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Phosphorus recovery from municipal wastewater

Literature Review

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Project task description

The phosphorus removal and recovery from municipal wastewater has received increased attention due to diminishing reserves of rock phosphates and an increased focus on a sustainable society. In the last decade various phosphorus recovery technologies have been developed, and some have been implemented at full-scale, while others are still at lab-scale.

This project will give an overview of state-of-the-art technologies that are used for recovery of phosphorus from municipal wastewater. The main phosphorus removal technologies will also be discussed, as method for removal is crucial to what method of recovery can be applied. For each P-recovery technology, different aspects will be considered such as process description, end product, application area, challenges, etc.

Abstract

The need for phosphorus recycling in municipal wastewater treatment plants (WWTPs) has received an immense attention the last decade as phosphate rock prices have risen and the direct application of sewage sludge to agriculture has been difficult due to high pollution levels (heavy metals and organic pollutants). Also an increased focus on a sustainable society has put more pressure on looking for alternatives to the use of phosphate rock for fertilizer production. Centralized municipal WWTPs represent a great phosphorus source, and even though it cannot cover the increasing phosphorus demand, it plays a key role for sustainable use of phosphorus.

Recently, various technologies have been developed to recover phosphorus in WWTP. They use different sources, such as phosphorus rich side streams, sewage sludge and sewage sludge ashes. Recovery of phosphorus from side streams has a recovery potential of max. 50% of the incoming phosphorus, while by recovering phosphorus from sewage sludge or sewage sludge ashes 90% of the incoming phosphorus can be recovered.

Three categories of technologies have been identified: crystallization, wet chemical and thermochemical technologies. The crystallization technologies have struvite or calcium phosphates as the final recovered product. These crystallization technologies typically require biological phosphorus removal to be applied in the WWTP. Struvite has been demonstrated as a high quality slow release fertilizer that can be used in agriculture. Currently, only struvite crystallization technologies have been commercialized on industrial scale. Crystallization technologies have also shown to bring other benefits, such as reduction of struvite problems in sludge handling and increased sludge dewaterability. Currently, only crystallization technologies of struvite from phosphorus rich side stream have had success on full scale.

Wet chemical technologies use acid or base to dissolve phosphorus from sewage sludge or sewage sludge ashes. Heavy metals are normally dissolved as well and needs to be removed before phosphorus can be recovered. The redissolved phosphorus can be recovered by different methods, but crystallization of struvite has been the most popular. Wet chemical technologies have been seen as the most complex technology among the three categories discussed, because of high chemical use and various processing steps.

Thermochemical technologies treat sewage sludge ashes by removing heavy metals and increase the bioavailability of the phosphorus in the ashes. Then the ashes can be used in fertilizer production. This is a promising method as high amount of phosphorus can be recovered and various types of phosphorus removal can be applied. However, it requires that the sewage sludge is mono-incinerated, and therefore is not applicable where incineration is not practiced.

Most importantly, this review of phosphorus recovery technologies demonstrates that there exist various options for phosphorus recovery. The economic feasibility of the phosphorus recovery technologies have been only briefly discussed in this project. Basic economic considerations give an indication that in the future (with increasing phosphate rock prices and optimization of the technologies) phosphorus recovery from WWTP can play a key role in fertilizer production and thus food production.

Preface

This project is part of the Master Program in Water and Wastewater Engineering at NTNU (Norwegian University of Science and Technology). It represents 7,5 ECTS credits and can be written on a topic suggested by a Professor or it can be written on a self-chosen topic. This project was written during the autumn 2013 on NTNU, Trondheim

Various researchers have put focus on the looming phosphorus crisis, where we deplete our rock phosphate reserves and have no replacement for phosphorus source to use in the production for artificial fertilizer and thus will have an immense food crisis. This spiked my interest in this subject and I chose phosphorus recovery from municipal wastewater as the subject of my project.

Not all phosphorus recovery technologies that are presented in the literature are included, due to the vast amount of literature that is produced in the last decade. The focus has been given on the most promising technologies.

I would like to thank Professor Stein Wold Østerhus for guidance during the semester and Thorbjørn Emdal for being a valuable discussion partner.

Ivar Urdalen
Trondheim, 19.12.2013

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List of terms and abbreviations

EBPR	Enhanced Biological Phosphorus Removal
PAO	Polyphosphate accumulating organisms
PHA	Poly-hydroxyalkanoates
SBR	Sequential Batch Reactor
VFA	Volatile fatty acids
WWTP	Wastewater Treatment Plant

1 Introduction

The aim of this project is to discuss and give an overview over popular phosphorus recovery technologies that are relevant for European countries. During the last decades a lot of research has been conducted with the objective to develop new phosphorus recovery technology, and this project aim to give an update of what has happened the last decades. The main processes that are implemented on an industrial-scale will be discussed, but also some technologies that are still on pilot and lab-scale will be discussed.

1.1 Global Phosphorus Situation

Phosphorus is an element that is essential to all life, as it is a part of DNA, proteins, enzymes, the energy carrier ATP. Plants, animals and bacteria are dependent on a reliable access to phosphorus to thrive. We get our phosphorus through the food we eat, thus phosphorus is an important part of food production.

Phosphorus is an essential part of synthetic fertilizers and the modern agriculture. Currently, the main source of phosphorus used in production of fertilizers is rock phosphates, which is a non-renewable resource. There are many different predictions for how long the remaining phosphorus reserves will last. The main challenge of making predictions of how long the phosphate rocks will last is that it is difficult to get good data on the amount of phosphate rock left (Gilbert 2009). However with current extraction rates and “business as usual”, the global reserves of rock phosphate have been estimated to last for about the next 100 years. See Schröder et al. (2010) for a more in depth discussion of the availability of rock phosphate reserves. It is important to emphasize that regardless of many years the remaining rock phosphates will last, the current use of phosphorus is unsustainable.

Phosphorus is an irreplaceable part in agriculture, but fortunately it is possible to recycle phosphorus. There are various strategies that can be used to achieve a sustainable use of phosphorus. In Cordell et al. (2011), Figure 1 was presented as a suggestion to a sustainable scenario of future phosphorus use. What is important to notice here is that a lot can be done with agriculture efficiency, food chain efficiency and changing diets to decrease the demand of phosphorus. However phosphorus recovery from human excreta (and thus wastewater) is also an essential part of achieving a sustainable phosphorus future.

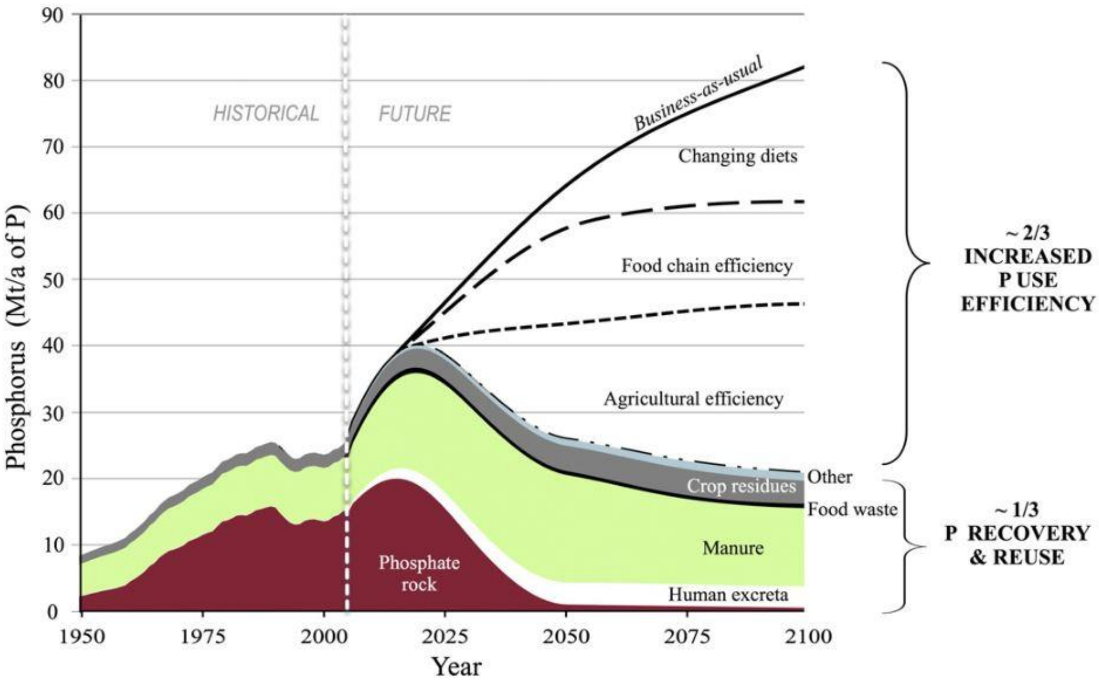

Figure 1 - A sustainable scenario for meeting long-term future phosphorus demand through phosphorus use efficiency and recovery (Cordell et al. 2011).

There are also different strategies that can be used to recover phosphorus from human excreta, such as separating the urine at the source and decentralized approaches. However in this project, centralized approaches to phosphorus recovery from municipal wastewater will be the main focus.

1.2 Difficulties with direct application of sewage sludge in agriculture

Phosphorus has already been “recovered” for many decades in European countries, as sewage sludge has been directly used as fertilizer for agriculture and this is still is the main disposal route in many European countries (Petzet et al. 2013). However, this practice is meeting increased resistance from EU, agriculture organizations and the public. The requirements to the quality of the sewage sludge for application to farm land has generally been tightened the last decades, and due to high heavy metal content and organic pollutants in sewage sludge it is not favorable to use as fertilizer. In various European countries landfilling of sewage sludge has been banned, and therefore incineration has become a major sink for phosphorus. Therefore there is a great potential and need for recovering the phosphorus from sewage sludge and sewage sludge ashes.

1.3 Other motivations for phosphorus recovery technologies

Typically the main reason for phosphorus recovery technologies is fertilizer production and recycling of phosphorus in a sustainable manner. However, there are other motivations to implement phosphorus recovery technologies at the WWTP.

Struvite formation cause serious operational problems in the processing of digested sludge and process water from anaerobic digesters in WWTP, as ammonium, magnesium and phosphorus are released during anaerobic digestion. Struvite precipitates in pipes, pumps and dewatering equipment, and thus clogs the system (Tchobanoglous et al. 2014). Struvite formation has particularly been a challenge in EBPR systems, due to a high amount of phosphorus is released from the sludge in the anaerobic digester. Figure 2 shows an example of struvite deposition in a pipe from anaerobic digester.

