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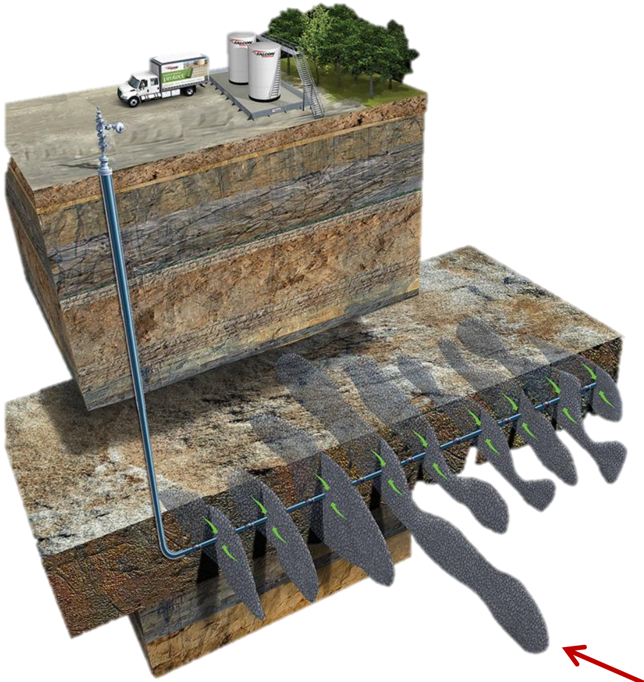
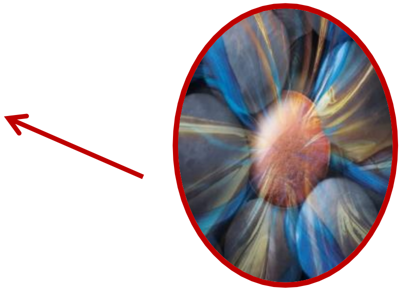




Tagged Nanoparticles for Fluid Flow Monitoring

Project Officer: William Vandermeer

Total Project Funding: $800,000

May 11, 2015

Richard A. Kemp, PI

Ryan Hess, Presenter

Sandia National Labs/CARBO

EGS: Tracers / Zonal Isolation / Geochemistry

Relevance/Impact of Research

Project Objective:

To prepare tagged nanoparticles (T-NPs) that will allow detailed information regarding the productivity of specific locations and zones within engineered geothermal systems. After deposition into porous proppants and loaded into specified fractures, T-NP release over time will allow us to determine precisely which zones are contributing to fluid flow as well, as the fluid flow rates.

Problem Addressed/Challenge:

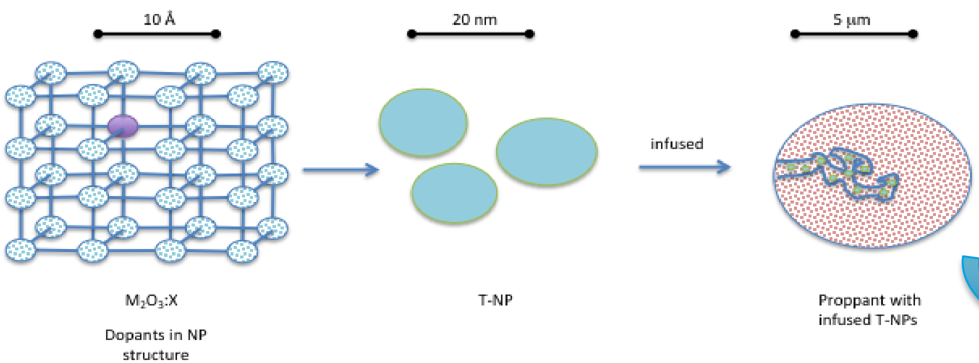
It is of high interest to be able to monitor underground fluid flows for extended periods of time to more efficiently extract product or energy from the reservoir. Additionally, it would be advantageous to have monitoring systems that are applicable to both aqueous and hydrocarbon environments. Porous ceramic proppants allow us to place rare-earth T-NPs precisely in zones of interest and by adjustment of the release characteristics we can monitor these zones over time.

