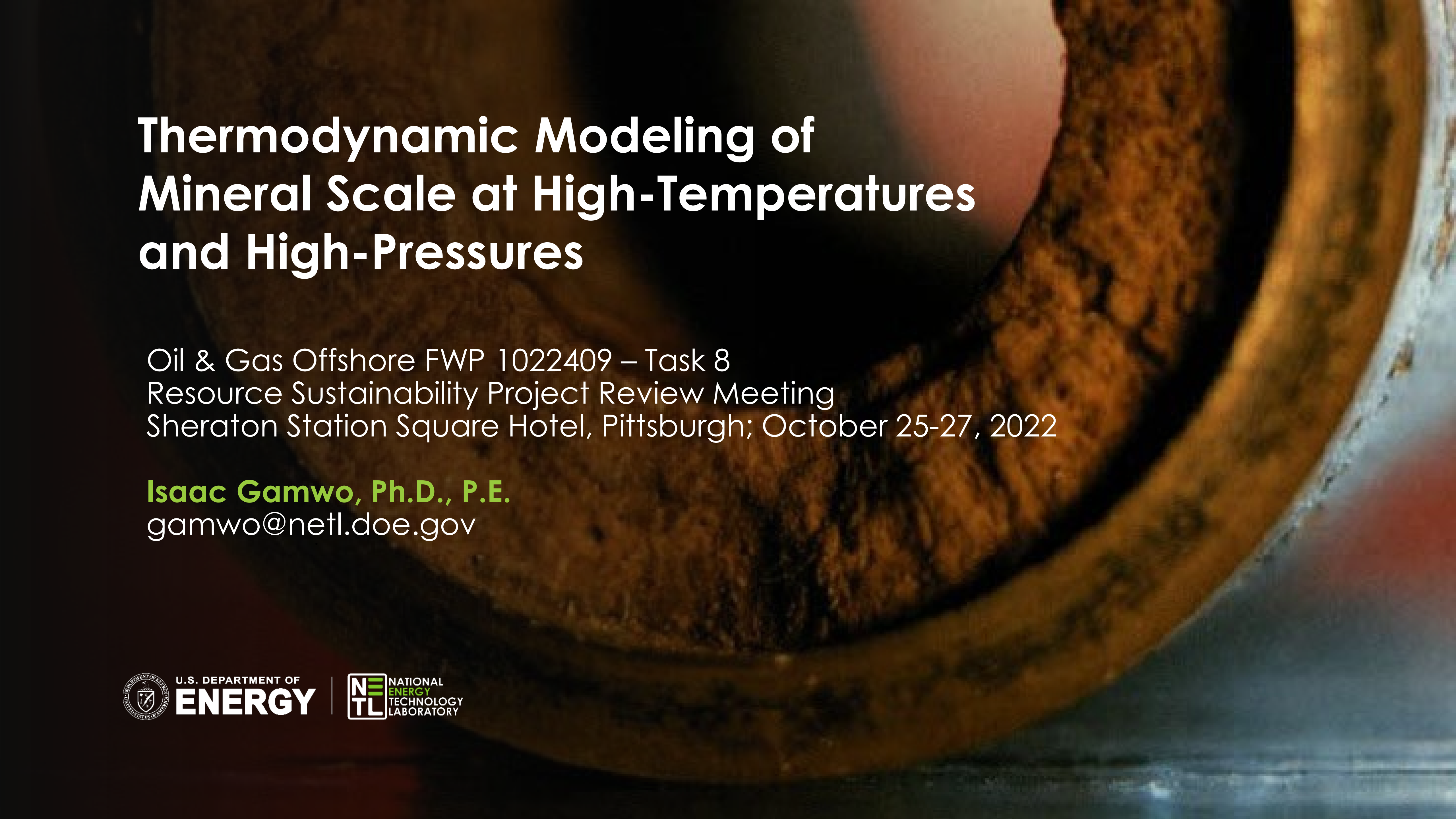

Thermodynamic Modeling of Mineral Scale at High-Temperatures and High-Pressures

Oil & Gas Offshore FWP 1022409 – Task 8
Resource Sustainability Project Review Meeting
Sheraton Station Square Hotel, Pittsburgh; October 25-27, 2022

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U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Mineral Scale Research Team – 2022-2023

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Task 8 - Thermodynamic Modeling of Mineral Scale at High Temperatures and Pressures (HTHP).

EY19	EY20	EY21	EY22	(Year 1 - 4)

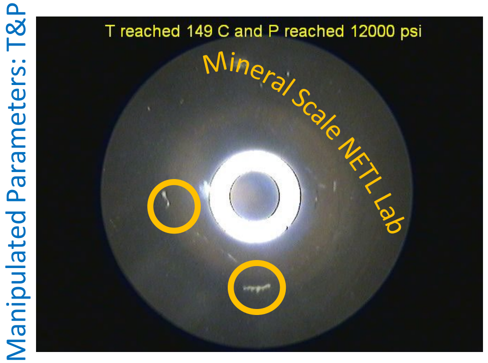
Need: Predictive model for HTHP mineral scale formation to proactively mitigate oil production losses. Existing models failed at ultradeep well conditions.

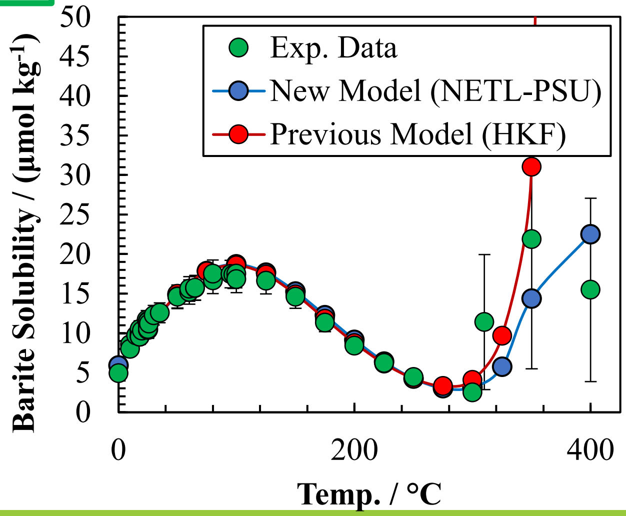
Research Questions: Why do scale prediction models fail in HTHP conditions? How can we develop a reliable model for HTHP conditions? Can we manipulate T&P in the lab to reproduce the scale formation?

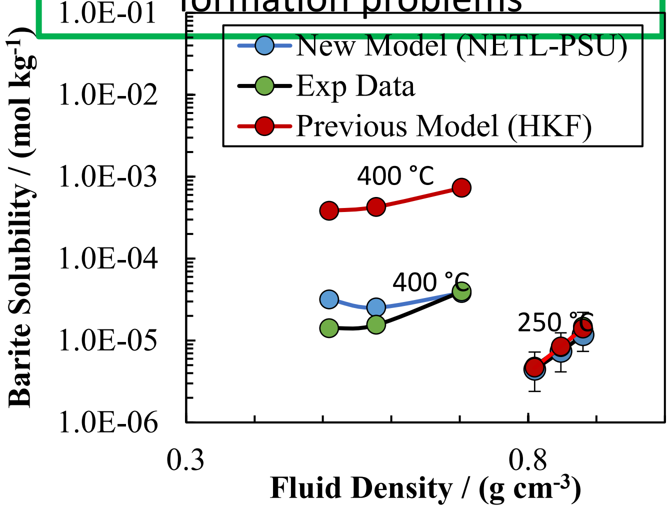
Approach: Combine theoretical, computational, and experimental approaches to reliably predict mineral precipitations at HTHP conditions

End Product: A validated mineral scale model at HTHP conditions.

Key Deliverable: collaborate with OLI to incorporate our new model into a commercial software uses in the petroleum industry to mitigate scale formation problems

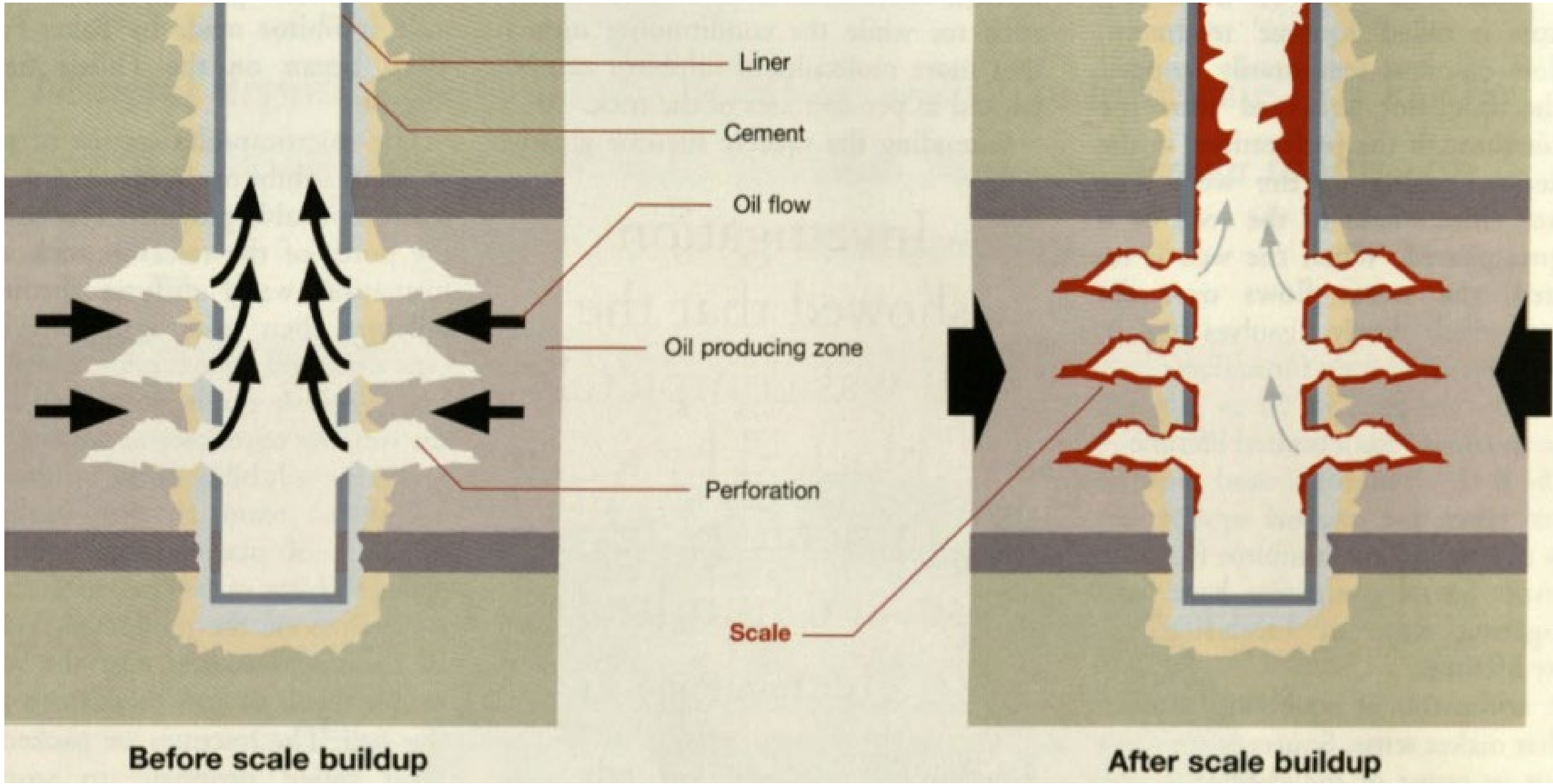






Real-World Example of Mineral Scaling Problem Production Threat

Miller North Sea Well: Oil production fell from 30,000 B/D to 0 in 24 Hours due to Scaling[1]



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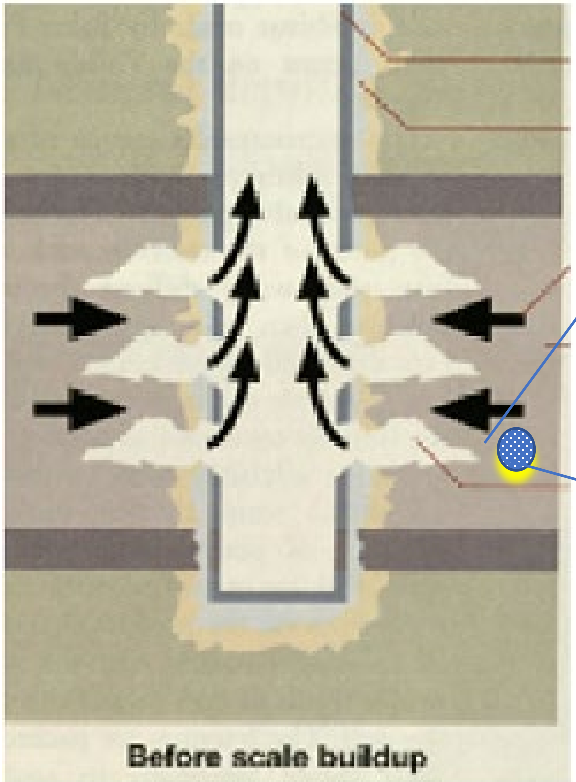
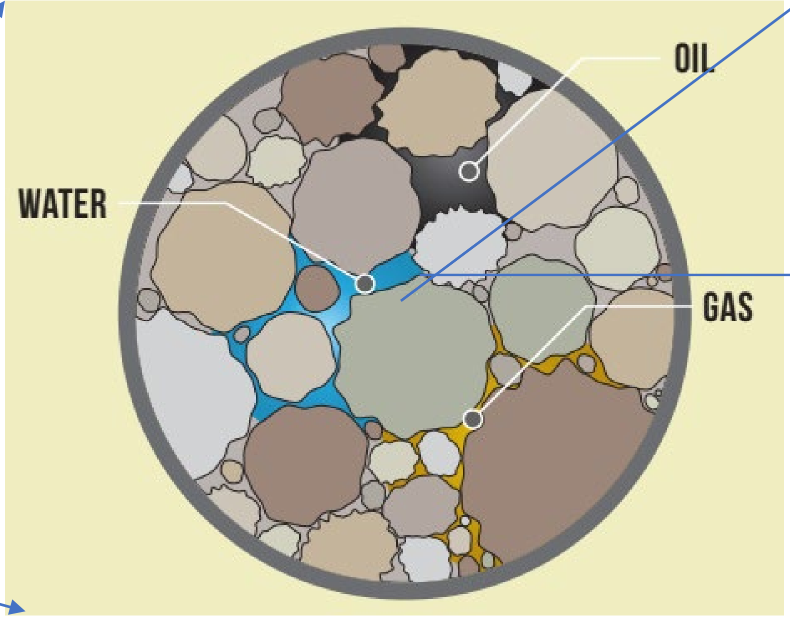
1. Brown, M., "Full Scale Attack," BP Technology Magazine, Review 30 (1998), p. 30-32.

