SYSTEMATIC APPROACH TO DYNAMIC MODELLING OF MULTIPLE AND COMPETING CHEMICAL PRECIPITATION REACTIONS IN WASTEWATER TREATMENT

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Crowne Plaza, Gold Coast, 15th June 2015
WHY SOLIDS PRECIPITATION?

- **Uptake**
- **Anaerobic digestion**
- **Precipitation**
- **Dissolution**

### Reactants and Products

- **Ca^{2+}**
- **PO_4^{3-}**
- **K^+**
- **Mg^{2+}**
- **O_2**
- **COD**
- **NO_x**
- **NH_4^+**
- **Fe^{3+}**
- **SO_4^{2-}**
- **FePO_4**
- **MgNH_2PO_4**
- **Ca_3(PO_4)_2**
- **MgCO_3**
- **CaCO_3**
- **NH_4^+**
- **CH_4**
- **N_2 gas**
- **H_2S**
- **FeS**

### Chemical Reactions

- **Aerobic oxidation**
- **Denitrification**
- **Decay**
- **Assimilation**
- **Uptake**
- **Reduction**
Need for a systematic approach to modelling precipitation reactions

$\frac{r}{k} = \frac{\downarrow p_{\text{PO}_4}}{\downarrow S}$

$X \downarrow \text{MeOH}$

Mathematical Process Simulation Models

ASM2d
pH/speciation
Non-ideality correction
Precipitation

ADM1
pH/speciation
Non-ideality correction
P and S modelling
Precipitation
STUDY OBJECTIVES

• Develop a generic mechanistic precipitation model to deal with multi-species systems.

• Evaluate this model on different types of experiments, with synthetic and real wastewater and for multiple precipitation reactions.
Precipitation Modelling Framework

Speciation Model

\[ \text{TOT}_{\downarrow j} = a_{\downarrow j} / \gamma_{\downarrow j} + \sum_{i=1}^{N_{\text{sp}}} v_{ij} a_{\downarrow i} / \gamma_{\downarrow i} \]

Fast/Equilibrium reactions – algebraic equations

Parameters: Thermodynamic equilibrium constants

Dynamic state variables - Dissolved species – Mineral solid state

Parameters: Rate coefficients

Precipitation Model

\[ \frac{dS_{\downarrow i}}{dt} = \frac{Q}{V} (S_{\downarrow j, i} - S_{\downarrow i, k}) + \sum_{k=1}^{N} q_{ij} N_{\downarrow l} \]

Gas Stripping Model

\[ r_{\downarrow \text{CO}_2} (g) = k_{\downarrow L} a_{\downarrow \text{CO}_2} (aq) - K_{\downarrow L} \]

Specific volumetric mass transfer

Parameters: \( K_{\downarrow L} \)
**PROPOSED PRECIPITATION MODEL**

\[ r_{\text{crys}} = k_{\text{crys}} X_{\text{crys}} \sigma^n \]

- **Kinetic rate coefficient**
- **Solid Mineral State**
- **Order of precipitation reaction**

\[ SI = \log_{10} \left( \frac{S_{\text{Ca}^{2+}} \times S_{\text{CO}_3^{2-}}}{K_{\text{sp, calcite}}} \right) \]

- **SI** = 0 \( \Rightarrow \) Solution is saturated
- **SI** > 0 \( \Rightarrow \) Solution is supersaturated
- **SI** < 0 \( \Rightarrow \) Solution is undersaturated

- **Only Contestable Parameter**: \( n = 2 \) or 3
- **Estimated by Optimization**

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[Image: University of Queensland logo]
PRELIMINARY VALIDATION WITH CALCITE

- Calcite precipitation
- $k_{\text{calcite}} = 0.0025 \pm 0.0004 \text{ min}^{-1}$
- Fitted with non-linear optimization ($lsqcurvefit$)
MINERALS IDENTIFICATION

- Modeller identifies relevant minerals

Prior knowledge and Process understanding

Model based analysis

Other indicators

- Mineral solid is important
- Model fit inclusion (CI)

SI values

log_{10} \left( \frac{S_{\text{Ca}^{2+}} \times S_{\text{CO}_3^{2-}}}{K_{\text{sp, calcite}}} \right)
## SYNTHETIC WASTEWATER WITH TITRATION

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Synthetic wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia (gNH4-N. m(^{-3}))</td>
<td>423</td>
</tr>
<tr>
<td>Calcium (g.m(^{-3}))</td>
<td>95</td>
</tr>
<tr>
<td>Magnesium (g.m(^{-3}))</td>
<td>120</td>
</tr>
<tr>
<td>Phosphorus (gP. m(^{-3}))</td>
<td>479</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
</tr>
</tbody>
</table>

\[ k_{DCPD} = 1.6 \ (±0.5) \ h^{-1} \]
\[ k_{Struv} = 3.2 \ (±1) \ h^{-1} \]
\[ k_{OCP} = 0.8 \ (±0.7) \ h^{-1} \]
CONFIDENCE REGIONS
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Piggery digestate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia (gNH$_4$-N. m$^{-3}$)</td>
<td>983</td>
</tr>
<tr>
<td>Calcium (g.m$^{-3}$)</td>
<td>207</td>
</tr>
<tr>
<td>Magnesium (g.m$^{-3}$)</td>
<td>126</td>
</tr>
<tr>
<td>Phosphorus (gP. m$^{-3}$)</td>
<td>96</td>
</tr>
<tr>
<td>Inorganic carbon (g.m$^{-3}$)</td>
<td>1150</td>
</tr>
<tr>
<td>pH</td>
<td>7.3</td>
</tr>
</tbody>
</table>

$k_{\text{Struv}} = 12 (\pm 9) \text{ h}^{-1}$

$k_{\text{CCM}} = 0.35 (\pm 0.03) \text{ h}^{-1}$

$k_La = 5.5 (\pm 0.49) \text{ h}^{-1}$
\( k_{\text{Struv}} = 4.6 \ (\pm 0.7) \ h^{-1} \)
\( k_{\text{ACP}} = 3 \ (\pm 0.5) \ h^{-1} \)
\( k_{\text{CCM}} < 0.22 \ h^{-1} \)
CONCLUSIONS

- A mechanistic precipitation model has been developed and validated.

- Model is identifiable: minimal number of parameters.

- Model is tolerant to a fast precipitation rate coefficient.

- Minerals could be classed as rapidly forming, moderately forming and slow forming.

- Model can be integrated with bio-kinetic models in plant-wide modelling (*Presentation 8.4*).
The Infinity is the Limit!

MANY THANKS FOR YOUR ATTENTION!