Poster No. 9

PULSE PROCESS: RECOVERY OF PHOSPHORUS FROM SLUDGE AND ITS PRODUCT QUALITY ASSESSMENT

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Need for P recycling? Phosphorous (P) is an essential element for all forms of life and is a finite resource. Mineral P is mainly produced from Phosphate rock, which was classified by the European Commission as a critical raw material in 2014. As a result, significant research has been directed towards finding economical ways of recycling P from waste streams which otherwise will be lost. The Phos4You (P4Y) project funded under the Interreg North-West Europe (NWE) Program is aimed at improving the recovery potential of P from municipal wastewater and sludge, which could substitute about 26% of mineral P demand in NWE. In the framework of the P4Y project 6 different technologies for recycling of P will be demonstrated. The university of Liège is developing one of the processes to be demonstrated which is called the PULSE (Phosphorus ULiège Sludge Extraction) process aimed at recovering P from dried sewage sludge. The work carried out at ULiège is also jointly supported by the Région Wallonne. The quality assessment of the novel products produced in P4Y project is lead by the Ghent University.

PULSE process development The PULSE process is a modification of the PASCH process developed at RWTH Aachen [1]. The concept of the PULSE process is shown in Fig. 1. The different process options possible for each unit operation of the PULSE process are evaluated using 'Cascaded Option Tree' methodology [2] to select the most feasible and optimum option. An example of the cascaded option tree for the drying operation in shown in Fig. 2. The most important process parameter of the PULSE process for the unit operations leaching, reactive extraction, and precipitation is pH. The pH controls the types of ions or complexes that exist in a solution and the species that will precipitate at equilibrium, knowledge of which is critical to optimize the process operation. Therefore, a modelling tool developed in MATLAB is used in order to simulate the SLLE based on the pH as shown in Fig. 3. As the model only considers pure substances, therefore in order to have good correlation between the experimental results and the model, a data fitting algorithm is also coupled with the speciation tool to fit the modelling parameters to experimental data.

