



Sustainable sewage sludge management fostering phosphorus recovery and energy efficiency



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List of abbreviations

WWTP	Wastewater treatment plant
MAP	Magnesium ammonium phosphate, struvite
PE	Person equivalents
EBPR	Enhanced biological phosphorus removal

1 Introduction

1.1 Objectives

This report gives technological information about processes for the recovery of phosphorus from sewage sludge or sludge liquor from municipal wastewater treatment plants. The processes included in the report are operated or have been operated in full scale or demonstration scale. For one exception (Budenheim process) the operation of a demonstration scale plant is presently in preparation.

The target of the report is to provide technological information about the processes regarding the process mechanisms, process design, operational conditions and type of phosphorus product. In order to fulfill this objective, each process is described in a standardized way in a separate chapter. The description contains the technological design of the process principal and site specific information of one or more installations.

The information given in this report aim at giving an overview of concepts for the recovery of phosphorus from sludge and are intended to allow a qualitative comparison between the different approaches. This report also describes the technological backgrounds of the processes compared by life cycle assessment (LCA) and life cycle cost (LCC) analysis. However, most figures stated in this report are site specific data. The LCA/LCC study, which is prepared after final editing of this report, includes the definition of a common base line for all processes, detailed process modelling and plausibility assessments. Thus certain figures are expected to differ between this report and the LCA/LCC study.

1.2 Background and context

Up to 90% of the phosphorus entering the waste water treatment plant (WWTP) is transferred into the sewage sludge [Pinnekamp et al., 2013]. Therefore, the recovery of phosphorus from the sewage sludge line offers a higher potential of phosphorus recovery in comparison to a recovery process from the effluent of the wastewater treatment plant. Almost all processes developed for phosphorus recovery and all processes described in this report focus on this fraction of the phosphorus originally contained in the raw wastewater.

The elimination of dissolved phosphate from wastewater and the transfer into sewage sludge is at least partly taking place by bacterial growth (38-45%) [Pinnekamp, 2004]. The phosphorus is used by the microorganisms in the activated sludge as nutrient and included into the biomass.

Tertiary wastewater treatment plants remove additionally around 30-52% of the phosphorus from wastewater into the solid sludge phase. There are two main concepts for phosphorus elimination:

- **Enhanced biological phosphorus removal (EBPR)** benefits from so called phosphorus accumulating bacteria. Under specific process conditions, these bacteria are able to store increased amounts of phosphorus – the so-called luxury uptake. Under anaerobic conditions and in presence of easily degradable organic compounds, the bacteria can use stored phosphorus as energy source which represents also an advantage in the competition with other

bacteria. As a consequence of applying subsequently aerobic conditions, the bacteria fill up again the phosphorus storage and even increase the phosphorus depot. The difference between the phosphorus uptake and the phosphorus release is called the net elimination [Seviour et al., 2003, Oehmen et al., 2007, Pinnekamp et al., 2007]. Therefore, sewage sludge from wastewater treatment plants with enhanced biological phosphorus removal contain phosphorus in form of biologically bound polyphosphates.

- **Chemical phosphorus elimination** applies dosing of aluminium, iron or calcium salts. The phosphorus is removed as hardly water soluble precipitation product, e.g. as strengite, variscite or apatite [Böchler & Siegrist, 2008]. Hence, the sewage sludge from wastewater treatment plants with chemical phosphorus elimination contains inorganic phosphates and biologically bound phosphorus. In wastewater treatment plants applying chemical phosphorus elimination larger amounts of sewage sludge are produced than in wastewater treatment plants using enhanced biological phosphorus removal.

1.3 Pathways and overview of concepts for phosphorus recovery

The phosphorus needs to be extracted in dissolved form out of the sludge matrix in order to obtain a secondary mineral fertilizer product. During digestion of the sludge, its biomass is degraded and therefore biologically bound phosphorus released into the liquid phase of the sludge as water soluble ortho-phosphate. This is especially the case for phosphorus taken up by phosphorus accumulating bacteria due to anaerobic conditions during digestion which lead to an enhanced release of phosphorus from the bacteria. The amount of phosphorus dissolved after the digestion is estimated to account for up to 23% of the phosphorus contained originally in the waste water [Cullen et al., 2013].

Four of the process concepts presented in this report are based on this fraction of the phosphorus which is dissolved directly after digestion of sludge coming from enhanced biological phosphorus removal (EBPR). One process applies a reactor in which the crystallization of a mineral phosphorus product occurs directly in the sludge (AirPrex®). The other three processes are applied on the process water after sludge dewatering by mechanical solid-liquid separation like e.g. centrifugation (Struvia process, Crystallactor, Pearl® Process). These three processes are also applicable to industrial wastewater containing significant concentration of dissolved ortho-phosphate.

To mobilize a higher percentage of phosphorus from the sludge, an extraction e.g. by acidic treatment of the sludge has to be applied. This disintegration is especially required for the recovery of phosphorus from sludge generated by chemical phosphorus elimination. In three of the seven processes (Gifhorn Process, Stuttgarter Process, Budenheim process) an additional acidic dissolution process is applied to make more phosphorus available for recovery from the liquid phase.

All these processes for phosphorus recovery from sludge provide a solid mineral phosphorus product by precipitation or crystallisation. An important target compound is struvite since it was evaluated as a slow release fertiliser offering a high plant availability [Römer et al., 2013]. According to the struvite solubility in water (around 200 mg/l), the struvite crystallisation processes is efficient for waste water containing more than 60-80 mg/l of soluble P-PO₄ and a soluble ammonia concentration higher than 50-70 mg/l of N-NH₄ (molar ratio N/P ≥ 2). Hence, recovery processes without an additional extraction step to transfer P into a soluble form are mainly applicable for digested sludge supernatant

from WWTPs with EBPR or for industrial wastewater with sufficiently high phosphorus concentrations. Other possible secondary mineral fertilisers from sludge or sludge liquor based processes are calcium phosphate compounds.

Due to the additional increase of the phosphorus dissolved in the sludge supernatant by acidic treatment, the processes with sludge extraction step are applicable for digested sludge from WWTPs with both EBPR and chemical P elimination. Figure 2 gives a categorization of phosphorus recovery processes from wastewater regarding level of implementation and specific source for the phosphorus recovery.

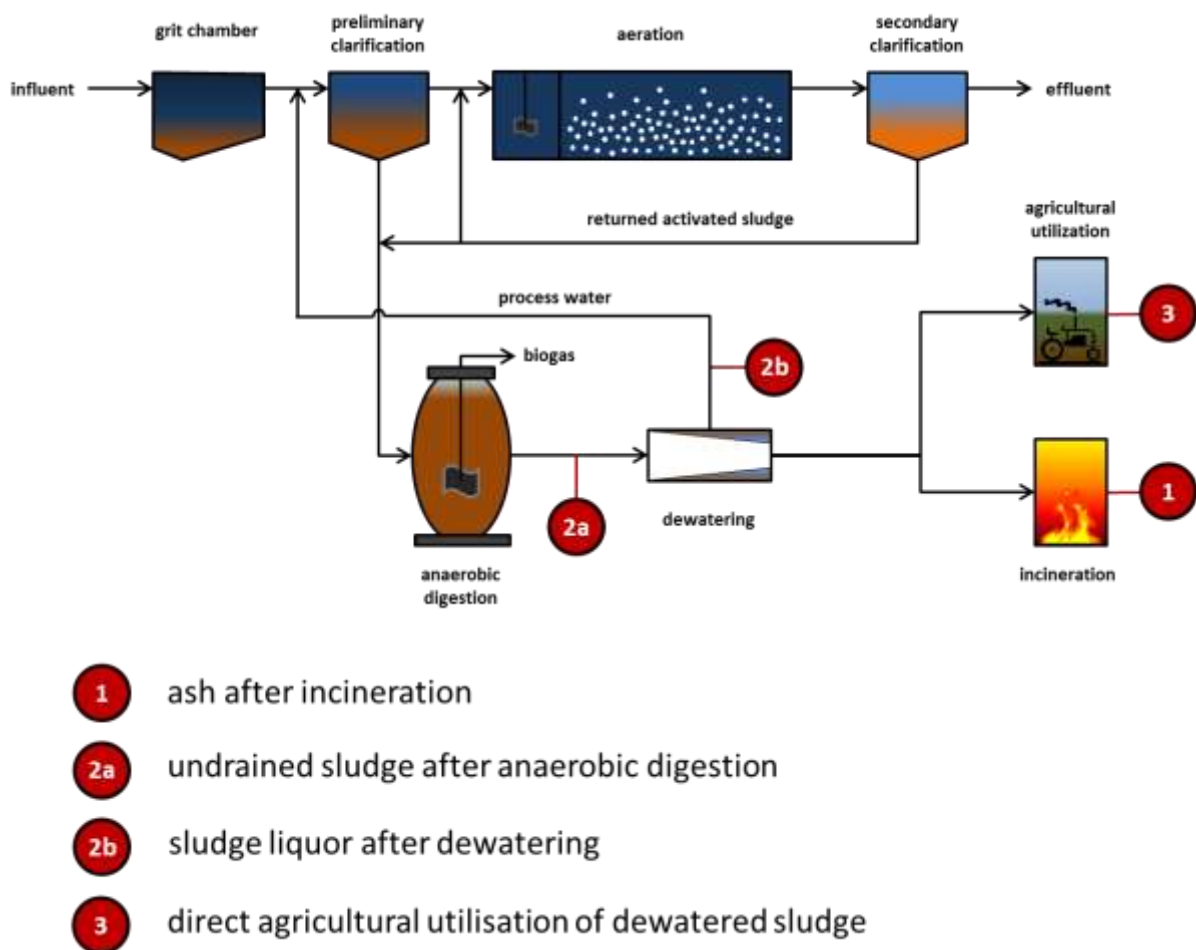


Figure 1 Phosphorus recovery processes in the context of the process chain of the wastewater treatment plant [amended from Pinnekamp et al., 2007]

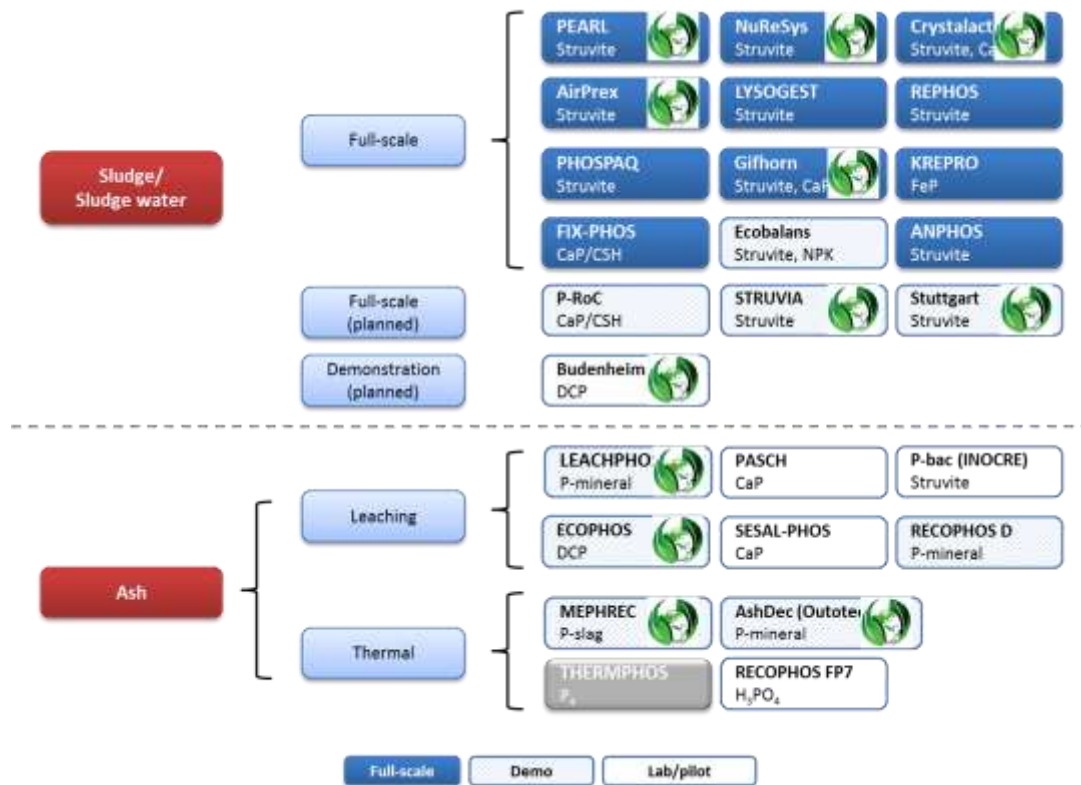


Figure 2 Classification of the Phosphorus Recovery Processes from sewage sludge or supernatant (blue = full scale operation, hatched = demo scale operation, white = lab scale operation) [Kabbe, 2014]

If the preferred way of final sludge disposal is mono-incineration, these processes have to be regarded in combination with processes for phosphorus recovery from sewage sludge ash. The positive influence on the operation of the wastewater treatment plant can justify a combination of recovering of the dissolved phosphorus with a process described in this chapter while the part of the phosphorus remaining in the solid sludge phase can be targeted by further processes treating the ash.

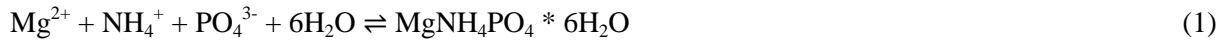
In Europe in 2010, about 42% of the sewage sludge disposed on land applications, about 27% incinerated, about 14% disposed by landfilling and about 17% by other disposal routes [van Dijk, 2013, Eurostat 2010, Milieu Ltd 2010 & Destatis 2011]. Kind [2009] showed that in general mono incineration is more energy efficient than co-incineration. However, under certain circumstances – as using alternative energy sources for drying - co-incineration can be more energy efficient.

These facts show that it can be expected that also other disposal routes beside mono-incineration will play an important role in the future. The combination of processes for phosphorus recovery from sludge or sludge liquor represent a beneficial option.

1.4 Background of struvite crystallisation

Struvite crystallisation is of high importance since it is an important mineral phosphorus recycling product and can spontaneously precipitate within pipes, pumps or centrifuges, causing severe operational problems in sludge handling and treatment.

Due to the degradation of the biomass, an important part of the phosphorus is remobilized as ortho-phosphate and therefore dissolved in the liquid phase of the sludge water typically with concentrations in the range of 80-300 mg/L [Lahav et al., 2013]. Normally, the concentration of ammonia is increased as well [being typically in the concentration range of 600-800 mg NH₄-N /L [Lahav et al., 2013] and if magnesium is present and the pH is high enough (optimum above pH 8), struvite (MgNH₄PO₄ x 6H₂O) precipitates according to the following reversible reaction:



Like all crystallization processes, also the struvite crystallisation is always in balance with re-dissolution of the crystals. The chemical balance is mainly influenced by stoichiometry (concentration) and matrix conditions (pH, temperature). A concentration of ortho-PO₄ above 50 mg/l and pH around 7.8 to 8.5 are known to be good conditions for struvite crystallization in presence of sufficient magnesium and ammonia.

