U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Novel Multidimensional Tracers for Geothermal Inter-Well Diagnostics

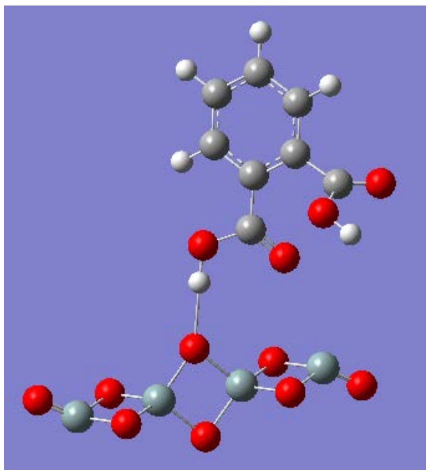
Project Officer: John Ma
Total Project Funding: $2,300,000
April 23, 2013

Principal Investigator : Yongchun Tang
Presenter: John Ma
Power Environmental Energy Research Institute

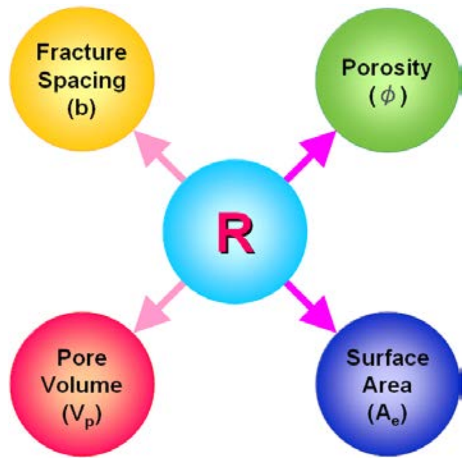
DE-EE0003032

Relevance/Impact of Research

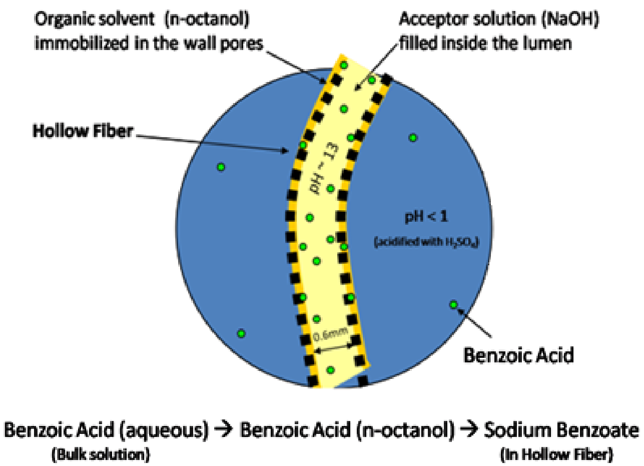
Objective: Develop a matrix of the smart geothermal tracer and its interpretation tools leading to information beyond well-to-well connectivity



Molecular modeling techniques: understanding the tracer-surface interactions



Interpretation development for subsurface characterization



Advanced sample pre-treatment technique for high resolution detection (10^{-12} gram per mL)

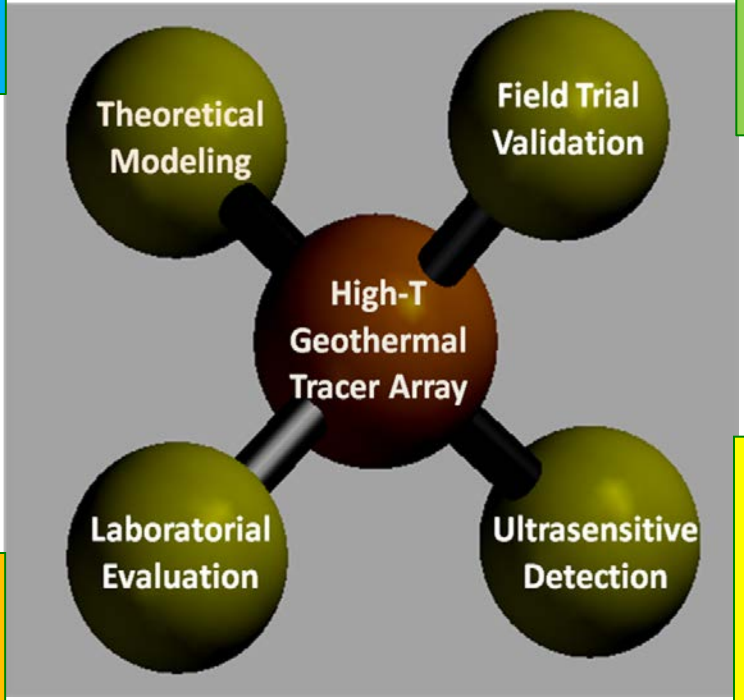
Anticipated Impacts: The integrated multiple tracer (smart tracer) and its interpretation system could have significant impacts on diagnostics of subsurface structures of geothermal reservoirs.

