Thermodynamic Modeling of Mineral Scale at High-Temperatures and High-Pressures

Oil & Gas Offshore FWP 1022409 – Task 8
Carbon Management and Oil and Gas Research Project Review Meeting
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U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Mineral Scale Team

NATIONAL ENERGY TECHNOLOGY LABORATORY

Isaac Gamwo (PI)

- **Theoretical**
- **Modeling**
- **Computational**
- **Deployment to Industry** — **Integrate Modeling and Experimental efforts**
- **(Experimental) Design/build/test scale and solubility experiments**
- **Experimental Model Validation**

Isaac Gamwo

Serguei Lvov

Derek Hall

PENN STATE NITTANY LIONS

OLI Studio analyzers+scalechem

Hseen Baled

Ward Burgess

Isaac Gamwo

University of Pittsburgh

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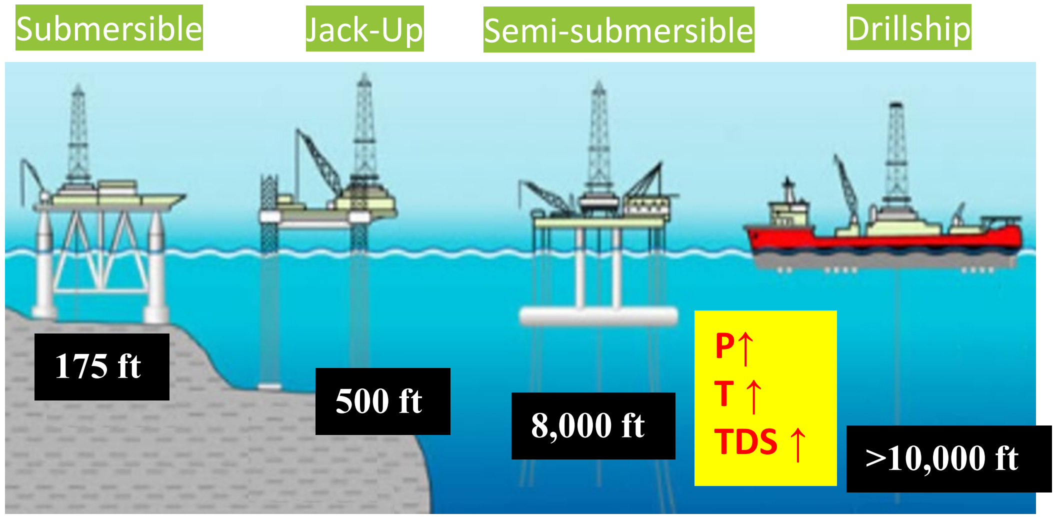
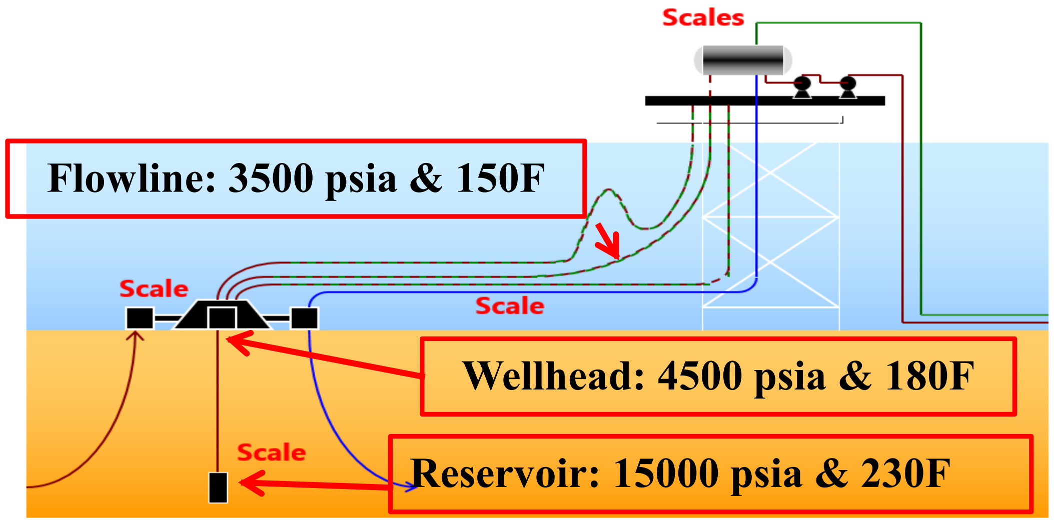
Identified An Oilfield Production and Safety Threat, Mineral Scale Deposition:





- Flow Restriction in Pipeline caused by mineral scale formation[1].
- Scales are hard crystalline salts that exceed their solubility under the given physicochemical conditions.

As an extreme example, oil production fell from 30,000 B/D to ZERO in just 24 hours because of scaling[2] in the Miller North Sea well.

$$Ba^{2+}(aq) + SO_4^{-}(aq) \rightleftharpoons BaSO_4(s)\downarrow$$

1. https://fqechemicals.com/contaminants/barium-sulfate-scale/
2. Brown, M., "Full Scale Attack," BP Technology Magazine, Review 30 (1998), p. 30-32.

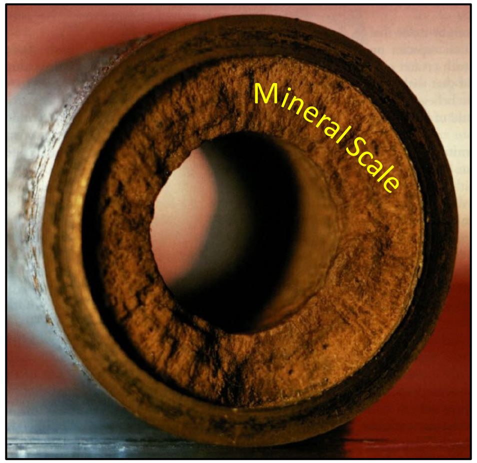
Goal & Challenges

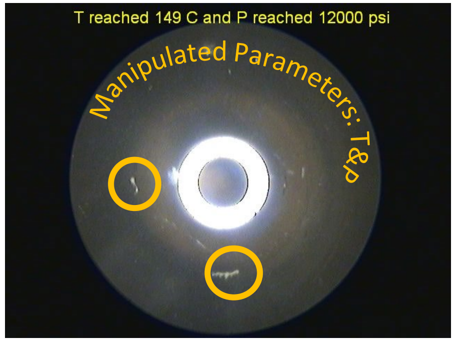
Motivation & Goal:

- Technology exists for preventing the occurrence of scale if scale formation can be predicted.
- Existing models fail to predict scale formation at ultradeep well conditions.
- Develop predictive model for HTHP mineral scale formation to proactively mitigate oil production losses, safety and environmental concerns.