The following basic information is a useful background for studying the process design for struvite crystallisation:

The process of crystallisation basically consists of two steps. The first step is the nucleation which means formation of the initial, smallest size crystals or “crystal embryos”. The second step is the crystal growth which means the mass transport of ions from the solution to the crystal surface and the incorporation of material into the crystal lattice. In order to produce a fertilizer product suitable for application, the growth of already existing crystals is more beneficial rather than the formation of a high number of very small crystals. The kinetics of nucleation and growth are mainly determined by the super-saturation of the liquid phase in struvite, the pH and the temperature. Over-saturation of struvite is defined as a state in which the solubility product is increased which means that the product of the activities of phosphate, ammonium and magnesium increase a certain value depending on temperature and ion strength. Bhuiyan [2007] determined solubility and solubility products as function of temperature and ion strength for digester supernatant.

The pH influences the over-saturation indirectly by the concentrations of NH₄⁺ and PO₄³⁻. The effects are contrarily, hence there is an optimal pH leading to the highest over-saturation. According to the literature this pH lies in the range of pH 8-10.7. Britton et al. [2005] determined for a pilot system of the Pearl® process the so called conditional solubility pP_S (product of magnesium, ammonium and phosphate concentration) as a function of the pH: $pP_S = -0.203 \text{ pH}^2 + 4.09\text{pH} - 11.76$. An additional important aspect is the release of protons as a consequence of struvite crystallisation. Therefore, the pH is required to be kept stable throughout the entire duration of the crystallisation process. According to the principles of thermodynamics every state of over-saturation will lead to a change of the system. Nevertheless, there are so called metastable regions in which the process of nucleation takes a significantly longer time. Crossing the limit of the metastable region will result in a sudden increase of crystallisation rate. Furthermore, the degree of over-saturation influences the growth rate of different crystal sizes. For higher super-saturation, smaller crystals grow faster than large ones because of diffusion mechanisms. For low super-saturation small crystals grow more slowly in favour of the growth rate of larger crystals due to the so-called Gibbs-Thomson or Ostwald-ripening effect.

1.5 Important definitions of yield coefficients

The following definitions are used in this report:

Overall phosphorus yield

The overall phosphorus yield is the phosphorus mass flow recovered in the final recycling product divided by the total phosphorus mass flow that enters the wastewater treatment plant. Therefore this yield shows which proportion of the total phosphorus content available in the wastewater can be recovered with the corresponding process:

$$\xi_{overall} = \frac{\dot{m}_{total P, recovered}}{\dot{m}_{total P, raw wastewater}}$$

Sludge specific phosphorus release-yield

The sludge specific phosphorus release-yield is the phosphorus mass flow in the sludge liquor phase (as dissolved $PO_4\text{-P}$) divided by the mass flow of phosphorus in the digested sludge. Therefore this yield shows which proportion of the phosphorus available in the digested sludge can be dissolved:

$$\xi_{release, sludge} = \frac{\dot{m}_{PO_4\text{-P}, sludge liquor}}{\dot{m}_{total P, digested sludge}}$$

Sludge specific phosphorus yield

The sludge specific phosphorus yield is the phosphorus mass flow recovered in the final recycling product divided by the total mass flow of phosphorus in the digested sludge. Therefore this yield shows which proportion of the phosphorus available in the digested sludge can be recovered with the corresponding process.

$$\xi_{sludge} = \frac{\dot{m}_{total P, recovered}}{\dot{m}_{total P, digested sludge}}$$

Liquor specific phosphorus yield

The liquor specific phosphorus yield is the phosphorus mass flow recovered in the final recycling product divided by the total mass flow of phosphorus in the sludge liquor phase. Therefore this yield shows which proportion of the phosphorus available in the sludge liquor phase can be recovered with the corresponding process.

$$\xi_{liquor} = \frac{\dot{m}_{total P, recovered}}{\dot{m}_{total P, sludge liquor}}$$

2 Technical descriptions of processes

2.1 Process 1: Airprex

- Crystallisation of struvite directly after the digester in the sludge phase of WWTPs with EBPR and prior sludge dewatering
- pH increase by CO₂ stripping
- Reactor design: airlift reactor with a loop stream providing a fluidized bed and conic bottom for sedimentation
- Four full scale installations in operation

2.1.1 Background

The AirPrex® process was developed by Berliner Wasserbetriebe (BWB) in cooperation with Technische Universität Berlin (TUB) to prevent undesired struvite incrustation after digestion in WWTPs applying EBPR such as the WWTP Wassmannsdorf at the Southern perimeter of Germany's capital Berlin. There, struvite incrustation threatened the plant's operational stability and caused high efforts for maintenance. The further development and the optimization of the AirPrex® process are made by Pollution Control Service GmbH (PCS).

After several tests with an existing storage tank refitted as struvite reactor, the design was optimized and a new Airlift prototype reactor was patented and erected in 2009. The 800 m³ reactor provides a capacity to treat 2'400 m³ sludge per day with a hydraulic retention time (HRT) of 8 hours. The construction of a housing around the bottom in 2010 optimized the wintertime operation.

The patented "Berliner Verfahren" is now commercialized by PCS under license of BWB as AirPrex® process. It is currently operated at several WWTPs with EBPR and sludge digestion in Germany and the Netherlands.

It was shown that this process is able to produce a fertilizer regulation conform product, marketed by BWB under the brand "Berliner Pflanze". (www.bwb.de/berlinerpflanze). "Berliner Pflanze" is the first product of AirPrex® with official fertilizer conformity approval and REACH registration, done by Berliner Wasserbetriebe.

Further information about reference installations are given in chapter 2.1.6.

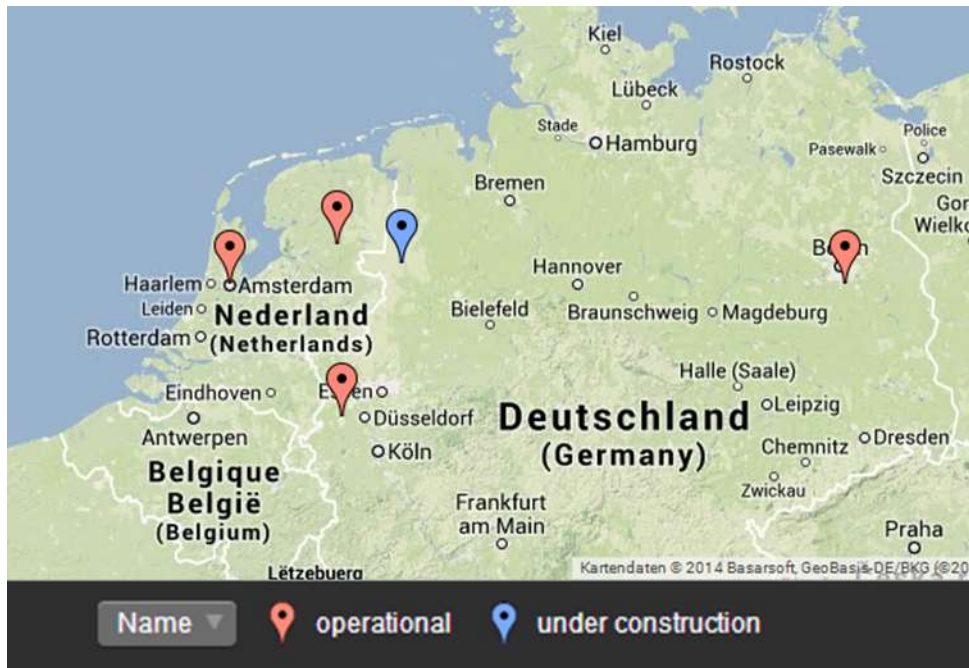


Figure 3 AirPrex installations and current operational status in Europe

2.1.2 Process design

The system is generally installed directly after the digesters and prior to sludge dewatering. In this way, the AirPrex® unit enables a controlled struvite formation and to crystallize a defined struvite without harming the WWTP's operation and performance.

The AirPrex® reactor recovers the phosphorus from the digested sludge. The deliberate crystallization of the mineral struvite is initiated under optimized conditions like pH ~8 and presence of sufficient magnesium after addition of magnesium chloride ($MgCl_2$) into the sludge inlet pipe of the reactor. The aeration with two aggregates can be adjusted between 0 and 3'000 m^3/h enabling the pH to shift from 7.5 in the digested sludge to 8 in the reactor.

The reactor is designed as airlift reactor, where air is pressed in through the bottom and released on top. Air compression for aeration requires considerable amounts of electric energy. On the other hand consumption of caustic soda for pH adjustment and energy consumption for dewatering are saved (or a lower water content and thus more efficient combustion is achieved). The internal reactor design includes a cylindrical wall, dividing the reactor into two compartments and promoting a streaming loop, where the sludge is moving upwards in the central compartment and flowing down in the outer ring. This looping moving bed allows for good contact between chemical reactants and enables the struvite crystals to grow and allows the bigger crystals to sediment in the conic bottom of the reactor, whereas the smaller particles are kept in the loop until they become large enough to settle down where the struvite can be extracted. The processed sludge is leaving the AirPrex® system on top of the outer reactor compartment towards the following dewatering step.

The airlift has two functions:

- pH increase by CO₂ stripping
- establishment of fluidized bed to enable crystallization and sufficient hydraulic retention time for crystal growth

Since the struvite product is crystallized within the wet sludge, it incorporates some sludge particles yielding a brownish color hue of the product. However, after separation from sludge, a subsequent sand washer removes the most co-precipitated and co-settled sludge particles from the struvite and improves the quality and purity of the crystals. The final fertilizer regulation conform product is collected and smoothly dried in containers and then sold to regional costumers. Figure 3 illustrates the mass flows relevant for the Airprex process, which are the following:

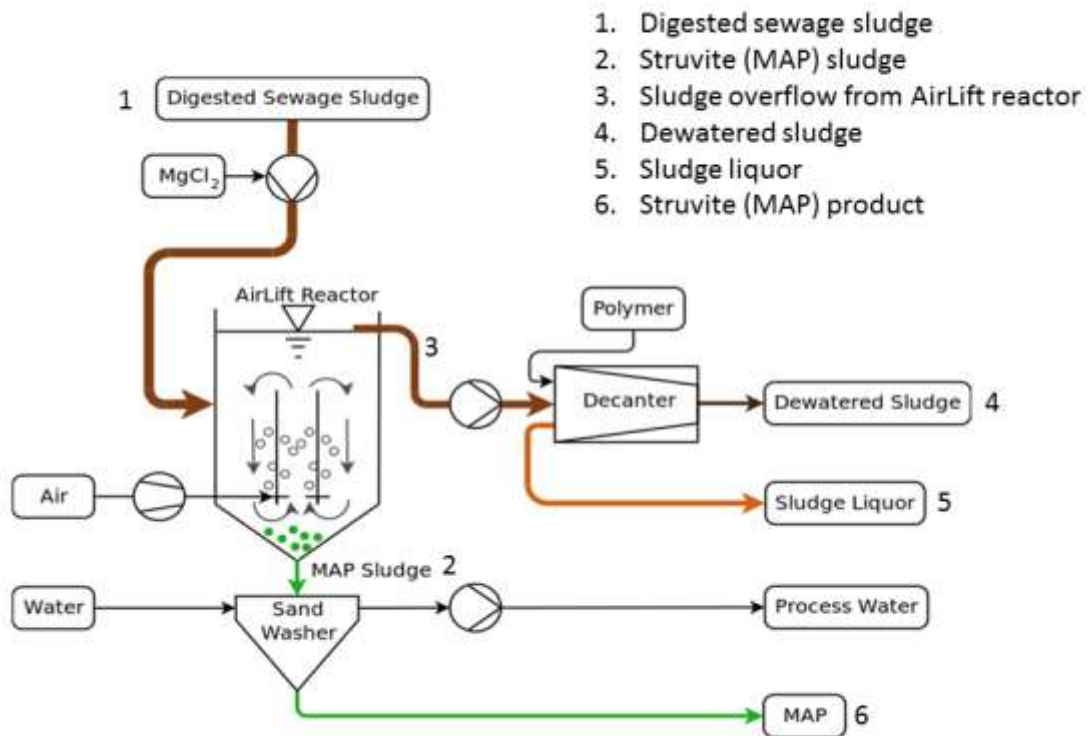


Figure 4 Flow chart of the Airprex process

2.1.3 Interactions

When crystallizing struvite directly after the digestion within the sludge but prior to dewatering, the efficiency of the sludge dewatering can be increased and the dry matter content can be raised by 3-6 % (Airprex 2014). In large WWTPs like Berlin Wassmannsdorf (Berliner Wasserbetriebe) or Neuwerk (Niersverband) this kind of optimization after installation of an AirPrex® unit led to substantial reduction of operational costs for the WWTP summing up to several hundred thousand Euros per year, even without selling the struvite [Reichert 2007]. These benefits are mainly achieved by reduced sludge disposal costs due to improved dewatering of sludge, less chemicals demand and lower

maintenance cost (pipe clogging and abrasion of centrifuges). A proven option to enhance the yield of struvite is a combination with thermal hydrolysis for disintegration of excess activated sludge. Besides improved biogas production in the subsequent digester, also insoluble or hardly soluble polyphosphates are transformed into soluble ortho-phosphate available for struvite crystallization in the sludge water.

Another benefit of this kind of phosphorus recovery is the reduction of the phosphorus and nitrogen load of the reject-water (sludge liquor), that comes as byproduct from the mechanical sludge dewatering and has to be returned to the wastewater treatment. This is a direct effect on the treatment capacity of the whole WWTP as well as a cost factor, since the removal of nutrients from the wastewater requires energy, chemicals and tank volume.

2.1.4 Options

The LysoGest® process is a combination of different processes: thermal hydrolysis of the waste-activated sludge upstream of the separate digestion of primary sludge and waste-activated sludge followed by phosphorus recovery from the fully digested waste-activated sludge with the AirPrex® procedure. The process chain for the waste-activated sludge is depicted in Figure 5 and can be described in detail as follows:

Primary sludge and waste-activated sludge are treated separately. Waste-activated sludge contains 90% of the phosphorus whereas the primary sludge contains 10% to 15% of the remaining phosphorus.

The waste-activated sludge firstly is thickened and then subjected to hydrolysis and digestion. Waste-activated sludge has a very high water absorbing capacity (due to the highly colloidal system and the exopolymeric substances (EPS)), and thus is considered the element in the sludge digestion system that is responsible for greatly reducing the degree of dewatering in proportion to its share. By subjecting waste-activated sludge to thermal hydrolysis in a pre-treatment step, poorly degradable substrates such as proteins and polysaccharides are modified such that micro-organisms can easily degrade them. This is followed by phosphorus recovery deploying the AirPrex® procedure. By deploying this procedure, the less desirable properties of the waste-activated sludge no longer have a negative impact on the good degradability and dewaterability rates of the primary sludge.

Primary sludge continues to be treated using the same technology as before. The sludge is removed from pre-treatment, fed conventionally to the anaerobic process stage and dewatered after digestion.

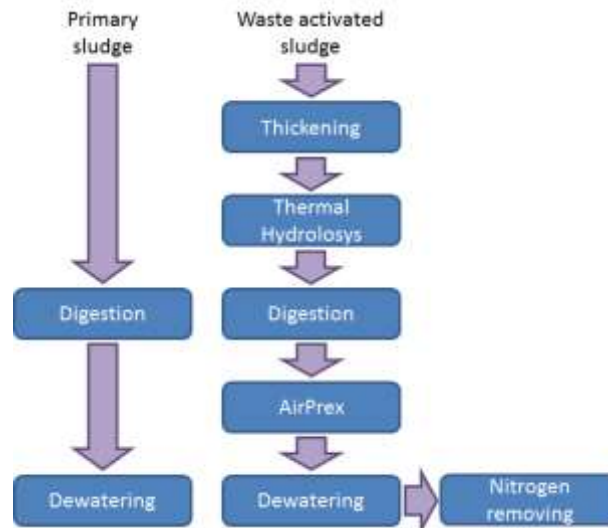


Figure 5 Flow scheme of the LysoGest®-Process

Process combinations regarding the AirPrex® process described above have been implemented at WWTP Lingen, Germany, as part of the research project “Plus-Energy Sewage Plant with Phosphate Recycling”.

