Phosphorous Recovery From Sewage Sludge Utilizing Reactive Extraction.

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Abstract Phosphorus (P) is indispensable nutrient in agriculture, essential for nutrition of mankind. To close the P loop, P must be recovered during wastewater treatment in Germany by the end of this decade. Other EU countries will follow with similar regulations. As part of an Interreg NW-Europe project, several pilot-scale processes were tested by industrial and research partners to validate them in industrial settings. At the University of Liège, the PULSE (Phosphorus University of Liège Sludge Extraction) process was developed. It consists of sludge drying, which is essential for good process performance, leaching with hydrochloric acid, reactive extraction to remove unwanted metals such as iron and heavy metals, and fractional precipitation. Since sewage sludge changes properties during storage, the mobile pilot plant was operated at three different locations with fresh sewage sludge from wastewater treatment. To adapt the operating parameters of PULSE to the specifics of the respective sludges, they were optimized with the aid of simulations, based on cascaded option trees. A key point is the thermodynamic description of the aqueous speciation equilibria, of the reactive equilibria during extraction and of those describing precipitation. In particular, the model allows considering different models for the non-ideality of electrolyte solutions up to concentrated systems. The simulation tool can also be used to fit unknown parameters such as the equilibrium constants of reactive extraction. It was shown that the model is able to describe well all equilibria at the different process steps in the system. On the other hand, the optimal operating parameters could be confirmed experimentally. Finally, it was shown that the process can be operated well at pilot scale. The product obtained after precipitation was tested by the project partners and showed good performance as a fertilizer component in pot trials and could be easily incorporated into the granulation of a commercial fertilizer formulation.

Keywords: circular economy, equilibrium modelling, heavy metal, phosphorous recycling, reactive extraction, sewage sludge

Introduction

At the University of Liège (Uliège), the PULSE (Phosphorus University of Liège Sludge Extraction) process was developed[i]. The concept of the PULSE process was developed based on the PASCH process[ii] and further adapted to treat dried sewage sludge to recover P. The scheme of the PULSE process developed at ULiège is depicted in Figure 1. The process shown produces calcium phosphate but can also be adapted to magnesium phosphate as final product.

The design and dimensioning of the PULSE demonstrator was carried out based on results of laboratory experiments that were established at ULiège and information from the PASCH process as well. While the equipment and parts for the PULSE demonstrator were ordered and procured, the optimization and evaluation of individual unit operations of the PULSE process was carried out at laboratory scale by making use of the cascaded option trees and equilibrium-speciation simulations. In order to carry out the equilibrium simulations for the

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unit operations of the PULSE process a MATLAB tool has been developed for calculation of solid-liquid-liquid equilibria (SLLE).
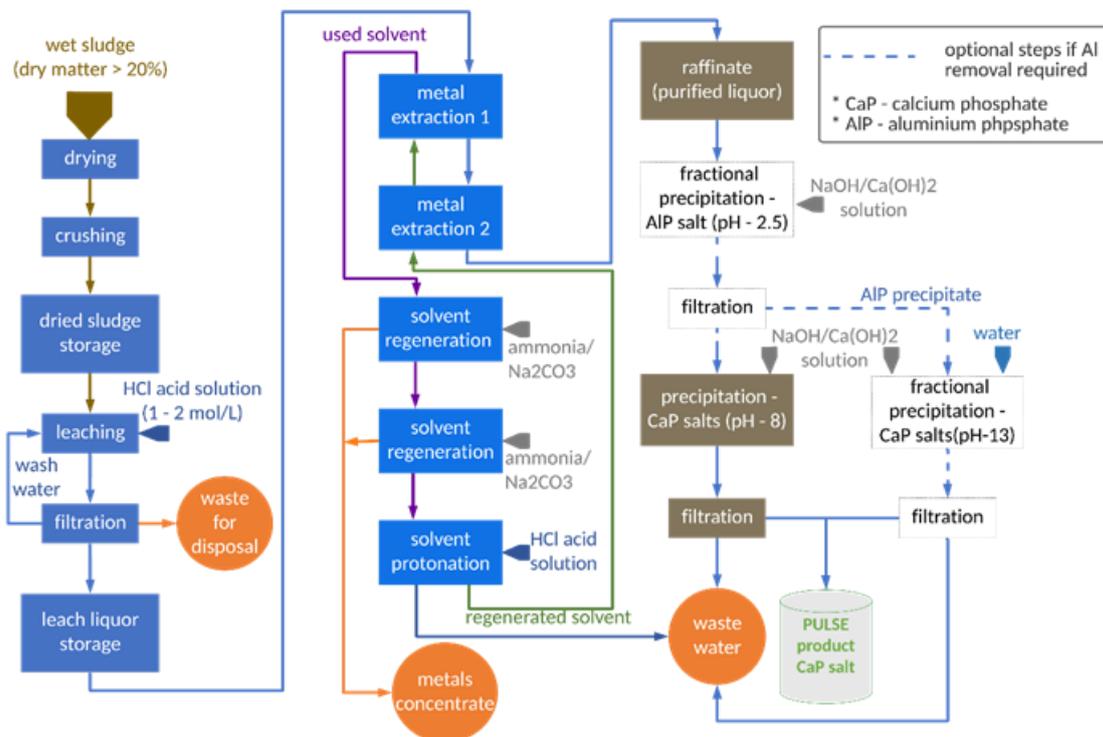
Figure 1: PULSE-process scheme.

