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## Need for P recycling?

Phosphorous (P) is an essential element for life and has a limited availability in nature. 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 to landfills. 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 for 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 fully or partially dried sewage sludge.



## Process development

The PULSE process is a modification of the PASCH process developed at RWTH Aachen [1]. In the PULSE process P is recovered from partially or fully dried sludge using acidic leaching. Purification of the leach liquor will be carried out by reactive extraction to separate P and other nutrients from the metals. Finally, depending on the leaching and extraction approach used above, the final product of the PULSE process can either be obtained as phosphate salt or phosphoric acid. The different process options for each of the unit operation will be evaluated using 'Cascaded Option Tree' methodology [2] to select the most feasible and optimum process option during process development.

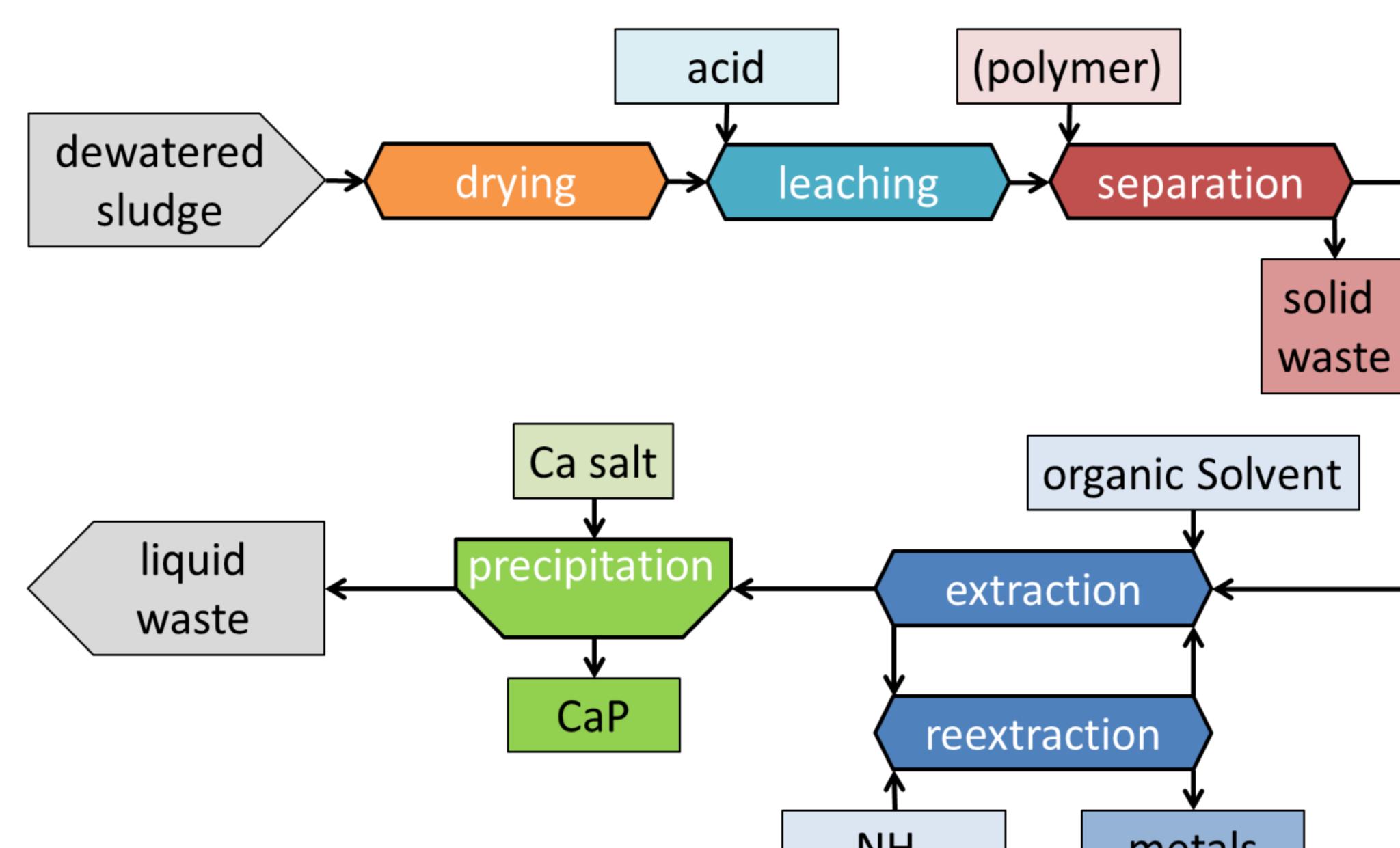
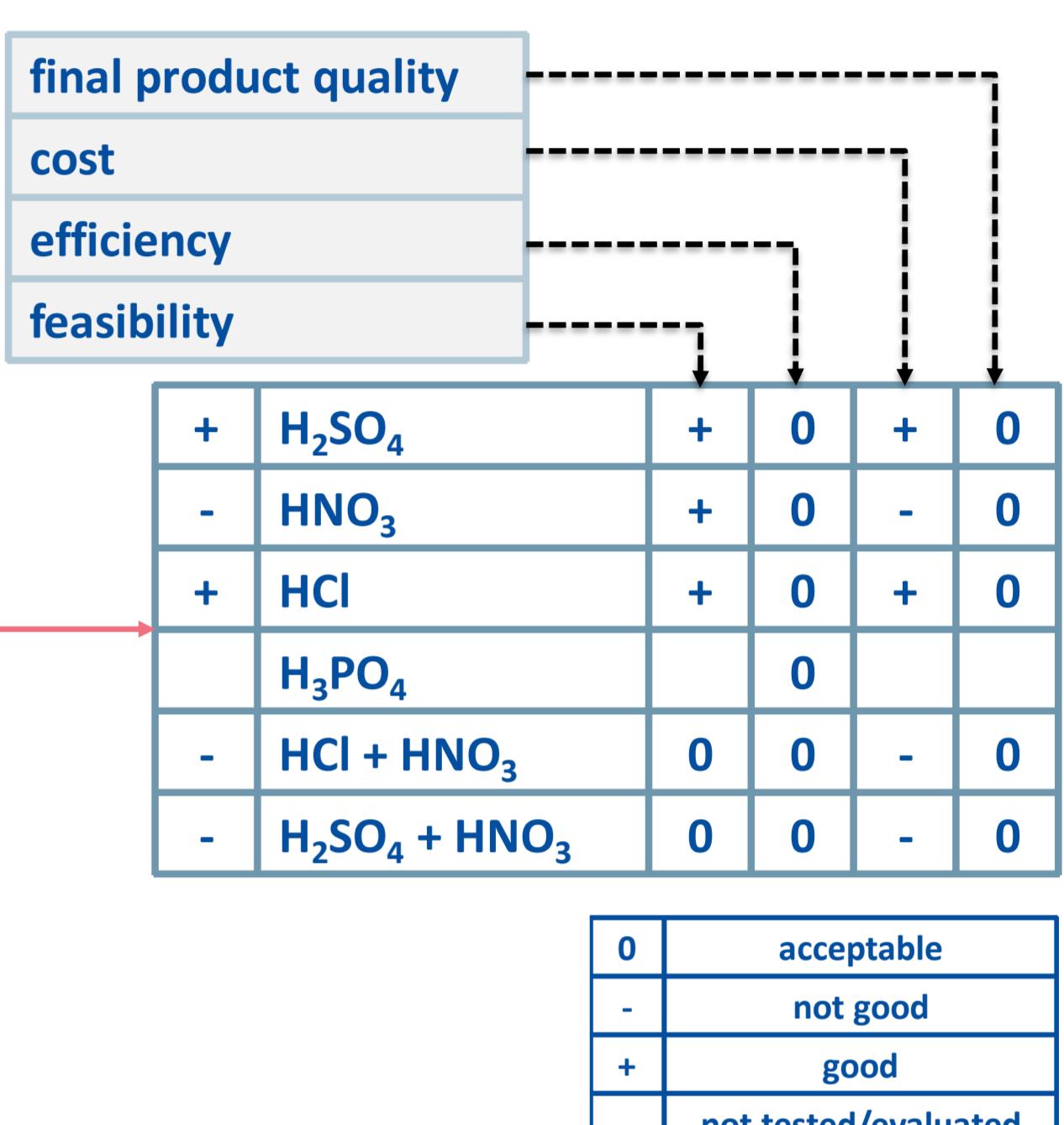


Figure 1. PULSE process concept



A cascaded option tree diagram for the PULSE process. The root node is 'acid leaching'. It branches into four options: + H<sub>2</sub>SO<sub>4</sub>, - HNO<sub>3</sub>, + HCl, and H<sub>3</sub>PO<sub>4</sub>. Each option leads to a 'final product quality' node, which further branches into cost, efficiency, and feasibility. A legend defines the symbols: 0 (acceptable), - (not good), + (good), and - (not tested/evaluated).

