Finding optimized process conditions to minimize precipitations in an SO_2 absorption process using thermodynamic process simulation

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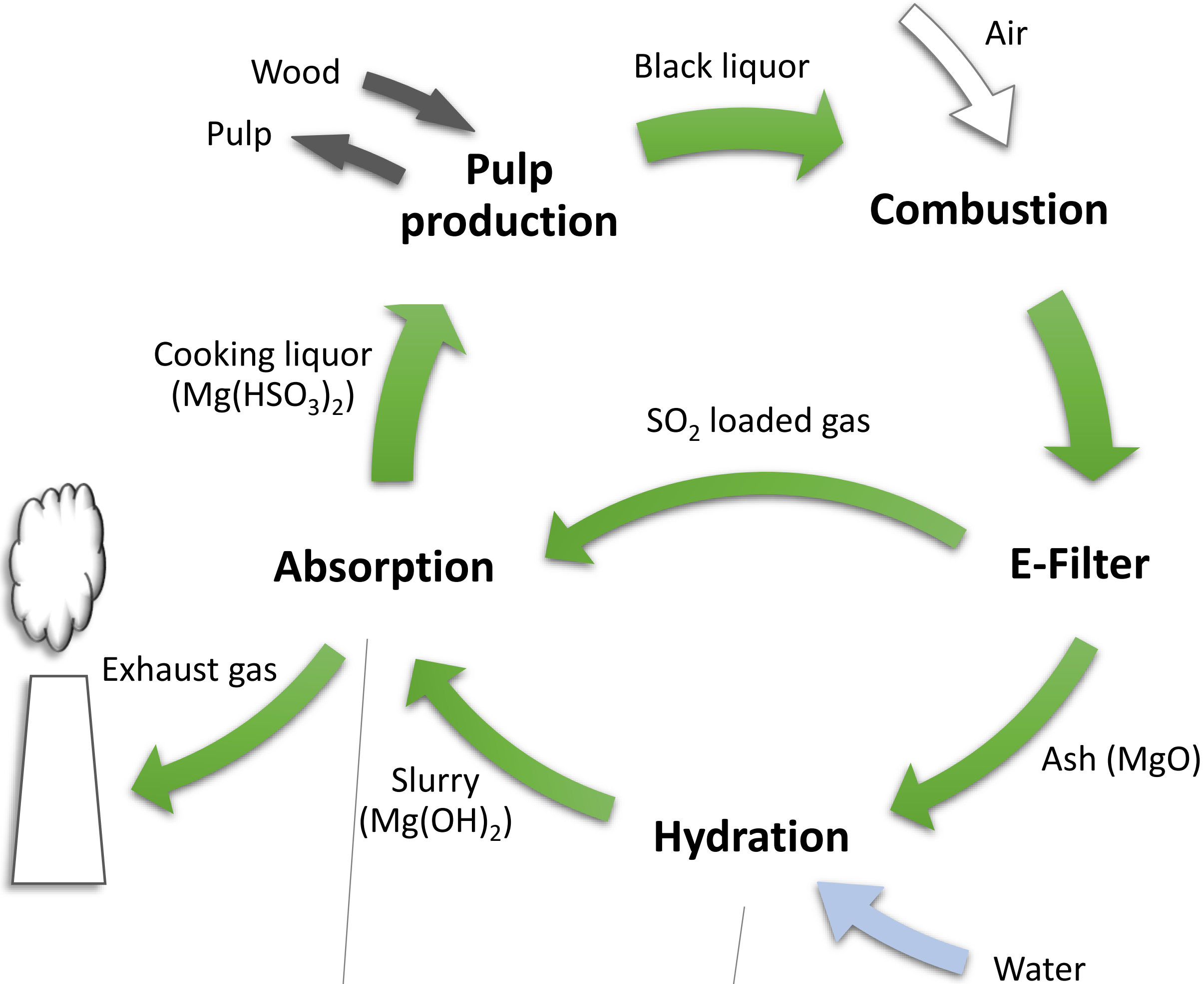
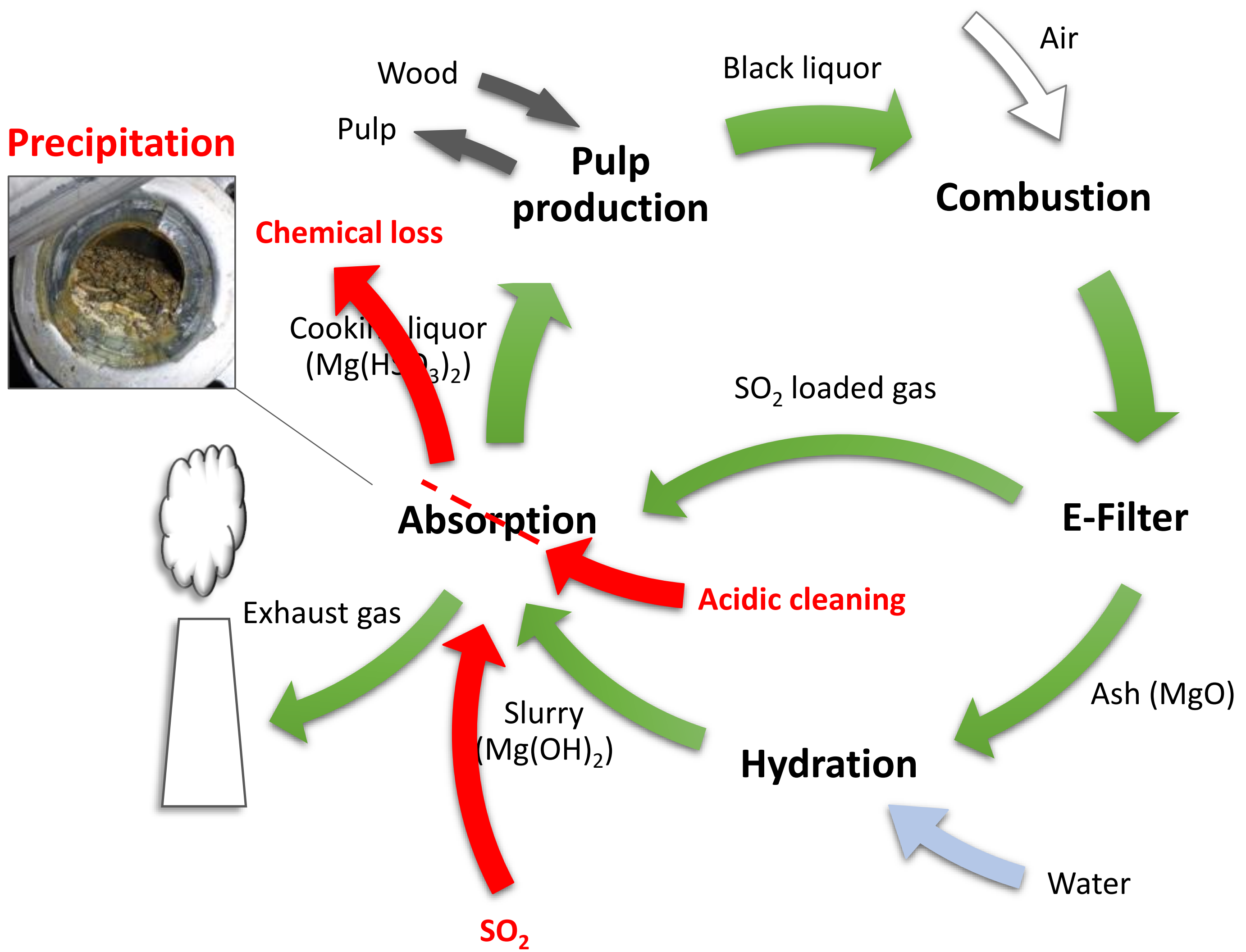
Chemical recovery



