# Scale management and mitigation utilizing a novel theoretical tool

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# Scope

- Impact of mineral scales in desalination operations

- Incorporation of Mixed-Solvent Electrolyte (MSE) model with Classical Nucleation Theory (CNT) for modeling scaling phenomena

- Modeling of induction time kinetics for common scales in absence of any inhibitors

- Thermodynamic modeling of scaling inhibitors

- Modeling of induction time kinetics for common scales in the presence of inhibitors

# Scaling risk in desalination technologies



**Management of the brine produced as a waste product of reverse osmosis is a major environmental and technical challenge**

- To achieve high water recovery and enable valorization processes, brines must be concentrated to high salinities (up to 250 g/L)
- Mineral scale formation limits the efficacy and lifespan of both membrane and evaporative technologies

**Scale is any crystalline deposit (salt) resulting from the supersaturation of mineral ions present in the process fluid**

- Scales typically consist of one or more types of inorganic deposit along with other debris (organic precipitates, sand (Silica), corrosion products, etc.) on processing equipment
- Common scale forming ions include calcium ($Ca^{2+}$), barium ($Ba^{2+}$), strontium ($Sr^{2+}$) cations along with carbonates $CO_3^{2-}$, sulfate $SO_4^{2-}$ anions

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# Mechanisms of mineral scale formation

Homogeneous nucleation occurs in the absence of a foreign substance where the scale particles do not necessarily deposit or grow onto a surface
- Usually do not cause depositional issues

Heterogeneous nucleation occurs in the presence of a foreign substance to trigger nucleation
- Nuclei or corrosion products, welds/stress points on metal surface, corrosion sites on metal surface, scratches on metal surfaces, or small particles of suspended solids
- Scale particles build up on solid surfaces causing problems
  - **Pressure increases and fluid flow is restricted in the formation, pipelines, and surface facilities and can potentially prevent production equipment such as downhole sub-sea safety valves or heat exchangers/motors on pumps from operating as expected**

Scaling tendency is the thermodynamic indicator for scaling risk
- Assess the supersaturation level in the solution pertaining to salt

$$SI = \log \frac{a_{M^{2+}} a_{X^{2-}}}{K_{sp}} = \log \frac{m_{M^{2+}} m_{X^{2-}} \gamma_{M^{2+}} \gamma_{X^{2-}}}{K_{sp}}$$

# Mixed-Solvent Electrolyte (MSE) model for phase equilibrium and speciation calculations
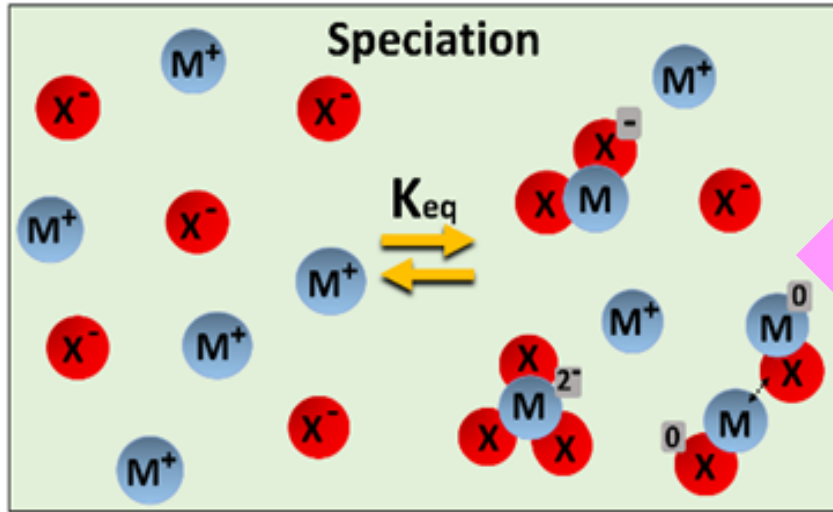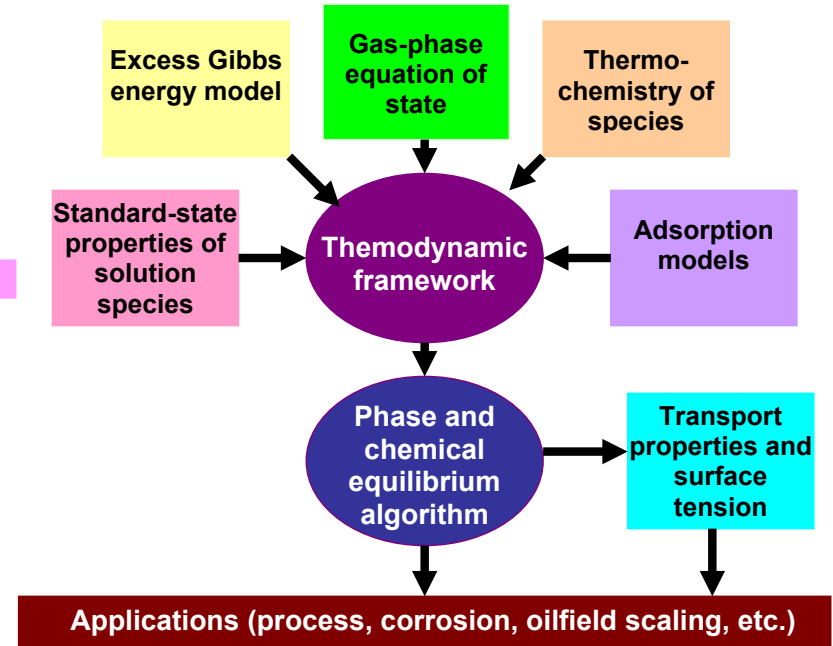


**Solution chemistry equilibria**

- Acid-base
- Complexation
- Redox
- Solid phase precipitation
- Surface complexation and other adsorption phenomena
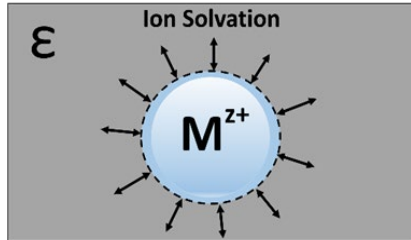
$$\sum v_i A_i = 0$$
$$\sum v_i \mu_i^L = 0$$

$$\mu_i^L = \mu_i^{L,0}(T,P) + RT \ln m_i \gamma_i (T,P,\mathbf{m})$$

Standard-state chemical potential (HKF model)
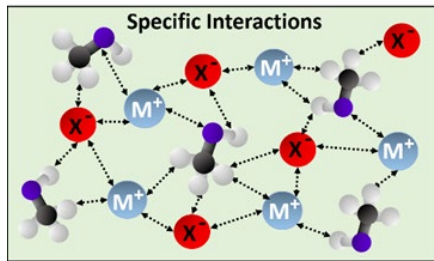
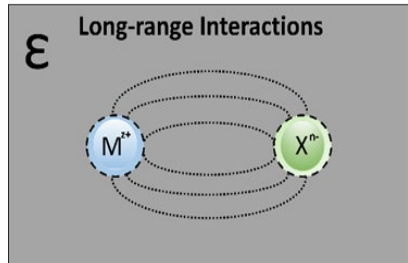Nonideality contribution: Activity coefficient (MSE $G^E$ model)

