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PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE ASHES BY WET CHEMICAL EXTRACTION: A FOCUS ON THE PRECIPITATION STEP

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Acknowledgements

Abstract

Phosphorus is a vital substance in human life, being a fundamental element for the formulation of fertilizers in agriculture. Unfortunately, it faces progressive shortage nowadays, and like other non-renewable sources, this element will sooner or later be depleted. Extracting phosphorus from waste streams that contain phosphorus can be a good alternative, especially sewage sludge ashes (SSA) which have a high amount of phosphorus (around 8%). For this reason, this study focused on the recovery of phosphorus from SSA. The wet chemical leaching method was used in this work because of its simplicity, good recovery rate, feasibility, and applicability at large scale. In detail, this work describes laboratory experiments aimed at investigating the capacity of combined acid leaching and subsequent precipitation to recover phosphorus as a plant available fertilizer from SSA. Four samples from an incinerator near Milan were collected and leached by sulfuric acid under optimal operating conditions (0.1M H_2SO_4, liquid-to-solid ratio of 20, reaction time of 2 hours). In the precipitation step, some preliminary tests were performed by NaOH to determine samples behaviour at different pH and rest time. pH 2.5, 3.5, 5, 8, and 2 hours as rest time were set as operating conditions for main precipitation experiments. In these tests, NaOH, $Ca(OH)_2$, and KOH were used to precipitate materials to investigate pH and reagent conditions resulting in high phosphorus extraction and low heavy metal contamination. Finally, high enriched phosphorus product was obtained (mean value of 16%) but heavy metals in the recovered material were beyond the European limits for content in fertilizer, indicating the need for pre-treatments or purification processes.

Keywords: sewage sludge ashes, phosphorus recovery, wet chemical extraction; acid leaching, precipitation, heavy metals, fertilizer, circular economy

Sommario

Il fosforo è una sostanza vitale per gli esseri umani ed è un elemento fondamentale per la formulazione di fertilizzanti in agricoltura. Attualmente, le riserve minerarie si stanno progressivamente riducendo e, come altre fonti non rinnovabili, questo elemento è destinato all'esaurimento. L'estrazione del fosforo dai flussi di rifiuti che contengono fosforo può essere una buona alternativa. In particolare, le ceneri derivanti dall'incenerimento dei fanghi di depurazione contengono un'elevata quantità di fosforo (pari circa all'8%). Per questo motivo, questo studio si è concentrato sul recupero del fosforo da tali ceneri. Un'alternativa valida è rappresentata dal processo di lisciviazione chimica ad umido per via della semplicità, del buon tasso di recupero, della fattibilità e dell'applicabilità su larga scala. Le attività sperimentali sono state indirizzate a studiare la capacità di estrazione mediante tale processo, finalizzata al recupero del fosforo come fertilizzante, con particolare interesse per la fase di precipitazione. Il processo di lisciviazione è stato applicato a quattro campioni provenienti da un inceneritore nell'area di Milano, utilizzando condizioni ottimali secondo la letteratura, ovvero 0,1 M H_2SO_4, rapporto liquido-solido di 20 e tempo di interazione di 2 ore. Nella fase di precipitazione, alcuni test preliminari sono stati eseguiti con NaOH per determinare il comportamento dei campioni a diversi pH e tempi di riposo. Successivamente, un piano sperimentale più ampio è stato condotto a pH 2,5, 3,5, 5, 8 e 2 ore come tempo di riposo. Come agenti precipitanti sono stati utilizzati NaOH, $Ca(OH)_2$ e KOH. In questo modo, si sono indagati l'efficienza di recupero di fosforo e il contenuto di metalli pesanti. La sperimentazione ha permesso di ottenere un prodotto ad alto tenore di fosforo (valore medio del 16%) ma i metalli pesanti nel materiale recuperato si sono rivelati oltre i limiti europei per il contenuto di queste sostanze nei fertilizzanti, cosicché si è mostrata la necessità di pre-trattamenti o altri processi di purificazione.

Parole chiave: ceneri da fanghi di depurazione, recupero del fosforo, estrazione chimica a umido; lisciviazione acida, precipitazione, metalli pesanti, fertilizzanti, economia circolare

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List of abbreviations

BA	Bottom Ash
CED	Cumulative Energy Demand
CF	CO_2 Footprint
CYC	CYClone ash
DAP	DiAmmonium Phosphate
DCP	DiCalcium Phosphate
DIO	DIOnized
EBPR	Enhanced Biological P Removal
EDTA	Ethylene Diamine Tetra Acetic acid
EE	Embodied Energy
ESCAPE	Evaluation of Sustainability of material substitution using CArbon footPrint by a simplified approach
HM	Heavy Metal
ISSASSA	Incinerated Sewage Sludge Ash
MAP	Magnesium Ammonium Phosphate
MSWI	Municipal Solid Waste Incinerators
P	Phosphorus
PEE	Phosphorus Extraction Efficiency
PolyP	PolyPhosphate
PR	Phosphorus Rock
SS	Sewage Sludge
SSA	Sewage Sludge Ash
SSP	Single SuperPhosphate
UP	Ultra Pure

1   Introduction

Phosphorus (P) is widely used in anthropic activities, but its primary application is in the agricultural industry as fertilizer. Humans use phosphorus in chemical forms to produce fertilizer, mostly single superphosphate (SSP), diammonium phosphate (DAP), dicalcium phosphate (DCP), and magnesium ammonium phosphate (MAP) (Li et al., 2019).

As the population grows, the need for food increases, and as a result, the need for phosphorus increases. Therefore, since phosphorus is a non-renewable substance, it is evident that only its extraction is not the right solution. It is necessary to find sustainable and environmentally friendly methods to reuse this valuable substance in the cycle (Szogi & Vanotti, 2009).

For this purpose, the use of various technologies for phosphorus recovery from the waste stream has been considered. Among them, recovery from sewage waste seems a valuable alternative because this stream is produced in large quantities and collected systematically, and contains an appropriate amount of P (Udaeta et al., 2018). Moreover, excess P in wastewater causes environmental problems like algal blooms and eutrophication of ponds and lakes (Vanotti et al., 2003). The European Water Framework Directive in 2000/60/EC set the maximum allowable amount of phosphorus at 0.15 mg_P/dm^3 (European Commission, 2000), so it is necessary to remove P before releasing wastewater in nature.

In this work, the focus is on P recovery from SSA (sewage sludge ash) because, this process is more economical, and it is characterized by a higher recovery rate; by incineration, this process reduces sludge volume and sanitizes it. Moreover, disposal of SSA and wasting P can cause environmental problems like leakage of leachate and groundwater contamination (Mitrano et al., 2017). Among all technology, wet-chemical extraction is interesting because of the lower energy consumption; it is cheaper to set up, operate, and has a greater capacity for large-scale use (Fang et al., 2020). In the wet method, at first, SSA is leached by an acid (like sulfuric acid or hydrochloric acid) then the solid and liquid phases are separated (usually by centrifuge, filtration, or both). Solid-phase usually goes for disposal. P-rich liquid after purification (like ion exchange column) goes for the final step, which produces sulfuric acid or other phosphorus products like calcium phosphate, which can be used as fertilizer (Donatello et al., 2010; Franz, 2008).

The goal of this work is to investigate the potential of extraction of P from SSA by the wet chemical extraction process and different methods for precipitation of recovered P to obtain a product that is plant available and has low impurities. Chapter 2 summarizes studies and research on P recovery from wastewater, including a review of different technologies for P recovery. Chapter 3 details the methods used in the experimental activity. Chapter 4 shows the experimental results, discusses them, and examines the process strengths and weaknesses, providing suggestions to solve existing issues.

2   State of the art

P is a non-renewable resource and plays an important role in human life, especially in agriculture, since it is an essential element for crop growth (Cordell et al., 2009). Humans use P in different fields. Around 80% of P is used in fertilizers (Van Vuuren et al., 2010) and approximately 12% in detergents and animal feed. However, due to its overexploitation, it has been estimated to be depleted in about 60 to 90 years (Cordell et al., 2009). Up to now, almost 30 countries have consumed their P mine. So, it is crucial to find a way to solve the P depletion problem. Besides, phosphorus minerals are not evenly distributed throughout the world, as 66% of phosphate rocks are in China, United States, Morocco, and Western Sahara (Jasinski, 2010). The major P users are the US, China, India, and less developed countries with a high population in Asia and Latin America, which contain almost 70% of the world population (FAO, 2015). So those countries that do not have enough resources need to import P, which, besides cost due to import and environmental problems because of transportation, somehow put their food security at risk because importing is not a long-term solution and there is always the possibility that exporter countries stop exporting.

Also, by population growth, P demand increases and, as a result, this exacerbates the P deficiency crisis (Reijnders, 2014; Van Vuuren et al., 2010). After some time of extraction from a specific source, the extraction cost increases. But on the other hand, due to the reduction of available phosphorus, this mineral price has increased. As the price increases, it makes the use of abandoned mines economically justifiable again. So scientists estimate a new time for P crises, which is around 300 years (Van Vuuren et al., 2010). But research shows that, as humans mine more, the quality of phosphorus rock (PR) decreases and contains more undesirable contaminants like (radioactive) heavy metals (HM) such as Cd, U, and Tl (Kratz et al., 2016). These contaminants in PR are a problem because there are limitations in using HM in soil. European countries have strict laws restricting the presence of heavy metals in fertilizers. For this reason, energy demand for mining and processing of P will increase and, in the not too distant future, the price of fertilizer will increase (EC, 2003). Moreover, as mentioned before, only a few countries have enough P sources; others need to import it and cause an unstable P price (World Bank, 2016).

The next issue is that extracting phosphoric acid from PR has adverse environmental effects; the most important one is phosphogypsum. It is composed chiefly of gypsum, containing high amounts of P, but even high levels of HM and other impurities such as fluorides, sulfates, and naturally occurring radionuclides such as radium, uranium, and thorium (Greenpeace, 2013). According to what was mentioned before, the European Commission listed P as a critical raw material (EC, 2014). Nowadays, the need for alternative supply of phosphorus is a priority of many countries.

Unfortunately, the efficiency of using phosphorus is not 100%, and humans are losing this precious element. Only around 20-25% of P consumed in agriculture is received by humans, and the other fraction is dissipated (Scholz & Wellmer, 2013). During mining and refining, up to 30-40% of P is lost. Globally only 50% of waste comes back to agriculture. P losses due to drainage and erosion were measured around 46% of the mined PR (Gorazda et al., 2013). Also, a large amount of P is lost from animal wastes and food wastes because of poor waste management (collection and processing). Various waste streams contain P and need to be treated before since they cause environmental problems if they are without treatment. For example, increasing phosphate concentration in surface water causes environmental problem like eutrophication (Schröder et al., 2011). Among all waste streams, the P amount in sewage is beyond all of them, and most of the population has been connected to the sewage system in all developed countries, and almost 95% of P is concentrated in sewage sludge (Krüger & Adam, 2014).

For these reasons, wastewater biological and chemical treatments are performed to respect regulations on phosphorus discharge, and these treatments generate sewage sludge that contain high amount of P in cellular matter or as an insoluble phosphate which is a good alternative for natural phosphate rock. Due to predicted P depletion, P recovery from sewage sludge has become more attractive in the last decades (Przewrocki et al., 2004). In central Europe, statistics show that municipal wastewater can cover around 50% of agricultural P needs (Zoboli et al., 2016). But it is impossible to use sewage sludge directly in agriculture because it contains HM, organic micropollutants, and pathogens (Ott & Rechberger, 2012).

There are several methods for P recovery such as electro-kinetic (Sturm et al., 2010), bioleaching and accumulation (Zimmermann & Dott, 2009), thermo-chemical (Adam et al., 2009), wet chemical methods, such as acid leaching (Biswas et al., 2009). The wet process is more economical and energy-efficient than the other process (Weng & Baptista, 1998; Pang, 2003). Other techniques have poor performance or an extended processing time needed. For example, the electro-kinetic process obtained a recovery of less than 1%, bioleaching and bioaccumulation need 11 days to complete, so they are not rational for industrial scale. On the other hand, the process of acid dissolution–alkali precipitation could achieve a 92% yield (Kaikake et al., 2009). Also, acid leaching of ashes from co-combustion of sewage sludge and wood has 50–80% yield (Pettersson et al., 2008). Another suitable method is two-step acid-base leaching of the incinerated sewage sludge ash (SSA), which has a recovery rate of 60–80% (Fang et al., 2020; Levlin et al., 2005; Petzet et al., 2011). P recovery from sewage as magnesium ammonium phosphate (struvite) has drawn a great deal of interest (Li et al., 1999; Suzuki et al., 2005). Many existing P industries try to use it instead of raw PR to produce phosphoric acid, mineral fertilizers, and even P in its purest type (P4) (Egle et al., 2016). Incineration of the sewage sludge transforms all P into an inorganic form and recovers energy (Gorazda et al.,

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2017) and reduces the sludge volume by around 80-90%, and sanitizes it (Donatello & Cheeseman, 2013; Kleemann et al., 2017). Also, SSA contains macronutrients like P, Mg, K, which are crucial for plants (Tan & Lagerkvist, 2011). From the economic point, the cost of recovered P fertilizer is 4-10 €/kg$_P$, which is higher than conventional fertilizer (1,6 €/kg$_P$). Still, the annual cost per population equivalent is less than 3% of all wastewater treatment costs (Ohtake et al., 2019).

2.1 Sewage sludge (SS)

Biological wastewater treatment produces sludge that contains a large amount of phosphorus and other elements like N, Ca, Mg, and K, also HM (Kupper, 2000), and even pathogens (Sahlström et al., 2004). Instead of disposal of this sewage sludge, it can be used for nutrient recovery. There are several ways to extract P from sewage sludge (SS), shown in Figure 1, and appendix B indicates them in detail. Below, wet-chemical and thermal treatment are explained briefly.
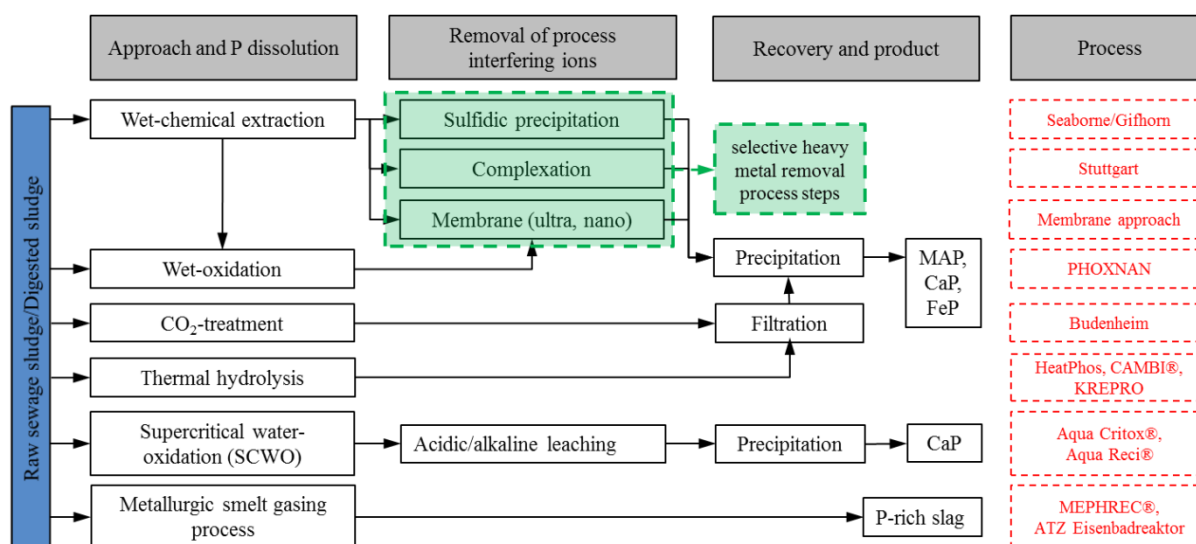
Figure 1 – Different P approach from SS (Egle et al., 2016).

2.1.1 Wet-chemical

Wet-chemical is for extraction of phosphorus from sludge through leaching process as well as minimal extraction of contaminants from it. This method is based on changing the pH to extracting desirable materials. In this approach, pH is reduced by an acid. At pH lower than two, around 80% of P dissolve simultaneously with undesired material (Seaborne/Gifhorn method (Esemen, 2013),

Stuttgart method (Antakyali et al., 2011)). If the pH is increased, the amount of undesirable substances decreases. However, this action reduces the extraction of phosphorus (30-75%).

Table 1 shows the amount of acid needed for reaching different pH. Data were collected from four different sources. Among those data, the maximum, minimum, and mean amount of acid required to reach the desired pH are given in the table. It shows that the P extraction efficiency (PEE) increases by decreasing the pH. In figures 2, PEE at various pH is reported and indicates that by reducing pH, PEE increases (data are collected from three different experiments). Figure 3 displays the range of elements extracted at pH 2 and demonstrates that in addition to phosphorus, other elements are extracted as well in large quantities; for instance, Fe extracted even more than P.

Table 1 - H_2SO_4 (98%) demand [kg kg^{-1}$_{TS}$] for various pH and P extraction efficiency in wet-chemical treatment of SS (Bouda et al., 2009; Esemen, 2013; Günther, 2011; Weidelener, 2010).

pH	Mean	Min	Max	P extraction %
1.5	0.55	0.45	0.65	> 90
2	0.5	0.36	0.59	75-90
3	0.35	0.23	0.39	50-75
4	0.27	0.2	0.34	30-55
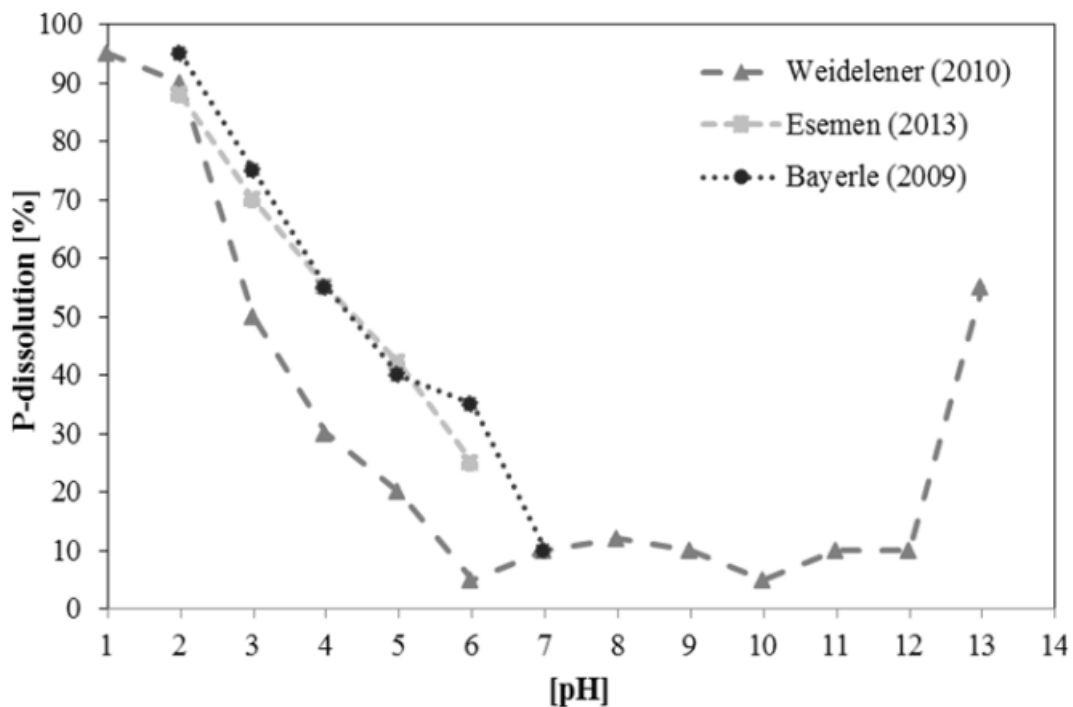
Figure 2 - P extraction from digested sludge in different pH.
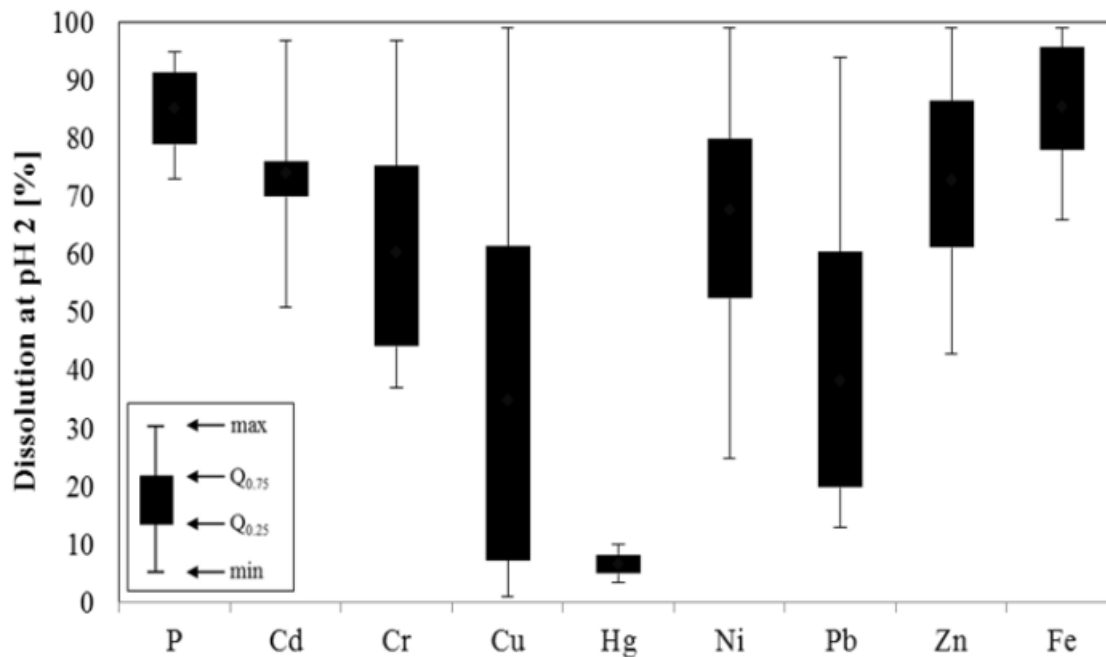
Figure 3 - Dissolution of different element at pH 2 - (first (Q0.25) and third quartile (Q0.75) and minimum (min)/maximum (max)) (Bayerle, 2009; Bouda et al., 2009; Günther, 2011; Naoum et al., 2001; Weidelener, 2010).

2.1.2 Thermal treatment

Thermal treatment is the technological solution under which solid materials like sediment, soil, or sludge are heated for improved mobility and organic pollutants extraction. For example, in EUPHORE, at first, reagents like alkaline (KCl) or alkaline chlorides ($MgCl_2$) or sulfates will be added to SS to cause heavy metal depletion and improve P solubility. SS is heated and dewatered in the second step, then moved to the reductive zone in the rotary kiln (pyrolysis step). Then in the reductive zone at a temperature higher than 650°C (anoxic process), metals are reduced and volatilized as chlorides gas to the atmosphere, and this gas is followed by a flue gas cleaning system. Finally, in the oxidation reactor with a temperature above 900°C (combustion stage, oxic process), materials sublime into phosphates. Because of the process's abrupt transition from reductive to oxidative situation, which coincides with high temperatures, the phosphate compounds in the ashes are extended and have a higher plant availability. As the final product is purified and has good plant availability can be used directly as a fertilizer (Kabbe et al., 2019).

2.2 Sewage sludge ash (SSA)

As mentioned, P recovery from SSA is more favourable because, with the incinerators, the sludge volume can be reduced by about 80-90%. In addition to reducing the volume and reducing the cost of disposal, this process also extracts energy and eliminates pathogens and toxic compounds in SS (Donatello & Cheeseman, 2013; Kleemann et al., 2017). The use of incinerators also increases phosphorus concentration in the ash by about five times (P concentration is about 8%, roughly the same concentration as low-grade PR) (Cieślik & Konieczka, 2017). In theory, this ash can be considered as a source for phosphorus extraction and an alternative source to reduce extraction from natural resources and help the environment, as well as reduce the economic impact of phosphorus extraction from its ore (Pasquali et al., 2018).

In incinerators, the temperature reaches about 800-900 °C. This temperature causes organic pollutants oxidation (DENG et al., 2009). 99.9% of the sewage sludge is collected in SSA. P and HM, except mercury, which has a low boiling point, transfer in SSA (Lederer & Rechberger, 2010). P in SSA is usually in a low soluble form. Besides, aluminium phosphate ($AlPO_4$) and iron phosphate ($FePO_4$) are usually present due to wastewater treatment. So P in SSA has low water solubility and low plant availability (Maier et al., 2007). These characteristics are comparable to those of unprocessed phosphate rock (PR). The P content of SSA varies between 50 and 100 g kg^{-1}_{TS}. On the other hand, raw phosphates from North Africa and Asia have a standard P concentration of 130-40 gP kg^{-1}_{ore} (IFDC, 2010). Mixing sewage sludge with other wastes should be avoided if it leads to a decrease in P concentration because it will increase the cost of recovery (Egle et al., 2014). The fluidized bed reactor is the favoured incineration technology for this purpose because it creates powdery ash and consequently simplifying subsequent process operations (Donatello et al., 2010). In Figure 4, different technologies for recovery from SSA are shown. Here, the most interesting ones are described, which are wet-chemical extraction and wet-chemical leaching.
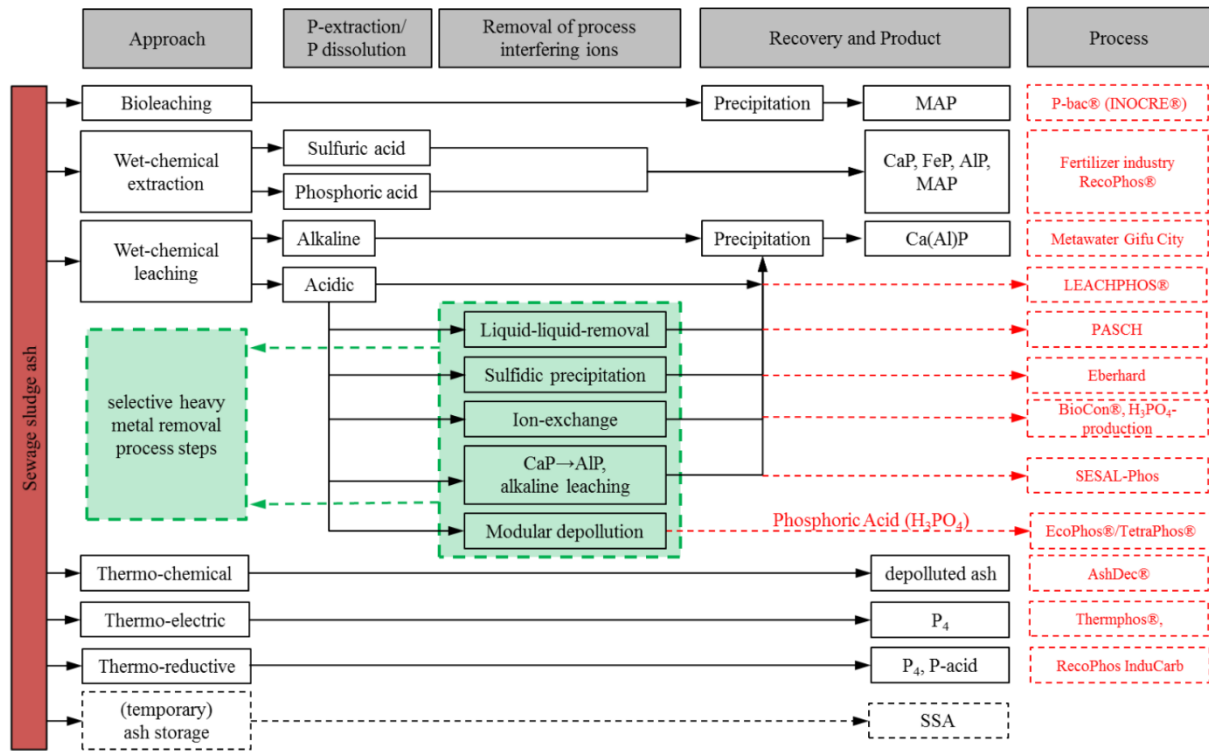
Figure 4 - Different P approach from SSA (Egle et al., 2016).

2.2.1 Wet-chemical extraction

This process converts water-insoluble phosphorus to water-soluble and plant available phosphorus. This process usually uses raw PR in fertilizer industries to produce fertilizers. By adding H_2SO_4 to natural PR, single superphosphate (SSP) is produced. Process characteristic reaction is reported in Equation 1. The amount of acid required in this process is 0.38–0.4 kg kg^{-1}_{ore} (Da Silva & Kulay, 2005).
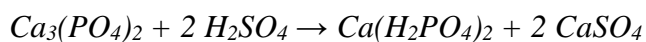
$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2\ CaSO_4 \qquad \text{Equation 1}$$

In the ICL Fertilizers (Israel Chemicals Ltd) process, it became clear that the same procedure can increase P availability from SSA (Ten Wolde, 2013). Aluminium-containing ashes are more soluble in water than iron-containing ashes. Moreover, Fe-rich ash has a sticky quality that makes subsequent treatment actions, including granulation and drying, complicated (Petzet, Cornel, 2011). To achieve a product with a higher P concentration, phosphoric acid (~52% H_3PO_4) is added to the SSA in a rotary kiln. The final product is something like triple superphosphate (RecoPhos process (Bohndick, 2012)). The process of producing calcium or magnesium phosphate is based on equation 2.

$$Ca_4Mg_5(PO_4)_6 + 12\ H_3PO_4 + 2\ H_2O \rightarrow 4\ Ca(H_2PO_4)_2 + 5\ Mg(H_2PO_4)_2 + 12\ H_2O \qquad \text{Equation 2}$$

Because of the lack of decontamination in wet-chemical extraction, all heavy metals were added to the final product, making it only suitable for fertilizer grade ashes (Weigand et al., 2013).

2.2.2 Wet-chemical leaching

Phosphorous from waste sludge ashes may be recovered by the wet chemical method by acid or base. The acid and liquid to solid (L/S) ratios are the key parameters that affect the leaching output. Also, solid particle size (surface area) is an essential factor because more surface area provides more contact with reagents. For this reason, the smaller particles have higher extraction efficiency (Donatello et al., 2010).

In this method, by changing the pH, the phosphorus bonds are broken and become soluble. By changing their pH by acid (H_2SO_4 or HCl) or base (NaOH), around 90% of phosphorus can be dissolved (Schaum et al., 2007). After leaching, the liquid part is separated and precipitate P from the liquid phase. Both alkaline and acid leaching are explained below.

2.2.2.1 Alkaline leaching

In this method, at a temperature of 50-90 °C, a strong base (NaOH or KOH) is added to the ash. By this work, about 60-70% is dissolved. Since HM are usually insoluble in bases, there is no need for HM purification. Then, liquid and solid phases are separated. In the next step, calcium hydroxide ($Ca(OH)_2$) is added to the P-rich leachate (the Ca:P molar ratio is 1.5:1). Almost all dissolved P precipitates as CaP. The existing supernatant can be reused in the leaching step. The rest of the solids after neutralization by acid can be used in the construction industry (LOTUS, 2007).

2.2.2.2 Acidic leaching

In this method, by using an acid, pH falls below 2. In 0.5-2 hours, about 90% of the P in the SSA is dissolved. After separating the liquid phase from the solid phase, both parts go for further treatment because the solid phase is acidic and needs to be neutralized before disposal. Also, the liquid phase contains undesired material (Al, Fe, HM). the amount of each element extraction in different pH and pH 2 in detail are shown in Figures 5 and 6 (Herr et al., 2013).