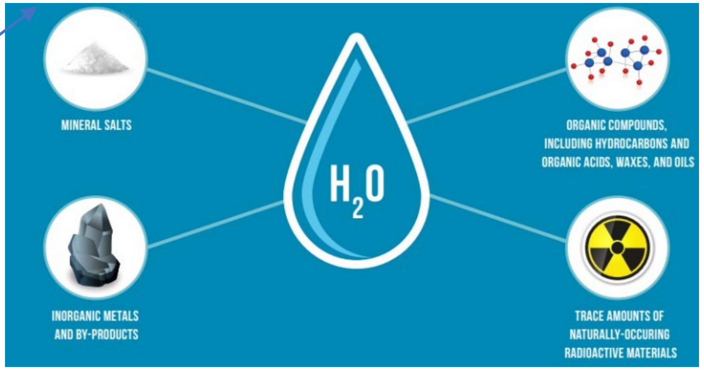
Why Do Mineral Scale Form?



Oil Flow in the Wellbore



Pore Space in the Reservoir



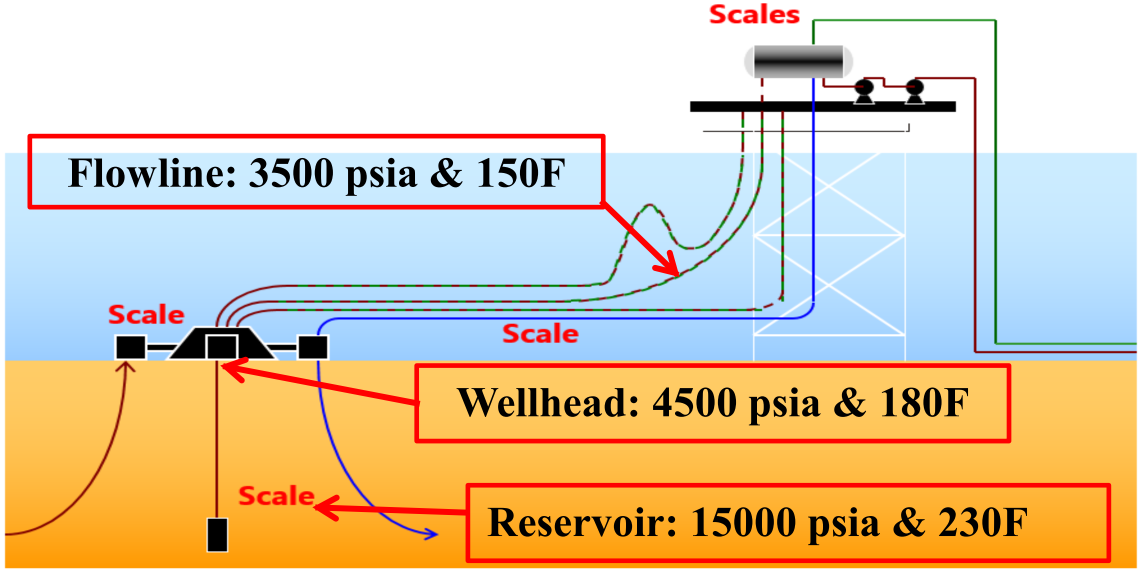
Formation Water Constituents

Example Formation Water Analysis Items:

Barium, Calcium, Magnesium, Potassium, Silica, Zinc, Iron, Strontium, Sulfate, Chloride, Carbonate, Sodium, etc…

Minerals can precipitate out of water and coat pipes

Offshore Oilfield Production and Safety Threat, Mineral Scale Deposition:



Flowline: 3500 psia & 150F

Wellhead: 4500 psia & 180F

Reservoir: 15000 psia & 230F

Scale in Flow Line[2] – Pipe is contaminated with Barium Sulfate.

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

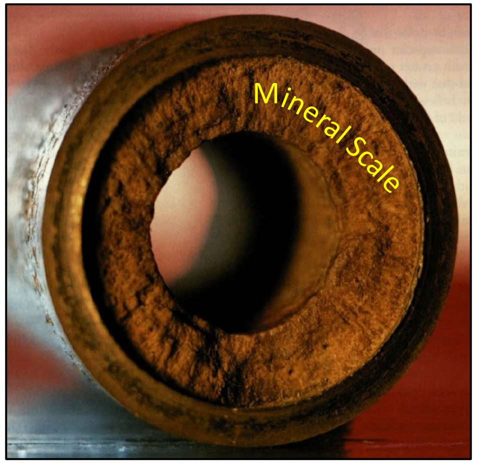
- Mineral scale is hard crystalline salt formed when its solubility limit is exceeded.
- Causes include: Changes in temperature, pressure, Ionic composition and pH

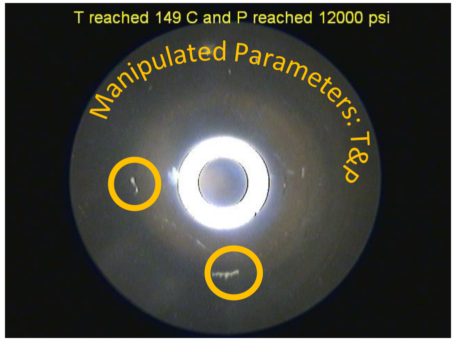
- Issues:
    - **Reduces oil production**
    - **Failure of safety equipment**
    - Causes corrosion of pipe walls

1. https://fqechemicals.com/contaminants/barium-sulfate-scale/

Motivation and 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.





Mineral Scale NETL Lab

Fundamental Understanding of Mineral Scale: How Does Mineral Scale Form?

Barium Sulfate Scales in Offshore Oilfields

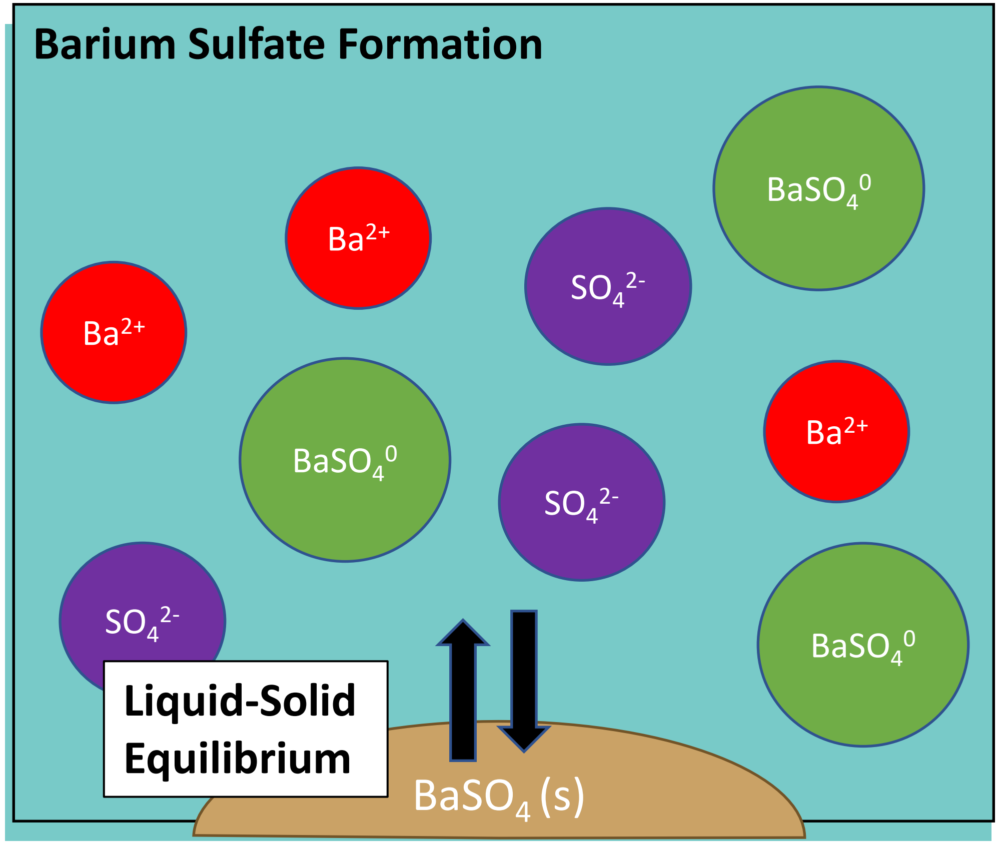
$$Ba^{2+}\,(aq) + SO_4^{2-}(aq) \rightleftarrows BaSO_4^0(aq)$$

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

Model Gibbs Energies of Reaction for predicting Barite scale, ΔG_r

Gibbs Energy of reaction, ΔG_r

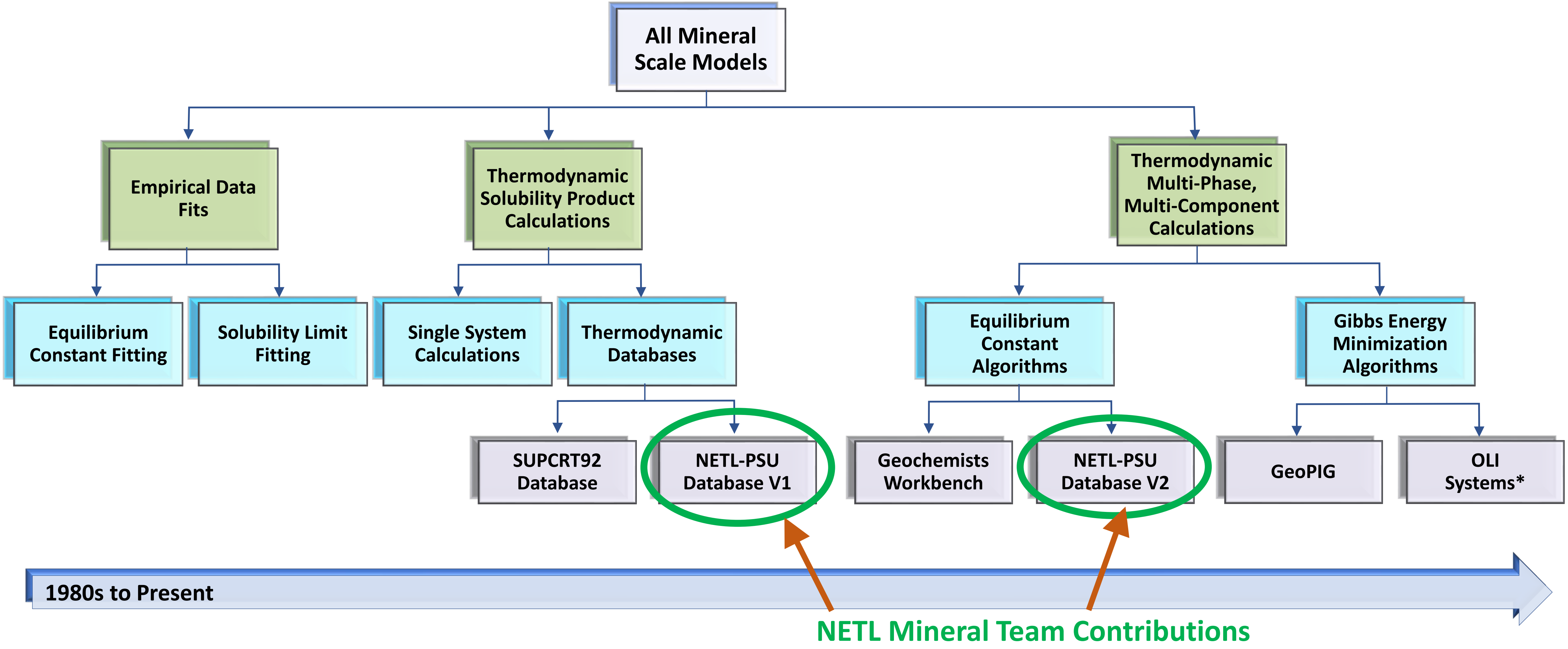
- Describes which way the reaction proceeds.



Post-Scale

Review of Mineral Scale Models Developed over the Past 40 Years

Model evolution tree of mineral scale solubility models from the 1980s to today. Sample techniques in grey boxes.