Methods

Cascaded Option Trees

In order to find suitable operating options and to optimize the unit operations of the PULSE process, the cascaded option-tree methodology[iii] was used. In this method, the options are evaluated against a set of operation-relevant criteria. The option with the most positive evaluation is chosen for the process. The information for evaluation of the options is obtained from literature, laboratory experiments, and SLLE modelling.

Solid Liquid Liquid equilibrium modelling tool

The chemical unit operations of the PULSE process, i.e. leaching, solvent extraction of metals and subsequent stripping of metals from the spent solvent for regeneration, and the precipitation of P salts are inter-dependent and sensitive to the pH of the respective operation among other operating parameters. As the characteristics of sludge can vary from day to day, it is imperative to understand the chemistry and reactions occurring as a function of pH in each of these operations. Therefore, a MATLAB tool for simulating SLLE was developed, which can be used to describe the chemical unit operations. With the help of this tool, it is possible to optimize the process for sludge with different characteristics minimizing experimental work.

The SLLE tool solves a set of nonlinear equations consisting of charge neutrality, mass balance and law of mass action constraints which describe the system[iv], including appropriate quantification of thermodynamic non-idealities, where e.g. the Debye-Hückel and the Davies model can be selected[v]. The solution of the non-linear system of equations leads to the concentrations of all chemical species that exist in the aqueous phase and/or in the organic phase as well as the solids that can precipitate at equilibrium as shown in Figure 3. In that example, representing undigested dewatered sludge used for performing experiments to develop the PULSE process, contained calcium, iron, and aluminum as the predominant metals besides phosphorus. Analysis of ferric and ferrous iron leached from the dried sludge revealed that about 70% of the iron were present as ferric, Fe^{3+}. Depending on the molar concentration of iron, a major fraction of inorganic phosphorus in sludge can be present as ferric phosphate ($FePO_4$). It can be seen from Figure 2, $FePO_4$ can remain undissolved if the pH is greater than 0.3.
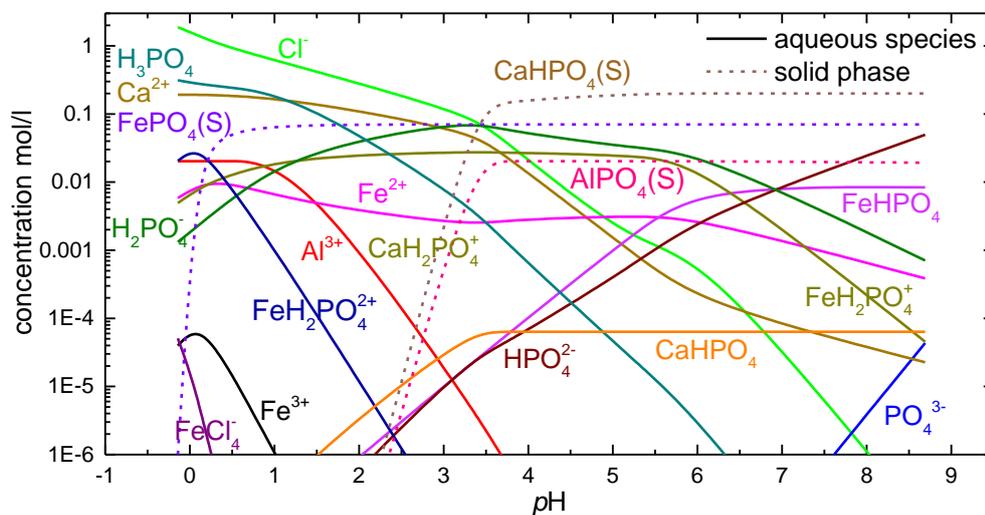
Figure 2: Speciation using the SLLE tool. Initial concentrations in [mol/L]: Fe^{3+}: 0.0703, Al^{3+}: 0.0203, HCl: varying, PO_4^{3-}: 0.348, Ca^{2+}: 0.2, Fe^{2+}: 0.03. The dashed curves show the precipitation equilibrium

