SAND2017-8531C

Spectroscopically sensitive salen and salen-type coordination compounds for long-term subterranean fluid flow monitoring

THE UNIVERSITY of NEW MEXICO

Orion Staples
Undergraduate Research Assistant
University of New Mexico/Sandia National Laboratories
Albuquerque, NM 87131
orion.staples@gmail.com

Sandia National Laboratories

University of New Mexico, Albuquerque, NM
Tefere E. Tesema, Jenny C. Sanchez, Terefe G. Habteyes, Richard A. Kemp

Sandia National Laboratories, Albuquerque, NM
Jeremiah M. Sears, Jeffrey A. Greathouse, Timothy J. Boyle, Richard A. Kemp

Carbo Ceramics Inc., Houston, TX
Todd M. Roper

Introduction

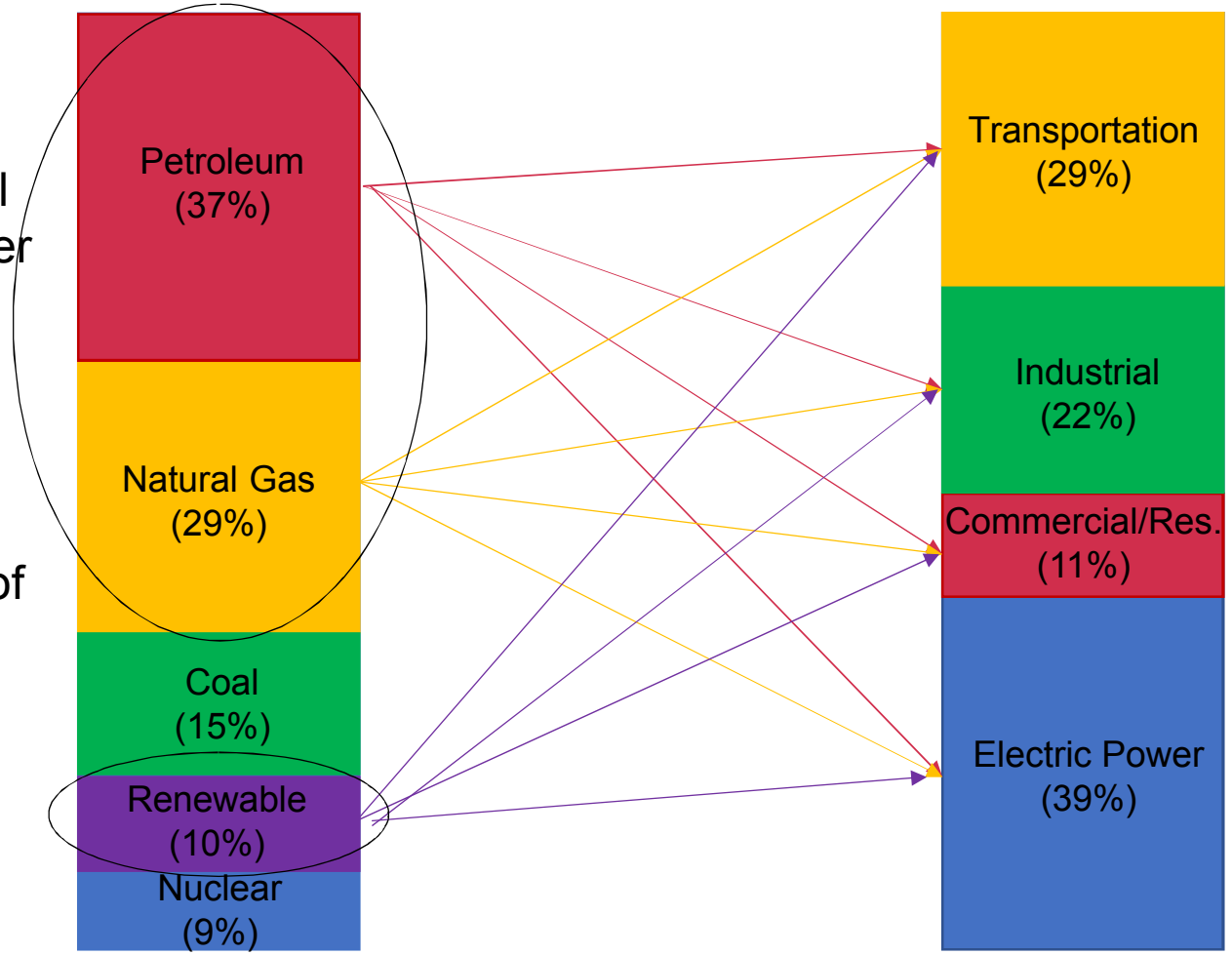
United States energy climate

U. S. is the largest producer of petroleum and natural gas hydrocarbons globally, as well as largest producer of geothermal power.

66.3% of the total national energy production 64.5 quadrillion Btu.

We aim to improve the energy acquisition efficiency of both of these methods.

Hydrocarbons alone account for: 95 % of the transportation market, 83 % or the industrial market, 99 % of the commercial market, and 28 % of electric power generation. (cm^{-1})



Introduction

Subterranean monitoring

Shale-oil and geothermal wells are of main interest as they produce petroleum, natural gas, and geothermal energy

Currently: radioisotopes are used to determine initial fluid flows

In progress: DNA, nanoparticles

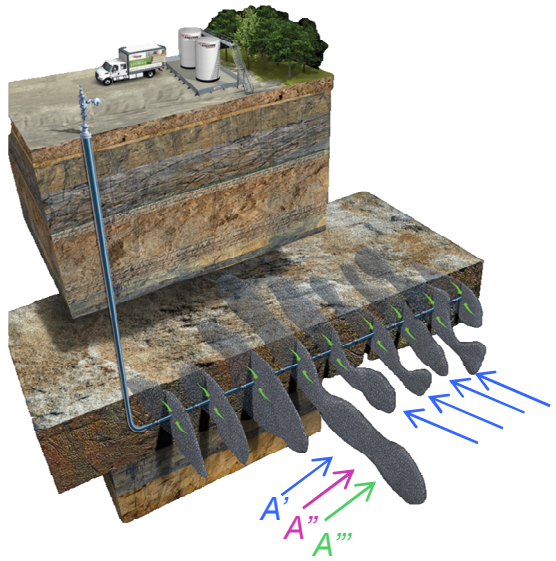
Our work: vibrational sensitive coordination compounds

Issues with current methods:

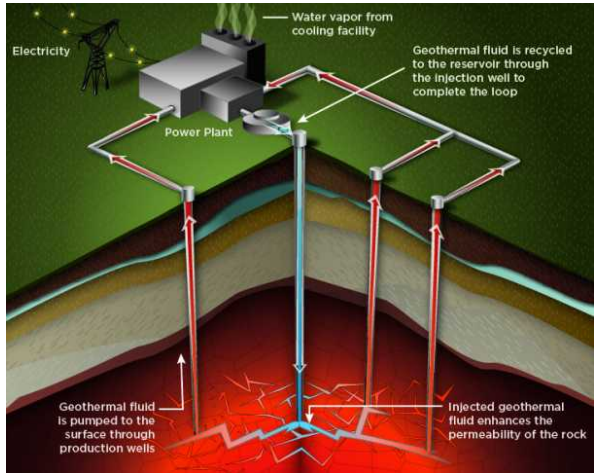
1. Radioisotopes require multiple injections (increased risk of radioactive exposure) and only monitor *initial* fluid flows.