# Mixed-Solvent Electrolyte (MSE) model



## Standard-state properties

- Helgeson-Kirkham-Flowers equation for ionic and neutral aqueous species
- Standard thermochemistry for solid and gas species

## Excess Gibbs energy



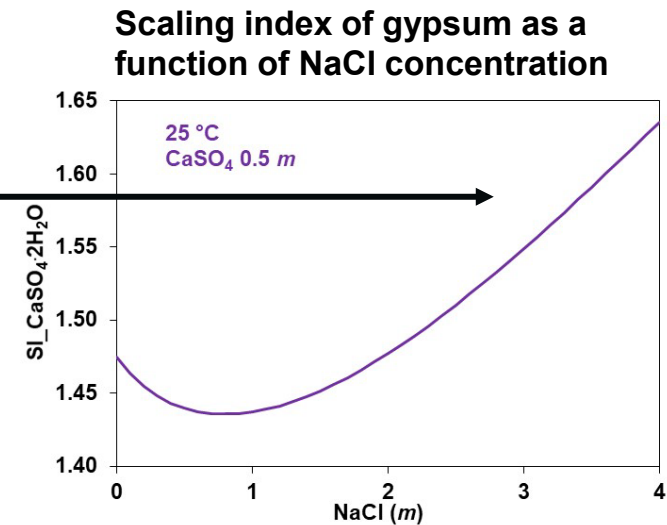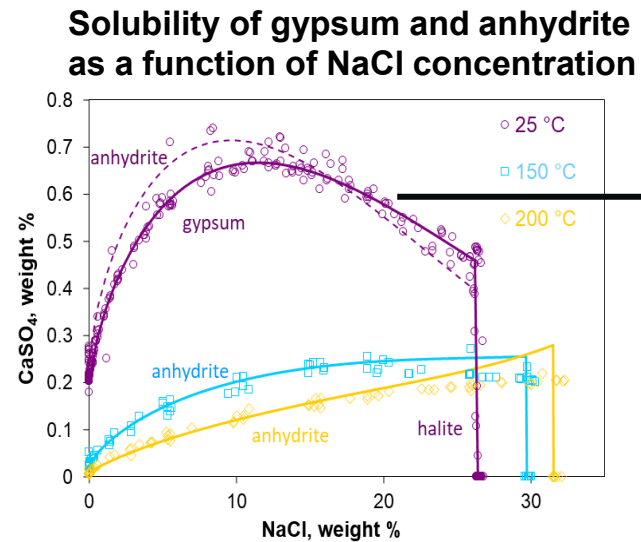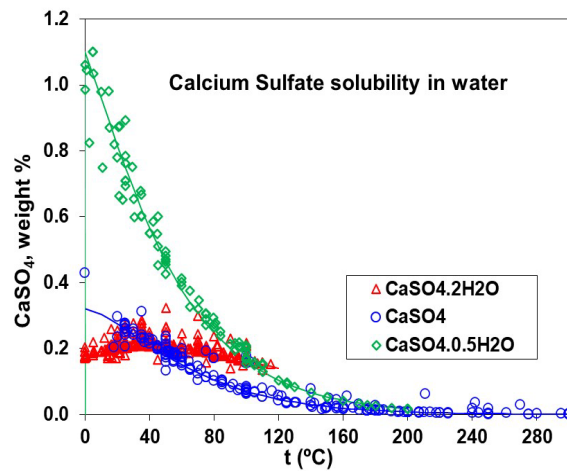$$\frac{G^{ex}}{RT} = \frac{G^{ex}_{LR}}{RT} + \frac{G^{ex}_{LC}}{RT} + \frac{G^{ex}_{II}}{RT}$$

LR   Long-range electrostatic interactions (Pitzer – Debye – Hückel)

LC   Local composition term for neutral molecule interactions (UNIQUAC)

II   Ionic interaction term for specific ion-ion and ion-molecule interactions

$$\frac{G^{ex}_{II}}{RT} = -\left(\sum_i n_i\right)\sum_i\sum_j x_i x_j B_{ij}(I_x)$$

# Thermodynamic framework for solubility and scaling tendency

**OLI's Mixed-Solvent Electrolyte (MSE) model accurately captures the solubility and thermodynamic properties of mineral scales including sulfates, carbonates, sulfides, silicates etc. in complex multicomponent brines**

- The model explicitly considers all essential solid phases along with aqueous species and complexes
- Enables precise estimation of scaling index, a fundamental parameter for the evaluation of induction time for scaling minerals



Solubility of gypsum and anhydrite as a function of NaCl concentration

Scaling index of gypsum as a function of NaCl concentration

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# MSE modeling of silica solubility

**OLI's Mixed-Solvent Electrolyte (MSE) model can accurately quantify silica solubility and supersaturation with consistent results across the wide ranges of temperature, pressure and pH**

- Silica supersaturation is driven by polymerization with rates are higher at higher initial monomeric silica concentrations
- Dissolved silica species is dominated by monomeric form, and pH is controlled by ionization
  - pH increases as polymerization proceeds (with decreased monomeric silica content)
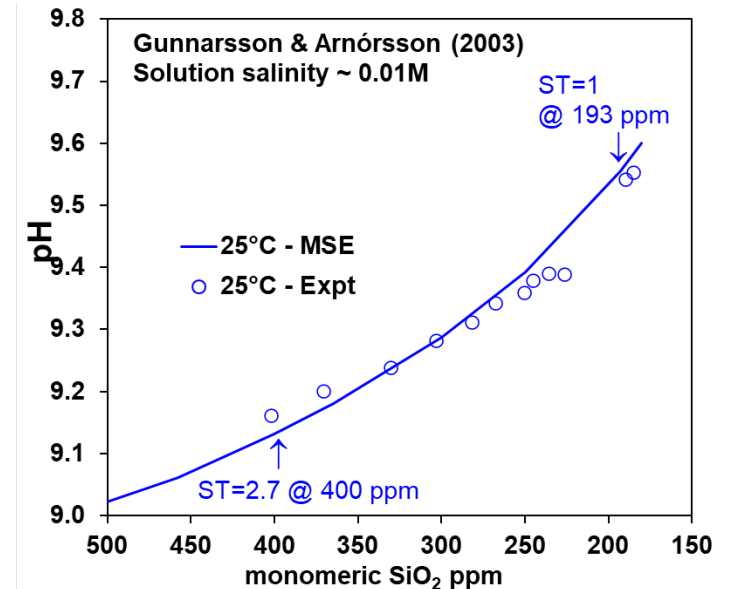