Figure 5 indicates the dissolution of different elements in various pH and shows that by increasing the pH in addition to phosphorus, other undesirable metals also dissolve. Figure 6 displays the range of elements extracted at pH 2.
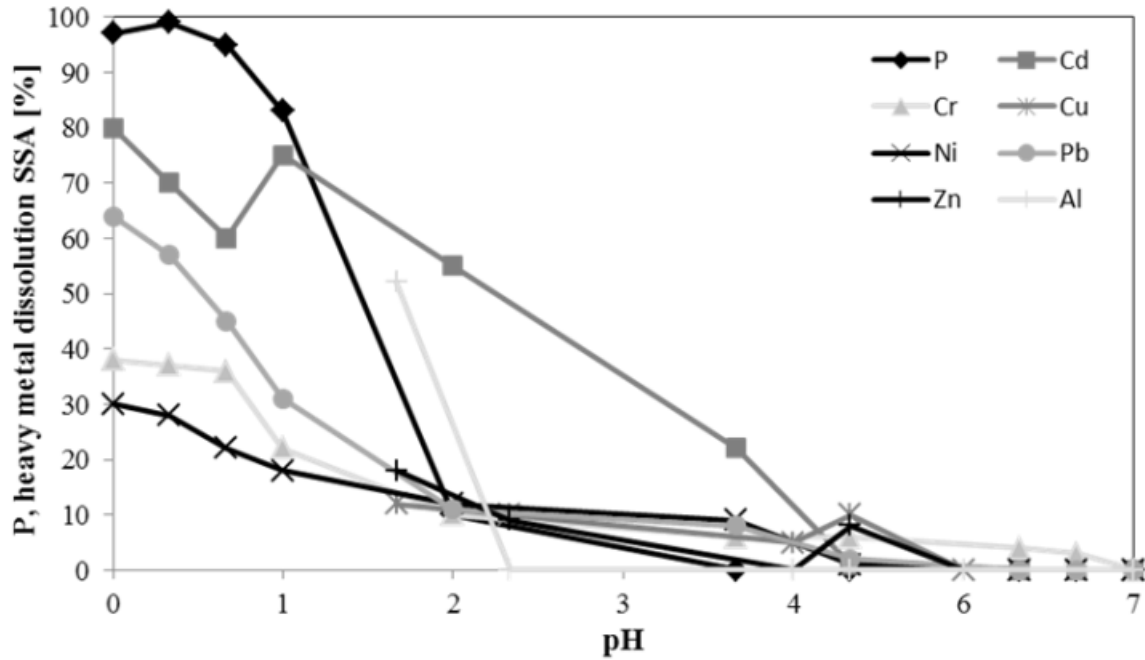
Figure 5 - The dissolution of selected elements from SSA at different pH levels (Herr et al., 2013).
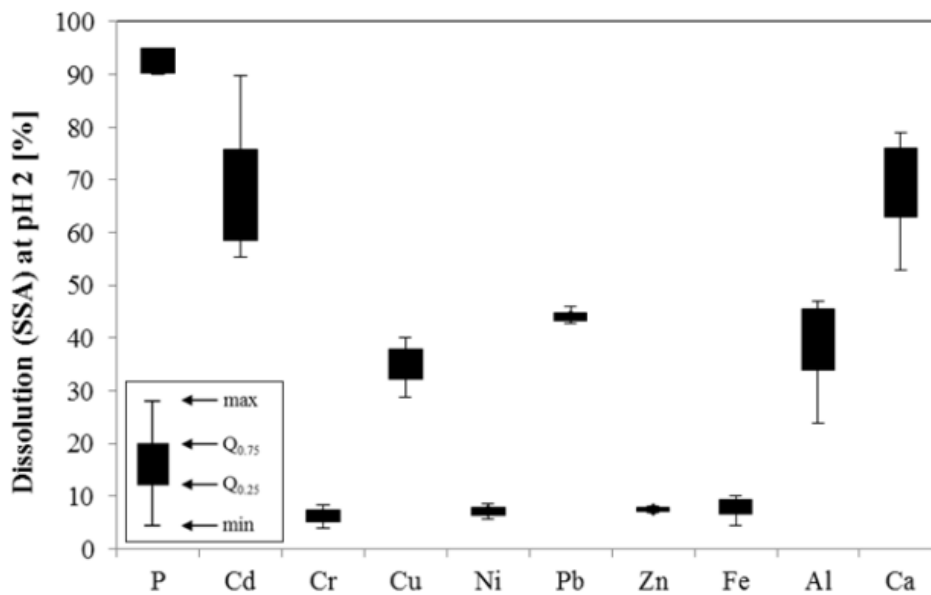
Figure 6 - Dissolution of different element in pH 2 - (first (Q0.25) and third quartile (Q0.75) and minimum (min)/maximum (max)) (Montag et al., 2011).

2.3 Choosing the most promising technology

The methodology is based on (Fahimi et al., 2021) works on a simplistic SUB-RAW index quantifying recovery technologies' sustainability relative to mining PR. There are two parameters in the SUB-RAW index, CO_2 footprint" (CF) and the "embodied energy" (EE). CF is expressed as CO_2 equivalent, which is an indicator of environmental influence and covers the corresponding greenhouse gas mass emitted into the air from the processing of 1 kg of material and calculated in kg_{CO_2} and EE is related to energy consumption. The EE indicates the energy required for the production of 1 kg of material. With SUB-RAW index, phosphorus recovery technologies can be compared with phosphorus extraction from PR (Bontempi, 2017). They may be normalized to an arbitrarily defined comparison framework and here normalized to 1 kg of P produced (kg_P).

ESCAPE (Evaluation of Sustainability of material substitution using CArbon footPrint by a simplified approach) is an approach suggested by Bontempi. It is based on the SUB-RAW index and evaluates the environmental impact of waste or by-products when are used instead of natural resources.

In many databases, EE and CF of the reagents used in P extraction technologies have been published. In this work CES Selector 2019 (Granta Design, 2019) (database: commercial Ecoinvent v. 2.2) and openLCA (GreenDelta, 2006) (database: free Ecoinvent v. 3.3) were used. Fahimi used Eco Audit Tool" of the CES Selector 2019 to calculate EE and CF for the overall power consumption of operation (Defined in Watts, W) for devices or heating. Then for every phase of the desired technology, EE and CF parameters were assessed, and the SUB-RAW index was determined by equation 3.

$$SUB-RAW\ index = \left[log(EE_{RAW}) - log(EE_{SUB}) + log(CF_{RAW}) - log(CF_{SUB}) \right]/2 \qquad \text{Equation 3}$$

EE_{RAW} (MJ/kg_P) and CF_{RAW} (kg_{CO_2}/kg_P) are for reference procedure that is P extraction from PR while EE_{SUB} (MJ/kg_P) and CF_{SUB} (kg_{CO_2}/kg_P) are for substituted procedure that is P extraction from SSA. From the equation can get SUB-RAW index is unitless and determine the level of sustainability of a substituted process. If it is positive, the recovery process is more sustainable than P-extraction from the PR.

The logarithm in the equation makes it possible for a straightforward and easy analysis by taking an average of the environmental effects and energy consumption. Table 2 indicates different technologies for P recovery from SSA. Class (a) technologies are those that the data for the method assessment was given in detail. For class (b), technologies, the required data on reagents input mass

flow, EE, and CF of reagents or power usage of electrical components are only partially available. For class (c) technologies, most of the data that is needed are missing.

Table 2 - Overview of P recovery technologies from SSA (Fahimi et al., 2021).

Nr.	Technology	Country initiative	Scale	Approach	Reference
1	AshDec[a]	Germany/Switzerland	Pilot	Thermo-chemical	Hermann and Schaaf (2018)
2	LeachPhos[a]	Switzerland	Pilot	Wet chemical leaching	Morf (2012)
3	Pasch[a]	Germany	Laboratory	Wet chemical leaching	Montag et al. (2009)
4	Recophos[a]	Germany	Full	Wet chemical leaching	Montag et al. (2015)
5	Recophos Inducarb[a]	Germany	Pilot	Thermo-reductive	Langeveld (2018)
6	ICL Fertilizers[a]	The Netherlands	Full	Wet chemical leaching	Ten Wolde (2013)
7	EcoPhos[b]	France	Full	Wet chemical leaching	De Ruiter (2014)
8	ThermPhos[a]	Kazakhstan	Industrial	Thermo-electric	Schipper et al. (2001)
9	Sephos[b]	Germany	Laboratory	Wet chemical leaching	Schaum et al. (2007)
10	BioCon[a]	Sweden	Laboratory	Wet chemical leaching	Levlin (2007)
11	LotusProject[a]	Japan	Full	Wet chemical leaching	Nakagawa and Ohta (2018)
12	Inocre P-Bac[c]	Japan	Pilot	Bio-leaching	Chi et al. (2006)
13	ED cell[c]	Denmark/Portugal	Laboratory	Electro-chemical leaching	Guedes et al. (2014)
14, 15	Takahashi et al. (2 runs)[b]	Japan	Laboratory	Wet chemical leaching	Takahashi et al. (2001)
16, 17	Eberhard (2 runs)[b]	Switzerland	Laboratory	Wet chemical leaching	Franz (2008)
18	Donatello et al.[c]	United Kingdom	Pilot	Wet chemical leaching	Donatello et al. (2010)
19, 20	Biswas et al. (2 runs)[c]	Japan	Laboratory	Wet chemical leaching	Biswas et al. (2009)
21	SesalPhos[c]	Germany	Laboratory	Wet chemical leaching	Petzet et al. (2011)
22	Wzorek et al.[c]	Czech Republic	Laboratory	Thermo-chemical	Wzorek et al. (2006)
23, 24	Stark et al. (2 runs)[b]	Sweden	Laboratory	Wet chemical leaching	Stark et al. (2006)
25, 26, 27	Mattenberger et al. (3 runs)[c]	Austria	Pilot	Thermo-chemical	Mattenberger et al. (2008)
28, 29	Vogel et al. (2 runs)[c]	Germany	Laboratory	Thermo-chemical	Vogel et al. (2010)
30, 31	Stemann et al. (2 runs)[c]	Germany	Laboratory	Thermo-chemical	Stemann et al. (2015)
32	PolFerAsh[b]	Poland	Laboratory	Wet chemical leaching	Gorazda et al. (2017)
33	Liang et al.[c]	China	Laboratory	Wet chemical leaching	Liang et al. (2019)
34	Greb et al.[c]	Germany	Laboratory	Wet chemical leaching/Thermo-chemical	Greb et al. (2016)
35	Wang et al.[c]	China	Laboratory	Wet chemical leaching	Wang et al. (2018)
36	Fang et al.[c]	China	Laboratory	Wet chemical leaching	Fang et al. (2018)
37, 38	Kalmykova (2 runs)[c]	Sweden	Laboratory	Wet chemical leaching	Kalmykova and Karlfeldt Fedje (2013)

P extraction by sulfuric acid from PR was considered as the reference technology. Figure 7 displays the position of technologies for P recovery calculated by the ESCAPE method. Numbers are the same numbers used in Table 2, as an example number 1 indicates the AshDeck process in both Table 2 and Figure 7. The reference process is named with "RAW" based on (Hutchins, 1993) works. The colors roughly show that the sustainability of the technologies in comparison to the reference process. The more the process is in the green area, the more sustainable it is, and the red zone is the reverse. As the estimation of reference technology includes the uncertainty of reagents gathered from the Ecoinvent database, a white area appears in the graph.

Some processes are not indicated in Figure 7 because their SUB-RAW index results were out of the graph range.
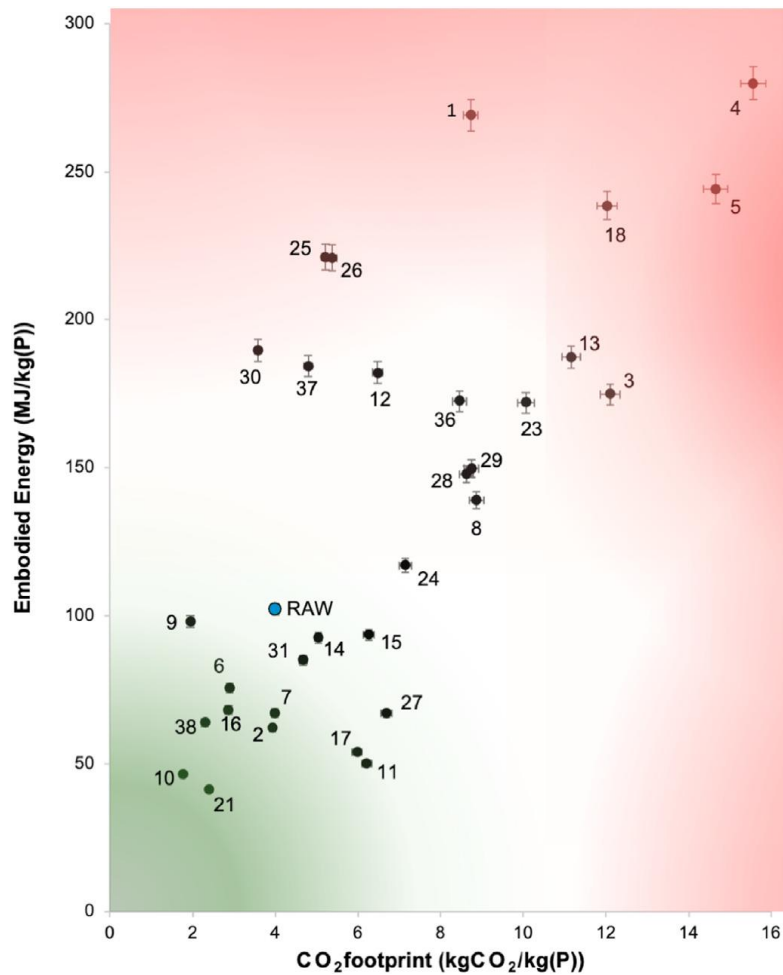
Figure 7 - EE and CF for all the P-recovery technologies reported in Table 2.

As an example, the procedure for Lutos method presents here. The Lotus Project, which is currently in progress in Gifu city in Japan, is a full-scale method for recovering P from SSA. The plant produces 200 tons of P recovered as hydroxyapatite per year. The P-extraction method is based on the wet alkaline-leaching technique, which is achieved by applying sodium hydroxide to SSA. NaOH (4%) is used as the reagent, and the ratio is 0.121 kg_{acid}/kg_{ash}, and the process temperature is 50-70 °C for 1.5 h. Then, a membrane is used to extract the leachate, and sulfuric acid is used to wash solid residues (H_2SO_4(98%), 0.04 kg_{acid}/kg_{ash} for 5-30 min at 50-70 °C). In the next stage, by applying hydrated lime ($Ca(OH)_2$, 0.431 kg_{acid}/kg_{ash} at 20-50 °C for 9 h, the leachate that is containing $AlPO_4$ precipitates as hydroxyapatite. The precipitated hydroxyapatite is eventually washed with water (3 kg_{water}/kg_{ash}) (Egle et al., 2016), filtrated, dried, and pelletized, and return the remaining liquid to the leaching reactor. This return does not take into account in the evaluation because the author considered uni-direction flow.

The overall electricity necessary for the process is 36 kW. This value was entered into the Eco Audit Tool to gain a yearly value for each pollution parameter. Then according to yearly mass flow, EE and CF calculated which are 0.8 MJ/ kg_{ash} and 0.07 kg_{CO2}/ kg_{ash}. the calculation was performed for sodium

hydroxide, sulfuric acid, hydrated lime, and water and finally got 4.23 MJ/kg_{ash} and 0.52 kg_{CO_2}/ kg_{ash} for EE and CF, respectively. for converting kg_{ash} to kg_P the author considers 8.45% of P in SSA, so EE_{SUB} = 50.13 MJ/ kg_P and CF_{SUB} = 6.21 kg_{CO_2}/ kg_P. By considering EE_{RAW} = 102.32 MJ/kg_P, CF_{RAW} = 4 kg_{CO_2}/ kg_P (Hutchins, 1993).

From technologies that are in class, (a) Leachphos, Biocon, Lotus Project, and ICL Fertilizers were more sustainable. The ICL Fertilizers process is close to the reference process, but instead of phosphate rocks, it uses SSA as raw material. Among class (b) processes, Sephos is in the green area but close to the reference technology. Besides that Sephos final product is not appropriate for agriculture due to high aluminum content further process is needed, which may cause that Sephos moves from the green area to the red area.

3   Material and methods

This study is aimed to investigate phosphorus recovery efficiency from sewage sludge ash by wet chemical extraction, maximizing P extraction while minimizing HM extraction.

Four separate sewage sludge ash samples were obtained from a grate furnace pilot plant near Milan (San Giuliano Ovest), which treats 150 kg of dried and pelletized sludge every hour. The samples were examined for ash characterization, particle size, and elemental composition with ICP-MS (inductively coupled plasma mass spectrometry). The first step of the recovery process consists in SSA leaching with acid for 2 hours. Then, the liquid and solid phases are separated, and with the help of a base, phosphorus is precipitated in plant-available form with the minimal amount of HM. All experiments were performed in the Department of Civil and Environmental Engineering at Politecnico di Milano. Table 3 indicates the chemicals used in this work with their formula and assay.

Table 3 – Chemicals used.

Chemical	Formula	Assay
Sulfuric acid	H_2SO_4	96%
Calcium hydroxide	$Ca(OH)_2$	$\geq 95\%$
Sodium hydroxide	$NaOH$	$\geq 95\%$
Potassium hydroxide	KOH	$\geq 95\%$

3.1   Sample preparation

Four separate sewage sludge ash samples were received. On any of the two trial campaigns, 2 kg of bottom ash (BA) and 2 kg of cyclone ash (CYC) were sampled and kept at room temperature in PET bottles (the first campaign was carried out from July 31st to August 8th, and the second campaign from October 24th to October 30th). During the campaigns, the pilot furnace was run continuously (24 h per day). The collected samples were the average of several sampling done during the week of work.

To assess the degree of burnout obtained during the process, samples were incinerated at 900 °C for 2 h in a typical muffle furnace (Model: Nabertherm LT 9/12/SKM). The samples were examined for ash characterization, particle size, and elemental composition with ICP-MS. BA was in pellet form (about 6 mm diameter), so it was necessary to crush and pulverize them to get a powder for better P extraction during the leaching test. The pounding was done with a hand mortar, while the CYC samples were fine enough and did not need further treatment. For the BA first campaign, two different crushing forms were used (mortar pounded and ball-milled), and then, according to the results, the best one was used for the second campaign (mortar pounded was chosen). The P content in the SSA was obtained by using acidic mineralization and chemical measuring kit (Hack Lange LCK 348),

aqua regia digestion was accompanied by ICP-MS analysis, and both toxic metals (As, Cd, Co, Cr, Cu, Ni, Pb, Hg, Sb, Tl, V, Zn) and most abundant elements (Ca, Fe, Al) were analyzed. Figure 8 shows the scheme of the pilot plant and the sampling points. BA corresponded to 90% of total generated ash, while CYC accounted for 5%. For this reason, BA were used for precipitation tests.
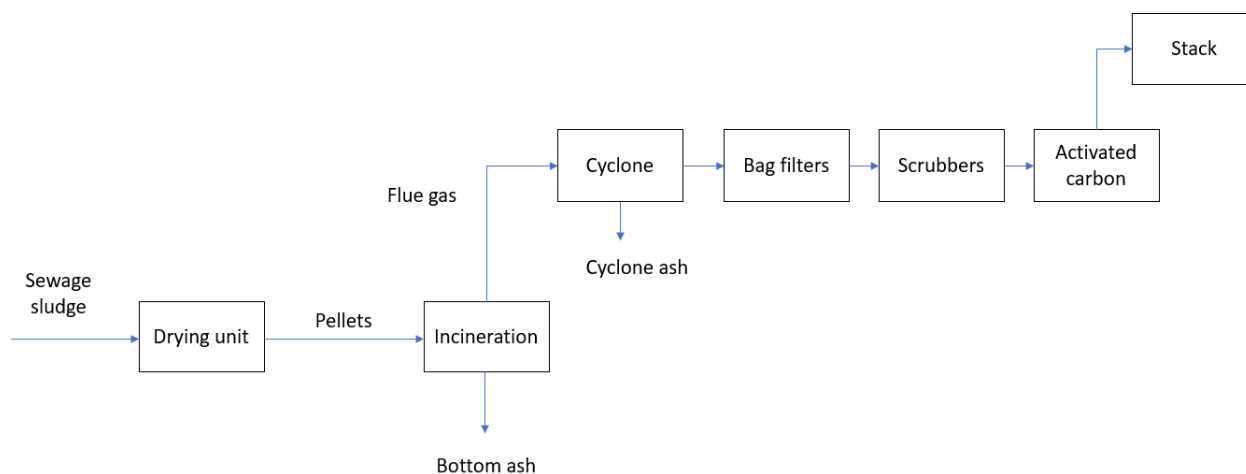
Figure 8 - Scheme of the pilot plant.

3.2 Leaching step

The experiment was performed twice on each fraction at ambient temperature. Acid extraction was performed with dilute sulfuric acid (with ultra-pure water) at acid concentration of 0.2 M and liquid to solid ratio of 20. A magnetic stirrer was used to agitate the mixture for 2 h (agitation helps avoid sedimentation and stagnant areas while improving diffusion and mass transport). The above conditions were determined as optimal for phosphorus extraction (Fang et al., 2018a; Franz, 2008). Centrifugation at 3500 rpm for 10 min and filtration (using Whatman^{TM} filter paper with a pore size of 0.45 µm and a diameter of 27 mm) are then carried out to improve the solid/liquid separation. Both solid and liquid parts were kept in PE bottles at ambient temperature for further analysis. Leachates were used for ICP-MS analysis to get elemental component. As CYC samples became opalescent soon, CYC samples were instantly stabilized after filtration by diluting it with 0.2 M HNO$_3$ (ICP-MS needs to have stable and acidic samples; dilution of samples only by water raises the pH significantly, causing some elements to precipitate). Also, P analysis was performed to the liquid phase to determine P extraction efficiency and also the amount of unwanted material inside leachate. For analysing the P content, the pH was modified to more than 8 by NaOH (35%) dosage, then the appropriate dilution was applied and the measure was performed. Subsequently, the solution was used for precipitation step. The procedure for this experiment is described in more detail in chapter 5.4.

For calculating PEE the following equation was used:

$$PEE = \frac{C_{P,\,leach} \cdot T}{C_{P,\,ash} \cdot (M_{in}/V_{in})} \times 100 \qquad \text{Equation 4}$$

$C_{P,\,leach}$ is the concentration of P in the leachate solution measured by the spectrophotometer (mg/L),

T is the dilution factor,

$C_{P,\,ash}$ is the concentration of P in the ash (mg/kg),

M_{in} is the mass of SSA before processing (kg),

V_{in} is the volume of the prepared leaching solution (L).

Also, the percentage of extracted material was determined based on the following equation:

$$\% \; extracted = \frac{C_{leach}}{C_{ash} \cdot (M_{in}/V_{in})} \times 100 \qquad \text{Equation 5}$$

C_{leach} is the concentration of metal in the leachate solution measured by ICP-MS (mg/L),

C_{ash} is the concentration of metal in the ash (mg/kg),

M_{in} is the mass of SSA before processing (kg),

V_{in} is the volume of the prepared leaching solution (L).

3.3 Precipitation step

Oversaturation of ions is needed to precipitate the phosphorus from the leachate solution. The initial pH was around 1.5, and by adding a base solution, it was possible to increase it. For this purpose, different kinds of base (lime water with 0.5% concentration, (0.1 M) KOH, (0.1 M) NaOH) were used, and the effect of each one on leachate was investigated. The same method previously described was used to determine the P content in the filtrate solution. For details about precipitation step, see chapter 5.7, and for the base solution preparation, see chapter 5.8.

3.3.1 Preliminary tests

Twenty tests were performed on different samples for phosphorus precipitation at ambient temperature. In these tests, the BA of the first and second campaigns were used. Each of them was performed under specific pH and rest time for sedimentation. In these experiments, the range of pH was increased from 2.5 to 7. Some tests were both performed in a single step or sequentially. In the

single step, the solution pH was raised to the final desired pH without stopping at any intermediate pH value. Sequential means that the final desired pH was reached by several intermediate steps of pH, then the solution pH was raised to the target pH and allowed to settle. Then, solid and liquid phase were separated by filtration, using Whatman™ filter paper with a pore size of 0.45 µm and a diameter of 27 mm. Finally, the filtrated solution was used for the precipitation tests by increasing the pH to the second intermediate pH step. These steps were continued until reaching the final pH. The amount of precipitated material and the amount of base required to change the pH were determined in both approaches. The rest time for sequential tests was 2 h, but for other samples were 2, 5, and 20 h. The purpose of this test was to get the behaviour of samples for precipitation.

3.3.2 Precipitation tests

For further tests, target pH of 2.5, 3.5, 5, and 8, and the rest time of 2 h were applied to leachates from second campaign BA. Three reagents (NaOH, $Ca(OH)_2$, KOH) were used to increase the pH and two methods were performed to increase pH (using single reagent and combined reagents). in combined reagents method for pH 2.5 and 3.5 only used NaOH but for pH 5 and 8 the ph first increased until 3.5, then the reagent was changed, and $Ca(OH)_2$ were used to increase pH until 5 and 8. In single reagent method the pH was increased by KOH until 2.5, 3.5, 5, and 8 without changnging the reagent. After reaching the target pH, a rest time of 2 h was applied while the beakers were covered with parafilm. Then, filtration was applied to separate the solid phase (the recovered material) from the liquid phase (the filtrate solution). ICP-MS was used to assess the levels of Al, Ca, Fe, Cu, and Zn in the filtrate solutions at various pH levels (these elements were selected because they were the most abundant in the ashes and in the leachate).

3.3.3 Calculation of precipitated materials

Equation 6 shows the concentration of the precipitated material, equations 7 and 8 indicate how to calculate precipitation efficiency.

$$C_{i,precipitated} = \frac{(V_{leachate} \cdot C_{i,leachate}) - (V_{filtrate} \cdot C_{i,filtrate})}{M_{precipitate}} \qquad \text{Equation 6}$$

$C_{i,precipitated}$ = Concentration of (i) in the precipitated material ($mg_{element,i}/kg_{precipitate}$),

$V_{leachate}$ = Volume of leachate (L),

$C_{i,leachate}$ = Concentration of (i) in leachate (mg/L),

$V_{filtrate}$ = Volume of filtrate solution (after increasing pH, rest time, and filtration) (L),

$C_{i,filtrate}$ = Concentration of (i) in filtrate solution (mg/L),

$M_{precipitated}$ = Mass of precipitated material (kg)

i = element (e,g., Fe, Al, HMs …)

$$Precipitation\ efficiency = \frac{Mass_{i,precipitate}}{Mass_{i,leachate}} \times 100 = [\%]$$

Equation 7

$Mass_{i,\ precipitated}$ = Mass of (i) in precipitated material (kg),

$Mass_{i,leachate}$ = Mass of (i) in leachate (kg).

$$Precipitation\ efficiency = \frac{(V_{leachate} \cdot C_{i,leachate}) - (V_{filtrate} \cdot C_{i,filtrate})}{V_{leachate} \cdot C_{leachate}} \times 100 = (1 - \frac{(V_{filtrate} \cdot C_{i,filtrate})}{(V_{leachate} \cdot C_{i,leachate})}) \times 100$$

Equation 8

3.3.4 Experimental plan

Figure 9 indicates an overview of experiments performed in this study. It should be noted that the results of the preliminary tests for the BA, first campaign, are not reported in this work because the method which was used to increasing the pH was sequential; it was not possible to analyze the P concentration in the filtrate solution.
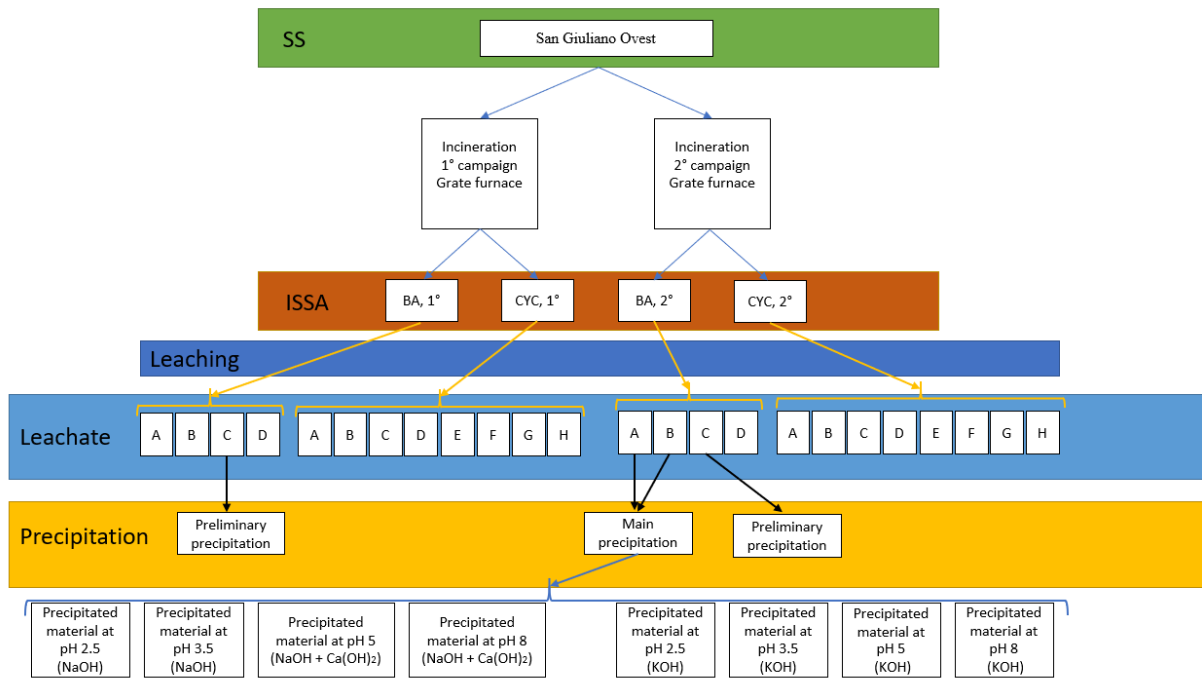
Figure 9 - Overview of experimental work.

4   Results and discussion

4.1   Ash characterization

The composition of the incoming SS and the incineration operation (e.g., burner technology, combustion zone temperature, and residence time) determine SSA characteristics. In combustion techniques, operating conditions affect different SS burnout grades and, consequently, the resulting ash carbonization (Krüger & Adam, 2014).

Figure 10 shows different ashes used in this work. Pelletized BA were characterized by heterogeneous aspect (different colours); black pellets resulted from unburned carbon. This is because the furnace temperature was not homogenous, and the side ash was exposed to colder air. First campaign BA presented 10% of unburned material, divided into 4% of unburned carbon, and 6% of metals bounded to hydroxides that did not react in the furnace. Second campaign BA had 20% of unburned material. The difference in unburned fraction between the two campaigns could have been determined by an increase in the grate speed during the second campaign, resulting in shorter contact time inside the furnace. According to DIRECTIVE 2010/75/EU ARTICLE 50, the overall slag and BA organic carbon content must be lower than 3%, or their loss on ignition must be lower than 5% of the dry weight of the material.

The red colour for the CYC sample could have been determined by the presence of iron, although similar iron content is reported in Table 5. Another reason could be related to the presence of lead oxide (PbO). In fact, it is worth noticing that CYC had higher Pb content with respect to BA.