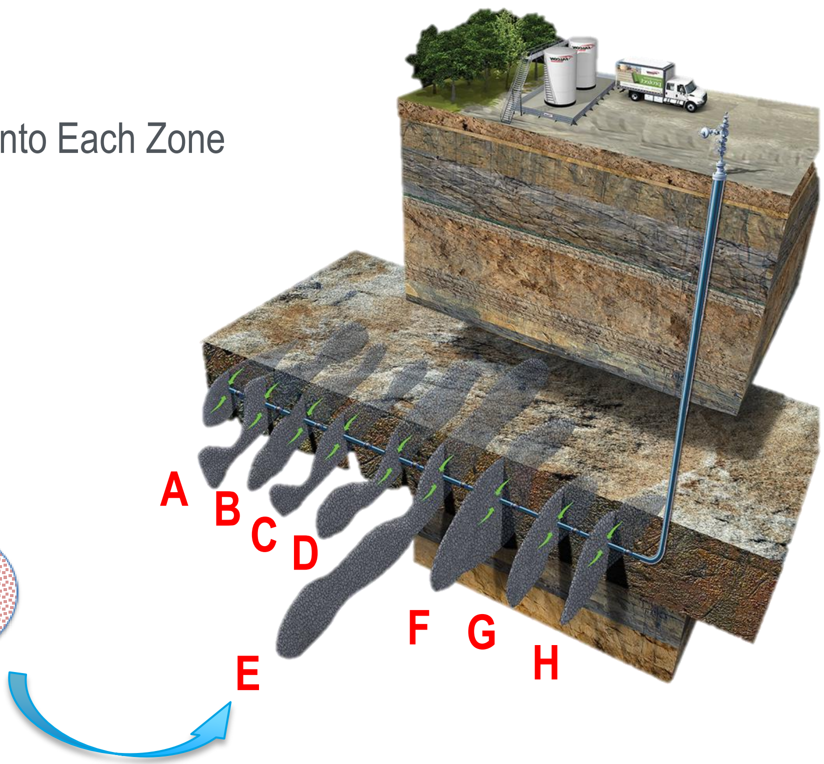
The ability to add unique tracers to multiple fracture zones in the same well that can be monitored over months will allow for the development of more accurate and predictive geothermal (and hydrocarbon) reservoir models describing the flow characteristics of each zone.

Overall Project Scheme

Hydrocarbon Reservoir Example

- Rare Earth (RE) Doped T-NP/Proppant Package Loaded into Each Zone
- RE Dopants in Each Zone Unique and Identifiable
- ~5% wt RE Element Doped Into Nano-Oxide Matrix,
  Thus Making T-NPs Which Can Be Infused Into Proppant





- Proppant/T-NP Package Coated with Polymer to Control Time-Release Characteristics
- Above Ground, RE Elements Identified by ICP
- Quantitative Analysis Allows For Fluid Flow Rate Determination

Scientific/Technical Approach

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- In This One-Year Project, Our Team's Technical Approach Is To…
  - Prepare and Characterize a Number of Monometallic Oxide NPs to Serve as a Base Matrix
  - Modify the NPs with ~5% Rare-Earth (RE) Elements to Provide Identifiable "Tags"
  - Controlled Deposition of the NPs into the Porous Ceramic Proppant
  - Control the Desorption Rate of the T-NPs by Surfactants, External Polymeric Coating
  - Understand the Desorption Rates by Utilizing Model Feeds, Test Wells
  - Provide Sufficient Technical Information for Larger-Scale Trials with Our Industrial Partner
  - Develop Analytical Measurement Techniques (*e.g*., ICP) to Measure RE T-NPs at Surface
- Although We Are Still Early On, Each Quarter's Emphasis Consists of…
  - Q1: *Design, synthesis, and characterization of the T-NPs;*
  - Q2: *Introducing the T-NPs to the proppant and understanding the interactions;*
  - Q3: *Understanding the rate of release of T-NPs in model/real feeds;*
  - Q4: *Integrating the entire package (T-NP/proppant) and delivering lab-scaled samples to CARBO.*
- Key Critical Technical Issues Are…
  - Preparing Appropriate T-NPs That Will Work in Either Water/Hydrocarbon Environments
  - Understanding and Measuring Both Qualitative *(Which Zone)* and Quantitative *(How Much)* Flow
  - Tuning the Time-Release Nature of the T-NPs to Allow for Multi-Month Monitoring