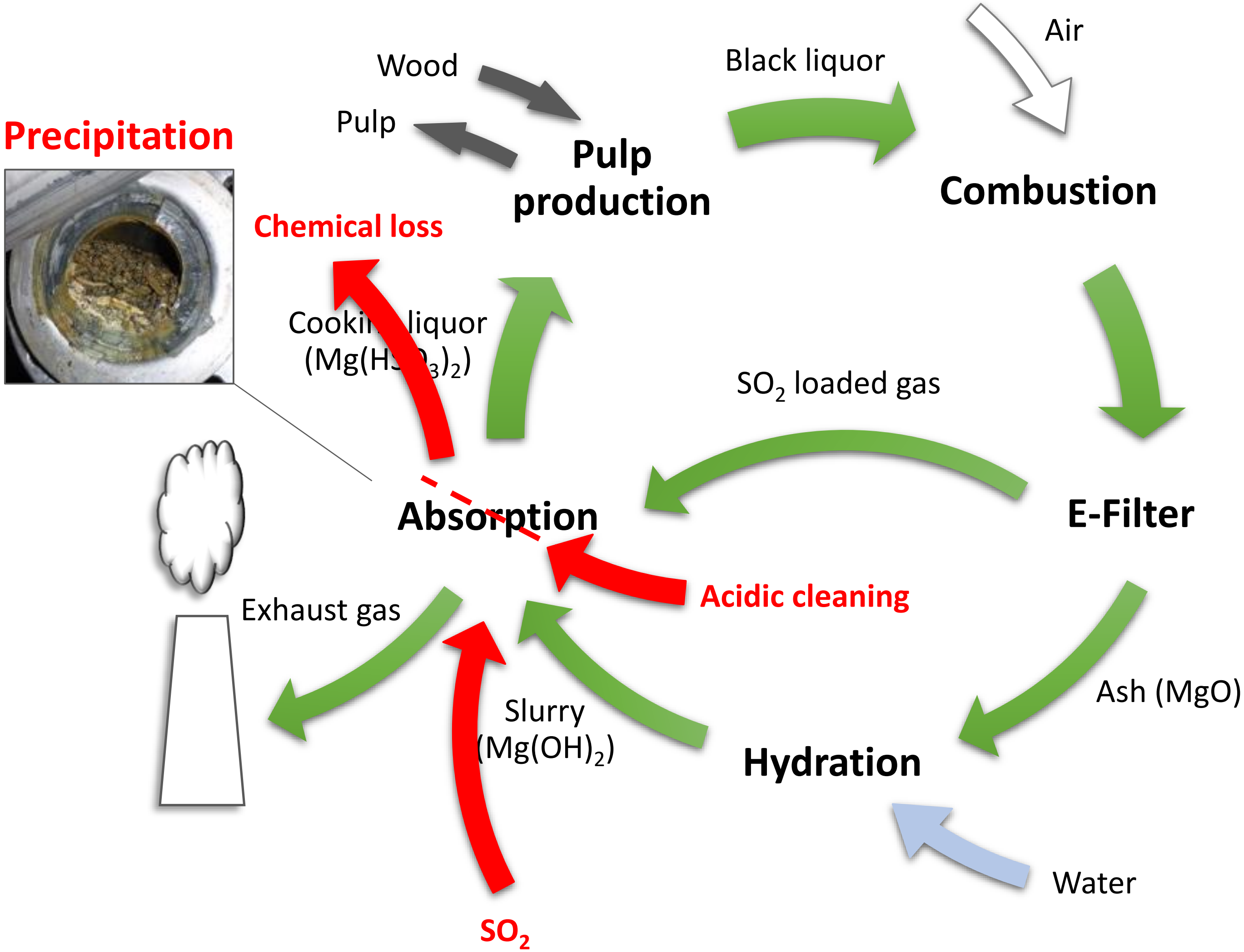
$$Mg(OH)_2 + SO_2 \rightarrow MgSO_3 + H_2O$$
$$MgSO_3 + SO_2 + H_2O \rightarrow Mg(HSO_3)_2$$

