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

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Jahrestreffen der ProcessNet-Fachgruppen
Fluidverfahrenstechnik, Adsorption und Extraktion
Berchtesgaden, 26 – 28 Feb. 2020

agenda

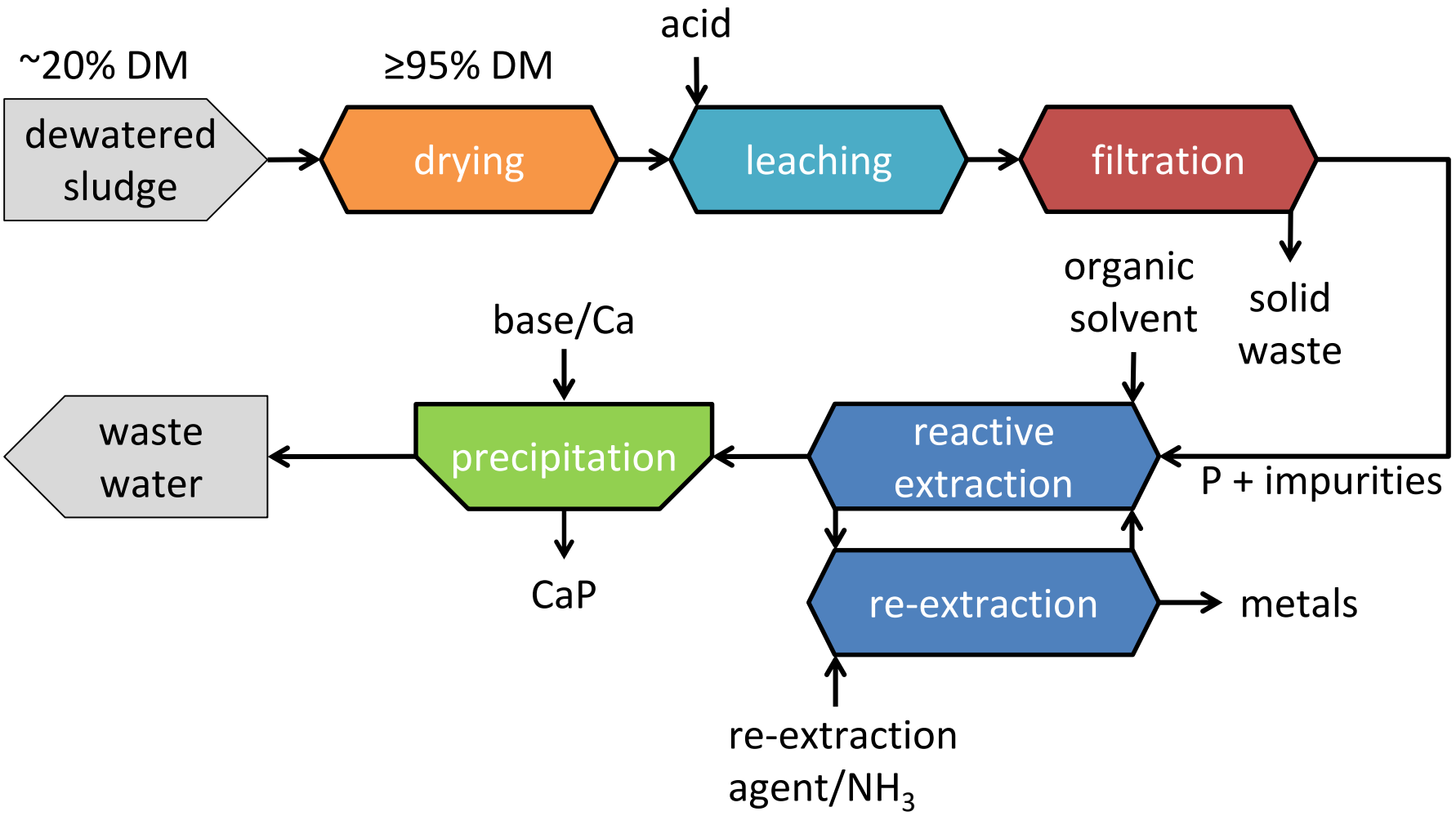
- Introduction to P recycling
- PULSE process
- SLLE tool
- results
- summary