Summary of Technical Accomplishments (Details on Following Slides)

- Three Families of Nanoparticle Oxides Based on Bi, Al, and Y Have Been Synthesized and Characterized; Rare Earth Doping Also Shown to Be Feasible
- Shapes of NPs Can Be Varied, Controlled – Due to Time Constraints, Rather than Developing New Fourth NP Option the Team is Focusing on These Three Matrices
- Two Routes to NPs Developed – Solvothermal (SOLVO) and Solution Precipitation (SPPT) – Both Give NPs of Different Shapes/Sizes *(Working to Reduce Size Further)*
- Initial RE Doping at ~5% wt Loadings into NP Oxides Is Promising
- Postdoctoral Fellow (Dr. Rico Treadwell) Recently Hired to Focus on RE Incorporation
- T-NPs and Molecular RE Species Infused Into/Onto Porous Ceramic Proppants
- Number of Samples of T-NPs/Proppants Delivered to CARBO to be Evaluated in Lab-Scaled Elution Studies to Determine RE Elution Rates in Model/Real Feeds
- Second Half of This Year’s Work Will Concentrate on Understanding Elution Rates
- **UNDERSPENT** by ~25% Due to Other Sandia Project Issues, Postdoc Hire Delayed

Accomplishments, Results and Progress

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Original Planned Milestone/ Technical Accomplishment	Actual Milestone/ Technical Accomplishment	Date Completed
1. Four doped NP base options to be verified by PXRD, TEM.	Three NP oxide bases using Bi, Y, and Al synthesized and characterized	Rather than going after fourth option, team concentrating on these three NPs (1Q 2015)
2. Lab scale consistent production of T-NPs and modified for water/oil	NPs have been loaded into proppants using hydrocarbon or water-based solutions	Ongoing in order to optimize loadings
3. Loading of T-NP $\geq$40 % theoretical capacity	High loading levels of Y NPs into proppant achieved (~10% wt NPs deposited)	(1Q 2015)
4. Fully assemble T-NP/coated proppant	Early samples have been delivered to CARBO for coating and evaluation; also, molecular RE test samples	*Not due yet*
5. Controlled release of T-NP elution.	Initial samples sent to CARBO for coating and evaluation of NP elution	*Not due yet*
6. Fully assembled T-NP/coated proppant demonstrated overall concept	End of project goal – steps to deliver this are ongoing	*Not due yet*

Selection, Synthesis, and Characterization of NP Oxide Matrices

- Directed to Focus on Monocationic Species
- Matrix Selection for RE (Ln) Incorporation Requires Particular Properties
  - 3+ charge
  - Size consistent with Ln dopant cation size
  - Stable over wide pH range
  - Amenable to surface modifications
  - Ceramic oxide monocationic NP selected include…
    - Yttria (Y_2O_3) – intermediate size for Ln cations
    - Bismuth oxide (Bi_2O_3) – equivalent to La: larger cation dopants
    - Alumina (Al_2O_3) – smaller ionic size but dopants can be added

SPPT

- Solution Routes Selected to Generate NP
  - Amenable to large scale
  - Facile doping
  - Solvothermal (SOLVO) – “bomb” preparation: high pressure and temperature
  - Solution precipitation (SPPT) – “cold precursor into hot solution”

