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**PHOSPHORUS RECOVERY FROM SEWAGE  
SLUDGE ASHES VIA WET CHEMICAL LEACHING**

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# Abstract

Phosphorus is a primary resource and an essential element for cells, crop's growth, living animals and human being. Nowadays it is facing gradual scarcity, and, in the next few decades, even depletion of natural sources (phosphate rocks). Incinerated sewage sludge ashes (ISSA) have recently become an interesting material for phosphorus recovery, thanks to its high phosphorus content (~ 8%). As a consequence, selective phosphorus acid leaching of sewage sludge ash has been investigated as a convenient and feasible option.

This present work presents lab-scale experiments to investigate the potential of phosphorus recovery from ISSA by acid leaching extraction under various operating conditions. Batch tests for six different samples of ashes from different incineration plants and from ashes obtained from muffle-furnace incineration were performed. The effects of type of acid, acid concentration, contact time and liquid-to solid ratio were examined. The overall results indicated that, depending on extraction operating conditions and treatment plant layout, phosphorus recovery rates between 40% and 90% can be obtained with low co-dissolution of heavy metals, except for arsenic. Three of the six ashes samples analysed achieved with sulfuric acid an extraction efficiency higher than 88% under the optimal conditions, which were 0.4 N H<sub>2</sub>SO<sub>4</sub>, 2 hours as contact time, at liquid-to solid ration of 20. Hydrochloric acid showed lower performances with a higher co-dissolution of heavy metals, especially lead.

Finally, chemical precipitation of phosphorus from the acidic leachate was carried out by dosing milk lime (1% suspension). After filtering and subsequent drying, the recovered product presents a phosphorus content between 3 and 9% (dry basis), with heavy metals content well below the limits for fertilizer application.

**Keywords:** incinerated sewage sludge ashes, nutrient recovery, phosphorus recovery, chemical extraction, acid leaching.

# Sommario

Il fosforo è una risorsa primaria e un elemento essenziale per le cellule, la crescita delle colture, gli animali e l'uomo. Oggi la risorsa si fa più scarsa e, molto probabilmente, nei prossimi decenni si assisterà al progressivo esaurimento delle riserve naturali (rocce fosfatiche). Le ceneri dei fanghi di depurazione, grazie al loro elevato contenuto di fosforo (~ 8%), sono recentemente diventate una interessante fonte secondaria. Di conseguenza, la lisciviazione selettiva dell'acido fosforo delle ceneri di fanghi di depurazione è stata studiata come un'opzione conveniente e fattibile.

Nel presente elaborato vengono descritti gli esperimenti a scala di laboratorio condotti per investigare il potenziale recupero del fosforo dalle ceneri dei fanghi di depurazione tramite lisciviazione acida. Sono stati condotti batch test per sei campioni differenti di ceneri provenienti sia da impianti di incenerimento a scala industriale, sia da ceneri ottenute in laboratorio con forno a muffola. Principalmente sono stati esaminati gli effetti sull'estrazione chimica dovuti al tipo di acido, alla sua concentrazione e al tempo di contatto.

A seconda delle condizioni operative di processo e dei processi depurativi presenti negli impianti di trattamento delle acque reflue, si è ottenuto un recupero del fosforo fino al 90%, con una contestuale bassa dissoluzione di metalli pesanti, ad eccezione dell'arsenico.

Tre dei sei campioni di ceneri analizzati hanno mostrato una efficienza di recupero con acido solforico maggiore dell'88% nelle seguenti condizioni: concentrazione 0.4 N, tempo di contatto 2 ore, rapporto liquido solido pari a 20.

L'acido cloridrico ha invece mostrato minore efficienza di estrazione del fosforo e contestuale maggiore dissoluzione di metalli pesanti, soprattutto del piombo.

Infine, si è condotta la precipitazione chimica del fosforo dall'eluato acido dosando latte di calce all'1%. Dopo una successiva fase di filtrazione ed essiccamento, il contenuto del fosforo del prodotto precipitato e recuperato è risultato pari al 3-9% su base secca, con un contenuto di metalli largamente inferiore al limite fissato dalla regolamentazione sui fertilizzanti.

**Parole chiave:** ceneri di fanghi di depurazione, recupero del fosforo, recupero dei nutrienti, estrazione chimica, lisciviazione acida.

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# 1 Scope of the work

The gradual depletion of phosphate rocks reserves is leading to a growing importance of several technological solutions emerged for its recovery from sewage sludge, which is an interesting secondary resource. Indeed, the content of phosphorus pentoxide ( $P_2O_5$ ) in the incinerated sewage sludge ashes usually ranges between 14 and 25% and can be comparable to the content of many phosphate rocks (R. Li et al., 2017).

An overview of the current methods applied for phosphorus recovery is presented. Brief description of different processes such as crystallization, precipitation, ion exchange, thermal treatments, wet oxidation, wet chemical leaching and thermo-chemical process is given.

Thus, selective phosphorus acid leaching from sewage sludge ashes turns out in a feasible and prominent option, which has been deeply examined.

The aim of this present work is to discuss and investigate the potential of nutrient recovery by acid leaching under various extraction operating conditions at lab-scale. Operating conditions for the extraction are indeed fundamental parameters in determining process efficiency.

Samples of ashes from different incineration plants, located in Germany and Switzerland, and from ashes obtained from muffle-furnace incineration of sewage sludge samples were analysed. These were obtained from various wastewater treatments plants built up near the city of Milan.

Experimental results indicated that leaching with sulfuric acid is an effective alternative for selective phosphorus recovery that can guarantee an extraction efficiency ranging between 40 and 90% with a minor release of trace elements. Experiments conducted showed that, under the operating conditions used for P recovery from incinerated sewage sludge ashes (ISSA), most of heavy metals remain in the solid residue after leaching, resulting in a very low contamination of the acidic solution.

Then, the extraction procedure involves precipitation of phosphorus from the leachate, which occurs mainly as calcium phosphate, and it is effective by dosing lime milk (1% suspension). The material recovered has a phosphorus content ranging between 3 and 9% with a heavy metal content that does not exceed the normative limits for fertilizer application.

## 2 Introduction

### 2.1 The importance of phosphorus

Phosphorus is a primary resource and an essential element for cells, crop's growth, living animals and human being. Indeed, it is present in the structure of DNA, RNA and it is a fundamental component of ATP and ADP involved in energy production, transport and storage activities (R. Li et al., 2017). Plants need phosphorus for doing photosynthesis and it accounts for about 2-4% of dry weight of most cells (Desmidt et al., 2015).

It exists in two major allotropes, namely white and red phosphorus, which have different chemical and physical properties. The most common form is the white phosphorus or tetra phosphorus ( $P_4$ ), which is extremely reactive and highly poisonous (Nieminen, 2010). Red phosphorus is instead more stable and exists as polymeric chains ( $P_n$ ). It is possible to convert white phosphorus to red, by heating it up to 250 °C in anoxic conditions or using the sunlight (Nieminen, 2010). However, because of its reactivity, phosphorus cannot be found as a free element, but it occurs in many minerals, mainly as calcium phosphate. The major forms are hydroxyapatite, fluorapatite and chlorapatite, which belong to the family of apatites ( $Ca_5(PO_4)_3(F,Cl,OH,Br)$ ). Although it is the 11<sup>th</sup> element most abundant in the earth crust, it is a non-renewable and limited resource. In nature, it can be found in the reserves of phosphorus rocks with an average content of  $P_2O_5$  ranging from 5 to 40%. These are distributed in more than 60 countries, but more than 80% of them are concentrated in Morocco, China and USA. The deposits can be furthermore divided in two categories that are sedimentary and igneous phosphate rocks. The latter can be found in Brazil, Canada, Russia and South Africa, which are often expensive to recover and low grade. Fig. 1 shows the distribution of phosphate rock reserves worldwide.

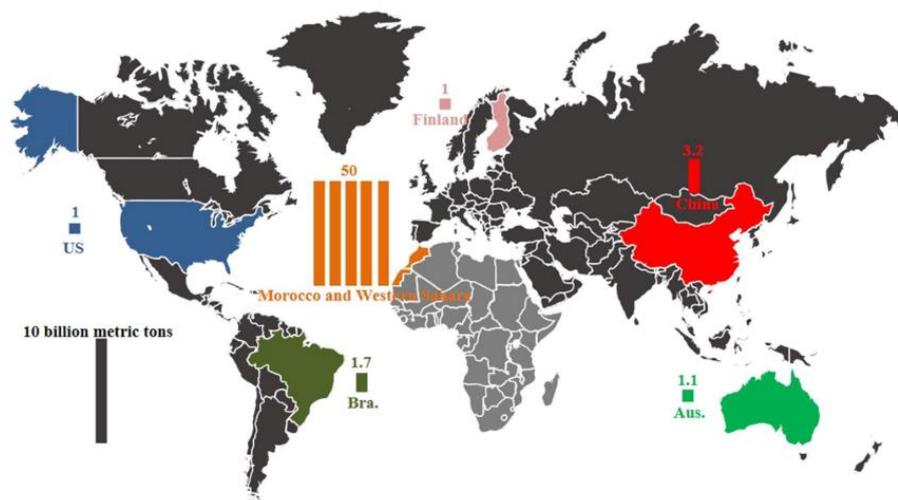


Fig. 1 Phosphate rocks reserves (Meng et al., 2019).

It is necessary to highlight that not only the total amount of phosphate ore should be considered, but also the quality of it. In fact, China accounts for 3,200 million metric ton reserves, but the average grade of phosphate ore is only 16.9% (Meng, Huang, Xu, Gao, & Yan, 2019).

Hence, many countries in Europe, such as Italy, strongly rely on the foreign exporters (El Wali, Golroudbary, & Kraslawski, 2019) and are affected by price volatility and geopolitical tensions. This dependency makes Europe vulnerable to future scarcity.

The European Commission put in 2014 phosphate rocks in the list of 20 critical raw materials ([https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical\\_en](https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en)).

In 2017, it has been estimated that about 70 million tons of phosphate rock ( $P_2O_5$ ) were consumed and, at the current rate of mining, phosphorus is expected to deplete within the next 100 years (B. Li et al., 2019). In addition, because high quality minerals have mined at first, the quality of phosphate rock is going to decline; hence concentration of impurities and heavy metals is increasing like the costs of mining, transport and refining (Desmidt et al., 2015). Indexmundi reports that the price of phosphate rocks almost doubled between 2004 and January 2020 reaching 72.7 US \$/metric ton (<https://www.indexmundi.com/commodities/?commodity=rock-phosphate>).

The high consumption rate of this fundamental resource can also be attributed to the low utilization efficiency, which is lower than 20% in many countries. 80% of losses can negatively affect the environment causing eutrophication phenomena, which compromise the quality of many surface water bodies and reduce the biodiversity. Van Dijk et al. (2016) reported that Europe uses 4 kg of reactive phosphorus to produce 1 kg of food, while China uses 13 kg of phosphorus to produce the same amount. The surplus can inevitably end up in soil and leach into the aquifers.

Because the world population is estimated to reach 9 billion by 2050, the food production may increase by almost 30% to ensure food security. This means that the demand for fertilizer will increase as well, putting more pressure on resource supply and environment. The typical fertilizers applied are ordinary superphosphate ( $Ca(H_2PO_4)_2$ ), triple superphosphate ( $Ca(H_2PO_4)_2$ ), monoammonium phosphate ( $NH_4H_2PO_4$ ) and diammonium phosphate ( $(NH_4)_2HPO_4$ ) (Nkebiwe, Weinmann, Bar-Tal, & Müller, 2016).

Shaddel et al. (2019) reported that, in Europe, 90% of the mined phosphorus is used for food production, split between fertilizers 79% and livestock farming 11%. Small percentages account instead for pharmaceuticals products, oil and detergents (Meng et al., 2019).

The world population's growth will inevitably cause an increase in the sludge production, which is referred to 50-70 g of dry sludge per person equivalent per day (Vouk, Nakic, Serdar, Donatello, & Cheeseman, 2017).

As a consequence, the production of European municipal sewage sludge will be expected to rise up to 25 million tons in 2020.

To close the gap between phosphorus demand and supply, recovery technologies and strategies must be implemented. Withers et al. (2015) suggested the 5R Strategy that states for **R**ealign P inputs, **R**educe P losses to water, **R**ecycle P in bio-resources, **R**ecover P from waste, and **R**edefine our food system (Withers et al., 2015). In particular, manure, meat, bone meal, agricultural waste, wastewater and sludge can be used as secondary resources, as indicated in Table 1.

*Table 1 Phosphorus concentration of different type of waste (Meng et al., 2019).*

Organic material	P (% P by weight)
Human urine	0.02–0.07
Human feces	0.52
Human excreta	0.35
Activated sewage sludge	1.4
Sludge (from biogas digester)	0.48–0.77
Cow dung	0.04
Poultry manure	1.27
Farm yard manure (FYM)	0.07–0.88
Rural organic matter	0.09
Vermicompost	0.65
Crop residues	0.04–0.33
Urban composted material	0.44
Oil cake (by-product from oilseed processing)	0.39–1.27
Meat meal	1.09
Bone meal	8.73–10.91

This can reduce the environmental impacts and decrease the amount of phosphate rock mined.

More than 30 technologies have been already investigated, but their implementation can be challenging, mainly for their economic feasibility.

For this reason, there are nowadays few commercial recovery facilities operating at full scale and there is a need for further industrial implementation. In fact, many factors should be considered such as resources available in the country, operation and investments costs, simplicity of the process layouts and national policies

Technologies should be chosen considering the local raw material availability, economic and ecologic situation (B. Li et al., 2019).

## 2.2 Phosphorus removal and recovery

As discussed in paragraph 2.1, to tackle the exhaustion of reserves and to ensure a sustainable development and circular economy, phosphorus can be efficiently recovered from wastewater because 90% of the wasted phosphorus concentrates in the sewage sludge (Desmidt et al., 2015).

By doing that, a significant fraction (40-50%) of the non-renewable mineral phosphorus can be replaced by this promising secondary source (Zoboli, Laner, Zessner, & Rechberger, 2016). Considering that Lombardy plants produce about 500 thousand tons per year of dry sludge (ARPA Lombardia 2017), of which 20% of dry matter, the potentially recoverable phosphorus would amount to 2,200 tons of phosphorus per year.

10% of phosphorus is usually removed with the primary sedimentation tank, producing the primary sludge, while approximately 20-30% of phosphorus can be incorporated into the biomass through biological treatment forming the waste activated sludge/secondary sludge (Cornel et al., 2009).

Because the effluent concentration must be lower than 1 mg/L (10,000-100,000 Population Equivalent) or 2 mg/L (>100,000 PE), according to the Council Directive 91/271/EEC, another 50% of the P load has to be removed chemically. This percentage contributes to the secondary sludge and summed up with the 30% corresponds to 80%, as reported in the flow sheet of Fig. 2.

Chemical precipitation with metal salts (Al (III), Fe (III)) or enhanced biological phosphorus removal (EBPR) are common approaches adopted. With EBPR, phosphorus accumulating organisms (PAOs) are able to incorporate the phosphorus into their cells, removing it from the wastewater, while with dosage of chemicals, phosphorus can precipitate in sludge. Fig. 2 summarized what has been already discussed.

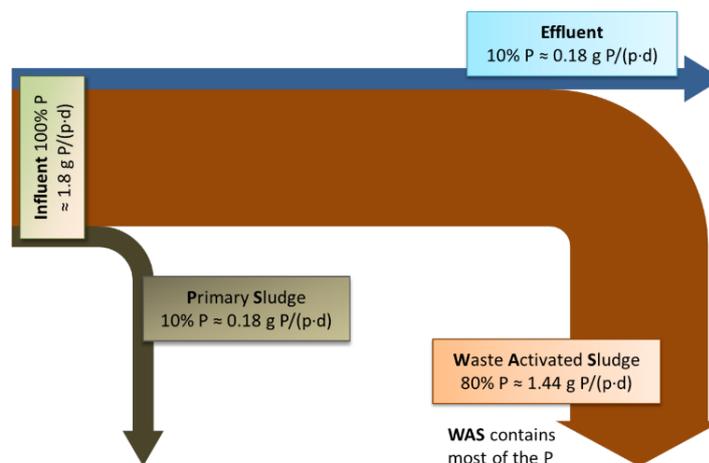


Fig. 2 Phosphorus percentage found in sludge and effluent (Kabbe et al., 2019).

The overall sludge usually contains an organic fraction (mostly composed by C), an inorganic fraction (Ca, Mg, Fe, Na, K, heavy metals) and pathogens, virus and bacteria coming from the human faeces. In general, phosphorus can be present bound as metal phosphate, as organic-bound phosphate or as dissolved phosphate. Before thickening and dewatering operations, the average content of water in the sludge ranges from 95 to 99%, while dry matter accounts for 1-5%. After the solid/liquid separation processes, the aqueous sludge fraction contains 5 to 20% of phosphorus in dissolved form, while the residual semi-solid fraction accounts for 80 to 95%. About 40-50% of phosphorus can be recovered from the liquid phase, while 80-90% can be recovered from the sludge or sludge ash. In the next section, the different recovery technologies and their efficiency are discussed.

### 3 State of the art

Thanks to the rising awareness about the concept of circular economy and sustainable development, processes and technologies for phosphorus recovery are constantly increasing. Over recent past years, different technologies, which mainly differ in type of process and phosphorus recovery efficiency, have been developed and improved to promote recovery and recycling. Netherlands, Germany, Belgium, Austria, Japan and United States are the leading countries operating with several treatment plants. Fig. 3 shows the location of the different treatment facilities indicating those that are in construction, planned, piloting and operating.



Fig. 3 Location of the treatment plants for phosphorus recovery (Kabbe et al., 2017).

It is important to highlight that the sludge management can vary a lot from one country to another because it is strongly influenced by the level of urbanization, available areas, wastewater treatment plant management and drainage systems. Fundamental aspects to obtain efficient phosphorus recovery are high recovery rate, high quality of the product recovered (the content of impurities should be low), low operating costs and low waste generated. Societal and political acceptance are key factors as well, because the resource recovered becomes a new product, that should be competitive to the market. For these reasons, there is not a one-size-fits all solution, but different strategies need to be adapted to the geographical context and local economy (Shaddel, Bakhtiary-Davijany, Kabbe, Dadgar, & Østerhus, 2019).

Considering a wastewater treatment (WWTP), phosphorus can be theoretically recovered from:

- Liquid phase,
- Sewage sludge,
- Sewage sludge ashes.

In Italy, in dense populated areas (> 100,000 PE), the influent phosphorus concentration ( $P_{tot}$ ) at WWTP is about 4- 5 mg/L, a lower value compared to values reported by Egle et al. (2016) (about 8-9 mg/L), while the effluent concentration is set at 1 mg/L for sensitive areas, according to the Italian regulation (Testo Unico 152/2006, Tab. 2 All. 5), and 2 mg/L for agricultural reuse (D.M. 02.05.2006).

Regarding the water purification line, the actual methods for phosphorus removal, which is mainly present in dissolved form as an orthophosphate ( $P-PO_4$ ), are based on the chemical process of precipitation with iron or aluminium salts, as mentioned in section 2.2. Precipitated material becomes then part of the total suspended solids 'fraction, which is going to form the sludge. This sludge should be then treated to recover the nutrients. It is widely accepted that phosphorus recovery from sludge and ashes is more convenient compared to the recovery form the liquid phase. In fact, the recovery rate ranges between 60 and -90% (L. Egle, Rechberger, Krampe, & Zessner, 2016).

The flow chart reported in Fig. 4, accurately indicates the access points for phosphorus recovery.

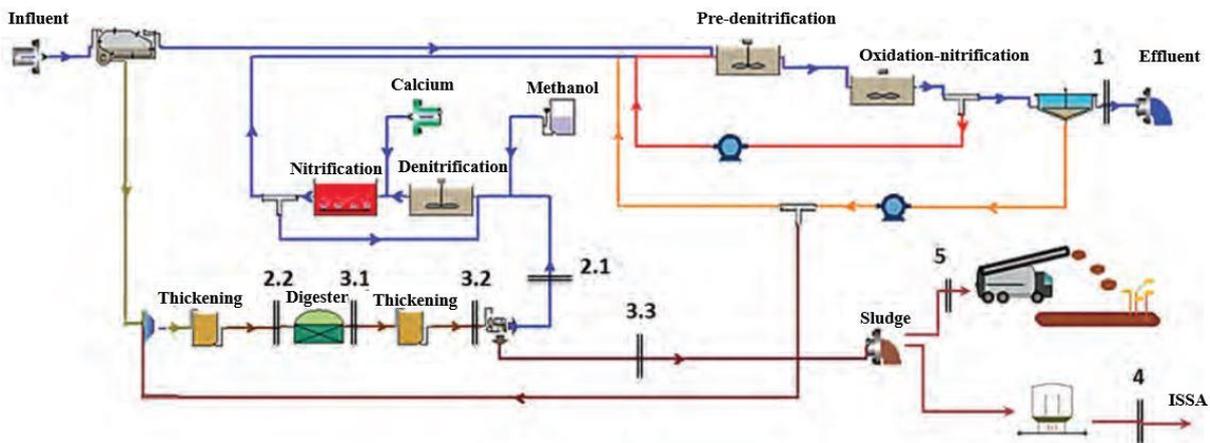


Fig. 4 Access points for phosphorus recovery (Canziani et al., 2018).

As shown in Fig. 4 phosphorus can be recovered from effluent (1) through precipitation or ion exchange and from digester supernatants (2.1) through precipitation/crystallization.

Regarding the sludge treatment line, it is possible to use the process of crystallization for sludge from pre-thickening (2.2), wet chemical leaching for digested sludge (3.1) and wet oxidation for digested

thickened sludge (3.2). Through gasification and hydrothermal carbonization, it is possible to extract phosphorus from dewatered sludge (3.3). Finally, through thermal-chemical process and chemical leaching phosphorus can be extracted from incineration ashes (4). A summary is reported in Table 2.

*Table 2 Processes for phosphorus recovery applicable for different matrix, in different sections of a WWTP (Canziani et al., 2018).*

Aqueous phase		Sewage sludge		Sewage sludge ashes	
Section	Process	Section	Process	Section	Process
1	Precipitation	3.1	Wet chemical leaching	4	Thermo-chemical based on chloride (e.g. MgCl <sub>2</sub> )
1.1	Ion exchange	3.2	Wet oxidation		Thermo-chemical based on sodium salts (e.g. Na <sub>2</sub> SO <sub>4</sub> )
2.1; 2.2	Precipitation/crystallization	3.2	Supercritical wet oxidation		Chemical leaching
2.2	crystallization	3.3	Melt gasification		
		3.3	Hydro-thermal carbonization		

Direct application of sewage sludge to agricultural land, which is an option largely diffused in Italy but not strongly adopted in Germany and Netherlands, is represented by access point (5) indicated in Fig. 4. This practice is regulated by Italian regulation (D.Lgs. 99/92) that sets normative limits for the content of pathogens, heavy metals and organic contaminants. Because these compounds can be transferred to crops and at the same time they can be accumulate in agricultural soil, emerging solutions to land spreading and landfill are nowadays rising.