Scientific/Technical Approach

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Theoretical Model and Molecular Design Tool (Working with California Institute of Technology (Caltech))

Field Tests and Industrial Application Evaluation
(Mt. Princeton Geothermal LLC
BJ Energy Service)



Establish Laboratory Protocols
(1) Thermal Stability
(2) Adsorption/Desorption
(3) Tracer Performance
(4) Tracer Evaluation

Developing tracer detections:
(1) Sample pre-concentration
(2) GC/LC analyses
(3) Nitrogen Phosphorus Detector (NPD)
(4) Techniques to improve sensitivity and accuracy of tracer detection limitations

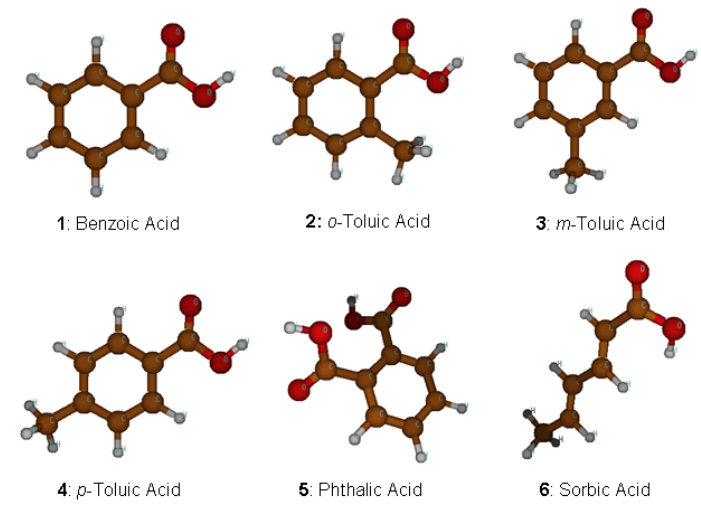
Accomplishments, Results & Progress

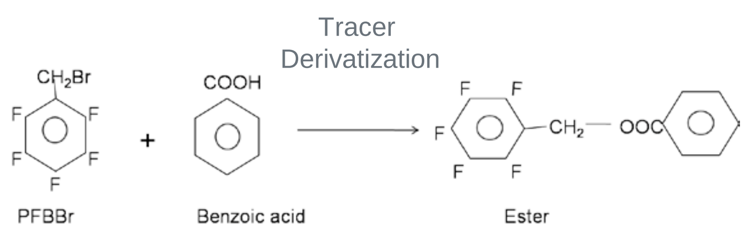
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Milestone 1: Completion of methodology developments and data collections	(1) A class of carboxylic tracers (2) Enhancing the tracer detection limit up to 1000x	July. 2010
Milestone 2: Identification of several sets of tracer candidates and data collection from Long-slim tube experiments	(1) Models for predictions of reserve characters (2) Potential to reduce tracer amounts for cost and environmental benefits	Sept, 2011
Milestone 3: Completion of field test and development of multidimensional tracer interpretation system	(1) Model Validation from field test (2) Evaluation of smart tracer application potentials	March, 2013

Carboxylic compounds as Multi-dimension Tracers

- Selection with structural variation → properties variation
  - Flow properties
  - Surface adsorption-desorption
  - Thermal degradation
- Tracer-matrix interaction → site characterization
  - Swept pore volume; surface area; fracture spacing … etc
  - Matrix composition
  - Temperature profile
- High sensitivity detection by GC-ECD through derivatization
- Low toxicity → environmental friendly