Solubility of silica at HTHP conditions
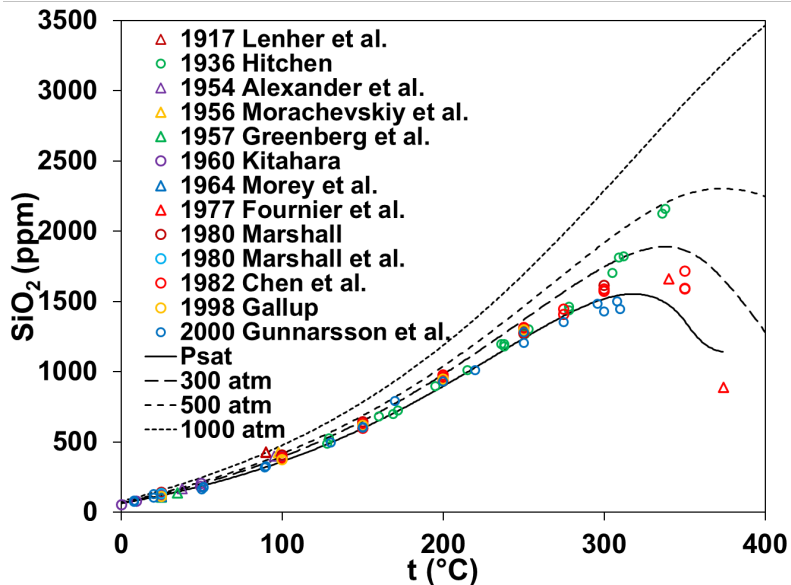
Solubility of silica as a function of pH
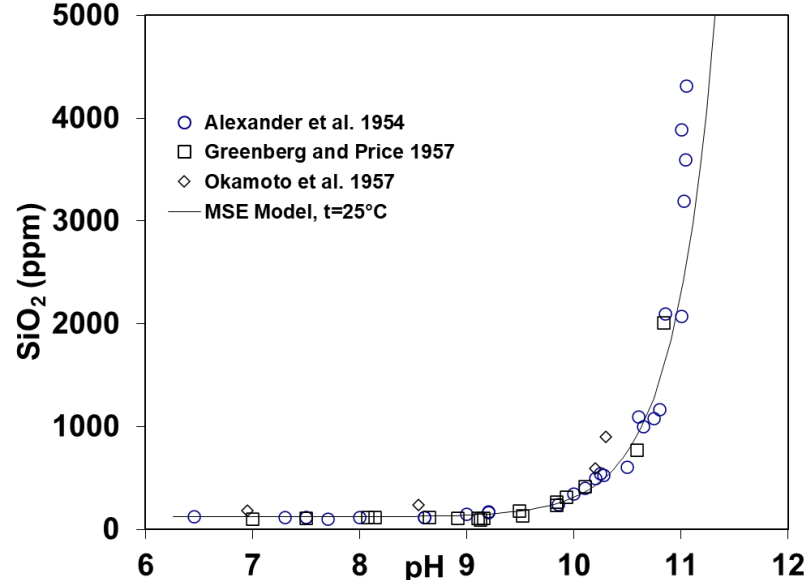
Effect of silica polymerization on solution pH

# Nucleation kinetics model

**Classical Nucleation theory (CNT) is based on the continuum thermodynamics treatment of clusters by imposing the capillarity approximation**
- Small clusters are considered to have the same properties as the bulk material

**Crystallization induction time period ($t_{ind}$)**
- Sum of the time for critical nucleus formation ($t_n$) and growth to detectable size ($t_g$), usually for heterogeneous nucleation; $t_n \gg t_g$

$$t_{ind} = J_s^{-1}$$

$J_s$=Steady-state nucleation rate

$$J_s = \Omega \exp\left[ -\frac{\beta \gamma^{s^3} V_m^2 f(\theta) N_A}{\upsilon^2 (RT)^3 \ln^2 S} \right]$$

$$\Omega = \Omega_{hom}, f(\theta) = 1$$
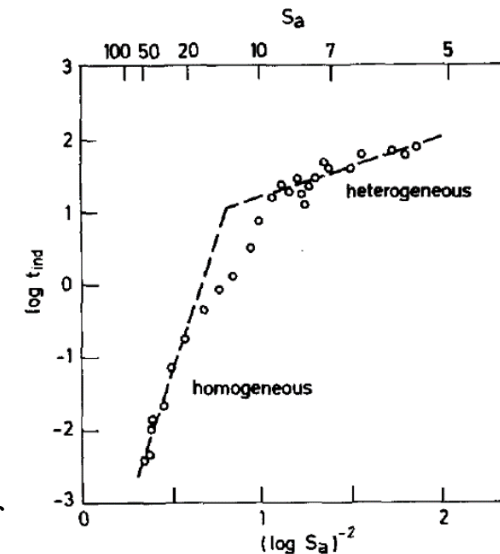$$\Omega = \Omega_{het}, f(\theta) < 1$$

$$\log(t_{ind}) = \left( B/T^3 \right) \log^2 S - A$$

$$B = \beta \gamma^{s^3} V_m^2 f(\theta) / (2.3RT)^3$$

$$A = \log \Omega$$

$$\gamma = \gamma_0 (1 + \sigma T)\left( 1 + \frac{a_1}{1 + e^{a_2 SI}} \right)$$

$\gamma_s$=interfacial energy
$f(\theta)$=correction factor,
$V_m$=molar volume,
$\beta$= geometric shape factor ($16\pi/3$)
$A$=frequency constant

$\sigma$ =coefficient to capture the effect of temperature on the interfacial energy

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# Induction time for sulfate scales

**CNT has been used to establish the correlation between the scaling index (obtained from MSE model) and induction time as evident in experimental data**

