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

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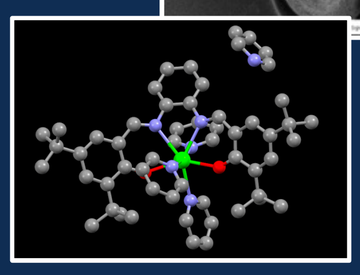
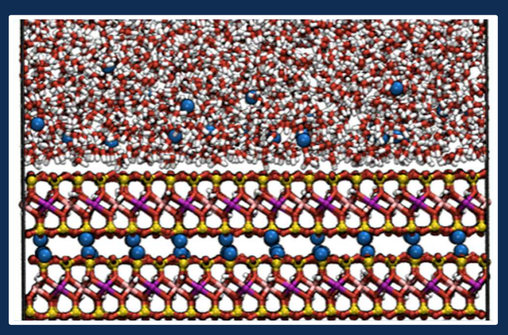
LDRD 2015-2017 (Two Year Project)



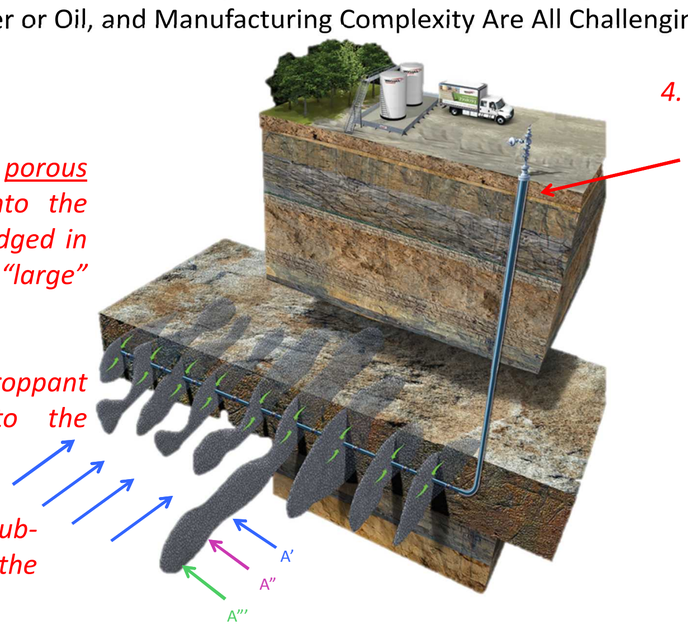


Objective/Problem to Be Addressed…

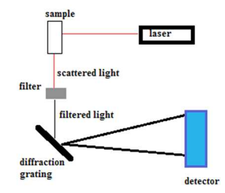
- Tracking Underground Fluid Flows in Oil/Gas Reservoirs or Engineered Geothermal Systems Over Extended Periods of Time Is Desired
- Currently, 60-70% of U.S. Hydrocarbon-Producing Wells are Hydraulically-Fractured, and Tools Exist for Monitoring Only Initial Fluid Flows (~1-2 months)
- ***Industrial 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 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" can be 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 analytical instrumentation.*
5. *In particular, we will exploit the sensitivity of Resonance Raman (rR) Spectroscopy for analysis at the wellhead of our tags.*



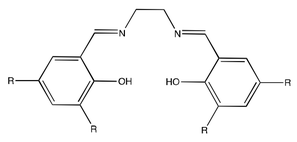
rR Spectroscopy: A sample is irradiated with monochromatic laser light at a frequency near the frequency of an electronic transition of the molecule, filtered, dispersed by the diffraction grating, and collected on the detector.

Development of 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

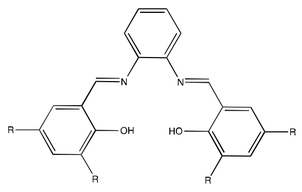
- Based on Salen-R derivatives these Species Were Readily Purchased or Synthesized to Alter Solubility (aqueous versus hydrocarbon) Using Existing Chemistry

H_2-Salen-R ligands



H_2-(salen)

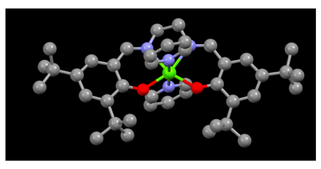
R = CH_3, $C(CH_3)_3$, Br, NO_2, [-CH2P(C6H5)][Cl]



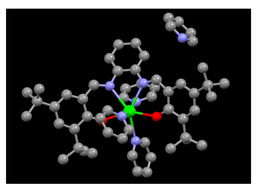
H_2-(salen-Ph)

- The variety of metals (1st Row metals) and ligands (8 types) synthesized and characterized has led to a novel family of compounds with varied solubilities.
- Numerous compounds isolated to date, including:*[(salo)Mg(py)$_2$] (**1**), [(saloPh')Mg(py)$_2$]$_x$ (**2**) [(py)$_2$Mg(salo-Bu^t)] (**3**), [(py)$_2$Mg(saloPh-Bu^t)] (**4**). [(py)$_3$Ca(salo-Bu^t)] (**5**), [(py)$_3$Ca(saloPh-Bu^t)] (**6**), [M(salo-Bu^t)] M = Ni (**7**), Co (**8**), [M(saloPh-Bu^t)] M = Ni (**9**), Co (**10**).*

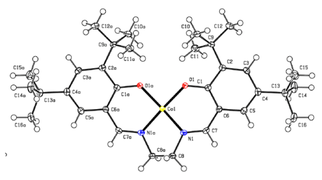
Examples of M-Salen-R compounds



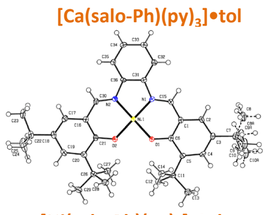
[Mg(salo)(py)$_2$]