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

rock phosphate

PULSE (Phosphorus University of Liege Sludge Extraction) process



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

$$\mathrm{Fe^{3+} + 4Cl^- \leftrightarrow FeCl_4^-}$$

$$\overline{R_3NHCl} + FeCl_4^- \leftrightarrow \overline{FeCl_4R_3NH} + Cl^-$$

- Precipitation of CaP

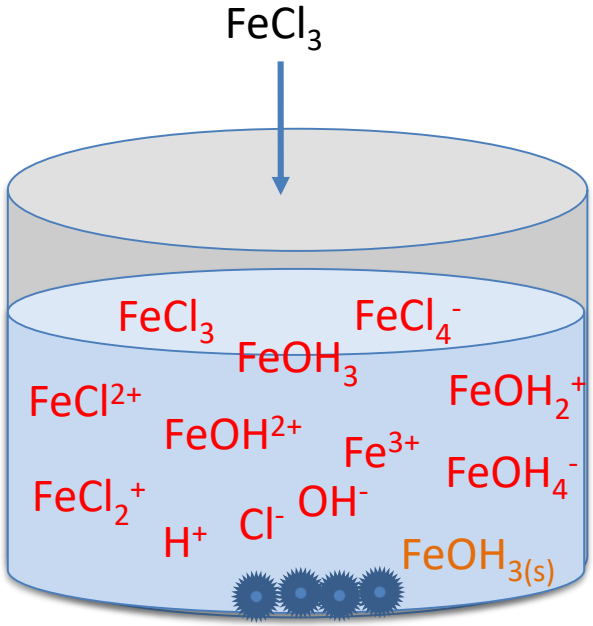
$$Ca^{2+} + HPO_4^{2-} \rightarrow CaH(PO_4)$$

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)
  - $Ctot_j = \sum_{i=0}^{n} \nu_{i,j} c_i$
- law of mass action (LMA)
  - $logK_m = \sum_{i=0}^{n} \nu_{i,r}\, log\, a_i$



