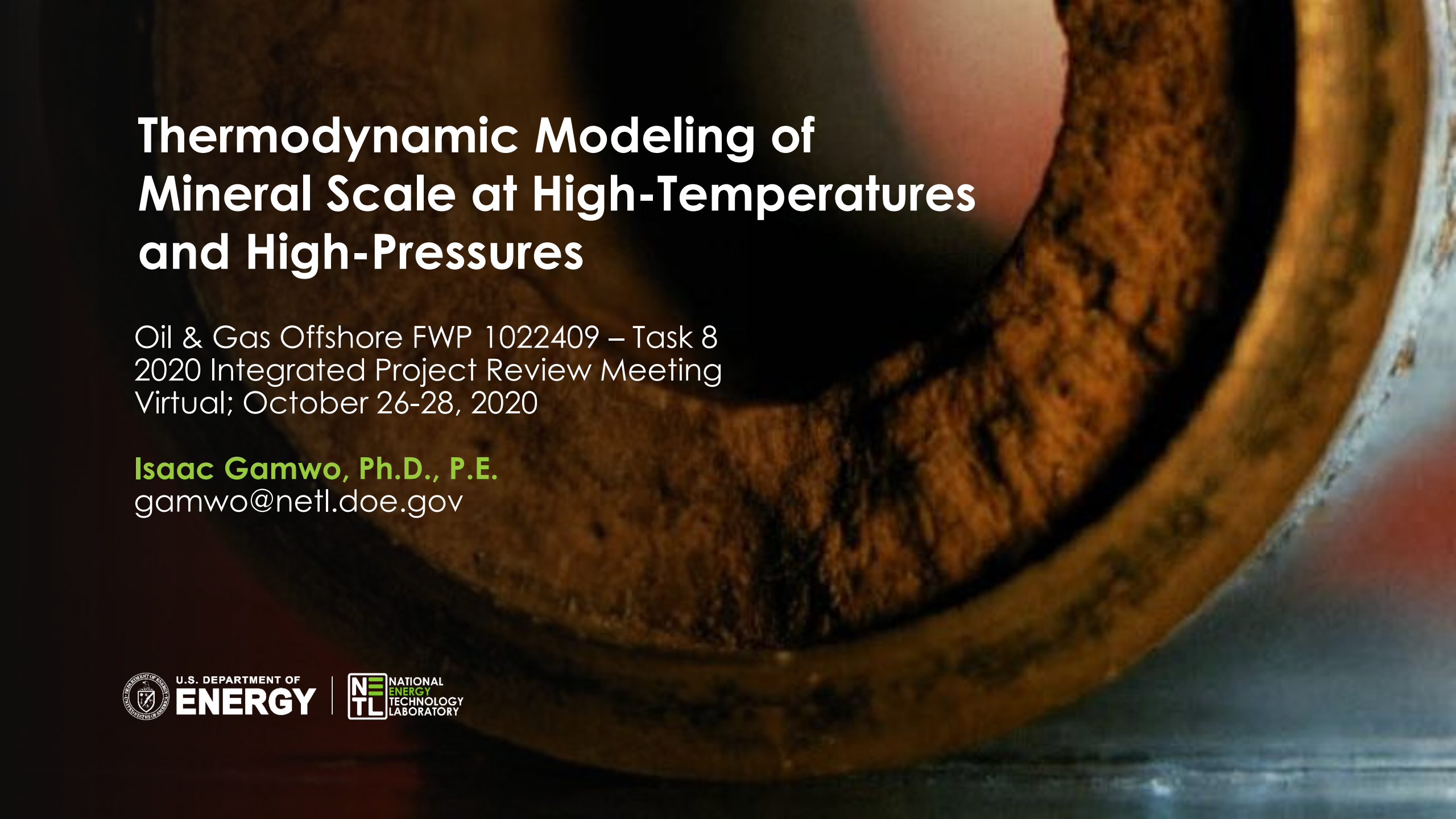

Thermodynamic Modeling of Mineral Scale at High-Temperatures and High-Pressures

Oil & Gas Offshore FWP 1022409 – Task 8
2020 Integrated Project Review Meeting
Virtual; October 26-28, 2020

Isaac Gamwo, Ph.D., P.E.
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U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Mineral Scale Team

EY19-EY21

Isaac Gamwo

(PI)

Theoretical

Modeling

Computational

(Experimental) Design/build/test scale and solubility experiments

Experimental Model Validation

Serguei Lvov

Derek Hall

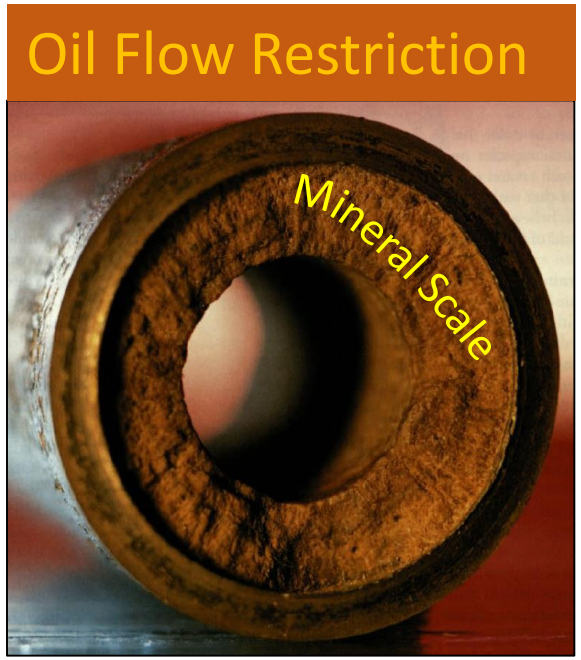
Deployment to Industry

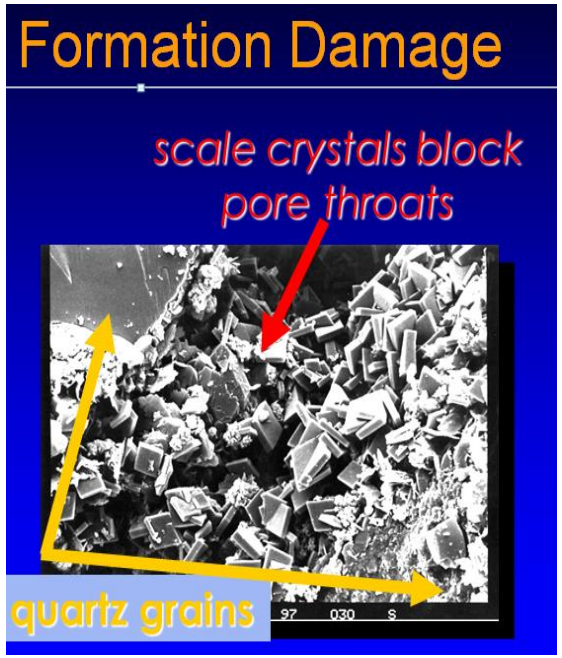
Integrate Modeling and Experimental efforts