2.1.5 Site specific information for the AirPrex® process

AirPrex-Berlin, WWTP Wassmannsdorf, Germany

This unit can be understood as prototype for the one-reactor configuration of AirPrex.

- Location of the air lift reactor: directly downstream of the digester unit and prior sludge dewatering
- Reactor volume: 800 m³ (treatment of the total quantity of digested sludge enabling a hydraulic retention time (HRT) of 8 hours)
- pH adjustment: by aeration (up to 3'000 m³/h)
- Magnesium dosage: MgCl₂-solution mixed into sludge in feeding pipe

In 2012 about 370 tons of struvite have been extracted and sold to regional agriculture. Optimization of crystallization, purification and drying are ongoing.

AirPrex-Mönchengladbach, WWTP Neuwerk, Germany

The AirPrex® process was integrated in the treatment processes at the WWTP in MG-Neuwerk in 2009. The AirPrex® unit is usually installed as a one-reactor system immediately downstream of the digestion process. Due to constructional particularities at the WWTP MG-Neuwerk (distance between the digester and the sludge collector/sludge dewatering unit is about 300 m) it was however necessary to split up the process into a staged system, which in this case consists of three containers, and to install the reactors at two different locations:

- Location of the digester (stand-alone unit): reactor 1 (stripping reactor)

- Location of the sludge collector/sludge dewatering unit (encased): reactor 2 (precipitation reactor) and reactor 3 (sedimentation reactor).

Table 1 Site specific data for two installations of the AirPrex-Process

	AirPrex-Berlin, Wassmannsdorf	AirPrex-MG, Neuwerk
Size of the WWTP [PE]	1,400,000	995'000
Throughput of sludge [m ³ /d]	1'820 m ³ /d digested sludge with 3.5 % TS	1'200 m ³ /d digested sludge with 3.9% TS
Liquor specific phosphorus yield [%]	95	83
Sludge specific phosphorus yield [%]	5-10	7.7
Energy consumption (without sludge dewatering) [kWh per m ³ sludge]	n.d.	0.5-1
Energy consumption [kWh per kg P in product]	n.d.	8-16
Molar ratio of magnesium to phosphate [-]	1.1 - 1.5	
Dry matter cont. without MAP recovery (%)	24-25 ¹	21 ²
Dry matter cont. with MAP recovery (%)	27-28 ¹	25-26 ²
Polymer without MAP recovery (100%) [kg/t _{DM}]	12-13 ¹	10-13 ²
Polymer with MAP recovery (100%) [kg/t _{DM}]	8-9 ¹	9-12 ²
Percentage of P in the product [weight%]	9	9

¹ [Ewert 2007] ² [Ewert 2009]

Further installations of the AirPrex® process

Some basic information about further sites with realized or planned installations of the Airprex® process is given in Table 2.

In addition, the geometry of the reactors was adjusted to suit the location requirements.

The first reactor (reactor 1) is located adjacent to the digestion chambers. It serves to precipitate the magnesium “naturally” occurring in the digested sludge as struvite (magnesium ammonium phosphate (MAP)). This prevents uncontrolled crystallisation, and the digested sludge can be fed to the sludge collector/sludge dewatering unit across a distance of 300 m. The pH value is increased to > 7.8 through air stripping. No additional precipitant is added to the first reactor. Magnesium is the pre-

precipitation parameter as it is precipitated in the first reactor stage to a level that makes it unnecessary to add crystallisation prevention agents to chemically protect the pipelines leading to the collector.

The crystals formed in reactor 1 are suspended in the sludge and fed to the actual phosphorus removal station (reactors 2 and 3) via the sludge pipeline using gravity flow.

At the collector site, in reactor 2, the struvite is almost completely crystallised by adding air and dosing magnesium solution (phosphorus concentrations in the sludge are reduced to almost zero, benchmark: $\text{PO}_4\text{-P} < 50 \text{ mg/l}$). Using gravity flow the digested sludge is fed to reactor 3 where the crystals mature and the precipitated MAP crystals settle down.

This procedure prevents further struvite crystallisation even if, during the sludge dewatering process for example, new magnesium ions enter the sludge due to the addition of polymer solution.

The struvite washer has been installed between reactor 2 and reactor 3. In the washer the crystals are cleaned, whereby 80% - 90% of all organic components are removed. The washed struvite is filled into containers and recycled as required.

Table 2 Basic data for further installations of the Airprex process

WWTP and plant size (person equivalents)	Operator	Sludge m^3/d	Struvite production capacity kg/d	Start of operation
Wassmannsdorf (Berlin) 1,400,000	Berliner Wasserbetriebe, DE	1,820	2,500	2010*
Mönchengladbach-Neuwerk 995,000	Niersverband, DE	1,500	1,500	2009
RWZI Echten 190,000	Reest & Wieden, NL	400	500	2013
Amsterdam-West 1,000,000	Waternet, NL	2,500	4,000	2014
Lingen 195,000	Stadtentwässerung Lingen, DE			2014

*2011 with housing

2.2 Process 2: Struvia process

- Crystallisation of struvite or calcium phosphate in one of the following streams or a mixture:
 - Centrate of thickened sludge from WWTPs with EBPR
 - Centrate of digested sludge from WWTPs with EBPR
 - Centrate and filtrate of sludge after thermal hydrolysis (Athos)
 - Industrial waste water
- Reactor design: two different configurations of continuous stirred tank reactors:
 - Turbomix® reactor with an additional lamella settler
 - Turboflo™ reactor combining intensive mixing and settling in a lamellar packing in only one reactor
- Laboratory, mini-pilot experiments and pilot study on the WWTP Brussels North with a reactor size of a 100-1000 L/h throughput

2.2.1 Background

Since the 1980ies, the Veolia group has significant experiences with struvite crystallisation technology in several areas, but mainly in Japan and in cooperation with its subsidiary company SKS. As a first step in phosphorus recovery, the company SKS developed the Phostrip® technology based on the combination of an anaerobic membrane bioreactor and a fluidized bed crystallizer producing struvite or calcium phosphate (hydroxylapatite (HAP)). The company SKS operated successfully one pilot plant and three reference WWTPs with HAP or struvite production. The optimal conditions applied on these installations in Japan colleagues are a reaction time of 1h, pH of 8, and a molar ratio Mg/P of around 1.1. A liquor specific phosphorus yield of 70-80% is obtained with the production of struvite with a particles size between 0.3 and 2 mm (0.2-0.5 mm for HAP).

Another concept by the Veolia subsidiary Nishihara uses seawater as the magnesium source necessary for struvite precipitation. A pilot study with a fluidized bed reactor has been performed at Kitakyushu city (Hiagari WWTP) showing liquor specific phosphorus yield > 70% by using 9-10 Vol-% of seawater.

The struvite product is finally integrated into an organo-mineral fertilizer produced and sold by the Veolia agronomic pole (pellets production).

During the P-REX demonstration tests, it was decided after the first months of operation to select the struvite precipitation instead of calcium phosphate (CaP) precipitation for several reasons:

- CaP and in particular HAP (HydroxyApatite) is less interesting from an agronomic point of view (P release for the plant) in comparison to struvite which is a slow release fertilizer, also reflected in the potential selling price.
- It can be more difficult to obtain CaP than struvite due to the possible competition with CaCO₃ precipitation in case of high alkalinity of the effluent. Precipitation of CaP can also lead to the formation of gel or fines which impacts the settling velocity.

However, CaP precipitation remains interesting for treatment of some acidic industrial waste water, e.g. for the food & beverage and chemistry sectors.

2.2.2 Process design

The Struvia™ technology consists of the crystallisation of struvite from waste water in a Continuous Stirred Tank Reactor (CSTR) and a liquid-solid separation. Today, this technology exists in two different configurations:

- Turbomix® configuration
- Turboflo™ configuration

In the first configuration, the process is divided into two steps: the struvite crystallisation is performed in the Turbomix® reactor, while the liquid – solid separation takes place in a lamella settler. The Turbomix® reactor is equipped with a vertical mixer, a draft tube and several baffles to optimize the mixing and the influent / chemical(s) injections. A struvite recirculation from the bottom of the lamella settler to the Turbomix® reactor is necessary to maintain a certain concentration of MAP crystals in the reactor in order to promote the crystals growth and avoid nucleation.

In the Turboflo™ configuration, the two steps - crystallisation and liquid/solid separation - take place in the same equipment, the Turboflo™ reactor. The mixing zone is similar to a Turbomix® reactor above which a calming zone and a lamellar packing are installed to retain the struvite particles in the mixing zone.

The two flow schemes given in Figure 7 and Figure 8 show all mass and energy flows relevant for the Struvia™ technology.

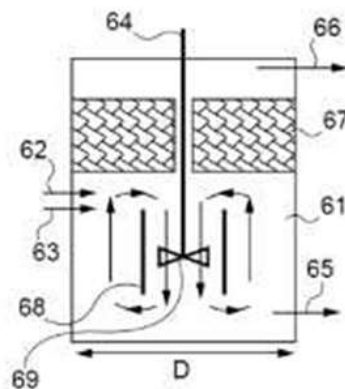


Figure 6 Simplified scheme of the Turboflo™ reactor

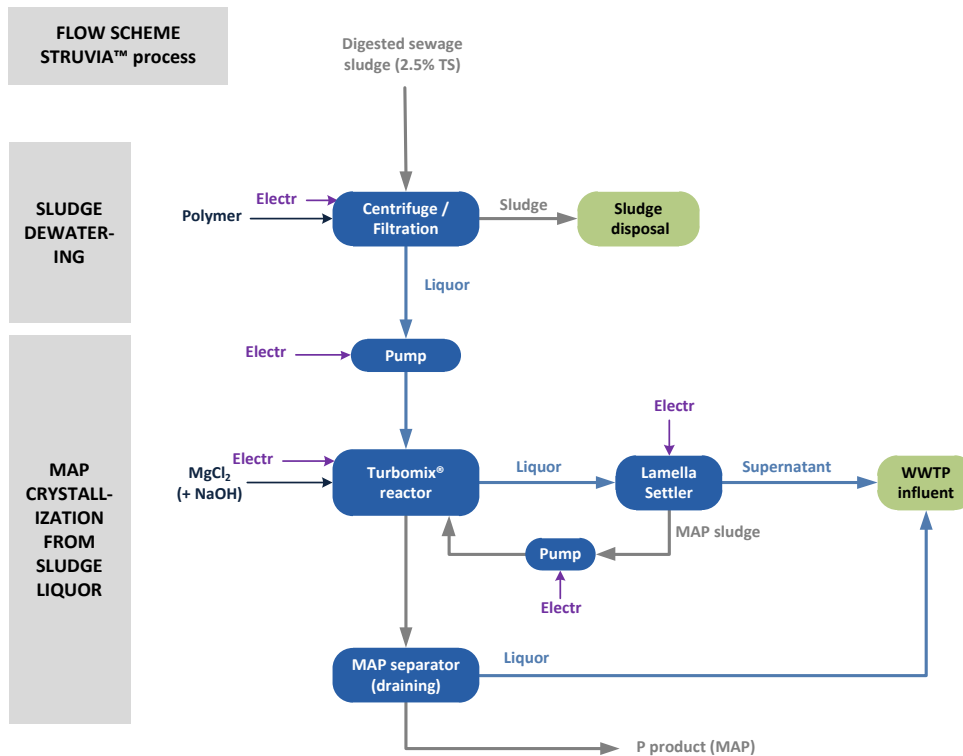


Figure 7 Struvia™ process - Turbomix® configuration

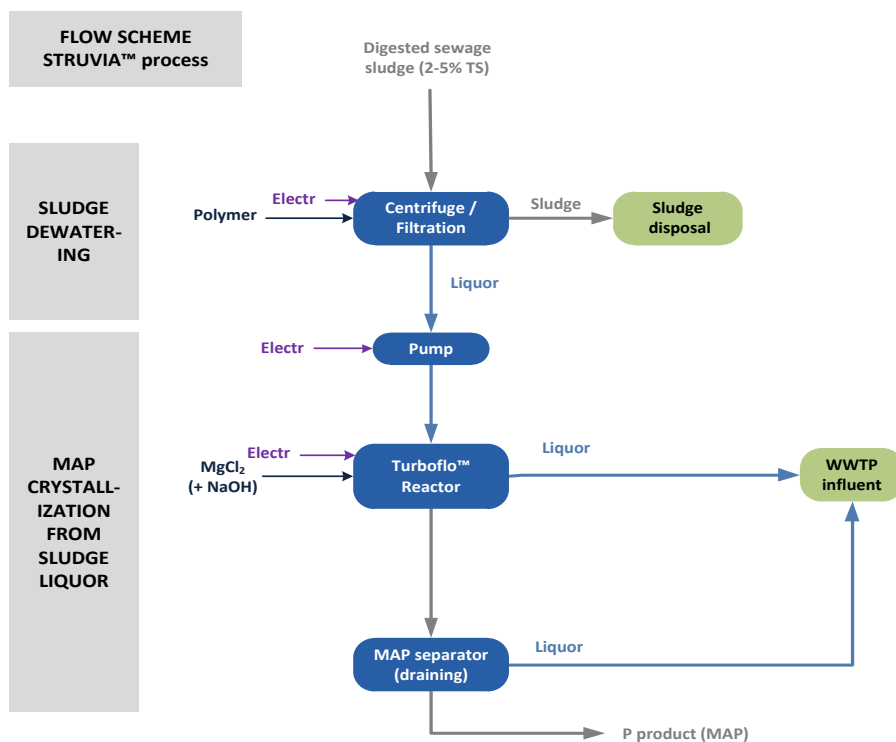


Figure 8 Struvia™ process - Turboflo™ configuration

In both configurations, the sludge liquor from digested sludge is pumped into the mixing and reaction zone. In the case of the first configuration, this is the Turbomix® reactor. In the case of the second configuration, this is the (lower) mixing zone of the Turboflo™ reactor. A magnesium source - usually

liquid magnesium chloride with a concentration of 33% - is added. The molar ratio Mg/P-PO₄ applied in the StruviaTM process varies from 1.1 to around 2 according to the quality of the liquor - in particular in term of TSS or calcium concentration - and the required quality of the struvite product. A sufficiently high Mg:P and Mg:Ca was demonstrated to be decisive for sufficient size of the struvite particles and low co-precipitation of calcium (see annex (4.1)).

If the pH is not optimal - i.e. between 8 and 9 -, caustic soda with a concentration of 30 or 32% can also be added. A pH probe is controlling the injection of caustic soda. The influence of the pH is exemplarily shown in Figure 9 (see also annex (4.1)).

After 30 min to 2 h of reaction, the waste water containing the struvite produced is:

- Either moved by gravity to a lamella settler, equipped with a scraper (in the Turbomix® configuration),
- Or passes through the lamellar packing located above (in the TurbofloTM configuration).