2. DNA degrade at high temperatures and pressures present in the wells

3. Nanoparticles bind unfavorably to subsurface strata



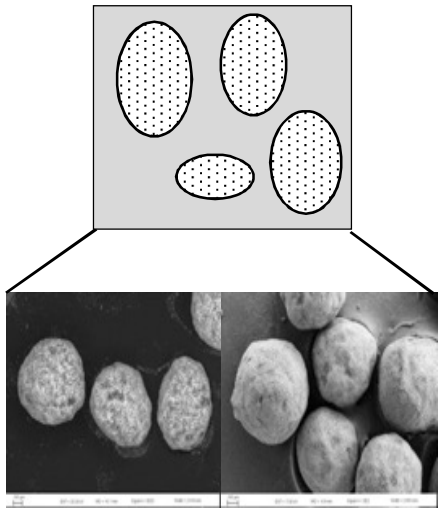
Horizontal shale-oil well



Injection geothermal well

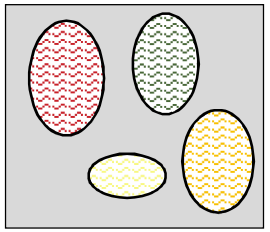
Approach

(i) Porous proppant



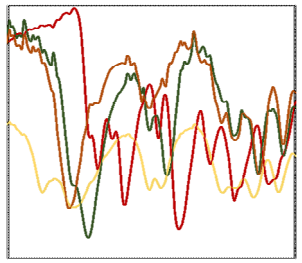
simple soaking

(ii) Fill with taggant

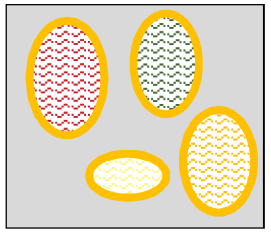


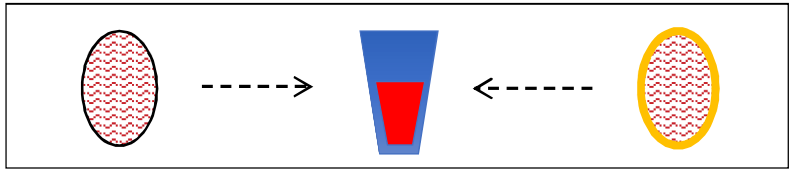
vibrational spectroscopy

(iii) Determine unique spectroscopic character

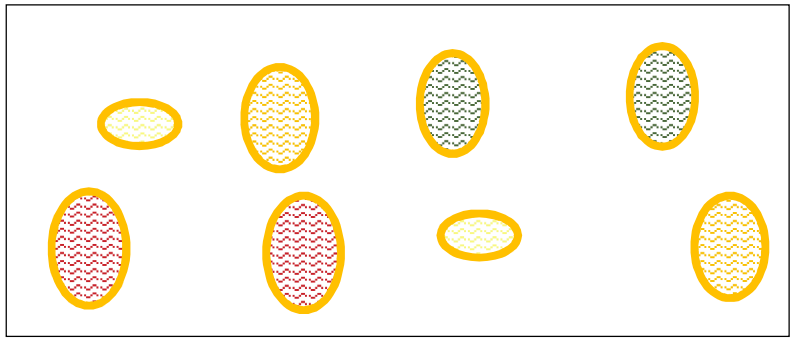


(iv) Coat with polymer ("time release")



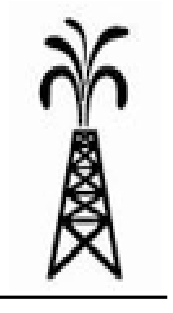


(v) Optimize long term release of ML-compound



(vi) In situ behavior determined by SNL (column tests) and industrial and/or academic partner(s)

industrial application



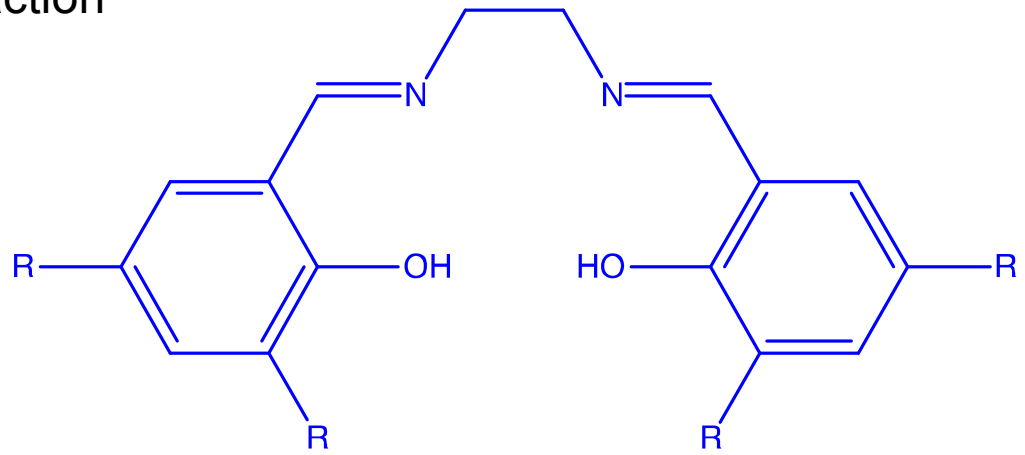
(vii) Increased efficiency in both hydrocarbon and geothermal energy liquid acquisition

Ligand Synthesis

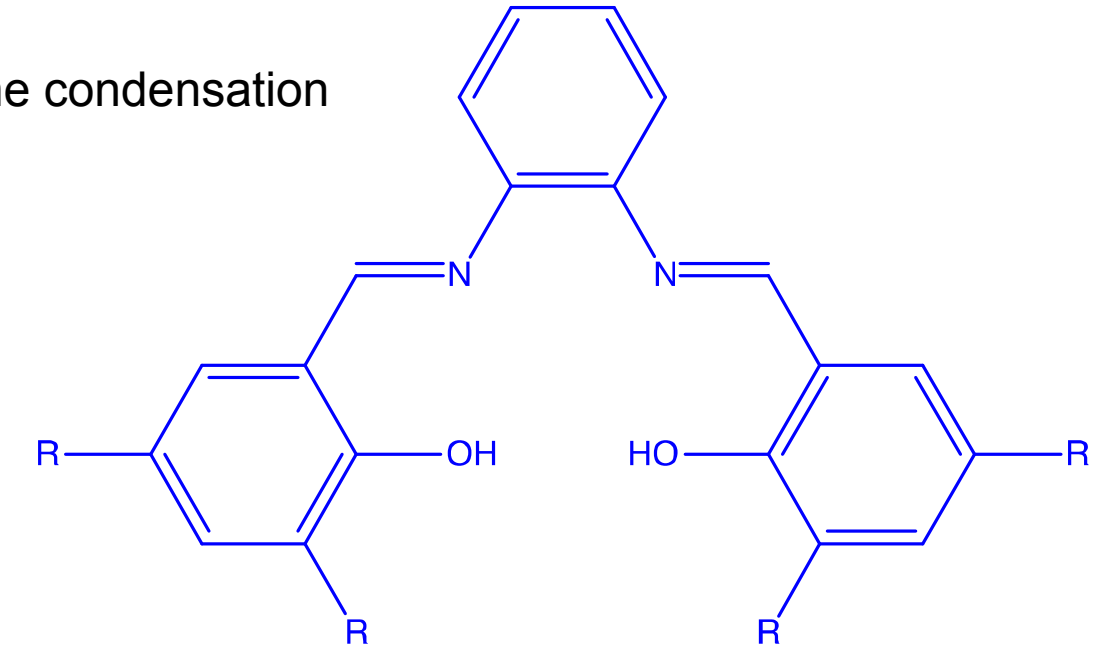
Commercially available salens and modified phenylene salen demonstrate poor solubility in both hydrocarbon and aqueous systems.