SOLVO

- Characterization of T-NP’s
  - PXRD
  - TEM/EDS

Accomplishments, Results and Progress

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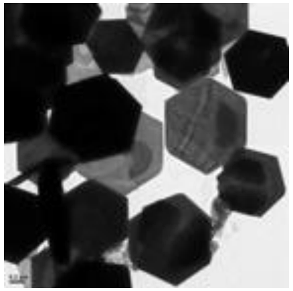
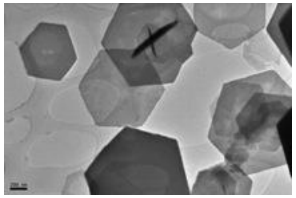
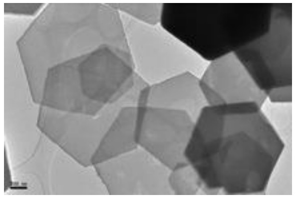
Bismuth oxide

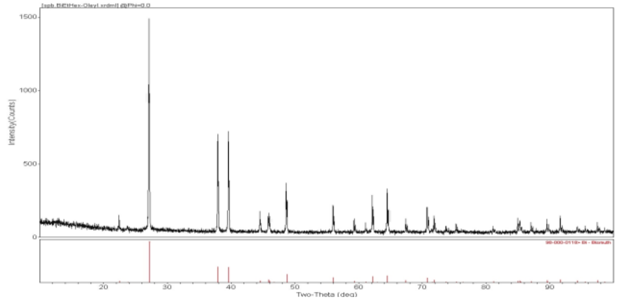
$Bi(NO_3)_3{\bullet}H_2O$

SOLVO H_2O/185 ^oC/12h