Figure 2 - Example of struvite deposition in a pipe from anaerobic digester (Bergmans 2011)

Crystallization technologies can help recover struvite in a controlled manner, and thus remedy this situation and decrease operational problems.

Phosphorus rich, digested sludge has typically a poor dewaterability. When crystallization technologies are used to recover struvite from the sludge treatment, an increase in the sludge dewaterability has also been experienced (Petzet et al. 2012a, Bergmans 2011). This helps lower the further sludge handling and transport costs.

As the phosphorus is recovered from the sludge, less phosphorus is returned to the inlet of the EBPR systems. That can help increase the stability and efficiency of the EBPR systems. It is important to be aware of these advantages as the savings in operations costs due to these advantages can be significant.

2 Phosphorus Removal Technologies

The efficiency of a phosphorus recovery technology is highly dependent on the method of phosphorus removal, and therefore the main phosphorus removal technologies will be discussed here.

2.1 General Phosphorus Removal

There are two main phosphorus removal technologies: chemical phosphorus removal and enhanced biological phosphorus removal (EBPR). During the last 50-60 years phosphorus removal technologies have advanced significantly and been implemented at various locations around the world. The main reason for implementing phosphorus removal at WWTP has been prevention of eutrophication, and the most popular technology has been chemical phosphorus removal. However, EBPR systems has received a wide interest due to lower chemical costs, lower sludge production and increased potential for phosphorus recovery (Morse et al. 1998).

As most of the phosphorus recovery processes and research have been focused on EBPR together with a phosphorus recovery process, the main focus will be given to EBPR as a phosphorus removal process. It has also been demonstrated in economic feasibility studies that phosphorus recovery is most attractive when EBPR is used (Jeanmaire et al. 2001, Gaterell et al. 2000).

Chemical phosphorus removal is still an important process as it is widely implemented and methods have been developed to recover the phosphorus from chemically precipitated sludge. See Section 3.3.3 and Section 3.3.4 for wet chemical and thermochemical technologies.

It is also possible to remove phosphorus with constructed wetlands, membrane filtrations and sand filtration, however these methods are not as widely implemented as chemical phosphorus removal and EBPR, and will not be discussed here.

The municipal wastewater characteristics are very site-specific, and depends on various factors such as, sewer infiltration, discharges of industrial wastewater, use of phosphate detergents, type of sewer system (combined or separated) (Petzet et al. 2013). It has been found that municipal wastewaters typically have a variation between 4 to 11 mg/L of phosphorus as P, where various places have an average between 6 and 8 mg/L (Cornel et al. 2009, Parsons et al. 2008, Tchobanoglous et al. 2014). In Germany, it was found that approx. 11% of the phosphorus could be removed using primary settling (Cornel et al. 2009). When using an activated sludge system about 15% to 25% of phosphorus can be removed as the bacteria use phosphorus for growth. The phosphorus is incorporated in the sludge mass and removed through the removal of the surplus sludge (Henze et al. 2008). However, effluent requirements are often below 1.0 mg/L or more than 90% removal, so the rest of the phosphorus has to be removed with an addition of other processes.

2.2 Chemical Phosphorus Removal

Chemical phosphorus removal is achieved by adding metals ions that are able to form precipitates with inorganic phosphates that are dissolved in the water. The most common metal ions that are used are aluminium (Al^{3+}) and ferric iron (Fe^{3+}). Calcium (Ca^{2+}) is also used, however calcium increase the chemical and sludge handling costs significantly more than aluminium and iron (Tchobanoglous et al. 2014). It is a very attractive technology as it is simple to operate and implement, and phosphorus levels below 1 mg P/L can be achieved in the effluent. Combined with good particle separation process, an even lower concentration can be achieved. However the disadvantages are a significant increase in sludge production and cost of chemicals (WEF 2011). The alkalinity is decreased if acidic salts are used (aluminum and iron salts) and the heavy metals concentrations of the sludge is increased (Petzet et al. 2013). It is also suggested that chemically precipitated sludge has a lower biogas production than biological sludge (Parsons et al. 2008).

With respect to phosphorus recovery, phosphorus bound to aluminum or iron is not especially attractive as it is difficult to use it in industrial processes (production of fertilizer) (Morse et al.

1998). It is also problematic to apply the sludge to agriculture as the phosphorus has a low availability for the plants (Kyle et al. 1995). European countries has strict regulations on the amount of metals in the sludge that can be applied to farm lands, so directly applying the sludge to farm lands has been difficult for European countries. However wet chemical and thermochemical technologies have been developed to recover phosphorus from chemically precipitated sludge (Section 3.3.3 and 3.3.4).

The common metal ions with their corresponding basic precipitation reactions are presented in Table 1. These reactions should be considered together with many other competing reactions and can therefore not be used to calculate dosage. The metal salts will react with other compounds in the water as well, and increase the consumption of metal salts.

Table 1 - Metals used for Chemical Phosphorus Removal (Tchobanoglous et al. 2014).

Name	Metal ion	Basic precipitation reaction
Aluminum	Al^{3+}	$Al^{3+} + H_nPO_4^{3-n} \leftrightarrow AlPO_4 + nH^+$
Iron	Fe^{3+}	$Fe^{3+} + H_nPO_4^{3-n} \leftrightarrow FePO_4 + nH^+$
Calcium	Ca^{2+}	$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2$

2.2.1 Process Configurations

Chemical phosphorus removal can be arranged in different ways and the process configurations have different names depending on the location of the addition of the metal salt.

- Pre-precipitation: Metal salts are added in the primary treatment and the phosphorus is removed together with the primary sludge
- Simultaneous precipitation: Metal salts are added in the biological reactor. It can be added in various places (influent, effluent, in the return sludge, etc.). The phosphorus is then removed together with the secondary sludge. This has been the most popular method.
- Post-precipitation: Metal salts are added after the secondary sedimentation tank. This configuration is normally used as a polishing step in order to achieve effluent total phosphorus concentrations of < 0.5 mg/L (Kroiss et al. 2011).

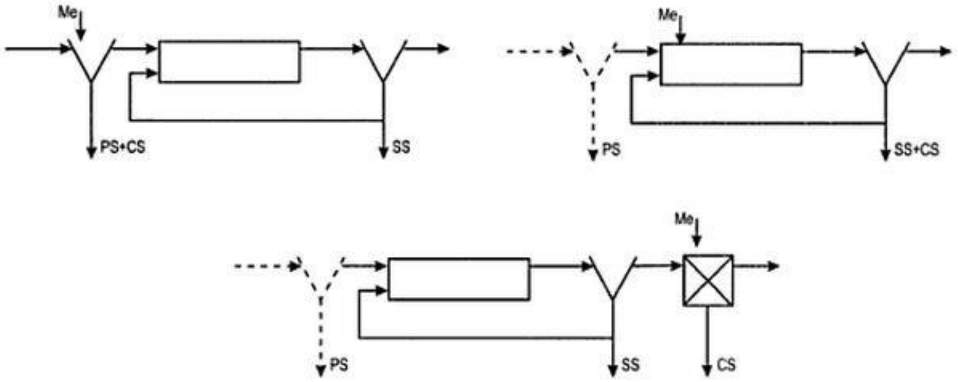

Figure 3 - Basic configurations of chemical phosphorus removal (Janssen et al. 2002). Pre-precipitation (above left), simultaneous precipitation (above right) and post-precipitation (bottom). Me = metal salt, SS = secondary sludge, CS = chemical sludge with phosphorus

2.2.2 Coagulant aids

It is also possible to enhance the precipitation of phosphorus by adding polymers. Özacar et al. (2003) found that organic polymers were able to increase the efficiency of alum to remove phosphorus.

2.3 Enhanced Biological Phosphorus Removal

In respect to recovery of phosphorus, EBPR is a much more favorable technology than chemical phosphorus removal. The phosphorus is taken up in the activated sludge and it is relatively easy to recover the phosphorus compared to chemical sludge. Due to the lack of chemicals used in this process, EBPR systems have lower sludge production, lower chemical costs and the sludge contains less metals. It has a higher value for agriculture as the phosphorus is not bound to metals, and is therefore more available to the plants. However, the EBPR process is very dependent on the wastewater characteristics and is less stable and flexible compared to chemical precipitation (Janssen et al. 2002, Tchobanoglous et al. 2014). It normally involves more complex control and larger reactor volumes as well. Normally, under favorable conditions, around 90% of the incoming phosphorus can be contained in the sludge (Petzet et al. 2013).

2.3.1 Principles

In normal activated sludge systems, phosphorus is removed by the microorganisms as they use phosphorus as a nutrient for growth. EBPR uses that fact that some organisms are able to take up more phosphorus than they require for cellular growth, often called “luxury uptake”. The workhorses responsible of EBPR systems are called polyphosphate accumulating organisms (PAO). There exist various types of organisms that are able to take up phosphorus in excess amounts as energy-rich polyphosphates, and the phosphorus content can reach up to 20-30% of the dry weight of the bacteria. For common heterotrophic bacteria the phosphorus content can be about 2% (Tchobanoglous et al. 2014). So the basis of EBPR is to maximize the fraction of PAOs in the wastewater to ensure optimal phosphorus removal.

To stimulate the growth of PAOs, two conditions have to be satisfied:

1. Alternating anaerobic and aerobic conditions (Can be achieved with an anaerobic reactor followed by an aerobic reactor, or with a sequential batch reactor).
2. Sufficient supply of volatile fatty acids (acetate, propionate, etc.) in the anaerobic reactor (Can be supplied by fermentative bacteria in the anaerobic reactor or have a separate tank where fermentation is occurring).

The stored polyphosphates are considered as a phosphate and energy reserves for the PAOs, and this helps PAOs get an advantage over other bacteria in alternating anaerobic and aerobic conditions.

