2015 Geothermal Technologies Office Peer Review
Summary: Tagged Nanoparticles

1. Tagged Nanoparticles for Fluid Flow Monitoring

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- Subcontractors and/or Participating Organizations: Carbo Ceramics, Inc., Houston, TX
- Project Start and End Date: 10/2014 – 9/2015

2. Project Objectives and Purpose

The overall project goal of is to develop a lanthanide (rare-earth, or Ln) tagged nanoparticle (T-NP) system that can be loaded into porous proppants to track underground fluid flows, either water or hydrocarbon-based. Current methods for conducting tracer studies typically involve the surface wellbore deployment of a bulk tracer. This results in the tracer being indiscriminately transported through all of the fractures near the injection wellbore and any nearby production wells. Our approach involves the synthesis of a series of nanomaterial tracers that have a unique Ln-based tag which are then deposited within a proppant, coated with what is essentially a time-release shell. This will allow for the placement of the tagged nanoparticles in the desired zones within a given system. Because a suite of particles containing different Ln elements will be used, it will be possible to assign specific tracers for each wellbore zone, thereby allowing for a higher degree of understanding of the underground reservoir fluid behavior. In particular, these T-NPs will generate information pertaining to specific active zones. This type of data has never before been available and should help produce a more useful reservoir model with greater fidelity than has previously been accomplished.

To achieve this objective, it is necessary to 1) understand how to prepare the specific T-NPs, including the required monometallic cation nano-precursor; 2) how to modify (or tag) the nano-precursors with the desired Ln cations; 3) how to deposit them into the porous proppants provided by CARBO; 4) how to alter solubility in hydrocarbon or water systems; and 5) manipulate and quantitatively measure the release of the T-NPs from the proppant into the fluid of interest and understand how to relate the measurements to fluid flows.

3. Project Timeline

Task 1.0 *T-NP component synthesis (monocation approach only) (M1-M6)*

- **Subtask 1.1** Synthesis and characterization of monocationic T-NPs (M1-M4)
- **Milestone 1:** A minimum of four uniquely-doped nanoparticle materials will be synthesized/characterized and verify their reproducibility and uniformity in target size to fit inside the proppant
- **Subtask 1.2** Surface functionalization of T-NPs (M2-M6)
- **Milestone 2:** Laboratory scale procedures for consistently and predictably modifying T-NP surfaces for compatibility (dispensability) in hydrocarbon and in aqueous based environments will be established and documented.

Task 2.0 *Integration of T-NP and Delivery System (M01-M10)*

- **Subtask 2.1** Proppant characterization (M01-M02)
- **Subtask 2.2 T**-NPs introduced to proppant (M01-M04)
- **Milestone 3:** Procedures for consistently and reliably loading a proppant to ≥ 40% of its theoretical capacity (based on pore volumes determined in ST 2.1) will be established and documented.
- **Subtask 2.3** T-NP elution from proppant without a rate-controlling resin shell (M03-M05)
- **Subtask 2.4** Development of a release-rate controlling shell (M03-M10)

- **Milestone 4:** At least one fully assembled T-NP/coated proppant package will be delivered to the next stage for elution work.

***Go/No-Go 2.1** If no T-NPs infused into proppants can be prepared; the effort will be terminated (M9)*

***Task 3.0** T-NPs in scale-up and pathway to implementation (M03-M12)*

- **Subtask 3.1** Well conditions and simulation (M01-M03)
- **Subtask 3.2** Verification of monocation stability (M03-M08)
- **Subtask 3.3** Detection of the T-NPs (M03-M09)
- **Subtask 3.4** Characterization and measurement of T-NP release (M03-M12)
- **Milestone 5:** Controlled release characteristics will be demonstrated and initial T-NP elution curves will be measured for at least one fully assembled T-NP/coated proppant package using the established CARBO approach and flow apparatus.
- **Subtask 3.5** Product definition and delivery (M06-M12)

4. Technical Barriers and Targets

In order to enhance energy production in both hydrocarbon and geothermal systems, more precise control over the solutions from these reservoirs is necessary. To achieve this goal, it is critically important to be able to track individual fluid flows underground for an extended period of time (months). If quantitative, this would allow producers to identify high- and low-producing zones, enabling a more efficient recovery process and better predictive capabilities for designing new wells. Previous tags for tracking subsurface flow patterns have suffered from either a limited ability to track multiple zones or a shorter period of tracking than desired. The approach taken here, when successful, will solve this issue by providing uniquely tagged (~10-12) zones of fluid flow that will be released and monitored over much longer periods of time (multi-months).

The 12-month targets are set to provide a porous proppant-based system that contains T-NPs built on a monocationic oxide nanomaterial, to demonstrate the methods for preparation of the taggant system at the laboratory scale, and to show proof of concept of the quantifiable elution of T-NPs. Information gained from this work will be used to help define a product line in concert with our industrial partner, CARBO. Prospects for scale-up and viability will be determined by the team. At this early stage, we are on track to meet our deliverables.

