

Enhanced Oil Recovery and CO₂ Flooding/Sequestration in Carbonates

The University of Kansas Tertiary Oil Recovery Project (TORP) has an extensive portfolio of research on improving oil recovery from carbonate reservoirs. Staffing in TORP is funded by the State of Kansas. Students and faculty in the Department of Chemical and Petroleum Engineering, and Department of Geology interact extensively in their courses, learning skills directly applicable to the oil and gas industry. Engineering staff of TORP and faculty in Chemical and Petroleum Engineering specialize in dual porosity/fractured reservoir systems in carbonates. Interdisciplinary studies among TORP, Chemical and Petroleum Engineering, the Department of Geology, and KGS are exploring a wide range of avenues related to enhance oil recovery and CO₂ sequestration in carbonates. Examples of some current and pending projects include:

Polyelectrolyte and Nanoparticle Stabilized CO₂ Foams for Enhanced Oil Recovery

Negar Nazari, Jyun-Syung Tsau and Reza Barati

SUBSURFACE APPLICATION: Mississippian limestone, Lansing Kansas City.

STATUS: Long-term project in progress

TIMING: To be completed in the future if funded

FUNDING: Kansas Interdisciplinary Carbonate Consortium (KICC)

Purpose

The overall objective of this project is to improve the stability of CO₂ foam systems, used for EOR purposes, using combinations of surfactants with polyelectrolytes and polyelectrolyte complex nanoparticles (PECNPs).

Project Description

Polyelectrolytes and their complexes can potentially reduce the dynamic movement of surfactants and prevent collapse of the formed lamellae. Moreover, polyelectrolytes have been found to reduce the critical micellar concentration of surfactants, thus potentially reducing the surfactant burden.

CO₂ foam has been used to overcome aforementioned problems by dispersing CO₂ within a surfactant solution. CO₂ foams are agglomerations of gas bubbles separated from each other by liquid films with 60-97% gas content. Up to 100 times gas mobility reduction can be achieved using CO₂ foam via permeability reduction and viscosity enhancement [1]. Moreover, CO₂ foams are shear thinning fluids, and are considered an environmentally friendly material [1]. In addition to being complex systems, suffering from surfactant adsorption and poor injectivity, CO₂ foam is a thermodynamically unstable system [2]. Reportedly, long-term stability, and stability in the presence of crude oil, has been a problem [3, 4]. Polyelectrolytes can potentially reduce the dynamic movement of surfactant [5, 6] and significantly strengthen the lamellae and making a more stable interface by interacting with surfactants of opposite charge, mainly through electrostatic forces.

Laboratory experiment will be conducted at reservoir pressure and temperature to find the most stable polyelectrolytes or PECNPs systems with a nonionic surfactant in foam durability and Interfacial Tension (IFT) test. A high pressure high temperature (HPHT) view cell will be used to select the chemicals of the best performance with and without crude oil in the system. Our preliminary experiments have showed significant improvement in stability of CO₂ foam due to application of PECNPs (*Figure 1*). Effect of molecular weight and structure of polycations on effectiveness of stabilizing the foam and viscoelasticity of the interface will be studied by measuring IFT and foam column durability. A flow loop experiment will be used to examine the flow behavior of foam generated by the selected chemical systems under shear and its rheological properties. Finally, core flood experiments will be designed to demonstrate the improvement of oil recovery with the proposed chemical system and optimize the performance of polyelectrolyte and nanoparticle stabilized CO₂ foam for enhanced oil recovery (EOR) by

measuring incremental oil recovery due to foam flooding and pressure drop along 10-inch cores (Figure 2).