BA Pelletized   BA Pound with mortar   BA milled with ball mill   CYC
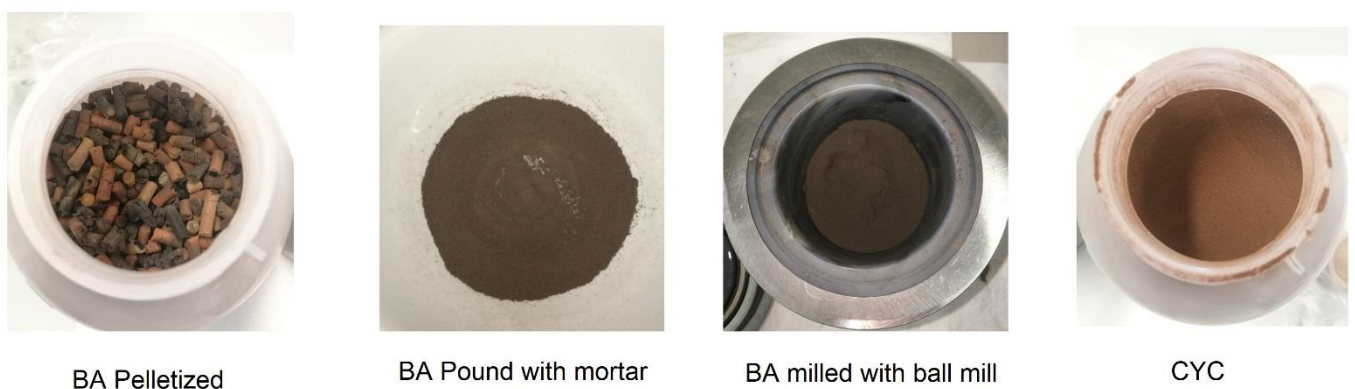
Figure 10 - Different ashes used in this work.

Figures 11 and 12 indicate particle size distribution in first and second campaign CYC and BA. As it was expected, CYC were composed by finer particles with respect to BA. Consequently, a higher

PEE is expected, since higher specific contact surface could enhance the contact between solid and liquid phases, as explained in chapter 4.2.
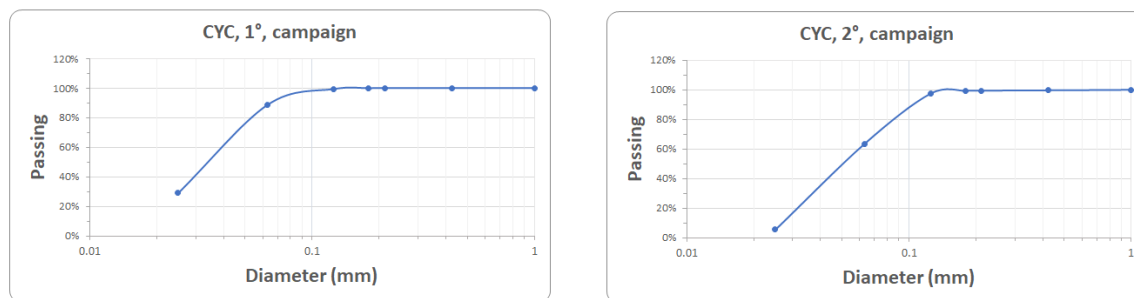
Figure 11 – CYC particle size distribution for first and second campaigns.
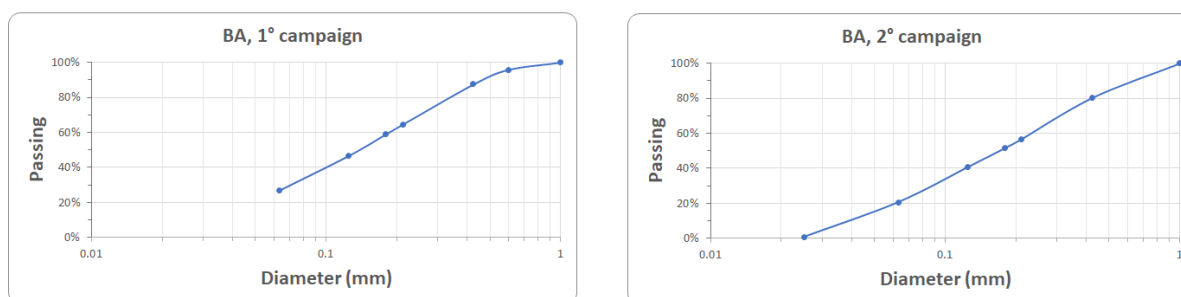
Figure 12 – BA particle size distribution for first and second campaigns.

Table 4 indicates most abundant elements in ashes and ashes humidity. The sample P content is slightly below expected average value, which is 8% (Biswas et al., 2009). By comparing the P content of these samples to Table 7, P content is similar to Taiwan average value, lower than the German, Korea, and Netherland average values, but higher than UK, Denmark, France, Hong Kong, and China average values. As P is a moderately volatile element, a higher amount in CYC is expected, and Table 4 proves it.

The quantity of Ca, Al, and Fe depends on the feed sludge nature and the choice of inorganic flocculants or dewatering agents. Al and Ca content affect the P extraction (Kalmykova & Fedje, 2013). According to (Gorazda et al., 2016), tested sample major element composition is similar to a plant in Szczecin in Poland.

Table 4 – Sewage sludge ashes (SSA) major elements for the different fractions.

	Element	P	Fe	Al	Ca	Humidity
	U.M	mg/Kg				%
First campaign	BA	72000	33729	60877	84835	0.94%
First campaign	CYC	75000	35135	67442	88811	0.34%
Second campaign	BA	72200	22087	57959	88805	4.62%
Second campaign	CYC	84700	20420	60526	91476	0.40%

Incineration increases the concentration of such metals by a factor of 4 or 5. For this reason, specific attention must be devoted to toxic metals like As, Cd, Hg, Ni, and Pb, whose presence in fertilizer must be controlled (Donatello, 2009).

Table 5 indicates the concentration of toxic metals in SSA. As expected, As, Cd, and Pb are higher in CYC because they are volatile metals. But Hg is volatile metal too, and a higher amount is expected compared to BA samples. Hg in cyclone is not higher than grate because mechanical collectors (e.g., cyclone) have poor ability to isolate submicron particles from flue gas; they are only expected to be capable of low mercury elimination. Less volatile elements like Cr, Cu, Ni are almost similar in both BA and CYC. The elemental composition for the Szczecin plant showed a similar result. Like other European SSA in Table 7, tested samples have a high content of Ni and Pb. The most abundant toxic element in all tested samples compared to other toxic elements in the same sample is Zn. According to Tables 5 and 7, the Zn content is similar to the UK, Hong Kong, and Korea average values, except for the first campaign CYC, which is identical to France average value.

Table 6 indicates the limits of toxic metals in inorganic fertilizers. It was found that the amount of toxic metals in ashes was more than the allowed limits for use as fertilizer (except As in the grate furnace ash). So, the direct use of SSA as fertilizer is not allowed, and treatments are needed.

Table 5 – Toxic metals in different SSA fraction.

	Element	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	Unit	mg/kg							
1° campaign	BA	32.9	0.31	441.6	1014.6	0.49	552	124.5	2381.6
1° campaign	CYC	92.2	76.8	468.8	1274	0.64	560.4	2522.8	6244.8
2° campaign	BA	25.8	0.51	426.4	1179.4	0.54	605.5	213.9	3229.7
2° campaign	CYC	49.7	37.1	640.2	1202.6	0.54	514.1	802.5	3197.2

Table 6 - Regulation (EU) 2019/1009 for inorganic fertilizer.

Element	Zn	Cu	Pb	Ni	Cr (VI)	As	Hg	Cd
LIMIT (mg/kg)	1500	600	120	100	2	40	1.5	1

Table 7 - Characteristics of various SSAs in different countries (Fang et al., 2020).

Country	Combustion technology	P (%)	Concentration of major contaminant elements of concern in case of fertilizer application (mg/kg)									References
			As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	
German (24 incinerators)	Fluidized bed/ grate firing/ multiple hearth firing/ fluidized bed gasification	4.9-11.9;	5- 19	2.1- 2.9				0.08- 0.47	58.6- 72.2	96.2- 124		Krüger and Adam (2015)
UK (7 incinerators)	Fluidized bed	5.3-7.6	7.1-42.5	0.1-9.4	N.P.	91.7-1031	492-828	0-3.9	4-351	130-627	1226-2737	Donatello (2009)
France	Fluidized bed	6.5	23	14	669	2636	2483	–	621	720	7103	Cyr et al. (2007)
Denmark	Fluidized bed	7.0/9.9	–	–	–	–	540/690	–	29/72	85/112		Ottosen et al. (2013)
Netherlands (2 mono-incinerators)	Fluidized bed	11.8	35	3.8				–	67	250		Ruijter (2018)
Hong Kong	Fluidized bed	4	107	–	–	–	839	–	85	97	2198	Fang, Li, Guo et al. (2018)
Taiwan	Brick-firing kiln	7.8	–	8.9	–	75.7	432.6	–	–	199.4		Lin et al. (2006)
Korea	–	10.7	29.8	12.5				–	86.9	823.9	2236	Lee and Kim (2017)
China	Muffle furnace	5.2-5.4	703-937	122-141	–	458-492	406-436	–	194-220	410-564	867-909	Liang et al. (2019)

Figures 13, 14, and 15 compare major and toxic elements in BA and CYC. Limits for toxic elements in inorganic fertilizers are reported. The Fe content is lower than most of the plant reported in literature (Fang et al., 2020; Gorazda et al., 2016); for example, Szczecin, Kraków, and Gdynia in Poland have 65000 (mg/kg), 113400 (mg/kg), and 90100 (mg/kg), respectively. The reason for such result could be related to the use of Al-salt instead of Fe-salt to precipitate P in WWTP.
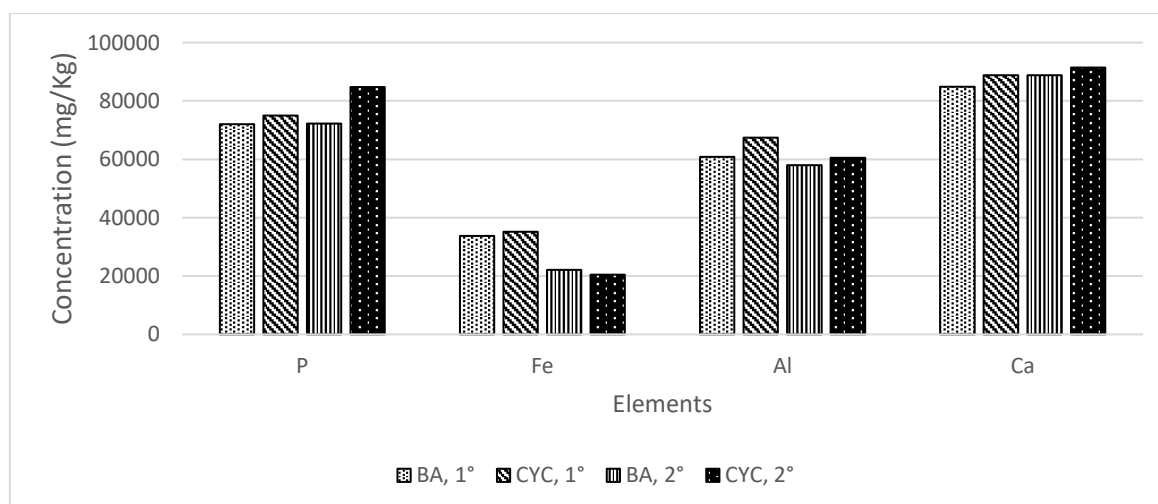
Figure 13 – SSA major elements in BA and CYC.
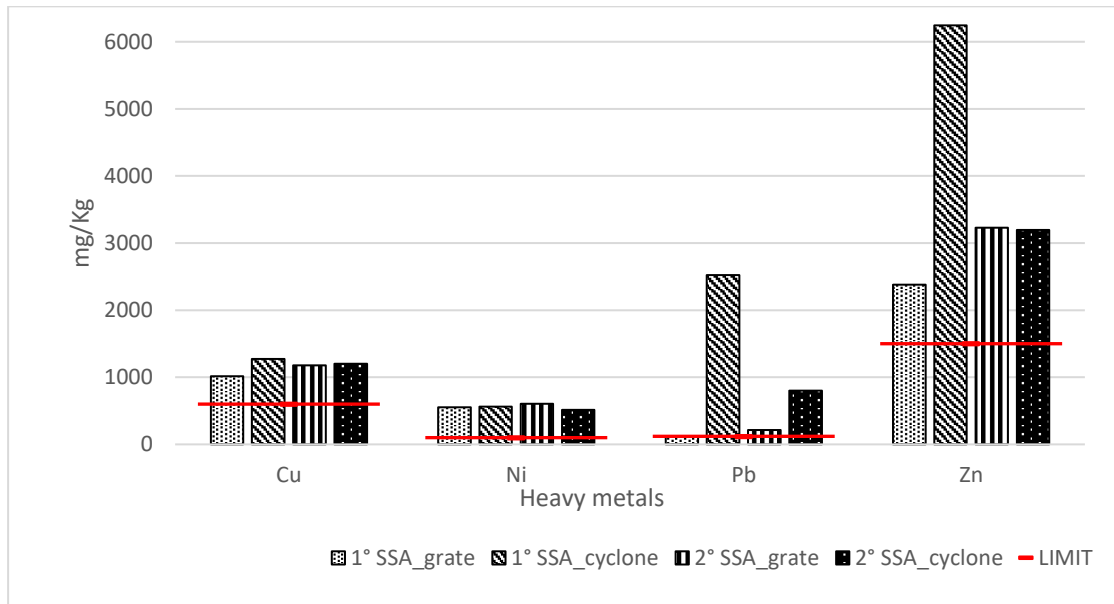
Figure 14 – SSA major HM in BA and CYC.
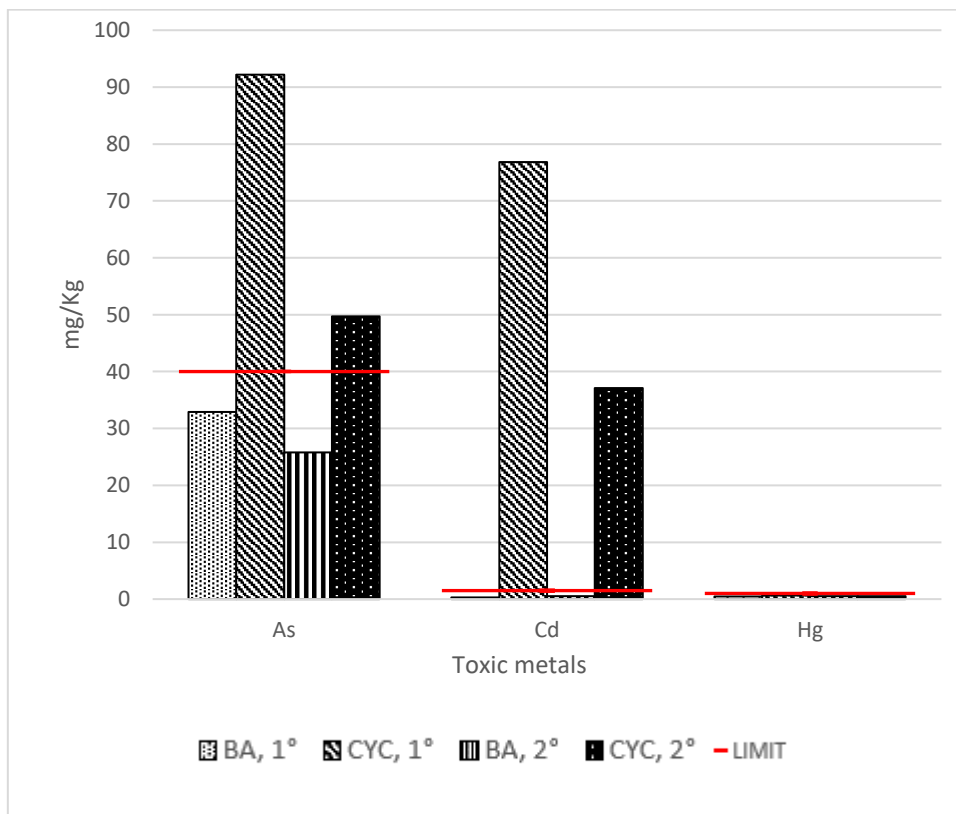
Figure 15 – SSA minor toxic elements in BA and CYC.

Figure 16 shows the amount of major elements in ashes and provides an idea about ash composition. Elemental composition was limited to Al, Fe, P, and Ca. Based on literature, 12-20% could be Si,

1.5-2% S, being a high amount of S expected because of the S content in the SS (approximately 0.75%), Cl 0.5-0.9%, Mg 1-3%, K around 1% and Na 0.5-2%.

	BA, 1°	CYC, 1°	BA, 2°	CYC, 2°
■ Other elements	74.9%	73.4%	75.9%	74.3%
☐ Ca	8.5%	8.9%	8.9%	9.1%
▨ Al	6.1%	6.7%	5.8%	6.1%
▥ Fe	3.4%	3.5%	2.2%	2.0%
⊞ P	7%	8%	7%	8%
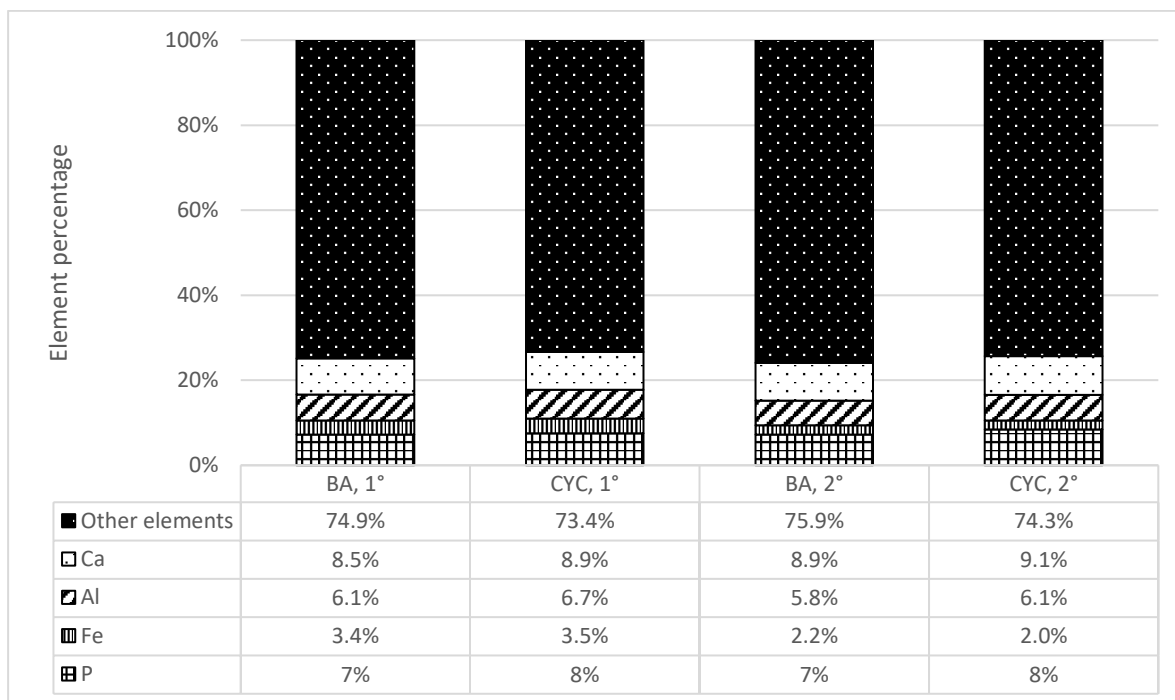
Figure 16 –Major elements in BA and CYC.

4.2 Leaching step

4.2.1 Phosphorus extraction

Figure 17 indicates the relation between particle size and PEE. It is known that as the solid particle size is smaller, the solid phase has better contact with the liquid phase and it improves extraction efficiency. Here, milled BA had the smallest particles, followed by pounded BA and pelletized BA. As it was expected, PEE was higher in samples with finer particles. It was found that the pounded BA is small enough (99.2% ash under 125 μm), and according to the results below, both milled BA and pounded BA resulted almost in the same PEE. Thus, mortar was chosen for the BA pounding.
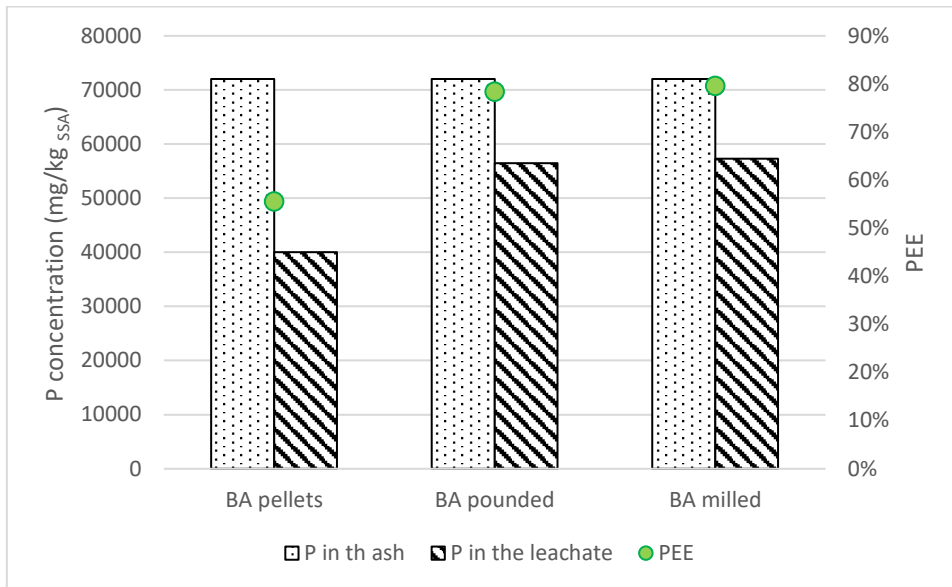
Figure 17 - Influence of SSA particle size on PEE

Generally, PEE for CYC samples was higher due to the presence of finer particles, as indicated in Figures 18 and 19, but higher variability was detected with respect to BA. This could depend on the higher number of tests for CYC (4 tests for BA and 8 for CYC); the reason for more tests over CYC is indicated in chapter 4.3. From descriptive statistics, it can also be deduced that suitable conditions for extraction have been selected because all samples showed good PEE (on average 80%) except pelletized BA due to large particle size and as BA .
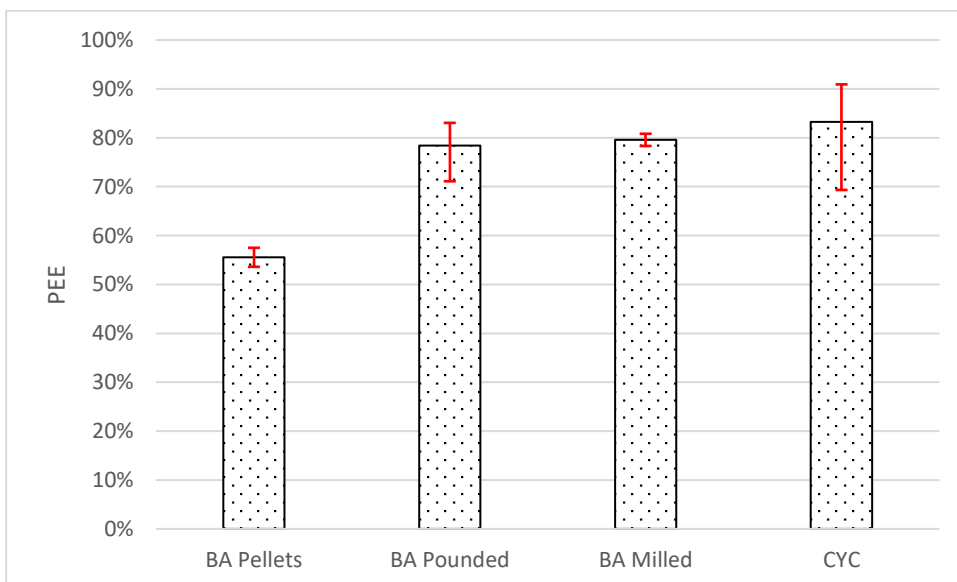
Figure 18 – PEE in BA and CYC (average±st.dev.) for first campaign.
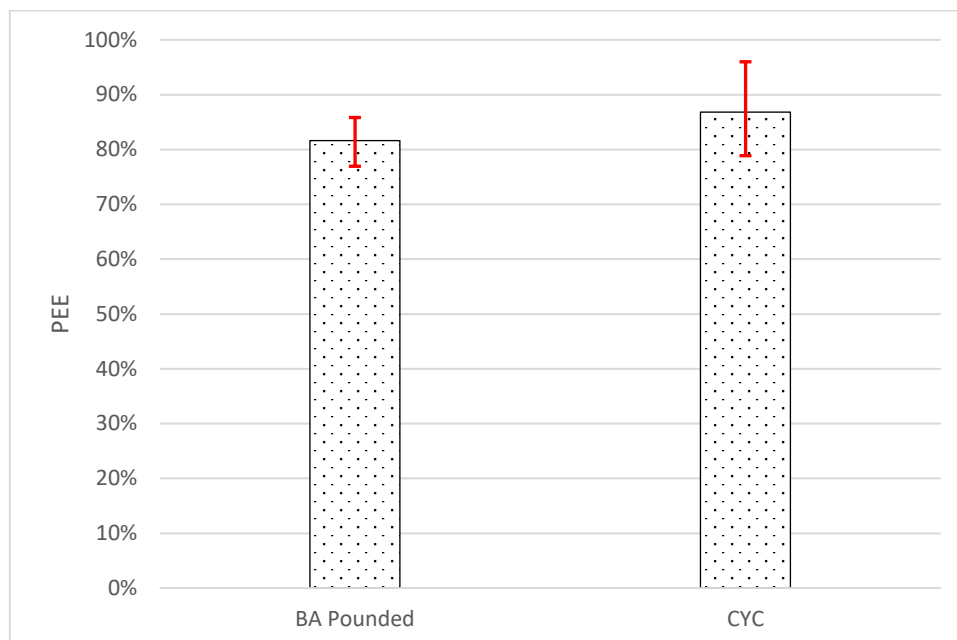
Figure 19 - PEE in BA and CYC (average±st.dev.) for the second campaign.

Table 8 shows P concentration and pH in samples from the first campaign. The amount of extracted phosphorus in both BA milled and BA pounded (by hand) is almost the same, so for the second campaign experiments, only the BA pounded was used.

Table 8 - P extraction for BA and CYC and their pH for the first campaign.

Sample	Name	P-PO4 (mg/L)	pH measured
BA, pellets	A	1930	<2
	B	2070	<2
BA, milled	A	2820	<2
	B	2910	<2
BA, pounded	A	2930	1.42
	B	2990	1.43
	C	2810	1.31
	D	2560	1.37
CYC	A	3410	<2
	B	3360	<2
	C	2600	<2
	D	2900	<2
	E	3270	<2
	F	3230	<2
	G	3070	1.92
	H	3140	1.94

Table 9 shows P concentration and pH in samples from the second campaign. Close results were expressed in the literature (Wang et al., 2018; Fang et al., 2018). In these articles, the same conditions used in this work were applied (using H_2SO_4, L/S = 20, and 2 h for reaction time). Leaching kinetics are generally regulated by several variables, including solubility and mass transfer (Franz, 2008). For this reason, as P has good acid solubility, and SSA has fane particles (Biswas et al., 2009) in several articles, 2 h is reported as the optimal reaction time. According to (Biswas et al., 2009), Phosphorus releases from ash are not affected by temperature changes in the range of 30-70°C, so all the tests were performed at room temperature. For a good recovery rate, the pH should be between 1 and 2; in the pH lower than 1, HM extraction is more noticeable (Franz, 2008). So in this work, all the leaching solutions had a pH between 1 and 2. The result for sample D for CYC was an outlier and did not consider in the evaluations.

Table 9 – P extraction for BA and CYC and their pH for second campaign.

Sample	Name	P-PO4 (mg/L)	pH measured
BA, pounded	A	2770	1.46
	B	2870	1.46
	C	3080	1.57
	D	3090	1.56
CYC	A	3290	<2
	B	3450	<2
	C	3000	<2
	D	920	<2
	E	3600	<2
	F	3730	<2
	G	3150	2.13
	H	3160	1.63

Figure 20 shows PEE and P content (as mass ratio) in comparison with Al and Ca. According to Kalmykova & Fedje (2013), the PEE is expected to decrease by increasing Ca and Al content. But this is not the case, since it did not result in a significant change.
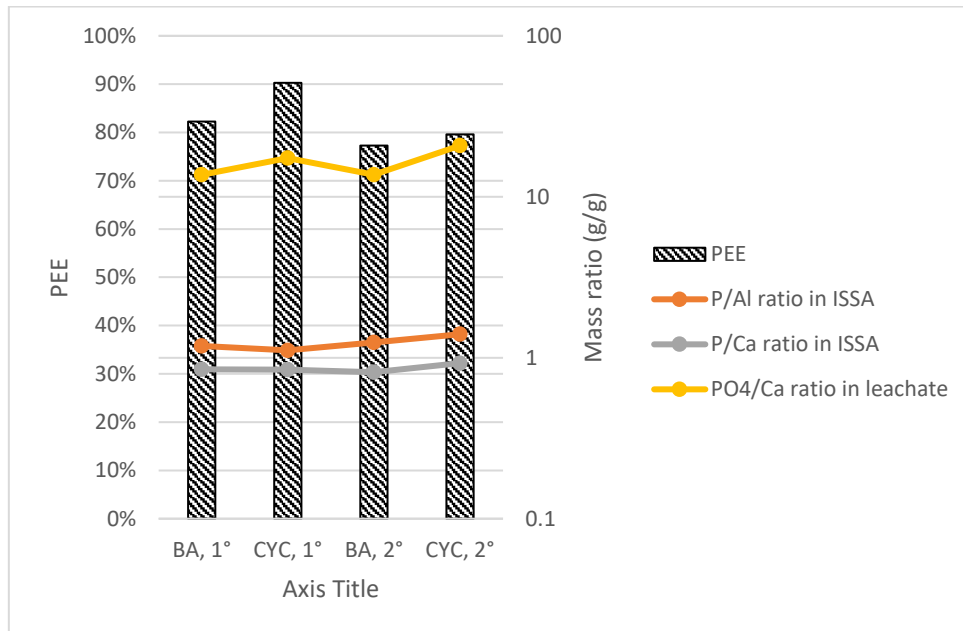
Figure 20 – PEE and P content (as mass ratio) in comparison with Al and Ca.

4.2.2 Metal extraction

Table 10 indicates the amount of analysed elements in the leachate.

Table 10 – Element concentration in the leachate for first and second campaign.

Element	U.M	BA 1°	CYC 1°	BA 2°	CYC 2°
Fe		591.54	723.14	472.83	676.26
Al		1210.28	2857.92	1420.99	3018.01
Ca		662.12	595.58	621.98	496.70
K	mg/L	88.80	191.52	87.72	150.61
Mg		335.85	370.73	304.88	336.66
Na		52.33	91.08	50.54	72.02
As		0.968	3.763	0.943	1.749
Cd		0.013	2.887	0.014	1.349
Cr		1.493	1.359	1.970	2.105
Cu	mg/L	19.507	25.308	21.760	28.204
Hg		0.004	0.012	0.004	0.006
Ni		2.075	2.339	3.280	4.171
Pb		0.200	3.529	0.309	1.123
Zn		41.600	89.721	48.250	39.425

According to Figure 21, the elements extraction efficiency was calculated. Most of elements moved to leachate (liquid phase). Also, since the percentage of Fe and Al passing in solution was high, a high amount of Al-P and Fe-P in the precipitated material was expected. These materials could affect

the quality of recovered material. Figure 21 also indicates that Ca is resistance to sulfuric acid and has low extraction rate.
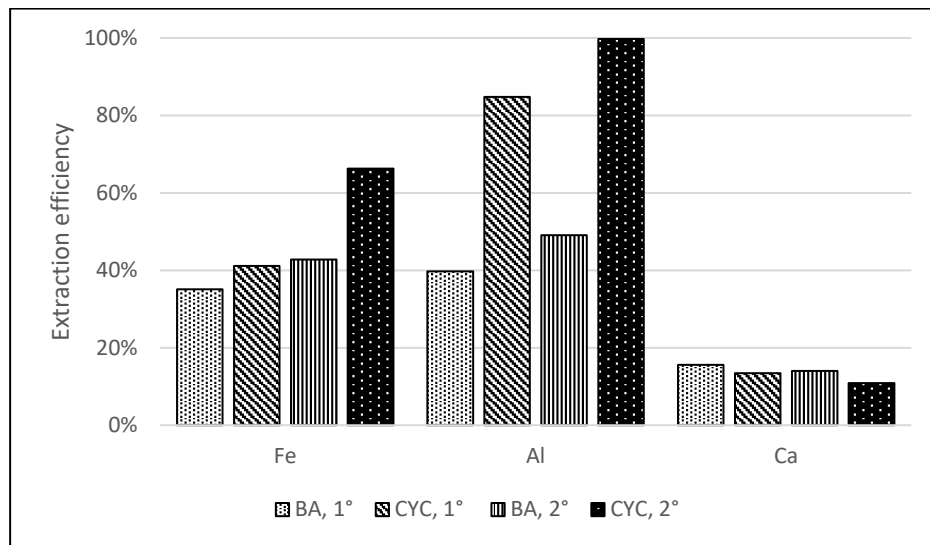
Figure 21 – Fe, Al and Ca extraction efficiency.