In recent years, innovative technologies have been established and the graph reported in Fig. 5 shows the phosphorus potential recovery for different processes. Green, blue and red bars refer to the recovery from liquid phase, sewage sludge and incinerated sewage sludge ashes (ISSA), respectively. According to the histogram, sewage sludge ashes provide a good opportunity for nutrient recovery. Indeed, the phosphorus recovery potential is about 85%, while the recovery from the liquid fraction doesn't exceed 50%. This is because 90 to 95% of the incoming phosphorus is incorporated in the produced sludge (Shaddel et al., 2019).

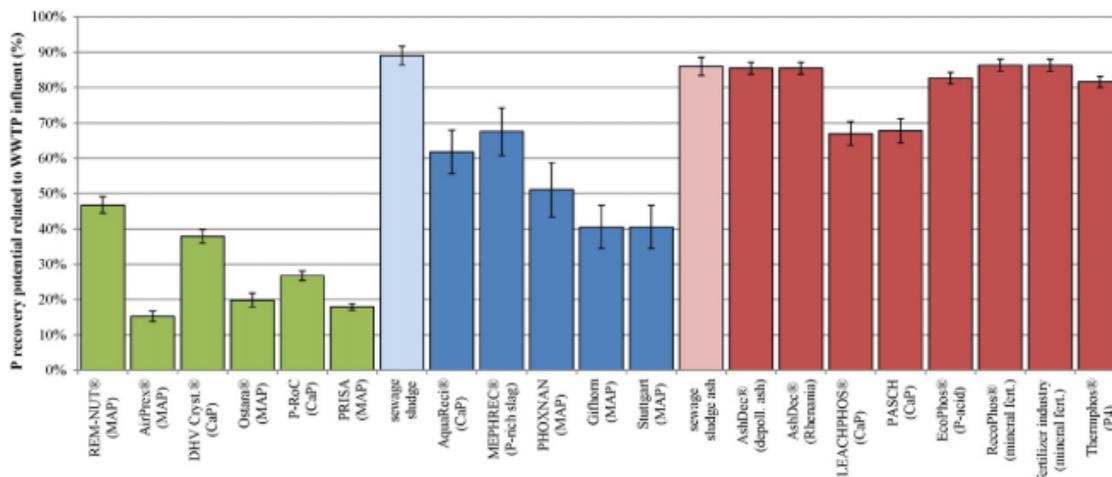


Fig. 5 Phosphorus recovery potential for different technologies (Egle et al., 2016).

### 3.1 Overview of the main phosphorus recovery technologies

This section includes a brief description of the different technologies presented in Table 2.

#### 3.1.1 Precipitation, crystallization and ion exchange

Precipitation and crystallization are two processes in which the soluble form of phosphorus (P-PO<sub>4</sub>) is transferred from the liquid to the solid phase.

To do that, a reagent such as MgCl<sub>2</sub>, MgO or Mg(OH)<sub>2</sub>, is usually added, followed by pH adjustment, if necessary. The obtained products are struvite, whose chemical formula is NH<sub>4</sub>MgPO<sub>4</sub>·6H<sub>2</sub>O (magnesium-ammonium-phosphate), also known as MAP, and hydroxyapatite, which refers to Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, also known as HAP.

The two processes differ in the reaction speed (crystallization takes more time), while both need a supersaturation of the reacting ions. From precipitation process usually an amorphous product is produced, while from crystallization a crystalloid product is obtained (Nieminen, 2010). Moreover, struvite can be used directly as a fertilizer because it is poorly soluble and has a low possibility to pollute the environment and cause eutrophication, whereas hydroxyapatite needs further treatments before it can be applied (Meng et al., 2019).

Ion exchange, instead, is a technology that uses resins and zeolites to separate phosphates from other compounds. An example is the RemNut (Removal of Nutrients) process, from which phosphorus is recovered from the effluent of the wastewater treatment plant as struvite. It uses a cationic resin (zeolite type) to exchange ammonium ions for sodium ions and an anionic resin to remove phosphates

ions exchanging chloride ions. Both columns are regenerated with sodium chloride and the ammonium and phosphate released are then precipitated as struvite. The phosphorus recovery rate related to WWTP influent is in the range of 50-70% (Liberti, Petruzzelli, & De Florio, 2001).

Fig. 6 shows the recovered products (struvite, calcium phosphate and phosphoric acid) and the names of the different technologies that can be applied. The pie chart indicates that the most common approach refers to the precipitation of struvite from sludge sidestream, followed by calcium phosphate precipitation, and phosphoric acid production.

It is important to underline that the amount of struvite that precipitates must be taken under control in order to prevent the scaling in pipe and the clogging of nozzles. This happens frequently in water rich in magnesium, with high phosphorus concentration in the supernatant (>100 mg P/L) and with pH ranging from 7 to 10.7 (Meng et al., 2019). Struvite precipitation is suitable for WWTPs with Enhanced Biological Phosphorus Removal (EBPR).

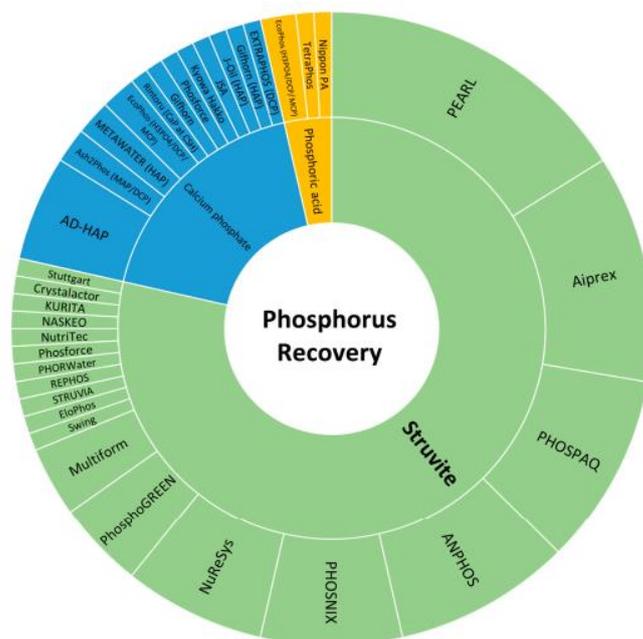


Fig. 6 Overview of main products for phosphorus recovery and related technologies (Shaddel et al., 2019).

### 3.1.2 Wet chemical leaching

Wet chemical process is able to recover phosphorus from sewage sludge or sewage sludge ashes by leaching them with an acid or base. The major extractants adopted include inorganic acids ( $H_2SO_4$ ,  $HCl$ , and  $HNO_3$ ), organic acids (citric, oxalic acids), alkali ( $NaOH$ ,  $CaO$ ) and chelating agents (Li et al. 2017), while the main parameters affecting the leaching efficiency are the acid concentration and the liquid to solid (L/S) ratio (Meng et al., 2019). Moreover, the efficiency of the solid-liquid

extraction is dependant form the interfacial contact area and pore characteristics. Therefore, sewage sludge ashes in form of dust can support a higher extraction efficiency with respect to sewage sludge.

Some authors reported that a higher phosphorus recovery rate can be achieved by using inorganic acids (Biswas, Inoue, Harada, Ohto, & Kawakita, 2009),(S. Donatello, Tong, & Cheeseman, 2010), (Petzet, Peplinski, Bodkhe, & Cornel, 2011),(Franz, 2008).

Petterson et al. (2008) obtained 94% of extraction efficiency by using 0.2 M H<sub>2</sub>SO<sub>4</sub> at L/S of 20, with 2 h as reaction time. Franz et al. (2008) obtained 66-99% recovery rate, while Stark et al. (2006) achieved 87% with 1 M HCl at L/S ratio of 50 for 2 h (Stark, Plaza, & Hultman, 2006). On the contrary, by using NaOH the P recovery efficiency reached only 40% (Biswas et al., 2009).

Moreover, sulphuric acid is more convenient from an economic point of view (Biswas et al., 2009). After the leaching process, which involves the co-dissolution of heavy metals, the dissolved phosphorus can be recovered with different methods such as chemical precipitation. If needed, also metals can be separated from the leaching solution using different techniques such as sulphide precipitation (Franz, 2008) or ion exchange columns (S. Donatello et al., 2010).

Processes like BioCon, Seaborne/Gifhorn, Stuttgart, RecoPhos P38, PASCH, EcoPhos and LEACHPHOS belong to this category.

BioCon is the only listed technology that uses the ion exchanges to recover phosphorus by separating it from metals. The first step includes the dissolution of incinerated ashes in diluted sulfuric acid. Then the solution passes through a series of four columns switching between cation exchanger and anion exchanger, to remove from the leachate ferric ions, sulphates ions, phosphate ions and other metals respectively. The products obtained are iron chloride and phosphoric acid with a phosphorus recovery of about 60% (Levlin, 1995). The other technologies considered are presented in more details in the following section.

As an introduction it is necessary to remind that phosphorus in digested sludge can be present in three different form: metal phosphates, organic phosphates and dissolved phosphate. After leaching, metal phosphates are converted to dissolved hydrogen phosphate (HPO<sub>4</sub><sup>2-</sup>), which can furtherly dissociate. The amount of dissolved phosphate is strongly dependent on metal salts used for phosphorus removal in the WWTP. It has been observed that precipitation by iron salts results in higher phosphorus dissolution. This is because iron phosphate can be much more easily dissolved by sulfuric acid (Ottosen, Kirkelund, & Jensen, 2013). However other authors such as Cieřlik et al. (2017) pointed out that using aluminium salts leads to a more efficient extraction of phosphorus.

### 3.1.2.1 Seaborne/Gifhorn process

Seaborne process was originally developed by a German company *Seaborne Environmental Research Laboratory*. Full-scale implementation is located in Germany at Gifhorn WWTP. At this site, the patented Seaborne process has been modified to meet the requirement of Gifhorn WWTP and to get a recovery rate of 45%.

Fig. 7 shows the three different phases of Gifhorn process that includes acid leaching of digested sludge with sulfuric acid, heavy metals removal and precipitation to recover phosphorus as struvite.

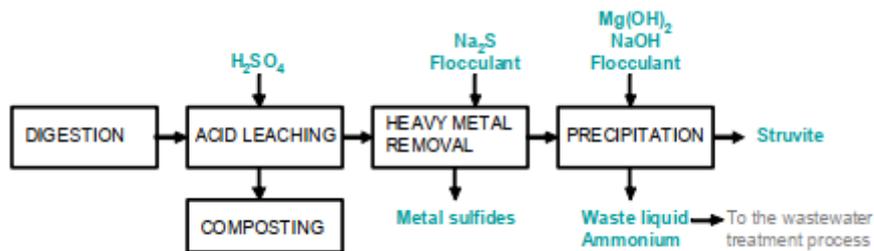


Fig. 7 Different phases of Gifhorn process (Nieminen, 2010).

The pH target value in the acid leaching stage was initially set to 2 and then risen to 4.5-5 for economic reasons. In fact, the dosage of sulfuric acid decreased from  $7.4 \text{ L/m}^3$  to  $4.5 \text{ L/m}^3$ . The residue of the leaching stage can be then either composted, thermal dried or incinerated, depending on the heavy metals content. Gifhorn WWTP managers decide to send it to compost, due to the considerable amounts of heavy metals separated in the liquid phase due to higher pH adopted.

Heavy metals are subsequently removed dosing  $Na_2S$  which is a flocculant that facilitates metal sulphides precipitation (about  $20 \text{ kg}_{\text{prec}}/\text{d}$ ). The solid material obtained is then dewatered using a belt filter and landfilled with costs of 200 €/ton (Nieminen, 2010).

For the third step, pH was increased to 8-9 with NaOH, and  $Mg(OH)_2$  was added to induce precipitation. The recovered product, struvite, was then dewatered by centrifuges.

It is important to highlight that high chemical dosage and energy consumption are necessary to reach high recovery rate by this process ( $\sim 40\%$ ) (L. Egle et al., 2016).

### 3.1.2.2 Stuttgart process

The Stuttgart process demonstrated the phosphorus recovery from digested sewage sludge in form of struvite at the pilot-scale. It consists of two steps, carried out in two different well-mixed reactors.

The first step involves the acidic leaching of metal phosphates from stabilized sewage sludge, which has undergone anaerobic digestion. After leaching, centrifugation/filtration process are applied to produce a phosphate-rich filtrate and a phosphate-depleted filter cake. To have a higher quality product, ultrafiltration module can be used.

The second step is devoted to the precipitation of struvite. Because it is important to produce high purity struvite, citric acid ( $C_6H_8O_7$ ) is first added to avoid metal transfer into struvite product. Then, MgO is used for the precipitation phase (it is not necessary to add ammonium, because nitrogen is usually present over stoichiometric)<sup>1</sup> and NaOH is dosed to raise the pH until 8. The precipitate is then dewatered using a chamber filter press to obtain the P-Recyclate. The phosphorus recovery rate is about 45% (Schaum, 2018. Chapter 21). Fig. 8 shows a flow sheet of the process described above.

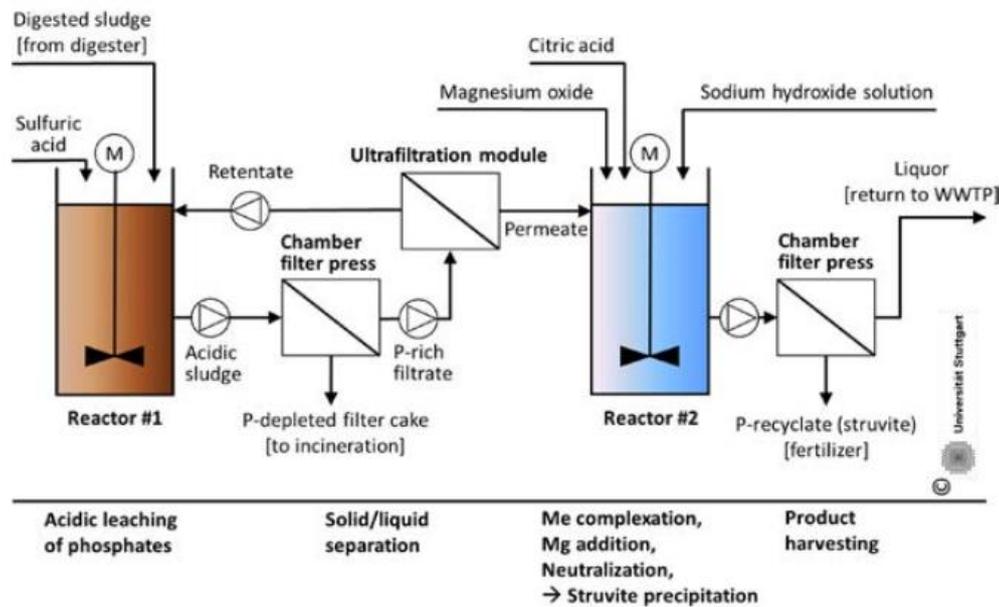


Fig. 8 Scheme of the Stuttgart process (Schaum, 2018).

<sup>1</sup> Struvite formation is promoted by alkaline conditions while the stoichiometric ratio is Mg:N:P = 1:1:1 (Canziani et al. 2018).

### 3.1.2.3 RecoPhos P38 process

RecoPhos P38 belongs to the wet chemical leaching process, because ISSAs are leached with industrial grade phosphoric acid (~52% H<sub>3</sub>PO<sub>4</sub>) to obtain a phosphate product, which is similar to the common fertilizer (triple superphosphate, TSP). After several tests conducted by German scientists that proved the benefits and applicability of this new type of fertilizer, 1,000 tons per month of RecoPhos P 38 are currently produced at industrial scale (Harald Weigand, Bertau, Hübner, Bohndick, & Bruckert, 2013). It shows a good water solubility with a phosphorus content of 16.6%. Fig 9 shows a simplified scheme of the process.

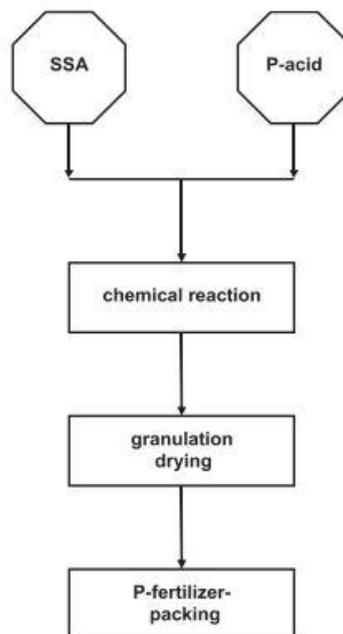


Figure 9 Simplified scheme of the RecoPhos P38 process (Weigand et al., 2013).

The following chemical reaction that takes place is suggested by Weigand et al. (2013):



As it can be seen, the primary minerals present in the ashes (stanfieldite) can react with phosphoric acid producing soluble calcium and magnesium dihydrogen phosphate, which is indeed the primary component of the RecoPhos P 38 fertilizer. However, it is important to highlight that because of the lack of decontamination step, high input quality regard phosphorus and heavy metal content in the ashes are required (Gorazda et al., 2017). The recovery efficiency is ~100% with respect to the ash input, and 85% with respect to the WWTP (H Weigand, Bertau, Bohndick, & Bruckert, 2011).

### 3.1.2.4 PASCH process

PASCH process, whose name refers to phosphorus recovery from ash, has been developed by the Applied Polymer Science institute at Aachen University (Germany). It is a lab-scale technology based on the wet chemical leaching, with an average phosphorus recovery rate of 60-70% with respect to WWTP influent (equal to a recovery rate 70-80% with respect to the ash input) (L. Egle et al., 2016). The products obtained are magnesium phosphate and calcium phosphate, which contain low amounts of metals and ensure an effective plant availability.

Fig. 10 shows a simplified scheme of the process that is composed by elution phase, filtration, liquid-liquid extraction and precipitation.

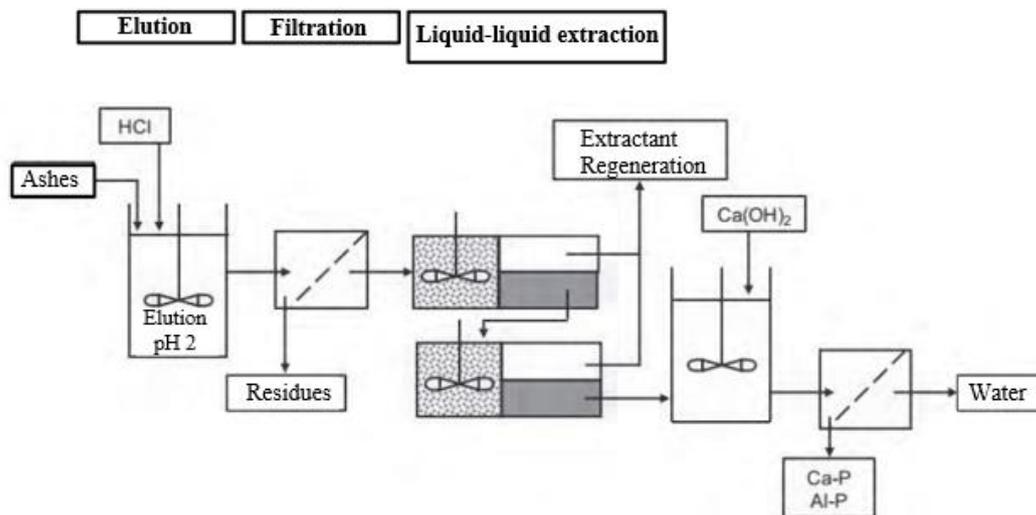


Fig. 10 Simplified scheme of PASCH process (Schaum, 2018).

Montag et al. (2011) have conducted different lab-scale tests and have obtained a phosphorus extraction efficiency equal to 94%. They used 25 g of ashes, mixed with HCl at 8%, with L/S of 5, 90 min reaction time and temperature of 30 °C (Montag et al., 2011).

They carried out also experiments by dosing H<sub>2</sub>SO<sub>4</sub> (at 8%), H<sub>3</sub>PO<sub>4</sub> (at 8%) and NaOH (at 17%) obtaining 92%, 57% and 30% as recovery rates, respectively.

To optimize the process, they investigated also different operating temperatures (from 30 to 90 °C) and observed that temperature is not a fundamental parameter for enhancing the phosphorus dissolution. In fact, the extraction efficiency did not increase significantly, while the higher iron dissolution at temperature higher than 30 °C affected negatively the process.

After the elution, the suspension was filtered (at 4-7 µm) and the residues washed with water and oven dried at 105 °C to be then disposed of.

Subsequently, a liquid-liquid extraction in two well-mixed reactors was performed to remove iron (Fe) and heavy metal (Cd, Pb, Cu, Zn), which are present in solution as chloro-complexes. The extraction was carried out by dosing two different reactants (Alamine 336 and tri-butyl-phosphate (TBP)), which have been mixed with the acidic solution for 5 minutes. Montag et al. (2011) reported a good extraction efficiency for Cd, Pb, Cu and Zn (>75%), while Cr and Ni cannot be extracted. Finally, the last phase is related to phosphorus precipitation, which involves the dosage of lime milk, a strong base. The process has been performed until pH is stable to 3,4-4 for 10-20 minutes without providing heat. To separate the final product from the suspension, a centrifuge has been applied. The product recovered shows a  $P_2O_5$  content of 24.5%, which is equal to about 11% of total P.

### 3.1.2.5 EcoPhos process

EcoPhos is a multistep process originally developed to produce phosphoric acid (PA) from low grade phosphate rock, but applicable also to sewage sludge ashes. There is a full-scale plant operating in Varna (Bulgaria), constructed in 2016 and dealing with phosphate rocks. Another full-scale plant is located in Dunkerque (France), using low-grade phosphate rock and producing 220,000 tons/y of  $CaHPO_4$ . A new line for processing the ashes is going to be constructed in the nearby future, whose goal is treating 10,000 tons of ashes in parallel.

The conventional process refers to the leaching of calcium apatite with sulfuric acid to dissolve phosphorus. However, co-dissolution of heavy metals, such as Cd and Pb, and radioactive elements can occur. Ohtake & Tsuneda (2019) reported that the conventional process produces a large amount of solid wastes and more specifically 21.8 tons of mine wastes and 6.5 tons of tailing are generated for each ton of PA produced. For this reason, alternative raw materials have been tested like sewage sludge ashes (SSA). The process is economically feasible from SSA-input volumes of at least 10,000 tons/y.