2.3.2 Biochemical Model

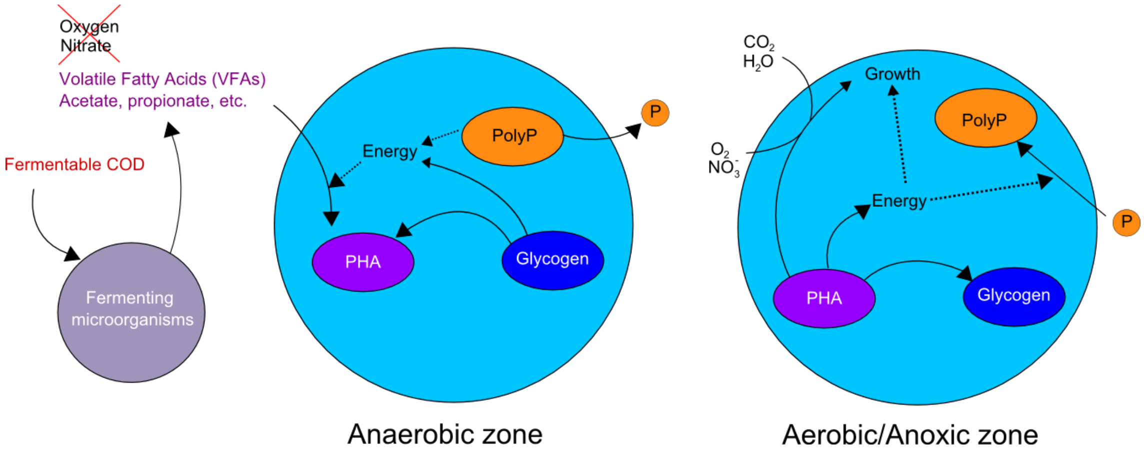

Figure 4 - Simplified biochemical model for PAOs under anaerobic and aerobic/anoxic conditions (Henze et al. 2008)

The general biochemical transformations in the metabolism of PAOs have been widely accepted in the literature and in textbooks. However there are still some disputes about the details of their metabolism. The Mino model is the generally accepted model and will be presented here (Grady et al. 2011).

In an EBPR system the incoming wastewater is mixed together with the activated sludge in an anaerobic zone. Here PAOs are able to use volatile fatty acids (VFA), such as acetate or propionate, to form poly-hydroxyalkanoates (PHA), which is a carbon storage product. The volatile fatty acids are already present in the influent or produced by fermentative bacteria present in the anaerobic tank. Fermentation is microbial degradation of organic compounds which occurs in the absence of oxygen and nitrate. So it is essential for the process that the anaerobic tank is free of any oxygen or nitrates, as this may interfere with the fermentation. It is also possible to use a separate tank dedicated to fermentation. To be able to form the PHAs, the PAOs use the stored poly-P and glycogen as an energy source. As the PAOs use poly-P, orthophosphate is released in the water, and often a concentration of 20 mg P/L can be observed in the anaerobic tank. See left side of Figure 4.

In the following aerobic or anoxic zone, either nitrate or oxygen is supplied. The PAOs are regenerating their poly-P reserves and are able to take up sufficient orthophosphate so that there is a net removal of phosphorus from the influent. To provide energy for the formation of the poly-P reserves, the PHAs formed in the anaerobic tank are oxidized by oxygen. The energy released is also used for replenishment of glycogen reserves and for growth. See right side of Figure 4. Figure 5 illustrates how the concentrations of the participating compounds are changing in anaerobic phase and aerobic phase.

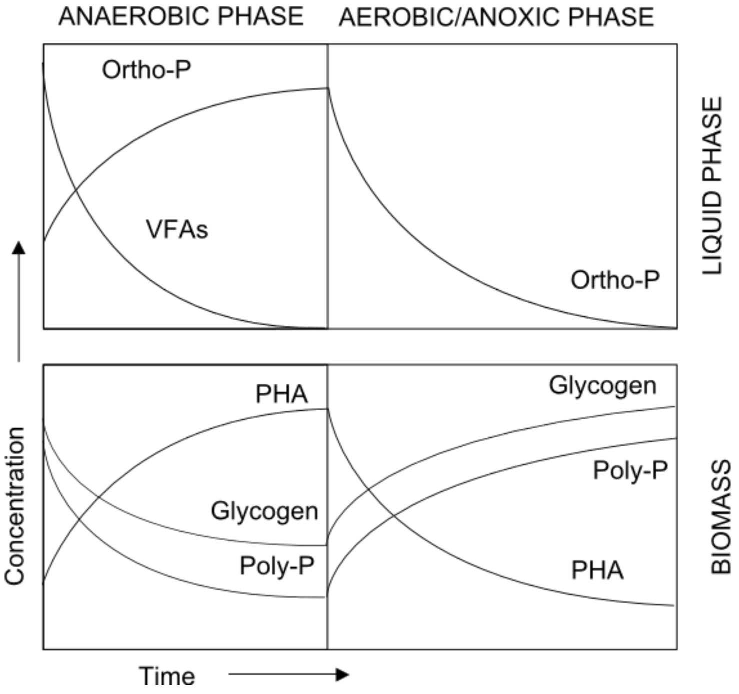

Figure 5 - Concentrations of participating compounds in anaerobic and aerobic reactor (Janssen et al. 2002).

2.3.3 Process configurations

There are different ways the requirement for alternating anaerobic and aerobic conditions can be fulfilled. The most basic configuration of a WWTP that applies EBPR is depicted in Figure 6. The anaerobic and aerobic zone can also be divided in time as a sequential batch reactor (SBR).

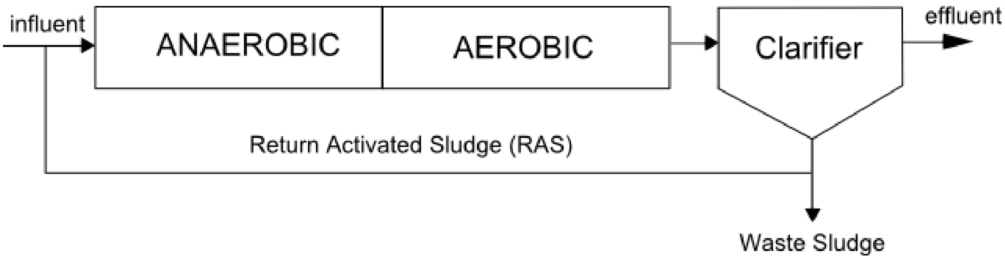

Figure 6 - Basic configuration of EBPR (Janssen et al. 2002)

Nitrogen is also an important nutrient that can be removed with biological processes and nitrogen removal has also been a requirement at various locations around the world. Therefore many process configurations have been developed that combine phosphorus and nitrogen removal (commonly called biological nutrient removal). It is beyond the scope of this project to discuss the different process configurations in depth. See Tchobanoglous et al. (2014) for a discussion of different process configurations for EBPR and biological nutrient removal systems.

3 Principles of Phosphorus Recovery

3.1 Locations of phosphorus recovery in WWTP

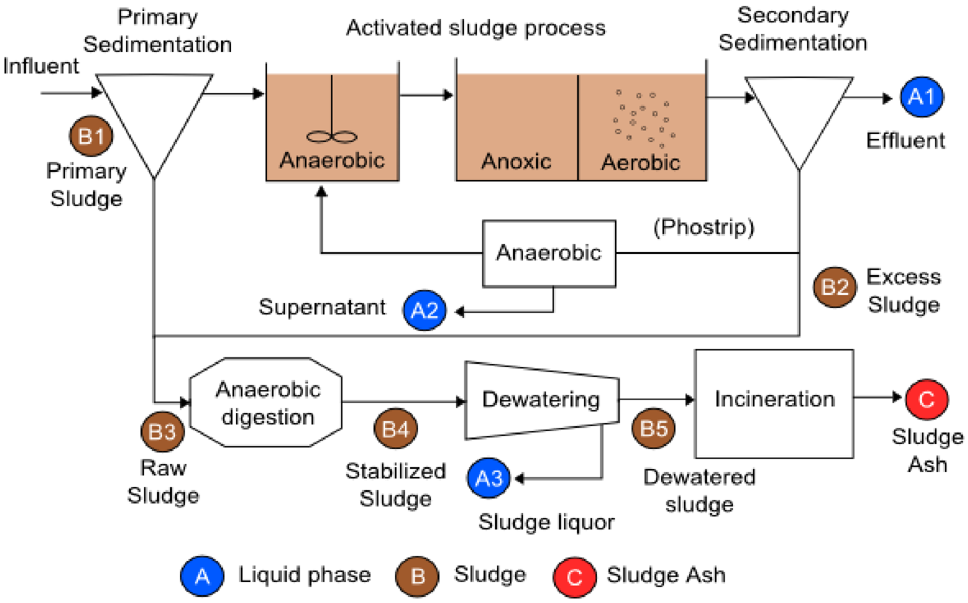

Figure 7 - Locations of phosphorus recovery in WWTP (Cornel et al. 2009)

There has been developed various technologies that can recovery phosphorus from different locations in the WWTP, and the possible locations in a conventional biological treatment plant have been illustrated in Figure 7. A1-3 shows locations where phosphorus can be recovered from the liquid phase. B1-5 shows locations where phosphorus can be recovered from sludge. C represents the sewage sludge ash after incineration. A couple of crystallization technologies have been developed where digested sludge is used as the raw source (AirPrex and FIX-Phos, see Section 3.3.2), however crystallization technologies are commonly used on phosphorus rich side streams. Wet chemical technologies and thermochemical technologies are used on sludge and sewage sludge ash (Table 2). Crystallization technologies are also combined with wet chemical technologies, see Section 3.3.3.

Table 2 - Applications of different technologies on different sources in a WWTP

	Crystallization	Wet Chemical	Thermochemical
Liquid phase	x		
Sewage sludge	x	x	
Sewage sludge ash		x	x

A summary of different phosphorus concentrations and recovery potential at different places in the WWTP, based on Germany experiences, are presented in Table 3. The effluent normally contains too low concentrations for phosphorus recovery to be economically feasible (Petzet et al. 2013). However, technologies have been suggested that use the effluent as a phosphorus source. It is based on the same principle of post precipitation of phosphorus removal, but changing the precipitant to a magnesium salt (Montag et al. 2009).

Table 3 - Phosphorus recovery potential from different locations in WWTP (Montag 2008).