According to Figure 22, almost all of As and Cd were extracted; this is a disadvantage because As, and Cd can contaminate the recovered material. Cu and Zn extraction had moderate efficiency, and Ni, Hg, Cr, and Pb had low extraction efficiency. Almost the same result was obtained by (Ito et al., 2013) except for Cu that is 67%. This difference could be because of higher residence time in Ito experiment.
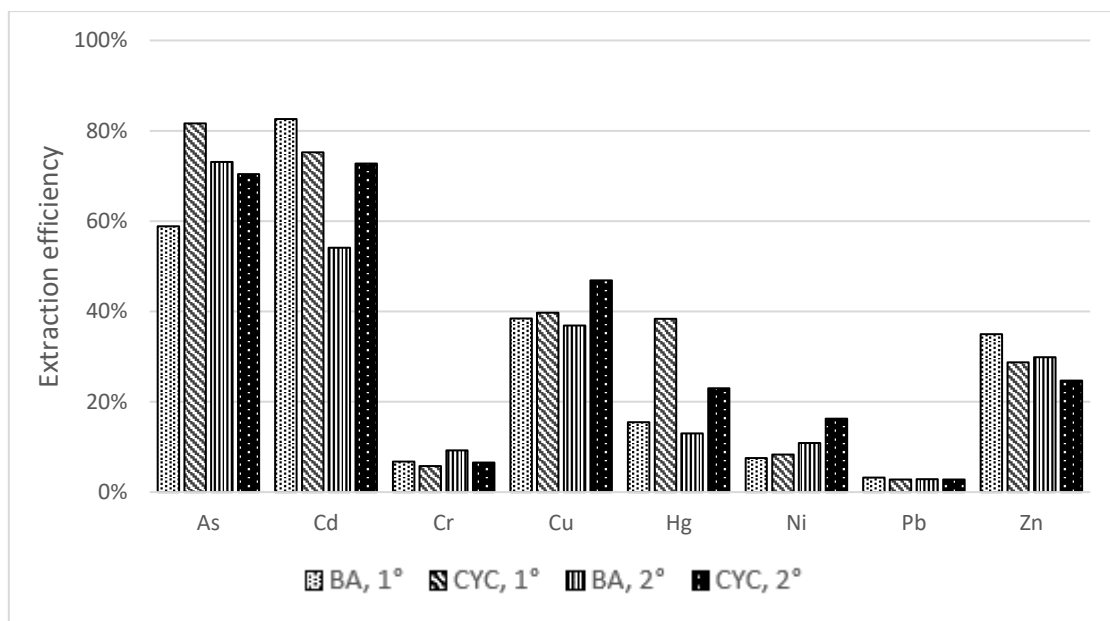
Figure 22 – Toxic element extraction efficiency.

4.3 Precipitation step

4.3.1 Preliminary tests

Several tests were performed to investigate the solution behaviour for different pH, precipitation methods, and rest time. Since the leachate of CYC became opalescent after a couple of hours, it was not possible to analyze the samples (a possible explanation for became opalescent is the quick precipitation of silica or metals bonded with sulfate). For this reason more tests were done over CYC to understand the behaviour of samples and to improve the stabilization procedure. The opalescent CYC samples are another reason for which BA samples were used for precipitation. Figure 23 shows the transparent and blurry samples.
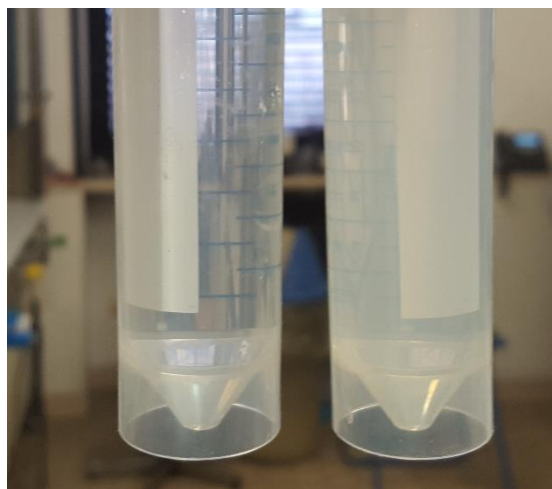
Figure 23 - Transparent CYC sample immediately after leaching and filtration (left) and blurry CYC sample after few hours (right).

Table 11 shows some of preliminary test results. As it was expected, by increasing the pH, the recovery rate increased as well. P started to precipitate in the early stage: it began with pH 2.5, but as the recovery rate was low, pH 2.5 was neglected for the following tests and the first target value for pH was pH 3. The percentage of P in precipitated material is reported in Table 11. Results evidenced that the P concentration decreases as pH increases. In other words, it can be understood that with increasing pH, in addition to growing phosphorus precipitation, the deposition of other substances also increases, and the sediment of different substances is more important than phosphorus, resulting in an overall reduction of the concentration of P in the precipitated material.

The volume of reagents dosed to precipitate P is shown in Table 11. After pH 5, further increase in pH seems irrelevant. For example, to raise P extraction by 1%, it is necessary to add a large amount of base, and this seems unreasonable because it increases the cost of reagents and waste of materials. The last column in Table 11 shows the amount of material recovered at different pH. Also, several sequential tests were done, but as most of the material precipitated at low pH (around pH 3), it was impossible to analyse precipitated material for high pH. For example, in one sample, 0.061 g was recovered at pH 3, 0.02 at pH 5, and 0.04 at pH 7. From Table 11, it can be seen that increasing the rest time of the solution raises P precipitation a bit, but this increase is only at low pH and has little effect at high pH. Moreover, by increasing the rest time, other undesirable material precipitates simultaneously; this effect can be seen in the precipitated material column. For these reasons, 2 h rest seems to be optimal for resting solution.

Table 11 – Experimental results obtained in preliminary tests using 0.1 M NaOH.

Sample name	Initial pH	Final pH	P prec	% P in prec mat	mL add (NaOH)	Δmol= mol(OH⁻)	mmol	g recovered
BA, 2°, rest for 2 h	1.9	2.5	23.6%	19.9%	22.69	0.0023	2.269	0.11
	1.8	3	59.8%	16.8%	40.57	0.0041	4.057	0.33
	1.6	5	94.2%	16.8%	59.39	0.0059	5.939	0.52
	1.9	7	96.5%	16.9%	74.57	0.0075	7.457	0.53
BA, 2°, rest for 5 h	2.0	3	48.0%	16.5%	34.83	0.0035	3.483	0.27
	1.6	5	94.1%	16.8%	63.11	0.0063	6.311	0.52
	1.9	7	96.2%	16.8%	68.49	0.0068	6.849	0.53
BA, 2°, rest for 20 h	1.5	3	84.1%	18.1%	45.90	0.0046	4.590	0.43
	1.9	5	94.2%	17.1%	61.90	0.0062	6.190	0.51
	1.8	7	96.0%	16.2%	75.22	0.0075	7.522	0.55

Figure 24 shows the amount of precipitated P at different pH and rest time. Rest time is relevant only at pH 3, while the precipitation efficiency overlaps at n pH 5 and 7, so there is no reason to increase the rest time.
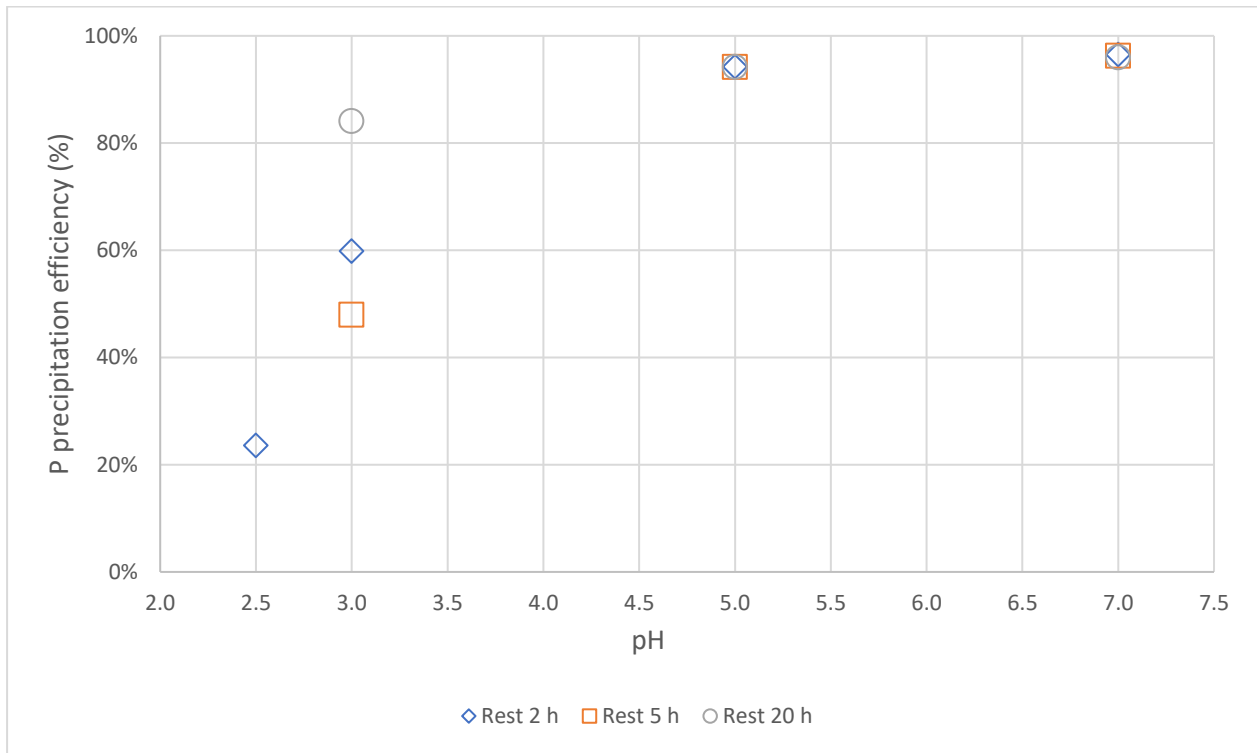
Figure 24 – P precipitation for BA second campaign in different pH and rest time.

According to Figure 25, which is from (Fang, Li, Guo, et al., 2018b), it seems that pH 2.5 is a good point to be set for the next experiments because of the large amount of Fe precipitated. In addition, at this pH P and Al start to precipitate significantly. pH 3.5 is a good point because a large amount of Al and P are precipitated. pH 5 has been set because almost all P and Al precipitated. pH 8 is also interesting because the totality of Fe, Al, and P is precipitated, and P and Al could experience re-dissolution. NaOH and Ca(OH)$_2$ were used to investigate the effect on the recovered product. For the same reason, KOH was used to investigate the combination of K in precipitated salts.
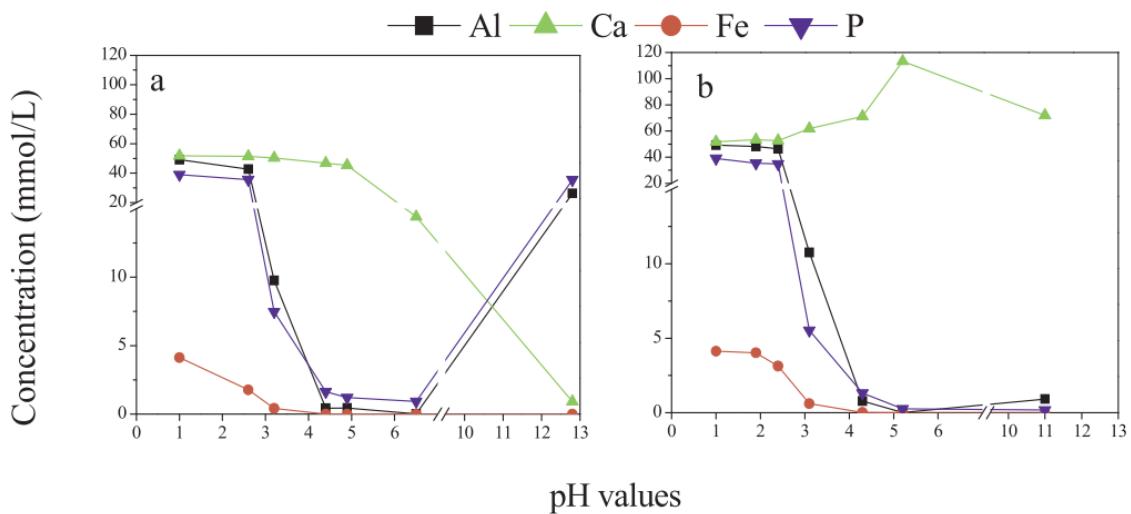
Figure 25 – Precipitation of different element*s* at various pH with NaOH (a) and Ca(OH)$_2$ (b) as reagents (Fang et al., 2018b).

4.3.2 Main precipitation tests

Table 12 reports the result of main precipitation tests. In case of P recovery, all reagents affect the process similarly: for a combination of NaOH and Ca(OH)$_2$, as it can be seen, at pH 8 nearly all P has been extracted, while for KOH, 4% remains, being a negligible amount. Since approximately 90% of the available phosphorus is recovered in all tests at pH 3.5, it seems that increasing pH to values higher than 3.5 is only a waste of resources to recover the remaining 10%. Moreover, increasing the pH increases the precipitation of heavy metals, so it seems that pH 3.5 is suitable to be set as target pH in precipitation tests. The initial pH does not affect the amount of phosphorus deposition. It is clear that if the initial pH is higher than 2, some phosphorus is already precipitated, and adding the base solution causes the remaining dissolved phosphorus to precipitate. Results collected in experiments performed in the preliminary tests (BA, second campaign) indicated that the amount of phosphorus deposition increases with increasing rest time. For example, for pH 3 and 2 h rest, the recovery rate was around 80%, but 90% of P was recovered at the same pH for 20 hours rest. But for the original sample (last tests), as target pH was 3.5 and 97% P was recovered in 2 h, a rest time equal to 20 h was not reasonable. Besides, waiting for 20 h makes the process industrial scale-up more complicated. The third column of Table 12 reports P content in the filtrate solution and indicates by increasing pH, the P concentration in the filtrate solution decrease, so it means that the more the pH, the more is precipitated P. The fifth column of Table 12 is the percentage of P in precipitated material and shows that enriched P product (average value of 16%) was obtained. Close result was obtained by (Ito et al., 2013), and as here the Al concentration in the leachate was high, it expected that P recovered as aluminum phosphate same as (Takahashi et al., 2001), according to that article, the ash was leached by sulfuric acid (decrease pH until 2) then increase the pH to 4 by sodium bicarbonate the concentration of P in recovered material was 19%.

Table 12 – Experimental result for main precipitation tests.

Sample Name	Initial pH	Final pH	P in solution mg/L	P prec	% P in prec mat	Molarity	mL add	Δmol= mol(OH⁻)	mmol	g recovered
BA, 2°, B	1.6	2.5	831	39%	22%	NaOH	33.29	0.0033	3.3289	0.15
	1.6	3.5	102	90%	17%	NaOH	57.56	0.0058	5.7560	0.46
	1.7	5.0	73	91%	16%	OH + Ca(O	77.46	0.0084	8.4330	0.48
	1.7	8.0	2.14	100%	15%	OH + Ca(O	138.66	0.0168	16.7655	0.57
BA, 2°, A	1.7	2.5	870	33%	21%	KOH	34.02	0.0034	3.4023	0.13
	1.6	3.5	91.9	89%	16%	KOH	69.52	0.0070	6.9521	0.46
	1.7	5.0	34.65	96%	17%	KOH	76.40	0.0076	7.6404	0.48
	1.6	8.1	21.6	96%	15%	KOH	106.09	0.0106	10.6086	0.53
BA, 2°, B	1.7	2.5	903	33%	20%	KOH	33.58	0.0034	3.3583	0.14
	1.6	3.5	77.7	91%	18%	KOH	70.40	0.0070	7.0404	0.44
	1.6	5.0	29.32	96%	17%	KOH	76.26	0.0076	7.6258	0.49
	1.7	8.2	24.1	96%	15%	KOH	109.05	0.0109	10.9053	0.55

Figure 26 shows that till pH 2.5 all reagents have the close behaviour but NaOH is stronger because although the sample for NaOH has lower pH than the sample for KOH. Because both samples reach to desire pH at the same time and the amount of NaOH used to reach that pH is a bit less than KOH. The reason is that although both reagents have the same (OH^-) concentration but NaOH can release (OH^-) easier.
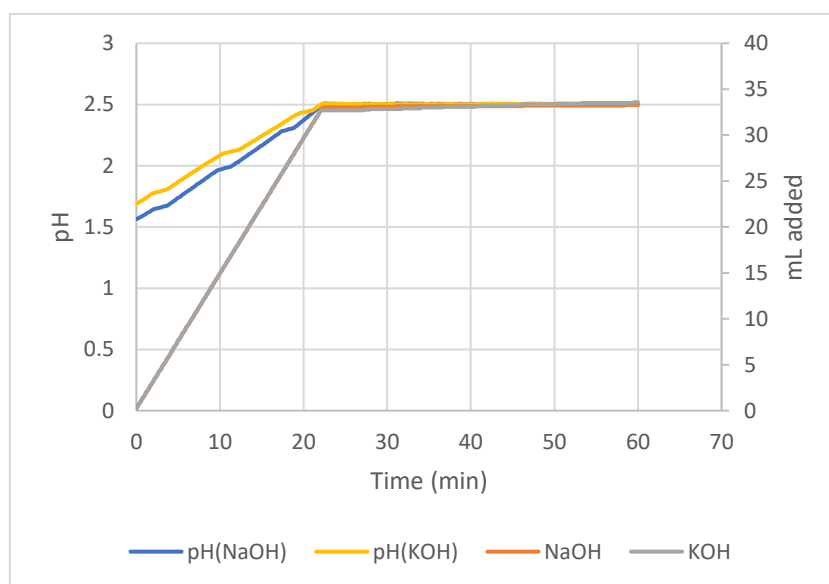
Figure 26 - Dosage of base (cumulative) at pH 2.5 and resulting pH change.

Figure 27 indicates that NaOH is stronger than KOH because it reaches pH 3.5 faster than KOH, also with less amount of NaOH. This behaviour is due to the fact that it is mentioned for pH 2.5, but as here more base solution is needed to reach pH 3.5, the difference between NaOH and KOH is clearer.
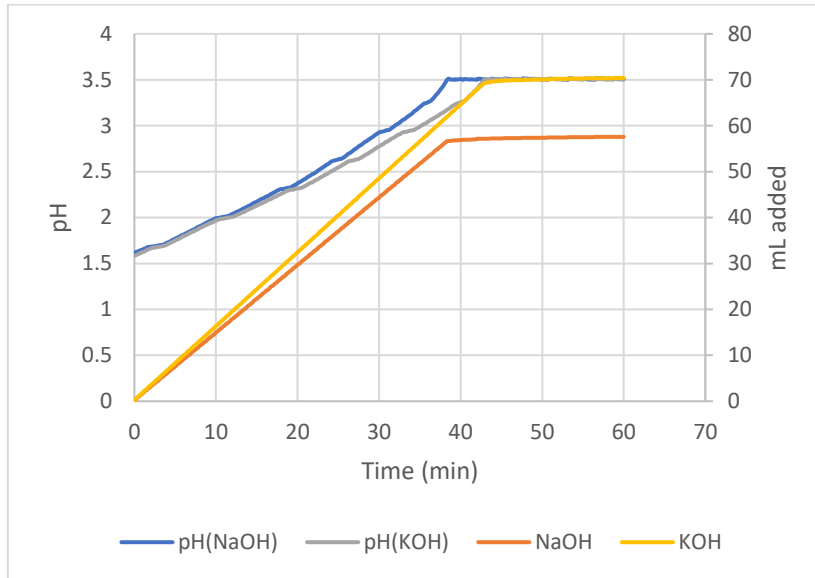
Figure 27 - Dosage of base (cumulative) at pH 3.5 and resulting pH change.

Figure 28 shows that NaOH + Ca(OH)$_2$ reaches the target pH faster, but the base added is similar to KOH. The reason could be because Ca(OH)$_2$ is weaker than both (because it is more diluted) NaOH and KOH. It is clear from the slope of the two graphs that the slope of KOH is slightly steeper than Ca(OH)$_2$ (after pH 3.5 when change the reagent). It was expected because, according to basic chemistry, as Ca(OH)$_2$ has a stronger bond, the kinetic of releasing (OH^-) is lower than KOH. This is another reason that KOH is a stronger and more soluble base than Ca(OH)$_2$.
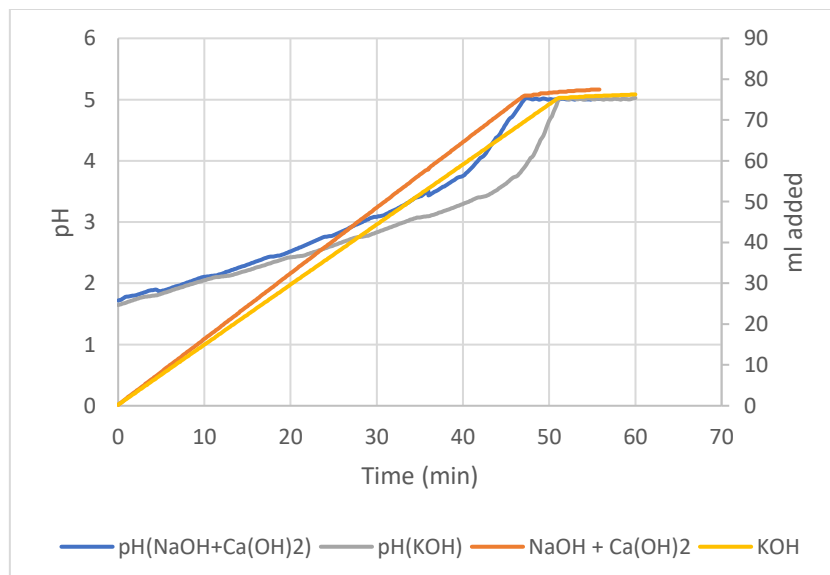
Figure 28 - Dosage of base (cumulative) for pH 5 and pH change.

Figure 29 indicates that Ca(OH)$_2$ is weaker than two other reagents, so that much more base needs to be added to reach target pH). As mentioned before, the order of the bases used in this work based on their strength is as follows: NaOH > KOH > Ca(OH)$_2$.
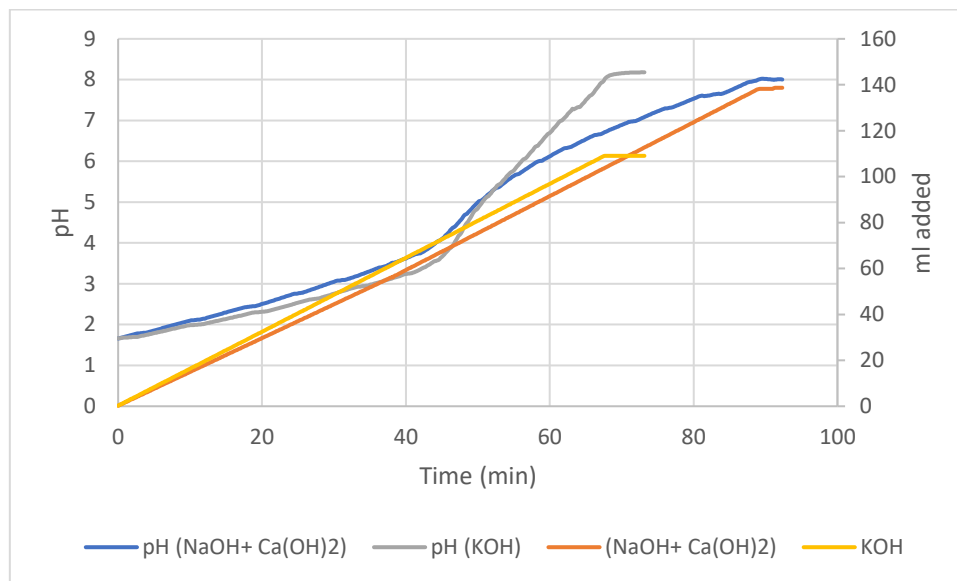
Figure 29 - Dosage of base (cumulative) for pH 7 and pH change.

According to Figure 30, the reagents have a similar ability to precipitate P, and using each of them does not make much difference in the P precipitation results because their P precipitation rate and P content in precipitated materials are almost identical. However, as from the previous figure, it is important to state that NaOH is more effective to precipitate material. The most important parameters for P precipitation are; P and precipitation agent molar ratio, pH, temperature, presence of suspended solids, COD content, and recirculation (Egle et al., 2017; Muster et al., 2013). The pH usually is changed by NaOH (Fattah et al., 2010) and is usually applied higher stoichiometrically at a rate of 5–50% (Doyle and Parsons, 2002). Sedimentation occurs when precipitants and P ions levels are greater than their solubilities at a certain pH. By this method, it is possible to recover P at the rate of 99.9% (Rahman et al., 2014).
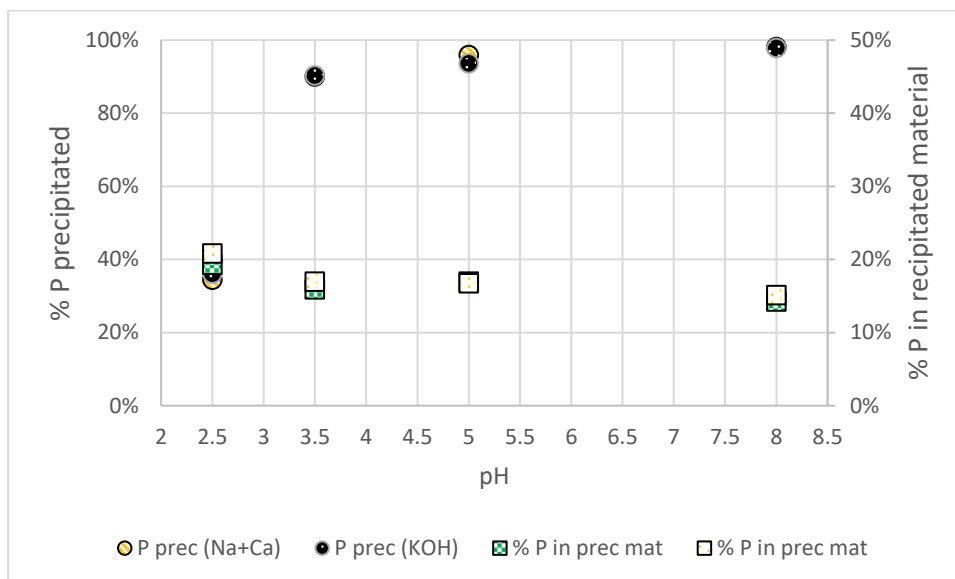
Figure 30 – The amount of % P precipitated and % P in precipitated material by using KOH and NaOH + Ca(OH)$_2$ in different pH ranges.

Figure 31 shows the amount of precipitates in the solution with KOH as precipitating reagent. By increasing the pH, as mentioned before, the amount of precipitated material increases. The amount of sedimentation increases because, by increasing pH, more material precipitates, and the amount of solution increases because more base needs to be added to increase pH. Precipitation by NaOH and Ca(OH)$_2$ resulted in the same behaviour.
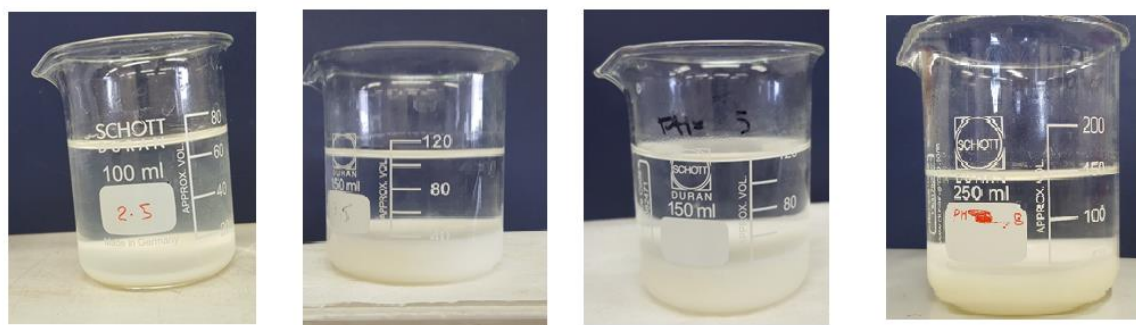
Figure 31 – Precipitation after 2 h in samples precipitated by KOH at different final pH (2.5, 3.5, 5, and 8).

Table 13 indicates the elemental content in the filtrate solution. Almost all elements precipitate at pH 8, except for Ca in samples precipitated by NaOH and Ca(OH)$_2$. At pH 3.5, a significant amount of elements precipitated. The same results are comparable to the literature Ito et al. (2013), Except for Cu, the recovery rate is higher here.

Table 13 – Elemental composition of the filtrate solution.