$$MgO + H_2O \rightarrow Mg(OH)_2$$

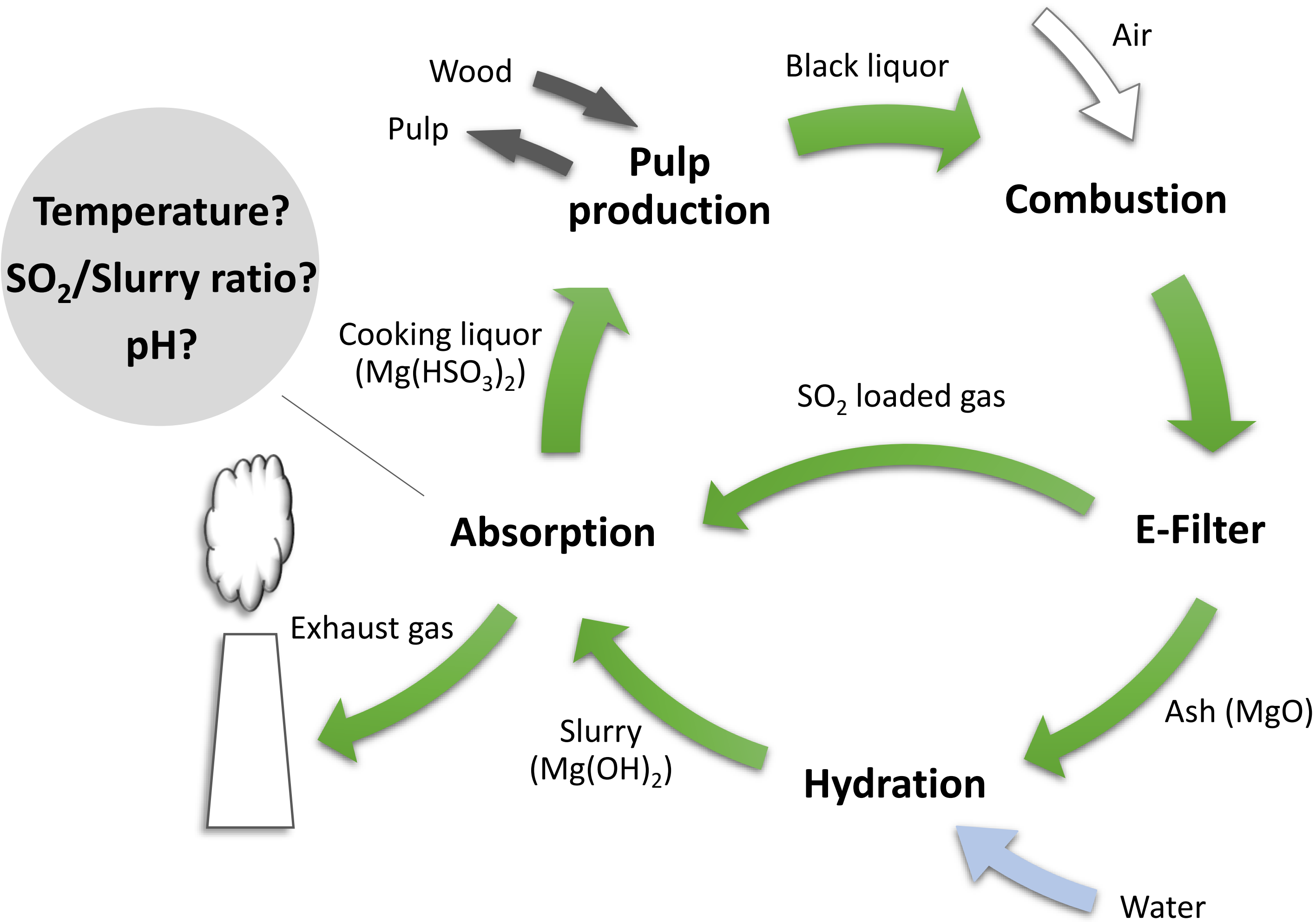
Chemical recovery



Chemical recovery

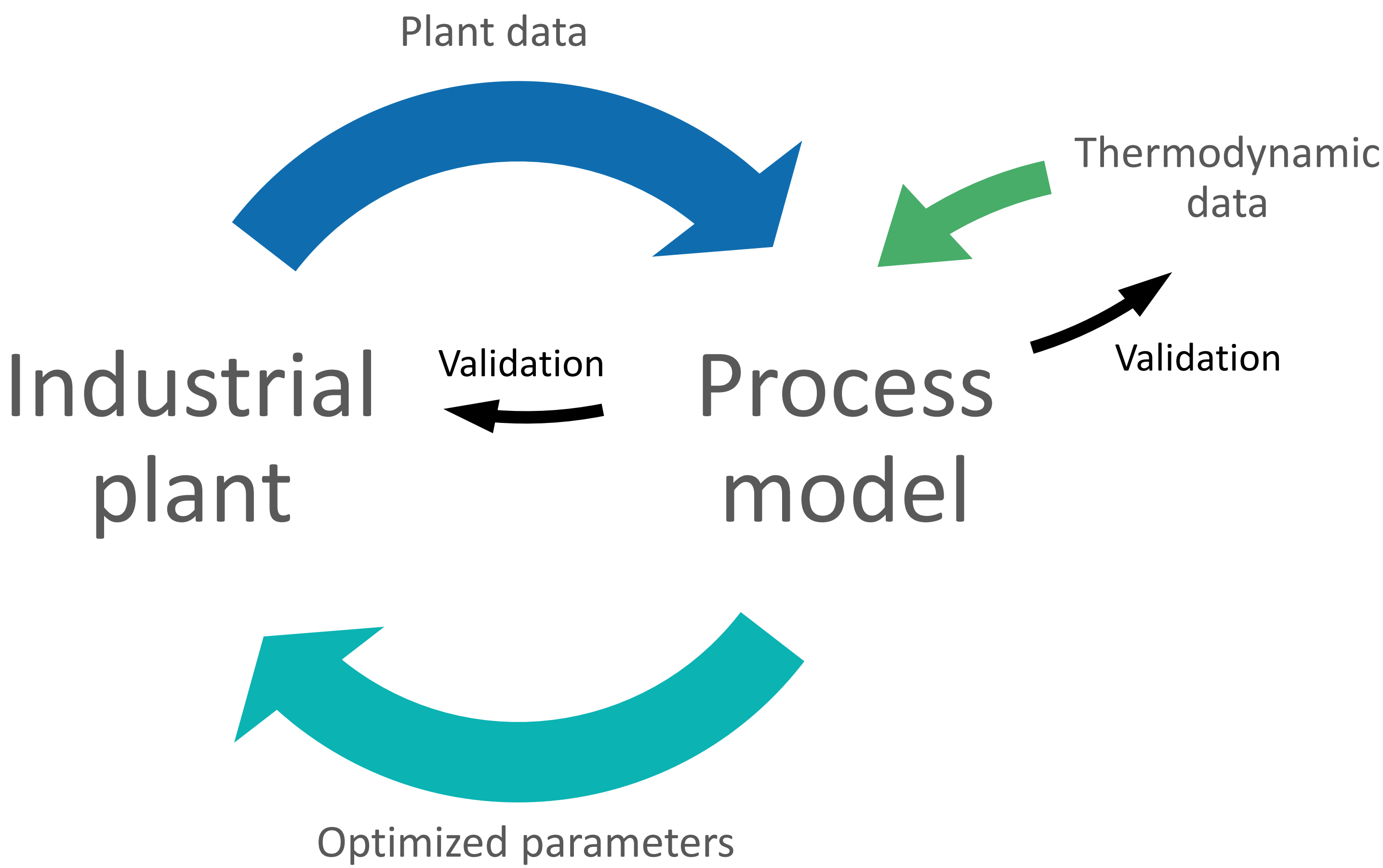


Chemical recovery

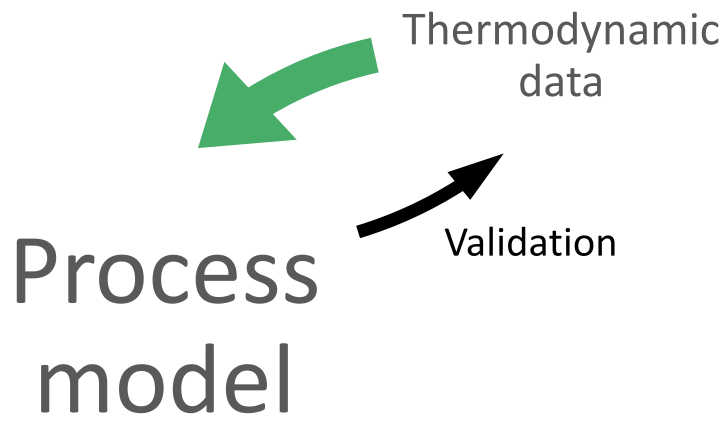


- **Optimizing process by minimizing precipitations**
- **Finding conditions under which precipitation occurs**

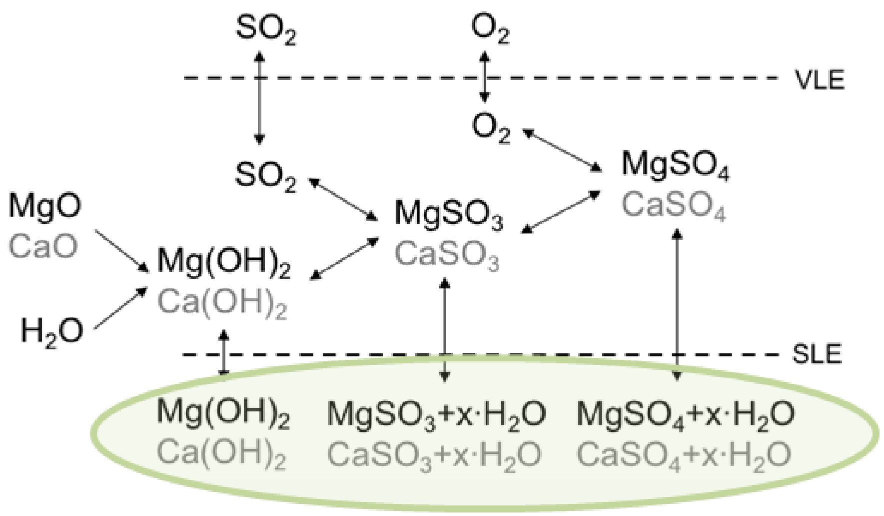
Process simulation for process optimization



Process simulation for process optimization



System to simulate



- Electrolyte system
  - Dissociation reactions
  - Equilibrium reactions
  - Precipitation reactions
- Henry components: SO_2, O_2, CO_2