A briefly description of the EcoPhos process, which is based on the HCl digestion process, is provided. Fly ashes are mixed in a digestion reactor with phosphoric acid to dissolve phosphorus. Then, there is a filtration unit to separate the insoluble solid residues from the leachate, followed by a multiple module of ion-exchangers to separate Al, Fe, Mg and Ca ions and, consequently, to purify the phosphate.

Resins applied in the process are usually regenerated with 0.9 L of HCl/kg ashes used (Canziani & Di Cosmo, 2018) and the phosphoric acid obtained has a concentration of approximately 25%  $P_2O_5$

(Ohtake & Tsuneda 2019). Thanks to the different modules used, the separation of valuable recovery by-products is possible.

As it can be seen in Fig. 12, part of the phosphoric acid recovered is recycled in the first stage of the process (digestion reactor), while the other part is sent to a concentration unit that uses steam to obtain phosphoric acid at commercial grade (~ 62%  $P_2O_5$ ).

So, 95 % of the phosphorus contained in the ashes can be recovered as phosphoric acid ( $H_3PO_4$ ).

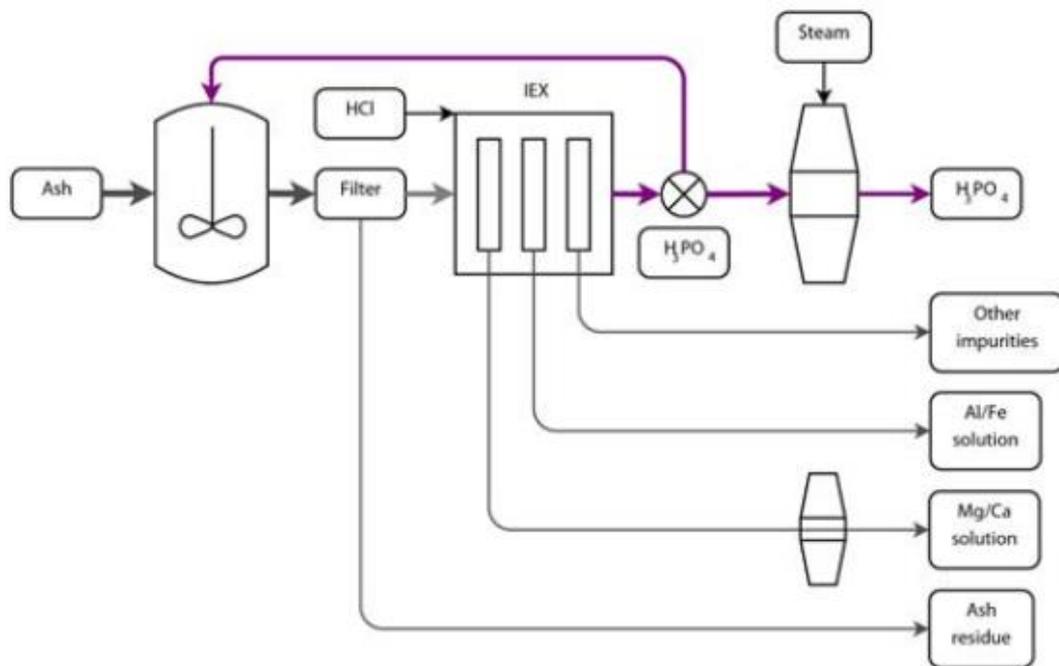


Fig. 11 Simplified Scheme of the EcoPhos HCl process (Schaum, 2018).

### 3.1.2.6 LEACHPHOS process

LEACHPHOS process has been developed in 2010-2012 by BSH Umweltservice GmbH at laboratory scale. It is based on the wet leaching process of sewage sludge ashes and the phosphorus recovery rate ranges from 80 to 90% (Schaum, 2018. Chapter 25) that correspond to a recovery of 60-70% if compared to the WWTP influent (L. Egle et al., 2016). The pilot plant in Bern recovered 6 tons of dry phosphorus product starting from 45 tons of sewage sludge ashes (BSH Umweltservice AG [https://www.umweltbundesamt.de/sites/default/files/medien/378/dokumente/buehler\\_bsh\\_leachphos.pdf](https://www.umweltbundesamt.de/sites/default/files/medien/378/dokumente/buehler_bsh_leachphos.pdf)).

Sewage sludge ashes from mono-incineration plant are put in a stirred batch reactor and mixed with diluted sulphuric acid to dissolve phosphorus contained in the ash. Then, a solid/liquid separation process takes place usually using a vacuum belt filter. The filter cake separated is withdrawn from the process and must be disposed of.

The next phase involves the dosage of NaOH and lime milk to precipitate phosphorus contained in the leached solution. The precipitate is a Ca-P rich product, whose phosphorus content expressed as  $P_2O_5$  is about 30%. Thus, it is extracted and filtered, as it can be seen in Fig. 11.

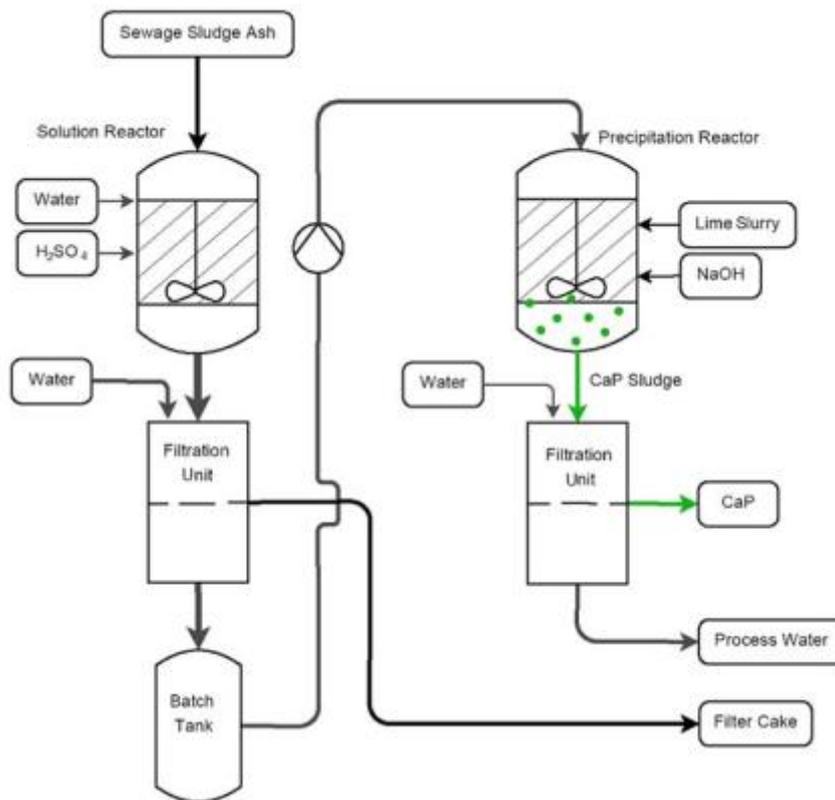


Fig. 12 Simplified scheme of the LEACHPHOS process (Schaum, 2018).

This technology is characterized by high flexibility, because many parameters can be varied and adapted to the characteristics of the input material, customer demand or legal requirements (Schaum, 2018). However, the main drawback is related to the large amount of chemicals used and the generation of high amount of waste (such as filter cake). Lema and Suarez (2017) reported that it is necessary to use 5.6 kg  $H_2SO_4$ /kgP, 0.6 kg NaOH/kgP and 3.9 kg  $Ca(OH)_2$ /kgP.

Moreover, Table 3 shows the mass flow of starting materials and products in a facility that operates with 15,000 tons/y SSA, where TMT 15 is used as precipitation agent for heavy metals. In fact, after precipitation and separation of the phosphorus product, the liquid waste stream must be processed to fulfil the legal requirements. Pb, Hg, Ni and Cr can achieve removal rate of 90%, while for Zn, Cu,

As and Cd it is between 60 and 90%, depending on the impurities and alkalinity of the ashes (Schaum, 2018. Chapter 25).

*Table 3 Mass flow of starting material and products (Schaum, 2018).*

	<b>Mass balance</b>	<b>P<sub>2</sub>O<sub>5</sub></b>
<b>Starting materials</b>		
SSA	2000 kg/h	14.4%
H <sub>2</sub> SO <sub>4</sub> solution (98%)	750 kg	
NaOH solution (40%)	30 kg/h	
Ca(OH) <sub>2</sub>	300 kg/h	
TMT 15	1 kg/h	
Water	15 m <sup>3</sup> /h	
<b>Products</b>		
Leached SSA	1800 kg/h	2.3%
LeachPhos product	675 kg/h	>30%
P-Recovery	70–80%	
Wastewater	15,000 L/h	
Waste product	50 kg/h	

### **3.1.3 Wet oxidation and supercritical wet oxidation**

Wet oxidation process has been developed on pilot-scale for phosphorus recovery from sewage sludge. Some authors reported that it may be environmentally favourable and more cost-effective than incineration (Svanström, Fröling, Modell, Peters, & Tester, 2004). PHOXNAN is an example of this technology that belongs to hydrothermal treatment. During the process, the organic content of sewage sludge is thermally degraded and oxidized producing CO<sub>2</sub>, H<sub>2</sub>O and nitrogen (Fytli & Zabaniotou, 2008).

The process consists in two different phases: in the first phase the sludge is oxidized at a relative low pressure (20 bar) in superheated water (200 °C) at pH 2, while in the second phase nanofiltration is applied to separate the solids from the leachate. Because the phosphorus recovery rate decreases with increasing iron concentration in the sludge, this process can be used for treatment plants with EBPR. Supercritical wet oxidation is based again on the oxidation of the sludge, but the reaction takes place in a liquid-gaseous solution at higher pressure and temperature (221 bar and 374 °C). Oxygen is added in the reactor for ensuring a complete oxidation with reaction time equal to 60 seconds and HRT of 5 minutes. By applying these parameters, 99% of the organic matter is decomposed to CO<sub>2</sub>, organic and inorganic nitrogen to N<sub>2</sub> (gas), as well as P is converted to P<sub>2</sub>O<sub>5</sub>. Phosphorus is recovered through a series of thickening batch process followed by filtration. Extraction is carried out in alkaline conditions, so lime is added. The recovery rate of Aqua Reci process, which belongs to this category, ranges between 45 and 65% of the phosphorus in the sludge. This corresponds to 40-60% of the phosphorus in the WWTP influent (L. Egle et al., 2016).

### **3.1.4 Hydro-thermal carbonization**

Hydrothermal carbonization is a process able to transform sewage sludge, even with elevated moisture content (up to 75-90%), into a more attractive and valuable product. Sewage sludge is put in contact with distilled water (so under wet condition) in a closed reactor at a temperature of 180-250 °C and a pressure of 10-20 bar. The sludge is converted into a solid carbonaceous fuel, which has higher carbon density and calorific value, and contains phosphorus as well (P<sub>2</sub>O<sub>5</sub> up to 52.55%) (Song, Park, & Kim, 2019). Hence, the char can be leached by an acidic aqueous solution obtaining dissolved phosphate in solution. To separate liquid from solid phase, filtration can be used, followed by precipitation to get hydrate calcium phosphate. Direct application of this fertilizer in agriculture is usually allowed.

### 3.1.5 Gasification

Melt gasification of sewage sludge belongs to thermo-chemical processes (Lema and Suarez, 2017), because the melting process of dewatered and dried sludge takes place in a cupola furnace under high temperature (1800-2000 °C) and with addition of coke. Sewage sludge is added in the form of dry briquettes (moisture content 4 %) to facilitate the passage of the gases. The slag formed  $\text{Ca-Si-PO}_4$  is rich in phosphorus (10-25%  $\text{P}_2\text{O}_5$ ), which is then granulated and further treated to form fertilizers, while the metal slag accumulates at the bottom part of the furnace because of its higher density.

Simultaneously, the synthesis gas is produced thanks to the carbon content of sewage sludge and it can be used for power and heat generation.

The main drawbacks of gasification process are related to the generation of a significant amount of aerosols and the accumulation of heavy metals in the final residue, making the disposal more problematic (Fytli & Zabaniotou, 2008).

The process called MEPHREC has been tested in a pilot scale plant at the Nuremberg WWTP and a scheme of it is reported in Fig. 13.

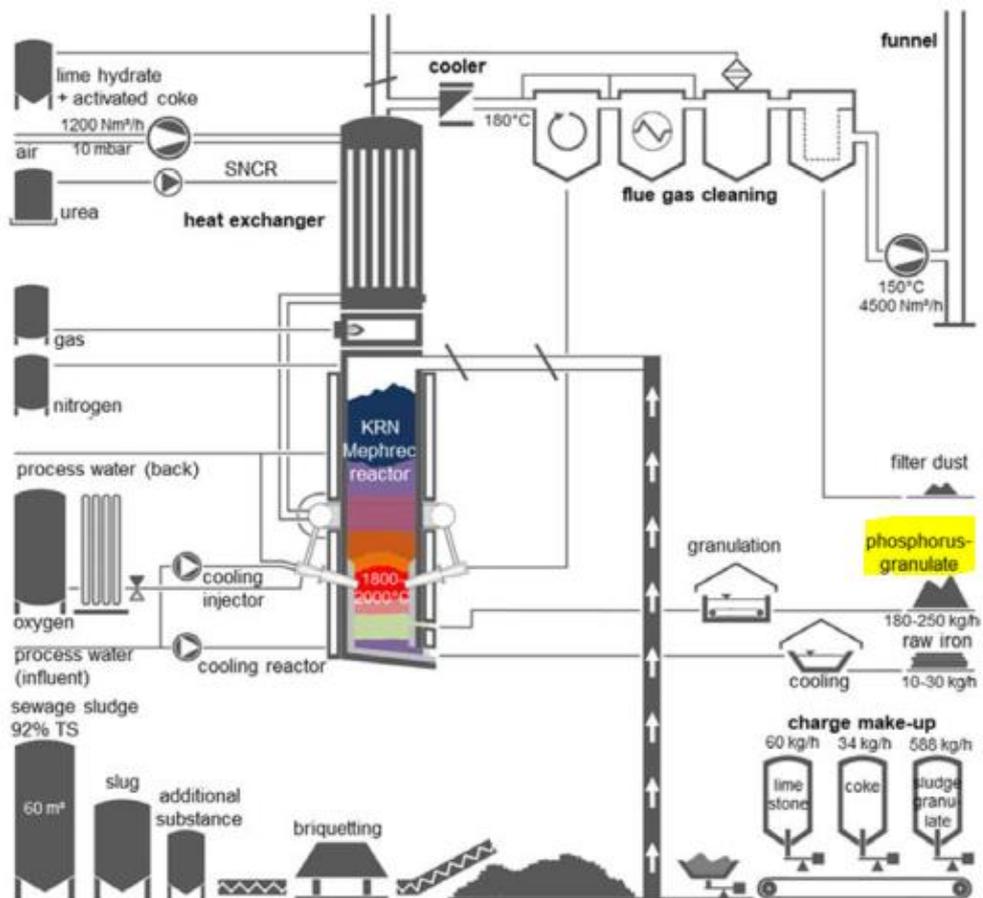


Fig. 13 Scheme of the Mephrec process (Schaum, 2018).

### 3.1.6 Thermochemical treatment

#### 3.1.6.1 AshDec process

The most common technology that uses a thermochemical process is the AshDec process, which has been developed by Outotec and German Federal Institute for Material Research and Testing (BAM) in the EU FP6 SUSAN project. It has been applied successfully for the first time at pilot-scale in 2008 in Leoben (Austria), treating up to 7 tons of ash per day, under continuous operation conditions.

The process can be classified in AshDec Depollution and AshDec Rhenania, depending on the type of additive applied. The term “Depollution” is used to define the processes needed to reduce the concentration of heavy metals in the recovered raw product. While the term “Rhenania” refers to the product obtained by the second AshDec process, which is indeed Rhenania phosphate.

AshDec Depollution uses a dosage of chloride additives (e.g.  $\text{MgCl}_2$ ) to SSA followed by thermal treatment at 850-1000 °C for 20-30 minutes to promote heavy metals decontamination (higher than 90% in the case of Cd, Cu, Pb and Zn, while As, Cr and Ni remain in the ashes) and P bioavailability (Gorazda et al., 2017). In this process, the heavy metals removal (in the form of volatile chlorides and oxychlorides) is more efficient, because chlorines can react with metals forming metal chlorides ( $\text{ZnCl}_2$ ,  $\text{CrCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{PbCl}_2$ ) that become gaseous at temperatures of 700-900 °C.

During the thermochemical process, new P-mineral phases (calcined phosphates) are built up. At 1000 °C calcium phosphate chlorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{Cl}_{1-x}(\text{OH})_x$ ), magnesium phosphate farringtonite ( $\text{Mg}_3(\text{PO}_4)_2$ ) and the calcium-/magnesium phosphate stanfieldite ( $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ ) can be present (Desmidt et al., 2015). Thus, thanks to the low heavy metal concentration, the final product obtained, which is usually in form of pellets or granules, is suitable for agricultural purposes. Hazardous waste produced must be then disposed of and flue gas cleaned, through filtration and adsorption methods. However, the major drawback is related to the lower phosphorus plant availability on alkaline soils that the output of the process has (Schaum, 2018. Chapter 27).

To improve the phosphorus bioavailability, the AshDec Rhenania process has been implemented. SSA are treated with  $\text{Na}_2\text{SO}_4$  (and not with chloride additives) in the rotary kiln at 900-1000 °C with a retention time usually kept around 20 minutes in order to get  $\text{NaCaPO}_4$  (Rhenania phosphate), which is a more soluble phosphate compound. On the other hand, a lower depollution rate is achieved (e.g., Cd: 80%, Pb: 50-70%, As and Zn: partial, Cu: none) (Lukas Egle, Rechberger, & Zessner, 2015).

Fig. 14 shows a simplified flow sheet of the AshDec Rhenania process.

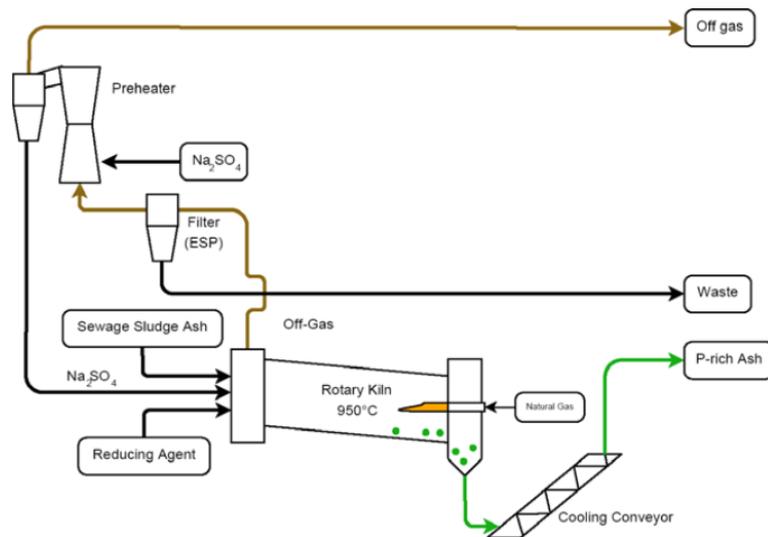


Fig. 14 Simplified scheme of the AshDec Rhenania process (Schaum, 2018).

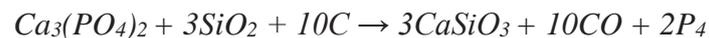
Table 4 summarizes what has previously been discussed. In both processes, 98% of phosphorus in the sewage sludge ash can be recovered with a waste flow (filter dust) equal to 2-3% (Schaum, 2018. Chapter 27).

Table 4 Overview of the AshDec process (Schaum, 2018).

Type of Process:	Thermochemical process
Operating temperature:	$900\text{--}950^\circ\text{C}$
Residence time:	15–20 minutes
Type of Plant:	Rotary kiln, preferably directly adjacent to a sludge-to-energy plant
Input Material:	Sewage sludge ash
Output Material:	Calcined phosphates or Rhenania phosphates or thermophosphate with $\text{CaNaPO}_4$ as the main phosphate-containing phase
P-concentration:	15–25% $\text{P}_2\text{O}_5$ depending on the phosphate concentration in the input materials
P recovery performance:	98% of P in the sewage sludge ash

### 3.1.6.2 RecoPhos/Inducarb process

RecoPhos/Inducarb is a full-scale process inspired by an European project that has been developed by a consortium including European universities (Montanuniversität Leoben, University of Stuttgart), small and medium enterprises and multinational industries (SGL Carbon GmbH, M.A.L., Inerco, InsPyro, H-CPE, M.I.T. and GCTU). Then, it has been acquired by a global manufacturer of products, ICL fertilizers, in March 2016, and operates nowadays in 4 different units of 9000 t/a P<sub>4</sub> in Europe and the United States (Schaum, 2018. Chapter 29). The process is based on the thermo-reductive approach aimed at phosphorus compounds reduction at temperature of 1300-1600 °C in an inductively heated coke bed. Carbon ensures a reducing atmosphere so phosphate contained in the ashes can be vaporized as pure phosphorus. The main chemical reaction involved in this process is shown by the following equation:



Then, gaseous phosphorus can be condensed to white phosphorus or oxidized to produce phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) (Canziani & Di Cosmo, 2018). Usually 100% of the phosphorus present in the sewage sludge ashes can be recovered (85% of the influent phosphorus at WWTP) (L. Egle et al., 2016). The main by-products of the process are *ferrophos* (an iron alloy), which is a mixture of elemental phosphorus (P<sub>4</sub>) and iron, and synthetic gas (mainly CO) that can be used for ashes pre-heating or steam/electricity generation. Finally, a flue gas treatment module is required to remove heavy metals that are vaporized. Process is illustrated in Fig. 15: ash is fed from the top of the reactor and smelts at the surface of the carbon balls. Thus, P<sub>4</sub> and CO are released as gaseous in absence of oxygen.