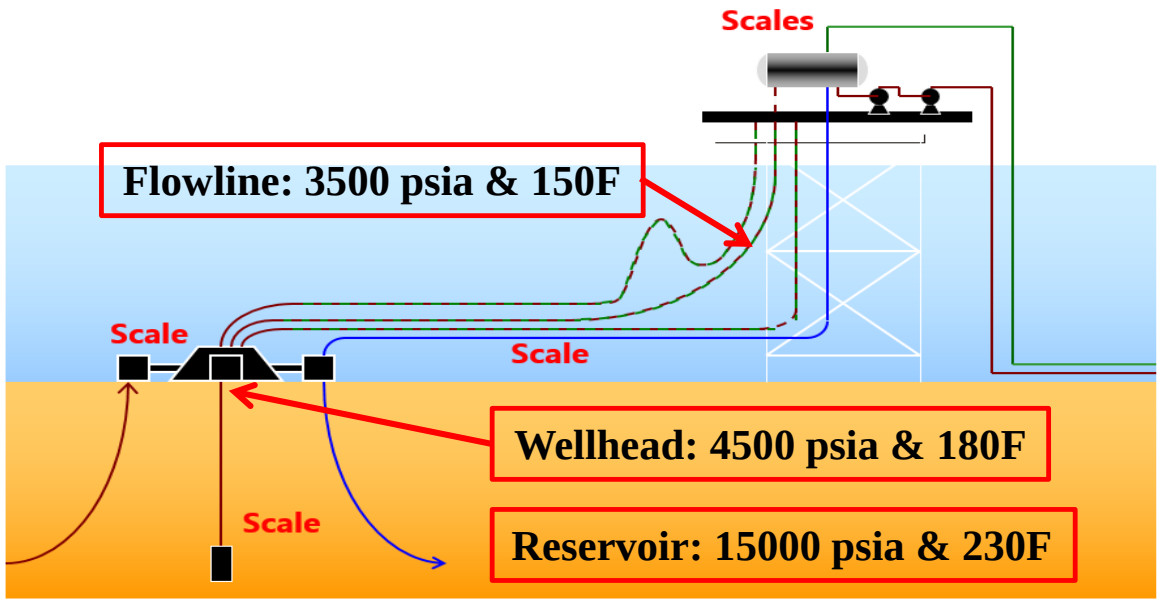
Hseen Baled

Ward Burgess

Oil Field Production Problems Caused by Mineral Scales: Inefficient unsafe Production







- Scale related loss accounts for approx. 0.25% of global GDP, that is ca. USD 200 billion
- Majority of loss comes from petroleum upstream:
  - Delayed production;
  - Non-production time (crew cost/equipment rental);
  - Chemical cost; corrosion
- As an extreme example, in a North Sea well, production fell from 30,000 B/D to zero in 24 hrs due to mineral scaling.

Storage)

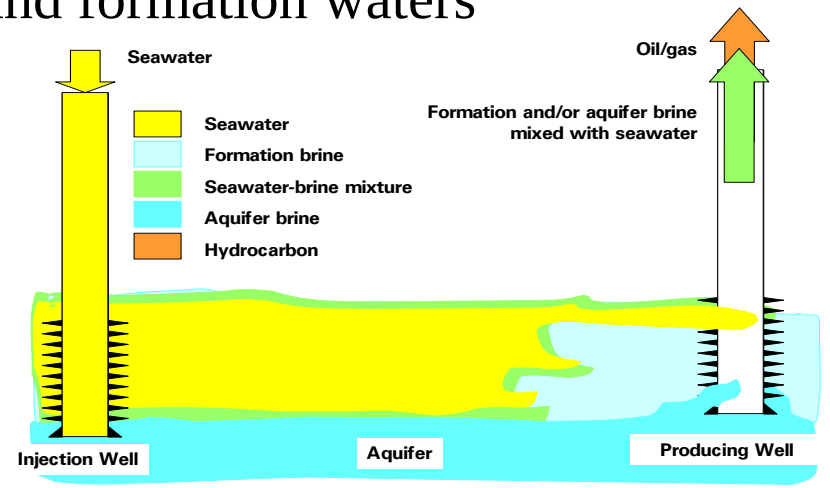
Common Oilfield Mineral Scales

- Scales are hard crystalline salts that exceed their **solubility** under the given physicochemical conditions
- Scale formation only occurs in water phase: no water, no scale.
- The most common oilfield scales include **carbonates** and **sulfates**
  - Carbonates, such as **$CaCO_3$ (calcite)**, form as a result of conditional changes

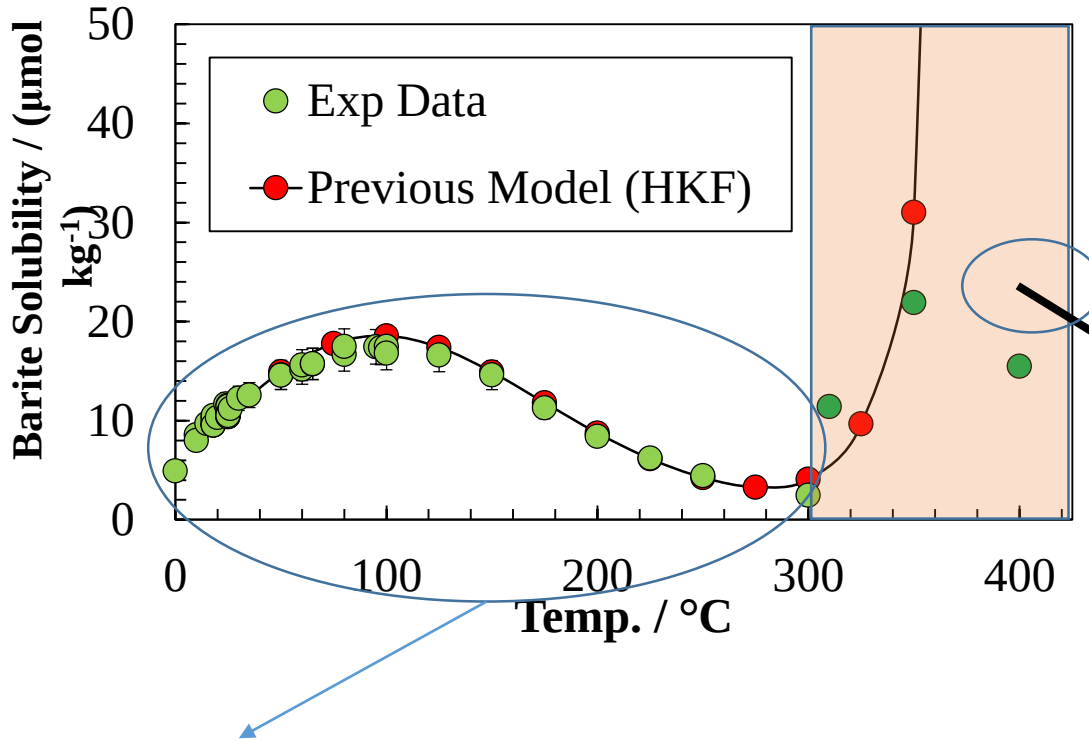
$$Ca^{2+}(aq) + 2\,HCO_3^-(aq) \rightleftharpoons CaCO_3(s)\downarrow + CO_2(g)\uparrow + H_2O(l)$$

  - Sulfates, such as **$BaSO_4$ (barite)** form due to mixing of sea and formation waters

