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PHOSPHORUS RECOVERY AND RECYCLING FROM MUNICIPAL WASTEWATER SLUDGE

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Instructor: M.Sc. (Tech.) Pirjo Rantanen

ABSTRACT OF THE MASTER'S THESIS

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The past decades have witnessed a rising awareness of the finite phosphorus resources and the importance of phosphorus recovery. The world phosphorus resources are estimated to deplete in 60 to 240 years and the world phosphorus production to peak in 2033, creating a need to discover alternative materials to replace phosphate ore. Municipal wastewater sludge is a phosphorus source worth considering, since modern technologies can transfer over 90% of the phosphorus from the wastewater to the sludge fraction.

The aim of this thesis is to discuss and overview the current methods for phosphorus recovery from municipal wastewater sludge, ash from sludge incineration, and the liquid phase after anaerobic treatment containing phosphorus in soluble form. The methods for recovery include crystallization and precipitation, wet chemical methods, and thermo-chemical methods. The crystallization and precipitation methods convert phosphorus into solid form with a chemical dosage and pH adjustment. The wet chemical methods recover the phosphorus bound in sludge or ash by leaching it with acid or base, and recovering the resulting dissolved phosphorus with various methods, the most common being the precipitation. The ash fraction after incineration can be treated with thermo-chemical methods by adding chloride chemical and bringing the ash to temperature higher than the boiling point of the resulted heavy metal chlorides, leading to their evaporation.

This study surveys processes based on these methods, both the operational full-scale applications and the pilot-scale and laboratory-scale processes. Most of the operational processes are based on crystallization or precipitation. Precipitation is a widely studied method that has proved to be economical compared to the wet chemical methods. The wet chemical methods require chemicals and offer limited amount of experiences from full-scale. Thermo-chemical methods do not yet have full-scale implementations.

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Viime vuosikymmeninä on alettu kiinnittää entistä enemmän huomiota maailman fosforivarojen riittävyyteen ja fosforin kierrätykseen. Arviot taloudellisesti hyödynnettävien fosforiesiintymien riittävyydestä vaihtelevat 60 ja 240 vuoden välillä ja maailman fosforin tuotannon arvioidaan saavuttavan huippunsa vuonna 2033. Tämän jälkeen fosforin tuotannossa on siirryttävä hyödyntämään vaikeammin saavutettavissa olevia ja heikkolaatuisempia malmivaroja. Vaikean saavutettavuuden vuoksi tuotanto hidastuu, ja heikompi laatu hankaloittaa malmin prosessointia. Tuotannon epävarmuus saattaa aiheuttaa nopeitakin heilahteluita fosforin hinnassa. Hupenevia fosforivaroja korvaamaan tarvitaan tulevaisuudessa vaihtoehtoisia fosforinlähteitä. Harkitsemisen arvoinen vaihtoehto on jäteveden puhdistusprosesseissa syntyvä liete, johon prosessin tehokkuudesta riippuen voi päätyä yli 90 % puhdistamolle tulevan jäteveden fosforista.

Tämän diplomityön tarkoituksena on tarkastella menetelmiä, jotka on kehitetty fosforin talteenottoon yhdyskuntien jätevesilietteestä, lietteen polton seurauksena syntyvästä tuhkasta sekä nestefaasista, johon fosfori on anaerobisessa käsittelyssä vapautunut. Talteenotto nestefaasista tapahtuu saostus- ja kiteytysmenetelmillä, joissa kemikaaliannostuksen ja pH:n säädön seurauksena liukoinen fosfori saostuu. Tuhkaan ja lietteeseen sitoutuneen fosforin talteenottamiseksi fosfori liuotetaan happo- tai emäskäsittelyllä. Liuenneen fosforin erottamiseen voidaan käyttää esimerkiksi saostusta, ioninvaihtohartseja tai nanosuodatusta. Tuhkan käsittelyyn voidaan soveltaa myös termokemiallisia menetelmiä, joissa tuhkaan lisätään klooriyhdisteitä ja seos kuumennetaan yli raskasmetallikloridien kiehumispisteen, jolloin syntyneet yhdisteet poistuvat kaasuna.

Työssä tarkastellaan menetelmiin perustuvia prosesseja: sekä toiminnassa olevia täyden mittakaavan laitoksia että kokeilu- tai laboratoriomittakaavassa olevia prosesseja. Suurin osa täyden mittakaavan sovelluksista perustuu kiteytykseen tai saostukseen. Näitä menetelmiä on kehitetty ja tutkittu eniten ja ne ovat taloudellisempia kuin märkäkemialliset menetelmät, jotka vaativat runsaasti kemikaaleja. Märkäkemiallisiin menetelmiin perustuvista täyden mittakaavan laitoksista on rajallisesti käyttökokemuksia. Termokemiallisia menetelmiä ei ole vielä toteutettu täydessä mittakaavassa.

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LIST OF TERMS AND ABBREVIATIONS

AF-BNR-SCP	Anaerobic Fermentation Biological Nutrient Removal Struvite Crystallization Process, a phosphorus recovery process
Aqua Reci	Phosphorus recovery process
ASH DEC	Phosphorus recovery process
B.V.	Limited liability company, Ltd.(Dutch)
BAM	The Federal Institute for Materials Research and Testing, Germany
BioCon	Phosphorus recovery process
BMBF	Bundesministerium für Bildung und Forschung, The German Federal Ministry of Education and Research
BMU	Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit, German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety
bsCOD	Dissolved organic matter
BWB	Berliner Wasserbetriebe
BOOM	Besluit Overige Organische Meststoffen, Other organic fertilizers decision
CSH	Calcium Silicate Hydrate
CSIR	Council for Scientific and Industrial Research
DAP	Diammonium Phosphate
DS	Dry solids
DüMV	Düngemittelverordnung, German fertilizer ordinance
EDX	Energy Dispersive X-Ray fluorescence
EPA	Environmental Protection Agency
EU-15	Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, the Netherlands, Portugal, Spain, Sweden, and the United Kingdom
EU-25	EU-15 and Cyprus, Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Slovakia, and Slovenia
EU-27	EU-25 and Bulgaria and Romania
GmbH	Limited liability company, Ltd. (German)
HAP	Hydroxyapatite

HRT	Hydraulic Retention Time
IAP	Institute of Applied Polymer science
ISA	Institute for Environmental Engineering of Aachen University
ITC-WGT	The Institute of Technical Chemistry – Water and Geotechnology Division
Kurita	Phosphorus recovery process
Ksp	Solubility product
MAP	Magnesium Ammonium Phosphate
p.e.	Population Equivalent
PAO	Phosphorus accumulating bacteria
PASH	Phosphorus recovery from Ash
PHB	Polyhydroxybutyrate
PRISA	Phosphorus Recovery by ISA
P-RoC	Phosphorus Recovery from wastewater by Crystallization of calcium phosphate compounds
Rem Nut	Removal of Nutrients. A phosphorus recovery process
RoHM	Removal of Heavy Metals
RTWH	Technical University of Aachen
SCWO	Supercritical Water Oxidation
SEM	Scanning Electron Microscopy
SEPHOS	Sequential Precipitation of Phosphorus
SNB	Slibverwerking Noord-Brabant
SSR	Supersaturation ratio
SUSAN	Sustainable and Safe re-use of Municipal Sewage Sludge for Nutrient Recovery
VFA	Volatile Fatty Acids
WAS	Waste Activated Sludge
WWTP	Wastewater Treatment Plant

1 INTRODUCTION

The past decades have witnessed a rising awareness of the finite phosphorus resources and the importance of phosphorus recovery. Phosphorus is a limiting factor in plant growth, making it an important part of fertilizers. Fertilizer industry processes the major part of the mined phosphate rock. In the US, the share is over 95% (U.S. Geological Survey 2010). Fertilizers are crucial for the modern efficient plant production and their lack can result in large crop failure.

The estimates of the phosphorus resources sufficiency vary between 60 to 240 years (Cornel and Schaum 2009) denoting that scarce phosphorus resources do not pose a short-term threat. However, the year 2008 saw a quick rise in the world market value of phosphorus resulting from the increased agricultural demand and tightened supplies (U.S. Geological Survey 2010), showing that temporary supply shortages can occur at any time. The depletion of good quality phosphate rock will conclude in uncertainty in the markets and rising costs in fertilizer production. Moreover, phosphorus cannot be synthetically produced, creating a need to discover substitutive sources for the phosphate rock.

One possible source of recycling phosphorus is municipal wastewater sludge. The past decades' problems with eutrophication in the surface waters have resulted in the present-day strict limit values for the effluent from sewage treatment plant. A modern wastewater treatment process removes phosphorus from sewage using an activated sludge process or a chemical precipitation process, transferring over 90% of the incoming phosphorus to the sludge fraction (Cornel and Schaum 2009).

A number of methods has been developed to recover phosphorus from the sludge and to convert it to a reusable form. Most implementation cases in full-scale are based on the largely researched technologies: the crystallization or precipitation of phosphorus as calcium phosphate (Giesen and van der Molen 1996, Berg *et al.* 2006a) or struvite (Ueno and Fuji 2001, Ostara 2010, Lengemann 2010a). However, these technologies can only reach the recovery efficiency of 50 to 60% of total phosphorus (Montag 2008) and are often implemented as a solution for the problems caused by the spontaneous precipitation of struvite.

Methods with higher recovery potential are typically wet-chemical. These methods aim at maximum phosphorus recovery, requiring a chemical consuming, thus expensive, leaching step with acid or base (Stark *et al.* 2006). The only full-scale application found in this study, the Seaborne process (Vesterager 2009), is currently neither feasible nor fully operational (Bayerle 2010).

Contributions to recover phosphorus from incinerated sewage sludge ash have lead to the development of the ASH DEC process (Boutoussov 2009), studied in the EU Project SUSAN (Sustainable and safe re-use of municipal sewage sludge for nutrient recovery) (2008). Incinerated ash can also be used as secondary material in phosphate industry (Schipper *et al.* 2001).

Although several researchers (Morse *et al.* 1997, Stratful *et al.* 1999, Cornel and Schaum 2009) have reviewed the existing technologies, these studies provide little information of the technical details and the problems occurring in the processes. The aim of this study was to gather more detailed information for assess the feasibility of future research projects. Information was assembled from literature, patents, and excursions to operational plants selected as the most representative in March 2010. The visited plants included two municipal WWTPs in Germany: Berlin and Gifhorn; and two other plants in the Netherlands: the sludge incineration plant Slibverwerking Noord-Brabant in Moerdijk and the chemical company Thermphos International B.V. in Vlissingen. The WWTP in Berlin has a recently started facility for struvite precipitation, and the only full-scale wet chemical process found within the limits of this study is located in Gifhorn. The Dutch plants show an interesting co-operation recycling the ash as secondary raw material in phosphorus chemicals producing process.

This thesis is structured as follows. Chapter 2 provides general information about phosphorus and phosphate rock, including the applications and processing of the ore to usable form. Chapter 3 discusses phosphorus flow in wastewater treatment process, chemical and biological phosphorus removal processes, means for sludge treatment, and phosphorus recycling. Chapter 4 introduces the locations, material flows, final products, and methods for phosphorus recovery. Chapters 5 and 6 describe the processes utilizing these methods and finally, Chapter 7 deals with the potentials and costs of phosphorus recovery.

2 PHOSPHORUS

2.1 Natural phosphorus cycle

Phosphorus is the eleventh abundant element in the Earth’s crust and an essential element in DNA, RNA lipids, proteins, enzymes, energy carrier ATP, as well as an important factor in development of teeth and bones. Phosphorus has no gaseous form in the nature but in water environment it occurs in small amounts limiting the metabolic activity. In water environment, other nutrients and energy, needed for the growth of biomass, are plentiful, therefore an increased level of limiting phosphorus can lead to eutrophication (Vesilind 1998). The past decades’ problems with eutrophication in the surface waters have resulted in the present-day strict limit values for the effluent from wastewater treatment plants (WWTPs). As a result, a major share of the incoming phosphorus is transferred into the sludge phase. Previously, organic waste was used in agriculture as a part of the natural phosphorus cycle presented in Figure 1. Increasingly stringent legislation and limitations in agricultural use led to decreased recycling of the nutrients bound in the sludge (Cornel and Schaum 2009).

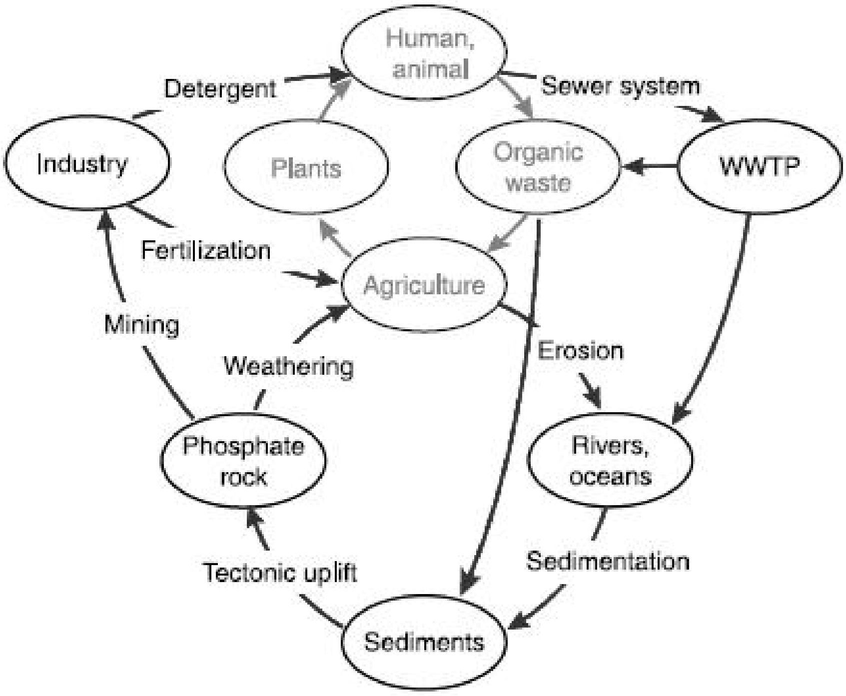

Figure 1: Inorganic and organic phosphorus cycle on land with human impact (Cornel and Schaum 2009).

Phosphorus has an inorganic geological cycle and two organic cycles occurring on land and in water. The geological cycle lasts several million years. It starts from the soil erosion transferring phosphorus to sea bottom. The phosphorus containing material sedimentates, finally slowly rising back to the upper soil by tectonic uplift. The organic cycle on land, starts from the plant uptake. The plants are utilized by humans and animals that later produce organic waste. The phosphorus in the organic waste can be used in agriculture or, as can be seen in Figure 1, join the geological cycle.

In Finland, the main source of phosphorus emissions to water environment from human actions is agriculture. In 2008 (Figure 2), about 67% (2600 t/a) of the whole phosphorus load to water environment (4105 t/a) originated from agriculture, while the fraction of municipal wastewater was only 4.8% (197 t/a). However, according to HELCOM (2009), emissions from municipal WWTPs to the Baltic Sea constituted 50% of total phosphorus load (37 000 t) in the whole catchment area.

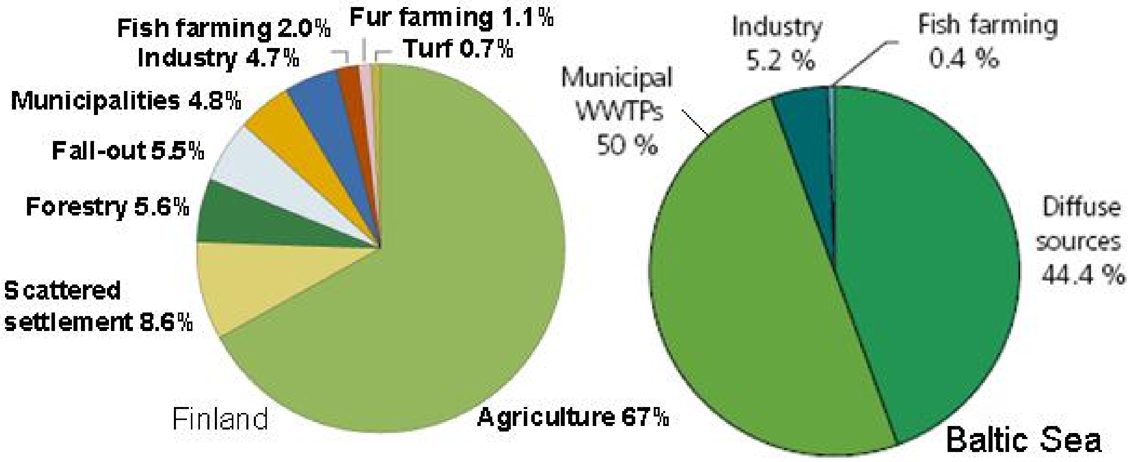

Figure 2: Total phosphorus by source into surface waters in Finland in 2008 (SYKE 2009) and within the catchment area of the Baltic Sea in 2000 (HELCOM 2009).

As Finland produces 10% of the phosphorus emissions to Baltic Sea, that is 3700 t/a, (HELCOM 2009) the phosphorus flow from Finnish WWTPs is considerable smaller compared to other countries in Baltic Sea area. The difference may be due to the untreated wastewater emissions to the sea from several countries.

2.2 World phosphate rock resources

The most important phosphate mineral, referred to as phosphate rock, is $Ca_5(PO_4)_3(F,Cl,OH)$ (Salminen 2006). It has three forms of calcium phosphate depending on the element of greatest share: hydroxyapatite, fluor apatite, and chloroapatite (Laitinen and Toivonen 1982). In addition to apatite, phosphate rock contains impurities such as arsenic, humic substances, and heavy metals, especially cadmium, uranium and zinc. Typically, phosphate rock contains 30 - 40% P_2O_5 (Schipper *et al.* 2001). The phosphorus content of ore or fertilizer is often expressed as oxide form due to earlier means to determine phosphorus content with gravimetric methods giving the result as %P_2O_5 (Lippert 2010). The amount of the element phosphorus in P_2O_5 is 43.6% by weight.

The largest reserves of phosphate rock occur in USA, China, and Morocco. In addition, large deposits have been detected in the continental shelves in the Atlantic Ocean and the Pacific Ocean. Recovering these deposits, however, is expensive. As for alternative sources, the phosphorus deposits on the ocean floor are considered when a profitable method of deep ocean mining is developed (U.S. Geological Survey 2010).

Figure 3 presents the consumption and supply of mined phosphate rock in the world. As can be noticed, USA is self-sufficient, although some amount of phosphorus is imported from Morocco (U.S. Geological Survey 2010). In Africa and the Middle East, production exceeds the consumption. The balance renders Africa, especially North Africa, the most important exporter in the world. In Asia, although the production level is high, the exceeding consumption leads to a need to import. Phosphorus resources of Europe are small, the Western Europe having no production, and the Eastern Europe producing just enough phosphorus for their own needs. The highest content of phosphorus rock in Eastern Europe occurs in Finland: Siilinjärvi mine produces apatite 850 000 t/a with phosphorus concentration as high as 36% P_2O_5 (Ylinen 2009).

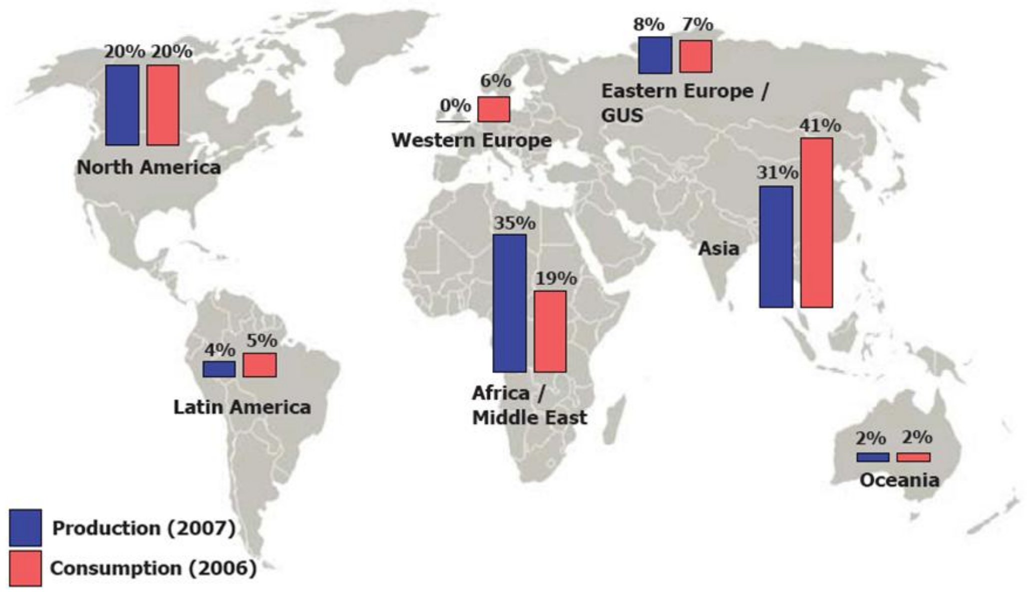

Figure 3: The World phosphorus production (Adam 2009).

In 2008, the price of the phosphate rock rose quickly worldwide (Figure 4), due to the increased agricultural demand and the tightened supplies of the phosphate rock. The price in the United States doubled, and the average spot price in exporting areas, such as North Africa, approached 400 €/t, which is five-fold compared to the average price in 2007 (U.S. Geological survey 2009). At the same time, the prices for other nutrients including potash, nitrogen and sulfur increased affecting the prices of the fertilizers even more. The prices have fallen since 2008, but the crisis showed, that temporary supply shortages and rising costs in fertilizer production can occur at any time, and the extinction of good quality phosphate rock will result in uncertainty in the markets.

Figure 4: Price development of phosphate rock in the U.S. (USD/t) (Mongabay 2010).

According to the U.S. Geological survey, the phosphorus mine production in the world has risen every year (Table 1). Due to the crisis in 2008 that decreased the production in the US, the production estimate for 2009 is a little lower than for 2008.

Table 1: Phosphorus production in the world (U.S. Geological survey 2009 and 2010).

	2006	2007	2008	2009 estimate
Mine production (Mt)	142	156	161	158

The estimates of the phosphorus resources sufficiency vary between 60 and 240 years (Cornel and Schaum 2009), the most common estimate being 100 years (Driver 1999, Balmér 2004). Another way to express the resources is the peak phosphorus indicating the time, when easily accessible high quality phosphate rock resources deplete. Thus, the production starts to diminish and the consumption will overrun the supply. Figure 5 shows that the estimated time for peak phosphorus is around 2033 (Cordel *et al.* 2009).

U.S. Geological survey (2010) estimates the economically feasible resources 16 000 Mt. The reserve base is 47 000 Mt, containing the reserves with specified minimum physical and chemical criteria related to current mining and production practices (U.S. Geological Survey 2009).

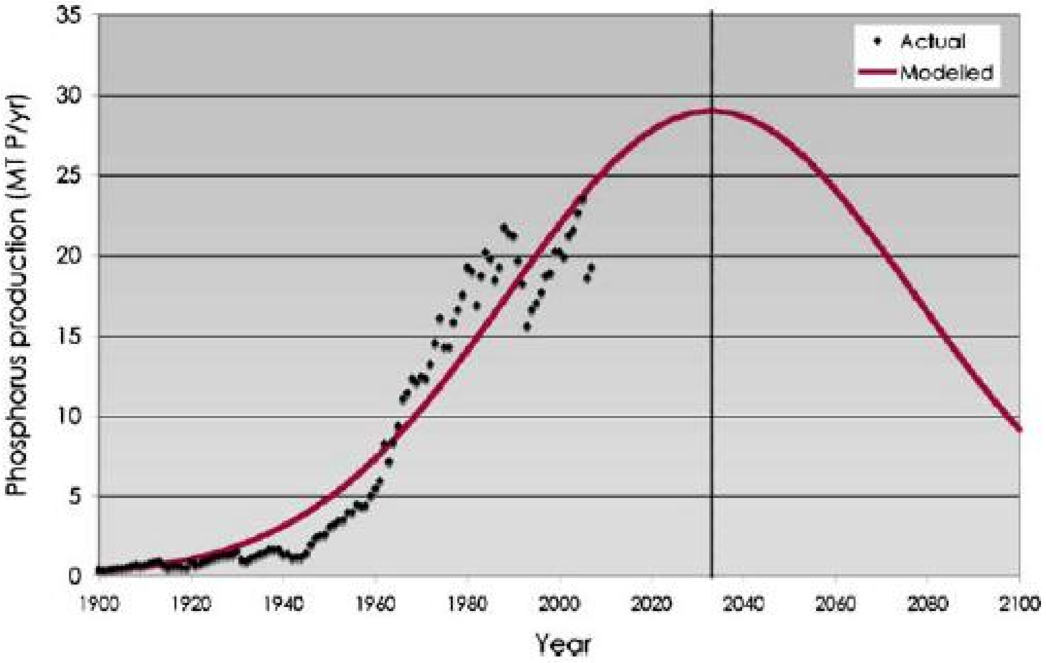

Figure 5: Peak phosphorus (Cordell *et al.* 2009).

2.3 Basic chemistry

Phosphorus has the atomic number 15, atomic mass 30.974 g/mol, and one naturally occurring isotope (^{31}P). The main oxidation states are -III, +III, and +V.

Phosphorus has three allotropes: white, red and black phosphorus. The most common form is white phosphorus, or tetraphosphorus P_4, also known as yellow phosphorus. Tetraphosphorus has an atomic mass of 30.97 g/mol, melting point at 44 ^{o}C, boiling point at 280 ^{o}C, and density 1.82 g/cm^3 (Laitinen and Toivonen 1982). Tetraphosphorus is highly poisonous, white, and waxy-looking. The main use is as starting point in production of other phosphorus chemicals. Having a strained bond structure it is extremely reactive. On skin contact, it causes serious burns, which is why it is used in military industry (Rayner-Canham and Overton 2006).

Other two allotropes are red and black phosphorus. Red phosphorus is not very reactive and is used in matches. White phosphorus transforms to red phosphorus in room temperature, or by heating it in airless conditions to 400 ^{o}C. The third allotrope, black phosphorus, has no significant commercial uses (Laitinen and Toivonen 1982).

As P_4 is extremely reactive, it has to be stored underwater, because when exposed to air it burns to tetraphosphorus decaoxide as in the Equation 1.

$$P_4\,(s) + 5\,O_2\,(g) \rightarrow P_4O_{10}\,(s) \qquad (1)$$

During this reaction, electrons fall to the lowest energy state causing a visible light. This glow in the dark has given the element its name, the bringer of light. P_4O_{10} is used as dehydrating agent because it reacts with water, and after several steps transforms to phosphoric acid. Phosphorus has another oxide, tetraphosphorus hexaoxide, formed when white P burns in shortage of oxygen as in Equation 2 (Rayner-Canham and Overton 2006).

$$P_4\,(s) + 3\,O_2\,(g) \rightarrow P_4O_6\,(s) \qquad (2)$$

Phosphoric acid is colorless and transparent viscous liquid with density of 1.885 g/ml and melting point at 42 ^{o}C. Typically, it is used as 85% water solution (Laitinen and Toivonen 1982). Phosphorus acid decomposes in water as shown in Equations 3 - 5.