Electrolyte system

Reaction	Type	Calculation of chemical equilibrium
$2\ H_2O \leftrightarrow OH^- + H_3O^+$	Equilibrium	build-in coefficients for K_{eq}
$2\ H_2O + SO_2 \leftrightarrow H_3O^+ + HSO_3^-$	Equilibrium	build-in coefficients for K_{eq}
$H_2O + HSO_3^- \leftrightarrow H_3O^+ + SO_3^{--}$	Equilibrium	build-in coefficients for K_{eq}
$H_2O + HCl \leftrightarrow Cl^- + H_3O^+$	Equilibrium	Gibbs free energy calculation
$H_2SO_4 + H_2O \leftrightarrow H_3O^+ + HSO_4^-$	Equilibrium	Gibbs free energy calculation
$H_2O + HSO_4^- \leftrightarrow H_3O^+ + SO_4^{--}$	Equilibrium	Gibbs free energy calculation
$MgOH^+ \leftrightarrow OH^- + Mg^+$	Equilibrium	Gibbs free energy calculation
$CaOH \leftrightarrow OH^- + Ca^{++}$	Equilibrium	Gibbs free energy calculation
$2\ H_2O + CO_2 \leftrightarrow H_3O^+ + HCO_3^-$	Equilibrium	build-in coefficients for K_{eq}
$H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{--}$	Equilibrium	build-in coefficients for K_{eq}
$Mg(OH)_2 \rightarrow OH^- + MgOH^+$	Dissociation	-
$Ca(OH)_2 \rightarrow OH^- + CaOH^+$	Dissociation	-
$MgSO_4 \rightarrow Mg^{++} + SO_4^{--}$	Dissociation	-
$MgSO_3 \rightarrow Mg^{++} + SO_3^{--}$	Dissociation	-
$CaSO_4 \rightarrow Ca^{++} + SO_4^{--}$	Dissociation	-
$CaSO_3 \rightarrow Ca^{++} + SO_3^{--}$	Dissociation	-
$MgCO_3 \rightarrow Mg^{++} + CO_3^{--}$	Dissociation	-
$CaCO_3 \rightarrow Ca^{++} + CO_3^{--}$	Dissociation	-
$Mg(OH)_2\ (s) \leftrightarrow OH^- + MgOH^+$	Salt precipitation	Gibbs free energy calculation
$Ca(OH)_2\ (s) \leftrightarrow OH^- + CaOH^+$	Salt precipitation	Gibbs free energy calculation
$MgSO_3 * 6\ H_2O \leftrightarrow Mg^{++} + SO_3^{--} + 6\ H_2O$	Salt precipitation	build-in coefficients for K_{eq}
$MgSO_3 * 3\ H_2O \leftrightarrow Mg^{++} + SO_3^{--} + 3\ H_2O$	Salt precipitation	build-in coefficients for K_{eq}
$CaSO_3 * ½\ H_2O \leftrightarrow Ca^{++} + SO_3^{--} + ½\ H_2O$	Salt precipitation	Gibbs free energy calculation
$MgSO_4 * H_2O \leftrightarrow Mg^{++} + SO_4^{--} + 1\ H_2O$	Salt precipitation	build-in coefficients for K_{eq}
$MgSO_4 * 7\ H_2O \leftrightarrow Mg^{++} + SO_4^{--} + 7\ H_2O$	Salt precipitation	build-in coefficients for K_{eq}
$CaSO_4 * 2\ H_2O \leftrightarrow Ca^{++} + SO_4^{--} + 2\ H_2O$	Salt precipitation	build-in coefficients for K_{eq}
$CaSO_4 \leftrightarrow Ca^{++} + SO_4^{--}$	Salt precipitation	Gibbs free energy calculation

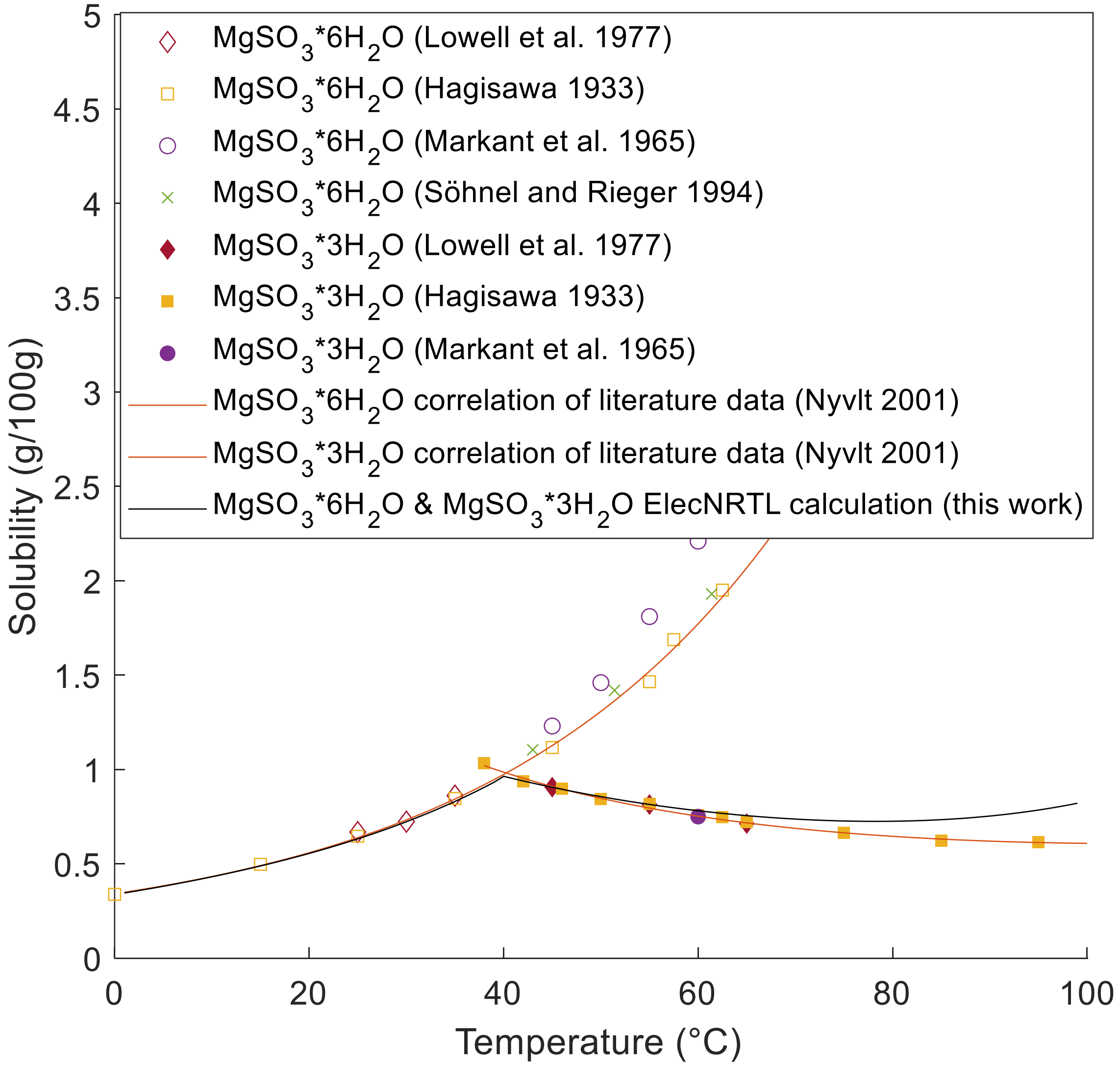
Thermodynamic simulation

- Electrolyte NRTL activity coefficient model
- Redlich-Kwong equation of state for vapor phase properties
- Chemical equilibrium calculated using
  - Build-in coefficients for K_{eq} or
  - Gibbs free energy
- Simulation performed in AspenPlus® V10