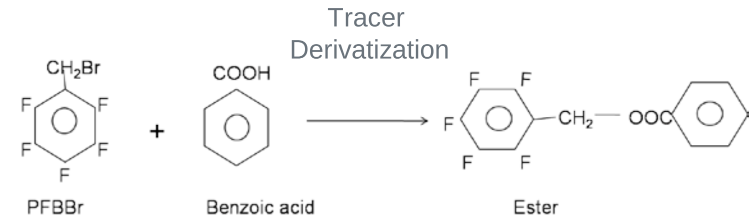


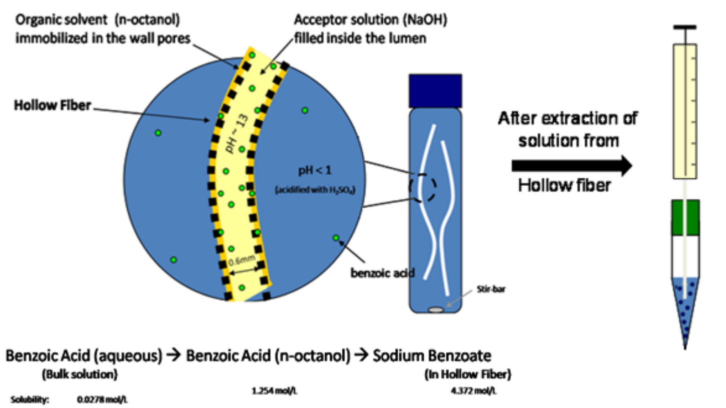


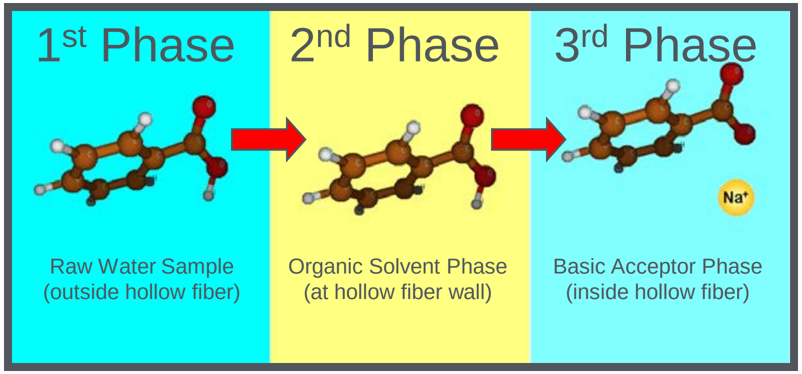
Detection Limit Improvement

- Derivatization technique: Carboxylic acids react with selective alcohol to form ester with high sensitivity detection by GC-ECD

- Advanced pre-concentration procedure development: Hollow-Fiber Liquid-Liquid Micro-Extraction (HF-LLME) based method to increase tracer detection limit up to 1000 times
  - 1st phase, the acidified raw water sample (bulk solution) outside hollow fiber;
  - 2nd phase, organic solvent soaked within the wall of the hollow fiber as transition phase for migration;
  - 3rd phase, basic acceptor solution (pH ~13) inside the hollow fiber

