

**Fundamentals of reservoir surface energy as related to  
surface properties, wettability, capillary action, and oil  
recovery from fractured reservoirs by spontaneous  
imbibition**

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## **PUBLIC ABSTRACT**

The objective of this project is to increase oil recovery from fractured reservoirs through improved fundamental understanding of the process of spontaneous imbibition by which oil is displaced from the rock matrix into the fractures. Spontaneous imbibition is fundamentally dependent on the reservoir surface free energy but this has never been investigated for rocks. In this project, the surface free energy of rocks will be determined by using liquids that can be solidified within the rock pore space at selected saturations. Thin sections of the rock then provide a two-dimensional view of the rock minerals and the occupant phases. Saturations and oil/rock, water/rock, and oil/water surface areas will be determined by advanced petrographic analysis and the surface free energy which drives spontaneous imbibition will be determined as a function of increase in wetting phase saturation. The inherent loss in surface free energy resulting from capillary instabilities at the microscopic (pore level) scale will be distinguished from the decrease in surface free energy that drives spontaneous imbibition.

A mathematical network/numerical model will be developed and tested against experimental results of recovery versus time over broad variation of key factors such as rock properties, fluid phase viscosities, sample size, shape and boundary conditions. Two fundamentally important, but not previously considered, parameters of spontaneous imbibition, the capillary pressure acting to oppose production of oil at the outflow face and the pressure in the nonwetting phase at the no-flow boundary versus time, will also be measured and modeled. Simulation and network models will also be tested against special case solutions provided by analytic models.

In the second stage of the project, application of the fundamental concepts developed in the first stage of the project will be demonstrated. The fundamental ideas, measurements, and analytic/numerical modeling will be applied to mixed-wet rocks. Imbibition measurements will include novel sensitive pressure measurements designed to elucidate the basic mechanisms that determine induction time and drive the very slow rate of spontaneous imbibition commonly observed for mixed-wet rocks. In further demonstration of concepts, three approaches to improved oil recovery from fractured reservoirs will be tested; use of surfactants to promote imbibition in oil wet rocks by wettability alteration: manipulation of injection brine composition: reduction of the capillary back pressure which opposes production of oil at the fracture face.

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## **INTRODUCTION**

### **Objectives**

The long-range objective of this project is to improve oil recovery from fractured reservoirs through improved fundamental understanding of the process of spontaneous imbibition by which oil is displaced from the rock matrix into the fractures. Spontaneous imbibition is fundamentally dependent on the surface energy. An initial objective is to determine the surface energy and relate the dissipation of surface energy to the mechanism of spontaneous imbibition. A parallel objective is to model the mechanism of spontaneous imbibition by a combination of network analysis and numerical modeling. Also fundamentally important, but not previously considered, parameters of spontaneous imbibition, the capillary pressure acting to oppose production of oil at the outflow face and the pressure in the nonwetting phase at the no-flow boundary (in effect within oil in the non-invaded zone of the rock matrix) versus time, will also be measured and compared with values predicted by the mathematical model. The next objective is to measure surface energy and related spontaneous imbibition phenomena for mixed-wettability rocks prepared by adsorption from crude oil. The dissipation of surface free energy must then be related to oil production at mixed-wet conditions. The final objective is to apply the results of the project to improved oil recovery from fractured reservoirs in three ways: reduction of the capillary force that opposes oil production at the fracture face; change in wettability towards increased water wetness; identification of conditions where choice of invading brine composition can give improved recovery.

## TASKS

### **Budget period 1, July 1, 2003 through June 30, 2005 – Ideas and Concept development: Fundamentals of Spontaneous Imbibition**

*Task 1. Work of displacement and surface free energy.* Obtain complementary sets of capillary pressure drainage and imbibition data and data on changes in rock/brine, rock/oil, and oil/brine interfacial areas with change in saturation for drainage and imbibition for at least two rock types (sandstone and carbonate). Determine free-energy/work-of-displacement efficiency parameters for drainage and imbibition for at least two rock types so that changes in rock/wetting phase/nonwetting phase surface areas can be closely estimated from capillary pressure measurements.