$H_3PO_4 + H_2O$ à $H_3O^+ + H_2PO_4^-$ pKa = 2.12 (3)

$H_2PO_4^- + H_2O$ à $H_3O^+ + HPO_4^{2-}$ pKa = 7.21 (4)

$HPO_4^{2-} + H_2O$ à $H_3O^+ + PO_4^{3-}$ pKa = 12.67 (5)

Phosphates occur in three different forms depending on the pH (Figure 6). Between pH 4 and pH 6, the most common form is dihydrogen phosphate $H_2PO_4^-$. In neutral pH area, hydrogen phosphate HPO_4^{2-} is the predominant form, and above pH 12.5, orthophosphorus PO_4^{3-} (Rayner-Canham and Overton 2006).

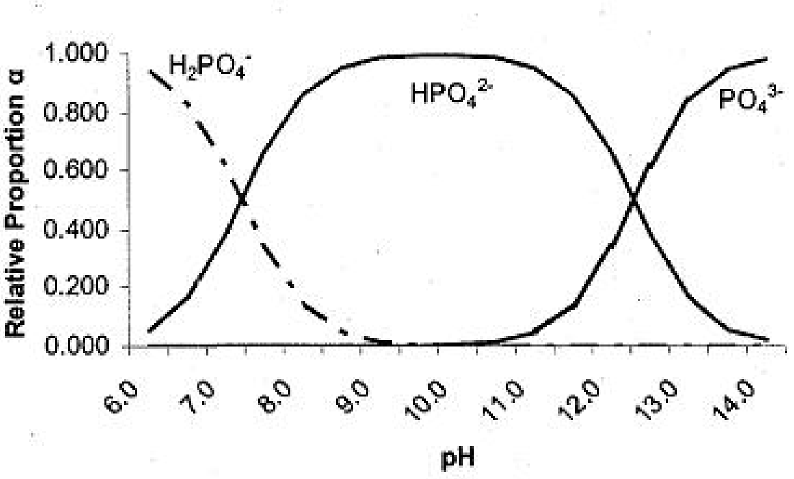

Figure 6. Relative proportions of orthophosphorus species (Lanning 2008).

Phosphates are, except for the monopositive alkali metals and ammonium phosphates, insoluble. Heavy metal phosphates are sparingly soluble. Water solutions of phosphates are alkaline as shown in Equation 6 (Laitinen and Toivonen 1982).

$PO_4^{3-} + H_2O \leftrightarrow HPO_4^{2-} + OH^-$ (6)

Typically, in natural environment, phosphorus occurs as the fully oxidized form orthophosphate PO_4^{3-}. Natural phosphorus levels in fresh water are low, 10 - 25 µg/l because Al, Fe, Mn and Ca bind PO_4–P by forming poorly soluble salts. Other forms of dissolved phosphate include inorganic polyphosphate and organic phosphorus compounds, mainly in complexes with organic acids (Salminen 2006).

2.4 Applications

2.4.1 FERTILIZERS

According to the U.S. Geological Survey (2010), the major part, about 80 to 90% of the mined phosphate rock is used in fertilizer industry. For example, the Unites States processed about 95% of all mined phosphate rock to phosphoric acid or superphosphoric acid. Both of the chemicals are needed in fertilizer production and in animal fodder supplements. About 45% of the phosphorus acid produced in the United States was exported as upgraded granular fertilizers MAP (magnesium ammonium phosphate) or DAP (diammomium phosphate).

Phosphorus together with nitrogen and potassium are the three primary nutrients. In addition, fertilizers can contain secondary nutrients (Ca, Mg, S) and micronutrients such as Mn, B, Zn, and Fe. Fertilizers need to have a suitable structure for easy apply to fields, nutrients in plant available form, and low concentrations of harmful substances (Ylinen 2009). The most beneficial fertilizer is DAP, containing both nitrogen and phosphorus in soluble form. Phosphorus solubility in citric acid is used as an indicator of bioavailability. Another indicator is the solubility in water. However, compounds with high water solubility can be easily washed away from soil to water system (SUSAN 2008). Another way to measure plant availability is the pot test, where certain plants are grown and fertilized in pots, and the phosphorus uptake is measured as mg/P/pot.

2.4.2 DETERGENTS

Phosphates are used in household cleaners for softening the water in order to enhance the washing process, for removal and prevention of encrustation on fibers, and as carriers of other detergent ingredients. Annually, the EU-25 countries, with total population of 456 million people, consume about 110 000 t of phosphorus as detergents. For comparison, the use of phosphates in fertilizers is equivalent to approximately 1.25 million t/a of phosphorus (EU Commission 2007).

The type of phosphate most commonly used in detergents is sodium tripolyphosphate (STPP). Concern over eutrophication has resulted in decreased use of phosphate containing detergents in many countries, and replacing phosphates with other chemicals.

The main alternative to STTP in laundry detergents is zeolite. However, dishwashing detergents are still mainly phosphate-based (EU Commission 2007).

2.4.3 OTHER

In addition to household cleaners, phosphorus compounds are used in other daily products such as toothpastes and shampoos. In food industry, they are part of baking powders, and are present in bottled soft drinks as phosphoric acid, preventing bacterial growth and buffering the pH. Metallic manganese, iron and zinc containers, especially those for food, are typically “phosphatised” to provide an inert and insoluble coating to prevent metal release to food and thus, metal poisonings (Rayner-Canham and Overton 2006).

Phosphate compounds (e.g. phosphoryl trichloride) are used in textiles and other flammable materials such as synthetic polymers, paints and protective coatings for wood. These materials are treated with phosphorus compounds to reduce the risk of fire. In electric devices, phosphorus oxychloride is used simultaneously as plasticizer and flame retardant to decrease the risks caused by the electricity and heat in the machines. High temperature lubricants contain phosphorus pentasulphide to reach a good lubrication, thermal stability and fire-resistant properties. Phosphoryl chloride can also be used in separation uranium and plutonium compounds (Rayner-Canham and Overton 2006).

In potable water treatment, phosphorus is used for iron, magnesium, and corrosion control, lead and copper removal, and scale inhibition. These ions occur in bivalent form in ground water and need to be removed for softening the water (Phosphate Forum of the Americas 2010).

2.5 Production

2.5.1 WET CHEMICAL PROCESS

As stated earlier in 2.4.1, most of the mined phosphate rock processed to phosphoric acid for fertilizer production. Typically, high quality phosphoric acid is not necessary in fertilizer industry. Thus, it can be produced straight from phosphate rock in wet chemical process that is more energy efficient than the electrochemical process producing elemental P_4.

In the wet process, phosphorus rock reacts with sulfuric acid producing phosphoric acid and calcium sulfate (Equation 7) (Schipper *et al.* 2001).

$$Ca_3(PO_4)_2\,(s) + 3\,H_2SO_4\,(aq) \rightarrow 3\,CaSO_4\,(s) + 2\,H_3PO_4\,(aq) \qquad (7)$$

Calcium sulfate is separated by filtration and can be used in building industry. However, a part of it must be landfilled since the demand of calcium sulfate is not high. Another waste stream occurs, as the acid is concentrated in the end of the process. Impurities precipitate and the resulting slime need to be disposed of in environmentally safe manner (Rayner-Canham and Overton 2006).

2.5.2 ELECTRO-THERMAL PROCESS

Electro-thermal process is a method for producing elemental phosphorus P_4 that can further be processed to high quality phosphoric acid or other phosphorus compounds. Production is expensive, but high purity level is needed in applications such as chemical and food industry, requiring the removal of more than 99% of the impurities in the raw material (Morse *et al.* 1998). The United States processes approximately 5% of mined phosphate rock in electro-thermal process (U.S. Geological survey 2010).

P_4 is very reactive and produced with extreme methods. Production requires great amount of electricity. For example, a phosphorus producing company Thermphos International B.V. uses 12 TJ annually (Thermphos 2010). It would be economical to locate the production plants in countries where electrical energy is available with low costs (Rayner-Canham and Overton 2006). Figure 7 presents an example of an electro-thermal process.

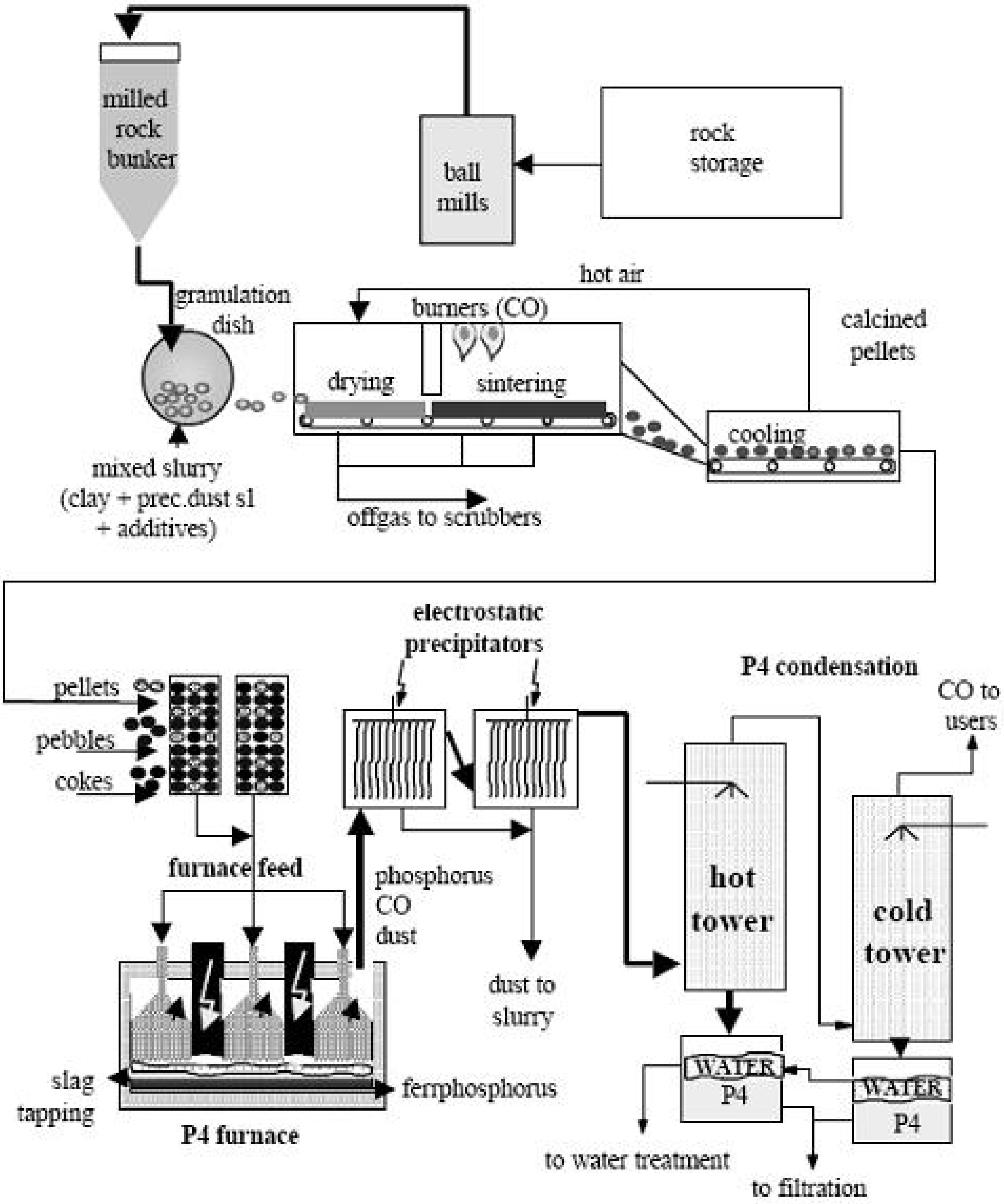

Figure 7: Electro-thermal production of elemental phosphorus (Schipper *et al.* 2001).

The first step prepares the raw material, calcium phosphate rich phosphate rock, for the actual electro chemical process. The phosphate rock is milled and ground to the particle size 1 to 2 cm, and dried and sintered to form pellets. In the second step, the pellets are mixed with sand (SiO_2) and coke before feeding them to the electric furnace. An electric current create a temperature of 1500°C in the furnace, producing elemental phosphorus, CO_2, CaO, as shown in the Equation 8. In addition, the furnace produces an amount of dust collected by electrostatic precipitators and recycled back to the pelletizing stage.

$$2\ Ca_3(PO_4)_2\ (s) + 10\ CO\ (g) \rightarrow 6\ CaO\ (s) + 10\ CO_2\ (g) + P_4\ (g) \qquad (8)$$

The gaseous P_4 is condensed by spraying it with water. Average production in electrochemical process using 180 000 A (500 V) current by 60-ton carbon electrodes is 5 t/h of tetraphosphorus (Rayner-Canham and Overton 2006). Further processing to phosphoric acid occurs by burning the white phosphorus, and adding water to the oxide, according to the Equation 9.

$$P_4O_{10}\,(s) + 6\,H_2O\,(l) \rightarrow 4\,H_3PO_4\,(l) \tag{9}$$

In the process, coke is used as a reducing agent in the reaction with CO_2 (Equation 10). The CO gas can be used as fuel in sintering step and furnace.

$$CO_2\,(s) + C\,(s) \rightarrow 2\,CO\,(g) \tag{10}$$

Calcium oxide reacts with sand forming calcium silicate slag as in the Equation 10. The slag needs to be tapped, cooled, and crushed, and is used in road constructions.

$$CaO\,(s) + SiO_2\,(s) \rightarrow CaSiO_3\,(slag) \tag{11}$$

Another by-product is ferrophosphorus Fe_2P, a dense liquid that is tapped from the bottom of the furnace. The ferrophosphorus containing about 75% of iron and 25% of phosphorus can be used as steel additive in specialty steel products (Schipper *et al.* 2001).

3 PHOSPHORUS REMOVAL

3.1 Phosphorus in wastewater treatment plant

Phosphorus content in the sewage systems derives from industrial and domestic sources. Main domestic sources are human metabolic waste, detergents and cleaning products. Human waste load to sewage is approximately 0.6 kg/a and load from detergents 0.3 kg/a per capita (Parsons and Smith 2008, Cornel and Schaum 2009).

An average phosphorus concentration in sewage is 4 to 16 mg/l (Metcalf & Eddy 2003). Approximately 50% is in soluble inorganic orthophosphate form, 35% are complex inorganic phosphates (polyphosphates) such as those from detergents phosphates, and 15% are organic phosphates found in organic matter and cell protoplasm (Vesilind 1998, Parsons and Smith 2008).

Phosphorus bound in the solid particles comprises about 11% of total phosphorus load to WWTPs and is removed in the primary treatment (Cornel and Schaum 2009). In the secondary treatment, phosphorus is needed in the activated sludge process as the substrate for micro-organisms. Activated sludge requires the BOD_5/P ratio of 1:100 that equals the requirements of any other biological process (Vesilind 1998). Therefore, biological treatment can remove 20 to 30% of phosphorus even without specific phosphorus removal process (Metcalf & Eddy 2003, Parsons and Smith 2008). The remaining phosphorus that is not bound in the activated sludge process, is removed with chemical precipitation or with biological phosphorus removal. These methods can be combined and used simultaneously, or, to have the chemical precipitation as back up to ensure the quality of effluent in varying conditions. Overall, with modern technology it is possible to remove over 95% of the incoming phosphorus (Metcalf & Eddy 2003).

The EU Directive 91/271/EEC defines the discharge limits for total phosphorus concentrations in WWTP effluent. In sensitive areas subject to eutrophication, the concentrations measured with molecular absorption spectrophotometer should be:

- 2 mg/l total phosphorus, when p.e. 10 000 – 100 000

- 1 mg/l total phosphorus, when p.e. > 100 000.

The minimum reduction in relation to the load of the influent is 80%. Depending on the local circumstances, it is possible to apply only one or both of the limit values. In Finland, the current requirement for large and medium sized WWTPs is 0.3 mg/l total phosphorus and at least 95% reduction. These requirements are met with chemical precipitation because the biological phosphorus removal process alone cannot ensure the required efficiency (Mäkelä 2004).

3.2 Chemical phosphorus removal

Phosphorus removal by chemical precipitation is a relatively simple and effective method, removing dissolved phosphorus from wastewater. The wastewater phosphorus is bound with coagulants containing two or three valent metal salt such as iron and aluminum chloride or sulfate, or calcium hydroxide. The coagulants react with phosphorus and other impurities in wastewater. The reactions are affected by side reactions that are dependent on alkalinity, pH, trace elements, and ligands. Thus, the chemical consumption can only be estimated from the stoichiometric molar ratios. The precipitation can occur in several steps in the wastewater treatment process, the most feasible step being the secondary treatment (Metcalf & Eddy 2003).

The most commonly used phosphorus removal chemical is iron coagulant containing Fe^{2+} and Fe^{3+} ions. The reaction between iron and water forms also ferric hydroxide. As can be seen in the Equation 12, the molar ratio $Fe:PO_4$ for phosphorus removal is 1:1. However, the ferric hydroxide formation creates a need for additional 10 mg/l of Fe (Vesilind 1998).

$$Fe^{3+} + y\,H_2O + x\,PO_4^{3-} \rightarrow Fe(OH)_y(PO_4)_x + y\,H^+ \qquad (12)$$

Vesilind (1998) estimates a dosage of 15 to 30 mg/l to precipitate 85 – 90% of the municipal wastewater phosphorus. Optimum pH range is 4.5 to 5 (Figure 7) but significant phosphorus removal can be obtained above pH 7.

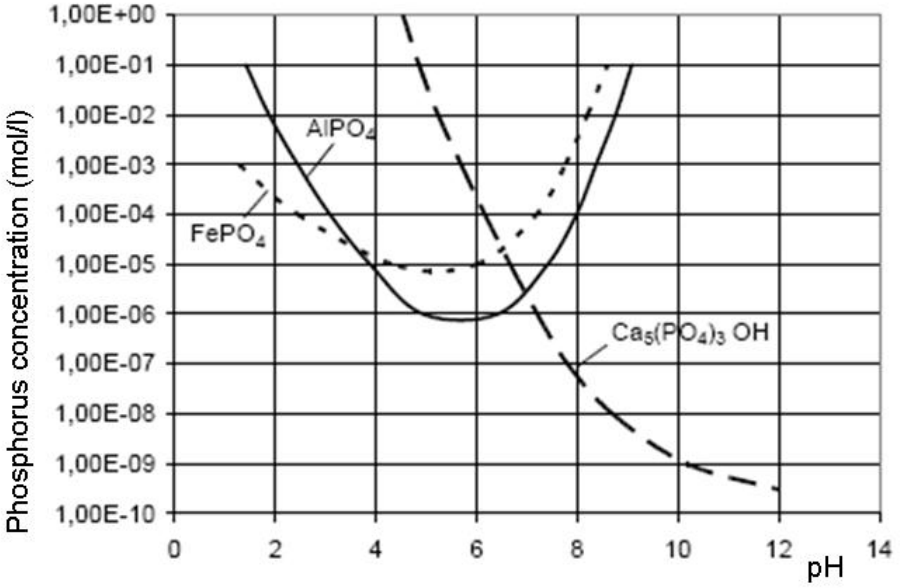

Figure 8: The phosphate precipitants and pH (Montag 2008).

Another common coagulant is aluminum that has the minimum solubility between pH 5.5 and 6.5. Aluminum sulfate results in a small depression in pH, so it can be operated in neutral area (Vesilind 1998). Aluminum reacts as in Equation 13.

$PO_4^{3-} + Al^{3+}$ à $AlPO_4$ (13)

Calcium is typically added to the water as $Ca(OH)_2$. The amount of calcium needed to precipitate phosphorus is dependent on the total alkalinity, because calcium reacts first with bicarbonates in water, forming calcium carbonate. Only above pH 10, the excess calcium reacts with phosphorus precipitating hydroxyapatite (HAP) as in the Equation 14 (Metcalf & Eddy 2003). The molar ratio $Ca:PO_4$ may vary between 1.3 and 2.0 because of the changes in the composition of the precipitated HAP. This is because the product calcium phosphate can precipitate in different forms as discussed later in Chapter 4 (Vesilind 1998).

$$5\ Ca^{2+} + 3\ PO_4^{3-} + OH^- \leftrightarrow Ca_5(PO_4)_3OH \qquad (14)$$

The flocks contain calcium carbonate formed in calcium reaction with bicarbonates. $CaCO_3$ is dense, and enhances the settling of the flock. Low alkalinity in wastewater results in small amount of calcium carbonate, thus decreasing the settleability of the flock. If alkalinity is high, excellent rates of phosphorus removal can be achieved in pH 9.5 to 10 (Vesilind 1998).

Phosphorus removal with calcium is typically not feasible due to the adjustment of pH before and after the precipitation, and the operational problems such as the handling, storage and feed of the chemical. Moreover, calcium precipitation produces larger amount of sludge compared to the iron and aluminum salts (Metcalf & Eddy 2003).

Although being an efficient way to remove phosphorus from wastewater, the chemical precipitation has negative effects downstream. In fact, a large amount of sludge is formed, requiring appropriate treatment. In digestion, especially iron result in lower biogas consumption (Parsons and Smith 2008). In addition, chemical phosphorus removal can rule out some of the phosphorus recovery possibilities.

3.3 Biological phosphorus removal

The driving forces of biological phosphorus removal are the phosphorus accumulating organisms (PAOs) for two reasons: they can storage excess amounts of phosphorus as polyphosphates in their cell under aerobic conditions, and secondly they can accumulate organic material in the anaerobic stage (Figure 9). The latter gives them a competitive advantage compared to other aerobes; in aerobic circumstances, they can immediately start utilizing available substances and their growth. The most commonly studied bacteria in biological phosphorus removal is *Acinebacter sp.* (Rantanen and Valve 1994).

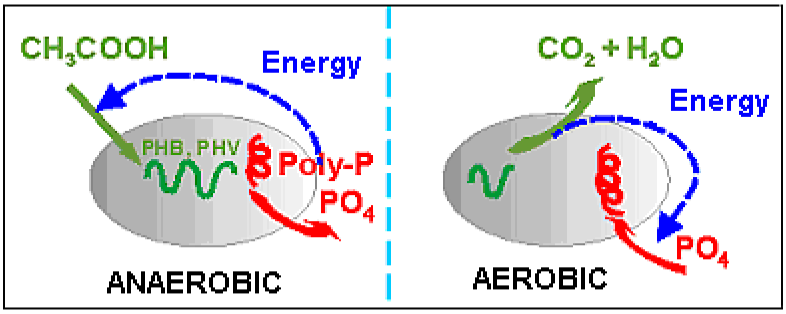

Figure 9: The principle of the cell operations for biological phosphorus removal (SYKE 2010).

When exposed to anaerobic conditions, PAOs start using their intracellular polyphosphates as an energy source to assimilate fermentation products from water. The most usable form of fermentation products for bacteria is volatile fatty acids (VFA) such as acetate. They are produced in water from fermentation of dissolved organic matter (bsCOD), which is easily assimilated by biomass. PAOs assimilate the VFAs as organic carbon polymers. For example, acetate is assimilated as polyhydroxybutyrates (PHB). At the same time, PAOs release phosphorus as orthophosphates (PO_4-P) with some amounts of magnesium, potassium and calcium. When PAOs are taken to aerobic conditions, they start to utilize the organic matter and phosphorus in water immediately, thanks to the energy from stored PHBs. As well as energy, oxidation of PHBs provides carbon for new cell growth, giving more space for polyphosphates assimilated from previously released orthophosphates and stored into the bacteria cells (Metcalf & Eddy 2003). Figure 10 presents the concentrations of the participating substances in the biological phosphorus treatment process.

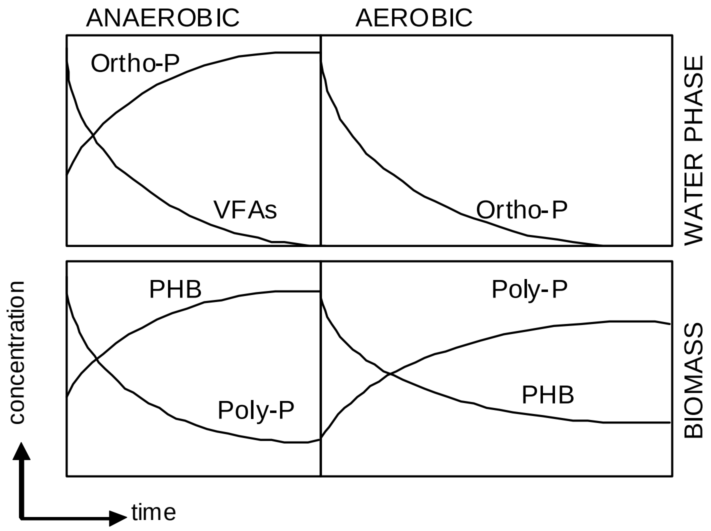

Figure 10: The concentrations of PO_4-P, VFA, PHB and polyphosphates in aerobic and anaerobic stage in water phase and in biomass (Janssen *et al.* 2002).

At its simplest, the biological phosphorus removal process has one activated sludge tank where the conditions can be altered from aerobic to anaerobic by scheduled aeration. Figure 11 presents, as an example, the A/O (anaerobic/oxic) process with one anaerobic and one aerobic section. More complicated processes can have an anoxic section in addition to several aerobic and anaerobic sections (Rantanen and Valve 1994).

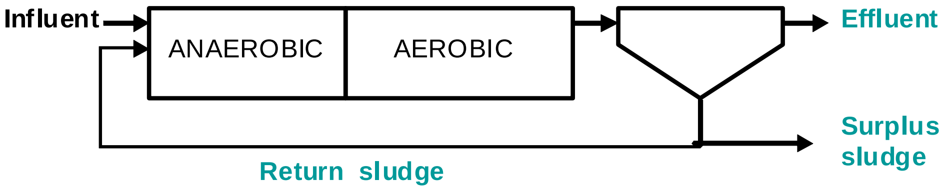

Figure 11: The A/O process (SYKE 2010).

Anaerobic stage of the process is very sensitive to molecular oxygen. Even a small amount of oxygen can prevent the phosphorus release, which is a condition to phosphate bonding. This problem may occur in the anaerobic stage when oxygen or nitrogen are present in the inflow. On the other hand, this property is beneficial, because in order to keep phosphorus bound in the sludge, aerobic conditions must remain. After aeration, the oxygen concentration in the sludge should be 2 mg/l to prevent the release of phosphorus (Rantanen and Valve 1994).