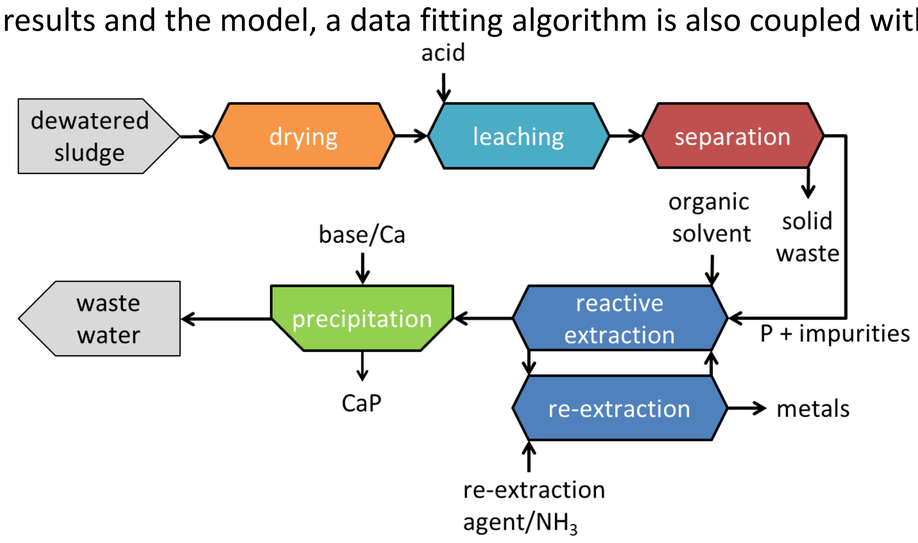


Figure 1. PULSE process concept

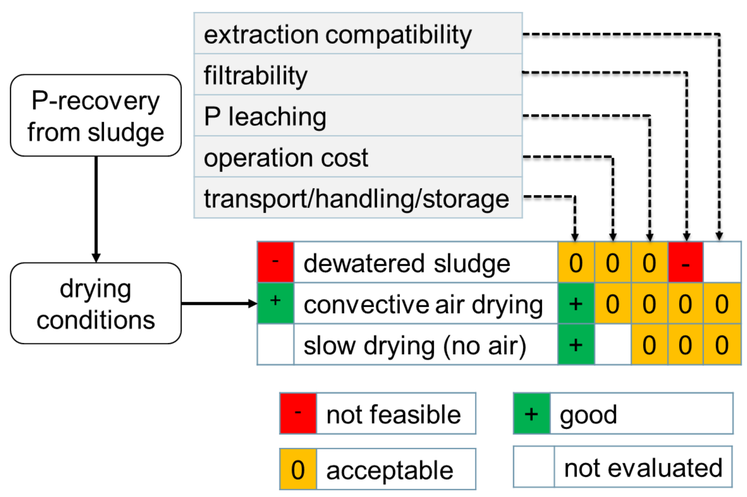


Figure 2. cascaded option tree evaluation for drying operation

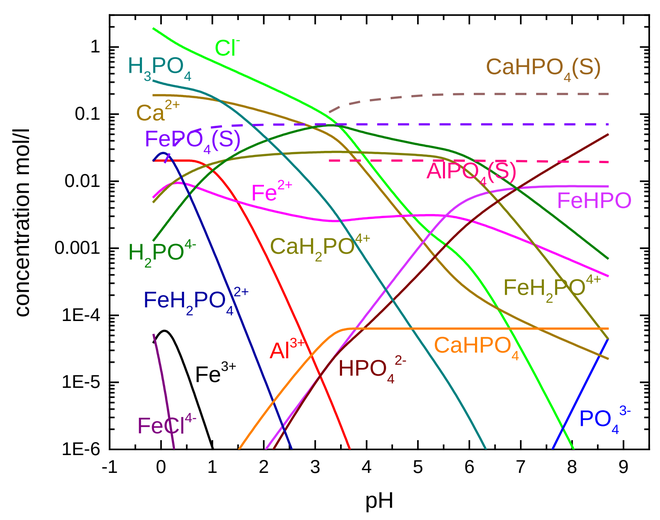


Figure 3. SLE speciation for Fe-Al-P and HCl system

Experimental results

- P leaching is independent of the acid used
- efficient extraction of metals could only be achieved in the presence of Alamine 336, which is a anionic extractant
- the extraction of metals, increased with the increase in Cl^- (anion) concentration
- Oxidation state of metals is also critical for extraction
- when 1mol/L H_2SO_4 was used as leaching acid, the extraction efficiency was < 20% for the metals considered