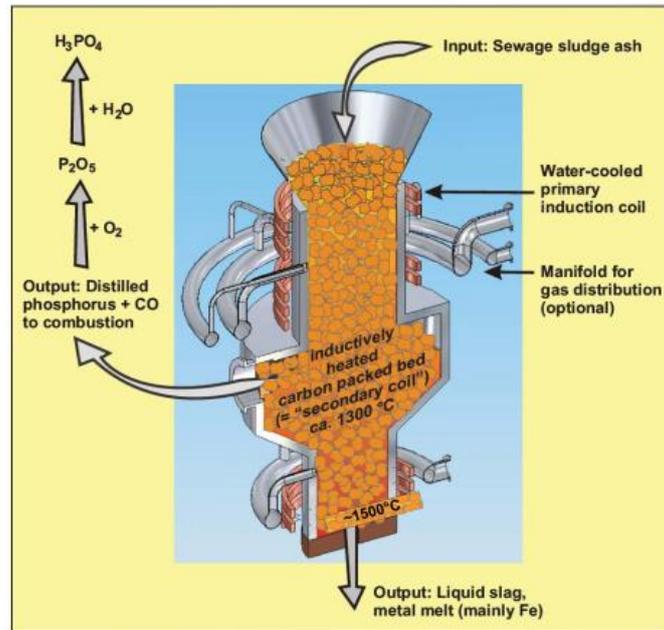


Fig. 15 Simplified scheme of the RecoPhos/Inducarb process (Ohtake & Tsuneda, 2019).

This technology is suited for high quality ash with low heavy metal content due to the lack of heavy metals removal steps. The process complexity is not high, and no waste stream is produced.

The amount of the by-products gained is 8.8 kg silicate-slag/kgP<sub>recovered</sub>, 1.3 kgferrophos/ kgP<sub>recovered</sub> and 9.7 kg syngas/ kgP<sub>recovered</sub>.

However, it is an energy intensive process, which uses 26 kWh/kg P<sub>recovered</sub> and 1.45kg<sub>coke</sub>/kg P<sub>recovered</sub> (Schaum, 2018). Thus, pre-heating the ash could be a good option for reducing the energy consumption up to 50 % (Schaum, 2018. Chapter 29).

## 4 Incineration

In relation to the scope of the present work, incineration will be the main process assessed.

Incineration belongs to thermal treatment of sewage sludge that has become more interesting over last years. This was determined by the introduction of more strict regulations on the direct application of sewage sludge in agriculture, which has been used intensively for decades. This caused a shift to other new and more sustainable technologies for sewage sludge treatment such as thermal treatment. Indeed, the amount of sewage sludge that have been incinerated in Europe in 2011 was 23.6% (Pellegrini, Saccani, Bianchini, & Bonfiglioli, 2016), percentage that is expected to increase in the next years.

Incineration is regarded as the best way to dispose sewage sludge because it can (Hartman, Svoboda, Pohořelý, & Trnka, 2005):

- *reduce waste volume,*
- *decompose organic pollutants,*
- *reuse the energy contained in the sludge,*
- *generate valuable by-products.*

The main technology examined will be the fluidized bed incinerator (section 4.3), while other types of technology such as multiple hearth furnaces (MHF), rotary kiln, cyclone and different types of smelting furnaces are not going to be investigated in this present work (Zhu, Yao, Lu, Gao, & Ouyang, 2015).

However, the common product obtained from a sewage sludge incineration process is the ash.

Phosphorus from incinerated sewage sludge ashes can be recovered through two different processes that correspond to thermo-chemical and wet extraction methods. AshDec and RecoPhos/Inducarb processes belong to the first category, while LEACHPHOS, EcoPhos, RecoPhos P38 and PASCH to the second, which have been described in paragraph 3.1.6 and 3.1.2, respectively.

This work focuses its attention on the second technology, which is based on dissolution in acidic environment of the ashes followed by separation/filtration and precipitation processes, as previously discussed. In general, the advantages of wet extraction are related to a high phosphorus recovery potential, high flexibility (ash composition and adjustable leaching parameters) and simple devices for extraction and phase separation (Gorazda et al., 2017). We decided to investigate the use of sulfuric acid and hydrochloric acid as the main extractants.

## 4.1 Incineration of sludge

Incineration of sludge is a common approach usually adopted in densely populated regions with low land availability, where high quantities of sludge are produced (Ciešlik, Namiešnik, & Konieczka, 2015). Currently, it is considered as one of the most effective alternatives for sludge disposal and stabilization and has been widely applied in many countries such as Germany, which generates about 300,000 tons of SSA per year (Herzel, Krüger, Hermann, & Adam, 2016).

There are two different terms usually applied in this field that are mono-incineration and co-incineration, whose main products are the exhausted gas, fly ash and slags (Ciešlik et al., 2015).

Incineration of sludge is defined as mono-incineration when sludge is the only material fed to the furnace, with the aim of volume reduction (~90%), destruction of pathogens and harmful substances, odour minimization and energy recovery, as mentioned before. Co-incineration instead relates to the combustion of sewage sludge together with municipal solid wastes (MSW). Lin et al. (2012) reported that co-incineration of 10% wet sludge with MSW can ensure the grate type furnace temperature, while 20% of semi-dried sludge can reach the same standard (Lin & Ma, 2012). As already discussed, the more the sludge is previously dried, the less supplementary fuel is needed to support the combustion process.

Furthermore, the increase proportion of sludge in MSW can cause the downward of the combustion temperature that inevitably leads to unburned wastes.

The already existing municipal incinerators can be more attractive if a WWTP is located nearby or if the plant has a modern flue gas cleaning technology. However, it is important to underline that these plants have a determined capacity that cannot be exceeded and mixing two different matrices with different phosphorus content does not ensure an efficient phosphorus recovery.

P<sub>2</sub>O<sub>5</sub> content of sewage sludge ashes ranges from 14 to 25% (Y. Li, Cui, Yang, Zhai, & Li, 2017), a higher value compared to P<sub>2</sub>O<sub>5</sub> content in the MSW bottom ashes (~13%) (Lam, Barford, & McKay, 2011) and sewage sludge (4-13%) (Pettersson, Åmand, & Steenari, 2008), because of the significant reduction (70-90%) in the volume of the incinerated material.

In more details, phosphorus maximum concentration in the ashes is up to 20% with an average value ranging from 5 to 11% (Ottosen et al., 2013) (Harald Weigand et al., 2013) (Ciešlik & Konieczka, 2017). Couto et al. (2015) reported that the concentration expressed in g/kg is from 70 to 134 g/kg (Couto et al., 2015). However, it must be taken into consideration that ashes from first and second sets of filters (generally electrostatic precipitators and wet scrubber, cyclones or bag filters) can differ. Therefore, different management methods should be designed properly.

Fig. 16 shows the distribution of phosphorus content in mono-incineration ashes in Germany. The red colour indicates the purely industrial sludge ash, the blue one the mixed mono-incineration of industrial and municipal sludge, and the green the purely municipal sludge ash.

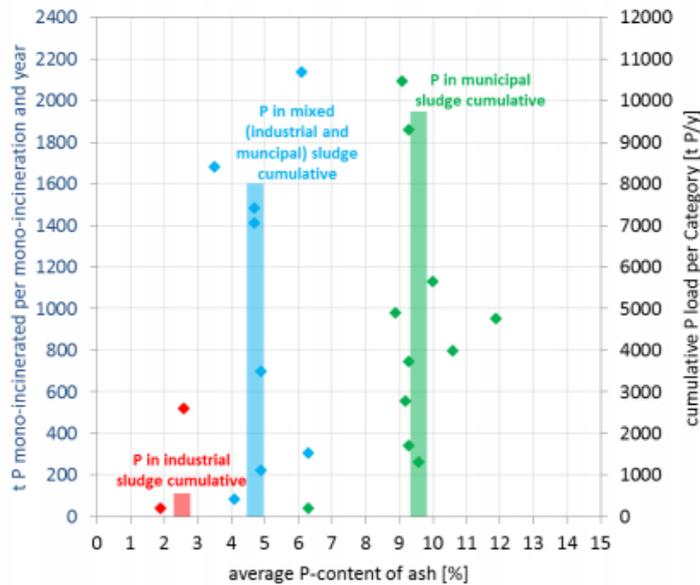


Fig. 16 Distribution of phosphorus content in mono-incineration ashes in Germany. Points refer to the primary y-axis, while bars to the secondary y-axis. (Kabbe 2019, based on Krüger and Adam, 2014).

However, the main drawback of sewage sludge incineration is related to the formation of hazardous air pollutants (HAPs) during the combustion. Fullana et al. studied in 2004 sewage sludge emissions and reported that considerable amount of chlorinated aliphatic compounds, chlorobenzenes, phenols and nitrogenated compounds can be generated (Fullana, Conesa, Font, & Sidhu, 2004). Thus, the formation of  $\text{NO}_x$  from the fuel-bound (organic) nitrogen cannot be avoided (Hartman et al., 2005). Because there are still some concerns related to emissions of gaseous pollutants, a good gas treatment system must be provided to remove particulates, acid gases and micropollutants, through a sequence of cyclones, bag filters and scrubbers and ensure the release of a safe exhaust gases to the atmosphere. These devices ensure a high efficiency, although they have a significant impact on process costs. In order to decrease capital and operational costs, the sludge fed to the incineration plant should be dewatered or dried in order to reach about 28-33% dry solid content to burn without any auxiliary fuel (Shane Donatello & Cheeseman, 2013). However, depending on the incineration technology used, different ranges are acceptable. Indeed, the fluidized bed incinerator allows to burn both wet and semi-dried sludge with a dry matter (DM) content that can vary between 41-65% (Fytli & Zabaniotou, 2008). Outotec Sewage Sludge Incineration Plant 100, for instance, burned dried sludge at ~ 40% DM. It will be discussed in more details in chapter 4.3.

Moreover, in the study by Ostojski et al. (2018) about the energetic potential of the municipal sewage sludge, a heating value of raw sludge of about 17 MJ/kg was reported, while values of about 15 MJ/kg and 11 MJ/kg were evaluated for activated sludge and stabilized sludge (digested), respectively. The latter value is similar to that of lignite, known as brown coal (Ostojski, 2018).

Table 5 shows the typical heating values of sewage sludge (Fytili & Zabaniotou, 2008).

*Table 5 Heating value of different type of sludge (Fytili et al., 2008).*

Type of sludge	Heating value (MJ/Kg of DS)	
	Range	Typical
Raw sludge	23–29	25.5
Activated sludge	16–23	21
Anaerobically digested primary sludge	9–13	11
Raw chemically precipitated primary sludge	14–18	16
Biological filter sludge	16–23	19.5

## 4.2 Characteristics of the incineration process

Incineration refers to an exothermic oxidation process involving several chemical reactions that generate CO<sub>2</sub>, H<sub>2</sub>O, ash, and a certain amount of heat. The main operation variables that strongly influences the efficiency of the combustion are bed temperature, freeboard region temperature, excess air and gas residence time. During sewage sludge incineration, it is fundamental to keep the temperature between 850 and 950 °C to avoid excessive odour emissions (that can occur below 850 °C) and sintering of the ashes (that can occur above 950 °C), as well as to get high energy production. Moreover, Hartman et al. (2005) claimed that the higher the temperature in the combustor is, the lower the N<sub>2</sub>O and CO emissions in the exit gas occur. Zhang et al. (2007) pointed out that temperature of 1250°C leads to a higher concentration of P in the dust fraction compared to the ash fraction (Zhang & Ninomiya, 2007). However, if we are dealing with incineration of different type of matrix like manure, temperature should keep below 700 °C to avoid the formation of insoluble hydroxyapatite in the ash (Thygesen, Wernberg, Skou, & Sommer, 2011).

About 30% of dry solids remains in the ashes that can be either disposed or reused as secondary raw material for construction purposes or as substituent to the traditional clay materials for glass-ceramics (Shane Donatello & Cheeseman, 2013). It is important to highlight that this method is able to concentrate the phosphorus in the SSA (Franz, 2008), whose inorganic fraction is mainly in the form of apatite phosphorus, bound to Ca/Mg ions which can be directly absorbed by plants (Adam, Peplinski, Michaelis, Kley, & Simon, 2009). Despite this, the main inorganic form of sewage sludge

is non-apatite phosphorus (NAIP), which is bound to Al/Fe/Mn ions. It exhibits low bioavailability, but it can be converted into apatite phosphorus with increasing temperature (R. Li et al., 2015).

It has been noticed that by increasing the temperature the ratio of AP/TP increased as well. This suggests that higher temperature promotes the conversion of NAIP to AP.

Zhao et al. (2013) suggested to add cotton stalk into sewage sludge to (i) improve the bioavailability of phosphorus in the fly ash during incineration and (ii) support the conversion of NAIP to AP (Zhao, Zhao, & Kearney, 2013). This mechanism can be promoted by the addition of CaO to the fluidized bed furnace.

### **4.3 Fluidized bed furnace**

Fluidized bed furnace is regarded as one of the best technologies that can ensure a higher combustion efficiency and a lower flue gas volume. The main parameters to deal with are the combustion temperature and the time that can ensure the completely burning.

In order to have an idea about the main units present in this type of configuration examples are provided. Firstly, different lab-scale studies conducted by Hartman et al. (2005) and R. Li et al. (2017) are presented, and, secondly, two full scale plants are illustrated.

Hartman et al. (2005) developed an experimental apparatus for the fluidized bed combustion with the following characteristics: 0,98 m height, 0,0936 m diameter, burning times equal to 20 s at 6 vol% O<sub>2</sub> and 5-6 s at 15 vol% O<sub>2</sub>. The dewatered sludge fed to the furnace contains about 65% of water with a particles size in the range of 1.4-1.6 mm. The resulting ashes had less than 1% of organic carbon left.

R. Li et al. (2017) designed a pilot fluidized bed as shown in Fig. 17. The main units are listed as follow: temperature controller (1), gas control panel (2), SSA collector (3), circulating fluidized bed furnace (4), cyclone separator (5), screw feeder (6), bag filter (7). Furnace height is 1700 mm, inner diameter 60 mm and the thermal power of fluidized bed incineration is equal to 20 kW. The dried sewage sludge is fed into the fluidized bed or mixed with CaO (to promote the conversion of NAIP to AP) at a rate of 5 g per minute. The sludge is combusted at 750-950 °C for a sufficient amount of time to ensure a complete combustion and SSA is then recovered as bottom ash, cyclone fly ash and fly ash from the bag filter (R. Li et al., 2017).

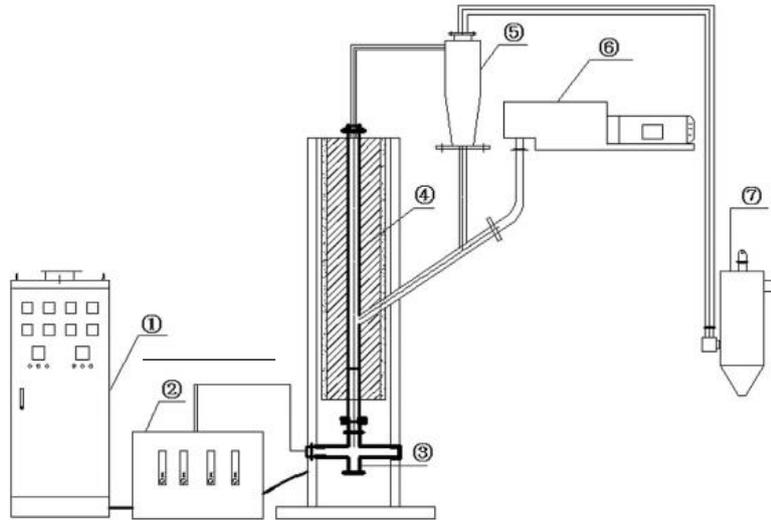


Fig. 17 Scheme of the pilot fluidized bed (Li et al., 2017).

An example of a full-scale implementation is given by the Outotec Sewage Sludge Incineration Plant 100, which has been developed in 2015 for the Disposal and Recycling Department of Zürich (ERZ). It is the largest thermal treatment facility of sewage sludge located in Switzerland that treats all the sludge coming from the Zurich canton area (~100,000 metric tons/a, which corresponds to a dry content of about 30,000 tons/a). The plant is self-sustaining, and the surplus of heat produced (~5 MW) is used for district heating. The main units are a sludge reception hall, a fluidized bed incinerator and a flue gas cleaning system.

(<https://www.outotec.com/references/sustainable-sewage-sludge-incineration-for-zurich-canton/>)

Fig. 18 shows a simplified scheme of the plant.

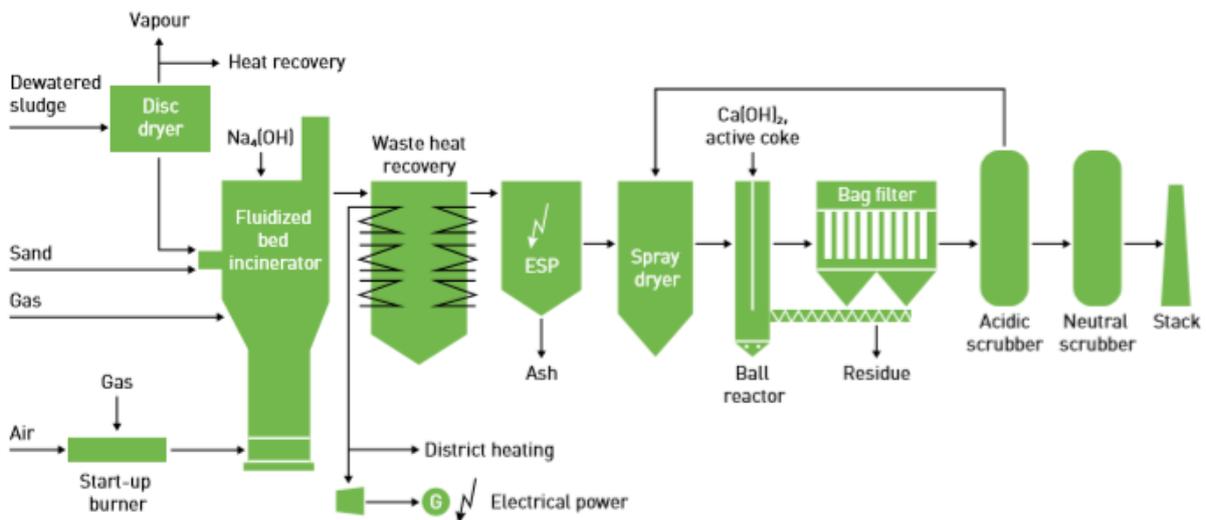


Fig. 18 Scheme of the Outotec Sewage Sludge Incineration Plant 100.

The sludge enters the dryer with a dry solid (DS) content of about 22-30% and exits with a value of 35-45% (which refers to a water content of about 55-65%). Then, the partly dried sludge is fed to the fluidized bed (FB) without the need of additional fuel. The air flow supplied is 16,000 m<sup>3</sup>/h with an oxygen content of 7-11 vol% dry and the combustion temperature is kept between 870 and 950 °C. The hot flue gases generated during the incineration process are used to pre-dry the sludge and to produce steam for a steam turbine. 99% of the ashes are collected from the electrostatic precipitator and the flue gas is then cleaned using a spray drying system, an adsorption reactor, baghouse filter and a two stages scrubber system to meet the environmental regulations. The emissions value guaranteed per m<sup>3</sup> of dry flue gas (at standard temperature and pressure) are reported in Table 6.

*Table 6 Emissions of the Outotec Sewage Sludge Incineration Plant 100.*

Dust	< 10 mg
Pb+Zn	< 1 mg
Hg	< 0.1 mg
Cd	< 0.1 mg
SO <sub>2</sub>	< 50 mg
NO <sub>x</sub>	< 80 mg
HCl	< 10 mg
HF	< 1 mg
NH <sub>3</sub>	< 5 mg
CO	< 50 mg
PCDD/PCDF	< 0.1 ng TEQ

Another example is given by the T-PARK, which is a sludge treatment facility located far from the residential areas of Hong Kong, in Nim Wan area, surrounded by sea and hills. It can treat up to 2,000 tons of sludge per day, because it is composed by four fluidized bed incinerators, grouped into two for the two plants. The ashes and residue produced are currently landfilled, but research to convert them into valuable products is going on (<https://www.tpark.hk/en/story/>).

The sludge coming from the 11 largest WWTPs in Hong Kong and reaching T-PARK is transported by 70% by vessel (to reduce the loading of road traffic) and 30% by truck.

The received sludge is then discharge to the bunker and can be used to feed the fluidized beds. Temperature of the combustion gases reaches 850 °C for at least 2 second to control the formation of organic pollutants. The heat produced during the incineration process is recovered and converted into electricity and the surplus is used to power up 4,000 households.

Moreover, the flue gas cleaning system is composed by three major components, which are the multicyclone (to separate large particle from fine), the dry reactor (to neutralise or capture acidic

gases, heavy metals and organic pollutants) and the bag filter (to remove fine particles), as reported in Fig. 19.

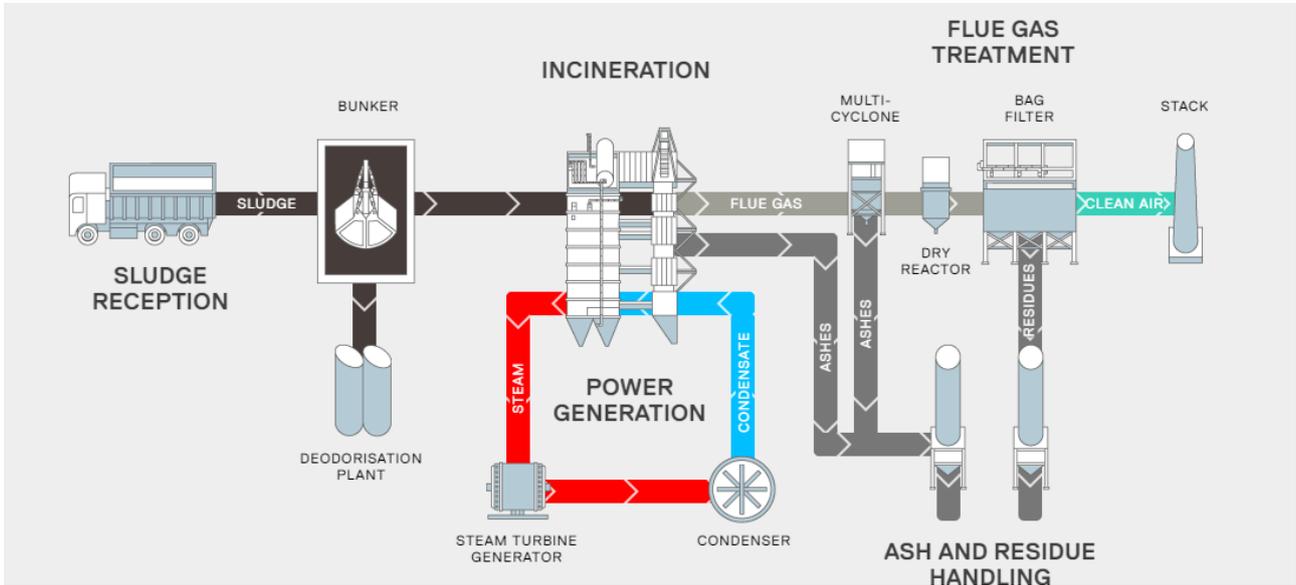


Fig. 19 Simplified scheme of the incineration process at T-Park (<https://www.tpark.hk/en/story/>).

