small amount of oil continuously added to the system. In all cases the foams proved to be less stable in the presence of crude oil [Mannhardt et al., 2000].

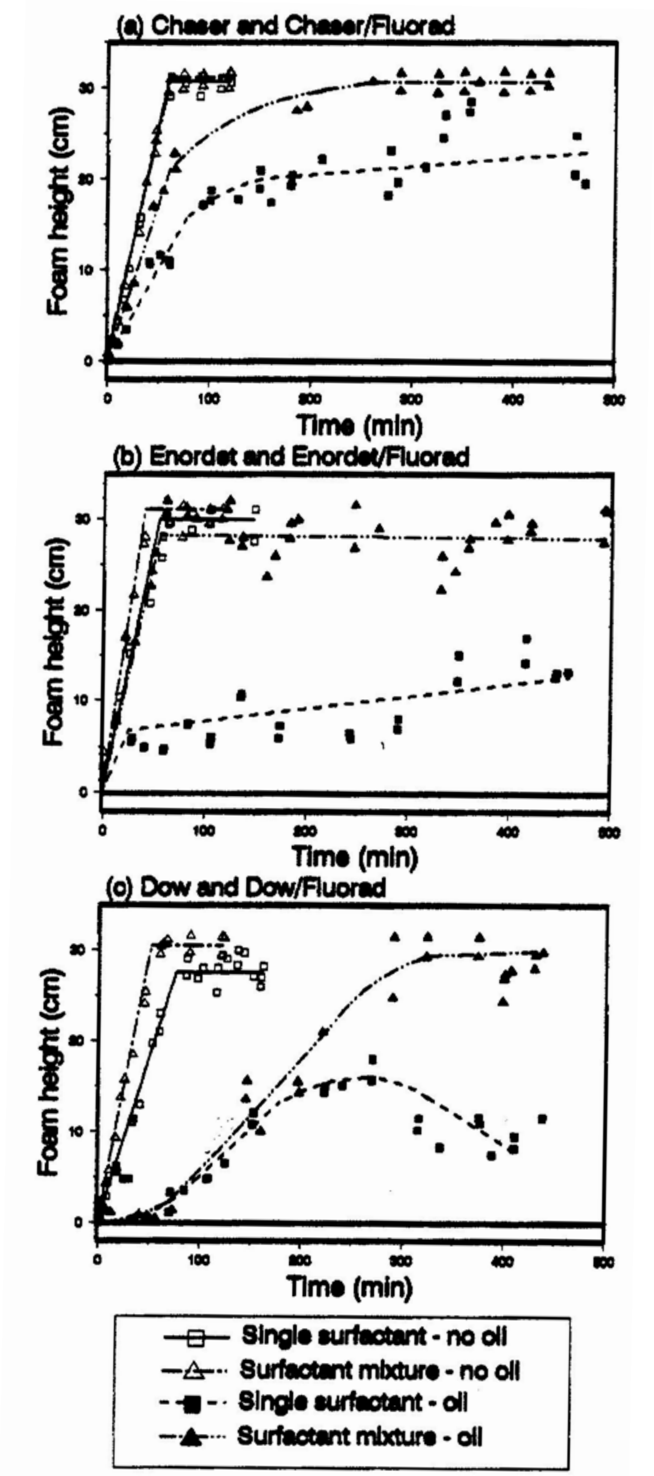


Figure 11.5. The addition of oil to the windowed cell resulted in less stable methane-in-brine foams [Mannhardt et al., 2000].

High-pressure foam tests conducted with windowed vessels have in some cases indicated that stable foams can be generated with excellent foaming surfactants such as Alipal CD 128, even when crude oil and crushed carbonate rock are placed in the cell [Bernard et al., 1980]. It has also been reported that the presence of an oil phase may even slightly enhance foam stability in specific cases [Dellinger et al., 1984].

Other assessments of the effect of oil have been conducted in an attempt to understand the effect of crude oil on foam effectiveness in porous media. Because the mobility reduction associated with foams is related to phenomena occurring between multiple phases at the pore level, high-pressure, 2-D, visual micromodels have been employed to provide direct visual observations of the effects of oil on CO_2 foams. These micromodels have either uniformly spaced and shaped flow paths for the fluids, or provide a flow path with an appearance similar to that exhibited by a sectioned portion of sandstone or limestone. For example, in SAG displacements conducted in a high-pressure visual micromodel, residual oil was seen either spreading along the CO_2-surfactant solution interface and being displaced along with the CO_2 phase or taking the form of individual blobs of oil floating in the surfactant solution and being displaced by the CO_2 phase [Chang and Grigg, 1994]. Another micromodel study has shown that the lamellae associated with oil-resistant foams pass over oil without rupturing. Other foams may have moderate stability to oil, as evidenced by the emulsification of oil that is contacted by lamellae and the subsequent transport of the emulsified oil with occasional lamella rupture. The most oil-sensitive foams, however, cause oil to emulsify into very small droplets that are imbibed into the foam lamellae and cause their frequent rupture [Mannhardt et al., 2000]. Kuhlman's micromodel results suggested that the foaming ability of the surfactant was diminished by hydrocarbons in the oil that were comparable in size to the hydrophobic, alkyl-based tails of the surfactants, even when a distinct, separate oil phase was not present. This effect was attributed to the disruption of the surfactant packing at the interface by the hydrocarbons [Kuhlman, 1990].

CT imaging of CO_2 foams flowing through porous media with and without some degree of oil saturation have been conducted in an attempt to understand the effects of oil on foams generated in situ [Farajzadeh, Andrianov, Bruining and Zitha, 2009; Farajzadeh, Andrianov and Zitha, 2009; Du et al., 2008; Wellington and Vinegar, 1985, 1988].

The effect of oil on CO_2 mobility has been reported by numerous investigators. For example, a recent study used pressure drops across cores of varying oil content to assess the integrity of CO_2-in-brine foams [Yin et al., 2009]. The results, shown in Figure 11.6, indicate that a significant decrease in pressure drop and increase in foam mobility occurs as the initial oil saturation increases.

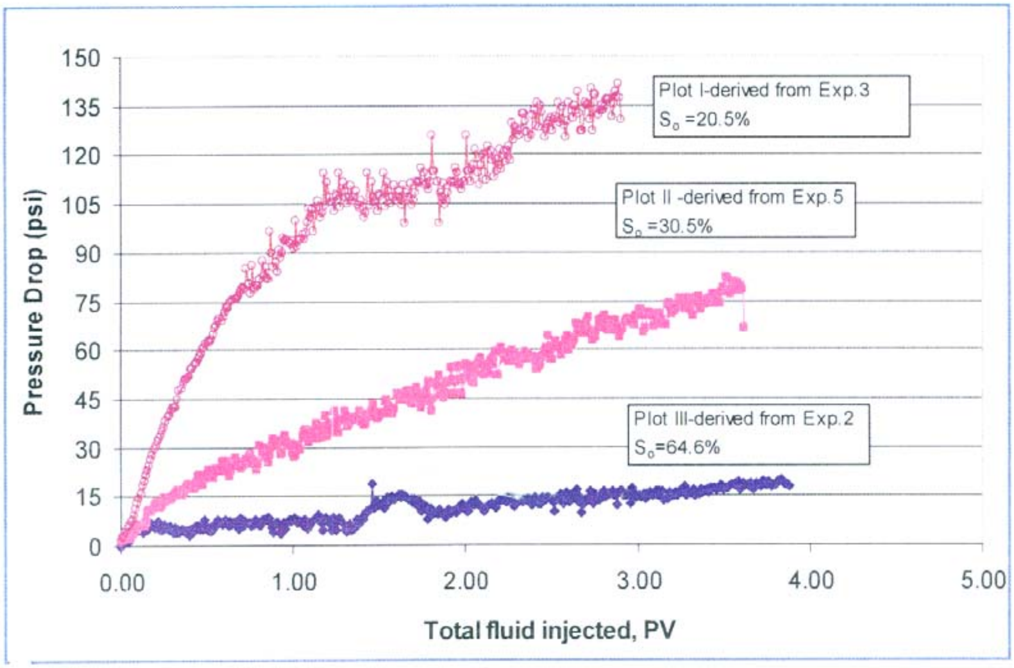


Figure 11.6 Pressure drop in response to foam injection at various oil saturations. [Yin et al., 2009]

It has been observed that at oil saturations greater than 5%–20%, oil tends to significantly reduce the effectiveness of foams during core floods [Schramm, 1994]. This observation, which has been confirmed by other researchers as described in the following section, suggests that the use of CO_2 foams as a secondary oil recovery mechanism may not be advantageous or widely feasible. Rather, CO_2 mobility control foams should be employed after a formation, or at least the highly permeable zones of a formation, have been flooded with CO_2.

Perhaps the most important assessments of the effect of oil on CO_2 foams are related to oil recovery tests intended to emulate the CO_2 EOR process. Numerous investigators have conducted CO_2-injection-into-core tests that have been waterflooded then oilflooded to residual water saturation to represent fields that are ready for a secondary recovery process, or a core that has been waterflooded, then oilflooded to residual water saturation, and then waterflooded to emulate a formation ready for tertiary recovery. An example of the former case, in which cores initially contained high oil and residual water saturation, was recently presented [Yin et al., 2009]. This study demonstrated that CO_2 foams were capable of reducing the residual oil saturation beyond that achieved by CO_2 floods when the foam flood occurred after the CO_2 flood, as shown in Figure 11.7. However, CO_2 injected after a CO_2 foam flood was not able to yield additional oil.

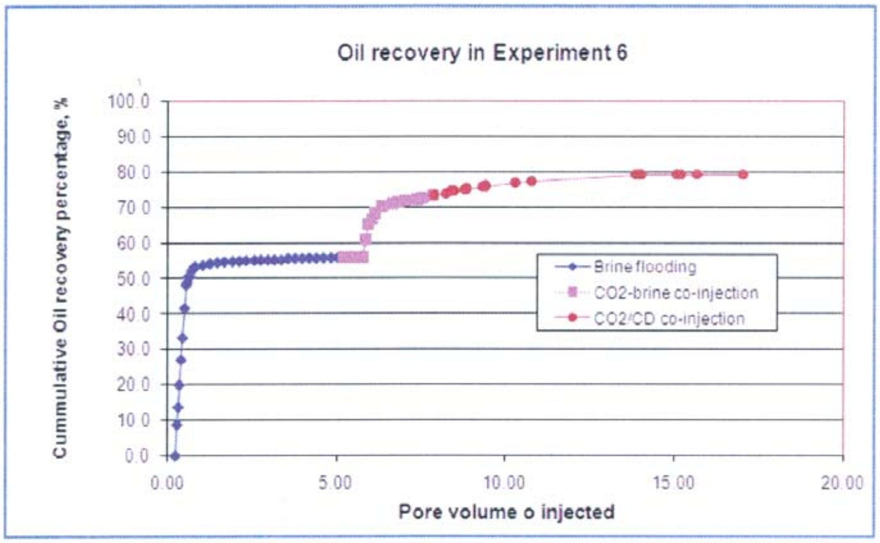


Figure 11.7. The recovery of oil from a sandstone core; waterflooding, followed by CO_2 WAG, followed by CO_2 foam [Yin et al., 2009]

Dual Permeability Core Floods

Researchers have also conducted CO_2 floods and CO_2 foam floods in composite, coaxial cores of dual permeability (a core fit inside the center of a second, annular core). In this study, the cores were waterflooded and then oil-flooded to residual water saturation. The cores were then subject to CO_2, CO_2 WAG, or CO_2 foam injection. The results shown in Figure 11.8 demonstrated the efficacy of the foams even at high oil saturations within the cores [Tsau et al., 1998].

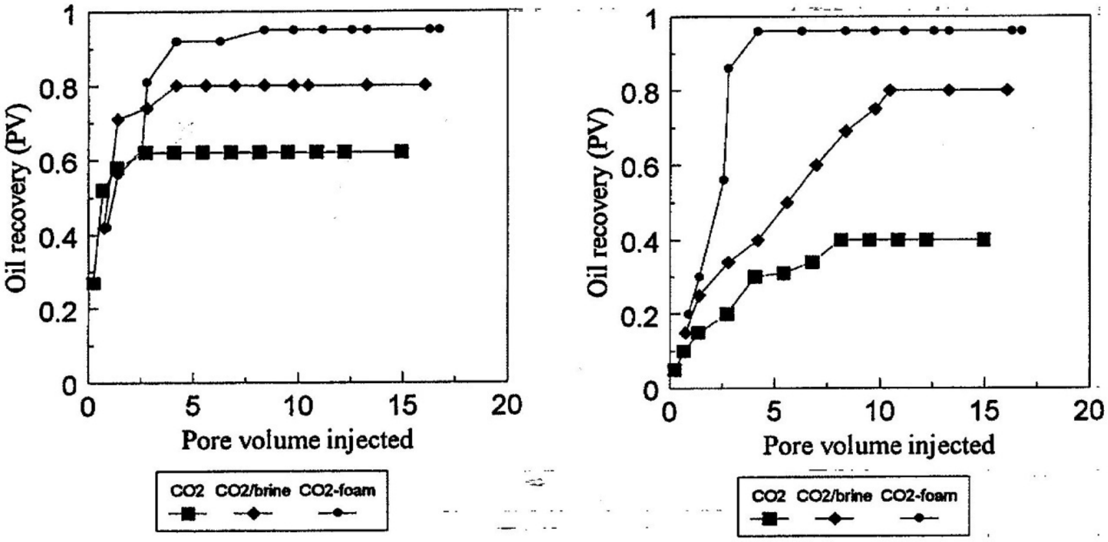


Figure 11.8. The recovery of oil from a co-axial core with varying permeability (590 and 120 mD) as a function of injection type and PV injected [Tsau, et al., 1998]

Efforts have also been made with dual perm experiments using waterfloods, CO_2 floods, and CO_2 foam floods to determine the optimal injection strategies to recover the most oil. Consider the various injection sequences assessed with a dual, parallel core system meant to simulate a layered formation with a high permeability flow path (154 mD) and a low permeability flow path (24 mD) [Casteel and Djabbarah, 1988]. In Figure 11.9 only CO_2 is injected into the previously waterflooded cores and oil is recovered only from the high perm core. Only 0.06 PV of CO_2 entered the low perm core, while 2.29 PV of CO_2 entered the high perm core. CO_2 breakthrough from the high perm core occurs after about 0.3 PV and the oil left behind by the waterflood is completely recovered from the high perm core at ~2.4 PV. This represents 39.7% of the oil in both cores.

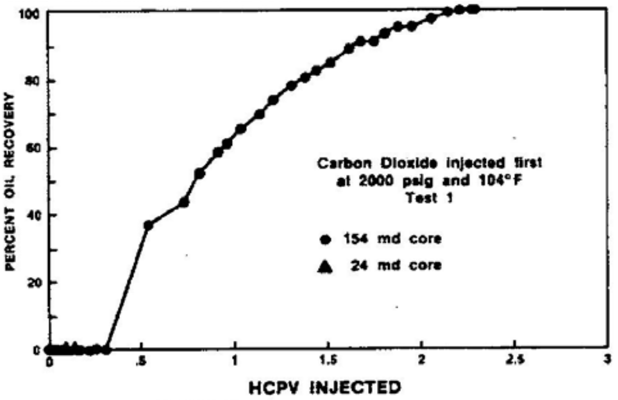


Figure 11.9. Oil recovery from two parallel cores that have been previously waterflooded; CO_2 injection into both cores, oil recovery only from the high permeability core [Casteel and Djabbarah, 1988]

Subsequently, WAG tests were conducted and the total oil recovery from the system ranged between 45% and 48% due to an increase in the percentage of oil recovered from the low perm core. Nonetheless, in the best case only 9% of the oil in the lower permeability core was recovered.

It was anticipated that a CO_2 foam could be more effective at recovering oil from the lower perm core; therefore, several surfactant solutions injection strategies were explored. In the first sequence, a 0.23 PV surfactant slug (based on the PV of both cores) of a 1% Witcolate 1247-H solution was injected into the water flooded cores prior to the CO_2 flood. The results, shown in Figure 11.10, illustrate that most of the surfactant solution entered the high permeability core, where it subsequently generated a fairly strong foam. Only 1.45 PV of CO_2 entered the high perm core and the oil recovery was only about 40%. A significant amount of the CO_2 was diverted to the lower perm core, where 99% of the oil was ultimately recovered after 10.24 PV of CO_2 were injected. Seventy-eight percent of the post-waterflood in the entire system was recovered in these tests, which were reproduced with a different surfactant and with a four slug sequence of surfactant-CO_2-surfactant-CO_2.

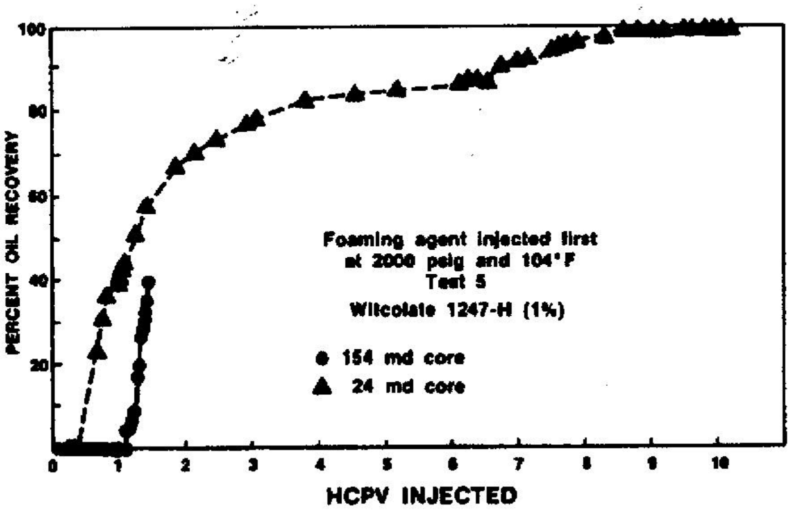


Figure 11.10. Oil recovery from two parallel cores that have been previously waterflooded; HCPV correspond to HCPV of each individual core; surfactant solution injection followed by CO_2 injection into both cores, partial oil recovery from the high permeability core, and complete recovery of oil from the low permeability zone [Casteel and Djabbarah, 1988].

In that the objective of this study was to recover as much oil as possible from *both* cores, another sequence was assessed. Carbon dioxide was injected first until oil recovery stopped (in an attempt to recover most of the oil from the high perm core), followed by a surfactant solution and more CO_2, which was intended to divert the CO_2 into the oil-rich low perm zone of the core. The results confirmed this behavior, and are illustrated in Figures 11.11 and 11.12.

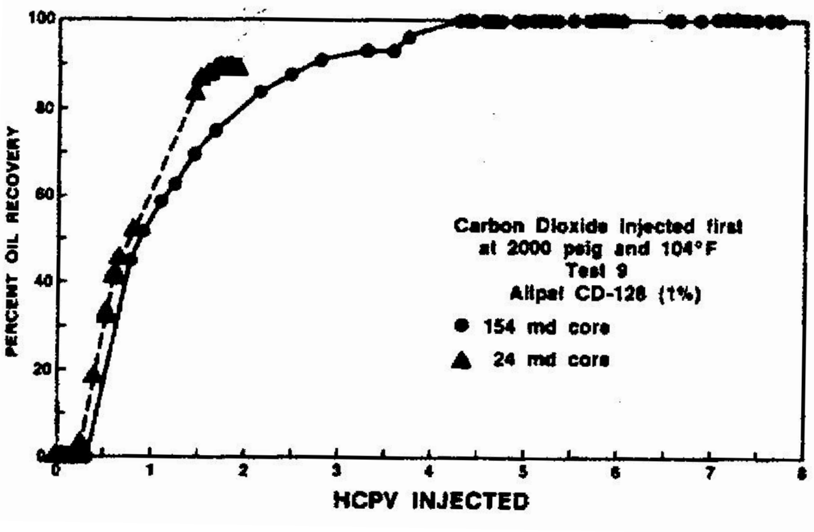


Figure 11.11. Oil recovery from two parallel cores that have been previously waterflooded; HCPV correspond to HCPV of each individual core; CO_2 injection until no further oil recovery (~100% of oil from high perm core; 0% from low perm core) followed by surfactant solution injection followed by CO_2 injection into both cores; 89% recovery of oil from the low perm zone subsequently attained [Casteel and Djabbarah, 1988].

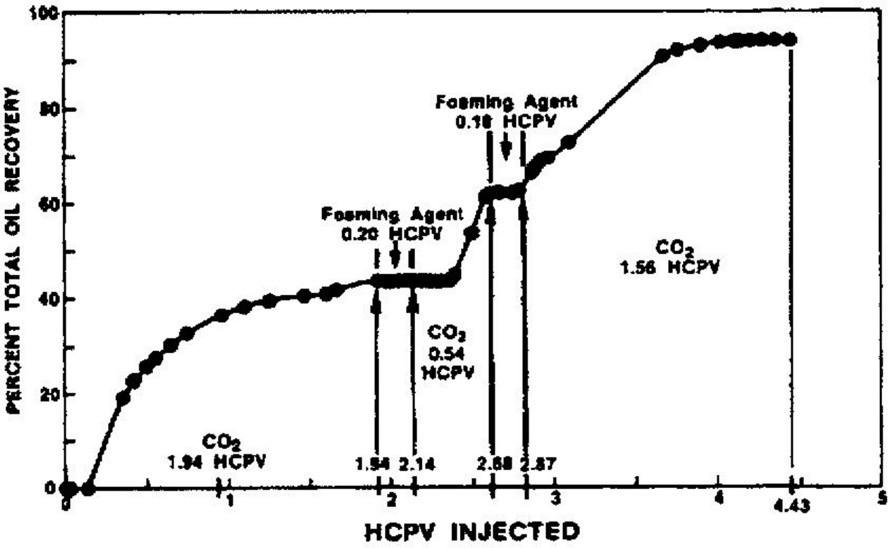


Figure 11.12.Same results as Figure 11.11, but with x-axis value of HCPV based on the total HCPV of both cores, and the oil recovery based on the total oil in both cores [Casteel and Djabbarah, 1988].

A dual core flood conducted by Chevron [Di Julio and Emanuel, 1989] also illustrated that most of the oil in two parallel cores of different permeability could be recovered by a waterflood, a CO_2 WAG that sweeps oil from the high perm core, followed by CO_2 foam that diverts CO_2 to the lower perm, oil-rich core, as shown in Figure 11.13.

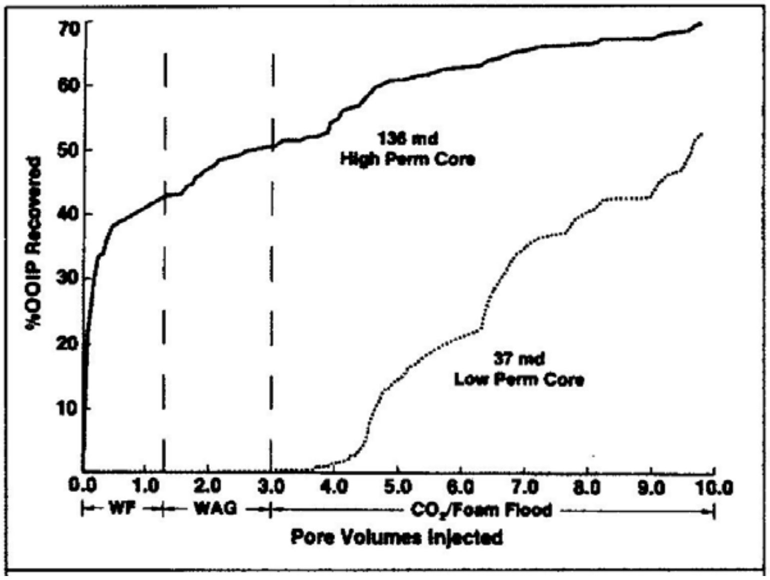


Figure 11.13. Oil recovery from dual parallel cores as a function of type of displacement process and PV injected; waterflood (WF) and CO_2 WAG recover oil from the high perm zone; the subsequent foam causes CO_2 to be diverted to the low perm zone [Di Julio and Emanuel, 1989]

These results suggest that it may be prudent to employ CO_2 WAG in a layered formation prior to introducing CO_2 foams in an attempt to recover oil from high perm zones before using strong foams that will form in the high perm zones and divert the subsequently injected CO_2 into lower perm oil-rich zones.

There have been several attempts to explain mechanisms responsible for the effect of oil on foam stability [Mannhardt et al, 2000], including oil spreading, emulsification of oil into lamellae, and pseudoemulsion film drainage.

In an aqueous foam, either oil or gas preferentially surrounds the high-pressure CO_2—conditions referred to as oil-spreading or water-spreading (oil non-spreading), respectively. Oil spreading typically occurs when oil saturation is high and gas-oil IFT is low. Although foams are more stable when water spreads and two-phase oil/water lamellae are not stable, spreading oil does not necessarily lead to the collapse of foam; it could even help to moderate the mobility of foam such that it becomes useful mobility control foam deep in the reservoir [Kuhlman, 1990]. Because spreading depends on saturations and interfacial tensions, each of which can change as a function of time and position in a formation, different spreading conditions can occur during a CO_2 flood. For example, water spreading is more likely to occur near the wellbore while oil spreading occurs at positions far removed from the wellbore. Spreading is shown schematically in Figure 11.14.

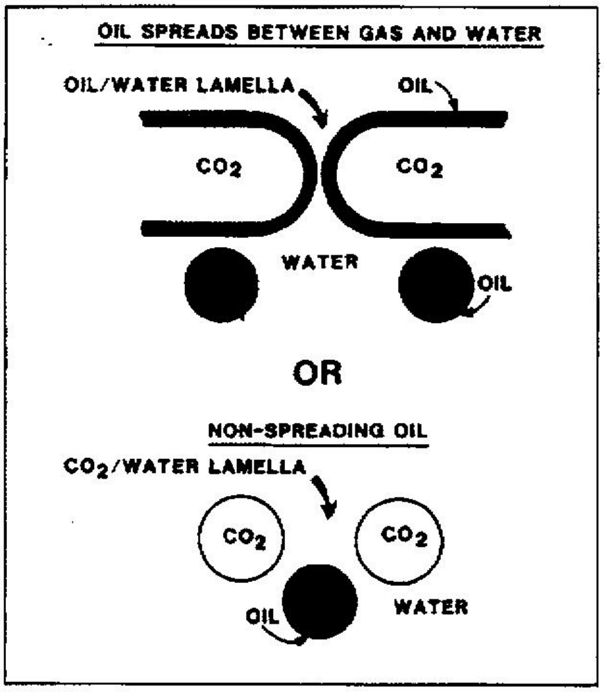


Figure 11.14.Cartoon illustration of spreading oil (oil is between CO_2 and gas) and non-spreading oil (CO_2 and gas in contact) [Kuhlman, 1990]

Another factor that may account for the typically negative impact of oil on CO_2 foam stability is related to oil emulsification. Oil can become emulsified and then imbibed into lamellae. The emulsified oil tends to de-stabilize the lamellae, which in turn leads to the degradation of the foam [Schramm and Novosad, 1990; Schramm and Novosad, 1992; Schramm and Novosad, 1993].

CT imaging of core floods conducted with mobile or residual oil can also shed light on the effect of oil on the performance of CO_2 foam. For example, Wellington and Vinegar [Wellington and Vinegar, 1988] demonstrated during a miscible flood that when CO_2 was injected into a horizontal core containing water and waterflood residual oil, the CO_2 (blue, injected on the left hand side) formed a single gravity tongue that overrode both the oil (doped to appear red) and the brine (yellow), as shown in Figure 11.15.

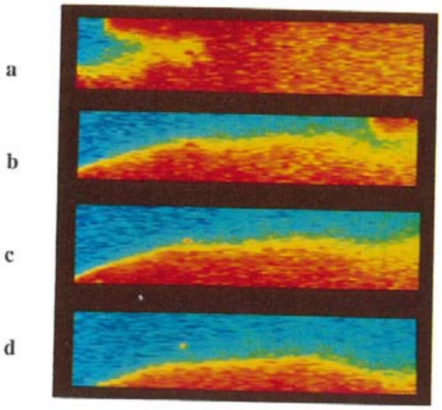


Figure 11.15. Gravity override as CO_2 (blue) is injected into a waterflooded core containing residual oil (red) and brine (yellow) [Wellington and Vinegar, 1988]

When the experiment was repeated with a 0.905wt% AEGS 25-12 surfactant solution injected prior to the CO_2, the occurrence of CO_2 foam behind the oil and brine became apparent, as shown in Figure 11.16.

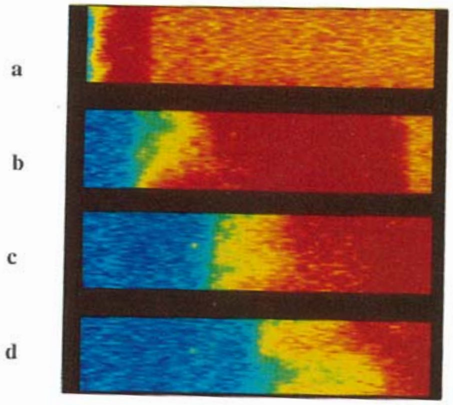


Figure 11.16. Foam formation as CO_2 (blue) in injected into a waterflooded core containing residual oil (red) and a surfactant solution (yellow) [Wellington and Vinegar, 1988].

When similar experiments were conducted with CO_2 at immiscible conditions ($P < MMP$) the oil phase prevented the CO_2 foam from forming, as shown in Figure 11.17 images [Wellington and Vinegar, 1987].

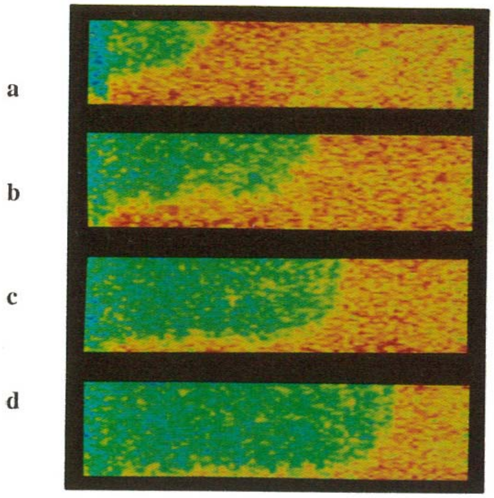


Figure 14a–d. CT reconstructions from Set No. 2, Experiment No. 1.

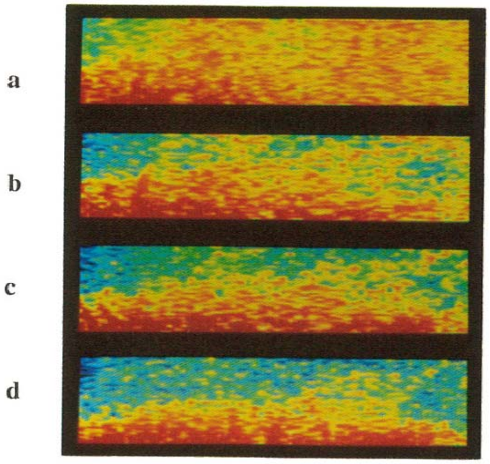


Figure 11.17. Gravity override occurs in the absence of a surfactant and in the presence of a surfactant solution at $P < MMP$. The CO_2 foam had difficulty forming (bottom set of images) and effectively displacing oil when the CO_2 was injected at immiscible conditions [Wellington and Vinegar, 1988].

A recent study [Farajzadeh, Andrianov and Zitha, 2009] confirmed their earlier findings [Farajzadeh, Andrianov, Bruining and Zitha, 2009] that foams can reduce the mobility of sub-critical or supercritical CO_2 if no oil is present in the core. The injection of an AOS surfactant solution into the core containing brine and oil at a pressure greater than the MMP prior to the introduction of CO_2 was shown to increase the utilization ratio of CO_2 (i.e., less CO_2 was required for the recovery of a given amount of oil). However, immiscible CO_2 foams were not advantageous compared to WAG because the oil prevented the formation of foams in the core. For example, consider the two displacements shown below (Figure 11.18) at immiscible CO_2

conditions: the top images correspond to the injection of CO_2 gas into a core that had been previously waterflooded, while the bottom images correspond to a waterflooded core in which a surfactant solution had been injected to generate foam in situ. In both cases, the aqueous phase (red) is predominant in the bottom half of the core at the start of the CO_2 flood, and residual oil (orange) is distinct as orange patches in the top half of the core. There is no evidence of a piston-like movement of a CO_2 front in the absence of a surfactant (top row of images) throughout the duration of the experiment. There is a distinct CO_2 front evident in the SAG process, however, as the CO_2 (blue) moves upward through the bottom half of the core (bottom row of images). However, as the CO_2 foam contacts the residual oil, the CO_2 front dissipates, indicating that the oil has de-stabilized the immiscible CO_2 foam.

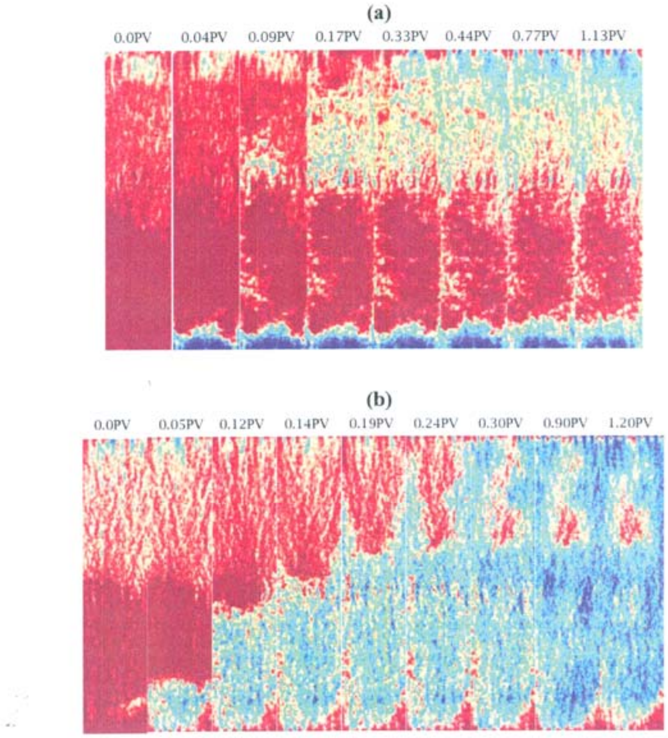


Figure 11.18. The deleterious effect of oil on immiscible CO_2 foam performance when the foam contacts the oil-rich top half of the porous medium [Farajzadeh, Andrianov and Zitha, 2009]

Surfactant Adsorption

One of the undesirable fates of surfactants intended to stabilize foams is adsorption. Surface active agents intended to stabilize foams by dissolving in the aqueous phase and then migrating to the CO_2/brine interface can also migrate to the surface of the porous medium. Tests are commonly performed with reservoir rock to assess the levels of adsorption (unfortunately, using a vast array of units of measure for the levels of adsorption). Simply put, the more surfactant that is lost to adsorption on rock surfaces, the less surfactant that is available for generating the mobility control foam and the more difficult it becomes to attain and maintain the desired level of mobility.