[Ca(salo-Ph)(py)$_3$]•tol

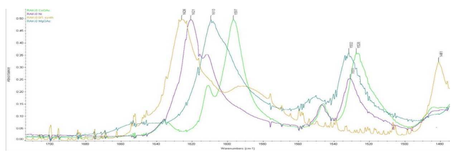


[Co(salo)py]



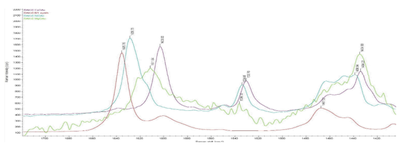
[Ni(salo-Ph)(py)$_3$]•tol

- FTIR and Raman spectroscopy has clearly demonstrated the unique signature of these compounds.



Compound	C=N peak absorbance frequency (cm^{-1})
Free RAK-0 Ligand	1626
RAK-0 Ni complex	1621
RAK-0 Mg complex	1610
RAK-0 Co complex	1597

Compound	C=N stretching Raman shift (cm^{-1})
Free RAK-0 ligand	1635.70
RAK-0 Ni complex	1628.75
RAK-0 Mg complex	1611.64
RAK-0 Co complex	1603.32

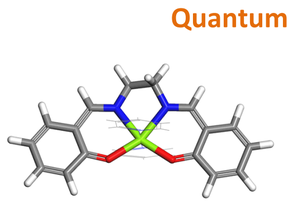


- Metal-Salen compounds are stable due to chelation.
- Initial investigations of exchange with dissolved cations has shown some possible exchange
- More studies underway to determine which M-L combinations are inert.

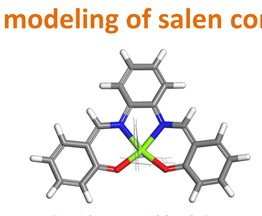
+ 4 undergraduates working on ligand and compound synthesis
+ 3 papers in preparation (Alkaline earth, transition metal derivatives, water derivatives)

Computational Modeling of Salen Derivatives

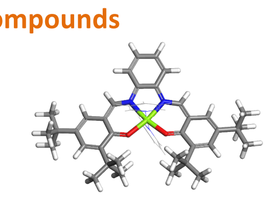
Quantum modeling of salen compounds



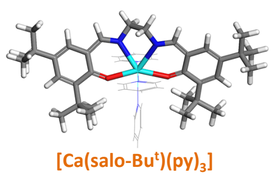
[Mg(salen)(py)$_2$]



[Mg(salo-Ph)(py)$_2$]



[Mg(saloPh-Bu^t)(py)$_2$]



[Ca(salo-Bu^t)(py)$_3$]

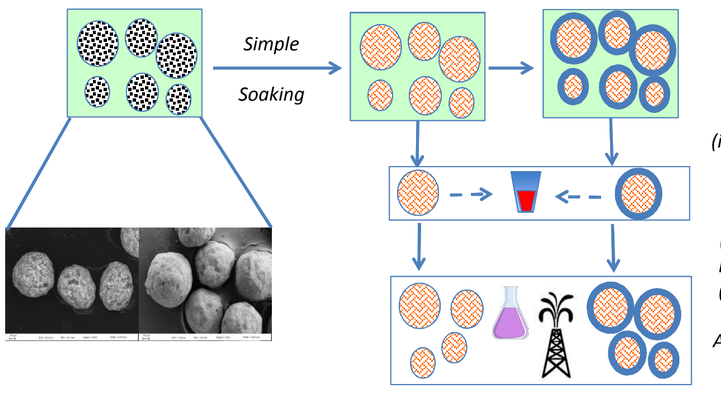
[Ca(saloPh-Bu^t)(py)$_3$]

- Results from gas-phase cluster models.
- Bond lengths and angles from computed structures are in good agreement with XRD.
- Non-planarity of ligands evident from Mg-N-C-C torsion angles.
- Fully coordinated metals have very low partial charge (0.6 – 1.0 *e*): *Electrostatic interactions with mineral surfaces should be reduced.*
- **FY17 plans:** MD simulations of tracer behavior in mineral pores.

FY17: Coated Complex-Proppant Preparation

(i) Proppants shown in lower left SEM image (and graphically above it) will be soaked (ii) with demonstrated high quality *Por* or *Pc* "tags" that have been synthesized/characterized;
(iii) These can also be coated with a polymer to prevent "flushing" of the tags;
(iv) These samples will be tested in the lab to determine/optimize utility; and
(v) Lab-approved prepared samples will be scaled-up and tested in the field.

(i) Porous Proppant *(ii) Fill with Taggant* *(iii) Coat with Polymer ("Time Release")*



(iv) Optimize Timing of L-M Complex Release

(v) In situ Behavior Determined by SNL (Column Tests) and Industrial and/or Academic Partner(s)

In situ Testing Will Validate Laboratory Synthesis and Diffusion of Taggants

Overall Project Expectations

We are developing 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 (Virtually Unlimited Number of Possible Test Candidates).
- A Few of the Compounds Developed for This Project are Shown Above. The Salen Ligand Has Been Emphasized Due to:
  - a) Ease of derivative syntheses to control solubility in either water (2 Ligands developed) or oil (4 ligands developed)
  - b) Novelty of prepared compounds and contributions to fundamental science, and
  - c) Porphyrins and phthalocyanines will be developed as [M(salo-R)] are explored for proppants and underground detection.
- 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/Licensing Upon Demonstration of Core Concept Possible, Including Industrial (Carbo) and DOE (EERE and subTER)

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