*Task 2. Imbibition in simple laboratory and mathematical network models.* Study imbibition in at least three simple tube networks that can be modeled analytically to establish and/or confirm fundamental aspects of the pore scale mechanism of dynamic spontaneous imbibition with special emphasis on determining how spontaneous imbibition is initiated and the key factors in how the saturation profile develops with time. Incorporate rules developed from laboratory measurements on relatively simple networks into the design of a computational network model. Use the network model to obtain an account of the mechanism by which imbibition is initiated, the saturation profile is developed, and the rate of spontaneous imbibition in terms of the dissipation of surface free energy that accompanies change in saturation.

*Task 3. Novel observations on fluid pressures during imbibition and the mechanism of non-wetting phase production at the imbibition face.* Make novel observations on the imbibition mechanism including details of the mechanism of oil production at the outflow rock face and the change in the nonwetting phase pressure at the no-flow boundary of the core during the course of spontaneous imbibition for at least 16 distinct combinations of rock/ fluid properties.

*Task 4. Network/numerical model and new imbibition data.* Develop a numerical simulator specifically designed for spontaneous imbibition. Incorporate the network model to obtain a network/numerical model that includes matching the measured pressure in the nonwetting phase at the no-flow boundary, and the pressure that opposes production of oil at the open rock face. Imbibition data will be obtained for at least 10 rocks with over six-fold variation in permeability, and at least 6 orders of magnitude variation in viscosity ratio, and at least 10 variations in sample size, shape, and boundary conditions.

*Task 5. Comparison with similarity solutions.* Compare results given by simulation with special case analytic results given by similarity solutions for spontaneous imbibition for at least five distinct cases of rock and fluid properties.

**Budget Period 2, July 1, 2005 through June 30, 2008 - Demonstration of concept:  
Application to mixed wettability rocks and improved oil recovery from fractures  
reservoirs.**

***Task 6. Rock preparation and Work of displacement and surface areas***

Obtain a range of rock types and identify and obtain crude oils that induce stable mixed wettability. Prepare at least 25 rocks with mixed wettability through crude oil/brine/rock interactions.

Determine work of displacement for drainage and imbibition and measure the variation in rock/brine, rock oil, and oil/brine interfacial areas during the course of drainage and imbibition for at least two examples of mixed wettability.

***Task 7. Novel imbibition measurements on mixed-wet rock and network models.*** Obtain, for at least six mixed-wet rocks, spontaneous imbibition data that includes measurements of the nonwetting phase pressure at the no-flow boundary, observations on the capillary pressure that resists production at the open rock face.

***Task 8. Application of network/numerical model to mixed wet rocks.*** Use network models to relate dissipation of surface energy to rate of spontaneous imbibition and to account for the frequently observed induction time prior to onset of spontaneous imbibition into mixed wettability rocks.

***Task 9. Increased oil recovery by spontaneous imbibition.*** The mechanism of increased recovery from mixed wet rocks by use of surfactants that promote spontaneous imbibition by favorable wettability alteration will be investigated for at least four distinct examples of crude oil/brine/rock/surfactant combinations.

The mechanism of increased recovery by manipulation of brine composition will be investigated for at least four crude oil/brine/rock combinations.

Addition of very low concentrations surfactants to the imbibing aqueous phase will be explored as a means of increasing the rate of oil recovery by reducing the capillary forces which resist production of oil at the fracture face. At least twelve combinations of rock and fluid properties including both very strongly wetted and mixed wet rocks will be tested.

## PROGRESS - BUDGET PERIOD 1

### Task 1. Work of displacement and surface free energy.

#### Introduction

The aim of this research is to understand the mechanism of the spontaneous imbibition, a process of key importance in oil production from fractured reservoirs. During the process of spontaneous imbibition, the surface free energy of the system is converted to work of displacement, for example as in the recovery of oil. The method proposed in this work utilizes thin section analysis from different core samples to determine fluid saturation and surface areas after solidification of epoxy resin. This information relates change in surface free energy to saturation.