A simple illustration of the early stages of anionic and amphoteric (i.e., zwitterionic) surfactant adsorption is provided in Figure 11.19 [Mannhardt et al., 1993]. In the case of the anionic surfactant in the presence of a negatively charged Berea sandstone surface, the electrostatic repulsions result in a relatively low level of adsorption (a). If there are divalent ions present in the brine, however, their presence near the surface can lessen the negativity of the sandstone, thereby increasing adsorption (c). In the presence of Ca $^{+2}$ ions either in the limestone at its negatively charged surface or in the brine (b), or in the presence of a positively charged limestone surface (d), adsorption of the anionic may occur to a greater extent than that observed in the sandstone. (It is for this reason that the infrequent use of cationic surfactants is associated solely with carbonates rather than sandstones.)

In the case of the amphoteric surfactant, which carries both a positive and negative charge with the molecule, adsorption occurs onto Berea sandstone as the negatively charged surface interacts favorably with the positively charged portion of the surfactant (e). The presence of a dissolved calcium ion promotes adsorption as it causes the amphoteric surfactant to fold, thereby enabling the negatively charged portions of the surfactant to interact with the surface (g), or by enabling the stretched surfactant to interact with the Ca^{+2} ion, which also interacts with the negatively charged sandstone surface (g). In the case of a negatively charged limestone surface with some Ca^{+2} ions at the surface or in the brine, adsorption can occur between the negative portion of a stretched surfactant and the dissolved or surface Ca^{+2} species, or the positive portion of the amphoteric surfactant and the negatively charged surface. Finally, in the case of the positively charged limestone, the negative portion of the folded surfactant can interact favorably with the positive surface or the Ca^{+2} species of the rock surface.

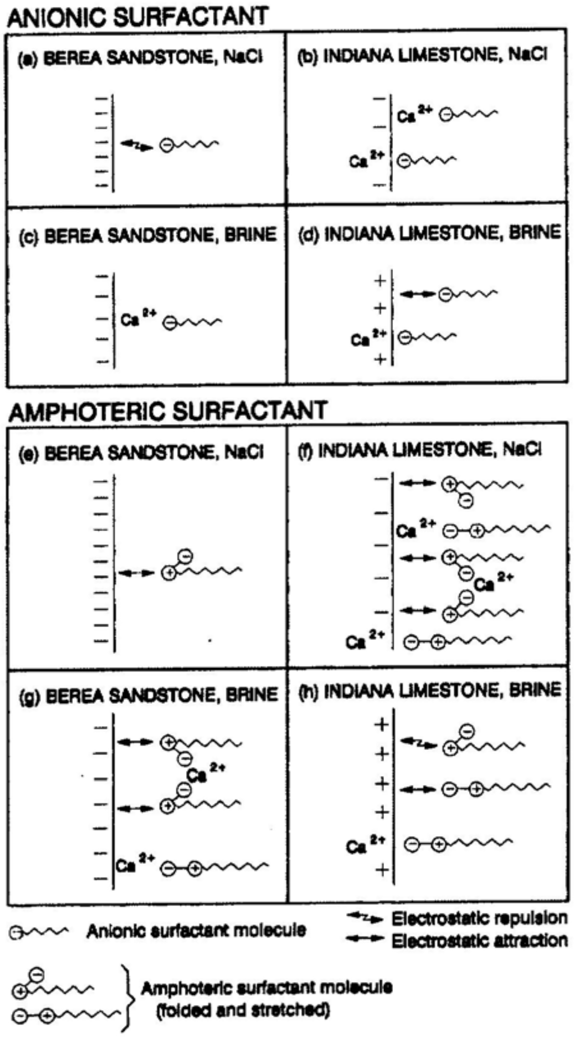


Figure 11.19.Attractive and repulsive interactions that can lead to adsorption of anionic or amphoteric surfactants onto sandstone or limestone; effects of dissolved or surface Ca^{+2} species are also illustrated [Mannhardt et al. 1993].

Because the surfaces of sandstone are typically positively charged, cationic surfactants (which have a negative charge on the surfactant and a positively charged counterion) are rarely employed in these studies. This is evidenced by the listings of water- and CO_2-soluble surfactants that have been selected for lab- and pilot-scale studies; anionic and non-ionic surfactants are predominant, while cationic surfactants are rarely employed. However, cationic surfactants may have broader applicability in carbonate reservoirs, where there may be reservoir conditions that can lead to positively charged surfaces and situations in which cationic surfactants exhibit lower levels of adsorption [Tabatabal et al., 1993]. It is also thought that in general, non-ionic surfactants are likely to yield the lowest levels of adsorption because they do not possess the positively or negatively charged functionalities within the surfactant molecule that are most likely to cause adsorption. The relatively few adsorption studies that include non-ionics, e.g., the work or Heller and Tsau [Heller and Tsau, 1992][Ren et al. 2011] confirm this assumption.

Numerous investigators have determined the extent of surfactant adsorption. One can employ a static test in which a crushed porous medium is immersed in a surfactant solution of known initial composition, and adsorption is measured as a function of time by observing the decline of surfactant composition in the brine. Alternately, one can flow a surfactant solution of known composition through a core during a dynamic test and determine the level of adsorption by measuring the concentration of surfactant found in the effluent stream. Desorption tests can subsequently be performed to determine how much of the adsorbed surfactant can be removed from the surfaces of the porous medium by the introduction of brine.

The results of several adsorption studies, which are reviewed in this section, will provide an understanding of the adsorption process and the levels of adsorption that are likely to occur during a CO_2 foam flood.

The generalized equilibrium relationship between the level of surfactant adsorption and surfactant concentration is illustrated in Figure 11.20 [Tabatabal et al., 1993].

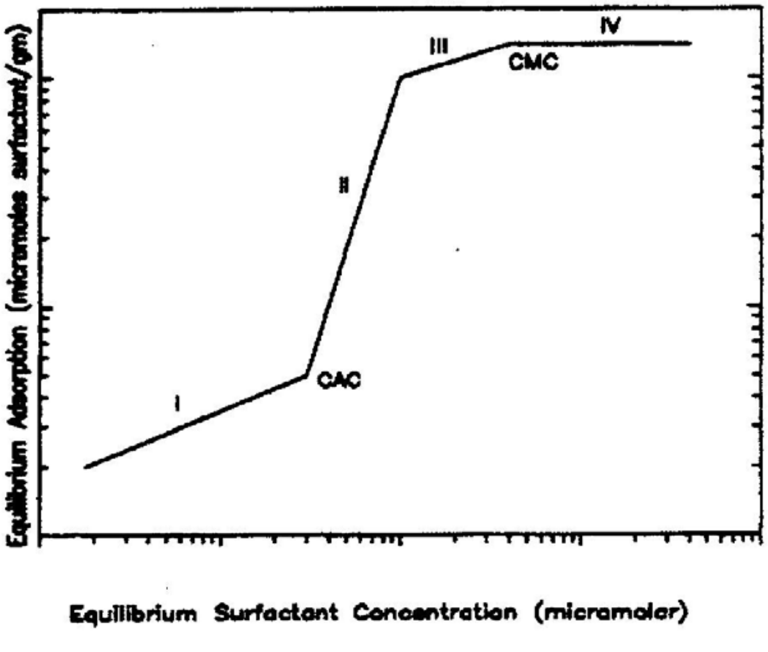


Figure 11.20. Equilibrium adsorption onto a rock surface as a function of surfactant concentration [Tabatabal, et al. 1993]

Within Figure 11.20, Region I corresponds to the lowest levels of surfactant concentration, well below the CMC. In this region there is a linear relationship between the adsorption of surfactant molecules and their concentration in the aqueous phase; therefore, this is referred to as a Henry's law region. In this range of concentrations, the adsorption is dominated by the electrostatic interactions between the surface and the surfactant molecule and there are low levels of surface coverage by the adsorbed species. Region II exhibits a sharp increase in adsorption for relatively small increases in surfactant concentration. This is attributable to the formation of monolayer (hemimicelle) or bilayer (admicelle) aggregates. Favorable thermodynamic interactions between the hydrophobic hydrocarbon tails greatly enhance the adsorption of surfactant in this region. Region III is denoted by a distinct or gradual leveling off of adsorption as surfactant concentration approaches the CMC. Region IV begins at the CMC, the concentration at which aggregates of surfactants self-assemble in solution, and extends to levels of higher surfactant with little additional adsorption occurring on the surface. The ability of the surfactant molecules to self-assemble into macromolecular assemblies in solution provides a competitive alternative to additional adsorption on the rock surface.

Similar results have been presented by others. For example, Figure 11.21 presents the generalized shape of the adsorption vs. concentration plot along with a Langmuir isotherm (which is commonly used to fit surfactant adsorption data) fit to surfactant concentration data above the CMC (Cf > 1 on the x-axis). At very low surfactant concentrations that fall below the CMC (Cf < 1 on the x-axis), however, the level of surfactant adsorption falls far below the level expected from the Langmuir isotherm typically used to describe adsorption [Kuhlman et al., 1992]. For this reason, Kuhlman and coworkers suggested the use of surfactants at very dilute concentrations (concentration < CMC) to generate

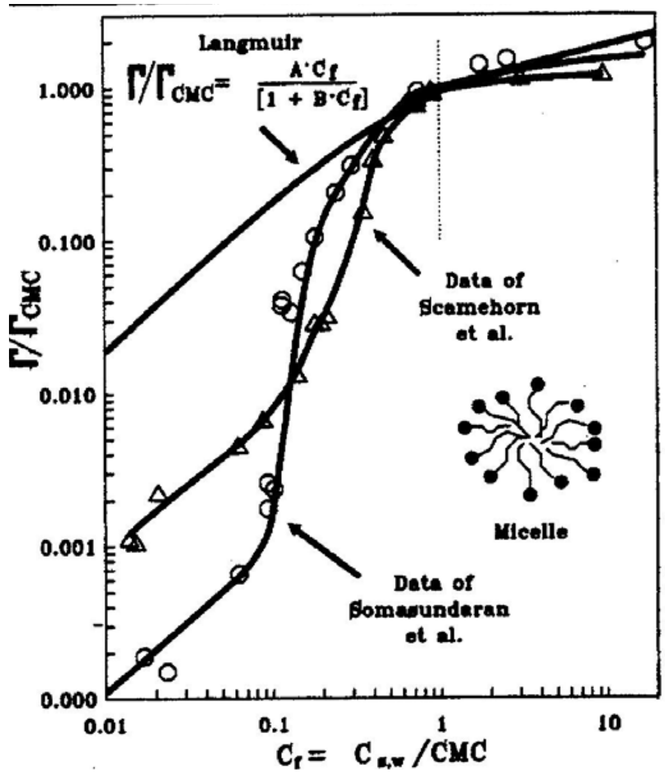


Figure 11.21. Generalized shape of the adsorption vs. concentration plot along with a Langmuir isotherm for an alkyl benzene surfonate [Kuhlman, et al., 1992]

One of the challenges of obtaining and interpreting equilibrium adsorption data is establishing that equilibrium conditions have been achieved. In Figure 11.22 three types of surfactant adsorption were monitored: adsorption from a solution onto crushed rock, adsorption from a solution into a small cube of the porous medium, and circulation of the surfactant solution through a core of the porous medium [Grigg and Mikhalin, 2007]. As expected, diffusion of a surfactant solution into a small solid cube of the porous medium is a very slow process, while the adsorption of the surfactant onto crushed porous media is quick.

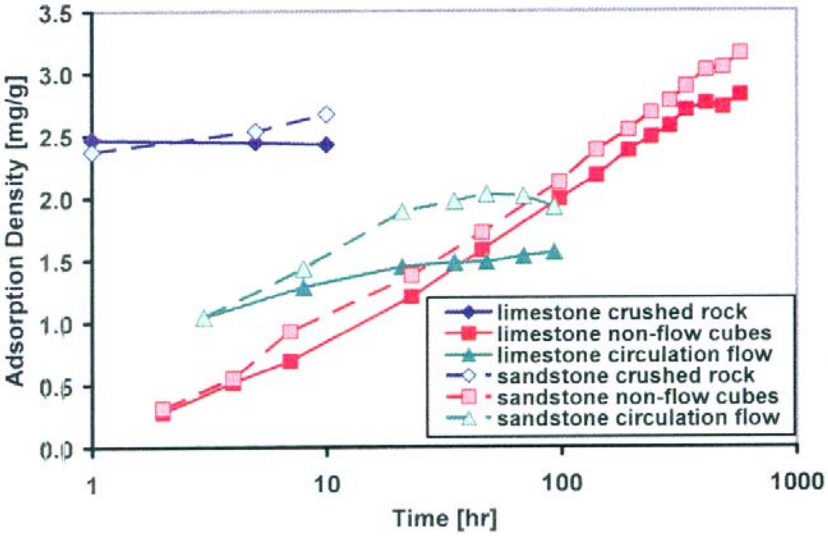


Figure 11.22. The time required to attain equilibrium conditions during adsorption experiments is related to the nature of the experiment: adsorption onto a crushed rock takes several hours; adsorption during a circulating experiment takes 10s of hours, and adsorption into a solid cube of the porous medium takes many hundreds of hours [Grigg and Michalin, 2007].

There are numerous reports of surfactant adsorption in the literature. Several examples are provided in this section to provide an understanding of the approximate amount of surfactant adsorption likely to occur for surfactants that have been considered for stabilizing CO_2-in-brine foams.

Bernard reported that roughly 0.1 pound of Alipal CD 128 surfactant, which was introduced to the core as a 1.0wt% CD 128 solution, was adsorbed per barrel of pore space [Bernard, 1980].

The levels of anionic surfactant adsorption as determined in static tests were determined over the 0.1–1.0wt% range for a crushed carbonate core and a crushed sandstone core as shown in Figure 11.23 [Casteel and Djabbarah, 1988]. Each surfactant is the ammonium salt of an ethooxylated, sulfated alcohol.

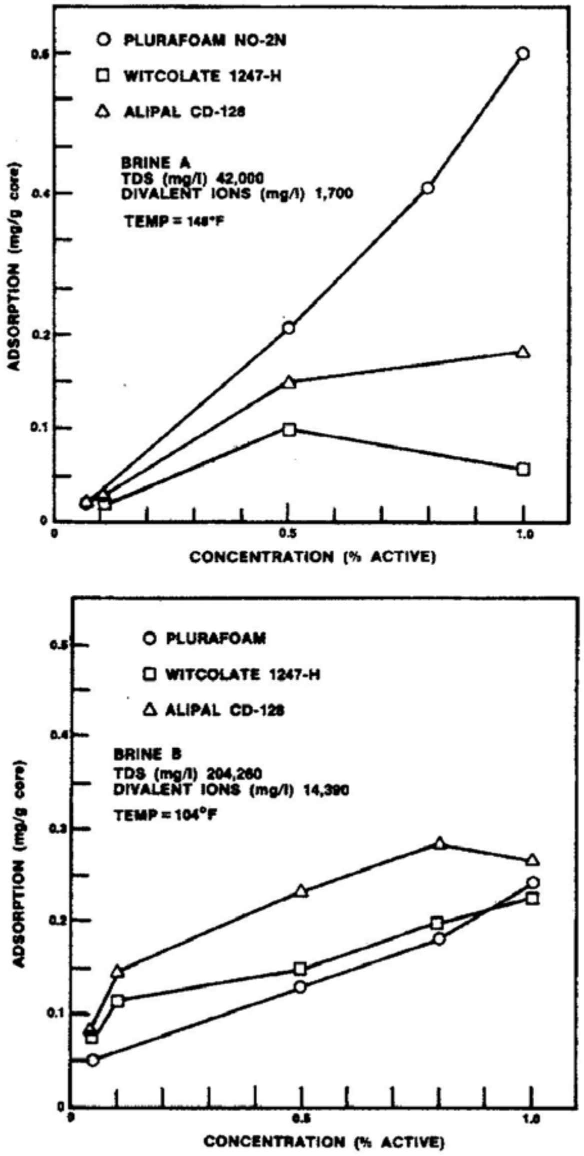


Figure 11.23. Static adsorption results for several anionic surfactants. Top: crushed carbonate rock. Bottom: crushed sandstone rock [Casteel and Djabbarah, 1988].

Figure 11.24 illustrates results from the adsorption of cationic surfactants on crushed dolomite and calcite [Tabatabal et al., 1993]. Under these conditions, the levels of adsorption associated with the cationic surfactant cetylpyridinium chloride were significantly less than the adsorption that occurred with the anionic surfactant sodium dodecyl sulfate.

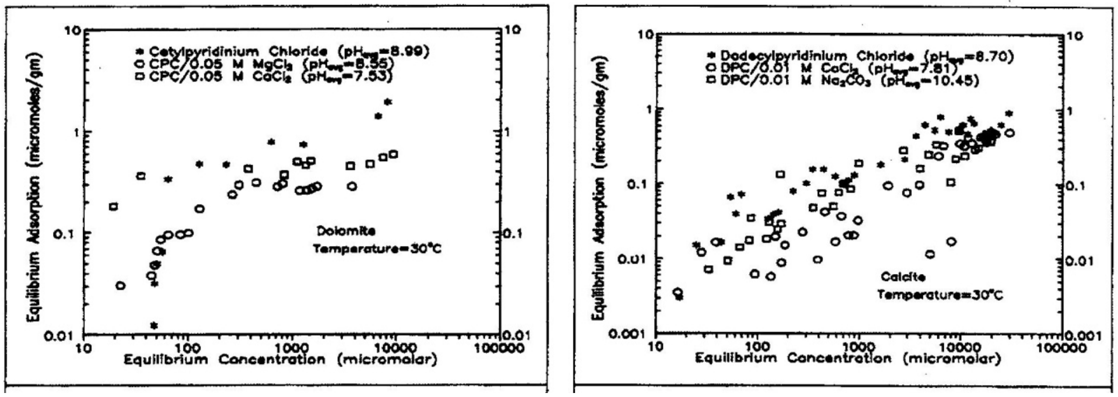


Figure 11.24. Equilibrium adsorption levels for the cationic surfactant cetylpyridmium chloride on crushed dolomite and calcite [Tabatabal, et al., 1993]

Figure 11.25 shows the adsorption as a Langmuir isotherm for the surfactant Chaser SD 1000 (designed for steam foam applications) at a variety of concentrations [Friedmann, Chen, and Gauglitz, 1991]. Surfactant adsorption decreases significantly as the temperature is increased from 120 °C to 220 °C.

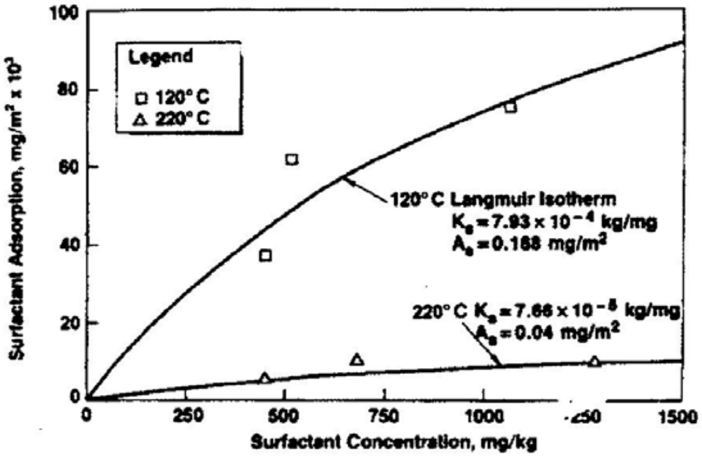


Figure 11.25. The effect of surfactant concentration and temperature on the adsorption losses [Friedmann, Chen, and Gauglitz, 1991]

The level of adsorption will be related to the properties of the rock surfaces, and varying levels of adsorption can be expected from the same surfactant solution for sandstones and carbonates, as shown in Figure 11.26 [Bai et al., 2010]. Not all surfactants reach equilibrium as quickly as shown (hours) in some thermal foam studies.

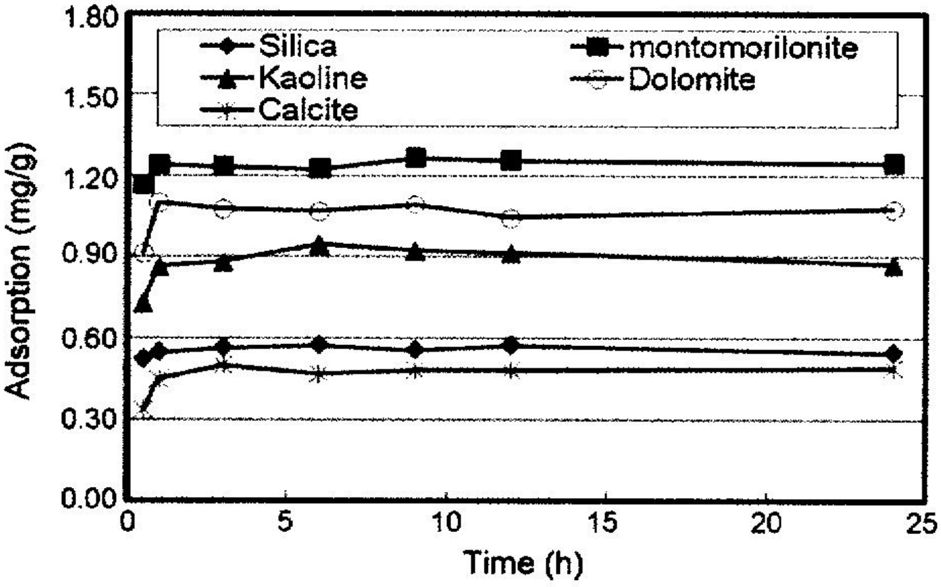


Figure 11.26. Varying levels of adsorption of anionic Chaser CD 1045 from a 500mg CD/liter 2% brine solution at 40 °C [Bai et al., 2010]

Figure 11.27 shows the typical surfactant adsorption results derived from data associated with the flow of an aqueous surfactant solution through a sandstone core [Bai et al., 2010]. Equilibrium conditions are attained in 10s of hours, and the level of adsorption increases with surfactant concentration.

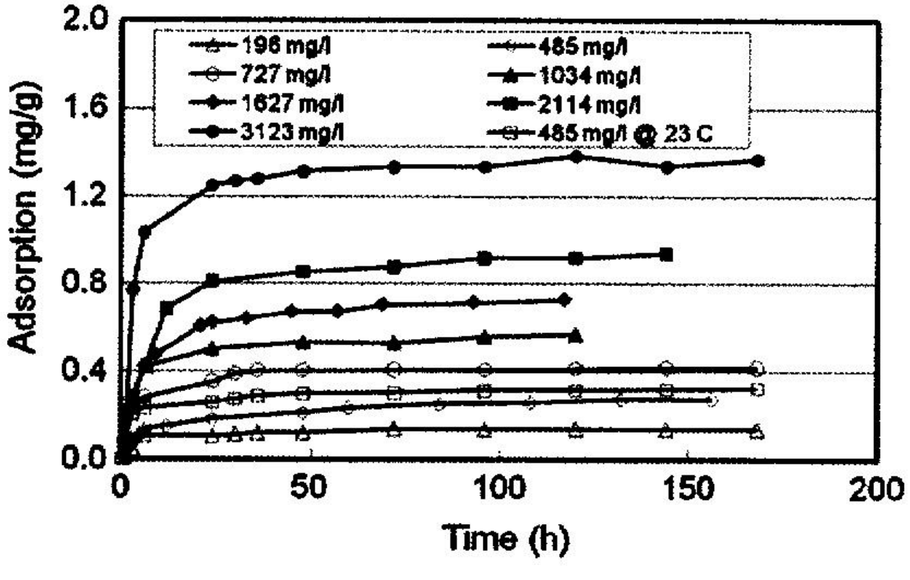


Figure 11.27. Adsorption of Chaser CD 1045 circulated through Berea sandstone at 23 °C from 2% brine solutions as a function of CD concentration in the brine [Bai et al., 2010]

While performing lab studies for a CO_2 foam project in Turkey, researchers [Alkan et al., 1991] measured the retention of Alipal CD 128 in brine onto the surfaces of a Bati Raman core and a fractured core, as shown in Figure 11.28.

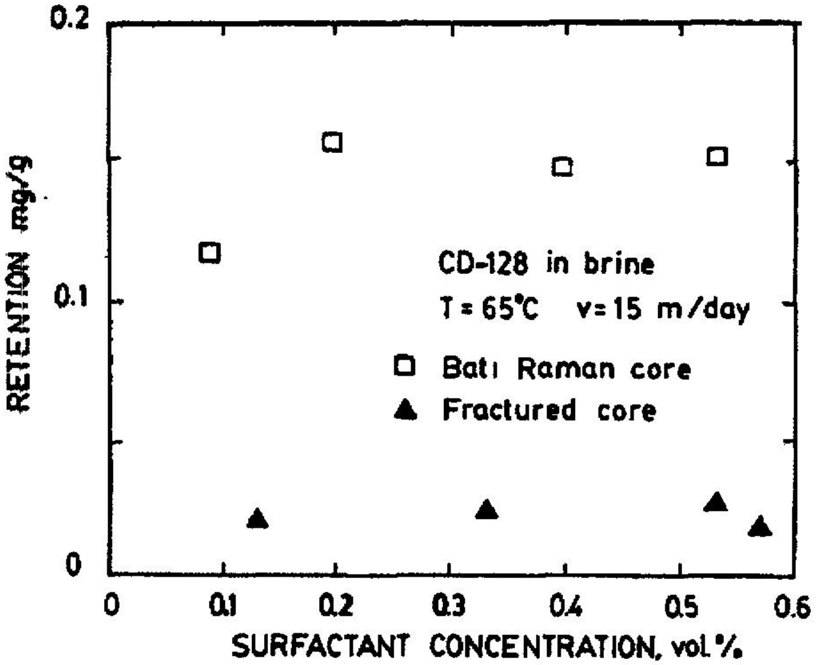


Figure 11.28. Adsorption of Alipal CD 128 onto a Bati Raman core and a fractured core [Alkan, et al., 1991]

In a study of foams being designed for mobility control applications, the levels of adsorption of commercial anionic and non-ionic surfactants on dolomite limestone cores designated as Type I (permeability from 15 to 26 mD, and porosity from 12.5% to 14.7%) or Type II (permeabilities ranging from 133 to 640 mD, and porosity from 13.2% to 18.6%) were assessed. Figure 11.29 illustrates the levels of adsorption at the relatively low surfactant concentrations associated with mobility control foams [Tsau and Heller, 1992].

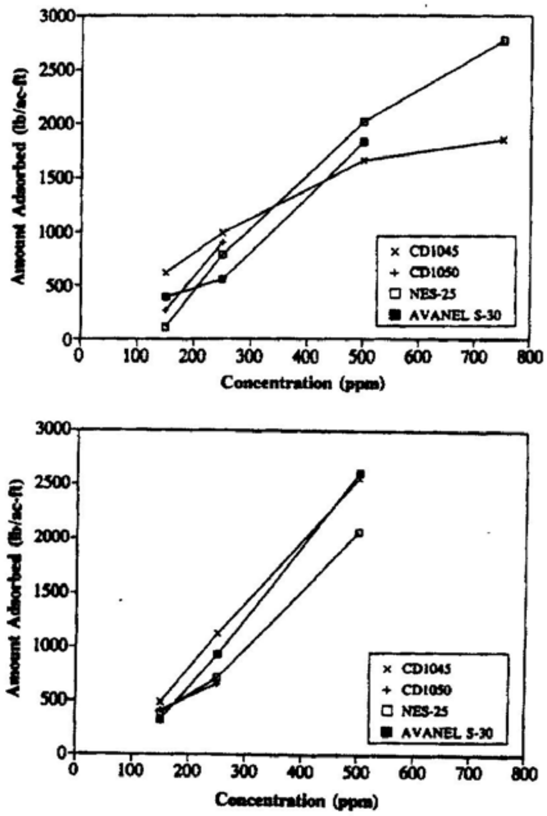


Figure 11.29. Top: Adsorption results for surfactant solution flowing at 10 cc/hr. into a 0.5 in. diameter low perm dolomite limestone core. Bottom: Adsorption results for surfactant solution flowing at 5 cc/hr. into a 0.5in diameter high perm dolomite limestone core [Tsau and Heller, 1992]

It was noted that for this particular dolomitic limestone field, at the 250–500 ppm (0.02–0.05 wt%) range of concentrations associated with mobility control foams, the non-ionic surfactant CD 1050 yielded relatively low levels of adsorption compared to the anionics, and also yielded foams that effectively reduced the mobility of the CO_2 [Tsau and Heller, 1992].

This study [Tsau and Heller, 1992] was also one of the few that recognized that adsorption results are presented in many different units of measure, and therefore they summarized their results in a table that allows one to appreciate how lab-scale measurements translate into field-scale units that can be used to estimate cumulative surfactant adsorption losses (pounds) in a field on known thickness (ft.) and area (acres).

Table 11.1. Amount of adsorption described by several different units of measure; adsorption losses increase from hundreds of pounds/acre ft. to thousands of pounds/acre ft. as surfactant concentration increases from 150 to 750 ppm [Tsau and Heller, 1992].

Surfactant Type	Rock porosity (%)	Surfactant conc. (ppm)	Amount of adsorption		
			mg/cc rock	lb/ac-ft	mg/gm rock
CD1050	18.6	150	0.098	265.70	0.0418
		250	0.331	900.11	0.1416
CD1045	13.2	150	0.226	616.57	0.0910
		250	0.364	989.18	0.1460
		500	0.609	1655.49	0.2443
		750	0.680	1849.38	0.2730
	18.7	150	0.254	690.93	0.1089
		250	0.352	956.14	0.1597
		500	0.728	1978.36	0.3118
		750	0.802	2181.53	0.3438
NES-25	16.6	150	0.040	108.24	0.0166
		250	0.290	787.70	0.1210
		500	0.740	2014.95	0.3096
		750	1.019	2771.80	0.4258
AVANEL S-30	14.6	150	0.143	387.78	0.0581
		250	0.204	554.53	0.0832
		750	0.672	1827.46	0.2742

Rock type: #109-110 (Type II)
Flow rate: 5 cc/hr

Figures 11.30 and 11.31 illustrate a dynamic adsorption test in which the effect of employing a sacrificial pad of surfactant prior to commencing co-injection of CO_2 and surfactant solution is observed [Liu et al., 2006]. During these tests, a solution of known surfactant concentration is injected into a core at a constant flow rate for a specified amount of time. The concentration of the surfactant in the aqueous phase leaving the core is measured as a function of time until a steady state is attained in which the surfactant concentration in the core and leaving the core is the same as the concentration entering the core. A material balance on the surfactant can then be used to determine how much surfactant is retained on the rock surfaces within the core of known porosity and mass. In this example, the use of a sacrificial pad of surfactant solution did not have an effect that was discernible given the level of scatter in the data.

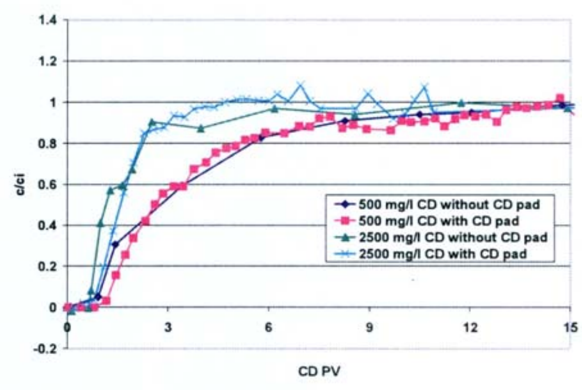


Figure 11.30. Concentration of surfactant in the core effluent relative to the injected concentration; the adsorption of Chaser CD 1045 on an Indiana limestone core [Liu et al., 2006]

The amount of retained surfactant that can be removed from the core during the injection of brine can be determined by monitoring the effluent concentration of the surfactant. In this example, desorption appears to be a slower process in which recovery of 100% of the adsorbed surfactant does not occur.

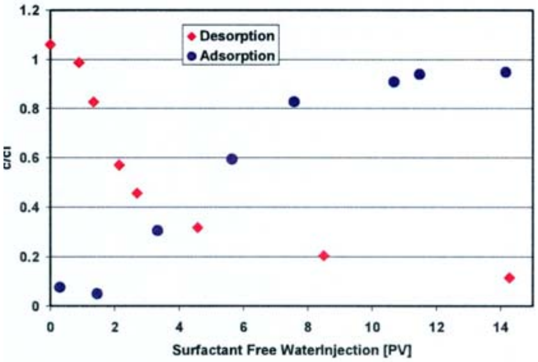


Figure 11.31. Desorption of the surfactant from the Indiana limestone core via brine injection [Liu et al., 2006]

The most common operational consideration that has emerged from these studies has been the introduction of a "sacrificial slug" of surfactant solution into the formation to satisfy the adsorption capacity of the formation prior to the SAG slug injections. Total adsorptive losses of the foam stabilizing surfactants can be high, especially if high concentration conformance control surfactant solutions are employed. For example, in the plots presented in this section of the report, levels of surfactant adsorption at surfactant concentrations of ~0.25–0.5wt% are on the order of 0.05–5.0 mg surfactant per gram of rock. To illustrate the magnitude of adsorption that can occur during a field application, consider a surfactant that is adsorbed at 2.5 mg surfactant/g sandstone; about 55,000 tons of surfactant would be adsorbed in a 10ft thick, one square mile formation (17,200 lb./acre ft. for the 6,400 acre ft. formation) [Grigg and Michalin, 2007].

12. Nanoparticle-Stabilized Foams

The tendency of extremely small particles to migrate to liquid-liquid interfaces has been exploited in the chemical engineering industry as a means of separating a mixture of extremely fine solids. For example, consider a mixture of fine hydrophobic and hydrophilic particles resting at the bottom of an aqueous phase. If a second liquid phase is added to this system, such as a hydrocarbon liquid that is less dense than water, and the liquids and solids are mixed and then allowed to settle under quiescent conditions, the hydrophobic particles will collect at the water-oil interface. A typical illustration of a model system in which a spherical particle suspended at a planar liquid-liquid interface is shown in Figure 12.1 [Perry and Green, 1997; Winitzer, 1973]. Models of these systems indicate that collection of particles at the interface is favored when the three-phase contact angle, as measured through the receiving or collecting phase, is between 0° and 180° [Winitzer, 1973; Henry et al., 1980; Smith and Van de Ven, 1981].

