Enhancing Unconventional Reservoir Ultimate Recoveries with In-Situ Nano-Catalysts

(TCF-18-15390)

Randall E Winans

Argonne National Laboratory

Robert Klingler(ANL), Robert Lestz(Greyhorse Engineering)

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Presentation Outline

1. Technical Status
2. Accomplishments
3. Lessons Learned
4. Synergy Opportunities
5. Project Summary

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Technical Status

- ANL has a patented nano-catalytic process that can convert solid hydrocarbons to liquids and reduce the viscosity of liquid hydrocarbons under in situ conditions.
- Prior to commercial down-hole testing, the catalyst preparation process needs to be matured. The metal catalyst will be transported down-hole as a metal halide and then reduced in situ. Here, we propose to develop in the lab optimized reducing procedures for commercial well conditions.
- This process has the potential to accelerate commercial improvements in ultimate recoveries and drainage areas from unconventional oil reservoirs through three primary means:
  1. Improving the transmissibility of the oil
  2. Increasing the reservoir's permeability by converting solid hydrocarbons (e.g., kerogens and paraffins) into producible liquids
  3. Improving overall economics by increasing drainage area and the reserves recovered by a well thus reducing the number of wells required and the environmental impact.

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First Stage Procedures

- The study will utilize shale core materials ground to 20 - 35 mesh <u>with the original mineral and clay content intact</u> to determine if the minerals interfere with the catalytic reactions previously observed using pure kerogen samples.
- *In the first stage*, metal ions such as Ni(II) or Cu(II) are chemically bound to carboxlyate groups that are natively part of kerogen and potential bound in clays. The metal ion is bound to the kerogen matrix so that subsequent reduction to Ni(0) results in nanoparticles that are fixed within the kerogen.
- The Ni(II) that is loaded into that kerogen will be determined using 1,2-cyclohexanedionedioxime reagent which forms a colored complex that can be quantitated by UV at 550 nm. This standard analytical method is used to follow the decrease in Ni(II) concentration while slurring.
- In addition, Ni X-ray absorption near edge structure (XANES) is used to verify that Ni ions have been absorbed into the structure