Challenges:

- Why do scale prediction models fail at HTHP conditions?
- How can we develop a reliable model for HTHP conditions?
- Can we manipulate T&P in the lab to reproduce the scale formation?

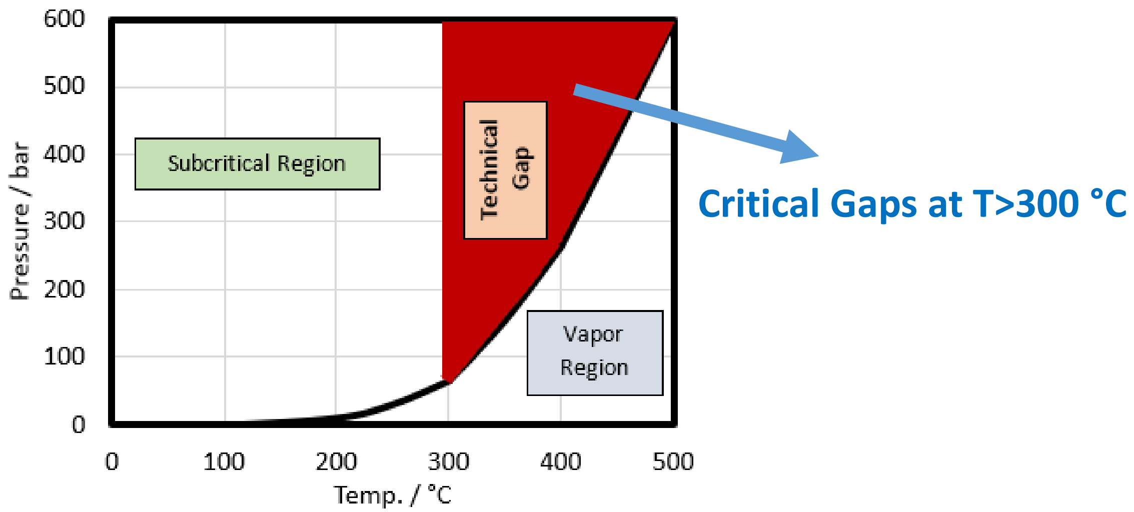




Mineral Scale NETL Lab

Technical Gap Identified in Scale Modeling

- Identified a knowledge gap[1] in the current state-of-the art models including OLI Studio[2]: ScaleChem.
- Software[1] lose accuracy at temperatures above 300 °C.
- OLI's commercial software is currently used worldwide by over 400 industrial companies including major oil and gas companies.
- The fundamental research question is why does the Helgeson–Kirkham–Flowers (HKF) EOS model fail at temperatures beyond 300 °C?



Red shows T &P region of interest (Technical Gap) where current thermodynamic models used by mineral scaling models break down.

<u>Limitations of the current OLI Thermodynamic Model</u>

Aqueous Phase

$X_{H2O} > 0.65$

$-50^{o}C < T < 300^{o}C$

0 Atm < P < 1500 Atm

$0 < I_{brine} < 30$

1. Johnson, J. W., Oelkers, E. H., & Helgeson, H. C. (1992). SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0 to 1000˚C. *Computers and Geosciences*, *18*, 899–947.
2. OLI Systems. (n.d.). *OLI Studio Stream Analyzer User Guide. V 9.5*.

Approach and Outcome

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- **Approach:**

Combine theoretical, computational, and experimental approaches to reliably predict mineral precipitations at HTHP conditions.

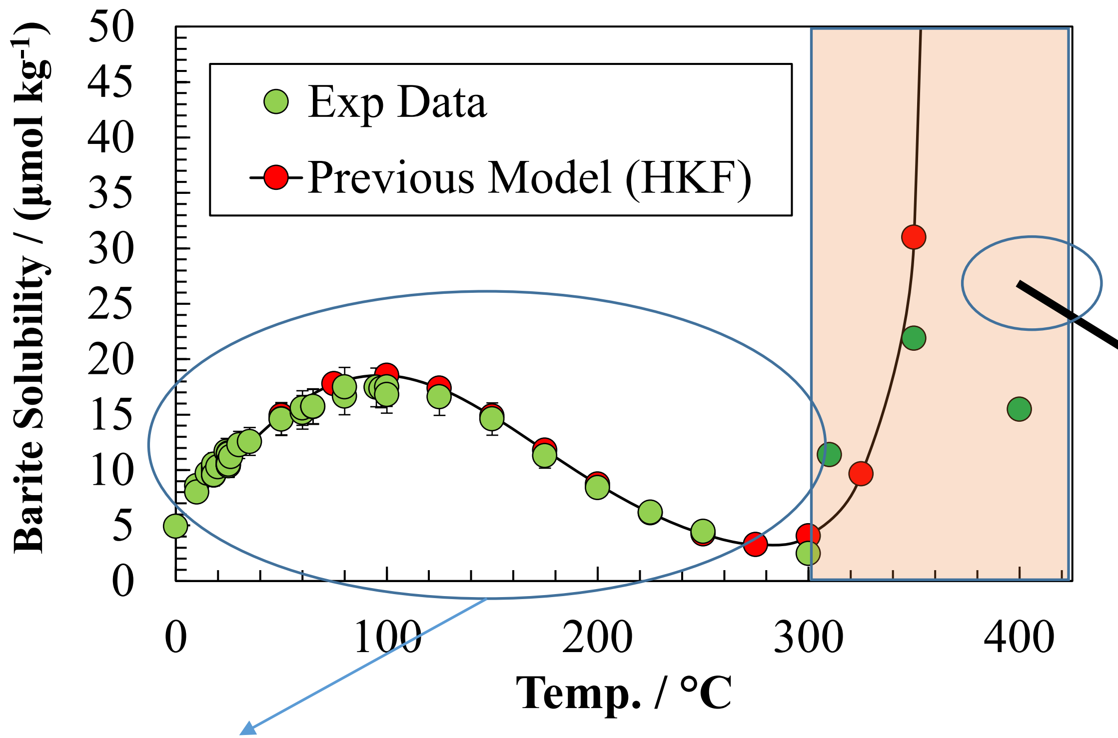
- **Outcome:**

A validated mineral scale model at HTHP conditions.

