Development of SLL equilibrium speciation and data fitting tool and its application to P recovery process from sludge

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agenda

- Introduction to P recycling
- PULSE process
- SLLE tool
- results
- summary
introduction

• essential element for all forms of life

• finite resource

• EU imports more than 90% of P

• sewage has potential to cover more than 20% of P demand in North-West Europe
PULSE (Phosphorus University of Liege Sludge Extraction) process

- Dewatered sludge (~20% DM)
- Drying (≥95% DM)
- Leaching (acid)
- Filtration

- Precipitation (base/Ca)
  - CaP

- Reactive extraction
  - Organic solvent
  - P + impurities

- Re-extraction agent/NH₃
  - Metals

- Solid waste
PULSE process

- Leaching of P and metals from sludge
  
  \[
  FePO_4 + 3HCl \rightarrow Fe^{3+} + H_3PO_4 + 3Cl^- 
  \]

- Reactive extraction of metals with organic solvent
  
  \[
  Fe^{3+} + 4Cl^- \leftrightarrow FeCl_4^- \\
  R_3NHCl + FeCl_4^- \leftrightarrow FeCl_4 R_3NH + Cl^- 
  \]

- Precipitation of CaP
  
  \[
  Ca^{2+} + HPO_4^{2-} \rightarrow CaH(PO_4) 
  \]
why SLL equilibrium modelling

- process development
  - evaluation of unit operations
- deeper understanding
- process optimization
- minimize experimental work
**liquid phase speciation**

- **charge balance (CB)**
  \[ 0 = \sum_{i=0}^{n} c_i z_i \]

- **mass balance (MB)**
  \[ C_{totj} = \sum_{i=0}^{n} v_{i,j} c_i \]

- **law of mass action (LMA)**
  \[ \log K_m = \sum_{i=0}^{n} v_{i,r} \log a_i \]

\[ a_i = \gamma_i c_i \]

\[ a_i = \text{activity of } i\text{th species} \]

\[ \gamma_i = \text{activity coefficient} \]

\[ c_i = \text{concentration} \]
solid-liquid equilibrium

- $AB_{\text{solid}} \leftrightarrow v_1 A + v_2 B$

- from law of mass action

$$K_{sp} = a_A^{v_1} a_B^{v_2} \text{ (at equilibrium)}$$

- Ion Activity product: $IAP = a_A^{v_1} a_B^{v_2} \text{ (actual)}$

- Saturation Index: $SI = \log IAP - \log K_{sp}$
  - $SI = 0$: $IAP = K_{sp} \rightarrow$ equilibrium
  - $SI < 0$: $IAP < K_{sp} \rightarrow$ undersaturated (dissolution)
  - $SI > 0$: $IAP > K_{sp} \rightarrow$ supersaturated (precipitation)
SLE MATLAB tool results

[Graph showing concentration mol/l vs pH with various chemical species labeled, such as CaHPO₄(S), FeHPO, HPO₄²⁻, PO₄³⁻, etc.]
experimental v/s SLE speciation results

- Degree of P leaching vs equilibrium pH for various acid combinations:
  - HCl
  - H₂SO₄
  - HNO₃
  - HCl+HNO₃
  - HCl+H₂SO₄
  - HNO₃+H₂SO₄
  - H₃PO₄

- Model comparison to experimental data.
non-linear data fitting

- deviation of modelling results
  - complex nature of sludge
  - P and metals bound to organic matter
- lack of thermodynamic data
  - fitting of multiple parameters - equilibrium constants and reaction stoichiometry
metal extraction from sludge liquor

TBP 10%; Exxal 3%; diluent – Ketrul;
LLE - non-linear data fitting

\[ \text{Log } K = 3.616 \]

stoich. Alamine: Fe \( (n) = 1.44 \)

\[ \text{FeCl}_m^- + nR_3NH^+Cl^- = \text{FeCl}_m(R_3NH)_n^- + nCl^- \]
summary

- MATLAB tool for simulation of SLLE with precipitation of multiple solid phases
- data fitting – lack of thermodynamic data and nature of sludge
- further development of the model
  - incorporate activity models for IS>1 mol/L
  - incorporate temperature dependence for logK
  - comprehensive tool to simulate the entire PULSE process
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References