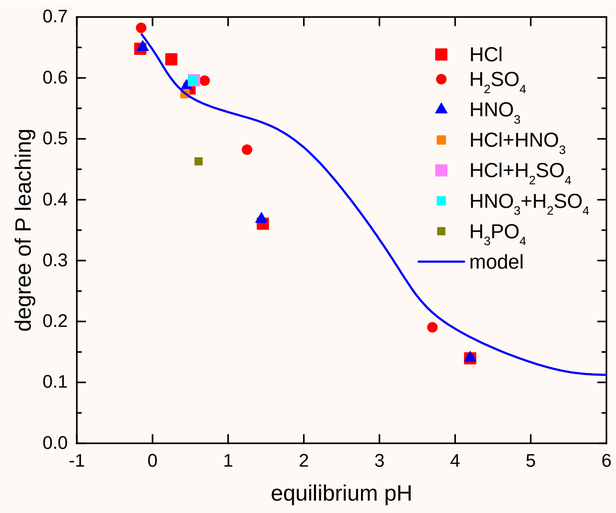


Figure 4. P leaching efficiency from undigested fully dried sludge

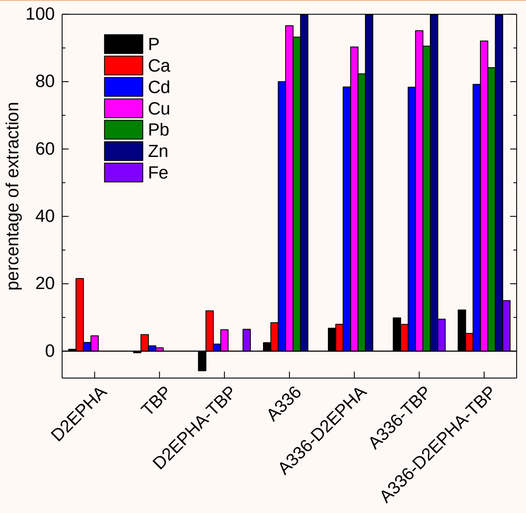


Figure 5. reactive extraction of metals from 1mol/L HCl dried sludge liquor

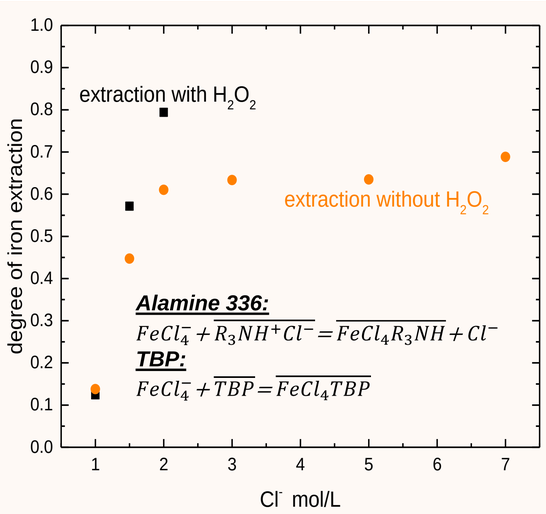


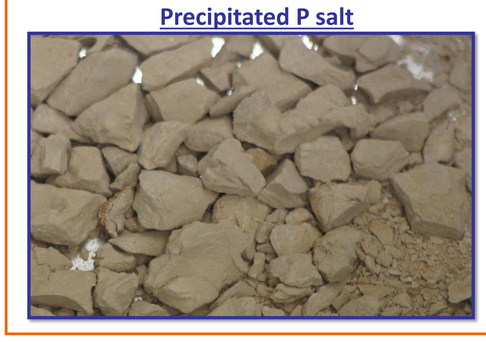
Figure 6. reactive extraction of iron using A336 10% + TBP 10% at different Cl^- concentrations

PULSE product quality assessment

Nutrient content ✓ rich

Element, %	Precipitated P salt	Recovery from sludge
P_2O_5	32±0.6	70
CaO	24±1	98
MgO	2.7±0.0	33
SO_3	0.52±0.0	5
K_2O	0.14±0.0	2

Precipitated P salt



Metal content ✓ safe

Element, mg/kg dm	Source sludge*	Precipitated P salt*	Legislative limit for fertilizers[3]
Cd	<DL	<DL	60
Cu	321±11	499±2	600
Ni	<DL	29.0±0.4	50-100
Pb	147±2	114±3	120
Zn	1309±23	4.5±0.5	1500
As	n.a.	18.0±1.2	40
Al	9603±96	15144±841	n.a.
Co	<DL	6.3±0.4	n.a.
Cr	306±5	1537±10	n.a.
Mn	1294±32	11093±167	n.a.
Fe	28445±881	17437±407	n.a.

*Method: Microwave digestion with nitric acid/or *aqua regia* and ICP-OES

Conclusion on final product-precipitated P salt

Advantages of novel fertilizer recovered from sewage sludge

- Relatively **high amount of P** (more than minimum of 3[3]-16%[4] P_2O_5)
- High amount of calcium (more than 12%[3] CaO)
- Significant amount of magnesium (more than 1,5%[3] MgO)

⇒ potential classification as compound fertilizer (>3% P_2O5; > 1,5% CaO and MgO; in total > 8-18%[3])

- reactive extraction succeeded in **removing Cd and Zn**
- reactive extraction **reduced also Cu, Fe and Pb**

Remaining potential concerns

- **Cr** and Pb are hazardous substances and should be further reduced (Cr is present at atypically high amount in the particular sewage sludge)
- Al and Fe may limit the nutrient availability of novel fertilizer
- Allowable limits for Cu may get more restrictive by the novel fertilizer legislation (expect for use in the areas with deficiency in this element)

Future work

- Precipitated P salt should be tested in a pot trial to check for its **nutrient availability** as well as other safety indicators

References:

[1] Doetsch, P., Pinnekamp, J., Montag, D., Rath, W., Grömping, M., 2010. Rückgewinnung von Pflanzennährstoffen, insbesondere Phosphor aus der Asche von Klärschlamm. Institut für Siedlungswasserwirtschaft, RWTH Aachen, Aachen.

[2] Bednarz, A., Rüngeler, B., Pfennig, A., 2014. Use of Cascaded Option Trees in Chemical-Engineering Process Development. Chem. Ing. Tech. 86, 611-620.

[3] EC, 2019. Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL laying down rules on the making available on the market of CE marked fertilizing products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009.

[4] Huygens, D., Saveyn H.G.M., Tonini D., Eder P., Delgado Sancho L., 2019. Technical proposals for selected new fertilizing materials under the Fertilizing Products Regulation (Regulation (EU) 2019/1009) - Process and quality criteria, and assessment of environmental and market impacts for precipitated phosphate salts & derivates, thermal oxidation materials & derivates and pyrolysis & gasification materials, Publications Office of the European Union, Luxembourg.