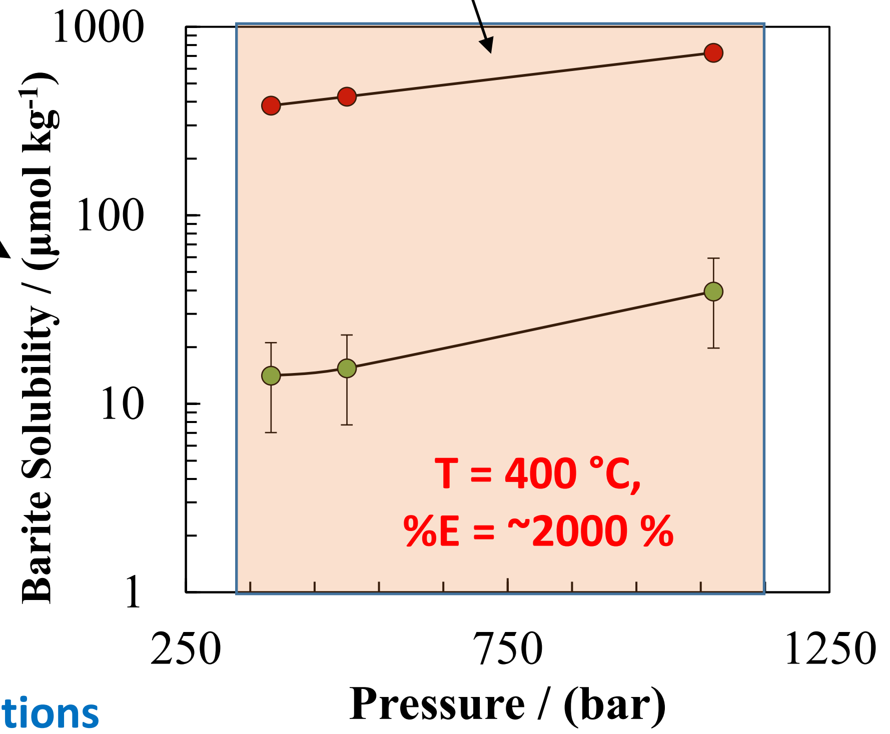
- **Key Deliverable**:

Incorporate our new model into a commercial software that is currently used in the petroleum industry to mitigate scale formation problems.

Problems with Current State of the Art Thermodynamic models for Scale



At high-temperature model loses accuracy; average % Error 2000%



Predicted and Experimental data agree at temperatures up to 300 ^{0}C

HKF Predictions - Failed at HTHP Conditions

Barium Sulfate Scales in Offshore Oilfields

Mixing of incompatible brines:

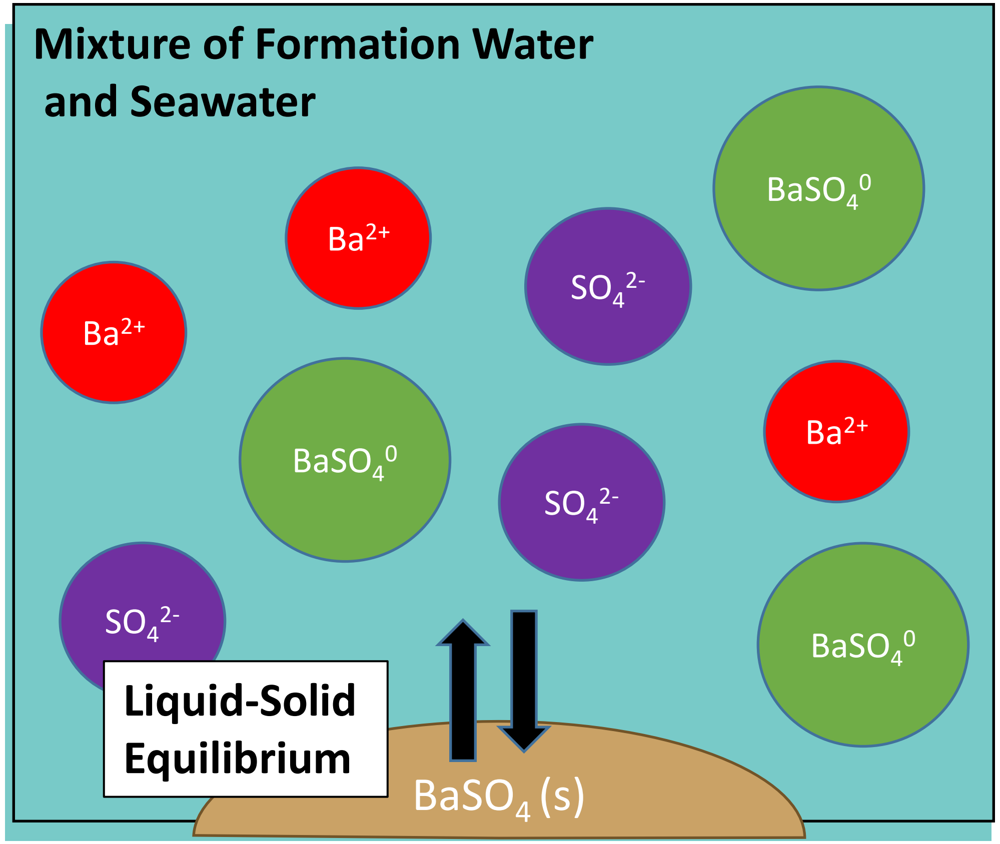
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightleftarrows BaSO_4^0(aq)$$