All Mineral Scale Models

Empirical Data Fits

- Equilibrium Constant Fitting
- Solubility Limit Fitting

Thermodynamic Solubility Product Calculations

- Single System Calculations
- Thermodynamic Databases
  - SUPCRT92 Database
  - NETL-PSU Database V1

Thermodynamic Multi-Phase, Multi-Component Calculations

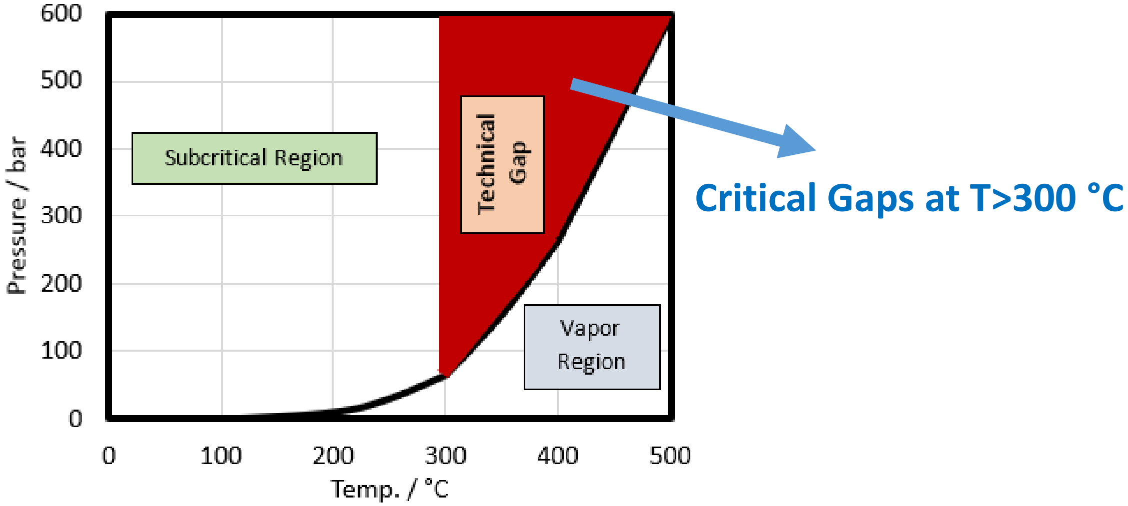
- Equilibrium Constant Algorithms
  - Geochemists Workbench
  - NETL-PSU Database V2
- Gibbs Energy Minimization Algorithms
  - GeoPIG
  - OLI Systems*

1980s to Present

NETL Mineral Team Contributions

Technical Gap Identified in Scale Modeling

- Identified a knowledge gap[3] in the current state-of-the art models including OLI Studio[2]: ScaleChem.
- Software[4] 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.

Limitations of the current OLI Thermodynamic Model

Aqueous Phase

$X_{H2O} > 0.65$

$-50^oC < T < 300^oC$

0 Atm < P < 1500 Atm

$0 < I_{brine} < 30$

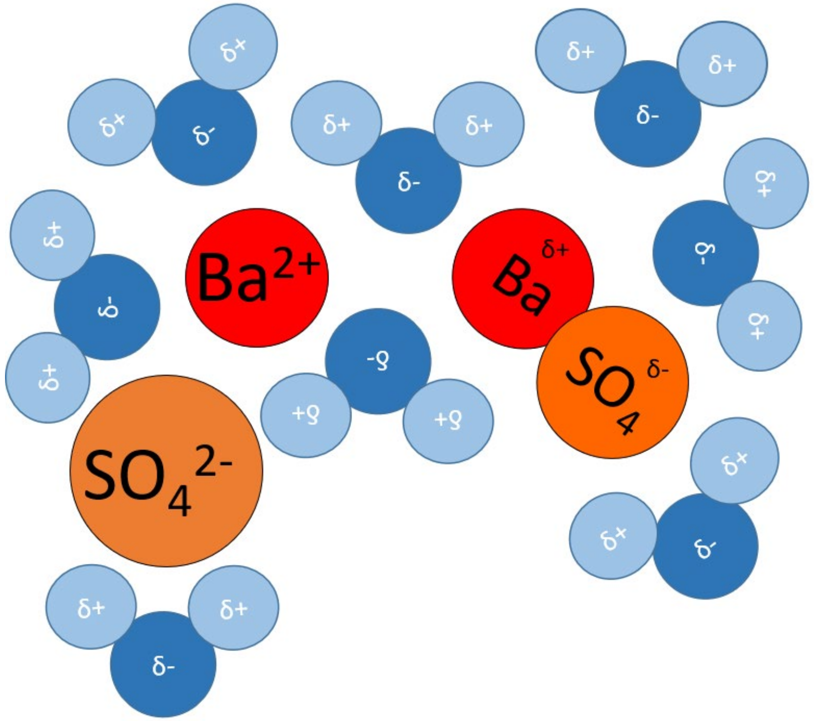
---

[3] 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.

[4] OLI Systems. (n.d.). *OLI Studio Stream Analyzer User Guide. V 9.5*.

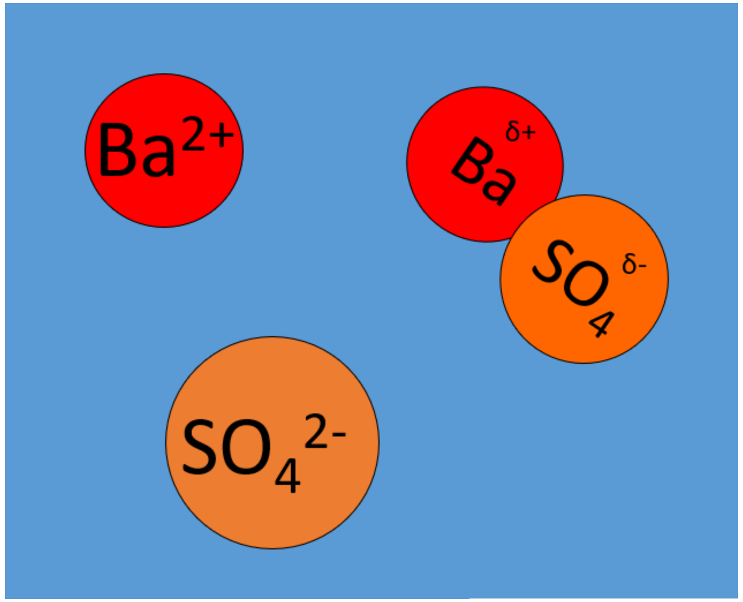
Why Did Previous Models Failed? New Model versus Old Model (1)

New Model Based on Molecular Statistical Thermodynamics (MST)



The new model uses the most sophisticated molecular statistical theory 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 in the Born equation for ion pairs which is fundamentally incorrect.

Why Did Previous Models Failed? New Model versus Old Model (2)

New Speciation Model

As an example, If 0.001 mol kg^{-1} of Ba^{2+}(aq) and SO_4^{2-}(aq) is detected in an aqueous solution, will barite precipitate at 25 C and 1 bar? (Let’s assume activity coefficients are equal to 1) IAP = $Q = a_{Ba2+}a_{SO42-} = 1 \times 10^{-6}$

$Q > K_{sp}$, barite will precipitate!

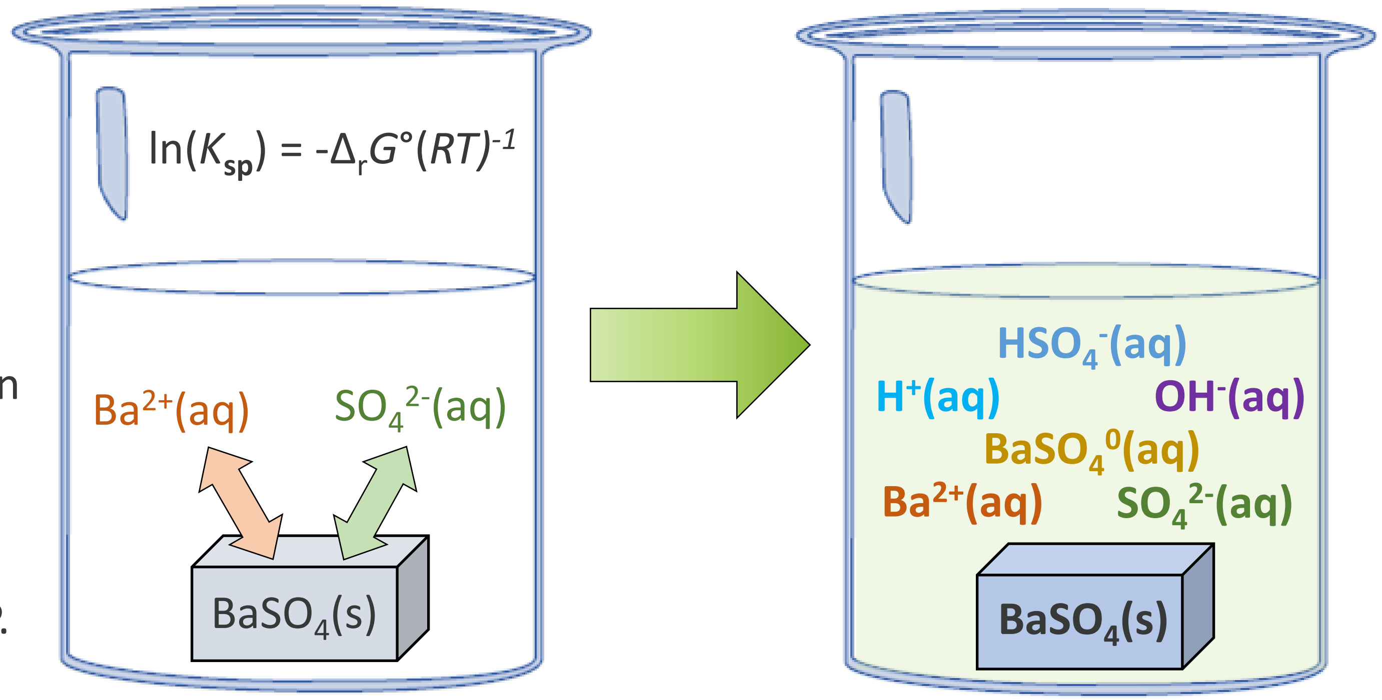
$\Omega = Q/K_{sp} = 8930$

Inputs

- One K_{eq} value determined via ΔG_i^0

Outputs

- Incorrect concentration of species at HTHP.
- Incorrect amount of solids formed for a given solution at HTHP.



Old Model

$\ln(K_{sp}) = -\Delta_r G°(RT)^{-1}$

Ba^{2+}(aq)

SO_4^{2-}(aq)

$BaSO_4$(s)

Simple $BaSO_4$(aq)-$BaSO_4$(s) System

New Model

HSO_4^-(aq)

H^+(aq)

OH^-(aq)

$BaSO_4^0$(aq)

Ba^{2+}(aq)

SO_4^{2-}(aq)

$BaSO_4$(s)

Improved $BaSO_4$(aq)-$BaSO_4$(s) System

Inputs

- Multiple K_{eq} values determined via ΔG_i^0
- Mass Balance Equations
- Charge Balance Equations

Outputs

- Correct concentration of all species at HTHP.
- Correct amount of solids formed for a given solution at HTHP.

The State of the Art Prior to Our Model – The HKF Model

Our model improves the terms and methods developed in the HKF model

$$\Delta G^0_{\mathrm{P,T}} = \Delta_f G^0_{Tr,Pr} - S^0_{\mathrm{Pr,Tr}}(T - T_r) - c_1\left[T\ln\left(\frac{T}{T_r}\right) - T + T_r\right] + a_1(P - P_r) + a_2\ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\left(\frac{\Psi + P}{\Psi + P_r}\right)$$

$$+\left[a_3(P - P_r) + a_4\ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right]\left(\frac{1}{T - \Theta}\right)$$

$$-c_2\left[\left(\left(\frac{1}{T - \Theta}\right) - \left(\frac{1}{T_r - \Theta}\right)\right)\left(\frac{\Theta - \mathrm{T}}{\Theta}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_r(T - \Theta)}{T(T_r - \Theta)}\right)\right]$$

$$+\omega\left(\frac{1}{\varepsilon} - 1\right) - \omega_{Pr,Tr}\left(\frac{1}{\varepsilon_{Pr,Tr}} - 1\right) + \omega_{Pr,Tr}Y_{Pr,Tr}(T - T_r)$$

Where,

H = Enthalpy
G = Gibbs Free Energy
V = Volume
Cp = Heat Capacity at constant Pressure
S = Entropy
T = Temperature
P = Pressure
Θ = 228 K
Ψ = 2600 Bar
ω = Temperature and Pressure dependent term for electrostatic nature of the electrolytes
Q = Pressure functions of the dielectric constant
ε = Dielectric constant of water
a1…a4 = Pressure dependent terms
c1, c2 = Temperature dependent terms

Empirical Terms

Two terms based on the Born equation

7 Empirical Parameters

- Despite is empirical nature, the HKF model works remarkably well up to 300 °C and is now the cornerstone of almost every aqueous thermodynamic database.