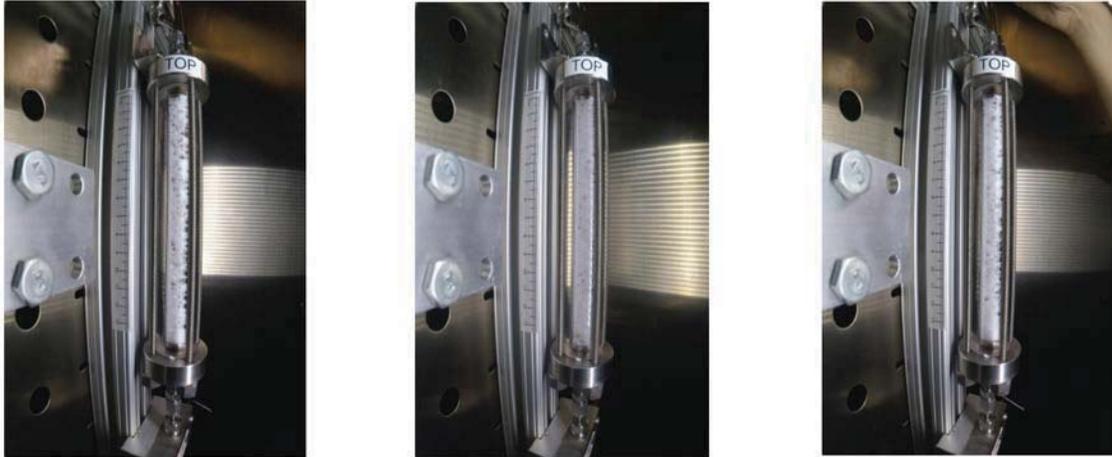


Figure 1. Foams generated without crude oil with surfactant (left) surfactant-PEI (middle) and surfactant-NP (right) at 40 °C and 1300 psi.

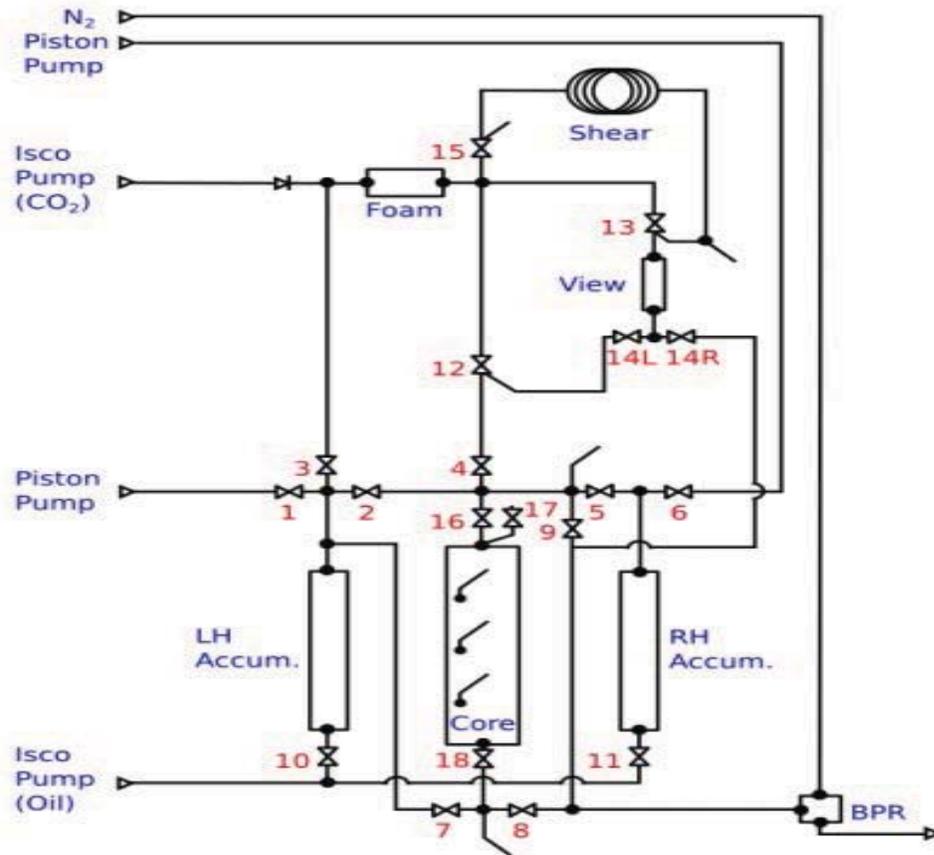


Figure 2. Core flood system prepared for the injection of CO₂-foam into a long core either 100% saturated with brine or brine at residual oil saturation.