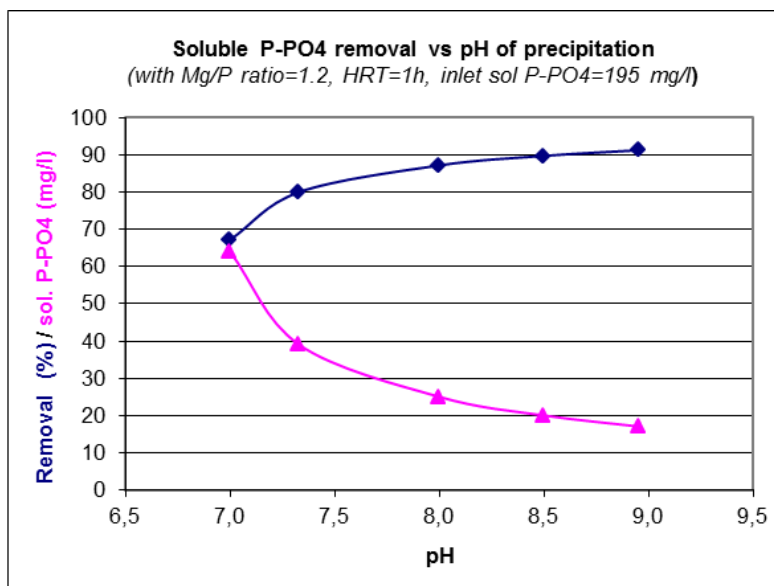


Figure 9 Example of soluble P-PO₄ removal according to the pH of struvite precipitation

The supernatant of the settler or of the TurbofloTM reactor returns at the inlet of the WWTP (in the case of digested sludge liquor). With the struviaTM process, at least 80% of the phosphorous and a certain percentage of ammonia - according to the inlet concentration - are removed. An on-line turbidity analysis of the supernatant allows checking the efficiency of the solid-liquid separation. As an option, an on-line P-PO₄ analyser can be installed in the supernatant to check in real time the efficiency of the chemical precipitation. Based on these results, the operational conditions (mixing velocity, pH, Mg/P ratio, TSS into the reactor) can be adapted if necessary.

In the Turbomix® configuration, the struvite crystals settle at the bottom of the clarifier (equipped with a scraper). Subsequently, a pump recirculates the crystals into the Turbomix® reactor. In the TurbofloTM configuration, the struvite crystals are retained directly in the reactor. Therefore, a certain concentration of struvite crystals (or TSS) is kept in the reactor to promote the crystals growth and avoid nucleation. A TSS probe (previously calibrated with the type and particle size of crystals concerned) records the average concentration of struvite into the reactor.

The struvite extraction from the reactor is sequenced. Hence a regular extractions takes place based on either the treated flow, time or struvite concentration in the reactor. Finally, the struvite is drained in a gravity draining system which allows to dewater struvite sludge. The final struvite dryness (measured at 40°C and not at 105°C, because the thermal decomposition of the struvite takes place from 50°C) is around 60-65%, only with gravity dewatering. Applying atmospheric drying by storage during several weeks in filtration bags a dryness of 80-90% is reached.

The Turboflo™ reactor configuration has several advantages. This configuration contains only one single reactor without separated settler. Due to the integration of the liquid/ solid separation in one process unit, neither the struvite recirculation loop nor a recirculation pump is required. This leads to decreased clogging risk, reduced footprint and hence lowers CAPEX and OPEX in comparison to the Turbomix® configuration.

2.2.3 Interactions

Struvite crystallisation from the centrate of digested sludge leads to a reduction of the phosphorous and ammonia load to the inlet of the WWTP. The additional dose of coagulant (iron or aluminium), used to achieve phosphorus removal by chemical precipitation, is reduced. Therefore, the production of chemical sludge (ferric or aluminium phosphate and hydroxide) is also reduced. According to the ammonia load reduction, there is a potential gain concerning aeration necessary for biological nitrification. Moreover, after the struvia™ process, the scaling risk in pipes is reduced and hence the maintenance costs are lower.

In the case of sludge liquor, struvite crystallisation is in direct interaction with the efficiency of the sludge dewatering. Indeed, the TSS concentration of the centrate has an impact on struvite (and also CaP) crystallisation. Ideally, TSS concentration should be less or equal to 1 g/l. The process can tolerate several g/l but with impact on the struvite quality with decrease of crystal growth and therefore on the settling and draining velocities due to the presence of organic matter.

In the case of certain industrial waste water, a high calcium, carbonate or soluble COD concentrations can have a bad effect on struvite crystallisation as a competition with other precipitation reactions (calcium phosphate, calcium carbonate, precipitable organic matter) can be observed. Certain organic compounds as e.g. acetats can act as antiscaling agents which are inhibiting crystallization reactions.

When these problems appear, the operational conditions must be adapted (i.e. the Mg/P ratio applied) and / or a specific pre-treatment can be necessary to reduce the cause of the problem upstream crystallisation.

2.2.4 Options

As explained before, the struvia™ technology can be implemented with two possible configurations: Turboflo™ and Turbomix® configurations. After the first months of pilot tests, the Turboflo™ configuration was selected as it was easier to operate. Instead of injecting caustic soda to adjust the pH of precipitation, an alternative is to have an air stripping reactor upstream the crystallisation reactor. The Turbomix® reactor may be replaced by a CSTR mixed with an air-lift device according to the reference installations in Japan. This concept is also used for the Airprex® and Nuresys processes.

Aeration leads to a slight pH increase of 0.5 to 1 pH units which can be sufficient to have an optimal struvite precipitation.

If the objective is to remove a high alkalinity concentration and prevent the formation of calcium carbonate in the reactor, CO₂ stripping must be realized at much lower pH and requires an acid injection.

If a high concentration of total suspended solids (TSS) of the waste water negatively affects the struvite crystallisation (reaction time too long, production of fines particles, slow settling and draining, final struvite containing too much organic matter), two options are possible: A TSS pre-treatment of the waste water by filtration and/or a struvite washing (before draining) with water coming from the reject of the WWTP. The second option is applied at Berlin-Wassmannsdorf to remove the organic matter and other colloids from the struvite produced and extracted from the struvite crystallisation reactor.

For treatment of acidic food & beverage and chemistry waste waters, calcium phosphate precipitation may be interesting. . Lime addition allows to increase the pH and to provide calcium necessary to precipitate phosphates. To control these two actions separately, it is possible to use caustic soda for pH adjustment to around 8 and to use pricier calcium chloride only as the precipitation agent. In both cases, soluble P-PO₄ removal is often higher than 95%. Sometimes flocculation step may be necessary if the produced CaP is too fine.

Drying of the product to a dryness > 99% is an option if required. It is important to operate the drying process at a temperature lower than 40-50°C as struvite decomposes into dittmarite (MgNH₄PO₄, H₂O) or in magnesium phosphate at higher temperature.

Another option is to associate the Struvia™ technology with ammonia stripping in order to increase global ammonia removal.

2.2.5 Site specific information for Pilot at Brussels WWTP

The pilot study conducted in the course of the P-REX project is located at Brussels North WWTP. Several internal partners are involved in this pilot study: Aquiris, VERI (Veolia R&D center) and the Veolia agronomic pole.

The objectives were to recover phosphorous from different waste water streams of Aquiris WWTP and to demonstrate that the following performance indicators can be achieved:

- Soluble liquor specific phosphorus yield $\geq 80\%$ for a maximum reaction time of 2 hours.
- Struvite quality in accordance with the specifications given by the Veolia agronomic pole.

At Brussels North WWTP, biological sludge extracted from the waste water treatment line is treated in two gravity thickeners. After storage, a post thickening dewatering by centrifugation allows to concentrate the sludge. Then thermal pre-hydrolysis (10 bars, 160°C) followed by mesophilic digestion is performed to reduce the volume of the sludge and to produce biogas. Digested sludge is transported to two Athos™ reactors (Wet Air Oxidation process – 50 bars, 250°C) where organic matter is oxidized and after filter press dewatering a final residue is produced called technosand which can be re-used in various industries. As this WWTP (with a capacity of 1,1 million p.e.) is

constantly overloaded, the sludge production exceeds the capacity of the Athos™ process. Therefore, a portion of the digested sludge is dewatered by centrifugation prior to incineration disposal.

Four different waste water streams identified for the pilot study are listed below and partly depicted in Figure 10:

1. Athos™ effluent (supernatant + filtrate)
2. Centrate of the digested sludge
3. Centrate of the thickened sludge (not alone as the ammonia concentration is not sufficient)
4. A fourth waste water, named industrial effluent, has been tested to simulate a Food & Beverage type effluent, after a biological treatment with the following characteristics:
 - pH = around 7
 - Dissolved. P-PO₄ = 150-200 mg/l (and punctually 300 mg/l)
 - Dissolved N-NH₄ = 150-850 mg/l
 - TSS < 100 mg/l
 - Total COD < 100 mg/l
 - Ca = 80-150 mg/l
 - Mg ≤ 30 mg/l

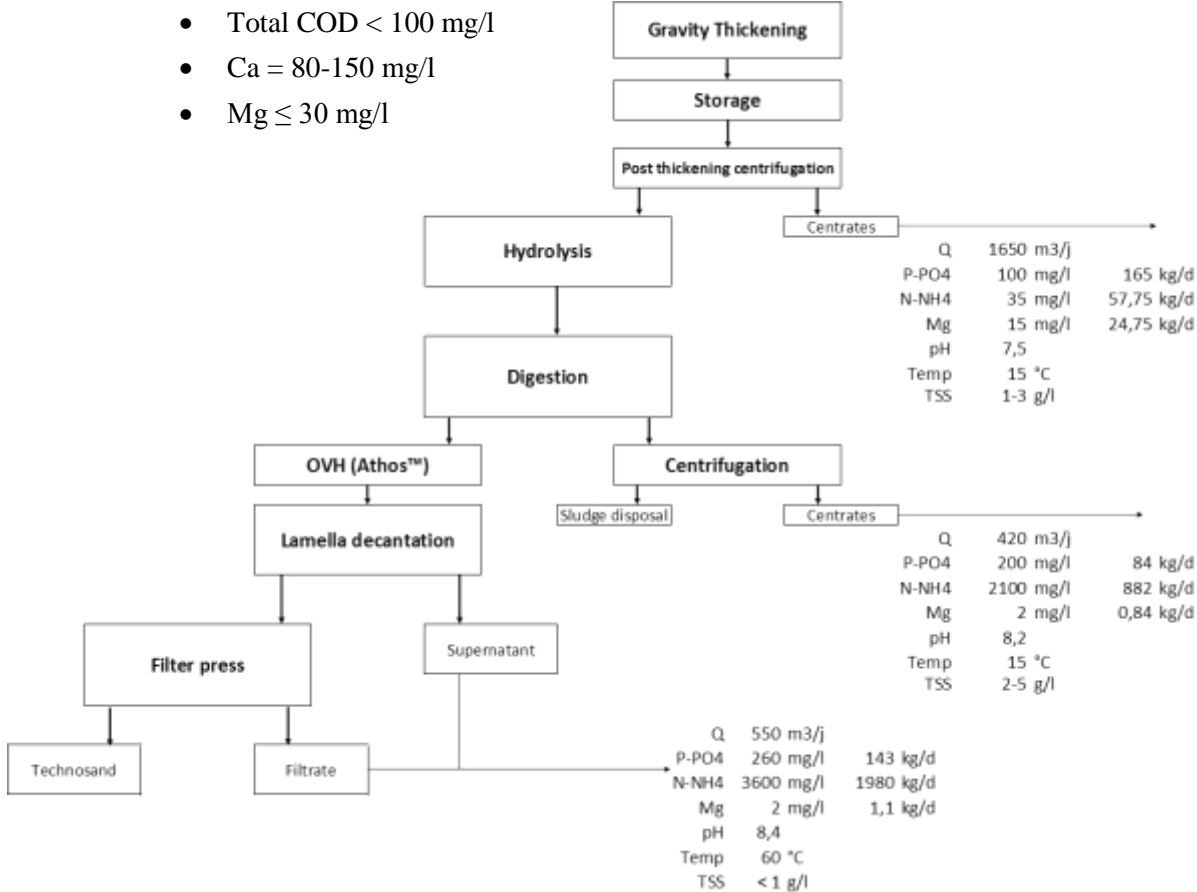


Figure 10 Aquiris sludge treatment and side-streams

The first steps of the pilot study (1st sem. 2013) were preliminary batch laboratory tests and a mini-pilot test with a reactor volume of 5 L. The results obtained in this experimental work are shown in the annex (4.2).

The P-REX pilot was installed and started-up at Brussels, in April-May 2013. The main characteristics of the pilot plant are presented in Table 3 and Figure 11.

Table 3 Summary of characteristics and process information Struvia®, Brussels

Characterisation of pilot	Throughput of centrate [m ³ /d]	100-1000 L/h
	pH control by	Caustic soda or lime injection
	Type of precipitation	Struvite or CaP
	Type of configuration	Turbomix or Turboflo
	Mixing velocity	30-300 rpm
	Total reactor volume	550 l (stainless 316L)
Operational data obtained from pilot study	Liquor specific phosphorus yield [%]	80-95%
	Sludge specific phosphorus yield [%]	<i>estimated at ~15%</i>
	Energy consumption [kWh per m ³ centrate]	≤ 0.3 (~0.2)
	Energy consumption [kWh per kg P in product]	~ 2 (1.7-2.5)
	NaOH (30%) [kg/m ³ centrate]	0-0.6
	Molar ratio of magnesium to phosphate [-]	1.1-2
	Percentage of P in the product [weight%]	12-13

**Figure 11 Struvia™ P-REX pilot**

A detailed description of the experimental results obtained for different types of effluent is given in the annex (4.1.2).

The chemical consumption is directly linked to the characteristics of the treated effluent. The range of dose is given in Table 3.

Up to now it is still difficult to accurately calculate the energy consumption of the struvia™ technology, since it has been operated in pilot scale which is around 1/50 compared to an industrial unit. In the Turboflo™ configuration, electricity is consumed by the feed pump which is estimated to consume maximal 0.1 kWh/m³_{treated flow} for an industrial unit and by the reactor mixer which consumes approximately 0.2 kWh/ m³_{treated}. The feed pump and the mixer run continuously but not at maximum speed. The energy consumption of the chemicals dosing pumps is negligible. According to the estimation, a full scale Struvia™ unit consumes a total of up to 0.3 kWh/m³_{treated}. Estimations for the specific energy consumption referring to the amount of recovered phosphorus are in the range of 1.7 to 2.5 kWh/kg_{p, recovered} (see also annex (4.1.2)). Table 3 summarizes the site specific information about the pilot installation of the Struvia® process in Brussels.

The quality of struvite varies according to the quality of effluent treated (see Table 4).

