Detection of Soluble Ligand-Tuned Molecular Tags for Subterranean Fluid Flow Monitoring Using Resonance Raman Spectroscopy

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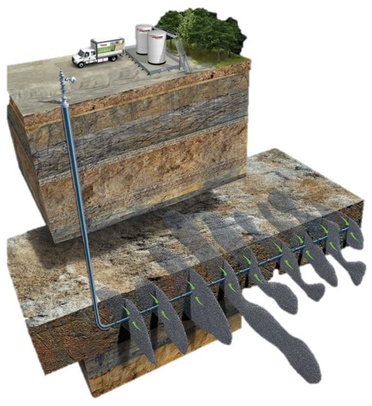
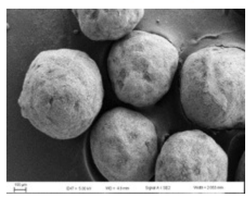
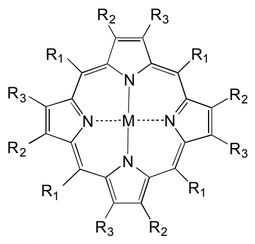
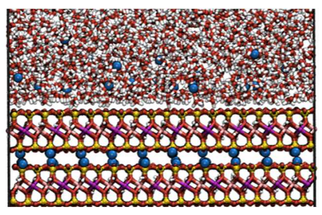
LDRD New Start 2015-2017 (Two Year Project)









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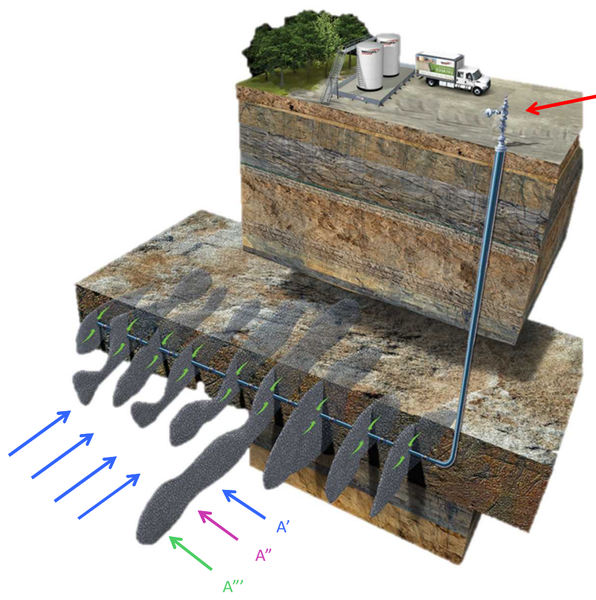
Objective/Problem to Be Addressed…

- Tracking Underground Fluid Flows in Oil/Gas Reservoirs or Engineered Geothermal Systems Over Extended Periods of Time Is Desired
- Currently, 60-70% of U.S. Hydrocarbon-Producing Wells are Hydraulically-Fractured, and Tools Exist for Monitoring Only Initial Fluid Flows (~1-2 months)
- ***Industrial Producers Strongly Desire Tracers that Last for 1+ Year***
- Improvements in Tracer/Tags for Monitoring Fluid Flows Underground Are Required for Improved Efficiencies In Energy Recovery
- Current Approach Funded by DOE-EERE OGS Uses Rare Earth (RE)-Tagged Nanoparticles (T-NPs) Loaded into Porous Proppants (Carbo Ceramics) and Investigate the Desorption into Oil/Water by ICP (inductively coupled plasma)
- However, Issues with RE Cost/Availability, Total Number of Possible Tags, Premature Deposition on Rocks, Preparing the T-NPs To Be 100% Soluble in Water or Oil, and Manufacturing Complexity Are All Challenging

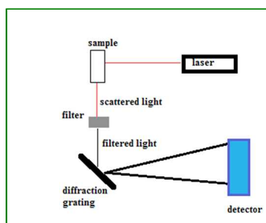
A Closer Look

1. *When a well is fractured, sand or porous proppants are also pumped into the zone fracture. These become and lodged in the cracks and keep the 'large' fractures from closing.*
2. *Each zone can have specific proppant (tags) selectively placed into the desired zone.*



3. *Further, for each zone, up to 5 'sub-zones' created by the selective placement of tags.*
4. *Tags from the different zone fractures will be transported to the surface by fluid flow and then analyzed by collecting samples at the wellhead. These will then analyzing for detectable species, using a variety of analytical tools.*
5. In particular, we will exploit the sensitivity of Resonance Raman (rR) Spectroscopy for analysis at the wellhead of out tags (see ***Project Methodology***).

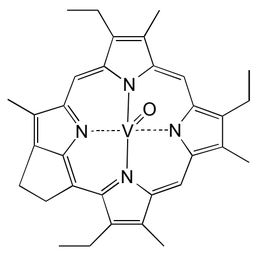
- *Classic Vibrational Raman Spectroscopy Is Less-Sensitive than Needed*
- *rR Modification Allows for 10^6 Increase in Sensitivity; 10^{-8} Molar Concentrations!*
- *Resolution of ~1-2 cm^{-1} Sufficient to Distinguish Different Molecules*
- *Vibrational Spectra Can Also Be Predicted Using Computational Tools*



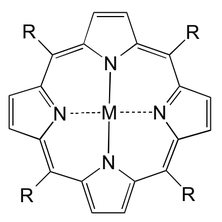
rR spectroscopy: A sample is irradiated with monochromatic laser light at a frequency near the frequency of an electronic transition of the molecule, filtered, dispersed by the diffraction grating, and collected on the detector.