		Al	Ca	Fe	Cu	Zn	P
		mg/L					
NaOH + Ca(OH)2	pH 2.5	579.8	268.2	26.8	9.05	16.6	837
	pH 3.5	41.4	180.2	1.33	5.95	10.0	93.85
	pH 5	0.26	293.4	0.062	1.06	4.60	51.35
	pH 8	0.02	226.6	0.02	0.005	0.02	1.845
KOH	pH 2.5	568.7	243.0	27.2	8.69	14.3	886.5
	pH 3.5	49.3	160.8	1.50	5.47	8.83	84.8
	pH 5	0.28	147.4	0.091	1.45	4.91	31.985
	pH 8	0.02	8.0	0.02	0.005	0.02	22.85

Figures 32 and 33 indicate the concentration of various elements at different pH. When the pH was increased, the elements in solution decreased because they precipitated, except for Ca that increased at pH 5 because $Ca(OH)_2$ was used as the reagent. Figures 32 and 33 also indicate that most of elements precipitate at pH 3.5. Also, for both reagents, the behaviour of elements was similar; this is more evident in Figure 33,
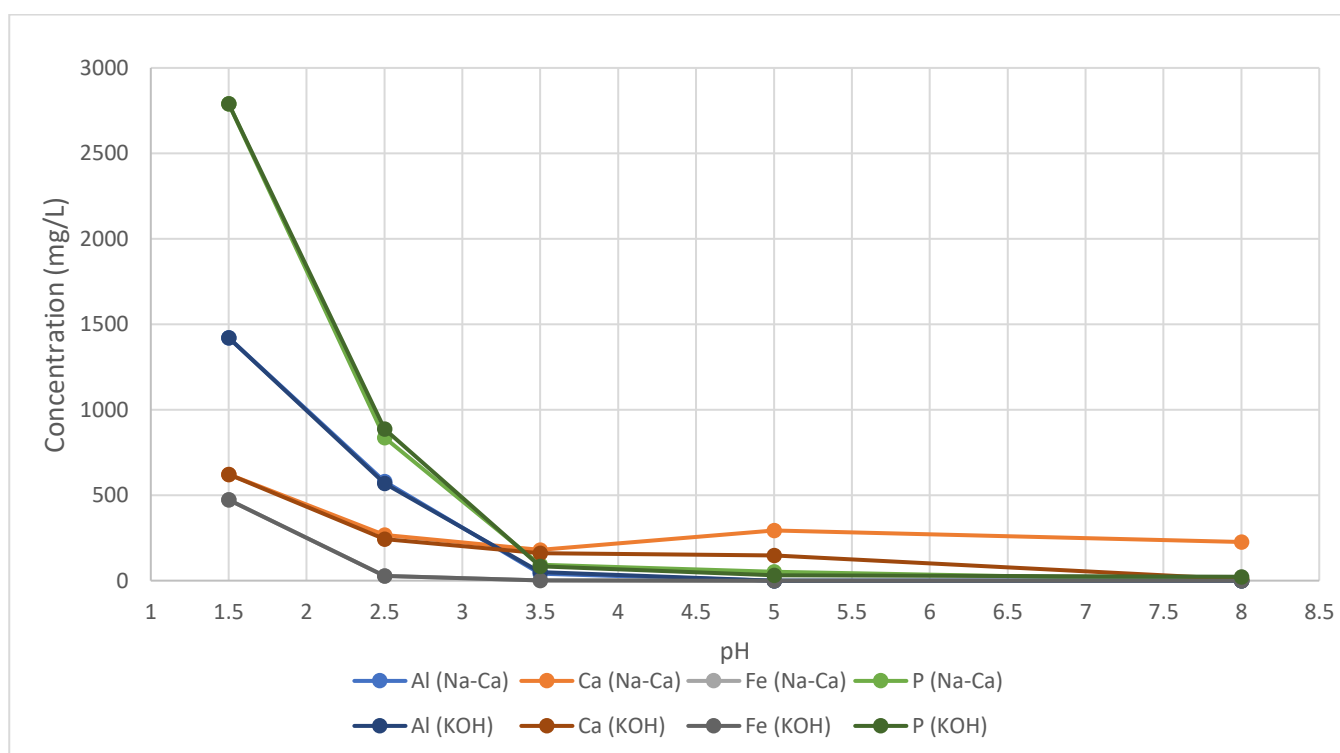
Figure 32 – Concentration of various elements at different pH for investigated reagents.
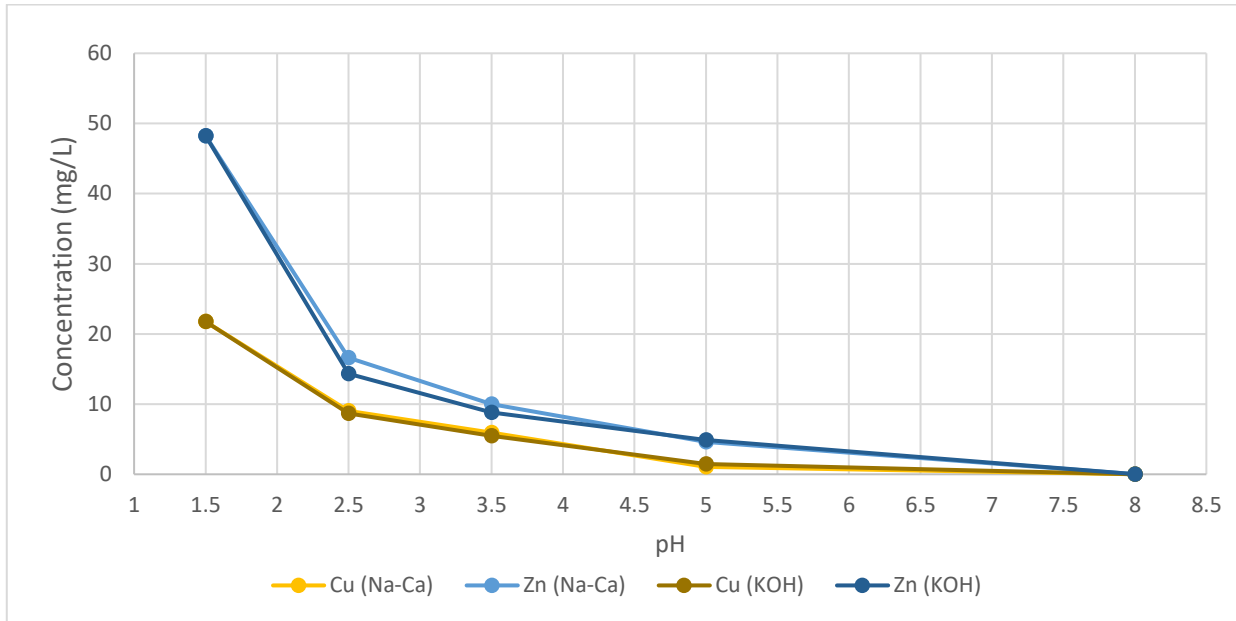
Figure 33 - Concentration of Cu and Zn elements at different pH for investigated reagents.

Table 14 shows precipitation efficiency for different elements. It indicates that most of Al, Fe, and P precipitated until pH 3.5 while less than 40% of Ca, Cu, and Zn precipitated. Ca is the most resistant element against precipitation among all reported in table 14. Figure 34 indicates metal phosphate solubilities at different pH and shows that calcium phosphate can not be recovered in low pH. Also dissolved metals and organic compounds in the leachate can influence calcium phosphate precipitation.

Table 14 - % Precipitated element at different pH based on the amount of elements in leachate.

		Al	Ca	Fe	Cu	Zn	P
		%					
NaOH + Ca(OH)2	pH 2.5	14%	9%	88%	12%	27%	37%
	pH 3.5	91%	15%	99%	20%	39%	90%
	pH 5	100%	-	100%	83%	66%	93%
	pH 8	100%	-	100%	100%	100%	100%
KOH	pH 2.5	15%	17%	88%	15%	37%	32%
	pH 3.5	88%	14%	99%	16%	39%	90%
	pH 5	100%	16%	100%	76%	64%	96%
	pH 8	100%	94%	100%	100%	100%	96%
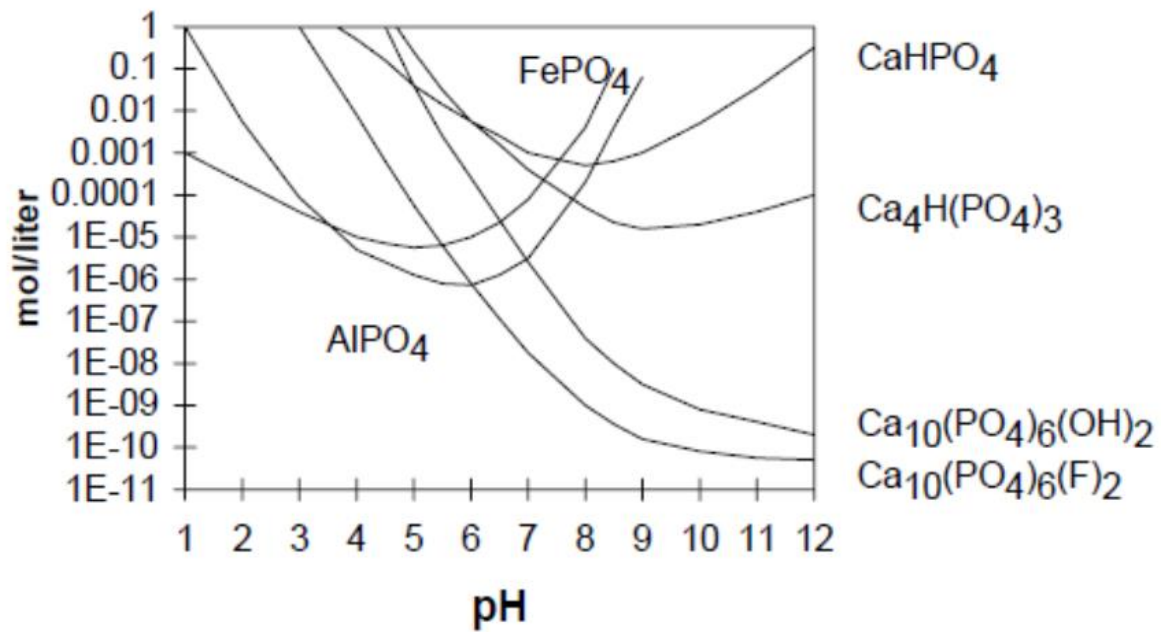
Figure 34 - Metal phosphate solubilities at different pH.

Figure 35 shows precipitation efficiency. It indicates that Fe precipitates faster than other materials, while Al and P precipitate with similar kinetics. The same result was obtained in Ito et al. (2013) and revealed that until pH 3 most of the toxic elements are still in the solution, except Cr that precipitated around 70%. According to Ito et al. (2013), 100% of all elements precipitate until pH 9 except As that precipitate only 40%.
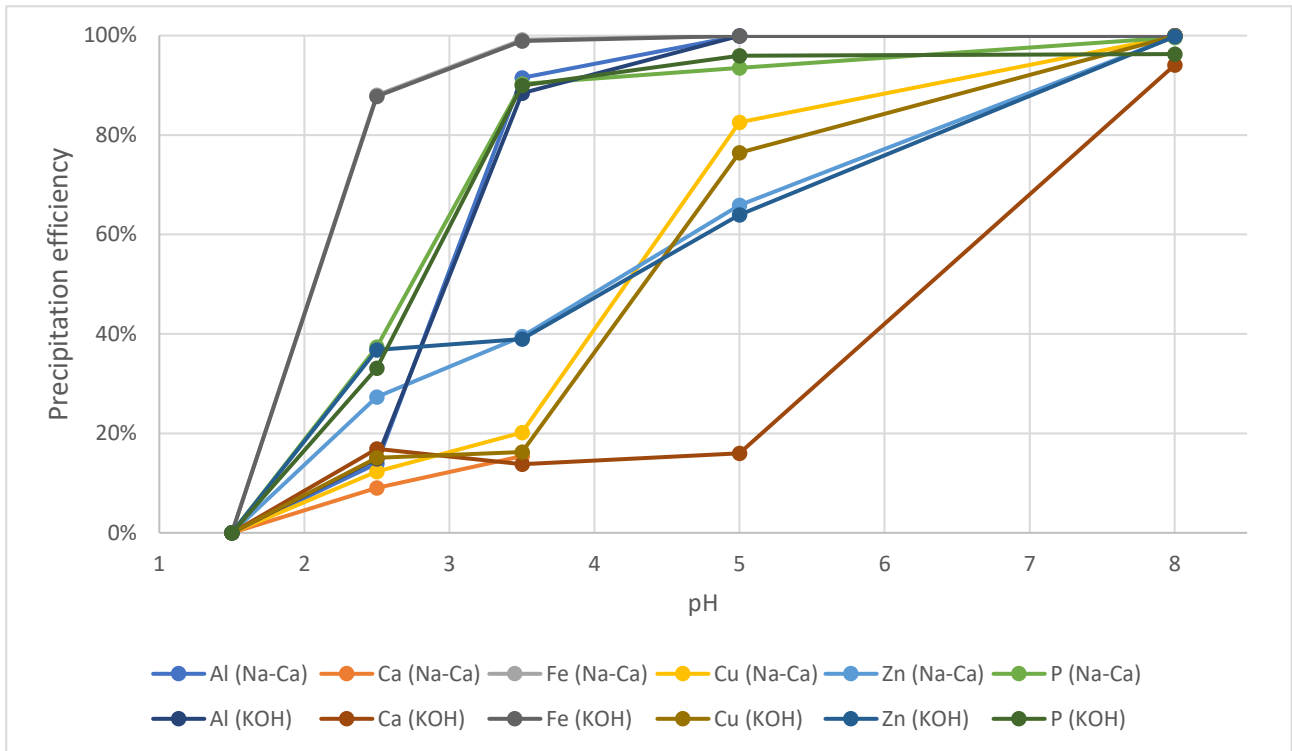
Figure 35 – Precipitation efficiency for different elements by using different reagents (KOH and NaOH+ Ca(OH)$_2$ in different pH.

Figures 36, 37, 38, and 39 indicate the concentration of toxic metals in precipitated material based on the assumption that they were completely precipitated. Except for a few of them, like Pb, toxic metal concentration exceeds regulations on fertilizers. The presence of Cu, Zn harms plant development, and Ni, while Pb and As harm cells (Rout and Das., 2009).
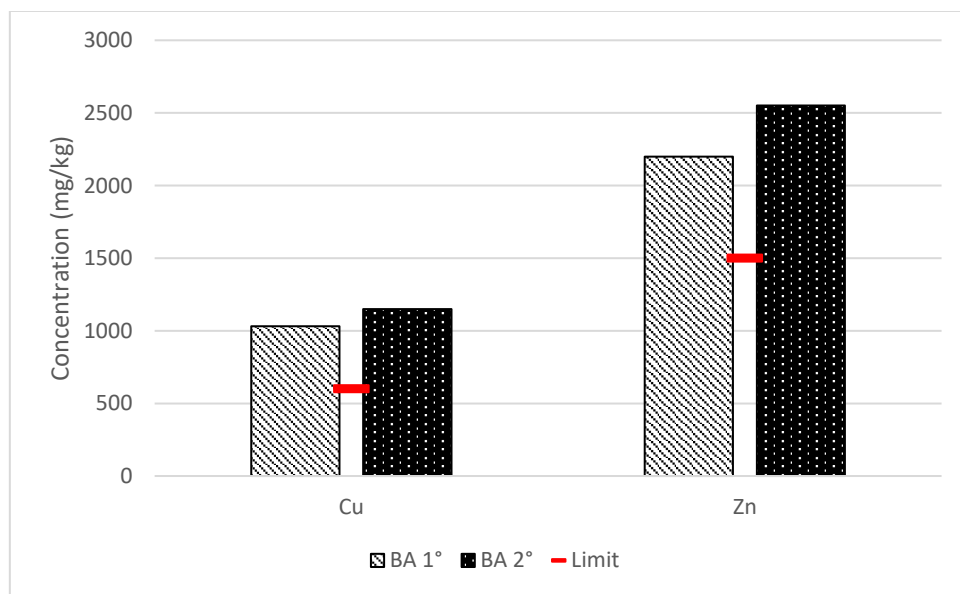
Figure 36 – Major toxic metals in precipitated material for BA.
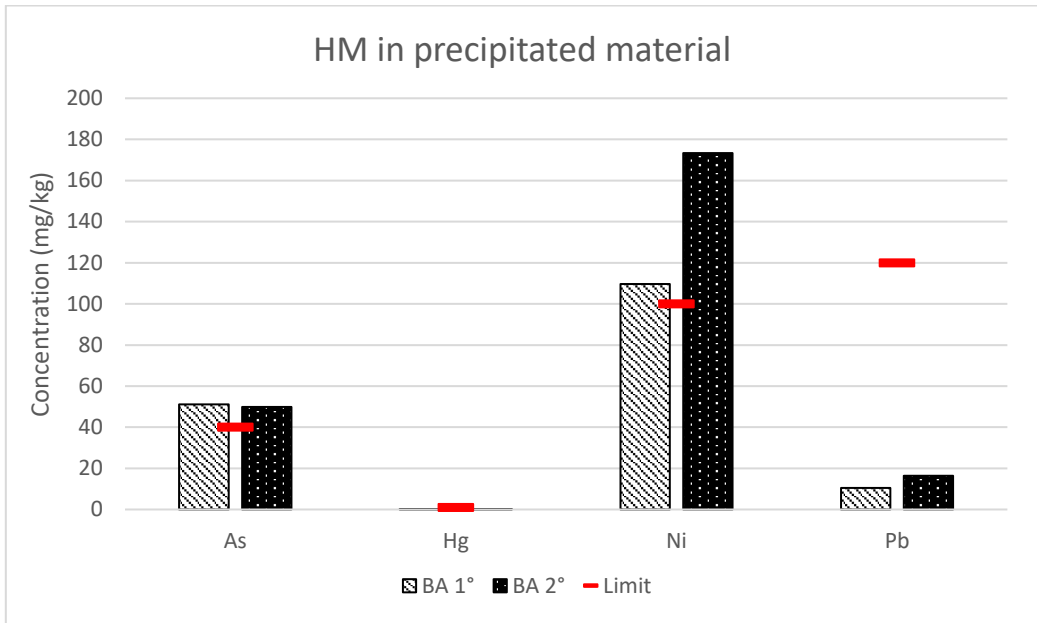
Figure 37 - Minor toxic metals in precipitated material for BA.
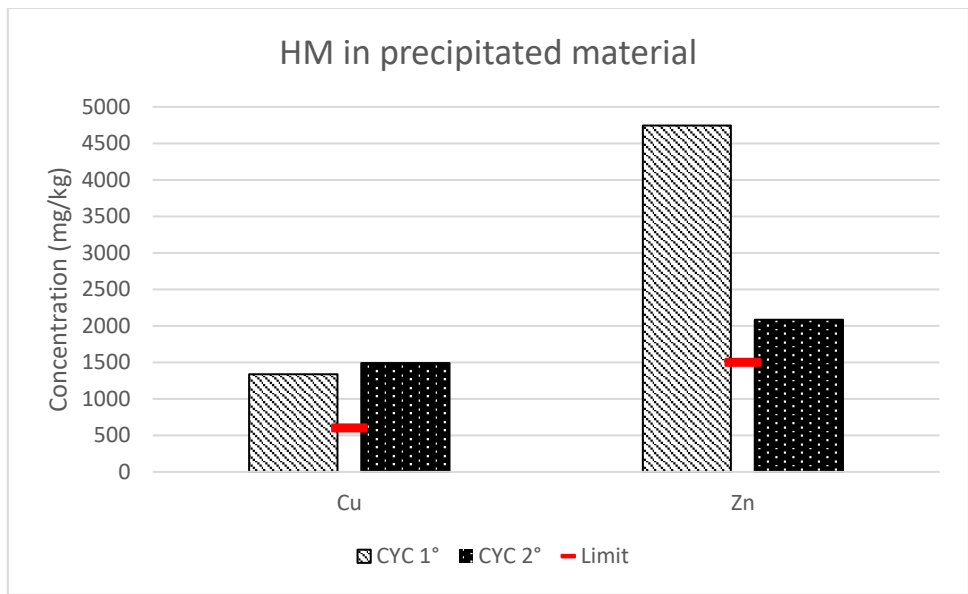
Figure 38 - Major toxic metals in precipitated material for CYC.
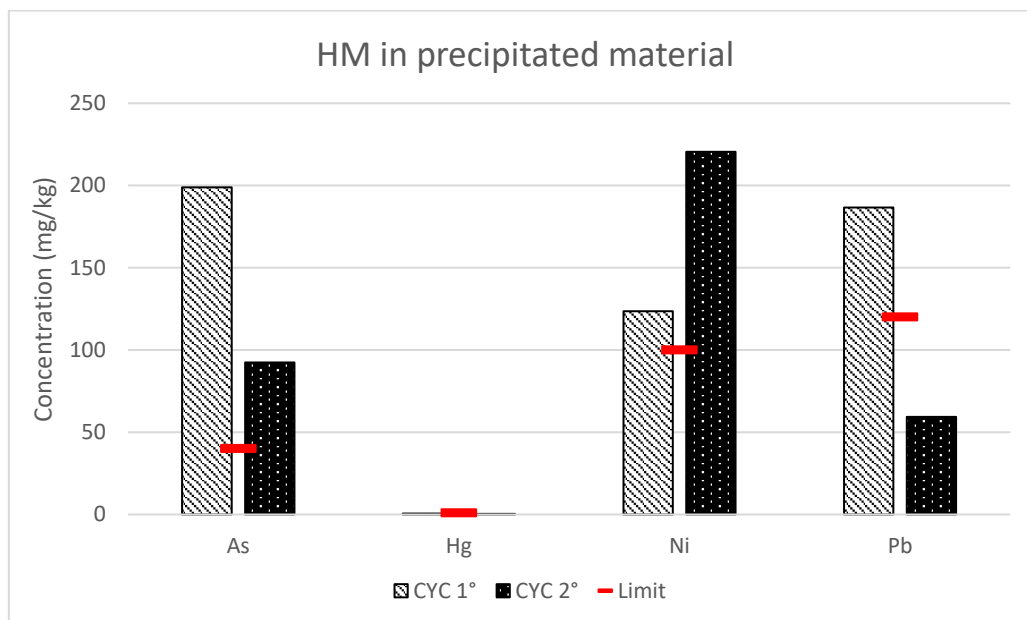
Figure 39 - Minor toxic metals in precipitated material for CYC.

Figures 40 and 41 show the element content of samples for all reagents. In Figure 40 the increases in Ca concentration after pH 3.5 is due to using Ca(OH)$_2$ as the precipitant reagent. They show that by increasing pH the concentration of undesired element increase and consequently P concentration decrease. The fact that each compound has its own behavior to precipitation and dissolution can be explained by their different solubility product constants. For example, ferric and ferrous iron has low solubility, and calcium phosphate is more stable, Fe precipitates rapidly. Aside from salt solubility, the kinetics of a precipitation phase may have a significant impact. Due to faster reaction kinetics, other less stable species can form in the as opposed to a stable phase (CEEP, 2001).

Element composition in the precipitatted material with NaOH + Ca(OH)2

	pH 2.5	pH 3.5	pH 5	pH 8
■ Other elements	67%	72%	62%	42%
⊞ Zn	0.25%	0.12%	0.20%	0.24%
■ Cu	0.05%	0.03%	0.11%	0.11%
▯ Fe	8%	3%	3%	2%
□ Ca	1%	1%	9%	34%
▨ Al	4%	8%	9%	7%
▯ P	20%	16%	17%	14%
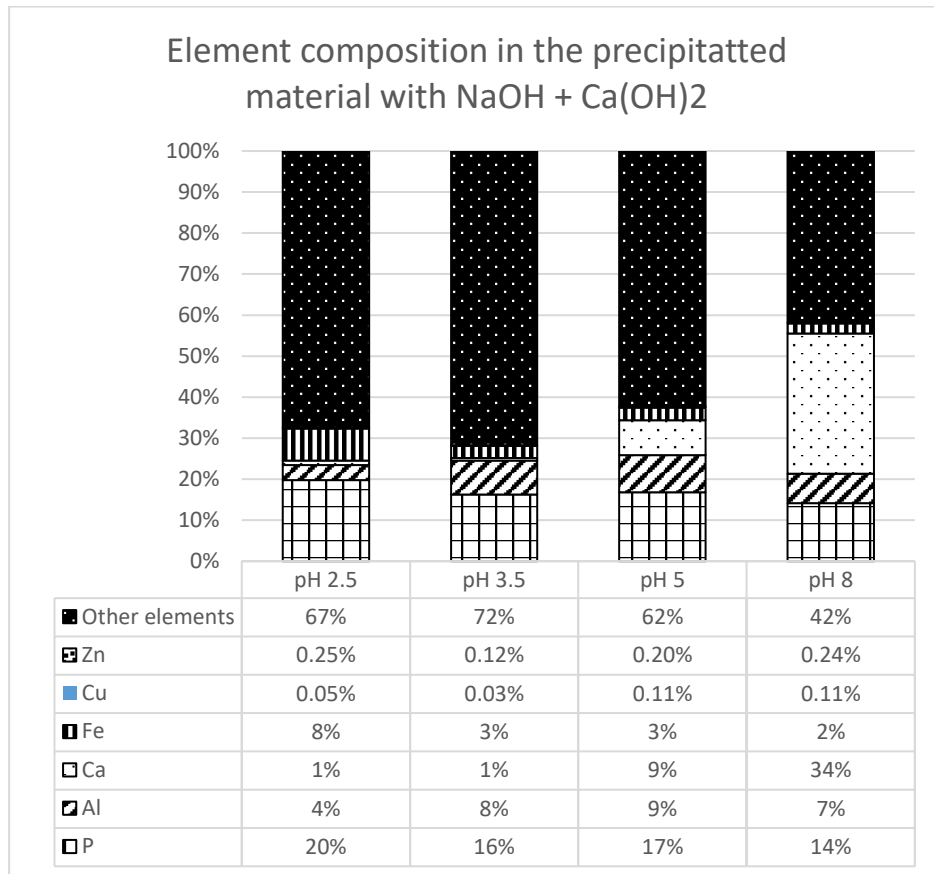
Figure 40 - Element composition in the precipitated material with NaOH + Ca(OH)$_2$.

Element composition in the precipitatted material KOH

	pH 2.5	pH 3.5	pH 5	pH 8
■ Other elements	63%	71%	71%	71%
⊞ Zn	0.39%	0.13%	0.19%	0.27%
■ Cu	0.07%	0.02%	0.10%	0.12%
▯ Fe	9%	3%	3%	3%
□ Ca	2%	1%	1%	3%
▨ Al	5%	8%	9%	8%
⊞ P	21%	17%	17%	15%
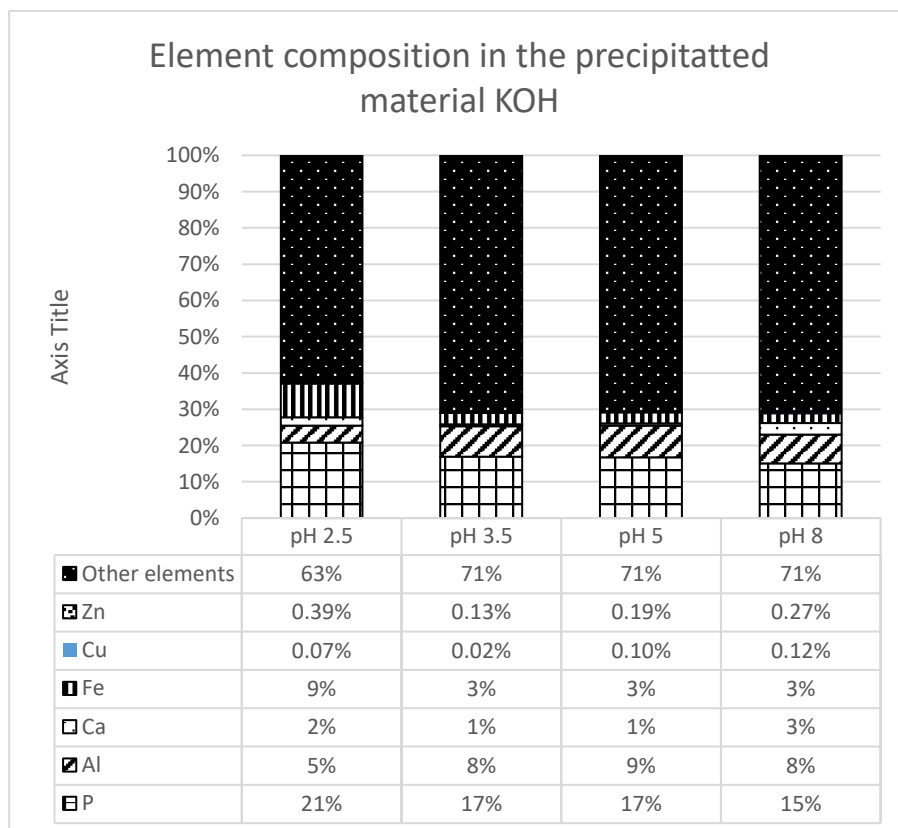
Figure 41 - Element composition in the precipitated material KOH.

In the precipitation process, the critical problem is eliminating iron and aluminum phosphate production while increasing the pH value. According to Le Châtelier's principle, the presence of specific ions or oversaturation can change the balance conditions to certain products. The conditions for calcium phosphate precipitation are improved by adding excess calcium ions to the leachate. The addition of calcium ions must be followed by an increase in pH to promote the precipitation of calcium phosphates since the deposition of hydroxides at higher pH levels prevent aluminum and iron phosphate formation. Consequently, calcium carbonate is an inexpensive option, providing both calcium ions and changing pH (Ehrnström, 2016). So further investigation can be done over this agent and other agents. The presence of sulfate ions remaining from sulfuric acid leaching is another issue. These ions can react in the right conditions with calcium to form gypsum (Ehrnström, 2016). Consequently, investigation over this situation would be another field for study.

5   Conclusions and further developments

The objective of this work was to study the possibility of extracting P from SSA by wet chemical extraction (based on acid leaching) with a focus on the precipitation step (by base dosage). As the goal is to use recovered P as a fertilizer, the final product must respect the legislation about the limits of toxic elements in fertilizer. The recovered materials need to be plant available and consider the environmental and economic aspects of the process. For this reason, by evaluation of different methods for P recovery, the current approach was chosen, and experimental results are summarized:

- Acid leaching experiments proved that the finer the SSA, the more is the extraction efficiency; since finer particles have a higher specific contact surface, they can improve the interaction between the solid and liquid phases.

- Acid leaching had a very good PEE; also, a high extraction efficiency for undesirable elements was obtained.

- In the precipitation step, by increasing the pH up to 8, almost all of the P was precipitated, as well as many other undesirable elements.

- As in pH 2.5 few amounts of P were precipitated, and in pH 5 and 8 the recovered materials had a lot of unwanted elements, pH 3.5 is considered as the optimum pH value because it had a reasonable P and undesirable elements extraction efficiency.

- Increasing rest time after precipitation step only affected pH 2.5. Therefore, 2 h can be the optimum rest time, which is also applicable for industrial scale.

- Different types of reagents with various molarity and the type of methods used for precipitating materials led to the same result. However, using a single reagent is preferable because using several reagents can increase capital and operational costs on the industrial scale. In addition, as 0.1M is stronger than 0.05M, less amount of base solution is needed. It should be noted that choosing of the reagents depends on their price.

- Finally, high enriched phosphorus product was obtained (mean value of 16%), but toxic elements were beyond the limits.

In the view of guaranteeing the regulatory compliance, dedicated treatments are needed. Some toxic elements can be separated before precipitation from leachate. For example, Fedje (2012) evidenced that by using solvent extraction reagents based on oximes, Cu can be retrieved (>90%) from MSWI (Municipal Solid Waste Incinerators) fly ash leachates. Another option could be chemical precipitation, ion exchange, or adsorption may purify P leachate. The base solution can be used to extract P instead of acid because most metals(loids) are not soluble in the base solution, but as this sample had the relevant amount of Ca, pretreatment of samples by acid is expected to reduce Ca concentration in the SSA (a few amounts of P can be extracted as well). It is proposed that before

starting the leaching test, the pre-treatment of ash should be performed. For example, by using ethylene diamine tetra acetic acid (EDTA), large amounts of metal(loid)s can be extracted, although some P will be lost. It follows acid leaching (sulphuric acid) to extract P from treated ash (Fang et al., 2018b). Perform selective precipitation using reagents such as EDTA, and citric acid to bound unwanted metals in the solution (Fang et al., 2020).

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Appendix A: Technologies for phosphorus recovery from SSA.

Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
AshDec (Depollution and Rhenania)	Thermal treatment	Depollution: Chloride additives (e.g., $MgCl_2$) are added to the sewage sludge ash before thermal treatment at 850-1000 °C to promote heavy metal decontamination. After a reaction time of about 20-30 minutes, a metal such as Cd, Cu, Hg, Pb, Zn can react with chlorines forming metal chlorides. As a result, the gaseous formed can easily evaporate, resulting in an excellent heavy metal removal efficiency (90-99%). Rhenania: A sodium carrier, usually Na_2SO_4, is added to sewage sludge ash in the rotary kiln at 900 °C for promoting the formation of a more soluble Ca-P compound. Using a retention time of about 20 minutes ensures the formation of $CaNaPO_4$, known as Rhenania phosphate. Due to the lack of chloride dosage, a lower depollution rate with respect to the Ashdec Depollution process is usually achieved (Cu: none, Cd:80%, Pb:50-70%, Zn: partial). 98 % of the input ash arrived in the form of granules toxic substance, while 2% of the input ash stays in the air pollution	~100% Related to P-flow	Calcined phosphates or Rhenania phosphates ($CaNaPO_4$, a highly citrate-soluble compound. P_2O_5 content of 15-20% depending on the input ash)	Semi-industrial (Pilot plant treating about 300 kgSSA/day)	Pros: - High plant availability of the ash-borne phosphates. - Effective heavy metal removal. - High P-recovery rates. - Effective fertilize. - The highest recovery rate among all technologies (98 wt.-%) and consequently lowest waste stream (2‑3 wt.-%). - Usage of biological or chemical phosphorus removal makes no problem for this technology. Consequently, don't need any upstream modification, only avoid dilution of P-concentrations by mixing municipal with industrial sludges or ashes. - Easily fit any modern sludge-to-energy plant. - The footprint of phosphate fertilizer over the environment is less than conventional mineral fertilizers or recycled organic fertilizers. - The concentrations of cadmium and uranium are 80‑99% lower. - No chance of transferring organic contaminants to the food and feed chain exists compared to organic fertilizers. - The lack of free acids enables urea and organic fertilizers to blend without undesired reactions. -phosphate supply on demand of crops due to releasing phosphorus only in the presence of crop root exudates avoiding P losses by runoff, leaching, and fixation - Water-insoluble but highly soluble in neutral citrate ammonium. Specific characteristics that the product has in common with thermo-phosphates produced from phosphate rock may favor its application in specific climatic and soil conditions. - TRL 7 Cons:	(Schaum, 2018 Chapter 27 and 31) (Egle, 2017)

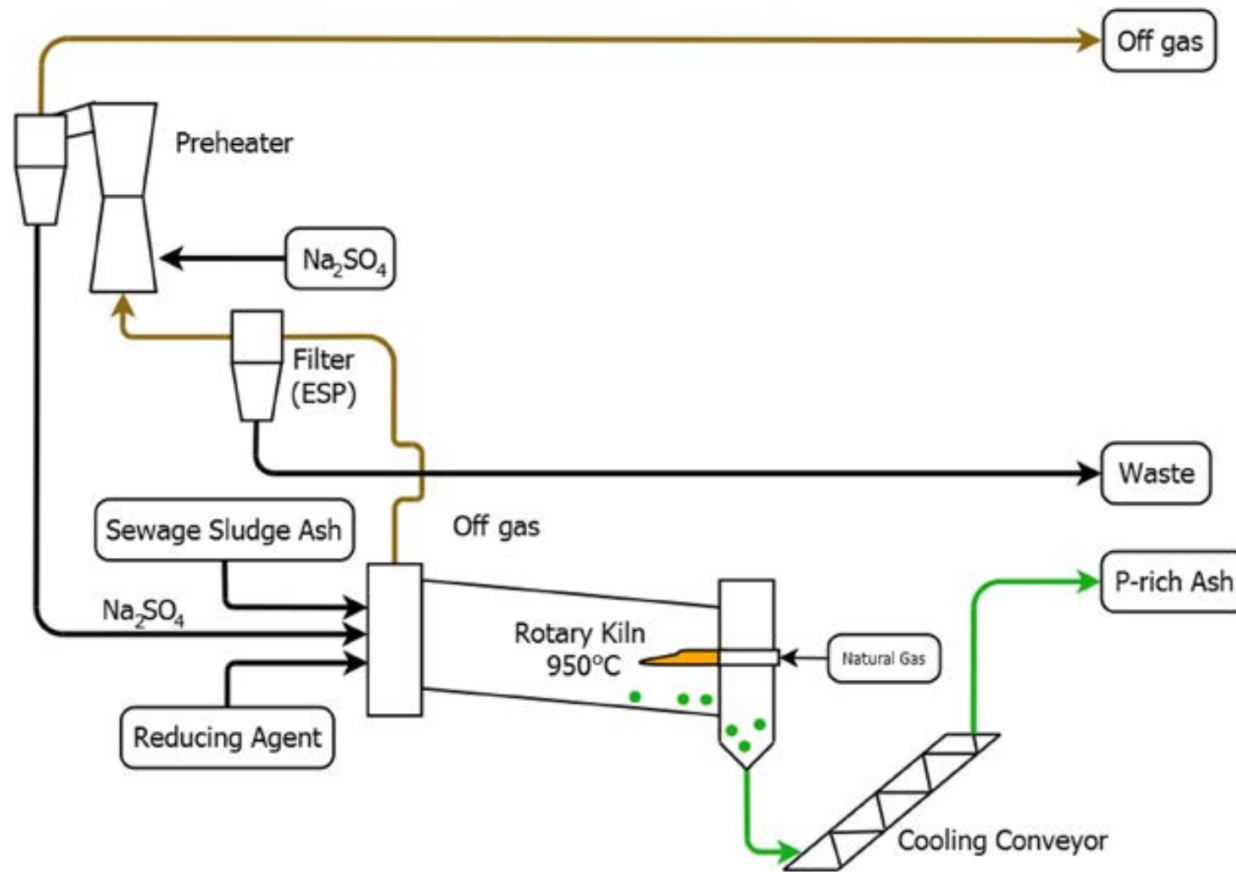| | | control system in a metal concentrate form.

A good off-gas treatment is required (e.g., Electrostatic precipitator, baghouse filter). The ashes retained from the filters (fly ash) are considered as a waste (small stream, for the Rhenania process, around 3% of the input material). In contrast, the bottom ash is a P-rich material. In order to meet the legal requirements for fertilizers application, the P-raw product obtained from the process can be blended with other nutrients such as N, K, S. | | | | - Expensive
- High energy requirement
- Gas emission
- Complicated
- Not direct applicability of the recovered products | |

Figure 42 – AshDec.

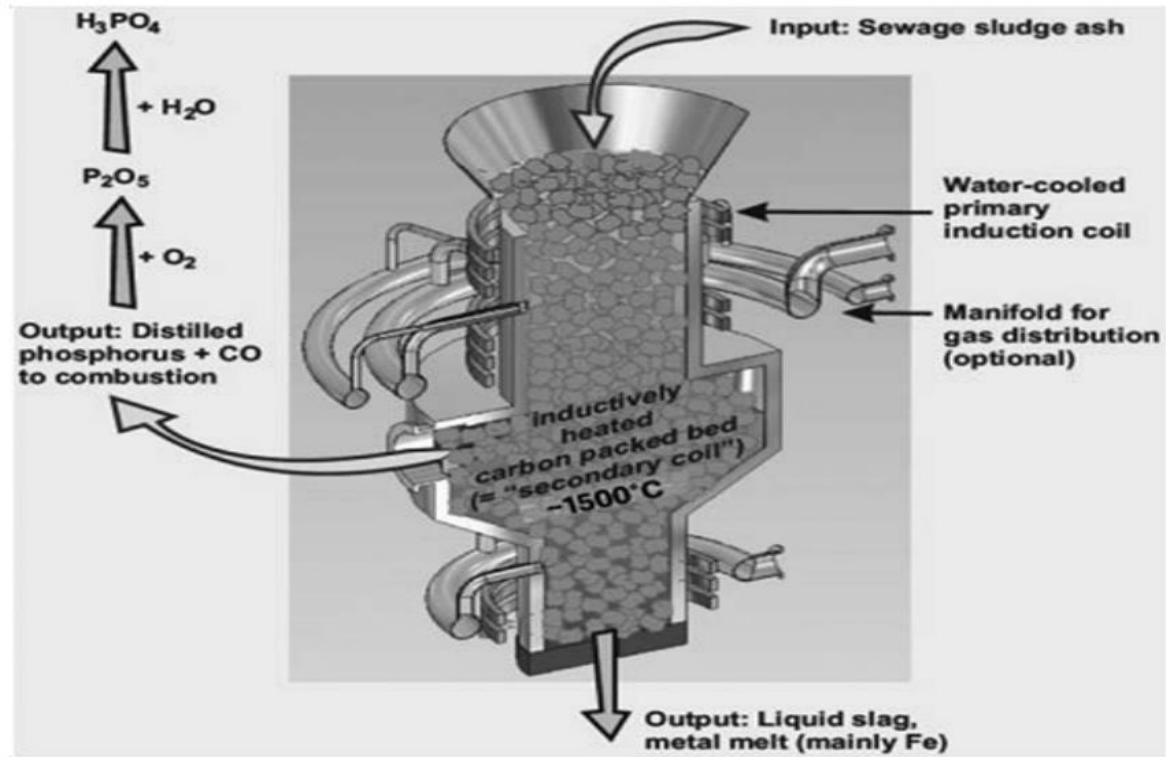| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
RecoPhos InduCarb	Thermal treatment	RecoPhos is based on the extraction of gaseous phosphorus (P_4) from sewage sludge ash by a thermal process under a reducing condition at 1500 °C in the InduCarb reactor. The following equation indicates the main reaction: $Ca_3(PO_4)_2 + 3SiO_2 + 10C \rightarrow 3CaSiO_3 + 10CO + 2P_4$. The packed bed of carbon (susceptors) is heated inductively. The ash is fed from the top of the reactor, melt, and release gaseous P_4, CO, and other volatile elements in the absence of oxygen. The gaseous phosphorus can oxidize, which leads to phosphoric acid (H_3PO_4) or condensed to produce white phosphorus (P_4). Liquid and non-volatile parts of the material will collect at the bottom as silica slag and Ferro-phosphates, which are products that can be used or go to the market. A flue gas treatment module is required to remove heavy metals that are vaporized.	80% related to P-flow	P_4, H_3PO_4	Pilot plant testing in Austria (10 kg SSA/h)	Pros: - Final product is valuable. - Possibility of installing decentralized production facilities due to the comparatively low ash treatment capacity and related investment cost points to a significant potential of the new process. - All by-products have a positive value - Can be used directly without any other process. - Silica, which is necessary for slag building is already present in sludge ash, but in phosphate rock, need to add it - Fully plant available - Applicability - High recovery rate - TRL 9 Cons: - Energy consumption is higher than most of the other technologies - Capacity of the reactor is 1500 tons P4 per year, so need InduCarb reactors in parallel - Expensive in case of implementation and operational cost	(Schaum, 2018 Chapter 15, 29, and 32) (Egle, 2017)

Figure 43- RecoPhos InduCarb.

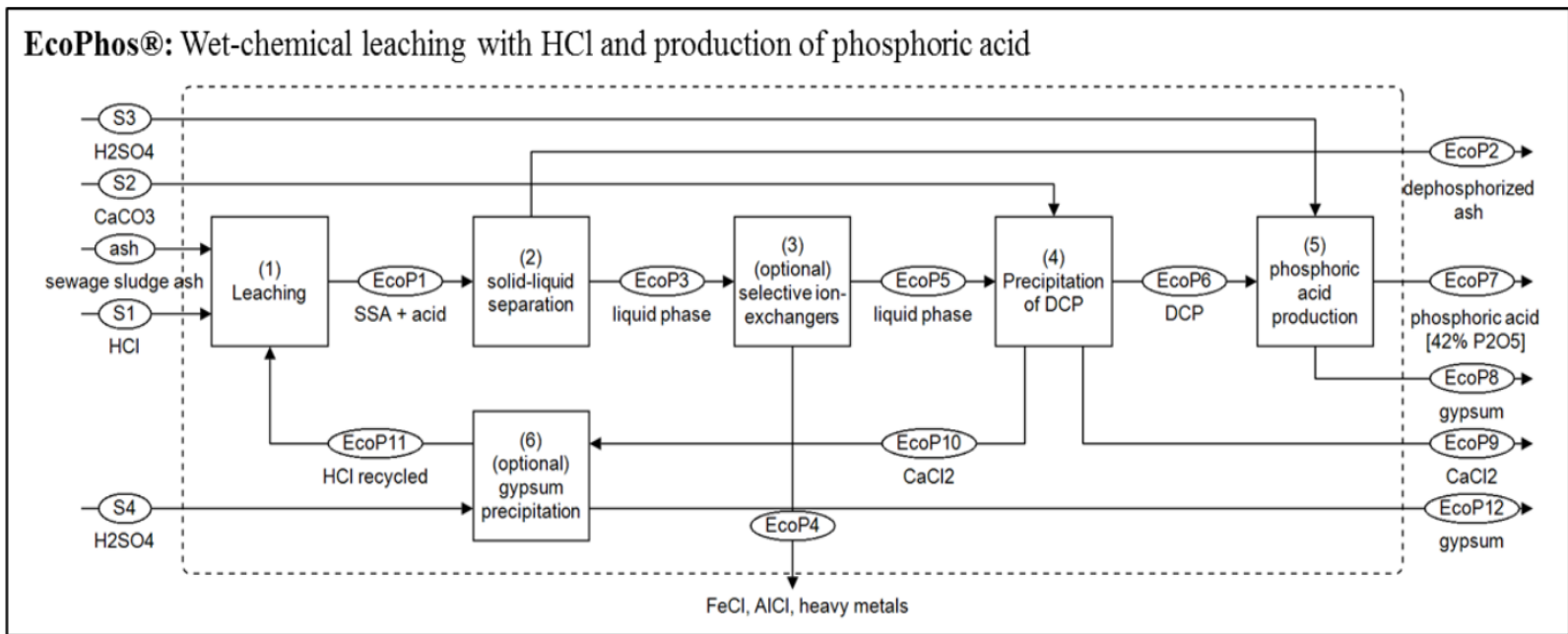| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
EcoPhos	acidic wet-chemical leaching	First, to dissolve phosphates, sewage sludge ash can be combined with HCl, H_3PO_4, or H_2SO_4 in a digestion reactor. The filtrate can be purified from heavy metals using a multiple ion-exchanger module after a solid-liquid separation device, and the solid residue is treated as a waste. Then, DCP can be produced by adding calcium carbonate ($CaCO_3$) to the leachate, which have already purified. It can be used directly or as a preliminary material to produce phosphoric acid (H_3PO_4). A fraction of H_3PO_4 will be used again in the leaching process, and the others to achieve the right conditions for the market will concentrate by a steam unit (62% P_2O_5). If are interested in producing gypsum, can add Sulfuric acid (H_2SO_4) to the last stage.	90% related to P-flow	H_3PO_4	Full-scale (Dunkerque, France) using low-grade phosphate rock as input material, producing 220,000 tons/y of DCP)	Pros: - By-products are valuable like Calcium chloride ($CaCl_2$), gypsum, silicate, iron- and aluminum chlorides. - It is compatible with any quality of ash, and it can be said that the only limitation is that it must have a certain amount of phosphorus. - The liquid phosphoric acid is the production of the EcoPhos operation, which has a good commercial value. - Great depollution of heavy metals but lower recovery capacity - TRL 9 Cons: -High CO_2 emissions -High cost of implementation and operating cost -Waste stream needs to be treated	(Ohtake and Tsuneda, 2019, Chapter 1 and 14) (Egle, 2017)

Figure 44- EcoPhos (HCl leaching).

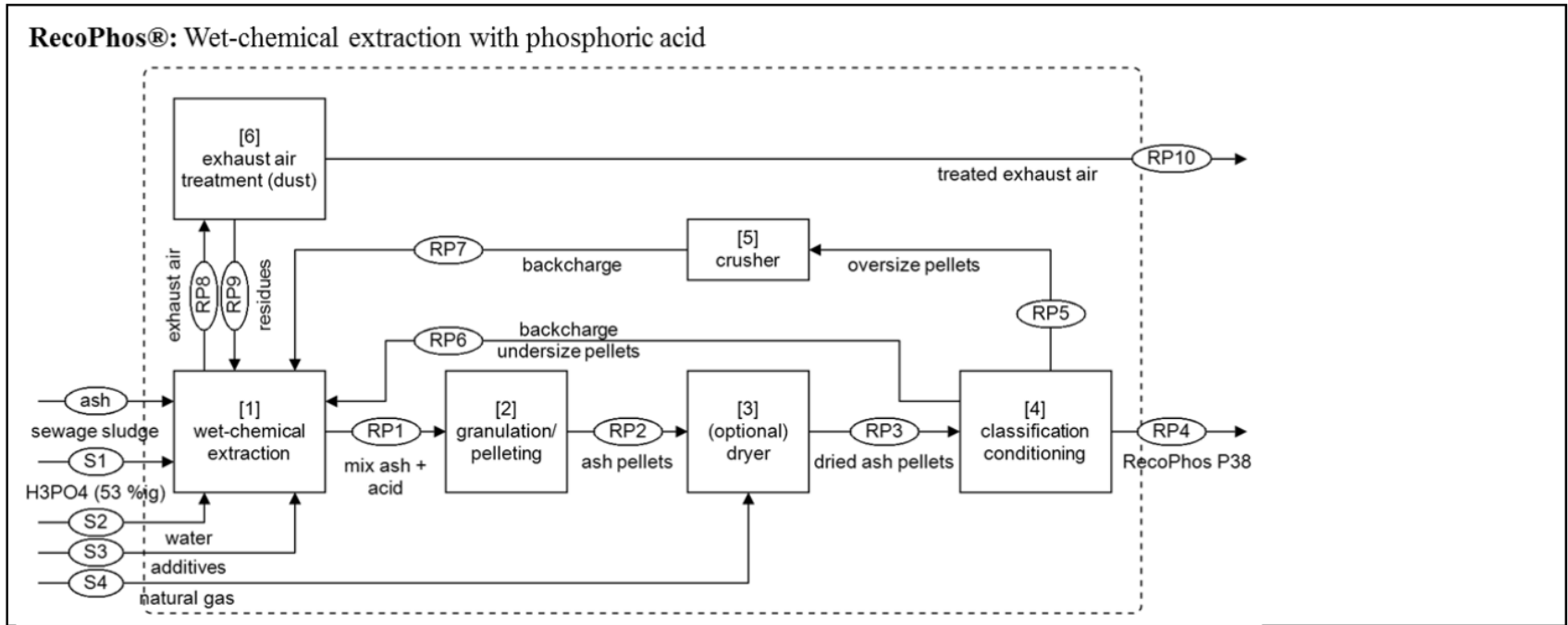| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
RecoPhos-P38	wet chemical extraction	The plant-available phosphate fraction is increased by the reaction of SSA with phosphoric acid (H3PO4). According to the elemental composition of sewage sludge ash, the following formula can be assumed. $Ca_4Mg_5(PO_4)_6 + 12H_3PO_4 + 2H_2O$ $\rightarrow 4Ca(H_2PO_4)_2 + 5Mg(H_2PO_4)_2 + 12H_2O$ The primary minerals are then converted into soluble calcium and magnesium dihydrogen phosphate, which are the main nutrient of the fertilizer RecoPhos P 38. This method consists of the manufacture of Triple Superphosphate with SSA instead of phosphate rock.	~100% related to P-flow	Mineral fertilizer	Industrial-scale	Pros: - The product is marketable. - water-soluble - TRL 9 Cons: - Need high-quality SSA - Almost the entire heavy metal load is transported to the product via the wet-chemical extraction processes Because of the absence of a decontamination stage. So this method is only applicable to ash-grade fertilizer.	(Weigand et al., 2013) (Egle, 2017)

Figure 45 - Recophos P-38.

Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
ICL fertilizer industry	wet-chemical extraction	Recovered phosphorus products are used as an alternative to phosphate rock in the fertilizer industry. During leaching of phosphate rock, it is possible to reach different products by changing acid or adding different materials. By using sulfuric acid, phosphoric acid, or combinations of both, by adding potassium chloride (MOP) or potassium sulfate (SOP) trace elements (Cu, Mg, Mn, Mo, Zn, etc.), can get a different kind of PKs. Also possible to use ammonium sulfate to produce NPKs. These methods are very good for secondary phosphate processing without any safety problems (contrary to other NPK processes). Usually, two kinds of secondary phosphates can be used in phosphate fertilizer production. one fraction from mono-incineration such as meat and bone meal ash, wood ash, sewage sludge ash the other is Struvite	100% related to P-flow	single super phosphate (SSP)	Industrial-scale	Pros: - MBMA (Meat and Bone Meal Ash) process would not face any environmental or biological danger, yet even decreases pollution due to the absence of fluoride and other gas-forming compounds. - In processes such as the ICL fertilizer industry, the use of Struvite as a raw material can decrease the risks of contamination to almost zero, as the Struvite will be subjected to a very acidic atmosphere and a high dryer temperature, eliminating all viruses and bacteria. - As MBMA and SSA (sewage sludge ash) have lower cadmium in comparison to most phosphate rocks, the finished goods containing a lower amount of cadmium. - Meat and bone meal ashes are the best applicable at the moment - By incorporating SSA into the fertilizer manufacturing process (fertilizer industry), negative CO_2 emissions can be detected due to positive H_2SO_4 credits. - TRL 9 Cons: - The main problem left is the regulations on the use of the outlets, which are currently perceived as waste. Struvite is also known to absorb pollutions encapsulated in its crystals, such as pathogens and pharmaceuticals. - Lack of depollution unit. - Struvite's processability varies as odor emissions and moisture content differs. These are concerns that should be held in mind, and each source of Struvite should also be independently checked and examined.	(L. Egle et al., 2016) (Ohtake and Tsuneda, 2019, Chapter 6 and 16)

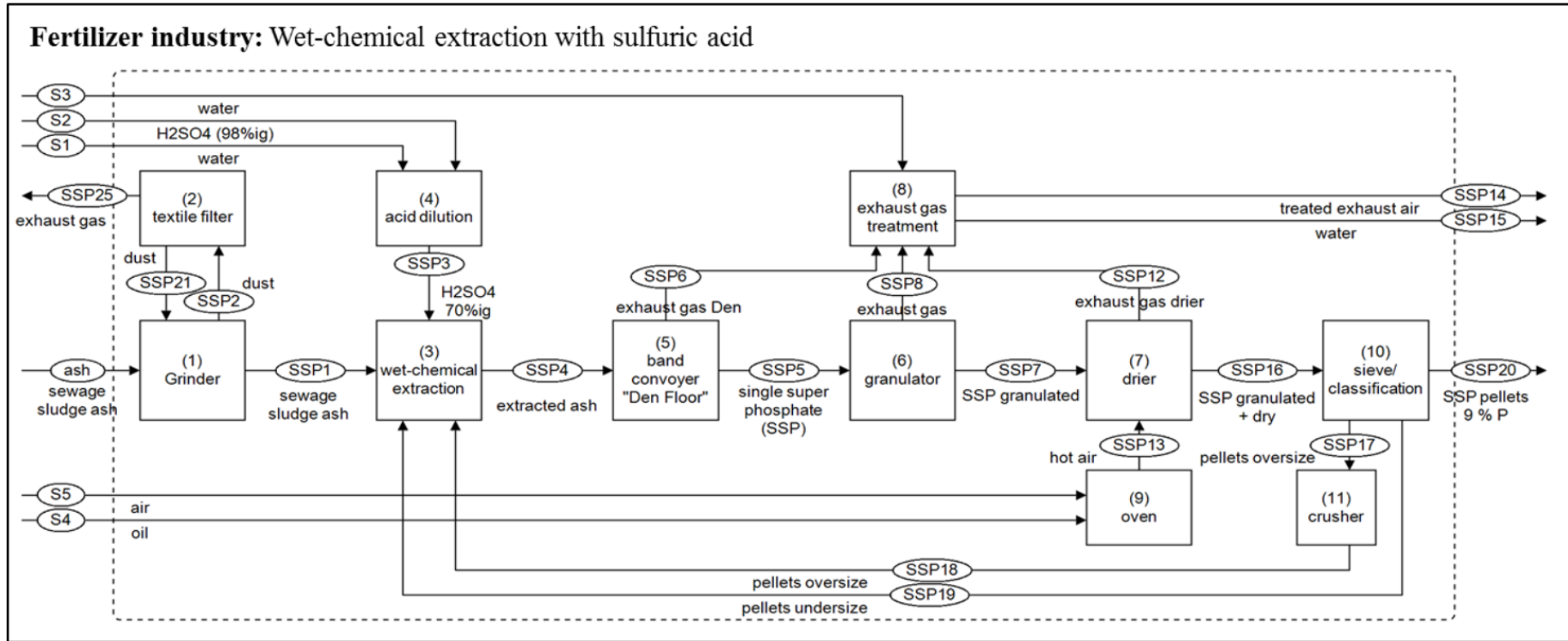| | | | | | | | - Using Struvite can decrease the emissions of fluorine and phosphate but smell issues from co-crystallized organic material | |

Figure 46 - ICL Fertilizer industry

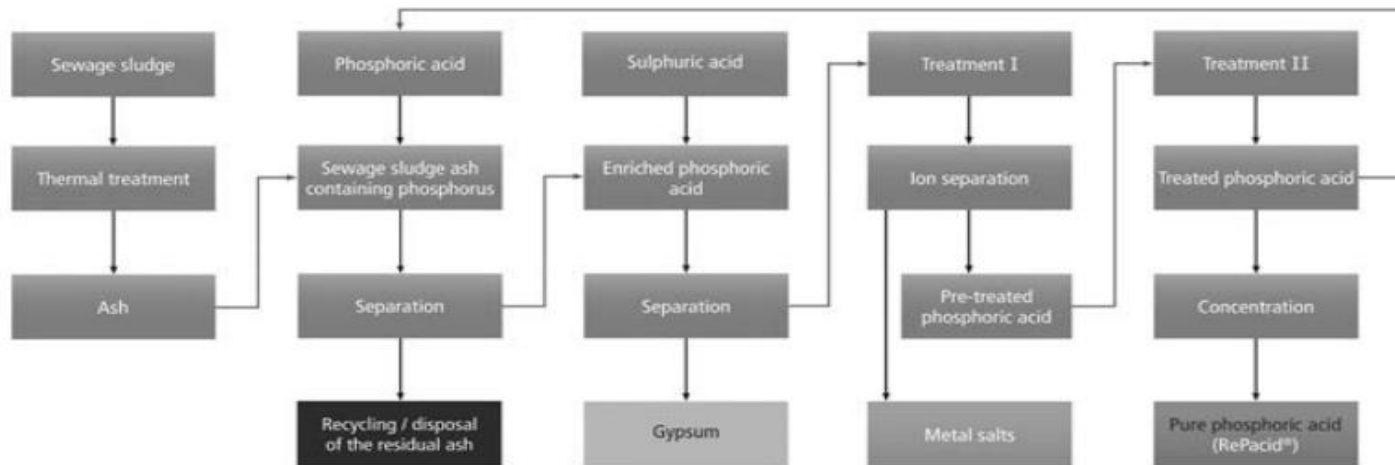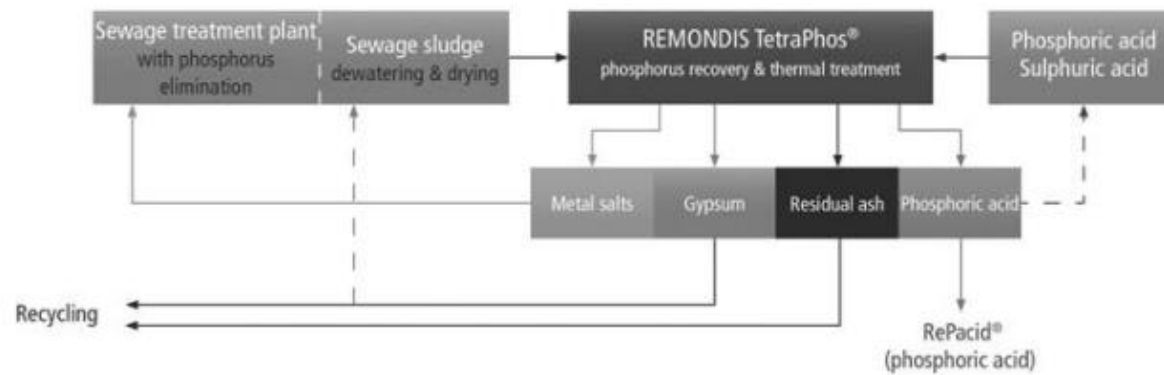| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
TetraPhos	Acid wet chemical leaching	Sewage sludge ashes are mixed with H_3PO_4 to dissolve phosphorus. Then H_2SO_4 is added to the liquid fraction to precipitate gypsum after solid-liquid separation. Additional treatments can be applied to purify the remaining liquid fraction by ion-exchangers. Metal salt solution (FeCl, AlCl) is generated by the regeneration of exhausted resins with HCl. It can be potentially used and recycled as precipitating agents in the chemical P-removal process at wastewater treatment plants (WWTP). At last, the produced H_3PO_4 can be concentrated.	90% related to P-flow	H_3PO_4	Pilot plant	Pros: - This method is commercially viable can be put down to the quality and the quantity of the marketable phosphoric acid - Highly pure phosphoric acid - For chemical precipitation of P in WWTP, it is possible to recycle metal salts (by-products of the process). Cons: - Lack of heavy metal decontamination step	(Egle, 2017) (Schaum, 2018 Chapter 24)

Figure 47 – Tetraphos.

Figure 48- Example: Integrating phosphate recovery into the City of Hamburg's WWTP.
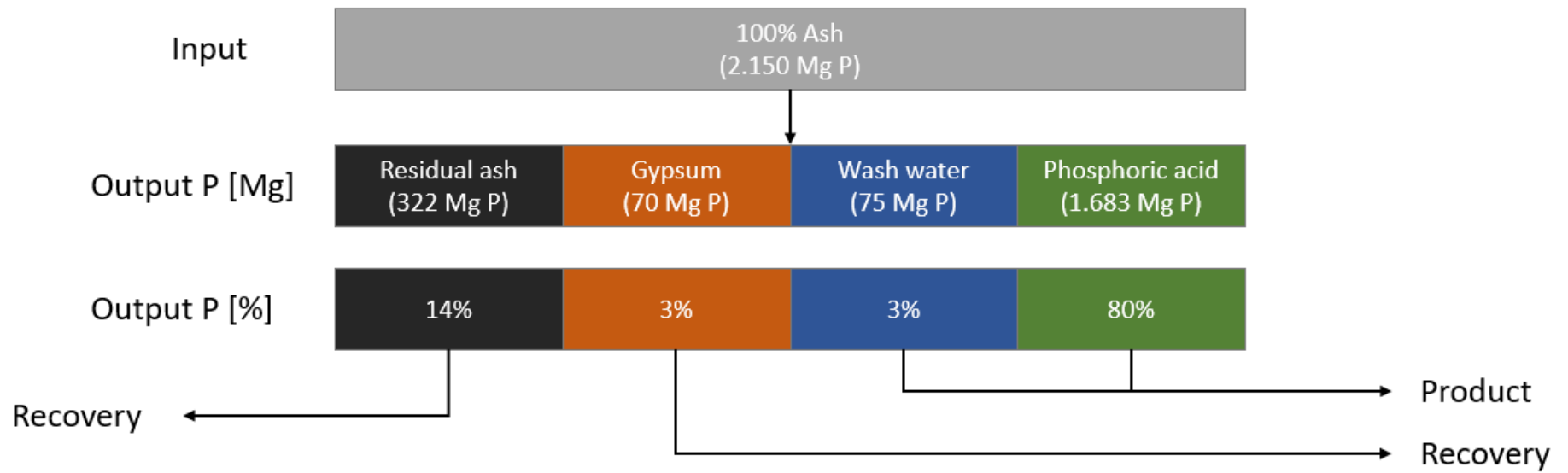
Figure 49- Phosphorus recovery at REMONDIS' TetraPhos® pilot plant at HAMBURG WASSER.