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

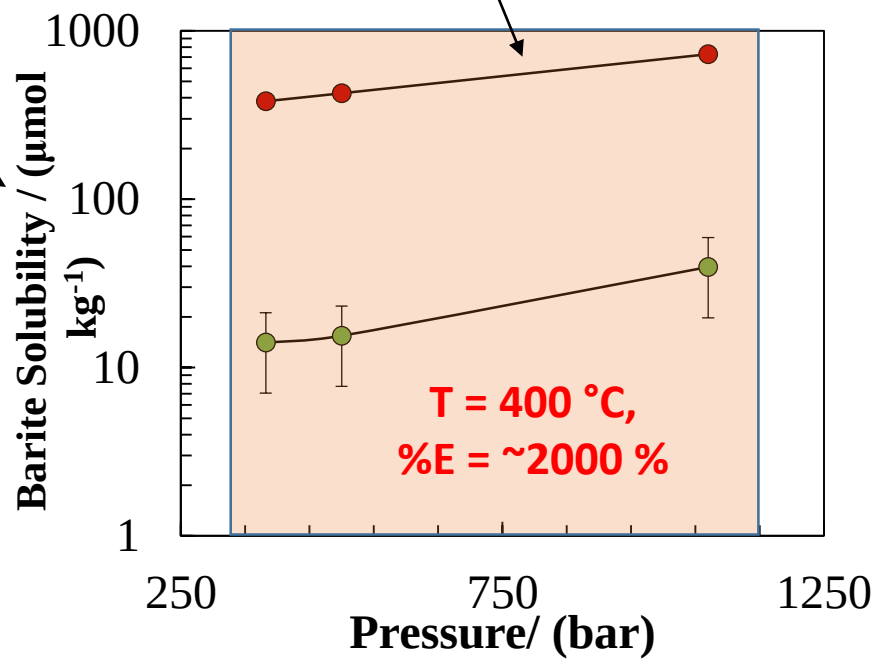


Problems with Current State of the Art Thermodynamic models for Scale Predictions- Failed at HTHP Conditions



Zoom

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



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

Project Goals

- Develop a thermodynamic model for simulating scaling in the high-temperature and high-pressure (HTHP) oil and natural gas production.
- Confirm modeling results by experimental studies on mineral solubilities at HTHP.
- Deploy Model to the Public -Implement this model into OLI Systems software-an industrial standard software for predicting scaling problems.

Project Planning, Execution and accomplishments (EY10-EY21) Future work EY22

	EY19	EY20	EY21	EY22
Modeling Effort to assist Scaling Experiments	**Review SLAC and NETL Scaling Projects** **Identify areas to optimize/expedite Experiments with modeling efforts**	Develop work Plan to collaborate with SLAC and NETL Scaling projects	Search for funding toe execute the Work Plan	Execute the work plan
Develop Advanced Thermodynamic models for HTHP scale predictions	• Review scale models • Assess Key knowledge gaps in HTHP Scale deposit models	• Modify models to address key gaps at HTHP conditions • Develop higher accurate scale formation models at HTHP conditions	• Validate models with experimental data • Pursue dissemination of models through OLI	• Implement into OLI
HTHP Scale Deposit Experiment	• Modify existing HTHP experimental cell to visualize scale deposits	• Generate experimental movies of scale formation at various T&P	• Design/build/test solubility cell • Validate new HTHP Scale formation models	

Planning

Execution

Accomplishments

Combine theoretical, computational and experimental approaches to address HTHP Scaling problems

Barium Sulfate Scales in Offshore Oilfields

Mixing of incompatible brines

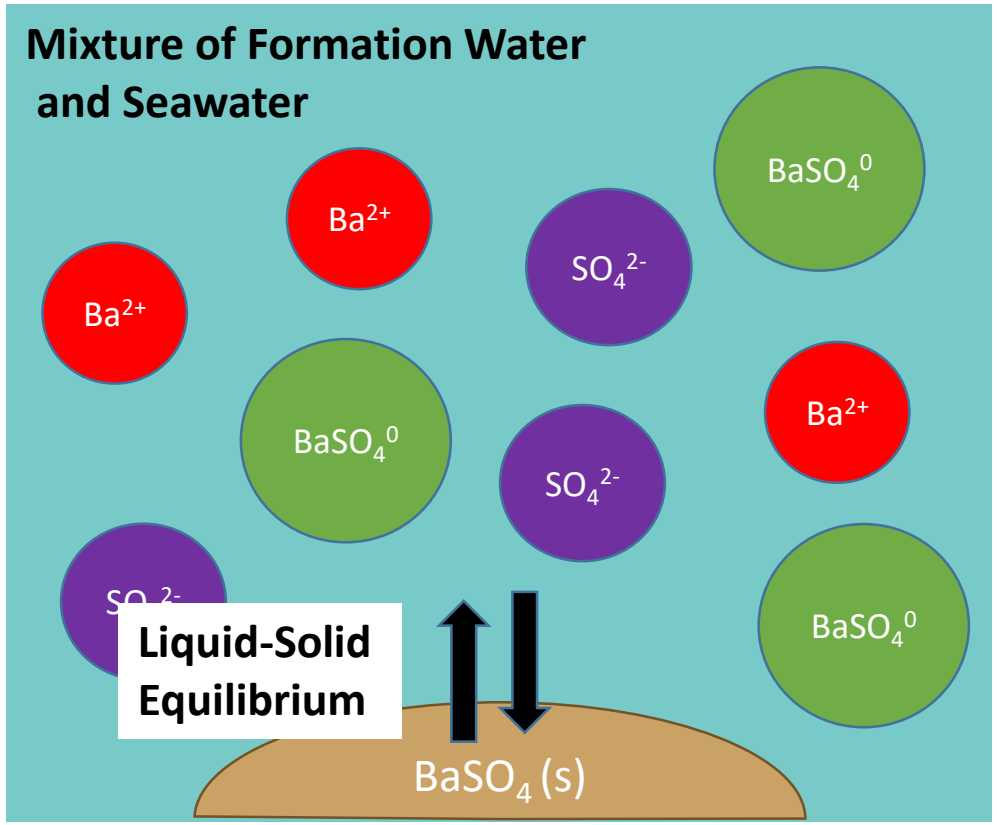
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightleftarrows BaSO_4^0(aq)$$

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

Model Gibbs Energies of Formation for predicting Barite scale, ΔG

Gibbs Energy of reaction, ΔG

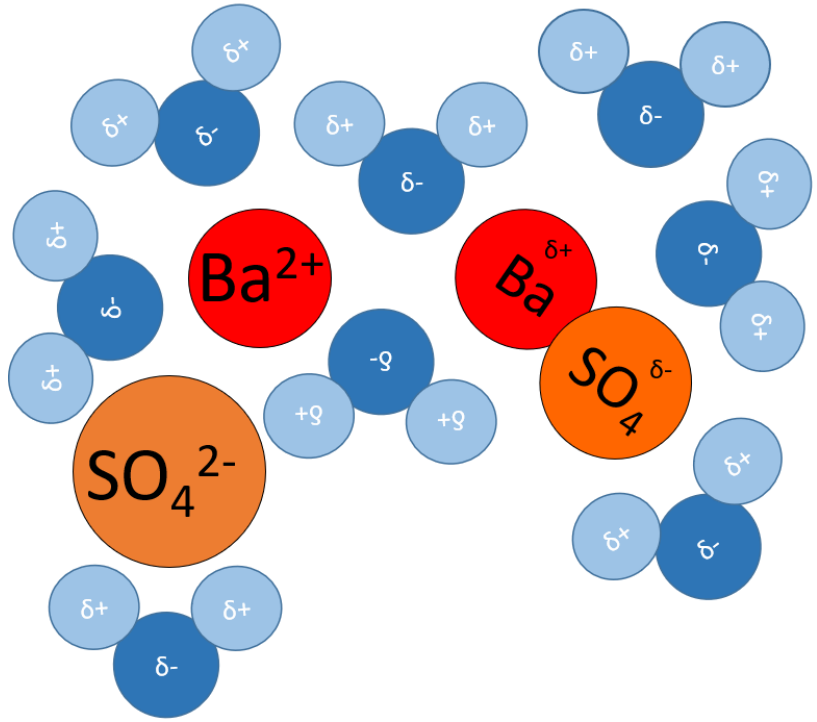
- Describes which way the reaction goes
- Can be either theoretically calculated or measured.