- All available experimental data from literature have been collected for sulfate scales (barite, celestine)
- Relationship between induction time and temperature has been evaluated and established
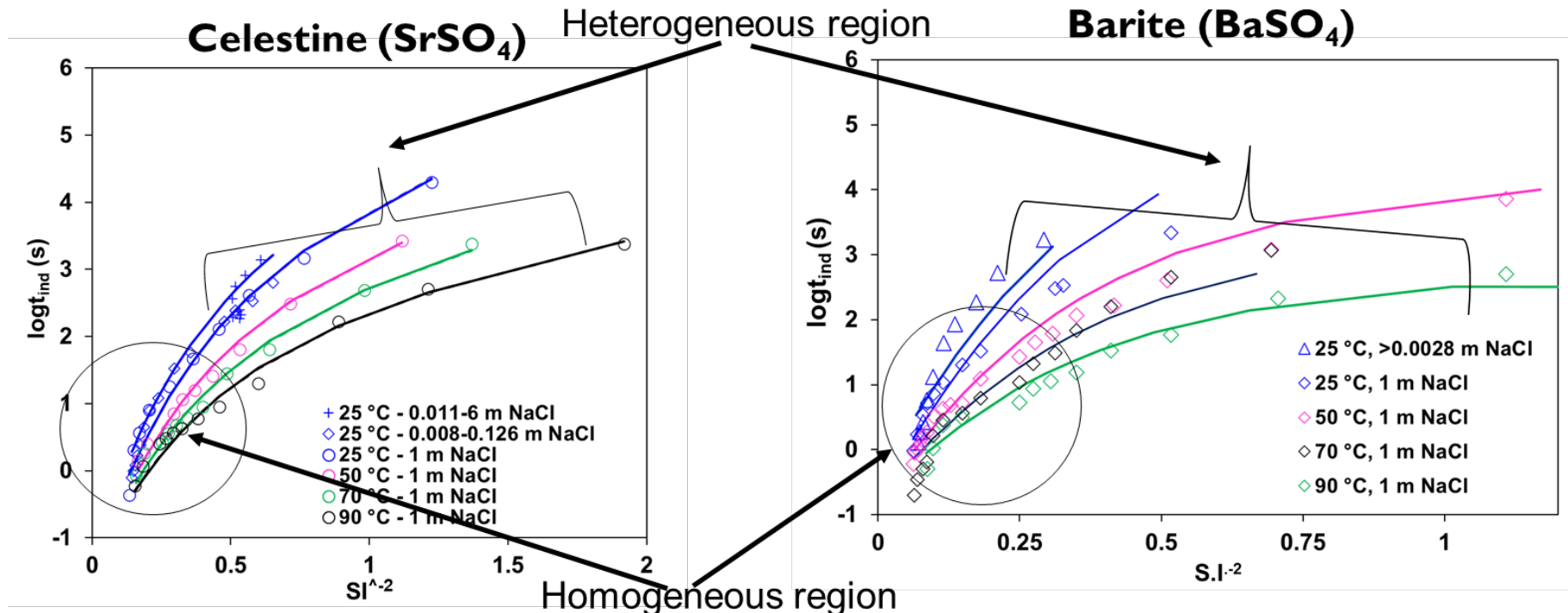
# Induction time for calcium scales

**Induction time characteristics of calcite and gypsum scales as a function of supersaturation level and temperature in the absence of any inhibitor**

- Induction time decreases rapidly with increase in temperature and saturation index as the kinetics for nucleus formation is enhanced

- Kinetics of gypsum scale formation is faster than the calcite scale
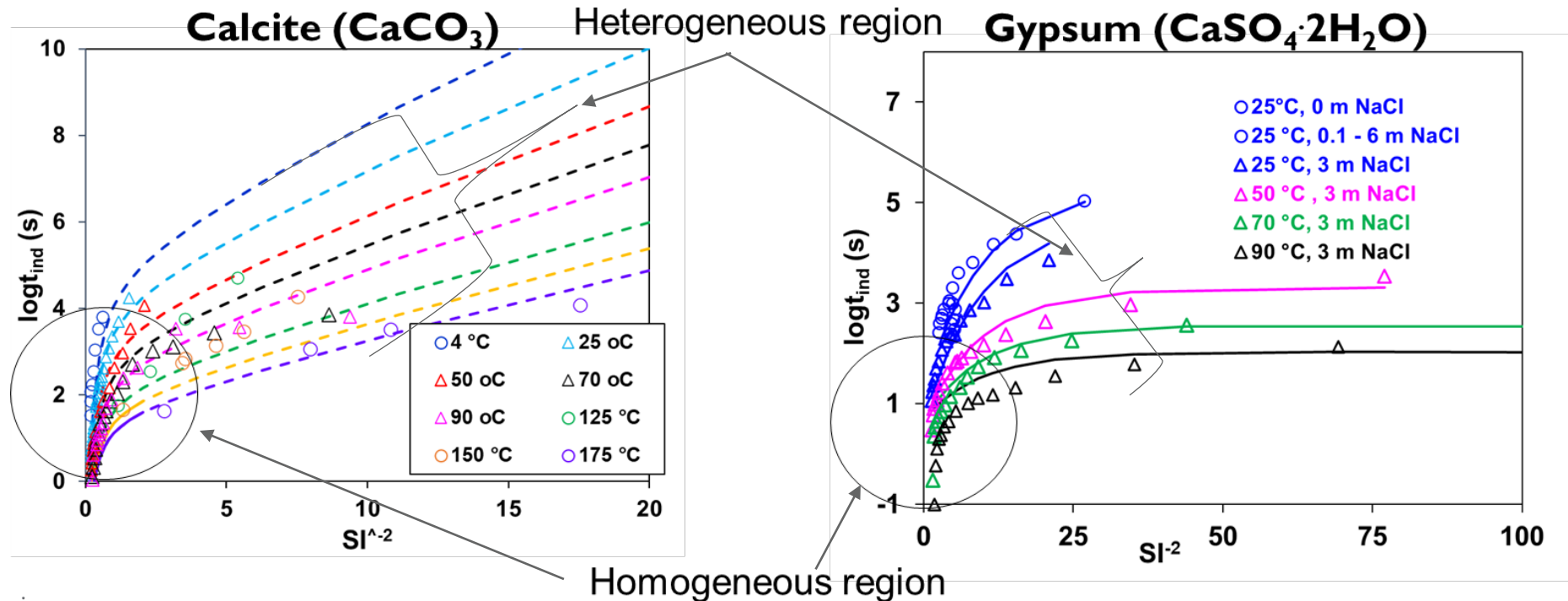
# Ionic strength dependance of the induction time

## The model captures the effect of background electrolytes through both kinetics and thermodynamics

- Effectively allows the theory to be more predictive and applicable over wide ranges of process conditions