	Volume/mass flow	Relative volume-mass flow	Concentration of phosphorus	Bond	Recovery potential
Effluent	200 l/cap/d	100%	< 5 mg/l	Dissolved	Max. 55%
Sludge liquor	1-10 l/cap/d	0.5-5%	20-100 mg/l	Dissolved	Max. 50%
Dewatered sludge	0.15 l/cap/d	0.075%	~10 g/kg TS	Biological/ Chemical	~90%
Sewage sludge ash	0.03 kg/cap/d	0.015%	64 g/kg	Chemical	~90%

3.1.1 Recovery from Liquid phase

Recovery from the liquid phase is limited to about < 50-60% of the incoming phosphorus as rest of the phosphorus is removed together with the sludge. Typically the recovery is from 10-40% (Cornel et al. 2009). If phosphorus is recovered from a phosphorus rich side stream, EBPR system most often used as the phosphorus needs to be easily released from the sludge. The recovered product is either struvite or calcium phosphate. One advantage for recovery from the liquid phase is that it typically involves addition of a small treatment step, and is therefore can easily be installed at existing plants (Kabbe 2013). Currently, only crystallization technologies of struvite from phosphorus rich side stream have had success on full scale.

3.1.2 Recovery from Sewage sludge

As 90-95% of the incoming phosphorus is incorporated into the sludge, technologies that recover phosphorus from the sewage sludge have a potential recovery of 90-95% (Table 3) (Cornel et al. 2009). Due to the high recovery potential from sewage sludge, a lot of interest has been given to recover phosphorus from sewage sludge. Historically, sludge has been applied as fertilizer. However it is not without problems as sludge typically contains contaminants such as heavy metals, pathogens and organic pollutants. Therefore technologies that recover phosphorus from sewage sludge must be able to handle these contaminants. Crystallization and wet chemical technologies have been developed to attempt to recover the phosphorus from the sludge and will be discussed in Section 3.3.2 and 3.3.3.

3.1.3 Recovery from Sewage sludge ashes

If the sludge is not landfilled or used directly on land it is often incinerated (typically in Europe), and the final residue is called sewage sludge ash. Only mono-incinerated sludge is attractive for phosphorus recovery as co-incinerated sludge (together with other wastes) often lower the phosphorus concentrations and increase the contaminant levels. When it is incinerated, the volume of the sludge is greatly reduced, as well as organic pollutants and pathogens are destroyed. About 90% of the phosphorus load to the WWTP is contained in the sewage sludge ashes. Sewage sludge ashes have a small volume and are easy to transport, therefore makes an attractive source for phosphorus (Petzet et al. 2013).

The characteristics of the sewage sludge ash and thus the feasibility of phosphorus recovery depends on the process used in the WWTP. If chemical phosphorus removal is used, high levels of aluminum or iron has to be dealt with. The sewage sludge ashes could potentially be used directly as a fertilizer, if the heavy metal contents satisfy the fertilizer legislation. However, the bioavailability of the phosphorus in the ashes is normally low compared to commercial fertilizer. Thermochemical technologies have been developed to primarily reduce the heavy metal content and increase the bioavailability of phosphorus in the sewage sludge ashes (Adam 2008).

3.2 Recovered Products

Phosphorus can be recovered as different products from the WWTP. Most methods are based on recovering the phosphorus in a way so it can be used for agriculture. Struvite (magnesium ammonium phosphate) and hydroxyapatite (calcium phosphate) has been the most popular products of recovery. Struvite and calcium phosphates are normally recovered as round pellets with low water quantity and high purity (Giesen 1999). The phosphorus can also be recovered as a sewage sludge ash with improved fertilizer qualities. General chemistry and applications of these products will be considered here.

Phosphorus can also be removed using aluminum and iron, but it has been found that when phosphorus is bound to aluminum or iron it is less available for plants and therefore these products are unattractive to use as a fertilizer (Kyle et al. 1995). If a method can be used to solubilize the phosphorus when phosphorus is bound to aluminium and iron, they can be used directly as a fertilizer. Various types of soil microorganisms have been found to be able to solubilize inorganic phosphorus, and these have been called phosphate-solubilizing bacteria (PSB) and phosphate-solubilizing fungi (PSF). One opportunity is therefore to favor the growth of these microorganisms in the soil. However, limited success have been achieved by this approach (Richardson et al. 2011).

It is also possible to improve the recovery of phosphorus from chemically precipitated sludge with wet chemical and thermochemical technologies. See Section 3.3.3 and 3.3.4.

3.2.1 Struvite (Magnesium Ammonium Phosphate)

In this section, the chemistry and applications of struvite will be considered. Magnesium ammonium phosphate hexahydrate, also known as struvite, has the chemical formula: $MgNH_4PO_4 \cdot 6H_2O$. Struvite has become a promising way to recover phosphorus from a WWTP and several technologies which recover phosphorus as struvite will be discussed later. It is normally recovered from EBPR plants as the sludge contains high amount of phosphorus which is not metal bound.

Struvite forms when molar ratio of magnesium, ammonium and phosphorus are approx. 1:1:1 and normally under slightly alkaline pH values. Other factors that are important for struvite formation are mixing energy, temperature, and the presence of other ions (Liu et al. 2013).

Figure 8 - Different particle sizes of produced struvite fertilizer from Ostara (Britton 2009)

Crystals of struvite will form when the concentrations of magnesium, ammonium, and phosphorus exceed the solubility limit and have a suitable location to grow. Seeding materials can be added to reactors to induce crystal growth. The formation of struvite can be described by this equation (Le Corre et al. 2009):

$$Mg^{2+} + NH_4^+ + H_nPO_4^{3-n} + 6H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O + nH^+$$

Struvite as a fertilizer

Struvite has been found to be an effective slow-release fertilizer and it provides both nitrogen and phosphorus. Struvite has a low water solubility (0.018 g/100 ml at 25 °C) (Bridger et al. 1962), which makes the nutrients less mobile compared to highly soluble fertilizers. A slow release rate is beneficial because (1) the plants are able to use more of the nutrients in the fertilizer, (2) a less frequent application rate can be applied and (3) decrease the loss of nutrients due to surface runoff or leaching into the groundwater (Münch et al. 2001). It has also been found that struvite recovered from digested sludge or anaerobic digesters in WWTPs usually have low or no heavy metal content (Liu et al. 2013).

The excellent fertilizing properties of struvite was already demonstrated in the 1960's by Bridger et al. (1962). Struvite can be used as a fertilizer for various purposes, such as turfs, tree seedlings, ornamentals, vegetables and flower boards (Münch et al. 2001). Various studies have also investigated the fertilizing properties of struvite recovered from various sources, such as landfill leachate (Li et al. 2003), swine wastewater (Liu et al. 2011), poultry wastewater (Yetilmezsoy et al. 2009) and industrial wastewater (El Diwani et al. 2007). All studies demonstrated that struvite has great fertilizing properties.

Currently struvite makes up only a small part of the slow-release fertilizer market, however there are companies that have successfully commercialized struvite fertilizer recovered from WWTPs (Ostara – Canada and Unitika – Japan) (Tchobanoglous et al. 2014).

3.2.2 Hydroxyapatite (Calcium phosphate)

Phosphorus can also be removed as calcium phosphates and the main product that is formed is hydroxyapatite, as it is the most thermodynamically stable form (Gray 2004).

Table 4 - Possible calcium phosphates that are formed (Gray 2004).

Name	Chemical Formula	Solubility product
Tricalcium phosphate	$Ca_3(PO_4)_2$	Variable, more soluble than crystalline phosphates
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	4.7×10^{-59}
Dicalciumphosphate dihyrate	$CaHPO_4 \cdot 2H_2O$	2.49×10^{-7}
Octacalcium phosphate	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$	1.25×10^{-47}

Hydroxyapatite (also called hydroxylapatite) has the chemical formula $Ca_5(PO_4)_3(OH)$, but is also written as $Ca_{10}(PO_4)_3(OH)_2$. Lately, calcium phosphates has become a less favorable as a product of phosphorus recovery, due to high chemical usage and proposed low fertilizer qualities compared to struvite (Tchobanoglous et al. 2014, Cabeza et al. 2011).

Calcium is normally added as lime $Ca(OH)_2$ and formation of hydroxyapatite follow this chemical reaction (Tchobanoglous et al. 2014):

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2$$

Calcium phosphates normally form in calcium and phosphorus rich water and with a high pH in the range of 8.0 – 9.0 pH. High oversaturation is needed for spontaneous precipitation of calcium phosphates. However, many technologies are based on adding a seed material such as sand or calcium silicate hydrate (CSH), and pellets of calcium phosphates are formed together with the seed material (Cornel et al. 2009, Piekema et al. 2001).

Calcium phosphates as a fertilizer

Calcium phosphates are more or less that same as mined phosphate rock, so it is possible to use calcium phosphates as a direct substitute in industrial production of fertilizer. It is also possible to mix together with other nutrients or apply it directly as a slow-release fertilizer (Tchobanoglous et al. 2014).

Cabeza et al. (2011) demonstrated by pot experiments that calcium phosphate has potential a fertilizer, however only in acid conditions. Bauer et al. (2007) investigated the quality of calcium phosphate recovered from swine wastewater, and demonstrated it has a potential as a fertilizer, however with a lower effectiveness than commercial fertilizer. The phosphorus uptake by the plants was also dependent on the particle size of the calcium phosphates.

Even though many pot evaluation studies have been conducted to investigate the fertilizer properties of calcium phosphates, it is important to perform long term field investigations to further evaluate the effectiveness of calcium phosphates as a fertilizer.

3.2.3 Sewage Sludge Ash

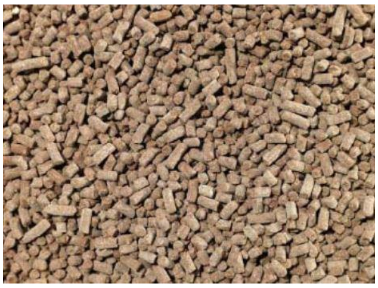

Figure 9 - Fertilizer produced from sewage sludge ash treated by the ASH-DEC process (Adam 2008)

The phosphorus can also be recovered from sewage sludge ash by using thermochemical technologies. Sewage sludge ash is produced by incineration of sludge from WWTP, and normally contains high levels of heavy metals. It is important to mention that sewage sludge is often co-incinerated together with other wastes that contain low amounts of phosphorus. These ashes are typically unattractive for phosphorus recovery as the ashes contains a low amount of phosphorus (Adam 2008). Therefore only mono-incinerated sludge is considered for phosphorus recovery.

When sewage sludge ash is the final product from a phosphorus recovery technology, the process includes:

1. Satisfactory reduction of heavy metal content.
2. Increase the bioavailability of the phosphorus.

The phosphorus is still incorporated in the sewage sludge ash, and the ash is used in fertilizer production or applied directly as a fertilizer. Mono incinerated sewage sludge ashes can have a high phosphorus content in the range of 15-25% P_2O_5 and is comparable to low grade phosphate rock (Adam et al. 2009).