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightleftarrows BaSO_4(s)$$

Model Gibbs Energies of Reaction for predicting Barite scale, ΔG_r

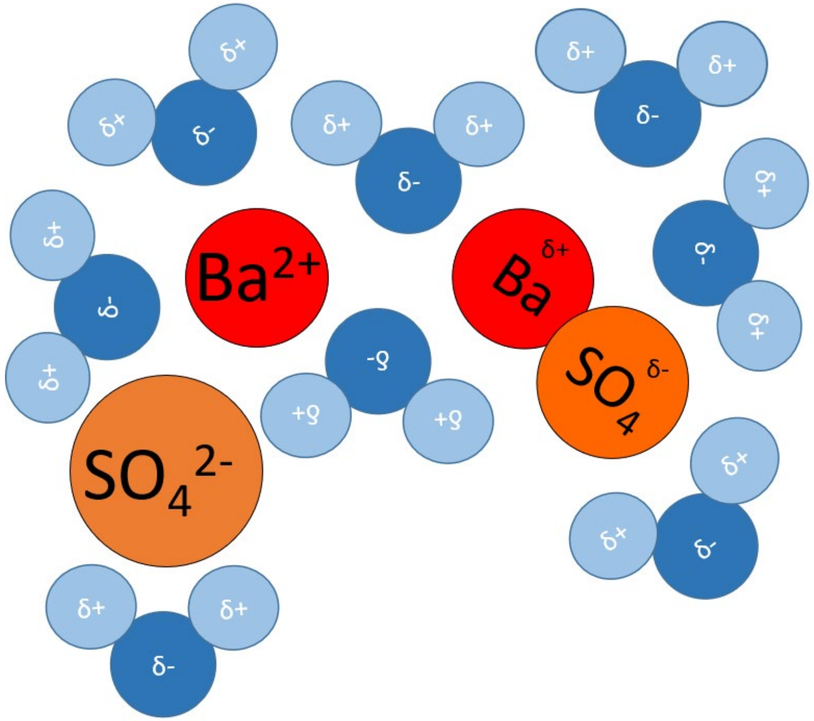
Gibbs Energy of reaction, ΔG_r

- Describes which way the reaction proceeds.
- Can be either theoretically calculated or measured.

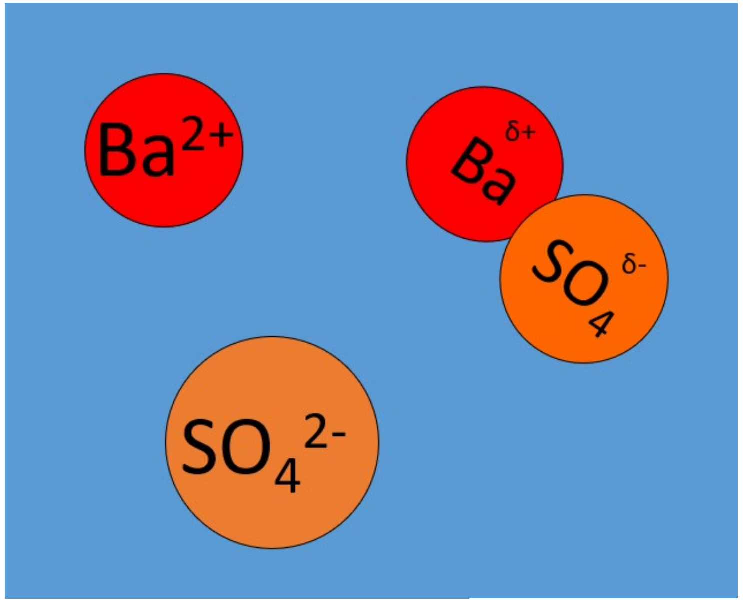


Post-Scale

New Model Based on Molecular Statistical Thermodynamics (MST)



Old Models Assume a Continuous Dielectric Medium (Classical Thermodynamics)



$$\Delta G = -\frac{N_A z^2 e^2}{8\pi\epsilon_0 r_0}\left(1 - \frac{1}{\epsilon_r}\right)$$

The new model uses the most sophisticated molecular statistical theory for ion-dipole and dipole-dipole interactions.

The old model also used negative diameters in the Born equation for ion pairs which is fundamentally incorrect.

Key Molecular Statistical Theory Equations

$$G_i = G_i^{IG} + G_i^{HS} + G_i^{ID} + G_i^{DD} + G_i^{SS} + G_i^{MS}$$

$$\frac{G_i^{HS}}{RT} = -\ln(1-\eta) + 3K\frac{\eta}{1-\eta} + 3K^2\left(\frac{\eta}{(1-\eta)^2} + \frac{\eta}{(1-\eta)} + \ln(1-\eta)\right)$$
$$-K^3\left(\frac{3\eta^3 - 6\eta^2 + \beta\eta}{(1-\eta)^3} + 2\ln(1-\eta)\right)$$

$$\frac{G_i^{ID}}{RT} = -Ne^2 z_i^2 \frac{(1-1/\varepsilon)}{\sigma_i + \sigma_w(\beta_6/\beta_3)}$$