Gypsum scale
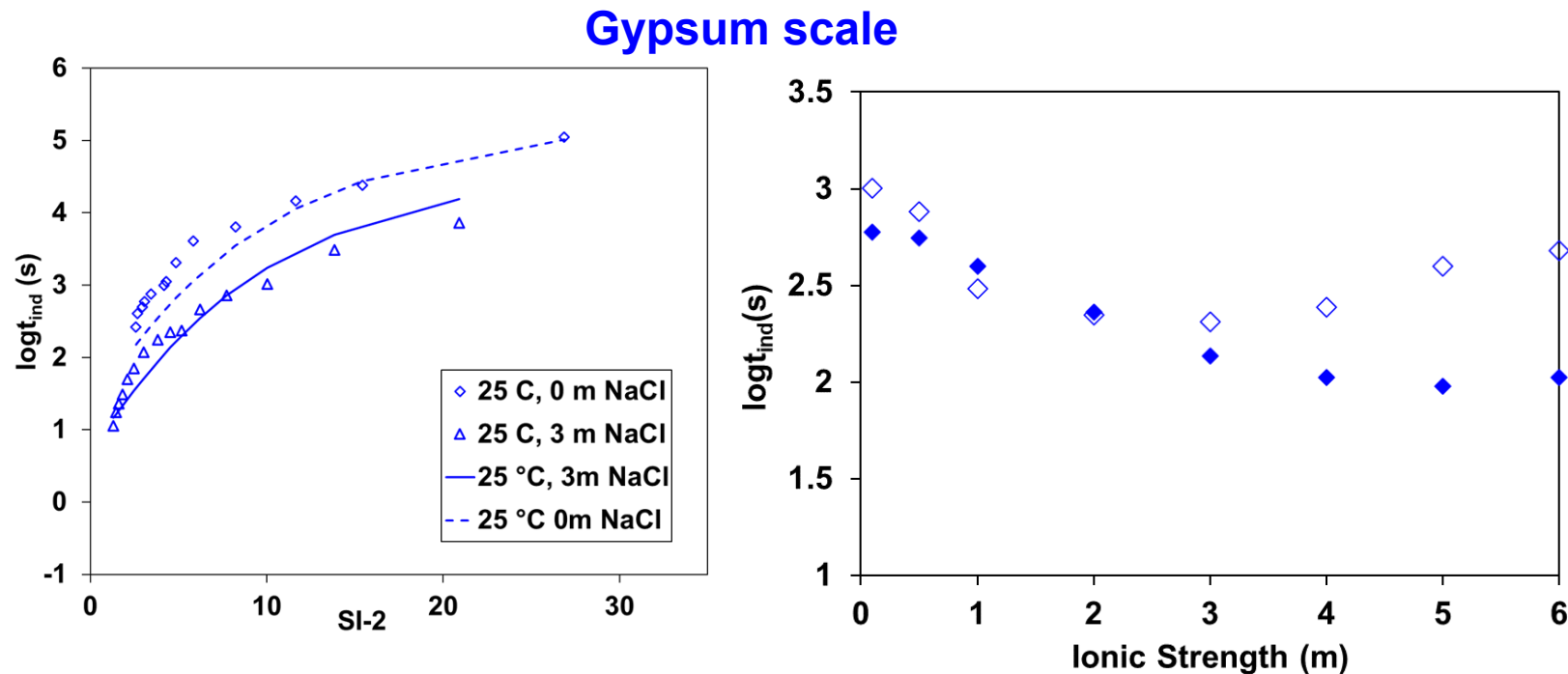
# Thermodynamic modeling of inhibitors: HEDP

**Thermodynamic models for key phosphonic acid-based inhibitors have been developed based on the primary and secondary solution chemistry data (titration, complexation constants and solubility)**

- Representation of the solution chemistry along with complexation characteristics in the presence of key cations is essential for reliable model development
- Provides a comprehensive understanding by illustrating the role of different active species in the inhibition phenomena

**Solution chemistry of HEDP with $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$ has been modeled using the MSE model**

- HEDP(aq), $HEDP^{1-}$, $HEDP^{2-}$, $HEDP^{3-}$, $HEDP^{4-}$ and $HEDP \cdot 1H_2O$ are considered as liquid species and solid respectively
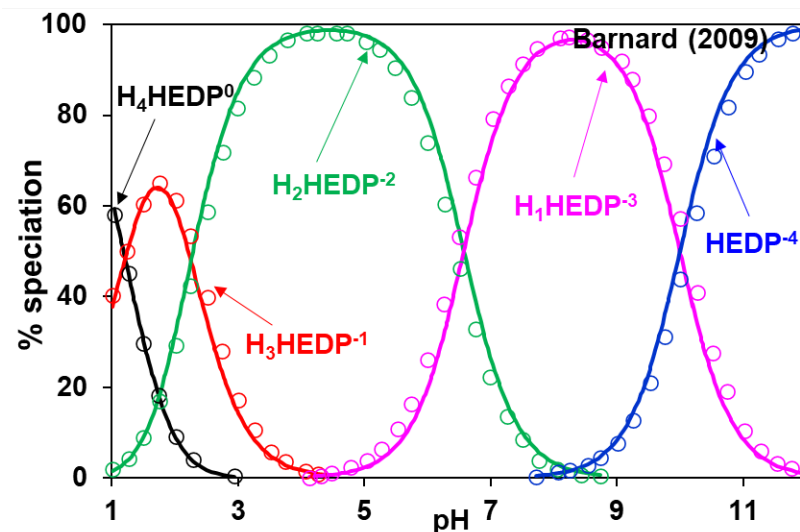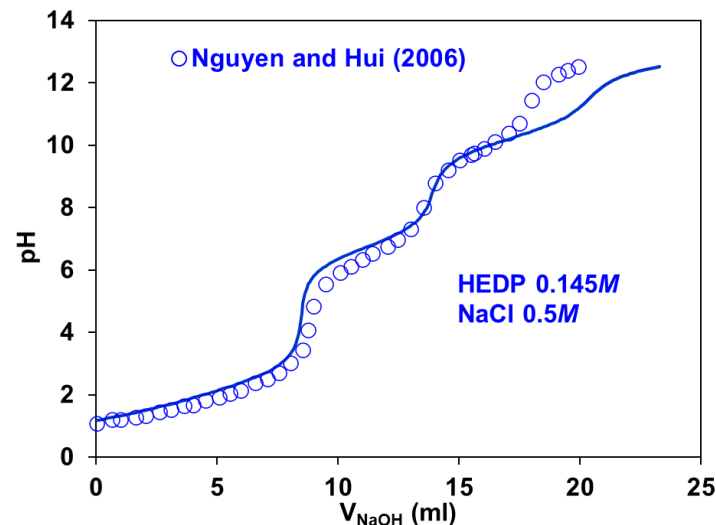


|  | pKa (Lit) | pKa (MSE) |
|---|---|---|
| HEDP(aq) | 1.6 | 1.349 |
| $HEDP^{1-}$ | 2.7 | 2.8219 |
| $HEDP^{2-}$ | 6.35 | 6.35 |
| $HEDP^{3-}$ | 11 | 11.695 |
| $CaHEDP^{2-}$ | 6.4 | 6.4791 |
| $CaHHEDP^{1-}$ | 4.2 | 4.1995 |
| $CaH_2HEDP$ | 2.63 | 2.6297 |
| SrHEDP | 4.8 | 4.7997 |
| SrHHEDP | 3.18 | 3.1798 |
| $SrH_2HEDP$ | 1.52 | 1.5199 |
| BaHEDP | 3.35 | 3.3494 |
| BaHHEDP | 2.72 | 2.7195 |

# Scaling inhibitors

- Speciation and titration curves elucidate the accuracy of theorical model in capturing solution characteristics of common inhibitors

- Influence of temperature, background electrolyte and complexation effect on the solution chemistry of the inhibitors has been explicitly modeled