Modification of the pendant phenyl rings achieves desired hydrocarbon or aqueous solution behavior

Simple and high yielding 2:1 molar ratio aldehyde to amine condensation reaction

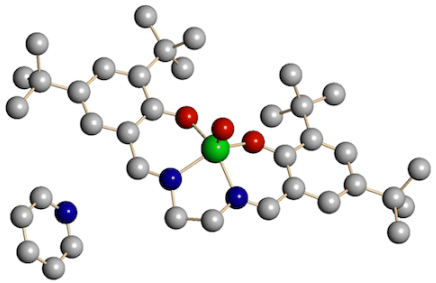


H_2-salo-R



H_2saloPh-R

Hydrocarbon soluble coordination



"V(salo-Bu^t)"

M-Isopropoxide

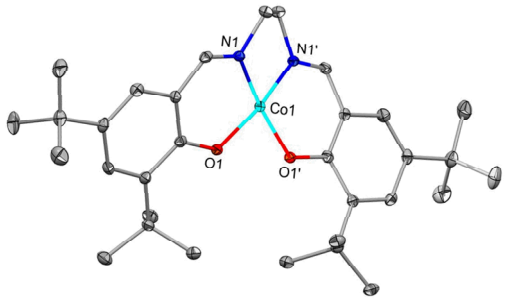
toluene, rt, 24 h

H_2-saloPh-Bu^t

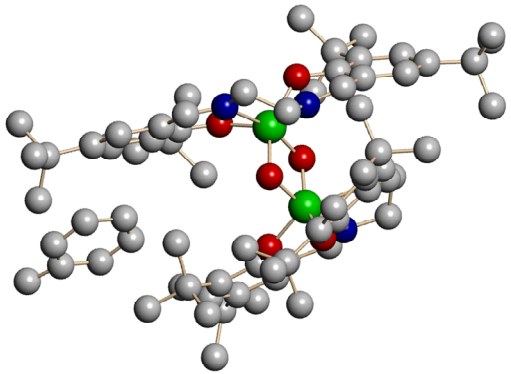
H_2-salo-Bu^t

M-Acetate

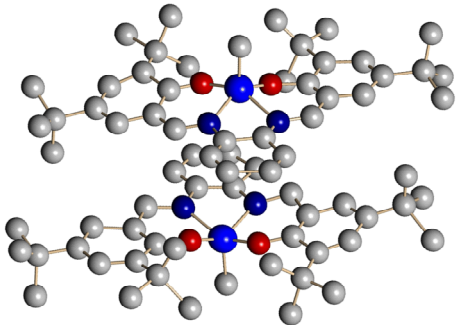
MeOH, rt, 24 h



"Co(salo-Bu^t)"



"Ti(salo-Bu^t)"

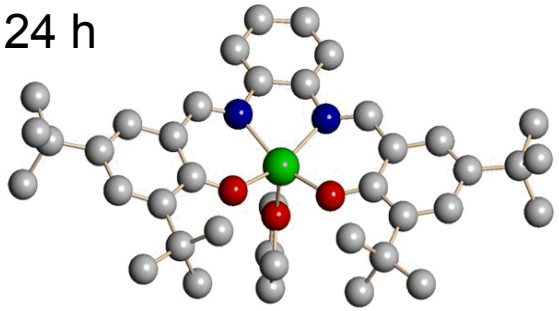


"Al(salo-Bu^t)"

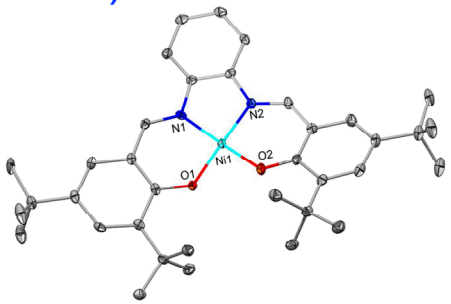
M-Alkyl

toluene

rt, 24 h



"Zn(saloPh-Bu^t)"



"Ni(saloPh-Bu^t)"

Aqueous soluble coordination

H_2-salo-PPh_3^{2+} $(Cl^-)_2$

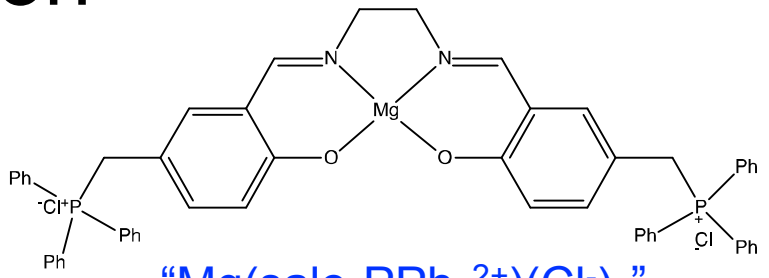
H_2-saloPh-PPh_3^{2+} $(Cl^-)_2$

H_2-saloPy-PPh_3^{2+} $(Cl^-)_2$

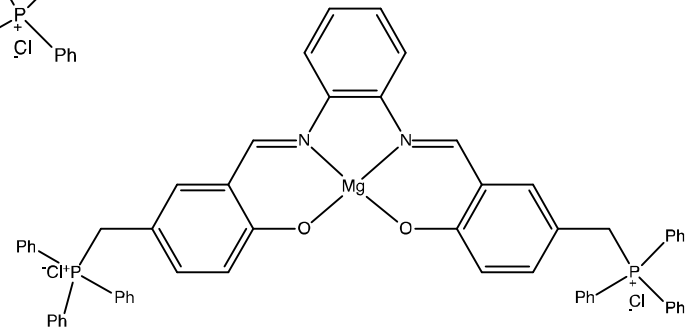
H_2-salo-Py^{2+} $(Br^-)_2$

M-Acetate

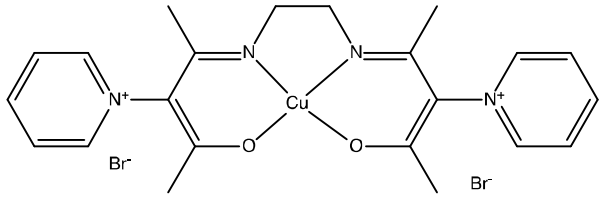
MeOH, reflux, 24 h



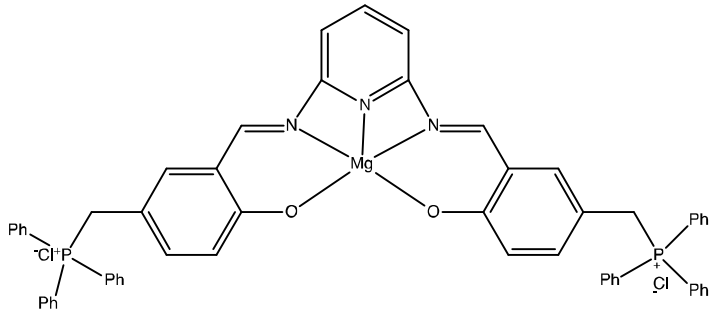
“Mg(salo-PPh_3^{2+})$(Cl^-)_2$”