Second Stage Procedures

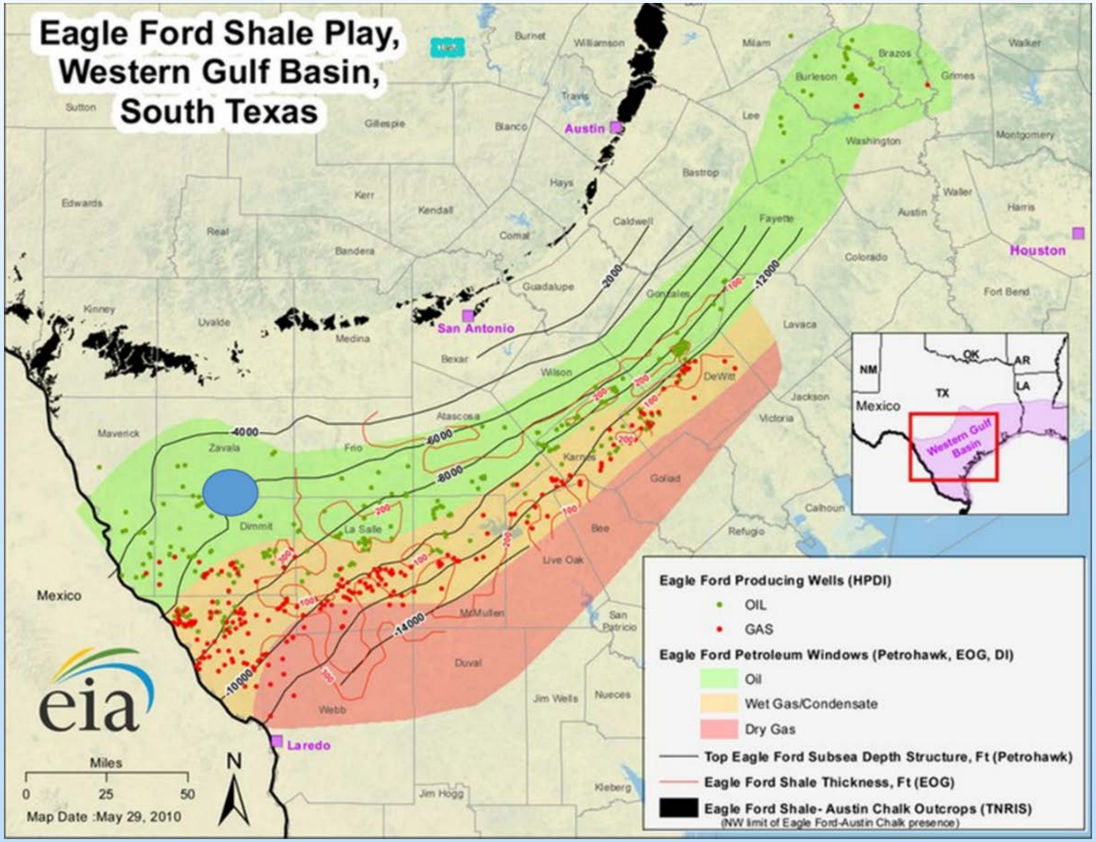
- *The second stage* involves the reduction of Ni(II)-kerogen to Ni(0)-kerogen. The two approaches that were used in the past will be used here
- The first method is a gas/solid reaction by passing hydrogen over the solid Ni(II)-core materials ground to 20 - 35 mesh contained in a porcelain boat that is placed in a Pyrex tube reactor operated at 1 atm pressure and temperatures from 150 to 350 ^oC.
- The extent of this reduction is followed as a function of temperature by XANES. The conversion of Ni(II) to Ni(0) is accompanied by a decrease in the white line peak intensity at 8350 ev and an increase in the edge region.
- Hydrocarbon products move down the tube to cooler portions of the oven. They are dissolved in methylene chloride and analyzed by GCMS. Different fractions are isolated by cutting the Pyrex tube into sections before extracting the product with solvent.

Second Stage Procedures

- The second approach to reducing the Ni(II)-kerogen is a solid/solution reaction where the Ni(II)-core materials ground to 20 - 35 mesh is reduced in solution phase by slurring the solid in the presence of chemical reducing agents, BH_4^- or N_2H_4.
- The extent of this reduction again is followed as a function of *time* by XANES.
- The reduced Ni(0)-kerogen solids from the chemical reduction will be loaded into tube reactors for catalytic reactions under hydrogen or N_2H_4 as described on previous slide.
- Hydrocarbon products move down the tube to cooler portions of the oven. They are dissolved in methylene chloride and analyzed by GCMS.

Sample

- Sample provided by Greyhorse Engineering & Technology, obtained from Core Lab, Houston.



Sample

- The core is from the oil window (6925 ft).
- From a larger 4" diameter core sample plugs were obtained in the horizontal and vertical directions for analysis.
- The remaining part of the core has been ground to 20 – 35 mesh and there is a -35 mesh sample.
- Pyrolysis (rock eval) data is available for this core (TOC 5.51 wt%).