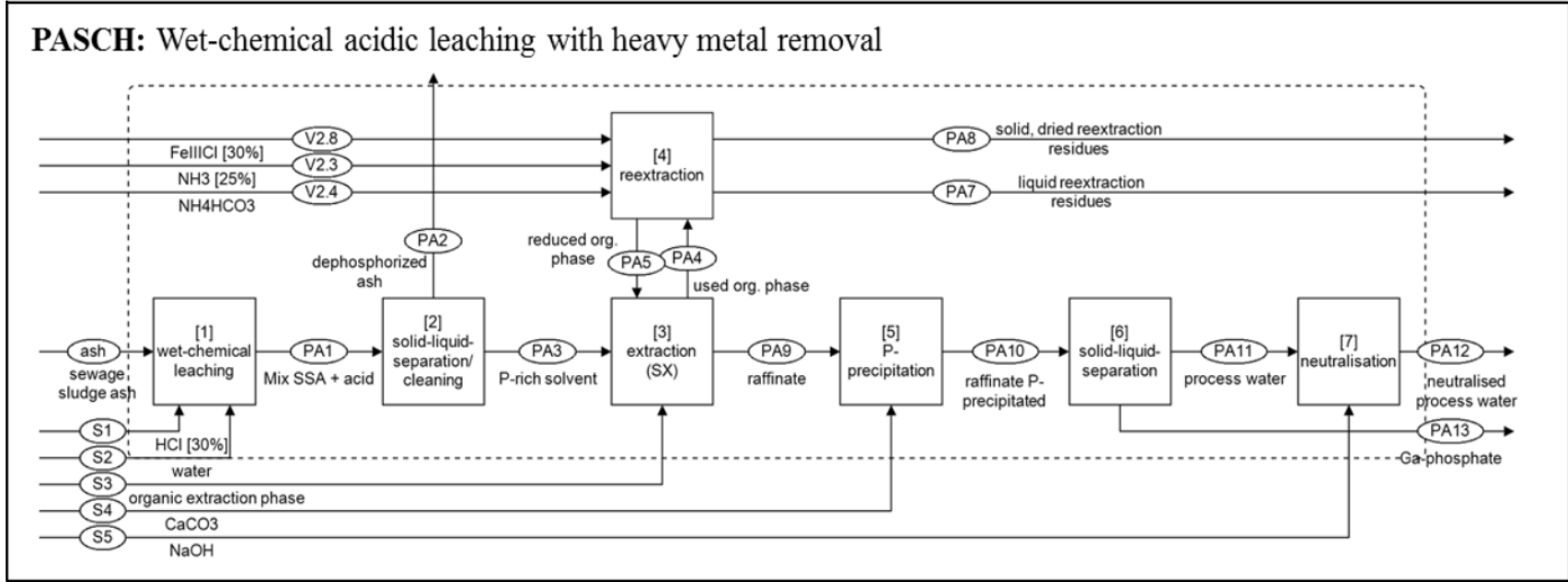| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
PASCH	Wet acidic leaching	In the first step of the process, SSA is mixed with an acid (HCl) for a sufficient contact time. Then, after a solid-liquid separation unit, the P-rich solvent obtained is subjected to the organic extraction phase for selective HM removal. Cd, Cu, Pb, Zn, and Fe can be efficiently removed at a rate of 80–99%, while Al, Cr, and Ni remain in the treated leach liquor. A re-extraction stage is usually applied to decontaminate the heavy-metal-rich solvent phase, producing solid and liquid residues that can be used in heavy metal removal. The last phase is related to the precipitation step: 98% of P passes through the solvent extraction stage and then precipitates as calcium phosphide (CaP) by adding lime and NaOH. After the solid and liquid separation, the supernatant from the precipitation process needs to be neutralized.	70-80% related to P-flow	CaP	Laboratory scale	Pros: - High rate of heavy metals removal from the ashes. - TRL 5-6 Cons: - In neutral and alkaline soils, the bioavailability of the recovered calcium phosphate content is slightly lower, while the calcium phosphate material is soluble in citric acid. - CED (cumulative energy demand) is in the range of 60 kWh kg P-1 and is higher relative to a fossil fertilizer based on raw phosphate rock - Higher costs and lower recovery potential compared to other technologies -High CO_2 emissions	(L. Egle et al., 2016) (Egle, 2017) (Schaum, 2018 Chapter 31)

Figure 50- PASCH.

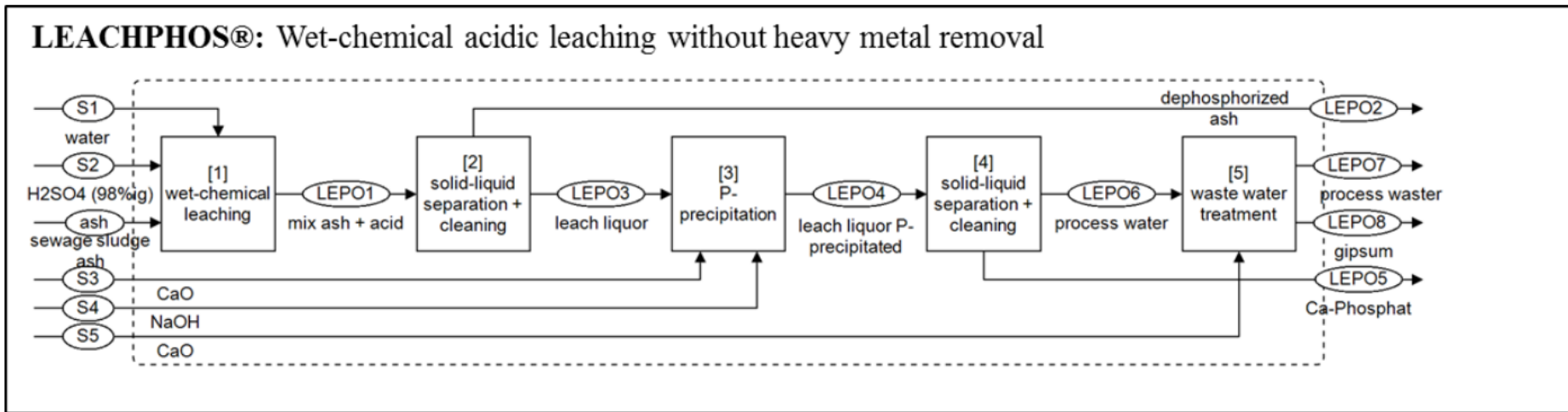| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
LEACHPHOS	Wet acidic leaching	In the first step of the process, SSA is mixed with an acid (diluted H2SO4), while in the second step, the mixed slurry produced undergoes a solid-liquid separation unit (usually filtration). The solid residue obtained corresponds to de-phosphatized ash and can be recycled or disposed of, while the leach liquor rich in phosphorus is conveyed to the precipitation unit. Finally, through the addition of NaOH and lime milk, P can be precipitated and separated from the process water through another solid-liquid separation unit.	70-80% related to P-flow	Ca-P (about 30% P_2O_5)	Pilot plant Bern (6 tons of P recovered from 45 tons of SSA)	Pros: - Good results in terms of solubility and good plant availability in both acidic and neutral soils - Applicability - High rate of removal of heavy metals from the ashes Cons: - High operation and implementation cost - High phosphorus recovery rate (80‑90% over the whole process) causes a less concentrated product, higher chemicals demand, and lower product purity. In terms of P concentration and impurities, the quality is greatly increased by reducing the recovery factor to 75-80 percent.	(Egle et al., 2016) (Egle, 2017)

Figure 51- LEACHPHOS.

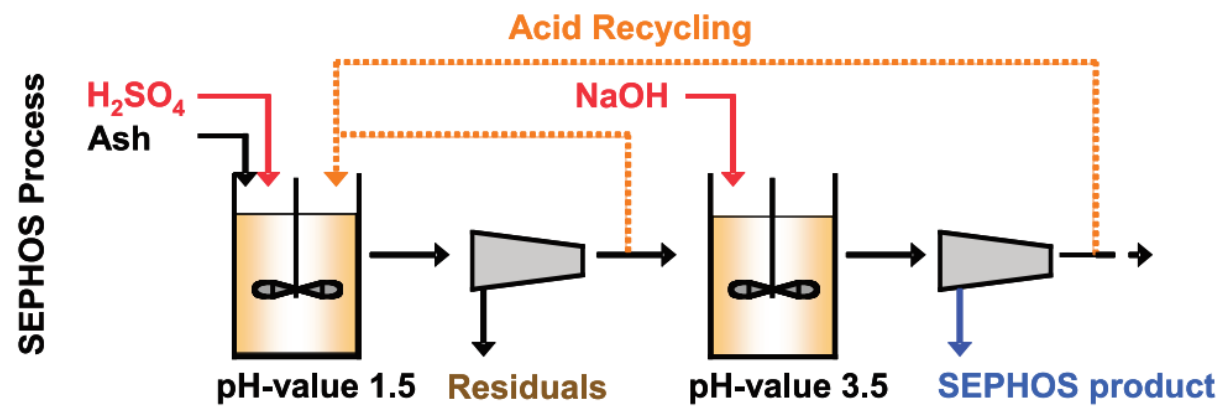| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
SEPHOS	Wet acidic leaching	In the SEPHOS (Sequential Precipitation of Phosphorus) method, as a first step, SSA is eluted with sulfuric acid. Then, after removing the undissolved residues, the filtrate's pH value is increased by dosing NaOH to induce the precipitation reactions. The pH regularly increases to about 3.5 for causing aluminum phosphate precipitation. Since copper and zinc only precipitate at a pH higher than 3.5 (around 4-5), can separate phosphorus from heavy metals. Finally, the phosphate-rich and heavy-metal depleted precipitate can be reused for different purposes (for example, Al-P material can be used in the electrochemical process of Thermphos prior to further treatment to reduce sulfur and sodium). However, according to Schaum et al. 2018, SEPHOS products cannot be used in agriculture due to the high amount of Al that can cause root destruction). To address this issue, a possible solution is the alkaline treatment of the Al-P phosphate (Advanced SEPHOS process), in which P and Al are firstly dissolved, followed by a calcium source added to induce Ca-P precipitation. Al that remains in the solution can then be recycled as a precipitant.	70-80% Related to P-flow	AlP, CaP	Lab-scale	Pros: - Aluminum phosphate” is a valuable raw material for the phosphorus industry, for example, the electro-thermal phosphorus industry. - Good heavy metal depollution. Cons: - Expensive - As SEPHOS product has high aluminum content, it is not suitable for agriculture	(Schaum et al., 2007) (Schaum, 2018) (Nieminen, 2010)

Figure 52 – SEPHOS.

Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
SESAL-Phos	wet acidic leaching	SESAL-Phos method has been designed for aluminum-rich ash, and the procedure is as follows: first, transform CaP to aluminum phosphate (Al-P) to make aluminum-rich ash by an acidic pretreatment for this purpose SSA leached by HCL to reach pH 3.5 and the residence time of 60 90 min. Then goes for a solid-liquid separation to separate acid from solid residuals, then solid phase (calcium-depleted sewage sludge ash) leached with NaOH to increase pH to 13, and as a consequence, Al-P dissolves again. About 75% of P can be dissolved, and unlike pure acid leaching, it doesn't contain (Cu, Ni, Pb, Zn) maybe a few redissolve (Cd, Cr). Then the dephosphorized ash is separated and neutralize and by adding Calcium chloride ($CaCl_2$). Almost 99% of P precipitated as hydroxyapatite ($Ca_5(PO_4)_3OH$). It is possible to use aluminum-rich supernatant in WWTP in the P precipitation unit.	70% Related to P-flow	CaP	Lab-scale	Pros: - P depolluted and recovered as calcium phosphate. - Aluminum can be recovered and reused as a precipitant. - chemical demand of the process is lower than other similar techniques. Cons: - It is not economically feasible due to its complexity and high chemical/energy demand.	(S. Petzet et al., 2011) (Sebastian Petzet & Cornel, 2012)
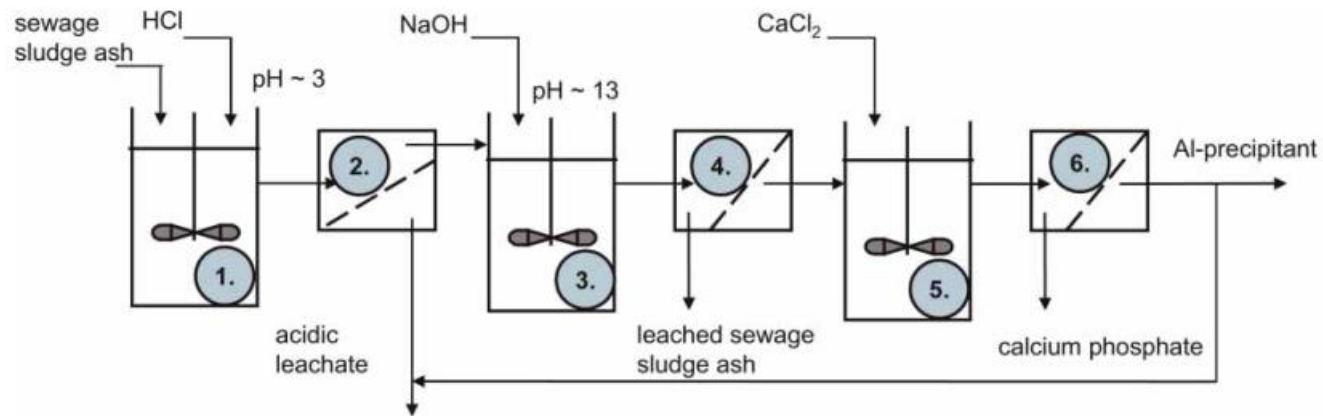
1. Acidic elution for calcium phosphate dissolution and simultaneous formation of aluminium phosphate
2. Separation of acidic leachate with dissolved Ca and heavy metals for neutralization. Precipitated heavy metals are disposed of.
3. Addition of NaOH for dissolution of aluminium phosphate
4. Separation of the alkaline leachate from the rest ash
5. Precipitation of the recovery product
6. Separation of the calcium phosphate. The dissolved Al may be reused as precipitant in wastewater treatment

Figure 53- SESAL-phos.

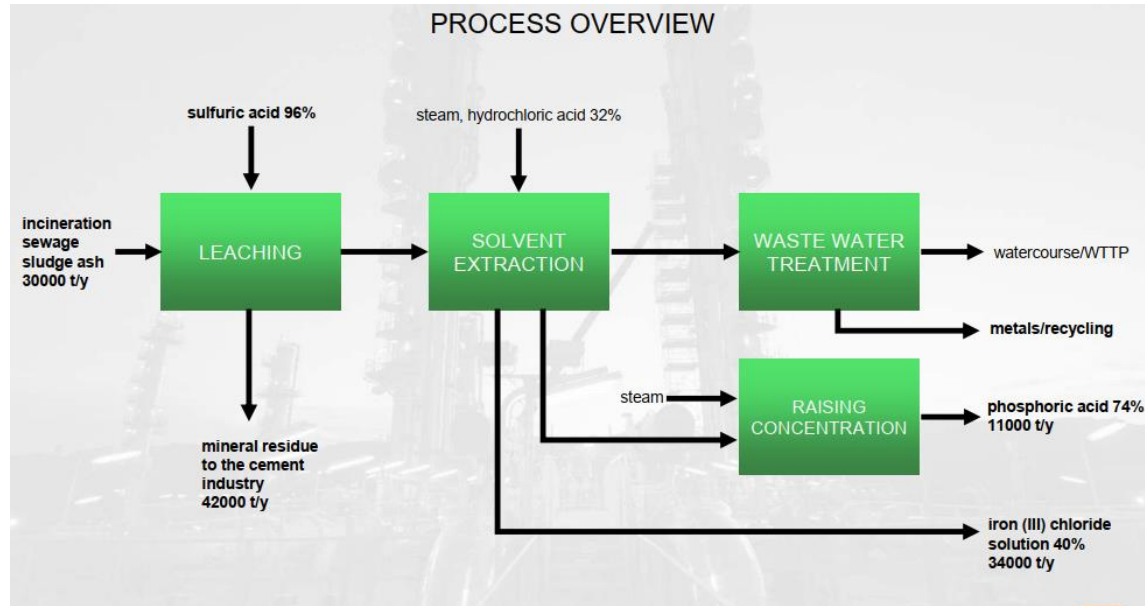| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
Phos4Life	Acid extraction	In the first step, SSA is mixed with sulfuric acid. After leaching, the solid mineral residue is sent to the cement industry, while the liquid solution goes into a solvent extraction unit using hydrochloric acid (HCl). Thanks to this unit, iron, aluminum, and heavy metals can be separated and recovered. Also, H_3PO_4 can be recovered and concentrated by evaporation.	More than 95% of P from the SSA	Phosphoric acid	Full scale	Pros: - The quality of the acid produced is like pure phosphoric acid - The goals of phosphorus recovery and resource processing of mineral residues can be entirely accomplished. - Iron recovery rate is more than 90% and can be used again in WWTP for P removal - Separated heavy metals (>85%) are extracted using current techniques in Switzerland and fed back into the flow of materials. - No structural or operational changes to the WWTP is necessary - High energy consumption and consequently high cost	(Fang et al., 2020) (Diaz Nogueira, 2017)

Figure 54- Phos4Life.

Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
Ash2Phos	wet chemical	This method is based on the wet chemical treatment of sewage sludge ash from mono-incineration or co-incineration. Phosphorus is first extracted in the form of calcium phosphate, a clean intermediate. After that, there are different ways to upgrade to consumer goods. First acid (HCl or H_2SO_4) and ash mix, in step two recyclable material separate from solution and the solution, is then neutralized, and heavy metals go for disposal. Undissolved residues, consisting mostly of silicates (sand), may be used in the cement industry after cleaning. Elements that were obtained in step two then separated from one another by a sequence of dissolution and precipitation steps. Input chemicals are recirculated internally so that their use is reduced. In the method, only lime is used. Phosphorus, iron, and aluminum are recovered in the form of the intermediate calcium phosphate, iron hydroxide, and aluminum hydroxide. In the last step of the process, the intermediates are processed into finished products. There are different choices for finishing based on the intended finished product. The intermediate calcium phosphate can be transformed into calcium chloride and ammonium phosphates (monoammonium phosphate, MAP or diammonium phosphate, DAP) by adding hydrochloric acid and ammonia in the cleanMAP process. In this process, the ammonium	90% of P-flow	Monocalcium Phosphate (MCP) Dicalcium Phosphate (DCP), Monoammonium phosphate (MAP), diammonium phosphate (DAP), phosphoric acid, Superphosphates	full-scale plant 30,000 ton/y ash in Sweden, planned 60,000 t/y in Germany Pilot plants are Sweden and Helsingborg treating 50 kg ash/day and 600 kg ash/day, respectively	Pros: - Compared to those of fertilizer quality, these ammonium phosphates are characterized by even lower heavy metal contents and complete water solubility - Recovery of clean, defined, and commercial phosphorus products (low HM content) - Recovery of Fe and Al, which are based chemicals for wastewater treatment plants - Energy-efficient process Cons: - Complicated - Difficult to manage	(Cohen & Enfält, 2018) (Kabbe & Rinck-Pfeiffer, 2019)

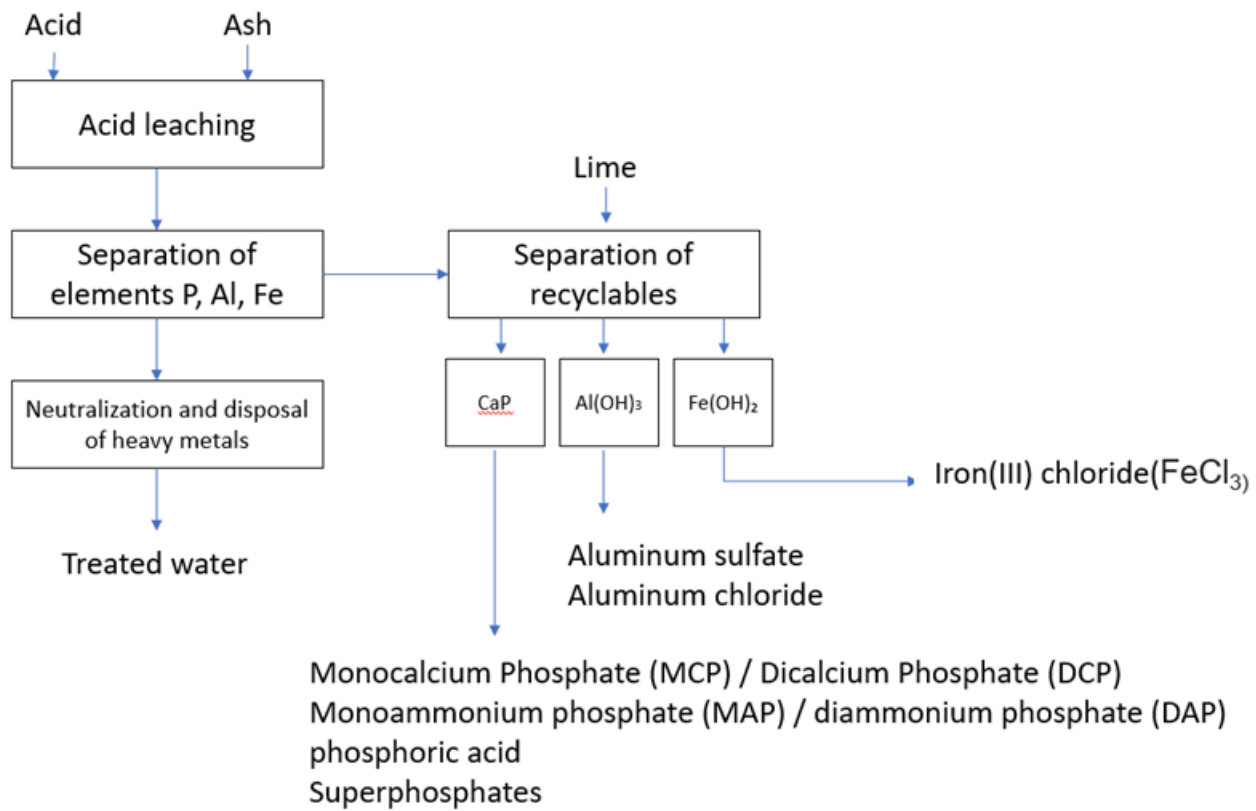|		phosphates of technical grade are produced and are pure and energy-efficient. This product has fewer metals in comparison to the fertilizer grade and is also completely solvent in water. A further refining choice is to transform the calcium phosphate intermediate to animal feed phosphates such as monocalcium phosphate (MCP) or dicalcium phosphate (DCP) by reacting with acid (phosphoric acid, hydrochloric acid, or sulfuric acid). Calcium phosphate can also be used to manufacture other phosphorus products, such as phosphoric acid or superphosphate. Precipitant iron chloride can be produced from intermediate iron hydroxide at a concentration that is customary on the market by reacting with hydrochloric acid. This can be used, among other things, as a precipitant for the removal of chemical phosphates in wastewater treatment plants. Aluminum hydroxide can be converted into aluminum sulfate or chloride by adding Sulfuric or hydrochloric acid.				

Figure 55 - Ash2Phos.

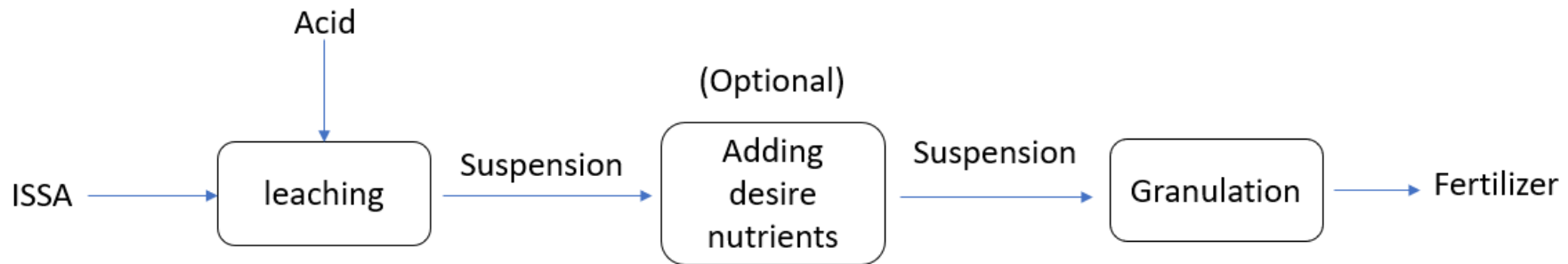| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
PHOS4green	Acid extraction	By acid leaching, a suspension gained (according to our need, other nutrients can be added), then it sprays and granulated in a fluidized bed apparatus (In order to homogenize the raw material, the phosphate conversion reaction is separate from the granulation process). In granulation, it allows liquids to be dried while at the same time creating dust-free granules with a lightweight, homogeneous shape, dense surface structure, and high abrasion resistance. In this way, valuable granules are produced, which can be used as high-quality phosphate fertilizers.		P or NPK fertilizers	Working on A full-scale plant	Pros: - 100% waste-free - Low cadmium and uranium and pollutant -High flexibility in terms of process control Cons: - HM remains in the final product	https://www.phos4green-glatt.com/

Figure 56 - PHOS4green.

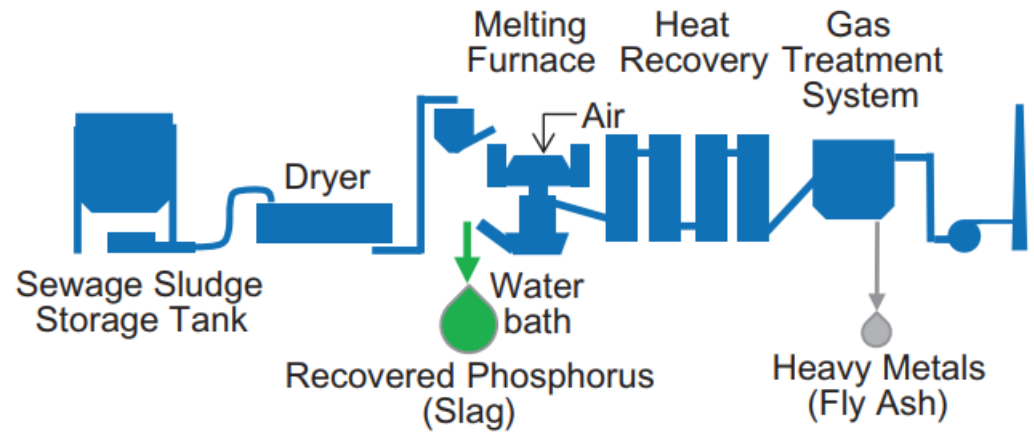| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
Kubota Surface Melting Furnace	Thermal treatment	Sewage sludge is heated at around 1300 °C, causing part of heavy metals volatilization (such as Cu and Zn), while iron oxide is applied to preserve phosphorus in solid slag. Calcium hydroxide can be applied to increase the abundance of phosphorus in slag. The KUBOTA surface melting furnace (KSMF) main reactor has a double melting furnace (KSMF). The space between the inner and outer cylinders is filled with the material to be treated, which is constantly fed into the furnace over the inner cylinder circumference by rotating the outer cylinder. The combustion area is the space near the inner cylinder. The ash portion melts and flows down through the slag port in the middle of the furnace floor. Organic matter in the sewage sludge is burning and decomposed at that temperature mentioned earlier. Based on the material process can be self-sustainable combustion (do not need external fuel). If the material is not self-sustainable (have low heating value), it is necessary to add external fuel.	90% refer to P-flow	P-containing slag	Full-scale	Pros: - Heavy metals can be separated - Sewage sludge treatment and phosphorus recovery at the same time - Good plant availability - Zero landfill Cons - High energy demand - High cost	(Schaum, 2018 Chapter 28)

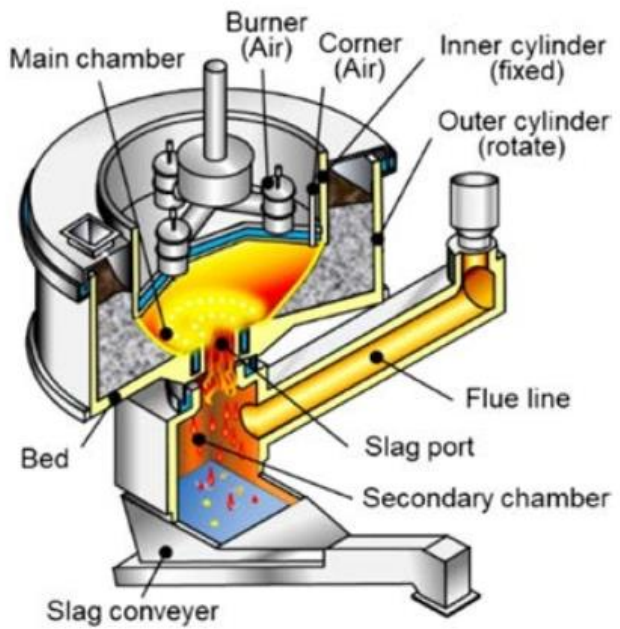Figure 57 - Kubota Surface Melting Furnace flow diagram.

Figure 58 - Sectional diagram of the KSMF.

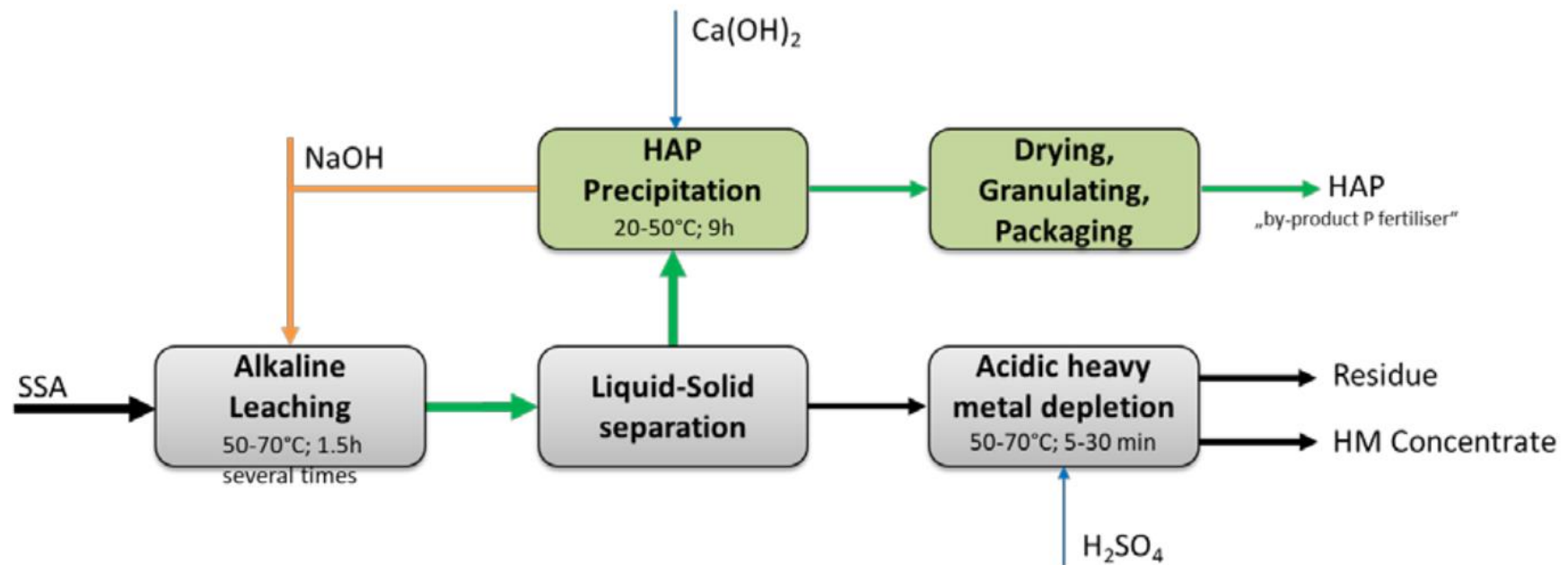| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
Metawater alkaline ash leaching	Wet chemical extraction	The first step is the leaching unit, which mixes the ash with sodium hydroxide (NaOH) at 50-70°C for 1.5 h. After a liquid/ solid unit, dissolve P Precipitated by adding Ca(OH)2 at 20-50°C for nine hours and producing HAP, then it washed, dried, and granulated. The NaOH can be recycled for use in the leaching unit again. The solid residual is treated by diluted acid H_2SO4 for 5-30 mins at 50-70°C for heavy metal extraction, then can be used in the road industry.	30% of p-flow	Calcium phosphate (hydroxyapatite)(HAP)	full-scale	Pros: - Low chemical demand - By incinerator's, surplus heat can cover process energy demand Cons: - For minimizing heavy metal extraction during leaching can recover 30% of phosphorus	(Kabbe & Rinck-Pfeiffer, 2019)

Figure 59 - Metawater alkaline ash leaching.