$a_i = \gamma_i c_i$

a_i = activity of ith species

γ_i = activity coefficient

c_i = concentration

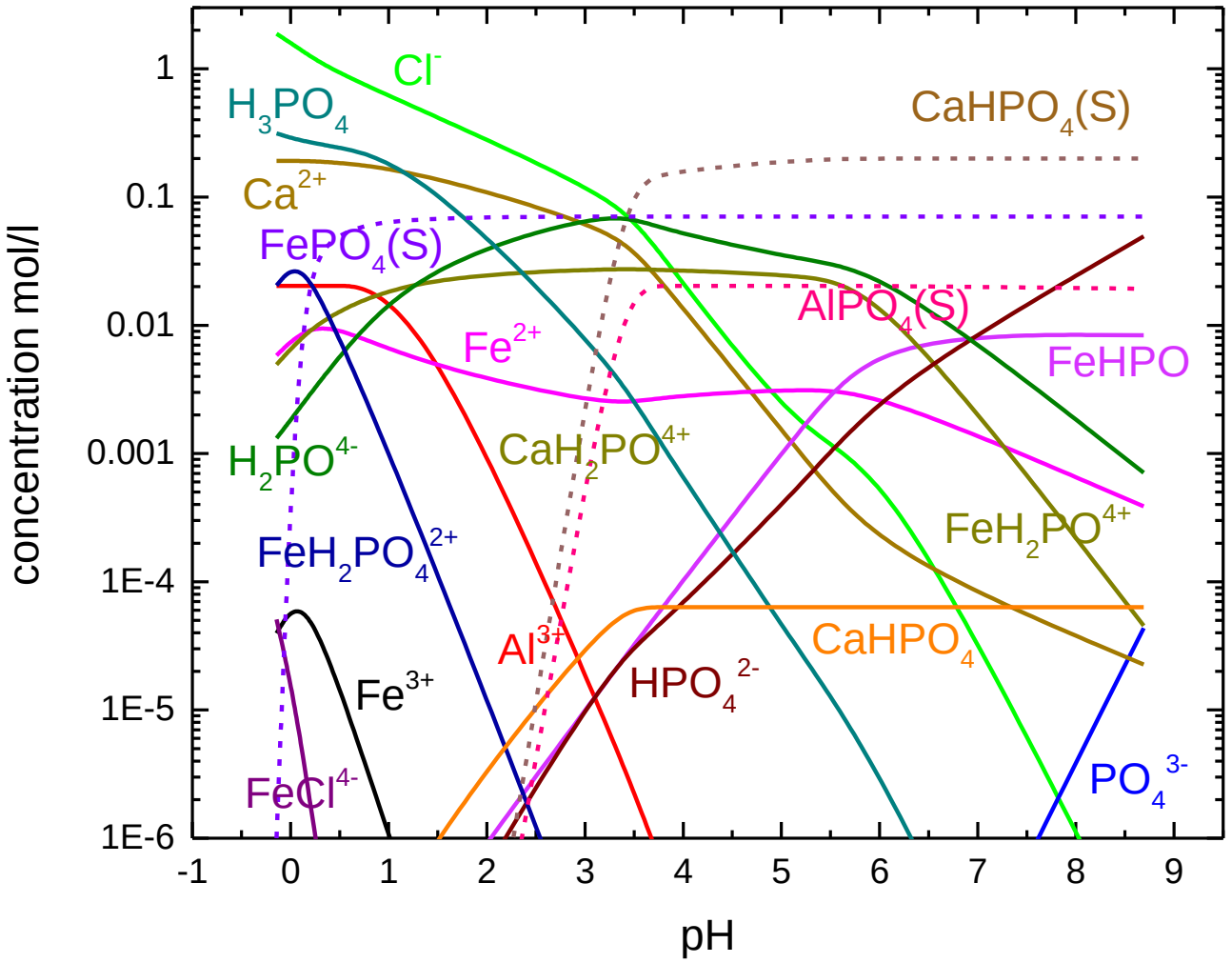
solid-liquid equilibrium

- $AB_{solid} \leftrightarrow \nu_1 A + \nu_2 B$
- from law of mass action

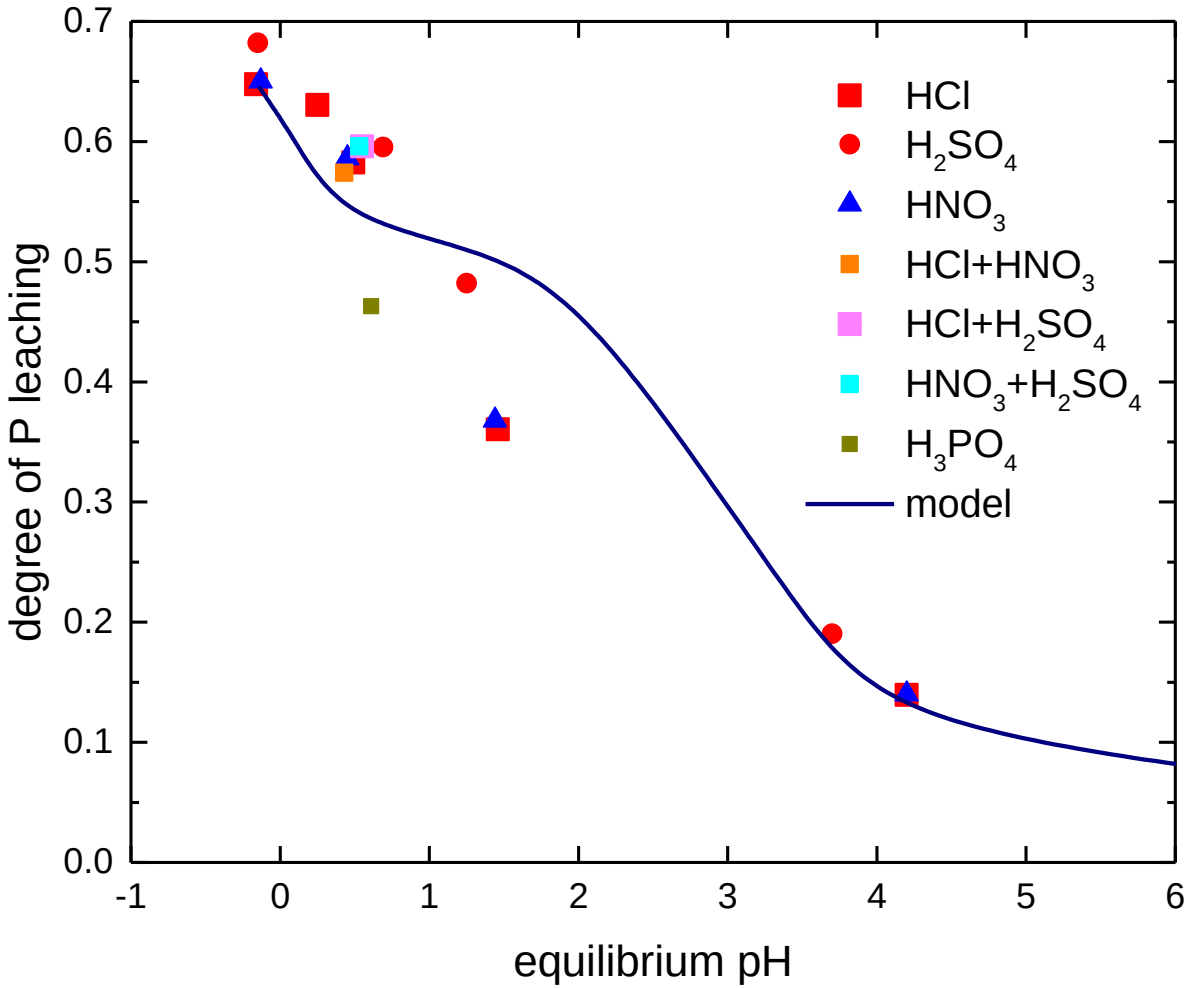
$$K_{sp} = a_{A0}^{\nu_1} a_{B0}^{\nu_2} \quad (at\ equilibrium)$$