## 5 Material and methods

The aim of this work is the evaluation of the phosphorus extraction yields from sewage sludge ash via wet chemical extraction. The experimental work studied ashes obtained from two different incineration plants located in Germany and Switzerland and from incineration in a laboratory standard muffle. Firstly, major components of the ashes (Fe, Al, Ca, Mg and P) and heavy metals were analysed through dissolution in aqua regia followed by inductively coupled plasma mass spectrometry (ICP-MS). Moreover, phosphorus concentration was determined using acidic mineralization and chemical measuring kits. Once the composition of each sample was determined, leaching tests were carried out at  $\text{pH} < 2$  with sulphuric acid and hydrochloric acid at different liquid to solid ratios. Finally, precipitation tests were performed to recover phosphorus in a form that can be more easily accepted by the fertilisers industry.

The following paragraphs present the methodology applied in order to evaluate the characterisation of the samples, the phosphorus extraction efficiency and the phosphorus content in the precipitate. Chemicals used in this work, formula and assay are presented in Table 7.

*Table 7 List of the chemical used.*

<b>Chemical</b>	<b>Formula</b>	<b>Assay</b>
Hydrochloric acid	HCl	37%
Sulphuric acid	H <sub>2</sub> SO <sub>4</sub>	96%
Calcium hydroxide	Ca(OH) <sub>2</sub>	≥ 95%

The acids used were then diluted with ultrapure water to get the proper concentration for each experiment. For filtration, filter papers with a pore size of 0.45  $\mu\text{m}$  and diameter of 27 mm from Whatman<sup>TM</sup> were used. All filtrates and solid fractions collected were stored in sealed PE-bottles at ambient temperature. All experimental apparatus used was provided by Department of Civil and Environmental Engineering at Politecnico di Milano.

### 5.1 Sample preparation

The incinerated sewage sludge ashes (ISSA) used in this study were collected from the mono-incineration plants located in Germany (Karlsruhe) and Switzerland (Zurich). The dewatered sludges from the two different wastewater treatment plants were incinerated at about 850 °C in a fluidized bed incinerator. The ISSA were then stored in sealed plastic bottle at room temperature and delivered

to the laboratory. Prior to testing, the collected sample from Zurich was oven dried at 105 °C because of its high humidity (about 21%).

Four other samples of dried sludges were collected from Italian wastewater treatment plants located near the city of Milan. Total solids and volatile solids have been determined. To simulate the incineration process, they have been incinerated in a standard muffle furnace at 900 °C for 2 hours. The six different ashes' samples were analysed to get phosphorus and heavy metals content. By using acidic mineralization and chemical measuring kit (Hach Lange LCK 348) the phosphorus in the ISSA was in the range of 7.5-9.6 %. These values are in accordance with the typically phosphorus content (5-12%) reported in literature (Biswas et al., 2009; Donatello et al., 2010; Franz, 2008).

The heavy metal content (As, Cr, Cu, Ni, Pb, Zn) was determined by aqua regia digestion followed by ICP-MS analysis. The presence of several elements (Ca, Mg, Fe, Al) was also investigated using ICP-MS and X-ray diffraction (XRD) in collaboration with the University of Brescia.

Concerning the contents of heavy metals, Zn is the most abundant with an average concentration of five samples investigated equal to 2200 mg/kg followed by Cu (980 mg/kg) and Cr (281 mg/kg).

As was present in low level (<75 mg/kg).

## 5.2 Leaching experiments

Leaching tests were carried out with the procedure reported in detail at page 40 and following, and repeated twice, while other possible procedures and data about the operating conditions usually reported in literature are listed in the Appendix.

Acidic extractions were carried out in batch tests at ambient temperature in glass beakers, using different operating conditions (type of acid: H<sub>2</sub>SO<sub>4</sub>, HCl; acid concentration: 0.4 N; liquid to solid ratio: 10, 20, 50) in order to achieve the best phosphorus extraction efficiency. Agitation was provided by a magnetic stirrer. Extraction solutions were prepared by adding correct amounts of pure sulfuric acid (96%) or hydrochloric acid (37%) diluted in ultrapure water.

The acid leaching process was optimised for one ISSA sample ("SGO (1)"), which shows an extraction efficiency >90% with the following conditions: 0.4 N H<sub>2</sub>SO<sub>4</sub>; L/S=20; contact time=2 h. The same result was achieved by (Fang et al., 2018).

The other five samples were tested using this optimal condition and for those that have shown an extraction efficiency lower than 85%, the L/S ratio was set to 50.

The leaching is then followed by centrifugation and filtration to enhance the solid/liquid separation. The leached filter cake that is formed, is discarded from the process and must be disposed of. Some

authors reported that dewatering the leached SSA could be a good option for diminish the costs of landfilling.

In addition, after drying the filter cake at 105 °C, we analysed the composition of it only once (for the sample of “SGO (1)”) to get an idea of the heavy metals and Ca, Mg concentration. As indicated in Table 8, the majority of the metals remain in the residue of the leaching tests except for As (>70% passes in solution).

*Table 8 Composition of the residue of the leaching test.*

<b>Element</b>	<b>Ashes at 900 °C (mg/kg)</b>	<b>Residue (mg/kg)</b>	<b>Percentage of elements in the residue</b>
<b>Ca</b>	80900	75195	92.9%
<b>Mg</b>	9970	3430	34.4%
<b>Zn</b>	1005.1	827.5	82.3%
<b>Cu</b>	700	433.5	61.9%
<b>Pb</b>	156	140	89.7%
<b>Ni</b>	279	190.5	68.3%
<b>Cr</b>	396	376	94.9%
<b>As</b>	34.1	8.35	24.5%

### 5.3 Precipitation

To precipitate the phosphorus from the leachate solution (initial pH less than 1.5), and make it available in a solid form, an oversaturation of ions is necessary.

Milk of lime at 1% (5 g Ca(OH)<sub>2</sub>/500 ml) was prepared and added to the solution until the pH reaches 8.5/9. Calibration of the pH-meter was performed in the desired range using two of the standard buffer solutions (at pH 7 and 10).

The suspension of lime milk was left on the magnetic stirrer at room temperature to have a homogenous solution. The final value of pH was set in accordance with the graph reported in Fig. 20, because at that pH most of the phosphorus precipitates as different form of calcium phosphates.

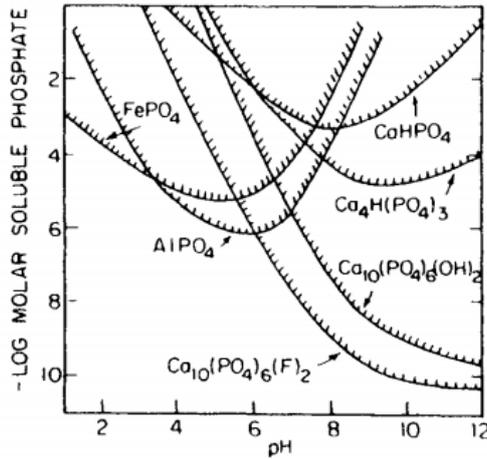
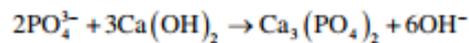


Fig. 20 Phosphate forms at different pH (Stumm & Morgan 1996).

The simplified reaction for precipitation is reported below (pH above 8):



Two tests were also carried out with lime water at 0.5% but the tests showed a need of larger volume of lime water to raise the pH until 8.5.

The procedure adopted is reported below.

#### Lime water @ 0.5% preparation

- Put 4 g of calcium hydroxide in an 800 ml clean glass beaker, in order to have a saturated solution.
- Fill the beaker with deionized water.
- Mix it with a magnetic stirrer for 10 minutes, then let it stand for 24 hours.
- Filter the solution through a 0.45  $\mu\text{m}$  filter paper, being careful not to stir up the sediment.
- Store the clear limewater solution in a glass bottle.

#### Milk of lime @ 1% preparation

- Put 5 g of calcium hydroxide in a 500 ml clean glass beaker.
- Fill the beaker with deionized water.
- Mix the suspension with a magnetic stirrer and use it for the tests.

A simplified scheme of treatment, which involves the acidic extraction and the precipitation of phosphorus as calcium phosphate, is reported in Fig. 21.

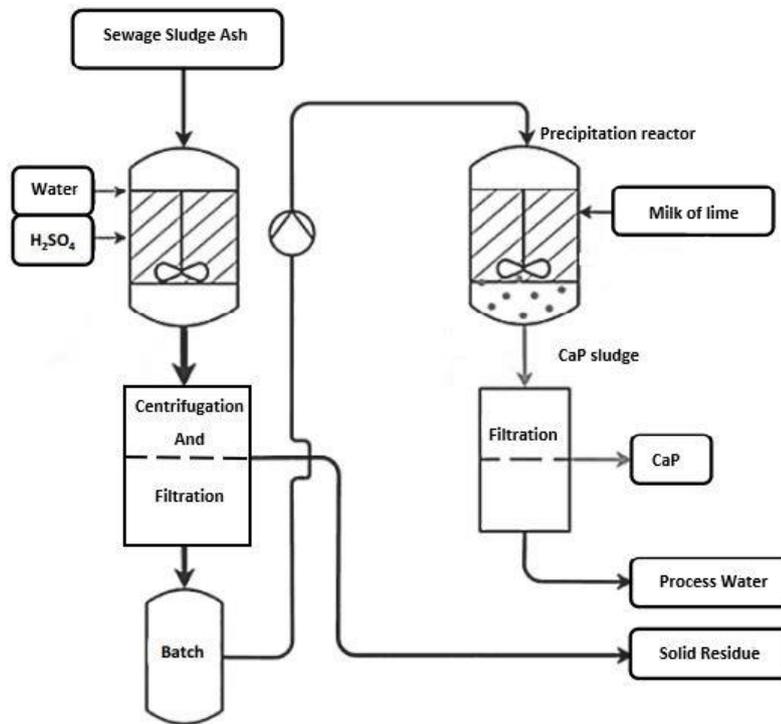


Fig. 21 Scheme of the process studied in this work (Adapted from Schaum, 2018).

## Procedure<sup>2</sup>

### 1) Sample preparation

- Determination of total solids (TS) at 105 °C.

Take 6 empty ceramic crucibles and oven dry at 105 °C for 1 hour. Put them in a desiccator for 40 min and weigh. Fill the crucibles with the sampled dried sewage sludge (total of about 200 g) and put them again in the oven at 105 °C for 2 hours. Afterwards, leave them in a desiccator for 45 min. Weigh the samples and subtract the tare weight to get the TS.

- Determination of volatile solids (VS) and ash at 600 °C.

Before getting the fraction of volatile solids (VS) and the ash at 600 °C it is necessary to pre-treat the samples using a hotplate under fume hood. Perform a heating curve of the hotplate from about 100 °C to 500 °C until the dried sludge stops emitting smoke. Leave the crucibles on the hotplate and let them cool down at ambient temperature to avoid the formation of fractures related to thermal stress (about 2 hours or more).

Put the crucibles in the muffle at 600 °C for 2 hours, let them cool down and put them in a desiccator for about 30 min. Weigh again the samples to get the ashes. Then calculate the VS/TS fraction as  $(TS - \text{ashes})/TS$ .

- To simulate the incineration process that usually occurs in a fluidized bed, put the ashes obtained as described above in the muffle at 900 °C for 2 hours. Leave them cool down, put them in a desiccator for about 40 min and weigh.

The incinerated sewage sludge ashes (ISSA) produced in this way are the starting point for the subsequently characterization and leaching experiments.

### 2) Characterization of incinerated sewage sludge ashes (ISSA)

- Oven dry the previously prepared samples at 105 °C overnight.
- Determine on two replicates:
  - phosphorus, aluminium and iron content,
  - heavy metal content<sup>3</sup> by mineralisation with aqua regia followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis.

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<sup>2</sup> Following: Fang, L., Li, J.-s., Guo, M.Z., Cheeseman, C.R., Tsang, D.C.W., Donatello, S., Poon, C.S. 2018 Phosphorus recovery and leaching of trace elements from incinerated sewage sludge ash (ISSA). *Chemosphere* **193**, 278-287.

<sup>3</sup> As, Cr, Cu, Ni, Pb, Zn

### 3) Leaching experiments:

- Transfer 20 g of dry ISSA to a 500 ml beaker, add 400 ml of leachant (about 0.4 N H<sub>2</sub>SO<sub>4</sub>), cover the beaker with a watch glass to avoid volatilization and mix for 2 hours with a magnetic stirrer.
- After leaching, centrifuge the samples at 3500 rpm for 10 min to allow solid-liquid separation and filter the leachates through a 0.45 µm filter paper.
- Determine phosphate in the leachate by using phosphate test kit (before using it, adjust the pH by adding few drops of phenolphthalein and NaOH. Dilute it in a conical Falcon and shake vigorously before performing the test),
- Determine heavy metals in the leachate after acid digestion with concentrated HNO<sub>3</sub> at a volume ratio sample: HNO<sub>3</sub> = 5:2, followed by ICP-MS.
- Dry the solid residues from the leaching tests at 105 °C and analyse heavy metals content by mineralisation with aqua regia, which is the same procedure that has been used for the characterization of the incinerated sewage sludge ashes.

### 4) Phosphorus precipitation:

- Take a representative volume of leachate (e.g. 50 ml) and put it in a glass beaker.
- Add gradually milk of lime at 1% and mix the suspension with a magnetic stirrer. Measure the pH and stop adding milk of lime when pH reaches about 8.5.
- Filter the suspension through a 0.45 µm filter paper.
- Determine phosphate in the filtrate by using phosphate test kit (adjust the pH if necessary)
- In accordance with the mass balance equation, calculate the phosphorus that has precipitated.

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

$$C_{prec} \cdot V_{prec} = C_{leachate} \cdot V_{leachate} - C_{filtrate} \cdot V_{filtrate}$$

## 6 Results and discussion

### 6.1 Ash composition

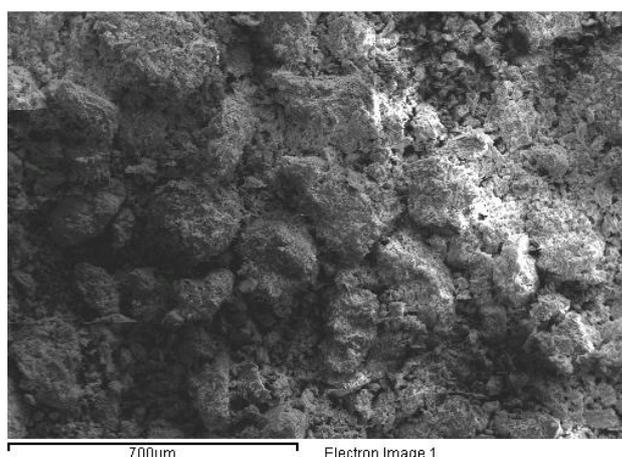
Table 9 shows the humidity, total solids and the ratio between volatile solids and total solids (VS/TS) of the different samples analysed. It emerged that the percentage of the ashes remained after incineration in the laboratory standard muffle refers to ~30%. This is because during the combustion process, sludge loses volatile materials, which mostly refers to organic substances.

*Table 9 Properties of the incinerated sewage sludge ashes (ISSA).*

sample	muffle incineration	humidity	TS	VS/TS
SGO (1)	yes	3.1%	96.9%	66.0%
S. Rocco 1	yes	9.2%	90.8%	72.8%
S. Rocco 2	yes	8.8%	90.25%	71.39%
SGO (2)	yes	15.5%	84.5%	67.1%
Zurich	no	21.0%	-	-
Karlsruhe	no	0.1%	-	-

Looking at the colour and granulometry of the ashes, it has been observed that black and dark brown ashes refer to higher humidity content ("S. Rocco 1", "S. Rocco 2" and "Zurich" samples), while brown colour and dusty sample ("SGO (1)") results in a lower content of humidity.

Fig 22 shows the SEM micrograph of particles in ashes from sample "SGO (1)", which have irregular shapes and seem to be rough with pores.



*Fig. 22 SEM image of ashes from sample "SGO (1)" (photo courtesy from Dept. of Chemistry, University of Brescia).*

As reported by R. Li et al. (2017), after extraction the structure changes because particles in ashes are broken down to smaller granules, even if agglomeration process can take place.

The content of Fe, Al, Ca, Mg and P in five different incinerated sewage sludge ashes (ISSA) samples and obtained by ICP-MS analysis, are summarized in Table 10. These elements are the most abundant in ISSA.

*Table 10 Most abundant elements in the ashes.*

<b>Origin</b>	<b>SGO (1)</b>	<b>S. Rocco 1</b>	<b>SGO (2)</b>	<b>Karlsruhe</b>	<b>Zurich</b>
Incineration in muffle	yes	yes	yes	no	no
<b>P (mg/kg)</b>	<b>75500</b>	<b>96000</b>	<b>84200</b>	<b>93000</b>	<b>86300</b>
Fe (mg/kg)	87200	26200	137900	20780	52000
Al (mg/kg)	49300	18710	24600	32890	17460
Ca (mg/kg)	80900	36800	47400	96300	111000
Mg (mg/kg)	9970	13700	7500	9100	12400

Phosphorus concentration is in line with the typical value reported in literature, which is approximately 8% (Biswas et al., 2009).

From basic chemistry, iron oxide and aluminium oxide can be derived. The average concentrations of samples “SGO (1)”, “S. Rocco 1”, “SGO (2)”, “Karlsruhe” and “Zurich” are 125 g Fe<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub>, 37 g Fe<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub>, 197 g Fe<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub>, 30 g Fe<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub> and 74 g Fe<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub>, respectively.

While aluminium oxide’s concentration is 93 g Al<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub>, 35 g Al<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub>, 46 g Al<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub>, 62 g Al<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub>, 33 g Al<sub>2</sub>O<sub>3</sub>/kg<sub>ss</sub> for sample “SGO (1)”, “S. Rocco 1”, “SGO (2)”, “Karlsruhe” and “Zurich”, respectively.

According to recent studies, it might be possible to substitute partially a fraction of apatite with sewage sludge ashes. To ensure a minor content of impurities this condition must be satisfied: Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub> < 1.5%. Because the ashes’ samples investigated showed a total percentage higher than 7% in all cases, the partial substitution is not possible.

Table 11 shows the heavy metal content by ICP-MS analysis. It clearly indicates that Zn is the most significant metal present at levels that ranged between 1,005 and 3,502 mg/kg. Similar results have been obtained by the 7 ISSA samples analysed by Donatello et al. (2010).

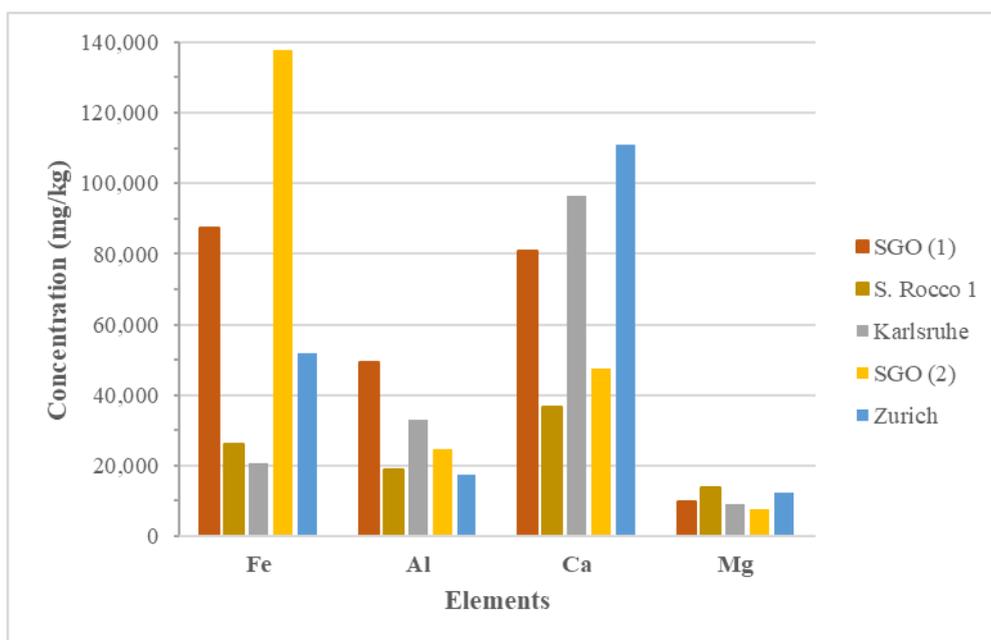
Table 11 Heavy metal composition for five tested samples.

	SGO (1)	S. Rocco 1	SGO (2)	Karlsruhe	Zurich
Zn (mg/kg)	1,005.1	2,792	1,910	3,502	2,024
Cu (mg/kg)	700	1,277	732	1410	783
Pb (mg/kg)	156	255	104	76	84
Ni (mg/kg)	279	233	131	74	46.3
Cr (mg/kg)	396	497	319	116	77.7
As (mg/kg)	34.1	12.1	74.2	5	17

Ni concentration in these ashes is instead higher than the average value reported by Donatello et al. (2010), while Pb concentration is less than the minimum reported.

The values of the different metals have been compared with the ones given from the Swiss regulation for agricultural land (compost) and resulted in most case exceeding them. The set of the limiting values agricultural application is listed as follow: Pb 120 mg/kg, Cr<sub>tot</sub> 100 mg/kg, Cu 100 mg/kg, Ni 30 mg/kg, Zn 400 mg/kg. Thus, these ashes cannot be directly used for agriculture purposes and need further treatments to decrease the metal concentration and to get plant available phosphorus.

The two graphs reported in Fig. 23 give a visual perception of what have been reported in Table 10 and 11.