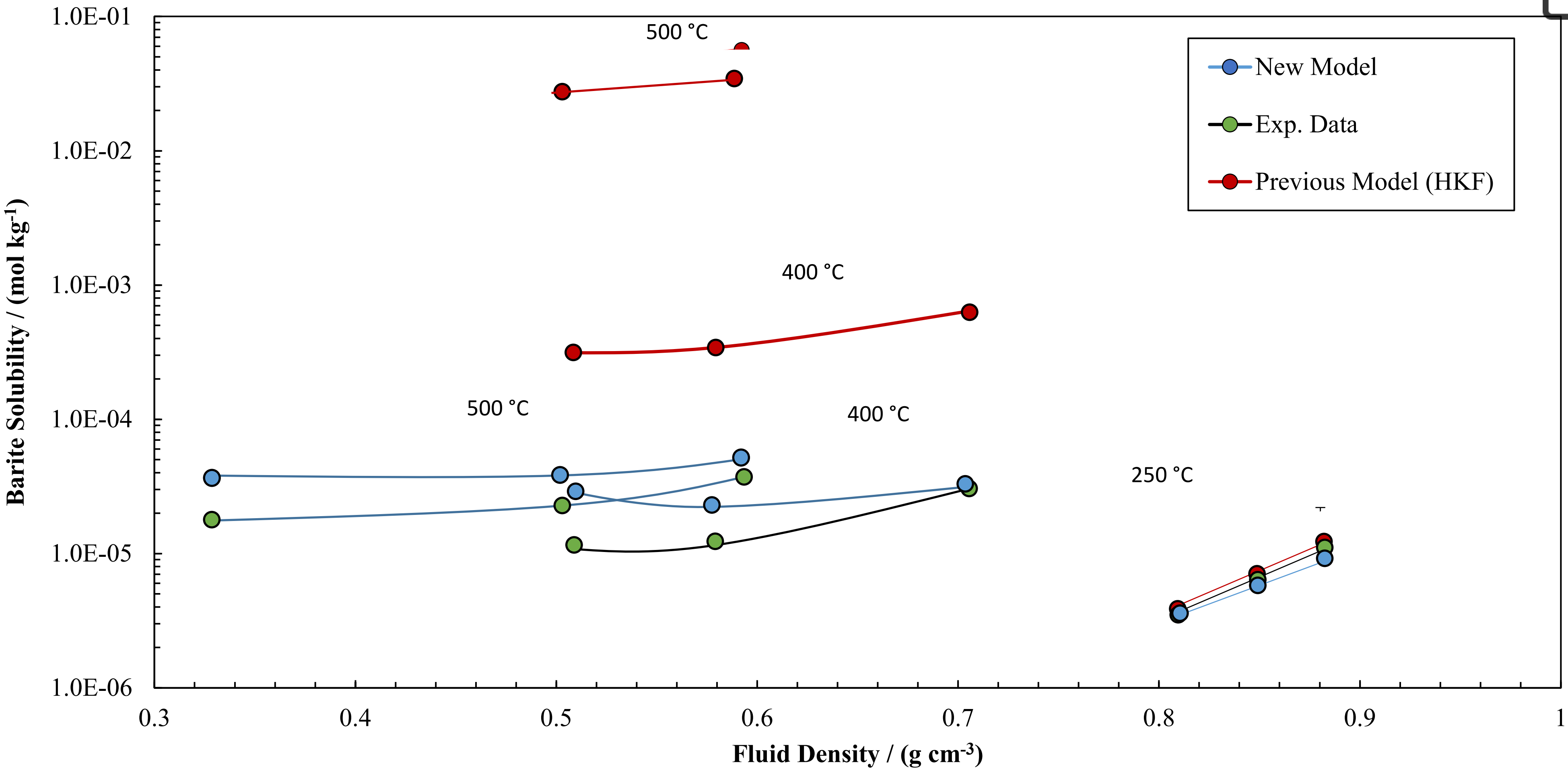
$$\frac{G_i^{DD}}{RT} = \frac{-8Np_i^2(\varepsilon-1)}{2\sigma_w^3\left(1-\frac{\beta_{12}}{\beta_3}\right)\left(\frac{\beta_{12}}{\beta_6}\right)^3 + 2\varepsilon\left(\sigma_i + \sigma_w\frac{\beta_6}{\beta_3}\right)^3 + \left(\sigma_i + \sigma_w\frac{\beta_{12}}{\beta_6}\right)^3}$$

$$\frac{G_i^{SS}}{RT} = -RTln(\rho RT/P^*)$$

$$\frac{G_i^{MS}}{RT} = -RTln(M_s/1000)$$

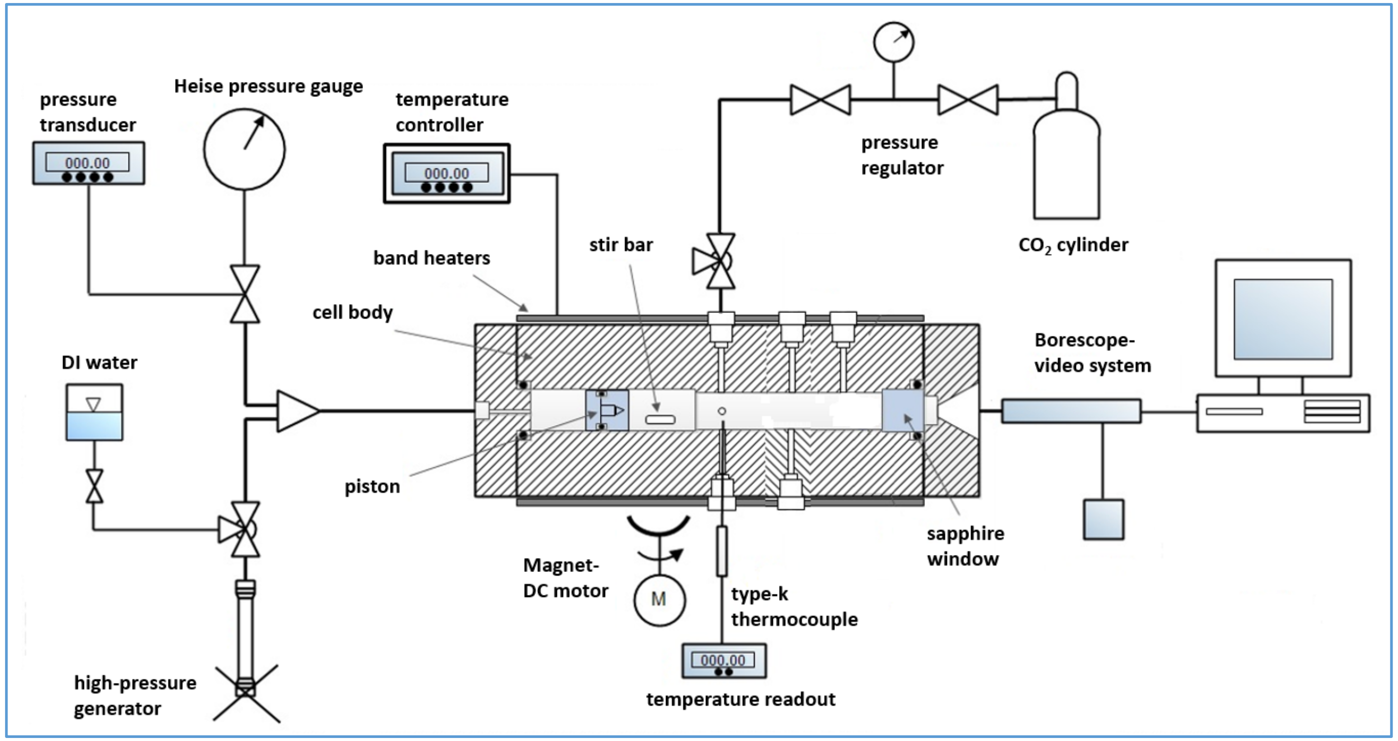
- **Modern molecular statistical thermodynamics provides a promising avenue to quantify the thermodynamic properties.**
- **Using perturbation theory, the standard Gibbs energy of formation, G_i , can be quantified as the sum of contributions.**
  - **Hard sphere**
  - **Ion-dipole**
  - **Dipole-dipole**
  - **Standard state**
  - **Molarity standard state**
- **Many of these contributions can be quantified through statistical mechanics expressions with some approximations.**
- **G_i values are used to calculate the Gibbs energy of a reaction.**