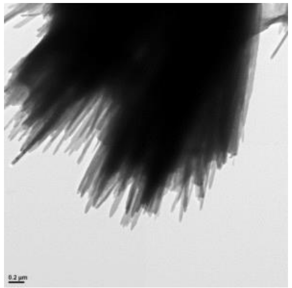
Terminated due to NP size restrictions

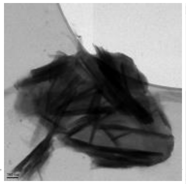
Alternative Bi_2O_3 NP being pursued

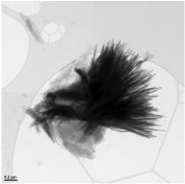
Yttria

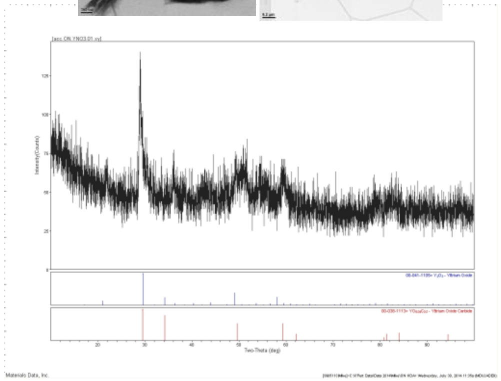
$Y(NO_3)_3{\bullet}5H_2O$

SPPT ON/310 ^oC/2h







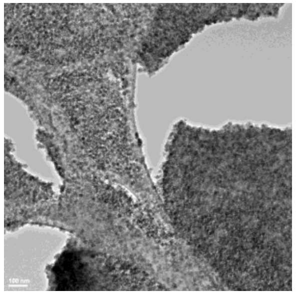


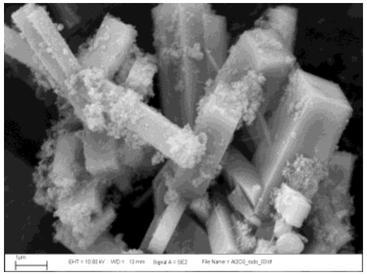
Doping with Ln underway