The composition of the sewage sludge ash is highly dependent on the treatment used in the WWTP. If chemical phosphorus removal is used, typically a high concentration of iron and aluminium can be found in the ashes (Petzet et al. 2012b).

3.3 Principles of Phosphorus Recovery Technologies

Phosphorus recovery technologies from WWTPs have received increased attention in the recent decade, and as a result various technologies have been developed. Hermann (2009b) provided an evaluation of over 30 different technologies and Sartorius et al. (2011) identified over 20. This demonstrates the significant increase in development of phosphorus recovery technologies, however only a few processes have been implemented on an industrial scale. Even though there are many phosphorus recovery technologies, many build on the same principles, and in this section the principles of the main phosphorus recovery technologies will be discussed.

3.3.1 Crystallization (Recovery from wastewater)

For treating high nutrient side streams, technologies based on crystallization of struvite has become a promising method, with several plants in full-scale operation. Especially wastewater with > 50 mg/L phosphorus have proved economically rewarding (Cornel et al. 2009). Crystallization of calcium phosphate has received much interest as well, but recently it has fallen out of favor due to higher chemical costs. Calcium phosphate recovery from other sources such as animal manure seems promising (SCOPE 2009). However, it has also been argued that too much focus has been given to struvite recovery, and that calcium phosphate still is a viable method of recovery due to its fertilizing properties and that it is possible to use it for industrial fertilizer production (Hao et al. 2013).

Crystallization can be used for treating phosphorus rich side streams, such as water from anaerobic digesters or dewatering, but it is also used in combination with wet chemical technologies as well and will be discussed later.

3.3.1.1 Crystallization basics

All crystallization technologies presented here are based on 3 fundamental stages: (1) supersaturation, (2) primary and secondary nucleation, and (3) crystal growth (Tchobanoglous et al. 2014). Supersaturation occurs when product of different ion activities exceeds the solubility product, and spontaneous nucleation and crystal growth occurs when the solution is supersaturated. Crystallization occurs as a mechanism of the system to return to equilibrium.

Nucleation is the process where ions come together to form a solid (crystal embryo or nuclei) in a supersaturated solution. The process is divided into primary and secondary nucleation. Primary nucleation is further divided into homogenous and heterogeneous nucleation (See Figure 10). Homogenous primary nucleation is the process where spontaneous nuclei formation occurs, and heterogeneous primary nucleation corresponds to the nuclei formation that occurs on foreign particles (sand, crystals, dust, colloids, etc.). In practice, as the influent contains suspended solids, heterogeneous primary nucleation is the dominant process (Le Corre et al. 2009).

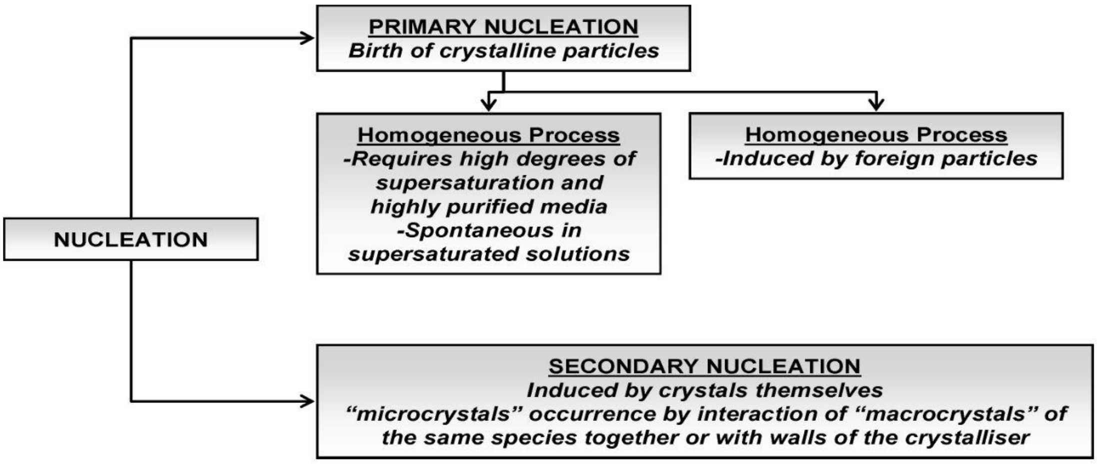

Figure 10 - The different nucleation processes (Le Corre et al. 2009)

Secondary nucleation is the process where new nuclei are formed, because small crystal particles leave the crystal surface due to shear forces in the water or contact with other crystals (Tchobanoglous et al. 2014).

Crystal growth refers to the process where, in supersaturated conditions, the crystal is growing due incorporation of ions into the crystal lattice. As larger particles are easier to separate from the liquid phase, larger crystals is a desired product and the processes are optimized with respect to factors that increase the crystal diameter.

3.3.1.2 Crystallization of struvite

See Section 4.1.1 and 4.1.2 for a description of commercial technologies from Ostara (Canada) and Unitika (Japan). For a discussion of basic chemistry of struvite and its use as a fertilizer, see Section 3.2.1.

The most important factors affecting the formation of struvite are (1) pH, (2) molar ratios of Mg^{2+}, NH_4^+ and PO_4^{3-}, (3) temperature and (4) the presence of foreign ions (Liu et al. 2013). Normally the phosphorus rich side stream is fed into a reactor together with seed material for crystal growth, magnesium source, and the pH is controlled either by NaOH or with CO_2 stripping.

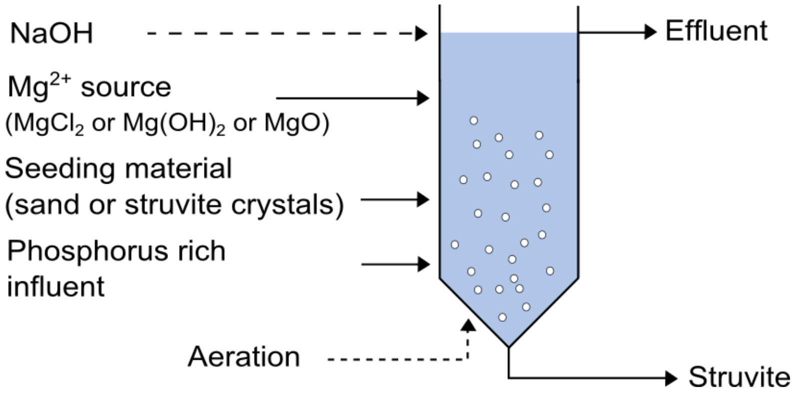

Figure 11 - General principle of struvite recovery from wastewater

Optimal molar ratios of Mg^{2+}, NH_4^+ and PO_4^{3-}

For the formation of struvite, a molar ratio of 1:1:1 of $Mg:NH_4:PO_4$ is needed. Magnesium is usually not present in sufficient quantities in the wastewater and needs to be added. However, usually more Mg^{2+} than the theoretical need for struvite precipitation is added, because other magnesium compounds will also form and Mg^{2+} will be consumed. A lot of research have been focused on finding an optimal ratio $Mg^{2+}:PO_4^{3-}$ and a ratio of 1.1-1.6:1.0 is often reported (Liu et al. 2013, Rahman et al. 2013). However, an optimal molar ratio of the constituents is dependent on the characteristics on the raw water. If the molar concentration of Mg^{2+} falls below the molar concentration of PO_4^{3-}, the system is not optimal with respect to the removal of phosphorus.

Optimal pH for struvite crystallization

MAP can be precipitated in a range of pH values (7.0 – 11.5) and the solubility of struvite is at a minimum at near pH 10.3 (Rahman et al. 2013, Ohlinger et al. 1998). Different optimal pH values for struvite recovery have been suggested by various authors, and based on a review of different studies, Liu et al. (2013) suggested an optimal pH value between 8.5 – 9.0 for wastewater. However, typically struvite recovery reactors is operated in the range of 8.0 - 8.8

to minimize the addition of chemicals and minimize the formation of other products such as calcium phosphates (Tchobanoglous et al. 2014).

In contrast to these results, Hao et al. (2008) found that highly pure (99.7%) struvite was found to formed at pH 7.0-7.5. Many researchers evaluate the struvite product using x-ray diffraction, which is often used as a qualitative assessment of the struvite. However, to evaluate the quality of the struvite crystals, a quantitative assessment is needed. The study found from elemental analysis of the precipitate that as pH increased (pH > 8.0), the purity of struvite decreased significantly. However, with pH values of 7.0-7.5 the precipitation rate is significantly reduced, and therefore a pH around 7.0-7.5 will not be employed in practice (Hao et al. 2008).

pH is normally controlled through the removal of CO_2 by aeration or by the addition of NaOH, and the choice of method depends among others on the characteristics of the influent, the preference of the designer/operator and availability of chemicals. Aeration also provides good mixing which is beneficial for crystal growth.

Source of Magnesium

In wastewater, the magnesium (Mg^{2+}) concentration is usually low relative to ammonium (NH_4^+) and phosphorus (PO_4^{3-}). Therefore addition of magnesium is necessary to achieve crystallization of struvite. Among the popular sources is magnesium chloride ($MgCl_2$), magnesium hydroxide ($Mg(OH)_2$) and magnesium oxide (MgO) (Tchobanoglous et al. 2014). An advantage with dosing $Mg(OH)_2$ is that pH will increase. Seawater has also been used successfully as a source of magnesium where the WWTP is located near the coast (Matsumiya et al. 2000). The choice of chemical is often based on the availability of the chemical and the cost of chemical.

Seed materials

To improve the crystallization process and ensure good crystal growth, a seed material can be added. This helps form good crystals that have an improved settleability and helps improve the struvite reaction rate. Different seed materials have been used in practice, such as sand, silica sand, granite, quartz and recycled struvite (Wang et al. 2006, Liu et al. 2013).

Using a seed material to enhance crystal growth also has some disadvantages. The purity of the product might be reduced if too much sand is added. The pumping and mixing energy needs to be increased with bigger particles, and the cost of operations increases (Liu et al. 2013, Battistoni et al. 2005). If recycled struvite is used as a seed material, a recycle stream needs to be introduced (See Unitika Process – Section 4.1.2). Wang et al. (2006) demonstrated the effect of seeding materials on struvite crystallization and evaluated different seeding materials (sand, granite, and struvite). Under their testing conditions they found that recycled struvite provided the highest efficiency with respect to phosphorus removal from the liquid.