Modeling - Demonstrated Research Accomplishment
Comparison old model, new model, and experimental data (250, 400, 500°C)



New model: State-of-the art model predictions compared to experimental HTHP data at a range of pressures from 90 to 1,100 bar and temperatures of 250 °C , 400°C, 500 °C.

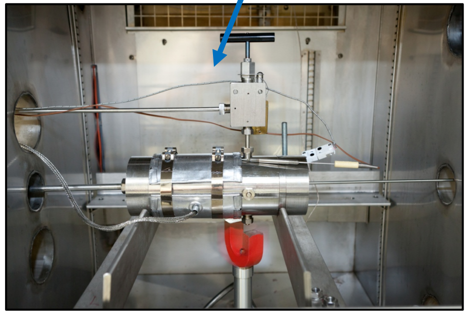
Current Experimental HTHP Scale Deposit Setup



Schematic NETL Scale Deposit Experimental Setup

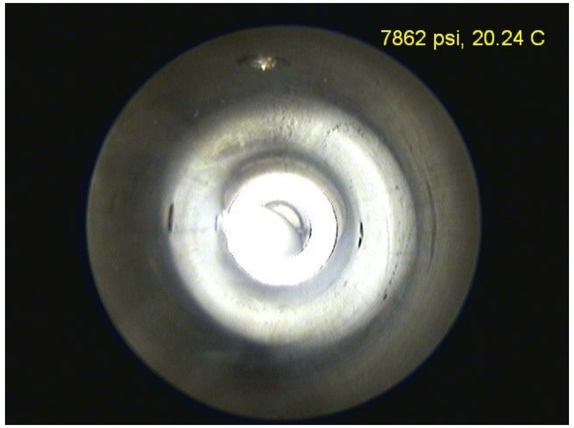
NETL HTHP Scale Deposit Experimental Setup

Operates to 600°F (315°C) and 40,000 psi (2,758 bar)

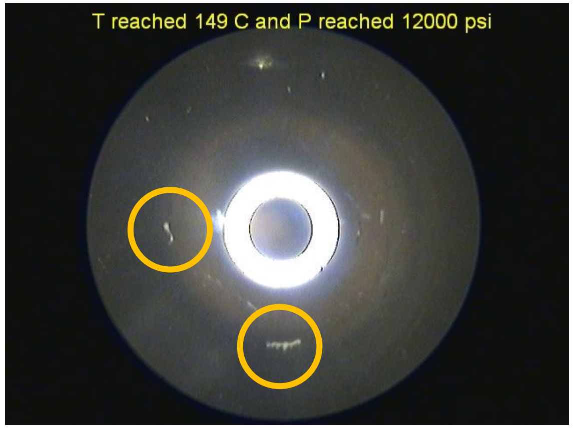


Experimental Still Images from-Experimental Scale Deposit Movie

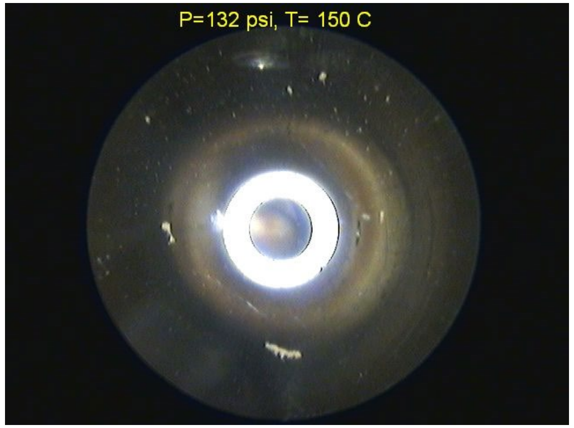
- Qualitative: Visualization of scale deposit at NETL's Experimental Facility
  Manipulated Parameters: T and P (Presented at the 2020 AIChE Virtual Meeting, Nov. 2020)



(1)
Clear calcite solution



(2)
Calcite deposits due to heating



(3)
More deposits due to depressurizing

- Quantitative: Developing New Capability to Measure Mineral Solubility at HTHP

Movie Experimental Scale Deposit in NETL HTHP Apparatus uploaded to YouTube
https://youtu.be/GI_My7bv-hE

Implementation into Commercial Applications

Technology-to-Market Path

- OLI Systems, Inc., a commercial software released a support letter. CTO specified steps needed to implement model in the commercial software.
- The model needs to be validated for an additional system with robust HTHP data (OLI Studio requested **sodium phosphate**).
- Conduct HTHP solubility experiments at NETL to validate the model (if Funded)
- Once completed, the model can be deployed to the public and added into OLI Studio to extend their robust speciation database that captures more than 6000+ species.
- Dr. Andre Anderko, CTO "… *we would be interested in implementing it in our software after it becomes sufficiently comprehensive for industrial applications…*"

OLI systems, Inc.

the chemistry right

OLI systems, inc.