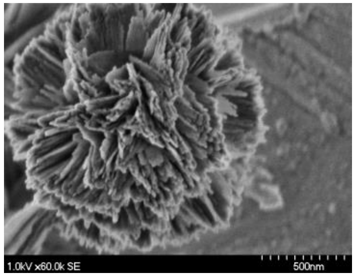
Alumina

$Al(OPr^i)_3/Al(NO_3)_3/\ Ce(NO_3)_3{\bullet}6H_2O$

SOLVO & SPPT

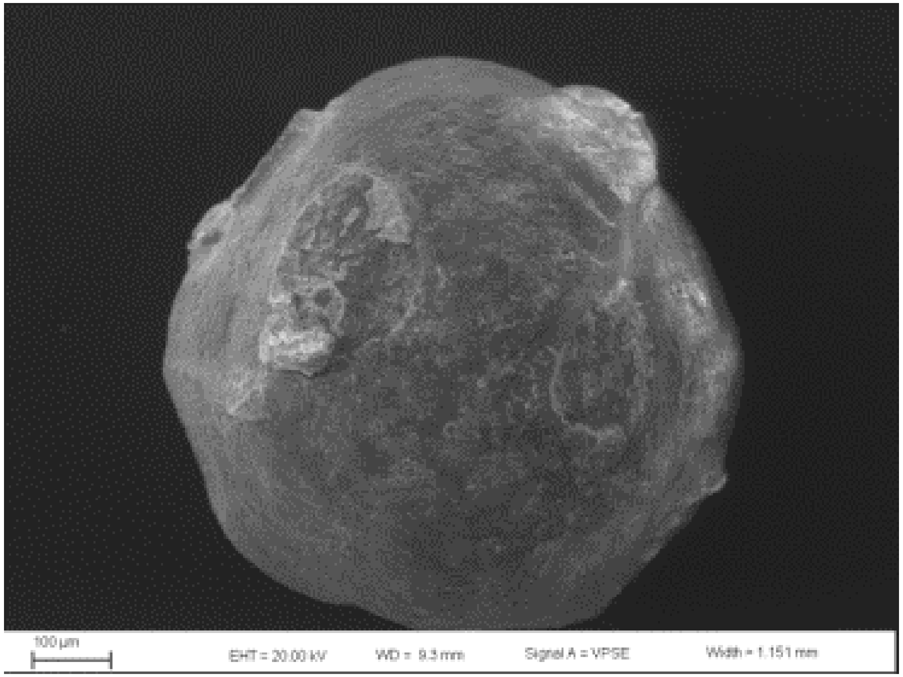


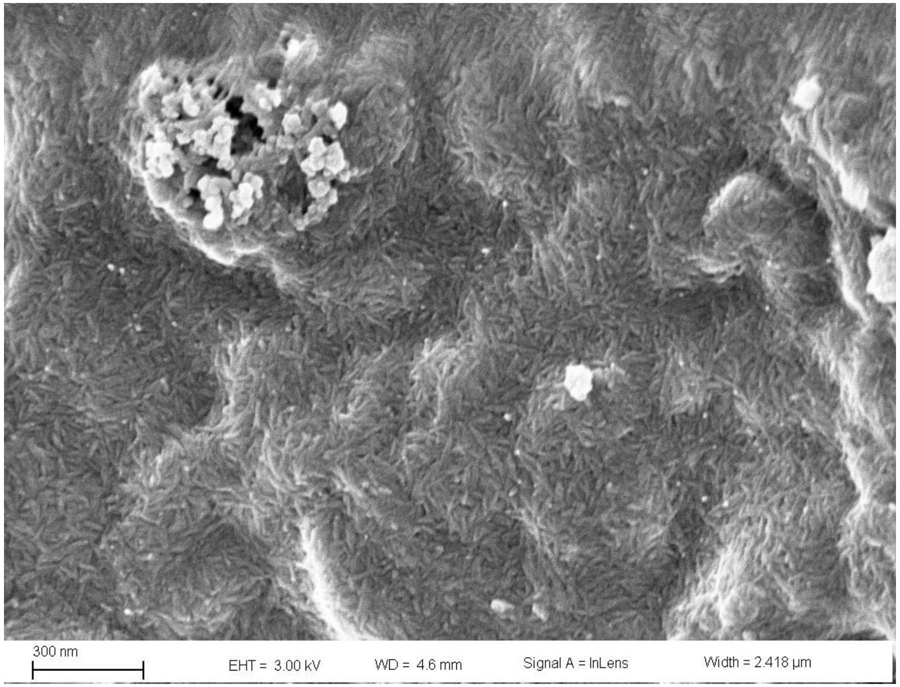




Synthesis of materials from previous routes - Optimization studies underway

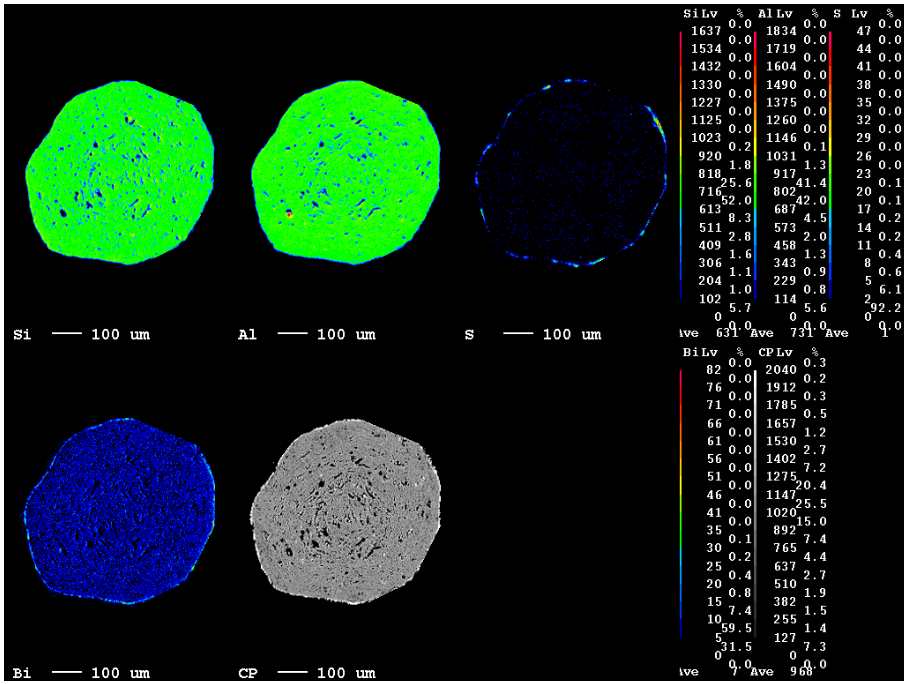
Scanning Electron Microscopy of Proppant and Surface Covered With NP Tags