Improved State of the Art model- NETL-PSU

Our model improves the terms and methods developed in the HKF model

$$\Delta G^0_{\mathrm{j}}(\mathrm{T,P}) = \Delta_{\mathrm{f}} G^0(T_{\mathrm{r}},P_{\mathrm{r}}) + [\, G^0_{\mathrm{j}}(T, P) - G^0_{\mathrm{j}}(T_r, P_r)] \qquad (1)$$

$$G^0_{\mathrm{j}}(T, P) - G^0_{\mathrm{j}}(T_r, P_r) = \{[-S_j^0(T_r,P_r) + \textstyle\sum_k S_j^k(T_r,P_r)]\,(T - T_r) + A_j(P - P_r) - C_j\left(T ln\frac{T}{T_r} + T_r - T\right)\} + (\textstyle\sum_k G_j^k(T,P) - \sum_k G_j^k(T_r,P_r)) \qquad (2)$$

MST model replaced HKF empirical terms with predictive statistical thermodynamic expressions – ID, DD, interactions

Insert (2) into (1) to obtain (3)

$$\Delta G^0_{\mathrm{j}}(\mathrm{T,P}) = \Delta_{\mathrm{f}} G^0(T_{\mathrm{r}},P_{\mathrm{r}}) + [-S_j^0(T_r,P_r)(T - T_r)) + \textstyle\sum_k S_j^k(T_r,P_r)\,(T - T_r) + A_j(P - P_r) - C_j\left(T ln\frac{T}{T_r} + T_r - T\right)] + (\textstyle\sum_k G_j^k(T,P) - \sum_k G_j^k(T_r,P_r))$$

HS, ID, DD, SS, and MS Gibbs energy contributions – shown in the next slide

HS, ID, DD, SS, and MS entropy contributions

k-th reference molecular statistical Gibbs energy contribution (=HS, ID, DD, SS, MS)

A New Entropy Term was Derived for the Dipole-dipole Interaction

Five entropy terms were included to the model, four were obtained from literature.

$$S_{j,ref}^{ID} = (d\varepsilon/dT)_{ref} N_A e^2 z_j^2 / (((\sigma_j) + (\sigma_w)(\beta_{6,ref}/\beta_{3,ref}))\, \varepsilon_{ref}{}^2) + N_A e^2 z_j^2 / ((\sigma_j) +$$

$$(\sigma_w)(\beta_{6,ref}/\beta_{3,ref}))^2\, (1/\varepsilon_{ref}{}^2 - 1)(\sigma_w)(db_2/dT)_{ref}(-(1/(6\beta_{3,ref})) - \beta_{6,ref}/(3\beta_{3,ref}{}^2))$$

$$S_{j,ref}^{SS} = -R\, ln(R\, \rho_{ref} T_{ref}/P_{ref}) - 1 + (T_{ref}/\rho_{ref})\, (-d\,\rho/d\,T)_{ref}/\rho_{ref}$$

$$S_{j,ref}^{HS} = -R(G^{HS}{}_{ref} - \eta_{ref} T_{ref} Y_{ref}\, (-d\,\rho/d\,T)_{ref}/\rho_{ref})$$

$$S_{j,ref}^{MS} = -Rln(M_s)$$

$$S_{j,ref}^{DD} = -8N_A p_j^2 (d\varepsilon/db_2)_{ref}/((\sigma_j/2)^3((1 + \mathrm{L}\,\beta_{12,ref}/\beta_{6,ref})^3 + 2\mathrm{L}^3\beta_{12,ref}{}^3 *$$

$$(1 - \beta_{12,ref}/\beta_{3,ref})/\beta_{6,ref}{}^3 + 2\varepsilon_{ref}(1 + \mathrm{L}\,\beta_{6,ref}/\beta_{3,ref})^3)) + 8N_A p_j^2(\varepsilon_{ref} -$$

$$1)(6\mathrm{L}^3\beta_{12,ref}{}^2(1 - \beta_{12,ref}/\beta_{3,ref})\,(d\beta_{12}/db_2)/\beta_{6,ref}{}^3 +$$

$$2\mathrm{L}^3\beta_{12,ref}{}^3\,(-(d\beta_{12}/db_2)/\beta_{3,ref}) + \beta_{12,ref}\,(d\beta_3/db_2)/\beta_{3,ref}{}^2)/\beta_{6,ref}{}^3 - 6\mathrm{L}^3 * \beta_{12,ref}{}^3 *$$

$$(1 - \beta_{12,ref}/\beta_{3,ref})\,(d\beta_6/db_2)/\beta_{6,ref}{}^4 + 6(1 +$$

$$\mathrm{L}\,\beta_{6,ref}/\beta_{3,ref})^2\varepsilon_{ref}(-(\mathrm{L}\beta_{6,ref}\,(d\beta_3/db_2)/\beta_{3,ref}{}^2) + \mathrm{L}\,(d\beta_6/db_2)/\beta_{3,ref}) + 3(1 +$$

$$\mathrm{L}\,\beta_{12,ref}/\beta_{6,ref})^2(\mathrm{L}\,(d\beta_{12}/db_2)/\beta_{6,ref} - \mathrm{L}\beta_{12,ref}\,(d\beta_6/db_2)/\beta_{6,ref}{}^2) +$$

$$2(1 + \mathrm{L}\,\beta_{6,ref}/\beta_{3,ref})^3(db_2/dT)_{ref})/((\sigma_j/2)^3((1 + \mathrm{L}\,\beta_{12,ref}/\beta_{6,ref})^3 + 2(1 + \mathrm{L}\,\beta_{6,ref}/\beta_{3,ref})^3(db_2/dT)_{ref}$$

$$2\mathrm{L}^3\beta_{12,ref}{}^3\,(1 - \beta_{12,ref}/\beta_{3,ref})/\beta_{6,ref}{}^3 + 2(1 + \mathrm{L}\,\beta_{6,ref}/\beta_{3,ref})^3 * \varepsilon_{ref})^2)$$

$$\sum_k S_j^k(T_r, P_r)$$

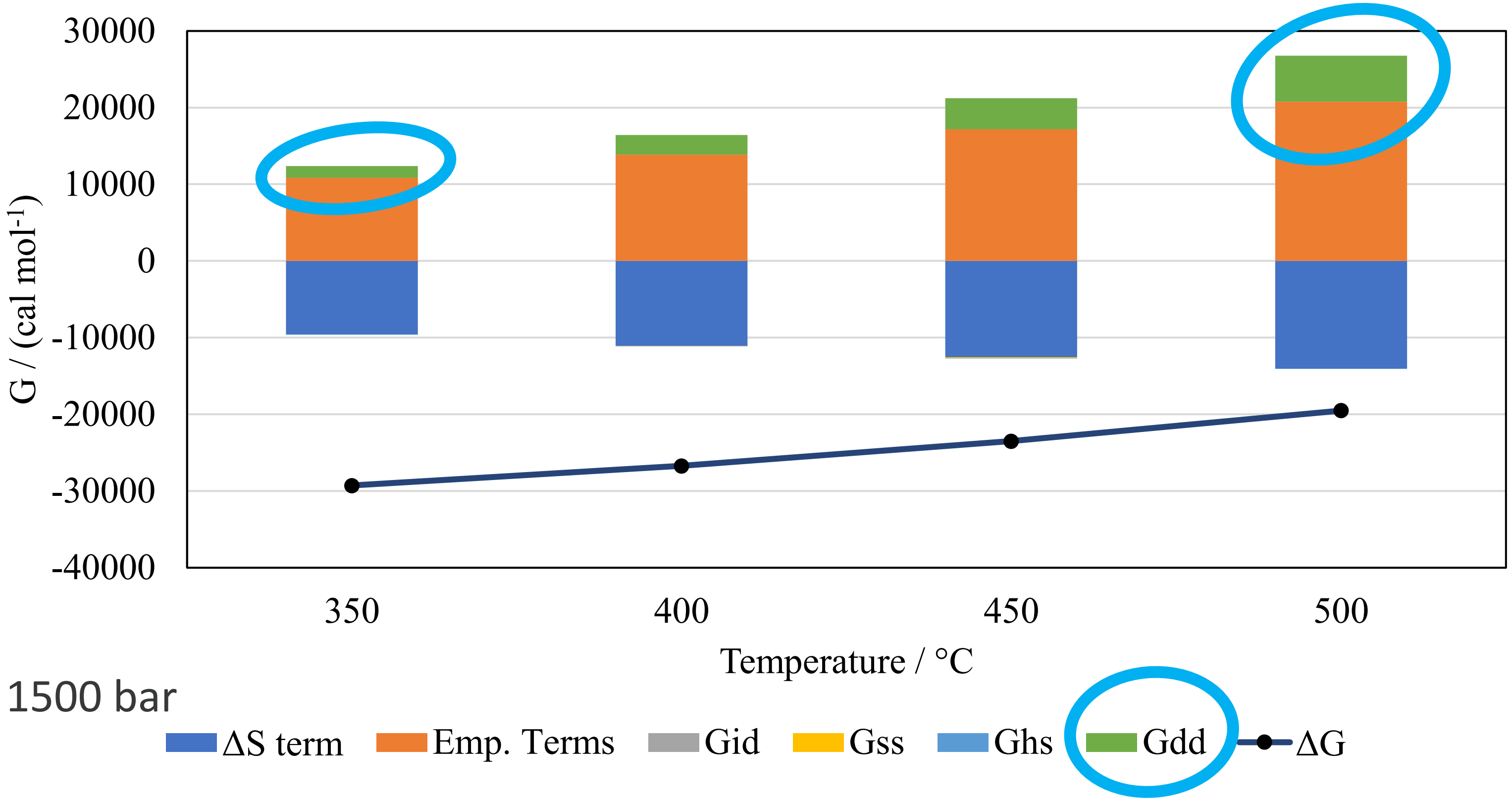
HS, ID, DD, SS, and MS entropy contributions

New dipole-dipole entropy term-important when ion-pairs appears & at T> 300 C

Lvov, S. N., Hall, D. M., Bandura, A. V., & Gamwo, I. K. (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.

Contributions of Each Term at HTHP

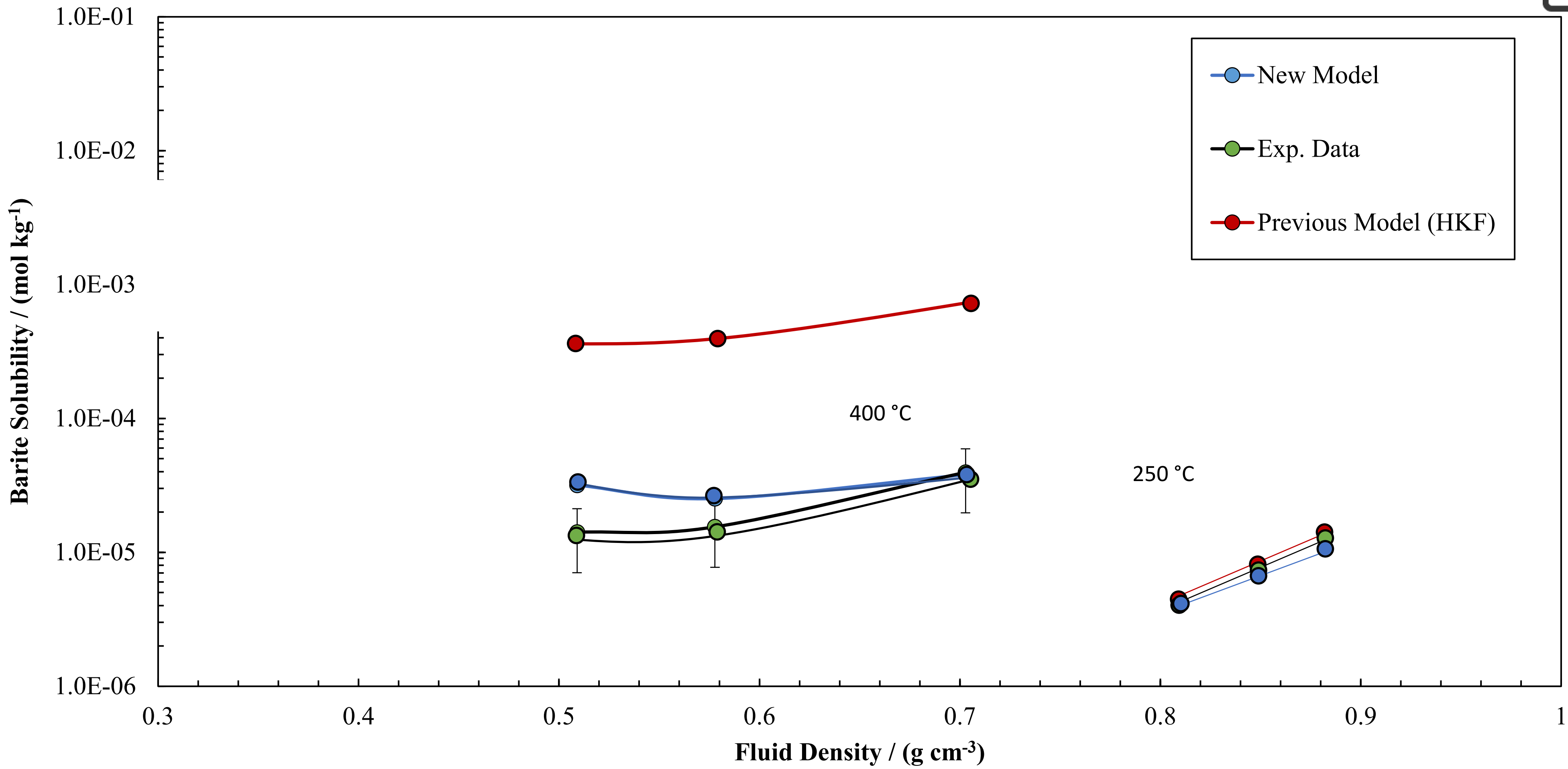
This example is for a neutral molecule to demonstrate the impact of the new terms.



P = 1500 bar

- New dipole-dipole contributions (both G and S) were dominant factors in HTHP regions.