Figure 2. Example of Cascaded option tree methodology for evaluation of process options

## Modelling and optimization

In the PULSE process, the most important process parameter for the unit operations leaching, reactive extraction, and precipitation is the 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 PULSE process operation. Therefore, a model was developed in MATLAB in order to simulate the SLE based on the solution pH as shown in Fig. 2. The activities of aqueous ions or complexes in a solution can be determined by non-linear system of equations consisting of laws of mass action (LMA), mass balance (MB) and charge balance (CB). In the current SLE model, two variations of Debye-Hückel model i.e. the Davies and Truesdell-Jones model are implemented for calculation of activity-coefficient. These models can be used to calculate ion activity in solutions with ionic strengths up to 1 mol/L. Once the activities of the aqueous ions have been determined, the next step is to check, if any solids are precipitating. Precipitation of a species depends on super-saturation of the solution which is governed by the saturation index. An example of the SLE simulation carried out using the developed MATLAB code for a simple system of aluminium-iron-HCl is shown in Fig. 3.

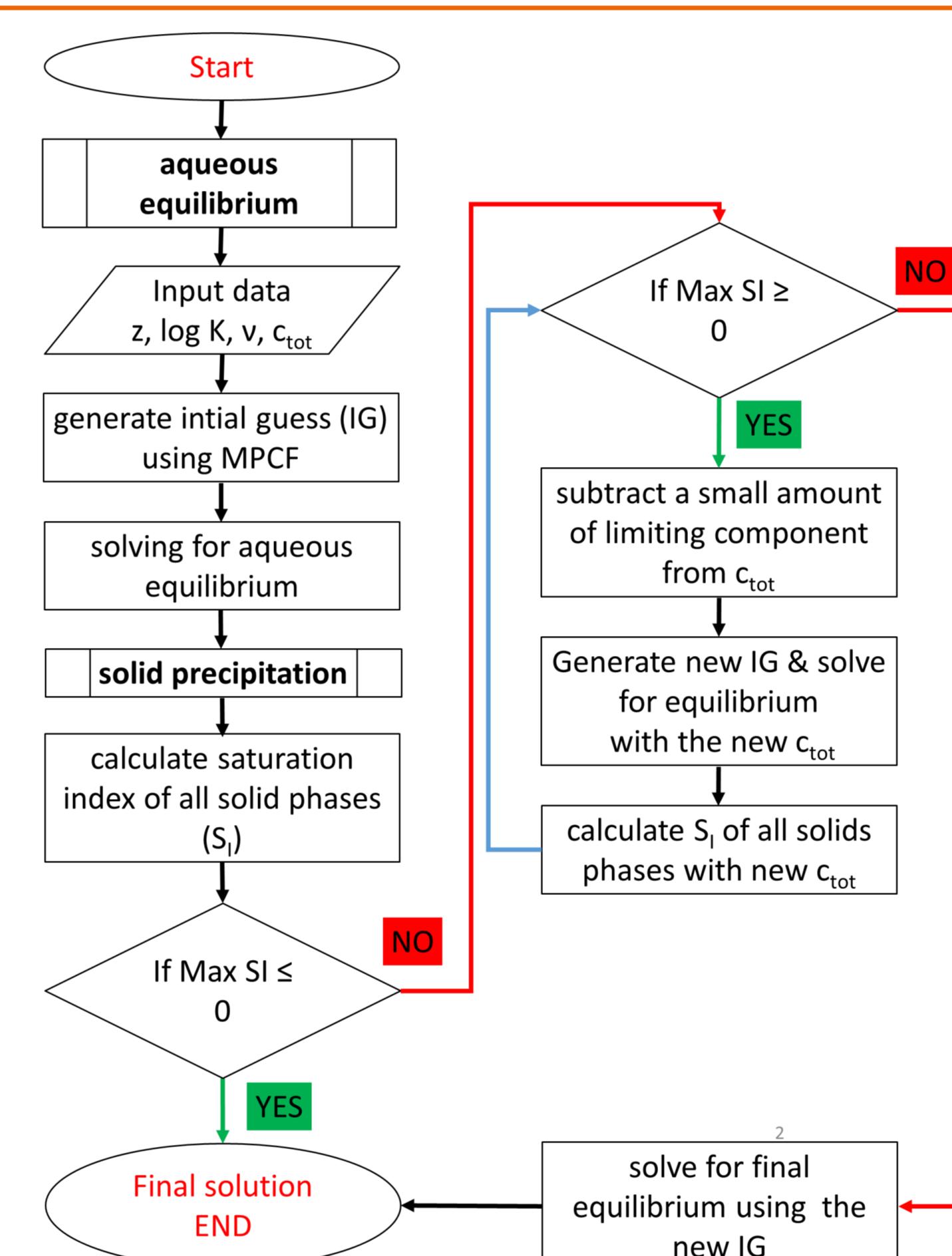


Figure 3. flowchart for the MATLAB solid-liquid speciation model

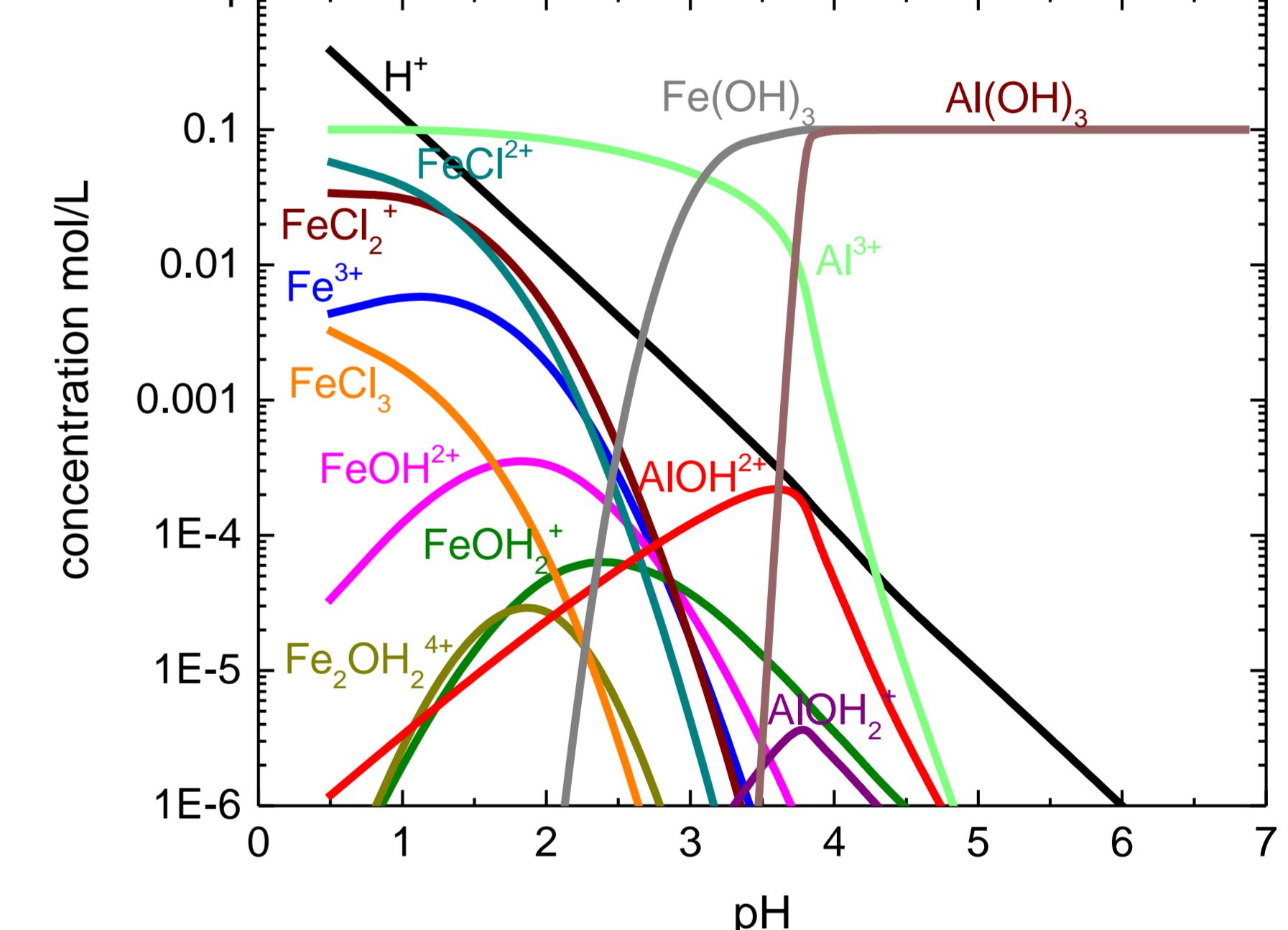


Figure 4. SLE of Al<sup>3+</sup>-Fe<sup>3+</sup>-HCl system as a function of pH. Total Fe = 0.1 mol/L; total Al = 0.1 mol/L; HCl = 1 mol/L - 10<sup>-6</sup> mol/L