Biological phosphorus removal has several benefits compared to chemical phosphorus removal. The sludge from biological process has better value in agricultural use due to the higher content of plant available phosphorus and the lack of the chemicals used in precipitation process. In addition, biological phosphorus removal created a possibility for a side stream phosphorus recovery process. The operating costs of chemical process are subject to change due to varying price of flocculants (Stratful *et al.* 1999). However, the biological process needs the addition of bsCOD, that can be costly. In addition it is not as flexible as the chemical process (Metcalf & Eddy 2003). The limit values for phosphorus concentration in WWTP effluent are strict. Thus, it may be necessary to use chemical phosphorus removal instead, or in addition to biological process.

3.4 Sludge treatment

3.4.1 ANAEROBIC DIGESTION

Anaerobic digestion is one of the most widely used methods for sludge stabilization at WWTPs. From the phosphorus recovery point of view, it creates a phosphate rich side stream that can be utilized in recovery processes. Anaerobic digestion reduces the amount of pathogens as well as the quantity of biomass by destructing volatile solids. The destruction level of volatile solids is 40 to 65% depending on the content of the easily degradable solids such as simple carbohydrates, cellulose, proteins and grease in the sludge. The solids affect the gas formation level and gas quality. Building the facility requires careful planning and the machinery increasing the investment cost (Vesilind 1998).

Anaerobic digestion is a result of complicated chemical and bacterial reactions. The process includes three steps: hydrolysis, formation of soluble organic compounds and short-chained organic acids, and methane formation. In the hydrolysis stage, the facultative anaerobic bacteria convert the volatile organic substances such as proteins, cellulose and lipids producing soluble compounds to soluble form. Hydrolysis is slow and often the limiting step in anaerobic digestion. In the second stage, the acid forming bacteria dissolve the compounds from the hydrolysis to soluble organic compounds such as long-chained fatty acids, and further to short-chained organic acids, such as acetate. The last stage, called methanogenesis, produces final products: methane gas, CO_2, H_2S, and mineral salts, such as Mg and K. The typical value of digested substrate is pH 7.5 – 8.5 (Vesilind 1998, Vesterager 2009).

3.4.2 MONO-INCINERATION

In order to use sewage sludge ash for phosphorus recovery, the sludge must be mono-incinerated without bark, solid waste or any other added material. Incineration is relatively popular method for sludge disposal: 20% of Europe is disposed of by incineration (Table 2).

Table 2: Sewage sludge production and mono-incineration facilities in selected countries (ASH DEC 2009).

	Sewage sludge (t/a DS)	Share of mono-incineration (%)	Operational plants
USA	8 200 000	22	170
Europe	8 330 000	20	~80
Austria	245 000	31	3
Germany	2 450 000	28	23
Switzerland	203 000	47	14
Japan	3 000 000	50	100

Sludge incineration has advantages such as energy integration and high mercury removal. In incineration process, phosphorus concentrates and absorbs in the ash. Organic pollutants including PCB’s, dioxins, hormones and POPs, are destroyed. The modern technology is reliable and the emissions controlled with specific flue gas cleaning system.

An example of a sewage sludge incineration plant is N.V. Slibverwerking Noord-Brabant (SNB), the largest sludge incineration plant in Europe, located in Moerdijk, the southern part of the Netherlands.

SNB processes more than 410 000 t/a of sludge. The sludge holding a 23% dry solid content is transported to SNB with trucks. The plant has storage facilities to buffer the seasonal changes of the incoming sludge: during winter and spring the amount of sludge is larger than in the summer. The trucks are unloaded in sludge bunker and the sludge is pre-dried. The sludge leaves the pre-dryer with dry solids content of 35 - 40% and enters the fluidized-bed furnace. The temperature in the furnace is 850 - 900 ^{o}C. Production of ash in SNB is 36 000 t/a containing approximately 10% of phosphorus (Korving 2010).

The process consists of four incineration lines one of which incinerates iron-poor sludge from biological phosphorus removal processes and processes using aluminum as precipitation chemical. The iron poor ashes can be recycled in the process of phosphorus chemical producer Thermphos as discussed later in the Section 3.5.2. SNB has tried to increase the amount of iron poor sludge by recommending WWTPs to change from the iron precipitants to aluminum precipitants, or to implement biological phosphorus removal.

Although the precipitation chemical is the main reason for iron concentrations in the sludge, relatively high iron concentrations occur in WWTP using biological phosphorus removal or aluminum precipitant. In these cases, the iron sources need to be searched up-stream. Several reasons have been detected including iron dosage to digesters to prevent the formation of H_2S; discharge of iron-containing sludge to sewer by potable water treatment plants; and the leakage of iron-containing groundwater to the sewage system (Korving 2010).

Korving (2010) estimated that in the future, the amount of mono-incinerated sludge ash recycled in phosphorus production in Thermphos could be maximally 50% of the incinerated sludge. However, a realistic estimate is 40%.

3.5 Phosphorus recycling

3.5.1 AGRICULTURAL USE

Municipal wastewater sludge contains nutrients and organic material that are needed in the agriculture as fertilizers. Spreading sewage sludge on the fields is the most economical route for disposal of biosolids (Andersen and Sede 2002), and simultaneously recycling the nutrients. However, unlike in the commercial fertilizers described in Section 2.4.1, the nutrients in the sludge may not be in the optimal form or quantity for plant production. In addition, the sludge contains micropollutants, pathogens and heavy metals that are subject to transmit to humans. Thus, the agricultural use of sludge has decreased, mainly because of the public opinion (Rantanen *et al.* 2008). For example, the agricultural use of sludge in Finland decreased from 33% in 1995 to 17% in 2003, reaching 3% in 2007 (Salado *et al.* 2009). Other reasons include high concentrations of heavy metals and organic substances. In addition, the use as a fertilizer is seasonal, creating a need to storage the material during the wintertime (Rantanen *et al.* 2008).

Table 3: Limit values for heavy metal concentrations in agricultural use.

	EU (mg/kg DS)	**Finland (mg/kg DS)**	**Germany (mg/kg DS)**	**Holland (mg/kg DS)**
	Directive 86/278	MMM 2007	DüMV 2008	BOOM
As	----	25	40	15
Cd	20 - 40	1.5	1.5	1.25
Cr	---	300	----	75
Cu	1000 - 1750	600	----	75
Hg	16 - 25	1	1	0.75
Ni	300 - 400	100	80	30
Pb	750 - 1200	100	150	100
Zn	2500 - 4000	1500	----	300

In the German fertilizer ordinance (DümV 2008), copper and zinc are considered micronutrients in concentrations 200 - 700 mg/kg and 200 – 5000 mg/kg, respectively (Petzet and Cornel 2009). In Finland, the spreading of phosphorus is limited by Ministry of Agriculture and Forestry (MMM 2007) to prevent the possible leaking of phosphorus containing water to the surface water and groundwater. The permitted amount of soluble phosphorus used in five year period in landscaping and agriculture is < 750 kg/ha and < 400 kg P/ha, respectively.

3.5.2 RECYCLING IN PHOSPHATE INDUSTRY

An example of recycling phosphorus in other than fertilizer industry is the co-operation between the chemical company Thermphos International B.V. and SNB. The former produces high quality phosphate chemicals for markets including pharmaceuticals, food and feed additives, beverages, flame-retardants and crop protection.

The company replaces the phosphate rock in the electro-thermal process (Section 2.5.2) with the mono-incinerated sewage sludge ash from the SNB incineration plant. This section discusses the quality requirements for the secondary material used in replacing phosphate rock in the process. Table 4 presents the requirements for phosphorus content as well as the most important substances disturbing the electro-thermal process: copper, zinc and iron. These values are compared to the ash from chemical and biological phosphorus removal process, and calcium phosphate from Geestmerambacht, the Netherlands, where phosphorus is recovered from sewage. As can be seen, the most beneficial secondary raw material would be calcium phosphate corresponding with phosphate rock (Morse *et al.* 1998, Schipper 2010). Thermphos used to receive 150 t/a calcium phosphate from Geestmerambacht, but high operational costs have restricted the plants phosphorus recovery and Thermphos utilizes only ash from SNB as secondary raw material in the phosphorus production process.

Table 4: Requirements for secondary raw material compared to ash from chemical and biological phosphorus removal process, and calcium phosphate (Schipper *et al.* 2001).

	P_2O_5 (g/kg)	Cu (g/kg ash)	Zn (g/kg ash)	Fe (g/kg ash)
Requirements for raw material	> 250	< 0.500	< 0.100	< 10
Sewage sludge ash from primary and secondary sludge	190	1600	3500	16
Ash from biological phosphorus removal process	360	1500	3100	< 10
Geestmerambacht $Ca_3(PO_4)_2$	260	1.6	35	---

Typically, P_2O_5 content of phosphate rock is 30 - 40%, which equals 13 - 17.5% of phosphorus (Schipper *et al.* 2001). Iron is the most harmful impurity in the raw material since it causes capacity problems by binding phosphorus, thus increasing the amount of produced ferrophosphate slag that has no commercial value and limited ways of use. Moreover, the slag requires a special cooling process increasing the energy consumption. Aluminum, on the other hand, replaces the SiO_2 needed in the process, thus not affecting the energy balance (Schipper *et al.* 2001).

Another problem is the volatile metals such as zinc, cadmium and lead. They are recycled in the process with the furnace dust, thus accumulating in the system and creating a need for purges. Due to isotopes, such as ^{210}Pb, the recycled material is slightly radioactive, increasing the disposal costs (Schipper *et al.* 2001).

Table 5 presents other substances with negative impact on the electro-thermal process.

Table 5: Impurities in secondary raw material and the ways and reasons of the interference of the process (Schipper *et al.* 2001)

Chloride	Causes corrosion in the sintering and granulation step.	
Copper	Ends up in the ferrophosphorus slag, decreasing it's value as steel additive.	Cu < 500 mg/kg ash
Moisture	Technical limitations, since the process is designed for dry material .	Low moisture content
Organic material, Alkali metal salts	Decreases the pellet strength after sintering, thus limiting the plant capacity	C < 5%
Ammonium	Volatilizes in the sintering step causing emissions or problems in gas scrubbing.	Struvite can not be used

As iron increases the energy consumption and the amount of produced slag, an important factor is Fe/P ratio, as illustrated in Figure 12. The normal Fe/P ratio in sewage sludge is 0.6 (Korving 2010), whereas Thermphos has set the limit to 0.2. Thermphos intends to replace 20% of the phosphorus rock used in the process with sewage sludge ash. Hence, as the process uses 600 000 t/a ash, 20% equals 120 000 t/a ash, equaling 8400 t/a phosphorus. SNB and Thermphos have negotiated setting the limit to 0.25, increasing the share of suitable sludge to 30 - 45%.

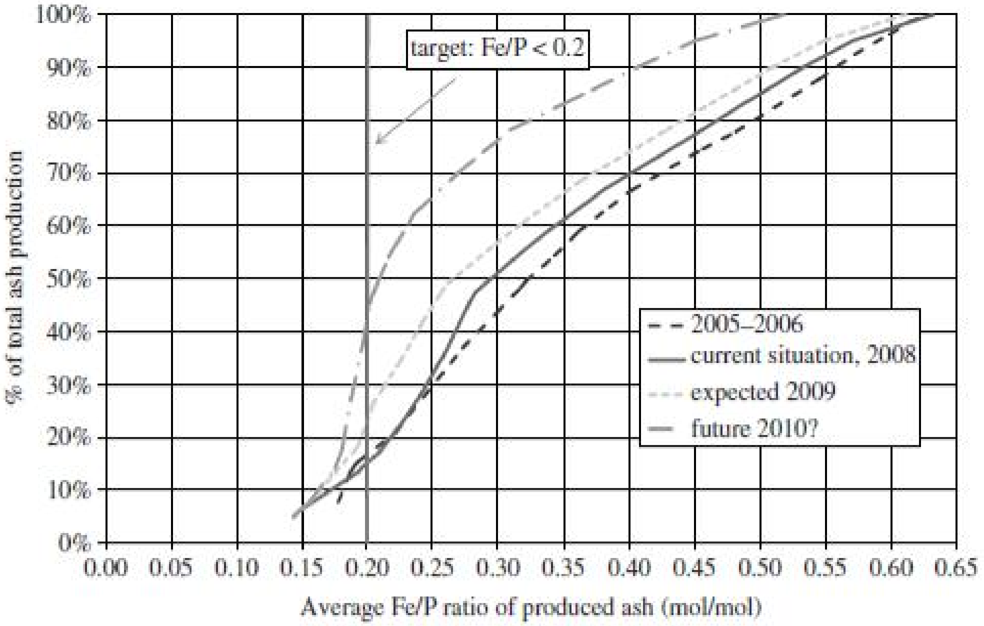

Figure 12: Fe/P in sewage sludge ash (Schipper and Korving 2009).

4 PHOSPHORUS RECOVERY

4.1 National policies

In Finland, phosphorus recovery has received little attention. Approximately 80% of the phosphorus is used in landscaping (Rantanen *et al*. 2008) and the only approach to nutrient recycling is a minor fraction of 3% through agriculture. However, the common interest towards the phosphorus recovery in Europe has arisen, and some countries have launched national goals to promote the matter.

In December 2002, the Swedish Environmental Protection Agency (SEPA) announced a long-term objective to recycle 60% of phosphorus from sewage by the year 2015 (SEPA 2002). The wastewater fraction should be returned to natural cycle or if not possible, be utilized as energy. The aim was to increase the fraction of biosolids in agricultural use to recycle the nutrients.

In March 2003, Germany announced the objective to develop new technologies in the branch of phosphorus recovery (CEEP 2003). In 2004, German Federal Ministry of Education and Research (BMBF) and German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) launched the funding program "Recycling management of plant nutrients, especially phosphorus" consisting of seven projects, as listed in Table 6 (BMBF/BMU 2010). The program aims at activating new processes for industry producing fertilizers, fertilizer components, or ingredients for the fertilizer industry using recycled products. In addition to phosphorus, the program wants the processes to recover other plant nutrients, such as nitrogen and potassium, present in the materials used for recovery, including sewage (water, sludge, ash) and by-products from food industry and agriculture, such as meat bone meal and manure. The recovered products should be usable as fertilizers or in fertilizer industry without further treatment, containing phosphorus and other nutrients in a plant available form, and having heavy metal and organic pollutant levels under limit values. The program has spawn at least one new process, the PASH (Phosphorus recovery from ash), described later in Chapter 6.

Table 6: The projects of the funding program "Recycling management of plant nutrients, especially phosphorus" (BMBF/BMU 2010).

Accompanying projects:	
PhoBe	Recycling of Phosphorus - Ecological and Economic Evaluation of Different Processes and Development of a Strategical Recycling Concept for Germany
Göttingen	Phosphorus recycling - Characterization of the effect of recycled phosphate fertilizers by field and pot experiments
Technical projects:	
PASCH	Recovery of plant nutrients, especially phosphorus from ash of sewage sludge as well as meat- and bone meal
Phoxnan	Optimized phosphorus recycling from waste water sludges by the combination of low pressure wet oxidation and nanofiltration
ProPhos	Phosphorus recovery from wastewater, sewage sludge and sewage sludge ashes
RECYPHOS	Phosphorus recycling - Sustainability contribution at the decentral wastewater treatment
PHOSIEDI	Phosphorus Recovery using Ion-Exchange and Electrodialysis

4.2 Locations for phosphorus recovery

A wastewater treatment process offers several locations for phosphorus recovery, presented in Figure 13. Raw material options for phosphorus recovery processes presented in this section include liquid phase (1), sludge (2), and mono-incinerated sludge ash (3).

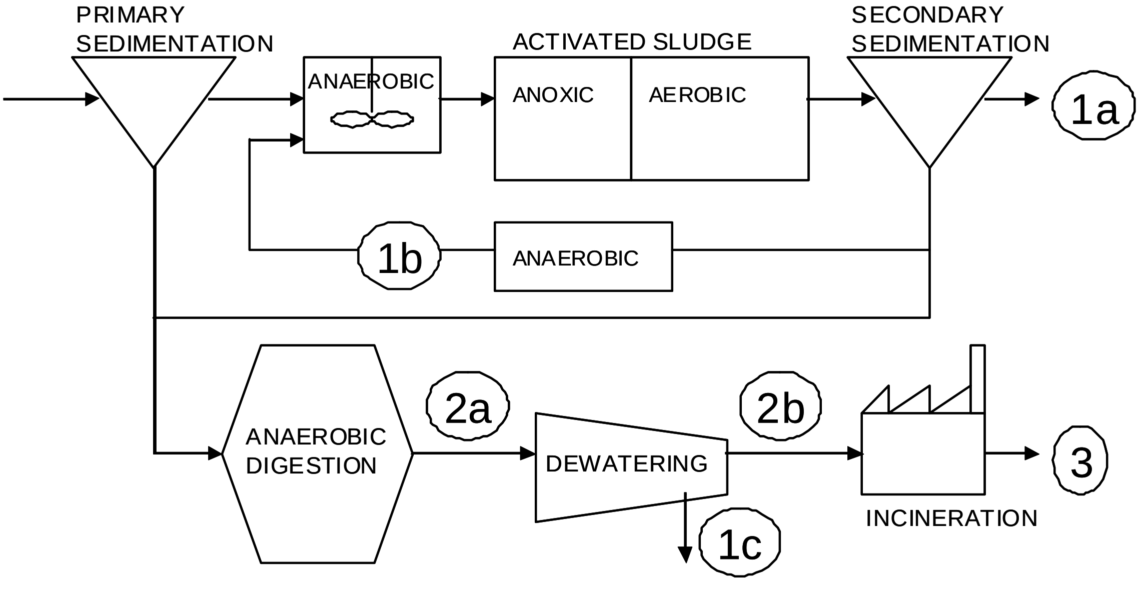

Figure 13: Possible locations for phosphorus recovery (modified from Adam 2009 and Cornel and Schaum 2009).

Phosphorus occurs in soluble form, expressed as orthophosphate PO_4-P, in several locations, including effluent from secondary sedimentation (1a), concentrated side stream from anaerobic treatment (1b), and sludge liquor from digested sludge dewatering (1c). The economically feasible recovery requires a liquid phase containing 50 - 60 mg/l of PO_4-P (Cornel and Schaum 2009, Ostara 2010).

As phosphorus concentration in municipal WWTP effluent (1a) is lower than 5 mg/l (Table 7), the concentrated side streams after anaerobic treatment, such as a separate anaerobic compartment (1b), or dewatering unit after anaerobic digester (1c), are usually better options for phosphorus recovery. These streams typically contain 20 - 100 mg/l of PO_4–P, but can reach concentration of 300 - 900 mg/l of PO_4–P (Lengemann 2010a, Ostara 2010). The phosphorus recovery methods from liquid phase are often located in WWTPs with biological phosphorus removal process.

Table 7: Phosphorus flow and concentrations (l/d per capita (modified from 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%

Sludge from digester before (2a) and after (2b) dewatering process contains phosphorus in chemically or biologically bound form. Especially after biological phosphorus removal process, PO_4-P is released in the sludge liquor (1c). Dried sludge contains phosphorus approximately 1 to 3% by weight (Montag 2008, Suomenoja 2009).

In the third option, the sewage sludge ash (3), phosphorus is in the most concentrated form. The decrease in volume results in decreased transporting and landfilling costs, as well as decreased consumption of chemicals in phosphorus recovery processes. Recovery from ash does not require major changes at the WWTP, although changing from iron-precipitants to aluminum-precipitants for better recyclability (section 3.5.2) may increase the total costs. From phosphorus recovery point of view, mono-incineration without any other material but sewage sludge is preferred method to co-incineration, as discussed earlier in section 3.4.2. Ash is discussed in detail in section 4.3.3.

4.3 Final Products

4.3.1 CALCIUM PHOSPHATE

Calcium phosphate is an attractive form of recovered phosphorus because it is directly comparable to phosphate rock. Thus, utilization as secondary material is possible in both phosphate and fertilizer industry (Schipper *et al.* 2001, Roeleveld *et al.* 2004).

Calcium phosphate crystals (Figure 14) form in phosphorus rich liquid as in Equation 15, when calcium is added and pH is in suitable range, typically above pH 8.

$$2\ PO_4^{3-} + 3\ Ca^{2+} \rightarrow Ca_3(PO_4)_2 \qquad (15)$$

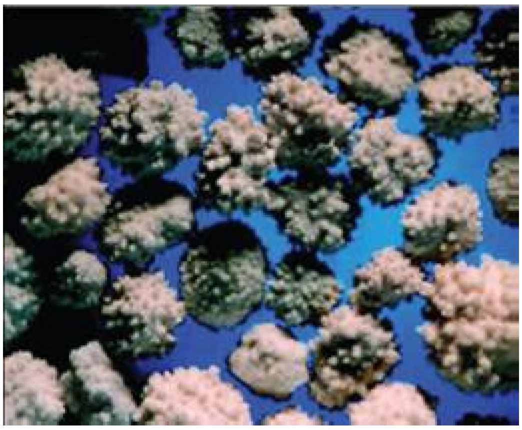

Figure 14: Calcium phosphate pellets (Giesen 2009a).

Calcium phosphate does not precipitate spontaneously in low concentrations. In wastewater, there is a selection of ions, so precipitation of calcium phosphate requires a very high oversaturation of component ions. For this reason, calcium phosphate precipitation requires seed material in the reactor. Seed material can be sand or calcium silicate crystals (Cornel and Schaum 2009).

Depending on the solution composition and pH, calcium phosphate crystallizes several forms presented in Table 8. The table shows the names of different calcium phosphates, chemical formulas, and thermodynamic solubility product.

Table 8: Calcium phosphate compounds (CEEP 2001).

Name of calcium phosphate	Formula	Thermodynamic solubility product
Brushite, dicalcium phosphate dihydrate	$CaHPO_4 \cdot 2H_2O$	$2.49 \cdot 10^{-7}$
Monetite	$CaHPO_4 \cdot 2H_2O$	$1.26 \cdot 10^{-7}$
Octacalcium phosphate	$Ca_4H(PO_4)_3 \cdot 2.5\ H_2O$	$1.25 \cdot 10^{-47}$
Amorphous calcium phosphate	$Ca_3(PO_4)_2$	$1.20 \cdot 10^{-29}$
Hydroxyapatite	$Ca_5H(PO_4)_3O$	$4.7 \cdot 10^{-59}$
Tricalcium phosphate	$Ca_3H(PO_4)_2$	variable

Thermodynamically the most stable form is hydroxyapatite (HAP). Other calcium phosphates that may form faster are eventually likely to turn into HAP (CEEP 2001).

4.3.2 STRUVITE

Struvite, or magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6\ H_2O$). consists of Mg^{2+}, NH_4^+ and PO_4^{3-} ions in molar ratio 1:1:1. The compound is referred to as MAP and it forms as given in Equation 16. The struvite crystals have an orthorhombic shape as in Figure 15.

$$HPO_4^{2-} + NH_4^+ + Mg^{2+} + OH^- + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + H_2O \qquad (16)$$

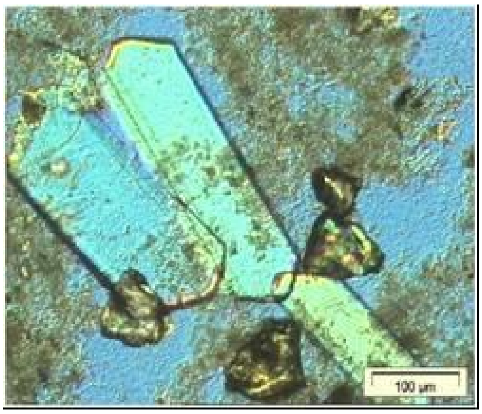

Figure 15: Struvite crystals (Heinzmann 2009).

Typically, the options for magnesium source are $MgCl_2$ and $Mg(OH)_2$. $MgCl_2$ is more common, because it is easier to handle and it disassociates faster, leading to shorter retention time. $Mg(OH)_2$ can be simultaneously used for pH adjustment and as magnesium source. However, the simultaneous use complicates optimization, and additional pH adjustment is needed (Jaffer *et al.* 2001). The minimum solubility of struvite, indicating the optimal circumstances for precipitation, occurs above pH 8.5 (Figure 16).

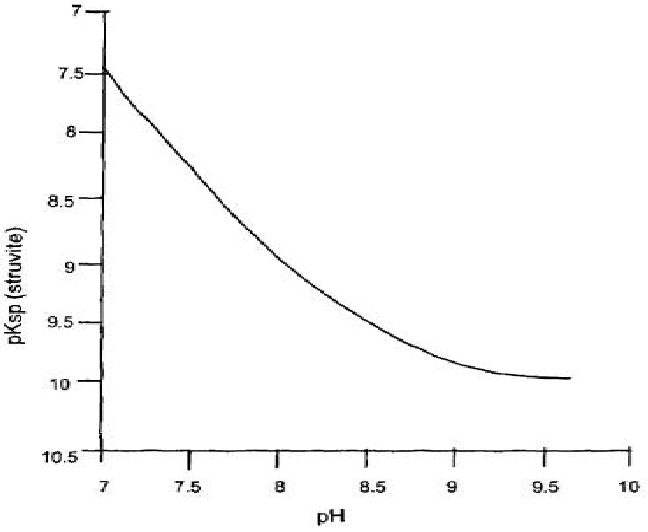

Figure 16: Struvite solubility vs. pH (Koch *et al.* 2009).

Since struvite contains two primary nutrients, phosphorus and nitrogen, and secondary nutrient magnesium, it would be beneficial to recover phosphorus as struvite for fertilizer industry. Unlike calcium phosphate, struvite is not suitable for replacing raw material in electro-thermal process due to the ammonia content (Schipper *et al.* 2001).

Experiences (e.g. Battistoni 2000, Nawa 2009, Kern *et al.* 2008) have shown that struvite is low in heavy metals and other pollutants, and that the nutrients are in plant available form, making struvite suitable for agricultural use as a slow release fertilizer. In their paper, Kern *et al.* (2008) conclude the share of water-soluble struvite approximately 3.6%, and citric acid soluble struvite 98.8%. The phosphorus uptake of examined plants, maize and wheat, was 66.7% and 85.9%, respectively.

As can be seen in Table 9, composition of struvite produced in the pilot plant at the Oxley Creek WWTP, Australia, and from Phosnix reactor in Japan, is comparable to the theoretical values calculated from the chemical formula of struvite. These processes are discussed in Section 5.2.3 and Section 6.4.

Table 9: Concentration by mass of Mg, N and P in struvite.