Although extensive thermodynamic data are available for aqueous phase reactions and precipitation, it is not the case for solvent extraction or organic-phase reactions. Since the description of these equilibria is required to optimize the PULSE process, the chemical equilibrium constants and reaction stoichiometry are determined in this case by performing equilibrium experiments and fitting the parameters to experimental data using the tool.

PULSE-process development and optimization with lab experiments

Lab-scale experiments for each unit operation of the PULSE process were established in order to obtain the necessary information for the design of the PULSE demonstrator and to develop and optimize the overall process. The materials and methods for these analyses are detailed in the project technical report[i]. Here, the general outcomes of the process development and optimization for the individual unit operations of the PULSE process are discussed below. All the laboratory experiments were carried out using undigested dewatered sludge from Oupeye wastewater-treatment plant (wwtp) in Liège, Belgium.

The PULSE process

In the following the resulting conditions for the unit operations of the PULSE are presented.

Sludge Drying

The P-leaching efficiency of dried sludge (DS) and dewatered sludge (DWS) was compared after leaching with hydrochloric acid (HCl) in order to select the optimal input material to the process. It turned out that the solid-liquid separation after leaching dewatered sludge directly was not possible as the solids were very fine and a sufficiently fine filter was blocked almost immediately. In contrast, for dried sludge the particle size could be controlled to a certain degree during crushing and removal of more than 80 % of the particles at 100 or 50 μm was possible by filtration. Considering the reduction in acid consumption during leaching and the ease of solid-liquid separation after leaching in case of dried sludge, a drying step was included in the PULSE process.

Leaching

The efficiency of overall P-recovery is largely dependent on the leaching operation. The results showed that the leaching of P depends only on the pH and not on the acid used. Also, the P leached is mainly stemming from the inorganic P while little or no organic P can be accessed around pH zero. The leaching of P estimated using the SLLE tool correlates well with the experimental data.

With respect to the different acids tested for leaching, HCl is one of the cheapest acids and it also provided better result with respect to solvent extraction of metals compared to sulfuric acid. Therefore, based on the cascaded option-tree evaluation of the different acids, it was decided to use HCl in the PULSE process. Further, based on the laboratory results, leaching time of 1 hour and an S/L ratio of 0.25 were chosen for the PULSE leaching.

Reactive extraction

The metals that are co-leached with P are not desired in the final product as they may be detrimental when the recovered P product is used as a fertilizer or they may reduce the P availability to plants. Apart from P and Ca, Fe is the most predominant metal leached from Oupeye sludge and 70 % of Fe is present in the form of Fe^{3+}. $FePO_4$ can precipitate even at a pH as low as 0.3, which would reduce the P availability to plants in the soil.

In the PULSE process, reactive extraction is used to remove Fe and other heavy metals from the leach liquor. Reactive extraction allows the selective extraction of metals as a function of pH and has a high capacity for metal loading. Based on the information obtained from the PASCH process and the mechanism of extraction, three extractants were evaluated, namely Alamine 336, which is an anion-exchange extractant, D2EHPA, which represents a cation-exchange extractant, and TBP, which is a complexing extractant. Ketrul-D80, which is a commercially available brand of desulfurized kerosene, was chosen as diluent. Kerosene is one of the most commonly used diluents due to the advantages it offers over other diluents such as low toxicity and high flash point. The extraction efficiencies of these extractants were evaluated using lab experiments.