Sample Characterization

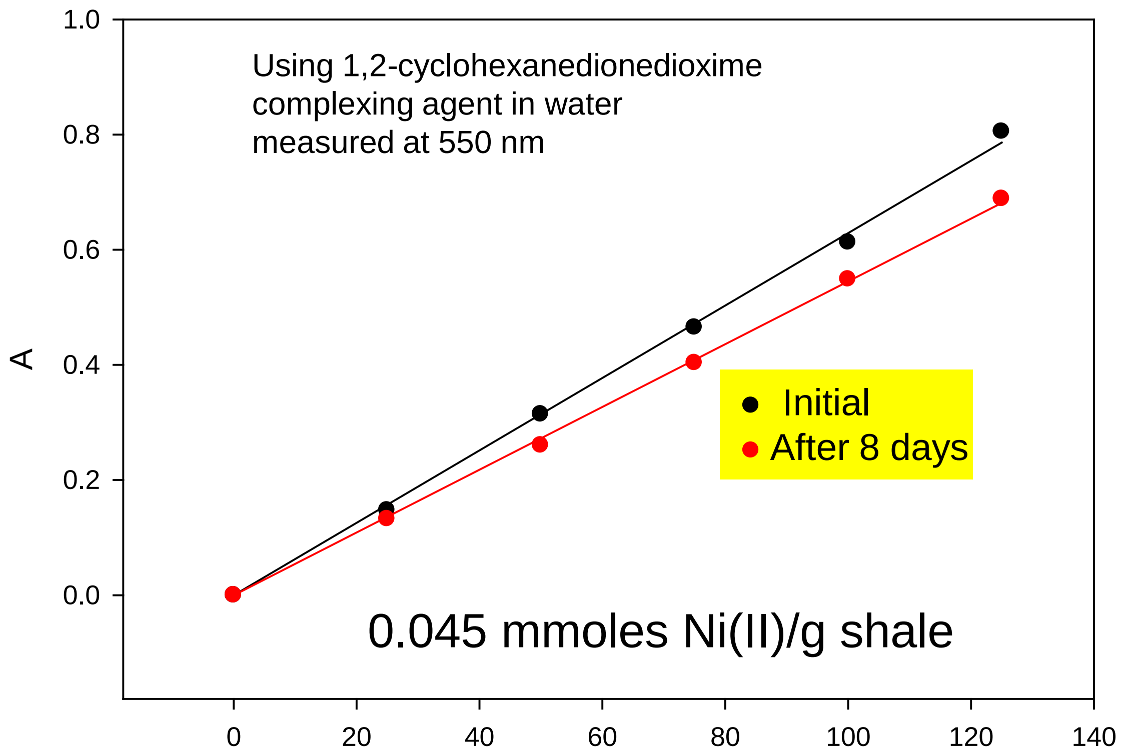
Mineral Content	Vol%
Calcite	52.00
Clay	18.60
Quartz	14.00
Kerogen	7.50
Pyrite	2.40

Leco	Wt%
TOC	5.51

Rock Eval 2		
S1	mg HC/g	3.84
S2	mg HC/g	11.85
S3	mg CO2/g	0.47
Tmax	^{o}C	452
H index	100*S2/TOC	215
O index	100*S3/TOC	9
Conc	S2/S3	25
Oil cont	S1/TOC	70
Prod index	S1/(S1+S2)	0.24