	Theoretical value from chemical formula		**Struvite from Oxley Creek (Münch and Barr 2001)**	**Struvite from Phosnix (Nava 2009)**
Mg	9.9%		9.1%	9.9%
N (NH_4)	5.7%	(7.4%)	5.1%	5.9%
P (PO_4)	12.6%	(38.7%)	12.4%	12.6%
6 H_2O	44 %		39 %	---

The solubility product (Ksp) and the supersaturation ratio (SSR) (Equations 17 and 18) have an effect on the formation of struvite crystals. The ideal value of SSR is between 2 and 5. Higher values above 4 and 5 decreases the crystal size hindering the formation of desired large crystals (Koch *et al.* 2009).

$$Ksp = [Mg^{2+}]_{eq} [NH_4^+]_{eq} [PO_4^{3-}]_{eq} \quad (17)$$
$$SSR = [Mg^{2+}] [NH_4^+] [PO_4^{3-}] / Ksp \quad (18)$$

Anaerobic digestion creates favorable conditions for struvite precipitation releasing PO_4-P and Mg^{2+} from the biomass and forming NH_4^+ from other ammonium compounds (Metcalf & Eddy 2003). Typically, municipal wastewater contains 3 – 20 mg/l of magnesium (Ostara 2010). Simultaneous change in pH leads to problems at WWTPs in form of spontaneous struvite precipitation into pipelines, valves and other sludge treatment equipment (Jeanmaire and Evans 2001). A practical example is given in Section 5.2.1.

4.3.3 ASH

Incineration concentrates the phosphorus contents of the sewage sludge to the resulted ash fraction. Incineration of sewage sludge decomposes the organic compounds including potentially toxic organics. Although the decomposing of the organic material is a benefit regarding to the hygiene and the processing with wet chemical methods, it increases the soil enrichment properties of the ash. In addition, the phosphorus bound in the ash is not in plant available form (SUSAN 2008). Since sewage sludge ash has little applications, it is typically landfilled, used in cement concrete industry or for road constructions.

Sewage sludge ash contains approximately 17% P_2O_5. The main chemical constituents of ash are SiO_2, CaO, Al_2O_3, Fe_2O_3, and P_2O_5. Figure 17 presents the average composition of ash in 16 European incineration plants that participated in the EU Project BioCrete (2007). The composition of ash varies depending on the type of the incinerated sludge. The precipitation chemical used in chemical phosphorus removal process plays an important role. The values can vary greatly; for example, the content of Fe_2O_3 in ash from different incineration facilities, varied between 3 and 27%, and the Al_2O_3 content between 6.5 and 34%. On the other hand, the P_2O_5 concentrations showed less variation with values between 9 and 27%.

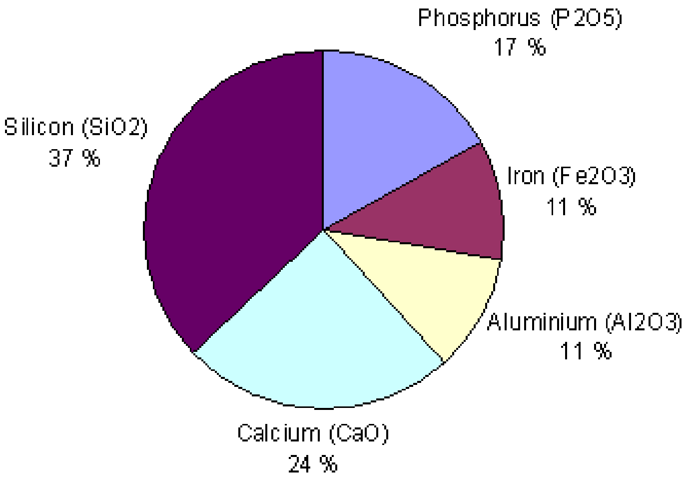

Figure 17: Average chemical composition of ashes from EU BioCrete project (2007).

As well as phosphorus, heavy metals concentrate in the ash. Table 10 shows heavy metal concentration of ash from several incineration facilities.

Table 10: Concentrations in ash from several incineration plants (Boutoussov 2009).

Source	P_2O_5%	Fe_2O_3%	Zn (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Cr (mg/kg)
Vienna (CH)	20.8	23.2	2 575	284	635	5.1	104
Vienna (CH)	20.1	18.6	1 978	220	543	3.4	92
St. Petersburg (RUS)	---	---	2 200	400	730	2.7	400
Berlin (D)	15.5	22.6	2 680	190	1 560	3.4	129
Wilhelmsheim (D)	18.1	19.6	2 030	156	552	2.7	150
Noord-Braband (SNB) (NL)	12.6	11	2 240	340	970	4.1	205
Average	**17.4**	**19**	**2 284**	**265**	**832**	**3.6**	**180**

The values show that heavy metal concentrations meet the values stated in Sewage Sludge Directive 86/278/EEC. However, the national restrictions can rule out the possibility of fertilizer use.

The ashes contain two fractions: the aerosol particles (flue ash) and the coarse particles (Table 11). The aerosol particles are finer and shaped differently than the coarse particles. The aerosol particles contain most of the heavy metals. Thus, separating them before further treatment can help in increasing the heavy metal concentration of the final product.

Table 11: Ash particle characteristics (Boutoussov 2009).

	Aerosol particles	**Coarse particles**
Diameter	0.5 µm	30 - 50 µm
Shape	Regular (rectangular or rod-shape)	irregular
Chemical composition	Heavy metal salts and oxides	Complex compounds such as aluminosilicates
Zn concentration	40 000 mg/kg	550 mg/kg
Cd concentration	100 mg/kg	30 mg/kg
Formed by	Volatile elements containing heavy metals	Partial melting of dust from the incinerated waste

4.4 The main phosphorus recovery technologies

4.4.1 CRYSTALLIZATION AND PRECIPITATION

In the 1970s, the phosphorus concentrations in the effluent became more strictly regulated leading to improvements in crystallization processes (Morse *et al.* 1998). Crystallization and precipitation technologies transform soluble PO_4-P from process liquid to solid form. As described in Sections 4.3.1 and 4.3.2, the main products are struvite and calcium phosphate.

The main difference between crystallization and precipitation methods is the reaction speed: precipitation is faster, often producing amorphous product, whereas crystallization takes more time producing crystalloid product. Both methods require supersaturation of the reacting ions. Formation of solid particles requires two steps: nucleation and crystal growth. Nucleation can occur spontaneously when the size of an individual nucleus exceed a critical size. The growth of the crystals transports the ions onto the crystal surface and into the lattice. Nucleation step can be avoided by increasing the crystal concentration in the solution with seed material. Thus, less energy is needed and the particle growth occurs on existing surfaces. The seed material is useful especially in wastewater environment, where impurities are present, offering a wide range of surfaces for the particle growth (CEEP 2001). Seed material can be for example sand or small struvite particles.

As the process requires a phosphate rich flow, it should be located after anaerobic compartment such as digester or the biological phosphorus removal process. Precipitation or crystallization occurs as the phosphorus ions in the flow and ions from added chemical react (Figure 18). In addition, pH adjustment with NaOH or CO_2 stripping can be necessary (Cornel and Schaum 2009).

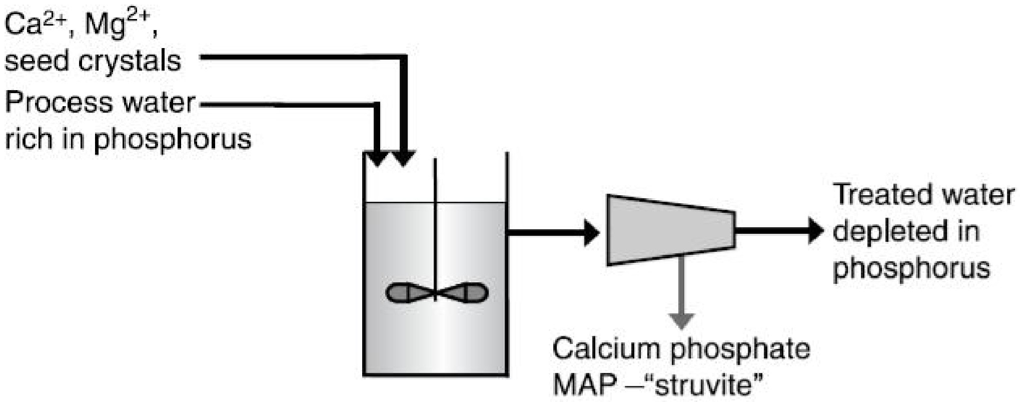

Figure 18: Principle of crystallization and precipitation process (Cornel and Schaum 2009).

The chemicals used in phosphorus removal: iron, aluminum and calcium, bind the phosphate ions, thus having a negative influence on the production (Güney *et al.* 2008). The suspended solids content below 150 - 200 mg/l in the liquid prevents problems such as impurities in recovered phosphorus, clogging of nozzles in the reactors and struvite crystallization onto anywhere else but the reactor seed material (Jeanmaire and Evans 2001). However, Ostara (2010) can operate with intermitted solids levels up to 3000 - 4000 mg/l, yet preferring levels below 1000 mg/l of TSS.

The treated flow from the precipitation reactor typically returns to the process. The decrease in the return phosphorus load decreases the load in phosphorus removal process, improves the dewaterability of sludge, thus decreasing the operational costs.

4.4.2 WET CHEMICAL TECHNOLOGIES

Wet chemical process releases chemically or biologically bound phosphorus from sludge or sludge ash with acid or base. As presented in Figure 19, non-soluble residue is separated and the remaining liquid phase treated for separating dissolved phosphorus. Methods include precipitation, ion exchange, nanofiltration and reactive liquid-liquid extraction (Cornel and Schaum 2009).

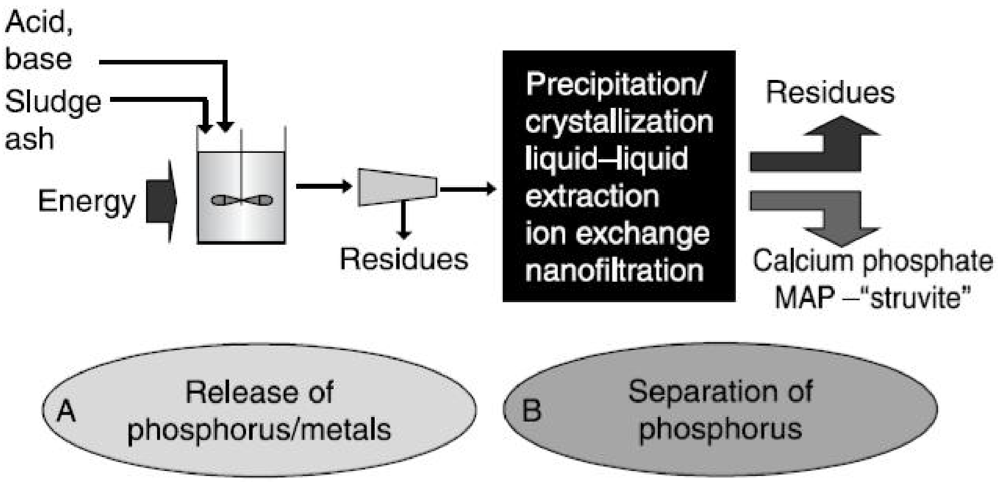

Figure 19: Principle of wet chemical process (Cornel and Schaum 2009).

Typically, leaching with acid releases more phosphorus compared to the leaching with base. Furthermore, the type of the feed material does not influence the result of acid leaching. With base, the release rate is higher from ash than from dried sludge (Stark *et al.* 2006). Schaum *et al.* (2005) studied the elution of phosphorus and heavy metals with different eluents. It was found that water caused no significant release of phosphorus and sodium hydroxide resulted in maximum 30% elution of phosphorus depending on the origin and formation of the ash. Sulfuric acid resulted in the release of over 90% of total phosphorus and part of heavy metals below pH 1.5. Montag (2008) performed experiments for phosphorus release from ashes with NaOH, H_3PO_3, H_2SO_4 and HCl discovering leaching of 25%, 50%, 80% and 90% of total phosphorus, respectively. Typically, wet chemical processes use sulfuric acid for phosphorus leaching (Bayerle 2009, Schaum *et al.* 2005). Figure 20 presents phosphorus and heavy metal solubility in sulfuric acid in respect of pH. It can be seen, that neutral pH 7 dissolves 10% of total phosphorus. The share of dissolved phosphorus increases linearly as pH decreases, the pH value 2 eluting 90% of total phosphorus.

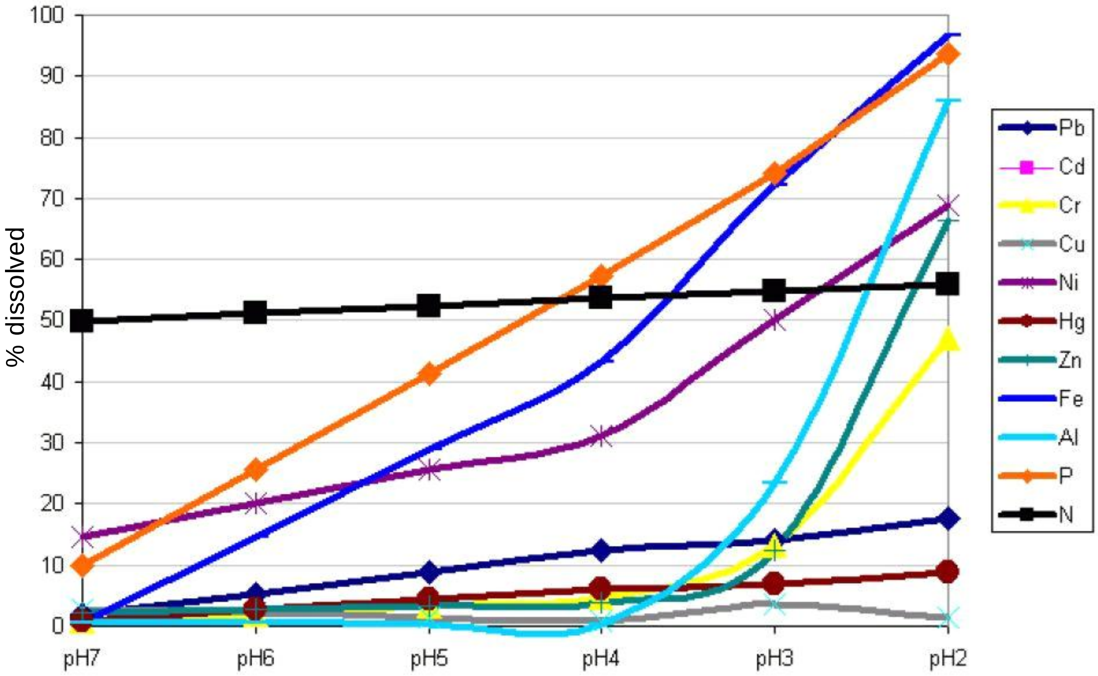

Figure 20: Dissolved components in sludge in respect to pH value (Bayerle 2009).

Nitrogen level stays at approximately 50% in solution regardless to the pH. Most heavy metals dissolve on pH below 3.5. However, lead, cadmium, copper and mercury stay in soluble form even at pH 2. Over 80% of iron and aluminum dissolve at pH 2 creating a possibility to recover precipitating chemicals simultaneously with phosphorus.

4.4.3 THERMO-CHEMICAL TREATMENT

Thermo-chemical technologies are used for removing heavy metals from sewage sludge ash. As stated in Section 4.3.3, ashes are hygienic, as the high temperatures in incineration process decompose the organic material. However, heavy metals concentrate in the ash together with phosphorus and can limit the utilization as fertilizer (Petzet and Cornel 2009).

An EU Project SUSAN (Sustainable and safe re-use of municipal sewage sludge for nutrient recovery) studied the possibility and technologies for removing heavy metals from sewage sludge ash with the method shown in Figure 21.

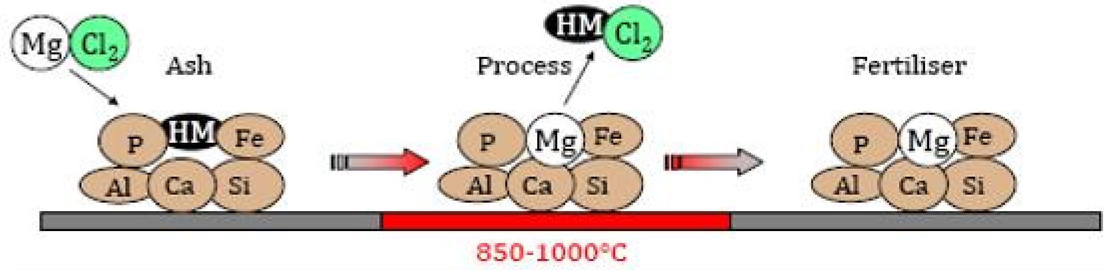

Figure 21: Thermo-chemical process principle (Hermann 2009b)

The process uses chloride additives such as earth alkaline salts, magnesium chloride and calcium chloride that react with heavy metals in the ash. The heavy metal chlorides evaporate as process temperatures rise over the boiling point of them. Typical temperatures are between 850 and 1000 ^{o}C. The results from the SUSAN project show removal rates of over 90% of Cd, Cu, Hg, Pb and Zn. In addition, thermal treatment increases the bio-availability of phosphorus in ash from 30 - 50% before incineration up to 100%. Thus, the product is suitable for fertilizer production (SUSAN 2008).

Other means of thermal treatment are based on metallurgy, treating dried sludge or ash in temperatures of 1500 - 2000 ^{o}C. These methods produce three material streams: a gaseous phase of volatile heavy metals and dust, a liquid metal phase, and a phosphorus rich slag. The slag is a typical by-product in steel industry and is comparable to Thomas phosphate, used as fertilizer in Germany (Hermann 2009).

5 INDUSTRIAL-SCALE PROCESSES

5.1 Crystallization of calcium phosphate

5.1.1 CRYSTALACTOR®

The Crystalactor® was developed in the 1970's by the Dutch company DHV Water B.V. Starting from the 1980's the process was applied in water treatment for potable water softening by limestone ($CaCO_3$) production, and for phosphorus recovery in wastewater treatment. Before the applications in water treatment, the process has been in use in other industrial branches such as chemical industry for zinc, nickel and aluminum recovery; and food industry for phosphate and ammonium recovery, where the process is still more popular than water treatment. (Giesen and van der Molen 1996).

Process description

The Crystalactor® is a crystallization process recovering phosphorus as calcium phosphate $Ca_3(PO_4)_2$ from concentrated side stream. Crystallization of other compounds, such as zinc phosphate or struvite, is possible by changing the type of added chemical (Giesen 2009a). The process consists of a cylindrical fluidized bed reactor (Figure 22) with seed material, which can be sand or minerals. The Crystalactor® reactor is relatively small, making the retrofitting it to most WWTPs possible.

The feed material is phosphate rich flow from the separation tank after biological treatment process and having a concentration of 60 - 80 mg/l PO_4-P. The recovery rate can reach 70 - 80% of PO_4-P (Cornel and Schaum 2009). The feed enters the reactor from the bottom and flows upwards with velocity of 40 – 100 m/h, keeping the reactor bed in fluidized stage.

The reaction surface is large, approximately 5000 – 10 000 m^2/m^3, making the crystallization efficient. The reaction starts after adjustment of pH with a NaOH dosage, and the calcium phosphate crystallizes on the surface of the seed material. As the pellets grow in size and mass, they sink to the bottom of the reactor from where they are periodically removed, typically once a day. The removed grains are replaced with smaller grains to keep their number constant (Giesen and van der Molen 1996).

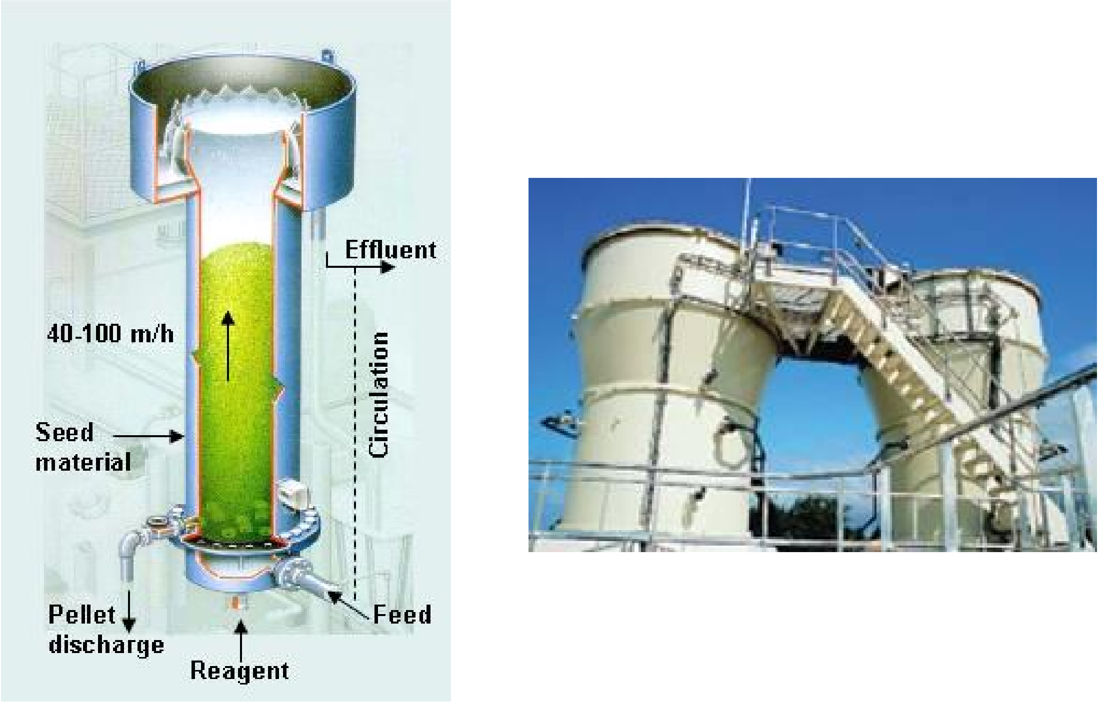

Figure 22: The Crystalactor® fluidized bed reactor (modified from Giesen 2009a) and the Crystalactor® reactors at the Geestmerambacht WWTP.

The reactor has a possibility to circulate the flow, thus making the reactor more flexible as wastewater with high concentration can be diluted by adapting the circulation ratio. The range of inflow concentration is wide: the treated water can contain 10 to 100 000 mg/l of the substance to be removed (Giesen and van der Molen 1996). The effluent, having a concentration of 15 – 20 mg/l, leaves the reactor from the top through an overflow gutter (Giesen 2009a).

Calcium reacts with carbonate ions in wastewater, causing unstable pellets that are problematic for recycling. To avoid the increased contents of calcium carbonate in the final product, the feed is first degassed from CO_2 by decreasing pH with 96% sulfuric acid (Stratful *et al.* 1999).

Information about the contents of the final product vary: according to Stratful (1999), the pellets contain calcium phosphates (Ca_xPO_{4y}) 40 - 50%, seed material (sand) 30 - 40%, $CaCO_3$ 10% and organic material 10%, whereas Gaanstra *et al.* (1998) report concentrations of 11% phosphorus (equaling 25% P_2O_5), and Schipper *et al.* (2001)

10.5% (equaling 26% P_2O_5). The estimated pellet production is 7 - 14 kg/p.e./a (Morse *et al.* 1998).

Experiences and costs

The first Crystalactor® application for phosphorus recovery was realized in 1988 in the municipal WWTP of Westerbork (12 000 p.e.), the Netherlands. Due to an increased use of phosphate-free detergents, the phosphorus concentrations in wastewater decreased, making the Westerbork crystallization unit no longer feasible. According to Giesen and van der Molen (1996), there have been two other installations of Crystalactor® in the Netherlands: Geestmerambacht (230 000 p.e.) and Heemstede (35 000 p.e.). In 2009, the only operational Crystalactor® application was the one located in Geestmerambacht, the Netherlands, at one of the WWTPs of the Waterboard Uitwaterende Sluizen (Giesen 2009b).

In Geestmerambacht, the present process was taken in use in 1994, and in 1997 the plant treated 10% of the 795 t of total phosphorus flow of the WWTPs of Waterboard Uitwaterende Sluizen. The WWTP in Geestmerambacht has a biological phosphorus removal process, design capacity of 231 600 p.e., total phosphorus load of 340 kg/d and inflow of 5000 m^3/d (Gaanstra *et al.* 1998).

The phosphate rich flow to the Crystalactor® originates from secondary sludge from a gravity thickener. The separation process is controlled by a sludge blanket measuring device. The flow containing 50 – 80 mg/l PO_4-P is collected in the buffer tanks and carbonates are removed in a cascade stripper before the flow enters the Crystalactor® reactor. The carbonate stripping occurs as pH is adjusted to 5 with H_2SO_4 (96%), however, in practice the stripping requires pH 3.5 due to technical problems (Gaanstra *et al.* 1998).

In the reactor, $Ca(OH)_2$ solution is added via separate nozzles and filter sand used as seed material. Calcium hydroxide dosage is controlled by pH measurement. Bed height is 4 to 4.5 m, controlled by extracting pellets near the bottom and subsequently adding sand.

Gaanstra *et al.* (1998) describe problems that occurred during the start-up of the Geestmerambacht Crystalactor®:

- Heavy abrasion occurred in the water nozzles. They were replaced by new nozzles of another material with 12 borings instead of 3.
- Feeding pumps were shut down by a clogging problems in return sludge pumps. The problem was solved as the control system was changed.
- Columns of “glued” pellets were formed in the reactor. For this reason, the reactors had to be emptied and started again. Problem was solved as new nozzles were installed and control system was fixed.

Investment for the side stream phosphorus recovery process was 4.2 M€ with the share of capital costs of 55%, and variable costs of 45%. Due to the applied new crystallation technology, the plant received 0.9 M€ governmental funding. The pellet production reached 180 240 t in 1998, with costs of 7.3 €/kg removed phosphorus. The produced pellets were used in the production of chicken fodder (Gaanstra *et al.* 1998) and later as secondary raw material at Thermphos (Giesen 2009b). Controlling the plant required no extra personnel.

Gaanstra *et al.* (1998) evaluate, that the investment and capital costs could be reduced to 5.9 – 6.8 €/kg removed phosphorus. The main problem is the high consumption of acid and base, forming 13% of the variable costs. Another problem is that the Geestmerambacht WWTP is underloaded: in 1998 the plant used only 60 – 65% of the designed capacity. Thus, the other crystallization reactor was shut down and used only as a reserve. In 2010 the situation has not improved: the other Crystalactor® reactor is about to be shut down due to the high operational costs and the age of the installation (Kaper 2010).

5.2 Crystallization / precipitation of struvite

5.2.1 AIRPREX PROCEDURE

The AirPrex procedure was developed by Berliner Wasserbetriebe (BWB), the company attending to the water treatment in Berlin (Germany) and is utilized at the WWTP Waßmannsdorf near the Schönefeld airport. The German company P.C.S. GmbH has a license to market the procedure under the name AirPrex and test runs for building a new AirPrex application are underway in Amsterdam.