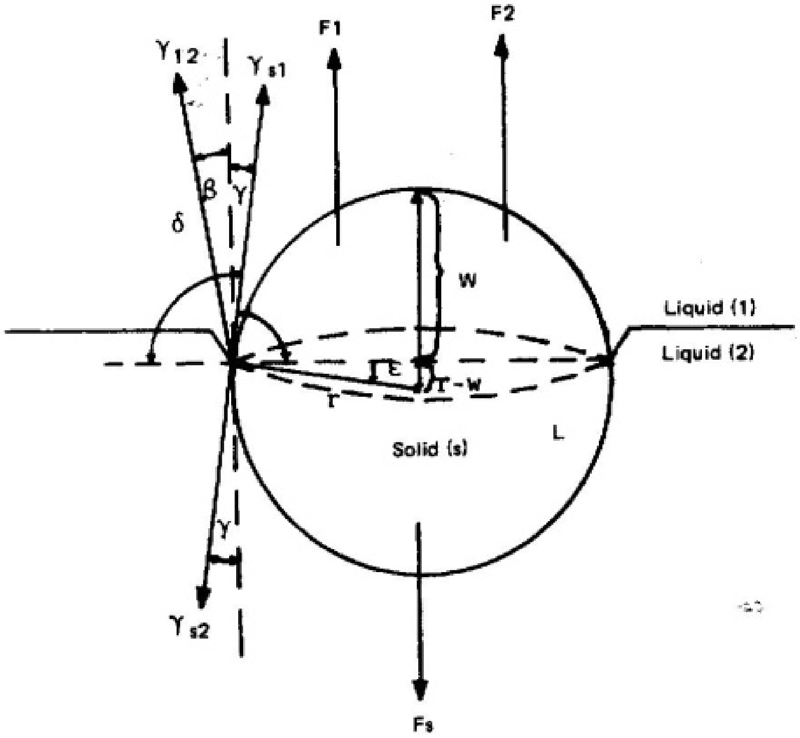


Figure 12.1. Illustration of the surface and buoyancy forces acting upon a spherical particle at a planar liquid-liquid interface [Perry and Green, 1997; Winitzer, 1973]

In general, small, hydrophobic particles can be drawn to the interface or coat the surface of small droplets of the hydrocarbon liquid, which may accumulate at the interface or settle to the bottom of the aqueous phase depending on the density of the particle-coated droplet.

Initially, these types of liquid-liquid separations were employed with conventional fluids that were relatively non-volatile at ambient conditions. For example, very fine ash particles could be removed from coal-derived liquids via the addition of an aqueous phase. Micronized coal particles could be drawn away from the water in which they originally resided via the addition of hexane, leaving the ash at the bottom of the aqueous phase and the coal particles at the interface. The activated carbon particles found in an aqueous slurry of fly ash and carbon could be recovered via the addition of hexane, which caused the activated carbon particles to accumulate at the water-hexane interface.

This concept was subsequently applied to several separations involving high-pressure liquid CO_2 as the hydrophobic phase. Chiang and co-workers developed the LICADO process and successfully tested it at the pilot-scale at the University of Pittsburgh [Chi et al., 1988]. In this process an aqueous slurry of micronized coal, composed of black hydrocarbon-rich particles and white liberated ash particles, was contacted with liquid CO_2. The coal fines were collected at the water-CO_2 interface while the ash particles were retained in the aqueous phase.

Enick and co-workers were able to separate pure gold particles from an aqueous slurry of micron-scale gold and silica via the addition of liquid CO_2. After mixing, the hydrophobic gold particles accumulated at the gold-CO_2 interface or formed small gold-coated droplets of CO_2. Attempts to recover liberated gold particles from an aqueous slurry of crushed Australian gold ore at the water-CO_2 interface were unsuccessful, however, because the liberated gold particles retained an extremely thin surface coating of quartz, rendering them hydrophilic [Shi et al., 1999; Shi et al., 2000].

Golomb, Ryan, and co-workers noted that small particles such as limestone could ameliorate seawater acidification concerns during ocean sequestration [Golomb et al., 2004]. In this process, droplets of CO_2 exiting a diffuser roughly 500 meters below the surface of the ocean would begin to form hydrates (with a density greater than that of the brine) that would sink to the ocean floor. The co-injection of an aqueous slurry of crushed limestone along with the liquid CO_2 would result in the limestone coating the CO_2 as it exits the diffuser. The $CaCO_3$-coated globules (particle-coated droplets) of CO_2-in-brine would tend to sink and form a dense emulsion plume of limestone-stabilized CO_2 globules in brine that would sink several hundred meters below the diffuser until neutral buoyancy was attained in the stratified ocean. After equilibration, these globules would fall out of the plume and head to the desired sequestration site—the ocean floor. Relative to injecting only CO_2 into the ocean waters at the diffuser, this co-injection of limestone slurry with the CO_2 would greatly diminish the amount of seawater acidification expected to occur around the release point. Golomb, Ryan, and co-workers continued their experimental studies of CO_2-in-water and water-in-CO_2 emulsions [Golomb et al., 2006] and modeling of the crushed limestone-enhanced ocean sequestration process [Golomb et al., 2007].

Johnston and co-workers pioneered the use of nanoparticulate silica for generating Pickering emulsions (particle-stabilized emulsions) of CO_2-in-water as an alternative to surfactant-stabilized CO_2 foams for "practical applications" [Dickson et al., 2004]. (Although not mentioned explicitly, given the expertise and experience of Johnston's group, it seems apparent that one of these applications would be mobility control foams for EOR.) Figure 12.2 illustrates that a contact angle θ of 0^o to 90^o was expected for CO_2-in-water emulsions to be stabilized.

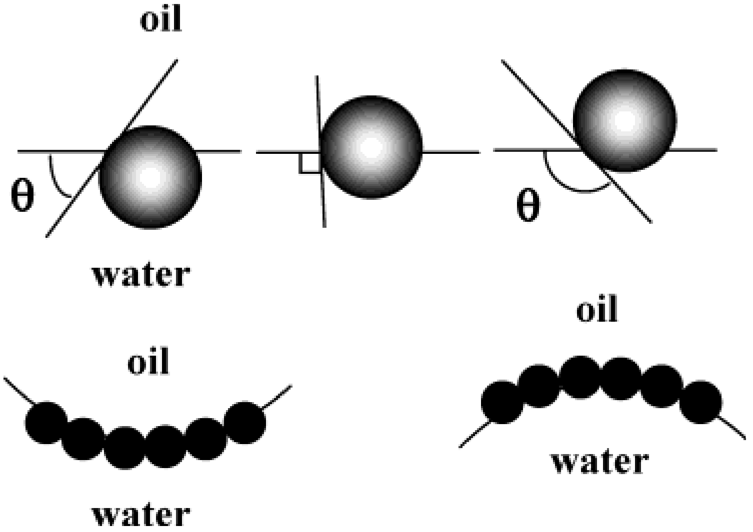


Figure 12.2. "(Top) Schematic demonstrating the relationship between contact angle (measured through the aqueous phase) and the position of a spherical particle at the planar oil-water interface; θ < 90° (left), θ ~ 90° (center), and θ > 90° (right). (Bottom) Expected emulsion morphology based on contact angle. For θ < 90°, o/w emulsions are favored (left), and for θ > 90°, w/o emulsions are expected." [Dickson et al., 2004]

Amorphous fumed silica particles with varying degrees of hydrophilicity were added to water in a concentration of ~2%, and CO_2 was then introduced. The mixture was then stirred and sheared, yielding CO_2-in-water emulsions. It was determined that emulsion stability increased with silica concentration, increased shear, and increased CO_2 pressure/density. Emulsion stability also increased when the hydrophilicity of the silica surface was decreased from its greatest degree of hydrophilicity (100% SiOH) to 76% SiOH, which lowered the contact angle and increased the attachment energy of the particles at the CO_2-water interface. Fumed silica samples at lower degrees of hydrophilicity, down to 20% SiOH, did not yield stable CO_2-in-water emulsions. (Subsequently, these researchers also generated water-in-CO_2 Pickering emulsions [Adkins et al., 2007].)

Although stabilizing foams with small particles may be easy to accept for large, agitated vessels, the notion of injecting an aqueous dispersion of particles into a porous medium may not appear to be a viable option. It is easy to envision the particles either being too large to enter the pores, or perhaps becoming trapped in restrictive pore throats. Although this would certainly be the case for micron-scale particles, the nanoparticles used in this technology are significantly smaller than the micron-scale pores associated with limestone and sandstone with permeability values commensurate with oil-bearing zones. Commercially available fumed silica particles can be obtained with primary (individual) particle diameters of ~5 nanometers. When dispersed in water, these particles (with diameters smaller than the visible wavelength of light) render the solution transparent. It is apparent that the displacement of such a dispersion into a porous medium could be readily accomplished under these conditions. Further, the subsequent or simultaneous injection of dense CO_2 into the porous medium could generate in situ mobility control foams.

Johnston and co-workers successfully generated CO_2-in-water foams in porous media composed of 180 micron glass beads packed in an HIP column using fumed silica as the stabilizer [Espinosa et al., 2010]. The idea of generating CO_2-in-brine foams in situ by co-injecting or alternately injecting an aqueous dispersion of nano-silica into a porous medium followed by the injection of CO_2 was intended to provide an alternative to surfactant-based CO_2 foams for mobility and/or conformance control. Advantages of this technology include the long-term stability of silica relative to surfactants, the ease of introducing a stabilizer that does not have to dissolve and remain dissolved in a fluid phase, an energy barrier to the desorption of the nano-particles from the CO_2-water interface, and the absence of adsorption losses that are analogous to those that occur with ionic surfactants. In their study, Johnston and coworkers tested a hydrophilic nano-silica with a covalently bound coating of PEG oligomers, and a "salt tolerant", proprietary nano-silica from 3M that was conjectured to have a more substantial PEG coating.

The results of this study are summarized in the following three photos in Figure 12.3 and described graphically in Figures 12.4 through 12.8.

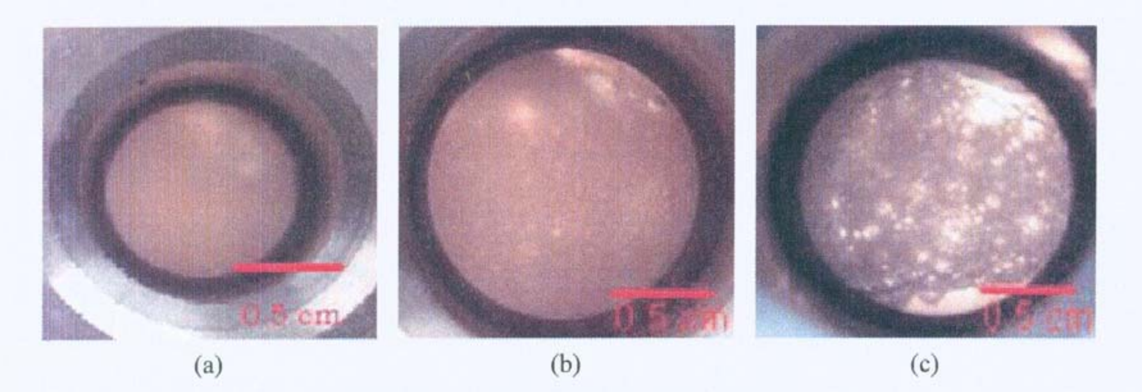


Figure 12.3. Various size CO_2 droplet sizes in nano-silica stabilized foams. The red bar is 0.5 cm, or 500 microns, long [Espinosa et al., 2010].

There appears to be a limiting concentration of the nanoparticles in brine (~ 0.04%) below which it is not possible to generate low-quality foam, and this concentration appears to increase to ~0.1wt% as the foam quality increases. There also appears to be an upper limit to the phase volume ratio between values of 20–30 (which corresponds to foam quality values of 95%–97%) above which a foam cannot be stabilized.

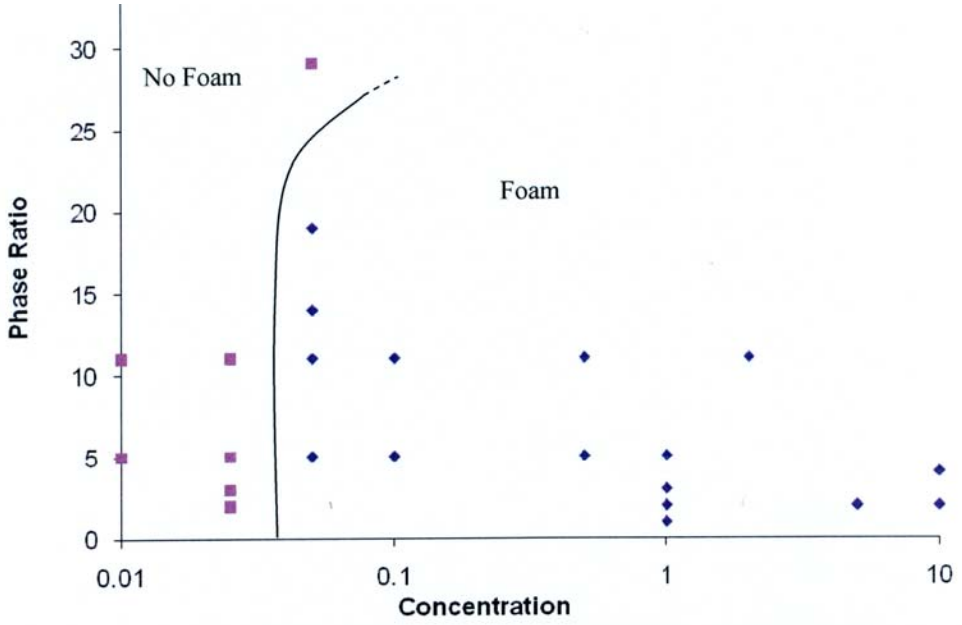


Figure 12.4. The effects of phase ratio (volume of CO_2/volume of water) and nanoparticle concentration on the ability to generate a foam [Espinosa, et al., 2010]

Capillary viscometry of the foams exiting this packed column was employed to provide an assessment of the degree of apparent viscosity enhancement that could be realized with particle-stabilized foams. As shown in Figure 12.5, the foams caused the pressure drop needed to displace the fluid through the same capillary tubing to increase by a factor of 2–20 times relative to displacing pure CO_2. Therefore, the foams had an apparent viscosity that was 2–20 times greater than that of CO_2—a value commensurate with mobility control foams. Higher apparent viscosity values were realized with higher quality (i.e., higher phase ratio) foams [Espinosa et al., 2010].

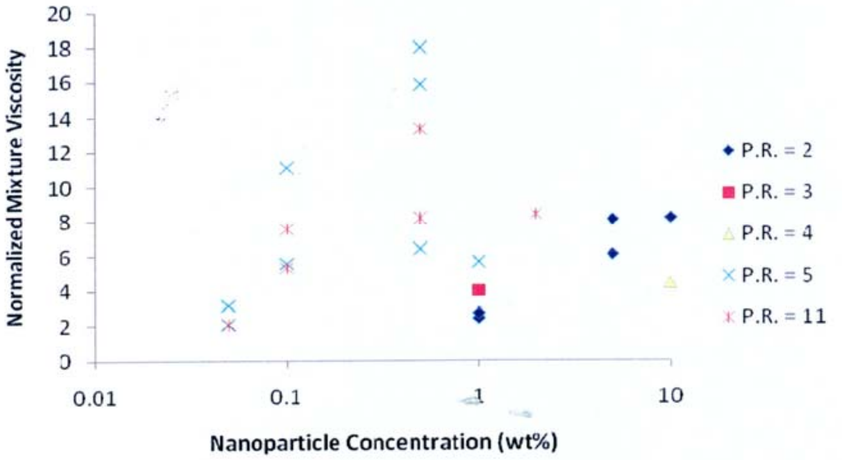


Figure 12.5. The effect of concentration and foam quality on the apparent viscosity of the nano-particle foam relative to pure CO_2 [Espinosa et al., 2010].

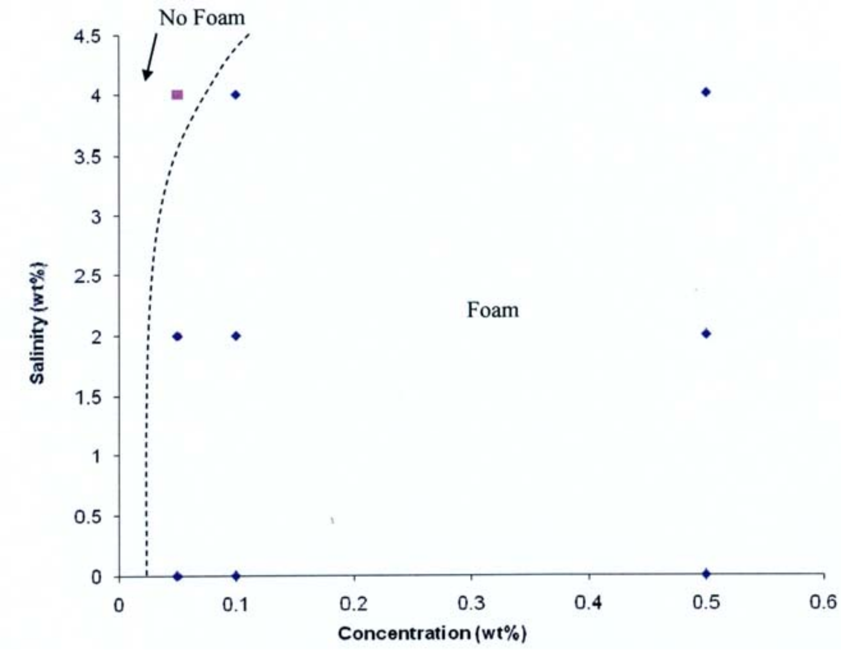


Figure 12.6. At a CO_2/brine phase volume ratio of 5, the ability to stabilize a foam with nanoparticles increases with decreasing salinity and increasing particle concentration [Espinosa et al., 2010].

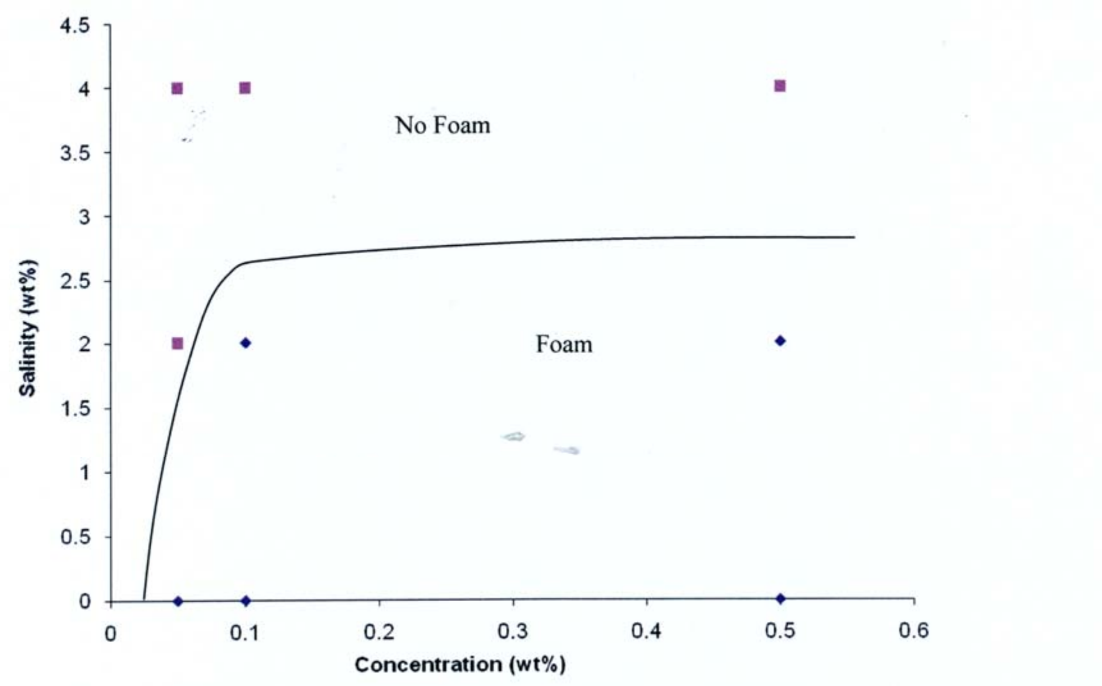


Figure 12.7. At a CO_2/brine phase volume ratio of 1:1, the ability to stabilize a foam with nanoparticles increases with decreasing salinity, increasing particle size, and decreasing phase volume ratio (compare with previous figure, Figure 12.6) [Espinosa et al., 2010].

An increase in TDS of the brine also makes it more difficult to stabilize a foam using nanoparticles, and this effect is enhanced at higher values of the phase ratio (i.e., higher quality foams) as shown in the following two figures [Espinosa et al., 2010].

There also must be sufficient shear in order to generate a nano-particle stabilized foam in situ. The results illustrated in the following figure below indicate a shear rate of roughly 4,000 s^{-1}; it may not possible to generate foam in this porous medium of glass beads [Espinosa et al., 2010].

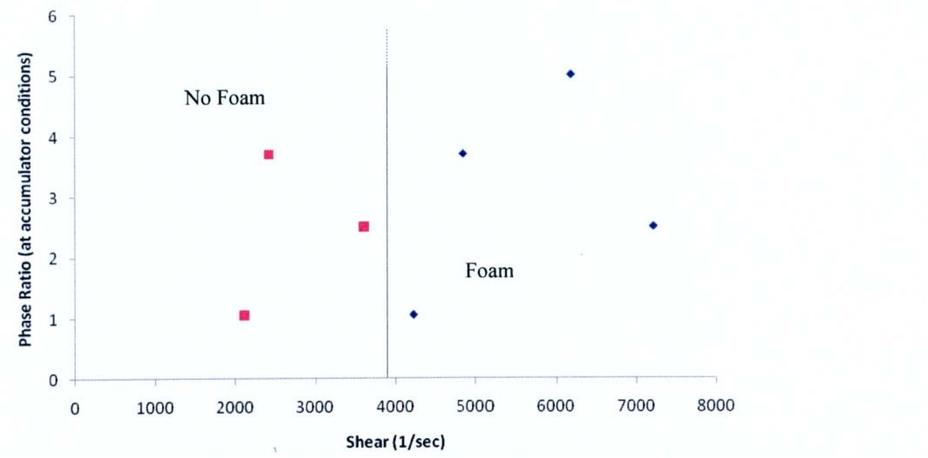


Figure 12.8. Foam generation in an HIP column packed with 180 micron glass beads requires a shear rate of approximately 4,000 s^{-1} [Espinosa et al., 2010].

In summary, nanoparticle-stabilized foams may provide a novel means of generating mobility control foams, and the use of alternating or simultaneous injections of aqueous nano-silica dispersions and CO_2 may provide an alternative to the use of surfactants, especially in very high temperature reservoirs where the surfactants may tend to degrade. It is possible to purchase massive quantities of fumed silica at ~$4/lb., and proof-of-concept tests in idealized porous media have shown that it is possible to propagate these dispersions through a porous medium without the nanoparticles being lodged in pore throats or retained at the surface of the porous media. Although there have promising preliminary laboratory-scale tests, this technology is still in its infancy and it is not surprising that there have been no core tests, lab-scale oil recovery tests, pilot tests, or field tests of these types of foams published to date.

13. Carbon Dioxide Field Tests Using Foam, Gel, Foam Gel, and Pre-formed Particle Gel

In this section, a review of mobility and/or conformance control foams in gas-injection field tests is provided based on prior reviews [Smith, 1988b; Turta and Singhal, 1998; Hanssen, Holt, and Surgechev, 1994] and descriptions of individual pilots found in the literature.

SAG Field Tests with Air as the Gas

Siggins Field Air Injectivity Tests [Smith, 1988b].

A surfactant solution-alternating-air SAG process was tested at the Siggins Field in an attempt to determine the effects of foam on injectivity of the fluids and the water injection profile. The injector well was surrounded by six producers. The surfactant solution was based on an alkyl sulfate with small amounts of amide stabilizers at concentrations of 0.5, 1.0, and 1.5wt% in water, and the gas was air. The air–aqueous volumetric ratio at reservoir conditions was 9:1, yielding a 90% quality foam with overall surfactant volumetric concentrations of 0.05, 0.1, and 0.15%. An alternating SAG injection scheme and a pre-formed foam generated in a packed bed of ceramic particles were compared. Three cycles of the sequential injection of air and surfactant solution reduced the injectivity of all fluids by ~20%. The subsequent injection of 0.2 PV foam further reduced water injectivity to 35% of its original value (a 65% reduction) while reducing air mobility by 50%.

ZhongYuan Oilfield Company's ZhongYuan Oilfield; Henan Province, China; Air Foam-Alternating-Air Injection (AFAAI); Conformance Control and Mobility Control [Yu et al., 2008].

The Hu-12 block in the ZhongYuan Oilfield is highly heterogeneous, containing both low permeability oil-rich layers and higher permeability mixed water/oil zones. The permeability values of these sandstones range from 100 to 1,000 mD, with an average porosity of 21%. The reservoir temperature is 90^{o}C and at this temperature the oil viscosity is 4 cP. The reservoir pressure has fallen from its original value of 25 MPa to its current value of about 20 MPa. The formation brine contains a high concentration of dissolved solids (200,000 ppm). The average net thickness of the formation is 16 m. After two decades of waterflooding, the oil recovery was only 21% and the water cut had risen to 95%. It was suspected that most of the injected water was bypassing the lower perm oil-rich zones and entering the high permeability, watered-out zones.

Nitrogen injection was attempted in 2005, but nitrogen breakthrough occurred in only three days. Soon thereafter, air and air foam injection was considered as a viable IOR technique for both conformance control (blocking the higher perm layers) and mobility control (increasing the sweep efficiency of the displacing fluids).

In May 2007, a field pilot test of the air foam-alternating-air injection (AFAAI) process was initiated in the Middle SaSan 8 unit, consisting of one injector—former water-injector Hu-12-

152—and four producers: Hu-12-32, 36, 153, and 83. Only 21.7 OOIP had been recovered from this unit by waterflooding, and the watercut just prior to the foam test was 97.2%. A pre-flush slug of 770 m^3 surfactant solution (unspecified surfactant and concentration) was first introduced and a 0.1 PV (based on the unit) main slug was injected. The first part of the main slug was an air foam composed of 23 E4 m^3 air and 2150 m^3 surfactant solution that were co-injected, which corresponded to a foam of roughly 50% quality. The second portion of the main slug was 23 E4 Nm^3 air. A backflush of 0.1 PV water was then injected. The results as of 2008 were favorable. Oil production increased by over 20% while water production decreased by 4%. No oxygen or nitrogen breakthrough was observed during the three months of AFAAI. Three months later only a small amount of nitrogen was detected in one of the producers. It was not possible at the time of their report to define the mechanism primarily responsible for the increased oil production, but the pilot test was still considered an operational and technical success.

SAG Field Test with Air or Nitrogen as the Gas

Chevron's Painter Field, Southwest Wyoming, 1986–1987; Co-injection; Conformance Control and Mobility Control [Kuehne et al., 1990].

The Painter reservoir, which is located in the Overthrust Belt of southwestern Wyoming, produces from the 1,000 ft. thick Jurassic Nugget sandstone. The top of the formation is a gas condensate while the lower third is light oil (44 °API). Pressure maintenance was initiated in 1980 by using nitrogen to increase reservoir pressure from 4,200 psia to 4,700 psia. Further, it was hoped that this would enhance the miscible displacement of oil with gas condensate. Nitrogen breakthrough occurred quickly, however, in the offset producers and in the dual-completion injector-producer wells. This channeling was attributed to stratigraphic communication between injectors and producers that favors flow along bedding planes rather than perpendicular to them as required for downward flow of the gas condensate into the oil zone; coning in the dual injector/producer wells that inhibits the production of oil into the well; and a complex sand dune geology with directional permeability.

Therefore, an attempt was made to mitigate these problems and improve sweep efficiency by injecting a low mobility nitrogen foam into Well 23-31B. The nitrogen and surfactant solution were injected simultaneously, with foam generation accomplished with a baffled pipe and right angle choke. A proprietary surfactant at a concentration of ~0.5 to 1.5wt% was used to generate a 60% or 80% quality foam, and adsorption losses were estimated at 1,540 lb./acre ft. (0.57 kg/m^3). The foam treatment began by re-saturating the near wellbore area with 6,000 bbl. water, the last 1,000 of which contained 0.25wt% surfactant, to satisfy some of the adsorption losses. A 20,400 bbl. slug of 60%–70% quality foam was then injected during the next seven weeks, followed by nitrogen injection. The wellhead pressure was closely monitored during the foam injection in an attempt to stay below the bottomhole fracture pressure of 6,800 psia due to the significant hydrostatic head associated with the 60% quality foam. The nitrogen foam reduced injectivity by a factor of about 10, and nitrogen injectivity recovered quickly after the foam treatment ended. Unfortunately, there was neither a reduction in the nitrogen cut or an increase in the oil production rate. There even appeared to be an increase in channeling noted in post-foam injection profiles that may have been induced by over-pressurization of the injector during foam injection that enhanced the significance of fractures. In retrospect, the operators concluded that the injection of a pre-formed foam was not the best choice because of the very low injectivity and possible over-pressurization of the formation. Further, their initial assessment of the geology overestimated the communication between injector and producer perforation in the dual completion wells, and underestimated the amount of produced nitrogen originating from nearby injectors that would not be affected by the near-wellbore foam treatments.

Shengli Oilfield Co.'s Shengli Oilfield, Chendong Block; SAG Polymer Foam; Conformance Control [Li et al., 2009]

The Shengli Oilfield is China's second largest oilfield, and polymer flooding has been used extensively in this field to promote oil recovery. The formation is ~1,125 m deep, has a net thickness of 6.5 m and has a porosity of 37%. The initial oil saturation was 62%. The average permeability (determined with air) is 2,304 10^{-3} µm^2 with a Dykstra Parsons permeability variation coefficient (DP) of 0.73. The reservoir temperature and original pressure are 60 ^{o}C and 11.27 MPa, respectively. At reservoir conditions, the oil viscosity is 74 cP and its specific gravity is 0.92. The produced oil is much more viscous, 1,619 cP, at typical ambient conditions. The reservoir brine currently contains 6,227 ppm dissolved solids, 130 ppm of which are divalent. The original brine had only 1,558 ppm of dissolved solids and 68 ppm divalent ions.

A recent nitrogen foam pilot test in the Chengdong block reflects interest in improving oil recovery beyond that which is associated with conventional polymer floods. The test area covers about 0.9 km^2 and retains 119x10^4 tons of oil. The pilot test area comprises four injection wells—C26-G9, C25-G10, C70-1, and C27-G10—three central production wells, and nine edge production wells. Prior to AFAAI, the water cut was 95.9% and the daily oil production rate was 4.5 tons/day. The polymer was 3530s from SNF Corporation, a high molecular weight (15 million) polyacrylamide (25% hydrolyzed); the surfactant was a 36% active aqueous solution of DP-4, and the brine contained 8,379 ppm of mixed ions.

The injection rate was set at 0.08 PV per year, which corresponds to a total rate of 520 m^3/d, or an average rate of 130 m^3/d per well. The injection sequence was composed of a 125-day pre-slug, a 1,248-day main slug, and waterflooding. The 0.03 PV sacrificial pre-slug contained 1800 ppm polymer and 1% (10,000 ppm) surfactant. This corresponded to a 6.4 10^4 m^3 solution containing 128 tons of polymer and 694 tons of surfactant. Pre-slug injection started in October 2004.

The 0.3 PV main slug was composed of nitrogen and an alternately injected aqueous solution of 1600 ppm polymer and 0.5% surfactant. This required 3.4 10^7 m^3 nitrogen (367,000 m^3), a 32.4 10^4 m^3 aqueous slug containing 577 tons of polymer, and 1,622 tons of surfactant. The quality of the main slug was roughly 60%. The main slug injection began in July 2005. At the time of the report in 2009, 55% of the main slug had been injected.

The reservoir pressure increased from 7.6 MPa before the treatment to 10.0 MPa after the pre-slug was injected. A very low gas-solution ratio (0.2:1 or 16% quality) was selected at the beginning of the main slug. The pressure did not rise until the ratio was increased to levels as high as 0.6:1, and a pressure increase to 12.0 MPa was attained. 2.8 MPa of this 4.4 MPa pressure increase was attributed to reservoir pressurization related to a neighboring polymer flood, while the remaining pressure increase was attributed to the foam. The Hall plot result indicated that the polymer foam had a resistance factor about twice as large as the polymer + surfactant pre-slug. Further, tracer monitoring and injection profile results indicated that the pre-treatment range of velocities in the various layers became more uniform and the proportion of fluids entering the least permeable zones increased notably (e.g., 16%–23% in the top 0.5 m of the C26-G9 well) indicating the increased resistance of the foam and a more uniform injection profile amongst the layers. The most promising results were related to the cumulative oil production in the 12 production wells. Before the pilot, the combined oil and production rate was 566 tons/day, only 23 tons/day of which were oil, and the water cut was 97.2%. Halfway through the pilot, the combined oil and production rate was 704 tons/day, the oil production rate was 36 tons/day, and the water cut was 94.9%.

PetroChina Daqing Oilfield Co.'s Sabei Field, Xing 7-1-33 and Bei 2-Ding 2-59 Well Clusters; SAG Polymer Foam; Conformance Control [He et al., 2010].

The Daqing oilfield is a multi-layer, heterogeneous sandstone system in an inland basin. The reservoir temperature of this 1,000 m deep formation is 45 ^{o}C. Oil viscosity at reservoir conditions range between 6 to 9 cP. The permeability of the sands reaches values as high as 1000 mD, and the Dykstra Parsons coefficient of permeability variation ranges from 0.4 to 0.7 [Dong et al., 2008]. During the late 1980s, a polymer flooding pilot was conducted at Daqing, which ultimately led to the initiation of the world's largest polymer flood in 1996. By the end of 2007, the polymer flood resulted in the production of more than 10 million tons (73 MM bbl.) of oil per year for six consecutive years.