“Mg(saloPh-PPh_3^{2+})$(Cl^-)_2$"



“Cu(salo-Py^{2+})$(Br^-)_2$”

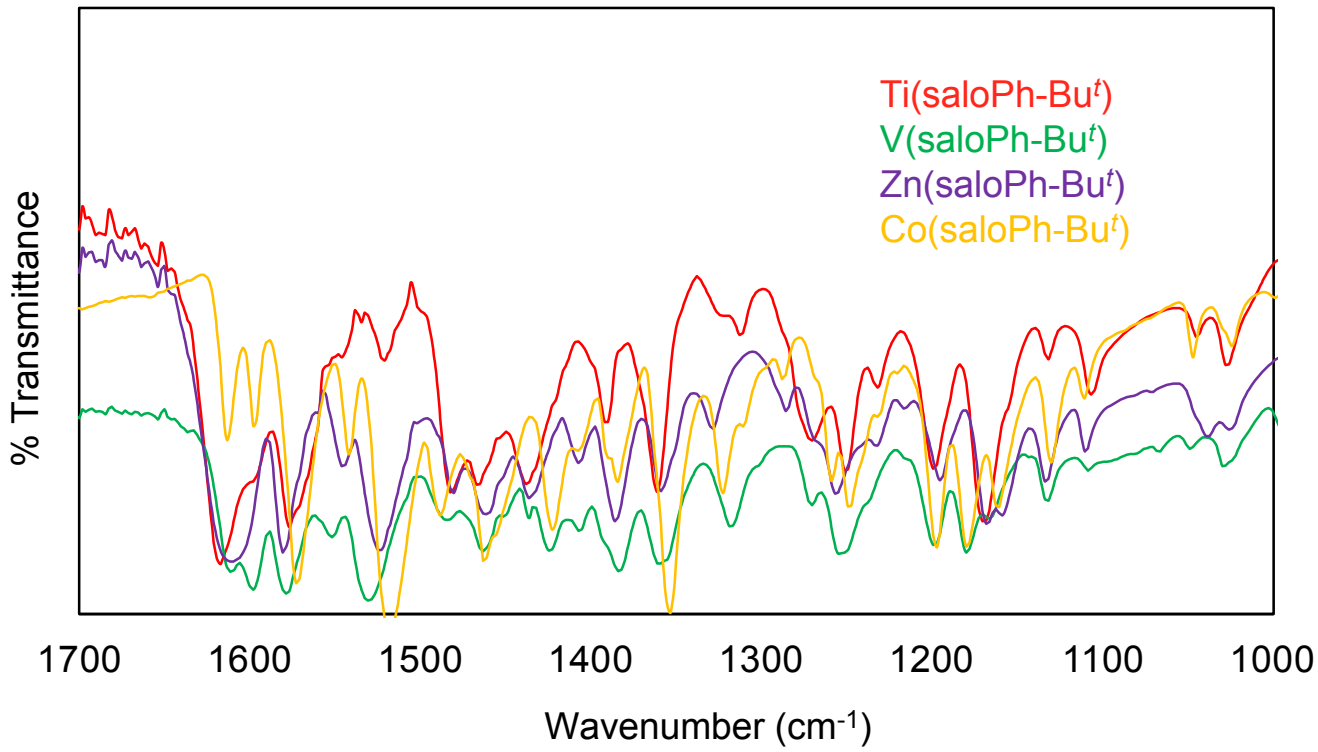


“Mg(saloPy-PPh_3^{2+})$(Cl^-)_2$”

Hydrocarbon FT-IR

	C=N (cm^{-1})	
Coordination	M[salo-Bu^t]	M[saloPh-Bu^t]
Free ligand	1626	1615
Ti	1636	1618
V	1616	1599
Co	1597	1614
Zn	1607	1612
Mg	1629	1604
Al	1631	1617

FT-IR shifts of C=N stretching in hydrocarbon soluble compounds

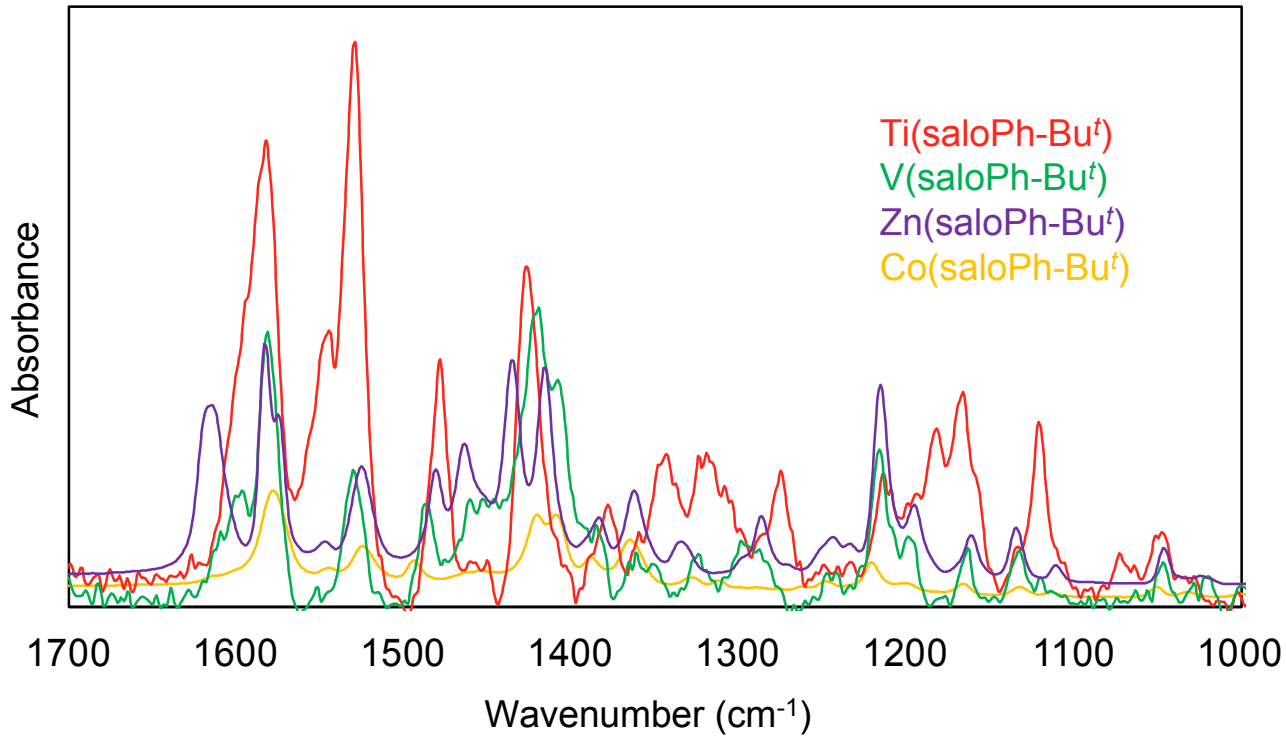


FT-IR fingerprint region of select hydrocarbon soluble compounds

Hydrocarbon Raman

Coordination	C=N (cm^{-1}) M[salo-Bu^t]	M[saloPh-Bu^t]
Free ligand	1632	1617
Ti	1646	1586
V	1612	1581
Co	1603	1578
Zn	1621	1615
Mg	1617	1642
Al	1664	1619