NTMP



DTPMP
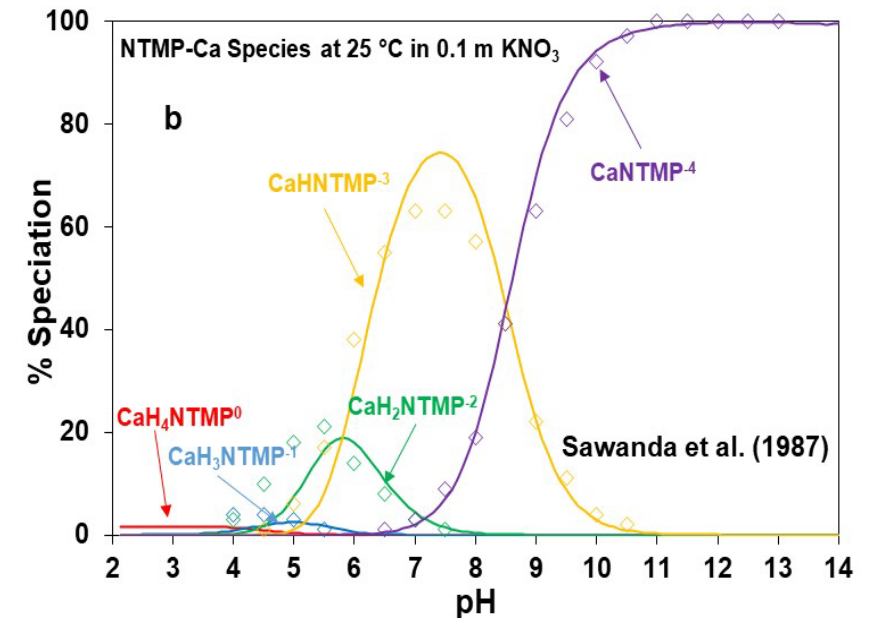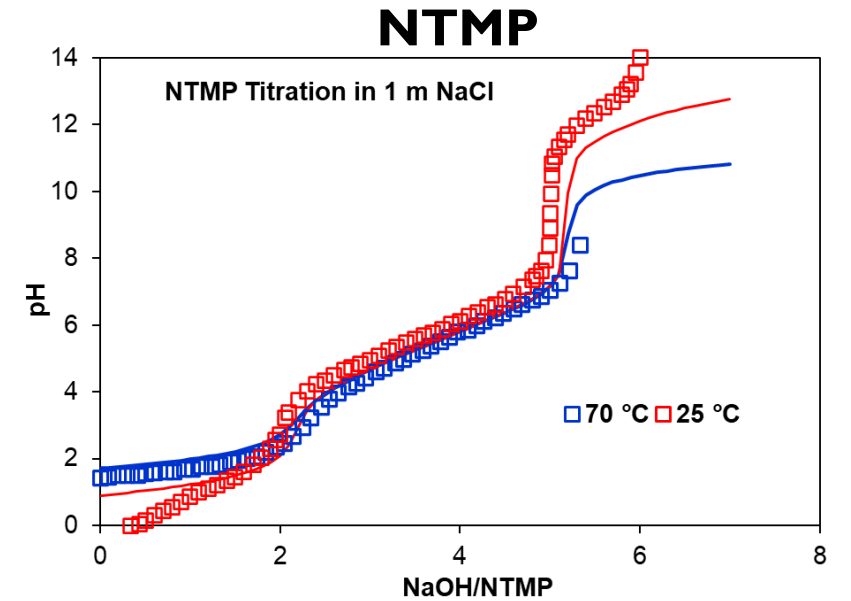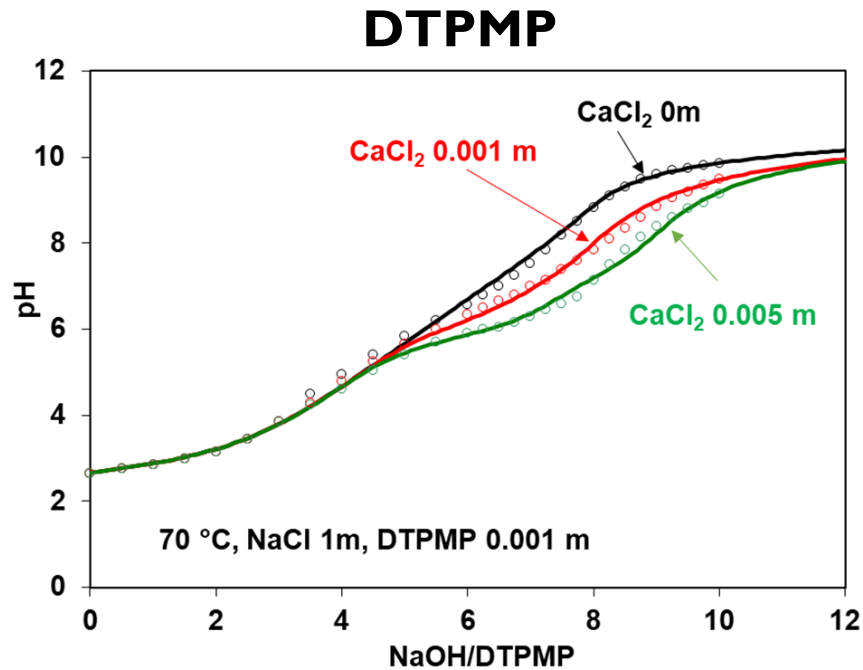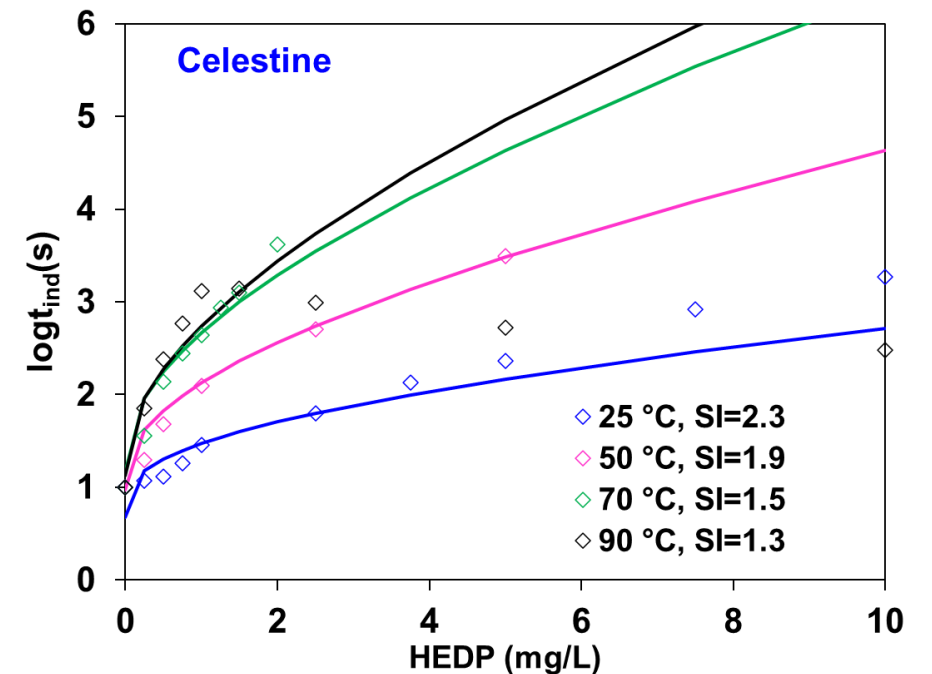
# Effect on inhibitor on induction time