Post-Scale

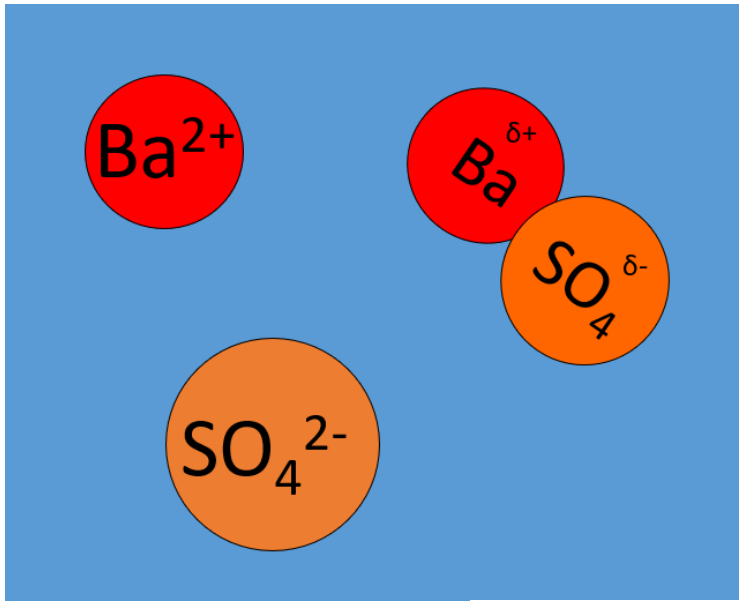
New Model versus Old Models

New Model Based on Molecular Statistical Thermodynamics (MST)



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

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 old model also used negative diameters for ion pairs which is fundamentally incorrect.

Key Molecular Statistical Theory Equations

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

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

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

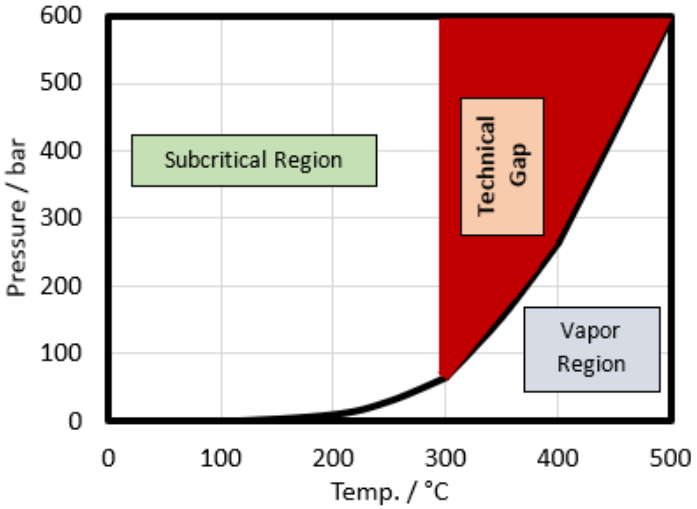
$$\frac{G_i^{DD}}{RT} = \frac{-8Np_i^2(\varepsilon-1)}{2\sigma_w^3\left(1-\frac{\beta_{12}}{\beta_3}\right)\left(\frac{\beta_{12}}{\beta_6}\right)^3 + 2\varepsilon\left(\sigma_i + \sigma_w\frac{\beta_6}{\beta_3}\right)^3 + \left(\sigma_i + \sigma_w\frac{\beta_{12}}{\beta_6}\right)^3}$$

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

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

- **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.**

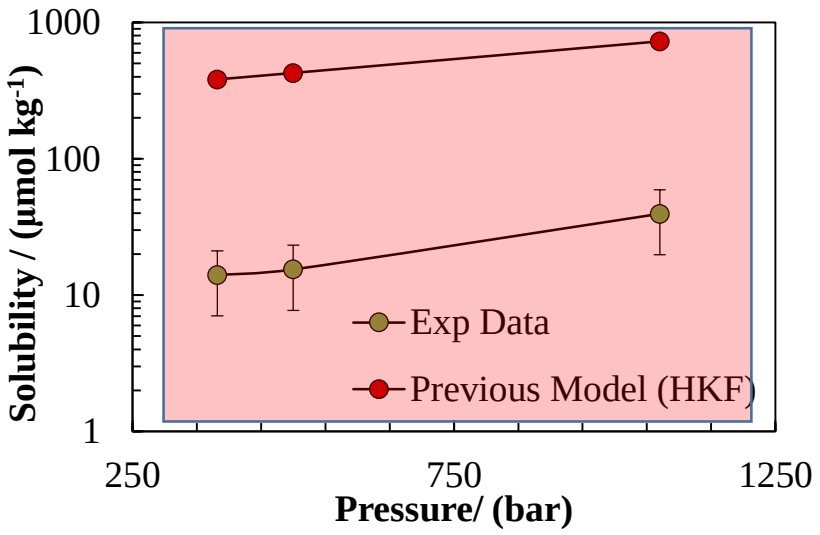
Improvement of New Model over Old Model in Technical Gap Regions:
Error decreases from 2000% to 60% at HTHP conditions