The main pay zone in Daqing has now been flooded for more than thirty years and is exhibiting water-cut values greater than 90%. Reservoir studies indicated that foam flooding could be a viable means of recovering the remaining oil in the main pay zone via improved sweep efficiency, while recovery of oil from the less permeable zones could be accomplished via conformance and mobility control. The Sabei field in Daqing was selected for a field pilot of polymer-stabilized nitrogen foam flooding because of its particularly high water cut of ~96% associated with the presence of very high permeability watered-out zones. A well cluster, Bei 2 Ding 2-59, in the eastern portion of Area Bei-3 of the Sabei field was selected for the pilot test to assess conformance control and oil production response.

It was anticipated that a relatively small, near-wellbore nitrogen foam treatment would effectively divert the subsequently injected nitrogen away from the thief zone, improve the injection profile, increase oil production, and decrease water production [He, et al., 2010]. The aqueous foaming solutions studied for this field contained 0.3–0.5wt% surfactant and 30–1,500 ppm of a polymeric stabilizer.

The Bei 2 Ding 2-59 polymer-stabilized nitrogen foam pilot was conducted from October 2005 to January 2006. The cluster is composed of two central production wells, three injection wells, and seven corner production wells in the peripheral zone. The targeted sandstone formations, Pu II and Gao I, are 900–1,200 m deep in these clusters with permeability values ranging from 140 –900 mD. The foam was injected into one well at a time, with a maximum injection period of one month per well. The cumulative injection into the three injectors was 4,477 m^3 of the aqueous foaming solution and 5,014 m^3 nitrogen with a gas–liquid ratio at reservoir conditions of 1.12:1 (foam quality of ~53%). The initial reservoir pressure of the pilot was 14.2 MPa. The 9,491 m^3 of injected fluids corresponded to 0.65% PV for the well cluster, which corresponded to a 20m radius from the wellbores. During foam injection, the pressure increased by 1.5–3.0 MPa in the three injectors during foam injection. Profile modification was evidenced by the number of layers receiving injected water increasing from pre-treatment values of 3 to 4 to post-foam treatment values of 4 to 6. Further, the amount of flow into highly permeable zones decreased while the proportion of flow into less permeable zones increased. For example, isotopic tracers injected into Bei 2-1-076 indicated that the amount of water entering the high permeability (800 mD) Pu II 6-9 (1) interval decreased from a pre-treatment value 57% to 24% after treatment, while the amount of water flowing into the lower permeability (360 mD) Pu II 6-9 (2) 2 increased from 27% to 33%. With regard to oil production, three of the nine producers exhibited no change while increased oil production was observed in the remaining six. The three unaffected producers were at the edge of the pattern and had previously exhibited the least connectivity with the injectors. For the six responding producing wells, the aggregate oil production rate increased from a pre-treatment value of 34.5 tons of oil/day to values as high as 50.9 tons of oil/day in the six months following foam injection. The water-cut for the combined six wells decreased from a pre-pilot test value of 93.9% to a post-treatment value of 90.2%.

These results were considered to be positive, and plans to identify more stable foaming formulations that would yield longer-lasting foams are underway for future tests.

14. SAG Full-scale Field Demonstration with Light Hydrocarbons as the Gas

Signalta Resources' Pembina/Ostracod 'G' Pool Field, Alberta, Canada; Solution Gas Foam; Co-injection; Mobility Control [Chad et al., 1988].

The Pembina Ostracod 'G' Pool is located in west-central Alberta, about 160 km west of Edmonton. The pool is a horizontal, 1,700 m-deep, 1 m-thick vuggy sandstone in the Lower Cretaceous Ostracod formation. The average porosity is 12%; the average permeability is 70 mD; the average water saturation is 35% of 70,000 ppm TDS brine; and the oil specific gravity is 0.8. Reservoir temperature and original pressure are 57 ^{o}C and 14 MPa, respectively. The 'G' Pool field contains thirteen producers and a single gas injector completed in the gas cap. By 1988, the reservoir pressure had dropped to 10.5 MPa, the gas saturation was 14%, and cumulative oil production totaled 73,000 m^3 and little water.

In 1985, secondary recovery was instituted by injecting a mixture of lean solution gas from the formation and make-up gas. Although this technique maintained oil production at 25 m^3/day, it was uneconomic. Therefore, a solution gas foam injection pilot test was conducted in an attempt to diminish gas mobility and increase sweep efficiency. A decision was made to co-inject a pre-heated surfactant solution and the solution gas through separate tubings to minimize the chances for hydrate formation. Foam quality of 95% was targeted. It was determined that a number of surfactants were soluble in the formation brine and capable of generating foams. Therefore, the investigators referred to previous reports of surfactant cost and adsorption during the process that led to the selection of the Dow Pusher XSS 84312.11, a mixture of C10 diphenyletherdisulfonate and C14-16 alpha olefin sulfonate [Mannhardt, et al., 2000] for the pilot test. The surfactant solution was composed of 0.6wt% surfactant dissolved in 3% KCl solution.

The first slug of 20 m^3 surfactant solution was introduced along with gas flow rate of 42.5 m^3/day. The surfactant solution flow rate was adjusted to attain 5% liquid, 95% gas foam. The injection pressure first increased from 10.8 MPa to 16.3 MPa due to the hydrostatic head of the water in the 32 mm tubing. As the surfactant solution entered the formation along with the gas, the pressure further increased from 16.3 MPa to 18 MPa. Within 24 hours after introduction of the surfactant solution slug, the injection gas pressure returned to its pre-pilot value.

A second, 97 m^3 surfactant solution slug of 0.65% surfactant in 3% KCl brine was injected over a five-day period in May 1987. Injection was stopped because the bottomhole pressure was approaching the facture pressure. A volume of 1718x10^3 m^3 of solution gas was introduced in this co-injection process. The gas injection pressure increased from 12.4 MPa to 21.5 MPa, indicative of foam formation. It required the introduction of about 0.1 PV (based on mobile gas) for the injectivity of the gas to return to its pre-treatment value, indicating that a foam bank was sustained for a short time in the formation. The level of mobility reduction in the field was only a factor of five, much less than that observed in short core lab tests. Nonetheless, the reduction in mobility was sufficient to increase oil production by 25% from 25 m^3/d to 33 m^3/d for three months after the addition of the surfactant solution containing about 750–800 kg surfactant.

Dome Petroleum's Triassic A Pool Field, Alberta, Canada; Patterns 1 and 7, Hydrocarbon Miscible Gas Foam; SAG; Mobility Control; Injectivity [Liu and Besserer, 1988].

The Kaybob South Triassic A Pool, which is located about 300 km northwest of Edmonton, was discovered in 1962. The producing zones are part of the Sulfur Mountain formation of the Spray River group. This dolomitized coquina formation is about 2,100 m deep at a temperature of 88 ^{o}C. The initial reservoir pressure was 17.8 MPa. The average permeability of the oil-bearing zones, which vary from 25 to 200 mD, is ~92 mD. The thickness of the net pay zone is 4.8 m and the average porosity of the pool is 11.5%. The OOIP of Unit 1 was estimated to be 150 million STB (11,300,000 m^3).

The field was developed with relatively large 160-acre spacing. Primary recovery from this formation occurred between 1962 and 1967. Waterflooding was initiated in Unit 1 in late 1967, with breakthrough occurring in 1973. Unit 2, with an estimated 85 million STB of oil and a 35 Bscf gas cap, was discovered in 1968. After several years of primary production, waterflooding began in Unit 2 in 1975.

A hydrocarbon miscible flood was planned for a portion of Unit 1 that included 9 injection wells and 38 production wells associated with 9 inverted nine-spot patterns. The miscible gas was composed primarily of ethane (44%), methane (33%), propane (18%), and butanes. It was anticipated that 12% HCPV of the solvent would be injected using a WAG that increases from 0.2 to 1.0 in the first two years, and by 1988 the WAG ratio was at a value of 2.0. Solvent injection started in mid-1984 and solvent breakthrough occurred by late 1984. Twenty-six of the production wells had experienced solvent breakthrough by mid-1987.

In an attempt to mitigate the effects of the high mobility and gravity override associated with the low viscosity, low density, miscible gas, foam flooding trials were planned for Patterns 1 and 7. Dowfax XS 84312.11 was selected as the foaming agent for the field trial based on laboratory tests. Foam injections were conducted during gas cycles of the WAG. A surfactant solution was injected after injection of the WAG water was completed and 0.3 m^3 of methanol was then injected to prevent hydrate formation. The hydrocarbon miscible gas was then introduced, followed by one cubic meter of methanol. Multiple SAG cycles were injected following this procedure. Four field tests were conducted in Pattern 1 from September 1987 until March 1988, and another two tests were conducted in Pattern 7 from February to March 1988.

Pattern 1 includes a single injector (4-3-62-20 W5M) and 6 active producers (2-3, 10-3, 12-3, 2-4, 10-4, and 10-33). Results included the injection of a single 10 m^3 slug of a very concentrated (5%) surfactant solution at the start of a two week gas-injection period. Gas injectivity with foam was roughly about half of the gas injectivity measured during WAG, and in both cases injectivity increased with time as gas saturation in the near wellbore region increased. After two weeks of water injection and two more weeks of gas injection the baseline injectivity was re-established, indicative that these foams would not induce permanent changes in injectivity and the foams could be dissipated, if desired, by water injection. In the second SAG test in Pilot 1 the same amount of surfactant was introduced via two 10 m^3 surfactant slugs injected during a two week gas injection period: a 4% slug at the beginning of the first week and a 1% solution at the beginning of the second week. The mobility associated with the use of a two surfactant slug

(4% and 1% surfactant) test was less than that of the injection of a single 5% slug over a longer period of time. Results that were comparable to the second test were obtained in the third test in Unit 1 when the surfactant concentrations in the two slugs were set equal to one another at 2%. The fourth test lasted six weeks (rather than two) to generate the foam further into the formation. At the beginning of the first five weeks of gas injection, 10 m^3 of a 2% solution was injected. At the beginning of the sixth and last week, 17 m^3 of a 2% surfactant solution was injected. It was noted that while injectivity decreases were distinct for the first three slugs, there was no drop in injectivity after that until the larger sixth slug was introduced. It was concluded that it may be beneficial in SAG to increase the volume of the surfactant slug as the SAG cycles progress. In February 1988, the GOR of production well 10-33 decreased by roughly two-thirds, while the GOR of well 2-3 decreased by about 20%. Smaller, but still appreciable reductions in GOR were observed in the other four production wells. There was not enough data to ascertain if the foam had increased incremental oil recovery, however.

Pattern 1 injectivity tests in well 4-11-62-20 W5M verified that there would be no problems associated with using foams; therefore, tests were conducted in the oil-rich Pattern 7. In the first test, two 2% 10 m^3 surfactant slugs were introduced during a two week gas injection cycle and, as observed in Pattern 1, injectivity decreased in Pattern 7. Similar results were obtained when this test was repeated in Pattern 7. At the time of the report, it was too early to detect either GOR reduction or an increase in oil production.

Evidence of the success of this project was not conclusive at the time of the report primarily because there was an appreciable reduction in GOR in Pattern 1 but no distinct increase in incremental oil that could be verified as a result of foam injection.

Esso's Judy Creek Beaverhill 'A' Pool Field, Alberta, Canada; Patterns 1 and 7, Hydrocarbon Miscible Gas Foam; SAG; Mobility Control; Injectivity [Turta and Singhal, 1998].

The Judy Creek Beaverhill 'A' field is northwest of Edmonton in Alberta, Canada. This limestone formation is 2,650 m deep and is composed of five producing zones with 67 m of net pay. Porosity ranges from 6 to12.5% and permeability values range between 40 and 170 mD. The reservoir is at 97 ^oC and the initial reservoir pressure is 24 MPa. Primary recovery started in 1959. Waterflooding was initiated in 1964 and by 1985, when tertiary recovery efforts began, 49% OOIP has been recovered. Ethane-rich (50%) hydrocarbon miscible gas was injected alternately with water at a 1:1 WAG ratio in 1.5 to 2.0 month cycles.

A foam pilot test for conformance and mobility control was initiated in 1992. The foam was injected solely in a mechanically isolated, 22 m thick portion of the formation in an attempt to divert flow from a 10 m thick high permeability streak, diminish gravity override, divert more solvent into the lower oil-rich zones, and improve sweep efficiency. Apparently, a 6-month long pilot was conducted in which a 0.35% surfactant solution of roughly 50% PV was injected alternately with the solvent. Fifty tons of surfactant were injected during this pilot. Although there was a 15% reduction in solvent injectivity, there was no increased oil production and no significant improvement in the injection profile.

Norsk Hydro's Snorre Field, Offshore Project in the Norwegian Sector of the North Sea; SAG or Foam-Assisted WAG; Mobility Control; 1997 – 2000 [Blaker et al., 2002; Skauge et al., 2002; Aarra et al., 2002; Blaker et al., 1999].

Snorre is a major oil field in the Tampen Area of the Norwegian Continental Shelf in the North Sea, about 150 km from the coast. The platforms are located at a depth of 300–350 m in the North Sea, and the Snorre formation is at a depth of 2000–2700 m [http://www.subseaiq.com/data/Project.aspx?project_id=204&AspxAutoDetectCookieSupport=1]. The estimated recoverable oil from this field (based on ~46% recovery of the 513 M Sm^3 stock tank oil originally in place (STOOIP)) is 234 million m^3, or 1.4 billion bbl. [Seldal et al., 2009]. This Brent-type sandstone reservoir is composed of an inhomogeneous, stratified, dipping (6^o to 8^o) fluvial deposit within rotated fault blocks comprising the Statfjord and Lunde formations of the Lower Jurassic to Upper Jurassic age. The formation temperature is 90 ^{o}C and the reservoir pressure is high at ~300 bar (or 4,350 psia). The light oil in the reservoirs is undersaturated because the reservoir gas and oil are miscible at pressures above 282 bar.

The field came online in 1992 with production being driven by a waterflood. In an effort to increase oil production, a down-dip, two-injector, three-producer, WAG pilot was conducted in the CFB. In 1995 a decision was made to more fully implement the WAG in the central, western and, eastern fault blocks. The gas used in the WAG was the produced low viscosity hydrocarbon gas, which is identical to the export gas and is rich in intermediate components. Rapid gas breakthrough was noted for injector/producer pairs in direct communication. For example, gas breakthrough times of roughly one month were observed even though the production well was more than 1 km from the injector (P25–P18). For producers with less direct communication paths with their respective injectors, a secondary gas cap forms, breakthrough is delayed, and GOR increases more slowly after breakthrough. In the Statfjord reservoir, the sands have good vertical communication and coarsening upward sequences. As a result, the gas tends to quickly gravity segregate and move up-dip below barriers, limiting the amount of gas-oil contact in the formation. It was therefore desired to test a technology that could lessen the mobility of the injected gas and increase the extent two-phase gas-liquid envelope in lower permeability zones, thereby increasing oil production and decreasing gas production. Promising candidate foams were selected for the Upper Statfjord reservoir zones S1 and S2. Laboratory tests originally conducted to provide insight into the design of surfactant solutions for injection into high permeability zones of a production well provided insight into the design of the mobility control foams [Svorstol et al., 1996; Vassenden et al., 1998].

Analyses of lab results led to the design of a surfactant solution with 0.5wt% AOS and a quality of 70%; enough water to ensure that the water saturation would not drop below the 15%–20% level required to prevent foam collapse. The mobility reduction associated with the foam was relatively constant until foam qualities exceeded 90%–95%. Water was heated to 40 ^{o}C to prevent hydrate formation, and a 23% active surfactant solution was added to water to form the dilute injection solution.

Surfactants have been considered in the Snorre field for stabilizing foams that can be used for reducing the GOR of producing wells, preventing fluids from flowing into high permeability layers, diminishing the mobility of a displacing gas [Hanssen et al., 1994], or to assist in deliquefying gas production wells [Schinagl et al., 2007].

The original application of surfactant-stabilized foams during 1996 in the Snorre field was as a means of reducing the GOR of producing well P-18 located in the Central Fault Block of the Snorre field [Svorstol et al., 1997; Aarra and Skauge, 1994] where 32 tons of C14-16 commercial grade α-olefin sulfonate (AOS) was dissolved at a 1wt% or 2wt% concentration in an aqueous solution that was injected into the targeted reservoir zone that had been isolated by a packer. Although the SAG foam generation was limited, strong foam was established via co-injection, and upon returning the well to production, the GOR was reduced by more than 50% over two months, accompanied by increased oil production from lower reservoir zones. (Excellent results were also realized in a gas coning situation [Aarra et al., 1996], and there also have been recent successes reported in 2007 concerning in the addition of batches of surfactant to promote gas lift in production wells [Schinagl, et al., 2007]; and 2–5 fold increases in the online duration of cycling wells and increases in oil production rates of up to 30% from these wells were observed).

The most important and substantial effort involving foams, however, was the full-scale field demonstration that in-depth mobility control foams can be used to successfully and profitably recover substantial amounts of oil. Mobility control tests were conducted from 1997 to 2000 in the Central and Western Fault Blocks, CFB and WFB, respectively, of the Snorre field [Blaker et al., 2002; Skauge et al., 2002; Aarra et al., 2002; Blaker et al., 1999].

A detailed description of the CFB FAWAG project [Blaker et al., 1999] indicates that the mobility control foam project was initiated with an injectivity study of CFB injector P25A in 1997. The mobility test was conducted from August through November 1998. First, three 0.5wt% AOS surfactant solution slugs were alternately injected with gas (SAG). Subsequently, a short co-injection scheme was used. The reservoir pressure was ~280 bar in this portion of the formation, and the fracturing pressure for P25A was 380–400 bar. After the injection of a water slug, there was—as expected—no significant increase in injectivity during the injection of the low viscosity surfactant solution. Injectivity was also observed to increase with pressure, indicating the formation of fractures. The gas injectivity was reduced by a factor of ten (relative to gas injection before the foam test) during the first gas cycle, indicative of near-wellbore foam formation in the sandstone matrix. The injectivity of the first gas slug was also comparable to the water injected prior to the first surfactant slug. Because the viscosity of the water at bottomhole conditions (0.7 cP) is about twenty times greater than that of the gas (0.03cP), the mobility of the gas flowing into the surfactant slug was decreased by a factor of 20 when compared to water flowing at high water saturation. The injectivity of the second surfactant slug was lower than the first slug because the surfactant solution was flowing into foam, which can trap gas in pores and diminish flow. During the introduction of this second surfactant slug, the pressure became elevated above the fracturing pressure, which slightly mitigated the injectivity decrease. Apparently, some surfactant solution was "lost" to the fractures because when the second gas slug was introduced at a pressure near the fracturing pressure, the extent of the fracture paths decreased and the gas would not flow into the portion of the surfactant solution that entered the open fractures. As a result, gas injectivity was actually lower at the end of the second gas cycle than the first. The third surfactant slug was injected at a pressure well above the fracture pressure, with fracture lengths increasing to 50–70 meters. The third gas cycle was injected at a much lower bottomhole pressure (BHP), and once again the gas injectivity increased due to the loss of surfactant solution to fractures that were inaccessible to the lower pressure third gas slug. This SAG project used 74,500 m^3 water, 75 MMm^3 gas, and 1,040 tons of 38% active AOS surfactant solution. Specifics of each half-cycle are found in the literature [Blaker et al., 2002]. Based on the use of 0.5wt% surfactant slugs, adsorption of 0.5 mg/g rock, a six meter net sand zone height, a porosity of 25%, and foam quality of 85%, the extent of the foam zone after SAG was estimated to be 85–150 m. A short co-injection process injection was implemented after the completion of a three cycle SAG. It was difficult to maintain the desired flow rates during this test. Further, the very low injectivity of the co-injected gas and surfactant solution caused the pressure to rise well above the fracturing pressure. In 1999 and 2002, it was deemed that the effectiveness of the foam as a mobility control agent that decreased gas production and increased oil production in CFB could not be readily assessed because of the complexity of the reservoir and the interruption of the CFB operation due to problems with the target injector well [Blaker et al., 1999; Blaker et al., 2002]. The major lessons learned from this CFB field test, which ended in November 1998, were to use SAG injection rather than co-injection, and to design foam floods where neither the injected surfactant solution nor gas would exceed the fracturing pressure of the formation. These findings were used to design another FAWAG field test in the WFB field test that followed in 1999.

The WFB was originally put into production during the fall of 1992, with WAG being introduced in 1995. The three injectors were P37, P32, and P21, and the four producers were P24, P33, P39, and P42A. (The WFB well pair later chosen for the FAWAG project was P32 injector and P39 producer, which are separated by 1,550 m.) The P32 injector injected water from March 1996 until November 1998. In late November 1998 gas injection began in P32, with 83.9 Mm^3 of gas injected over the following months. Gas breakthrough occurred between January 7 and January 25, 1999, implying that the maximum travel time for gas between P32 and P39 was ~60 days. The injection of a second gas slug of 105.8 Mm^3 into P32 commenced on June 7, 1999. A distinct increase in GOR was observed 29 days later in P39. The quicker gas breakthrough time was attributed to the absence of a secondary gas cap in the area, establishment of a trapped gas saturation, reduced gas-oil mass transfer, and/or the second slug following the path of the gas injected in the first slug. Water injection was implemented in P32 during the late summer of 1999. These two WAG cycles were used to establish a baseline or control project in which oil and gas production attributable to WAG could be defined for subsequent simulations that compared the oil and gas production associated with SAG and WAG processes.

The SAG process was initiated in November 1999 with the injection of a 15,262 m^3 slug of 0.49% AOS solution over 9.5 days during which time the rate was restricted to prevent the BHP from exceeding the fracture pressure. Subsequently, 82 MMm^3 gas was introduced at a relatively constant wellhead pressure and the normal gas injectivity limit was realized about 100 days later. A small GOR increase was observed in P39 5–6 weeks after SAG gas injection started. The GOR stabilized at about 250 m^3 gas/m^3 oil, a value significantly lower than the values of >400 associated with WAG. A second slug of surfactant solution was injected from February 26 through March 17, 2000, and consisted of 31,733 m^3 of a 0.2% AOS solution. Trailing gas injection of 116 million m^3 continued for 175 days until September 14, 2000, at which time the revision shutdown of the field occurred. The GOR in P39 remained at a value of about 175 during the injection of the second SAG gas slug. After the revision stoppage, the GOR increased significantly and a tritiated methane gas tracer added during the start of the second SAG gas slug was produced in P39, both of which indicated that gas breakthrough had occurred. A total of 380 tons of 38% AOS solution was used during the WFB SAG project: 208 tons in the first cycle and 172 tons in the second.

There was a significant amount of oil production associated with both of the WAG cycles and the subsequent SAG cycles. The efficacy of the SAG process in the WFB was then determined using simulations that attempted to quantify the amount of oil that would have been produced from P39 had there been no surfactant in the two SAG cycles. In other words, an analysis was made that compared predictions of the amount of oil that would have been recovered with two additional WAG cycles from November 1999 to September 2000, rather than the two additional SAG cycles. Both conventional simulations and the STARS foam mechanistic simulator were employed in this effort. This analysis concluded that the SAG contribution to oil recovery was 250,000 m^3 of oil. This corresponds to ~$31 million at an oil price of only $20/bbl. A material balance on the gas in the WFB indicated that as much as 350,000 m^3 of oil could have been displaced by stored gas, representing a value of $44 million. Because the cost of the surfactant treatment was only $1,000,000, this project was considered a technical and economic success.

A StatOil presentation on the Snorre field given in 2006 by one of the scientists who was heavily involved in the FAWAG development [Svorstol, 2006] indicated that these FAWAG projects were highly regarded and indicated that mobility control foams could have great potential. The success of the project was attributed to a small, enthusiastic team of advocates who were permitted to explore this technology. Foams were being considered for future injector and producer applications in the 2007–2008 time-frame. A 2008 review of North Sea EOR projects conducted between 1975 and 2005 included the FAWAG projects in the CBF and WFB of the Snorre field [Awan et al., 2008]. Despite the substantial amounts of oil recovery attributed to FAWAG in Snorre by its operators, this review article was much more guarded in its assessment of the project. The authors concluded that FAWAG was still immature and that a good understanding of foam propagation within the reservoir was still lacking, especially in fields where interwell distances were great. Further, FAWAG processes were deemed as needing additional and more careful well monitoring efforts.

15. Field Tests with Foams Generated with Water-soluble Surfactants Using Dense CO_2 as the Gas

Carbon dioxide foams can be tailored to provide long-term, in-depth, relatively modest mobility reduction for mobility control during a CO_2 flood, or conformance control via the generation of stronger foams in high permeability zones in the near-wellbore region. Mobility reduction can be considered as a form or sub-set of conformance control technology in that the generation of foams in a layered formation will be capable of both diverting CO_2 from the most highly permeable zones into the less permeable oil-rich zones and inhibiting the formation of viscous fingers of CO_2 [Sydansk and Romero-Zeron, 2011], especially if the foam is designed to exhibit higher mobility reductions in the higher permeability watered-out zones and more modest decreases in mobility in the lower permeability zones that retain significant oil saturations. Nonetheless, most CO_2 field studies of foams refer to either the use of stronger foams formed with smaller volumes of higher surfactant concentration solutions designed primarily to block thief zones as conformance control foams, and weaker foams made with larger volumes of less concentrated surfactant solutions intended to inhibit fingering throughout the formation in the oil-bearing zones as mobility control foams.

Although surfactant-based foams are the only chemical-based, in-depth, CO_2 mobility control option that has been available for pilot-testing, relatively few field tests have been conducted with the specific intent of attaining in-depth mobility control. Rather, nearly all of the uses of CO_2 foam in prior pilot tests described in the previous section were directed at achieving a reversible, inexpensive means of conformance control. With the notable exception of the on-going Kinder Morgan SACROC pilot test of foams generated in situ with CO_2-soluble surfactants, however, there have been very few reports of CO_2 foams being employed for either mobility or conformance control since the mid-1990s.

Vikor Resources' Joffre Viking Field, near Red Deer, Alberta, Canada; 1989, Co-injection Foam; Mobility Control [Stephenson et al*.*, 1993]

The Joffre Viking Field produces from a reservoir that is a Cretaceous, Lower Colorado group, Viking formation sandstone deposited as overlapping sand lenses. The formation is approximately 9' thick. Primary recovery via fluid expansion and solution gas drive and secondary waterflooding resulted in the recovery of about 42% OOIP by the mid-1960s. In the early 1980s, based on promising lab tests and simulations, there was renewed interest in tertiary recovery in the field using CO_2. In 1991, Vikor initiated the operation of the miscible CO_2 flooding project for the Alberta Oil Sands Technology and Research Authority and the working interest owners. It was evident from the beginning of operations that there would be a need for mobility control in that the CO_2 was ~22 times as mobile as the oil and brine in the reservoir. Further, the CO_2 density was 80% of that of the oil and 60% that of the brine, leading in part to the CO_2 entering only the top third of the formation. Therefore, Viking explored a number of options in an attempt to mitigate the anticipated viscous fingering and gravity override. The options included continuous CO_2 injection, WAG, co-injection of CO_2 and water, and CO_2 foam.

Pattern B was selected for the CO_2 foam pilot test because it was well characterized. Further, it was nearing the end of its economic life thus any oil lost to irreversible injectivity losses would not have resulted in a significant loss of oil production. Therefore, the first part of the pilot was directed more at understanding short-term injectivity changes than documenting long-term incremental oil increases. Co-injection of CO_2 and surfactant solution yielded a ~300 psia bottomhole pressure increase, indicative of low mobility foam generation. Further, co-injection yielded longer-lasting reductions in mobility than alternate injection of a surfactant solution followed by CO_2 and water co-injection. Therefore, a more extensive foam test was conducted. A sacrificial slug containing 900 kg of active surfactant in a 0.5wt% aqueous solution was followed by the co-injection of 10,000 kg of active surfactant (at a 0.2wt% aqueous concentration) and CO_2. Although an increase in BHP was again observed during the first three weeks, the BHP leveled off, indicating that the foam was not continuously expanding away from the well in the sandstone during the five months of CO_2-surfactant solution co-injection. Further, there was no change in the GOR of the production wells and the modest rise in oil production was apparently due to the increased amount of CO_2 injected into the reservoir rather than to the effects of the foam. The foam apparently propagated only a few meters from the wellbore, and the pilot test was therefore judged as neither a technical nor economic success. Ultimately, the co-injection of CO_2 and water was found to be the most effective tertiary CO_2 flooding strategy.

Amoco's Wasson ODC Unit, Yoakum County, Texas, 1994; Conformance Control Foam; Single Cycle SAG [Henry et al., 1996].

Carbon dioxide flooding in the Wasson ODC Unit in Yoakum County, Texas, began in late 1984. The extremely high cyclic gas production rates that were observed in Well 455 in 1992 were attributed to the cyclic injection of CO_2 into Well 324. It was determined that the CO_2 was cycling through a high permeability thief zone at the total depth of the wells. The objective of the foam treatment was to reduce the high gas cycling rate associated with flow of CO_2 through a thief zone at the total depth of the well while maintaining injectivity into the other layers. Communication through fractures was ruled out as a problem.

The foam treatment started with injecting 2,665 bbl. of surfactant solution over seven hours. Eight-hundred bbl. of water were subsequently injected over four hours to displace surfactant from the tubing and openhole, and then more water was injected at 82 bbl. /hr. for 13 hours. This 24-hour sequence was repeated for the next four days. Surfactant solution and water injections at 200 bbl. /day were followed by CO_2 injection on the fifth day.

The diminished injectivity of the foam was evidenced by a decrease in the injection flow rate at a constant wellhead pressure of 1,000 psia from roughly 3,000 Mscf/d to 2,000 Mscf/d. Relative to pre-foam conditions, CO_2 breakthrough was delayed from 8 to 22 days and CO_2 production was reduced from roughly 2,000–2,500 Mscf/d to 1,000–1,500 Mscf/d. As injectivity and gas production slowly increased and approached pre-treatment levels after a month of CO_2 injection, small slugs of water were introduced to rehydrate the foam. The first rehydration slug, which was followed by a month of CO_2 injection, was more effective in decreasing injectivity and gas production than the second rehydration slug. It was also determined that there may have been a marginal increase in sweep efficiency, but the volume of the surfactant slug was too small to draw a conclusive finding. The placement of the foam in all of the injection layers, rather than solely in the thief zone, also inhibited a discernible increase in sweep efficiency. While this pilot was deemed a technical success in that cycling was reduced, it was considered to be uneconomic because of the low compression cost associated with gas cycling. For example, the surfactant costs alone were \$19,000 while the compression savings were only \$5,500. It was suggested that better placement of larger injection volumes of surfactant, which could result in improved sweep, decreased gas production, and increased oil production, could render a more economic success.

Phillips' East Vacuum Graysburg/San Andres Unit (EVGSAU), Lea County, New Mexico; 1991 – 1993, Conformance control SAG [Butler et al., 1993; Chang and Grigg, 1994; Grigg, Tsau and Martin, 2002; Harpole, et al., 1994; Martin, Heller, Weiss, and Tsau et al. 1992; Martin, Stevens and Harpole, 1995; Stevens, Harpole, Zornes and Martin, 1992; Tsau, Heller, Moradi-Araghi, Zornes, and Kuehne, 1994].

Despite yielding favorable CO_2 flooding results, the EVG/SAU CO_2 flood in Lea County, NM was characterized by significant CO_2 breakthrough in some portions of the field, especially in the wells/patterns ultimately selected for the foam test. The foam test was funded by EVGSAU Working Interest Group, the state of New Mexico, and the USDOE, while the PRRC of NMIMT and a Joint Project Advisory Team provided technical and planning support. Well log and observation well data were used by Schlumberger to assess the path of the CO_2 or the response times of different carbonate layers. This is one of the most thoroughly documented field tests of CO_2-in-brine foams.

Carbonate laboratory core floods carried out at reservoir conditions of 101^{o}F and 2,100 psia with Chaser CD 1045 at 0.25wt% and 0.10wt% at interstitial velocities of 0.36–34'/day and foam qualities of 66–86vol% CO_2 were found to be 3 to 63 times less mobile than CO_2, with adsorption losses estimated to be roughly 0.4mg surfactant/cm^3 of porous media (~1,100 lb. /acre ft.).

Initially, the EVG/SAU was considered as a candidate for either mobility control or conformance control. A decision was made to establish the CO_2-in-brine foam for near-well fluid diversion using a short duration, small (~1% hydrocarbon pore volume (HCPV)), relatively high concentration foam slug rather than a larger, longer duration, lower concentration mobility control slug. Apparently, it was thought that the economics of the shorter term surfactant solution injection for conformance control would be more favorable than a mobility control project. Because a 1% HCPV slug would occupy a cylinder about 100' in radius surrounding the injector, it was expected that the surfactant could be expected to propagate no more than several hundred feet from the injector.

The first field test began with a modified WAG cycle that was meant to simulate the SAG process, but not include surfactant; it was agreed that this would facilitate the interpretation of how the surfactant, rather than a change in the injection schedule, changed the performance. Therefore, during the first half of the CO_2 injection cycle, five short cycles of WAG were conducted in the exact same manner as prescribed for SAG, but without any surfactant. During the second half of this cycle, CO_2 was continuously injected.

A sacrificial Chaser CD 1045 surfactant solution pad designed to inhibit the adsorption of subsequently injected surfactant intended for foam generation was then injected. This pad, which contained 90,000 lb. of surfactant at 2,500 ppm concentration, took three months to inject.

The SAG injection was designed to occur within the first half of a normal WAG cycle. Because ~2%PV of CO_2 was being injected during every CO_2 cycle of a WAG, about 1% HCPV of an 80% quality foam was generated during the SAG half-cycle. Each (surfactant solution-CO_2) cycle within the SAG half-cycle consisted of injecting a 2,500 ppm surfactant solution at 1,000 bbl./day (~3,000 reservoir barrels/day) for three days followed by 12 days of injecting CO_2 (12,000 reservoir bbl.) in an attempt to generate an 80% quality foam. There were five CO_2-surfactant solution cycles in the SAG half-cycle. The project injected 15,000 lb. of Chaser CD 1045 surfactant during the SAG half-cycle. The SAG half-cycle was followed by continuous injection of a half-cycle of CO_2, which was followed by the injection of brine.

Substantial pressure increases when CO_2 was injected after the surfactant indicated the formation of foam in situ. In situ mobility values that were generated from Hall-plot slopes and falloff tests for the injection well indicated that the mobility of the CO_2 was reduced by one-half to one-third that of CO_2 and the foam apparently persisted for several months. Approximately 12% of the fluids typically entering a thief zone were diverted to other zones at the beginning of and during foam generation, but after the SAG cycles ended the distribution of injected CO_2 reverted to its pre-foam status. Observation well logging experiments demonstrated that fluids were diverted away from the highest permeability watered-out zone at CO_2 residual oil saturation, while a gradual decrease in oil saturation and increase in CO_2 saturation occurred in a lower perm zone, indicative of mobile oil displacement by foam. The most dramatic change caused by SAG was evident in an offending well (a low oil-producer from which the CO_2 typically was produced quickly after breakthrough), which experienced a positive oil response, delayed CO_2 production (by a factor of ~2), and reduced CO_2 production (by a factor of ~ ½). Although the effects were less dramatic, increased oil cut was also observed in two other producers.