The Waßmannsdorf WWTP is one of the six treatment plants of BWB, largest by BOD_5 load, and the second largest in terms of the influent flow. The plant has a capacity of 230 000 m^3/d, with an average influent flow of 180 000 m^3/d during dry weather conditions. Table 12 shows concentrations of the influent and effluent flow in Waßmannsdorf WWTP in 2006.

Table 12: Concentrations (mg/l) of the influent and effluent at WWTP Waßmannsdorf in 2006 (Berliner Wasserbetriebe 2007).

	COD	**BOD_5**	**P_{total}**	**NH_4-N**	**NO_3-N**	**N_{total}**
Influent	1087	389	13.7	65.7	---	---
Effluent	54	4	0.4	0.2	11.6	12

The WWTP at Waßmannsdorf has secondary treatment process with biological phosphorus removal. To ensure the quality of the effluent, the plant can provide iron(III)sulfate precipitation when needed. The waste activated sludge (WAS) holding a dry solids (DS) content of 1% is thickened to 3% DS by flotation and dewatered to 8% DS with centrifuges. The dewatering is aided with 7.5 kg/t DS flocculants. The dewatered WAS is stored in a mixed sludge collection tank with the sludge from primary sedimentation. In the tank, the sludge is heated with heat exchangers to 33 ^oC before pumping it into the mesophilic digestion process.

For the digestion process, the WWPT Waßmannsdorf has six digesters of 8000 m^3 each. The process provides biogas for energy production covering over 60% (90 000 KWh/d) of the total 140 000 KWh/d energy demand of the plant (Lengemann 2010c). The heat generated during the electricity production is used for heating the sludge and the buildings (Berliner Wasserbetriebe 2007).

The flow to the sludge treatment facility is 2000 m^3/d of digested sludge. First, the sludge is dewatered with a centrifuge to 27% DS. Two thirds of the dewatered sludge are transported to a lignite-fired power plant for energy production. The remaining 1/3 is treated in a dryer to reach a dry solid content of 97% and used in a power plant to replace coal (Lengemann 2010a).

Process developement

Spontaneous precipitation of struvite was a problem at Waßmannsdorf WWTP causing incrustations to the sludge treatment equipment. The digested sludge at Waßmannsdorf holds a magnesium concentration of 10 mg/l. Figure 23 presents a bend joint pump and an intake aperture from the centrate pumping station after 319 and 180 operating hours, respectively. Analyses from the incrustations showed that the precipitated material was mainly struvite with small portions of calcium phosphate (Heinzmann 2009).

Figure 23: A Pump and aperture with struvite incrustations (Heinzmann 2009).

The problem was solved by developing a method for controlled precipitation of struvite in co-operation with Technical University of Berlin. The method described here is “the old method” that was operational eight years before the AirPrex procedure, described in the following section. Figure 24 shows the principle of the method and the old precipitation tanks. The digested sludge was transferred to the aerated precipitation tank and stripped from CO_2 with a flow of air. The stripping of CO_2 causes an increase in pH value, and the simultaneous dosage of $MgCl_2$ balances the molar ratio of Mg^{2+}, $NH_4^+$and PO_4^{3-}, inducing the precipitation.

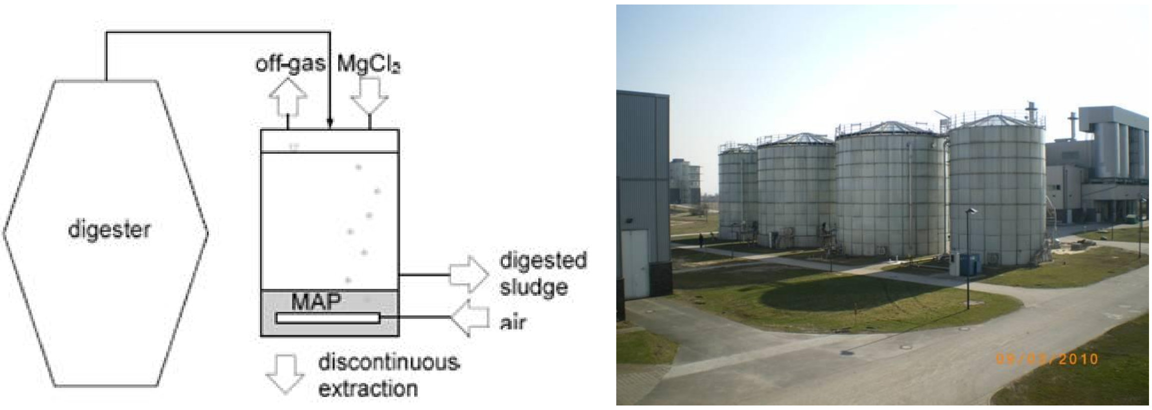

Figure 24: The old method for struvite precipitation (Heinzmann 2009) and the old precipitation tanks (Picture: P. Rantanen) at Waßmannsdorf WWTP.

The process precipitated 20 tons of struvite in 3 months period. Being discontinuous, the aeration and precipitation needed to be stopped while the tank was emptied. Not having a permission for fertilizer use, the struvite was landfilled with disposal costs of 140 €/t. Moreover, there was no efficient method for separating the product from the sludge phase, although different separation methods such as hydrocyclones had been tested (Heinzmann 2009). Nevertheless, the PO_4-P content in the sludge decreased during the precipitation from 300 mg/l to 50 mg/l PO_4-P (Figure 25), decreasing the phosphorus recycle flow and improving the dewaterability of sludge (Lengemann 2010c).

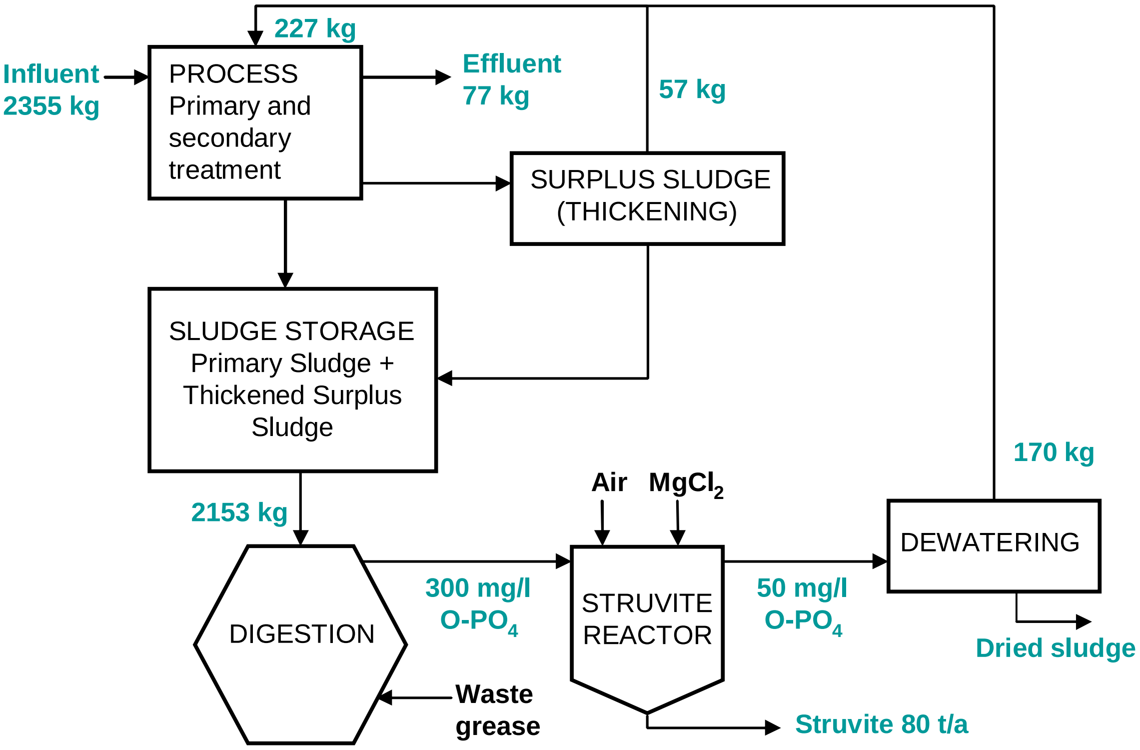

Figure 25: The daily phosphorus balance (kg/d) at WWTP Waßmannsdorf with the "old method" (modified from Lengemann 2010a).

As can be seen from the Figure 25, the primary and the secondary treatment transfer 97% of the phosphorus into the sludge. Comparison between the influent and effluent from the struvite reactor show that the struvite precipitation removed over 83% of PO_4-P. The total internal phosphorus load returning to the process was 227 kg/d consisting of the 57 kg/d flow from the secondary sludge clarifier and 170 kg/d from the sludge dewatering process (Lengemann 2010a).

Process description

The AirPrex Procedure (Figure 26 and in further detail in Figure 28) replaced the old precipitation tanks in 2010. The principle in the AirPrex is the same as in the old method: air-stripping of CO_2 to adjust pH and a dosage of $MgCl_2$ to induce the struvite precipitation. The main difference is the possibility to remove struvite continuously from the bottom of the reactor. In addition, it provides more efficient phosphorus recovery: whereas the effluent from the old precipitation tanks contained 50 mg/l PO_4-P, the new reactor can reach concentrations as low as 5 mg/l PO_4-P showing a decrease of 98% in the PO_4-P content (Figure 27).

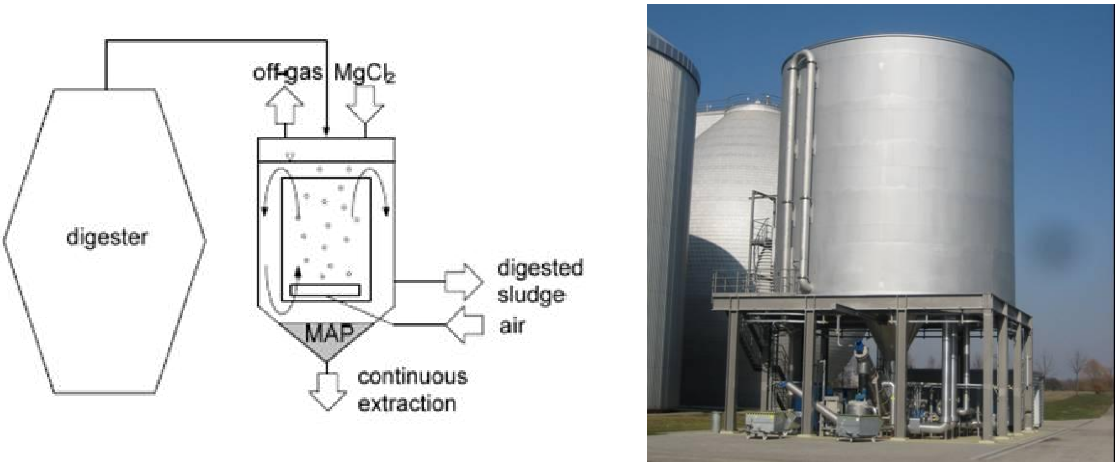

Figure 26: The AirPrex procedure (Heinzmann 2009) and reactor (Picture: J. Nieminen).

As can be seen in the Figure 26, another difference between the new and the old method is the circulating movement of sludge. The air bubbles lift the sludge upwards in the aerated zone in middle of the reactor. After reaching the surface, the sludge settles in the tranquil zone in the outer part of the reactor. The precipitated struvite settles in the bottom of the funnel part as the sludge enters the aerated zone again.

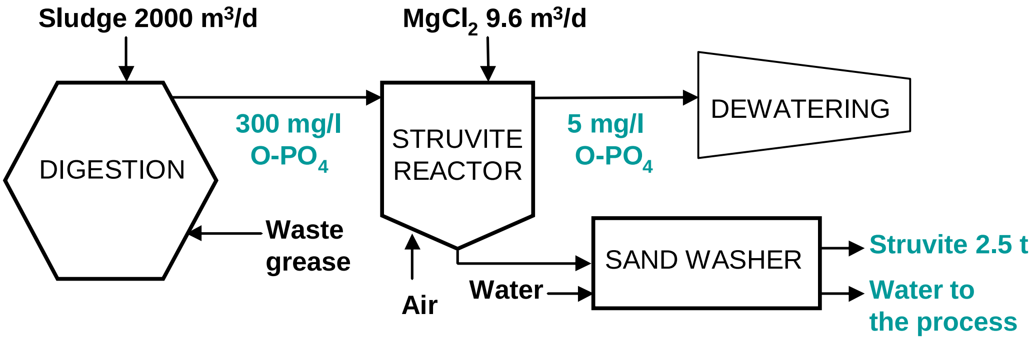

Figure 27: The AirPrex procedure (Lengemann 2010a).

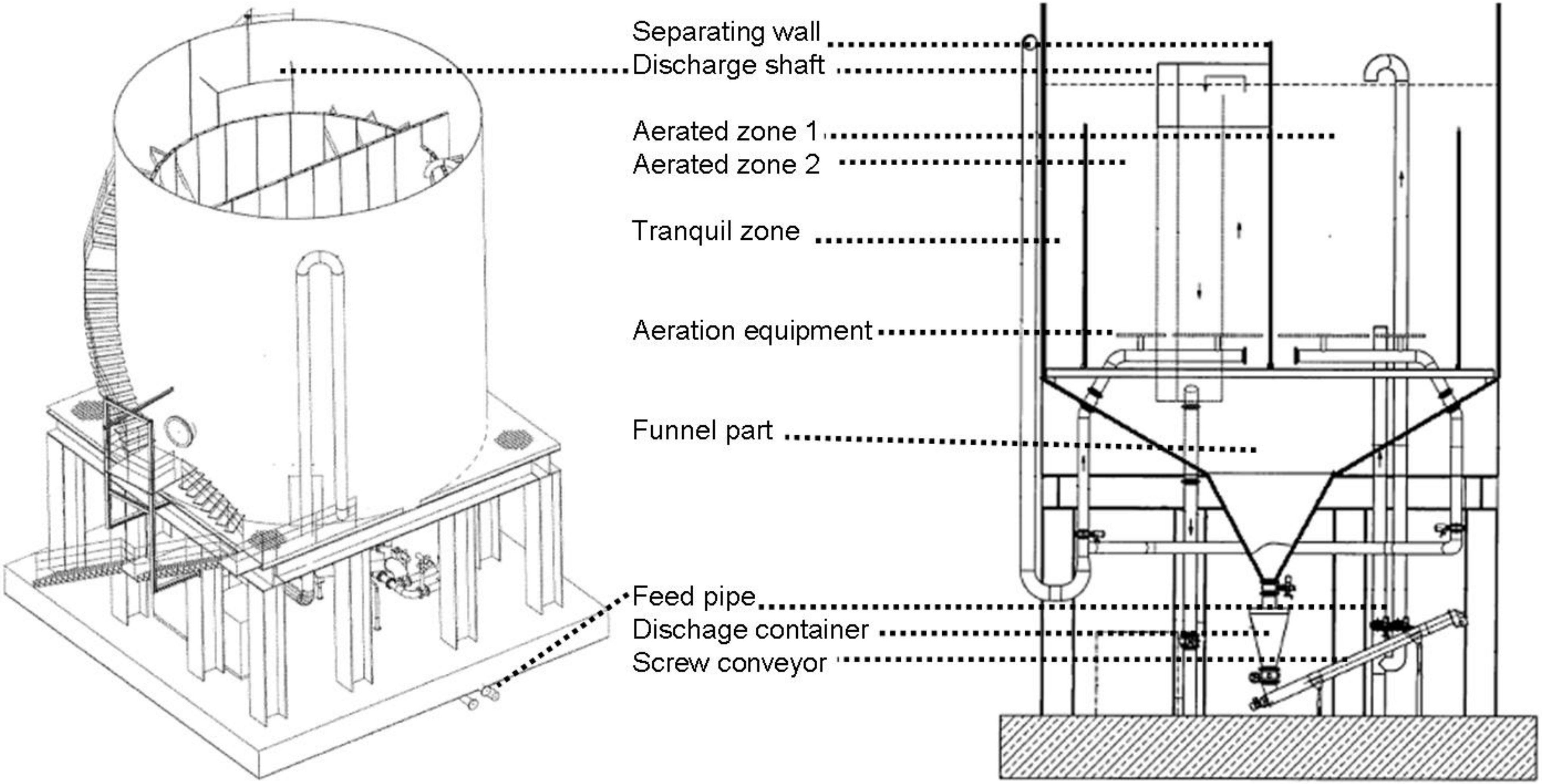

Figure 28: The AirPrex Reactor from above (Lengemann 2010a) and side (Hannemann *et al.* 2009).

The AirPrex reactor at Waßmannsdorf WWTP measures approximately 17 m in height, 10 m in diameter, and 500 m^3 in volume. The HRT in the reactor is 8 hours, during which the sludge is aerated with airflow of 2840 Nm^3/h. The target pH in the reactor is approximately 8, with typical values varying between 7.2 and 7.4. The magnesium chloride solution containing 10% of magnesium is added into the sludge feed pipe just before the sludge enters the reactor. The feed rate of the $MgCl_2$ solution is approximately 400 l/h. The pipeline between digester and reactor is still subject to incrustations, creating a need for anti-incrustation agent (Lengemann 2010a and 2010b).

From Figure 28, it can be noticed that a wall rising above the sludge surface divides the reactor in two zones. The aerated zone 1 removes most of the CO_2. The sludge circulates down the tranquil zone returning to the aerated zone under the aeration equipment. As the sludge enters the aerated zone 2 the rest of the CO_2 is stripped. The sludge leaves the reactor through the discharge shaft in the upper part of the zone 2 (Figure 29). As the sludge travels through the tranquil zone, the struvite settles to the funnel part of the reactor (Hannemann *et al.* 2009).

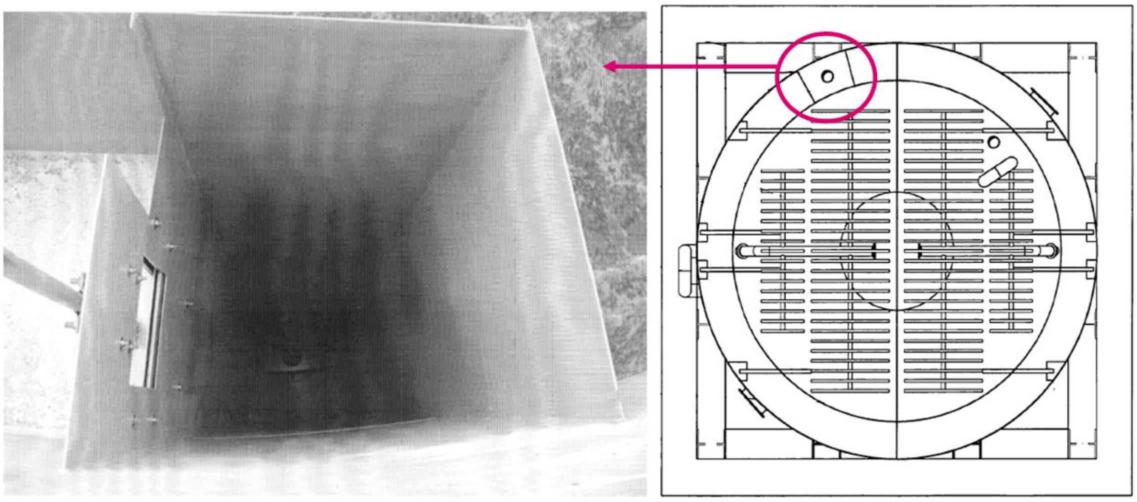

Figure 29: The discharge shaft (Lengemann 2010a) and the cross-sectional view of the reactor (Hannemann *et al.* 2009).

Figure 30 presents the bottom of the reactor with the tip of the funnel part, the discharge container, and the separation machinery with the sand washer, screw conveyors and the metal container trolleys.

Figure 30: The bottom of the AirPrex Reactor.

The funnel needs to be emptied from struvite six times a day. A valve at the bottom of the funnel part prevents the sludge entering the discharge container. As the valve is opened the struvite falls to the discharge container from where it is transferred with a screw conveyer to the sand washer. The sand washer uses water that is afterwards transferred to the wastewater treatment process. The washed struvite is stored in the container trolleys. Targets for the future are a continuous struvite removal process and a storage container for struvite measuring 10 m^3 (Lengemann 2010a).

Experiences and costs

Struvite production is 2.5 t/d and the quality meets the limiting values given in the German fertilizer ordinance. The struvite is sold to be used as raw material in fertilizer production, where it is mixed with another fertilizer. According to Lengemann (2010a), the investment for the new process was 2.5 M€ and the ideal price of the struvite is 50 €/t. This value is calculated taking into account all the costs of the new plant. Converted to €/t phosphorus, the value is 400 €/t.

5.2.2 THE OSTARA PEARL® PROCESS

The Ostara Pearl® process (Figure 31) was developed in University of British Columbia (Canada), and it holds an U.S. Patent 7622047 B2. It has a fluidized bed reactor recovering nutrients from sludge liquor as struvite. The Ostara Group markets the final product struvite under the name Crystal Green™ used as slow release fertilizer at golf courses and municipal lawns. Since 2001, pilot tests have been performed in six different pilot plants for periods from 1 to 8 months. The first industrial scale reactor opened in Edmonton, Canada in May 2007, and other reactors located in the U.S. in Portland (Oregon) and Suffolk (Virginia) started in 2009 and 2010. The fourth reactor will start operating in York (Pennsylvania) in the fall of 2010 (Ostara 2010).

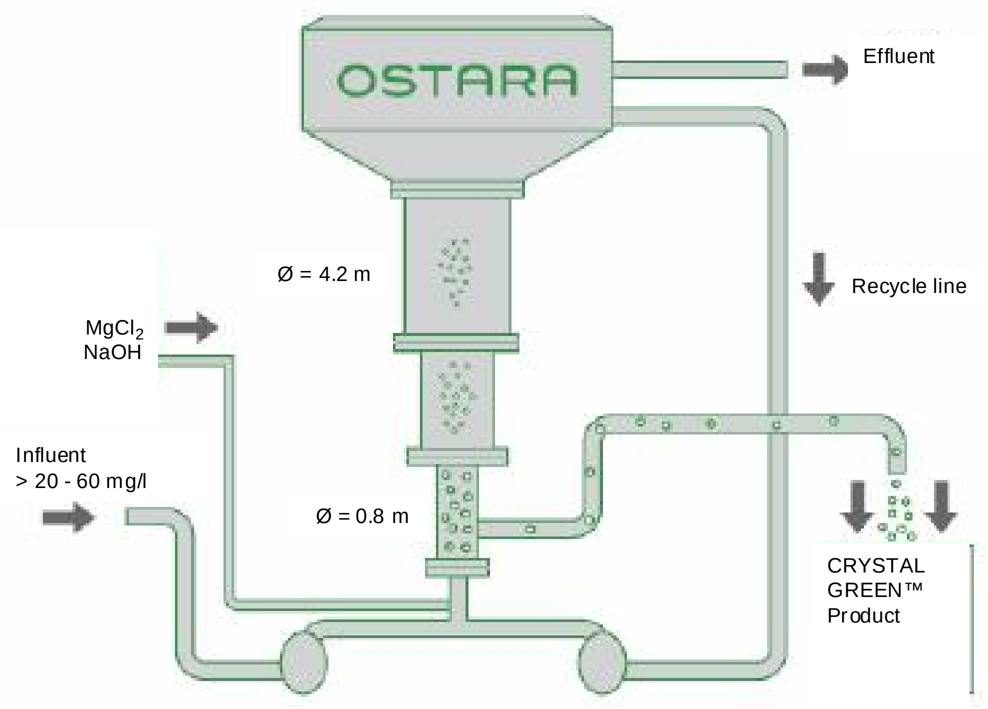

Figure 31: The Ostara struvite precipitation reactor Pearl® (modified from Ostara 2010).

As can be seen, the diameter of the reactor enlargers to the top, the lowest part having a standard diameter of 0.8 m and the settling zone on the top having a standard diameter of 4.2 m. Ostara is developing a larger reactor. The influent is sludge liquor from dewatering process typically containing 100 - 900 mg/l PO_4-P if the WWTP has biological phosphorus removal. With conventional activated sludge process, the concentration of PO_4-P is approximately 60 - 150 mg/l. The minimum flow to the reactor with the nutrient contents needed for economically feasible process can be seen in Table 13. These values ensure the sufficient production of struvite. Concentrations as low as 10 mg/l PO_4-P can be processed, but the limit for feasibility is 20 - 30 mg/l PO_4-P, the preferable concentration being above 60 mg/l PO_4-P. The process could remove even more phosphorus, but the economical feasibility lies in the range of 75 – 95% PO_4-P. Typically, the process removes 85 % of phosphorus and 10 – 15% of ammonium (Ostara 2010).

Table 13: Ostara Pearl® information (Ostara 2010).

Reactor size	
Height	7.3 m
Diameter	0.8 - 4.2 m
Influent	
Flow	500 m^3/d
Minimum PO_4-P flow	70 kg/d
Minimum NH_4-N flow	32 kg/d
Suspended solids content	< 1000 mg/l
Final product	
Struvite production	500 kg/d
Ammonia removal	10 - 50%
Operational parameters	
pH	7.2 - 8.0
Energy consumption	7.2 - 13 kW

Electricity consumption needed for drying the pellets, varies depending on availability of waste heat. One full time equivalent covers the maintenance of the process. The chemical used for precipitation and the pH adjustment are $MgCl_2$ and NaOH, respectively. Struvite production rate is 500 kg/d; the final product is marketed under the name Crystal Green®, having a nutrient formula N-P 5-28, also containing 10% of magnesium.

Ostara offers a turn-key solution for WWTPs that includes the Ostara PEARL® reactor vessel with peripherals such as access platforms, pumps and instrumentation, as well as equipment for chemical handling, screen dryer, and bagging equipment. Before the implementation, Ostara rents a mobile pilot-plant in a scale of 1/100. The capital costs are estimated 2 - 4 M€ the paid-back time being 3 - 5 years.

5.2.3 THE PHOSNIX PROCESS

The Phosnix process was developed in Japan by Unitika Ltd Environmental and Engineering Div. The process is a side stream process that can treat water from a number of processes including digester, industrial, and biological nutrient removal systems. A full-scale application has been in use in lake Shinji Eastern Clarification Center of Shimane Prefecture (SECC), Japan, since 1998. Figure 32 presents the two Phosnix reactors at SECC, the larger treating a stream of 500 m^3/d and the smaller 150 m^3/d. Phosnix can treat flows with 100 – 150 mg/l PO_4-P, recovering 80 - 90% of PO_4-P as struvite. Another reactor of 500 m^3/d started operating in 2000 in Osaka South Ace Centre (GEC 2010).