Tested Model for the Barium Sulfate Scaling System

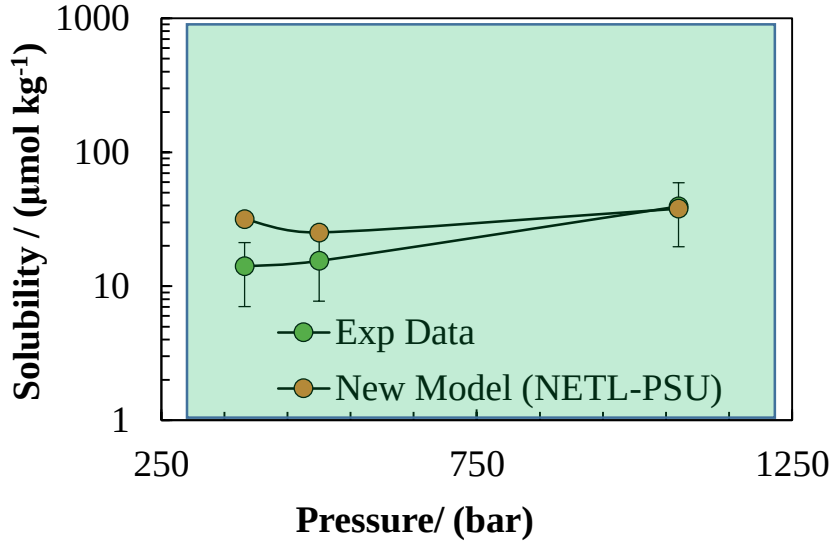
Previous Model

T = 400 °C,
%E = ~2000 %



New NETL-PSU Model

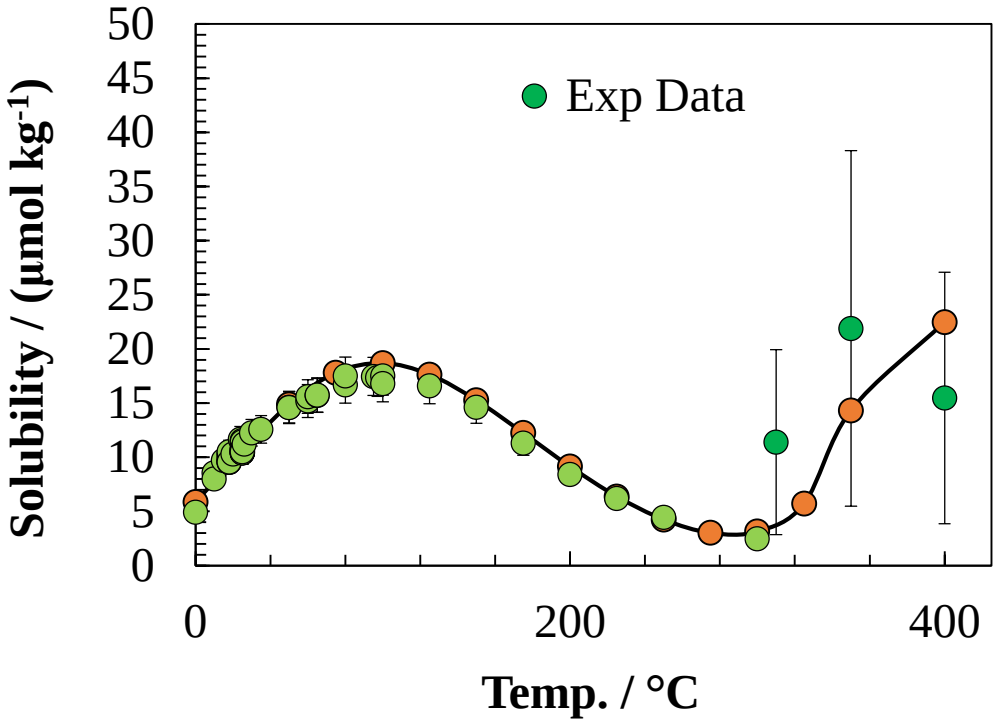
T = 400 °C,
%E = ~60 %

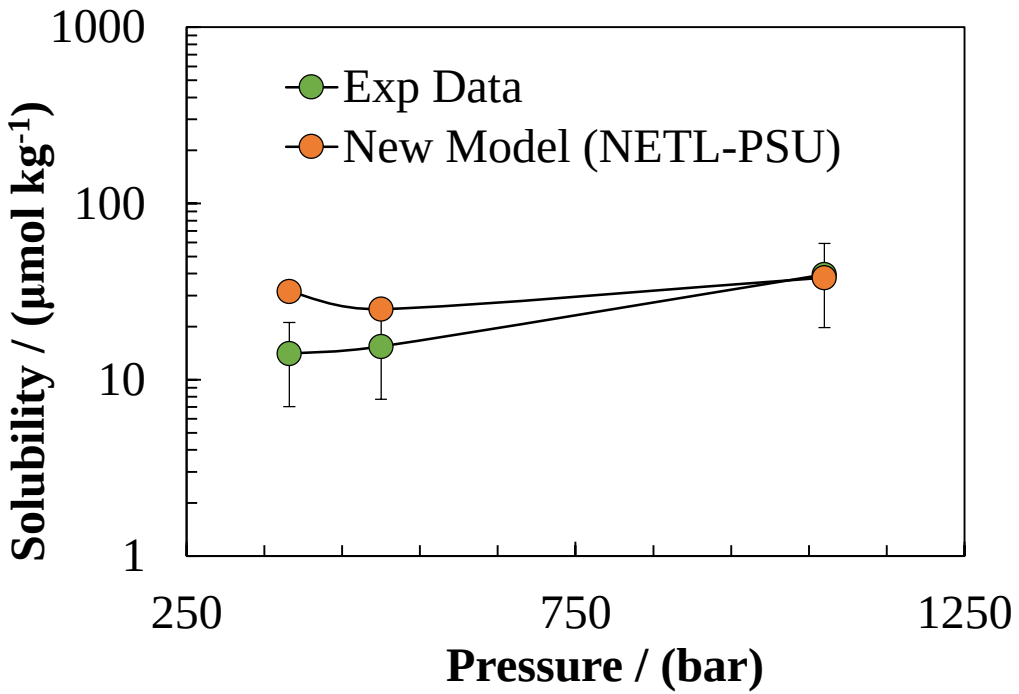


Comparison Between Predicted and Experimental Barite Solubility

HTHP Issues Corrected by Our New Model

Comparison Between Experimental and Predicted Barite Solubility – NETL-PSU Model

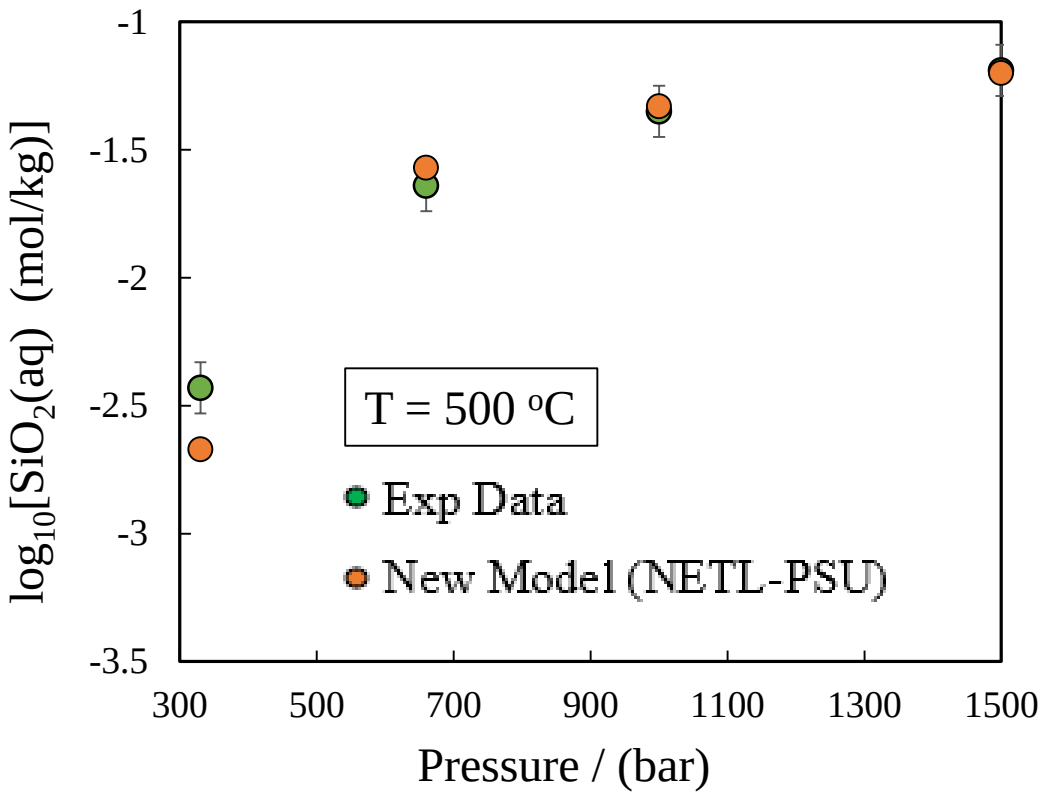


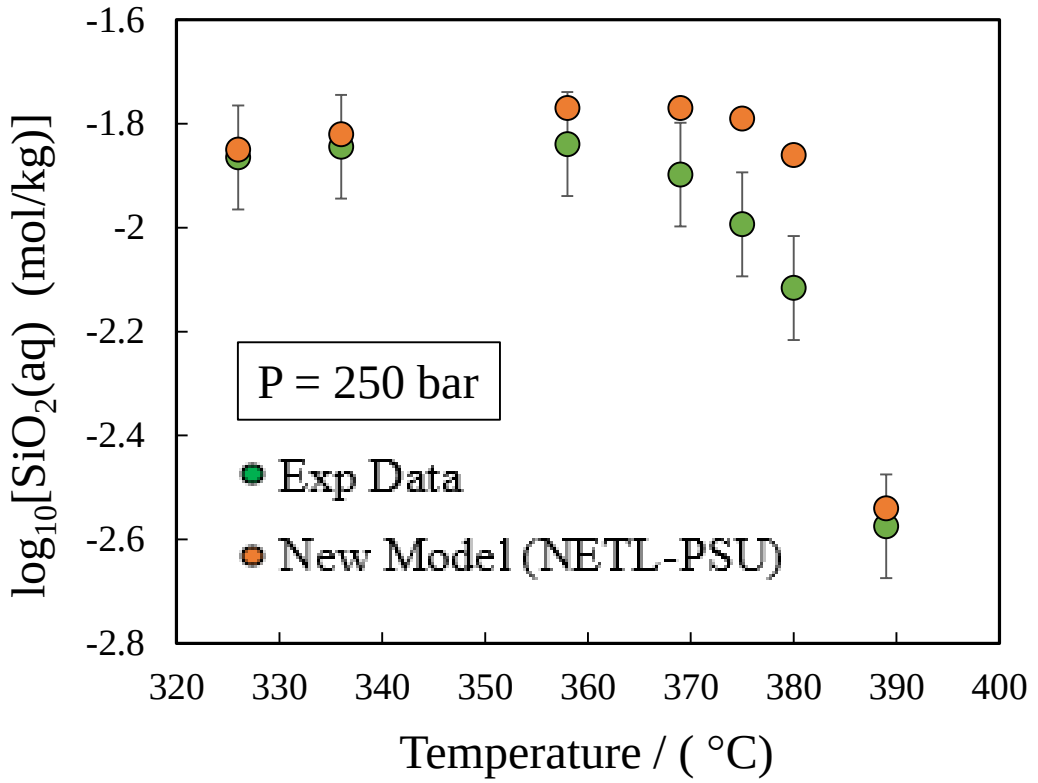


- HTHP comparisons between experimental data and our new model based on the molecular statistical thermodynamics (MST) show the dramatic improvements can be made in the scaling predictions.
- Predictions errors of up to 2000% were reduced to ranges within experimental error.