#### Experimental

In order to determine the change in surface free energy a dyed liquid epoxy resin will be used as the wetting phase. After establishing a specific saturation the resin is solidified. A second epoxy was then injected at high pressure and solidified before preparation of the thin section. After both the epoxies have been set in place thin sections (28 microns thick) from the samples are made. Then laying a grid over the thin section a point count is done to determine the relative amount of area corresponding to oil-water and oil solid interfaces. The change in surface free energy of the system is given by:

$$\Delta F = \sigma_{ow}(\Delta A_{ow} + \Delta A_{so} \cos\theta)$$

Where,

$\Delta F$  is change in the surface free energy

$\sigma_{ow}$  is the oil – water interfacial tension (measured by drop volume method)

$\Delta A_{ow}$  is the oil – water interfacial area

$\Delta A_{so}$  is the oil – solid interfacial area

#### Epoxy Mixture

Initial studies have been focused on choosing the type of epoxy to be used for saturating the pore space. The desirable properties in the epoxy are:

1. Low viscosity, to allow easy mixing, removal of air from the epoxy mixture prior to vacuum saturation of the core, and establishing an initial wetting phase saturation by centrifuging before the epoxy starts to harden.
2. Long setting time to allow completion of all the steps i.e., vacuum saturation, high pressure injection and centrifugation. In all, these steps take around 8 hours to complete. Hence the ideal epoxy should give us atleast 12 hours of time before it starts to set up.
3. The epoxy, after setting up, should be hard enough to cut.

## Results and Discussion

The following resins have been tested:

1. Epoxy DER 331 diluted with n-butyl glycidyl ether to reduce the viscosity of the DER 331 from 14,000 cPs at 25 °C to around 200 cPs. The hardener used was Diethylenetriamine (95 %). The setting time was found to be around 3 hours and hence we could not use this epoxy in our research.
2. Epoxy DER 736 with n-butyl glycidyl ether and Diethylenetriamine (95 %). As before the setting time was not found to be adequate and also it was seen that after the epoxy was set it was not very hard, infact it was somewhat spongy. Hence for these two reasons this epoxy was also ruled out.
3. VCD (vinyl – 4 – cyclohexene diepoxide) and n-OSA (octenyl succinic) anhydride with Diethylenetriamine (95 %) were also experimented with however like the previous two epoxy mixtures they too were found to be inadequate. Also VCD is a strong carcinogen and hence for safety reason it could not be used.
4. Araldite 502 (modified Bisphenol A epoxy CAS # 84-74-2) epoxy with DDSA (Dodenyl Succinic Anhydraide CAS # 26544-38-7) as the hardener and BDMA (Benzylidimethylamine CAS # 103-83-3) as curing agent was finally selected for our research purposes as it all fulfilled all the criterion mentioned above. The following composition by volume was used for the experiments

Araldite 502	20 ml
Dodenyl Succinic Anhydraide	22 ml
BDMA	1- 1.2 ml

The dye used for these epoxies were Kriegrosol Blue Supra, Rhodamine B and two other fluorescent dyes (lemon yellow and aztec gold) obtained from Edgar Plastics.

### Measurement of Surface Areas

A petrographic microscope manufactured by Olympus<sup>®</sup> (Model BX 51) has been purchased and initial training in use of the microscope has been completed. The microscope has two different light sources, halogen and mercury. The halogen lamp is use for transmitted light whereas the mercury is used in conjunction with a UV filter to look at the sample under UV light using a fluorescent dye. Small cracks/fractures and microporosity with features even smaller than the wavelength of visible light show up very well under UV light. These cracks may be a part of a well connected network of pores and in some cases, like the tight gas sands, maybe the only pathway for the fluids to flow. The microscope also has a green filter that allows emission in the 590 nm range to look at the cracks and microporosity. The use of this filter is recommended with the Rhodamine B dye. A digital camera output for gathering real time picture has been used to capture high quality digital images. The microscope is also equipped with analyzer/polorizer combination to look for crystals of a specific type.