Raman shifts of C=N stretching in hydrocarbon soluble compounds



Raman fingerprint region of select hydrocarbon soluble compounds

Aqueous FT-IR

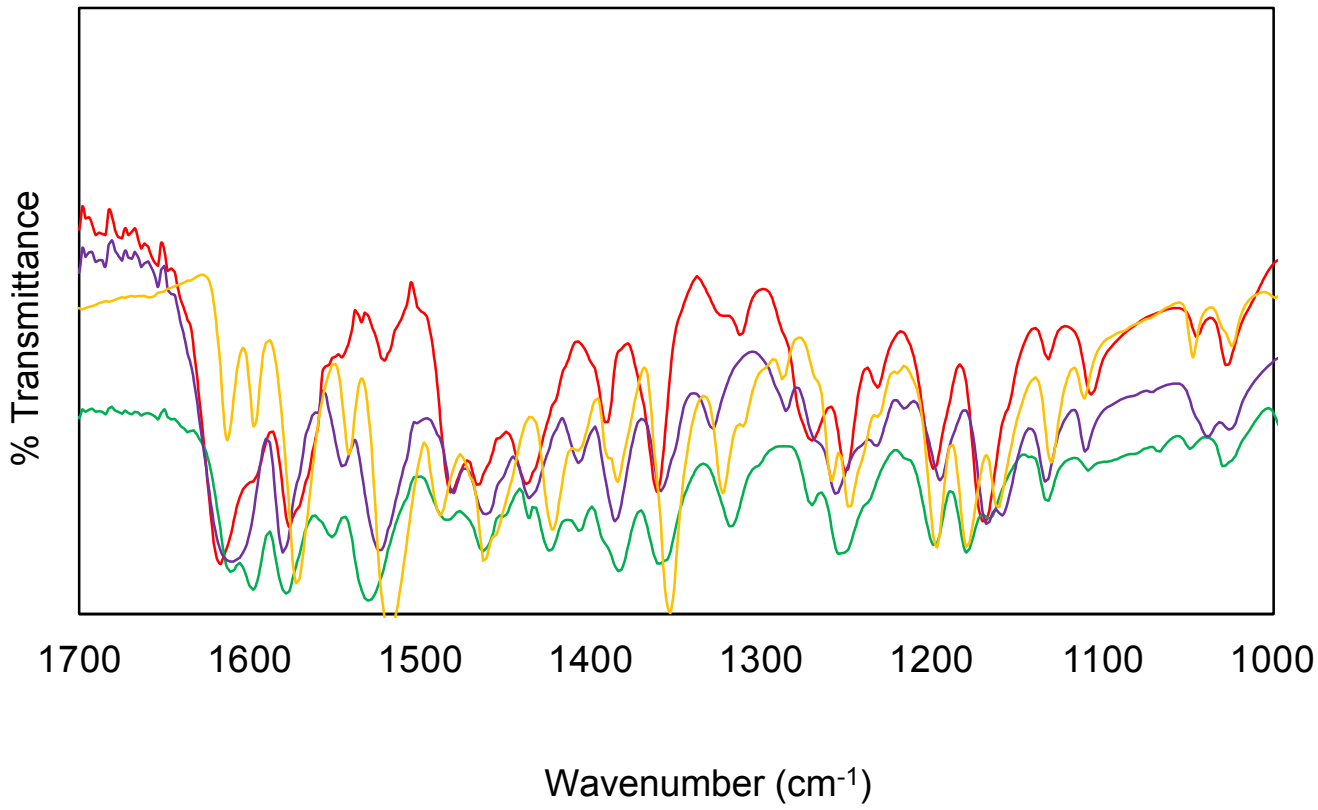
C=N (cm^{-1})

Coordination	M[salo-Py^{2+}] $[Br^-]_2$
Free ligand	1625
Co	1620
Cu	1622
Mg	1626

C=N (cm^{-1})

Coordination	M[salo-PPh_3^{2+}] $[Cl^-]_2$	M[saloPh-PPh_3^{2+}] $[Cl^-]_2$	M[saloPy-PPh_3^{2+}] $[Cl^-]_2$
Free ligand	1631	1652	1726, 1607
Co	1620	---	1585, 1563
Mg	1709	1675	- - -

FT-IR shifts of C=N stretching in water soluble compounds



FT-IR fingerprint region of select water soluble compounds

Aqueous Raman

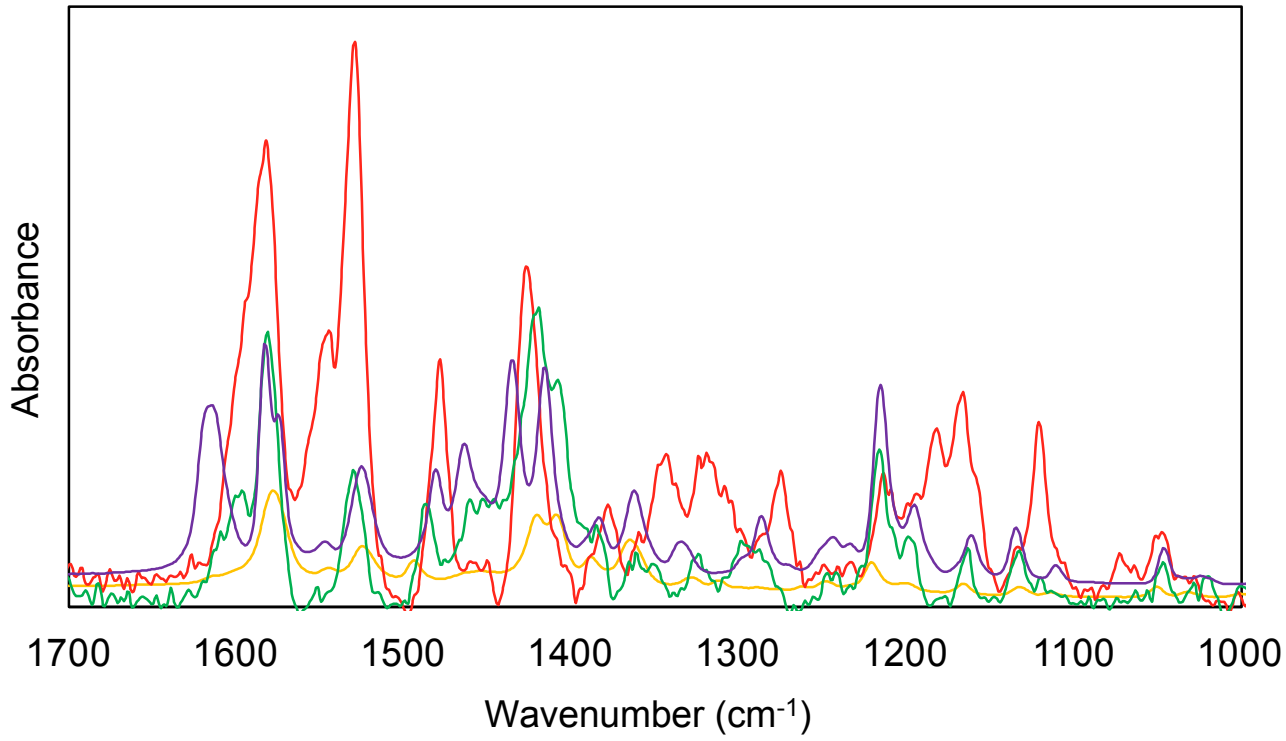
C=N (cm^{-1})