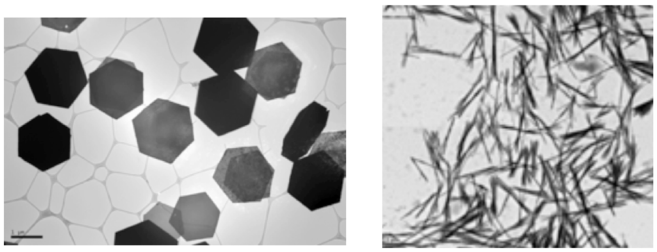
5. Technical Approach

In this work, metal oxide-based nanoparticles will be prepared that can be doped with Ln ions to produce the T-NP materials. These T-NPs will be subsequently loaded into porous ceramic proppants, which are then encapsulated by a porous polymeric coating. This coating will to moderate and control the release characteristics of the T-NP. During the fracturing process, the T-NP-loaded proppant will be delivered to a specific fracture zone(s) of a reservoir. The gradual release of the T-NPs into the fluid flowing out of the reservoir is monitored over time above-ground *via* ICP elemental analysis that will provide both qualitative and quantitative information about the collected fluid. For example, this information will provide data concerning the origins of the fluid within the well, the relative contributions of each zone to the whole, and potentially, information pertaining to the rate of zone's flow. In order to maximize versatility of these T-NPs, modifications (*i.e.*, surfactants) to the nanomaterials prior to infusion into the proppant will be performed to adjust oil/water solubility.

The unique approach of this work will allow the independent monitoring of ~10-12 different zones for an extended period of time. In addition, a sufficiently-high loading of these nanomaterials into the proppant will allow a desired multi-month observation period. Further, the flow rates may be determined as the quality of the data is optimized.

6. Technical Accomplishments

The synthesis of the two prime candidate materials based on optimal cation size/ charge for Ln doping: (i) yttria (Y_2O_3) and (i) bismuth oxide (Bi_2O_3) have been successfully realized. These particles have been prepared following solution routes (*i.e.*,.solvothermal (SOLVO) and solution precipitation (SPPT)). Commercially-available precursors were surveyed to generate the desired NP supports, among them acetate, nitrate, and chloride. For both Bi_2O_3 and Y_2O_3 systems, using water as the solvent, the nitrate derivatives appeared to generate optimal particles. The Bi_2O_3 species were generated by a SOLVO route and made a hexagonal shaped nanoparticle as indicated by TEM analysis. PXRD indicate a stable bismuth oxide phase was formed. These are fairly large (100 – 200 nm) compared to the expected pore size of the proppant but are being explored to elucidate the experimental induction of particles and if they will fit into the proppant. Work to modify the size is underway. The Y_2O_3 samples were prepared by a SPPT route and found to form long thin wires by TEM analysis and were phase pure as determined by powder XRD (PXRD) studies. These are being treated (similar to the Bi_2O_3 route) for intercalation into the proppant. A third candidate material being explored for doping is aluminum oxide (Al_2O_3) nanoparticles. Similar to Bi_2O_3 and Y_2O_3, both SOLVO and SPPT synthetic routes along with hydrothermal and sol-gel processing are being used with commercial precursors. Characterization of the products by PXRD has shown amorphous product formation and additional heat treatments are being conducted to crystallize the oxide.



Pure Bi_2O_3 Hexagons (left) and 5%Ce/Y_2O_3 Nanowires (right)

In an alternative approach, a systematic series of <u>molecular</u> samples were loaded *via* the precipitation of Ln salts within the pores of the proppant. While these $Ln_2(SO_4)_3$ infused salts are not technically nanomaterials, these 4%-loaded proppants will help understand the deposition chemistry of the T-NPs into the proppant as well as to understand more fully the elution of the Ln-materials into the reservoir. Additionally, the use of these "model" compounds loaded into proppants also gives us an ability to follow the elution of the Ln and thereby develop analytical techniques for quantitative identification that will be needed for analyzing the T-NPs in real systems.

7. Challenges to Date

At this early point of the study, no notable changes to the plans or schedule have been made. The most important technical issues and challenges remaining are a) to understand the modification chemistry of the Ln tags to provide reproducible small sizes of nanoparticles in both water and oil; b) to follow the gradual release of the T-NPs into the fluids in order to determine a quantitative assessment; and c) deliver the entire functional package at the end of the project. We will continue with the plan that we set forth earlier in order to solve these outstanding issues.

8. Conclusion and Plans for the Future

As we are still in the first half of this one-year project, we are intent on continuing the agreed-upon path. To this point, no showstopper issues have arisen to our knowledge and progress towards our goals is being made. Our immediate future plans are to understand and control the addition of Lnions into the nano-metal oxide, and to develop the chemistry of the nanoparticle coating to allow solubility in oil orwater. Lastly, developing the release model that correlates [Ln] concentration to fluid flow must be developed.

9. DOE Geothermal Data Repository

At this point, data generated has been primarily characterization-based. Information on the proppant physical and chemical properties has been obtained and will be deposited. Electron micrograph images of all of the synthesized monocationic oxide nanoparticles have been obtained. A significant amount of TEM/SEM and microprobe data has also been obtained on the metal oxide nanoparticles, which examines the distribution of the nanoparticles throughout the porous proppant. These images and raw data, alongwith the synthetic procedures on how to control their size and shapes, will also be uploaded.

10. Supplemental Information

- A patent application broadly covering this technology listing Sandia/CARBO co-inventors was filed in late 2014.

Publications and Presentations, Intellectual Property (IP), Licenses, etc.

- A broad patent application covering this technology with Sandia/CARBOas co-inventors was filed in late 2014.