The experimental results indicated that only the reactive extractant Alamine 336 provided a quantitative extraction of metals. The degree of extraction of iron is very low at a HCl concentration of 1 mol/l. It was found to increase with the concentration of HCl, as Cl^- is exchanged against negatively charged ferric-chloride complexes that are formed at low pH.

Based on the cascaded option tree evaluation, the solvent system containing Alamine 336, TBP and Exxal 10 dissolved in Ketrul D80 was chosen to be employed in the PULSE process. Exxal 10 is a modifier that is required to improve the solubility of Alamine 336 in the diluent and to prevent the formation of a third phase upon extraction.

In the PULSE demonstrator, a battery of four mixer settlers of 150 mm diameter and 1500 mm length is employed to carry out the different steps involved in extraction, i.e. protonation of solvent using acid, reactive extraction of metals in two counter-current stages and stripping of metals from solvent.

Precipitation

In the PULSE process, it is possible to precipitate P either as calcium phosphate (CaP) or as magnesium phosphate (MP). Since precipitation of MP requires an additional step for the removal of calcium as calcium sulphate by fractional precipitation, it is preferred to precipitate P as calcium phosphate.

The different calcium-phosphate phases that could precipitate at different pH were evaluated based on the SLLE model considering the solubility-product constant of the various calcium-phosphate phases and the Ca/P ratio that was found in the precipitate. The precipitation of different phases is quite complex as at first a less stable phase such as di-calcium phosphate di-hydrate ($CaHPO_4 \bullet 2H_2O$) or amorphous calcium phosphate ($Ca_3(PO_4)_2$) is precipitated which transforms into the more stable hydroxyapatite (HAP) ($Ca_5(PO_4)_3OH$)[vi]. The time for transformation of the precursors to HAP depends on various factors such as temperature, saturation, presence of other ions such as magnesium and carbonates.

For the demonstrator tests, it has been decided to use a pH between 5 and 6 for the precipitation. As $Ca(OH)_2$ is cheaper compared to NaOH, it is more desirable to use $Ca(OH)_2$ compared to NaOH for the precipitation.

The PULSE Demonstrator

The PULSE demonstrator was designed and built as a mobile pilot plant so that it could be transported in containers and tested at different locations within the Phos4You project. The PULSE demonstrator consists of two 20-feet containers which can be placed parallel and opened on the long side as well as the short side. A tent can be installed between the two containers in order to create an enclosed space where the mixer settlers (MS) for solvent extraction can be assembled as all the sites where the demonstrator was operated do not have an enclosed space.

The unit operations were dimensioned to realize a capacity of 100 kg of dewatered sludge per day. Considering a typical DM content of 20 % this relates to a daily capacity of 20 kg of dried sludge. The unit operations were realized in batch mode for leaching, filtering, and

precipitation. The extraction and stripping steps were operated in quasi-continuous mode, i.e. procedures were established that the continuous mixer-settler units could be switched off and restarted with only limited disturbance of their content. In Figure 3 the mixer-settler units are shown while being run in the technical hall during commissioning.
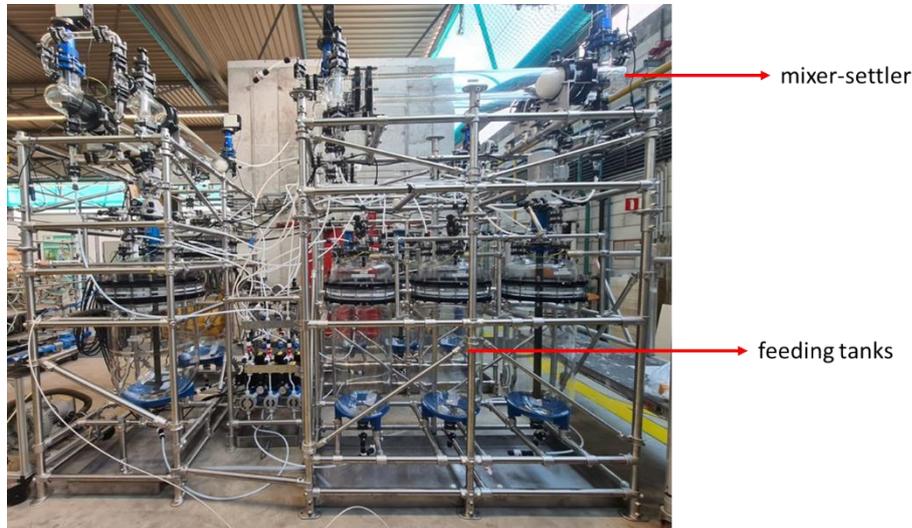
Figure 3: 5 stage mixer-settler equipment for solvent extraction tests in the PULSE demonstrator (Photo: ULiège/Z.A. Shariff)