## Results and future work

- leaching of P is mostly dependent on the pH of the leaching solution
- efficient extraction of metals could be achieved with Alamine 336 (A336), which is an anionic extractant from HCl leaching acid
- the extraction of iron was <15%, which is one of the predominant metal in the sludge considered
- when H<sub>2</sub>SO<sub>4</sub> was used as leaching acid, the extraction efficiency was < 10% for the metals considered
- the inefficient iron extraction could be due to the form of iron present in the leach liquor and more investigation will be carried out in this regard
- further experiments will be conducted to optimize the extraction process and the final product precipitation
- in the second step of research, the process will be tested on pilot scale at different locations

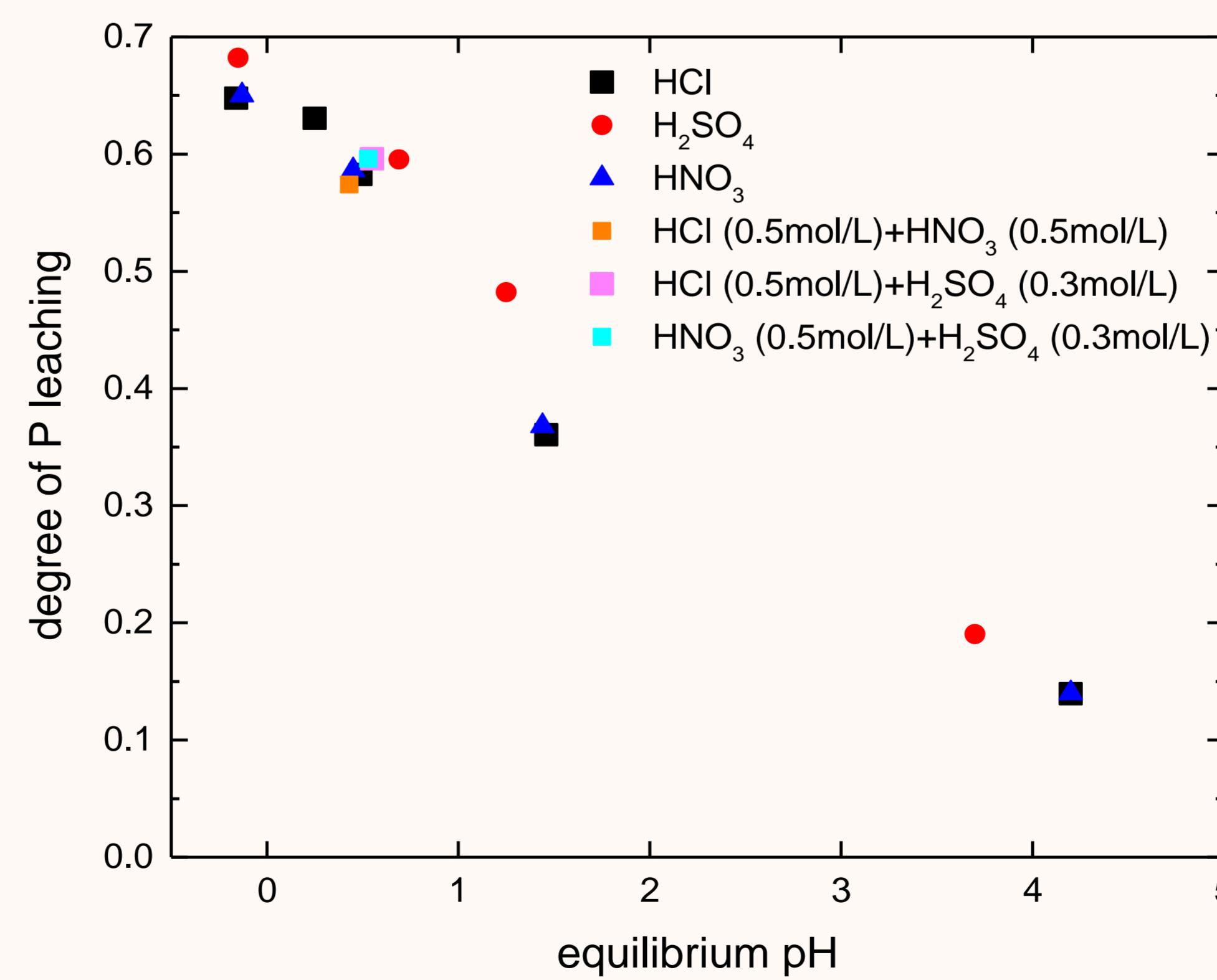


Figure 5. efficiency of P leaching from undigested fully dried sludge with different acids and at different pH