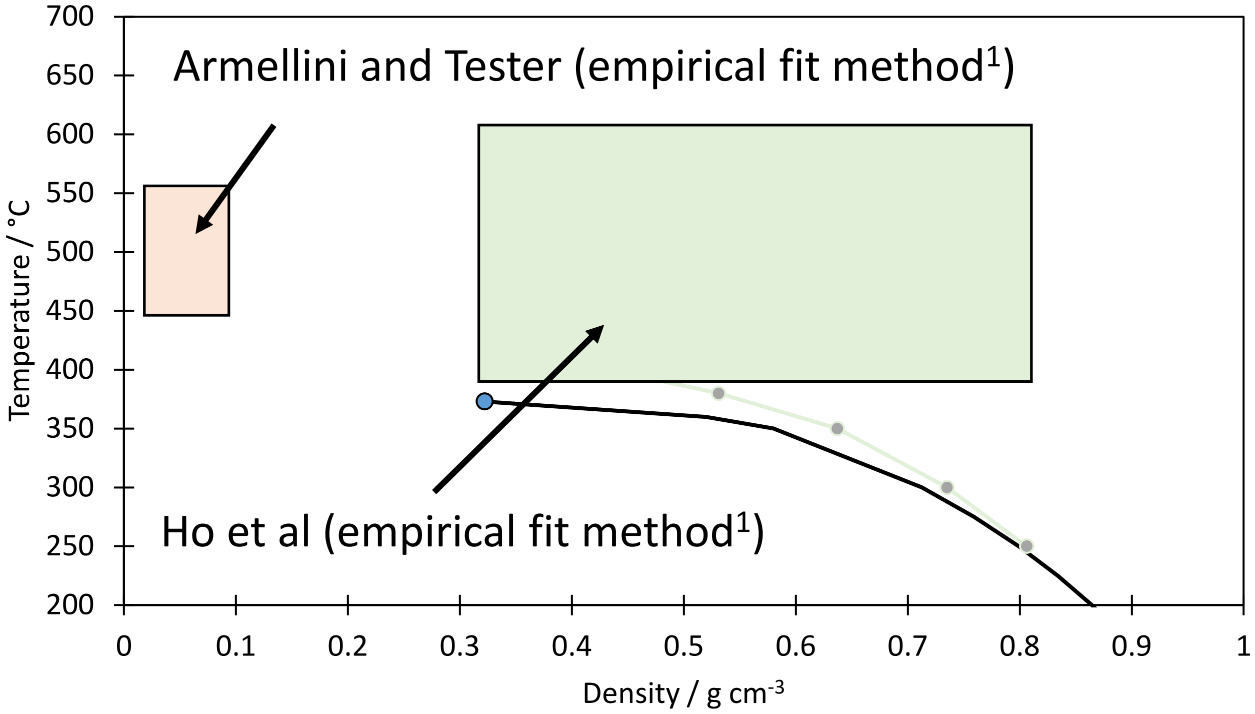
Comparison old model, new model, and experimental data (250, 400, 500°C)



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

Currently <u>two different models are needed</u> to cover low densities (0.03-0.1 g cm^{-3}) and high densities (0.3-0.8 g cm^{-3}) for HT systems.

Identified that $NaCl^0$(aq) has the largest dataset in HT conditions



This figure shows experimental data from NaCl(aq) solutions for two regions that currently require two different models as HKF model cannot cover both regions.

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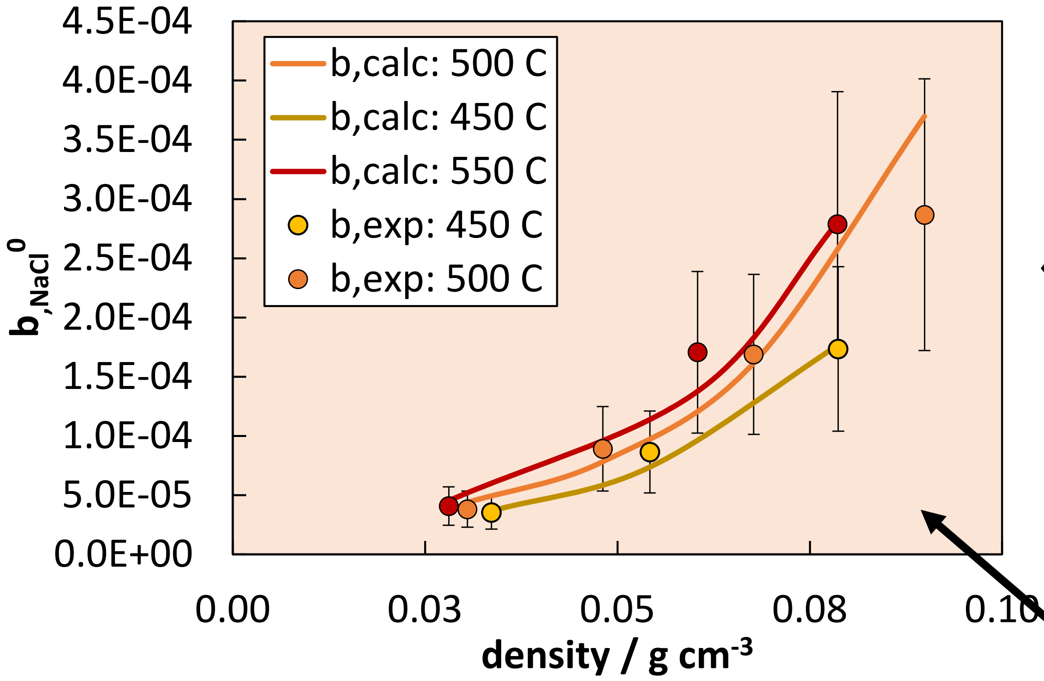
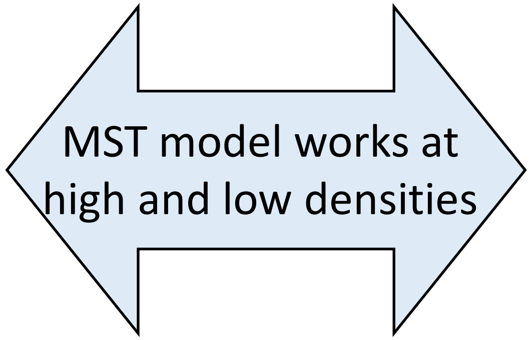
[1] Hall, D.M.; Lvov, S.N.; Gamwo, I.K. Thermodynamic Modeling of Mineral Scaling in High-Temperature and High-Pressure Aqueous Environments. *Liquids* **2022**, *2*, 303–317.

New model works across the density ranges in HT systems

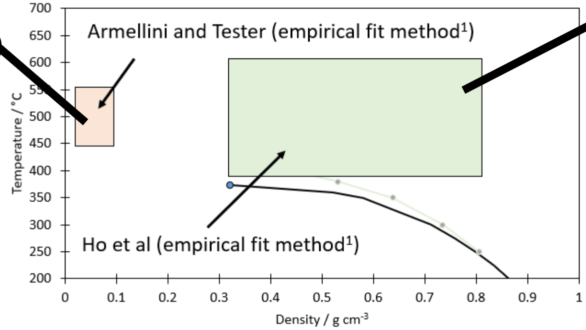
The MST model can capture experimental trends for $NaCl^0(aq)$ down to 0.03 g cm^{-3}; which is an order of magnitude lower than what is possible with the HKF model.

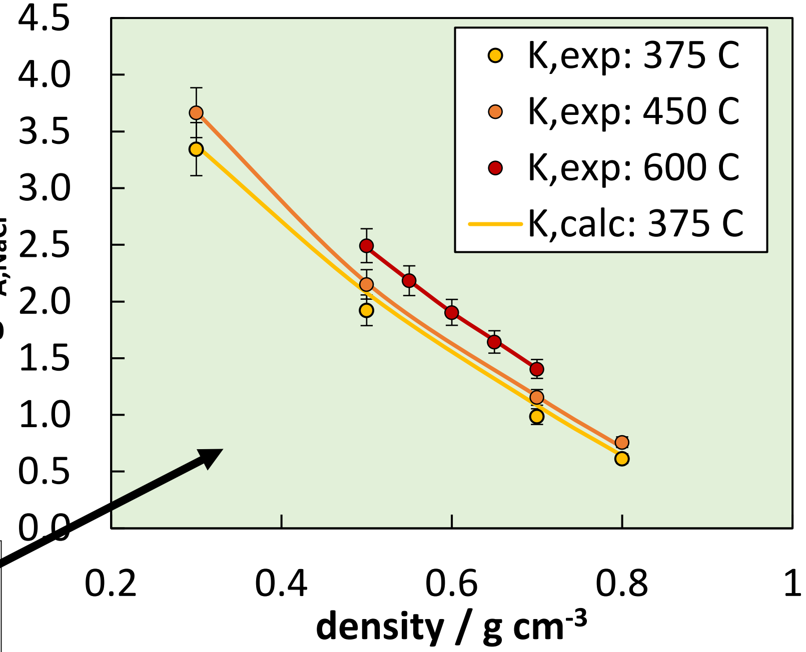


MST calculations compared to the Armellini and Tester dataset.



MST model works at high and low densities





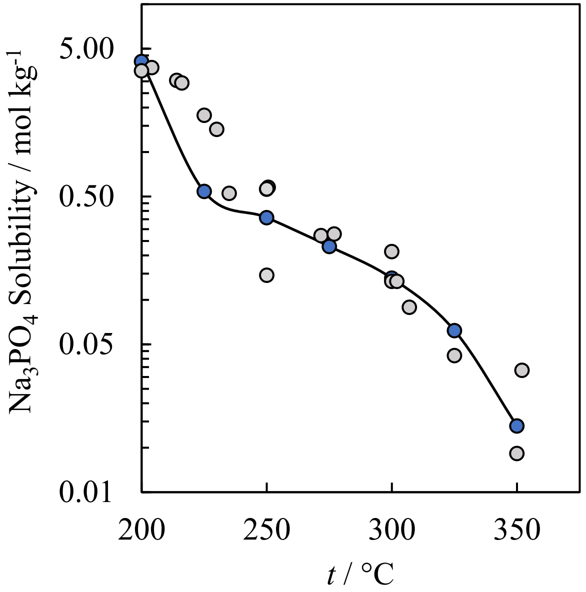
MST calculations compared to the Ho et al. dataset.

Successfully tested our model using experimental data found in literature for three salts over a wide range of parameters

Trisodium phosphate, Na3PO4(s)

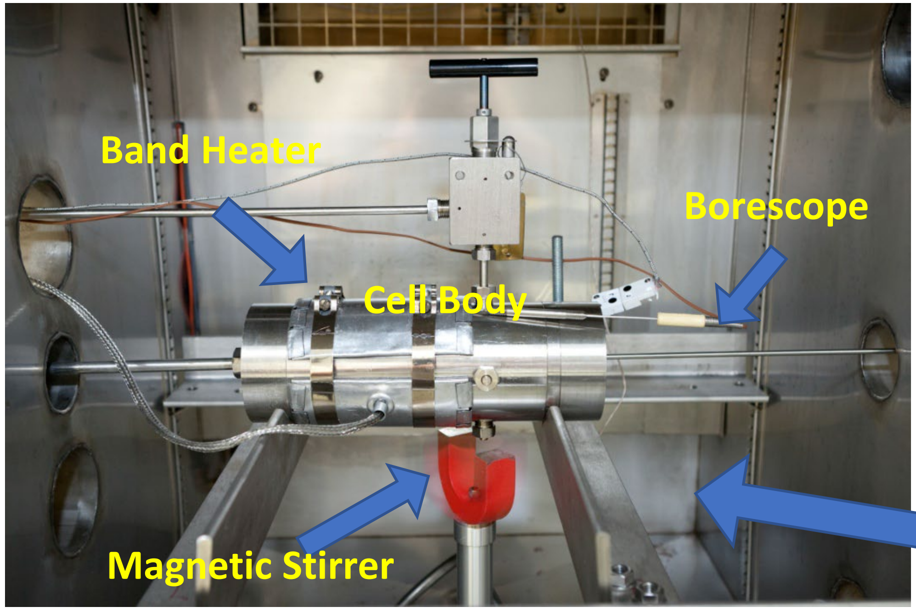
Barium Sulfate, BaSO4(s)

Sodium chloride, NaCl(s)

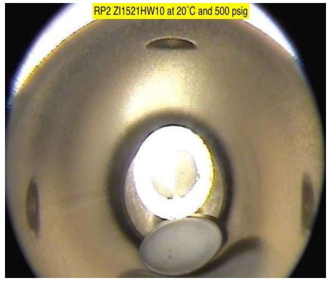


Mineral scale solubility limit for trisodium phosphate predicted using six chemical reactions and 9 chemical species.