Deliverables

Successful completion of this project will provide a novel chemical system to improve mobility control for CO₂ application in EOR with stabilized foams. A surfactant-polyelectrolyte (s) system capable of generating stable CO₂-foam in the presence of crude oil, showing stable rheological properties under shear, and incremental crude oil and stable pressure drop across long cores is aimed to be the main deliverable of this research.

References

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Understanding the Underlying Mechanisms of Low Salinity and Modified Salinity Water-Flooding Processes for Limestone Formations

Tugba Turnaoglu and Reza Barati

SUBSURFACE APPLICATION: Lansing Kansas City limestone intervals, Oread and Foraker

STATUS: Long-term project in progress

TIMING: To be completed in the future if funded

FUNDING: Kansas Interdisciplinary Carbonate Consortium

Purpose

The goal of this study to investigate the effect of salinity modification on Lansing-Kansas City (LKC) limestone intervals via the evaluation of incremental oil recovery, relative permeability and capillary pressure curves, interfacial properties between crude oil and brine and the ion exchange mechanism.

Project Description

The potential of incremental oil recovery via reduced/modified salinity brine, low/modified salinity waterflooding (LMSW), from sandstones has been well studied. Incremental oil recoveries of 2-10% have been also reported for carbonates due to modification of injected water composition (Strand et al. 2008; Ligthelm et al. 2009; Romanuka et al. 2012). Despite the controversy regarding the LMSW mechanisms, the effect of these mechanism(s) on relative permeability and capillary pressure curves has been postulated and used for the simulation of LMSW processes. However, even though the relative permeability and capillary pressure has been used to match the displacement results (Romanuka et al. 2012), a complete study of the effect of LMSW on carbonate rocks is yet to be done.

LKC reservoirs have been exposed to waterflooding for many years (Allison, 1959) and have contributed to the 47% oil production of the State of Kansas that comes from Pennsylvanian formations (Evans and Newell, 2013). The low/modified salinity waterflooding will potentially bring an economically viable option to enhance the income even for small producers in the State of Kansas.

To obtain full characterization of the LKC limestones, three sets of LKC core plugs will be used. The cores will be cleaned using a Dean-Stark apparatus and then saturated with synthetic LKC brine. Initial water saturation will be established for all core plugs. The cores will be aged in LKC crude oil to simulate the initial reservoir conditions. The following experiments will be conducted with various salinity and brine compositions:

- The first set of core plugs: Spontaneous imbibition tests will be conducted to study the wettability state of the cores.
- The second set of core plugs: The oil/water relative permeability curves will be generated. These cores will be flooded with brine with similar composition at the reservoir brine and at their residual oil saturation to study modified salinity waterflooding as an improved oil recovery method.
- The third set of core plugs: Capillary pressure curves.

- To investigate the effect of salinity modification on interfacial properties between oil and water for LKC, IFT and contact angle measurements will be conducted by Pendant Drop Method. The interfacial properties will be correlated to oil-water and oil-water-rock interface properties.
- To study the effect of salinity modification on ion exchange between rock and oil-water system, a baseline ion exchange test will be conducted. Cores which will be saturated in synthetic brine which is analogue to LKC formation will be flooded with various salinity and composition of brines for at least 20 PV. The brine effluents will be analyzed by Inductively Couple Plasma Optical Emission Spectroscopy (ICP-OES).
- A simulation study of the lab experiments will be conducted next to extract properties for the field scale modified waterflooding simulation for LKC reservoirs.
- An inverted 5-spot pattern will be selected in a LKC reservoir in order to conduct a pilot test of low salinity waterflood and analyze the production and injection data.

Deliverables

This project will provide full characterization of the LKC limestone formation including LKC crude oil properties, wettability alteration (contact angle, Amott Harvey test and relative permeability), the interaction between crude oil and brine (dynamic and equilibrium IFT) as well as oil displacement studies. Moreover, a correlation will be sought between wettability and SCAL properties for different water salinity and compositions.