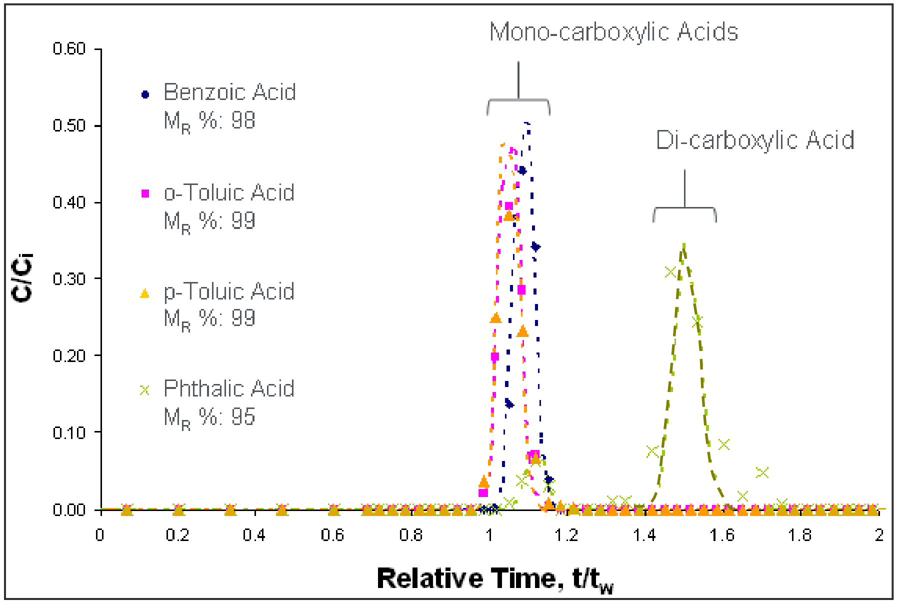






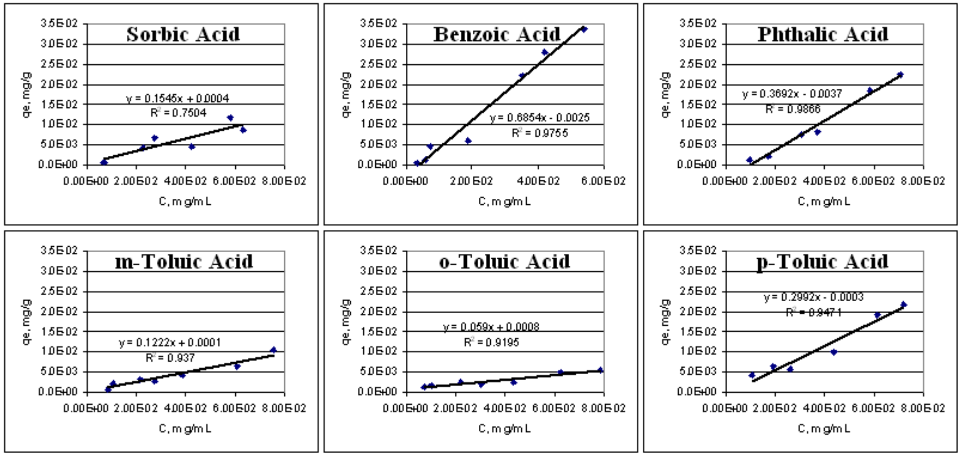
Laboratory Calibration

Dynamic Adsorption Studies to determine K on Silica



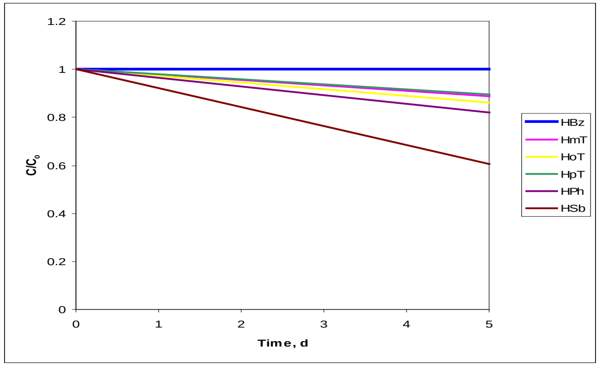
	p-Toluic Acid	*o*-Toluic Acid	*m*-Toluic Acid	Benzoic Acid	Sorbic Acid	Phthalic Acid
K, mL/g	0.006	0.006	0.007	0.014	0.016	0.081
K_a x10^6, m	0.372	0.397	0.459	0.833	0.968	5.027

Static Adsorption Test to determine of K on Calcite



benzoic > phthalic > p-toluic > sorbic > m-toluic > o-toluic

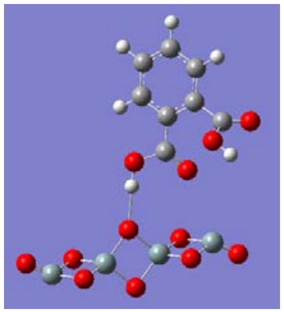
Thermal Degradation of Tracers



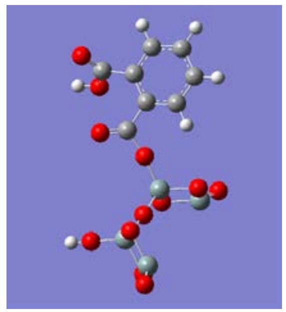
Degradation at 250°C

Tracer-Matrix Interaction Mechanism

Fundamental understandings of tracer-matrix interactions



Weak Tracer-Matrix Interaction
(H---O bond: Before Deprotonation)

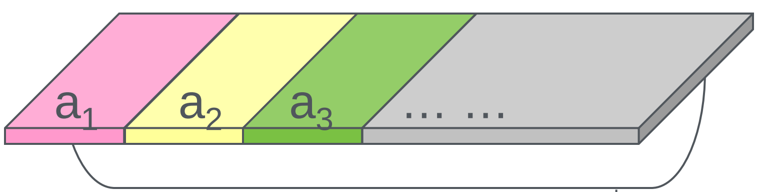


Strong Tracer-Matrix Interaction
(O---Si bond: After Deprotonation)