Figure 32: The Phosnix Process at the lake Shinji Eastern Clarification Center of Shimane Prefecture (SECC), Japan (Nawa 2009).

As can be seen in Figure 33, the inflow to the reactor is liquid phase from sludge dewatering, containing approximately 120 mg/l PO_4-P. The figure success, that the reduction of 100 mg/l PO_4-P, equaling 83% of the influent phosphate concentration.

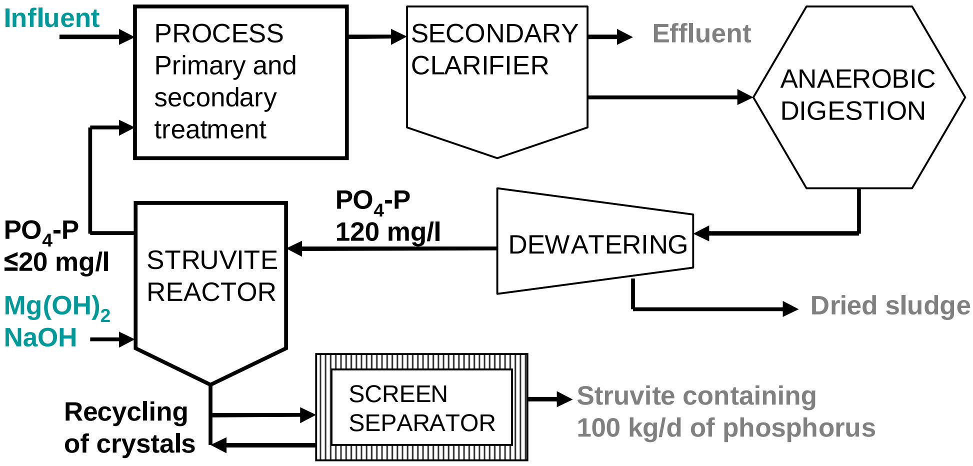

Figure 33: The Phosnix process (Nawa 2009).

The amount of precipitated phosphorus, 100 kg/d, is for a plant with capacity of 1000 m^3/d. The effluent from the Phosnix reactor is transferred to the beginning of the wastewater treatment process (Nawa 2009). The process reduces the need for precipitation chemicals in the activated sludge process as well as in the sludge dewatering step (Ueno and Fuji 2001).

The reactor is an air-agitated column with chemical dosing equipment (Stratful *et al.* 1999). The sludge liquor is pumped to the bottom of the reactor and the chemicals, sodium hydroxide and $Mg(OH)_2$, are added for precipitation and pH adjustment to pH 8.5 – 8.8 (Nawa 2009). Crystals grow, and sink to the bottom of the column where they are removed periodically. Fine struvite particles separated from the product struvite, are fed back to the reactor as seed material. Struvite granules of 0.5 – 1.0 mm form in ten days retention time. The product is dewatered for 24 hours in filter bag system or natural drying in an ambient temperature. (Stratful *et al.* 1999) The water content of the final product is <10% (Nawa 2009).

The produced struvite is sold to fertilizer company for 250 €/t. Transport costs are covered by the purchaser. The company mixes the struvite with other products and adds potassium to produce a fertilizer sold in 20 kg bag for 100 – 200 € (CEEP 2001). Estimated savings using phosphorus recovery as part of the water treatment process are 171 000 €/a, calculated with a price of struvite 210 €/t. In his paper Stratful *et al.* (1999) states that Unitika claims total operation cost of a plant with 500 m^3/d influent containing 50 mg/l PO_4-P 70 £/d (83 €/d at the current conversion price), including maintenance. The estimate is considerably lower compared to costs of similar sized plant with chemical phosphorus removal with aluminum sulfate, 420 £/d (284 €/d at the current conversion price) (Stratful *et al.* 1999).

5.3 Wet chemical process

5.3.1 THE SEABORNE PROCESS

The Seaborne Process is a complex network of unit operations, suitable for recovering nutrients from various biomasses, such as sludge from wastewater treatment plants, manure, and agricultural waste. It was developed and patented by a German company Seaborne Environmental Research Laboratory (EPM AG). The first full-scale implementation is located at Gifhorn WWTP in Germany. Earlier, the thickened sewage sludge from the Gifhorn WWTP was utilized in agriculture as fertilizer, but the general interest, limits in heavy metal content, pressures created by discussion concerning organic toxins and drug residues led to a need for new sludge treatment method (Bayerle 2010).

The Gifhorn WWTP has an influent flow of 6500 m^3/d corresponding to 50 000 p.e. The secondary treatment consists of three activated sludge tanks (2900 m^3 each) and three clarifiers (2700 m^3 each). Digestion capacity consists of two mesophilic digesters (2000 m^3 each), built in 1972 (Bayerle 2009). The inflow to the digester consists of 60 m^3/d primary sludge, 40 m^3/d of secondary sludge, and 20 m^3/d of waste grease from food industry. A storage tank levels off volume changes in the flow from the digester, the feed to the process being 110 m^3/d.

Process development

The construction of the process at Gifhorn WWTP started in 2003, being ready for the basic mass balance monitoring in 2004. In co-operation were the Institute of Sanitary and Environmental Engineering at the Technical University of Braunschweig and the institute of Waste Quality and Waste management at the University of Hannover. The operation started in 2005 and a testing period before continuous operation lasted until 2007 (Müller *et al.* 2007).

Figure 34 presents a partial view from the Gifhorn process hall. The first figure has centrifuges in the front and the precipitation step tanks in the back. The other shows the RoHM (Removal of Heavy Metals) unit.

Figure 34: Partial view of the Seaborne Process at Gifhorn WWTP.

The original patented Seaborne process needed modifications to meet the economical requirements of Gifhorn WWTP. The modifications and solutions for the Gifhorn process are presented is Table 14. Figure 35 presents the patented process as described by Vesterager (2009) and Figure 36 in the next section presents the implemented process in Gifhorn.

Table 14: Summary of the modifications at Gifhorn plant.

Patented version	The Gifhorn Process
Acid leaching	
Circulation between two units with different pH.	The target pH value is 2, but due to the increased price of sulfuric acid, the process uses pH 4.5 - 5.
The patent does not include a detailed treatment for organic residues, but suggests incineration	The residue can not be incinerated due to the heavy metal content, but is composted instead.
Oxidizing agent	Not used
Separation unit	Separation with centrifuge
Removal of heavy metals	
pH adjustment with base, NaOH preferred	Higher pH in the previous step reduces the consumption of the base.
Digester gas is exploited to precipitate the heavy metals simultaneously cleaning the gas from sulfides.	Na_2S replaces the digester gas.
Separation	Separation with band filter
Precipitation	
Me^{2+}, preferably MgO for the precipitation.	MgO is mixed with water producing $Mg(OH)_2$.
Stripping	
Stripping unit for producing ammonium rich flow to be used in fertilizer industry.	The stripping unit is not in use due to problems with calcium precipitation.

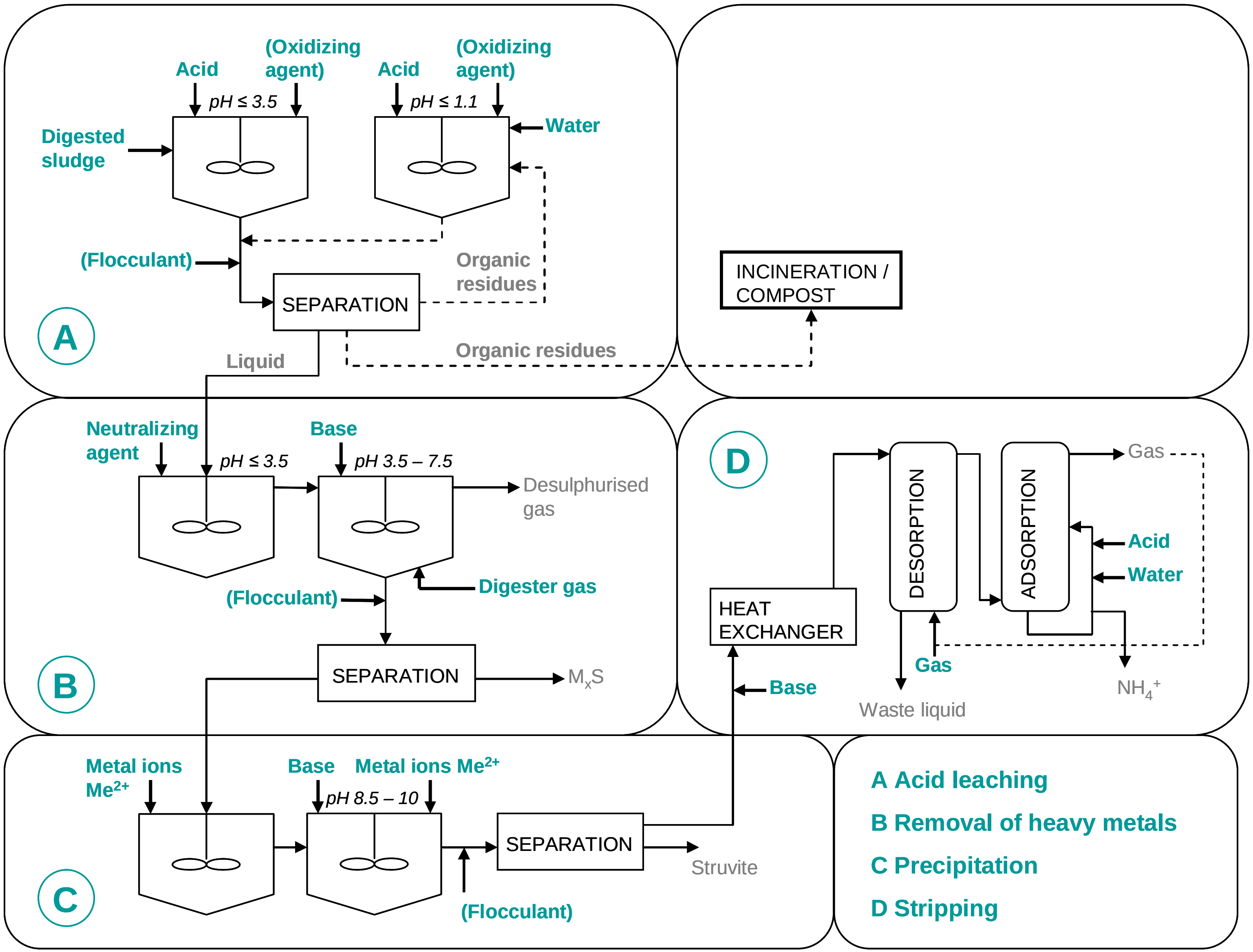

Figure 35: The patented version of the Seaborne process (modified from Vesterager 2009).

Process description

The process consists of three main steps presented in Figure 36: acid leaching, removal of heavy metals and the precipitation of struvite. In addition to these steps, the process contains stripping unit for ammonium recovery. Due to problems with calcium precipitation, the stripping unit is not at the moment operational and the ammonium rich flow returns to the beginning of the process (Bayerle 2010). The designed concentrations of nitrogen and phosphorus in the influent are 1800 mg/l and 1000 mg/l, respectively (Bayerle 2010). However, according to Bayerle (2010), the phosphorus concentration entering the Seaborne process is 600 mg/l.

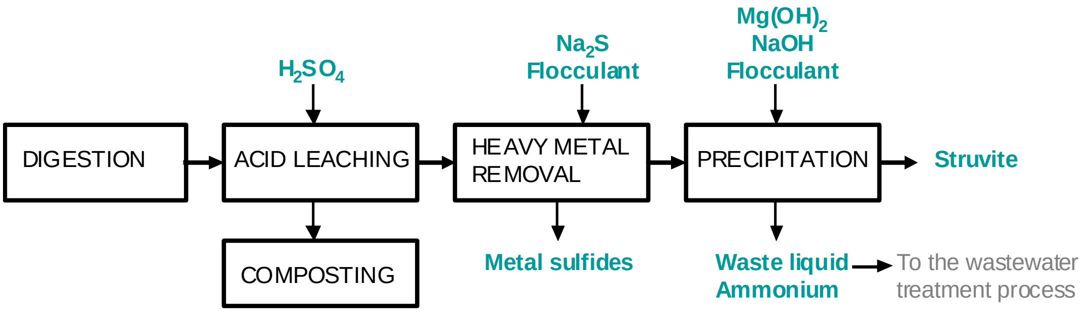

Figure 36: Flowchart of the Seaborne process at Gifhorn (Bayerle 2010).

In the acid leaching step in the patented method, the digested sludge is mixed with an acid (H_2SO_4) and an oxidizing agent (H_2O_2) to lower the pH below 3.5. The oxidizing agent is optional but it improves the dissolution of the heavy metals and phosphates. If included in the process, the oxidizing agent can be added simultaneously with the acid or after it. The mixture is circulated to another leaching tank with pH 1.1 for thorough dilution (Vesterager 2009). The Gifhorn process has only one acid leaching stage with a target value of pH 2. Reaching this value would require 7.4 l/m^3 sulfuric acid. For economical reasons, the operational area was set to pH 4.5 - 5 reached with 4.5 l/m^3 sulfuric acid. Compared with the start of the project in 2006, the chemicals prices have more than doubled (Bayerle 2010). After two hours, the insoluble part is separated in a centrifuge. To improve the separation, flocculent is added before the mixture enters the centrifuge. Options for the treatment of the residue are incineration, thermal drying and composting.

The operational area pH 4.5 – pH 5 dissolves approximately 50% of the total phosphorus but do not transfer considerable amounts of heavy metals to the liquid phase. Hence, most of the heavy metals are removed with the undissolved part from the acid leaching step excluding incineration as treatment option. Nevertheless, according to Bayerle (2010), this is not a problem, since the concentrations of heavy metals are low in the sludge.

The liquid phase containing dissolved phosphorus, nitrogen and heavy metals goes to the removal of heavy metals (RoHM) step. As the pH is already on the target level at pH 4 – 4.5, NaOH dosage is not necessarily needed. Removal of heavy metals is not executed by exploiting digester gas as in the original Seaborne process, but with a substituting chemical Na_2S. Since the dissolved heavy metal fraction in the acid leaching step is smaller than designed, only a about 20 kg/d of heavy metal sulfides precipitate. The solid material is separated in a belt filter and landfilled with costs of 200 €/t.

The third step is the struvite precipitation. The pH is increased to 8.7 - 9 with NaOH and $Mg(OH)_2$ added to induce precipitation. The magnesium hydroxide is prepared in situ from MgO delivered in sack, and mixed with water. The magnesium dosage is controlled by observing daily the precipitation reactor effluent. The flow leaving the process contains about 5 - 6 mg/l phosphorus and 250 mg/l nitrogen. Precipitated product is dewatered by centrifuges (Bayerle 2010).

The last step in the process is the stripping of the excess ammonium removing the NH_3/NH_4 from the liquid phase. The stripping unit is not operational due to the problems with calcium precipitation in the column. The patented method for stripping is to increase the pH value to pH 8.5 – pH 10.5 by adding a base (NaOH), after which the temperature is raised to 50^oC in a heat exchanger. The warm liquid enters the desorption unit where, together with a high specific surface, the counter current gas flow transfers the NH_3 from the liquid phase to the gas phase. The gas from desorption is sent to the adsorption unit where the gas containing NH_3 is washed with a counter current of an acidic solution (water and H_2SO_4). The reaction between the ammonia and the acid produces NH_4^+ transferred to the liquid phase. The liquid phase is recirculated in the adsorption column (Vesterager 2009). The concentrations of NH_4-N and PO_4-P in the stripping effluent were estimated < 40 mg/l and < 6 mg/l respectively, the planned product being 38% $(NH_4)_2SO_4$ diammonium sulfate. As the solution for the stripping unit problems is studied: an increase of the share of calcium phosphate in the final product would remove calcium before the stripping columns (Bayerle 2010).

The formed product contains $MgNH_4PO_4$, $Mg_3(PO_4)_2$, $Ca_3(PO_4)_2$, $(NH_4)_3PO_4$, $MgHPO_4{\cdot}3H_2O$ $CaHPO_4{\cdot}nH_2O$ and $(NH_4)_2HPO_4$ (Bayerle 2010). The precipitated product is not crystalloid as the Waßmannsdorf struvite; about 90% is amorphous and crystal content is about 10% (Bayerle 2009). Figure 37 shows the produced struvite: the first beaker contains struvite after atmospheric drying, the second after centrifuge separation, and the third the liquid phase from the centrifuge.

Figure 37: Amorphous struvite from Seaborne process after atmospheric drying and after centrifuge separation, as well as the liquid phase from the centrifuge.

Costs and experiences

The complicated process has faced many challenges; by March 2010, the process had been working properly only for two weeks after the start-up (Bayerle 2010). The problems with pH adjustment result in decreased struvite production that is currently 250 t/a, the maximal production with pH 2 being 500 t/a. The produced struvite with 50 % DS has been sold for 5 €/t to be used as fertilizer. As can be seen in Table 15, the major part of the costs derive from chemical consumption, showing also that with pH 4, the specific cost for recovered phosphorus is approximately 15 €/kg PO_4^{3-}, equalling 46 €/kg phosphorus.

Table 15. Costs and chemical consumption of the Seaborne process with several pH values (Bayerle 2009).

pH value	**Chemical consumption (kg/kg DS)**			**Specific costs**	**Yield**	**Cost distribution**	
	H_2SO_4	NaOH	$Mg(OH)_2$	(€/kg PO_4^{3-})	(kg PO_4^{3-}/a)	Depreciation and Maintenance costs	Chemical costs
7	0	7.1	0.7	20.19	4.715	62%	38%
6	5.7	10.1	0.4	17.30	6.800	50%	50%
5	10.7	14.2	0.3	15.68	9.823	38%	62%
4	15.3	19.4	0.8	14.72	13.010	29%	71%
3	19.9	28.4	1.4	14.22	17.681	23%	71%

Table 16 presents the investment costs of the Seaborne process in Gifhorn. The federal-state of Lower Saxony funded the project with 3822 M€, covering 50.6% of the total costs (Adam 2009).

Table 16: Investment costs of the Seaborne process in Gifhorn (Bayerle 2010).

	M€
The process shed building	1274
Digestion, energy, miscellaneous	1284
Technical costs	2987
Engineering costs	1012
Technical and scientific monitoring	1000
Total	**7557**
Lower Saxony funding (50.6 %)	3822
Gifhorn	3735

Although, the Seaborne is not feasible now, a re-evaluation should occur in 5 – 10 years. Possible future Seaborne processes should be designed more simple with larger reactors. In addition, operating a plant twice or three times larger or collecting sludge from several plants would increase the feasibility (Bayerle 2010).

5.4 Summary of the full-scale processes

The five industrial-scale processes described in this Chapter represent crystallization and precipitation, and wet chemical methods. The processes showing the best operative performance include AirPrex, Ostara Pearl® and Unitika Phosnix recovering phosphorus as struvite from sludge liquor. Crystalactor®, using calcium phosphate crystallization, has experienced difficulties related to the feasibility of the process, and Seaborne at Gifhorn WWTP is described as "a big pilot" by Bayerle (2010). Table 17 lists the processes described in this Chapter.

The operational processes are all located at WWTPs with anaerobic digestion. The final product has a value and is sold to fertilizer industry or used as fertilizer. As can be seen in Table 18, the production rate of struvite is about 1 kg struvite per 100 m^3 influent (Shu *et al.* 2006), when the influent has a concentration of about 100 mg/l PO_4-P. In addition, the table presents the flow to the WWTP and the inflow to the process with estimated concentration of phosphorus and the production rates.

The Seaborne is the first industrial-scale implementation, thus an important landmark for wet chemical processes. Although the Seaborne process is not yet feasible, a re-evaluation should occur in 5 - 10 years to see the developments in the prices of fertilizers and chemicals. According to Bayerle (2010) the future plants should treat sludge from several WWTPs or one large WWTP to increase the feasibility. The process should be twice or three times larger than the Gifhorn process.

Table 19 lists the main chemicals used in the processes.

Table 17: The industrial-scale processes.

Full-scale process	Owner	Developer	Location	Start-up	Feed material	Method	Final product
AirPrex	Berliner Wasserbetriebe / License: P.C.S GmbH	Berliner Wasserbetriebe	Waßmannsdorf, Berlin, Germany	2010	Digested sludge / sludge liquor	Crystallization	Struvite
Crystalactor®	Waterboard Uitwaterende Sluizen	DVH Water BV	Geestmerambacht, the Netherlands	1988	Liquid	Crystallization	Calcium phosphate
Ostara Pearl™	Gold Bar WWTP, Edmonton	University of British Columbia / Ostara	Edmonton	2007	Liquid	Crystallization	Struvite
Phosnix	The lake Shinji Eastern Clarification Center of Shimane Prefecture (SECC)	Unitika Ltd.	Shimane Prefecture, Japan	1998	Liquid	Crystallization	Struvite
Seaborne	The city of Gifhorn	Seaborne Environmental research laboratory	Gifhorn, Germany	2005	Digested sludge	Acid leaching, crystallization	Struvite

Table 18: The flow of the processes.

	Inflow of the WWTP		Feed material flow	P concentration in influent	P concentration in the effluent	Production
	m^3/d	p.e.	m^3/d	mg/l PO_4-P		kg/d
AirPrex	180 000	230 000	2 000	300 mg/l	< 5mg/l	2 500
Crystalactor®	120 000	230 000	6 000	50-80 mg/l	15-20 mg/l	4 600
Ostara Pearl™	n.f.	700 000	500	100 - 900 mg/l	n.f.	500
Phosnix	45 000	n.f.	500 + 150	100 - 110 mg/l	10 mg/l	500 - 550
Seaborne	6 500	50 000	110	600 mg/l P_{tot}	5 - 6 mg/l P_{tot}	680

n.f. Not found

Table 19: Chemicals used in the processes.

	Chemical	Purpose	Consumption	Additional information
AirPrex	$MgCl_2$	Magnesium source for struvite precipitation	400 l/h	(33% Mg) Brenntafloc ML 200
	Rockaway PX 60 N	Incrustation preventing agent		Marketed by: P.C.S GmbH
	Flocculent Praestol® 40560			Material: 737092, Ashland
Crystalactor	Sand	Seed material		
	NaOH	Adjusting pH for crystallization		
	$Ca(OH)_2$	Calcium source for crystallization		
Pearl	NaOH	Adjusting pH for struvite precipitation		
	$Mg(OH)_2$	Magnesium source for struvite precipitation		
Phosnix	NaOH	Adjusting pH for struvite precipitation		
	$Mg(OH)_2$	Magnesium source for struvite precipitation		
Seaborne	H_2SO_4	Acid leaching	240 000 t/a	
	Na_2S	Precipitation of the heavy metals	12 t/a	
	NaOH	Adjusting pH for struvite precipitation	100 t/a	
	MgO	Magnesium source for struvite precipitation	20 t/a	
	Flocculent Praestol® K 255 L			Material: 371792, Ashland

6 PILOT AND LABORATORY SCALE PROCESSES

6.1 Crystallization / precipitation

6.1.1 P-RoC

The P-RoC process (Phosphorus Recovery from wastewater by Crystallization of calcium phosphate compounds) was developed in Germany, at Forschungszentrum Karlsruhe GmbH, ITC-WGT (the Institute of Technical Chemistry – Water- and Geotechnology Division) in co-operation with Universities of Karlsruhe and Darmstadt and the Leibniz University Hannover (Hermann 2009a).

The P-RoC (Figure 38) is a crystallization process using calcium silicate hydrate (CSH) as seed material to produce calcium phosphates from concentrated side stream. The maximum recovery potential is estimated 45% of total phosphorus (Hermann 2009a).

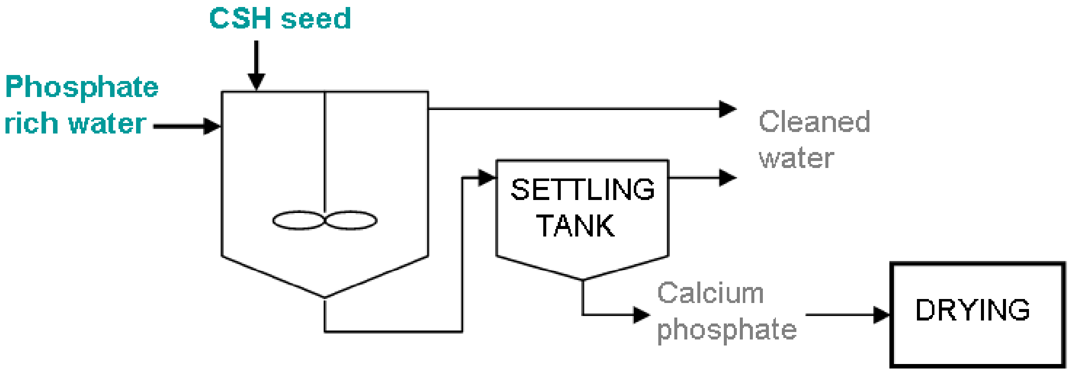

Figure 38: The P-RoC process flow chart (Berg and Schaum 2005).

CSH, or Tobermorite (Figure 39), is a by-product in building material industry. Due to the calcium content of the compound, it can be utilized as the calcium doner in the process. Due to the seed material CHS, a simultaneous increase in pH occurrs and the process requires no additional chemicals (Berg *et al.* 2006a). The mixture of phosphorus rich water and seed material is agitated in a reactor for two hours after which the product is separated and dried (Hermann 2009a). The proposed separation and drying methods are a settling tank and utilization of solar power (Berg *et al.* 2006a).

Figure 39: CSH granules (Petzet and Cornel 2009).

Berg *et al.* (2006a) tested the P-RoC both in laboratory-scale and in pilot-scale with fixed bed, stirred, and expanded bed reactors. The stirred reactor was proved to be the economical and technical optimum, although further studies are needed to prevent the seed material escaping the reactor. The final product was analyzed for total phosphorus, mineralogical composition, and surface morphology with Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Fluorescence (EDX). The analyses showed that calcium phosphate crystallized on the surface of CSH and over time, the seed completely transformed into calcium phosphate (Hermann 2009a).

The pilot-scale tests show that the production of crystals with 13% phosphorus content equaling 30% P_2O_5 is possible. Furthermore, the iron, cadmium and uranium levels are below those in natural phosphate rock. Hence, the product is suitable for phosphate industry as a substitute raw material (Berg *et al.* 2006a).

In their study, Berg *et al.* (2006b) evaluate the costs for the total phosphorus recovery process including the investment and running costs for a plant of 45 000 p.e. with hydraulic load of 250 l/d per capita. Maintenance costs were estimated 0.5% of the investment costs per year. The sales value of the product was not included in the estimate, presented in Table 20). If the problems with the seed material loss are solved, the continuous stirred process in large scale is the most economical choice (Berg *et al.* 2006b).