October 29, 2019

...eral Engineering
...rsity

I am writing to express our interest in your work in collaboration with the National Energy Technology Laboratory on a new molecular model for predicting the standard-state properties of aqueous species in a wide range of temperatures and densities. I strongly believe that this work has the potential to significantly advance the state of the art of thermodynamic modeling of aqueous systems at high temperatures.

OLI Systems is engaged in modeling the thermodynamic properties of aqueous systems for various applications including upstream oil and gas production, petroleum refining, power generation, chemical processes, metals and mining and fundamental research focused on energy and materials. The OLI software is used by over 400 industrial companies across the world and is a de facto standard for simulating aqueous-based chemical processes involving electrolytes.

Accurate computation of standard-state properties is an extremely important part of our modeling technology. It is the essential starting point for predicting ionic speciation, solubility and other thermodynamic properties, which are a *sine qua non* for simulating industrial processes. For calculating standard-state properties, we currently use the well-known Helgeson-Kirkham-Flowers (HKF) equation of state. While the HKF equation of state is highly accurate in dense aqueous systems, it loses its accuracy in less dense, high-temperature systems, especially at temperatures above 300 °C and pressures below 500 bar. Faced with these limitations, we are prevented from solving our clients' problems at such conditions. In fact, we are often forced to turn down potential users who are interested in simulating chemical systems at conditions close to or above the critical point of water. Such conditions are of great importance for geothermal energy production and power cycle chemistry in power generation. Furthermore, they occur in oil and gas production as the industry moves to increasingly deeper wells.

OLI Systems is keenly interested in following your work. Ultimately, we would be interested in implementing it in our software after it becomes sufficiently comprehensive for industrial applications. From our side, we would like to assist you and your team in your development by providing future use cases and discussing the application areas for the new model.

Sincerely yours,

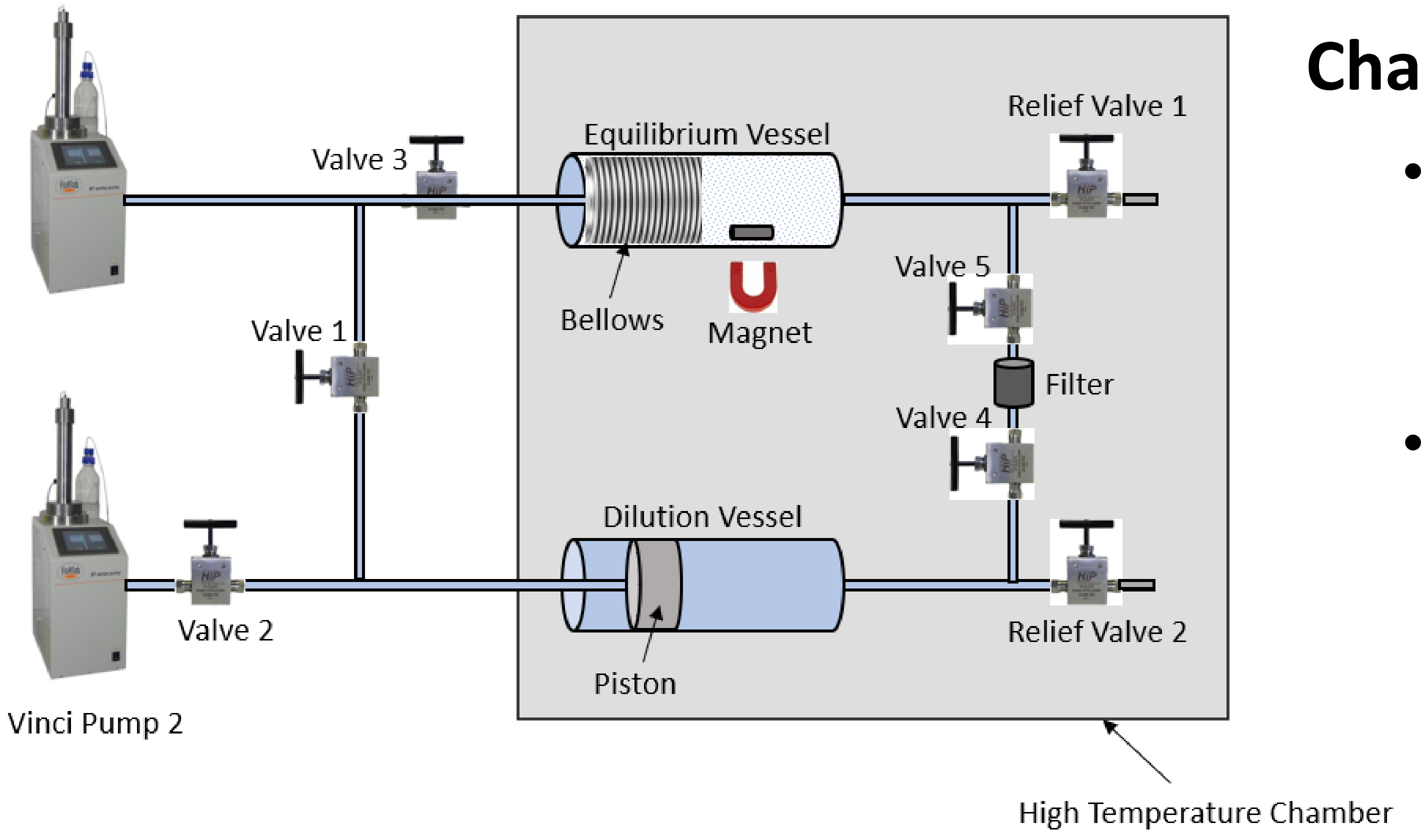
Andre Anderko, PhD, FNACE
Chief Technology Officer
Phone: +1 973-539-4996 ext. 25
Email: aanderko@olisystems.com

www.olisystems.com

OLI systems, inc.