**The influence of the adsorbed inhibitors on mineral surface is described by a Langmuir type adsorption isotherm**

- Theory will allow the adjustment of induction time data pertaining to mixed inhibitor systems

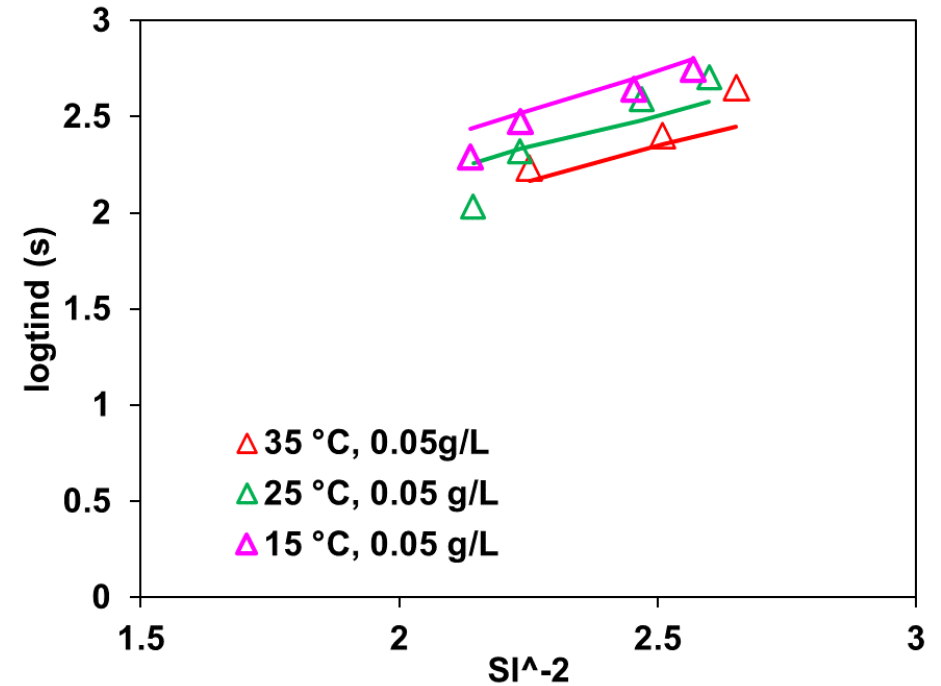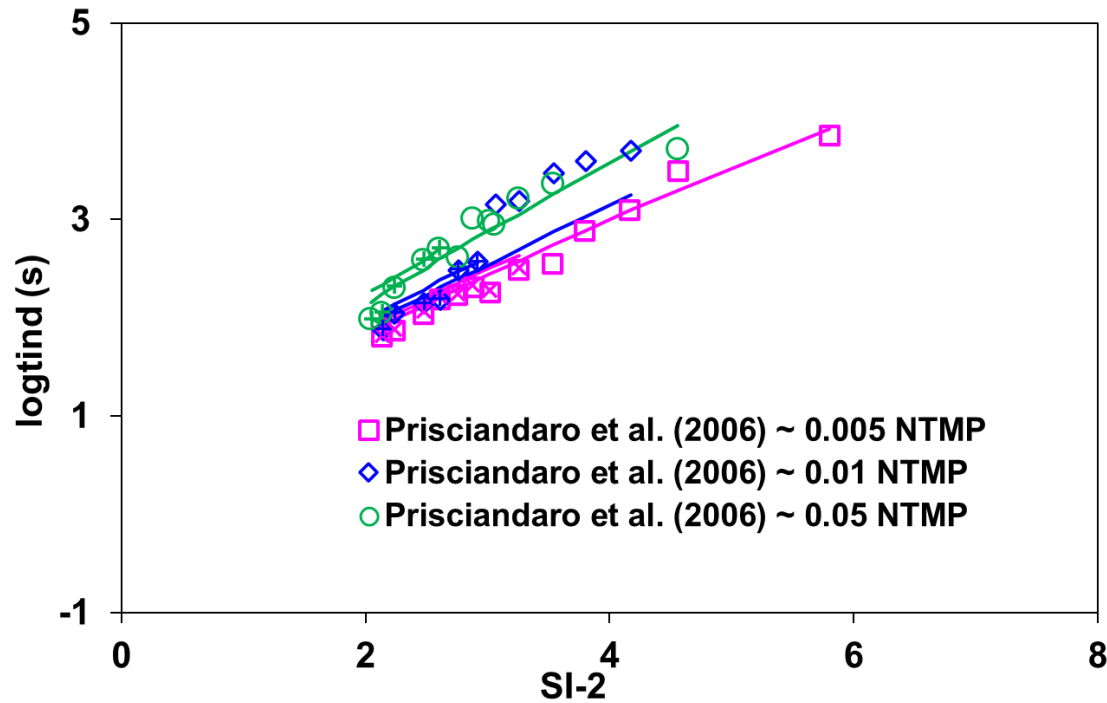$$\gamma_{winh} = \gamma_{w/oinh} + (1 + \sigma T)\gamma_{inh}$$

$$\gamma_{inh} = \frac{\left(\sum_{i=1}^{inh} \sum_{j=1}^{inh} (B\gamma)_{ij} K_{L,ij} \frac{[inh,i][inh,j]}{[inh,tot]} (1 - k_{ij})\right)^{0.4}}{1 + \sum_{i}^{inh} K_{L,i}[inh,i]}$$