## **Conclusions**

The microscope will be used for petrographic analysis including point counts of the thin sections. It will also be used to obtain saturations and interfacial areas for two phase distribution of wetting and nonwetting phases. The thin section analyses will be performed for West Texas Crème (Carbonate) and Berea Sandstone.

## **Task 2. Imbibition in simple laboratory and mathematical network models.**

### **Experimental**

Simple network models have been designed and are currently being constructed with glass tube.

## **Task 3. Novel observations on fluid pressures during imbibition and the mechanism of non-wetting phase production at the imbibition face.**

### **Experimental**

The process of displacement of a nonwetting phase (NWP) from a porous medium by spontaneous imbibition of a wetting phase (WP) is often countercurrent. In core analysis studies, imbibition measurements are usually made on cylindrical cores with all faces open to imbibition. Use of cylindrical cores with only one end face open provides an effective approach to experimental investigation of linear displacement and analysis of the imbibition process; the volumetric flow of WP and NWP is opposite and equal at all distances from the open face. Conditions have been identified under which the existence and location of imbibition fronts are well defined. (Li et al., 2003). Under such conditions the history of the imbibition is independent of the dead end space defined by the distance from the front to the no flow boundary at the end of the core.

During counter current spontaneous imbibition (COUCSI), displaced NWP appears as bubbles at the open face. After detachment of the bubbles by snap-off, pore throats refill and must be repenetrated by a local drainage process before a new bubble of NWP is formed at the open face. During this process, there are local pressure fluctuations because of local changes in curvature including snap-off of the bubble (Roof, 1970). The capillary back pressure,  $P_{cb}$ , associated with these interfaces opposes production of NWP.  $P_{cb}$  is determined by the interfacial tension and locally selected large throats through which NWP exits the core.

One approach to elimination of the capillary back pressure is to allow NWP to vent from the otherwise sealed end of the core. Wang showed that this increased the rate of recovery of air by imbibition of oil by about an order of magnitude (Wang, 1999). However, under these conditions, there is a distinct change in the mechanism of imbibition. Both  $P_{cb}$  and relative permeability effects associated with counter-current flow are eliminated and there is a very small pressure gradient in the NWP region ahead of the front because the imbibition process becomes co-current.

In the present study of COUCSI, the pressure in the NWP,  $P_{nw, de}$ , contained in the dead end space ahead of the imbibition front will be monitored via a pressure tap at the end of the core. The location of the imbibition front and production versus time will also be recorded. Results for very strongly wetted conditions were obtained for displacement of mineral oil by water and air by mineral oil for a selection of Berea sandstone cores. The information obtained by experiment will be matched by numerical simulation to determine  $P_{cb}$  and  $P_{cf}$ , the saturation at the imbibition front, and the development of pressure and saturation profiles along the core.

### Conclusion

Preliminary results have been obtained for imbibition which includes the amount of imbibition versus time, the location of the imbibition front, and the change in pressure in the nonwetting phase dead space ahead of the imbibition front. The experimental designs for water/oil and oil/gas spontaneous imbibition are shown in Figs 1 and 2 respectively.