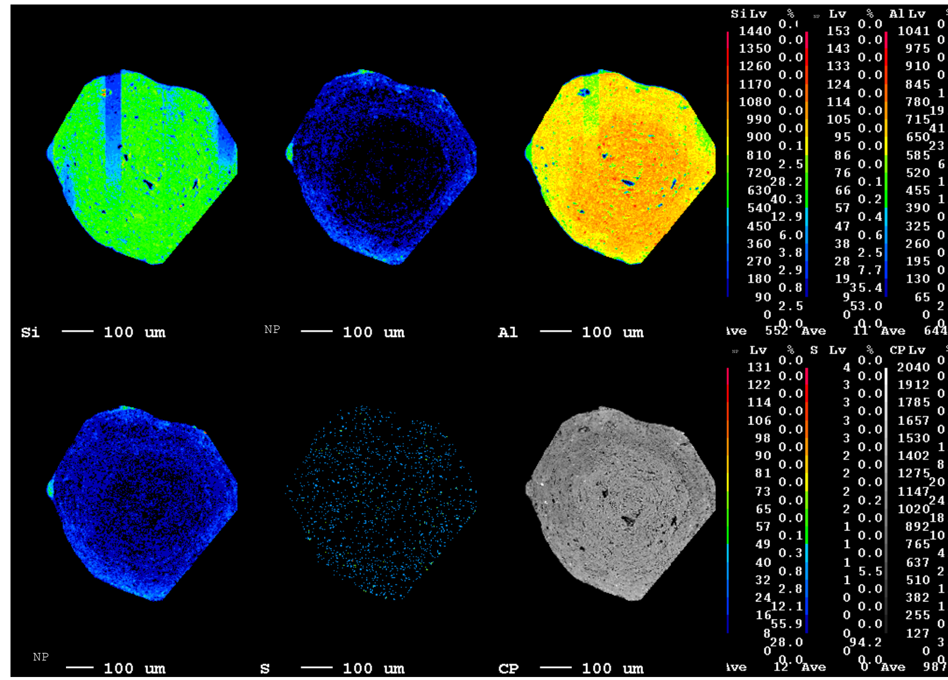




NP tags can coat surface and…

Cross-Sections of Proppant Indicating NP Inclusion Within Pores





NP tags can coat surface and enter pores!

Future Directions

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- Highly Ambitious One-Year Project to Invent, Optimize, and Deliver a T-NP System for Implementation by CARBO Ceramics, Others
- Initial Deployment of This Technology is Expected To Be in Hydraulic Stimulation Area
- Natural Outlet in Hydrocarbon Recovery with Our Industrial Partner CARBO (early 2016)
- Key Activities for Remainder of 2015 *(End of This Project, 9/2015)*
  - Smaller Size T-NPs
  - Controlled Doping of REs into NPs
  - Optimize Surfactant/T-NP Relationship for Both Hydrocarbon Fluid and Water Systems
  - Optimize Coating/T-NPs for Long-Term Elution Rates
  - Model the Elution of the T-NPs in Order to Usefully Estimate Lifetime of RE Elution
  - Analysis of T-NPs in Real Feeds

- At This Point, We Have No Major Changes to Our Plans for the Next Six Months *(next slide)*
- Due to Unexpected and Critical Sandia Needs in Other Areas Early in the Project and the Delay in Hiring a Postdoc, We Are Slightly Behind on Spending Overall; *However, We Are Continuing to Meet Our Technical Targets*

- Depending on Level of Success in Next Six Months, Will Be Looking Forward to Implementation and Exploitation of this Technology in 2016

Future Directions

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May, 2015 – September, 2015 Milestone Timeline

Milestone or Go/No-Go	Status & Expected Completion Date
4. Fully assemble T-NP/coated proppant	Ongoing – initial systems have been demonstrated (to be completed by 7/2015)
5. Controlled release of T-NP elution.	Ongoing – initial systems have been demonstrated (to be completed by 9/2015)
6. Fully assembled T-NP/coated proppant demonstrated overall concept	To be completed by 9/2015 (end of project)

Go/No Go Decision at 9 Months:

Demonstrate T-NP Elution in at Least 2 Systems

Mandatory Summary Slide

- In this One Year Project, We Have Prepared Three Unique NP Systems Based on Bi, Y, and Al Oxides
- RE (Ln) Doping of These NP Oxides Has Been Initially Demonstrated
- Complete "Packages" of T-NP Loaded into Proppants and Coated Produced
- Elution of RE (Ln) Has Been Demonstrated Using Molecular Ln's as Models

- Despite Short One-Year Timing of this Project, We Are On Track to Produce a Scale-able System by the End of this Fiscal Year, Although Some Work to Implement Commercially May Be Pushed into 2016

- Overall Superb Working Relationship Between Sandia and CARBO Scientists

- Primary Team Members:
  - <u>Sandia National Laboratories:</u> Richard A. Kemp (PI), Timothy J. Boyle, Bernadette Hernandez-Sanchez, James E. Miller, Ryan F. Hess, and LaRico J. Treadwell
  - <u>Carbo Ceramics, Inc.:</u> Chad Cannan, Todd Roper

Additional Information

- Patent Application Filed in December, 2014, Jointly by Sandia National Laboratories/CARBO Ceramics Personnel

- Cadet Kevin Petow, From the U.S. Coast Guard Academy, Has Been Selected by the Military Academic Collaborations (MAC) Program to Aid in Summer Research at Sandia on This Project.