Table 4 Main components and impurities of the produced struvite after drying at 40°C

P_{total}	P₂O₅	N_{total}	Mg	Ca	K	SiO₂	SO₄	Fe	Al
[%w]				[g/kg]			[mg/kg]		
12-13	28-29	4.5-5.5	9.5-10.5	0.5-3	0.5-1.5	0.1-2	250-350	200-400	10-100
Mn	Zn	Cu	Cr	Ni	Pb	Cd	Sn, Se, As		Hg
[mg/kg]									
30-40	30-40	3.8	2.4	0.9	0.5	0.1	<0.5		<0.1

In addition to the one-year P-REX demonstration study at Brussels, other laboratory and pilot studies from different industrial effluents have been realized:

- Acid chemical industry effluent (CaP precipitation)
- Centrate from co-digestion of different organic wastes (MAP precipitation)
- Starch industry effluent (MAP precipitation)
- Acid Food & Beverage effluent (CaP or MAP precipitation – Preliminary anaerobic treatment essential to decrease the COD concentration)

2.3 Process 3: Crystalactor

- Crystallisation of struvite or calcium phosphate generally from centrate from WWTPs with EBPR, wastewater treatment plant effluent and industrial waste water
- Reactor design: cylindrical reactor with a fluidized bed, usually sand as seedings, recirculation at defined volume flow to realise a sharp phase separation, retaining particles in the reactor
- Full scale installations have been in operation starting from 1988

2.3.1 Background

This crystallisation process was first developed in the 1970ies for a different application: for the softening of drinking water, i.e. the crystallisation of CaCO_3 from drinking water. The process was developed and patented by the company DHV Water BV Water together with the Municipal Water Works of Amsterdam [Giesen and Van der Molde, 1996; Hermann, 2009]. In the 1970ies around 50 plants for drinking water softening were built internationally with crystallisation reactors of the Crystalactor design [Hermann, 2009]. In the following years, this process was also applied in full-scale for the removal of phosphorus from municipal and industrial wastewater.

The first installation took place in 1988 on the municipal wastewater treatment plant in Westerbork, Netherlands which has a size of 12'000 p.e.. In this application the crystallisation was done from the main stream, i.e. from the effluent of the biological treatment followed by filtration. The phosphorus concentration was reduced from 10 mg/L to below 0.5 mg/L. The crystallisation product – calcium phosphate – was used by the phosphorus processing industry. This installation was operated successfully and economically due to the relatively high concentration of dissolved phosphorus in the municipal wastewater. Due to reduced application of phosphorus containing detergents, phosphorus concentration in the effluent of the biological treatment decreased. As a consequence the application of this crystallization technology in the main wastewater stream became economically unattractive and the operation of the Crystalactor in Westerbork was stopped [Piekema and Giesen, 2001, Giesen, 2009, Hermann, 2009].

As an alternative the Crystalactor technology was applied in the side stream of wastewater treatment plants with enhanced biological phosphorus removal. In 1994, a plant started operation on the wastewater treatment plant Edam, Geestmerambacht, Netherlands (230'000 p.e., 250 m³/h). In this installation, phosphorus was recovered from the supernatant from surplus sludge as calcium phosphate, reducing the concentration of 60-80 mg_p/L to 15-20 mg_p/L [Piekema and Giesen, 2001, Giesen, 2009].

A similar installation was built in 1993 in Heemstede, Netherlands [Piekema and Giesen, 2001, Giesen, 2009].

Further installations were operated in full scale in several industrial sectors: potato processing industry, food industry, and dairy industry. The products yielded from these applications include calcium phosphate and struvite [Piekema and Giesen, 2001, Giesen, 2009].

2.3.2 Process design

The core process of the Crystalactor technology is the crystallisation reactor with feed pump, dosing of chemicals, dosing of seeding and recirculation.

Figure 12 shows the configuration of the Crystalactor process and the connection between different parts of the system and with the WWTP [Houwelingen, personal communication].

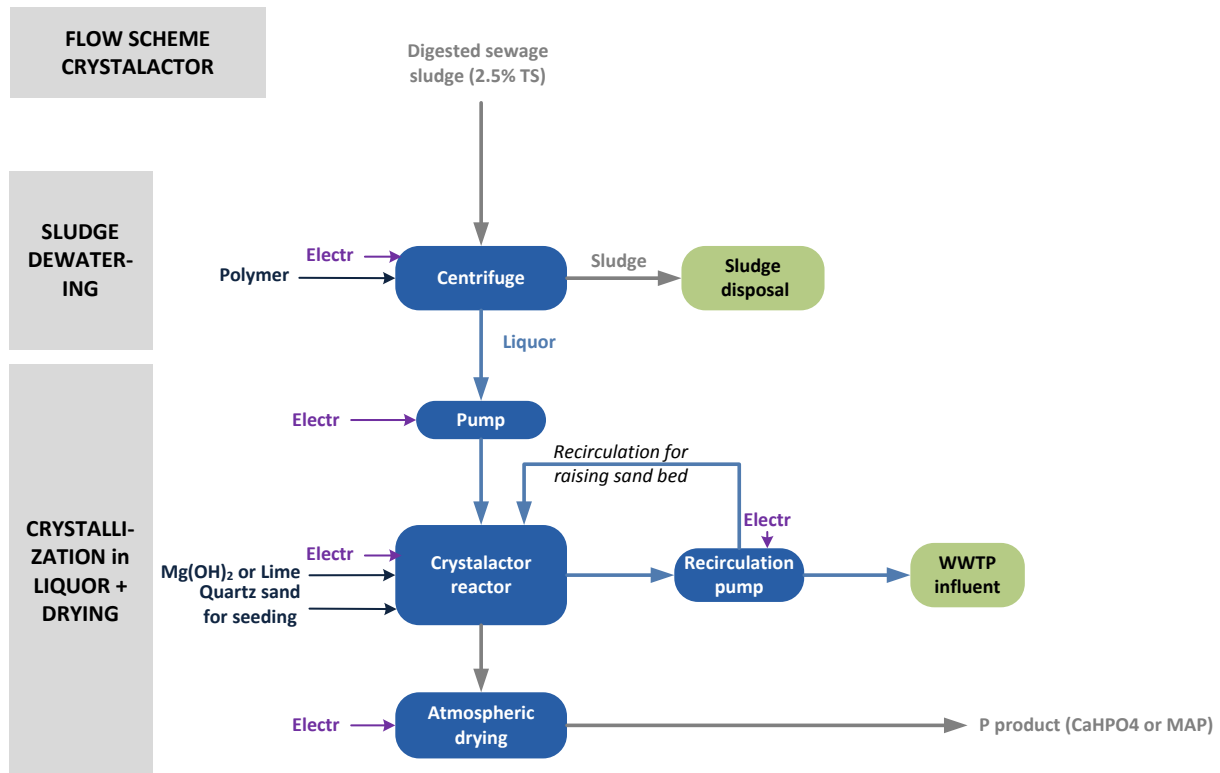


Figure 12 Flow chart of the Crystalactor Process [based on Houwelingen, personal communication]

The general principle of the Crystalactor technology is a controlled crystallisation of phosphate on seeding particles producing a phosphorus product with relatively high particle size. The crystallisation process is operated in a cylindrical up flow reactor containing a fluidized bed of seeding material. Fine sand of a particle size of around 1 mm is often applied as seeding pellets.

In order to adjust the chemical and hydrodynamic conditions in the reactor, a part of the reactor overflow is recycled into the dosing zone at the bottom of the reactor (see Figure 13). The recirculation ratio applied for this process lies in the range of 2.5-3 [Piekema and Giesen, 2001].

The sand is usually stored in a silo and dosed in batches using a vibrating feeder or dosing screw into the funnel of an ejector pump. The sand mixes with the motive water in the ejector and the slurry is pumped into the reactor. The function of the sand dose is to keep the number of grains in the bed relatively constant; ideally one sand grain should be dosed for each pellet that is discharged from the reactor. This objective is reached with the help of a control system for sand supply and pellet discharge that closely approximates the correct dosing rate to maintain a nearly constant number of pellets in the reactor. Sand batches are dosed a couple of times per day. The dosing of sand is typically

around 5% by weight of the struvite removed. Sand is dosed and pellets are discharged during normal operation while the bed is fluidized [Houwelingen, personal communication].

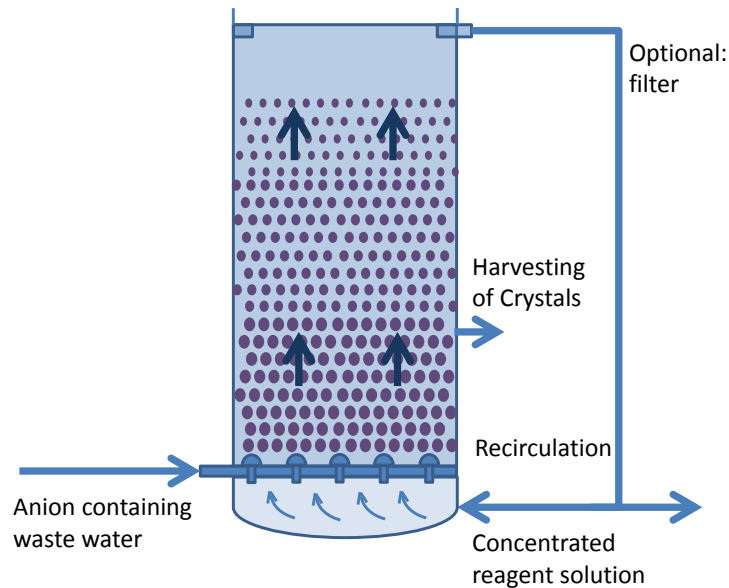


Figure 13 Principle of the reactor with recirculation [based on Giesen and Van der Molen, 1996]

The fluidized bed provides a large crystallization surface in the magnitude of $5'000-10'000 \text{ m}^2/\text{m}^3$ [Giesen and Van der Molen, 1996]. The large crystallization surface enables a high crystallization efficiency despite the compact reactor design. The liquor specific phosphorus yield lies typically around 70% [Houwelingen, personal communication].

The up flow velocity in the reactor is adjusted to a value which is typically between 40 and 120 m/h. As a consequence the pellet bed is kept in the fluidized state and a sharp phase separation between the supernatant and the fluidized bed is obtained at the top phase of the reactor [Giesen and Van der Molen, 1996]. In general, a hydraulic load of 40-75 m/h has shown to lead to good results [Piekema and Giesen, 2001].

The dosing of chemicals depends on the type of phosphorus product. For the production of calcium phosphate, lime is added and the pH adjusted to about 8 [Houwelingen, personal communication].

For the production of struvite, usually $\text{Mg}(\text{OH})_2$ is dosed. Hence the Mg:P ratio is increased and the pH is raised simultaneously. Alternatives are dosing of MgCl_2 and pH adjustment by CO_2 stripping or NaOH dosing [Houwelingen, personal communication].

In general the chemical conditions are adjusted in a way that the super saturation does not exceed a critical limit in order to avoid nucleation and hence the formation of a high number of very small crystals. At optimal conditions an overdose of $0.5-5 \text{ mol}/\text{m}^3$ is applied [Piekema and Giesen, 2001].

In order to avoid disturbance of the crystallisation, the concentration of suspended solids should not be higher than 250 mg/L and the inorganic carbon below 1 mmol/L. Hence monitoring devices such as scum baffles in the thickener, sludge blanket detection in the thickener, turbidity monitor in the reactor influent line are beneficial. In case of too high inorganic carbon, acid dosage in form of carbon dioxide and stripping in a cascade tower are applied [Houwelingen, personal communication].

2.3.3 Interactions

Two main situations of applying the Crystalactor are distinguished:

If the Crystalactor is applied for phosphate crystallisation from the centrate of sludge dewatering, the load of nutrients which is recycled into the aerated tank is reduced significantly. In the case of crystallisation of struvite, both phosphorus and nitrogen loads are reduced. In the case of calcium phosphate only the phosphate load is reduced. As shown below in chapter 0, it is estimated that with a similar process around 30% of the total ammonium load of the biology can be removed in this way for plants with enhanced biological phosphorus removal. This is an important advantage for the wastewater treatment plant saving costs and capacity. For plants with enhanced biological phosphorus removal this leads to a more stable operation of the process, saving additional dosing of chemical precipitants, reduction of the amount of sludge produced and preventing uncontrolled precipitation of struvite leading to encrustations in pipes and other devices.

2.3.4 Options

An optional pre-treatment of the centrate or waste water is the stripping of CO₂. A possible configuration is to dose sulphuric acid to convert the carbonic acid into CO₂. This pre-treatment is beneficial in the case of crystallisation of calcium phosphate. In this case the formation of calcium carbonate is a competing reaction. The formation of carbonate is reduced by removing the carbonic acid. This option is less relevant in the case of producing struvite or magnesium phosphate [Houwelingen, personal communication].

Since large crystals with particle size larger than 1 mm are produced the pellets can normally be dewatered by atmospheric drying. Usually a reduction of the water content below 5-10% can be achieved by atmospheric drying [Giesen and Van der Molen, 1996].

Further cleaning, sieving and drying processes can improve further the product quality.

In cases in which the Crystalactor is applied in the main waste water stream before discharge into surface water – hence in the effluent of the wastewater treatment plant – filtration might be required. By the filtration suspended solids are removed in order to meet the discharge regulations. For an application on centrate from sludge dewatering this optional process is not required since the water is recycled into the influent of the aeration tank where a certain concentration of suspended solids is not critical [Houwelingen, personal communication].

2.3.5 Site specific information

For the installations in operation, it was observed that crystallization efficiency (Liquor specific phosphorus yield) of 70% was achieved.

The final product – the calcium phosphate pellets – typically contain 40-50% calcium phosphate, 30-40% sand and up to 10% calcium carbonate.

2.4 Process 4: Pearl® (Ostara)

- Crystallisation of struvite from centrate from WWTPs with EBPR
- Reactor design: stepwise increase of reactor diameter, self-seeding reactor, fluidized bed, recirculation to maintain low over-saturation
- Several full scale installations in operation in North America, one full scale installation in operation in Europe.
- Product is marketed as slow release fertilizer for special applications

2.4.1 Background

Studies about fundamental mechanisms of struvite crystallisation in digester supernatant were performed at the University of British Columbia, Vancouver. Comprehensive studies about the thermodynamic solubility product of magnesium ammonium phosphate and dependency of this on process parameters as ionic strength and temperature were conducted. Investigations about the nucleation and growth kinetics and the identification of the fluidized bed reactor provide important basic knowledge for optimized design and operation of struvite crystallisation reactors [Bhuiyan, 2007]. The university provided results with a pilot scale crystallisation reactor using model solutions and digester supernatant from Canadian wastewater treatment plants [Huang et al., 2006]. Furthermore, the technology was tested in pilot-scale at the Advanced Wastewater Treatment Plant of the city of Pentincton and the Greater Vancouver Regional District's Lulu Island wastewater treatment plant [Britton et al., 2005, Severs, 2005].

The process developed as a result of this research activity was commercialized in 2005. The company Ostara Nutrient Recovery Technologies Inc. was founded in 2005 as a spinoff of the University of British Columbia for bringing the process to the market. The nutrient recovery process is marketed under the name Pearl® with the reactor sizes ranging from 5 kg P/day to 10 t P/day. A series of WWTP mainly in North America installed the Pearl® process and first was installed by Thames Water in Slough (London) in 2013.

The fertilizer product is marketed under the name Crystal Green® and received fertilizer certification. Hence it is not considered biosolid or “waste-derived” product but fertilizer.

The strategy of Ostara for the implementation of cooperation with the operators of wastewater facilities are public-private partnerships. Ostara sells the reactors to the operators of the wastewater treatment plants and signs a contract for buying the fertiliser product. Hence Ostara is responsible for providing of the plant and for the marketing and selling of the fertilizer product. Systems have been delivered under various procurement models, including Design-Build, Design-Build-Finance-Operate, and Design-Bid-Build.

2.4.2 Process design

The flow scheme (Figure 14) illustrates the Pearl® process and shows all relevant mass and energy flows. The core of the process is the Pearl® reactor which is an up flow reactor with several different diameters (see Figure 15). The reactor inside is filled with growing struvite crystals forming a fluidized bed due to the digester supernatant flowing upwards in the reactor.