References

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Development of an Environmentally and Equipment Friendly Alternative for Matrix Acidizing and Acid-Fracturing Applications

Reza Barati and students

SUBSURFACE APPLICATION: Mississippian limestone, Lansing Kansas City limestone intervals, Arbuckle, Austin Chalk, Buda limestone, Bakken, Eagle Ford, Niobrara

STATUS: Proposed project

TIMING: Preliminary results available; to be completed in the future if funded.

FUNDING: Seeking funding

Purpose

The overall objective of this project is to evaluate the performance of Ultraseries FF-01 (FF-01) as an environmentally- and equipment-friendly alternative for HCl that can be used for matrix acidizing and acid fracturing of wells producing from limestone formations. Specifically, this project will focus on developing this new product for the Mississippian Limestone Play (MLP) reservoirs in Kansas by evaluating the performance of FF01 as a single component product to be injected followed by evaluation of blends of FF01 and different polymers used in hydraulic fracturing of limestone formations.

Project Description

Well acidizing is one of the most common practices in the oil industry. Hydrochloric acid (HCl) has been used as the main acid for limestone stimulation purposes [1]. However, serious concerns regarding the health and safety of the field crew, corrosive nature of the acids for the tubular and equipment, environmental effects of the produced HCl, and rapid spending rate of HCl that prevents deep penetration into the formation has led the industry towards a more environmentally and equipment friendly product [2]. FF01 is an environmentally- and equipment-friendly product of 101st Earthborn Environmental Technologies LP, which is a conversion to an organic carrier to maintain very low pH as a vehicle for aggressiveness, along with the creation of buffers and surface tension relievers for the effectiveness and safety [3]. Low pH, linear reaction with limestone, small amount of residue after reaction, longevity and higher viscosity than water with shear thinning behavior are the properties of this product.

The Mississippian Limestone Play (MLP) has become an important source of income for both Kansas and Oklahoma with hundreds of horizontal wells drilled and completed and millions of dollars of extra income [4, 5]. Acid treatment of oil wells with the purpose of increasing their productivity is a very common practice in the MLP. Considering the millions of barrels of fluids that are being used for acid treatments, use of a more environmentally- and equipment- friendly product will both save the companies money on their equipment and prevent the exposure of the acidizing crew and surface environment to HCl, both in liquid and vapor forms.

A complete lab study of this product including rheological, core-flooding and fracture conductivity tests at reservoir and ambient conditions will be followed by a matrix acidizing field test in a MLP production well.

During the research and development phase of this project:

- Rheological measurements will be conducted for FF01 and blends of FF01 with guar and hydrolyzed polyacrylamide (HPAM) products used for hydraulic fracturing of wells.
- HPHT reaction experiments will be conducted using a rotating disk setup and reaction parameters will be calculated by measuring the Ca concentration vs. time as a result of the acid reaction.
- Core-flooding experiments using different concentrations and blends of FF01 with each fracturing polymer as viscosifying agents and fracturing fluids will be conducted at reservoir conditions.
- Fracture conductivity measurements for fractures generated using the selected fluids will be conducted at reservoir conditions. Base cases will also be conducted using HCl for both ambient and reservoir conditions.

The final products most suitable for matrix acidizing and acid fracturing will be selected and the conditions of different wells owned by the producer will be studied to select a MLP well with the most appropriate conditions for matrix acidizing. The field test will be designed and conducted. Post-treatment data will be analyzed.

Deliverables

The deliverables are: 1) an optimized recipe and designed blends using acid alternatives and hydraulic fracturing polymers including a comparison of rheological properties (Figure 1), 2) Comparison of reaction parameters for commercial blends used in the industry with this novel environmentally-friendly product, 3) incremental permeability induced by matrix acidizing and acid fracturing using this new product (Figure 2) compared with HCl, and 4) improvement in the overall productivity due to acid fracturing using HCl alternatives.