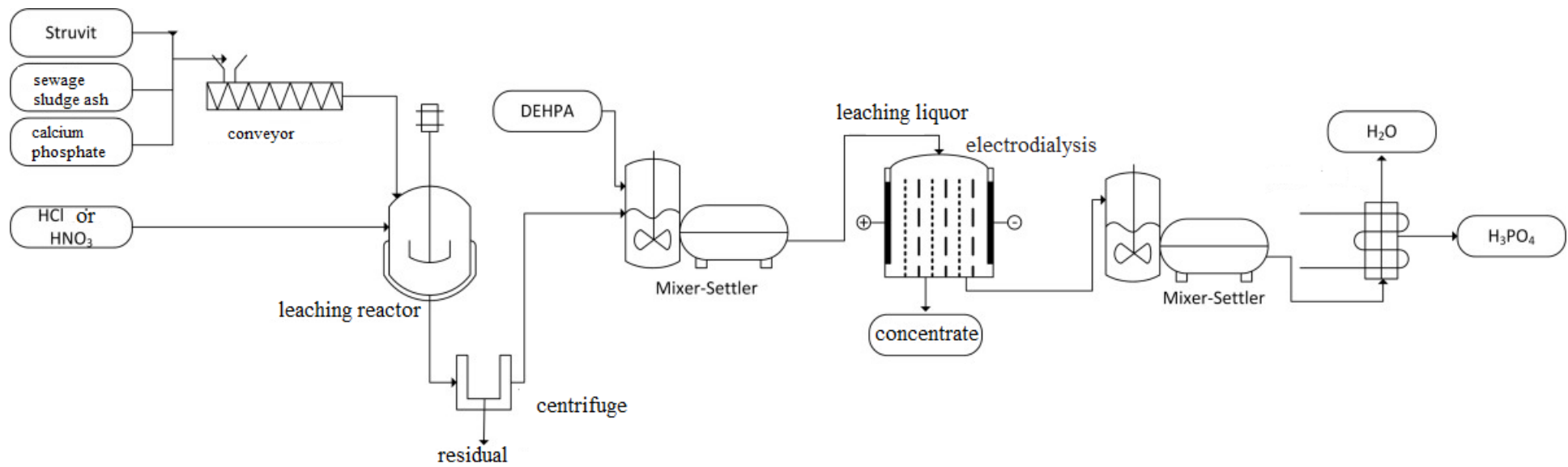| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
Parforce	Wet chemical extraction	This process is suitable for different kinds of input material: struvite, SSA, or calcium phosphate. In the first step, input material is leached by mineral acids such as HCl or HNO3 to dissolve P.In the case of using SSA, other elements such as Ca, Mg, Fe, and Al can be dissolved. Second, for purification, extract Al and Fe by DEHPA (di-(2-Ethylhexyl)phosphoric acid) or using HCl and produce iron and aluminum chloride solution to reuse them in phosphorus removal unit in WWTP. Then according to Schaum, 2018 Chapter 26." Within the electrodialysis stack, chloride ions are separated by monovalent anion exchange membranes from trivalent phosphate ions, and the remaining concentrate liquor of calcium chloride and diluted phosphoric acid is concentrated in further steps."	80% related to P-flow	Phosphoric acid	pilot plant	Pros: - Low waste Cons: - High cost - High energy demand, especially by using SSA as input material	(Schaum, 2018 Chapter 26)

Figure 60 – Parforce.

Appendix B: Technologies for phosphorus recovery from SS.

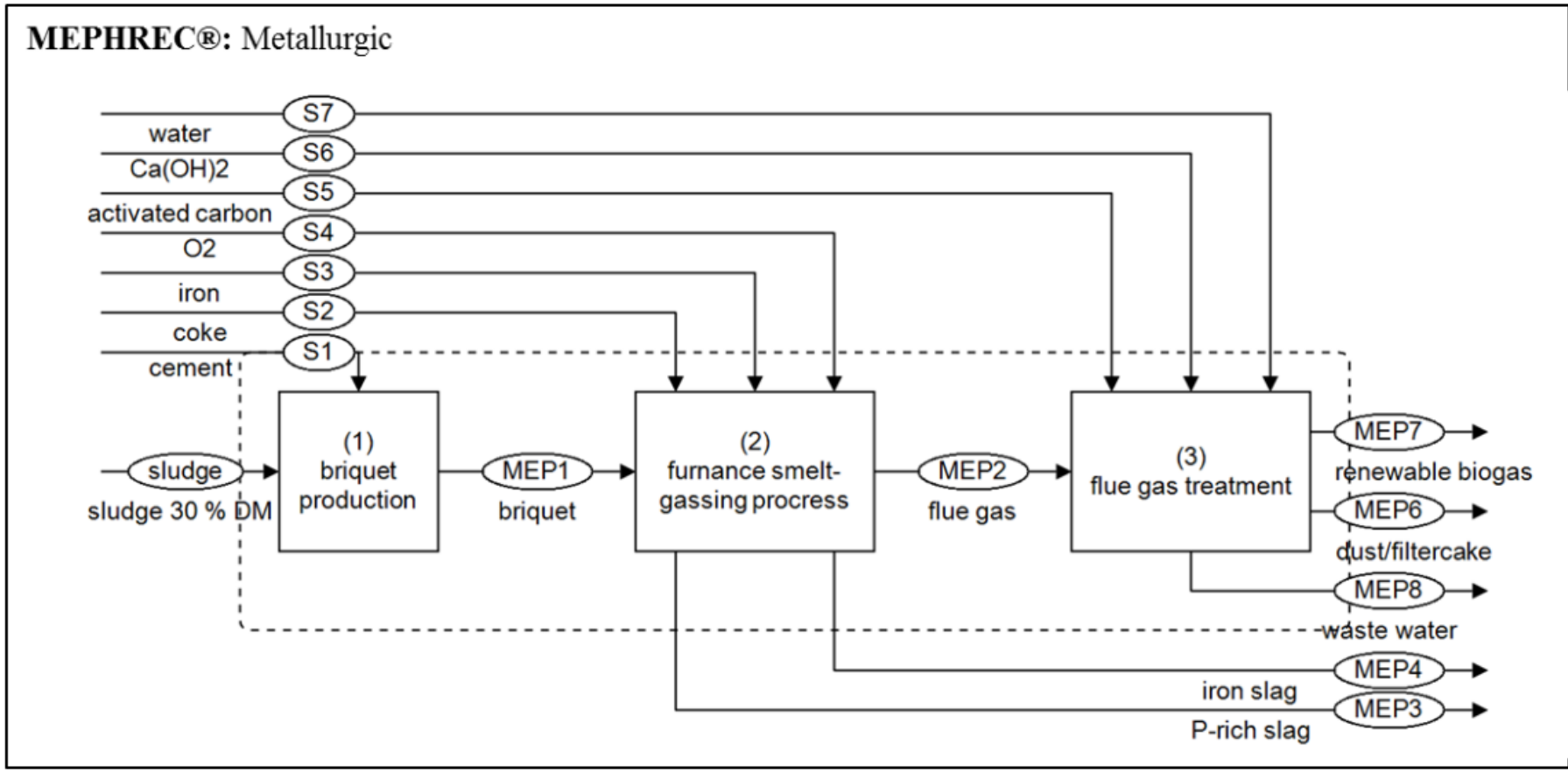| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
MEPHREC	Thermal treatment (metallurgic smelt-gassing process)	Press the sewage sludge into the cement briquettes and place it in the cupula furnace at temperatures which is higher the ash melting point (>1450°C). In the furnace, all organic matter degasses, mineral elements are melted and mixed with other additives (limestone) and coke ash to create a P-rich liquid slag, while the metal slag accumulates below due to its higher density. The liquid slag rich in P is then tapped separately and released into a water bath where it forms fine grained porous granules.	80% related to P-flow	Phosphorus-rich slag	Semi-industrial (large scale plant)	Pros: - Salable impure carbon monoxide (as fuel) - Recovery of energy that kept in the sewage sludge without need to transport it to incineration plant. - Nearly complete destruction of organic matter - Waste material can be disposed of without the need for treatment - No chemical demand - High bioavailability in neutral soil (50–100%) and low in acidic - TRL 5-6 Cons: - Necessary drying of sludge before to feeding - Selling the fuel off-gas is vital for feasibility	(L. Egle et al., 2016) (Lukas Egle et al., 2015) (Schaum, 2018 Chapter 23)

Figure 61 – MEPHREC.

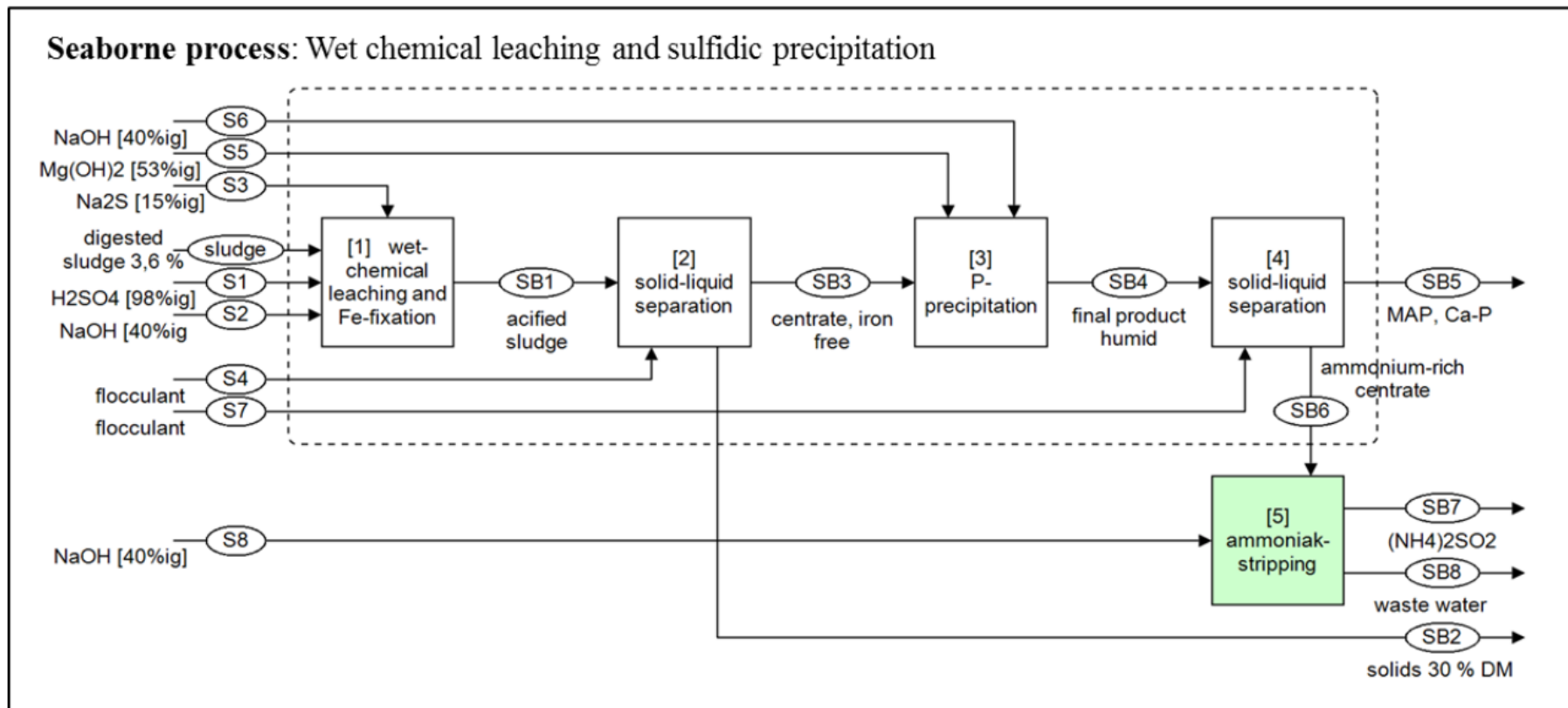| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
Seaborne	With leaching (insert the reactants used)	First, dissolve P by adding an acid (the amount of acid which need is proportional to dry matter in sludge). The lower the pH the higher P recovery (usually pH 2) but also undesirable material will dissolve, so need purification and need to fix iron before solid-liquid separation. After that pH of the liquid phase increased then by using sodium sulfide (Na_2S) and then P recovery. in this process, pH increase in several steps first increases to 3 then 5, and 5.5 to reduce acid consumption and flocculation chemicals during the dewatering step.	50% related to P-flow	CaP on CSH, Struvite	Full scale	Pros: - Very good depollution (up to 98% for all heavy metals) - Good plant availability in acidic soils and middle in alkaline soils, and not soluble in water - Organic micropollutants exist but much lower in comparison to SS Cons: - High operation and implementation cost - Some amount of P stayed in (acidified) sludge or other organic residues that must be disposed of. so some amount of P irretrievably lost. - High energy and chemicals are needed and consequently highest CED demand (170‑270 kWh kg P-1). - SO_2 emissions are high	(Schaum, 2018 Chapter 31) (Egle, 2017)

Figure 62 – Seaborne.

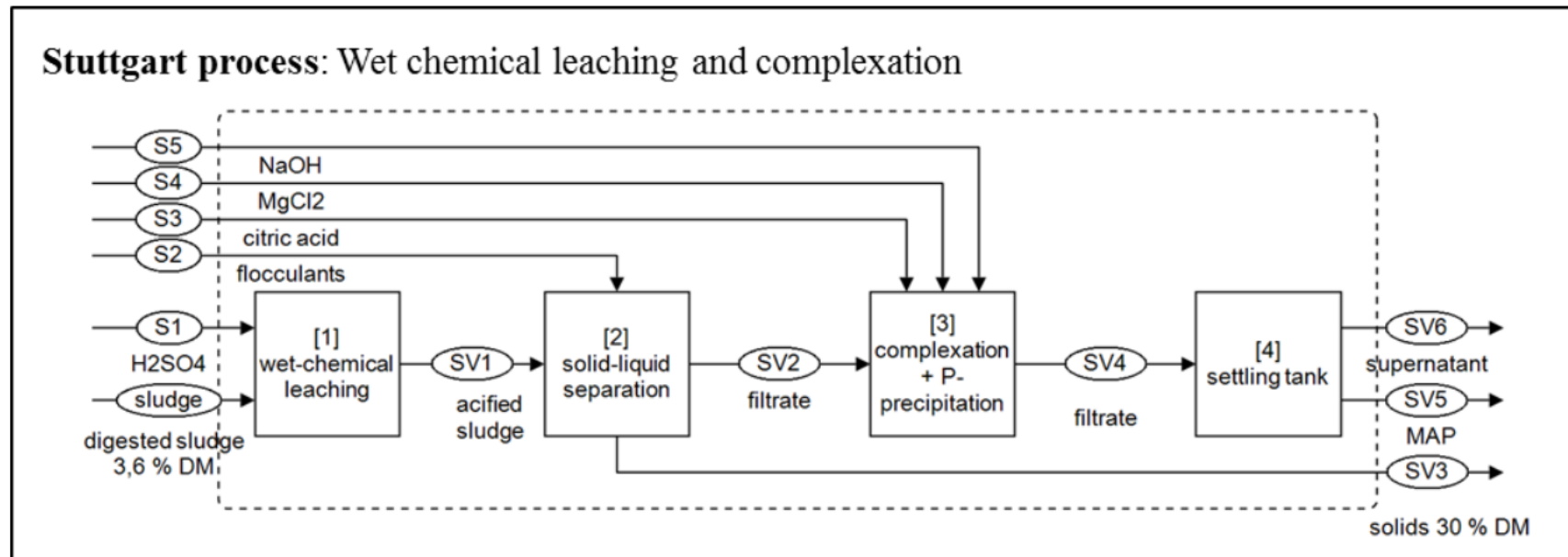| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
Stuttgart	With leaching (insert the reactants used)	Similar to seaborne but avoid precipitation of dissolved undesirable ions by complexation with citric acid in the digester supernatant. After wet-chemical leaching and then solid-liquid separation then by adding MgO or Mg(OH)$_2$ and NaOH, pH increase and cause the precipitation of Struvite. The supernatant is rich in complexed ions and returns to the WWTP influent, this cause increase in heavy metal load so a cation-exchange membrane need for metal ion removal (Al, Ca, Fe) of the supernatant for more pure Struvite but it could be still contaminated and not follow the limits	50% Related to P-flow	Struvite, MAP	Full scale (pilot plant)	Pros: - Very good depollution (up to 98% for all heavy metals) - Good plant availability in acidic soils and middle in alkaline soils, and not soluble in water - Organic micropollutants exist but much lower in comparison to SS - TRL 5-6 Cons: - Some amount of P stayed in (acidified) sludge or other organic residues that must be disposed of. so some amount of P irretrievably lost. - 20‑50% more costly compared to the defined reference system - High CO_2 emissions are surprising. - High energy and chemicals are needed and consequently highest CED demand (170–270 kWh kg P-1). - SO_2 emissions are high	(Egle, 2017)

Figure 63 – Stuttgart.

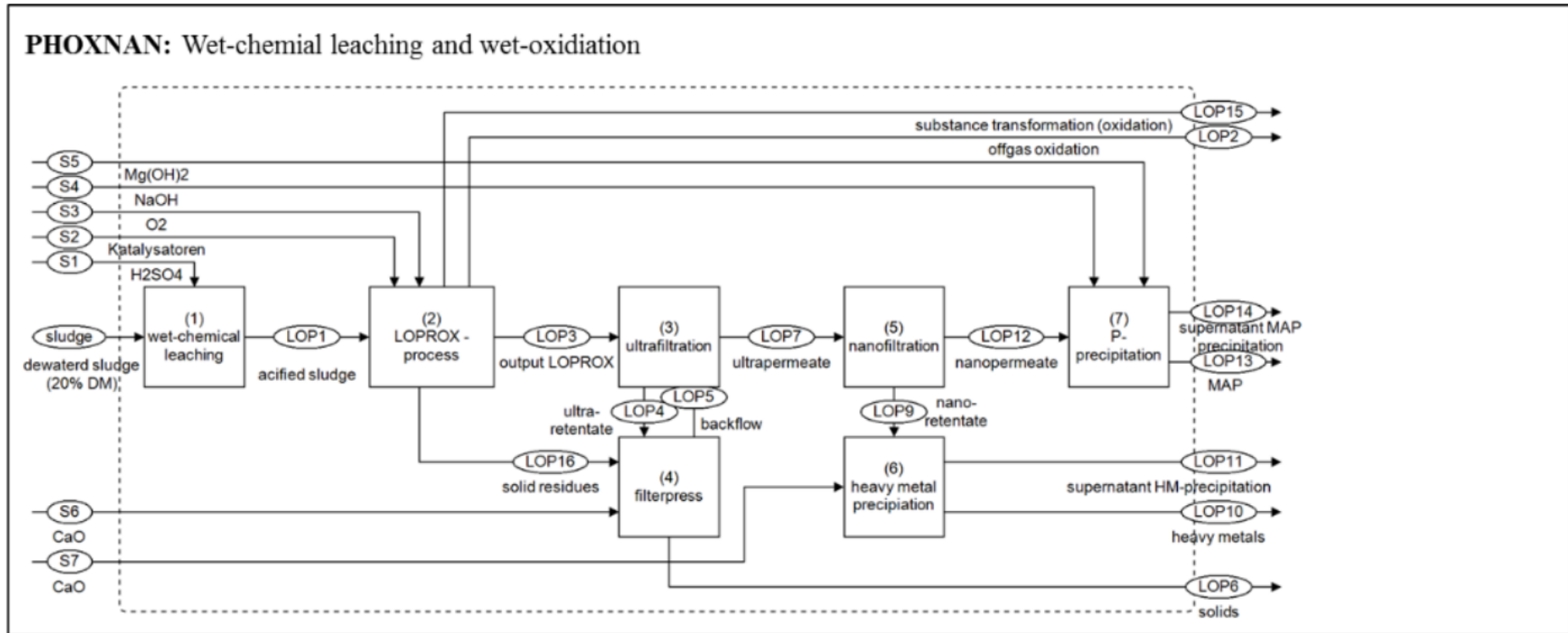| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
PHOXNAN	Wet-oxidation, with leaching (insert the reactants used), precipitation	First, by wet-chemical leaching pH decrease (pH 1.5-2 by H_2SO_4) the low pH prevents the formation of FePO4. then it goes to a low-pressure wet oxidation tank (1–4 h, 160–200°C, ~20 bar) amount of oxygen that added depends on the COD load (1 kg O_2 kg COD^{-1}), as it is an exothermal process the excess heat can be used. organic content (less than 5%) which has good settling properties separate from the liquid phase that contains P and other ions. Then two filtering unit (ultra-filtration and nanofiltration) are used to separate Fe, Al, and heavy metals (as it contains heavy metals needs further treatment) from the solution. Then solution goes for P precipitation.	55% Related to P-flow	Phosphoric acid	Full scale	Pros: - As the output wastes are inert can be disposed of without further treatment Cons: -The cost is high, but revenues, such as the heat that can be recovered or converting sludge to an inorganic product and the value, can cover the expense a lot - SO_2 emissions are high	(Egle, 2017) (Lukas Egle et al., 2015) (Sartorius et al., 2011)

Figure 64 – PHOXNAN.

| Process name	Method	Process description	PEE	Products	Operational scale	Pros & Cons	References
Aqua Reci	Supercritical water oxidation, with leaching (insert the reactants used), precipitation	It is based on recovery of SCWO (Supercritical Water Oxidation) ash. In this approach using HCl or NaOH to dissolve P from ashes (up to 90%). Then P can be recovered by precipitation process.	80% Related to P-flow	FeP, AlP, CaP	Lab scale/Full scale	Pros: - Really high depollution capacity (up to 98 per cent for all heavy metals considered) for sewage sludge. The transition of heavy metals to the final product, and consequently agriculture, is poor. - Reasonable cost Cons: - Some amount of P stayed in (acidified) sludge or other organic residues that must be disposed of. so some amount of P irretrievably lost. - Bioavailability of recovered calcium phosphate products is slightly lower in neutral and alkaline soils, while calcium phosphate is soluble in citric acid (like MAP).	(Egle, 2017) (Stendahl & Jäfverström, 2004)
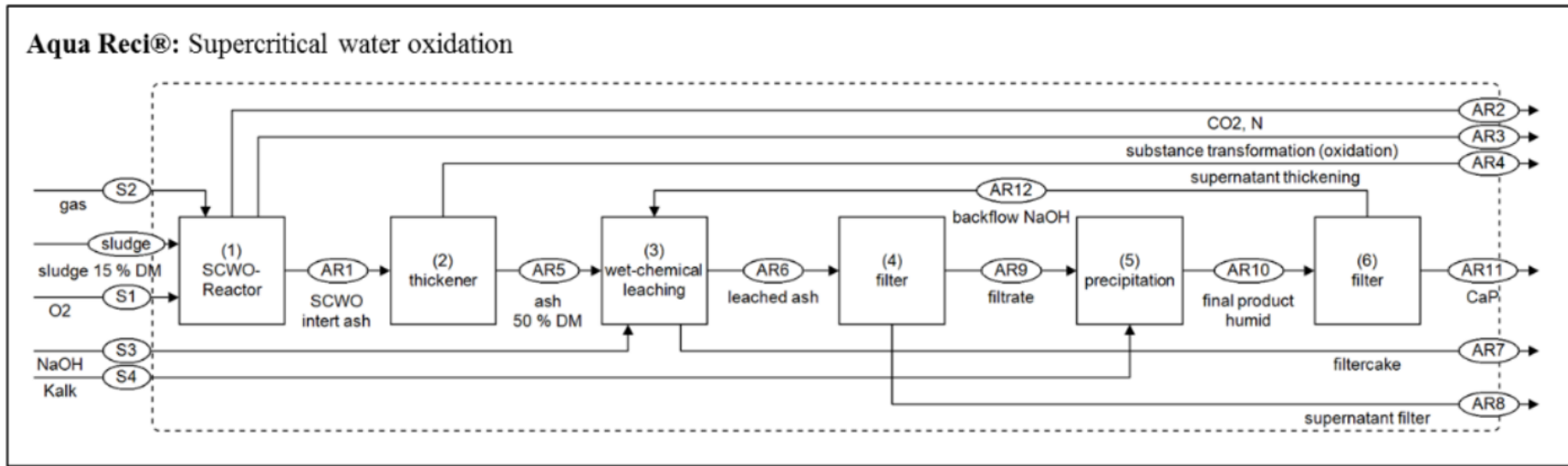
Figure 65 – Aqua Reci.

6 Appendix C: Detailed experimental procedures.Step by step procedure

6.1 Sieve analyses

1) Take 210 g of ash for the grate-pounded and 220 g for the cyclone.

2) Order the sieves by their pore size from large to small (in this experiment (the pore size is in mm): 0.425, 0.212, 0.18, 0.125, 0.063, 0.025, bottom)

3) Weigh each sieve to get the tar weight.

4) Add the ash and shake for 10 min

5) Weigh each sieve (final weight)

6) The difference between final weight and tar weight for each sieve is the amount of ash which has that particle size obtain

6.2 Finding humidity of the ash

1) Take an aluminum container that is resistant to heat.

2) Weigh the container (tar weight).

3) Add few grams of ash (for example, 10 g) to the container.

4) Put them inside the oven at 105 °C for 24 h.

5) Weigh them to get the dry weight.

6) By equation 9, humidity can be found.

$$Amount\ of\ ash\ added = Wet\ net\ weight$$
$$Final\ weight\ (after\ oven) - Tar\ weight = Dry\ net\ weight \qquad \text{Equation 9}$$
$$Humidity = 1 - \left(\frac{Dry\ net\ weight}{Wet\ net\ weight} \right)$$

6.3 Determination of unburned material in the ash

1) Take a ceramic container that is resistant to heat.

2) Weigh the container (tar weight).

3) Add few grams of ash (for example, 10 g) to the container.

4) Put them inside the muffle oven at 900 °C for 24 h.

5) Weigh them to get the dry weight.

6) By equation 10, humidity can be found.

$$\text{Unburnd material} = 1 - \left(\frac{\text{Dry net weight}}{\text{Wet net weight}} \right)$$
<div align="right">Equation 10</div>

6.4 Leaching process

1) Pour 20 grams of SSA into a glass beaker with 500 mL capacity.

2) Add 400 mL diluted acid (0.2 M sulfuric acid) (to make a diluted acid, add 11.14 mL of 96% concentrated acid in a one-L flask and fill it with ultra-pure (UP) water and shake and let it rest to reach ambient temperature).

3) Put the beaker over the magnet stirrer and mix for 2 h (put the watch glass over the beaker to water evaporation during mixing).

4) After 2 h pour the solution in 50 mL falcon and centrifuge them at 3500 rpm for 10 min to separate the solid phase from the liquid phase.

5) Do filtration using Whatman^{TM} filter papers with a pore size of 0.45 µm and a diameter of 27 mm.

6) Keep the filtrated solution in PE bottles for further tests.

7) Keep also solid residuals and wash them with DIO (deionized) water as reported in chapter 3.4.4.

6.5 P analyses

1) Add 25 mL of leachate in a falcon.

2) Add few drops of phenolphthalein (which is a pH indicator) and shake.

3) Gently add NaOH to increase pH and shake (add till the solution becomes pink)

As the phosphorus kits have a limited range that can analyze the amount of P in solution, it is necessary to dilute the samples to reach the acceptable range. In this case, need to dilute it 1000 times.

4) Add UP water till the water level reach 50 mL and shake.

5) By micropipette, take 1 mL of solution and add it to a 500 mL flask (shake again before taking the sample).

6) Add UP water to the flask till reaching 500 mL level and shake.

Now the samples are correctly diluted, and they are ready for analysis.

7) Use a spectrophotometer for P-analyzes.

6.6 Washing solid residual from the leaching process

1) Extract solid residuals from falcon and pour them in glass becker.

2) Add 100 mL of DIO water to solid material and mix well.

3) Do filtration using Whatman^{TM} filter papers with a pore size of 0.45 µm and a diameter of 27 mm.

4) pour the solid material over the filter to glass becker and again add 100 mL DIO water and mix well.

5) Again, do filtration by using Whatman^{TM} filter papers with a pore size of 0.45 µm and a diameter of 27 mm.

6) Keep the solid material over the filter paper for further analysis.

6.7 Precipitation

1) Using the solutions from the leaching test.

2) Add 30 mL of solution in a glass beaker with proper volume(the volume depends on the desired pH, of course, for high pH, as it is necessary to add a more basic solution, a larger beaker is needed.

3) To reach the desired pH, Martina (Multiple Analysis, which is a programmable Titration Analyser from Spes) was used (Martina add a specific amount of base step by step to get the aimed pH) and over the stirrer for one h and evaluate the variation of pH by adding a particular amount of base till reaching the aimed pH.

4) After that, let the solution rest for 2 h and cover them with parafilm to avoid CO_2 exchange.

5) Filtrate the solution use Whatman^{TM} filter papers with a pore size of 0.45 µm and a diameter of 27 mm. The material that traps by the filter is kept for more analyses (they contain P and maybe other elements).

6) Keep solid residual in a desiccator for 48 h then keep them in proper containers for further analysis.

7) The liquid phase goes for P analyses to measure the liquid's P content (adjust pH if necessary).

8) By equation 11, it is possible to calculate P in precipitated material.

$$C_{leachate} \cdot V_{leachate} = C_{filtrate} \cdot V_{filtrate} + C_{precipitated} \cdot V_{precipitated}$$

$$C_{precipitated} \cdot V_{precipitated} = C_{leachate} \cdot V_{leachate} - C_{filtrate} \cdot V_{filtrate} \qquad \text{Equation 11}$$

6.7.1 Precipitation methods

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Precipitation did over two fractions of ash grate and in two method

6.7.2   First method

1) Take four samples of each fraction (each sample 30 mL).

2) First and second samples for reaching pH 2.5 and pH 3.5 by adding NaOH (0.1 M).

3) third sample for getting pH 3.5 by NaOH (0.1 M), then change the reagent, and use $Ca(OH)_2$ (0.05 M) and reach pH 5.

4) fourth sample for getting pH 3.5 by NaOH (0.1 M), then change the reagent, and use $Ca(OH)_2$ (0.05 M) and reach pH 8.

6.7.3   Second method

1) Take four samples of each fraction (each sample 30 mL).

2) Each of these samples is intended to reach a certain pH. The pHs used in this experiment are 2.5, 3.5, 5, and 8, and the reagent was KOH (0.1 M).

6.8   Base solution prepration

6.8.1 Lime water with 0.5% concentration

For this purpose, 5 g of $Ca(OH)_2$ will mix with 1 L of UP water

1) Add some UP water in the flask with 1 L capacity.

2) Gently add $Ca(OH)_2$ and shake

3) Let the suspension cool down and add ultrapure (UP) water till it reaches 1 L capacity.

4)

6.8.2 (0.1 M) KOH preparation

For this purpose, 5.6 g of KOH will mix with 1 L of UP water

1) Add some UP water in the flask with 1 L capacity.

2) Gently add KOH and shake

3) Let the solution cool down and add UP water till it reaches 1 L capacity.

6.8.3 (0.1 M) NaOH preparation

For this purpose, 4 g of NaOH will mix with 1 L of UP water

1) Add some UP water in the flask with 1 L capacity.

2) Gently add NaOH and shake.

3) Let the solution cool down and add UP water till it reaches 1 L capacity.