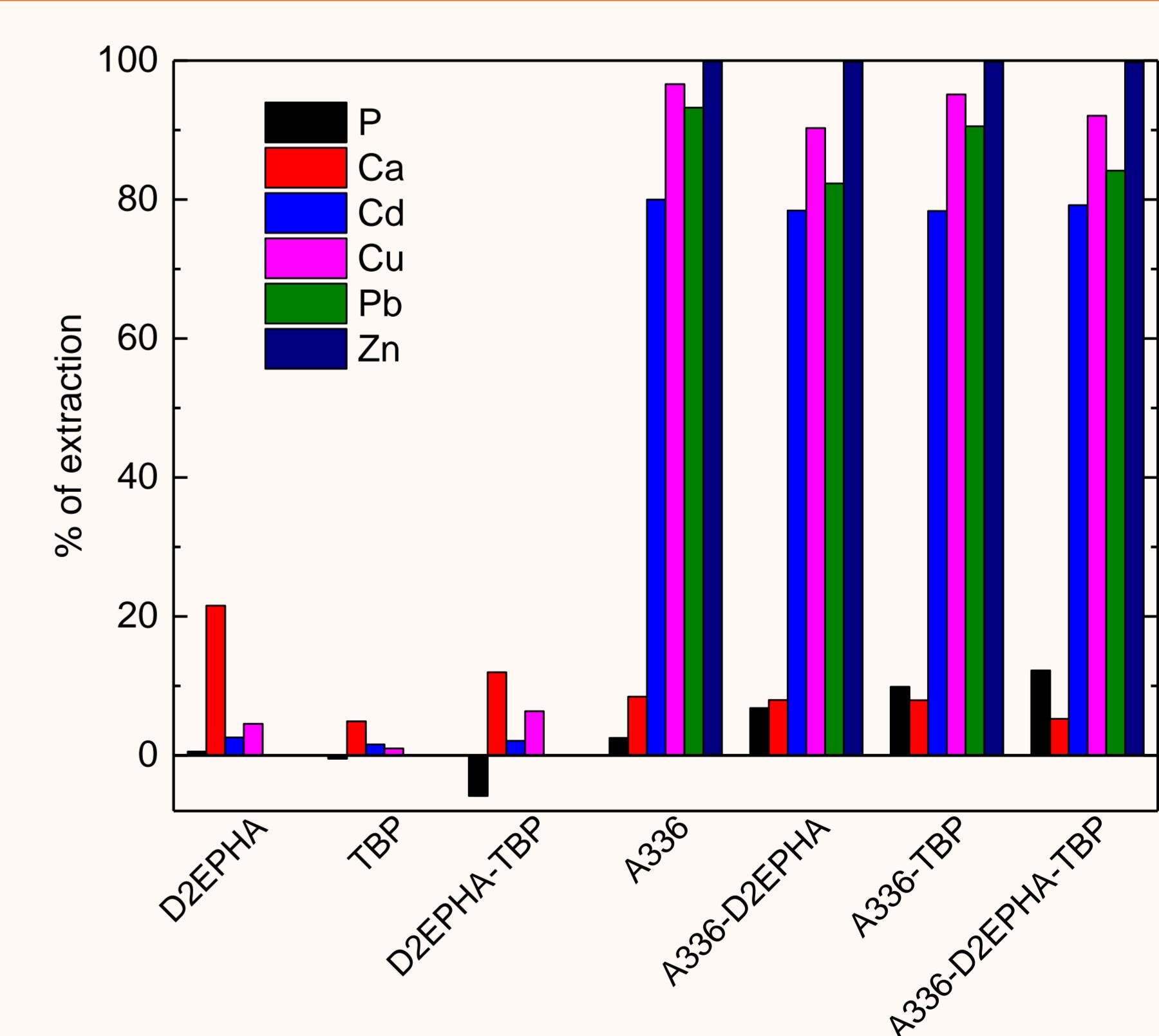


Figure 6. reactive extraction using different extractants from HCl leach liquor (pH of aqueous phase = 0.7)

## 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.

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