OLI's Chief Technology Officer's (CTO) Letter of Interest to collaborate on Task 8

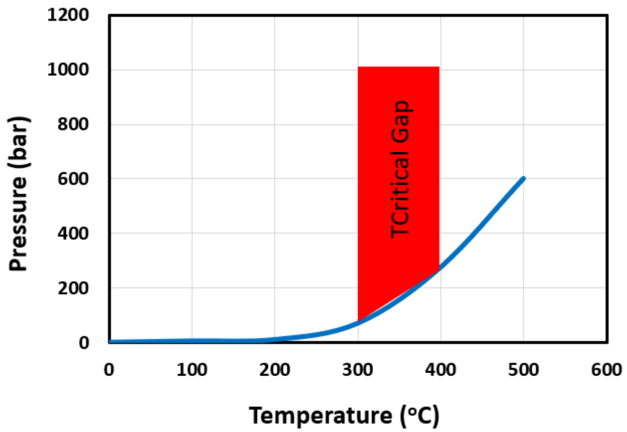
Future Work: New NETL Solubility Experimental Set-up



Challenges

- Long lead times for the delivery of the materials ordered.
- Long lead time to complete the design and wiring by Leidos Engineers.

Experimental studies of the effects of pressure, temperature, pH, and ionic strength on the solubility of $CaSO_4$-NaCl-H_2O, $BaSO_4$-NaCl-H_2O, and Na_3PO_4-NaCl-H_2O



Accomplishments

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- Extended state-of-the art scaling models to HTHP conditions to close the technical gap. Successfully tested the new model on barium sulfate, a common oilfield mineral.
- Documented the model and barium sulfate results in a book chapter manuscript accepted for publication.
- Collaborating with OLI to implement the newly developed thermodynamic scale model into OLI Studio: ScaleChem software.
- **Developing a new experimental capability to measure mineral solubility at HTHP conditions.**
- Mineral scale model under development is being solicited by OLI to incorporate into their mineral sale deposit software. OLI is used by over 400 Companies worldwide.
- Results from this research would be helpful in pro-active mitigation of scale formation in HTHP reservoirs.
- Wide range of applications including Geothermal Energy

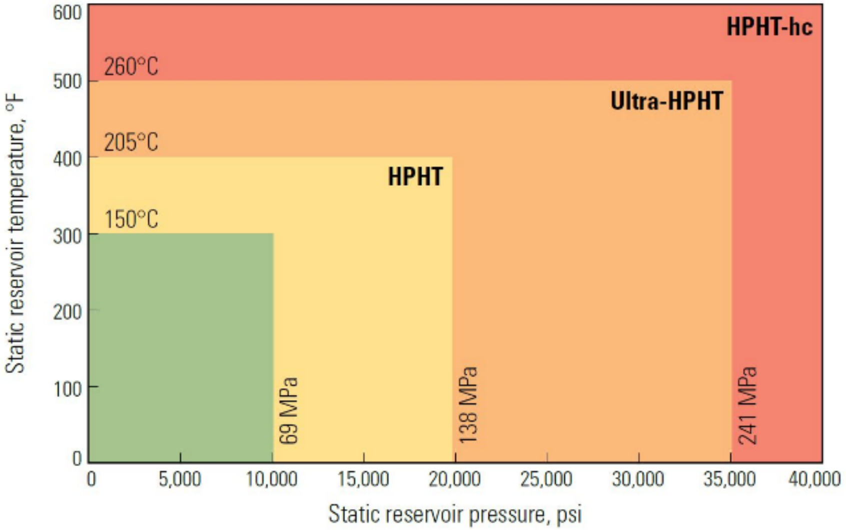
Outreach Product Released

NATIONAL ENERGY TECHNOLOGY LABORATORY

- **Gamwo, I. K., Hall, O.D., Lvov, S., Baled, O., H, Modeling Barium Sulfate Precipitation in High Temperature Systems based on Molecular Statistical Thermodynamics Model, 2021 AIChE Annual Meeting, Boston, MA, November 7-19, 2021.**

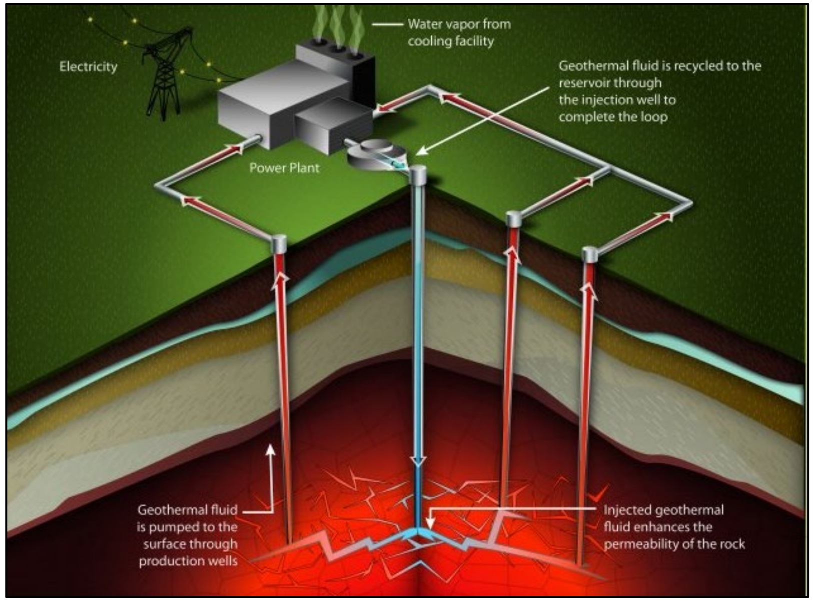
- **Hall, D.M., Lvov, S.N, Gamwo, I.K, Prediction of Barium Sulfate Deposition in Petroleum and Hydrothermal Systems, *Solid–Liquid Separation Technologies: Applications for Produced Water*, CRC Press Taylor & Francis, cat. 351983, accepted, 2021.**

Wide Range of Applications of Extended HTHP Mineral Scale Models



HPHT Oil and Gas Wells

Fossil Fuel Powerplants



Geothermal Energy

THANK *YOU FOR YOUR ATTENTION*

QUESTIONS?

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