A second foam test using a lower concentration at 0.10wt% was yielding favorable results, but mechanical problems abruptly ended the test after only a short (CO_2-surfactant solution) cycle. Gas production decreased and oil production increased in several wells.

The operator estimated that 14,700 bbl. and 4,460 bbl. of incremental oil were produced as a result of the first and second SAG tests, respectively, accounting for $144,244 and $35,764 in oil revenue. At the time of the first and second tests, the price of oil was $17.50 and $15.45, respectively. This total of $180,008 in additional oil revenue was accompanied by $44,250 in compression savings. The surfactant cost was $176,000 for 105,000 lb. While the net revenue of $48,258 was encouraging, it did not provide an attractive rate of return. Subsequent analysis of the EVG/SAU SAG tests conducted by PRRC suggested that the economics could be enhanced by combining inexpensive lignosulfate surfactants with Chaser CD 1045 as a sacrificial agent and SAG solutions, or to use less surfactant for the sacrificial pad. Further, it was noted that “these results suggest that surfactant-generated foam could prove economic in times of slightly higher oil process (> $20/bbl.)” [Martin, Stevens, and Harpole, 1995].

Chevron's SACROC Field Test, 1984, SAG Conformance Control [Smith, 1988b; SPE Forum Series, 1987].

The foam pilot test at SACROC has not been published in the literature, but it has been discussed at a conference. The surfactant chosen for the SAG cycle was Alipal CD 128, a mixture of alkyl ethoxy sulfates with 8–10 carbons in the alkyl tail and an average of 2.5 ethoxy groups in the EO chain. The test yielded neither adverse nor beneficial effects, and was thought by most to be a demonstration that dual-porosity reservoirs (those exhibiting substantial open fractures and intergranular pores of carbonates) are not the best candidates for foams. In this case the in situ generated foams were not capable of diverting fluid flow through the very high permeability open fractures.

Unocal/Long Beach Oil Dev. Co. Wilmington Immiscible Trial, Long Beach, California; 1984; SAG Conformance Control [Smith, 1987b; Holm and Garrison, 1988]

In 1982, after two decades of waterflooding, an 85:15 molar mixture of CO_2:N_2 (flue gas) was injected into the Tar Zone of Fault Block V of the Wilmington, California field. The injection pressure of 1,100 psia was well below the 3,000 psia MMP associated with this heavy oil (14^o API gravity). At any time during the WAG process, two injectors were used for CO_2 while the remaining eight injection wells were used for water injection. The wells used for CO_2 injection were rotated amongst the 10 injectors. Although the WAG was responsible for increased oil production from the three unconsolidated sands with permeability values ranging between 100 to 1,000 mD, there was extremely high CO_2 production in some wells and an uneven distribution of the injected fluids between the three zones. Therefore, a decision was made to implement a CO_2 foam in hopes of alleviating both of these problems by diverting the CO_2 away from the high permeability "S" zone and into the other two less permeable, more oil-rich sands, most notably the "T" zone.

Alipal CD 128, a mixture of alkyl ethoxy sulfates with 8–10 carbons in the alkyl tail and an average of 2.5 ethoxy groups in the EO chain was selected as the surfactant for foam generation. This surfactant is sold as a 58% active surfactant in water because the neat surfactant is a solid. Each of the eight injection cycles consisting of ~2,600 bbl. of a 1wt% surfactant solution in reservoir brine was followed by the injection of nine times that volume of the CO_2:N_2 gas mixture in an attempt to generate 90% quality foam. Therefore, a total of 21,000 bbl. of surfactant solution was injected during this test.

Gas and water injection profiles indicated that as little as 57% of the gas injected during SAG flowed into the S sand, rather than the 98.7% value that occurred during WAG. The T zone received as much as 43.3% of the injected gas, a dramatic increase from the 1.3% value prior to SAG. Further, at a constant injection pressure the gas flow was reduced by a factor of about two-thirds. Pressure falloff tests also verified that the skin factor in the well was reduced and that in-depth permeability reduction occurred. Because no gas tracer was introduced to the CO_2:N_2 mixture during SAG, it was not possible to confirm whether the continued gas production from surrounding wells was due to a problem with the foam diversion, channeling from the T zone, or gas influx from other injection wells.

Although it was initially planned to continue gas injection following the SAG to assess how long the foam could last without continued surfactant injection, the well was returned to water injection because of the continued high gas production rates. After about three times the volume of water compared to the volume of surfactant solution used in the SAG was injected, gas injectivity returned to pre-SAG conditions. The foam had dissipated or collapsed as a result of water injection. The operators concluded that either CO_2 injection should have resumed immediately after SAG or a surfactant solution, rather than brine, should have been introduced after the SAG.

Pennzoil's Rock Creek Field Test, Roane Co., West Virginia; 1984–1985; Co-injection Mobility Control [Smith, 1988b; Heller, Boone, and Watts, 1985a; Heller, Boone, and Watts, 1985b]

The Rock Creek oil field has been produced since 1906 from the high clay content, low permeability Big Injun sandstone. Primary production accounted for 10% of the OOIP. Although waterfloods and a steam flood were subsequently attempted, the first and most successful secondary recovery method proved to be the low-pressure gas recycling that began in 1935 and was extended in 1972 when Pennzoil purchased a new portion of the field. It was estimated that gas-recycling produced another ~10% of the OOIP. Both the oil characteristics (43 ^{o}API gravity, paraffinic, 3.2 cP, 1,000 psi MMP) and the reservoir characteristics (22% porosity, 21.5 mD, 73 ^{o}F, 34% oil saturation, ~2,000 ft. depth) made this field an attractive candidate for CO_2 miscible displacement. Water pressurization and injection from 1976 to 1978 preceded CO_2 flooding in two adjacent five-spot patterns from 1979 to 1982. Data from observation wells and pressure coring indicated that CO_2 could reduce residual oil saturation from the ~33% post-waterflooding value to values less than 2% in regions swept effectively. However, much higher residual oil saturations were detected in most cores. Therefore, it was thought that mobility control could greatly enhance oil recovery.

Ultimately, the CO_2 foam mobility control mini-pilot was conducted with a single injector (PI 2) and a single observation well (OB 2) 75 ft. away. This field project was designed specifically to alleviate frontal instability caused by an unfavorable mobility ratio. There was no intent to design a foam that would divert CO_2 from a high permeability layer. Therefore, Rock Creek is one of the few pilot tests aimed specifically at mobility control rather than conformance control. A "thickened" slug of CO_2 in the form of foam was attained via co-injection of CO_2 and surfactant solution, rather than the implementation of a SAG process. The foam was designed to induce a modest decrease in the mobility that would result in a favorable mobility ratio, rather than extremely low mobility foam for conformance control. Lab tests indicated that a foam of ~80% quality formed with a 0.05wt% Alipal CD 128 solution would be 0.4 – 0.2 times as mobile (i.e., 2.5–5 times as "viscous", respectively) as brine, which would result in the foam having a mobility quite comparable to that of the oil. It was anticipated that injectivity measurements would signal the formation of a foam, and that the formation and flow of a mobile oil bank would be detected at a nearby observation well, which was perforated to allow for the production of 8–10 bbl./day.

The injection sequence was planned to consist of (a) the injection of a slug of ammonium thiocyanate consisting of 15 kg NH_4SCH in 371 bbl. water; (b) a "short" water spacer to prevent the tracer from interacting with the surfactant in the sacrificial pad; (c) a 2,764 bbl. sacrificial pad of 0.1wt% active Alipal CD 128 in water; (d) the co-injection of 0.05wt% active surfactant in a low total dissolved solids (TDS = 500 ppm) and sour grade CO_2 that was heated and pressurized to 65 ^{o}F and 1,000 psia; and (e) chase water. The fluids were mixed at the injection, and it was thought that the CO_2 and surfactant solution would flow down the injector as slugs; it was highly unlikely that small cell-sized CO_2-in-brine foam formed in the well because the pressure required to inject such a dispersion would have been very high. Although there were no surprises during the injection of the tracer, an unexpected and reversible decrease in injectivity was noted during the injection of the sacrificial surfactant pad. The co-injection of surfactant solution and CO_2, which began on November 6, 1984, caused a gradual decrease in injectivity that brought injection to a stop on December 22, 1984, after the injection of 3,522 bbl. of CO_2 foam because flow ceased at the allowable pressure of 100 psia. Spotty injection was attained during January and February of 1985, and after repair of a casing seal leak in the injector, the targeted 10,608 bbl. of a 75% quality CO_2 foam was realized in August 1985.

The operators of this pilot were frustrated in that the chances of detecting a mobile oil front hinged on that front passing through the observation well, and it appeared that the injected fluid and any mobilized oil did not do so. Neither the tracer nor oil was produced from OB 2. Production of CO_2 occurred about seven months after its co-injection, however, and surfactant was detected about 10 months after the injection of the sacrificial pad. The injection rate of the co-injected fluids was about 73 bbl./day at 1,000 psia, whereas the average water injection rate was about 120 bbl./day, which appears to indicate that the foam was about 1.6 times as viscous as water—a modest degree of thickening for this mobility control project.

Amoco's Wertz Field; Wyoming; ~ pre-1991; Conformance Control SAG [Borling, 1994]

The Wertz Tensleep in Sweetwater and Carbon Counties, Wyoming, is a 470 ft. thick sandstone with 240 ft. of net pay characterized by 10% porosity, 13 mD permeability, and some natural fractures. The sandstone is preferentially oil-wet and the crude is light (35 ^{o}API) and sour. At the bottomhole temperature of 165^{o}F, average reservoir pressure was 3,300 psia, well above the MMP of about 2,300 psia. Waterflooding of the field was initiated in 1980, and tertiary CO_2 flooding was implemented in 1986. The need for conformance control and initial attempts to alleviate these problems using sand or cement techniques were ineffective. Therefore, an attempt was made to divert CO_2 using SAG. Although details of the process were not provided, a slug of surfactant solution was introduced to the formation, and conformance control foam was then generated in situ as CO_2 was injected. The conformance control was short-lived, however, and considered unsatisfactory. Diversion by in situ generated foam was particularly ineffective in the fractured portions of the formation. The field operators then abandoned SAG in favor of two types of polymer gel conformance control in ten wells [Sydansk, 1988; Sydansk and Smith, 1988].

Chevron's North Ward-Estes (NWE); 1990 – 1991; Conformance control SAG [Chou et al. 1992].

The North Ward-Estes (NWE) field, located in Ward and Winkler Counties Texas, was waterflooded from 1955 and CO_2 flooding commenced in 1989. Seventy-seven million bbl., or roughly 54% of the OOIP remained after secondary recovery (waterflood), residing in eight sands separated by dense dolomite layers. Poor sweep efficiency was evident from the beginning of the CO_2 flood, as evidenced by early CO_2 breakthrough and low tertiary oil recovery that peaked very quickly. Foams were selected only for conformance control because the mobility of the CO_2 was only slightly greater than that of the oil and a 1:1 WAG yielded a 50% reduction in CO_2 mobility. A particularly problematic producer was identified and the injector responsible for high gas production, high GOR, and early breakthrough in that producer was selected for foam injection.

Laboratory tests indicated that good foams were generated using Chaser CD 1040, an α-olefin sulfonate, at surfactant concentrations of 0.2–0.5wt%. Foam mobility was 20 to 200 times less than that of CO_2 and decreased with increasing permeability, thus decreasing flow rate and quality in the 60–80% range, and increasing surfactant concentration, A dramatic increase in foam mobility in the lab tests was noted at surfactant concentrations below 0.1wt%.

Therefore, the field test employed a pre-foam surfactant slug of 0.21–0.43wt% surfactant. The surfactant concentration used in the aqueous solutions of the SAG process varied between 0.19 and 0.28wt%. Foams of 50%–80% quality were generated with an alternating injection sequence of surfactant solution one day and CO_2 the next. Four foam treatments were conducted and it was observed that CO_2 injectivity was reduced by 40%–85% for periods of time ranging between one to six months. The foam appeared to successfully divert CO_2 from a high permeability zone, as evidenced by a reduction in CO_2 production at the problematic producer and an increase in CO_2 production at other offset producers. There appeared to be incremental oil recovery due to improved mobility and conformance control. It was concluded that the foam was significantly more effective at reducing flow into the higher permeability zone than the WAG process. Due to the small size of this flood and an economic analysis that did not include capital depreciation, interest, or royalty, the operators were reluctant to present firm economic conclusions. However, a simple comparison of the performance expected if the injector was (a) continued in the WAG mode, (b) changed to water injection only, or (c) converted to SAG indicated that the process would have (a) lost $400,000, (b) broke even, or (c) generated $118,300, respectively. The key economic benefit of SAG was related to the reduction of CO_2 recycling (due to the reduction of CO_2 from a problematic producer); therefore, it was suggested that future foam floods be directed at generating a strong foam that can effectively block a thief zone rather than generating a weak foam for mobility control, even if the strong foam required much more surfactant.

Chevron's Rangely Weber Sand Unit, Rio Blanco County, Colorado; 1989–1990 Conformance Control SAG; [Jonas, Chou and Vasicek, 1990].

The Rangely Weber Sand Unit produces from the Pennsylvanian-Permian Weber formation, a sequence of various sandstones, siltstones, and shale at a depth of 5,500–6,500 ft. The six producing sands are separated by five fluvial shales that occur across the entire field. The average porosity and permeability of the effective sands are 11% and 10 mD, respectively. The initial development of the field on a 40-acre spacing was completed in 1949, and peripheral water injection commenced in 1958. Reinjection of produced hydrocarbon gas continued until 1969, when pattern waterflooding started. Infield drilling occurred from 1963 until the mid-

1980s. Primary recovery resulted in the production of ~18% OOIP and secondary recovery yielded ~24% OOIP.

Chevron initiated a CO_2 flood in the Rangely Weber Sand Unit in October 1986. A 1:1 WAG injection scheme was used to reduce the mobility of CO_2 in this heterogeneous reservoir. Nearly all of the injectors had been previously fractured, and it was thought that the existence of both macroscopic heterogeneities and hydraulic fractures facilitated early breakthrough of CO_2 and poor sweep efficiency. Significant CO_2 production was a concern, as 40% of the 250 MMscf/day of injected CO_2 was recycled gas from CO_2 producers. Selective injection equipment (SIE), consisting primarily of multiple packers and mandrels, was first employed in an attempt to control injection into specified layers. CO_2 production remained a problem even when SIE was used.

Therefore, a pattern in which gas production was particularly problematic was selected for a CO_2 foam conformance control trial and mobility control in an attempt to divert the CO_2 away from watered-out thief zones and into less permeable oil-rich layers. The test pattern included a (previously) fractured injection well, Gray A 10, which was in communication with several offset producers including A.C. McLaughlin 4, Gray A 15, Gray A 22X, and Associated 4X. For example, A.C. McLaughlin 4 produced 2 MM scf/day of CO_2-rich gas and no tertiary incremental oil within 10 days of CO_2 being injected into Gray A 10.

The baseline injectivity test that preceded the foam flood consisted of a day of simultaneous CO_2 and water injection, followed by a three-day water injection cycle during which a multi-rate test was performed. The subsequent conformance foam consisted of the injection of (a) a 12,000 bbl. sacrificial surfactant slug of 0.43% Chevron Chaser CD 1040. Fifty-five thousand bbl. of a ~80% foam slug was then injected via the simultaneous injection of 11,000 bbl. of Chaser CD 1040 solution (with an average 0.47wt% concentration solution) and 44,000 bbl. of CO_2. A CO_2 chase was injected following the foam at approximately constant pressure until CO_2 injectivity or gas production at A.C. McLaughlin 4 reached pre-foam levels. This was followed by water injection until a 1:1 ratio of aqueous solution and CO_2 was attained for the foam flood. In early 1990, a two-month co-injection of CO_2 and water was conducted in order to contrast the effects of the CO_2-surfactant solution co-injection with the CO_2-water co-injection. The performance of these co-injection cycles was assessed using injectivity results, determination of CO_2 injection profiles, pressure transient analysis, and production results. The injectivity and CO_2 injection profiles indicated that the foam was placed in the formation despite the presence of a hydraulic fracture in the injector. The foam injection also caused A.C. McLaughlin 4 to exhibit lower gas production and higher oil production. Upon the injection of the CO_2 chase, injectivity was reduced for two months while the McLaughlin gas production was diminished for one month. In general, the operators found the results encouraging and that the foam project, which resulted in the incremental production of roughly 50 BOPD during April and May 1989, paid out by May 1989. At this time, they considered the CO_2 foam (which doubled the injection cost of CO_2) to be a less expensive conformance technique than the use of polymer gels. Polymer gels were also tested in this field several years later (as described in the polymer gel section of this report).

Mobil's Slaughter Field, East Mallet Unit, Well 31, Hockley County, Texas; SAG; Conformance and Mobility Control; 1991 [Hoefner and Evans, 1995]

Mobil's four field tests (described in this section and the following three sections) were designed in recognition that foams can, in general, provide both conformance and mobility control. Mobil considered foams as the conformance control of choice (rather than cement-, gel-, or resin-based profile-control methods) when a reversible method was desired. Specific examples of situations that are most appropriate for foams include (a) multiple thin intrazone thief zones, (b) thief zones that are not vertically differentiated from target zones, and (c) thief zones still capable of producing oil if mobility control can be established within them. In its attempt to study two surfactants and two types of injection strategies, Mobil conducted four field tests in patterns that were characterized by high gas flow rates, high GORs, low wellhead pressure in the injection well, rapid interwell transit of the injected CO_2, and a readily distinguishable thief zone.

The East Mallet Unit produces from the San Andres formation of the Slaughter field in the Permian Basin. The Slaughter field is composed of several units that produce from the layered, highly dolomitized, San Andres formation at a depth of 4,000 to 5,500 ft. This formation exhibits a wide variation in permeability. Miscible CO_2 flooding was initiated in 1989 using 20 acre well spacing in chicken wire patterns. Laboratory tests indicate that CO_2 foams 3 to 10 times less mobile than CO_2 could be generated—even in the presence of oil—via SAG or co-injection of surfactant and CO_2. The foams did not cause any damage to the cores.

A total of 20,200 lb. of active Rhodapex (previously marketed as Alipal) CD 128 surfactant was formulated into a 1wt% aqueous solution and injected into Well 31 with very short cycles via the SAG process. Foam formation was evidenced by reduced gas injectivity determined from increases in wellhead pressure. Injection profile logs indicated that fluids were completely diverted from the top 20 ft. of the injector perfs, which included the thief. Surfactant utilization for this field was 0.58 lb. active surfactant per 1 psi change per MMscf of CO_2. Gas production was cut by as much as 50% in Well 98. While a portion of this decrease may have been attributable to decreased CO_2 injection rate during SAG, the diminished gas flow continued for eight weeks after the SAG process ended, indicating that the foam was also responsible for the reduced gas flow. While oil production decreased in one well, oil production in the entire pattern increased by about 26%, or 19 BOPD.

This particular Mobil field test provided the most conclusive evidence of the four trials that SAG was an effective conformance and mobility control technique.

Mobil's Slaughter Field, East Mallet Unit, Well 68, Hockley County, Texas; Co-injection and SAG; Conformance and Mobility Control; 1991–1992 [Hoefner and Evans, 1995]

The objective of this test was to compare the SAG technique (Well 31) with the co-injection technique (Well 68). After co-injection in Well 68, SAG was also performed to provide a comparison of co-injection and SAG in the same well (Well 68), and a comparison of SAG performance in two wells (31 and 68). These two patterns were chosen due to the similarity of their injection and production history and wellhead pressure and log data.

The co-injection was intermittent in that the simultaneous co-injection of CO_2 and a 1wt% surfactant solution was followed by injection of CO_2 alone. Nine such cycles were employed during this intermittent co-injection. This strategy led to very large pressure increases, which in turn led to injection rate decreases designed to prevent the pressure from exceeding the maximum allowable wellhead value. Foam quality was also decreased from 80% to 60% to 30% to 20% in an attempt to increase injectivity and flow rate. Not surprisingly, operators had numerous difficulties in metering flow during these low injectivity periods.

The subsequent SAG injection of CO_2 and surfactant solution, including a final cycle with Chaser CD 1045 (rather than Rhodapex CD 128) yielded injectivity changes quite similar to those observed in Well 31. Surfactant utilization for this field was 0.17 lb. active surfactant per 1 psi change per MMscf of CO_2. This pattern exhibited neither a reduction in gas production, an increase in oil production, nor the production of surfactant. The producing wells were inadvertently stimulated prior to the designated end of the foam test; therefore, it was difficult to assess how much of the resultant dramatic oil production rate increase was caused by the foam. Although it was not considered to be conclusive evidence of the benefits of foam, the increase in oil production was more significant than increases observed in similarly stimulated WAG producers.

Mobil's Greater Aneth Field, McElmo Creek Unit, Well P-19, San Juan County, Utah; SAG; Conformance and Mobility Control; 1992 – 1994 [Hoefner and Evans, 1995].

The Mobil Greater Aneth field test—the third of the four Mobil pilots—was conducted in a platform carbonate reservoir with larger well patterns (160 acres) than the Slaughter field tests (40 acres). Further, the objective was to more thoroughly assess the potential for increased oil production.

The McElmo Unit is part of the Greater Aneth Field in the Paradox Basin, and CO_2 miscible flooding started there in 1985. Just before the foam pilot test oil production was about 6,000 BOPD. Because of the high mobility of CO_2, the field was operating at the capacity of the gas plant, high gas producing wells were routinely shut-in, and CO_2 injection cycles were commonly shortened. The Lower Ismay and Desert Creek II were identified as the thief zones, with CO_2 targeted at the more oil-rich Desert Creek I layer. Based on lab tests, it was expected that a resistance factor of ~7 could be realized with foams.

The injection strategy was changed from WAG to continuous CO_2 injection prior to SAG in this pattern. The subsequent SAG foam test was conducted by maintaining a targeted injection rate and injecting foam when the injection pressure fell below the selected minimum value. Rhodapex CD 128 was used from April 1992 until February 1993, while Chaser CD 1045 was used from May to December 1993. No sacrificial slug was employed because of the apparent likelihood the slug would not necessarily flow into the same portion of the formation as the CO_2 foam. For each surfactant, the total volume of surfactant solution was injected in two cycles, with a CO_2 slug between them.

The average wellhead pressure increased from 900 to 2,100 psia in Well P 19. Surfactant utilization for this field was only 0.053 lb. active surfactant per 1 psi change per MMscf of CO_2, a value substantially lower than that of the EMU wells. A relatively long period of higher surfactant utilization early in the flood may have been attributable to surfactant adsorption losses. Further, it was determined that the performance of Rhodapex CD 128 was quite similar to that of CD 1045. A reduction of CD 128 surfactant concentration from 1.0wt% to 0.5wt% had no effect on the foam performance when the results were compared on a per-pound-of-surfactant basis.

The SAG process was found to increase the amount of flow into Desert Creek I from 15% in the test previous to SAG to an average value of 19% during SAG; however, the average of seven pre-foam tests indicated that about 29% of the foam was entering DCI during WAG. During WAG, gas production averaged 0.41 Mscf gas/ Mscf CO_2 injected; during continuous CO_2 injection the value increased to 11.1, and during the subsequent SAG the value decreased to 0.6. Oil production increased by ~10% as the pilot was changed from WAG to continuous CO_2 injected at nearly twice the flow rate. This higher oil production rate was maintained during the subsequent SAG, but it was not possible to affirm that this increase was due to increased sweep of the foam.

Mobil's Greater Aneth Field, McElmo Creek Unit, Well R-21, San Juan County, Utah; SAG, Co-injection; Conformance and Mobility Control; 1992 – 1993 [Hoefner and Evans, 1995].

The extremely high gas production rate of Well R-20 was found to be attributable to injector R-21, which was therefore selected as the foam injection well for the last of Mobil's four pilot tests. In this case the thief zone was a high perm streak in the DCI zone. Because this thief zone was not capable of being vertically isolated from the CO_2 target interval, it was deemed that foam, rather than more permanent measures such as gels, was the most appropriate means of attaining conformance control. Thirty-three thousand seven-hundred pounds of active surfactant was injected into R-21 using SAG, the first two-thirds of which was injected in a manner similar to the MCU P-19 test to allow a direct comparison of the injector response of the two MCU pilots. Injectivity was found to be similar, but due to operational problems no conclusive production response was identified.

Subsequently, an attempt was made to co-inject the CO_2 and surfactant solution in an attempt to reduce injectivity. In order to avoid the extremely high reductions in injectivity experienced in the EMU Well 68 test, continuous co-injection of higher quality foam was employed without any intermittent CO_2 cycles. Although 95–98% quality foams were found to be more effective than SAG at reducing injectivity on a per pound surfactant basis, this injectivity reduction was quickly lost when injection was returned to CO_2. Unfortunately, plugging at the wellhead, possibly due to freezing or hydrate formation, frustrated efforts to conduct a longer and more thorough test.

16. Field Tests with Foams Generated by CO_2-soluble, Water-soluble Surfactants Using Dense CO_2 as a Gas

DuPont Oil & Gas and KinderMorgan's WAGS SACROC Unit; 2008-2010; Pilot Test [Sanders, 2010]

The SACROC unit of the Kelly-Snyder field is located in Scurry County, Texas. This field produces from the Canyon Reef of the Horseshoe Atoll in the northeast portion of the Permian Basin. The SACROC unit, which is on the eastern side of the Horseshoe Atoll, produces from a 6,700 ft. deep limestone carbonate formation that has a net pay thickness of ~260 ft. with 800 ft. of closure, an OOIP of 2.8 billion bbl., an average porosity of 7.6%, and permeability values that range from less than 10 to hundreds of mD with an average of 19 mD. A review of the unit's history [Larkin and Creel, 2008] reveals that the Kelly-Snyder field was discovered in November 1948 and by 1952 about 1,200 wells had been drilled. The solution gas drive resulted in a rapid pressure drop from 3,120 psia at discovery to an average pressure of 1,546 psia, well below the 1,976 psia bubble point value. This resulted in the design of a line drive waterflood along the spine of the structure in 1953. In 1970, a second row of wells was converted to injectors that increased reservoir pressure to 2,300 psia. In 1971, preparations for a unit-wide CO_2 flood began with the conversion to a 160-acre inverted 9-spot pattern. CO_2 flooding began in 1972, but the initial response was disappointing primarily because of the limited supply of CO_2. About six years later—after two years of CO_2 flooding, four years of waterflooding, and the elimination of depletion allowable limits—oil production peaked at 211,000 BOPD. Over the next 20 years, oil production declined despite infield drilling, waterflooding, and deepening of the wells to the oil-water contact. The lowest oil recovery rate of 7,000 BOPD occurred in 1997. Continued pattern size reduction via infield drilling to 20-acre spacing, coupled with larger CO_2 slugs and reduced WAG ratios, resulted in an oil production rate of about 27,000 BOPD in 2008. Not surprisingly, this massive unit has numerous injectors that communicate directly with offset producers. It was previously mentioned in this report that conventional CO_2 foams were assessed in SACROC, albeit with limited success because the pilot was apparently conducted in a portion of the unit were there were significant vugs and massive flow paths that are not well remediated by foams.

On the basis of relatively recent identification or design of relatively inexpensive surfactants that dissolve in CO_2 and generate CO_2-in-brine foams in situ, Dow and KinderMorgan are currently conducting a pilot-scale test of Dow Oil & Gas' proprietary surfactant, Enhance CO_2. This family of non-ionic surfactants is soluble in CO_2 to approximately 0.1–0.2wt% at typical CO_2 flooding conditions at SACROC. The first phase of the pilot involved injectivity analyses in a single pattern, with plans for a subsequent four-pattern pilot to assess both injectivity and oil recovery. The patterns that were chosen for this test, 225-3A, 225-8, 225-10, and 225-11, have an OOIP of 8.7 MM bbl. of oil. Tertiary recovery as of 2011 was ~13%. Further, the injectivity of four injectors indicates that fluids flow away from the wells through the rock matrix where foams can be an effective conformance and/or mobility control strategy, rather than in extremely high permeability, open channels where foams exert little influence on conformance control. (Note that in cases where fracture communication between injectors and producers was responsible for poor sweep in other SACROC patterns, swellable-preformed, crystallized copolymer particles were recently employed and compared to conventional pre-formed metal crosslinked particles.) This crystallized polymer effort is detailed in the "Preformed Polymer Particle" section of this report.

The success criteria were specified as a 10% increase in CO_2 usage for the pattern over 6 months and a 1% increase in oil production on the dimensionless curve for the pattern. During the first phase of the pilot, the CO_2 plus surfactant solution was injected in a single well in an attempt to validate the lab tests, determine concentrations, and develop an injection strategy for the subsequent expansion. During the second phase, which was underway in 2010, injectivity and oil production were to be carefully monitored from all four patterns.

The results of the first phase of the pilot test were promising. The injection of CO_2 or the CO_2-surfactant solution was constrained by the compression system maintaining a constant wellhead pressure. There was no indication of extremely high permeability voids in this pattern. Relative to the injection of pure CO_2, the injection rate dropped from roughly 6,800 BPD (during the period from 200 to 500 hours following the injection of CO_2) to roughly 4,600 BPD (during the period from 300 to 550 hours following the injection of CO_2 plus surfactant solution). This represents a reduction in injection rate by one-third compared to CO_2, which indicates that the in situ generated foam had an apparent viscosity about 50% greater than pure CO_2. Another injectivity test began with three weeks of concurrent surfactant and CO_2 injection, after which surfactant addition was terminated while CO_2 injection continued. The consistent increase in the cumulative CO_2 volume injected vs. time at constant injection pressure indicated that (for the duration of this test) the foam propagated through the matrix for 500 hours following the introduction of surfactant. Further, injection profiles indicated that about 30% of the injected CO_2 was diverted to a lower portion of the formation while only 1% of the CO_2 flowed into this zone prior to the addition of the surfactant.