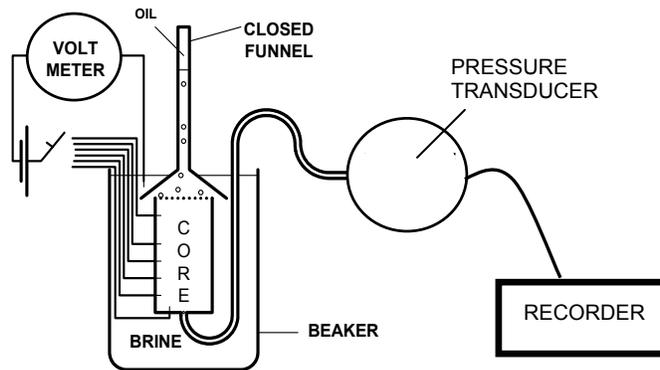


Fig.1. Apparatus for water/oil tests

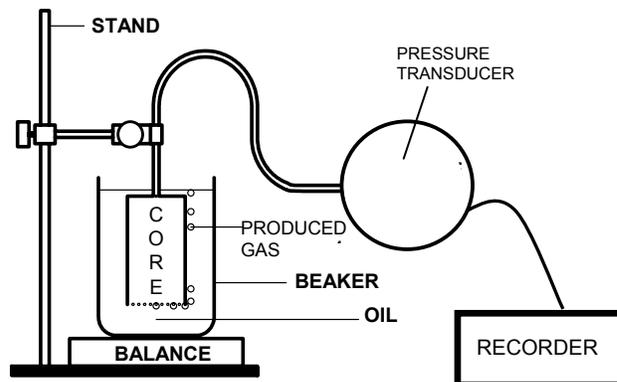


Fig.2 Apparatus for oil/air tests – change to pressure transducer

## Task 4. Network/numerical model and new imbibition data.

### Introduction

Spontaneous imbibition measurements will be made for a wide range of viscosity ratios as part of the program designed to give 6-fold variation in viscosity. The use of glycerol as a viscosifying agent for aqueous solutions is being investigated. A systematic study is being made of the physical and interfacial properties of glycerol/water or brine solutions. The solutions are Newtonian with viscosity ranging from 1-1800[cp] at ambient temperature. There was no significant change in volume with mixing. For example, densities increased linearly from 1.02[g/cm<sup>3</sup>] for seawater to 1.262 [g/cm<sup>3</sup>] for 99.5[%] glycerol (as supplied). All measurements were made at ambient temperature.

### Experimental

#### Fluids

Glycerol (provided by EM Science, assay min. 99.5 [%]), a synthetic formation brine termed as seawater (Table 1) and mixtures of both were used as the aqueous phase in this study. Two refined oils, Soltrol 220 ( $\mu_{oil}$ = 3.9[cp]) and pure n-decane ( $\mu_{oil}$ = 0.92[cp]) were utilized as the oil phase. Prior to their application the oils had to be both purified by means of passing the oils through aluminum and silica gel columns and degassed.

NaCl	56	[g/2L]
KCl	1.87	[g/2L]
MgCl <sub>2</sub> *6H <sub>2</sub> O	22.89	[g/2L]
CaCl <sub>2</sub> *6H <sub>2</sub> O	4.696	[g/2L]
NaN <sub>3</sub>	0.2	[g/2L]

#### Density

A Paar Density Meter DMA 48 was used to measure the density. Figure 1 shows the results over the entire range from 0% to 100% by weight glycerol concentration. The phase density increases linearly with increasing glycerol concentration from 1.024 [g/cm<sup>3</sup>] to 1.262 [g/cm<sup>3</sup>] for pure glycerol as provided. The linear dependence of liquid density with glycerol concentration indicates that there is no significant change in volume with mixing.