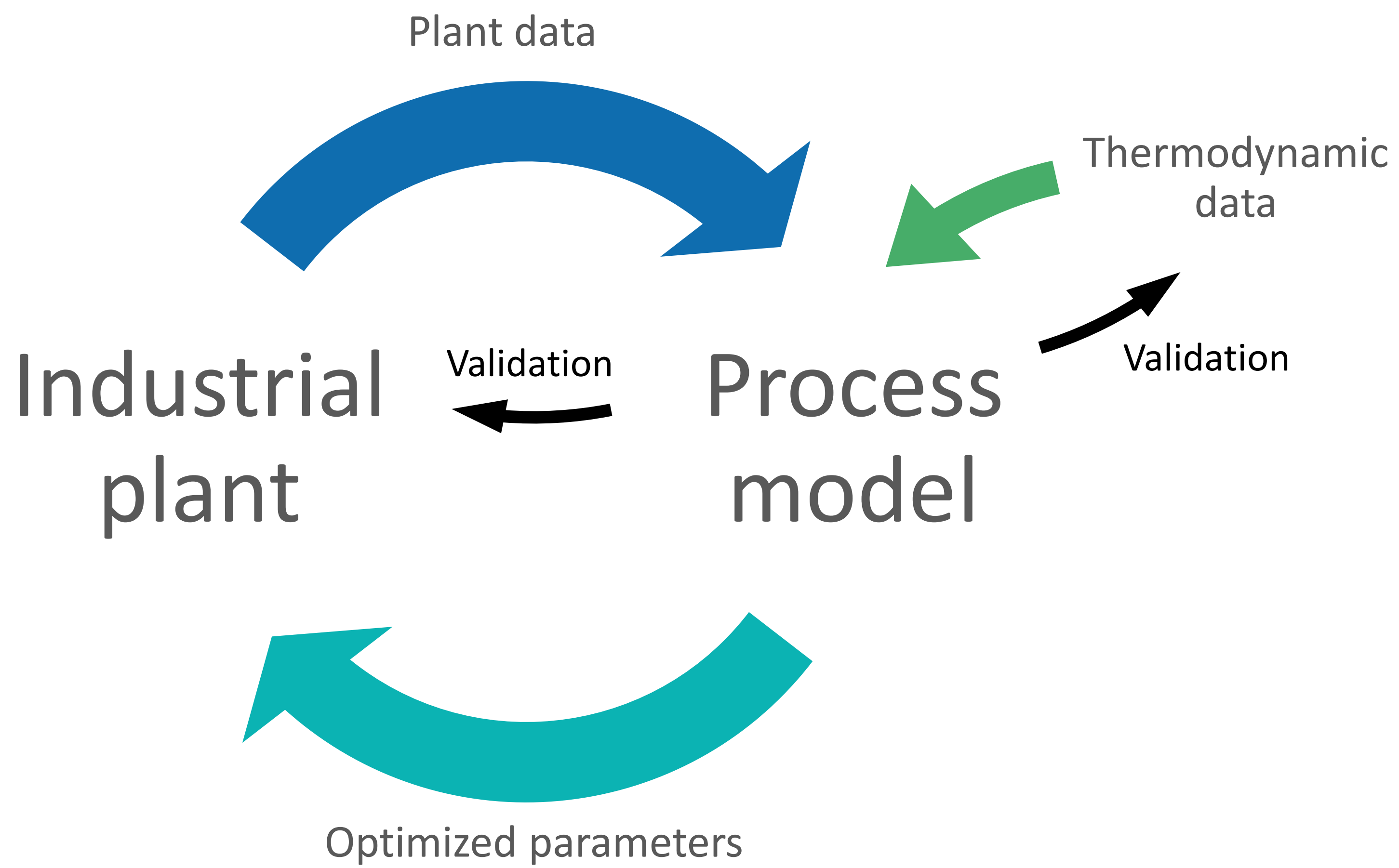
Validation

✓ Calculating solubility of SO_2 and potential salt precipitates and comparing with literature data

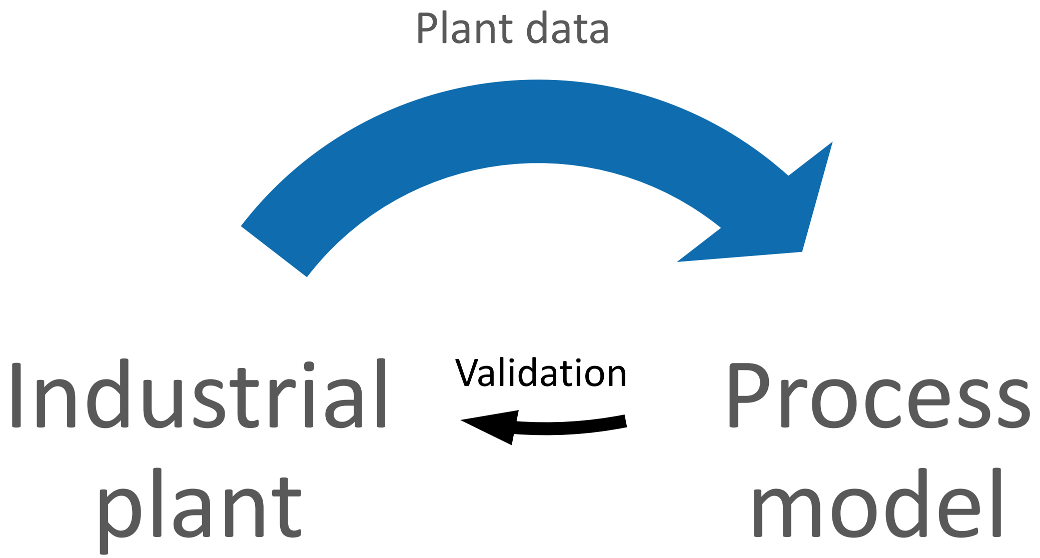
Example: Solubility of $MgSO_3$ in Water



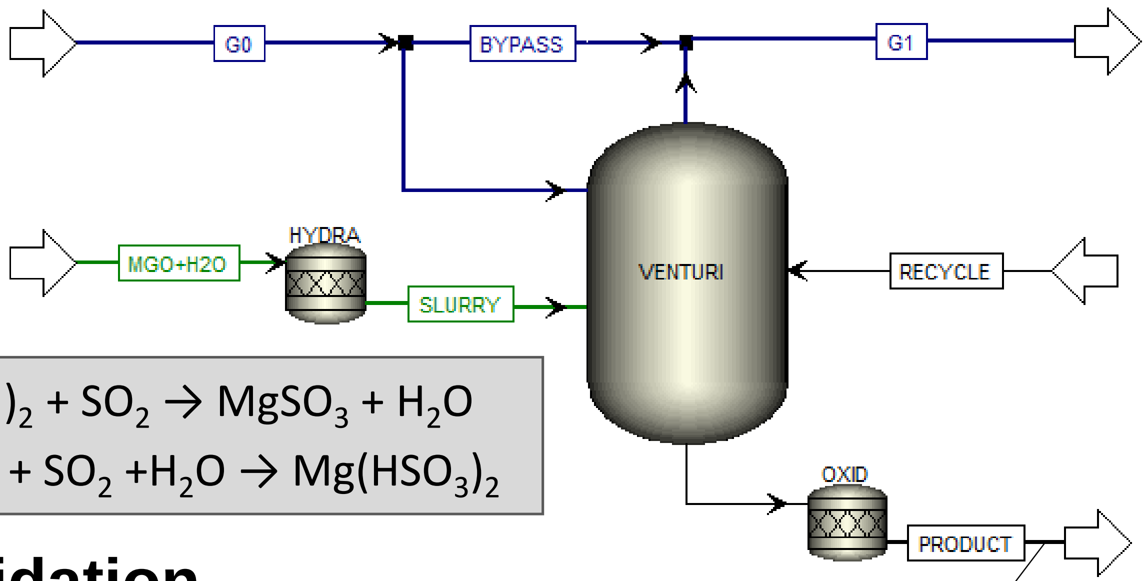
Process simulation for process optimization