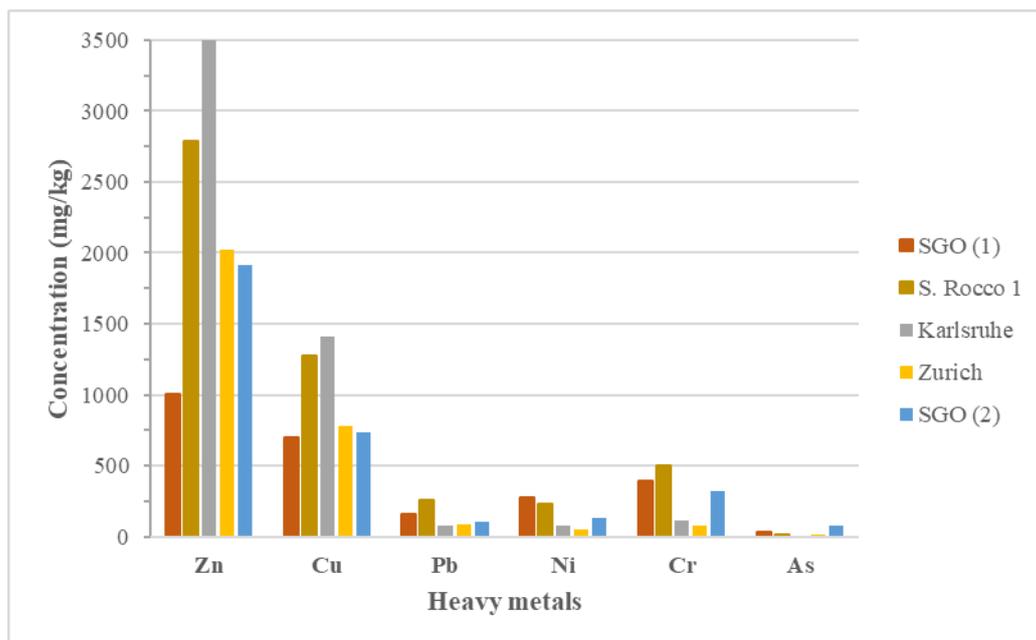


Fig. 23 Characterization of the ISSA: major elements and heavy metals composition.

In the following paragraphs a comprehensive experimental assessment highlights the influence of extraction operating conditions on phosphorus recovery and heavy metal leaching from incinerated sewage sludge ashes.

## 6.2 Release of phosphorus to the liquid phase

The determination of the presence of orthophosphate in the liquid phase was given by spectrophotometry as mg/L of P-PO<sub>4</sub>. Because the colour of the leached solution appears transparent, no interferences with the measurement have been observed. We assume that all the phosphorus present in the leachate is in the form of orthophosphate. Even if minor amounts of phosphorus could be present as particulates (probably P<sub>2</sub>O<sub>5</sub>), this fraction can be neglected.

Dissolution of 40-90% of phosphorus from ISSA by sulfuric acid is feasible, as indicated in Fig. 24. The brown bars correspond to the phosphorus content of the ashes, while the blue bars the phosphorus present in the leachate.

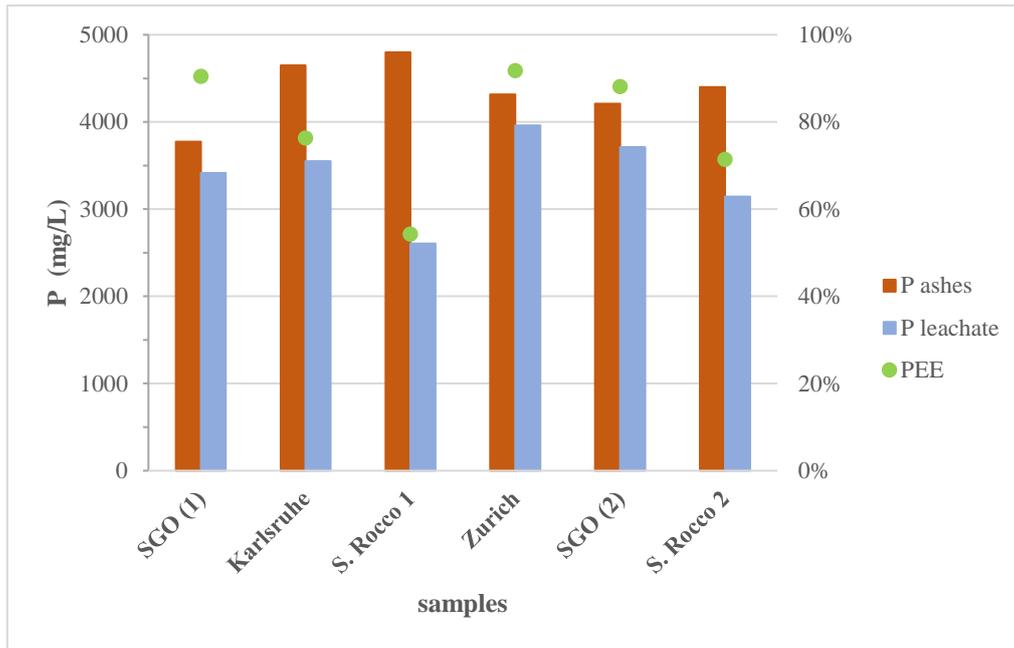


Fig. 24 Phosphorus concentration (in ashes and leachate) and phosphorus recovery efficiency for six tested samples using 0.4 N  $H_2SO_4$  as leaching agent with 20 liquid to solid ratio.

Table 12 summarizes the values of the phosphorus extraction efficiency obtained performing different leaching tests. It derives that it can be controlled and enhanced by changing fundamental parameters such as acid concentration, time of contact ( $t_c$ ) and liquid to solid ratio (L/S), depending on the chemical composition of the ashes.

Table 12 Average values of phosphorus extraction efficiency depending on operating conditions.

SGO (1)				
Type of extractant	Acid concentration (N)	L/S	$t_c$ (hours)	P extracted (%)
$H_2SO_4$	0.4	10	2	80.53
		10	3	79.21
		20	2	90.46
10		71.52		
HCl		20		84.77

SGO (2)				
Type of extractant	Acid concentration (N)	L/S	$t_c$ (hours)	P extracted (%)
$H_2SO_4$	0.4	20	2	88.12

<b>Karlsruhe</b>				
Type of extractant	Acid concentration (N)	L/S	t <sub>c</sub> (hours)	P extracted (%)
H <sub>2</sub> SO <sub>4</sub>	0.4	10	2	42.10
		20		76.34
		50		85.38
H <sub>2</sub> O	-	10		<1

<b>S. Rocco 1</b>				
Type of extractant	Acid concentration (N)	L/S	t <sub>c</sub> (hours)	P extracted (%)
H <sub>2</sub> SO <sub>4</sub>	0.4	10	2	52.19
		20		54.27
		50		58.13

<b>S.Rocco 2</b>				
Type of extractant	Acid concentration (N)	L/S	t <sub>c</sub> (hours)	P extracted (%)
H <sub>2</sub> SO <sub>4</sub>	0.4	20	2	71.48
		50		68.30
	1	50		79.20

<b>Zurich</b>				
Type of extractant	Acid concentration (N)	L/S	t <sub>c</sub> (hours)	P extracted (%)
H <sub>2</sub> SO <sub>4</sub>	0.4	20	2	91.77
H <sub>2</sub> O	-	10		<1

As stated in the literature review, a contact time of 2 hours can guarantee a sufficient contact between the solid particles and the extracting solution. Donatello et al. (2010) and several authors suggested 2 hours as optimum, because in this condition, almost complete dissolution of phosphorus can be achieved. For this reason, this experimental work does not deeply investigate the influence of retention time, even if a couple of experiments were conducted.

Shiba et al. (2017) found that increasing the reaction time to 3 h or more, can promote different reactions and processes such as crystallization and precipitation of insoluble compounds, which negatively affects the phosphorus recovery. Thus, the chemical bonds formed are harder to be break down. This is consistent with the result obtained by leaching sample “SGO (1)” for 3 h by sulfuric acid at 0.4 N and L/S=10, which shows a marginal decrease of the P extraction efficiency (79%), while the percentage of the heavy meals leached remained almost unchanged.

Moreover, Biswas et al. (2009) and Hong et al. (2005) reported that the phosphorus extraction rate is usually fast thanks to the acid soluble nature of the ISSA and the small particle size, which increases the specific surface. It is known that the rate of leaching kinetics is usually governed by many factors such as the solubility and mass transfer rate (Franz 2008).

It is necessary to highlight that all experiments were conducted at room temperature, thanks to the previous literature findings. These indicated a relatively weak temperature dependence, so no external heating is provided during the leaching process. This reduced the equipment required (heating systems) and recovery system for an efficient energy process. Biswas et al. (2009) reported that the release of phosphorus from ashes is not affected by increasing the temperature in the interval 30-70°C.

Also, the pH of the leaching solution is a parameter that should be taken into account. Franz (2008) indicated that for obtaining a satisfactory phosphorus dissolution, a pH lower than 2 is required. Indeed, he observed an increase of the P-PO<sub>4</sub> concentration in the extracting solution by decreasing the level of pH; at around 1.8 a plateau can be reached. However, he recommended to maintain a pH higher than 1 to minimize the heavy metal dissolution. Shiba et al. (2017) pointed out that by decreasing the level of pH the thickness of the electrostatic double layer decreases as well. This means that the electrostatic repulsion between ash's particles and viscosity can be reduced. So, the mass transfer rate is promoted, and a higher phosphorus extraction efficiency can be achieved.

In addition, Fang et al. (2018) reported that a pH in the range of 0.5-1 could be appropriate for leaching phosphorus. The extraction efficiency as a function of the pH has not be accurately investigated in this project. However, the result of this laboratory investigation confirms that the pH of the different leaching solutions analysed were between 0.7 and 1.4, which can theoretically ensure a satisfactory recovery rate.

### 6.3 Influence of sludge type

The precipitation agents used for the phosphorus removal in wastewater treatment plants can effectively influence the form of phosphorus present in the sludge, as reported in paragraph 2.2.

In fact, if chemical removal is applied, phosphorus is mainly present in the form of iron or aluminium phosphate ( $\text{FePO}_4$  or  $\text{AlPO}_4$ ). While in the case of enhanced biological phosphorus removal (EBPR), most of phosphorus is stored in the flora cells in the form of adenosine triphosphate (ATP), which refers to a long chain polymer (Cieřlik & Konieczka, 2017). This strongly influences the effect on phosphorus recovery.

Some authors agreed that sludge coming from EBPR can ensure a higher phosphorus dissolution in acidic environment, because phosphorus is mainly present as dissolved phosphate. Therefore, dissolution is promoted.

Cieřlik et al. (2017) indicated that using aluminium as flocculating agent allows a more efficient phosphorus extraction, while Ottosen et al. (2013) suggested using iron salts, because sulfuric acid can dissolve iron phosphate more efficiently. They reported that Al-rich ashes have a higher buffering capacity and more acid for the extraction is required, while Shiba et al. (2017) found that, at pH 1, it is easier to extract phosphorus from Al-rich ashes. However, at pH 2.5, no differences have been observed (Shiba & Ntuli, 2017).

This is apparently in contrast with our findings.

The maximum extraction efficiency was obtained from samples "SGO (1)" and "Zurich", which have a much higher Fe and Al content in the ashes compared to other samples (see below "S. Rocco 1"). Iron concentration corresponds to 87,200 mg/kg for "SGO (1)" and 52,000 mg/kg for "Zurich", while Al is 49,300 mg/kg and 17,460 mg/kg respectively, for the two samples. These concentrations are similar to the one reported by (Krüger, Grabner, & Adam, 2014) and (Ottosen et al., 2013).

The lowest extraction efficiency was instead obtained from sample "S. Rocco 1", which does not exceed 60% in all tests performed, and "Karlsruhe" with the following operating condition: acid concentration of 0.4 N, L/S of 10, 2 hours as contact time.

Even if sample "S. Rocco 1" has a lower Fe and Al content (26200 mg/kg and 18710 mg/kg, respectively) and comes from a WWTP that mostly uses EBPR, it showed a lower phosphorus extraction efficiency. This can be attributed to many other factors such as alkalinity of the ashes or characteristics of the incineration process that took place in a standard laboratory muffle. Thus, further investigations are required.

## 6.4 Release of heavy metals

Fig. 25 shows the percentage of heavy metals dissolved from sample “SGO (1)”. Leaching tests were conducted at room temperature with a contact time of two hours, as previously indicated. Conditions reported indicate the type of acid and the liquid to solid ratio used.

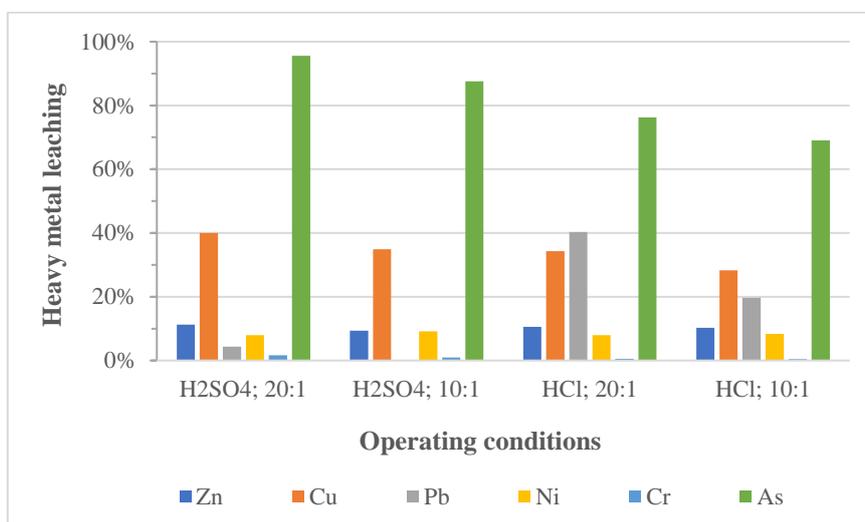


Fig. 25 Heavy metal leaching of sample “SGO (1)”.

Arsenic showed the higher extraction efficiency in all experiments, followed by copper and by lead when using HCl. In general, extraction with HCl resulted in a higher heavy metal extraction efficiency if compared to H<sub>2</sub>SO<sub>4</sub>. In addition, to an increased liquid to solid ratio corresponds a higher extraction efficiency.

Table 13 reports a detailed characterization of the leached solutions for sample "Karlsruhe", "S. Rocco 1", "SGO (2)" and "Zurich", obtained with different operating conditions.

In addition, extraction rate of Fe and Al were investigated for sample “SGO (1)” and “SGO (2)”. It has been found that 1.30% (SGO 1) and 2.13% (SGO 2) of the initial Fe is leached, while the leached Al accounts for 40.16% (SGO 1) and 41.46% (SGO 2). Experiments were conducted at liquid to solid ratio of 20 with a contact time of 2 hours.

Table 13 Percentage of total elements in the leachate. Operating conditions: acid used; acid concentration; liquid to solid ratio; contact time.

Operating conditions	Ca	Mg	Zn	Cu	Pb	Ni	Cr	As	sample
H <sub>2</sub> SO <sub>4</sub> ; 0.4 N; 20:1; 2h	9.6%	84.1%	41.5%	60.6%	0.3%	18.7%	9.9%	-	Karlsruhe
H <sub>2</sub> SO <sub>4</sub> ; 0.4 N; 50:1; 2h	28.8%	86.3%	42.6%	32.3%	4.4%	15.4%	16.3%	-	
H <sub>2</sub> SO <sub>4</sub> ; 0.4 N; 20:1; 2h	27.6%	70.6%	59.5%	23.3%	2.5%	6.9%	2.6%	70.2%	S.Rocco 1
H <sub>2</sub> SO <sub>4</sub> ; 0.4 N; 50:1; 2h	96.9%	85.6%	60.9%	28.8%	9.0%	7.2%	3.1%	66.7%	
H <sub>2</sub> SO <sub>4</sub> ; 0.4 N; 20:1; 2h	19.0%	-	43.9%	37.8%	3.3%	14.7%	2.8%	76.5%	SGO (2)
H <sub>2</sub> SO <sub>4</sub> ; 0.4 N; 20:1; 2h	8.4%	89.4%	38.1%	63.3%	0.3%	19.6%	7.2%	84.9%	Zurich

In general, it emerged that Al and Mg are the most soluble ions, while Fe and Ca have a limited solubility with sulfuric acid 0.4 N and liquid-to solid ratio of 20.

According to the results obtained from Donatello et al. (2010), the amount of ferric ion released to the leachate was less than 10% in all experiments. This is related to the presence of Fe<sub>2</sub>O<sub>3</sub> in the ashes, which is insoluble in acidic environment. In fact, iron compounds need higher energy (in term of higher temperature or higher acid concentration) to be dissolved. Biswas et al. (2009) observed a higher release of iron at temperature around 50 °C. Low concentration of total iron in the leached solution can be attributed to the slow dissolution kinetics, which affects the formation of FePO<sub>4</sub>·H<sub>2</sub>O. This condition is favourable for phosphorus extraction, because it leads to lower contamination of the leachate.

## 6.5 Effect of acid type on leaching

As reported in chapter 3.1.2 different type of acid, organic or inorganic can be used for the leaching process. Several studies conducted showed that sulfuric acid can successfully be applied, because higher phosphorus extraction efficiency can be achieved with a minor co-dissolution of heavy metals. This happens due to the fact the fewer complexation reactions occur (Cieřlik & Konieczka, 2017).

Moreover, using sulfuric acid has the following advantages:

- is the cheapest extractants,
- can be easier transported due to the lower volatility,
- less volume needed because it can be concentrated up to 96 to 98%,
- minor amount of heavy metals can be leached during wet chemical extraction.

However, the possibility of gypsum formation must be considered. It can affect the phosphorus extraction rate and the future use of the material recovered, because gypsum increases significantly the volume. If the remaining ash will be used as construction material, this can be an important drawback.

Others inorganic extractants, such as hydrochloric acid, ensure a good phosphorus extraction rate as well, but with a larger release of trace elements. In fact, adding chloride ions to the leached could promote the formation of soluble complex with most of the heavy metals present resulting in higher metal contamination (Pettersson et al., 2008), (Shiba & Ntuli, 2017).

Lead, for instance, can be leached three times more by using HCl as extracting medium. This finding is in line with our investigations, because the percentage of Pb extracted in 0.4 N at L/S=20 with  $t_c=2h$  at room temperature increases from 4% to 40% by using HCl, as presented in Fig. 25.

Moreover, the amount of acid required is linked to the chemical composition of the incinerated sewage sludge ashes and specifically to the phases containing phosphorus. In accordance with the characteristics of our samples analysed, phosphorus could mainly exist as  $FePO_4$ ,  $AlPO_4$ ,  $Ca_3(PO_4)_2$  or as a mixed form of these compounds.

Franz pointed out that the major consumers of acid are CaO and  $P_2O_5$ , while minor consumers are MgO,  $Na_2O$  and  $K_2O$ .  $Al_2O_3$  and  $Fe_2O_3$  are instead partially attacked.

## 6.6 Effect of acid concentration

Previously studies conducted have shown that leached phosphorus and trace elements gradually increased as the acid concentration increases. This is consistent with the results obtained for sample "S. Rocco 2". The acid concentration has been increased from 0.4 to 1 N promoting a higher phosphorus dissolution. It changed from 68% to almost 80%. During leaching tests, operating conditions have been kept constant: L/S=50,  $t_c=2h$ , room temperature.

Shiba et al. (2017) found that this trend can be observed for acid concentrations that are below 1 M, because at higher concentration the amount of phosphorus recovered started to decrease by 10%.

Biswas et al. (2009) pointed out that if the acid concentration increases with no change in the release of heavy metals, it might be that the remaining metals' fraction are present as nucleation particles in the centre of the matrix.

At the same time, some authors reported that a further increase of the acid concentration would increase the content of heavy metals in the leachate. For instance, Fang et al. (2018) reported that by rising sulfuric acid concentration from 0.1 to 0.5 M, higher amounts of Ni and Pb were extracted, while Cu, Zn and As remained stable.

## 6.7 Effect on liquid to solid ratio (L/S)

Liquid-to solid ratio is another parameter that strongly influences the dissolution process. The tests have revealed that the percentage of leached phosphorus increases with increasing the liquid to solid (L/S) ratio, possibly because contact between ashes and the extractant is enhanced (S. Donatello et al., 2010),(Shiba & Ntuli, 2017).

Indeed, sample “SGO (1)” with L/S ratio of 10 dissolved around 80% of total phosphorus, while at L/S of 20, 90% of phosphorus has been extracted. Fig. 26 shows the percentage of phosphorus extracted by using sulfuric acid with varying the liquid to solid ratio.

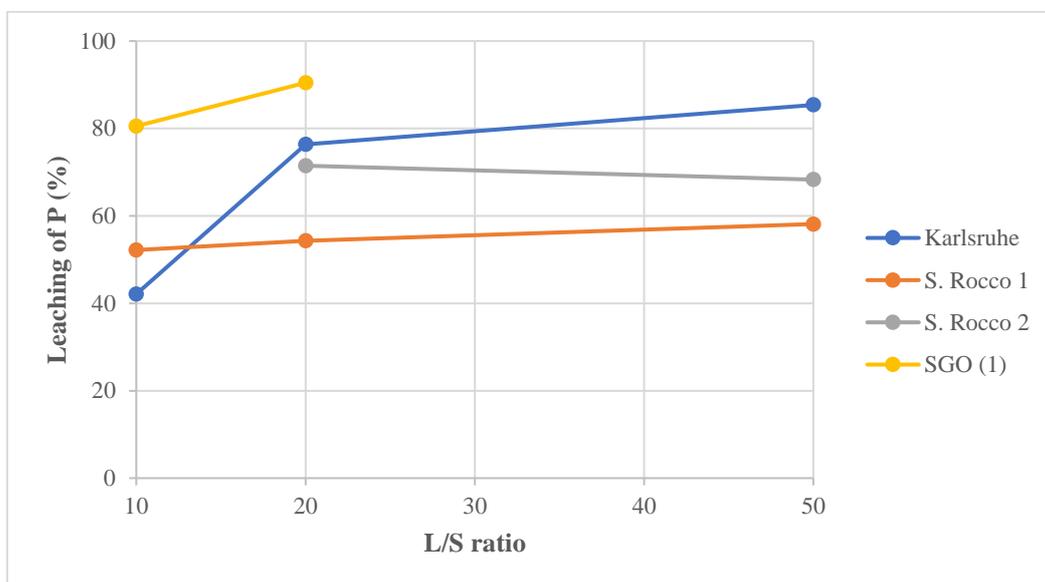


Fig. 26 Leaching of P at different liquid-to solid ratio.

It can be noticed that sample “S. Rocco 1” does not achieve a high extraction efficiency (<60%). This might be attributed to the characteristics/major alkalinity of the ashes, morphology, incineration conducted in a laboratory standard muffle etc. Ntuli et al. (2013) reported that the limitation on recovery can be attributed to the metals present that can act as nucleation particles in the centre of the matrix. So, phosphorus is attached to the metals resulting in a decrease of the amount that could be extracted (Ntuli, Falayi, Mhlungu, Thifhelimbilu, & Material, 2013).

However, also another sample taken from the same WWTP but at a different time, called “S. Rocco 2”, shows some anomalies. In fact, an L/S=50 results in a lower phosphorus leaching compared to the result obtained at L/S=20, which is in contrast with the previous findings. A possible explanation is that the buffer capacity of sample “S. Rocco 2” was higher than the previous sample and, indeed, a good extraction efficiency (~80%) has been achieved only with increasing the acid

concentration to 1 N. Also, Donatello et al. (2010) pointed out that the buffer effect of a alkaline ashes can be depleted by using strong acids.