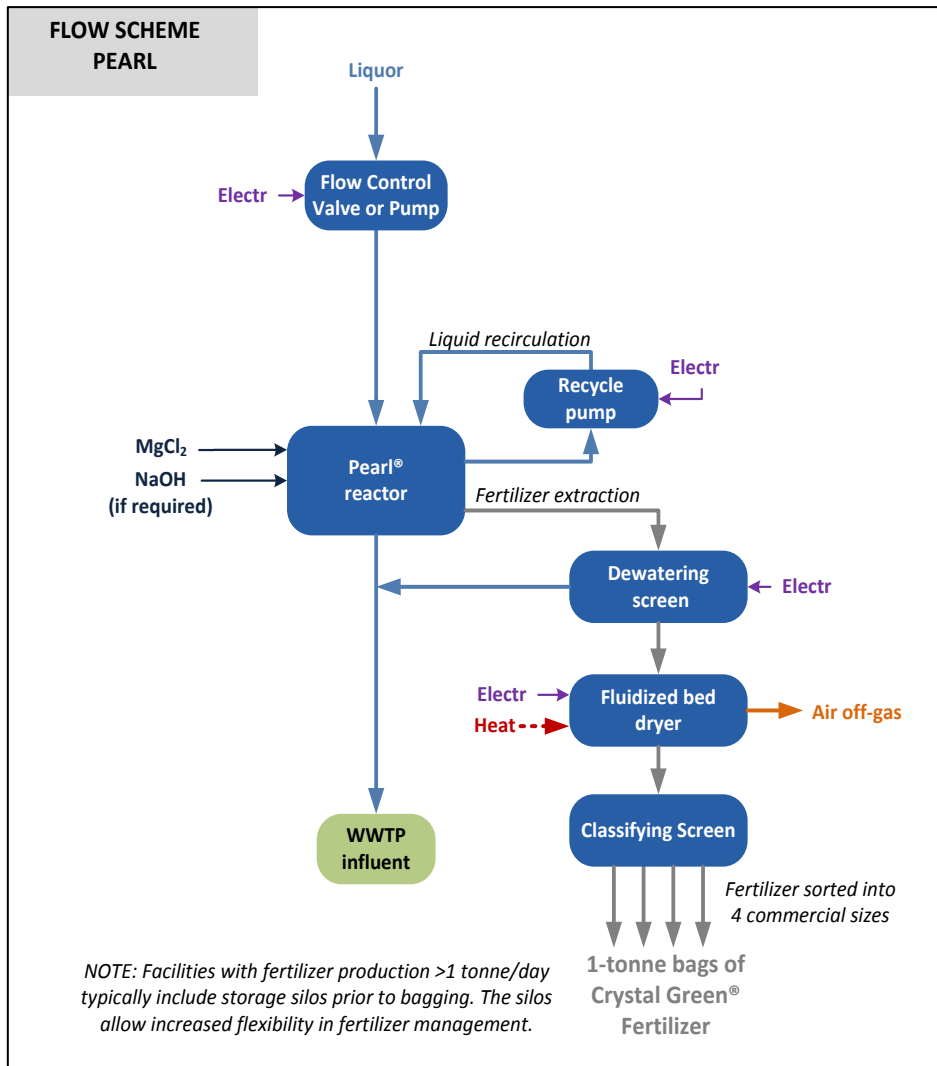


Figure 14 Flow scheme of the Pearl® process

The lowest cylindrical part of the reactor is designed for dosing of input and harvesting. The digester supernatant is separated from sludge by centrifugation or thickening and dosed with a feed pump first from a buffer tank into the dosing zone of the Pearl® reactor.

The upper part of the reactor – the last reaction zone – is designed as clarifier with a weir overflow. Here a solid-free liquid phase is separated and recycled, partly with another pump directly again as feed into the Pearl® reactor, partly into the biological treatment of the wastewater treatment plant.

In the initial starting phase of the process during construction, seedings are added in form of 1-3 mm struvite prills. Afterwards the reactor is self-seeding and does not require further addition of struvite particles.

In order to reach a oversaturation of magnesium-ammonium-phosphate and enable the crystallisation, magnesium chloride is added in the dosing zone at the bottom of the reactor, in some cases also caustic soda to adjust the pH.

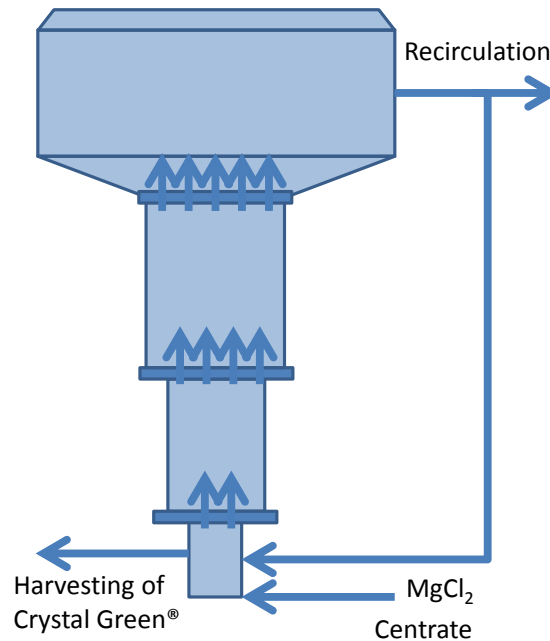


Figure 15 Scheme of Pearl® Reactor based on Cullen et al. [2013]

Due to the increasing diameter of the reactor, the upflow velocity decreases stepwise from bottom to top when entering in the next reaction zone. This reactor design leads to a certain classification according to the particle size. Furthermore the sudden change in diameter and hence upflow velocity at the entrance into the next reaction zone leads to turbulence in form of eddies which supports maintaining sufficient mixing and the fluidized bed.

The process has been optimized in order to produce a high quality struvite fertilizer which includes high purity and crystals of big particle size and hardness.

In the case of the Pearl® process the growth of already existing crystals is more beneficial rather than the formation of a high number of very small crystals.

For the Pearl® process, this means that the operation in the metastable region would be favourable since only minor nucleation takes place but already existing crystals grow further since the solution is over-saturated.

The process is operated at a relatively low over-saturation which is achieved by a recirculation stream diluting the centrate entering the reactor. Process saturation is controlled automatically and can be monitored remotely. During the growth process small struvite crystals aggregate and form struvite prills. It was observed that long retention time and higher magnesium dosage increase aggregation and hence lead to larger prills of increased hardness Britton et al. [2005], [Huang et al., 2006].

According to information from the literature, The recirculation ratio, defined as the total volume flow entering the reactor divided by the volume flow of fresh supernatant coming from the dewatering of digested sludge, is varied in the range of 4-20 [Huang et al., 2006, Baur et al., 2009]. .

For operation of the full scale system, the molar ratio of magnesium to phosphate is adjusted in the range of 1-1.5 [Huang et al., 2006, Rieck, personal communication, Garcia et al., 2013, Britton et al., 2005].

Very high TSS concentrations might affect the crystallisation negatively. Garcia et al. [2013] mentions a security limit of 1 g/L which should not be exceeded for extended time periods. Nevertheless, it was shown at full scale that at a concentration of 15 g/L a successful operation was possible [Garcia et al., 2013].

Harvesting of the struvite product takes place from the lowest section of the reactor. These particles are fluidized in a special pipe for harvesting and removed using process water as carrier water [Baur et al., 2009, Cullen et al., 2013].

There are several steps for product finishing applicable according to the requirements regarding the product quality:

Dewatering of the struvite prills is usually done using dewatering screen [Cullen et al. 2013].

Furthermore, the surface moisture can be removed with a fluidized bed dryer [Cullen et al. 2013].

Classification by sieving can narrow the size distribution of the fertilizer product further [Cullen et al. 2013].

2.4.3 Interactions

In the operation of a wastewater treatment plant with enhanced biological phosphorus removal without struvite recovery, the load of phosphorus and ammonium recirculated with the centrate from dewatering of activated waste sludge represents an important part of the total load. For the Durham Advanced Wastewater Facility in Tigard (Portland), Oregon it was mentioned that 30% of the ammonium load is coming from the process water recycling. Recirculated phosphorus loads are also roughly 30% of total phosphorus load.

Crystallisation of struvite leads to reduced recycling of nutrients into the biological treatment step. The installation of the Pearl® process in the Durham Advanced Wastewater Facility lead to a reduction of 14-15% of recycled load of ammonium and 82-85% reduction of the recycled load of phosphorus [Cullen et al., 2013].

As a consequence the operation of the enhanced biological phosphorus removal is more stable and the capacity of the wastewater treatment plant is increased. Hence the additional dosing of chemical precipitants is reduced. For the Durham Advanced Wastewater Facility a reduction of 20-39% of aluminium dosed for phosphorus precipitation was observed due to the operation of the Pearl® reactors [Cullen et al., 2013]. A related effect is the reduced amount of chemical sludge production due to less dosing of chemical precipitants. For the Durham Advanced Wastewater Facility a reduction of roughly 15% in the total dry mass of sludge produced at the plant was observed as a result of centrate treatment using the Pearl® process.

2.4.4 Options

With the first operational experiences of the Pearl® process it became clear, that the phosphorus and ammonium load of the biological treatment could be significantly reduced and a stable production of struvite could be achieved. Nevertheless, still a significant precipitation of struvite in the digester was observed. In order to increase the phosphorus recovery performance, the so-called Waste Activated

Sludge Stripping to Recover Internal Phosphate (**WASSTRIP®**) **process** was developed and patented [Baur, 2009].

The WASSTRIP process includes stripping of phosphorus and magnesium from waste activated sludge before this sludge is digested (see Figure 16). The stripping is operated under anaerobic conditions, and can be accelerated by adding volatile fatty acids, e.g. using supernatant from dewatering of fermented primary sludge [Prasad and Schauer, 2012]. Under these conditions the phosphorus accumulating organisms release a significant part of the stored phosphorus and magnesium as counter ion [Cullen et al., 2013]. Due to this process combination, an additional phosphorus release from the activated waste sludge an increase of struvite production by 60% is possible [Cullen et al., 2013]. WASSTRIP has been installed at full scale in the Saskatoon WWTP, the Durham AWWTP and the Nine Springs WWTP. It is in development as part of numerous other Ostara nutrient recovery projects.

WASSTRIP benefits wastewater treatment plant operators in various ways. Removing magnesium and phosphate prior to anaerobic digestion prevents struvite formation. Without WASSTRIP struvite forms as scale encrustations (causing maintenance costs) and as grit/sand like particles (which occupy volume and decrease digester performance). WASSTRIP's positive effect on digestion was found to reduce the total dry mass of sludge produced at the Durham AWWTP by roughly 10% (in addition to the 15% previously observed when treating dewatering centrate only). WASSTRIP also cause potassium to be stripped prior to digestion. Potassium impacts digested sludge dewaterability due to its monovalent positive charge. Full scale testing of WASSTRIP has found an improvement in dewatered cake dry solids content of 4%, and also a significant reduction in polymer demand.

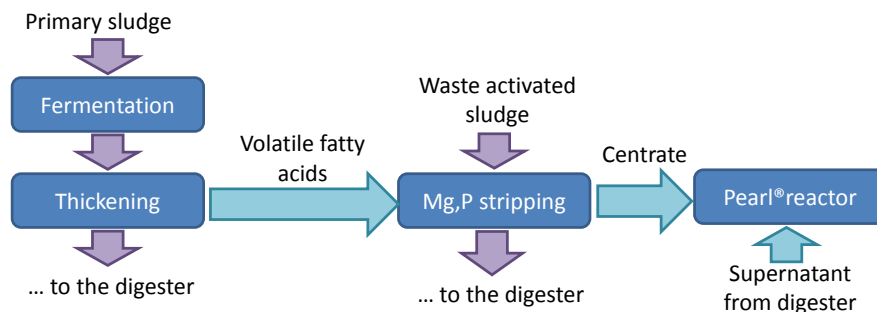


Figure 16 Flow scheme of the WASSTRIP process including the optional step of volatile fatty acid dosing (adapted from Cullen et al., [2013])

2.4.5 Site specific information

Site specific data is provided for five installations of the Pearl®process – three full scale and two pilot scale applications. The information is shown in Table 5. For the estimation of the sludge specific phosphorus yield no data was available from the sites directly. Therefore the liquor specific phosphorus yield given for each site was used together with an estimation for the phosphorus dissolution ratio in the digester. For the latter, a value of 23% was assumed based on Cullen et al. [2013].

Table 5 Site specific data for five installations of the Pearl®process, *estimation based on the data given by Cullen et al. [2013] about the dissolution ratio in the digester (23%)

	Rock Creek (Full scale)	York (Full scale)	Nansemond (Full scale)	Durham (Pilot)	Edmonton (Pilot)
Size of the WWTP [m ³ /d]	132'475	75'700	75'700	94'625	32'800
Throughput of centrate [m ³ /d]	2'653	473	394	19	21
Liquor specific phosphorus yield [%]	83%	90%	90%	90%	85%
Sludge specific phosphorus yield [%]	19%*	21%*	21%*	21%*	20%*
Energy consumption [kWh per m ³ centrate]	0.36	0.89	1.34	1.19	0.45
Energy consumption [kWh per kg P in product]	3.3				
NaOH (50%) [kg/kg P recovered]	0.55-2.3	0.22-0.93	0.15-0.62	0.17-0.69	n.a.
Molar ratio of magnesium to phosphate [-]	0.97	0.94	1.24	1.04	n.a.
Percentage of P in the product [weight%]	13.5				

2.5 Process 5: Gifhorn process

- Acidic phosphorus extraction from digested sludge from WWTPs with EBPR or chemical phosphorus elimination
- Iron and aluminium precipitation with dosing of sodium sulphide
- Precipitation of a mixed product of struvite and hydroxylapatite from the centrate
- Combined with ammonia stripping
- Full scale installation in Gifhorn

2.5.1 Background

The beginning of the Seaborne technology from which the simplified installation called “Gifhorn process” derives, was originally developed by the German company Seaborne Environmental Laboratory (EPM AG) to create a procedure for the production of fertilizer from liquid manure, in order to receive the nutrients for a sustainable feedback into the nutrient cycle. The application of the process was extended to other organic residuals (sewage sludge, bio wastes, fats etc.) and thereby increased in complexity.

The idea behind was to develop a process for nutrient recovery for a great variety of organic materials, simultaneously eliminate pollutants of the treated biomasses (mainly heavy metals from municipal sewage sludge) and utilize the energy content of the organic materials.

The seaborne technology started with a pilot plant for 10'000 p.e. in Owschlag, Germany which started operation in 2000 (Schulz, 2003).

The first full-scale installation was established in a modified way at the WWTP Gifhorn, Germany in 2005 (50'000 p.e.). It has a capacity of approx. 1'000 tons of dry solids per year (120 m³ digested sludge per day). Planning and construction were carried out by Seaborne EPM AG together with the engineering company Wittig. The technical and scientific monitoring of the implementation of the seaborne process was carried out by two university institutes (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) in cooperation with the engineering company PFI from Hannover.

After the beginning of continuous operation in 2005 several full-scale investigations accompanied by laboratory scale experiments were conducted to overcome operational problems and to increase the economic efficiency of the seaborne process at the Gifhorn plant. Central problems were iron in the digested sludge (in Gifhorn significant amounts of iron flocculant are used to support the biological phosphorus elimination) and thereby high calcium concentrations in the subsequent ammonia stripping unit which led to serious scaling effects. As a consequence the originally installed seaborne technology was simplified and the process operation modified.