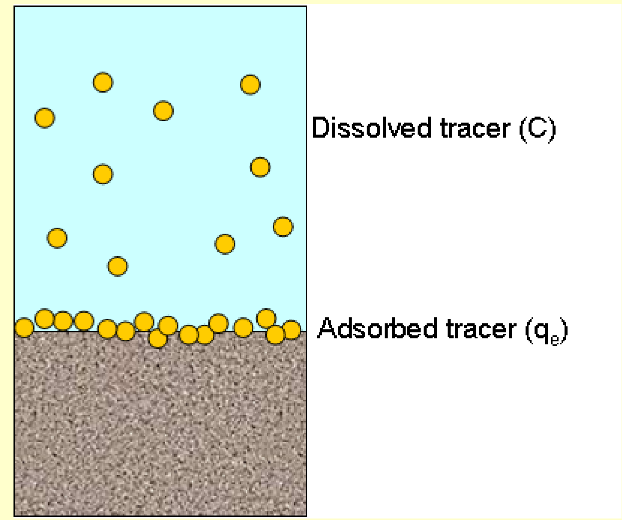
Silicate

Calcite

Hematite

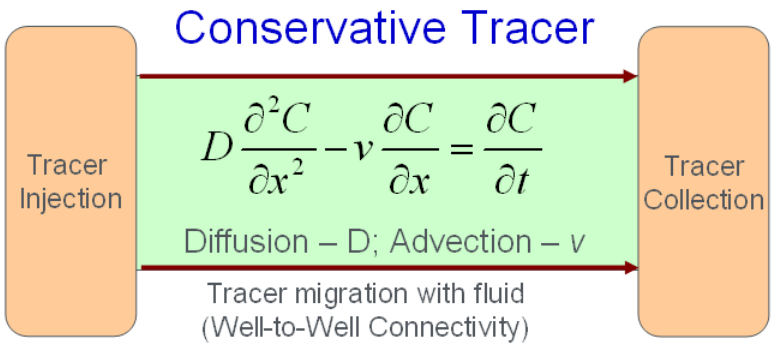


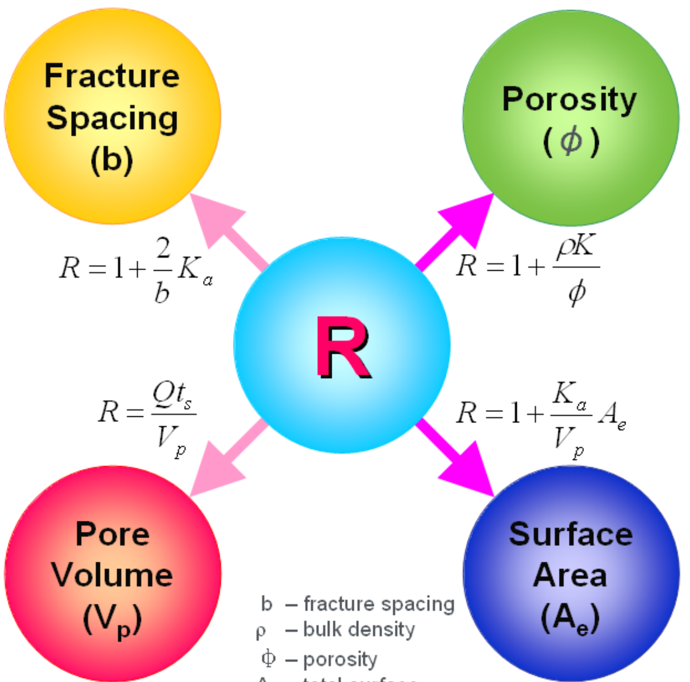
Rock matrix: composite of different mineral surfaces



- Partition of tracer in liquid/solid phases
- Depend on tracer-matrix interactions
- Constant at low tracer concentration
- Different K_s for different tracers
- Determined from static or calibrated tests

Interpretation Development





b – fracture spacing
ρ – bulk density
ϕ – porosity
A_e – total surface
V_p – pore volume
Q – total Flow

Adsorptive Tracer (need to know t_w)

$$R = \frac{t_s}{t_w}$$

t_s: Travel time of adsorptive tracer

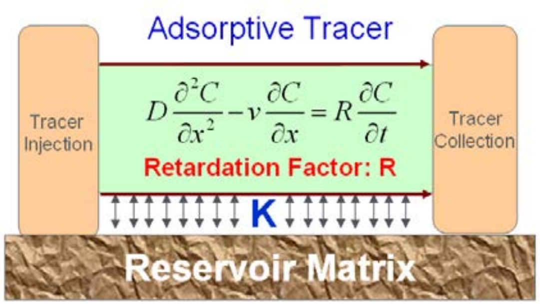
t_w: Travel time of water (or one conservative tracer)

"Smart" Tracer (at least two tracers)

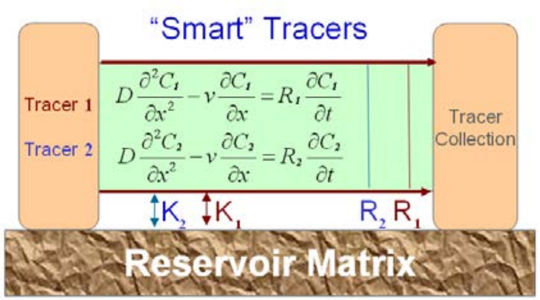
$$\frac{R_1}{R_2} = \frac{t_1}{t_2}$$

t_1: Travel time of tracer 1;

t_2: Travel time of tracer 2.



K: Distribution of tracer in fluid and matrix



Pore Volume

$$V_p = Q\frac{K_2 t_{s1} - K_1 t_{s2}}{K_2 - K_1}$$

Porosity

$$\phi = \frac{\rho(K_1 t_{s2} - K_2 t_{s1})}{t_{s1} - t_{s2}}$$

Surface Area

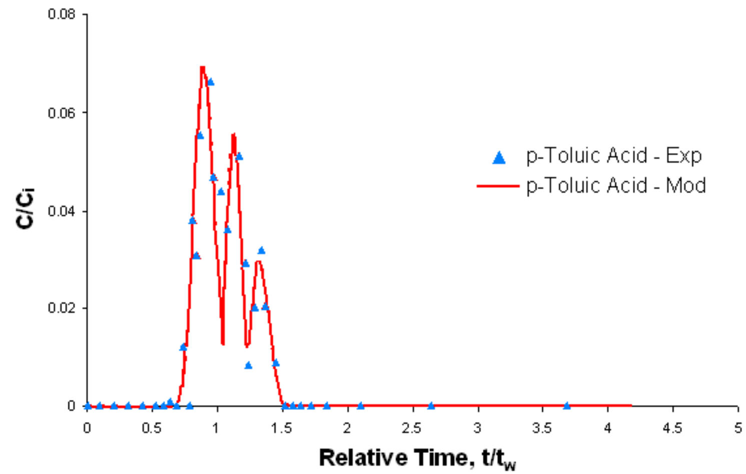
$$A_e = \frac{V_p(t_{s1} - t_{s2})}{K_{a1}t_{s2} - K_{a2}t_{s1}}$$