Table 20: Cost evaluation for the P-Roc Process with reactor options (Berg *et al.* 2006b).

Process	Annual costs (€/p.e./a)
Phostrip	0.79
Pre-treatment	0.32
Crystallization	
Fixed bed	1.71
Stirred reactor, discontinuous batch	1.30
Stirred reactor, continuous flow	1.10
Expanded bed	0.95 - 1.24
Solar drying	0.09
Total	**2.14 - 2.90**

The future development aims at the implementation in full scale and concentrates on the optimization of the stirred reactor process, the material selection and the suitability studies of the final product for fertilizer use (Berg *et al*. 2006b).

6.1.2 PRISA PROCESS

The PRISA (Phosphorus Recovery by ISA) process was developed in RWTH Aachen University (Germany) at the Institute of Environmental Engineering (ISA). The process aims at phosphorus and ammonium recovery precipitating struvite from supernatant liquor separated from the sludge in the thickeners before and after anaerobic digestion (Montag *et al.* 2007). Figure 40 presents the simplified flow chart of the PRISA process.

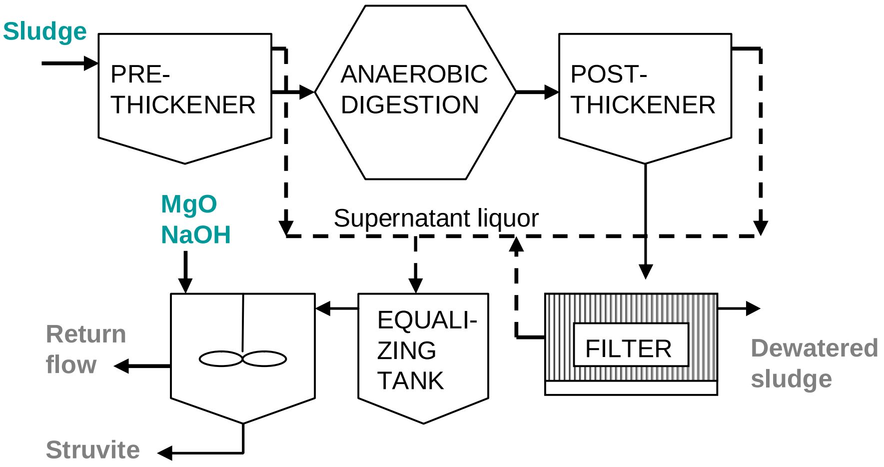

Figure 40: Simplified flow chart of the PRISA process (Montag *et al.* 2007).

The first step in the pre-thickener acidifies the sludge, thus releasing phosphorus to the liquid. The acidification is achieved by an extended HRT and periodical stirring. Montag *et al.* (2007) establish that HRT of three days and stirring the sludge once or twice a day result in dissolution levels of over 20% of dissolved PO_4-P. The equalizing tank collects the supernatant flows from the pre-thickener, the post-thickener, and the filter. In the reactor, a dosage of MgO and pH adjustment with NaOH precipitate struvite. Montag *et al.* (2007) found that pH above 9.2 and Mg:N:P ratio of 1.5:6:1 precipitate over 90% of the PO_4-P.

6.1.3 THE REM NUT® ION EXCHANGE PROCESS

Process development

The Rem Nut® (Removal of Nutrients) process was developed in the mid-1980s at Italy's National Council. The principal of the method is to remove nutrients from secondary treatment effluent with ion exchange columns using cationic resin for ammonium ions, and basic resin for phosphate ions. The regeneration of the resins produces nutrient containing eluents that are mixed with magnesium salt precipitating the nutrients as struvite. Because of this process step, the process was profiled under the struvite precipitation section. The process is directed to small to medium sized WWTPs that can integrate the process to ensure the quality of the effluent after secondary treatment (Liberti *et al.* 2001). However, the regulations for phosphorus concentrations in effluent, that at the times did not create a need for further polishing of the nutrient levels in the secondary effluent (CEEP 2001).

Originally, the process was designed for nutrient recovery on teh basis of the ammonium content in the process liquid. As ammonium concentrations compared to phosphorus concentrations in wastewater are five-fold, the method required a dosage of both magnesium and phosphorus to precipitate the ammonium, resulting in high chemical costs. Thus, the Rem Nut® was re-evaluated and modified to "P-driven" process (Figure 41) aiming at the recovery of phosphorus rather than ammonium. The new method reduced the capital costs, equipment size, operating and chemical costs. However, removal of the excess ammonia needed to be performed with other methods (CEEP 2001).

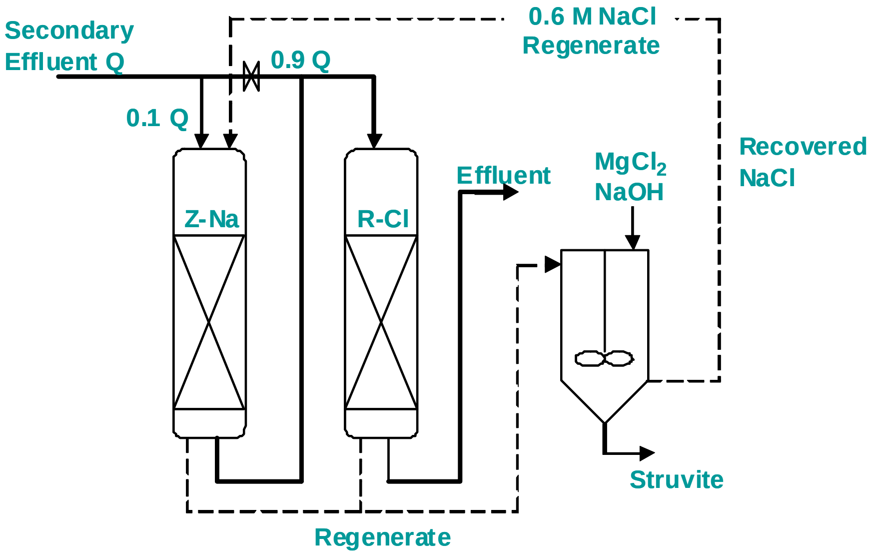

Figure 41: The "P-driven" Rem Nut® ion exchanger process flowchart (Liberti *et al.* 2001).

As can be seen in the Figure, the "P-driven" Rem Nut® processes the whole influent stream in the anionic resin column, whereas only 1/10 is passing through the cationic resin (Liberti *et al*. 2001).

Process description

As described by Stratful *et al.* (1999) the liquid from secondary treatment is controlled for pH and temperature, and the flow is measured with rotameter. The liquid enters the cationic resin column with 0.45 m^3 natural zeolite (Clinoptilolite), where ammonium ions are removed. Then the flow is led to the anionic column with 0.43 m^3 strongly basic resin removing phosphate ions. The reactions in the columns are:

$$\text{Z-Na} + NH_4^+ (K^+) \leftrightarrow \text{Z-}NH_4 + Na^+ \qquad (17)$$

$$2\text{R-Cl} + HPO_4^{2-} \leftrightarrow R_2\text{-}HPO_4 + 2Cl^- \qquad (18)$$

Where Z = zeolite, R = anion exchanger (Liberti *et al.* 2001).

The process consists of two columns with both resins, thus enabling continuous process during regeneration. Regeneration is needed every 3 hours with a flow rate of 30 m^3/cycle (Stratful *et al.* 1999). Seawater can be used in regeneration when possible, resulting in estimated savings of over 80% of chemical costs. Otherwise, 0.6 M NaCl solution is recirculated four times as a closed loop (Liberti *et al.* 2001). Cationic resin is regenerated with 2.6 m^3, and the anionic resin with 2 x 0.86 m^3 of the NaCl solution. The elutes are mixed and the lacking substances for struvite precipitation ratio are added. The final product is stored in filter bags letting the supernatant drain off before returning it to the process. At this point, the product is sludge-like with high solids concentration (Stratful *et al.*1999).

Costs and Experiences

Typical negative factors in ion exchangers include relatively high cost, environmental impact of regeneration eluents, and the fouling of ion exchangers. These effects are decreased by a closed loop technology developed for Rem Nut® (Liberti *et al.* 2001). Additional problems in anionic resins are poor selectivity towards phosphates leading to low operative retention capacity, inefficient regeneration, and gradual loss of the loading capacity due to the fouling phenomena (Petruzzelli *et al.* 2003). NH_4-selective natural zeolite and commercial anion exchanger seem to be able to remove phosphorus to meet the requirements for effluent quality. However, commercial availability is weak for synthetic and natural zeolites because they are limited to specialized applications in the US and the United Kingdom (Liberti *et al.* 2001).

The process has been tested in pilot-scale: in 1983, a fully automatic pilot plant with capacity of 240 m^3/d was located at West Bari WWTP in southeast Italy. Another pilot plant was opened in 1986 at South Lyon in Michigan, USA (Liberti *et al.* 2001). Intentions to build a full-scale plant failed in 1998 as the readily planned application with financial approvals lost the buyer of the produced struvite in the closedown of the nearby fertilizer factory (CEEP 2001).

Liberti *et al.* (2001) estimate that the total investment of the Rem Nut® process in a WWTP with an influent flow of 11 000 m^3/d, would be 440 000 €, the operational costs 336 900 €/a, and the net unit cost 0.048 €/m^3. The production of struvite is estimated 285 t/a.

Petruzzelli *et al*. (2003) tested a phosphate selective resin, based on the commercialized DOWEX 4195. The resin was based new promising ion exchanger that, according to previous tests, shows good selectivity towards phosphates. It was developed in USA at Lehigh University, Pennsylvania. The reference materials are based on the use of commercial weak base anion exchanger saturated with copper ions. The resin was first tested in laboratory for the phosphate selectivity. The tests showed that the phosphorus level stayed below 1 mg P/l during 400 bed volumes, and the phosphorus recovery rate was over 95% in regeneration (Petruzzelli *et al.* 2003). The resin was tested in the pilot plant with the capacity of 0.1 m^3/d. The pilot for this study was located at the Grottaglie-Monteiasi WWTP, having an inflow of 3 000 m^3/d and 20 000 p.e. The experiments showed half the capacity detected in the laboratory-scale experiments. The leakage stayed below 1 mg P/l during 150 - 200 BV. Regeneration was performed using 1M NaCl pH 4.3 with 2 BV and resulted in over 95% recovery. No fouling of the polymer matrix was observed, but the results were not encouraging in terms of performance improvement of the new sorbent. Although the resins are improving, the feasibility of the process has to be evaluated. Often the ion exchangers are too expensive in full-scale use (Petruzzelli *et al.* 2003).

6.2 Wet chemical

6.2.1 THE SEPHOS AND THE ADVANCED SEPHOS PROCESS

The SEPHOS process (Sequential Precipitation of Phosphorus) was developed in the Technical University of Darmstadt (Germany), at the Institute of Water Technology (WAR) as part of a two-year project funded by the federal state of North Rhine-Westphalia. The SEPHOS Process is based on the studies of Schaum (2007) on the wet chemical approach of phosphorus recovery from sewage sludge ash.

First step of the SEPHOS process is the elution of ash with H_2SO_4 to reach pH value below 1.5 dissolving phosphorus and most of the metals (Figure 42). Undissolved residues are removed from the mixture and pH increased stepwise with caustic soda to pH 3.5.

Aluminum phosphates precipitate below pH 3.5 whereas heavy metals remain dissolved. The produced aluminum phosphate is separated and suitable for the electrochemical process of Thermphos, although more development is needed on the product quality, such as reduction of sulfur and sodium. Due to the high aluminum content, the SEPHOS product is not suitable for agriculture, since aluminum can cause root damage (Schaum *et al.* 2005).

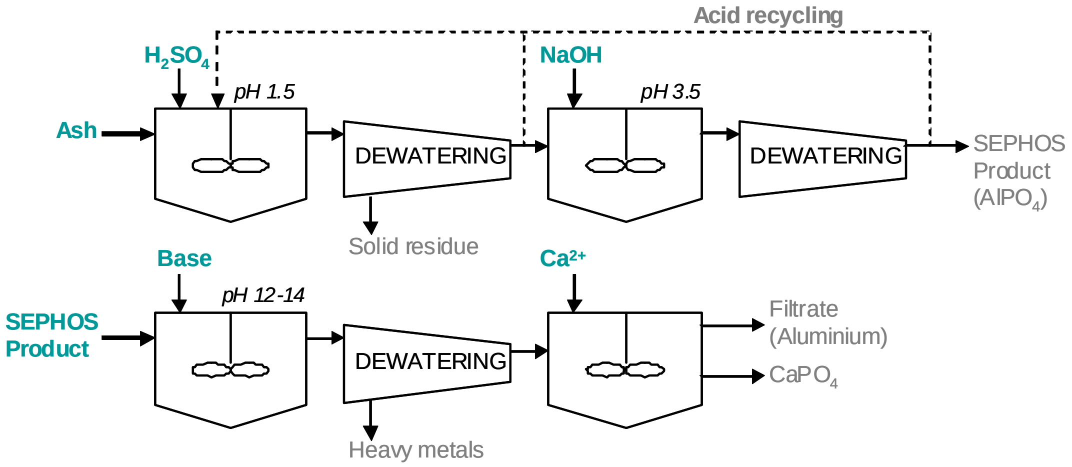

Figure 42: The SEPHOS Process and the Advanced SEPHOS Process (modified from Schaum *et al.* 2005).

Further processing with the advanced SEPHOS process recovers calcium phosphate that can be used in agriculture. The SEPHOS product is treated with base in pH 12 - 14. This dissolves aluminum and phosphate, but the most heavy metals remain solid and can be separated. The liquid rich in dissolved phosphorus and aluminum is transferred to a reactor where a dosage of calcium ions precipitate calcium phosphate (Schaum *et al.* 2005).

After phosphorus removal from the liquid, the remaining aluminum can be reused as precipitant at a WWTP. Crystallization with P-RoC process, using CSH as seed material has been tested with promising results to replace the precipitation (Schaum *et al.* 2005).

The analyses from the product showed that the SEPHOS product had a phosphorus content of 12% whereas the phosphorus content in the ash before treatment was 9.8%. Compared to the test on the aluminum ash before and after SEPHOS treatment, the heavy metals content had reduced about 70 to 90% (Schaum *et al.* 2005). By adding sulfides before increasing the pH, it is possible to lower the amount of Cd and Cu in the SEPHOS product. In their paper, Schaum *et al.* report 50% and 90% lower concentrations of cadmium and copper, respectively, in the laboratory experiments when using sodium sulfate Na_2S precipitation before pH increase.

Figure 43 presents estimates of the mass flow in SEPHOS process (Schaum 2007).

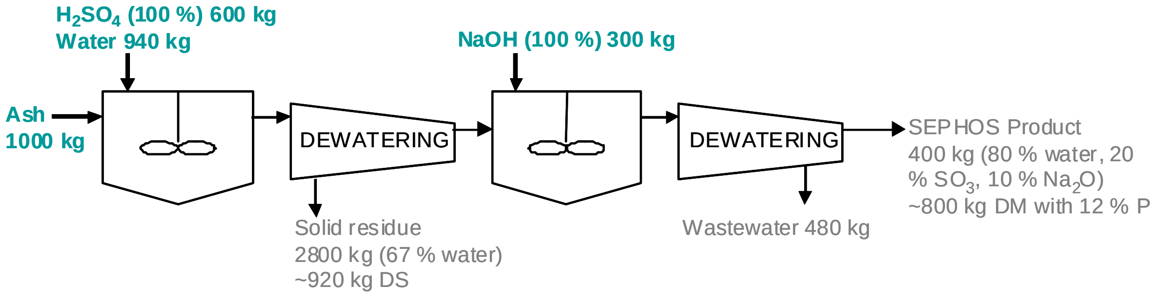

Figure 43: Mass flow in the SEPHOS Process (modified from Schaum 2007).

The price of the SEPHOS Product is estimated on basis of the chemical costs and is about 2 to 3 times higher compared to the price of raw phosphorus (Schaum *et al.* 2005).

6.2.2 THE PASH PROCESS

Developed in the Institute of Applied Polymer Science (IAP) at Aachen University (Germany), the PASH (Phosphorus recovery from Ash) process recovers phosphorus as calcium phosphate from incinerated sewage sludge ash and also meat and bone meal ash. The PASH process was developed during the PASCH project launched as part of the German government funded program "Recycling management of plant nutrients, especially phosphorus" (BMBF/BMU 2010). Figure 44 presents the simplified flow chart of the process. The process utilizes liquid-liquid extraction for heavy metal and iron separation after acid leaching with HCl. The precipitation chemical determines the final product; lime or magnesium compounds are possible options (Montag 2008, Montag and Pinnekamp 2009).

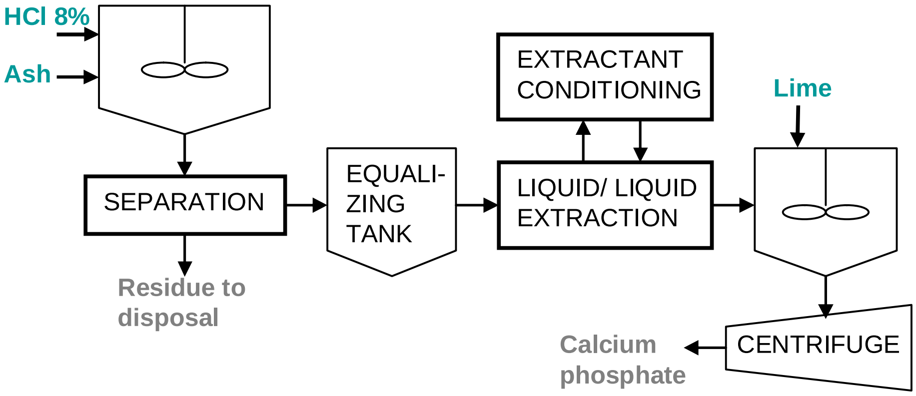

Figure 44: The PASH process flow chart (modified from Montag 2009).

Montag and Pinnekamp (2009) experimented phosphorus solubility with NaOH, H_3PO_3, H_2SO_4 and HCl with results of 25%, 50%, 80% and 90%, respectively. The highest solubility was achieved using HCl (8%) and HRT of 60 minutes. No heating is required in the dissolution since the experiments showed almost complete dissolution of phosphorus with temperatures as low as 35 - 40 ^{o}C. In fact, the increase in temperature was found to have a negative affect on the process; at temperatures above 40 ^{o}C, the concentration of released iron increased significantly.

After the acid leaching, a lamella separator and filter separate the residue. The filtrate, containing phosphorus, calcium, and metal compounds, is treated in the extraction step with Alamine 336 and tri-butyl-phosphate (TBP) and reaction time of 15 minutes. Reduction in the heavy metal concentrations is over 95% and iron over 99%. The final step precipitates the phosphate as struvite or calcium phosphate. According to Montag and Pinnekamp (2009), a dosage of lime precipitated calcium phosphate in pH 3.3 – 3.6 with reaction time of 15 minutes. The phosphorus content was relatively high: 16%.

The estimated costs are presented in Table 21. The designed plant has a design capacity of 30 000 t/a recovering 1 700 t/a of phosphorus. The estimated specific cost of phosphorus is relatively low: 3 €/kg recovered phosphorus.

Table 21: The cost evaluation of the PASH process (Montag and Pinnekamp 2009).

Investment costs	
Building and civil engineering works	2.0 M€
Mechanical equipment	2.4 M€
Electrical equipment	0.6 M€
Operational costs	4 M€/a

6.2.3 THE BIOCON® PROCESS

The BioCon® process recovers phosphorus as phosphoric acid from sewage sludge ashes. The process was developed in Denmark by PM Energi A/S. Now, the brand BioCon® belongs to a subsidiary of Veolia Water, a Danish company Krüger A/S located in Aalborg. The process consists of three parts: sludge drying, sludge incineration, and recovery unit with ion exchangers. According to the company website (Veolia Water 2010), the process is available only with the sludge drying and sludge incineration process, without the recovery unit. However, this Section discusses only the recovery unit (Figure 45). Due to the acid leaching step, the process was profiled under the wet chemical methods Section.

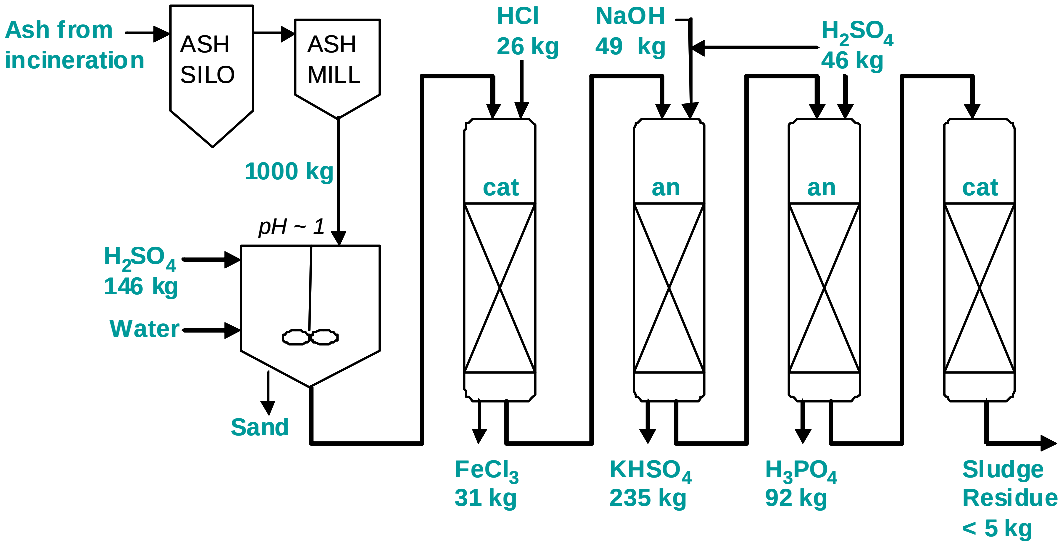

Figure 45: The recovery unit of BioCon® Process with mass flow information from the pilot plant at Brønderslev WWTP (modified from Levlin 2002 and Hultman *et al*. 2001).

The first step of the process dissolves the phosphorus and heavy metal contents with sulfuric acid from the ground feed material (Hermann 2009a). The addition of the acid and water in the stirred reactor leads approximately to pH 1 (Berg and Schaum 2005). The solution passes through a series of ion exchangers. The first exchanger is cationic, separating Fe^{3+} ions. It is regenerated with HCl producing $FeCl_3$. The following exchanger is anionic, collecting potassium ions, and after regeneration with sulfuric acid produces potassium hydrogen sulfate. In this step, NaOH is used for both pH adjustment and regeneration (Hultman *et al.* 2001). The final exchanger collects phosphates. Regeneration with hydrochloric acid produces a stream of phosphoric acid (Lundin *et al.* 2004). The effluent needs to be further treated due to heavy metals remaining in the liquid (Hermann 2009a).

The method has been tested in pilot scale in WWTP of Brønderslev, Denmark. The plant has biological phosphorus removal process and the sludge from the process, holding iron 200 mol/t DS, is incinerated without digestion step. A permit for a large scale incineration plant with BioCon® application has been applied in Falun, Sweden (Levlin *et al.* 2001).

Ion exchangers are not considered economical due to considerable ion concentrations, numerous regenerations. Lundin *et al.* (2004) evaluated the total cost of 155€/t DS consisting of capital costs 88 €/t DS and operational costs 67 €/t DS.

6.2.4 THE AQUA RECI PROCESS

The Aqua Reci process was developed jointly by Feralco and Chematur Engineering AB. A pilot plant is located in Karlskoga, Sweden. The process uses supercritical water oxidation (SCWO) with conditions of $p > 221$ bar and $T > 374$ °C. Under these conditions, pure oxygen is added for complete oxidation of sludge constituents. Reaction time is 60 seconds in the reactor, the total retention time being five minutes. Energy for heating is needed only in the start-up of the process because the oxidation reaction is exothermic generating sufficient energy to maintain the reactor temperature (Stendahl and Jäfverström 2004, Hermann 2009a). During the process, 99.9% of organic substances decompose to CO_2, organic and inorganic nitrogen oxidizes to N_2, and phosphorus to P_2O_5. The inorganic ash from the SCWO process is very reactive. Thus, the metal oxides and phosphorus are easily soluble. The phosphorus recovery step, presented in Figure 46, follows the SCWO.

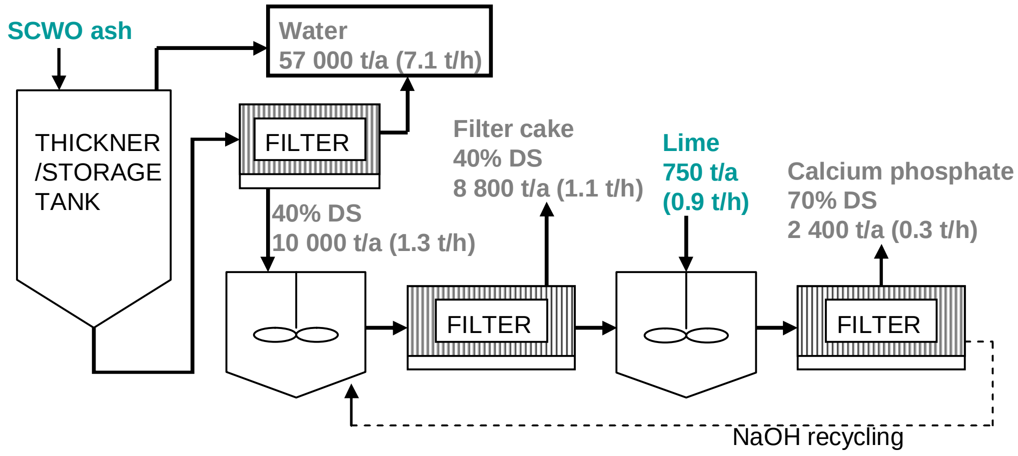

Figure 46: The recycling step after SCWO in the Aqua Reci process (Stendahl and Jäfverström 2004).

Phosphorus can be extracted using base. Since heavy metals are insoluble under alkaline conditions, they can be separated from the mixture. Phosphorus is recovered as calcium phosphate by adding lime.

Table 22: Cost evaluation for Aqua Reci investment (Stendahl and Jäfverström 2004).