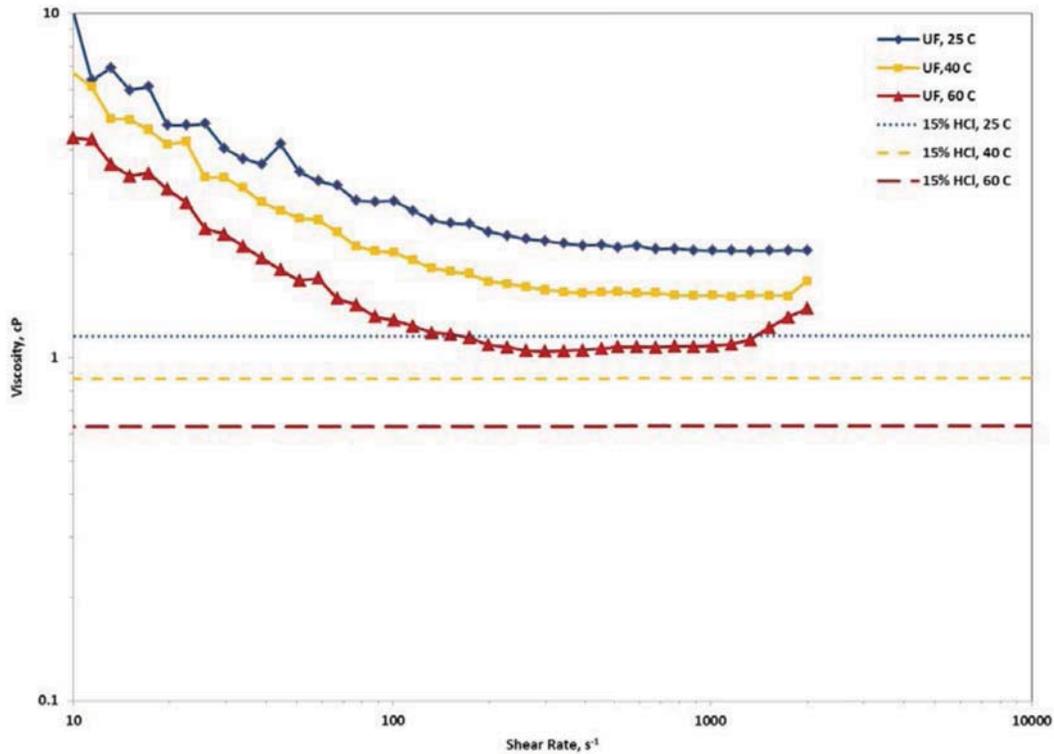


Figure 1. Viscosity versus shear rate for FF-01 and 15% HCl at 25 °C, 40 °C, and 60 °C.

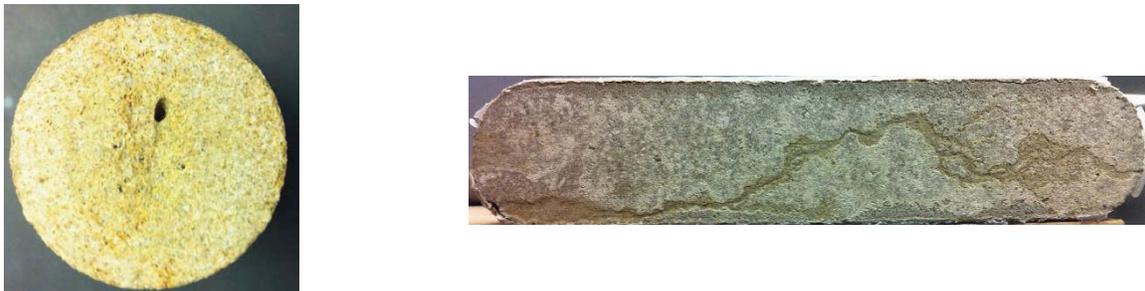


Figure 2. The LHS picture presents a core sample after a matrix acidizing experiment is performed. The RHS picture is a core sample after an acid fracturing experiment was performed.

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Microbial Enhancement of In Situ CO₂ Sequestration

Jennifer Roberts and David Fowle

SUBSURFACE APPLICATION: Applicable to Mississippi Lime; Arbuckle Aquifer and other reservoirs targeted for tertiary recovery via CO₂ injection or aquifers targeted for CO₂ storage.