Coordination	M[salo-Py^{2+}] $[Br^-]_2$
Free ligand	1625
Co	1620
Cu	1622
Mg	1626

C=N (cm^{-1})

Coordination	M[salo-PPh_3^{2+}] $[Cl^-]_2$	M[saloPh-PPh_3^{2+}] $[Cl^-]_2$	M[saloPy-PPh_3^{2+}] $[Cl^-]_2$
Free ligand	1631	1652	1726, 1607
Co	1620	---	1585, 1563

Raman shifts of C=N stretching in water soluble compounds



Raman fingerprint region of select water soluble compounds

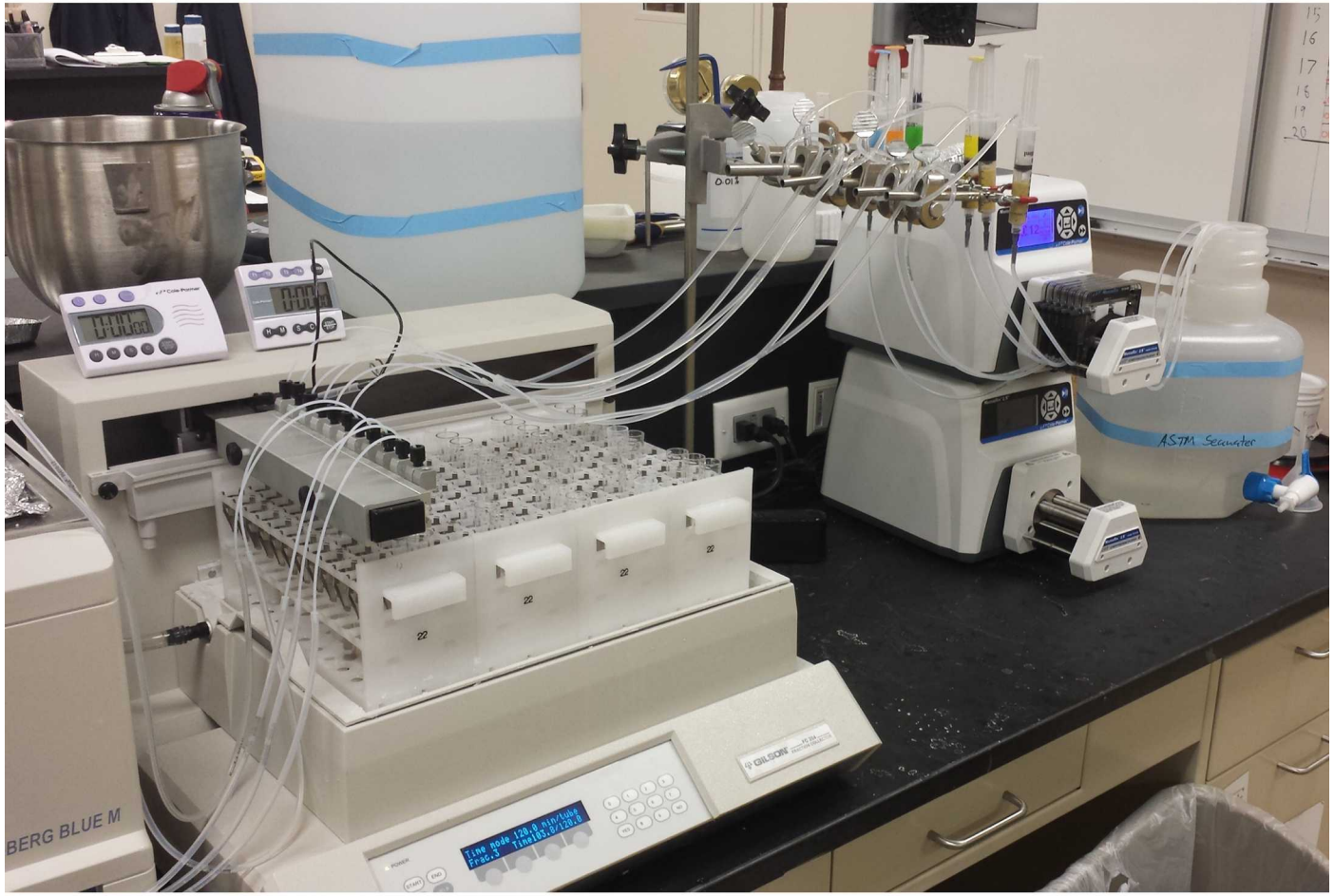
Elution kinetics