	Costs (€)
Energy 3 000 MWh @ €50	150 000
Oxygen 8 750 tons @ €80	700 000
Sulfuric acid 3 300 tons @ €40	132 000
Magnesium oxide 1 170 tons @ €120	140 000
Staff, 2 people	60 000
Miscellaneous	100 000
Total annual operative costs	1 282 000
Operative costs €/ton DS	128
Total annual capital costs	1 200 000
Total annual costs	2 482 000
Total costs €/ton DS	248
Total costs €/ton 25% DS	62

6.2.5 NANOFILTRATION

Güney *et al.* (2008) used Nafion 117 (DuPont) cation exchange membrane to remove metals from digested sludge in order to recover phosphorus as struvite. In the study, four types of sludge were used: original, diluted, centrifuged and incinerated sludge from the digester. It was found that the most important factors to successful filtration are adequate mixing and low concentration of suspended solids (SS) and organic material, both for avoiding problems in cake layer and giving the metal ions a change to a good contact with the filter surface. The best material for metal ion removal was the incinerated sludge, because it has the minimum amount of organic material and solids to interrupt the filtration. It also holds a high metal content. The removal rate with incinerated sludge was the highest of all four: 98%, 97% and 80% of Al, Ca and Fe, respectively, was removed. After removal of metal ions the phosphorus rich solution was brought to pH 8.5, the residue of metal phosphates was filtered and struvite production was initiated by adding NH_4Cl and $MgCl_2$. More than 65% of influent phosphorus was recovered as struvite with high quality. The mass fraction of produced struvite was close to the mass fraction of pure struvite, and met the requirements of DümV (Güney *et al.* 2008).

6.3 Thermo-chemical

6.3.1 THE ASH DEC PROCESS

The ASH DEC process treats mono-incinerated sewage sludge ashes by a chloride dosage and thermal treatment in order to remove heavy metals making the product suitable for agricultural use. The development of the process started already in 2002, but was completed as a part of the EU Project SUSAN (2008) with the pilot-scale implementation and the experiments for the fertilizer use of the final product.

Process description

The process can treat ashes with phosphorus concentration from 5 to 30%. In the first step, the ash is mixed with an environmentally acceptable chloride donor such as alkali metal chloride, alkaline earth metal chloride, or both. Preferred chemicals are $CaCl_2$, KCl, and $MgCl_2$, that can be added in powder or aqueous solution. The crystallization water content of the additive is insignificant. The amount of chemical varies between 60 to 95% of ash and 5 to 40% of metal chloride by weight based on the total weight of the mixture

(Boutoussov 2009). A molar surplus of chloride compared to heavy metal concentration is required (Berg and Schaum 2005).

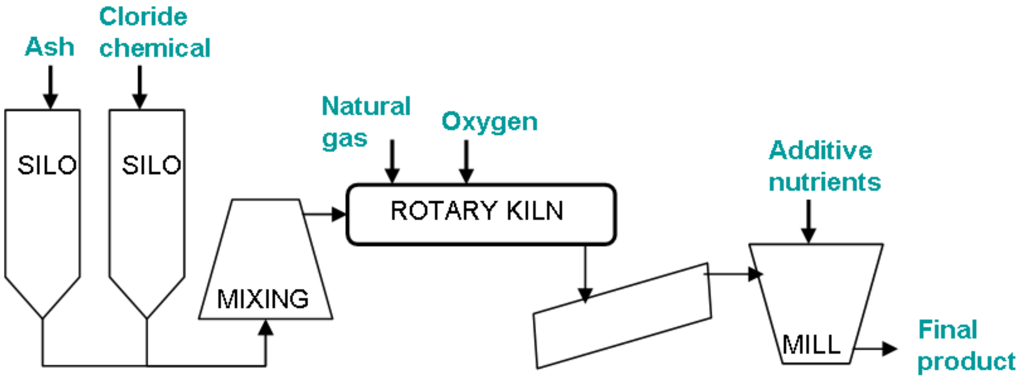

Figure 47: The flowchart of the ASH DEC Process (modified from ASH DEC 2010).

Addition of fillers affects the composition of the end product and enables design for specific applications. Fillers can be finely ground coal, alumina, ground sewage sludge, fine wood waste or finely ground waste paper. The particle size of the fillers should be less than 1000 µm. Especially useful are inorganic materials that do not form toxic gases in temperatures above 900 °C, such as lime. Use of liquid fillers is also possible, for example 30% H_3PO_4. The mixture should be as homogenous as possible, containing about 55 to 90% of ash, 5 to 40% of metal chlorides and 1 to 50% (preferably 3 to 20%) of filler material. The mixture is pelletized or granulated producing pellets of 3 to 30 mm (Boutoussov 2009).

In the second step, the granules are heated to the temperatures above the boiling point of the heavy metal chlorides, thus separating them. Heating in two stages increases the effect of the MeCl removal: first, a constant temperature below the boiling point of the heavy metal chloride, typically less than 300 °C, is kept for at least 30 minutes for drying and heating the granules, thus minimizing the energy consumption in the following thermal process. The second thermal step, lasting maximum 60 minutes, raises the temperatures above the boiling point of heavy metal chlorides, typically to 900 – 1100 °C (Boutoussov 2009). However, it is shown in the pilot-scale process, that thermal treatment at 1000 °C up to 20 minutes is sufficient.

Temperatures above 1100 °C can cause sintering of the granules decreasing the yield. Optimal yield with heavy metal removal occurs at 1000-1100 °C (Boutoussov 2009). The flue gasses need to be cleaned for instance with a wet flue gas cleaning system. The resulting hazardous waste needs to be disposed accordingly.

Experiences and costs

ASH DEC has a pilot plant in Leoben build in 2008 and designed to treat about 7 to 10 t/d ash in continuous operation. The ash is stored in two 24 m^3 silos, treated in 1000 °C up to 20 minutes and cooled down in water-cooled screw conveyors. The output is about 110% of the ash input. The material flows can be seen in Figure 48. The process removes 99% of Cd, Hg, and Pb; over 90% of Cu and Zn; and about 50% of Sn and Mb. 75% of chlorides are recovered and recycled (ASH DEC 2009). The energy demand is estimated to be 600 – 800 kWh/t (Adam 2009). The process is ready for full scale implementation and plans for building a 15 000 t/a plant are underway (ASH DEC 2010).

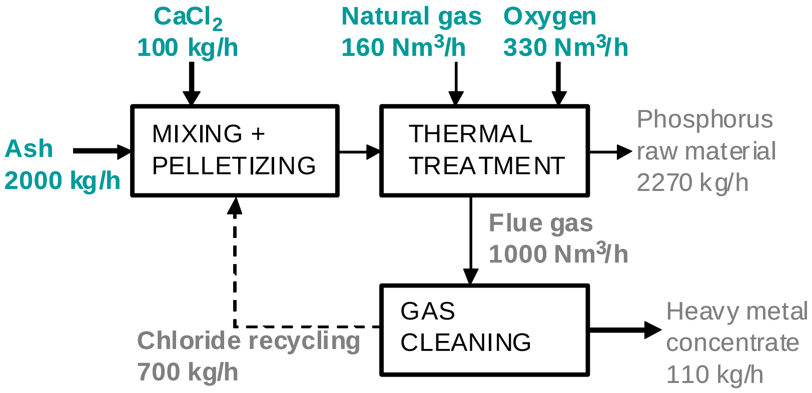

Figure 48: The ASH DEC Process and estimated material flow of a full-scale plant with feed of 2000 kg/h of ash (ASH DEC 2010).

The final product from the furnace is round pellets or granules, sized 2 to 5 mm with porosity of 20 to 40%, and P_2O_5 content above 10%. Tests show, that 80 to 100% of the phosphorus in the pellets is soluble in citric acid, and over 70% insoluble in water. The product contains Zn, Cd, Pb, and Cu, 0.025%, 0.00015%, 0.001%, and 0.01% by weight, respectively (Boutoussov 2009). The product, marketed by name PhosKraft®, has been fully licensed for fertilizer use in March 2006 in Austria and in Germany in 2008 (ASH

DEC 2009). PhosKraft® is marketed as a high quality PK 12-20 fertilizer with calcium, and NPK 20-8-8 fertilizer. The sales prices are comparable to commercial fertilizers (Hermann 2009b).

Investment on full-scale plant is estimated 15-18 M€ in 2008. Typical design capacity is 4 t/h equaling 30 000 t/y. Expected sales revenues are 13 to 24 M€/a, and the payback time 3 to 4 years. The price varies according to whether the plans are to build a plant producing ready-made fertilizer or a plant purifying the raw material ashes. Either way, the production costs result in prices significantly higher than those of phosphate rock (ASH DEC 2010).

6.3.2 THE MEPHREC PROCESS

The Mephrec (Metallurgical Phosphorus Recovery) process was developed by the German company Ingitec. The process (Figure 49) recovers phosphorus and energy from dried sludge.

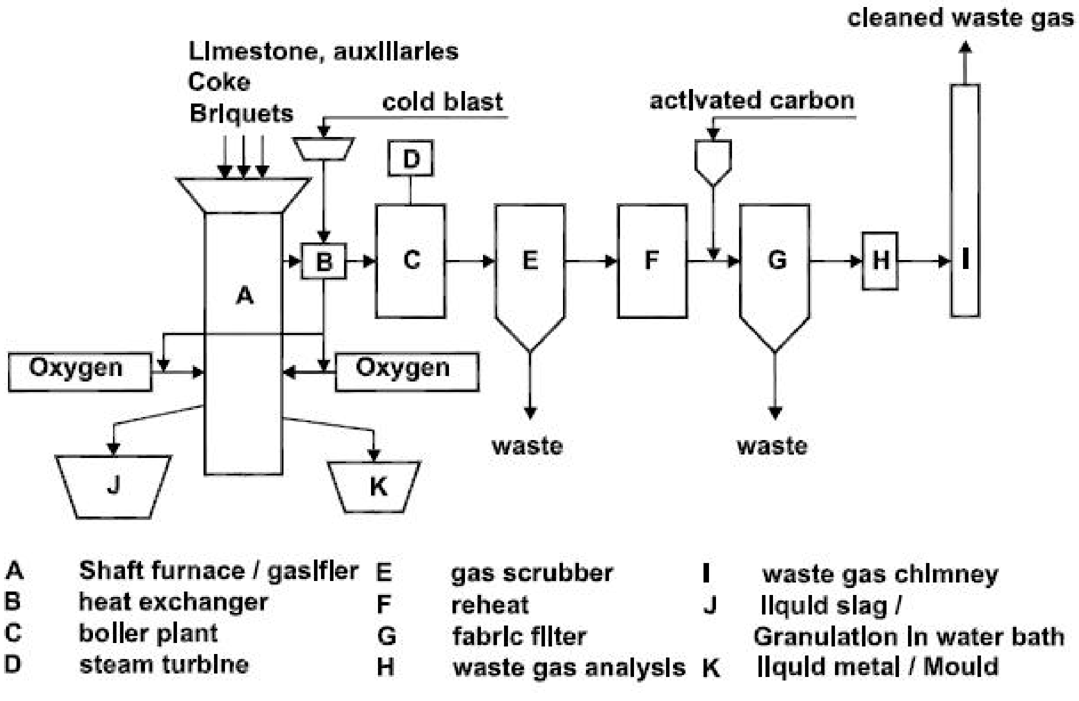

Figure 49: The Mephrec process (modified from Ignitec 2010).

Dried sludge is briquetted with slag forming substances and coke. The mixture is treated in 2000 ^{o}C transferring phosphorus into the mineral slag and heavy metals to liquid metal phase (Fe, Cu, Cr, Ni) or to gaseous phase (Hg, Cd, Pb, Zn). The silico phosphates containing slag is separated from metal phase after being tapped at 1450 ^{o}C (Adam 2009). The final product contains 4.6 - 12% P_2O_5 with over 90% citric acid solubility. The content can be varied by mixing sewage sludge with animal meal. With sewage sludge ash, the P_2O_5 content can reach 20%, but the energy recovery is not possible. The process has been tested in a pilot plant with a capacity of 8 t/h briquettes. A feasible process should have a minimum capacity of 40 000 t/a briquettes (Ingitec 2010).

6.4 Summary of the pilot and laboratory scale processes

The processes in pilot and laboratory-scale include three crystallization or precipitation processes, five wet chemical processes, and two thermal processes. Only one of the crystallization processes, the P-RoC process, uses crystallization as calcium phosphate from process liquid. The P-RoC operates with no chemical dosage the seed material providing everything needed for the crystallization. This decreases the chemical cost which is important as the experiences from the industrial-scale Crystalactor® show that the method is not economically feasible.

The processes using wet chemical approach with phosphorus leaching step with acid or base separate the phosphorus with crystallization, sequential precipitation, nanofiltration, and ion exchangers.

Two processes, the Rem Nut® and the BioCon® use an ion exchanger process step with the difference that RemNut® is designed to remove phosphorus from liquid phase as struvite and BioCon® uses acid leaching of phosphorus from sludge ash, producing H_3PO_4 after regeneration. These methods do not seem to be feasible until ion exchange resins develop.

Table 23 presents the basic information of the processes including the place of development, location, feed material, method, and the final product. Not all processes found in the table are dicussed in detail in this Chapter.

The laboratory-scale processes are presented in Table 24. Literature search provided more information of SEPHOS than other processes. The recently established and yet developing processes include ATZ, LOPROX, and ERPHOS, whereas PECO, CSIR, Kurita, AF-BNR-SCP, Sydney Water Board process, and processes based on the high gradient magnetic separation were found in the literature published before 2000.

Table 23: The summary of the pilot-scale processes.

Pilot-scale process	Developer	Location	Feed material	Method	Final product
Aqua Reci	Feralco AB	Karlskoga, Sweden	Sludge	SCWO, precipitation	Calcium phosphate
ASH DEC	ASH DEC Umwelt AG	Leoben, Austria	Ash	Thermal method	Ash, purified from heavy metals / Fertilizer
BioCon	PM Energi A/S	Falun, Sweden	Sludge/ Ash	Acid leaching, ion exchange	H_3PO_4
KREPRO	Kemira Oyj	Helsingborg, Sweden	Sludge	Thermal hydrolysis, acid leaching, precipitation	$FePO_4$
PASH	RWTH Aachen	Aachen, Germany	Ash	Acid leaching, liquid-liquid extraction, precipitation	Calcium phosphate / struvite
PRISA	RWTH Aachen	Aachen, Germany	Sludge liquor	Precipitation	Struvite
Mephrec	Ingitec	Freiberg, Germany	Dried sludge/ Ash	Metallurgical method	Silico-phosphate
P-RoC	Institut ITC-WGT	Karlsruhe, Germany	Liquid	Crystallization	Calcium phosphate
Oxley Creek	Unitika Ltd.	Brisbane, Australia	Sludg liquor	Crystallization	Struvite
Rem Nut	Bari polytechnics	Grottaglie-Monteiasi, Italy	Liquid	Ion exchange and Precipitation	Struvite

Table 24: The laboratory-scale processes.

Laboratory-scale process	Developer	Feed material	Final product	Chemicals	Process description
PECO	TU Braunschweig, Germany	Liquid	Struvite	Sea water, NaOH	Struvite precipitation after anaerobic treatment using sea water as magnesium source.
LOPROX	RWTH Aachen, Germany	Digester sludge	H_3PO_4	n.f.	Acid leaching of metal ions with acid and nanofiltration of the liquid phase.
ATZ	ATZ Entwicklumszentrum, Germany	Sludge/ ash	Phosphate rich slag	n.f.	Thermal treatment in an iron bed reactor
Sydney Water Board Process	Sydney water board, Australia	Liquid	Amorphous calcium phosphate	Gypsum, magnesia	Contact bed reactor for crystallization
SEPHOS / Advanced SEPHOS	TU Darmstadt, Germany	Ash / SEPHOS product	Aluminum phosphate / Calcium phosphate	H_2SO_4, NaOH, Ca^{2+}	Acid leaching and sequential precipitation
CSIR	Council for Scientific and Industrial Research	Secondary effluent	Calcium phosphate, struvite	Quartz sand (0.5 - 1.2 mm), NaOH	Fluidized bed reactor for crystallization
Kurita	Kurita, Japan	Secondary effluent	Calcium phosphate	Phosphate rock (0.5 – 1.0 mm) as seed material, CaCl, NaOH	Fixed bed reactor for crystallization
EPHOS	TU Darmstadt	Ash	n.f.	n.f.	Electro-kinetic method
AF-BNR-SCP	n.f.	Enriched digester stream	Struvite	n.f.	Anaerobic fermentation biological nutrient removal struvite crystallization process
High Gradient Magnetic Separation Technique	n.f.	Tertiary flow	n.f.	Precipitation chemical, Magnetite (Fe_2O_3),	Precipitated phosphorus is mixed with fine grained magnetite (Fe_2O_3). The magnetite is separated from phosphate by shear forces in a drum separator. Separated phosphate sludge needs to be processed for final use. High energy costs are expected.

7 POTENTIAL AND COSTS

The sludge treatment costs are presented in Table 25 listing the estimates of Andersen and Sede (2002) updated to 2009 level by Salado *et al.* (2009). The total costs consist mainly of investment and operating costs, the external costs representing less than 15% of the total costs. The calculation take into account the diminished need for fertilizers estimating the agronomic value 10 - 30% of the cost of landspreading.

Table 25: Total costs of disposal of sewage sludge (Salado *et al.* 2009).

	€ / t DS
Agricultural use (landspreading)	
Semisolids	198
Semisolids, digested	198
Solids	255
Composted sludge	374
Incineration	
Co-incinerat	298
Mono-incineration	384
Landfilling	308

As can be seen from Table 25, the landspreading of semisolids is the least expensive method with total costs less than 200 €/t DS. The three most expensive methods with total costs over 300 €/t DS are mono-incineration, landspreading of composted sludge and landfilling. Table 26 presents the recovery potential of sludge, assuming the sludge production as presented by Salado *et al.* (2009) and the phosphorus content in dewatered sludge 2% by weight of total phosphorus. The Table assumes that the recovery from liquid phase could reach 50% of the total phosphorus in the sludge, and 90% represents the recovery potential from sludge or ash. However, the estimates in the Table appear to be lower than those presented in the literature. For example, Adam (2009) estimates the recycling potential in Germany 60 000 t/a, and in the Netherlands 8000 t/a, and Hermann (2009) 293 000 t/a in the EU-15 countries.

Table 26: Phosphorus recovery potential from municipal wastewater sludge.

Sewage sludge	**Population***	**Sludge production (t/a DS) ****	**Total P (t/a)**	**Recovery 50% (t/a)**	**Recovery 90% (t/a)**
Finland (2005)	5 300 000	150 000	3 000	1 500	2 700
the Netherlands (2003)	16 500 000	550 000	11 000	5 500	9 900
Germany (2007)	82 000 000	2 100 000	42 000	21 000	37 800
EU-27	499 000 000	10 130 000	202 600	101 300	182 340
* Eurostat (2010), ** Salado *et al.* 2009					

The limit values for heavy metal and organic substance concentrations in the Sewage Sludge Directive 86/278/EEC have been subject to tightening. In 2002, Andersen and Sede published a report concerning the possible change in the Directive, including more stringent requirements for sludge pretreatment and heavy metals concentration as well as introducing limits for certain organic pollutants. The report estimated the total implementation cost 1 billion €/a in the EU-15 countries by 2025. The cost would be higher in countries with low limit values for pollutants, and those, using sewage sludge in agriculture (CEEP 2003).

Another consultation report for changes in the Directive was published in 2009, introducing five options for the future changes in the Directive:

Option 1: do-nothing, keeping the Directive as it is.

Option 2: stringent standards, especially for heavy metals, standards for some organics and pathogens, and more stringent requirements on the application, sampling and monitoring of sludge.

Option 3: stringent standards across all substances and bans on application of sludge to some crops.

Option 4: total ban on the sewage sludge agricultural use.

Option 5: repeal of the Directive.

Table 27 presents estimated total costs resulted from the options. The economic costs include costs due to further treatment, increased landfilling costs, increased incineration costs, quality assurance related costs and fertilizer replacement costs. As can be seen, even the option 2 with moderate changes can result in over 2 billion euro costs in EU. In

Finland, the option 2 would result in 1.9 - 3.2 M€ costs. The costs result from the sludge failing to fulfill the requirements for agricultural use, increasing the need to use other disposal routes such as incineration and landfilling.

Table 27: Estimated costs of the four options presented in the Consultation Report on Options and Impacts (Salado *et al.* 2008).

	Economic costs M€		**Environmental / Human health costs M€**
Present value costs	**Low**	**High**	
Option 1 - No change	---	---	
Option 2 - Moderate changes	2470	2940	243
Option 3 - More significant changes	5660	6860	576
Option 4 - Total ban	7100	9400	1369
Annualized costs			
Option 1 - No change	---	---	
Option 2 - Moderate changes	295	352	29
Option 3 - More significant changes	677	821	69
Option 4 - Total ban	849	1124	164

The world market price of phosphorus depends on the quality, demand and the capacity of the phosphorus industries, as well as politics and stock market speculations (Cornel and Schaum 2009). In 2004, Roeleveld *et al.* (2004) estimated the total costs of phosphorus recovery about 22 times higher compared to mined phosphate rock, the price for the phosphate rock in Northern Europe being 320 €/t. According to Bayerle (2010), the market price of fertilizer phosphorus is 400 €/t.

Table 28 presents the estimates of price for recovered phosphorus including the values for crystallization processes Crystalactor® and AirPrex, and the wet chemical process Seaborne. Additional costs are presented in the discussion of each process. Cost estimations for thermo-chemical methods were not found in literature. However, the cost of mono-incineration is 384 €/t sludge (Table 25). Assuming the average phosphorus concentration in dried sludge is 2%, the cost of transferring phosphorus to ash is 19 000 €/t. However, this estimate includes the disposal costs of the residues, that can be deducted if the ash is used in phosphorus recycling.

Table 28: The price of recovered phosphorus (€/t).

Process	Phase	Product	€/t P	Reference
Crystalactor®	Liquid	Calcium phosphate	7 300	(Gaanstra *et al.* 1998)
---	Sludge	Struvite	1 235 - 2 833	(Jeanmaire and Evans 2001)
---	Liquid	---	3 600	(Balmér 2003)
---	Sludge	---	8 800	(Balmér 2003)
Seaborne	Sludge	Struvite	40 000	(Bayerle 2010)
AirPrex	Sludge liquid	Struvite	390	(Lengemann 2010a)
PASH	Ash	Calcium phosphate	2 900	(Montag and Pinnekamp 2009)

As can be seen, compared to the cost of calcium phosphate recovery, the expenses of struvite production are lower. Indeed, the operational processes mostly recover struvite whereas the only calcium precipitation plant, Crystalactor® is about to be shut down. Furthermore, the phosphorus recovery as struvite from the AirPrex reactor results in costs as low as 50 €/t of struvite (Lengemann 2010a), being even lower than the market price for N-P-K fertilizer 400 €/t (Bayerle 2010). Jaffer *et al.* (2001) calculated that 97% of the chemical costs in a struvite precipitation process are due to the pH adjustment with sodium hydroxide, which is not used in the AirPrex procedure. Shu *et al.* (2005) estimate a payback period for a recovery process located in a WWTP with an inflow of 55 000 m^3/a, using struvite precipitation, five years. The estimate includes the savings due to reduce sludge handling and disposal.

The wet chemical methods recover phosphorus with higher costs. Balmér (2003) estimates the cost of phosphorus recovery from wastewater about 40% of the costs from the recovery from sewage sludge. Experiences from the Seaborne application in Gifhorn show that the costs depend on the used pH value and thus, the leaching chemical, as well as the pH adjustion chemical. The magnesium chemical used in the precipitation step does not have a major effect on the chemical costs.

A careful re-examination of the costs is needed, since during the literature search it was not always clear if the evaluation was calculated as produced struvite or as recovered phosphorus. Cost evaluation presented as €/t of recovered phosphorus would result in comparable data.

8 CONCLUSION

Phosphorus recovery has received increasing attention as the phosphate rock resources deplete and the need for finding a replacing source of phosphorus becomes ever more important. At the same time, a great amount of sewage sludge is disposed off by using methods that do not ensure the sustainable recycling of the nutrients bound in the sludge. Furthermore, as the most economical way to dispose the sludge, the agricultural use, appears to be increasingly restricted, new technologies are needed to recover phosphorus from sludge and to process it into a suitable form for fertilizing purposes.

The three raw material options for phosphorus recovery from municipal WWTPs include: sludge, ash from sludge incineration, and liquid phase after anaerobic treatment containing phosphorus in soluble form. These options provide a maximum recovery potentials of 90% from sludge or ash, and 50 - 60% of total phosphorus from concentrated side streams. Although the recovery potential is higher with sludge or ash, recovery from these materials requires chemical leaching of phosphorus or energy consuming thermal treatment, resulting in higher costs than methods recovering phosphorus from liquid.

The methods for phosphorus recovery discussed in this thesis include crystallization and precipitation, wet chemical methods, and thermo-chemical methods. The crystallization and precipitation methods convert phosphorus into solid form with a chemical dosage and pH adjustment. The wet chemical methods recover the phosphorus bound in sludge or ash by leaching it with acid or base, and recovering the resulting dissolved phosphorus with various methods, the most common being the precipitation. The ash fraction after incineration can be treated with thermo-chemical methods by adding chloride chemical and bringing the ash to temperature higher than the boiling point of the resulted heavy metal chlorides, leading to their evaporation. Other thermal methods, based on metallurgical approaches, produce phosphate rich slag in high temperatures.

Phosphorus recovery technologies have several operational examples, especially of precipitation technologies. This study suggest that the precipitation is more feasible economically and technically than methods using wet chemical or thermo-chemical methods. Furthermore, the precipitation of struvite is more feasible than calcium phosphate crystallization. In terms of technical feasibility, struvite producing processes offer a relatively simple and functional method with long operational history.

The wet chemical methods offer experiences from shorter period of time with only one full-scale process, the Seaborne. The process is currently not feasible due to the high chemical costs and low influent flow to the plant. The preferred flow to the plants of future implementatios should be at least two-fold compared to the process at Gifhorn WWTP, having the influent flow of 6 500 m^3/d and population equivalent of 50 000. Many researches expect the increase of the phosphate rock prices solve the feasibility problems and a re-evaluation should occur in 5 - 10 years to see the development of the fertilizer and chemical prices. In addition, centralizing the treatment facilities would result in higher feasibility by increasing the volume of the feed material. However, centralizing increases the transporting costs and the transportation of sludge requires dewatering of the sludge. Nevertheless, being the first industrial-scale wet chemical implementation, the Seaborne is an important example and has already granted several experiences for future full-scale wet chemical applications.

The thermo-chemical processes have high energy consumption and they require sludge incineration plants in addition to the thermo-chemical process itself: in countries lacking incineration facilities, the implementation of such plant would require large investments. Thus, these methods can be suitable in countries already using incineration as a common approach to sludge disposal. Thermo-chemical processes have indefinitely been implemented only in pilot-scale. However, plans for a plant utilizing ASH DEC technology are nearly completed, and a full-scale application is expected in the near future.

It is necessary to recognize the consequences of the depletion of the phosphorus resources nationally on the governmental level as well as globally. The developments of the recovery methods conserve the remaining phosphorus resources, and ensure that reliable technology will be available, when the secondary raw materials become increasingly important source of phosphorus.

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