Instead of conventional seeding material that gets incorporated in the final product, crystal accumulating devices has also been investigated. Le Corre et al. (2007) demonstrated that a stainless steel mesh placed on the top of a fluidized bed reactor can be used as a surface which captures crystals formed in the solution. The crystals accumulate on the mesh, and then the mesh can be removed together with the crystals. Subsequently struvite can be removed from the stainless steel mesh.

Temperature

The temperature has an effect on the solubility of struvite and on the crystal growth. The rate of crystal growth often increase with temperature and affect the shape and the size (Le Corre et al. 2009). The solubility has been found to generally increase up to a limit around 60 ^oC, where the solubility drops significantly (Aage et al. 1997). The temperature is often controlled in lab studies, however it is not economic viable to control temperature in industrial processes.

3.3.1.3 Crystallization of calcium phosphates

For a discussion of basic chemistry of hydroxyapatite and its use as a fertilizer, see Section 3.2.2.

Most approaches that use crystallization of calcium phosphates are often connected to high chemical use, and have therefore fallen out of favor as a technology of phosphorus recovery from municipal wastewater. However it is seems that it can be effective in recovery of phosphorus from other sources such as animal manures (SCOPE 2009). Ways to avoid high chemical costs with crystallization of calcium phosphates will be discussed here.

Normally a fluidized bed reactor is used as a crystallization reactor. The principle is much like the crystallization of struvite, where a seeding material is added to induce the deposition of calcium phosphates and pellets are grown that are easily removed as they sediment to the bottom of the reactor. The most important operational parameters that affect the crystallization of calcium phosphates are (1) pH, (2) seeding material, (3) supersaturation of calcium and phosphorus and (4) bicarbonate concentration. Figure 12 demonstrates the general method for calcium phosphate recovery from wastewater.

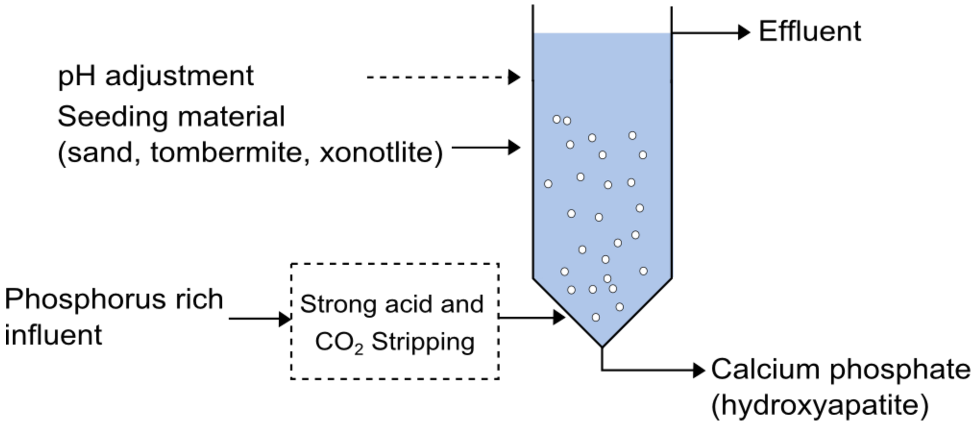

Figure 12 - General principle of calcium phosphate recovery from wastewater (Tchobanoglous et al. 2014)

Temperature is an important parameter for the crystallization of calcium phosphates, however it is seldom controlled (Tchobanoglous et al. 2014).

pH

To achieve optimal conditions for crystallization of calcium phosphates, crystallization technologies normally require a pH of 8.0 – 9.0 (Tchobanoglous et al. 2014), depending on the seeding material. When tobermite-rich construction waste was used, there is no need for pH adjustment, and the process can be maintained at 7.0-7.5 (Berg et al. 2005). If pH needs to be adjusted, it is typically controlled by dosing lime or NaOH (Donnert et al. 1999).

Problems with $CaCO_3$ formation

A serious disadvantage with dosing lime is that it will react with bicarbonate in the wastewater and form calcium carbonate, as illustrated in the following equation (WEF 2011):

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \leftrightarrow 2CaCO_3 + 2H_2O$$

To prevent the formation of unwanted calcium carbonate, the common strategy has therefore been to acidify the water to a pH less than 4-5 by using a strong acid, and CO_2 is subsequently stripped off. Then lime is dosed to increase the pH and calcium phosphates are formed (Tchobanoglous et al. 2014, Donnert et al. 1999). This strategy leads to high chemical costs, and therefore a lot of research has dedicated to achieve crystallization of calcium phosphates without this costly pretreatment. A possible solution is to use different seeding materials.

Seeding Material

It has been found that different seeding materials can help to avoid the problems with $CaCO_3$ formation. Most wastewater is already supersaturated with calcium and phosphate, however spontaneous precipitation does not occur. To initiate the crystallization of calcium phosphates it is found beneficial to provide a seeding material, which provides a surface for the deposition of calcium phosphates (Berg et al. 2006).

The first application of crystallization of calcium phosphates for phosphorus recovery was developed by DHV in the Netherlands (DHV Crystalactor) and used quartz sand as a seed material, however this led to the major disadvantage of costly pretreatment with acidification and CO_2 stripping (Cornel et al. 2009).

A process called P-ROC (developed at Karlsruhe Institute of Technology in Germany) have successfully applied tobermite-rich construction waste compounds (calcium silicate hydrates) as a seeding material (Berg et al. 2005). The process does not apply any form of pH adjustment or CO_2 removal. The pH of the initial water was around 7.2-7.5. The formation of hydroxyapatite was demonstrated, and the final product was found comparable to phosphate rock. The process has only been implemented on lab-scale.

Other seeding materials that have been investigated and seems promising are calcite (Song et al. 2006), xonotlite (calcium silicate hydrate) (Chen et al. 2009). The goal with these seeding materials is also to avoid the costly pretreatment with acidification, CO_2 stripping and subsequently increase the pH.

3.3.2 Crystallization (Recovery from sludge)

The crystallization technologies presented in the previous section were all based on a phosphorus rich side stream as the source for phosphorus. However, there are also crystallization technologies that have been developed that use the mainstream in the sludge treatment as a phosphorus source, and thus use sludge as the phosphorus source. The products are then crystallized within the sludge.

The major advantages with this method are struvite scaling on sludge treatment equipment can be avoided, and dewaterability is increased. A smaller phosphorus return load to the inlet of the WWTP is also achieved. These advantages can cause significant savings in operational costs. A major challenge with this method is the increased difficulty of separating the recovered product from the sludge and reduced purity of the product. (Petzet et al. 2013).

These technologies have many similarities with conventional crystallization technologies, but it is worth to mention the differences with using sludge as the phosphorus source. There are mainly 2 technologies that have developed – AirPrex and FIX-Phos (Table 5).

Table 5 - Crystallization technologies - Recovery from sludge

Name	Organization	Recovered product	Chemicals used	P Recovered (of influent)	Scale	Reference
AirPrex	Berliner Wasserbetriebe, Germany	Struvite	$MgCl_2$	~80%	Semi-industrial	Heinzmann et al. (2003)
FIX-Phos	TU Darmstadt, Germany	Calcium phosphate	Calcium silicate hydrate (CSH)	21-31%	Pilot	Petzet et al. (2012a)

It is also important to mention that these technologies are developed to be used together with EBPR systems, and therefore are not usable together with chemical phosphorus removal.

AirPrex

This technology was developed by Berliner Wasserbetriebe (Berlin Water Works), and the objective was to recover phosphorus in a reusable manner, but also prevent struvite incrustation in the anaerobic digester (which can cause big operational problems). A schematic diagram is shown in Figure 13.

The recovered product is struvite, so a magnesium source needs to be added and the pH needs to be increased. This process uses $MgCl_2$ for magnesium source and CO_2 stripping by aeration for pH increase. The aeration also causes a good mixing in the reactor. An air-lift reactor design makes sure the sludge is well mixed. The struvite crystallizes, and when the crystals grow to sufficient size they will settle to the bottom and be removed. The sludge is sent to dewatering and further treatment (Tchobanoglous et al. 2014).

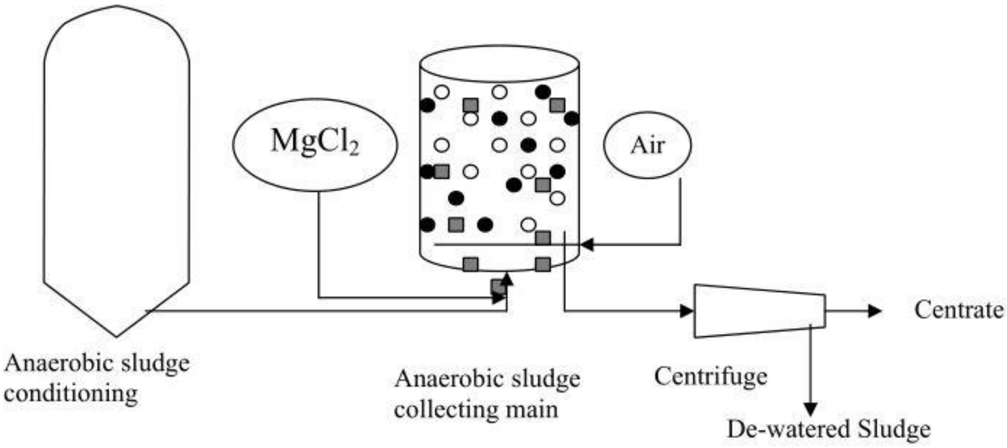

Figure 13 - General schematic diagram of AirPrex process (Heinzmann et al. 2003)

FIX-Phos

Another process recovers phosphorus from sludge by adding calcium silicate hydrate (CSH) to the waste activated sludge before the anaerobic digester. The CSH used in the process is a waste product from the construction industry. The CSH particles are able to induce crystallization of calcium phosphates without any need for pH adjustment in the anaerobic digester. The calcium phosphates are then separated from the digested sludge (Figure 14).