STATUS: Project Proposed

TIMING: To be completed in the future if recommended by membership, funded, or staffed

FUNDING: None

Purpose

In recent years there has been significant advancements investigating aquifers, mine tailings, and oil fields as a long-term storage solution for carbon dioxide. One potential fate for injected CO₂ is sequestration of CO₂ into sparingly soluble carbonate minerals. Whereas microorganisms are known to facilitate precipitation of carbonate minerals, it remains unclear whether they promote carbonate precipitation in CO₂-injected reservoir systems. Here we will investigate: 1) the extent that microorganisms and other functionalized particles influence carbonate precipitation under reservoir temperatures and pressures in the presence of super critical CO₂ and high partial pressures of CO₂, and; 2) strategies to enhance precipitation kinetics through stimulation of *in situ* native microbial communities or injection of natural or engineered materials.

Project Description

The introduction of high partial pressures of CO₂ into the subsurface will influence mineral solubility. The dissolution and precipitation of mineral phases will lead to changes in reservoir permeability, and the potential sequestration of CO₂ into insoluble carbonate minerals. These abiotic processes have been investigated at the bench (e.g., HANSEN, et al., 2005) and field scale (e.g., KHARAKA et al., 2006) yet influences on these processes by native microorganisms and other charged surfaces remain unclear. Because microorganisms have been shown to be integral to carbonate mineral formation in some environments (Figure 1), in this study we will develop strategies to enhance carbonate mineral precipitation under reservoir conditions. We hypothesize that:

- Microbial activity and reactive surfaces can enhance rates of carbonate mineral precipitation; and
- By distinguishing the mechanism of precipitation, we can engineer protocols to enhance these processes *in situ*.

These hypotheses will be tested using controlled laboratory batch experiments containing native consortia from reservoir fluids. We will characterize precipitation of carbonate phases as a function of solution chemistry and the presence/absence of cells; and characterize precipitation of carbonate phases as a function of solution chemistry and active metabolic pathways.

Deliverables

We expect precipitation of carbonate phases will be facilitated by both metabolic activity and cell wall interactions. By characterizing the abundance and types of microorganisms in a specific system we can produce better estimates of sequestration and devise approaches to enhance sequestration. Specific deliverables include: 1) quantitative data to assess the rate of carbonate precipitation under reservoir conditions as a function of biomass; 2) implementation of experimental data in conjunction with site specific characterization of microbial populations into predictive models; and 3) engineered approaches for enhancing carbonate precipitation *in situ* including enhancement of carbonate-precipitating metabolic activities or bioaugmentation.

References

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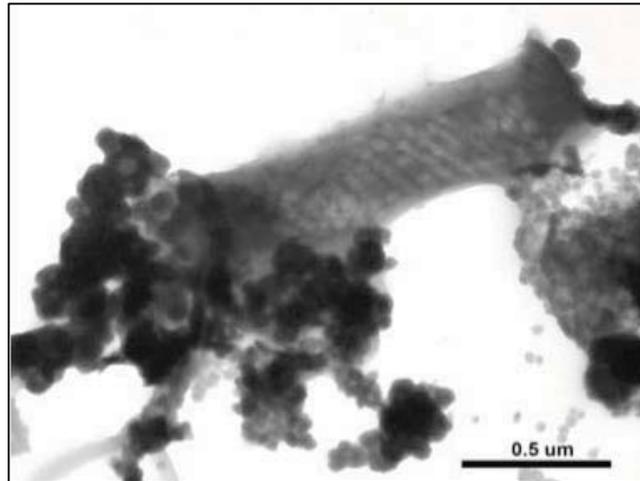


Figure 1. TEM photomicrograph of a microbial surface coated in carbonate precipitate.

Experimental Studies of Geofluid Interactions with Carbonate Rocks in Sedimentary Basins

Jennifer A. Roberts and David A. Fowle

SUBSURFACE APPLICATION: Applicable to modeling carbonate reservoir diagenesis or testing hypotheses of “production-induced” diagenesis in produced carbonate reservoirs.

STATUS: Project Proposed

TIMING: New laboratory and analysis June 2014-February 2015

FUNDING: Seed funding from KICC awarded.