Process simulation for process optimization



Simplified flowsheet of one absorption unit



$Mg(OH)_2 + SO_2 \rightarrow MgSO_3 + H_2O$

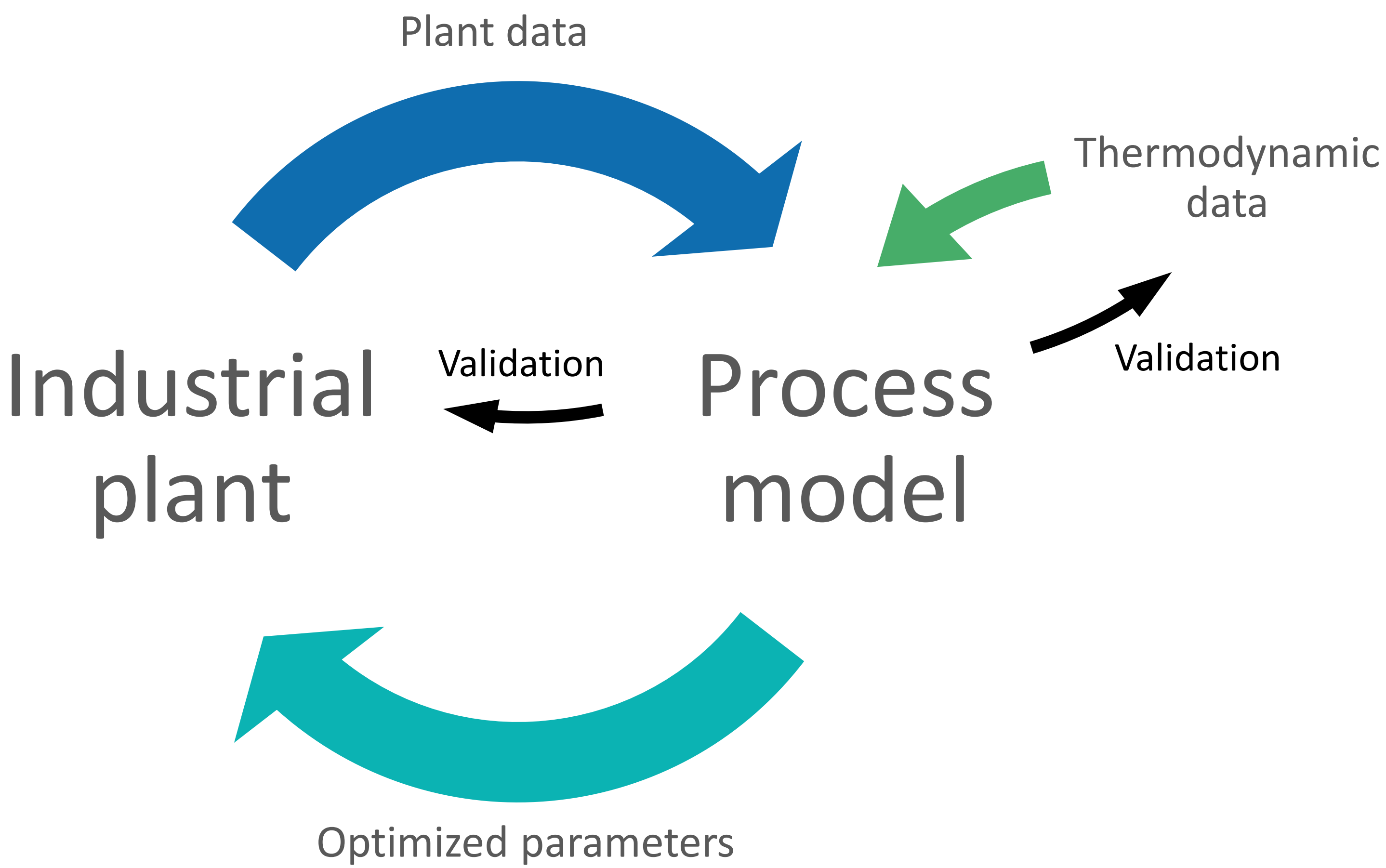
$MgSO_3 + SO_2 + H_2O \rightarrow Mg(HSO_3)_2$

Validation

	Units	Calculated	Plant data
pH		5.47	5.18 $\sigma = 0.07$
$SO_3^{--} + HSO_3^{-}$	mass-% SO_2	2.94	3.04 $\sigma = 0.22$
SO_3^{--}	mass-% SO_2	0.13	0.39 $\sigma = 0.09$

✓ Calculating flowsheet and comparing with plant data

Process simulation for process optimization



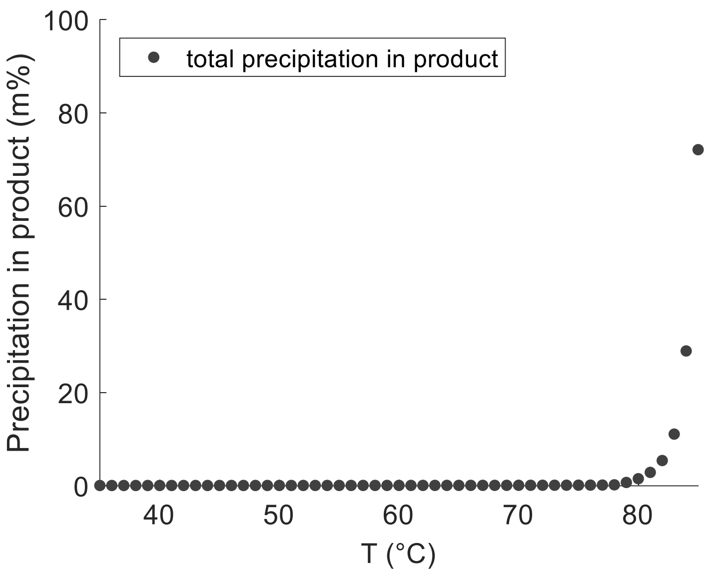
Process simulation for process optimization