Interpretation Expansion

Multiple-Path Tracer Envelope

$$C(x,t) = [Q_1 C_1(x,t) + Q_2 C_2(x,t) + Q_3 C_3(x,t) + ...] / Q_T$$

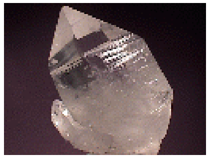
- Differentiate into several path-groups
- Same model for each path
- Specific paths' characterization



Surface Characteristics

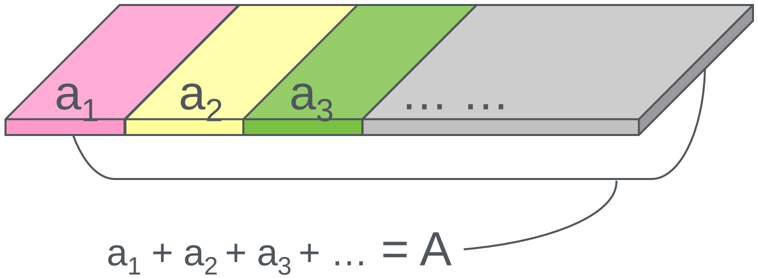
$$K_{obs} = (a_1 K_1 + a_2 K_2 + a_3 K_3 + ...) / A$$

- Adsorption studies on surface with different minerals – calcite
- Adsorption strength on calcite:
  benzoic > phthalic > p-toluic > sorbic > m-toluic > o-toluic
- Estimate rock surface composition