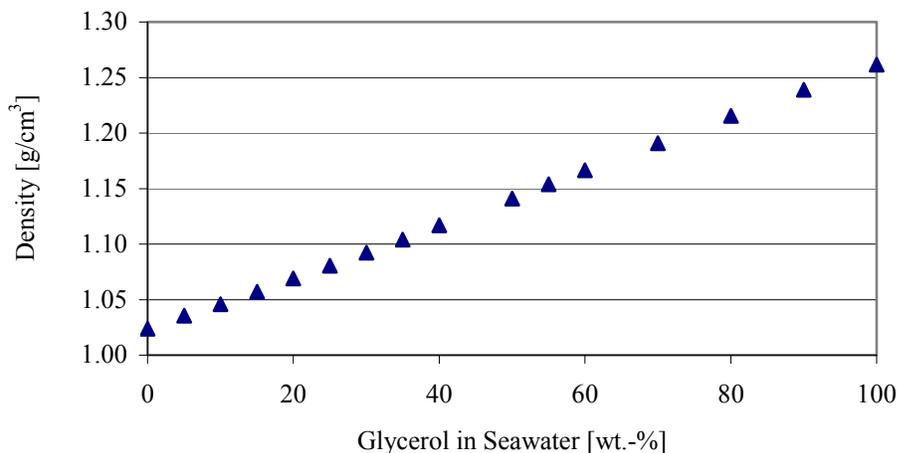


Fig.3: Aqueous phase density as a function of glycerol concentration

### Viscosity

The viscosity of seawater/glycerol mixtures was measured with capillary tubes (Cannon-Fenske viscometers). Three measurements were performed with each mixture and the viscosity was calculated from the average

### Results and Discussion

The results in Fig.4 show that low glycerol concentrations (up to about 50 [wt.-%]) gave moderate increase of the aqueous phase viscosity. At higher glycerol concentrations (up to 8-fold) the viscosity increased to nearly 100[cp]. Very high glycerol concentrations result in aqueous phase viscosities that range up to 1,800[cp] given by pure glycerol.

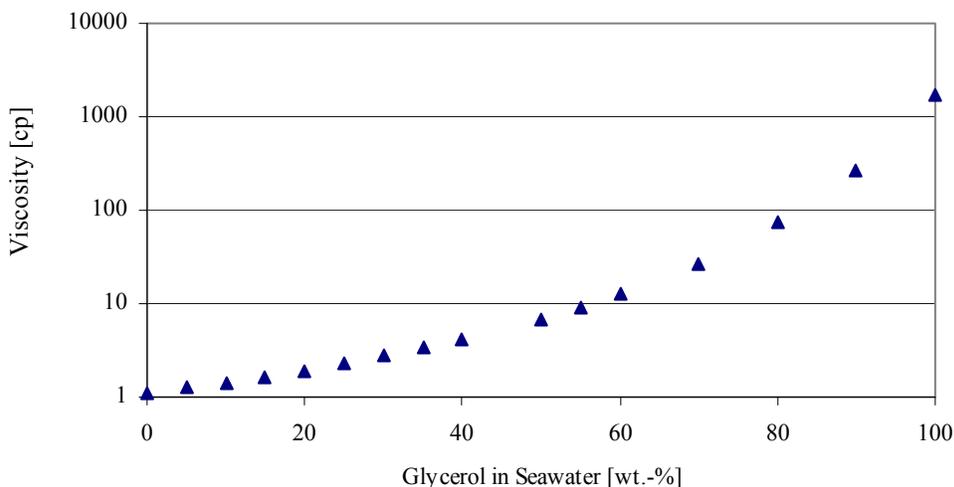


Fig.4: Aqueous phase viscosity as a function of glycerol concentration

### **Surface and Interfacial Tension**

Oil/water and gas/oil interfacial tensions are currently being measured and will be reported in the next quarterly report.

#### **Conclusion**

Good progress has been made in development of a numerical simulator for spontaneous imbibition.

### **Task 5. Comparison with similarity solutions.**

#### **Conclusion**

Work is progressing on developing a closed analytic solution for linear spontaneous imbibition.

### **REFERENCES**

Li, Y., Morrow, N.R. and Ruth, D., "Similarity Solution For Linear Counter-Current Spontaneous Imbibition" *JPSE*, 39, 3-4, 2003, 309-326.

Roof, J.G., "Snap-off of Oil Droplets in Water-Wet Cores", *Soc. Pet. Eng. J.*, March, 1970, 85-90.

Wang, R., 1999, Gas Recovery from Porous Media by Spontaneous Imbibition of Liquid, MS Thesis, University of Wyoming.