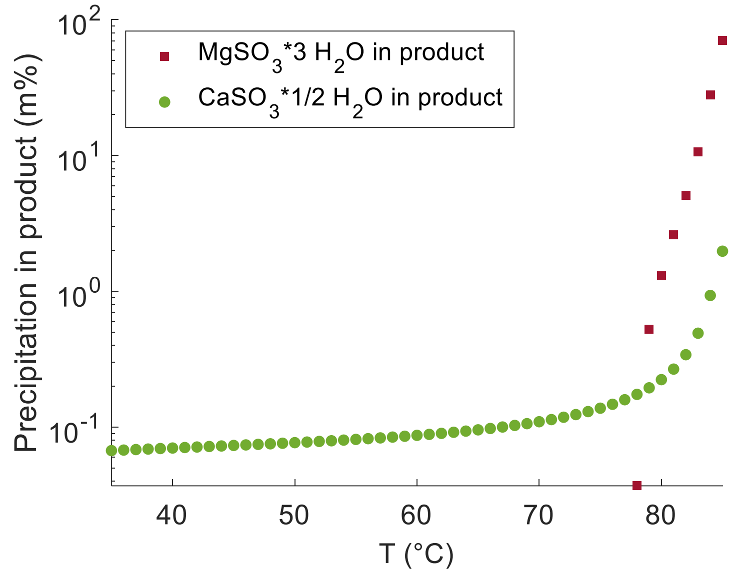
Industrial plant

Process model

Optimized parameters

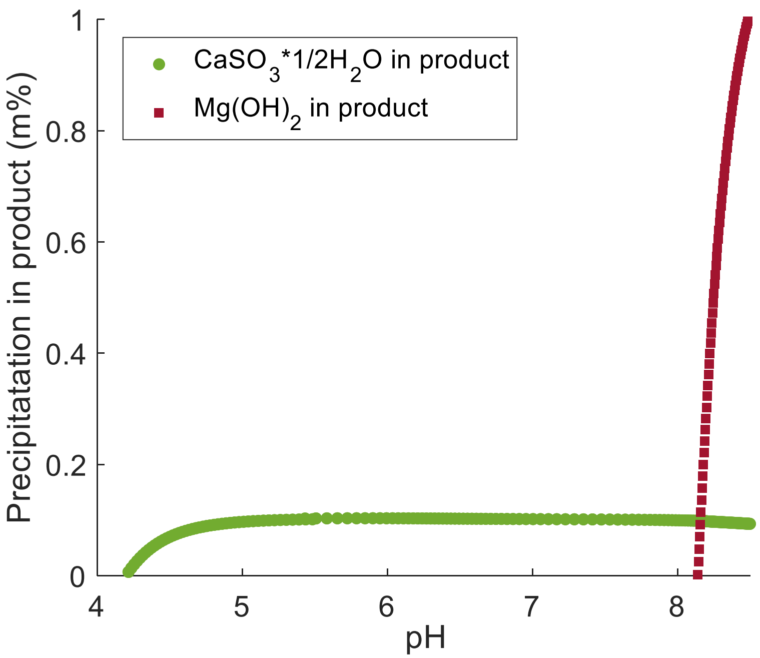
Precipitation as function of temperature





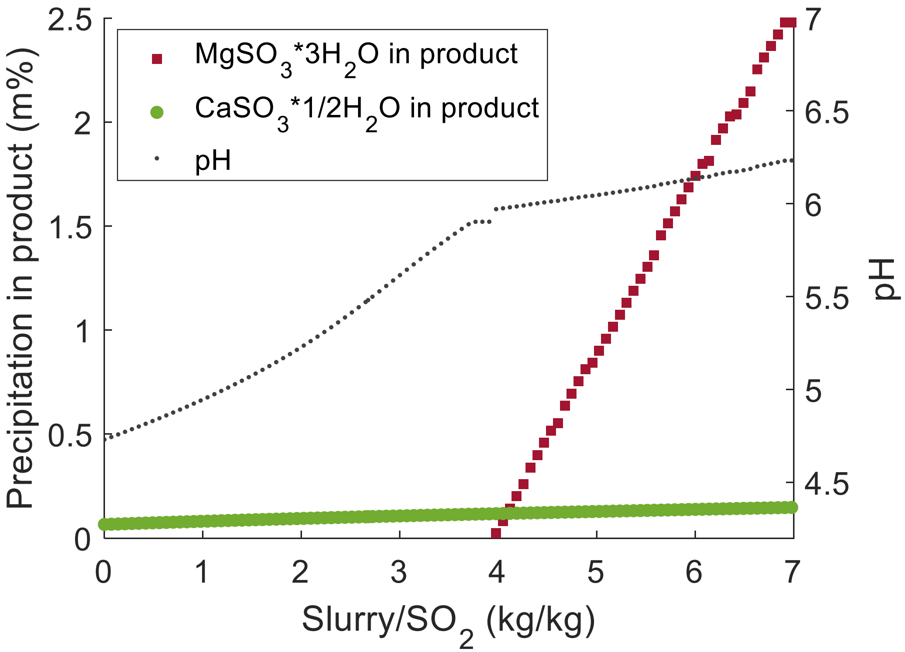
- $CaSO_3$*1/2 H_2O
- T > 78 °C: $MgSO_3$*3H_2O
  - Shift in VLE
  - Transition from $MgSO_3$*6H_2O to less soluble $MgSO_3$*3H_2O

Precipitation as function of pH



- $CaSO_3$*1/2 H_2O
- pH > 8: $Mg(OH)_2$ almost not soluble

Precipitation as function of Slurry/SO_2 ratio



- Slurry/SO_2 ratio > 4: $MgSO_3*3H_2O$
- $CaSO_3*1/2\ H_2O$

$Mg(OH)_2 + SO_2 \rightarrow MgSO_3 + H_2O$

$MgSO_3 + SO_2 + H_2O \rightarrow Mg(HSO_3)_2$

Summary

- Process model in good agreement with plant data

- Precipitating salts under studied conditions:
  - $CaSO_3$*1/2 H_2O
  - pH > 8: $Mg(OH)_2$
  - $MgSO_3$ * $3H_2O$
    - T > 78 °C
    - Slurry/SO_2 ratio > 4

- Findings correspond to solubility reports found in literature

Constraints and outlook

- Ratio of SO_3^{--} and HSO_3^{-} in the liquid product deviates from plant data

  - Measurements using infrared spectroscopy for further evaluation of model

- Model does not depict local concentration differencies

  - Implementation of electrolyte reactions in 3D resolved fluid dynamic model

Thank you for your attention!