- Ion Activity product: $IAP = a_A^{\nu_1} a_B^{\nu_2}$ *(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



experimental v/s SLE speciation results

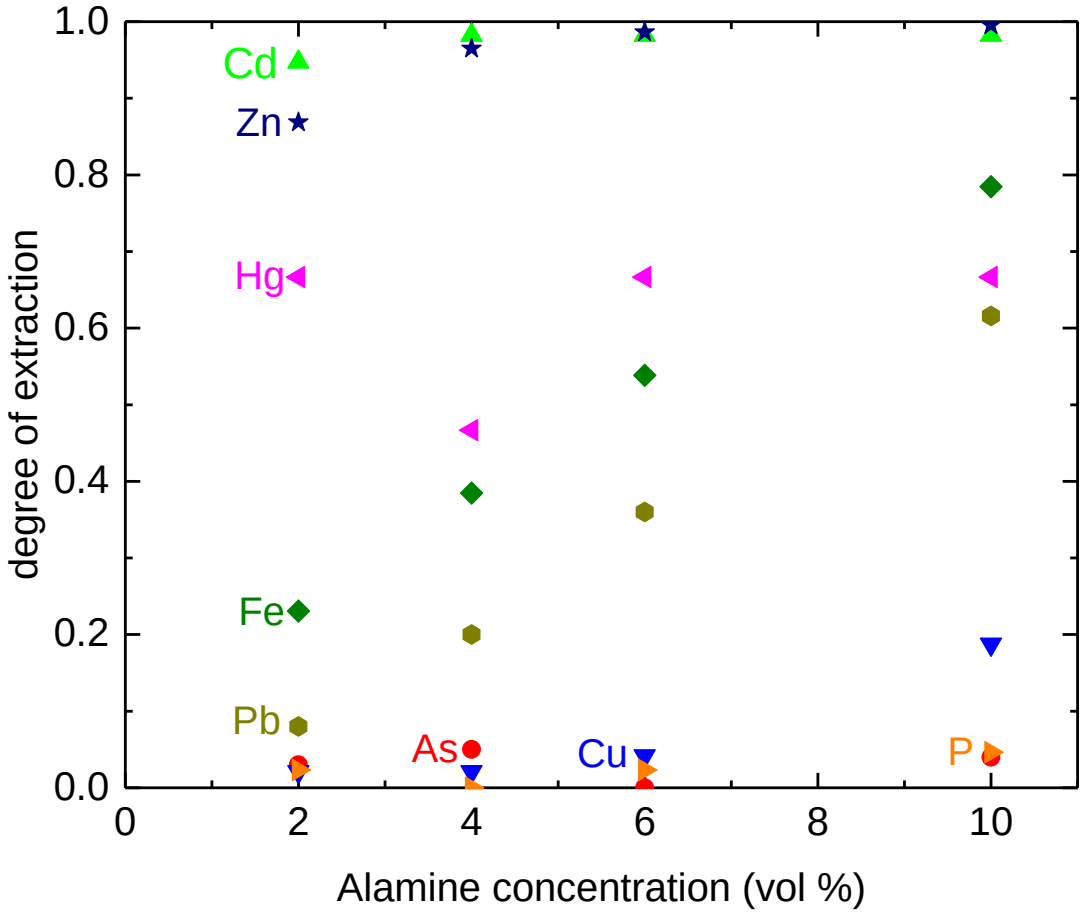


non-linear data fitting

- deviation of modelling results
  - complex nature of sludge
  - P and metals bound to organic matter