First Stage - Exchange

Beer's Law Determination of Ni(II) uptake by Eagle Ford Shale

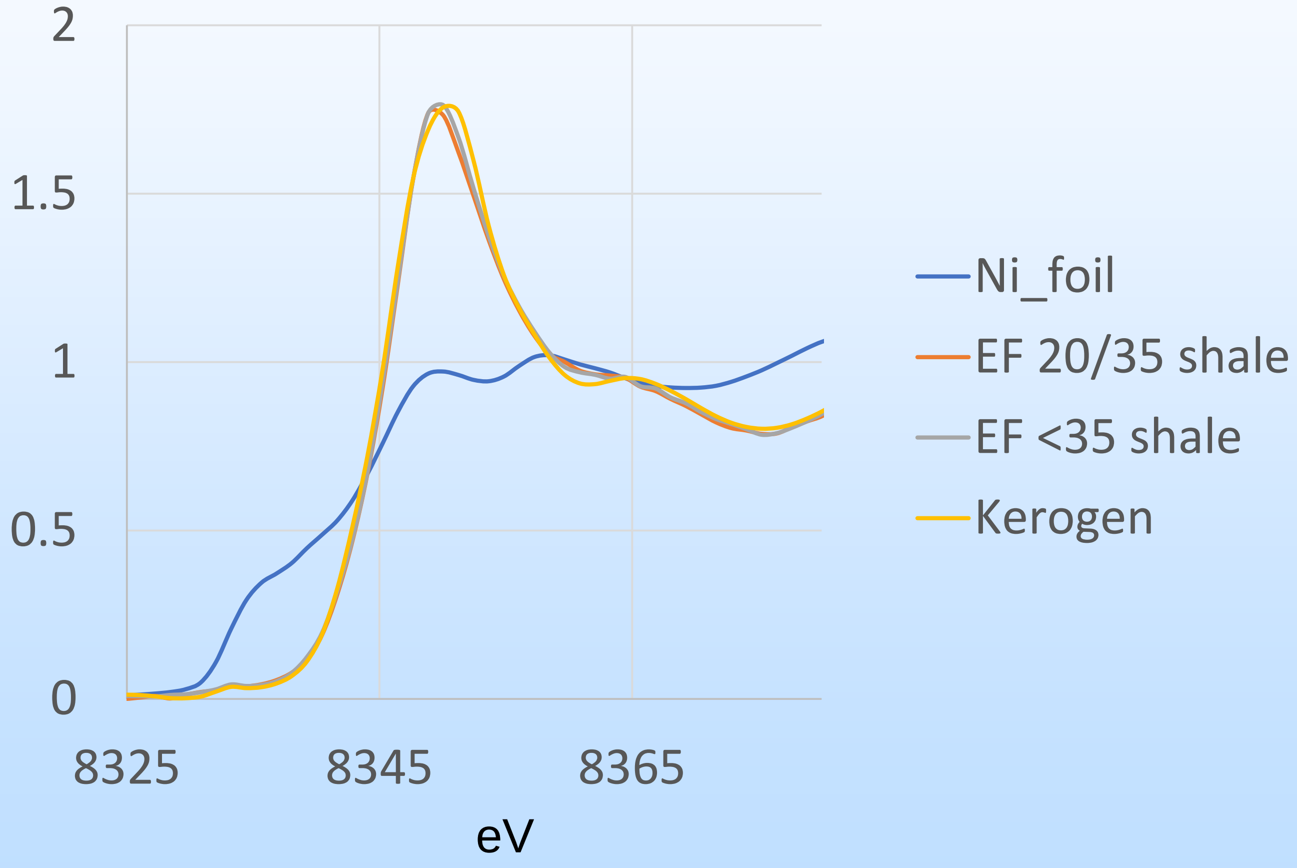


Vol(reaction)/Vol(complexing agent) x 10^5

With isolated kerogen exchange takes 1 day

First Stage - Exchange

Verification via Ni X-ray absorption near edge structure (XANES)
12BM Sungsik Lee



Accomplishments to Date

- Identified characteristics of sample required.
- Acquired sample, ground and with characterization information.
- Developed testing protocol and procedures.
- Completed assembly of the required lab equipment (reaction vessel).
- Completed lab safety review and approved to proceed.
- Ni exchange has been accomplished

Lessons Learned

- Transparent objectives and communications has accelerated cooperation among all parties and 3rd party involvement
- Industry has demonstrated a strong desire to improve recoveries and economics through technology but there is a general lack of willingness to be an early adopter in the upstream oil and gas industry.
- Experimental/lab phase is just in the beginning stages, but it is clear that the rate of reactions are slower in shale compared to kerogen. In addition, since most of the clay is bentonite, the amount of Ni ions absorbed by this clay will be measured.

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Synergy Opportunities

- Greyhorse Engineering’s industrial relationships and their oil and gas fundamental understanding offers ANL a window of opportunities to commercially transferring this technology through a “hydrocarbon conversion” platform.
- Lessons learned from this project have synergies impacting various diverse paths to commercialization through applications beyond the shale oil being investigated both thru in situ and ex situ conversion.

Project Summary

- We have obtained the appropriate, well characterized sample for this study
- A study of the effects on the minerals in this two step process has begun:
  1. Exchanging in the metal salts onto the carboxylic acids in the kerogen has been accomplished.
  2. Reduction of the salts to metal nanoparticles and subsequent breaking of C-C bonds in the kerogen to release smaller hydrocarbons is next.