HTHP Scale Predictions for Silica

Tested Model for Silica Scaling System





- **Good agreement was found for a simple one species system, $SiO_2(aq) \rightarrow SiO_2(s)$**
- **Now, we need to focus on systems with multiple species such as barite.**

Lvov, Serguei N., Derek M. Hall, Andrei V. Bandura, and Isaac K. Gamwo. 2018. "A Semi-Empirical Molecular Statistical Thermodynamic Model for Calculating Standard Molar Gibbs Energies of Aqueous Species above and below the Critical Point of Water." *Journal of Molecular Liquids* 270:62–73.

Scale Deposit Experiments

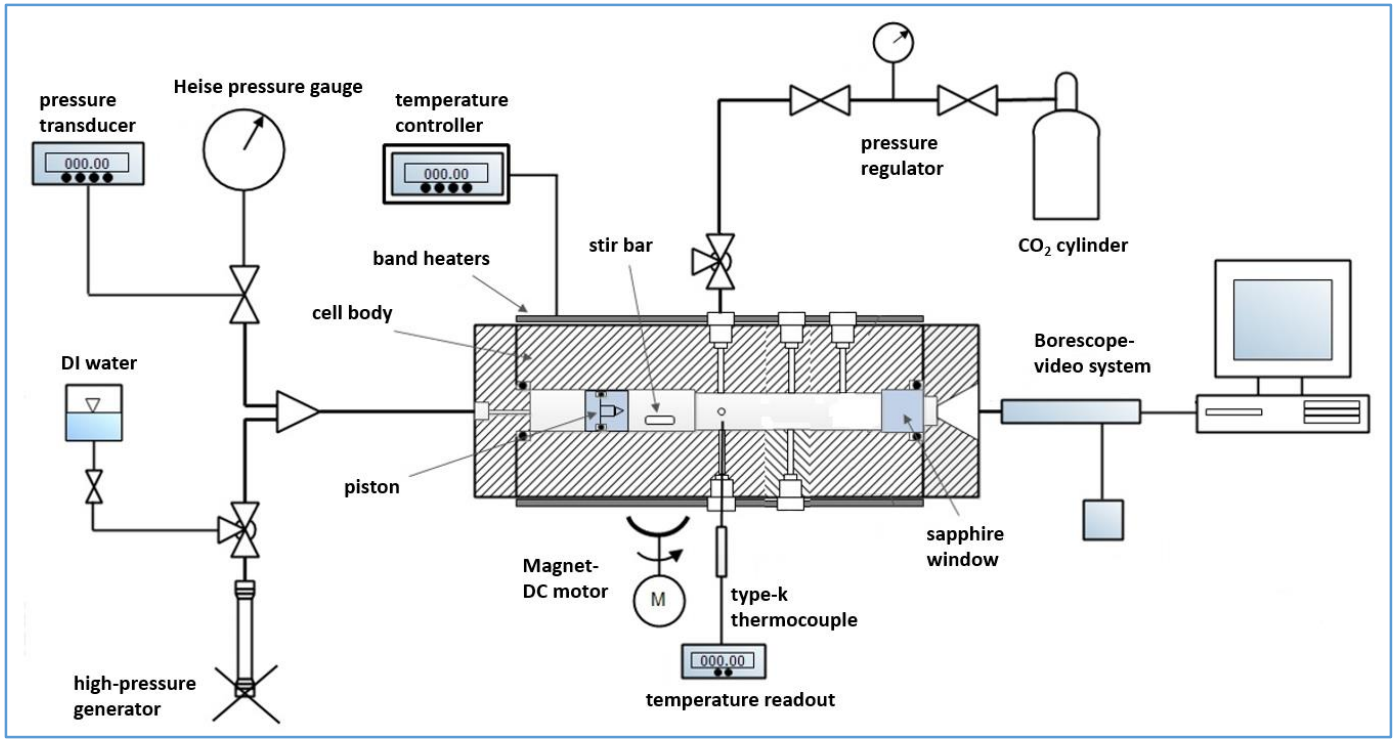
Objective

- Validation of modeling results via experimental studies on mineral solubilities at high-temperature, high-pressure (HTHP) conditions.