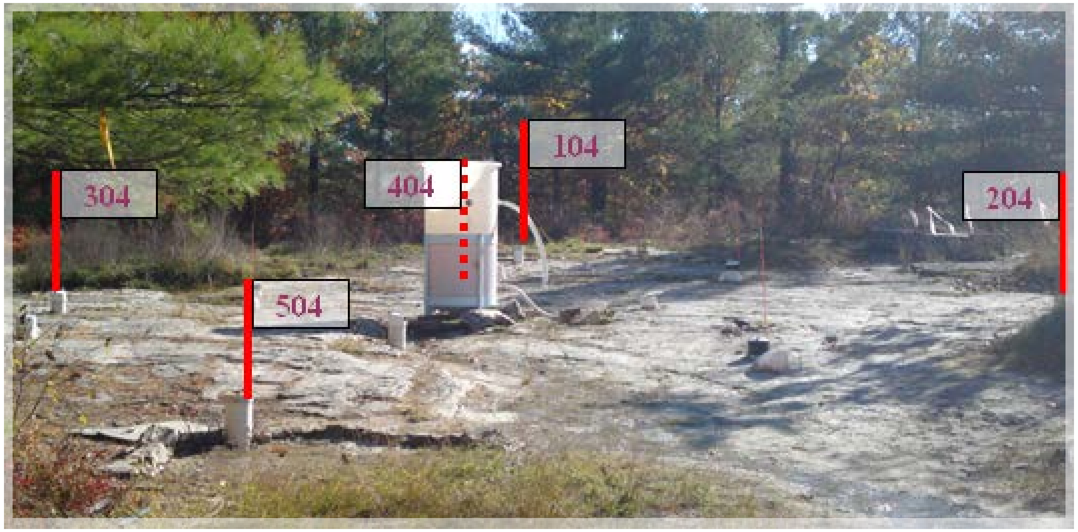

Silicate

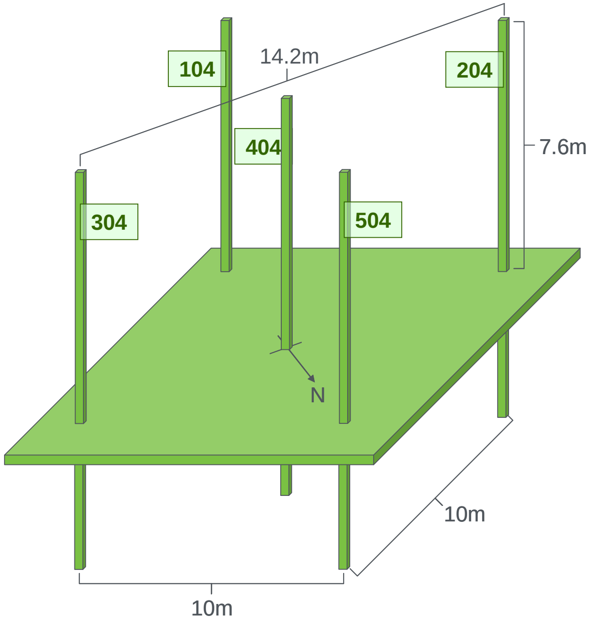

Calcite


Hematite



Field Validation: Altona Flat Rock at Plattsburgh, NY

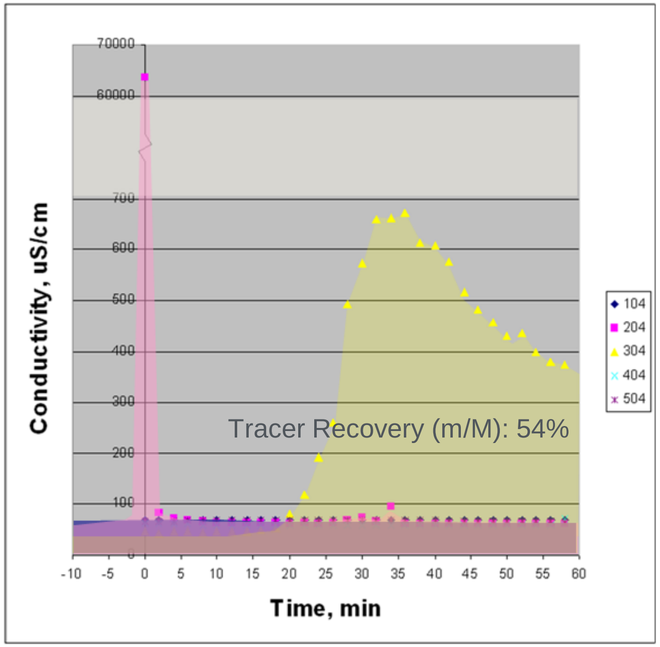


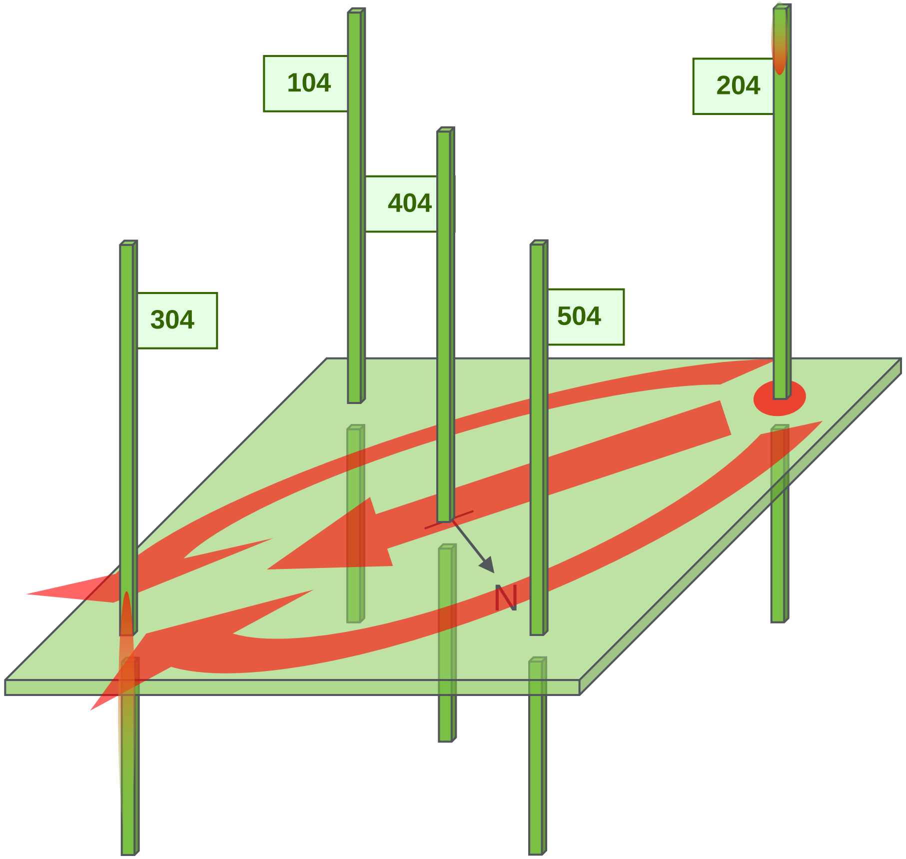


- Potsdam sandstone: nearly pure quartz
- Fractures with transmissivity of $5 m^2/day$
- Mean aperture (b) ~ 0.45mm from literature

Field Test: Inorganic (Conservative) Tracer

- Ionic tracers (NaCl, LiBr, etc)
- High concentration (>10000ppm)
- Data-logger system: detect wells' conductivity variation
- Wells' connectivity; breakthrough
- Pore volume swept: $0.12 m^3$