**Inhibition of SrSO$_4$ scaling using phosphonate inhibitors at different temperatures and saturation levels**

# Effect on inhibitor on gypsum scale inhibition

## Inhibition of $CaSO_4.2H_2O$ scaling using NTMP at different temperatures and scaling conditions
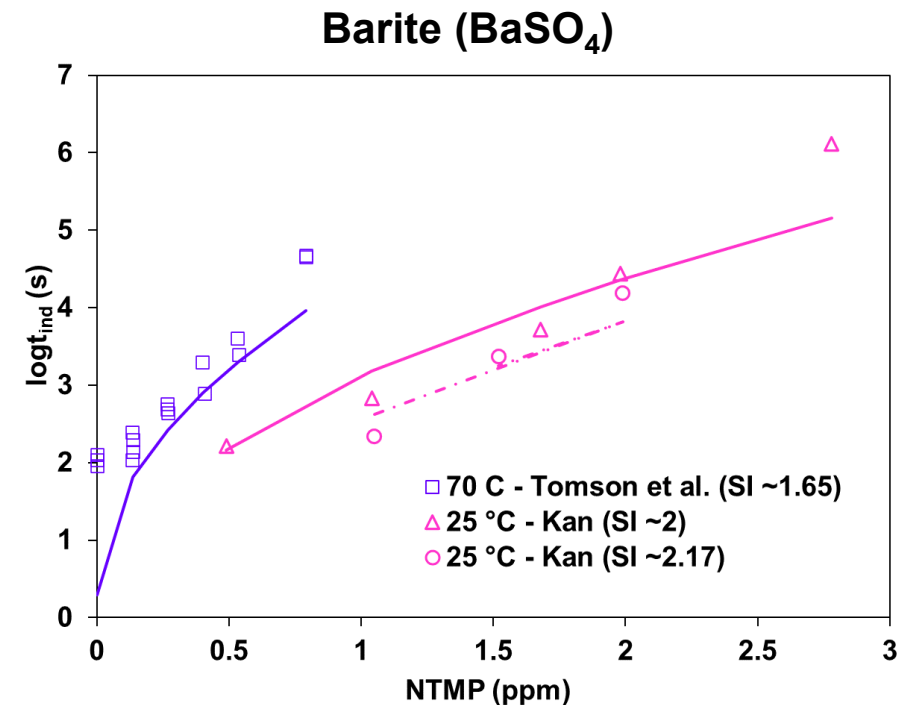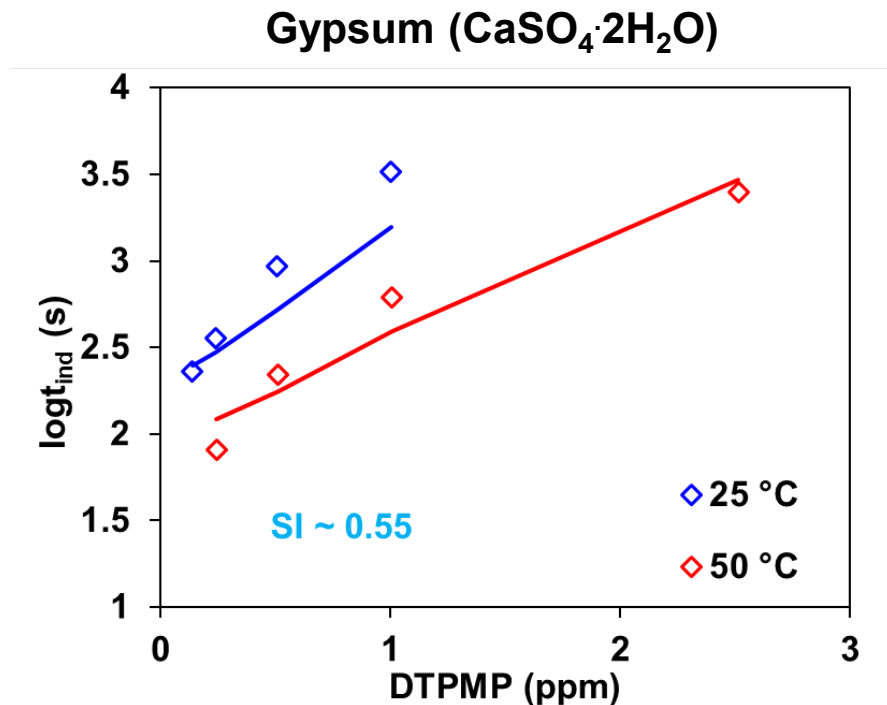
# DTPMP effect on sulfate scale inhibition

## Inhibition of barite and gypsum scaling using DTPMP at different temperatures and scaling conditions

- Theoretical approach provides appropriate correlation between temperature and inhibitor dosage level as evident from experimental data

**Gypsum (CaSO$_4$·2H$_2$O)**

**Barite (BaSO$_4$)**



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# DTPMP effect on calcite scale inhibition

## Effect of DTPMP in enhancing the induction time for calcite formation as a function of dosage levels at different saturation levels

- DTPMP, a common inhibitor, shows almost 3 orders of magnitude effect in delaying the induction time with the increase of dosage level from 0-3 ppm
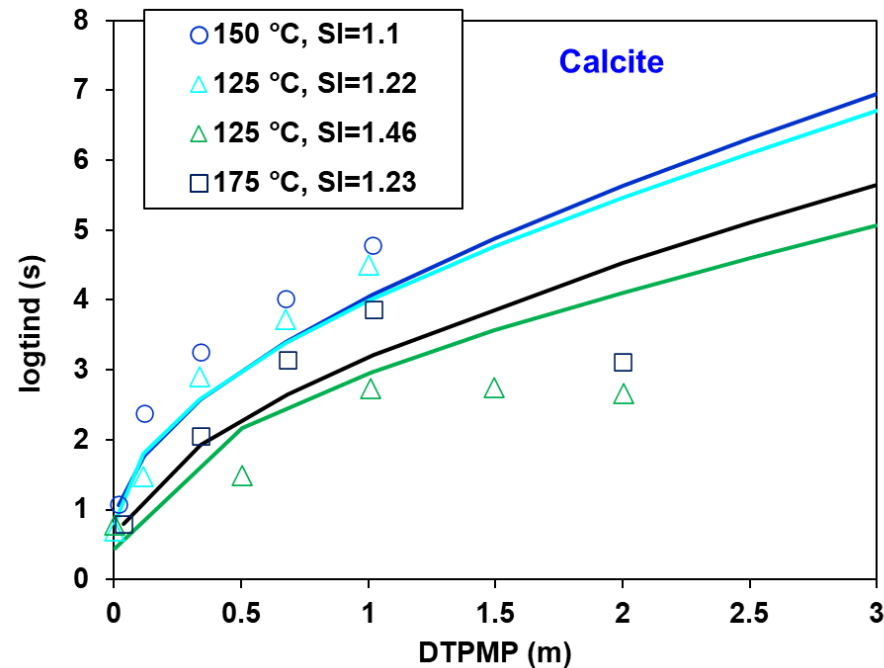
# Conclusions

A model has been developed by combining MSE with CNT for studying the induction time kinetics for common scales in the presence and absence of phosphonic acid-based inhibitors

- The model accounts for the effect of temperature and inhibitor speciation on the interfacial surface energy parameter

MSE model has been used to model solution characteristics of the inhibitors while considering appropriate solution species, complexes and precipitating solid phase

- Provides an accurate representation of experimental speciation and titration curves

The MSE+CNT model has been successfully applied to study characteristics of induction time curves as a function of saturation index and temperature

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**Thank you**

Q&A

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