Fluid flows from right to left

Proppant is packed in a plastic syringe to simulate well-packing

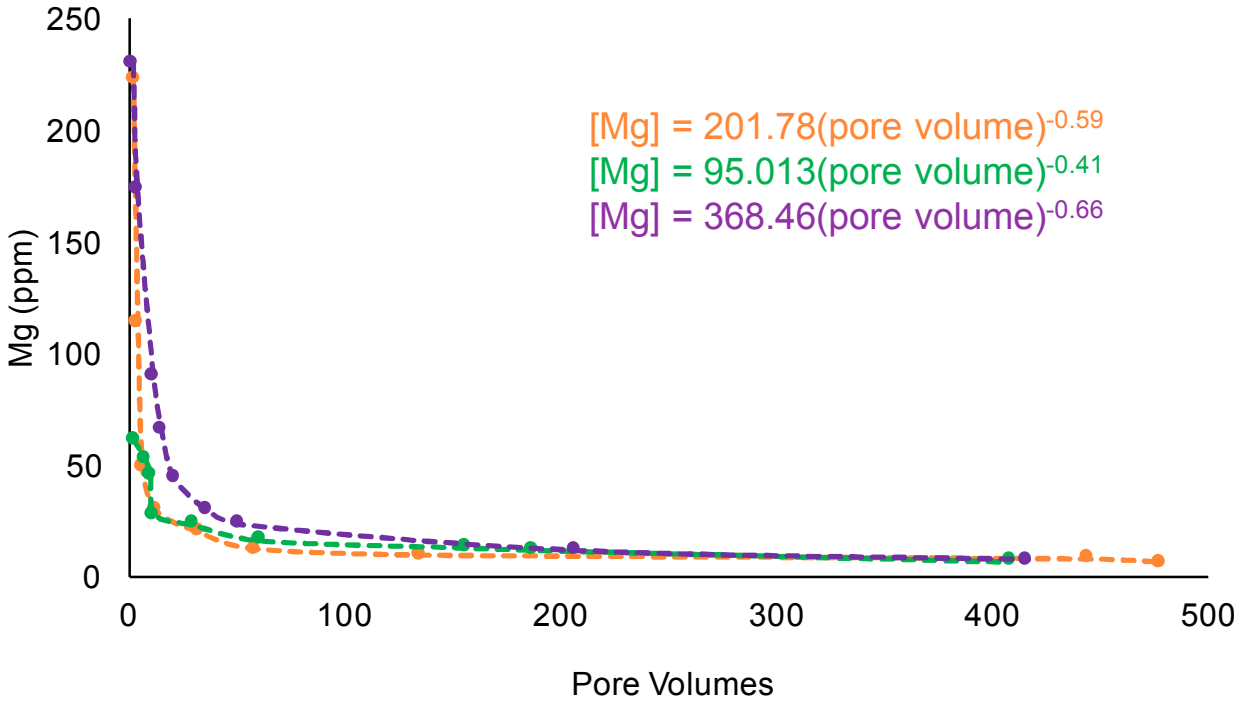
Fractions are collected per pore volume

Analysis performed by ICP

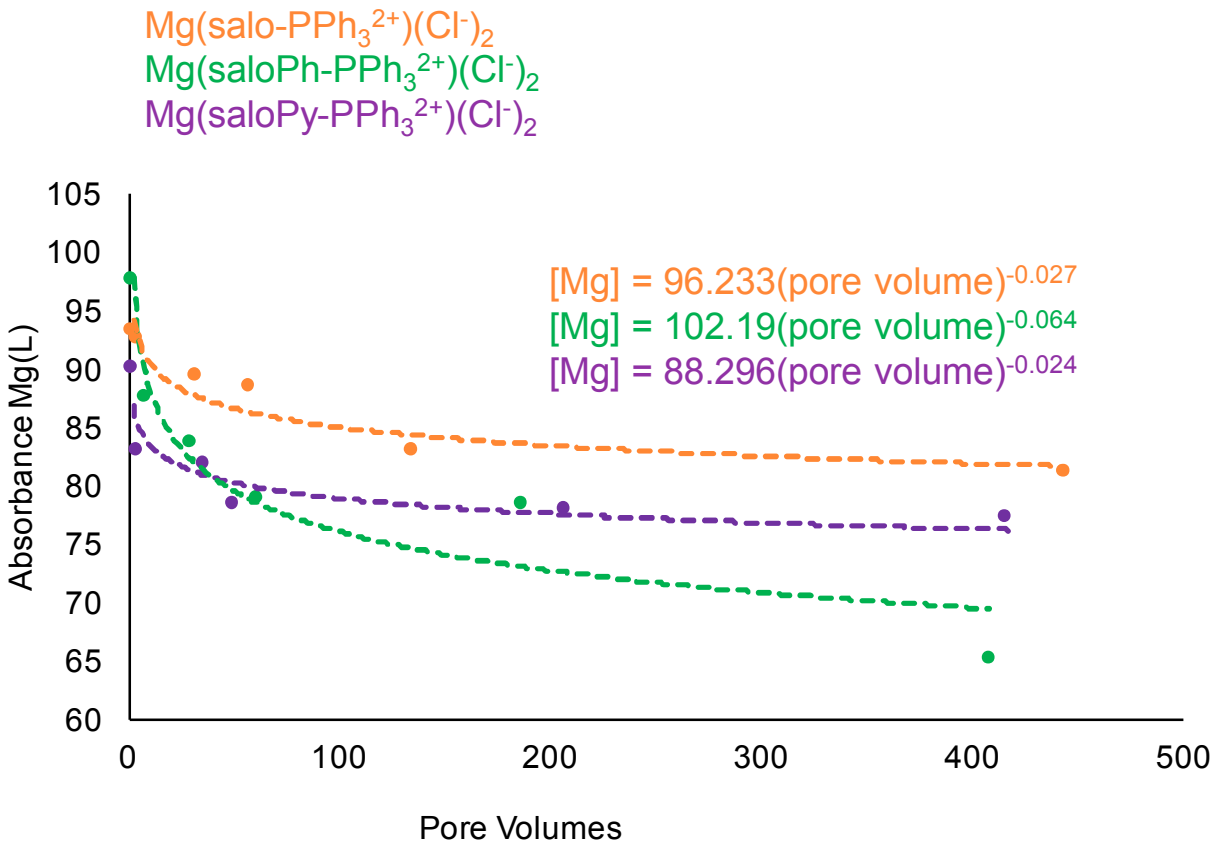


Elution kinetics testing setup at Carbo Ceramics

Elution kinetics



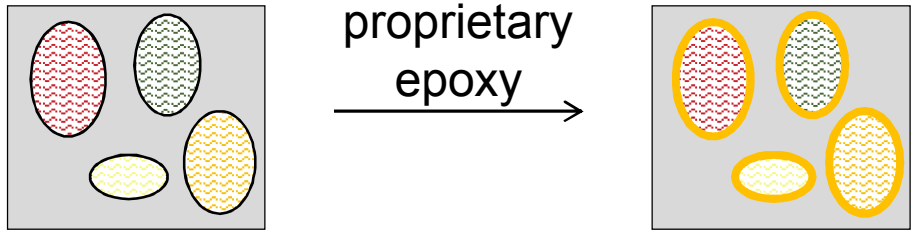
Elution results of uncoated proppants run in ASTM seawater solution, ICP results