As a result of the lab-scale experiments, process conditions were found and demonstrated on full-scale operation which allowed an efficient separation of iron and a high phosphorus sludge related recovery yield (~50%) with moderate demands of auxiliary chemicals and allowed a safe operation of the ammonia stripping unit.

Due to the necessary modifications, the simplified sludge treatment and nutrient recovery technology in operation at Gifhorn became called “Gifhorn process”.

Currently the sludge treatment at the Gifhorn WWTP is operated with limited functionality for economic reasons, which means that the ammonia stripping unit and heavy metal separation is not in operation. As a consequence the phosphorus yield rate is significantly lower and the plant availability of the resulting product is reduced.

2.5.2 Process design

As pointed out above the process conditions which are described here are based on full-scale experiences of the seaborne plant in Gifhorn which successfully demonstrated phosphorus and nitrogen recovery units in operation for a period of about one month.

Since only a part of the original process equipment and periphery is needed for the simplified Gifhorn process the following process design is based only on the necessary process equipment for obtaining the phosphorus recovery results as described in the following.

The relevant process steps and mass flows are shown in Figure 17. The whole process chain is carried out in steel batch reactors.

Extraction and simultaneous iron precipitation reactor

First the digested sludge is pumped in the extraction unit, which consists of two redundant stainless steel reactors with 16 m³ each operated in batch mode.

1. Step: Phosphorus extraction

The extraction is started by addition of sulphuric acid (2.8 l/m³ H₂SO₄ (96%)) to adjust a pH around 4. Lowering the pH leads on the one hand to a transformation of not readily soluble phosphate species into better soluble phosphate species (H₂PO₄⁻/HPO₄²⁻) (Falbe et. al, 1995). On the other hand pH values below 5 (Kunst, 1991) can induce cell destruction and therefore result in phosphorus release. After a reaction time of 0.5 h a PO₄-P concentration of around 500 mg/L was achieved, which means that roughly 66% of the total phosphorus content of the sludge was brought into solution. In comparison to other literature references the obtained phosphorus dissolution rate is rather high which could be explained by the anaerobic conditions during extraction. The acidification also lead to a strong release of calcium and magnesium (both around 80%) and iron (60%). Most of the heavy metals were not released at the given pH and kept in the solid phase, only nickel (24%) and cobalt (17%) showed a considerable dissolution rate.

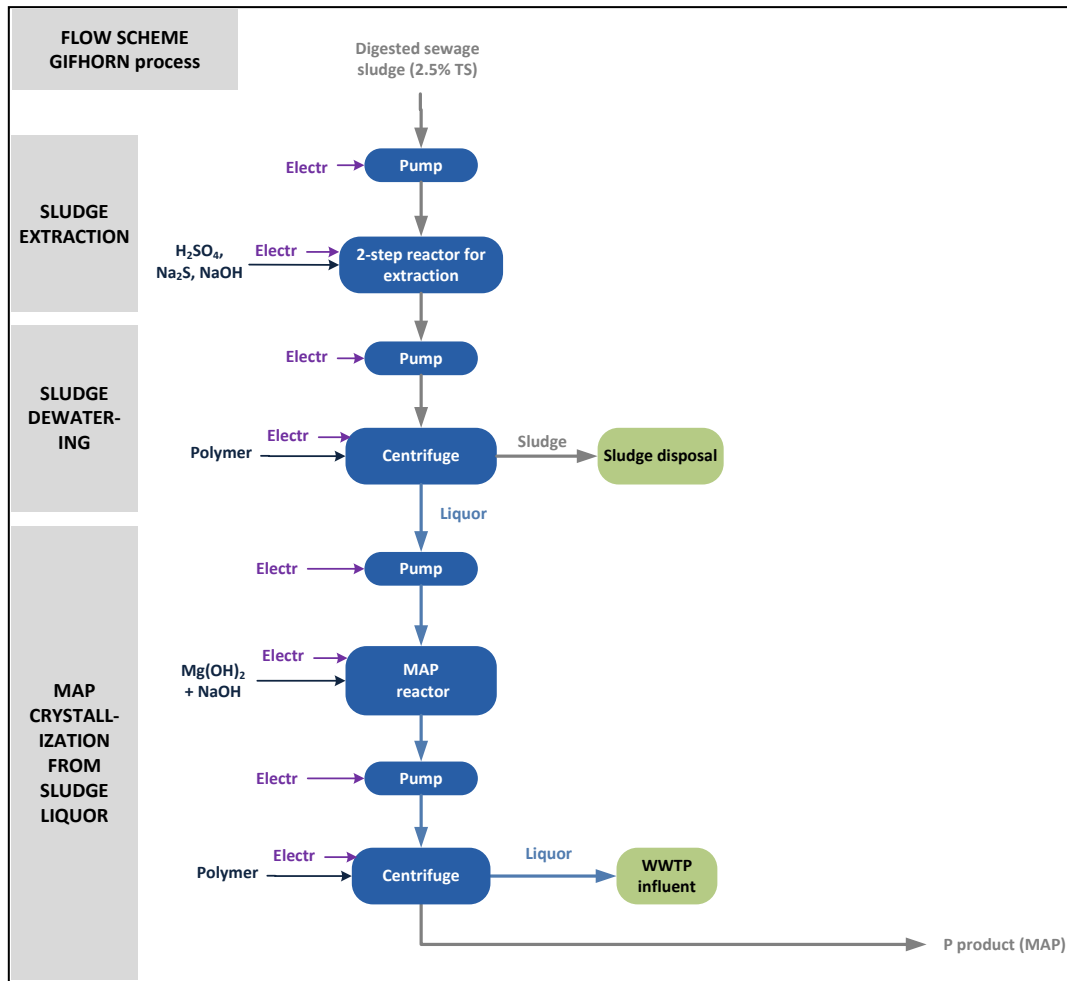


Figure 17 Flow chart of the Gifhorn process

2. Step: simultaneous iron precipitation

A central problem of the original seaborne process for the subsequent nutrient recovery units was the dissolution of iron which led on the one hand to a high content of iron phosphate in the recovered phosphorus product and on the other hand to a significant amount of unprecipitated calcium which prevented operation of the nitrogen recovery unit.

As a solution an iron precipitation step between extraction and dewatering by addition of sodium sulphide ($2.7 \text{ l/m}^3 \text{ Na}_2\text{S}$ (15%)) was introduced. The dosage of sulphide is about stoichiometric with reference to iron. To ensure a quantitative elimination of iron and prevent losses of phosphorus (as iron phosphate), calcium and magnesium, a pH of 5.5-5.7 is required.

In full-scale operation exact pH control was difficult. As a result a pH range of 4.9-6.1 was achieved by dosing a mean amount of 0.6 l/m^3 of $NaOH$ (50%). The reaction takes place in the same reactor.

After a reaction time of 0.5 h, solids (organic compounds, precipitated iron, etc.) are separated by a centrifuge and the addition of polymer (around 12 kg effective substance/ton of dry solids). An average elimination of 75% of the iron content after extraction was obtained by sulphidic precipitation. Lab experiments revealed that a better control of the pH increase iron elimination up to 90%. As intended, nutrients almost completely remained in solution and only minor losses of calcium, magnesium and phosphorus were observed after the first dewatering step.

Phosphorus precipitation reactor

After the first separation step the remaining liquor which contains most of nutrients (phosphorus, ammonium, calcium and magnesium, etc.) is pumped in the phosphorus recovery unit, consisting of two redundant stainless steel reactors with 16 m³ each operated in batch mode.

The precipitation process is initiated by dosage of magnesium hydroxide (0.15 l Mg(OH)₂ (53%) per m³). Due to the alkaline properties of the hydroxide the pH is slightly raised to pH 6-6.5. After a reaction time of 0.5 h sodium hydroxide (1.74 l NaOH (50%) per m³) is dosed to the solution to raise the pH to 9.3-9.4. After 0.5 h reaction time the precipitated nutrients are separated from the process solution by a centrifuge and the addition of polymer. The dosage of magnesium is under-stoichiometric with reference to phosphate in solution to force precipitation of calcium which would otherwise induce scaling in the subsequent ammonium stripping unit.

The elementary analysis of the product by ICP implies that it consists mostly of magnesium ammonium phosphate (struvite) and calcium phosphate presumably in form of hydroxylapatite. Probably 40% of the phosphate in the product is bound as struvite (MgNH₄PO₄·6H₂O), 5% as vivianite (Fe₃(PO₄)₂·8 H₂O) and 55% as calcium phosphate (supposedly hydroxyapatite with low calcium content: Ca₉(PO₄)₅(HPO₄)OH). The heavy metal content is generally very low; many heavy metals are slightly above or under the limit of detection. The product obtained directly after dewatering has a solid content of 35-40%, which increases quickly by air-drying to >80%.

2.5.3 Interactions

A central reason for modifying the seaborne process was the iron and aluminium content of the digested sludge which originated from the use of chemical flocculants (aluminium and iron salts) in the biological stage of the WWTP. Both active agents, aluminium and iron, form phosphate compounds which have a low plant availability when transferred to the nutrient product. Besides the use of aluminium leads to a lower phosphorus recovery rate under the chosen extraction conditions (pH 4) since aluminium phosphate needs a lower pH (<3) to get into solution. If the phosphorus elimination of the WWTP was predominantly biological it would be possible to omit the simultaneous iron precipitation step which would simplify the whole process.

Other main interactions with the WWTP are the treatment of the digested sludge and change of the nutrient chargeback caused by the sludge liquor. A crucial effect of the Gifhorn process is that the chargeback with phosphate and ammonium by recirculation of the sludge liquor back to the biological stage of the WWTP is reduced. The phosphorus chargeback is reduced to almost zero whereby ammonium reduction is limited by stoichiometry between nitrogen and phosphorus since for the precipitation reaction for each ammonium molecule a phosphate molecule is necessary.

For comparison with a WWTP without phosphorus recovery it has to be taken into consideration that the first dewatering step of the Gifhorn process substitutes the sludge dewatering which is usually an integrated part of a WWTP.

Due to the enhanced extraction of phosphorus from the digested sludge by acidic treatment the phosphorus content of the disposed sludge is lowered. Depending on the adaptation of the dewatering conditions to the changed sludge properties (i.e. selection of adequate polymers) the dewatering

efficiency and the polymer demand may be influenced. In case of the Gifhorn process dewatering was adjusted in such a way that dewatering efficiency did not change considerably.

2.5.4 Options

Increase of struvite content in phosphorus product

The so-called Gifhorn process was developed to recover not only phosphorus but also ammonium which is not part of the evaluation of the P-Rex project. To guarantee the operation of the ammonium stripping unit the concentration of scaling agents like calcium and magnesium after phosphorus precipitation must be low. This was achieved by using an under-stoichiometric dosage of magnesium, so that also the majority of calcium ions were eliminated in the nutrient precipitation step. If only the phosphorus recovery step of the Gifhorn process was realised at a WWTP, calcium scaling could be disregarded so that a higher magnesium dosage would help raising the struvite content and thereby improve the nutrient properties of the product especially the plant availability.

Increase phosphorus recovery rate

To increase the phosphorus recovery rate the extraction could be operated under more acidic conditions. This would also increase the consumption of operating supplies such as sulphuric acid and sodium hydroxide. As lab experiments have shown (Esemen, 2012) the specific acid consumption significantly increases at pH values below 3.5. Besides, it had to be taken into consideration that at lower pH the release of heavy metals is raised and dewatering could be more difficult (adaption of polymer would be required).

Several other process options are described in the PhD thesis of Esemen (2012), some of these will be represented shortly in the following:

Sea water as magnesium source

As seawater contains significant amounts of magnesium and calcium ions, it can be used as source for the struvite precipitation as substitute for the magnesium salts for WWTPs located near the coast.

Phosphorus release by thermal hydrolysis instead of acidic extraction

Instead of releasing phosphorus by acidification from digested sludge by applying chemicals, thermal hydrolysis (i.e. Cambi/Lysotherm) could be applied on secondary sludge from WWTPs applying EBPR. Lab experiments (Esemen, 2012, Bormann et. al., 2009) showed that average phosphorus release rates of 40% were achieved. If hydrolysed secondary sludge is mixed with primary sludge and then stabilised in an anaerobic digester, most of the released phosphorus is refixed in the sludge matrix so that a potential phosphorus recovery step should be applied directly after hydrolysis and before digestion. An alternative would be a separate digestion of secondary sludge as phosphorus apparently stays in solution after digestion (Bormann et. Al., 2009).

Alternative product separation

Although separation by centrifugation works fine (93% recovery of P from liquid phase), energy consumption is relatively high (8.7 kWh/kg P, 3.1 kWh/m³ only for centrifugation). On the one hand centrifugation itself is one of the more energy demanding dewatering processes on the other hand the throughput in Gifhorn is very low (4.5 m³/h, typical volume streams are 20-30 m³/h). Besides, to obtain satisfying dewatering efficiency synthetic polymers are used which end up in the P-product.

Alternatively sedimentation technologies like lamella clarifiers could be a possibility for the product separation.

Product optimization

The application of a drying process after dewatering could help increasing the market acceptability of the product.

2.5.5 Site specific information for Gifhorn

Table 6 shows site specific data for the installation of the process in Gifhorn discussed in this chapter.

Table 6 Site specific data for the Gifhorn process

Size of the WWTP [p.e.]	50'000
Throughput of digested sludge [m ³ /d]	108 (with 2% TS)
P-Extraction rate from sludge	66.1 % (for pH 4)
Liquor specific phosphorus yield [%]	93.3%
Sludge specific phosphorus yield [%]	48.7%
Energy consumption including dewatering [kWh per m ³ sludge]	7.6
Energy consumption without dewatering [kWh per m ³ sludge]	4.5
Energy consumption including dewatering [kWh per kg P in product]	21.6
Energy consumption without dewatering [kWh per kg P in product]	12.9
H ₂ SO ₄ (96%) [kg/kg P recovered]	14.6
Na ₂ S (15%) [kg/kg P recovered]	8.9
NaOH (50%) [kg/kg P recovered]	2.3
Polymer (100%) [kg/t _{DM}]	14
Molar ratio of magnesium to phosphate [-]	0.19
Percentage of P in the product [weight%]	11.0-12.0

2.6 Process 6: Stuttgarter Process

- Acidic phosphorus extraction from digested sludge from WWTPs with EBPR or chemical phosphorus elimination
- Solid liquid separation with chamber-filter-press
- Complexation of metal ions to avoid co-precipitation by dosing of citric acid
- Struvite precipitation
- Operation of demonstration plant in Offenburg

2.6.1 Background

In the year 2003, the Institute for Sanitary Engineering, Water Quality and Solid Waste Management at the University Stuttgart started the development of the Stuttgart process in cooperation with the engineering company iat (Stuttgart). The main objective was to design a technology for recovering phosphorus as struvite (Magnesium-Ammonium-Phosphate, MAP) from digested sludge from WWTPs which use iron salts for chemical phosphorus elimination. The process development was supported by lab experiments in 2003 and 2004. As a result a pilot scale plant with a reactor volume of 1 m³ was constructed and operated with digested sludge from the WWTP Vaihingen(Enz)-Strudelbach. By acidification at a low pH value of 2, approximately 80% of the sludge's phosphorus was transferred into solution, and almost 60% of the phosphorus could be recovered as struvite. A first full-scale installation of the Stuttgart process was built at the WWTP Offenburg (160,000 p.e.), Germany, and put into operation in 2011. The plant is designed to treat a partial flow of the digested sludge, corresponding to 8'000 p.e. It has a capacity of 170 tons dry solids per year (21.6 m³ digested sludge per day with 2.7-2.8 % DS, which equals two charges/d). At the moment a maximum of one charge per day is processed. The project was realized by the project partners Abwasserverband Raum Offenburg, IB iat Ingenieurberatung für Abwassertechnik GmbH and the Institute for Sanitary Engineering, Water Quality and Solid Waste Management at the University Stuttgart and funded by the state of Baden-Württemberg. The whole process equipment was installed in an existing building at the WWTP Offenburg.