The PULSE demonstrator was operated at ULiège with German sludge that had been shipped from Dortmund-Deusen wwtp, at Oupeye wwtp near Liège, and at the Waste-Water Development Centre of Scottish Water in Bo'ness.

Results

Some results obtained with the demonstrator are presented in the following. A broader overview can be found in the technical report of the PhosForYou project[i].

From 60 kg of dried sludge from the Dortmund-Deusen wwtp about 6.8 kg of product were obtained. The product concentrations are characterized in Figure 4 together with the reduction ratios that are be required to reach EU legal limits for fertilizer ingredients. For the critical components these limits are clearly met. The only exception is Cr, the content is not reduced relative to P for the sludge from Oupeye wwtp. The high concentration of Cr is due to a specific industry present within the Oupeye wwtp catchment. The results with the German sludge indicate, that it is in principle possible to reduce the Cr content relative to that of P. The final product contains a rather high Cl concentration. This can be easily avoided by additional washing of the product before drying, which was not realized for this set of demonstrator runs.

Conclusion

It has been shown that the PULSE process can efficiently recover P from sewage sludges of various origins. In particular, metallic impurities such as heavy metals can be sufficiently removed to meet the strict legal limits. The process can be easily adapted to the specific

conditions of a particular wastewater treatment plant using the SLLE tool. For example, it is possible to adjust the number of extraction stages depending on the metal concentrations, optimize the phase ratio, etc. to minimize process costs.
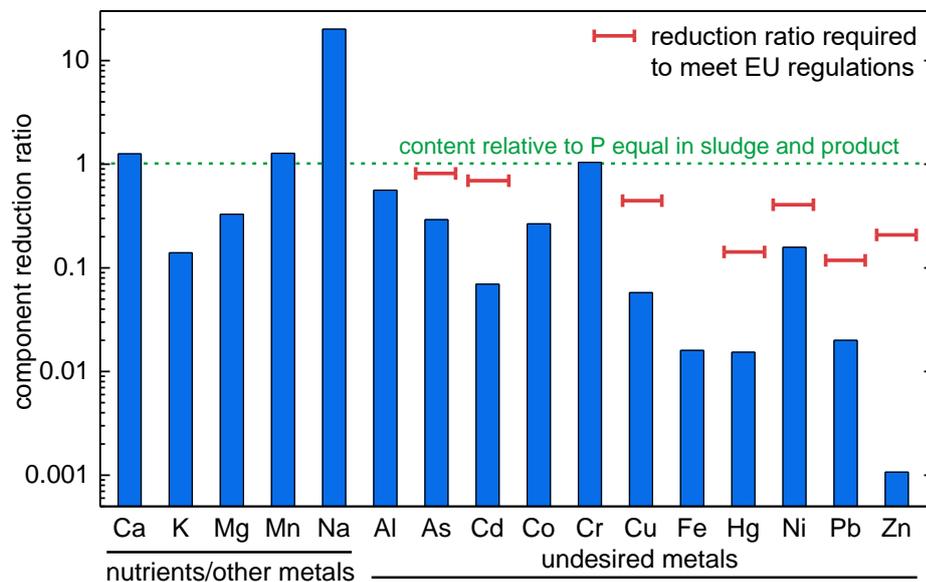
Figure 4: Reduction ratio relative to P (g/g P) between product and sludge and minimum reduction legally required for contaminants for the Oupeye sludge[vii]

ACKNOWLEDGMENT

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