Experiments

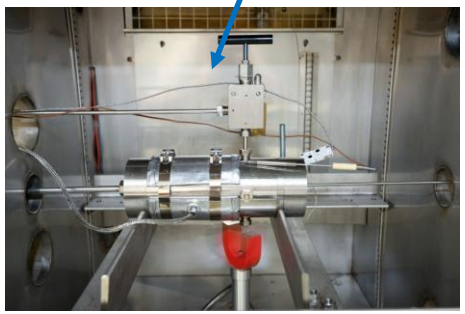
- Visualization of scale deposits at NETL's Experimental Facility.
- Design of the most appropriate setup for the HTHP solubility experiments?

Current Experimental HTHP Scale Deposit



Schematic NETL Scale Deposit Experimental Setup

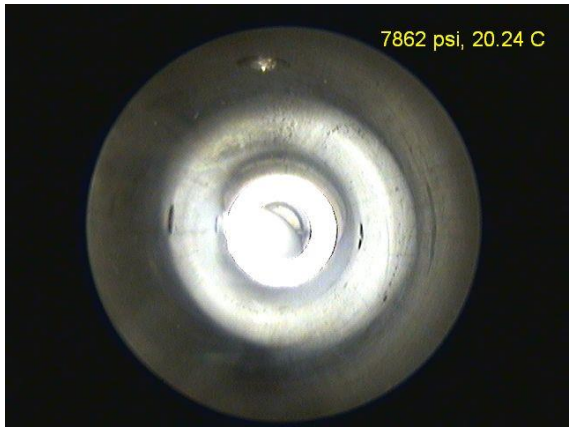
NETL HTHP Scale Deposit Experimental Setup
Operates to 600°F and 40,000 psi



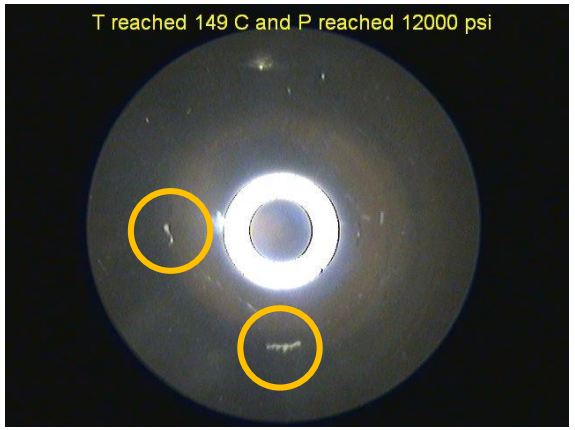
Still Images from Experimental Scale Deposit Movie