TABLE 16.1.A SUMMARY OF FIELD PROJECTS AND THEIR PERFORMANCE

Field	**Gas**	**Location**	**Geology**	**T**	**P**	**Depth**	**Porosity range %**	**Perm range mD**	**Net pay**	**# layers**	**Oil viscosity at res/API gravity/SG**	**Brine**	**Primary**	**Secondary**	**Tertiary**
Siggins	Air	US	Pennsyl. Sandstone	65F		400 ft.	19	56	30–50 ft.		25 cP		1906	1940s	~1970
ZhongYuan	Air	China	Sandstone	90 C	25 MPa orig.		21	100 - 1000	16 m		4 cP	200000 ppm		Two decades ~21%	2005 Nitrogen injection; breakthrough in 3 days
Painter	Nitrogen	US	Jurassic Nugget Sandstone								44 º API				1980 Pressure maintenance via nitrogen injection; fast breakthrough
Shengli	Nitrogen	China	Unconsol. sandstone	60 C	11.27 MPa	1125 m	37	2304 DP 0.73	6.5 m		74 cP; SG 0.92	Orig. 1558 ppm; 6227 ppm (130 divalent)	1964		Extensive polymer flooding
Sabei	Nitrogen	China	Sandstone	45 C		~1000 m		140 – 190			6 – 9 cP				World's largest polymer flood started in 1996; 10 million tons of oil/yr. 2002 - 2007
Pembina Ostracod 'G' Pool	H.C. gas	Canada	Sandstone	57 C		1730 m	12	70	1 m	1		70000 ppm	1978 16%	No	1985
Kaybob South Triassic 'A' Pool	H.C. gas	Canada	Dolomitic limestone	88 C		2100 m	11.5	92	4.8 m	1	0.42 cP		1962	1967	1984
Judy Creek Beaverhill Lake 'A' Pool	H.C. gas	Canada	Limestone	97 C		2650 m	6 – 12.5	40 - 170	67 m Foam inj. in top 22 m	5	0.4 cP		1959	1964 49%	1985
Snorre Central Fault block and Western Fault Block	H.C. gas	Norway	Brent-type sandstone	90 C	300 bar 30 MPa	300-350 m water; 2000 – 2700 m	25	400 S2–3500 S1 50-80 S3	6 m	2 S1 and S2			-	1992	1995 WAG; 1 mo. breakthrough for wells 1 km apart
JoffreViking	CO_2	Canada	Sandstone	56 C		1500 m	13	500	3 m	1	1 cP		1953	1957 42%	1984; 44% HCPV, 6 month breakthrough; WAG 1.5:1; 5 month 5 month; 32 ha
Wasson	CO_2	Texas	Dolomite (fractured)			1550 m	10-20	10	10 m		1 cP		1936	1966	1982; 8 ha; 4 month breakthrough
EVG/SAU	CO_2	New Mexico	Dolomite (weakly fractured)	101 F		610 m	21.7		7.6 m				1941	1980	1985; 40% HCPV; WAG 2:1; 8 mo. : 4mo; 24 ha
SACROC	CO_2	Texas	Limestone carbonate (dual porosity)	58 C		2100 m	8	~19	42 m		0.4 cP		1949	1953	1972; CO2

Field	**Gas**	**Location**	**Geology**	**T**	**P**	**Depth**	**Porosity range %**	**Perm range mD**	**Net pay**	**# layers**	**Oil viscosity at res/API gravity/SG**	**Brine**	**Primary**	**Secondary**	**Tertiary**
Wilmington	CO_2 Immiscible	California	Clastic sands							3					
Rock Creek	CO_2	West Virginia	Sandstone	73 F	<1000 psia	610 m	21.7	21.5	7.6 m	1	3.2 cP; 43 °API		1906 10%	1935, 1972; gas cycling	1979; CO2 pilot
Wertz	CO_2	Wyoming	Sandstone											1980	1986 CO2
North Ward Estes	CO_2	Texas	Sandstone			800 m	18	15 DP 0.85	18 m	8	1.4 cP		1929	1955	1989; 40% HCPV; 8 ha
Rangely Weber	CO_2	Colorado	Sandstone			5500 – 6500 ft.	11	10		6			1949	1958	1986 CO2
EMU 31	CO_2	Texas	Dolomite			1520 m	1 - 18	0.01 - 28	30 m	3			1940	1964 30-40%	1989; 35% HCPV; 16 ha
EMU 68	CO_2	Texas	Dolomite			1520 m	1 - 18	0.01 - 28	30 m	3			1940	1964 30-40%	1989; 35% HCPV; 16 ha
MCU 19	CO_2	Utah	Carbonate												
MCU 21	CO_2	Utah	Carbonate			1750 m	3-12	0.01 - 1000	15 m	19			1956	1962	1985; 40% HCPVWAG <1:1; 6 mo:6 mo.; 32 ha
SACROC	CO_2	Texas	Carbonate	58 C		6500 ft.	8	~19	42 m				1949	1953	1972 CO2

TABLE 16.2. GAS-IN-WATER FOAM FIELD TESTS

	Purpose of Foam	Gas Phase	Years of Foam Test	P at Start	Surf.	Conc. Wt.%	Quality % at res cond.	Inj. Strategy	Slug Size	SAG ratio	Duration	Inj. profile imp?	Inc. in Inj P?	Dec injectivity ?	Dec in GOR?	Inc. in Oil Prod?	Technical Success?	Economic Success?
Siggins	Injectivity decrease	Air			Alkyl sulfate	0.5 – 1.5	90	SAG		1:9				20-65% mobility reduction for water and air			Yes	
ZhongYuan	Conf. Control; Mobility control	Air	2007	20 MPa reservoir			~50%	Air foam – alternating – air; AFAAI	0.1 PV							20% increase	Yes; oil prod increase and 4% drop in water production	
Painter	Conf. control; mobility control	Nitrogen	1986-1987		Proprietary	0.5 – 1.0	60-70	Co-injection	20,400 res bbl. of foam		~2 mo.			Yes,10-fold decrease in nitrogen injectivity	No	No	No; co-injection led top overpressurization	No
Shengli	Conf. control	Nitrogen	2004 pre-slug; July 2005 main slug	7.6 MPa	DP-4 surfactant and high MW polyacrylamide (25% hydrolyzed)	0.5% surfactant; 1600 ppm polymer; 2316 tons surf.	~60%	Pre-slug, main SAG foam slug, waterflooding	0.3 PV main slug		4 years; main slug 55% complete in 2009	Yes	To 10 MPa	Yes		Increased from 23 to 36 t/day; 7894 ton incr. oil	Yes; decrease in water cut; increase in oil cut and prod.	Yes
Sabei	Near wellbore; 20m; thief zone	Nitrogen	2005 - 2006	14.2 MPa	Industrial foaming agent	0.3-0.5% surf; 30 – 1500 ppm polymer stab.	~53%	SAG	0.65% PV	1:1.12	4 mo.	Yes	1.5 – 3.0 MPa	Yes		Increased in 6 of 9 prod.; incr. from 35 to 51 tons oil/d for 6 mo.	Yes; decrease in water cut; increase in oil cut and prod.	Yes
Pembina Ostracod 'G' Pool	Mobility control; Override?	H.C. gas	1987	11 MPa	Dow Pusher XSS 84321.11	0.6	95	Co-injection			6 days			Yes 18 MPa possible fracture	Yes	25% for 4 months	Yes; although mobility reduction was less than that anticipated from lab tests	
Kaybob South Triassic 'A' Pool	Mobility control; Override?	H.C. gas 68% C2+	1987	18 MPa	Dowfax XS 84312.11	2 - 5	90	SAG	12%					2 times	Yes	Not distinctly related to foam		
Judy Creek Beaverhill Lake 'A' Pool	Mobility control; Conf. control; Override	H.C. gas 50% C2+	1992	24 MPs	No info 50 tonnes	0.35	50?	SAG?			6 months	Not significant		15%	No	No	No	No

	Purpose of Foam	Gas Phase	Years of Foam Test	P at Start	Surf.	Conc. Wt.%	Quality % at res cond.	Inj. Strategy	Slug Size	SAG ratio	Duration	Inj. profile imp?	Inc. in Inj P?	Dec injectivity?	Dec in GOR?	Inc. in Oil Prod?	Technical Success?	Economic Success?
Snorre CFB and WFB	In-depth mobility control; CFB injectivity test, WFB in-depth mobility control	H.C. gas 70% C1	1997 - 2000	280 bar	AOS	0.5-0.2 a total of 1420 tons of 38% AOS were used in the two mobility control tests; 1040 CFB, 380 WFB	85	CFB: SAG and short co-injection; WFB SAG	CFB: 85-150 depth into form,; 74.5km3 water; 75 MMSm3 gas; 1040 tons 38% active AOS WFB							WFB: 250000 Sm3 oil attributed to FAWAG	Yes	Yes WFB: 250000 Sm3 oil, $1000000 cost for FAWAG
JoffreViking	Mobility Control	CO_2	1990	16 MPa	No info	0.2		Co-injection; SAG			6 months		2 MPa	Moderate	No	Difficult to Assess	No	No
Wasson	Conf. Control; Thief zone	CO_2	1994		Chaser CD 1045	0.5		SAG; Single slug			5 days	No		Yes	30%	No?	Yes	No Poor surfactant placement and small slug size
EVG/SAU	Conf. control; Near-well; thief zone	CO_2	1992	2100 psia res 14.5 MPa	Chaser CD 1045	0.25	80	SAG; fast cycles			4 years	10-20%	3.5		Yes	Yes	Yes	Positive net revenue, but low rate of return
SACROC	Conf. Control; Thief Zone	CO_2	1984	12.4 MPa	Alipal CD 128	N/A		SAG				No			No	No	No	No foam not effective in dual porosity formation
Wilmington	Conf. control	CO_2	1984		Alipal CD 128	1.0						yes	yes	yes			Partial; water injection after foam formation collapsed foam	No
Rock Creek	Injectivity; 2 well test; Mobility control; Override	CO_2	1984	10 MPa	Alipal CD 128	0.05	80	Co-injection					Yes	Yes			No; foam did not flow past observation well	No
Wertz	Conf. control	CO_2	Pre 1991		N/A	N/A											No; the conformance control foam was short-lived	No
North Ward Estes	Conf. control; Thief zone	CO_2	1990	10 MPa	Chaser CD 1040	0.2 – 0.5	50-80	SAG fast cycles			2 years	Yes	2.1	40 - 85%	9 times	15 times	Yes	Yes; based on extrapolated numbers from this small foam flood
Rangely Weber	Conf. control	CO_2	1990 - 1991		Chaser CD 1040	0.5						Yes	Yes	Yes	Yes	Yes	Yes	Yes

	Purpose of Foam	Gas Phase	Years of Foam Test	P at Start	Surf.	Conc. Wt.%	Quality % at res cond.	Inj. Strategy	Slug Size	SAG ratio	Duration	Inj. profile imp?	Inc. in Inj P?	Dec injectivity ?	Dec in GOR?	Inc. in Oil Prod?	Technical Success?	Economic Success?
EMU 31	Conf. control and mobility control	CO_2	1991	14 MPa	Alipal CD 128	1.0		SAG			0.5 yr.	Yes	2.6	Yes	2	31%	Yes	Yes
EMU 68	Conf. control and mobility control; co-injection	CO_2	1991	14 MPa	Alipal CD 128 and Chaser CD 1045	1.0	80-20	Co-injection			0.7 yr.	No	Too high	Too much	No	0	No	No
MCU 19	Conf. control and mobility control	CO_2	1992		Alipal CD 128 and Chaser CD 1045	0.5 - 1.0							Yes			Yes, 10%, but not conclusively linked to foam	Inconclusive	No
MCU 21	Conformance control; Thief zone	CO_2	1992		Alipal CD 128 and Chaser CD 1045	0.5 – 2.0		SAG; Co-injection			>1 yr.			Yes		No; test was too short	No; operational problems	No
SACROC	Conf. Control	CO_2	2008		Dow's Enhance CO_2; a CO_2-soluble nonionic	~0.1 – 0.2%		GS; surfactant dissolved in CO_2				Yes		Yes		Phase 1 injectivity only	Yes; Phase 1	On-going Phase 2, oil production

17. CO_2 Pilot Tests Conducted with Alternate Conformance Control Technologies

It is likely that one of the reasons for the decline in interest in CO_2 foams for conformance control has been the aggressive development of alternative conformance control technologies that are applicable for oil recovery. In general, these alternative conformance control treatments consist of aqueous solutions or dispersions that, once in place in a high permeability zone, form extremely low mobility gels or gelled foams. The fundamental advantage of such techniques is that the fluids are injected into the formation while they exhibit a relatively low viscosity, which allows the majority of the solution to preferentially flow into the higher permeability "thief" zones, after which significant increases in viscosity are then triggered in situ by polymerization or crosslinking reactions. Placement of these gelling solutions in the targeted thief zone can be improved if the thief zone can be mechanically isolated in the injection well. This is a far more effective strategy for blocking off a zone than injecting a highly viscous solution, which would tend to distribute itself more evenly throughout the layers of varying mobility. These strategies therefore provide the operator of a CO_2 flood with many other options for conformance control if the objective of the treatment is primarily conformance control. None of these gel strategies can be employed for in-depth mobility control, however, if an operator is considering the use of a mobility control foam. *In fact, it would be possible to first use a gel technique for conformance control and then employ a CO_2 foam for mobility control (rather than using only CO_2 foams or only gels).* Although likely to be more expensive and less reversible than foam, these gels and gelled foams may be the more robust and effective conformance control agents.

Several of these alternate conformance control strategies have been used in CO_2 floods; therefore, a brief review of chemical-based conformance control technologies that have been employed during CO_2 floods in the field will now be presented. A review of the fundamental science and lab-scale testing of these conformance control techniques is beyond the scope of this report, but a more thorough overview of reservoir conformance improvement can be found in an excellent book by Sydansk and Romero-Zeron on this topic that has been recently published by SPE [Sydansk and Romero-Zeron, 2011] and in a recent summary of PPG conformance control technology [Bai et al., 2009].

Crosslinkable monomer solutions

If one desires to inject an aqueous conformance control solution such that the slug flows preferentially into the problematic thief zone and not into the less permeable oil-bearing zones, the slug should be designed to have a very low viscosity. Designing a gel solution that has a viscosity comparable to water is most readily achieved by dissolving a water-soluble monomer and a crosslinking agent in the water and having both the polymerization and crosslinking occur after the solution has flowed into the thief zone. The fundamental drawback of this technique, however, is that monomers and monomeric solutions are inherently more hazardous to workers and the environment than polymeric solutions.

Crosslinklable polymer solutions

It is possible to dissolve a polymer or biopolymer in water along with a crosslinking agent. This enables the polymer solution to be introduced to the formation prior to crosslinking, thereby allowing the solution to flow preferentially into the watered out zones. The crosslinking reaction is then initiated via a “trigger” such as the passage of time occurring since the solution was prepared on the surface and/or the increase in temperature the solution experiences as it flows into the reservoir. This is probably the most common means of conformance control in CO_2 flood pilot tests. The foremost disadvantage of these systems is that they may not be effective in formations characterized by extremely high permeability paths such as voids, vugs, and large fractures.

Crosslinkable surfactant/polymer foams

One can attempt to enhance the durability and reduce the mobility of CO_2 foams by enabling the thin, aqueous lamellae that bridge across pore throats to gel once the foam is in place. This can be accomplished via the addition of a relatively small concentration of polymer and crosslinking agent to the surfactant slug. Further, prior to crosslinking, the low density foam is more likely to flow into regions of the reservoir where CO_2 is likely to flow than aqueous crosslinkable polymer solutions. There may also be an economic advantage in that dense CO_2 in a typical EOR project is less expensive on a mass basis than the aqueous solution of surfactant, polymer, and crosslinking agent. This makes gelled foams particularly attractive for injection into very large portions of the field where gas breakthrough is particularly severe. Foam gels have been reported much less frequently than polymer gel solutions, however, perhaps due to increased complexity of the chemistry, on-site preparation, and injection logistics.

Inorganic gels

Although silicate gels have been explored for conformance control, these inorganic gels are beyond the scope of this report and have not yet been employed in CO_2 field tests.

Dispersions of swellable, pre-formed particles in water

Preformed particle gel (PPG) conformance control is a promising technology that offers robust conformance control for wells characterized by extremely high permeable features such as voids, vugs, and large fracture networks. Millimeter-scale gel particles are synthesized and dispersed in water prior to being introduced to the formation. This eliminates the inherent in situ gelation difficulties such as uncontrolled gelation times, variations in gelation due to shear degradation, and unforeseen reactions that may occur when the solution gel contacts reservoir minerals and fluids. Because the only reaction that occurs in situ is the enlargement of the particles as they absorb water, PPG dispersions are relatively environmentally benign and safe to handle. Unlike crosslinkable monomer solutions, polymer gel solutions, and foam gel solutions, PPG slurries consist of very fine preformed gel particles dispersed in water or produced water. As such, they are well-suited for entering voids, fractures, or fracture-feature channels, but not the matrix of sandstone or carbonate porous media. They can conceivably be used in conjunction with polymer gel solutions, however, if it is desirable to first block extremely high permeability open flows paths with PPG and then block the pore network of a highly permeable watered-out zone with a crosslinkable polymer solution [Sydansk and Romero-Zeron, 2011].

18. Field Tests of Gels with Hydrocarbon Miscible Gas

Amoco's South Swan Hills Field, Northeast of Edmonton, Alberta, Canada; 1975–1977; Polymer Gel Conformance Control [Wagner and Weisrock, 1986].

Following primary production, Amoco began secondary hydrocarbon miscible flooding in the eastern portion of the South Swan Hills (SSH) field in 1973. This SSH miscible unit (SSHMU) produced from the Beaverhill Lake formation at a depth of 8,500 ft. and reservoir temperature of 225 ^{o}F. Because of the low viscosity of the hydrocarbon solvent, alternating injections of water and solvent were employed to reduce solvent mobility. Severe channeling of both water and solvent through a thief zone was detected in the northwest quarter of the SSHMU. Therefore, lignosulfonate gel conformance control was implemented in nine injection wells. The treatment was designed to gel in situ after injection of the solution was complete.

Lignosulfonate is a biopolymer with an average molecular weight of 10,000 derived from pulp industry byproducts. Lignosulfonates are capable of being crosslinked by chromium III ions in a manner similar to polyacrylamides. The time-setting nature of these solutions is related to the reduction of Cr VI to Cr III in solution in the presence of wood sugars. The solutions injected into the wells had a viscosity comparable to water and contained 2–3 wt% lignosulfonate and 0.5–3.0% dichromate, but formed viscous sludges or stiff gels in situ. Injected volumes varied from 8,500 to 14,000 barrels at an average cost of $147,000(Can.)/well.

Not surprisingly, there was no immediate response in oil production when the solution was injected. Subsequent to gelation, however, there was an improvement in the fluid distribution profile. For example, in Well 201, 58% of the injected fluids flowed into Zone 2 prior to gelation treatment, but two months later that zone was receiving only 18% of the injected fluids.

The oil production from the 56 offset producers in the SSHMU was monitored for many months (up to 30) to judge the effectiveness of the gel treatments. Thirteen of these producers had a significant increase in incremental oil, and the total incremental oil production from this project was 3,300,000 barrels. The increase in revenue was $33,000,000 while the total costs of the nine injection treatments was $1,300,000 (Canadian dollars). The project was considered a technical and economic success.

19. Field Tests of Crosslinkable Polymer Solutions and Crosslinkable Monomer Solutions with CO_2

Phillips' Lick Creek Field, Bradley and Union Counties, Arkansas; 1978; Conformance Control; Crosslinkable Anionic Polymer Gel [Woods et al., 1986].

The Lick Creek Meakin Sand Unit contains 61 wells on 20 acre spacing. Production comes from the unconsolidated, fine-grained Meakin Sand of the Ozan formation of the Cretaceous age. This formation is 2,550 ft. deep and about 8' thick, with an average permeability, porosity, and initial water saturation of 1200 mD, 0.30, and 40%, respectively. The viscosity of the 17 ^{o}API crude oil at initial reservoir conditions of 118 ^{o}F and 1,200 psia was 160 cP. The field was discovered in 1957 and primary oil production ensued until 1976. CO_2 injection began in February 1976, and WAG was established for mobility control in January 1979.

By 1978 it was evident that channeling was resulting in diminished oil recovery. Thief zones with permeability values as great as 3,000 D were detected. Initially the use of foams was considered for conformance control, but tests indicated that the foams would not be effective in sands with permeability values greater than 150 D.

Therefore, a crosslinkable anionic polymer was employed in 1978 in an attempt to block the thief zones via in situ gelation of the polymer-crosslinker solution. Although gelation did occur, conformance control was effective for only a few WAG cycles. It was thought that the gel, which was based on an anionic polymer, may not have been able to withstand the acidic environment caused by the dissociation of a small amount of the dissolved CO_2, which forms carbonic acid. Subsequently, Phillips injected a monomer solution that formed a non-ionic polymer in situ, which then crosslinked to form a gel (see the next section).

Phillips' Lick Creek Field, Bradley and Union Counties, Arkansas; 1984–1985; Conformance Control; In situ Polymerization and Crosslinking Gelation [Woods et al., 1986].

Initial attempts to attain conformance control in the Lick Creek field were focused on CO_2 foams and in situ gelation of an anionic polymer (see the prior section). When it became apparent that neither of these techniques was suitable for this field, Phillips decided to use a low viscosity, aqueous monomer solution that contained an organic crosslinker. It was thought that the gelation of a non-ionic polymer would yield a gel that was more robust in the low pH, high salinity environment of an aqueous phase in contact with high-pressure CO_2. Both the polymerization of the monomers into a non-ionic polymer and the crosslinking of the polymer occurred in situ.

Two problematic injection wells, 27-3 and 4-1, were identified and gel treatment slugs of 500 barrels and 400 barrels, respectively, were injected. The treatment, which occurred during the injection of a water half-cycle during WAG, consisted of 4 bbl. of a 1,000 ppm fluorescein dye solution, a 50 bbl. spacer, the gel solution, and a 2% KCl post flush capable of displacing the solution from the entire wellbore. When dye was detected in a producer, the well was shut-in for five days and gas-lift pressure was maintained on the casing in order to prevent the gel from forming in the production wellbore

The production of incremental oil and the increase in injection pressures after the treatments demonstrated that the gels did form in situ. The incremental oil production attributable to these treatments was 65 BOPD, totaling 25,000 bbl. by November 1985. This project was considered an economic success in that payout occurred in 1 ½ months, and the ability to effectively block the entire channel was considered to be a key aspect of the effectiveness of the treatment.

Chevron's Rangely Weber Sand Unit, Rio Blanco County, Colorado; 1994–1997; Conformance Control; CO_2 gel; In situ Gelation of a CC/AP Polymer Solution [Hild and Wackowski, 1998; Friedman et al*.*, 1999; Sydansk and Southwell, 2000].

The Weber Sand Unit (described in the previous section on CO_2 foams) was tested with foam along with other near-wellbore treatments during the late 1980s. Because the field had matured and both conformance and mobility control problems were becoming more significant in the mid-1990s, Chevron decided to employ a technique involving the injection of a very large volume of a diverting agent that could occupy a substantial portion of the interwell region in the high permeability, watered out zones. The gel solution was an uncrosslinked polymer solution that was intended to flow primarily into the high perm zone, gel, and then divert flow into lower perm zones that (hopefully) did not receive a significant amount of the gel solution.

During CO_2 flooding, it became apparent that an extensive fracture network existed throughout the field, as evidenced by the identification of over 100 pairs of injector-producer wells that exhibited early CO_2 breakthrough. Research conducted at NMIMT [Seright and Liang, 1996] indicated that a Cr (III) acetate polymer gel system requires a permeability of at least several hundred millidarcies for placement of the matrix. Therefore, this solution was selected because the high permeability zones and fractures had a greater permeability than the minimum amount needed for the gel to form, while the zone targeted for post-gelation CO_2 recovery had a permeability of roughly 10 mD, meaning that the gel solution should not block this oil-rich zone.

Cr (III)-carboxylate/acrylamide polymer gels (CC/AP) are aqueous solutions that form gels when the polyacrylamide is crosslinked by a Cr (III)-carboxylate-complex, typically in the form of chromic triacetate. Two major formulations of the gel are used for two distinct applications. If near-wellbore (<15ft.) total fluid shutoff treatments are desired for unfractured rock, small volumes (typically < 500 bbl.) of fresh water solutions containing high concentrations (3.5–7.0 wt.%) lower molecular weight (200,000–2,000,000) polymers are used. If fractures or multiple darcy permeability zones are prevalent, as is the case at Rangely, large volumes (500–40,000 bbl.) of a produced brine solution containing low concentrations (0.3–2.0wt%) of high molecular weight (>4,000,000) polymer are injected. Details of the chemistry associated with CC/AP gels are found in Marathon's review of 12 years experience using this technology in a wide array of applications, including conformance control, during CO_2 floods at the Rangely and Wertz fields [Sydansk and Southwell, 2000].

CC/AP can be used in many scenarios, and it was deemed to be appropriate for the Rangely field because this gel is insensitive to the low pH characteristic of CO_2 floods if the degree of hydrolysis of the polymer is in the appropriate range. A typical injection treatment of an injectivity test consists of one week's injection of water to displace CO_2 from the near wellbore region, the injection of 70 bbl. of water at 1 barrel per minute (bpm), the injection of 50 bbl. of 0.3wt% polymer solution at 1 bpm, 50 bbl. slugs of polymer solution with polymer concentrations of 0.4wt%, and 50 bbl. at a concentration of 0.5 wt%. Subsequently, the crosslinking agent was introduced, followed by injection of 10,000–15,000 bbl. of 0.5wt% solution. Finally, 100 bbl. slugs of polymer solution were injected at concentrations of 0.6, 0.7, and 0.8wt% polymer in order to establish a strong gel in the near-wellbore region that could survive the higher pressure gradients in the vicinity of the injector well. A 100 bbl. flush of water was then introduced to flush the wellbore, and the well was then shut-in for a week, followed by a return to water injection.

Forty-nine wells were treated in this manner between 1994 and 1997. Detailed examples of the performance of several individual treatments are provided in the literature [Hild and Wackowski 1998]. An aggregate assessment of these treatments showed that although some treatments yielded no discernible improvements, 80% of the treatments were considered to be successful. The increase in the incremental oil production rate for the successful treatments averaged 21 bpd, while incremental water production diminished by 98 bpd. Although incremental gas production increased by 98 Mscf/d the increase in CO_2 injection rate was even greater. The $2,060,500 investment yielded 685,000 incremental barrels of oil, which resulted in a 365% rate of return and an 8-month payout period. The net present value relative to a 10% interest rate was $3,226,000.

Amoco's Wertz Field; Wyoming; 1992-1994; Conformance Control; CO_2 Gel; In situ Gelation of a CC/AP Polymer Solution [Borling, 1994; Sydansk and Southwell, 2000].

The Wertz Tensleep field in Sweetwater and Carbon Counties, Wyoming, is a 470' thick sandstone with 240' of net pay characterized by 10% porosity, 13 mD permeability, and some natural fractures. The sandstone is preferentially oil-wet and the crude is light (35 API) and sour. At the bottomhole temperature of 165^{o}F, average reservoir pressure was 3,300 psia, well above the MMP of about 2300 psia. Waterflooding of the field began in 1980, and tertiary CO_2 flooding was implemented in 1986. Diversion by in situ generated foam was particularly ineffective in fractured portions of the formation. The field operators then abandoned SAG in favor of two types of polymer gel conformance control in ten wells [Sydansk, 1988; Sydansk and Smith, 1988]. Matrix-type workover repairs were employed by mechanically isolating the target zone and then injecting about 1,000 bbl. of low molecular weight (250,000–500,000) polyacrylamide at concentrations of 2.5–5.0wt% with a chromium (III) time-delayed crosslinker. Conformance control used in wells with fractures employed about 15,000 bbl. of high molecular weight (8,000,000–12,000,000) polyacrylamide at concentrations of 0.5–0.8 wt%, with a chromium (III) time-delayed crosslinker. These workovers extended the economic life of the field by two years by enabling the production of 35,000–140,000 barrels of oil per pattern. Therefore, in the Wertz field, polymer gel conformance control was considered to be clearly superior to SAG-based conformance control.

Occidental Petroleum's Anton Irish field; Conformance Efforts; 2003-2005; In situ Crosslinking of a Polymer Solution [Smith et al., 2006; Larkin and Creel, 2008].

The Anton Irish field was unitized in 1950 for produced gas pressure maintenance. Waterflooding began in 1969, and CO_2 flooding was initiated 1997. Early breakthrough of water and CO_2 has occurred in this field during secondary and tertiary recovery, and in 2003 an effort was made to reduce the excess cycling, increase oil recovery, and reduce the rate at which production wells were shut in. Several near-wellbore treatments were then attempted, including the injection of 900 barrels of a polymer solution in 1991, and a 1993 effort to introduce 25 barrels of monomer solution that polymerized and gelled in situ. These efforts were unsuccessful, and a thorough assessment of the field led to the conclusion that long, large voids were responsible for the rapid communication between wells. These substantial openings were originally generated as induced fractures, and then became more significant as the carbonate porous media dissolved in the low pH brine and was eroded by fluid flow. Eventually extensive void space conduits several inches in diameter formed between injectors and producers. The operators concluded that the prior near-wellbore treatments were much too small in volume to divert fluids from these massive void spaces. Therefore, they decided to employ large volumes of gel solutions and foamed cement to block these extensive voids.

Because it was determined that seven injector wells were in communication with two producers (wells 251 and 252) the polymer gel solution was injected into the producing wells. The formulation of the gel solution was adjusted after the first two wells were treated in December 2003. The improved formulation employed for the treatment of the next three producing wells, 282, 284, and 292, in 2005 comprised 6,000 barrels of a high molecular weight (16–18 million) polyacrylamide at a concentration of 0.4wt% followed by 2,000 barrels of the same polymer at a concentration of 0.6wt% followed by 2,000 barrels of foamed cement. The polyacrylamide solutions gelled in place due to the presence of a chrome (III) crossslinking agent in the treatment. In this manner, the treatment was strongest near the wellbore (foamed cement) and was less rigid deep into the reservoir (0.4wt% gel).

The combined increase in oil production rate for all five producing wells was 490 BOPD. Gas production rate was reduced by 30 MM scf/d. As of March 2006, the increase in oil production rate was 320 BOPD and the gas production rate was only 5 MM scf/d less than the pre-treatment value. At the time of the first report [Smith et al., 2006] the first two gel treatments survived for two years and the other three well treatments lasted a year.

In 2007 the status of these five wells was updated [Larkin and Creel, 2008]. The chrome-linked polymer gels that were placed in the first two producers, 251 and 252, in 2003 were still effective after three-and-a-half years. Of the three producers treated in 2005—wells 282, 284, and 292—two were still exhibiting production rates superior to pre-treatment rates, while it appeared that one of the three wells was beginning to lose its integrity.

In cases where fracture communication between injectors and producers was responsible for poor sweep in the Anton Irish field, swellable-preformed, crystallized copolymer particles were employed and compared to conventional pre-formed metal crosslinked particles. (This crystallized polymer effort is detailed in the "Preformed Polymer Particle" section of this report.)

Turkish Petroleum's Bat Raman field; Turkey; 2002; In situ Crosslinking of a Polymer Solution; Conformance Control [Topguder, 1999; Sahin et al., 2007; Topguder, 2010; Karaoguz et al., 2007; Karaoguz et al., 2004].

The Bat Raman field is located in southeast Turkey. It produces from the 4,300 ft. deep, 210 ft. (gross) thick, heterogeneous, fractured Garzan Limestone formation of the Cretaceous age. The crude is a heavy (10–15 ^{o}API), viscous (450–1,000 cP) oil that contains little solution gas. As a result, oil production from primary recovery between 1961 and 1986 was quite low, only 2% OOIP. The formation pressure declined during this period from 1,800 psia to values as low as 400 psia.

A cyclic CO_2 injection scheme was piloted in 1986 in a 1,200 acre portion of the formation. CO_2 huff-n-puff was then investigated. In 1988 the CO_2 injection was converted to a CO_2 flood and soon thereafter the entire field was CO_2 flooded. Although the matrix permeability was 10–100 mD, effective permeability values obtained from well tests were in the 200–500 mD range, which is indicative of the existence of fractures, vugs, and connecting cracks. The presence of this secondary permeability, combined with fingering due to the very unfavorable mobility ratio and gravity segregation caused by the density difference between CO_2 and the oil, led to early gas breakthrough and poor sweep efficiency.

Laboratory tests indicated that polyacrylamide-based gels that would crosslink in situ via Cr^{+3} acetate could provide effective conformance control. For near wellbore treatments, a solution of 3wt% Allied Chemical relatively low molecular weight Alcoflood 254S and 1.46% Cr^{+3} acetate was tested, while large volume, deep penetration formulations were based on 1wt% of a moderately high molecular weight Alcoflood 935 and 0.1wt% Cr^{+3} acetate [Topguder, 1997]. Given the extensive vuggy and fractured zones, a decision was then made to use the latter formulation.

About 10,000 bbl. of treatments were injected into a typical well over a two-day period. Preparation of the polymer solution required low shear mixing and fresh water hydration of the polyacrylamide, precise addition of the crosslinker at the wellhead, sampling during the operation, and monitoring of the injection pressure, injection flow rate, and cumulative injected volume of the solution. Three wells—BR-109, 116, and 124—were treated in July 2002, with four more planned for 2004.

In general, there was little initial change in injection pressure as the solution apparently filled the highest permeability vugs, but then the injection pressure increased during the remainder of treatment. Therefore, the injection flow rate was gradually decreased to prevent formation fracturing. After the treatment was injected, the well was shut in for a week, and then the CO_2 injection was incrementally ramped up to 1,200 psia over a month to prevent gel damage due to the sudden application of high-pressure (1,200 psia) CO_2. In one of the treatments, an offset producer exhibited changes in fluid level indicative of communication with the injector, but after gelation the communication was lost. This provided direct evidence of the gel's ability to plug a high permeability fracture path between these two wells. A year after the gel treatments, oil production from the 19 offset producers was 720 BOPD, a 12% increase over the pre-gel value of 645 BOPD. The payout time for the project was 12 months, which led to the expansion of this project to four additional wells in 2004. An update of the field's performance in 2007 [Sahin et al., 2007] indicated that all seven treatments yielded "short term" improvements in oil production and GOR reduction. The duration of these short term improvements was about one year, which was about the same amount of time required for the project payoff. A recent update of the effectiveness of seven treatments indicated that CO_2 injection pressure at a constant rate increased and maintained reduced injectivity for a long time, but the decrease in gas production and increase in oil production was relatively short-lived [Topguder, 2010]. Apparently, while the gel reduced injectivity in the near-wellbore region, the CO_2 was able to find new high permeability paths that that flowed toward the production well and even joined with high permeability flow paths that the CO_2 had passed through previously.

Occidental Permian's Slaughter Field, Central Mallet Unit, Hockley County, Texas; CO_2 Gel; In situ polymerization and crosslinking gelation [Creel et al., 2001; Honnert et al., 2005].

A description of the Slaughter field is found in the "Foam" section of this report describing a CO_2 foam test in the East Mallet Unit. The Central Mallet Unit (CMU) was selected for conformance control field tests. In cases where poor performance was attributable to channeling through high perm streaks and fingering, an aqueous monomer-initiator solution with a viscosity comparable to water was injected. Once in place, the monomers would react to form polymers that, in turn, would crosslink to form a gel.

The use of monomers, rather than polymers, enables the viscosity of the treatment solution to be essentially the same as water. Monomers are inherently more reactive, dangerous, and environmentally suspect than polymers; therefore, care should be taken in the preparation of large volumes of these solutions. An acid-resistant acrylate monomer was selected because of the low pH environment of the aqueous phase during CO_2 floods. In order to make the acrylate solution more environmentally benign, an organic "azo" initiator was employed rather than chromium III. The solution can be designed to become activated in the 70–200 ^{o}F range; therefore, it was deemed appropriate for this 115 ^{o}F formation.

The first two in situ generated polymer (IGP) conformance treatments were performed on CMU Well 273 and Well 275 in January 2000. The next two IGP treatments were injected into CMU Wells 15 and 274 during September 2000, and two more treatments in Wells 276 and 279 were conducted in early 2001. When the aggregate post-treatment performance was compiled for the six injection wells and the associated offset producers, oil production was maintained at the rate attained just prior to the treatments, CO_2 injection was reduced by 1.2 MMcf/d, and gas production was reduced by 0.81 Mscf/d. Therefore, oil revenues remained constant while CO_2 purchasing and processing costs went down. Based on this success, four more injection wells were treated with IGP in December 2003. The oil decline was reduced, CO_2 injection was reduced by 2 MMscf/d, and gas production was reduced by 1 MMscf/day. Ten additional treatments in the CMU during 2005 were also successful in maintaining a flat oil production rate while reducing CO_2 injection and production. These treatments were also considered an economic success in that projects completed in CMU and five additional well treatments in the nearby Slaughter Estate Unit paid out in about seven months. As of 2006, plans were in place for 31 more treatments in the CMU and 14 in the SEU.

Denbury's Brookhaven Field, Lincoln County, Mississippi; 2008–2009; Conformance Control; In situ Crosslinking of a Polymer Solution with Organic Crosslinker [Cain, 2010].

This field was discovered in 1943. The producing sands are located in the Mississippi Interior Salt Basin. The structure is a salt-cored 4-way anticline that produces from the Upper Cretaceous Tuscaloosa formation. The faulting, which occasionally affects production, trends north-south and typically has 100–200 ft. vertical displacements. The thickness of the sands ranges from ~1 to 42 ft. for individual sands, which can coalesce and become about 70 ft. thick. The porosity averages 22% but can be as high as 42%, while the permeability averages 182 mD but can be as high as 5,830 mD. All of the sands were shot in the injectors and producers. Pressure maintenance was initiated in 1945 to promote oil recovery and waterflooding commenced in 1957. Denbury acquired the field in 2002 and continuous CO_2 injection began in 2005. This field is operated under relatively high injection pressure conditions where CO_2 miscible flooding occurs and production wells flow without need for artificial lift.

Not surprisingly, early CO_2 breakthrough, high GOR, and by-passing of lower permeability, oil-rich zones occurred during CO_2 flooding of this heterogeneous field. A decision was made to forgo near-wellbore selective perforations in this heterogeneous formation because there are no shale breaks that effectively isolate zones. Cement squeezes also were not selected because it was thought that the CO_2 would migrate through weak spots in the cement. Therefore, in 2008 and 2009, gel treatments were applied to four injectors and one producer. Treatments composed of 1,500–7,000 bbl. of polymer solution and organic crosslinker were injected into the formation at polymer concentrations of 0.3–0.9 wt % at a rate of ~1 bbl. per minute. The wells were shut in after treatment to allow the gel to crosslink. Although injectivity decreased in three of the four injectors, improvements in the injection profile were modest and the effect on oil production was difficult to ascertain. It was concluded that the volumes of gel solution injected into the wells were too small. Subsequent treatments will consist of much larger volumes of solution. (WAG is also being assessed at Brookhaven.)