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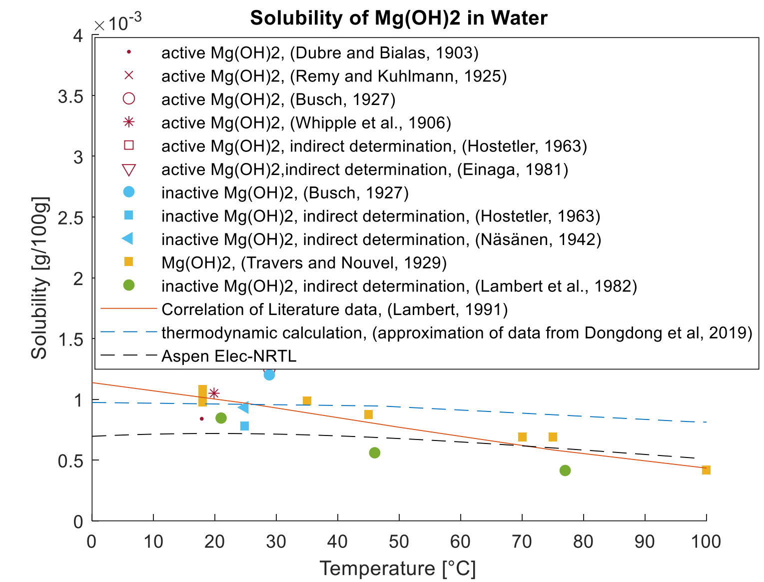
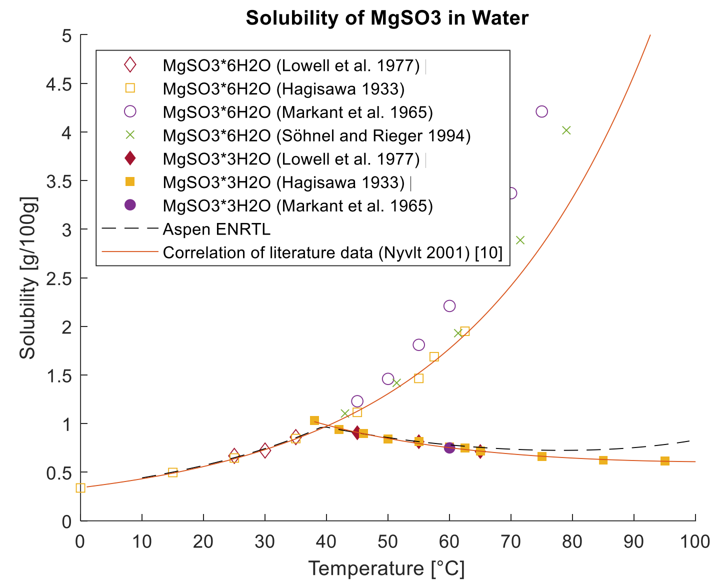
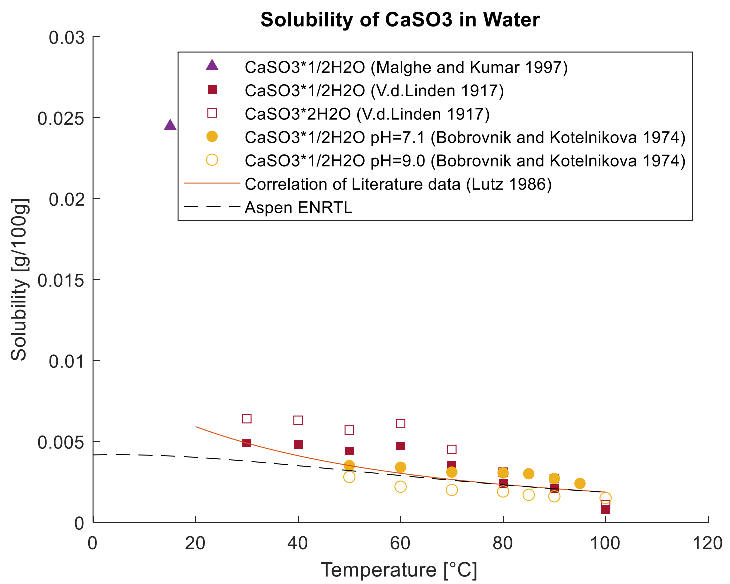
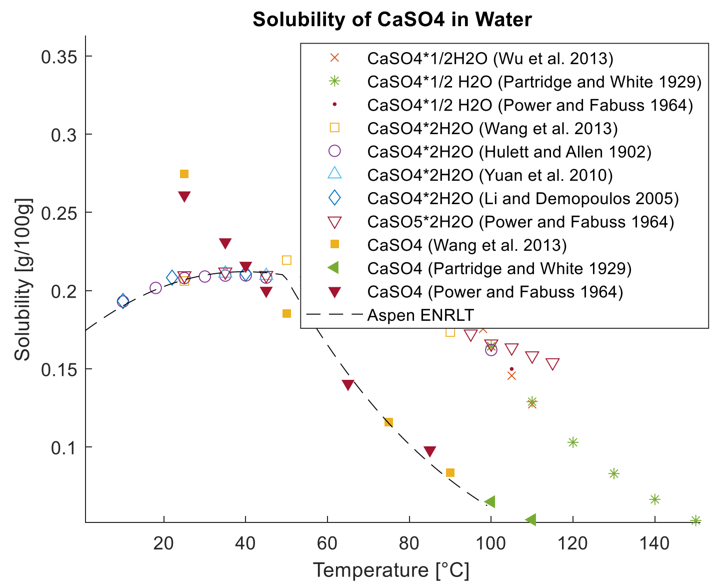
Thermodynamic validation

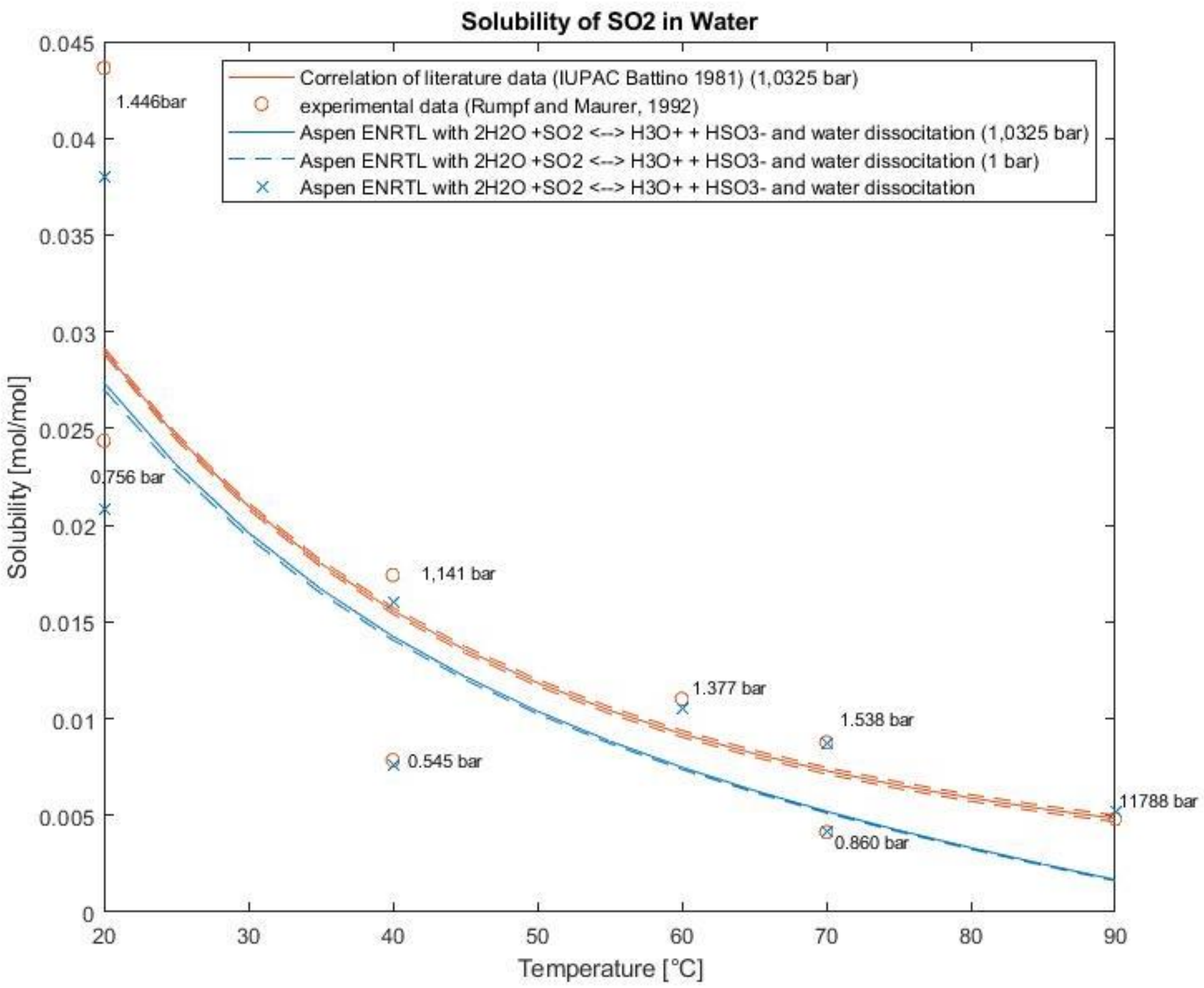








Evaluation of ElecNRTL



Sensitivity analyses to study the effect of

- Temperature
- pH
- Input ratio of Slurry and SO_2

on the precipitation of the potential salts

- Hydroxides
  - $Mg(OH)_2$, $Ca(OH)_2$
- Sulfites
  - $MgSO_3 * 3H_2O$, $MgSO_3 * 6H_2O$, $CaSO_3 * ½H_2O$
- Sulfates
  - $MgSO_4 * H_2O$, $MgSO_4 * 7H_2O$, $CaSO_4 * 2H_2O$, $CaSO_4$