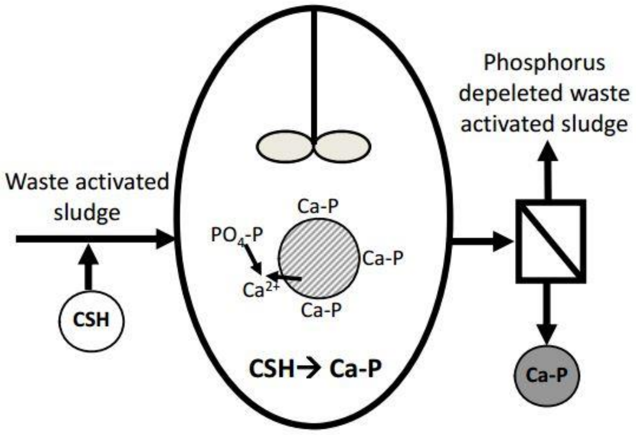

Figure 14 - General schematic diagram of FIX-Phos process (Petzet et al. 2013)

3.3.3 Wet chemical technology (Recovery from sludge and sewage sludge ash)

Wet chemical technologies are defined as technologies that apply a strong acid/base to release the phosphorus that is bound in sludge (digested or dewatered sludge) or sewage sludge ash. The phosphorus can also be released by heating the sludge, applying pressure and a combination of these. When dosing acids, typically sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) is used. When the phosphorus is dissolved by using chemicals, heavy metals are dissolved as well, and needs to be removed from the water before phosphorus can be recovered. After metals are removed, the phosphorus can be recovered in different ways (ion exchange, crystallization, nanofiltration, etc.), however it is typically combined with crystallization of struvite or calcium phosphates (Cornel et al. 2009). It has yet to be found that ion exchange or nanofiltration is an economically or technically feasible solution for the recovery of phosphorus in wet chemical technologies (Petzet et al. 2012b). The general principles of wet chemical technologies are depicted in Figure 15.

Due to the high amount of chemicals and processing steps that are needed by wet chemical technologies, they are considered significantly more complex than the crystallization technologies.

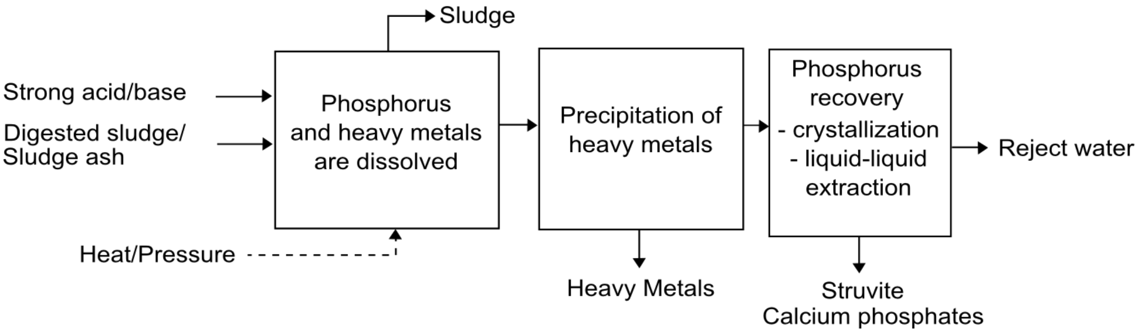

Figure 15 - Principle of wet chemical technologies (Adapted from Cornel et al. (2009)).

Alkaline or acidic treatment?

Whether the raw material should be treated by dosing acids or base depends on the characteristics of the raw material, such as calcium and aluminium content. High amounts of calcium in the sludge reduces the efficiency significantly of alkaline treatment (Petzet et al. 2012b).

When using sewage sludge ash as raw material, Stark et al. (2006) demonstrated that using a strong acid, instead of strong base, results in a higher release of phosphorus. For acidic treatment, the pH needs to be < 2 to ensure a high dissolution of the phosphorus from the raw material. Normally sewage sludge ashes contains phosphates in the form of calcium, aluminium and iron phosphates, and especially calcium and aluminium phosphates will dissolve under acidic treatment (Petzet et al. 2012b).

Alkaline treatment

With alkaline treatment (dosing NaOH), a low amount of heavy metals is dissolved and the phosphorus can be recovered as calcium phosphates ($pH > 13$) with a high purity. Iron is dissolved in small quantities as well, and about 60-70% of phosphorus can be dissolved (Petzet et al. 2013). When the sludge ash contains a low amount of calcium, it is possible to use alkaline treatment to dissolve high amounts of phosphorus. High amounts of calcium phosphates in the raw material makes alkaline treatment unfavorable.

When using aluminium rich sludge ash, Petzet et al. (2012b) found that alkaline treatment with acidic pre-treatment increased the phosphorus recovery, compared to only acidic or alkaline treatment. This result was because calcium phosphates in the sludge (which is alkaline-insoluble) was converted to aluminium phosphate. Aluminium phosphate can be easily dissolved with alkaline treatment, and the phosphorus can be subsequently precipitated as calcium phosphates with the addition of $CaCl_2$ or $Ca(OH)_2$.

When raw material contains a low amount of calcium, it is possible to treat the sludge ashes directly with alkaline treatment. In Japan, recovery of 75% of total phosphorus in a wet chemical plan was achieved with direct alkaline treatment. The sludge was low in calcium content and high in aluminium (Petzet et al. 2012b).

Metal removal
The heavy metals can be precipitated as metal sulfides by using sodium sulfide (Na_2S) or by using biogas from digester containing H_2S (Muller et al. 2007).

3.3.4 Thermochemical technologies (Recovery from sewage sludge ash)

The thermochemical technologies are based on treating the sewage sludge ashes that come from incineration of the sludge. The main objective of the treatment is to remove heavy metals and increase the bioavailability of the sludge.

A major advantage with this method is that most types of sewage sludge ashes can be treated, and therefore is less dependent on the characteristics of the sewage sludge ash compared with wet chemical technologies (Petzet et al. 2013). It is also a favorable method if chemical phosphorus removal is used in the WWTP.

The main thermochemical technology were developed in an EU project called SUSAN (Sustainable and safe re-use of municipal sewage sludge for nutrient recovery), and the basic principle is demonstrated by Figure 16. The ashes are fed into a furnace together with chlorine compounds, such as magnesium chloride or calcium chloride. It has been found that magnesium chloride showed the best performance, with respect to bioavailability of the phosphorus (Adam 2008).

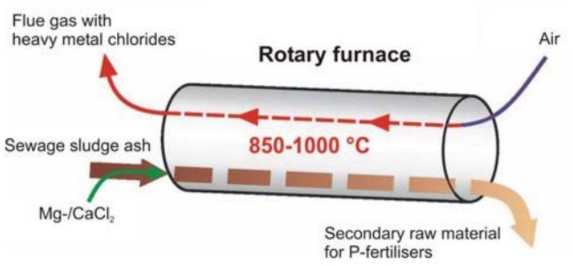

Figure 16 - Principle of thermochemical phosphorus recovery (Adam 2008).

Under high temperatures (850-1000 ^{o}C), the chlorides will react with the heavy metals, and form heavy metal chlorides, and these will vaporize and thereby the heavy metals are removed (Figure 17). The removal rates of cadmium, lead and copper were found to be over 90%. Also, the bioavailability of phosphorus increased significantly under thermochemical treatment. This was due to chemical transformations of the phosphorus during the treatment, from mainly aluminum and calcium phosphates to more bioavailable phosphates such as magnesium phosphates and new types of calcium phosphates (Adam et al. 2009). It was found through greenhouse pot experiments and field trails that sewage sludge ash treated with thermochemical technology was an excellent fertilizer and was comparable to commercial fertilizers (Adam 2008).

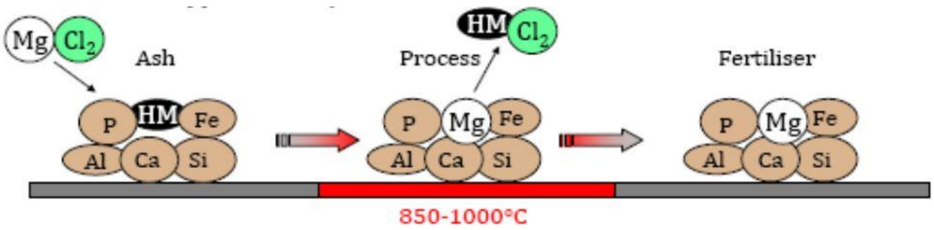

Figure 17 - Magnesium chloride reaction with heavy metals under thermochemical treatment (Hermann 2009a)

4 Case studies of Phosphorus Recovery Technologies

In the following section, 3 short case studies of successful phosphorus recovery technologies will be presented.

4.1 Crystallization and precipitation

4.1.1 Ostara Pearl Reactor

Country: Canada
Input source: Wastewater, phosphorus rich
Process description: Crystallization of struvite in fluidized bed reactor with addition of $MgCl_2$
Phosphorus recovery rate: 80-90 % from influent to crystallization reactor.
Product: Slow release fertilizer in form of struvite, marketed as Crystal Green
Stage: Industrial scale

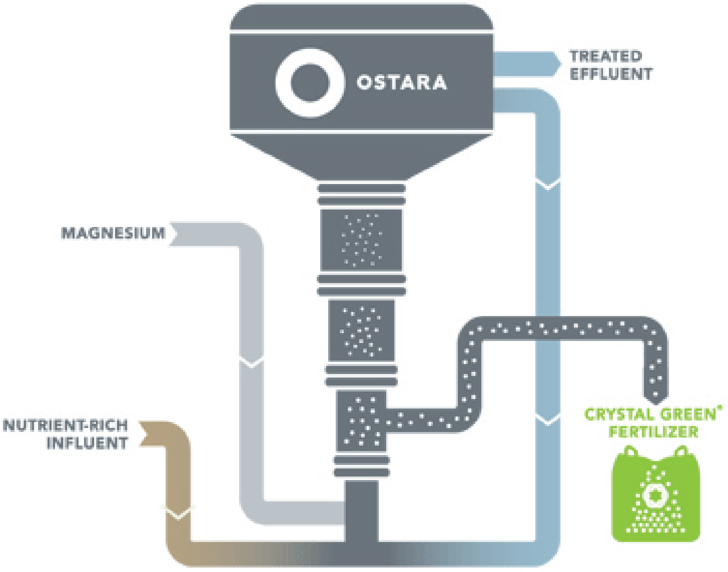

Figure 18 - Illustration of the Ostara Pearl Reactor (Ostara 2013)

One of the most successful companies in terms of commercialization of phosphorus recovery from WWTPs can be said to be Ostara (Canada). Ostara have won numerous awards in the last years and have successfully been able to sell their recovered struvite as Crystal Green. The company was founded in 2005 in Vancouver, Canada and the technology was developed at University of British Columbia.