Because extraction of phosphorus is adversely influenced by the co-dissolution of heavy metals (metal-phosphorus bonds are broken down), Fig. 27 show percentages of the extracted metals in sample "SGO (1)" by reducing the L/S ratio from 20 to 10. Concentration of sulfuric acid was 0.4 N and contact time equal to 2 hours, while leaching tests were conducted at ambient temperature. As previously reported, the extraction efficiency increases with increasing the L/S ratio.

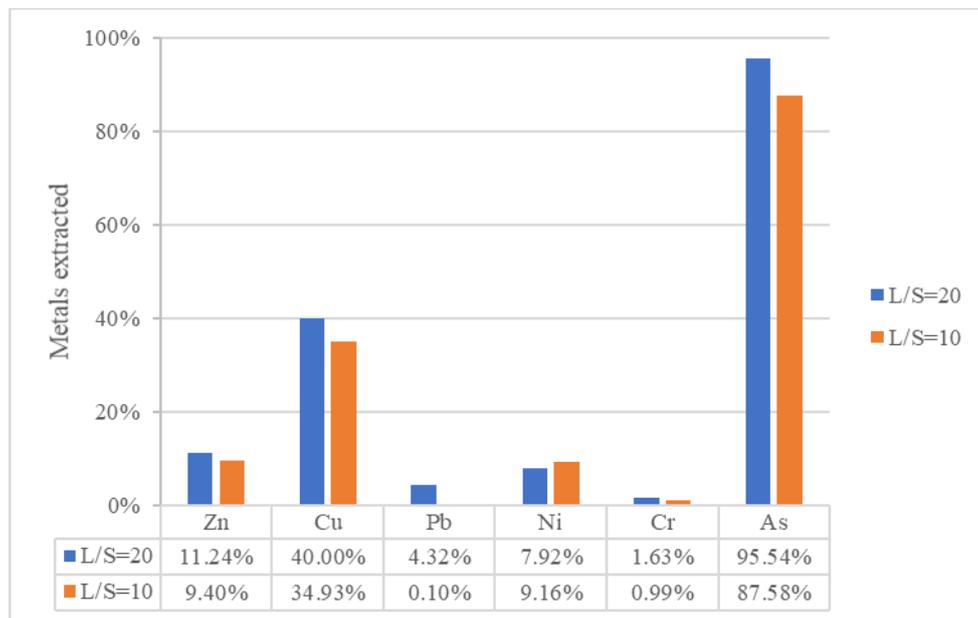


Fig. 27 Heavy metals extracted for sample "SGO (1)" by reducing the L/S ratio from 20 to 10.

It can be seen that arsenic was extracted to the highest percentage (>85%), while other metals were leached in minor amount. This means that the majority of heavy metals remain in the solid residue of the leaching test, not passing in solution contaminating the leachate.

## 6.8 Recovery of phosphorus from acid leachate

First experiments were conducted by taking 25 ml of acid leachate, which refers to sample "SGO (1)". Initial pH was determined when starting the gradual dosage of limewater at 0.5%. At pH around 2.5 the colour of the suspension became off-white, suggesting the precipitation of some compounds. Fig. 28 shows the trend of the pH as a function of the limewater added; initial pH were 1.27 for sample A and 1.2 for sample B.

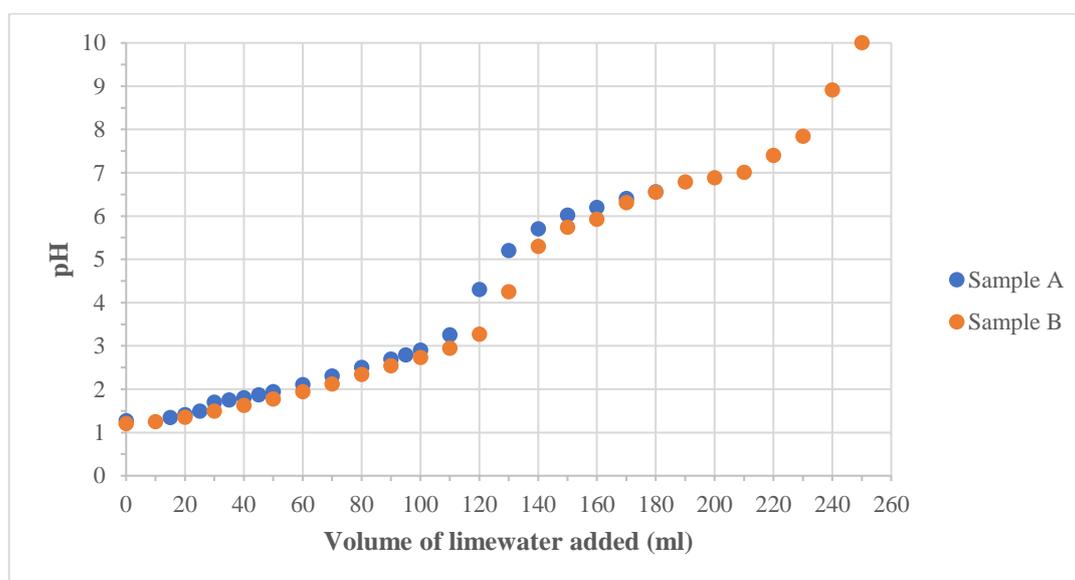


Fig. 28 Trend of pH in the precipitation process.

It can be seen that pH rose with a linear trend in the beginning of the experiment reaching a value of 3 after adding 100 ml of the 0.5% limewater suspension (it took 6 minutes). Then, it increased rapidly exceeding the value of 6, followed by a further sharp increase. After addition of 250 ml (after about 20 minutes), precipitation reactions are completed, and pH stabilized at about 10. Because a large amount of limewater has been used (250 ml for the precipitation of 25 ml of leachate), following experiments were conducted using milk of lime at higher concentration (1%). The volume of the leachate was set to 50 ml, and around 80 ml of milk of lime was added for each test. It emerged that 99% of the phosphorus present in the leachate precipitated as calcium phosphate and in some cases the P-PO<sub>4</sub> concentration determined by spectrophotometry was lower than the minimum detectable value (0.5 mg/L).

The phosphate slurry was then filtered at 0.45  $\mu\text{m}$ , dried at room temperature and ground to obtain a recycling phosphate fertilizer. In order to determine the phosphorus content in the recycled material the dried product obtained was weighed. Then, assuming that  $\sim 100\%$  the phosphorus present in the

leachate precipitated, the grams of phosphorus recovered were calculated. By dividing it over the total mass of the dried product, the phosphorus content was derived. It ranges between 3 and 9%. At the same time, heavy metal content was determined. It has been assumed that, according to the pH reached ~9-10, all the metal present in the leachate can precipitate.

Therefore, the following equation has been considered:

$$C_{HM\_leachate} \cdot V_{leachate} = C_{HM\_precipitate} \cdot V_{precipitate}$$

Finally, the heavy metal content was compared to the limit values set for fertilizers. The two graphs reported in Fig. 29 show that no value exceeds the limit. Pb, Ni and As concentrations detected were lower than 5 mg/kg.

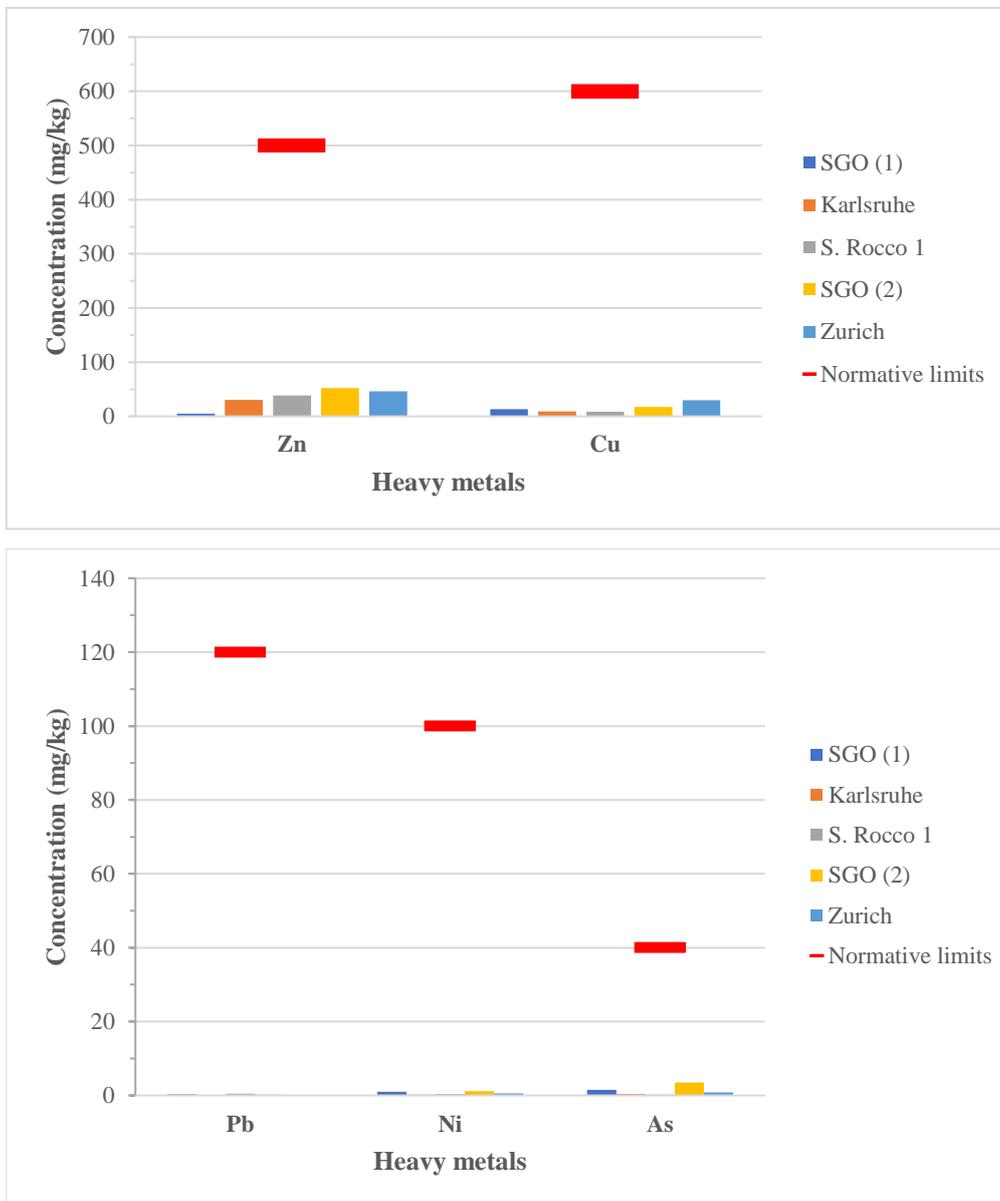


Fig. 29 Heavy metal concentration of the recovered P-rich material and normative limits.

Fig. 30 shows the suspension obtained after adding milk of lime at 1% and left to rest for 10 minutes, while Fig. 31 presents the dried residue of the precipitation process, which is the recovered product.



*Fig. 30 Suspension obtained after adding lime milk.*



*Fig. 31 Recovered material after precipitation and drying (number 19045 refers to sample "SGO (2)", 19048 to sample "Zurich", 19039 to sample "SGO (1)", 19043 to sample "Karlsruhe" and 19044 to sample "S. Rocco I").*

## 7 Application perspectives

Wet chemical precipitation is not the only way to recover phosphorus from ISSA, but also thermochemically, as already discussed previously (Chapter 3.1.6).

In this section literature data collected about AshDec and RecoPhos P38 are compared through SWOT analysis (Strengths-Weaknesses-Opportunities-Threats) as a first approach to highlight the main factors involved in the different technologies and get some indications about which might be the most convenient process. Future work, outside the scope of this thesis, will consider more complete DSS approaches and quantitative evaluation tools.

The main factors considered are the phosphorus removal efficiency, the depollution rate, the annual costs including the capital and operating costs, the consumptions in term of electricity/natural gas/chemicals, the complexity of the process and the temperature adopted, the waste stream generated, the characteristics of the recovered material and the major environmental impacts.

AshDec Depollution<sup>4</sup> process has a high phosphorus removal efficiency and high depollution rate for some heavy metals. Indeed, Cd, Cu, Pb and Zn contained in the ISSA can be reduced up to 90%, while As, Cr, and Ni still remain in the ashes at high percentage (L. Egle et al., 2016). The complexity of the process is high, as reported by Schaum (2018), and the temperature achieved in the rotary kiln is around 950-1000 °C.

The final product obtained is calcinated phosphate with 15-25% of P<sub>2</sub>O<sub>5</sub> that has to be pelletized (2-5 mm) for direct application. The plant availability is usually low; thus, the recycled material contains 8.5% P<sub>tot</sub>/kg<sub>DM</sub> from which only 2% is phosphorus plant available. The relative fertilizer efficiency is high in acidic and neutral soil (75-90%), but low in alkaline soil (4%) (L. Egle et al., 2016). Nevertheless, significant improvement of the plant availability and solubility can be achieved with the use of the AshDec Rhenania<sup>5</sup> process.

The annual cost of the both AshDec technologies is in the range of 2 €/kg P<sub>recovered</sub>, with a low population specific cost (~ 1€ Pe<sup>-1</sup>y<sup>-1</sup>). More specifically, the electricity consumption of AshDec Rhenania is about 0.8-0.9 kWh/kg P<sub>recovered</sub>, while the consumption of the natural gas can vary between 3.5 and 5.5 kWh/kg P<sub>recovered</sub>, depending on the type of the plant. In fact, the first value refers to integrated plant, while the second to a standalone plant.

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<sup>4</sup> The term “Depollution” is used to define the processes needed to reduce the concentration of heavy metals in the recovered raw product.

<sup>5</sup> The term “Rhenania” refers to the product obtained by the AshDec Rhenania process, which is indeed Rhenania phosphate.

The main drawback is related to the high dosage of chemicals that accounts for 3.3 kg Na<sub>2</sub>SO<sub>4</sub>/kg P<sub>recovered</sub>, 0.1 kgCa(OH)<sub>2</sub>/kgP<sub>recovered</sub>, 0.1 kg NaOH/kgP<sub>recovered</sub> and 1.3 kg dry sludge/kg P<sub>recovered</sub> (Lema & Suarez, 2017). On the contrary, the waste stream produced, which comes mainly from filter dust, is tiny and accounts for 2-3% of the ash input.

Dealing with environmental indicators, damage unit (DU), cumulative energy demand (CED), global warming potential (GW) and acidification potential (AP) are the main factors considered in the life cycle analysis (LCA) conducted by Amann et al. (2018).

DU is a harmfulness coefficient expressing the pollution load. It is useful to compare the recovered material in term of heavy metal content and phosphorus recovered. So, low DU refers to low pollutant content in relation to the amount of phosphorus recovered and vice versa.

As reported in the formula below, DU is calculated by dividing each heavy metal concentration in the recovered material (C<sub>i</sub>) by the reference concentration of heavy metal in the reference material (C<sub>i</sub><sup>reference</sup>). Then the quotients are summed up and the value obtained is divided by the phosphorus content of the product (P concentration).

$$C_{DU} = \frac{\sum_{i=1}^n \frac{C_i}{C_i^{reference}}}{P \text{ concentration}}$$

Taking into account the two different AshDec processes, which are AshDec Depollution and AshDec Rhenania, their DU are 0.05 and 0.21, respectively (L. Egle et al., 2016). The second process has a higher DU because the heavy metal removal decreases with the replacement of chloride source with sodium sulphate, which is usually applied in the AshDec Rhenania to increase the phosphorus available to crops.

CED expresses the energy requirement taking into account the direct energy demand (electricity/gas needed to get the final product) and the indirect demand (energy necessary to produce the resources needed). GW considered the gaseous emissions of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O expressed as CO<sub>2</sub> equivalent (CO<sub>2</sub>-e), while AP refers to SO<sub>2</sub>, NO<sub>x</sub>, HCl and NH<sub>3</sub> emissions referred as SO<sub>2</sub>-e. These have a direct impact on soil acidity and can affect the fertilizer efficiency (Amann et al., 2018).

Therefore, the values adopted in the reference system of the LCA analysis correspond to 20 kWh Pe<sup>-1</sup>y<sup>-1</sup> (CED), 9 kgCO<sub>2</sub>-e Pe<sup>-1</sup>y<sup>-1</sup> (GW) and 42 gSO<sub>2</sub>-e Pe<sup>-1</sup>y<sup>-1</sup>(AP). The results with respect to the AshDec process fed with hot ashes showed negative percentage for all the indicators thanks to the credits gained for phosphorus fertilizer replacement. They are equal to -21%, -16% and 64% for CED, GW and AP.

Also, the process RecoPhos P38 shows a high phosphorus removal rate, but a low depollution rate. In fact, about 100% of the heavy metal load in SSA is incorporated into the recovered material. Nevertheless, a good fertilizer product can be obtained. Indeed, a study conducted by Weigand et al. (2011) confirmed that the output of the RecoPhos P 38 process complies with the limit values for soil fertilizers given by the German Fertilizer Ordinance (H Weigand et al., 2011). Table 14 shows a comparison between the metals content in RecoPhos P 38 and Yara, which refers to the conventional phosphorus fertilizer. Data are expressed as mg/kg<sub>dry matter</sub>.

*Table 14 Metals and metalloids content in RecoPhos P 38 and Yara (Amann et al., 2018).*

<i>Element</i>	<i>Recophos P 38</i>	<i>Yara</i>	<i>Element</i>	<i>Recophos P 38</i>	<i>Yara</i>
As	9.10	8.30	Ni	47.4	55.1
Cd	2.16	20.0	Pb	51.4	1.82
Cr	118	120	Se	3.83	5.40
Cu	664	36.5	Tl	0.20	0.42
Hg	0.70	< 0.054	Zn	1600	439

It can be seen that the fertilizer derived from SSA has higher content of Cu, Zn, Pb and Hg and a lower content of Cd, Ni and Tl. Levels of As and Cr are instead comparable. However, the limit values of metals with respect of the German regulation are fully satisfied.

Looking at the annual cost, it accounts for 2-3 €/kg P<sub>recovered</sub>, a slightly higher value compared to both AshDec process. This is due to the enrichment of the ashes with phosphoric acid (PA). The population specific cost is instead 6€/ Pe<sup>-1</sup>y<sup>-1</sup>, almost six times more than AshDec, as it can be seen in Fig. 32.

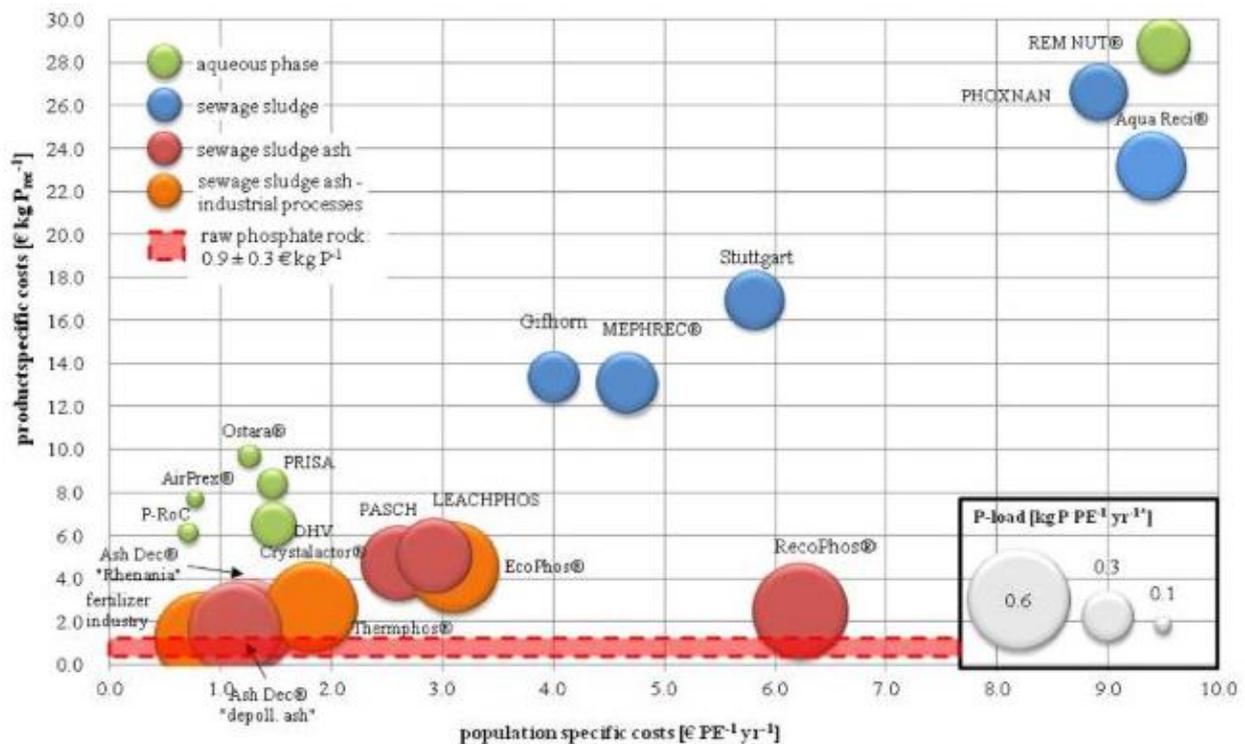


Fig. 32 Product-and population specific costs for different phosphorus recovery technologies (source: Egle et al., 2016).

The size of the bubble indicates the phosphorus that can be recovered per population equivalent and year. So larger bubble refers to higher amount of recovered phosphorus. Savings and revenues are not taken into account.

The main product obtained from the RecoPhos P38 process is elementary P<sub>4</sub>, which can further oxidize to get PA. It can be direct applied as fertilizer, because it shows good plant availability; the total phosphorus content accounts for 15.3% P<sub>tot</sub>/kg DM where 11% is plant available (L. Egle et al., 2016). Weigand et al. (2011) reported that 1,000 metric tonnes are usually produced at marketable price every month. The estimated value is then 1,300€/ton (Schaum, 2018).

Looking at the environmental indicators previously discussed, the DU is equal to 0.15 while CED is -112%, GW -56% and AP -55% (Amann et al., 2018). Negative values can be reached thanks to the high credits obtained for fertilizer substitution. In fact, the use and production of PA increases the GWP, but it is well balance by the credits.

In accordance with the data, reference and results obtained, Tables 15 and 16 show in the following page the SWOT analysis of the two processes investigated.

Table 15 AshDec SWOT analysis.