Field Tests of Foam Gels

Chevron's Rangely Weber Sand Unit, Rio Blanco County, Colorado; 1996 Conformance Control CO_2 Foam Gel [Friedman et al., 1997; Friedman et al., 1999; Hughes et al., 1998; Hughes et al., 1999].

The Rangely Weber Sand Unit had been previously tested with a SAG field test in the early 1990s, with the pilot yielding promising decreases in injectivity and increases in incremental oil recovery for several months [Jonas, Chou and Vasicek, 1990]. Chevron subsequently explored the use of a foamed gel in the Rangely CO_2 flood. An ideal foamed gel will behave like a typical SAG or co-injected CO_2-in-brine foam during the injection period. Gelling is designed to occur only after the foam injection is complete. In general, a gel will make the porous media impermeable until a critical pressure gradient is reached. At or above this pressure gradient, the gelled lenses will rupture and the media will become conductive, but the gel debris that becomes trapped in pore throats may continue to provide a measure of resistance to fluid flow. The advantage of gelled foam, relative to an aqueous gel treatment that was also tested at Rangely

[Hild and Wackowski, 1998], is that the average density of the foam will be less than that of the brine (CO_2 density at field conditions is ~0.7 gr/cm^3). Therefore, the gelled foam is more likely to flow into regions of the reservoir where CO_2 is likely to flow, such as the upper regions of fractures of thief zones. Further, CO_2 in this project is inexpensive relative to the aqueous phase; therefore, is it possible to inject much larger volumes of gelled foams than aqueous gels in an injector. This makes gelled foams particularly attractive for injection into very large portions of the field where gas breakthrough is particularly severe.

The aqueous liquid used to form the foam gel in the formation at 160 ^oF at a pH of ~3.9 was composed of Rangely brine and (a) 10 mg/liter of a scale inhibitor; (b) 6.3 active gr/liter partially hydrolyzed polyacylamide (PHPA) with 0.5%–1.0% degree of hydrolysis (DH); (c) 130 ppm Cr(III) as acetate for crosslinking; (d) 0.5wt% of an anionic surfactant to stabilize the aqueous lamellae during foam generation without degrading gel strength; (e) 3 gr/liter of urea that acted as a delayed release bicarbonate buffer that decomposed to form 0.05 mol/liter of bicarbonate that, in turn, maintained the pH above the critical pH value of 4.00–4.25 required for gelation to occur; and (f) a sodium lactate inhibitor with concentration ramped down from 1.8 to 0 times as much as the crosslinker (molar basis) that enabled gelation to a flowing gel consistency (Gel Strength Code 3) to vary from 276 hours for the initially injected mixture to 24 hours for the last position of the mixture.

The first field test involved the injection of 36,400 bbl. of CO_2 gelled foam that was placed in the Hagood A-9X injector in an attempt to improve volumetric sweep efficiency [Friedman et al., 1997; Friedman et al., 1999]. The recovery of the 16 million barrels was low due to rapid communication between Hagood A-9X and three offset producers. The rapid breakthrough of CO_2 was attributed in part to the high mobility of CO_2 through fractures. Initial tests with CO_2 and brine showed phase segregation in the well, with CO_2 entering the top zones and brine entering the lower zones. Upon the addition of polymer and surfactant (but no crosslinker) foam was formed at the wellhead, no phase segregation occurred in the well, and the CO_2 and brine entered the zones in approximately the same ratio. It was determined from these trials that a 2 barrel/minute gelled foam injection rate was achievable, with CO_2 pressure limited by the compressor to 2,100 psia. The quality of the foam was ~0.8 (0.2 liquid volume fraction [LVF]). The injection of the CO_2 and aqueous solution caused the injection pressure to increase from 1,540 to 1,630 psia and was followed by 200 barrels of a non-foamed MARCIT^{TM} gel intended to protect the foamed gel in the near wellbore region. The injector was then shut-in for three weeks, more than long enough for gelation to occur. Injection profiles indicated that CO_2 was flowing into new sands, with no flow into the top thief zones. Pressure fall-off tests indicated that the flow changed from a pre-treatment vertical 154' half-length vertical fracture with linear flow to a post-treatment short period of linear flow through a much shorter half-length fracture of 25', followed by radial flows at longer times. The reduction of the fracture effect and the radial flow are both consistent with the successful formation of gelled foam. CO_2 breakthrough times in one of the offset producers increased from pre-treatment values of 9–14 days to post-treatment values of 15–29 days, indicative of improved sweep. CO_2 production from the pattern remained relatively constant after the foamed gel treatment. The most promising result, however, was the change in the oil production trend from a pre-treatment value of -126 BOPD/yr. to a post-treatment value of +36 BOPD/yr. for nearly two years after the foamed gel treatment. This November 1996 treatment increased the oil production rate from ~260 BOPD in March 1997 to

~330 BOPD in August 1998. A very conservative estimate of the incremental oil production of 40,000 barrels of oil was provided by the operators.

Due to the success of this test, two additional foamed gel tests were conducted [Hughes et al., 1998; Hughes et al., 1999]. The second 43,450 barrel treatment injected into well Gray A-10 in Aug./Sept. 1997 increased the oil production rate from 430 BOPD in March 1998 to ~470 BOPD in August 1998; an increase of ~ 56 BOPD/yr. The third treatment of 44,700 barrels of gelled foam solution was injected into A.C. McLaughlin 70X during Oct./Nov. 1997. It resulted in an increase in oil production from 330 BOPD in May 1998 to ~375 BOPD in July and August 1998. At the time the paper was published, a firm estimate of incremental oil was not made for either pattern.

In conclusion, the cost of the foamed gels was roughly 40%–50% less than the MARCIT^{TM} gel because CO_2, which constituted ~80% of the foam, is much less expensive than the aqueous liquid that contains all of the chemicals required for foaming and gelation. An attempt to increase foam quality to 85% led to injectivity problems (the injection pressure to maintain the desired rate approached the CO_2 compressor limit). About twice the volume of foamed gel could be injected than a conventional gel for the same cost. During the treatments, oil production was stabilized and, in two of the three cases, a reduction in gas production occurred. Positive oil responses were noted about 6 to 8 months after the treatment. In general, the foamed gel was considered to be a cost-effective means of attaining in-depth conformance control in fractured reservoirs.

Field Tests of Pre-formed Particle Gels

Occidental Petroleum's Anton Irish Field; Conformance Efforts; 2003–2005; Injection of Pre-formed Particle Gels [Larkin and Creel, 2008; Smith et al., 2006]

The introduction to the Anton Irish Field is provided earlier in this chapter because polymer gel solutions were also tested in this field [Smith et al., 2006; Larkin and Creel, 2008].

In 2007, injection well 63 was treated with preformed particle gels. Video imaging and step-rate injection test results indicated that the injection fluid was flowing into voids and large fractures. A decision was made to inject a dispersion of crosslinked, water-swellable—but not water-soluble—polycrystalline polymer particles into the voids. The particles would swell significantly after injection, resulting in the voids being filled.

The treatment consisted of ~120,000 gallons of a dispersion composed of 0.25 lb. polymer particles/gallon and a density of 9.5 lb./gallon (a 35:1 ratio of particles to water). Thus (for the 30,000 lbs. of pre-formed particles) each pound of solid would swell and absorb 35 lb. of water. Following injection, the well was shut in for 1.5 days. Afterwards, the well had to be cleaned out because it exhibited no injectivity. After the wellbore was cleaned, there was no significant change in injectivity. At the time of the report, a ~1,000 bbl. foamed cement squeeze was being planned after the wellbore was further cleaned and the post-treatment profiles established. Plans also were being made for injecting pre-formed particle gels in another injector, number 104.

KinderMorgan's SACROC Field; Conformance Efforts; 2006; Injection of Pre-formed Particle Gels [Larkin and Creel, 2008]

A description of the SACROC unit has been provided and attempts have been made to deal with early breakthrough of CO_2 or water at offset producers with SAG foams or foams generated with nonionic CO_2-soluble surfactants. Because the formation is highly heterogeneous, exhibiting features such as lateral and vertical discontinuities of porosity and permeability, micro-fractures, and vuggy porosity, a field assessment of pre-formed particle gels was initiated. After a review of conformance control treatments, KinderMorgan settled on the injection of a super-absorbent crystallized copolymer (CP). These sodium acrylate polymers, which consist of a polymerized acrylic acid monomer that has been almost completely neutralized with sodium hydroxide, are crosslinked during their production, and then cooled, extruded, chopped, and bagged for shipment. The product used by KinderMorgan was resistant to bacteria, degradation by CO_2 or mildly acidic water, and reservoir temperatures below 275 ^oF. After being dispersed in fresh water at ~110 ^oF, the pre-formed polymer particles will begin to hydrate and swell in about 20 minutes and will ultimately absorb roughly 10–800 times their mass. If the particles are dispersed in brine, the initiation of hydration is delayed until about 45 minutes have elapsed and the particles have absorbed 5–100 times their mass.

The twelve injection wells selected for treatment were found in patterns in which three or more producers had GOR of 30,000 scf gas/BO, low water/oil ratio to improve oil response time, injection/withdrawal ratios of ~1 to minimize the risk of added complications, and no tailpipe below the injection packers to allow bullheading of the materials and rig-less work. The particles were either 2 mm or 4 mm in size, and roughly 1000 to 10,000 lbs of particles were used in each treatment; in one example, 8200 lb. of particles were dispersed in 5,000 gal of fluid. Nine treatments caused improvements in sustained conformance control and two other treatments induced little change. Only one treatment was deemed a failure, and the cause of the poor performance was attributed to the polymer swelling too quickly in the freshwater used to disperse particles. Details of the results from five well treatments are provided in the paper [Larkin and Creel, 2008]. In general, understanding the cause of the communication between the injector and producer was critical; the 75% technical success rate was considered to be very good, the treatments were found to be cost-effective, and maintaining injection below established limits was found to extend the durability of the treatment.

20. Challenges in Transitioning to Wider Application

It became increasingly evident during the course of this literature review that many of the projects listed in Table 16.1 were one-time field pilots. Although many of the pilots were reporting technical success and on occasion positive financial returns, the literature was devoid of reports of follow-on documentation of the application, either from industry operators or chemical suppliers. In general, one could concur that seemingly successful pilots of CO_2 viscosifiers and CO_2 (gas) diverters/profile modification technologies did not make the transition to field-wide implementation. There may be a variety of reasons for lack of publication of follow-on applications. This section attempts to capture what developers and field applicators — "practitioners"—conducting the tests voiced as reasons, with most of them expressing disappointment and concern with the challenges of scale-up. Each project must be analyzed individually to determine the reason for absence of follow-on documentation for application, which was beyond the scope of this study.

In discussions with a number of experienced personnel (asset managers, lead technologists, field implementers, field team members, economists, and/or chemical suppliers, including working and retired personnel with decades of experience in taking R&D projects to the field) who have operated successful pilots (as reported in the SPE or CIM literature), there were myriad reasons given why successful pilots did not make the transition to wider field implementation. These teams often had a number of successful and unsuccessful pilots under their belt and were called upon by their respective companies to provide solutions to overcome reservoir geology, improve oil production or gas usage, and attempt to improve the bottom-line for their respective assets. Many of the responses, although directed toward CO_2 or other gas injection (steam, flue gas) using chemicals, tended to be broadly encompassing and would apply to any chemical use in EOR.

The following comments (often paraphrased) were made in reference to foams or polymer enhanced foams used in steam diversion, CO_2 direct thickeners, CO_2 diversion by a multitude of chemical methods, or chemical and mechanical methods of CO_2 and hydrocarbon diversion to improve sweep efficiency. Companies rarely divulge their decision making processes and so there is a scarcity of written "how and why" decisions made at a specific time and under a specific forecast oil price. Decisions on go/no-go expansion often required analysis of numerous previous pilots. Often, answers to problems of transition to larger scale or broader application were unclear and based not on science or economics but rather on the comfort level of one or more persons involved in the approval process. Hurdles in transition to wider implementation can be just one, or as most practitioners voiced, "most often a combination of factors that are both defined (quantified) risk or perceived risk" including:

Economics

- Low oil prices (compared to relatively constant chemical cost) and often fluctuating future oil prices precipitated decisions to shelve new technology.
- Practitioners consistently voiced that it was difficult to make a case to go to full-scale implementation given the prevailing economics of the late 1980s and

early 1990s; however, a different decision would have been made had oil prices increased to over $75/bbl.

- Foams for profile modification accelerated recovery and made operations easier, but did not necessarily dramatically improve overall oil recovery.
- The NPV was slightly greater due to accelerated recovery (after chemical application), but there were greater (relatively uncertain) operating costs.
- Transition from pilot-scale to wider field application often meant exposing the technology to higher level of scrutiny, where it had to compete with other opportunities for investment—mainly exploration and drilling—which can add reserves to a company's portfolio.
- From an operator's point of view there was no economic benefit to publishing results and giving competitors an advantage. The opposite was true for chemical companies supplying materials or technology.
- There were U.S. government programs during the 1980s and 1990s to encourage EOR and thus gain royalty relief. Although there was significant oversight, there was not a lot of research to evaluate how well the programs would work.
- Many of the projects were shut-in during periods of low oil prices and were subsequently branded as non-economic in general.

Technology:

- The SOR did not decrease much when foam was used as diverter.
- High permeability zones were treated with squeeze cements or foamed cements.
- Alternate technologies, such as infill drilling and horizontal wells, were used rather than in-depth chemical modification.
- Inability to properly model processes.
- A case of chemistry phobia.

Comfort Level:

- Asset managers are often experienced field engineers with years of field operation experience, including drilling, completion, etc., and have a level of comfort in applying mechanical solutions to reservoir problems. The application of massive amounts of chemicals is new and thus their chemistry phobia inhibits expansion from successful pilot to wider field application.
- Corporate culture varies from company to company. Companies that have a number of successful pilots (in a similar technology) within their technology portfolio are more apt to transition the technologies to wider field implementation.
- Cautious implementation of chemical systems to wider field implementation is often displayed by companies transitioning to wider field application. Each expansion must provide an economic return before application is expanded to other areas or at an accelerated rate.

- Perceived “ownership” of the project plays a role. Attitudes such as “this is R&D’s project” or “this is a field project where R&D is helping us” or “this is my project” as well as company culture play roles in transitioning successful pilots to wider field implementation.
- A frequently voiced practitioner comment that “there was at least one person in management who did not believe the economics” was combined with “many of the pilots were completed when future oil prices were on the way down it was less risky to perform WAG or do nothing.”
- Technologies involving chemicals (as opposed to more widely practiced mechanical fluid diversion) are often rejected by people in decision making roles who have had a previous negative experience with them. (Technologies are often rejected based on guilt by association and not the merit of the process applied to a specific asset.)
- There were U.S. government programs during the 1980s and 1990s to encourage EOR and thus gain royalty relief. Although there was significant oversight, certain practitioners viewed some of the projects (especially some of the smaller projects) as “tax floods” and may not have performed enough research to effectively evaluate their likelihood of success.
- Familiarity with the technology: “Just re-inject more CO_2, it is something that the existing infrastructure is designed to do and we know how to apply.”
- Operators in the U.S. require that proposed new technology be successfully performed many times and have little risk. Proposed applications must have been wildly successful (ROI in the 100%–200% range) in previous projects before operators will invest money in them. (This does not hold for certain countries like China where a different set of incentives apply.)
- Risk includes both personal (career) and company (capital and lost opportunities) risk. Although the petroleum industry takes significant drilling and exploration risks, the production side of the industry is much more risk averse. There is no culture of risk taking within some companies. Personnel perceive there to be few tangible benefits resulting from field-scale chemical EOR success and any number of negative consequences for failure. This does not apply to mechanical systems where a certain number of failures are anticipated.
- *Development of higher level champions within companies is the key to future application.*

Asset Turnover:

- Dilution of experience and removal of champions.
    - Teams that worked on successful pilots are often reassigned (either individually or as members of new teams) to work on other asset problems.
    - The lead champion for the technology often moves on to other problem solving or management opportunities within the company.
    - Dilution of experienced talent devoted to continuing deployment often makes future expansions less economically viable.

  - Loss of the management champion or asset champion due to promotion, reassignment to another asset, or retirement leads to loss of continuity. The replacement wants to leave their own mark and reinvents a solution to the asset problems.
- Training of future operators or implementers of the technology is rarely part of the pilot and thus at the conclusion of a successful pilot, replacement staff skilled in implementation and problem solving are not available.
- Some of the more successful chemical applications were by those whose laboratory, field, or specific asset knowledge became available through retirement or by the sale of assets.
- The asset is removed from the technology scenario.
  - The field was sold; the operating company was sold or acquired by another entity (a common occurrence from the 1980s to mid-2000s). A minimum of files were transferred during many of these consolidations, with R&D notes, field application reports, and economic studies of various technology applications being deleted from the asset files because they may pose a future liability.

Application as a Service:

- Successful profile modification pilots are more apt to become routine if the technology can be applied by a service company and thus seldom are summarized in the literature as a follow-up unless hundreds of applications are analyzed and reported. Individual jobs can be expensed.
- Successful mobility control in a gas flood seldom makes the transition from pilot to full-field due to the volume of chemicals and the investment and time required.
- Some of the more successful chemical applications were by those whose laboratory, field, or specific asset knowledge became available through retirement or by the sale of assets.
- Chemical applications for profile modification and mobility control are not the primary focus of major oil field service companies who specialize in pumping services (cementing, acidizing, hydraulic fracturing, sand control, etc.) thus major service companies in most countries do not have enough technical support to support field-wide application.
- Most successful profile modification companies are small, specialized, regional companies who publish on occasion when clients permit. Most of their presentations are to prospective clients and are based on their experience and license of technology from developers they contract with for the chemicals they apply. Most of these companies have long-term, nearly exclusive agreements with specific operators to provide services.

- Slow Implementation of Chemical Profile Modification in a CO_2 Floods:
  - Slow implementation of chemical systems to wider field implementation has been shown in field-wide application of chemical profile modification in a

CO_2 flood. One example is Chevron's Weber Sand Unit in the Rangely, Colorado field and in some of the Permian Basin CO_2 floods where chemical profile modification is practiced on a limited scale but operators do not want competitors to obtain the same economic advantage.

Bigger Target Focus:

- Most major companies changed their focus in the late 1990s to assets in deep water or outside the U.S., but the current focus is development of huge source rock shale (and carbonate) plays worldwide. Advances in seismic, horizontal drilling, hydraulic fracturing, massive data processing, and analysis have changed company focus towards the huge natural gas, natural gas liquids, and oil shale plays. This draws attention and assets away from improvements that could be made to existing CO_2 EOR assets.

- During the last few decades CO_2 EOR has been constrained by CO_2 supply. Expansion of new CO_2 floods was slow both in the Permian Basin and the Rocky Mountains; however, new CO_2 floods are being brought online in the Rocky Mountains, U.S. Gulf Coast, and the Middle East due to increased availability of CO_2 (Moritis, 2010). The use of gas diversion, viscosifiers, and foam will probably return, but only when these newer source rock plays run out of drill and frac resources or the price of oil rises sufficiently.

Although much of the above section illustrates that companies have not published much beyond pilots, this does not mean that field application and field tests have not been continuing. Current projects in CO_2 mobility control and diversion continue but are proprietary.

CONCLUSIONS

There have been about four decades of lab-scale research and field-scale pilot tests dedicated to improving mobility or conformance control during CO_2 floods via the addition of CO_2 or water-soluble chemical additives. In general, two distinct strategies were considered: CO_2 thickeners and CO_2 foaming agents.

CO_2 Thickeners

Two types of CO_2 thickeners have been considered: small molecules that self-assemble into long macromolecules, and polymers with associating groups.

Two types of molecules have been considered in the design of CO_2 thickeners: small, lower molecular weight compounds that dissolve in CO_2 and then self-assemble while remaining in solution to form a non-covalently bound macromolecular network, and very high molecular weight polymers.

Small Molecule, Associating Thickeners

Inexpensive, small molecule oil thickeners cannot thicken CO_2 unless prohibitive amounts of co-solvent are introduced, and novel small molecule thickeners designed specifically for CO_2 induce very modest increases in viscosity and are too expensive because they contain fluorine

The notion of identifying a compound that could dissolve at very dilute concentrations (~0.1 wt %) in CO_2 at typical injection conditions and remain in solution at reservoir conditions was very alluring. The ability to thicken light alkanes such as propane, butane, pentane, and hexane with dilute concentrations of "small molecules" such as hydroxyaluminum disoaps (the surfactant used to thicken gasoline) and tributyltin fluoride gave numerous researchers hope that the task of thickening CO_2 would not be insurmountable. These thickeners struck a delicate balance in that they were able to dissolve in the fluids without heating and then self-assembled and remained in solution, forming long, linear macromolecules that dramatically increased the fluid viscosity. If an analogous small "direct thickener" could be identified for dense CO_2, it would have the advantage of providing a simple means of precisely adjusting CO_2 viscosity by changing thickener concentration. Further, it appeared possible that the thickener could be easily designed to be water-insoluble (and possibly even crude-oil insoluble) thereby minimizing reductions of CO_2 viscosity due to partitioning of the thickener into other fluid phases.

Despite a flurry of activity by academic and industrial researchers in the 1980s and 1990s, attempts to thicken CO_2 with small self-assembling molecules or ultra-high molecular weight polymers were unsuccessful. The fundamental problem with the small molecule thickening candidates was that they would typically not dissolve in CO_2 (let alone thicken it) unless prohibitive amounts of organic co-solvents were used. These direct thickeners typically consisted of a CO_2-philic segment that promotes the dissolution of the compound in CO_2, and a CO_2-phobic portion that enables the compounds to associate with one another in solution.

Although CO_2 is a reasonable solvent for light alkanes that may serve as CO_2-philes, CO_2 is a notoriously poor solvent for polar, ionic, or hydrogen bonding groups commonly used to establish the viscosity-enhancing intramolecular interactions or associations. These associating groups are so CO_2-phobic that the favorable interactions between CO_2 and the CO_2-philic portion of the thickener are insufficient to enable the compound to dissolve. Although the addition of a strong organic co-solvent to the CO_2 enabled some small molecule thickeners to dissolve in CO_2 in lab-scale tests, the use of such large volumes of a solvent in the field would not be realistic.
In the late 1990s and early 2000s, efforts to design CO_2 thickeners resorted to extraordinarily CO_2-philic fluorinated segments. Although several fluorinated small compound CO_2 thickeners (trifluoroalkyltin fluorides and surfactants with a divalent cation and two branched fluorinated tails) were developed, unacceptably high concentrations were required to attain very modest increases in viscosity. Current research is focused on the systematic reduction and then elimination of fluorine atoms from small molecule thickener candidates.

Polymeric and Associating Polymer Thickeners

Silicone oils can thicken CO_2 if significant amounts of toluene are added as a co-solvent (e.g., 10% toluene, 90% CO_2), and a single CO_2-thickener (a fluoroacrlyate-styrene copolymer) has been designed that is both effective at <1wt% and does not require a co-solvent. Both of these thickeners are too expensive to employ in pilot tests, however.

A multitude of high molecular weight polymers was also considered for thickening CO_2. Silicone oils were capable of dissolving in CO_2 and inducing significant increases in viscosity, but only if a co-solvent such as toluene was added in a concentration of ~10% to the CO_2 (90%). The most CO_2-soluble, high molecular weight oxygenated hydrocarbon was determined to be polyvinyl acetate, but pressures of roughly 9,000–10,000 psi (pressure values far beyond MMP values) were required to achieve dissolution. The most CO_2-soluble polymer yet identified capable of increasing the viscosity of CO_2 at temperature and pressure values commensurate with CO_2 EOR is polyfluoroacrylate (PFA). Although capable of thickening CO_2, the concentrations required to attain large increases in viscosity are too high (e.g., a three-fold increase in viscosity at 50 ^oC at ~3,400 psi requires ~3.7g PFA/cm^3 CO_2).

An extremely effective high molecular weight co-polymeric CO_2 thickener, designated "polyFAST", was designed and synthesized. This random copolymer was composed of two monomers: fluoroacrylate and styrene. The fluoroacrylate portion of polyFAST promoted dissolution in CO_2, while the pendent aromatic rings of the styrene promoted viscosity-enhancing intermolecular associations referred to as π-π stacking. PolyFAST dissolved in CO_2 at typical reservoir conditions after being stirred vigorously, forming a transparent, thermodynamically stable, shear-thinning, CO_2-rich phase. At concentrations of 0.2–1.0wt%, significant increases in CO_2 viscosity were observed in both falling object viscometers and mobility measurements in Berea sandstone (e.g., ten-fold increase in viscosity at polyFAST concentrations of 1wt% and a superficial velocity of 1ft/day).

In the late 2000s, attempts were made to replace the fluoroacrylate monomer of polyFAST with an extraordinarily CO_2-philic, non-fluorous monomer. Nearly all of these copolymers were CO_2-

insoluble. The only modest success was polyBOVA, a copolymer of 5% benzoyl (a monomer with a phenyl group in the side chain for intramolecular associations) and vinyl acetate (the most CO_2-philic oxygenated hydrocarbon segment) that increased the viscosity of CO_2 by only 40% at a concentration of 1wt% at 25 ^{o}C, but required ~9,000 psi for dissolution.

No pilot field tests of CO_2 thickeners have been conducted and none are currently being considered.

CO_2 Foaming Agents

There are many affordable, commercially available, water-soluble surfactants capable of stabilizing CO_2-in-brine foams for mobility control and/or conformance control that have been tested in the lab and field, and there has been recent lab-scale testing of silica nanoparticles as foam stabilizers.

The second strategy for reducing the mobility of CO_2 with chemical additives deals with the in situ generation of CO_2-in-brine foams. Three distinct types of foam-stabilizing compounds have been considered: water-soluble surfactants, CO_2-soluble nonionic surfactants, and nanoparticles. There are an extremely large number of findings associated with lab-scale research and more than a dozen pilot tests of CO_2 foams formed with surfactants dissolved in brine; a much smaller amount of recent lab-scale activity along with an on-going pilot test involving a CO_2-soluble surfactant; and a very recent report of laboratory experiments related to foam stabilization using fumed silica nanoparticles.

Water-Soluble Surfactants as Foam-Stabilizing Agents

Many surfactants can be used to form an aqueous surfactant solution that is injected with CO_2 to generate foams in situ, and several of these surfactants (i.e., Chaser CD 1040, Chaser CD 1045 and Alipal CD 128) have been employed in 13 pilot tests (11 conformance control, 2 mobility control) that yielded promising results in five successful applications, a partial success, an inconclusive result, and six unfavorable or problematic tests. Gels, foam gels, and pre-formed particle gels have emerged as alternative conformance control techniques for CO_2 floods.

There are a multitude of commercially available, inexpensive surfactants that can dissolve in water or brine, and many of them are also capable of stabilizing CO_2-in-brine foam to varying extents. Therefore, a great deal of research has been conducted in the lab related to CO_2-in-brine foams. Reducing the mobility of CO_2 by alternating the injection of soap solutions and CO_2 in order to form surfactant-stabilized lamellae in the pore network of a rock is quite complex. Lamellae can be generated by the leave-behind mechanism, lamellae division, and snap-off. This in situ foam generation mechanism and foam mobility and foam durability are affected by the structure of the surfactant, brine salinity, surfactant concentration, ratio of surfactant solution to CO_2, injection flow rate, fluid velocity, frequency of the surfactant solution and CO_2 cycles, duration of the SAG process, oil saturation, and the permeability, wettability, and nature of porosity of the rock. Further, one typically must design the foam to provide in-depth mobility control or near-wellbore conformance control. Despite the multitude of factors that can influence the CO_2 foam properties, significant progress has been made in understanding the properties of CO_2 foams because (unlike identifying the elusive CO_2 thickener) there are many surfactants that can dissolve in brine and stabilize a foam. Numerous general trends were recognized thereby providing useful guidelines for designing a field test. A few examples of these trends are provided in the following paragraph.

The surfactant must be soluble in reservoir brine at reservoir conditions. The mixed anionic/nonionic/amphoteric surfactant blend, Chaser CD 1045, and the anionic surfactant, Alipal CD 128 (an ammonium salt of ethoxylated sulfated linear alcohol), are examples of excellent foam stabilizers. Cationic surfactants are not appropriate for negatively charged sandstone or carbonate rock because there would be a strong driving force for adsorptive losses; therefore, cationic surfactants are suitable only for carbonate layers with a positively charged surface. As velocity increases from extremely low values to higher values the foam mobility can increase over a narrow range of the lowest velocity and then decrease over a broad range of higher velocity values. Foam mobility decreases with increasing surfactant concentration and then levels off at a concentration above the CMC. Foams of 60%–80% quality typically exhibit the lowest mobility. Foams are shear-thinning. Foam mobility increases with increasing oil saturation. Mobility reductions are usually more significant in high permeability watered out zones. By manipulating surfactant composition, surfactant concentration, and foam quality it is possible to attain modest decreases in mobility suitable for mobility control or very large declines in mobility needed for conformance control. Foams can be degraded via the injection of water. Adsorption losses can be significant, especially for ionic surfactants at concentrations above the CMC. The highest recovery of oil from two parallel cores is obtained by CO_2 flooding until oil recovery from the high permeability zone is nearly complete and little oil is producing from the low permeability zone, and then forming CO_2 foam in situ via SAG that diverts the subsequently injected CO_2 into the lower permeability oil-bearing zone.

There are many exceptions to these trends, and enough uncertainty in attempts to accurately predict foam performance that pilot floods have been preceded by lab-scale mobility measurements and oil recovery floods conducted with reservoir cores and reservoir fluids at reservoir conditions. Despite laboratory foam literature making frequent reference to the use of CO_2 foams for mobility control or conformance control, only two CO_2 foam pilots dedicated solely to assessing mobility control were conducted. The Joffre Viking test was unsuccessful because the foam propagated only a few meters from the injector. The Rock Creek pilot results were inconclusive because the reservoir fluids and the in situ generated foam did not flow past the observation well as expected, although injectivity results indicated that the foam was about 1.6 times as viscous as water. The remaining foams generated in field tests were primarily intended for near-wellbore, relatively short-term, conformance control (e.g., blocking out watered-out thief zones). CO_2 conformance control results at the following fields had a mixed bag of successful and unsuccessful technical results, and the economic results associated with the technical successes ranged from modest successes to unfavorable outcomes. The 1984 Wilmington pilot was a technical success in that CO_2 was diverted away from the high permeability zone during the SAG process, but the subsequent water injection dissipated the foam. During the 1984 SACROC pilot the foam was unable to divert CO_2 from very high permeability open fractures. The 1989–1990 Rangely Weber Sand Unit demonstrated that foam was produced in the formation despite the presence of a hydraulic fracture in the injector that resulted in lower gas and higher oil production during a project that paid out quickly. The ~1991 Wertz Field conformance control foam was short-lived and ineffective in fractured portions of the reservoir. The 1990–1991 North Ward-Estes pilot was a technical success and illustrated that more promising economics are associated with the use of conformance control foams that reduce expensive CO_2 recycling rather than mobility control foams. The 1991 Slaughter Field, East Mallet Unit, Well 31 SAG foam was successful in that it diverted CO_2 from the thief zone and caused gas production decrease and oil production increase in the pattern. The 1991–1992 Slaughter Field, East Mallet Unit, Well 68 was co-injection foam that resulted in very large injection pressures and the effect of the foam on increased oil production was somewhat difficult to analyze because of operational difficulties. The 1991–1993 EVGSAU foam pilots were a technical success but the rate of return was considered unacceptable due to the $20/bbl. oil price. The 1994 Wasson ODC Unit foam pilot was deemed a technical success but economic failure. In the 1992–1993 Greater Aneth Field, McElmo Creek Unit, Well R-21 pilot, a SAG foam was used for conformance control rather than a more permanent gel because the thief zone could not be vertically isolated, and although injectivity reduction was observed no conclusive production response was identified; subsequent attempts to employ a high quality co-injected foam were frustrated by freezing or hydrate formation at the wellhead. The 1992–1994 Greater Aneth Field, McElmo Creek Unit, Well P-19 pilot foam test exhibited diversion of CO_2 into the targeted oil-rich DCI zone and a decrease in gas production but it was not possible to affirm that the ~10% increase in oil production was attributable to the increased sweep of the foam.

Reports of CO_2 pilot tests ceased to appear in the literature in the mid-1990s. Perhaps this was due to the somewhat inconsistent pilot results from the preceding decade, nearly all of which were designed for conformance control. This may have also been due in part to the emergence of other technologies for achieving conformance control. These include monomer solutions that polymerize and crosslink (gel) in situ, polymer solutions that crosslink in situ, foams that gel in situ, and pre-formed particle gel dispersions. It was, and still is, generally recognized that the CO_2 foams are relatively inexpensive conformance control techniques that are not very likely to induce permanent damage to a formation. Nonetheless, the marked reductions in mobility associated with these more robust conformance control alternatives, the improving ability to precisely place them in targeted zones, and their ability to block extremely high permeability flow paths that foams could not treat seems to have made these gel technologies very popular alternatives to CO_2 foams. In short, this suite of conformance control chemistries may be more expensive than foams, but if carefully placed, they appear to be more effective for achieving robust, long-term conformance control.

There have been numerous reports associated with CO_2 floods of aqueous monomer solutions that polymerize and gel in situ or aqueous polymer solutions that gel in situ. Crosslinking anionic polymer solutions and in situ polymerization/crosslinking solutions were both tested at the Lick Creek Field in 1978 and 1984–1985, respectively, with better results occurring with the latter treatment. In situ gelation of a CC/AP polymer solution was tested in 49 wells at the Rangely Weber Sand Unit from 1994 to 1997; 80% of the treatments were deemed successful and the economics of the project were highly favorable. In situ gelation of a CC/AP solution was also tested in 10 wells of the Wertz Field in 1992–1994, with the results being superior to those previously achieved using CO_2 foam. The occurrence of massive void space conduits between injectors and producers at the Anton Irish field called for the use of foamed cement and gel solutions from 2003 to 2005. These treatments, which were used in five offending production wells, increased oil production, decreased gas production, and retained their integrity for at least several years. Conformance control during the 2002 CO_2 flooding of the Bat Raman field in Turkey, which is characterized by a viscous crude and substantial secondary permeability, was tested in seven injection wells using a polymer solution that crosslinked in place. Each treatment yielded short term improvements in oil production and GOR reduction that lasted roughly a year, which was about the same duration as the payout period. Although definitive evidence was obtained that the gel plugged a high fracture path between injector and producer, it appeared that the CO_2 was eventually able to find new high permeability flow paths to the producer. Conformance control in the Slaughter Field, Central Mallet Unit, was accomplished with low viscosity solutions that polymerized and gelled in situ. Six injection well treatments resulted in the maintenance of the oil production rate with a reduction in CO_2 purchasing and processing costs. Similar results were achieved with 14 more treatments from 2003 to 2005, and plans were in place for 31 more treatments in this unit. In situ crosslinking of a polymer solution with an organic (rather than metallic) crosslinker was employed in four injectors and one producer from 2008 to 2009 at the Brookhaven Field. Although injectivity decreased in 3 of the 4 injectors, improvements in the injection profile were modest and the effect on oil production was difficult to ascertain, probably because the volumes of gel solution injected were too small.