NETL Solubility Experimental Setup
Temperature Effect on Mineral Solubility



Rated to 40,000 psi (275 MPa)
and 600°F (315°C)



EXPERIMENTAL EFFORTS

Reliable data - Used to validate System

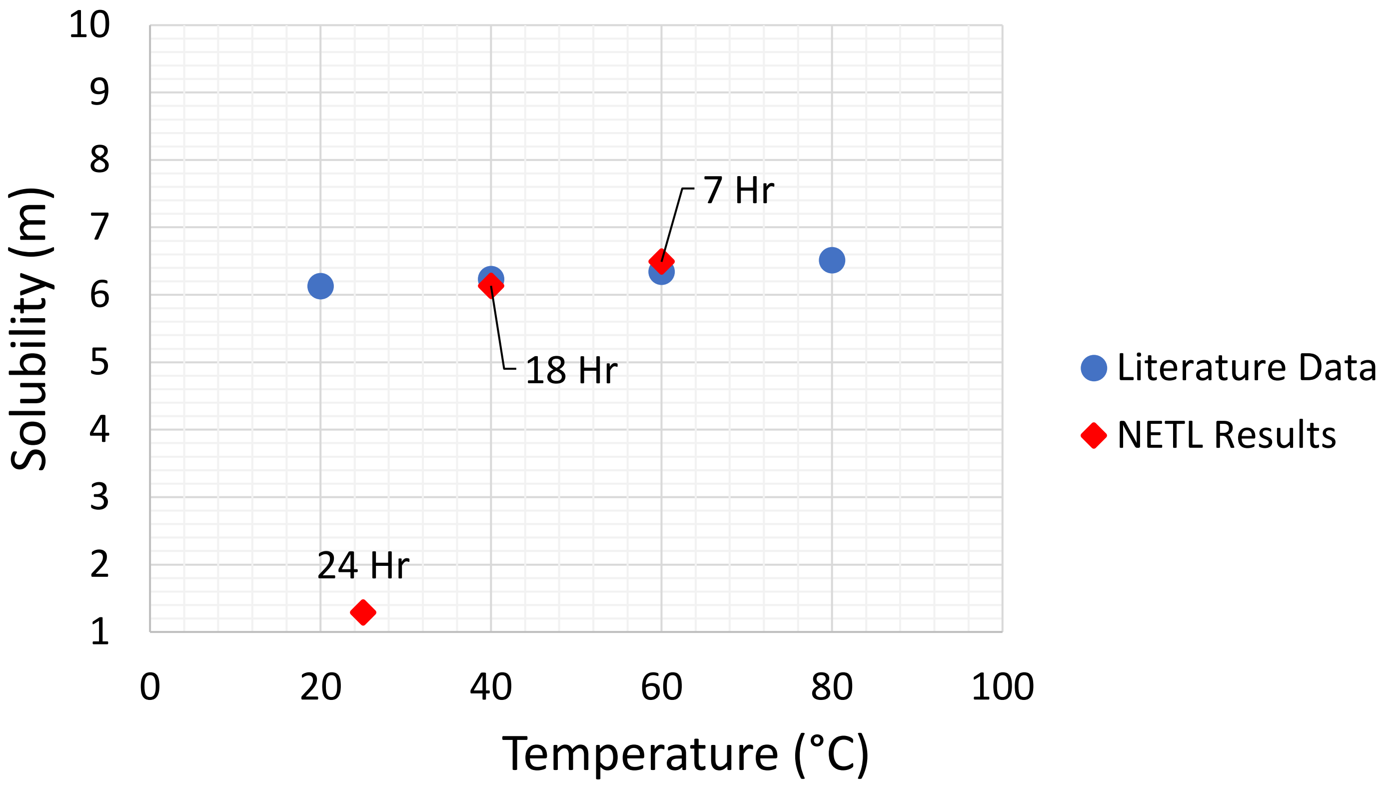
Halite (NaCl)

Common minerals in oil field production

Calcite ($CaCO_3$)

Barite ($BaSO_4$)

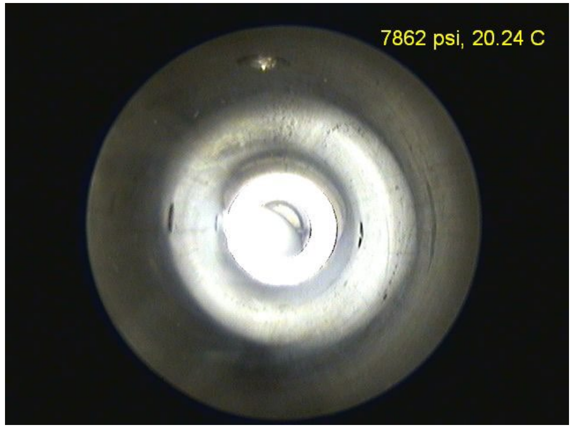
(Halite, NaCl); Comparison of NETL Results vs. Literature Data



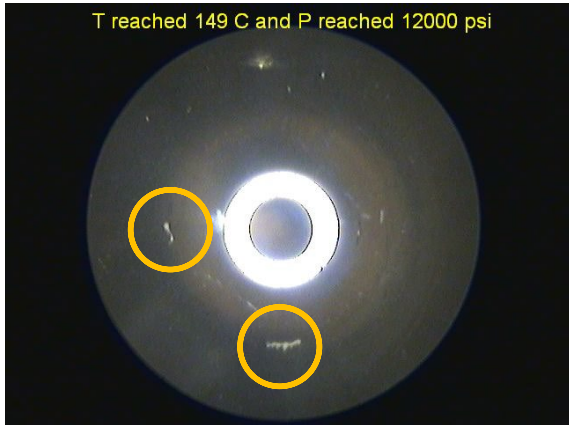
- NETL and Literature Halite data agree well at 40°C and 60 °C
- Poor Comparison @ 25°C – Experimental Errors

Experimental Still Images from-Experimental Scale Deposit Movie

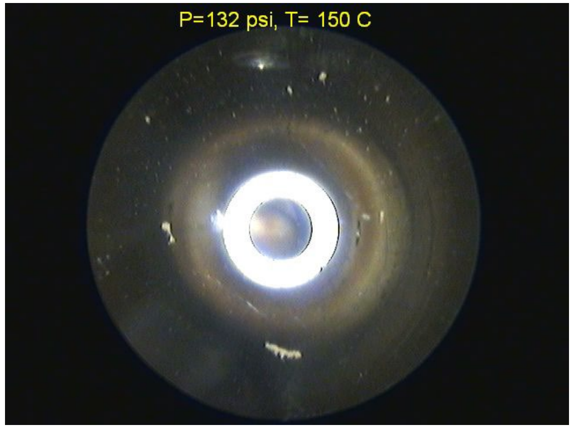
- Qualitative: Visualization of scale deposit at NETL's Experimental Facility
  Manipulated Parameters: T and P (Presented at the 2020 AIChE Virtual Meeting, Nov. 2020)



(1)
Clear calcite solution



(2)
Calcite deposits due to heating



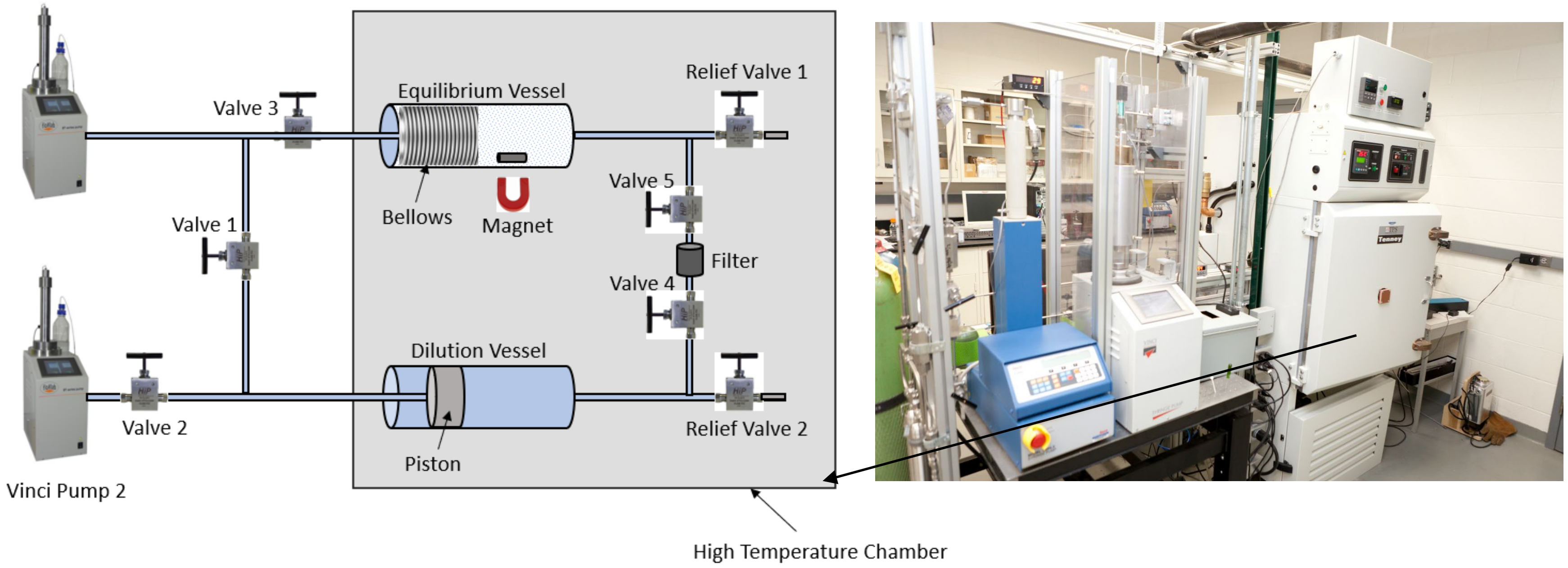
(3)
More deposits due to depressurizing

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

Movie Experimental Scale Deposit in NETL HTHP Apparatus uploaded to YouTube
https://youtu.be/Gl_My7bv-hE

New NETL Solubility Experimental Setup – (under construction)

Effects of Temperature and Pressure



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

- Data will be used to fill literature technical gap, validate model and provide the necessary model parameters
- Challenge: Long lead times for the delivery of the materials ordered.

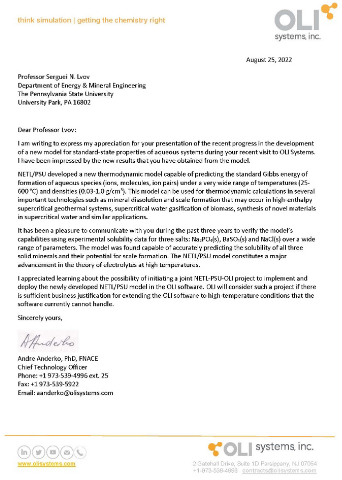
Implementation into Commercial Applications

Technology-to-Market Path

- OLI Systems, Inc., a commercial software released a support letter.
  CTO commended our new model and agreed to collaborate to implement our new model into OLI Studio to extend their capabilities in HT regions.
- Dr. Andre Anderko, CTO, August 25, 2022 (Letter)

"The NETL/PSU model constitutes a major advancement in the theory of electrolytes at high temperatures"

"I appreciated learning about the possibility of initiating a joint NETL-PSU-OLI project to implement and deploy the newly developed NETL/PSU model in the OLI software."



think simulation | getting the chemistry right

OLI systems, inc.

August 25, 2022

Professor Serguei N. Lvov
Department of Energy & Mineral Engineering
The Pennsylvania State University
University Park, PA 16802

Dear Professor Lvov:

I am writing to express my appreciation for your presentation of the recent progress in the development of a new model for standard-state properties of aqueous systems during your recent visit to OLI Systems. I have been impressed by the new results that you have obtained from the model.

NETL/PSU developed a new thermodynamic model capable of predicting the standard Gibbs energy of formation of aqueous species (ions, molecules, ion pairs) under a very wide range of temperatures (25-600 °C) and densities (0.03-1.0 g/cm^3). This model can be used for thermodynamic calculations in several important technologies such as mineral dissolution and scale formation that may occur in high-enthalpy supercritical geothermal systems, supercritical water gasification of biomass, synthesis of novel materials in supercritical water and similar applications.

It has been a pleasure to communicate with you during the past three years to verify the model's capabilities using experimental solubility data for three salts: $Na_3PO_4(s)$, $BaSO_4(s)$ and NaCl(s) over a wide range of parameters. The model was found capable of accurately predicting the solubility of all three solid minerals and their potential for scale formation. The NETL/PSU model constitutes a major advancement in the theory of electrolytes at high temperatures.

I appreciated learning about the possibility of initiating a joint NETL-PSU-OLI project to implement and deploy the newly developed NETL/PSU model in the OLI software. OLI will consider such a project if there is sufficient business justification for extending the OLI software to high-temperature conditions that the software currently cannot handle.

Sincerely yours,

Andre Anderko, PhD, FNACE
Chief Technology Officer
Phone: +1 973-539-4996 ext. 25
Fax: +1 973-539-5922
Email: aanderko@olisystems.com

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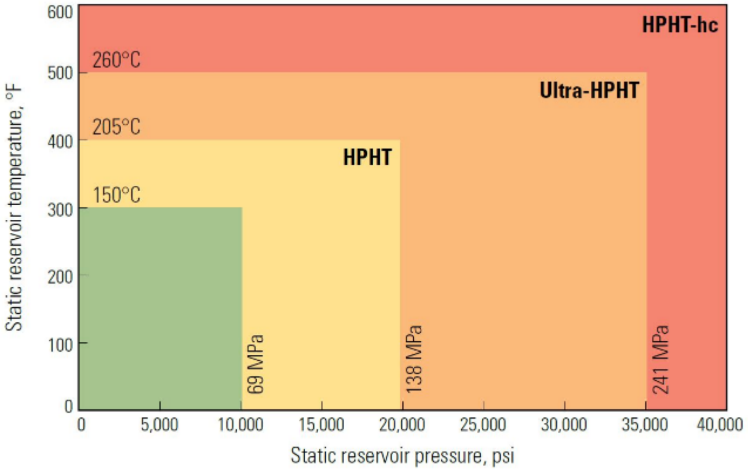
OLI's Chief Technology Officer's (CTO) Letter to praise the new model and interest to implement novel model developed on Task 8 into OLI. Dated August 25, 2022.