Purpose

Due to experimental limitations, thermodynamic and kinetic data for mineral dissolution and precipitation typically are extrapolated to the temperatures and pressures appropriate for sedimentary basins. These data are central to reactive transport and basin evolution models used for prediction of reservoir quality. Extrapolation of these data are questionable, and new data from experiments conducted at conditions appropriate to the deep subsurface remain integral for understanding both the formation and evolution of porosity and permeability in sedimentary basins. Model experimental systems are critical to able to predict, for example, how fracking fluids or supercritical carbon dioxide will impact the integrity of shales and other seals, how mobile radionuclides, sourced from reservoir and seal dissolution, will behave in deep repositories, and how reservoir carbonates form and evolve under basinal temperatures and pressures (e.g. Cantucci et al., 2009; Kazuba et al., 2003). Furthermore, these systems lack any conceptual framework regarding the role of microorganisms in these processes, which are critical to the kinetics of many early diagenetic reactions below temperatures of 80 °C (e.g. clay diagenesis, carbonate cementation).

The goal of the proposed study is to generate preliminary data in our new high-temperature, high-pressure experimental geofluids laboratory generating rates of carbonate mineral precipitation and dissolution under reservoir temperatures and pressures.

Project Description

As principal investigators in a collaborative US Dept of Energy (DOE) project modeling carbon dioxide sequestration in a deep saline aquifer and a depleted oil reservoir, we have undertaken experiments to study shale cap rock dissolution, and precipitation reactions and kinetics at high temperatures and pressures in the presence of microbes and supercritical CO₂ at a DOE national lab. Specifically, we have developed protocols for high T and P experiments in batch reactors and flow through reactors that are comparable to reservoir conditions. The experimental data produced can be coupled to high-resolution x-ray CT scanning and *ex situ* geochemical and gas phase analysis to provide new mechanistic insights into diagenetic and reservoir reactions, products, and rates (after Regnault et al., 2009). Through funding in hand from the University for the experimental geofluids laboratory we propose to develop a line of research focused on Carbonate Reservoirs in collaboration with KICC and ultimately industry sponsors.

We will begin our studies by investigating the impact of a gradient of temperature and pressure on a variety of carbonate sediment samples, including primary dolomites

produced in our laboratory (e.g. Kenward et al, 2013; Roberts et al. 2013), Arbuckle dolomite, and so-called “oil shales” (e.g. Pierson Formation) in the overlying Mississippian units. Specifically, we will 1.) investigate how mineral equilibria change under CO_{2(SC)} injection, 2.) quantify the rates of dissolution and precipitation reactions, and 3.) assess how these reactions will impact reservoir and seal porosity and permeability. A critical and unique aspect of the proposed project will include microorganisms as a variable to investigate whether native microbial communities, their metabolic byproducts (e.g. organic acids, dissolved organic carbon) or cells themselves influence the rates, mechanism and outcomes of the previous questions. These experiments will be conducted using individual minerals, complex mineral mixtures and core samples from the basins of interest in collaboration with KICC and industrial partners. Fluid geochemistry and microbial communities will be modeled on reservoir brines characterized from drill stem tests and swab fluids. Reaction progress will be followed using solution chemistry, stable isotopes, pore and surface area measurements, XRD, and electron microscopy.

The initial work and deliverables for the proposed work will focus on reactions with Arbuckle and Mississippian materials in the presence of CO_{2(SC)}. We will also use this as an opportunity to observe “ripening” processes in our laboratory-precipitated dolomite, however these efforts will be purely exploratory at this point in time.

This work will provide a first step in understanding critical thermodynamic and kinetic parameters necessary to predict basin scale pore water and reservoir evolution based on sorption, precipitation/dissolution kinetics, and biological activity.

Deliverables

Specific deliverables include: 1) The first results for experimental microbial geochemistry of carbonates at high temperatures and pressures; 2.) Preliminary mechanistic, morphological and kinetic data on *in situ* of carbonate precipitation and dissolution with and without reactive microbial surfaces in the same environments, 3.) At least one manuscript and development of a larger NSF or industry supported proposal.