The process is based on crystallization of struvite in a fluidized bed reactor. The influent is normally taken from the dewatering side stream. Magnesium is added by $MgCl_2$ and pH is adjusted if necessary with NaOH. The process is installed in full scale at various locations in North America and Europe (Portland, Edmonton, Saskatoon, London and more) (Ostara 2013).

According to the firm the cost savings from reduced uncontrolled struvite precipitation, reduced phosphorus load on the plant, and revenue from fertilizer sale may payback the investment costs in 3-5 years (Schröder et al. 2010).

4.1.2 Unitika Phosnix

Country: Japan
Input source: Wastewater, phosphorus rich side stream
Process description: Crystallization of struvite in air agitated reactor with addition of $Mg(OH)_2$ and recycling of struvite crystals for enhanced crystal growth.
Phosphorus recovery rate: 80-90 % from influent to crystallization reactor
Product: Slow release fertilizer in the form of struvite
Stage: Industrial scale

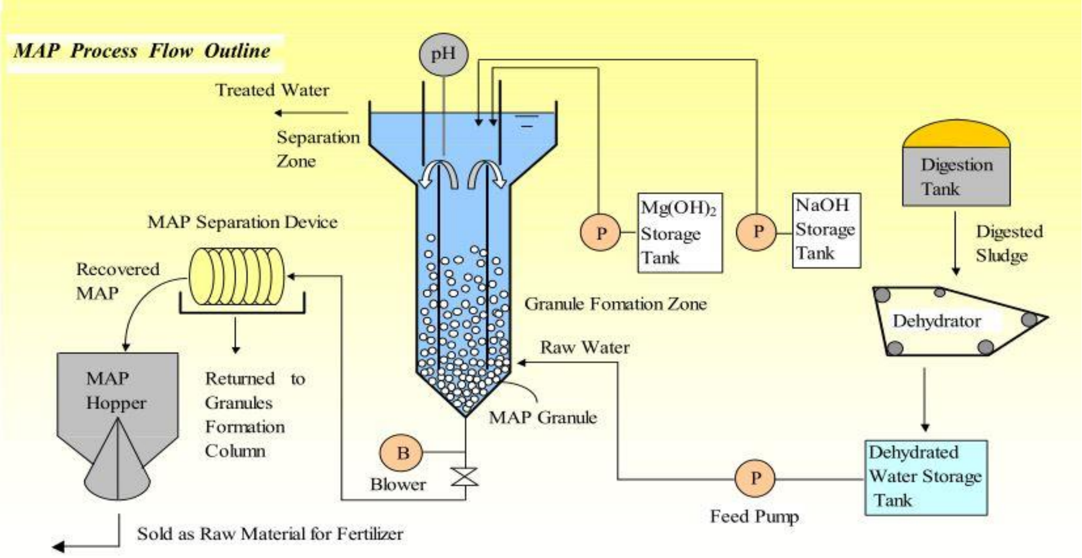

Figure 19 - Schematic diagram of the Phosnix process (Nawa 2009)

The Phosnix process from Japan has many similarities with the Ostara Pearl Reactor process. Their first full scale plant was completed in 1998. Normally, side stream from dewatering is used. However, any phosphorus rich side stream can be used. It uses $Mg(OH)_2$ for a magnesium source and NaOH for pH adjustment. Struvite pellets with 0.5 – 1 mm diameter is produced after a retention time of 10 days. For improving crystallization of struvite, small struvite crystals are recycled back to the reactor and acts as a seeding material. The reactor is operated with a pH ranging from 8.2 – 8.8 (Ueno et al. 2001).

4.2 Thermo-chemical methods

4.2.1 Outotec/ASH DEC process

Country: Austria/Germany/Finland
Input source: Sewage Sludge Ash
Process description: Thermochemical treatment (reduction of heavy metals and improved bioavailability of phosphorus). $CaCl_2$ or $MgCl_2$ are used for removal of heavy metals.
Phosphorus recovery rate: > 90% of the phosphorus inflow to the WWTP
Product: Sewage sludge ash
Stage: Pilot Scale

The ASH DEC process is a thermochemical treatment that was developed as a part of the EU research project SUSAN. The principles of the technology are discussed in Section 3.3.4. A Austrian company was created called ASH DEC, however the technology and company was recently bought by the Finnish company Outotec (Outotec 2011).

A pilot plant was constructed in Leoben, Austria in 2008, treating 7 tons of sewage sludge ashes per day. After the ashes were treated thermochemically, they were mixed with other nutrients (NH_4NO_3, K_2SO_4, KCl) to create multi nutrient fertilizers with nitrogen, phosphorus and potassium. These fertilizers were found to be comparable to commercial fertilizers (Adam 2008).

The main advantages of this technology is that is has the highest possible phosphorus recovery rate (> 90% of incoming phosphorus in WWTP) and it doesn’t require any changes to the existing wastewater and sludge management infrastructure (Hermann 2009a).

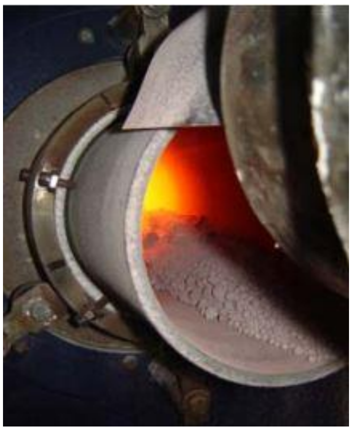

Figure 20 - Operation of the medium-scale rotary furnace (Adam 2008)

5 Economics of phosphorus recovery

Through the development of various technologies, the technological feasibility of recovering phosphorus from municipal wastewater has been demonstrated. Then likely the most important question for wide implementation of phosphorus recovery: Is phosphorus recovery feasible from an economic perspective?

For a complete evaluation of a phosphorus recovery technology, the economics of the process should be thoroughly discussed and evaluated. However, many technologies have not reached industrial scale and the recovered products have yet to be fully accepted by the agriculture organizations and government. Therefore it is difficult to predict the cost of operations of such a technology. It is beyond the scope of this project to go into an in depth discussion of the economics of phosphorus recovery, however some basic considerations are presented here.

The cost of various phosphorus recovery technologies based on lab-scale and pilot-scale projects were presented by the German Water Association (Petzet et al. 2013), and are presented in Table 6. These costs do not take into account savings in the operational costs in the WWTP or sludge handling, or revenues from fertilizer sale as they are often highly specific.

Table 6 - Cost of phosphorus recovery (Petzet et al. 2013)

Source	Cost [€ / kg P]
Liquid phase	9 - 15
Sewage sludge	2 – 25
Sewage sludge ash	2.6 – 7.5

The great variation in cost of recovery from sewage sludge is caused by high cost from wet chemical treatment (high chemical costs) and low costs by FIX-Phos process (Section 3.3.2).

The price of phosphate rock has had a great variation between 1 and 3 €/kg P during the last 5 years (Dockhorn 2009). Currently the phosphate rock price is ca. 1 € / kg P and thus phosphorus recovery technologies cannot compete with phosphate rock as a source for phosphorus (Petzet et al. 2013). However, if operational savings is taken into account and if the phosphate rock prices rises to previous levels, many technologies can be economical.

6 Conclusion

The need for phosphorus recycling in WWTPs has received an immense attention the last decade as phosphate rock prices have risen and the direct application of sewage sludge to agriculture has been difficult due to high pollution levels (heavy metals and organic pollutants). Also an increased focus on a sustainable society has put more pressure on looking for alternatives to the use of phosphate rock for fertilizer production. Centralized municipal WWTPs represent a great phosphorus source, and even though it cannot cover the increase in phosphorus demand, it plays a key role for sustainable use of phosphorus.

Phosphorus recycling technologies have been developed during the last decade and different approaches have been taken. They have primarily used three different sources: liquid phase, sewage sludge and sewage sludge ashes. Recovering phosphorus from sewage sludge and sewage sludge ashes represents the greatest recovery potential as all the phosphorus that is removed from the WWTP is incorporated in the sludge and ashes. At the best, 90% of the incoming phosphorus to the WWTP can be recovered from sludge or ashes, while at optimal performance about 50% of the incoming phosphorus to the WWTP can be recovered with only crystallization technologies.

The recovery of phosphorus is dependent on the method of phosphorus removal, and chemical and biological phosphorus removal have been briefly been reviewed. Chemical phosphorus removal tend to decrease the bioavailability of the phosphorus in the sludge and the phosphorus needs to either be redissolved with wet chemical technologies or treated with thermochemical technology which increases the bioavailability. Most crystallization technologies require that EBPR is used to remove the phosphorus.

Struvite crystallization has been successfully commercialized by different companies and especially Ostara is expanding rapidly. Struvite crystallization adds additional benefits to the WWTP as it prevents operational problems related to unfavorable deposition of struvite, increases the dewaterability of the sludge and lower the phosphorus load on the WWTP. The final product has also been demonstrated as an excellent slow-release fertilizer.

Crystallization of calcium phosphates are likely to be unfavorable method for recovery of phosphorus for municipal wastewater as it requires high chemical costs due to reaction with alkalinity. However, different seeding materials have tried to remedy this costly pre-treatment.

Thermochemical treatment of sewage sludge ash seems particularly favorable as it is able to treat a wide range of input sources, avoid the high chemical costs associated with wet chemical technologies and have a high recovery rate of phosphorus. The treatment can also be performed with low cost compared to other technologies and if incineration is already a part of the existing sludge handling infrastructure, no big changes is needed in the existing sludge handling infrastructure. However, the sewage sludge ashes have to be mono-incinerated and if incineration is not already a part of the sludge handling infrastructure, this process requires considerable investment costs. Thermochemical treatment has yet to be implemented on a full scale.

Economics of the processes have not been the aim of this project. However, basic economic considerations show that phosphorus recovery from municipal wastewater is feasible if savings in operational costs are taken into account. It will also likely be more favorable in the future as the phosphate rock price is expected to increase, and as the technologies will be optimized in terms of cost-efficiency.

It also important to emphasize once again that sustainable use of phosphorus cannot be achieved by phosphorus recycling from WWTPs alone, but can be achieved by taking a holistic perspective on the whole phosphorus cycle and improve among other aspects, agriculture and mining efficiency.

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