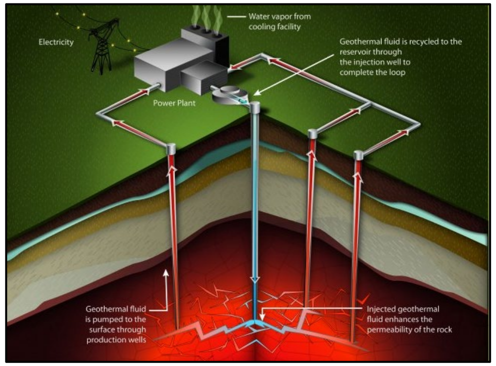
Potential Applications

- Results from this research would be helpful in pro-active mitigation of scale formation in high-temperature, high-pressure oil and gas reservoirs.

- Model can be used in Geothermal applications and fossil fuel powerplants for mineral scale mitigation



HPHT Oil and Gas Wells



Geothermal Energy

Fossil Fuel Powerplants

Summary of Accomplishments

- Completed the review of thermodynamic mineral scale models developed over the past 4 decades.

  None of the models has the capability to accurately predict mineral solubility at temperature above 300 ^{0}C and densities below 0.7g/cm^3

- NETL-PSU developed new thermodynamic model capable of accurately predicting mineral solubility over a very wide range of temperatures (25 - 600 °C) and densities (0.03-1.0 g/cm^3)
- New model predictions show very good agreement with experimental data for a comprehensive range of temperatures and pressures.
- OLI Systems, Inc., a commercial software, has agreed to collaborate to implement our new model to extend their capabilities in HT regions.
- Developing a new experimental capability to measure mineral solubility at HTHP conditions.

Outreach Product Released

Publications

Journal

- Hall, D.M.; Lvov, S.N.; Gamwo, I.K. Thermodynamic Modeling of Mineral Scaling in High-Temperature and High-Pressure Aqueous Environments. *Liquids* **2022**, *2*, 303–317.

Book Chapter

- Hall, D.M.; Lvov, S.N.; Gamwo, I.K. Prediction of Barium Sulfate Deposition in Petroleum and Hydrothermal Systems. In *Solid–Liquid Separation Technologies: Applications for Produced Water*; Gamwo, I.K., Ogunsola, O., Eds.; CRC Press Taylor & Francis, 2022; pp. 101–121.

Presentations

- Gamwo, I.K., Hall, D.M., Lvov, S.N. Baled, H.O. Modeling Barium Sulfate Precipitation in High Temperature Systems based on Molecular Statistical Thermodynamics Model, paper 425c, AIChE Annual Meeting, Boston, MA, November 7-11, (2021).
- Gamwo, I.K., Hall, D.M., Lvov, Baled, H.O. Status of Modeling and Visual Observation of Mineral Scaling in High Temperature Aqueous Solutions. AIChE Annual Meeting. (2020)

More Details in 2022 Journal Article…

liquids

MDPI

Review

Thermodynamic Modeling of Mineral Scaling in High-Temperature and High-Pressure Aqueous Environments

Derek M. Hall [1,2], Serguei N. Lvov [1,2,3] and Isaac K. Gamwo [1,*]

1 National Energy Technology Laboratory (NETL), Research and Innovation Center, U.S. Department of Energy, Pittsburgh, PA 152356, USA
2 Department of Energy and Mineral Engineering, The Pennsylvania State University, University Park, PA 16802, USA
3 Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
* Correspondence: isaac.gamwo@netl.doe.gov

Abstract: Methods of predicting mineral scale formation have evolved over the years from simple empirical fittings to sophisticated computational programs. Though best practices can now solve complex multi-phase, multi-component systems, they are largely restricted to temperatures below 300 °C. This review examines critical gaps in existing mineral scale modeling approaches as well as strategies to overcome them. Above 300 °C, the most widely used model of standard thermodynamic functions for aqueous species fails when fluid densities are below 0.7 g cm^{-3}. This failure occurs due to the model's reliance on an empirical form of the Born equation which is unable to capture the trends observed in these high temperature, low density regimes. However, new models based on molecular solvent-solute interactions offer a pathway to overcome some of the deficiencies currently limiting high-temperature and high-pressure mineral scale predictions. Examples of the most common scale prediction methods are presented, and their advantages and disadvantages are discussed.

Keywords: mineral scale; high temperature; high pressure; review scaling models; aqueous species; partial molar Gibbs energy; equilibrium constants; Gibbs energy minimization

check for updates

Citation: Hall, D.M.; Lvov, S.N.; Gamwo, I.K. Thermodynamic Modeling of Mineral Scaling in High-Temperature and High-Pressure Aqueous Environments. Liquids **2022**, 2, 303–317. https://doi.org/10.3390/liquids2040018

Academic Editors: Juan Ortega Saavedra and William E. Acree, Jr.

Received: 13 August 2022
Accepted: 20 September 2022
Published: 28 September 2022

1. Introduction

The safety and reliance of many engineering applications rely on the prediction of operating scenarios that lead to severe mineral scale formation events. A classic example of the immediate and dramatic effects of scale formation is an event that occurred during early production from the Miller oil field which brought production of 30,000 barrels a day to zero in 24 h [1]. Knowledge of scaling conditions inform operating decisions that directly affect lifetime and safety [2]. As such, methods of modeling mineral solubility, which is the driving force for scale formation, date back to the early 1900s and are still being improved today. When available, mineral scale models can be used to (i) avoid mixing of incompatible brines, (ii) determine if scale inhibitors are needed and (iii) predict when scale removal maintenance is required [2,3]. Some common mineral scales are sulfate-based (Ba, Sr, Ca), oxides/hydroxide-based (Fe, Mg), and carbonate-based (Ca, Mg, Fe) [2]. However, the development of models to predict the formation of all these possibilities is an ongoing effort with many challenges due to the number of possible conditions that lead to mineral scale formation.

Determining the thermodynamic favorability of mineral scale formation is the first and most important step in combating mineral scaling. Thermodynamic favorability is governed by a mineral's solubility limit (b_{sat}) and whether a particular fluid is above or below that limit. As such, knowing b_{sat} is paramount to effective mineral scale control. To better predict b_{sat}, the modeling of how it changes with system conditions has evolved from simple polynomials [4,5] to sophisticated thermodynamic programs [6–9] containing

https://www.mdpi.com/journal/liquids

Liquids **2022**, 2, 303–317. https://doi.org/10.3390/liquids2040018

"Thermodynamic Modeling of Mineral Scaling in High-Temperature and High-Pressure Aqueous Environments. *Liquids* **2022**, *2*, 303–317.
https://doi.org/10.3390/liquids2040018

In the Special Issue of *Liquids* "Modeling of Liquids Behavior: Experiments, Theory and Simulations

THANK YOU FOR YOUR ATTENTION

QUESTIONS ?

Isaac.gamwo@netl.doe.gov

EY23 – EY25 Proposed Research- Phase II

❑ MODELING

Deploy the new model to the public and industry via two routes:

1. Deploy an online user-friendly calculator for solubility limits for oil field minerals to the public

2. Deploy the new model to the oil industry via commercial software OLI used by over 400 companies worldwide

❑ EXPERIMENTAL

1. Conduct solubility using a pseudo formation fluid with more than one mineral and other impurities found in real produced water

2. Collaborate with OLI for experimental studies of solubility of several minerals that can be used for obtaining the necessary model parameters

PROJECT MILESTONES

Task 8 - Thermodynamic Modeling of Mineral Scale at HTHP

Schedule

Milestone A - Completed 7/2019. Complete review capabilities of OLI Studio: ScaleChem software as it relates to the SLAC National Accelerator Laboratory and NETL's onshore projects.

Milestone B – Completed 11/2019. Complete experimental setup and design of scale deposit experiments.

Milestone C - Delayed to 01/2023. Complete experiments of scale formation (Long lead time to setup solubility experiment- Limited Lab access).

Milestone D – Completed 11/2020. Extend state-of-the art scaling models to HTHP conditions.

Milestone E – On track -12/2022 Stretch: Collaboration with OLI to implement the newly developed thermodynamic scale model into OLI Studio: ScaleChem software.

Advances Made by Our Model - MS Gibbs Energy Contributions

Our model is the first to include molecular statistical thermodynamic (MST) equations

- Of the G_j MST equations, all but the dipole-dipole interaction were published previous.
- The novelty of our model was to include all of these terms together to formulate a useful Gibbs energy model substitutable for the HKF model.
- Additionally, the entropy terms for the ion-dipole and dipole-dipole were developed by us to complete the model. This accounts for entropy differences between MST entropy terms and real entropy values at standard conditions.

The sum of the new MST expressions

$$\sum_k G_j^k(T,P) - \sum_k G_j^k(T_r,P_r))$$

MST expressions

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

$$\frac{G_j^{ID}}{RT} = -\frac{N_A e^2 z_j^2(1-1/\varepsilon)}{\sigma_j+\sigma_w(\beta_6/\beta_3)}$$

$$\frac{G_j^{DD}}{RT} = \frac{-8N_A p_j^2(\varepsilon-1)}{2\sigma_w^3\left(1-\frac{\beta_{12}}{\beta_3}\right)\left(\frac{\beta_{12}}{\beta_6}\right)^3 + 2\varepsilon\left(\sigma_j+\sigma_w\frac{\beta_6}{\beta_3}\right)^3 + \left(\sigma_j+\sigma_w\frac{\beta_{12}}{\beta_6}\right)^3}$$

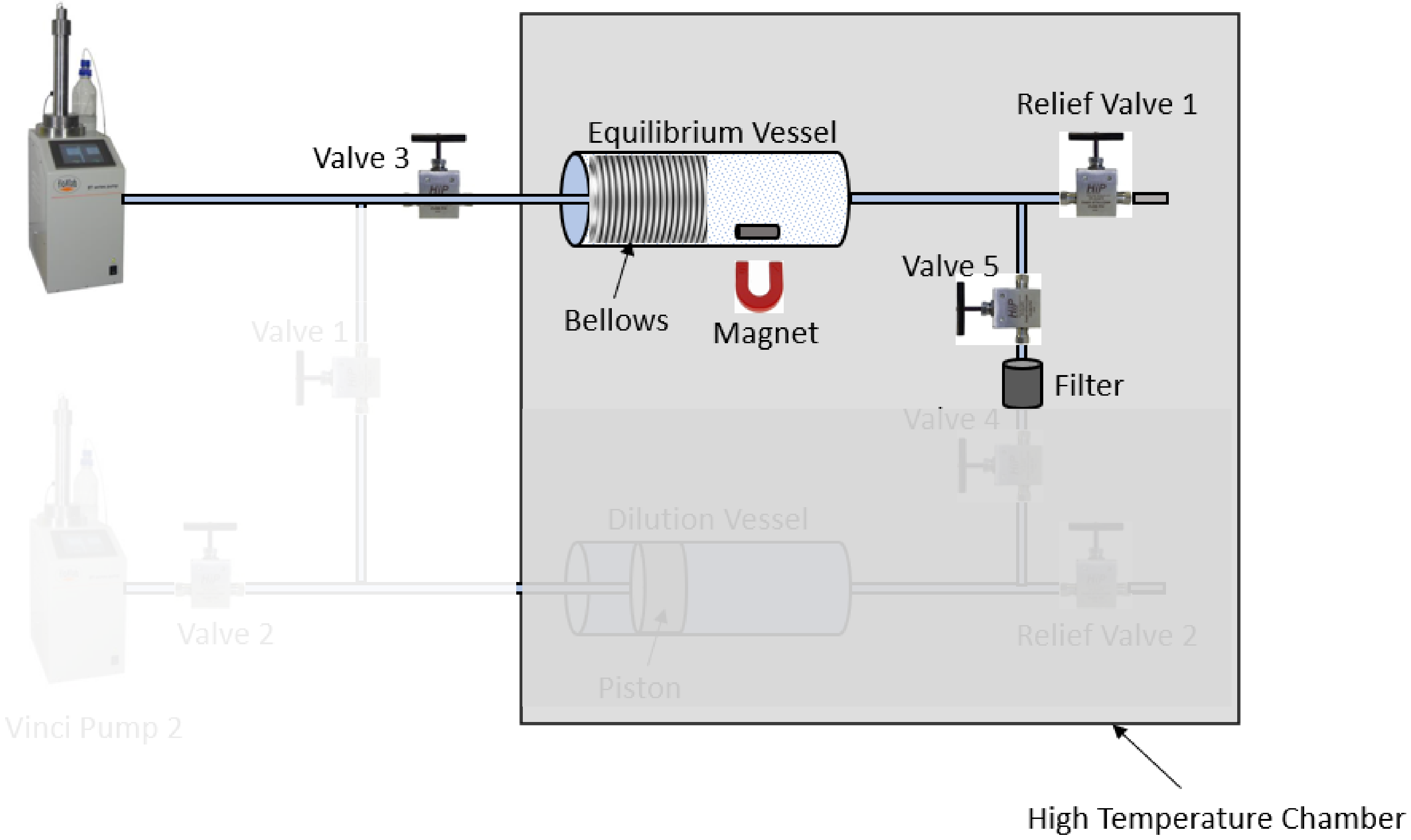
$$\frac{G_j^{SS}}{RT} = -ln(\rho RT/P^*)$$

$$\frac{G_j^{MS}}{RT} = -ln(M_s/b^0)$$

HS, ID, DD, SS, and MS Gibbs energy contributions

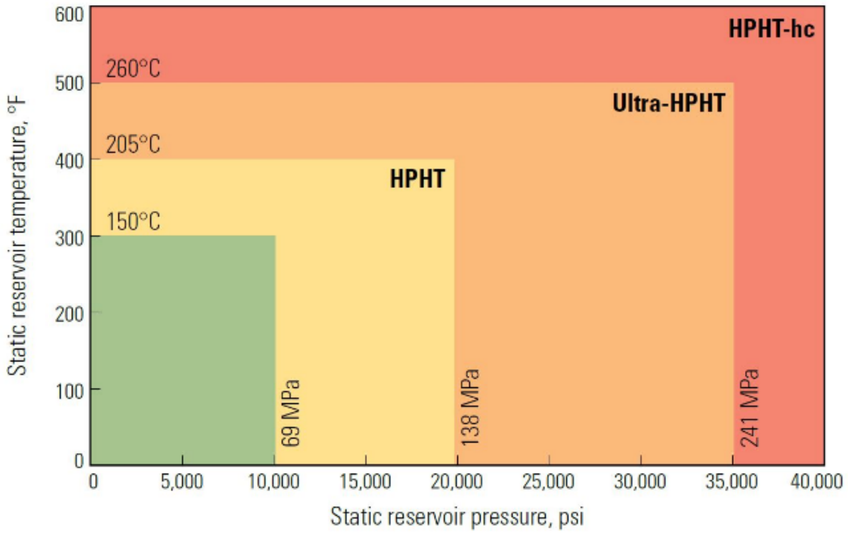
Lvov, S. N., Hall, D. M., Bandura, A. V., & Gamwo, I. K. (2018). A semi-empirical molecular statistical thermodynamic model for calculating standard molar Gibbs energies of aqueous species above and below the critical point of water. *Journal of Molecular Liquids*, *270*, 62–73.