Appendix

Benefit to the Program

- FE-UFET: Unconventional Fossil Energy Technologies from Petroleum - Oil Technologies
- Without stimulation, unconventional oil reservoirs lack sufficient permeability to produce at economical rates.
- Today's existing technology is focused on pumping extremely large hydraulic fracturing jobs (up to 50 million lbs of proppant and 40 million gals of water) to artificially create a reservoir. Fundamental reservoir engineering fluid flow principles are based on Darcy's law which states viscosity is inversely proportional to flow rate. Thus a reduction of the liquid hydrocarbon viscosity will improve the oil transmissibility and lead to greater recovery for the same drawdown.
- Additionally, the nano-catalysts' ability to cleave bonds from the solid hydrocarbons will not only convert these compounds into producible liquids, but will also enhance the permeability of the reservoir by creating pore volume and flow paths.
- This combination of generating more liquid hydrocarbon content and increasing effective permeability will result in dramatic ultimate recovery improvements.

Project Overview

Goals and Objectives

- Argonne National Laboratory has a patented nano-catalytic process that can convert solid hydrocarbons to liquids and reduce the viscosity of liquid hydrocarbons under in situ conditions. This process has the potential to accelerate commercial improvements in ultimate recoveries and drainage areas from unconventional oil reservoirs
- Goal: Prior to commercial down-hole testing, the catalyst preparation process needs to be matured. The metal catalyst will be transported down-hole as a metal halide and then reduced in situ.
- Objectives:
  - Develop optimized reducing procedures for commercial well conditions
  - Understand possible mineral interference with the processes.

Organization Chart

- Argonne National Laboratory, Robert Klingler and Randall Winans
  - Reaction studies with in situ characterization and product characterization

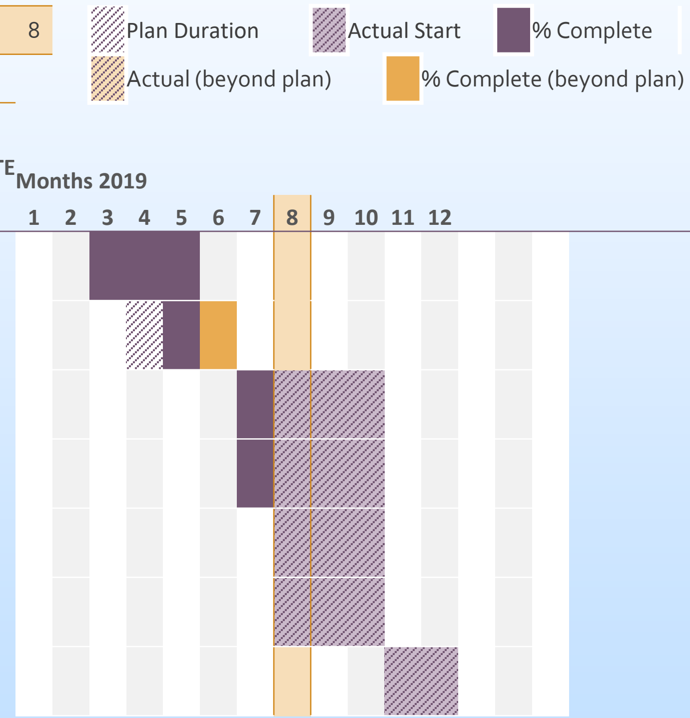
- Greyhorse Engineering and Technology, Robert Lestz, President
  - Provide access to samples and characterization information and engineering assistance. Eventually provide access for down hole tests.
  - Mr. Lestz is a petroleum engineer with 34 years of industry experience. He co-invented the LPG Fracturing technology and worked at GasFrac as their CTO. He spent 22 ½ years at Chevron working in the areas of fracturing, artificial lift, completions, and well operations.

Gantt Chart

ANL- Greyhorse TCF-18-15390

Period Highlight: 8

ACTIVITY	PLAN START	PLAN DURATION	ACTUAL START	ACTUAL DURATION	PERCENT COMPLETE
Specify Sample	3	3	3	3	100%
Acquire Sample	4	2	5	2	100%
Stage 1	7	4	7	4	25%
Stage 2 H2	7	4	7	4	25%
Stage 2 N2H4	8	3	8	3	0%
Stage 2 NaBH4	8	3	8	3	0%
Final Report	11	2	11	2	0%



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