<b>AshDec</b>	
<p style="text-align: center;"><b>Strengths</b></p> <ol style="list-style-type: none"> <li>1. High phosphorus recovery rate (85% with respect to the WWTP-influent phosphorus)</li> <li>2. High depollution rate for some metals (Cd, Cu, Pb and Zn in AshDec Depollution)</li> <li>3. Technology suited for EBPR and chemical phosphorus removal at WWTP</li> <li>4. Relatively low annual costs</li> <li>5. Low population specific costs</li> <li>6. Relatively low electricity consumption</li> <li>7. Direct application of recovered product</li> <li>8. Low environmental impacts</li> <li>9. Tiny waste stream</li> </ol>	<p style="text-align: center;"><b>Weakness</b></p> <ol style="list-style-type: none"> <li>1. Low depollution rate for As, Cr and Ni (AshDec Depollution)</li> <li>2. Low plant availability</li> <li>3. Low fertilizer efficiency in alkaline soil</li> <li>4. High process complexity</li> <li>5. Raw material ash should be fed after pelletizing (2-5mm)</li> <li>6. Large use of chemicals and additives</li> </ol>
<p style="text-align: center;"><b>Opportunities</b></p> <ol style="list-style-type: none"> <li>1. Savings associated with waste disposal</li> <li>2. Valorisation of a waste, which can be turned into a valuable raw material,</li> <li>3. Possibility to decrease the dependence from phosphorus imports and price variability</li> <li>4. High phosphorus recovery efficiency</li> <li>5. Decrease the use of conventional fertilizers</li> </ol>	<p style="text-align: center;"><b>Threats</b></p> <ol style="list-style-type: none"> <li>1. High cost of implementation and operating cost</li> <li>2. Rollout potential</li> <li>3. Public opposition/societal acceptance</li> <li>4. Lack of incentives supporting phosphorus recovery and lack of organizations financing the innovations</li> </ol>

Table 16 RecoPhos P38 SWOT analysis.

<b>RecoPhos P38</b>	
<p style="text-align: center;"><b>Strengths</b></p> <ol style="list-style-type: none"> <li>1. High phosphorus recovery rate (85% with respect to the WWTP-influent phosphorus)</li> <li>2. Relatively low annual costs</li> <li>3. Low process complexity</li> <li>4. Near zero waste process</li> <li>5. Raw material ash can be fed without pelletizing</li> <li>6. Direct application of recovered product</li> <li>7. Good plant availability</li> <li>8. Low environmental impacts</li> </ol>	<p style="text-align: center;"><b>Weakness</b></p> <ol style="list-style-type: none"> <li>1. Low depollution rate</li> <li>2. High electricity consumption</li> <li>3. High population specific costs</li> </ol>
<p style="text-align: center;"><b>Opportunities</b></p> <ol style="list-style-type: none"> <li>1. Savings associated with waste disposal</li> <li>2. Valorisation of a waste, which can be turned into a valuable raw material,</li> <li>3. Possibility to decrease the dependence from phosphorus imports and price variability</li> <li>4. High phosphorus recovery efficiency</li> <li>5. Decrease the use of conventional fertilizers</li> </ol>	<p style="text-align: center;"><b>Threats</b></p> <ol style="list-style-type: none"> <li>1. High cost of implementation and operating cost</li> <li>2. Public opposition</li> <li>3. Lack of incentives supporting phosphorus recovery and lack of organizations financing the innovations</li> </ol>

It emerged that from an economical point of view, AshDec is the most convenient process because it costs less and at the same time ensures a high recoverable phosphorus load. This is clearly presented in Fig. 32. However, the RecoPhos P 38 process is able to produce a fertilizer, which can show good plant availability and can be competitive in the global market. It can effectively substitute the conventional fertilizer (Yara), decreasing the pressure on primary phosphate reserves. Indeed, the process is able to treat over 400,000 t/y of sewage sludge ashes (Schaum, 2018) and thus it can be applied in densely populated area at large scale, decreasing the costs of waste management. Also, the years of application of this product, measured until a critical concentration is reached, are higher (~ 5000 yr) compared to the AshDec process (1000-3000 yr). Moreover, almost no wastes are generated, reducing the environmental impacts and the by-products obtained, such as silicate slag, can be used

as binder in the cement industry. So, technologies that can offer multiple benefits may be more successful compared to technologies that offer only phosphorus recovery (Schaum, 2018).

Our ashes' sample Zurich can theoretically be applied in RecoPhos P 38 process to get the valuable fertilizer. In fact, the heavy metal content of these sewage sludge ashes can be compared to the one proposed by Weigand et al. (2011), which resulted to be conformed to the required input quality of the process.

The same preliminary approach can be used to decide which technology investigated based on the acidic wet chemical leaching is preferable. Surely, as it can be seen in Fig. 32, technologies such as PASCH, LEACHPHOS and EcoPhos are more expensive than AshDec process, because the product specific costs account for 4-5 €/kg  $P_{\text{recovered}}$ , while the specific cost per unit equivalent population served is 3 €  $PE^{-1}y^{-1}$ . However, relative high phosphorus recovery efficiency and depollution rate can be achieved. In fact, 70-80% of the phosphorus present in the ash input can be recovered by PASCH and LEACHPHOS process, while EcoPhos reaches 95% (L. Egle et al., 2016). EcoPhos is in fact an interesting process because it produces pure PA, which is a market-oriented product (Schaum, 2018). Moreover, the phosphorus content in the recovered material ranges between 13 and 17% for PASCH and LEACHPHOS processes, with a high percentage of plant available phosphorus. Also, the DU of these two technologies are equal to 0.03 and 0.13, respectively (L. Egle et al., 2016). Lower values compared to AshDec and RecoPhos P38 processes. If we look at the CED, GWP and AP, instead, it emerged that PASCH and LEACHPHOS have higher energy requirements and environmental impacts, because the credits obtained for the substitution of fertilizer are lower, as it can be seen in Fig. 33 (Amann et al., 2018).

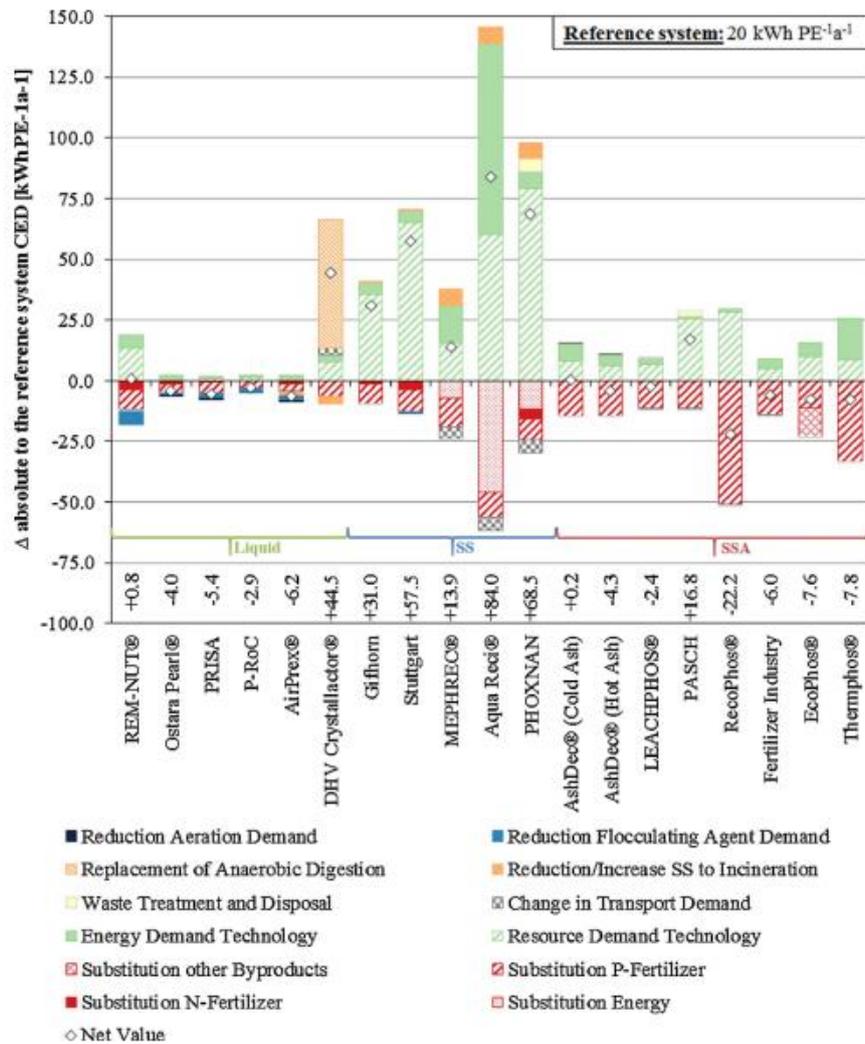


Fig. 33 Changes in the energy demand related to the reference system (Amann et al., 2018).

In the wet leaching processes, operational parameters can be changed and controlled more easily than in other processes. In fact, they can be adapted to the type of input material or customer demand. In conclusion, despite the type of technology to choose, the main problem is related to the full-scale implementation. Indeed, this is linked to the economic feasibility, legislation and national policies (Desmidt et al., 2015). So, governments play an important and fundamental role, because they can support and enforce the recovery and recycling, rising public awareness and acceptance for a new fertilizer and creating a sustainable market for recycled phosphate products. For instance, Germany, Austria, Netherlands and Switzerland encourage the recovery from sewage sludge ashes through stringent requirements on land spreading of the sludge. The specific context in Europe is not yet fully motivating, although this need has been cited at point (58) of the introductory considerations of the recent Regulation on Fertilizers (EU, 2019) and phosphorus recovery must be supported more, especially within the Circular Economy Action Plan within the Green Deal (<https://ec.europa.eu/environment/circular-economy/>).

## 8 Needs for future research

It is well established in literature that sewage sludge coming from EBPR treatment can show a higher phosphorus extraction efficiency, because phosphorus is mainly present as dissolved phosphate and can be easier leached by an acidic extractant. While if chemical phosphorus removal takes place at WWTP, the sludge obtained contains mainly metal bound phosphorus. This is because precipitating agents (aluminium or iron salts) ended up in the sludge, increasing the metal content.

Some authors suggested to use preferably aluminium salts rather than iron salts to promote the phosphorus dissolution, but contrasting point of views emerged, as previously discussed in section 3.1.2.

However, our results are apparently in contrast with the previous findings reported in literature. In fact, the sludge samples "S. Rocco 1", which comes from a WWTP that uses EBPR, showed a lower phosphorus extraction efficiency, compared to the other samples investigated.

Sample "SGO (1)", instead, achieved the best recovery rate, even if its iron and aluminium content was high. It may happen that other factors such as the buffering capacity of the ashes, the form of phosphorus present in the ashes and the suboptimal incineration, which takes place in a laboratory standard muffle, can affect the final result.

Sample "Karlsruhe", for instance, may have had a higher buffering capacity of the ashes, because it was necessary to increase the L/S ratio until 50 to have a phosphorus extraction efficiency higher than 85%. Moreover, an additional leaching test was carried out using water instead of an acidic extracting agent, resulting in a strong basic pH of the leachate (pH of about 12). In addition, incineration in a laboratory muffle does not reproduce the actual conditions of the combustion process that usually occurs in a real furnace and this may have affected the results.

Nevertheless, the overall experimentation has led to very promising results that will be useful for the scale-up of the process and developments on an industrial scale. Further investigations at a larger scale will be necessary for the optimization of the design, operating conditions and consumption of reagents on ISSAs produced by different sludge treatment processes.

# APPENDIX

## Procedure A<sup>6</sup>

### 1) ISSA characterization

- Collect and store the samples of ISSA in desiccators at room temperature until use.
- Determine:
  - The average water content of the ISSA by heating the sample to 105 °C for 24 h,
  - The particle size distribution. Place the ISSA sample (10 g) on the top sieve and shake it to achieve separation into fractions. Particle size ranges (< 53, 53–75, 75–150, 150–300, and > 300 μm),
  - The major crystalline phases by using X-ray diffractograms at 30 mA and 40kV.

### 2) Leaching experiments:

- Before starting with leaching experiments, treat all glassware in a solution of 10% HNO<sub>3</sub> for 24 h and wash them with deionized water.
- Take an Erlenmeyer flask and add approx. 500 mL of 0.05 M H<sub>2</sub>SO<sub>4</sub> to 3,33 g to make a L/S ratio of 150 mL/g. <sup>7</sup>Put the flask into a water bath to maintain a constant temperature (30 °C) and stir the whole slurry with a magnetic stirrer.
- Take out the samples at defined intervals from and suspension and filter the slurry with a 1 μm ashless filter paper.
- Analyse the filtrate to determine phosphorus and metals content with ICP/AES spectrometry, perform the tests in triplicate and take the average values.

### 3) Phosphorus recovery

- Pour the Zr(IV)-loaded SOW gel in conical flasks to adsorb phosphorus from the acid leachate (about 10 mL) at 30 °C for 24 hours.
- Measure the concentration of phosphorus and metal ions before and after equilibration

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<sup>6</sup> Biswas, B. K., Inoue, K., Harada, H., Ohto, K., & Kawakita, H. (2009). Leaching of phosphorus from incinerated sewage sludge ash by means of acid extraction followed by adsorption on orange waste gel. *Journal of Environmental Sciences*, 21(12), 1753–1760.

<sup>7</sup> It is possible to vary the amount of ISSA, acid concentration and L/S ratio to optimize the process. Take 200 mg of ashes and vary the concentrations between 0.01-2.0 mol/L and the L/S ratio from 20 to 250 mL/g.

## Procedure B<sup>8</sup>

### 1) ISSA characterization

- Collect and store the samples of ISSA in desiccators at room temperature until use.
- Determine:
  - the particle size distribution,
  - the chemical composition by XRF (P<sub>2</sub>O<sub>5</sub> content and heavy metals content),
  - the mineral composition by XRD.

### 2) Leaching experiments:

- Take a 2 L wide-mouth plastic bottle, fill it with 200 g ash and add 400 mL of H<sub>2</sub>SO<sub>4</sub> (its concentration can vary between 0.5 and 3 mol/L).
- Seal the bottle and mix immediately the slurry with a Heidolph electroic stirrer at 1200 rpm for 10 min.
- Take a 2 L barrel of a Sartorius pressure filtration unit with a filtration area of 130 cm<sup>2</sup> and an operating pressure of 5 bars, filtrate the slurry at 0.45 μm suing a mixed cellulose ester membrane (diameter 142 mm) and collect the filtrate in a glass beaker.
- Measure the pH (Mettler Toledo pH electrode), heavy metals content (Fe, Cu, Zn, Cd) and PO<sub>4</sub> by photometry according to DIN EN 1189.

### 3) Heavy metals extraction

- Take 60 mL of leachate and add 5 mL of Na<sub>2</sub>S solution with a concentration between 10 and 80 g/L to promote the sulphide precipitation.
- Stir the solution for 5 minutes.
- Filtrate the slurry at 0.45 μm to separate the black precipitate.

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<sup>8</sup> Franz, M. (2008). Phosphate fertilizer from sewage sludge ash (SSA). *Waste Management*, 28(10).

#### 4) Precipitation

- Take a 1L plastic bottle and fill it with 200 mL of the heavy metal-free acid leachate.
- Add lime water with 20% CaO and stir the solution at 1200 rpm for 15 minutes.
- Filter the slurry with a Bucher funnel.
- Dry the filter cake overnight at 105 °C and prepare a white powder in a mortar.
- Finally determine:
  - the weight of dried precipitate and its chemical composition by XRF,
  - the heavy metals content with ICP after aqua regia dissolution.

## Procedure C<sup>9</sup>

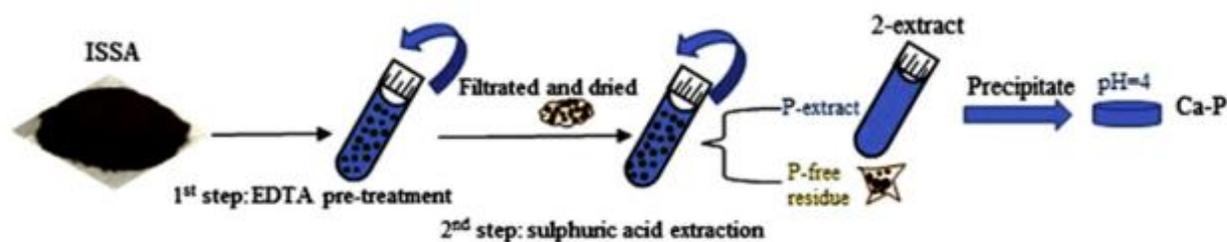


Fig. 34 Two steps extraction method (Fang et al., 2018).

### 1) First step: Pre-extraction with ethylenediaminetetraacetic acid (EDTA)

- Weigh 1.0 g of dried and homogenized ISSA and transfer it into a 50 mL centrifuge tube.
- Add the EDTA reagent (0.02 mol/L, reaction time 120 min, L/S=20) and perform an end-over-end mechanical rotation at 30 rpm.
- Then, centrifuge the mixture at 4000 rpm for 10 min.
- Filtrate the suspension using 0.45  $\mu\text{m}$  mixed cellulose ester membrane filter paper.
- Analyse the filtrate for metal and phosphorus content using inductively coupled plasma optical emission spectroscopy (ICP-OES) and colorimetry after molybdenum blue complex formation, respectively.
- Wash the solid residues with deionized water to remove excess EDTA and then dry them at 105  $^{\circ}\text{C}$  overnight.

### 2) Second step: sulphuric acid

- Perform the extraction in triplicate.
- Pour the solid residues obtained in diluted  $\text{H}_2\text{SO}_4$  at 0.2 M with liquid to solid ratio of 20.
- Mix it for 2 hours and filtrate the solution at 0.45  $\mu\text{m}$
- Calculate The extracted mass of P and metal(loid)s using this equation:

$$\text{Extracted mass}(\text{mg}\cdot\text{g}^{-1}) = \frac{c \times T \times V}{M_0}$$

<sup>9</sup> Fang, L., Li, J. shan, Donatello, S., Cheeseman, C. R., Wang, Q., Poon, C. S., & Tsang, D. C. W. (2018). Recovery of phosphorus from incinerated sewage sludge ash by combined two-step extraction and selective precipitation. *Chemical Engineering Journal*, 348(April), 74–83

where:  $c$  is the concentration of the metals or phosphorus in mg/L;  $T$  is the dilution factor;  $V$  is the volume of extract in L; and  $M_0$  is the mass of the ISSA before processing in g.

### 3) Precipitation

- Put 40 ml of the extract in a beaker.
- Mix it with a magnetic stirrer and increase the pH by adding NaOH or Ca(OH)<sub>2</sub> to reach the target pH.
- Centrifuge the suspension obtained at 4000 rpm for 10 min.
- Filter it at 0.45 μm and analyse the supernatant to determine phosphorus and metals content.
- Dry the remaining precipitate at 105° C overnight.
- Analyse it with XRD to get the crystalline-phases and use X-ray fluorescence (XRF) to get the elemental composition.
- Analyse the morphology of the precipitate with scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX).

Table 17 Literature data about leaching experiments with sulfuric acid.

Extractant	Concentration (N)	P extracted	Dried ash sample	L:S ratio	Contact time	Filtration	Temperature	pH leachate	References
<b>H<sub>2</sub>SO<sub>4</sub></b>	0.4	94%	-	20:1	2 h (30 rpm)	-	-	0.9	(Fang et al., 2018)
	0.8	90%	30 g (SSA-1)	20:1	-	0.45 μm	ambient	-	(Abis, Calmano, & Kuchta, 2018)
	0.2	88.3 %	2 g	20:1	2 h (30 rpm)	0.45 μm	-	1.49	(Wang, Li, Tang, Fang, & Poon, 2018)
	1	>70%	-	10:1	2h (30 rpm)	0.45 μm	-	0.89	(J. shan Li et al., 2017)
	0.38	72-91%	1 g	20:1	2 h	3 μm	20 °C	-	(S. Donatello et al., 2010)
	0.1	100%	3.33 g	150:1	4 h (140 r/min)	1 μm	30 °C	-	(Biswas et al., 2009)
	5.2	>90 %	200 g	2:1	10 min (1200 rpm)	0.45 μm	-	-	(Franz, 2008)
	2	100%	-	-	-	-	-	-	(Hong, Tarutani, Shinya, & Kajiuchi, 2005)
	1	89-93%	-	-	10:1	2 h	-	-	(Takahashi et al., 2001)

Table 18 Literature data about leaching experiments with hydrochloric acid or nitric acid.

Extractant	Concentration (N)	P extracted	Dried ash sample	L:S ratio	Contact time	Filtration	Temperature	pH leachate	References
HCl	0.5	95%	0.5 g	50:1	2 h	-	-	-	(Xu, He, Gu, Wang, & Shao, 2012)
	0.1	~ 100%	-	150:1	4 h (140 r/min)	-	30 °C	1.5	(Biswas et al., 2009)
	1	87%	-	50:1	2 h	-	-	-	(Stark et al., 2006)
	1	100%	-	6.4:1	-	-	-	-	(Hong et al., 2005)
HNO <sub>3</sub>	0.5	>70%	-	10:1	2h (30 rpm)	0.45 μm	-	0.85	(J. shan Li et al., 2017)
	2.71	94.89%	-	0.45 g/g acid to ash mass ratio	-	-	-	-	(Gorazda, Kowalski, & Wzorek, 2012)

Table 19 Literature data about leaching experiments with ethylenediaminetetraacetic acid or oxalic acid or citric acid.

Extractant	Concentration (M)	P extracted	Dried ash sample	L:S ratio	Contact time	Filtration	Temperature	pH leachate	References
<b>EDTA</b>	0.02	20%	-	20:1	3 h	-	-	2	(Fang et al., 2018)
	0.05	<30%	-	10:1	2h (30 rpm)	0.45 μm	-	-	(J. shan Li et al., 2017)
<b>C<sub>2</sub>H<sub>2</sub>O<sub>4</sub></b> (oxalic acid)	0.5	>95%	20 g	20:1	2h (30 rpm)	0.45 μm	-	-	(Fang et al., 2018)
	0.4	56-100%	5 g	20:1	1 h	-	ambient	-	Abis et al. 2018
	0.5	>70%	-	10:1	2h (30 rpm)	0.45 μm	-	1.01	(J. shan Li et al., 2017)
<b>C<sub>6</sub>H<sub>8</sub>O<sub>7</sub></b> (citric acid)	0.2	80%	20 g	20:1	2h (30 rpm)	0.45 μm	-	-	(Fang et al., 2018)
	0.5	>70%	-	10:1	2h (30 rpm)	0.45 μm	-	1.7	(J. shan Li et al., 2017)

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## Sitography

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