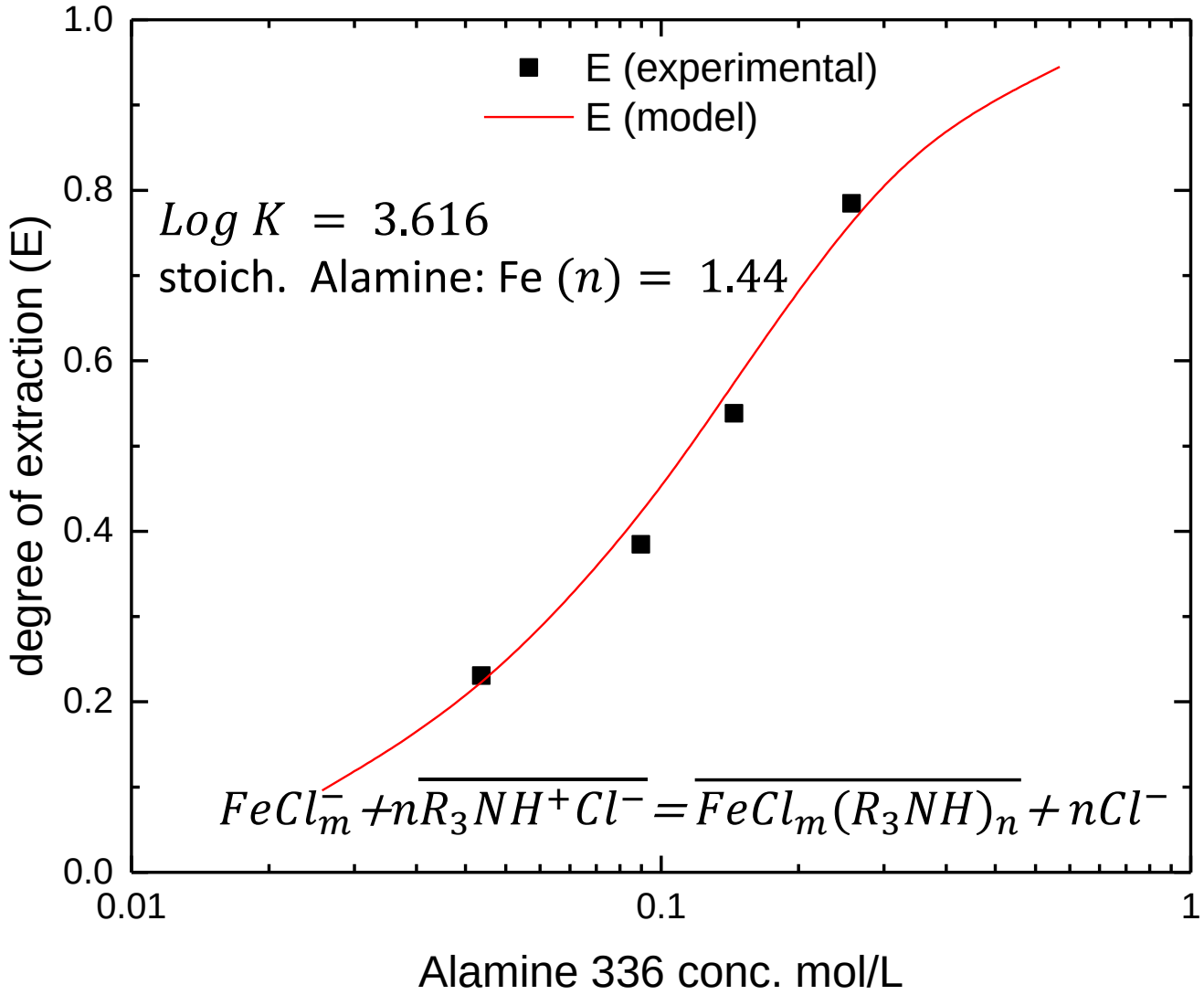
- lack of thermodynamic data
  - fitting of multiple parameters - equilibrium constants and reaction stoichiometry

metal extraction from sludge liquor



TBP 10%; Exxal 3%; diluent – Ketrul;

LLE - non-linear data fitting



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

- http://www.nweurope.eu/projects/project-search/phos4you-phosphorus-recovery-from-waste-water-for-your-life/
- Doetsch, P., Pinnekamp, Johannes, Montag, D., Rath, W., Grömping, M., 2010. Rückgewinnung von Pflanzennährstoffen, insbesondere Phosphor aus der Asche von Klärschlamm (Abschlussbericht PASCH). Institut für Siedlungswasserwirtschaft der RWTH Aachen, Aachen.
- Morel, F., & Hering, J. G., 1993. Principles and applications of aquatic chemistry. New York (N.Y.): Wiley
- Carrayrou , J., Mosé , R., & Behra, P., 2002. New efficient algorithm for solving thermodynamic chemistry. AIChE, 894-904.
- Andalibi, M.R., Kumar, A.S., Srinivasan, B., Bowen, P.L., Scrivener, K.L., Ludwig, C.H., & Testino, A., 2018. On the mesoscale mechanism of synthetic calcium–silicate–hydrate precipitation: a population balance modeling approach. J. Mater. Chem. A, 6, 363