Field Test: Carboxylic Tracers

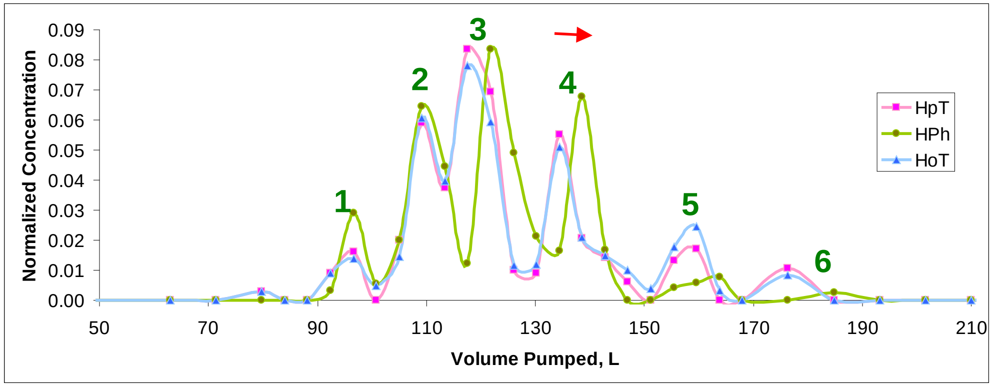
- Low concentration (<1000ppm)
- Insignificant conductivity variation
- Breakthrough pattern → multiple paths
- Tracer-matrix interaction → Path characteristics
- Swept pore volume (total) match result from conservative tracer
- Fracture aperture (b) match literature's value

$$V_p = Q\frac{K_2 t_{s1} - K_1 t_{s2}}{K_2 - K_1}$$

$$A_e = \frac{V_p\left(t_{s1} - t_{s2}\right)}{K_{a1}t_{s2} - K_{a2}t_{s1}}$$

$$b = \frac{2\left(K_{a1}t_{s2} - K_{a2}t_{s1}\right)}{t_{s1} - t_{s2}}$$

Path Group	V, L	A_e, m^2	b, mm
1	5.65	15.03	0.38
2	30.88	24.77	1.27
3	37.14	337.39	0.11
4	30.75	98.18	0.33
5	10.84	30.40	0.36
6	5.30	54.58	0.10
Total swept volume = **0.12m^3**		Average b = **0.42mm**	



Mandatory Summary Slide

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Q1 – Q4

Smart Tracer Selection
Thermal stability
Solubility
Structural variety
Delectability
Environmental friendly
Field Applicability

Analytic Protocol
Esterification reaction
HF-LLME pre-concentration
GC/ECD/NPD analysis
Molecular modeling

Major Accomplishments
(1) A class of Carboxylic tracers
(2) Enhancing the tracer detection limit up to 1000x

Q5 – Q8

Interpretation Model
Tracer-matrix Interaction
Adsorptive tracers
Retardation for differential tracers
Distribution for matrix characters
Multiple-Paths

Laboratory Validation
Static adsorption tests
Column filtration studies
Slim-tube dynamic tests

Major Accomplishments
(1) Theoretical models to predict reserve characters (porosity, fracturing spacing, surface area, heterogeneity etc)
(2) Potential to reduce tracer amounts for cost and environmental benefits

Q9 – Q12

Field Tests
Quartzose sandstone matrix
Inorganic tracer
Smart tracer

Model Improvement
Rock surfaces characters
Flow characters
Thermal Degradation

Major Accomplishments
(1) Model Validation from field test
(2) Engineering and economic assessment of smart tracer applications

Future Directions

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

The current project has officially completed. Continue developments of "smart" tracers as diagnostic tools for the geothermal resources as well as other unconventional energy resources will be pursued. Suggested directions of the further developments are discussed below:

Milestone or Go/No-Go	Status & Expected Completion Date
Continuous development and evaluation of new "smart" tracer compounds for subsurface diagnostic tools	N/A
Further development of basics for the interaction of the "smart" tracer with different surface structures for accurate prediction of subsurface information	N/A
Conduct long-term field validation and applications of "smart" tracer for geothermal resource system	N/A
Exploring applicability of the developing "smart" tracer system for other geological systems (shale, tight sand reservoir etc.)	N/A

Project Management

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Title

Novel Multidimensional Tracers for Geothermal Inter-Wall Diagnostics

Awardees

Lead Organization: Power Energy Environmental Research (PEER) Institute

Partners: **California Institute of Technology**

Mt. Princeton Geothermal LLC,

BJ Energy Service Company

Academics

Materials and process Simulation Center (MSC)
California Institute of Technology (Caltech)
Co-PI: William A. Goddard III

Industries

Mt. Princeton Geothermal LLC
co-PI: Fred Handerson

Industrial Partner BJ Energy Services

Planned Start Date	Planned End Date	Actual Start Date	Current End Date
01/29/2010	12/31/2012	04/29/2010	03/31/2013

Federal Share	Cost Share	Planned Expenses to Date	Actual Expenses to Date	Value of Work Completed to Date	Funding needed to Complete Work
$1,840,000	$460,000	$2,300,000	$2,300,000	100%	0