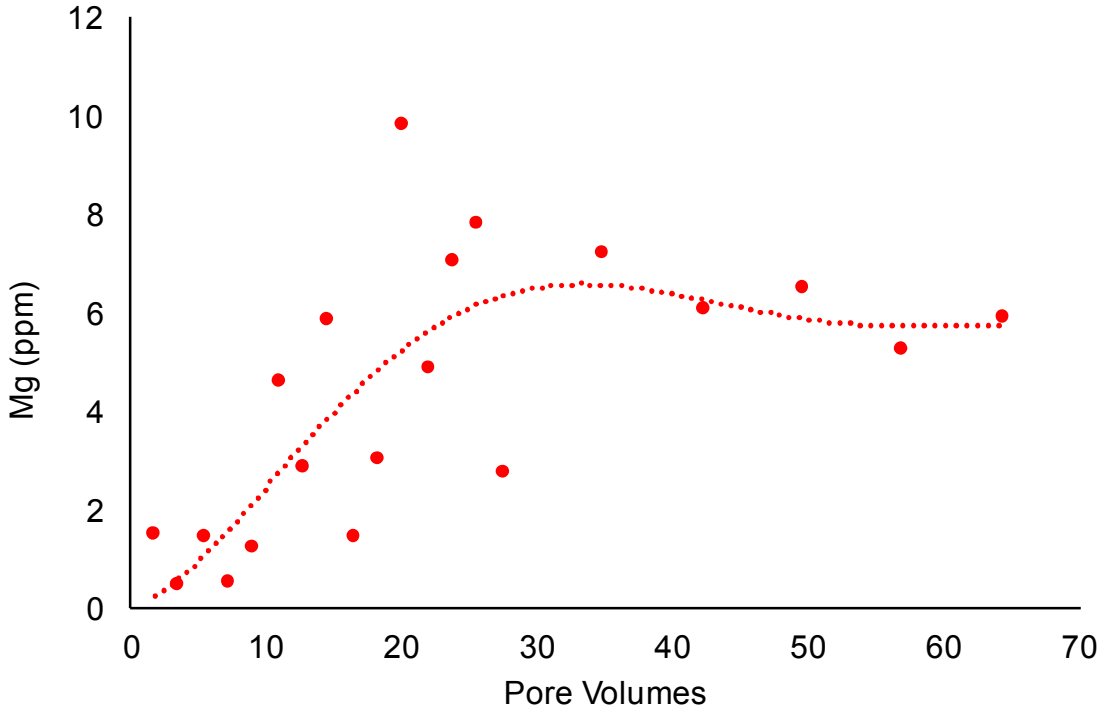


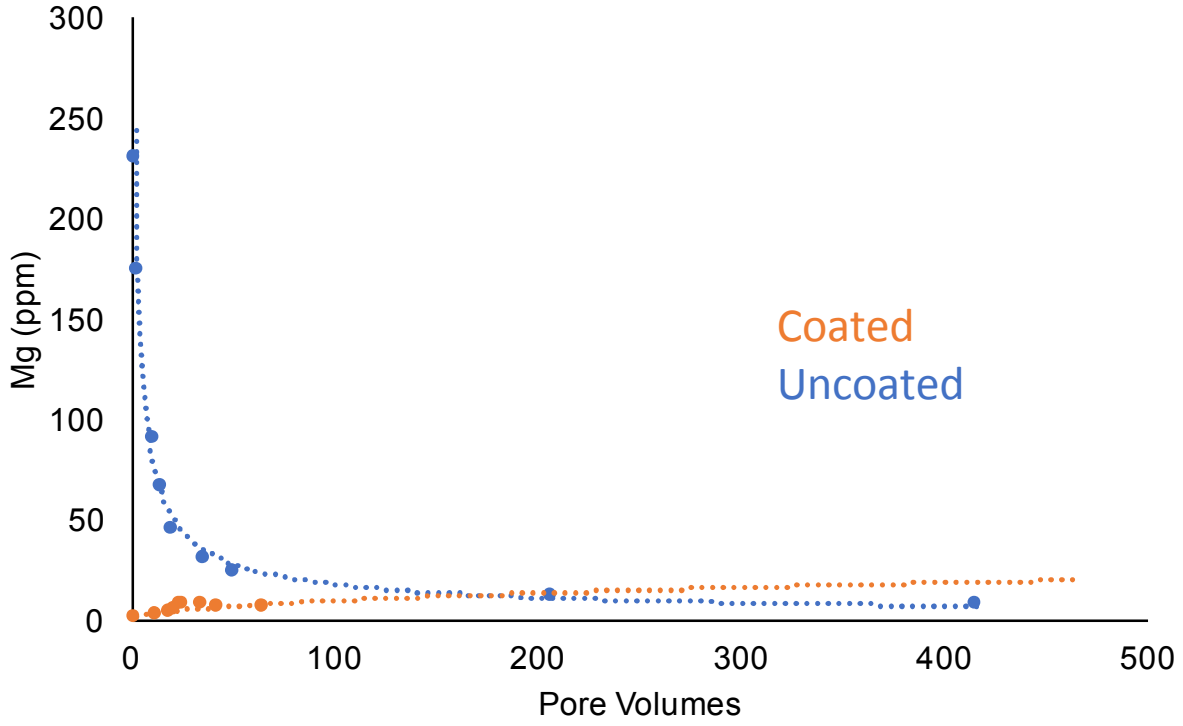
Elution results of uncoated proppants run in ASTM seawater solution, Initial Raman correlation

Optimization of elution kinetics

"Mg(saloPy-PPh_3^{2+})(Cl^-)$_2$" loaded proppant coated with epoxy to provide long-term monitoring capabilities







Optimize time-release of ML-complex from proppant

- ✓ Initial elution data recorded by ICP for metal concentrations in both aqueous and hydrocarbon liquids
- ✓ ICP correlated to Raman absorbance intensities for a cheap and quick method of determining fluid flow rates at the well head
- ✓ Coated proppants provide more favorable kinetics

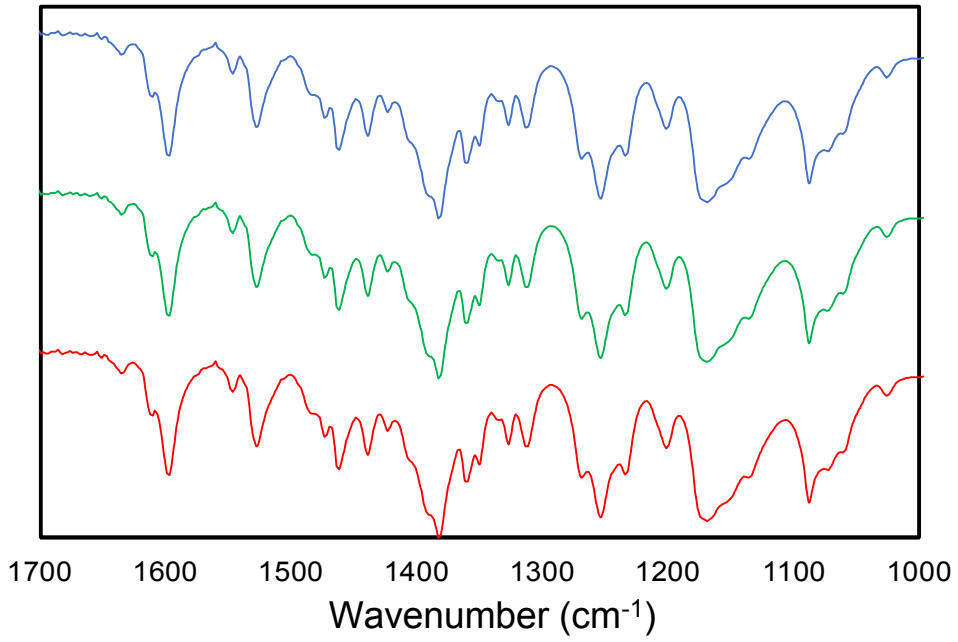
Issue 1: long term monitoring capability ***resolved***

Stability analysis

Temp: 150 °C
Reactive conditions: Mg^{2+} and Ca^{2+} ions, pH ~ 8.5

M(salo-Bu^t)

Octanes
Brine
$Ca(OH)_2$
$Ba(OH)_2$
150 °C, 24 h



Inert:

-"Co(salo-Bu^t)"
-"Ni(saloPh-Bu^t)"
-"V(saloPh-Bu^t)"
-"V(salo-Bu^t)"
-"Ti(salo-Bu^t)"
-"Ti(saloPh-Bu^t)"
-"Zn(saloPh-Bu^t)"
-"Zn(salo-Bu^t)"
-"Cu(salo-Py^{2+})(Br$^-$)$_2$"

Reactive:

-"Al(salo-Bu^t)"
-"Al(saloPh-Bu^t)"

Issue 2: high pressure and temperature stability ***resolved***

Subsurface binding

Column testing in sand

Compound	Amt. dissolved (g)	Solvent	Amt. retained (g)	%
Mg(saloPh)	0.100	50 mL toluene	0.000	0
Mg(salo-Bu^t)	0.100	50 mL toluene	0.000	0
Mg(saloPh-Bu^t)	0.100	50 mL toluene	0.000	0
Co(saloPh-Bu^t)	0.100	50 mL toluene	0.000	0
(Mg(saloPh-Bu^t))$_2$	0.100	50 mL toluene	0.026	26
Cu(salo-Py^{2+})(Br$^-$)$_2$	0.100	50 mL DI H_2O	0.000	0

Issue 3: Unfavorable binding to subsurface strata ***resolved***

Review

-Designed and synthesized a family (>40 species) of variably soluble salen-type coordination compounds
-Unique spectroscopic character exists
-Loaded proppants to test these compounds under “assumed well conditions”

Results:

- ✓ Long term fluid flow capabilities achieved
- ✓ Stability and non-reactivity achieved
- ✓ A majority of the compounds do not adsorb onto subsurface strata