Phase 1: Experimental Apparatus for Solubility Diagram –Effect of Temperature

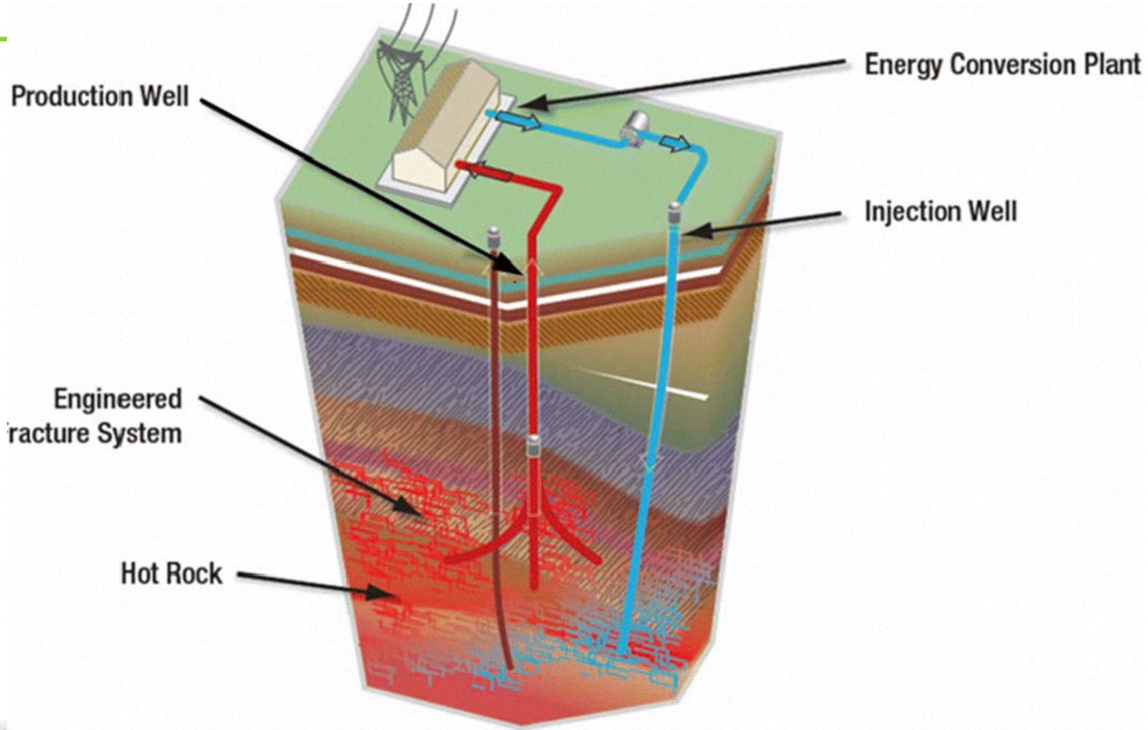


Experimental studies of the effects of pressure, temperature, pH, and ionic strength on the solubility of $CaSO_4$-NaCl-H_2O, $BaSO_4$-NaCl-H_2O, and Na_3PO_4-NaCl-H_2O

Wide Range of Applications of Extended HTHP Mineral Scale Models



HPHT Oil and Gas Wells

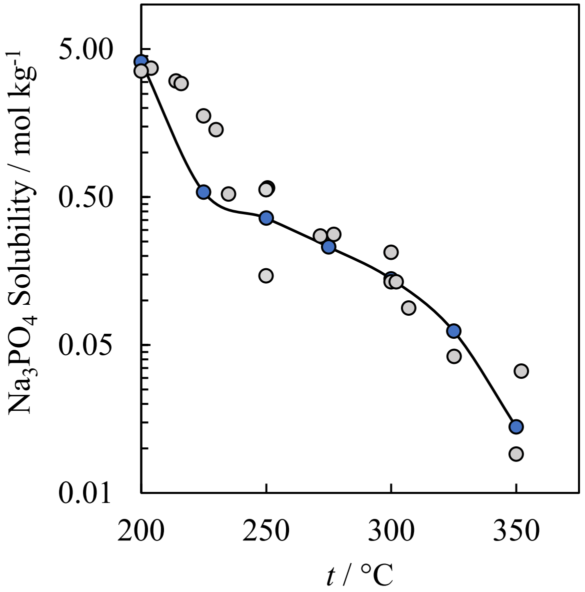


Geothermal Energy

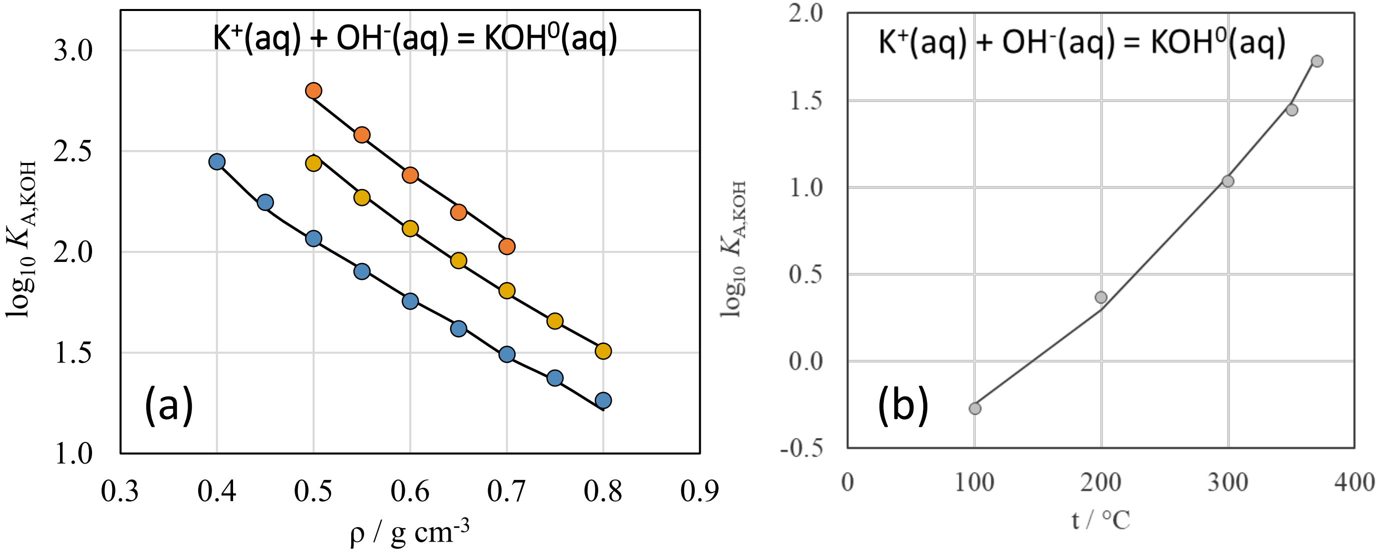
Oil Spill Prevention

Successfully tested our model using experimental data found in literature for a range of reaction types and chemical species

We added several molecules needed for new scaling and ion association reactions important to HT systems.

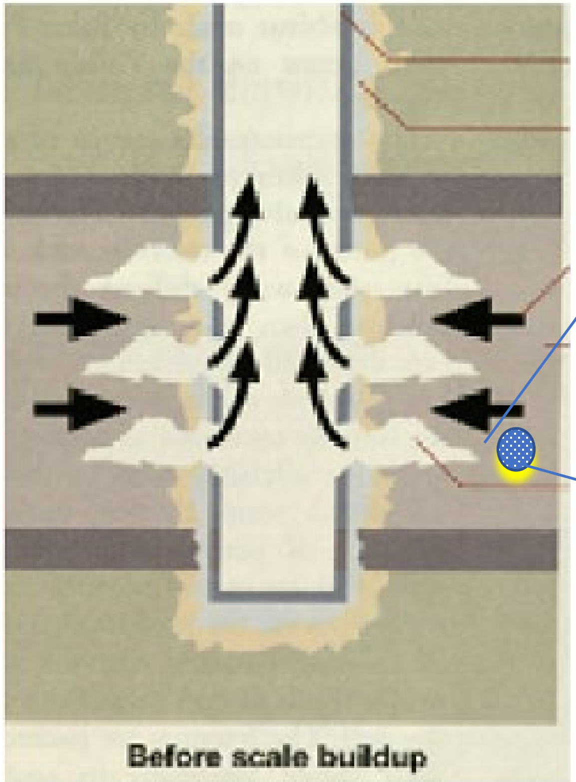


Mineral scale solubility limit for trisodium phosphate predicted using six chemical reactions and 9 chemical species.

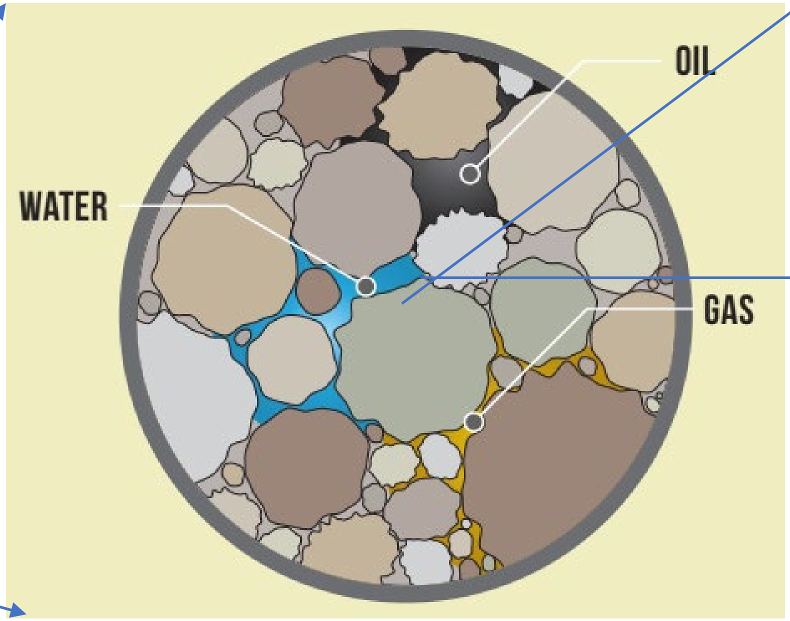


Comparison of experimental data with model predictions (black lines) for an ion association reaction with three chemical species. (a) supercritical association constant data (K_A) for $KOH^0(aq)$ at T = 400°C (blue circles), 500 °C (yellow circles) and 600°C (orange circles), and (b) subcritical conditions at P_{sat} (gray circles).

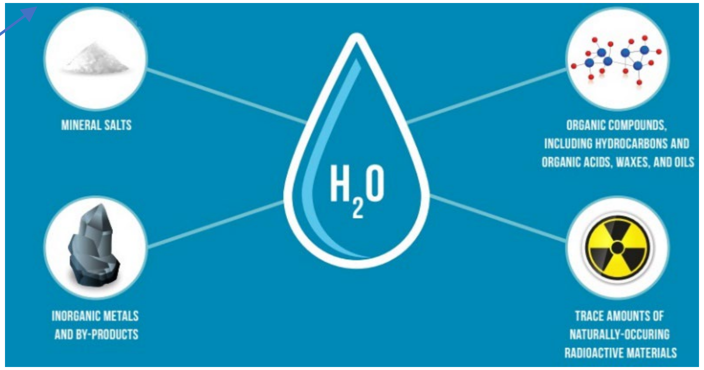
Why Do Mineral Scale Form?



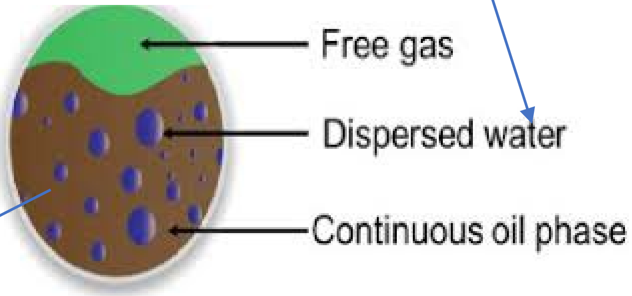
Oil Flow in the Wellbore



Pore Space in the Reservoir



Formation Water Constituents



Oil Flow in the horizontal Pipe

Minerals Precipitate out of Water and coat pipes