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CO₂ Flooding to Improve Oil Recovery in Carbonate Reservoirs

TORP Staff, Graduate student

SUBSURFACE APPLICATION: Arbuckle reservoirs in Kansas or other similar type of reservoirs with operation pressure below minimum miscibility pressure

STATUS: Long-term project

TIMING: Significant results to be reported – Results currently available to membership

FUNDING: TORP

Purpose

Carbon dioxide (CO₂) injection for enhanced oil recovery is a proven technology. It is also considered as one of the most promising methods for carbon sequestration in geologic formations. CO₂ injections are normally operated at a pressure above the minimum miscibility pressure (MMP), which is determined by crude oil composition and reservoir conditions. However, many reservoirs in the United States and around the world are at shallow depths or geologic conditions exist such that they operate at pressures below the MMP. When CO₂ injection operates at a pressure below the MMP, displacement efficiency decreases as a result of the loss of miscibility but is still better than that in a waterflooding process. This better recovery has been attributed to possible improvement of the mobility ratio displacement and an extraction process, which are all closely related to operating pressure. To increase the resource base for CO₂ flooding and substantially increase the production from reservoirs, there is a need to characterize the near miscible conditions of reservoirs and investigate the feasibility of CO₂ displacements at near miscible pressures by conducting appropriate experimental work and reservoir simulation.

Project Description

Arbuckle reservoirs historically have been viewed as fracture-controlled karstic reservoirs with porosity and permeability influenced by basement structural patterns and subaerial exposure. These reservoirs have produced an estimated 2.2 billion barrels of oil representing 35% of the 6.1 billion barrels of oil of total Kansas oil production and are a significant resource in Kansas for improved oil recovery. Initial studies of CO₂ miscible flooding indicated that miscibility is not achievable at the reservoir operating pressure in most Arbuckle reservoirs. On the other hand, if the reservoir operating pressure is above the MMP, CO₂ miscible process can be considered to improve the oil recovery. An example of such a reservoir is located at a depth of about 2900 feet in Hall Gurney Field, Russell County, Kansas.

The objective of this project is to investigate the feasibility of applying CO₂ displacement at miscible or near miscible pressure to increase the resource base for CO₂ flooding and substantially increase the production from these reservoirs. The proposed work includes experimental and simulation studies. The experimental study will 1) systematically characterize the miscible and near miscible condition and study recovery of waterflood residual oil using CO₂ displacement at near miscible pressure, and 2) identify key parameters in phase behavior and flow tests for simulation modeling. The simulation

study will develop a representative model to simulate miscible and near miscible displacement physics and 2) assess the potential of recovery processes at miscible and near miscible pressures.

Deliverables

The project will develop a methodology to design field application of carbon dioxide injection at near miscible and miscible condition. Economics of pilot/demonstration and field application on carbonate reservoirs of interest will be evaluated.

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Chemical Flooding for Improved Oil Recovery in Carbonate Reservoirs

TORP Staff, Graduate student

SUBSURFACE APPLICATION: Trembley oilfield in Kansas

STATUS: Long-term project

TIMING: Significant results to be reported

FUNDING: Partial from DOE

Purpose

Successful field applications of chemical flooding rely on a high-quality design. Laboratory evaluation to determine an efficient chemical formulation for an oil/brine/reservoir system, and reservoir simulations to predict performance and economic evaluation of the process are key elements of the design. The principal objective of this project is to supply the design work for chemical flooding processes that is necessary for oil producers to make an informed assessment for implementation of a pilot or demonstration project.

Project Description

Generally, more than half of the oil is left in the ground at the end of waterflooding operations due to partial sweep of the reservoir by the water and the residual oil that is left where the water has invaded. Chemical flooding has the potential to displace and produce a significant portion of that remaining oil. A slug of a chemical formulation is injected and displaced through the reservoir. The chemical formulation, which includes surfactants, solvents, polymer and/or alkali, is designed for the particular oil/brine/reservoir rock system. TORP is presently classifying Kansas reservoirs for their chemical flooding potential. The proposed work includes 1) conduct laboratory testing under reservoir conditions to screen different chemical formulations for carbonate reservoirs of interest, 2) determine field responses to chemical flooding by reservoir simulations, and 3) evaluate economics of pilot/demonstration and field applications.

Deliverables

The project will develop a database of carbonate reservoirs that are used to screen, rate and study for future field application. Laboratory and simulation results will be used to assess the potential oil recovery at carbonate reservoirs of interest.

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