There has been a single report of a CO_2 foam gel associated with the 1996 pilot test in the Rangely Weber Sand Unit. Although the chemistry and field application may be relatively complex, the advantages of gelled foam are that the average density of the foam will be less than that of the brine so the foam is more likely to form in the upper regions of fractures of thief zones, and that the aqueous solution of chemicals is more expensive than dense CO_2; therefore, is it possible to inject much larger volumes of gelled foams than aqueous gels for the same cost. The initial result at the Rangely Weber Sand Unit was promising; the oil production trend increased from -126 BOPD/yr. to a post-treatment value of + 36 BOPD/yr. for nearly two years after the treatment, and two other treatments were undertaken.

There have also been reports of the use of pre-formed particle gel during CO_2 floods characterized by highly heterogeneous formations containing lateral and vertical discontinuities of porosity and permeability, micro-fractures, and vuggy porosity. Foams are generally recognized to be inadequate for treating such high permeability secondary porosity flow paths, and the introduction of an aqueous slurry of polymer particles that swell in situ is a promising means of closing these paths. These PPG treatments were being implemented in five wells of the Anton Irish field in the 2003 to 2005 period, four of the treatments were considered effective in 2007 and a sixth well was then treated. PPG treatments were also used during 2006 in 12 offending production wells at SACROC field; nine were successful, two induced little change, and only one failed.

CO_2-Soluble Surfactants as Foam-Stabilizing Agents

There has been recent activity in lab- and pilot-scale testing of commercially available liquid, non-ionic surfactants that can be dissolved in the high-pressure CO_2 that is injected into the formation.

Although the concept of adding surfactants to high-pressure CO_2 (rather than brine) was first suggested more than 40 years ago, only recently has there been significant progress in making this idea a reality. It is thought that the addition of a dilute concentration of a surfactant into the CO_2 (about 0.02–0.2wt %) would ensure that the surfactant is delivered only to the regions where the CO_2 flows. Because the reservoir, especially the thief zones, already contain a high saturation of water, the injection of a CO_2-surfactant solution could lessen or possibly eliminate the need for alternating injections of aqueous slugs. CO_2-soluble surfactants would be the only viable foam-stabilizing agent available for field operations dedicated to the continuous injection of CO_2.

The identification of CO_2-soluble, foam-stabilizing surfactants has been hampered by the very poor solvent strength of CO_2 for ionic compounds. The "CO_2-philic" portion of the surfactant should contain hydrocarbon groups known to interact favorably with CO_2. Further, the surfactant should be more water-soluble than CO_2-soluble in order to stabilize the thin aqueous lamellae of a CO_2-in-brine foam in the pores of the rock, and the surfactant should be more water soluble than CO_2-soluble. It appears that the most promising surfactants for this application may be single- or multiple-tailed, branched, water-soluble, non-ionics. Based on research conducted at the University of Texas at Austin, Dow Oil & Gas has developed a proprietary non-ionic surfactant, referred to as CO_2 Enhance, for this application, which is currently being assessed in a SACROC pilot flood. The injectivity results from the single-well injector tests were promising, and oil production results from a four pattern pilot are currently being assessed. Based on research conducted with commercially available surfactants from several companies at the University of Pittsburgh and NETL, inexpensive, CO_2-soluble branched alkylphenol ethoxylates appear to be more effective than branched ethoxylates, although both may be adequate for generating CO_2 foams in situ. A single-well pilot test involving one of these surfactants is being considered for the SACROC field.

Nanoparticles as Foam-Stabilizing Agents

Recently, the notion of stabilizing foams with nanoparticles (rather than surfactants) has been considered; these particles (e.g., nanosilica) can be readily dispersed in the brine that is injected alternately with CO_2.

Johnston and co-workers at the University of Texas at Austin pioneered the use of nanoparticulate matter for generating Pickering emulsions (particle-stabilized emulsions) of CO_2-in-water as an alternative to surfactant-stabilized CO_2 foams. Nano-silica is an excellent candidate because it is ready available at reasonable prices for lab-scale experiments or in bulk (~$4/lb.) for pilot tests. The nanoparticles would be dispersed in an aqueous solution and then injected alternately with slugs of CO_2. Because the primary particle size of nano-silica can be as small as several nm, the dispersion of these particles in brine yields a transparent solution that can readily flow through porous media with pore throats that may be ~1,000 nm in diameter. Unlike surfactants, such particles could be used without loss of the foam-stabilizing agent to adsorption or chemical degradation. Initial lab tests—especially for the generation of mobility control foams—appear to be promising, but the process has yet to be fully assessed in lab tests, reservoir cores, or in a pilot test.

Could Combining Gel Conformance Control with CO_2 Foam Mobility Control Work?

Although both gels and CO_2-in-brine foams can provide conformance control, only CO_2 foams can be employed for mobility control.

It is apparent that the interest in the use of SAG foams formed with water-soluble surfactants for conformance control has diminished during the past 15 years, perhaps due in part to the emergence of several relatively expensive but very effective conformance control technologies. As a result, many field operations appear to be using monomer or polymer gel solutions, foams, gels, and PPG dispersions for conformance control that block watered-out zones and high permeability flow paths, and WAG for mobility control in the oil-bearing zones.

Unlike these conformance control gel techniques, CO_2 foams can be designed for conformance control *or* mobility control. Given the few CO_2 foams that were tested in the field for mobility control/sweep improvement, perhaps weak CO_2 foams stabilized with water-soluble surfactants, CO_2-soluble surfactants, a combination of CO_2-soluble surfactants and water-soluble surfactants, or nanoparticles should be reconsidered as a tool for mobility control in conjunction with conformance control gels. Perhaps pilot tests involving gels for conformance control followed by either WAG or SAG for mobility control could rekindle interest in CO_2 foam technology.

Summary of conclusions

There has been considerable lab-scale progress in thickening CO_2, most notably with the fluoroacrylate-styrene copolymer, polyFAST, and silicone oil–toluene solutions, but an inexpensive thickener capable of being tested at the pilot-scale has not yet been designed. There have been a multitude of successful lab-scale tests involving water-soluble surfactants capable of stabilizing CO_2-in-brine foams. These achievements led to 13 published reports of pilot-tests conducted between 1984 and 1994, most of which were aimed at attaining conformance control. Five pilot tests were successful, two were inconclusive, and six were either unsuccessful or hampered by operational difficulties. It appears that the emergence of robust gel-based conformance techniques coupled with WAG for mobility control may have led to a decline in the use of foams as a conformance control technique. Given the ability of foams to be designed for mobility control, it may be prudent to conduct a pilot-test in which gels are employed for conformance control and CO_2-in-brine foam (rather than WAG) is used for mobility control. Recently, CO_2 foams generated with CO_2-soluble nonionic surfactants have been successfully tested in the lab and in an on-going pilot-test. Further, lab-scale testing of foam stabilization with water-dispersible nanoparticles has been initiated in an attempt to circumvent problems, such as adsorption losses and chemical instability of the surfactant, often associated with surfactant solutions flowing for extending periods of time through a porous medium.

21. APPENDIX A

CHARACTERISTICS OF CO_2

CO_2 Properties that Influence EOR and CO_2 Viscosifiers

Although carbon dioxide has been used commercially in EOR to recover oil from geologic formations for nearly 40 years, a number of figures in this section illustrate some of the challenges in conducting laboratory and numerical modeling of systems, especially systems for viscosifying CO_2 that would meet field conditions. The systems should be evaluated not only by the additives added to the CO_2 at a given temperature and pressure but also by factors such as hydrocarbon composition or a range of compositions; salinity (including divalent ions); pH; other gases that may be co-injected in the gas stream (hydrocarbon, H_2S, N_2, etc.); adsorption of the additive on the rock surface (the mineralogy and adsorption area); and changes in composition of the fluids between wells (between injector and producer throughout and over the life of the flood where fluid composition—such as hydrocarbon composition—changes with time); and the implications for vicosifiers if pressure decreases (as CO_2 viscosifiers are often more soluble at higher pressure CO_2).

The influence of hydrocarbon composition on minimum miscibility pressure (MMP) and the fractionation (stripping of components) within the hydrocarbon phase are covered in SPE Monograph 8 "Miscible Displacement" [Stalkup, 1983]; for impure CO_2 gas mixtures [Sebastian, 1985]; and when related to field conditions, covered in SPE Monograph 22, "Practical Aspects of CO_2 Flooding" [Jarrell, et al., 2002].

CO_2 Properties

The Intergovernmental Panel on Climate Change (IPCC) has compiled reports on CO_2 capture, transport, and sequestration. The 2007 IPCC Special Report [Freund et al., 2007] on carbon dioxide capture and storage contains Annex I "Properties of CO_2 and Carbon-Based Fuels". It covers not only CO_2 properties in Si units, but also highlights health and safety issues, as well as fuel properties that are usually found only in scattered references. OSHA [1986] also provides information on Health and Safety of air contaminants, including CO_2.

Carbon dioxide behaves as a gas at standard temperature and pressure (STP) and becomes a liquid at low temperature or high pressure (Appendix Table 1 and Figure A.1). CO_2 behaves as a solid ("dry ice") over a narrow temperature range at atmospheric conditions; the entire envelope is shown in Figure 20.1. If CO_2 temperature and pressure are both increased from STP to levels at or above the critical point, CO_2 can adopt properties midway between those of a gas and a liquid. More important for EOR, CO_2 behaves as a supercritical fluid above its critical point (31.1 °C) and pressure (0.73 atm, 7382 kPa).

APPENDIX TABLE 2. CARBON DIOXIDE PHYSICAL PROPERTIES [CRC, 1968]

English Units			Normal Boiling Point (1 atm)		Gas Phase Properties @ 32°F & @ 1 atm			Liquid Phase Properties @ B P & @ 1 atm		Triple Point		Critical Point		
			Temp.	Latent Heat of Vaporization	Specific Gravity	Specific Heat (Cp)	Density	Specific Gravity	Specific Heat (Cp)	Temp.	Pressure	Temp.	Pressure	Density
Substance	Chemical Symbol	Mol. Weight	° F	BTU/lb.	Air = 1	BTU/lb. °F	lb./cu. ft.	Water = 1	BTU/lb. °F	°F	psia	°F	psi	lb./cu ft.
Carbon Dioxide	CO_2	44.01	-109.3	245.5	1.524	0.199	0.12341	1.18	--	-69.9	75.1	88.0	1074	29.2

Metric Units			Normal Boiling Point (101.325 kPa)		Gas Phase Properties @ 0°C & @ 101.325 kPa			Liquid Phase Properties @ B P & @ 101.325 kPa		Triple Point		Critical Point		
			Temp.	Latent Heat of Vaporization	Specific Gravity	Specific Heat (Cp)	Density	Specific Gravity	Specific Heat (Cp)	Temp.	Pressure	Temp.	Pressure	Density
Substance	Chemical Symbol	Mol. Weight	°C	kJ/kg	Air = 1	kJ/kg °C	kg/m3	Water = 1	kJ/kg °C	°C	kPa abs	°C	kPa abs	kg/m3
Carbon Dioxide	CO_2	44.01	-78.5	571.3	1.539	0.85	1.9769	1.18	--	-56.6	517.3	31.1	7382	468

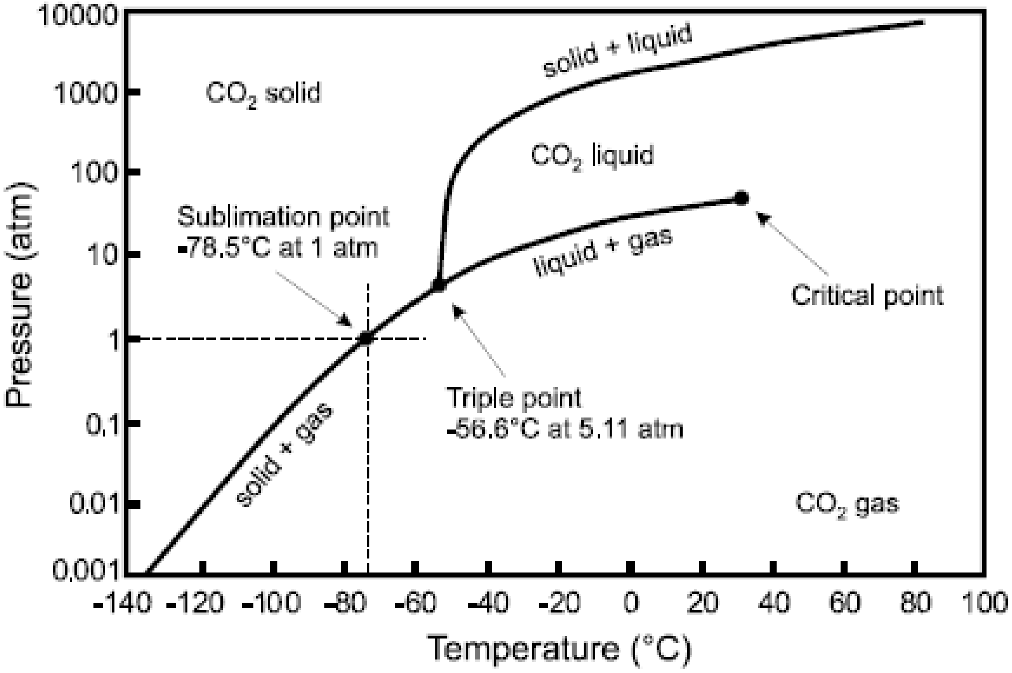


Figure A.2. Carbon Dioxide Phase Behavior [Shakhashiri, 2008]

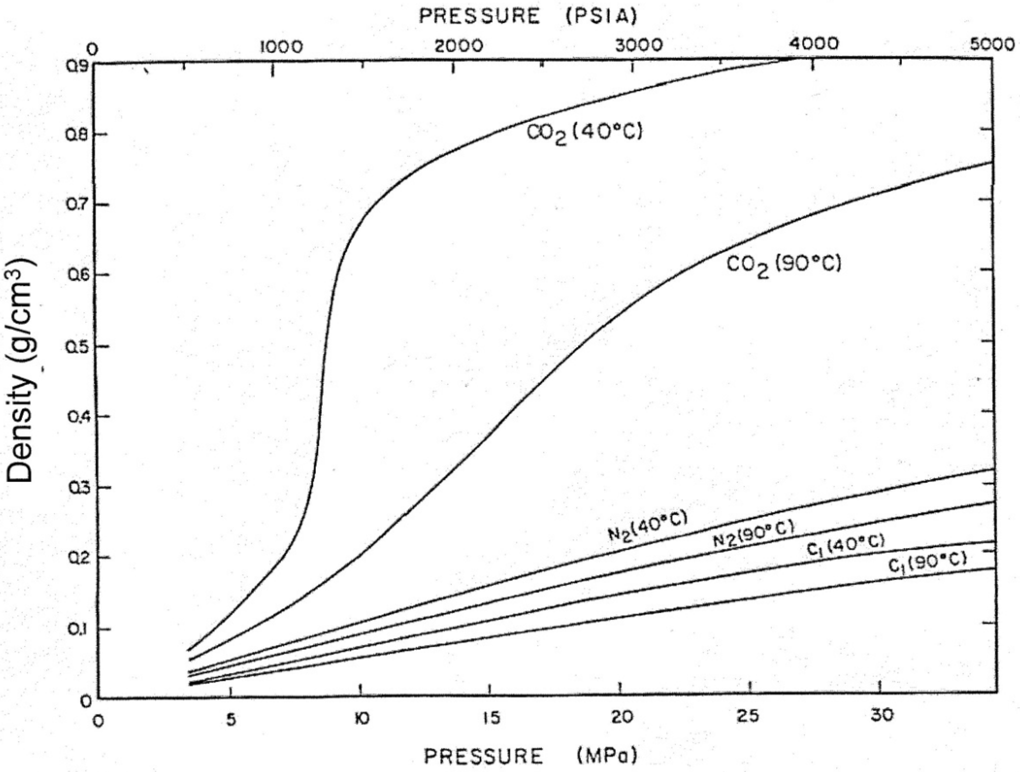


Figure A.3 Comparison of CO_2, N_2, CH_4 Density [Stalkup, 1983]

The density of pure CO_2, N_2, or CH_4 as a function of temperature and pressure are well defined (Figure A.2). The tie-lines for density and viscosity (Figure A.3) of CO_2 as a function of temperature and pressure are shown. The black, irregularly dashed lines in Figures A.3 show variation of density and viscosity in a sedimentary basin, assuming a normal hydrostatic pressure gradient and a geothermal gradient of 30 °C/km of depth.

Regardless of whether the CO_2 source is natural or anthropogenic, it is not economic to purify the flue or exhaust gas, or the gas from natural gas processing plants to the extent necessary to inject pure (100%) CO_2; a range of CO_2 compositions (often >95% CO_2) are used for EOR. Other gases (such as CO, SO_X, NO_X, N_2, H_2S, O_2, hydrocarbon, and H_2O) are anticipated in various concentrations depending on the fuel being burned, the unit operating conditions of the combustor, and the operating conditions of the CO_2 separation/dehydration units. Gas concentrations range from trace quantities to a few percent, which impact phase behavior, solubility, and chemical reactivity of the injected gas. Depending on the types and concentrations of the impurities, an impurity in the CO_2 injection stream affects the CO_2 EOR process and process efficiency. The presence of H_2S and intermediate hydrocarbons, such as C3 or C4, reduces the minimum miscibility pressure (MMP) and generally improves the oil displacement efficiency. Impurities such as N_2 significantly increase the MMP and decrease oil displacement efficiency [Sebastian, 1985]. Thus when evaluating a material for its potential to viscosify CO_2, tests with an impure CO_2 gas are recommended. The SPE monographs and industry handbooks, including the *GPSA Engineering Data Book* [GPSA, 2004], the *Natural Gas Engineering Handbook* [Gao and Ghalambor, 2005], Perry's *Chemical Engineers Handbook* [Perry et al., 1984] and the National Institute of Standards and Technology (NIST) Standard Reference

Database Number 69 [NIST Webbook, 2003] have various phase behavior nomographs for various gas compositions. However, only plots of pure CO_2 solubility in aqueous solutions have been included in the rest of the section. Introduction of an electrolyte into H_2O-CO_2 fluids causes dramatic effects on the fluid phase equilibrium, molal volumes, fugacity coefficients, and equilibrium compositions of coexisting phases [Bowers and Helgeson, 1983].

When dry injected gas (CO_2 or flue gas) enters the geologic formation, it will encounter formation water; the temperature, pressure, and fluid compositions within the reservoir are anticipated to significantly impact CO_2 phase behavior. The impacts to phase behavior include changes in

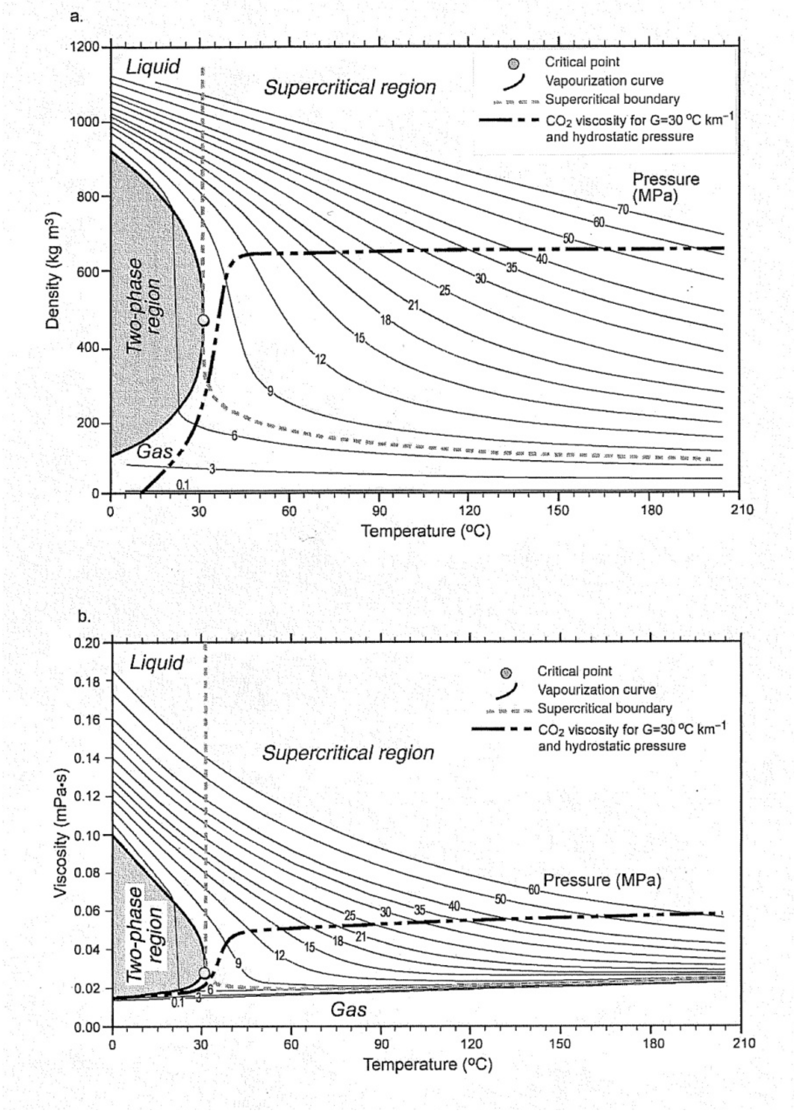


Figure A.4. CO_2 properties as a function of temperature and pressure by (a) density and (b) viscosity [Gunter, Bachu and Benson, 2004]

solubility, viscosity, density, injectivity (rate and pressure), volume that can be injected, and chemical reactivity (pH and reaction of CO_2 or other gases with ions in solution and the formation that form precipitates). Some of these impacts on phase behavior are shown in Figures A.4 through A.8.

Pure, dry CO_2 is relatively non-corrosive. However, it forms carbonic acid in the presence of water, which corrodes metal surfaces and reacts to dissolve carbonate materials within the reservoir, increasing reservoir heterogeneity, especially near the injector. The primary environmental factors that affect corrosion rates are the partial pressure and flow rate of CO_2, operating pressure and temperature, water content, and contaminants such as H_2S. Pure CO_2 exerts a very high partial pressure that leads to reduction in pH. At temperatures below 70 ºC the corrosion rate progressively increases up to an intermediate temperature range (70 ºC to 90 ºC), and then drops [Kermani and Morshed, 2003]. Corrosion affects CAPEX and OPEX economics of CO_2 floods, thus it is essential to include the necessary corrosion-related considerations in the project. Corrosion introduces metal ions that could influence CO_2 viscosifiers and mobility control agents. Detection of corrosion and monitoring of corrosion rates are essential components of project management. Data collection on wells improves the chances of accurately predicting and managing corrosion risks. Test coupons, caliper surveys, sonic-thickness logs, and probes are some of the options that do not require pulling the tubing for inspection.

When the injected gas enters the geologic formation, the temperature, pressure, and fluid composition within the reservoir is anticipated to impact CO_2 phase behavior.

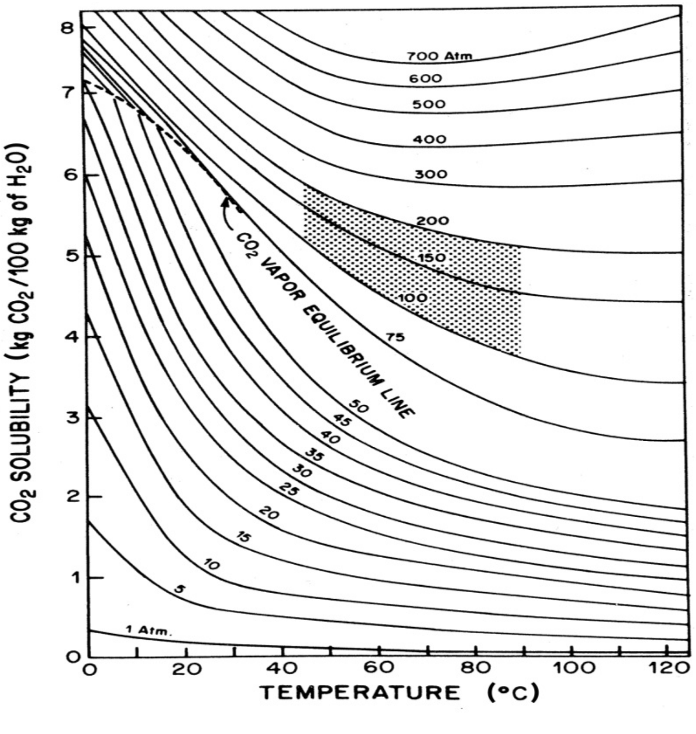


Figure A.5. CO_2 solubility as a function of temperature and pressure [Dodds, et al., 1956; Bowers, 1983].

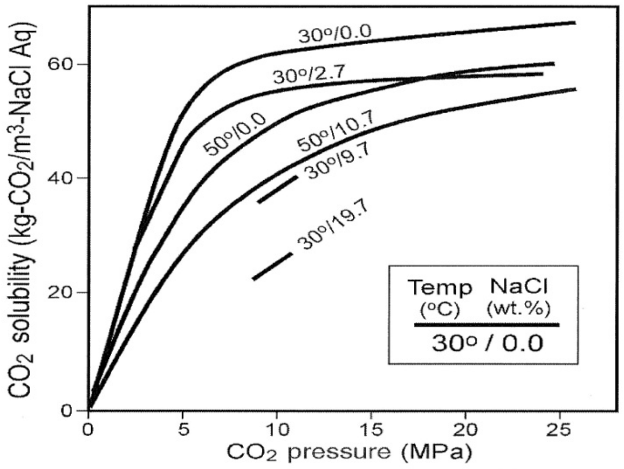


Figure A.6. CO_2 solubility in water (various NaCl salinities and temperature) [Koide, et al., 1993].

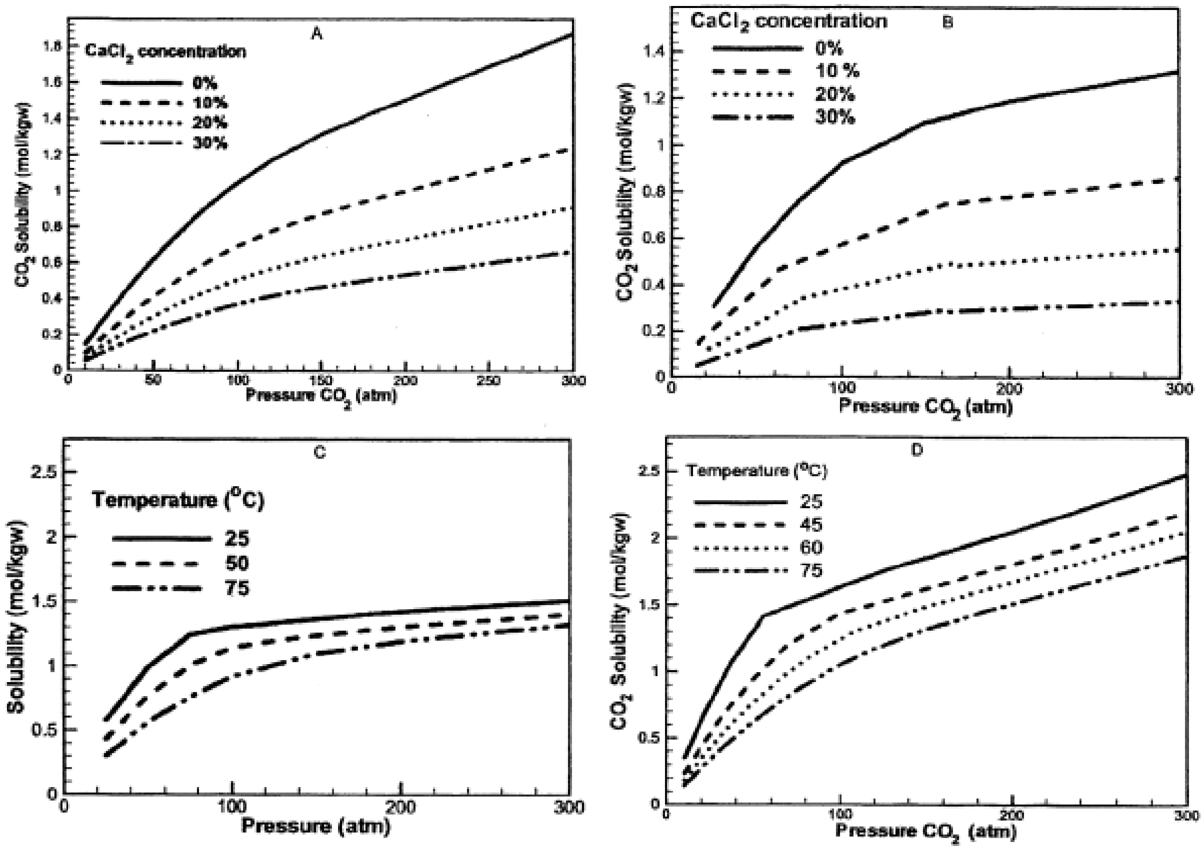


Figure A.7. Solubility of CO_2 in pure water and $CaCl_2$ brines as a function of pressure (A) at various concentrations (wt.%) of $CaCl_2$ and 75 °C — experimental results from Prutton and Savage [1945]; (b) at various concentrations (wt.% $CaCl_2$) and 75 °C — calculated using GWB (Bethke, 2002); (c) in pure water at various temperatures — experimental results [Wiebe and Gaddy, 1939; Wiebe and Gaddy, 1940]; and (d) in pure water at various temperatures— calculated using PHREEQC [USGS, 2008].

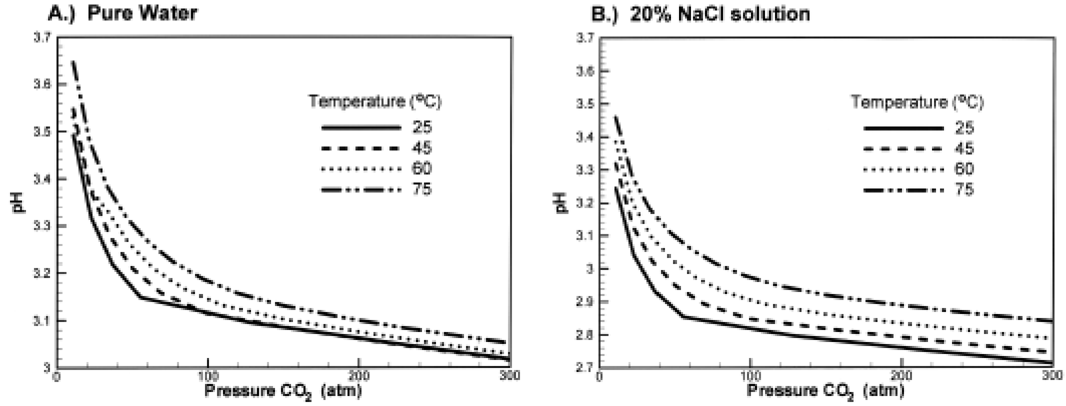


Figure A.8. Hydrogen ion concentration (pH) of CO_2 in H_2O (a) and carbonated brines (water containing 20% NaCl) and (b) as a function of pressure at 25, 45, 60, and 75 ^{o}C. The results in pure water were estimated using PHREEQC, while the brine results were estimated using GWB [Bethke, 2002].

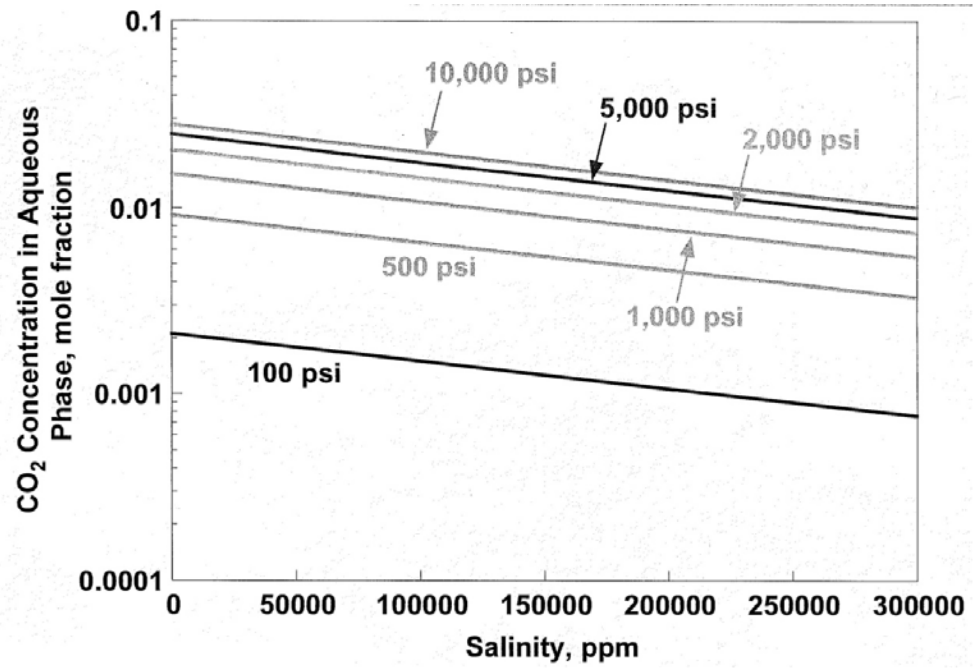


Figure A.9. Increasing brine salinity reduces CO_2 solubility in aqueous phase [Courtesy of Gary Pope, 1995].

Since the formation rock (mineralogy and distribution) and brine composition are unique to the formation, laboratory compatibility tests of CO_2 viscosifiers are required.

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