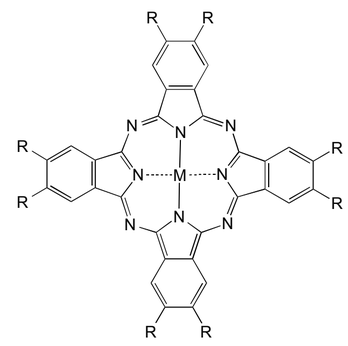
Project Methodology – Use Soluble Molecular Species as Tags

- *It Should Be Possible to Solve Every Issue Associated with the Nanoparticles (EERE project) by Utilizing Soluble, Metal-Containing Complexes that "Mimic" Natural Crude Oil Components*
- Based on Porphyrins or Phthalocyanines (see Figure on right), These Species Can Be Readily Synthesized and Modified to Alter H_2O/Oil Solubility Using Existing Chemistry
- Observable by Traditional Vibrational Spectroscopy Techniques, Including rR; Each Metal-Ligand Complex Gives a Unique rR Spectrum, and rR is Sensitive Enough to Quantifiably Measure Levels to a *Minimum of Low ppm Range*
- Metals Complexes Are Highly-Stable Due to Thermodynamically-Favored "Chelate Effect" Seen with Multi-site Binding Ligands
- **Any Commonly-Found Metal Ion Can Be Used** – Not Restricted to RE's! Initial Results Indicate that Presence of Metal Ions Also Improve Signal/Noise!
- High Loadings of Complexes In Proppants Allow for Much Longer Tracking Times



Example of a Natural Biomarker found in Venzuelan Crude Oil

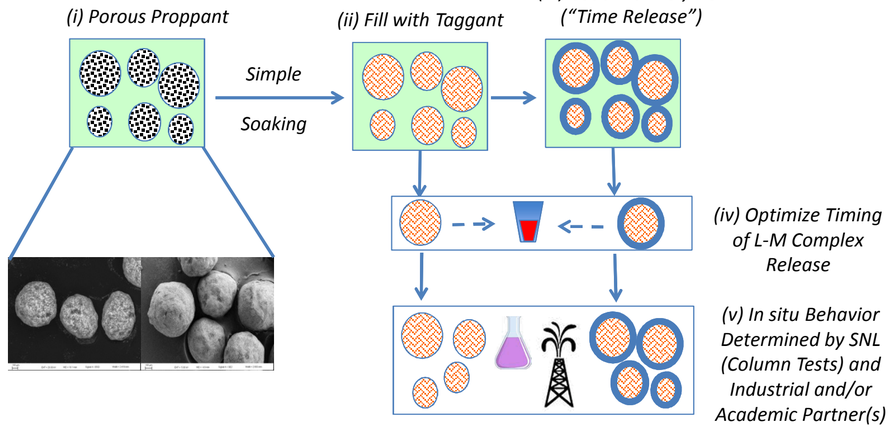




R = –COOH, $-SO_3H$, R_3N^+, rR tag, etc.

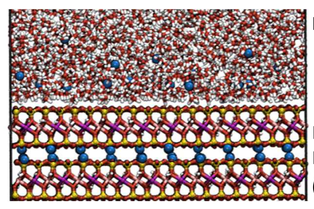
Coated Complex-Proppant Preparation

(i) Proppants shown in lower left SEM image (and graphically above it) will be (II) soaked with demonstrated high quality 'tags' synthesized/characterized.
(iii) These can be coated with a polymer to prevent 'flushing' of the tags.
(iv) Both will be tested in the lab to determine/optimize utility.
(v) Approved samples will be tested in field



In situ Testing Will Validate Laboratory Synthesis and Diffusion of Taggants

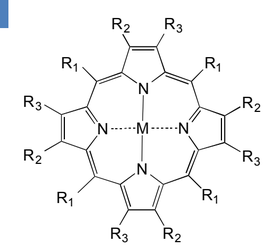
Modeling



Fluid – Oil and/or Water

\+ Taggant

Representative Mineral Phase *(Illite or Montmorillonite)*



Methods

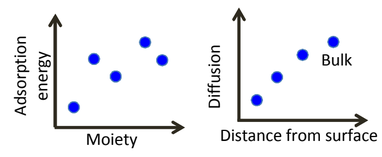
- Classical Molecular Dynamics (MD) Simulations of Adsorption and Intrapore Diffusion
- Based on Established Methods to Model L-M Complexes (Marques and Brown, *Coord. Chem. Rev.* **2002**) and Mineral Interfaces (Greathouse and Cygan, *Handbook of Clay Sci.* **2013**)
- Use of Sandia's LAMMPS MD Package and Analysis Tools Developed in Org 6915

Questions

- *What Metal/Ligand Properties Control Adsorption and Surface Diffusion?*
- *How Does Changing the Moiety Affect Partitioning of Water/Oil/Taggant w.r.t. the Clay?*

Impact

Results Will Be Used to Inform Experimental Choices by Understanding the Influence of Clay Surfaces



Overall Project Expectations

We Will Develop a Unique, Proppant-Loaded System Based on Soluble Tags That Can Be Used for Precise Tracking of Underground Hydrocarbon/Aqueous Fluid Flows That Utilizes Common Synthetic Organic Chemistry and Inexpensive Earth Abundant Metals

- Site-Specific Libraries of Tags Possible
- Molecular Modeling Will Guide the Laboratory Effort by Establishing Trends in Metal-Ligand Properties (Metal, Ligand Functionalization)
- Highly Interactive Project Allowing for Leverage – Contacts Have Been Made in Industry (Carbo) and Academics as Well as Within Sandia
- Sources of Follow-on Funding Upon Demonstration of Core Concept Possible, Including Industrial (Carbo) and DOE (EERE and subTER)
- If Successful, Licensing Possibilities for Sandia are Significant

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