Visualization of scale deposit at NETL's Experimental Facility

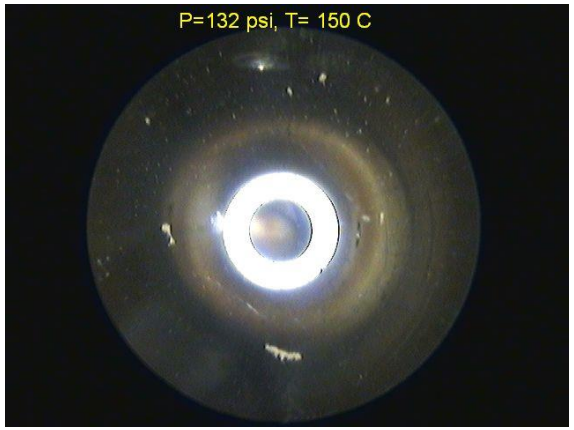
Manipulated Parameters: T and P



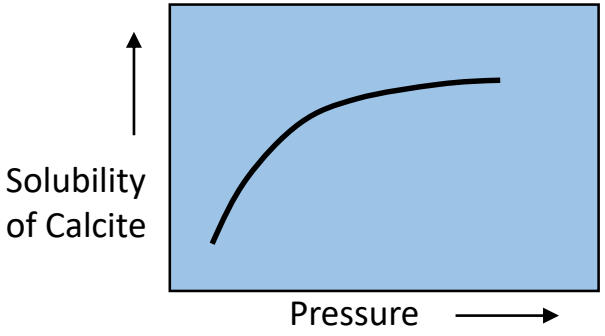
(1)
Clear calcite solution

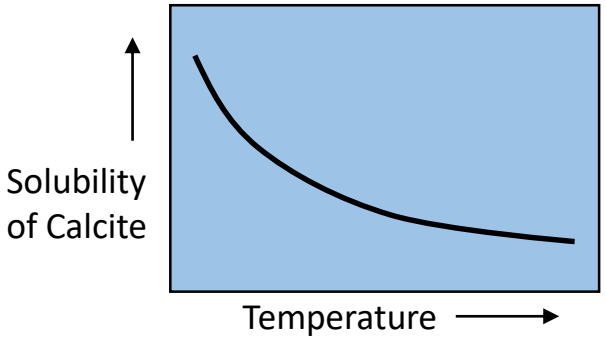


(2)
Calcite deposits due to heating



(3)
More deposits due to depressurizing

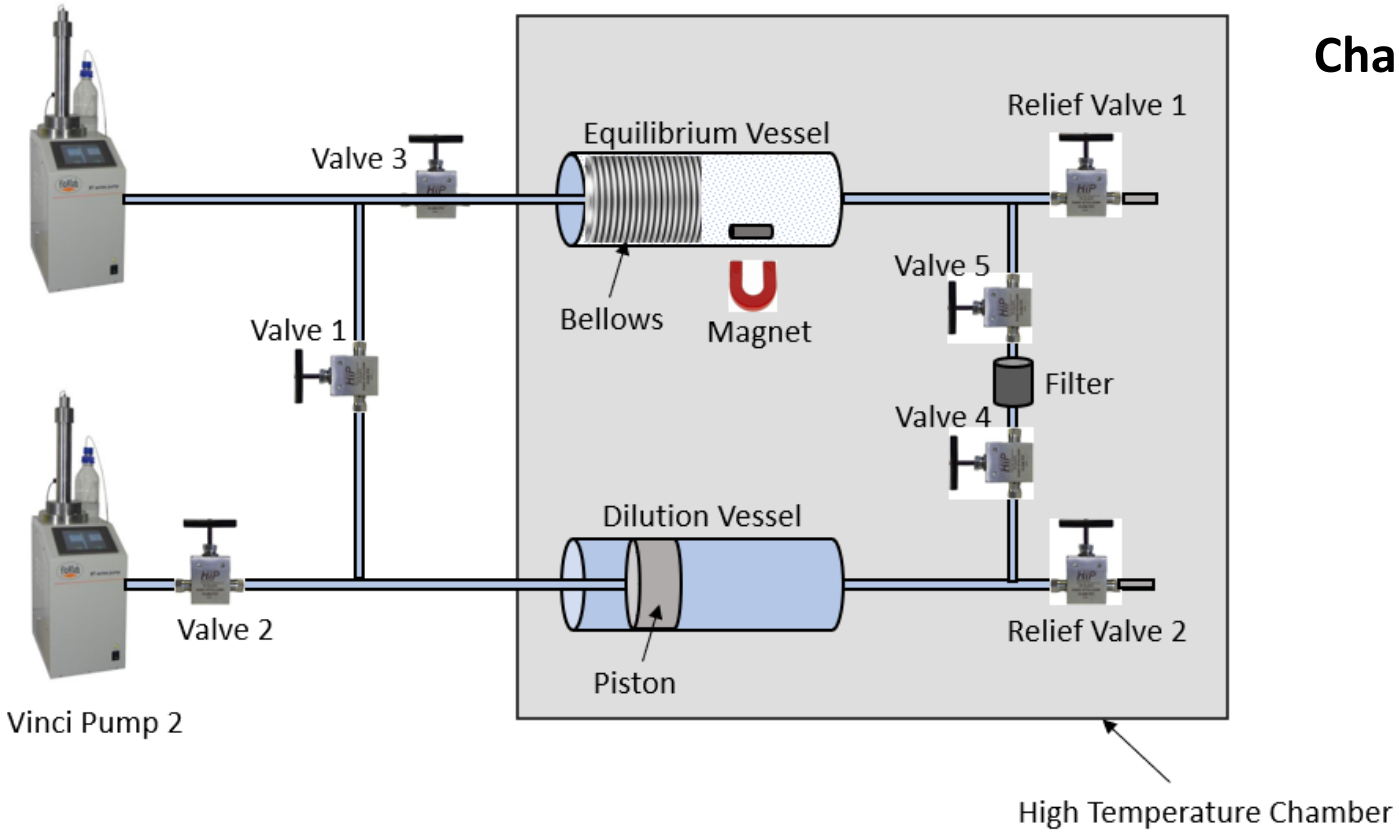




Movie Experimental Scale Deposit in NETL HTHP Apparatus

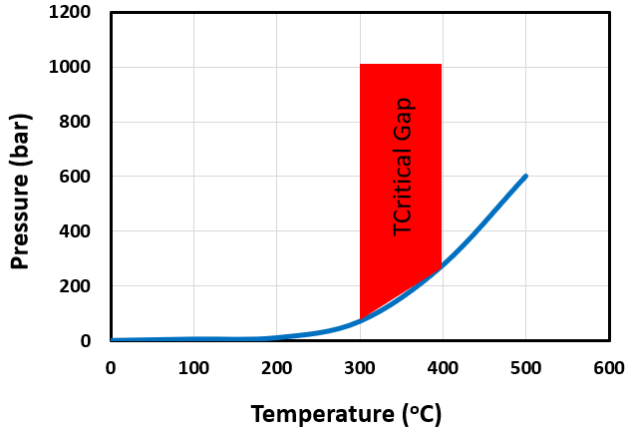
https://youtu.be/Gl_My7bv-hE

Future Work: New NETL Solubility Experimental Set-up



Challenges

- Insufficient funds to cover the costs of the new solubility experimental setup
- Long lead time to complete the design and wiring by Leidos Engineers. If funding becomes available, it will take 6 months to get the experimental setup ready.
- Long lead times for the delivery of the materials ordered.



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

Implementation into Commercial Applications

Technology-to-Market Path

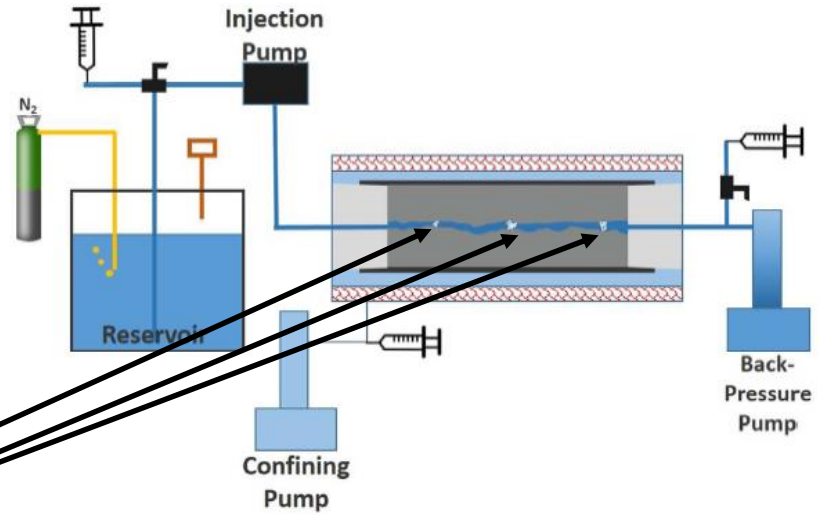
- OLI Systems, Inc., a commercial software released a support letter. CTO specified steps needed to implement model in the commercial software.
- The model needs to be validated for an additional system with robust HTHP data (OLI Studio requested **sodium phosphate**).
- A new database will need to be developed that provided model parameters for all necessary aqueous species in the sodium phosphate system.
- Once competed, the model can be 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*…"

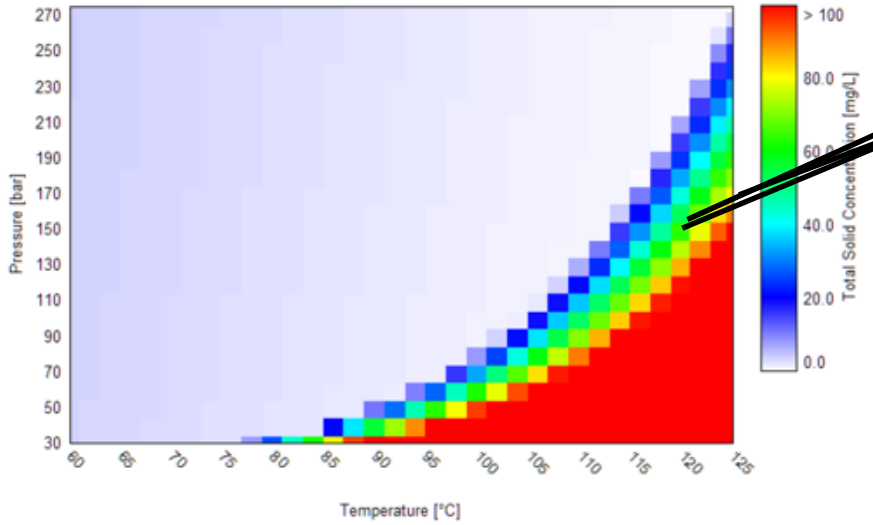
OLI's Chief Technology Officer's (CTO) Letter of Interest to collaborate with Task 8

Preparing Project for Next Steps

Possible Collaborations with experimental groups at SLAC National Lab and NETL

- The flow through and batch systems used by NETL onshore and SLAC can be modeled using OLI Flowsheet software.
- Corrosion rate measurements (not shown here) can also be modeled by OLI Corrosion Analyzer software to provide insights into possible reaction pathways.
- Possible collaboration with LBNL to incorporate our model into LBNL transport model including reservoir geometry





Concluding Remarks

Applicability of technology to Fossil Energy

- Our new model predicts a phenomena that threatens production rates in oil and gas operations.
- The model also applies to petroleum midstream and downstream as well as to the hydrothermal water cycles found in powerplant water cycles.
- Geothermal technology can also benefit from outcome of this project.

Define project's next steps and current technical challenges

- Validate for the sodium phosphate system as HTHP, another multiphase, multicomponent, multi-reaction system.
- Implement this tool into OLI Systems software; an industrial standard software for dealing with scaling problems. OLI software is used worldwide by over 400 companies including Shell, Chevron, ConocoPhillips, Marathon Oil, Total, etc…

Latest News

Dr. Isaac Gamwo has been selected as a 2020 AIChE-MAC Eminent Chemical Engineer

THANK YOU FOR YOUR ATTENTION

QUESTIONS?