2.6.2 Process design

The relevant process steps and mass flows are shown in Figure 18. The pilot plant consists of two reaction tanks and one sedimentation tank (each 12 m³), a chamber filter press and storage tanks for sodium hydroxide (18 m³), citric acid (20 m³) and sulphuric acid (20 m³). The Stuttgart process starts with the acidic sludge leaching (H₂SO₄) of the digested sludge in the first reactor. Subsequently, a chamber filter press is used for the solid/liquid separation of the acidified sludge suspension. Usually, this dewatering step is an integral part of the sludge treatment of the WWTP. The filtrate which contains the dissolved fraction of the phosphorus but also several metals in solution is pumped into a second reactor where citric acid is dosed as a complexation agent for metal ions. In a second step, magnesium (MgO) and sodium hydroxide (NaOH) are added to start the precipitation of struvite (MAP). The MAP crystals are separated from the liquid phase by sedimentation. Crystal growth is supported by recycling a part of the settling tank's supernatant. When sedimentation is complete the phosphorus depleted supernatant is fed to the activated sludge tank of the WWTP.

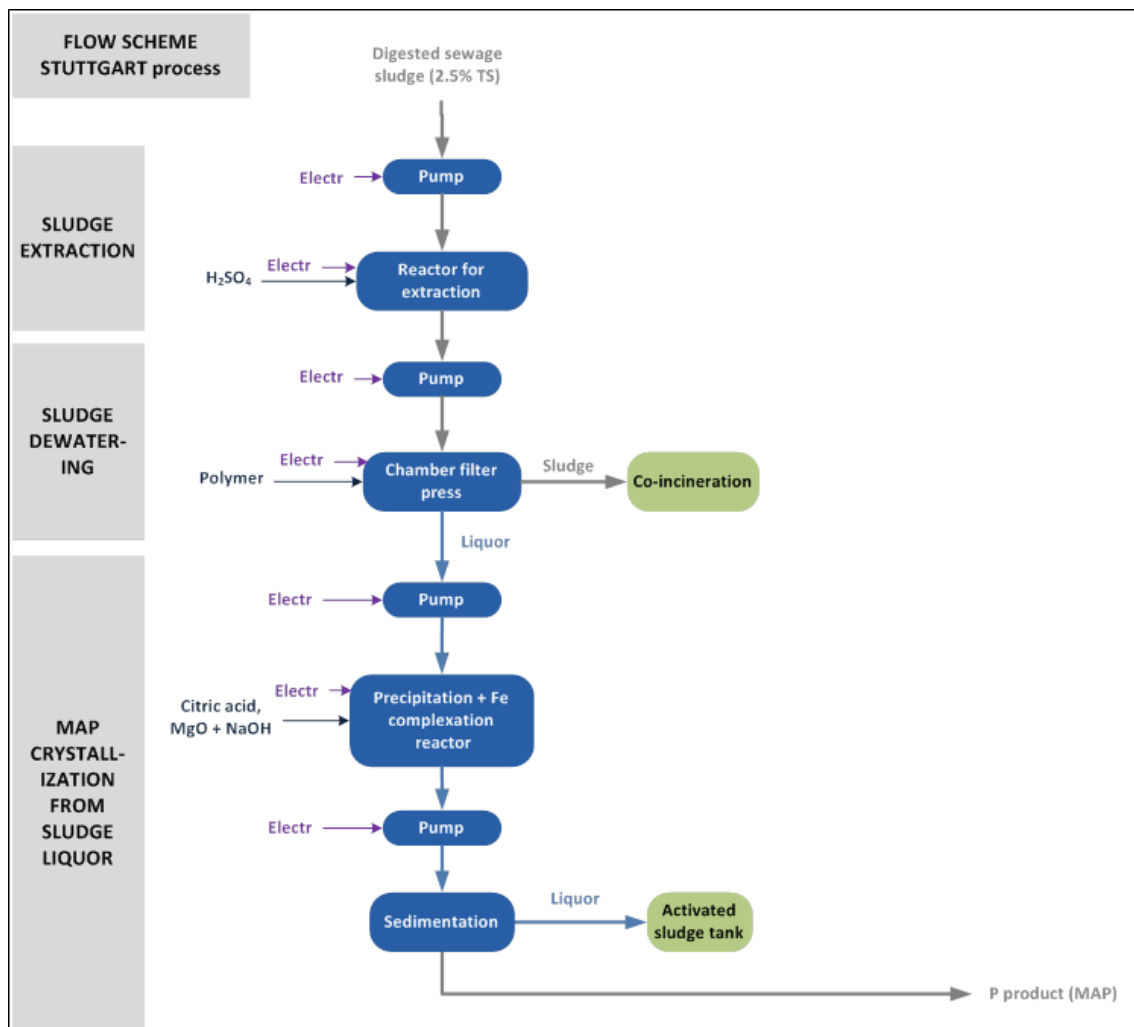


Figure 18 Flow chart of the Stuttgarter Process

Since the beginning of the operation of the full scale plant at the WWTP Offenburg different process conditions were tested to see how recovery results and process conditions correlate. As a consequence, it is difficult to describe standard conditions for a regular operation. In the following, the different

process steps with its varying process conditions are explained. The whole process is designed in a batch operational mode which allows the treatment of a maximum of two charges per day.

Extraction reactor

First, the digested sludge is pumped in the encapsulated extraction reactor (12 m³). To control foaming during acidification a part of the reactor volume is used as freeboard, so that approximately 10.8 m³ digested sludge can be treated per charge.

Phosphorus extraction

To reduce foaming, digested sludge (2.5-3.0 % DS) and sulphuric acid are introduced simultaneously into the extraction reactor. During the operation of the last years different values of pH were tested in the range of pH 3 to pH 5. One experience was that lower pH values than 4 have a negative influence on the sludge's dewaterability by the chamber filter press, so that the polymer dosage had to be increased. Therefore, the process was operated in the later phases at a pH of 4.5 which required an average dosage of 5.0 l sulphuric acid (78%) per m³. Carbon dioxide which is produced during the acidification process is released into the atmosphere. Depending on the process conditions (pH), phosphorus dissolution rates from 39% to 83% were obtained with an average of approx. 52%.

Separation of solids and organics

After a reaction time of 1 h the acidic sludge is dewatered by a chamber filter press. The dewaterability varied in a wide range from 15 to 30% DS, strongly dependent on the pH. Below pH 4 the dewaterability decreases significantly, and the consistency of the filter cake becomes more liquid and sticky. The specific polymer dosage was in a normal range for digested sludge.

Complexation and precipitation reactor

The filtrate of the chamber filter press is pumped in the complexation and precipitation reactor (12 m³).

Complexation

To prevent metal precipitation, citric acid is added to the filtrate. The ratio between the molar amount of citric acid and the main metal ions in solution which are iron, aluminium, calcium and magnesium was between 0.2 and 1.4. Currently, the citric acid is dosed stoichiometric (1.8-12.7 l citric acid (50%) per m³ filtrate). After a reaction time of 10 min magnesium dosage is started.

Precipitation

To start precipitation first MgO is dosed over-stoichiometric in relation to phosphate in solution (factor 1.5-2, average dosage 0.9-1.8 kg MgO (92%) per m³ Filtrate). After a reaction time of 20 min a target pH for precipitation of 8.5 is adjusted by adding 3.2-12.6 l (for leaching at pH 4.5 to 5) NaOH (22%) per m³ filtrate.

Sedimentation tank

After precipitation the filtrate is pumped into a sedimentation tank (12 m³) from which the precipitated product is separated, dewatered by sieves and air-dried in small containers.

Analyses of the latest recovery products show that they contain mainly struvite (approx. 95 wt%). The iron (phosphate) content as well as concentrations of several harmful substances (heavy metals, persistent organic pollutants) is very low compared to raw digested sludge and mineral fertilizers. The sludge specific phosphorus yield was in the range of 38% to 62% mainly depending on the pH of the leaching step. An average regular phosphorus recovery rate of 50% is obtained with a leaching pH of 4.5.

2.6.3 Interactions

Similar to the Gifhorn process the main interaction of the Stuttgart process with the WWTP are the treatment of the digested sludge and the change in the chargeback by the sludge liquor. Since sludge disposal is one of the cost constituting parts of a WWTP the influence on the dewaterability has a great impact on the overall cost of waste water treatment.

On the one hand the phosphate chargeback with the sludge filtrate is reduced by the Stuttgart process. The metal ions leached from the sludge and complexed by the citric acid are going back to the waste water process (activated sludge tank) which could lead to an enrichment of these compounds in the WWTP. Additionally, the citric acid acts as a carbon source in the biological stage of the WWTP.

For comparison with a WWTP without phosphorus recovery it has to be taken into consideration that the first dewatering step of the Stuttgart process substitutes the sludge dewatering which is usually an integrated part of a WWTP.

2.6.4 Options

The application of a drying process after dewatering helps to increase the market acceptability of the product.

In this context an increase of the crystal size of the struvite would be advantageous.

2.6.5 Site specific information for Offenburg

Table 7 shows site specific data for the installation of the Stuttgarter Process at the wastewater treatment plant Offenburg.

Table 7 Site specific information for the installation of the Stuttgarter Process in Offenburg

	Configuration 2012	Configuration 2013
Size of the WWTP (average load) [p.e.]	160'000	
Size of the phosphorus recovery unit [p.e.]	8'000	
Throughput of digested sludge [m ³ /d]	10.8 with 2.8-3% TS	
pH used for extraction	3-5	4.5-5
Sludge specific phosphorus release-yield	36-82 %	30-50%
Liquor specific phosphorus yield [%]	>90%	
Sludge specific phosphorus yield [%]	38-62%	45-50%
Energy consumption including dewatering [kWh per m ³ sludge]	3.5	
Energy consumption including dewatering [kWh per kg P in product]	8	
H ₂ SO ₄ (78%) [kg/kg P recovered] ([kg/m ³ _{sludge}])	8-34 (6-12)	11-23 (6.8-9.35)
Citric acid (50%) [kg/kg P recovered] ([kg/m ³ _{sludge}])	1.5-83 (1.1-29)	4-38 (2.2-16)
NaOH (22%/25%) [kg/kg P recovered] ([kg/m ³ _{sludge}])	5-112 (3.7-39)	7-39 (4-16)
Molar ratio of magnesium to phosphate [-]	1.5-2	
Percentage of P in the product [weight%]	12	

2.7 Process 7: Budenheim

- Phosphorus extraction using carbon dioxide
- Solid liquid separation with filtration or centrifugation
- Precipitation of calcium phosphate
- Operation of laboratory tests, installation of pilot unit is going on

2.7.1 Background

The Budenheim Carbonic Acid Process was first developed in 2010 by the company Budenheim in Germany. The investigation of the process concept started with lab-scale experiments and a patent was filed in 2009.

In cooperation with the Fraunhofer association an experimental plant was installed in Pfinztal, Germany with an extraction volume of 20 litres. The conclusions of the operation of the experimental plant led to a first scale-up. A second experimental plant was built in Budenheim with an extraction volume of 50 litres in January 2012. Both experimental plants were funded by the Investment- and Structure-bank, Rhineland-Palatinate, Germany. The phosphorus recovery rate at the plants is about 50 %. In 2014 the first pilot plant will be installed directly at one WWTP with an extraction volume of 1 m³.

2.7.2 Process design

In the Budenheim process, phosphorus is extracted from sewage sludge by using carbon dioxide. No other chemicals are necessary in the extraction step which leads to an environment friendly process. Also, there is no need for a thermal input in the process. The used carbon dioxide is recycled back into the process. Hence, there are no climate relevant emissions. The Budenheim Carbonic Acid Process is applicable both to WWTPs with EBPR and WWTPs with phosphorus removal by iron or aluminium compounds. The end-product of the process is a calcium-phosphate which represents a plant available fertilizer compound. The sewage sludge which contains less phosphorus after the process can be disposed for example in co-incineration.

The individual process steps illustrated in Figure 19 and Figure 20 are explained in more detail in the following sections.

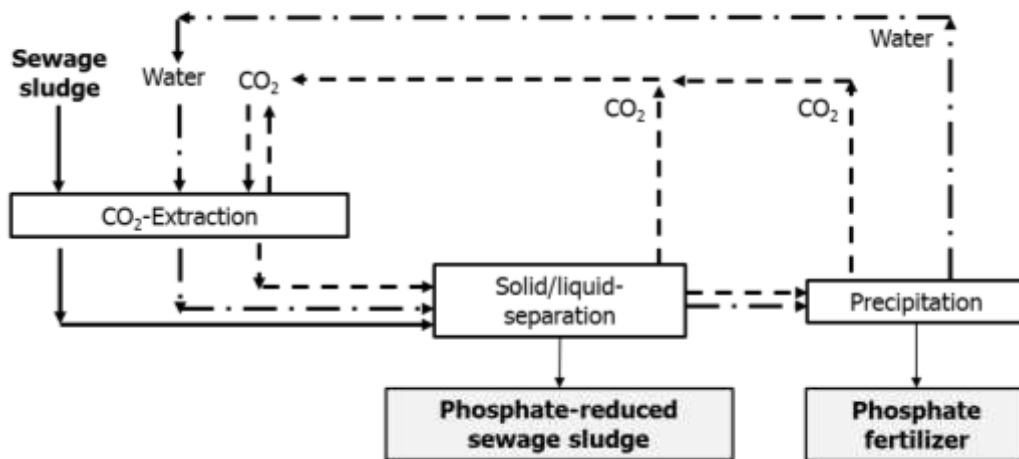


Figure 19 Flow chart of the Budenheim Carbonic Acid Process

Carbon dioxide is brought into the system of sewage sludge and water under pressure. The carbon dioxide dissolves in the water and reacts to carbonic acid. The pH value in the reaction vessel decreases and the phosphates in the sewage sludge are resolved. Afterwards the sewage sludge is separated from the liquid phase in a filtration unit.

Afterwards, the dissolved phosphates are precipitated by outgassing the carbon dioxide. After drying the phosphates, a phosphorus-rich fertilizer can be produced.

The carbon dioxide is captured, compressed and used again for the reaction in the pressure vessel. This way the carbon dioxide moves in a circle and is not emitted into the atmosphere. The process water used for conditioning the sewage sludge is also circulated. There are also no emissions of exhaust-air or waste-water which might be critical for the environment.

In earlier projects the basic principles of the process were investigated and an experimental plant was built in the technical centre in Budenheim. In the new project, the technical expertise will be used to scale-up the process and will lead to the installation of a larger plant. At this pilot plant the scale-up parameters can be assessed and the conditions for a full-scale production unit can be developed including information on costs.

Another positive aspect is a raise of the calorific value of the sewage sludge because non-combustible contents of the sewage sludge are separated before combustion. Sewage sludge ash from sewage sludge treated with the Budenheim Process contains a lower concentration of phosphorus and may be used in the building-material-industry. Here a low phosphorus content may be beneficial in order to avoid instability or insufficient quality of building materials such as cement.

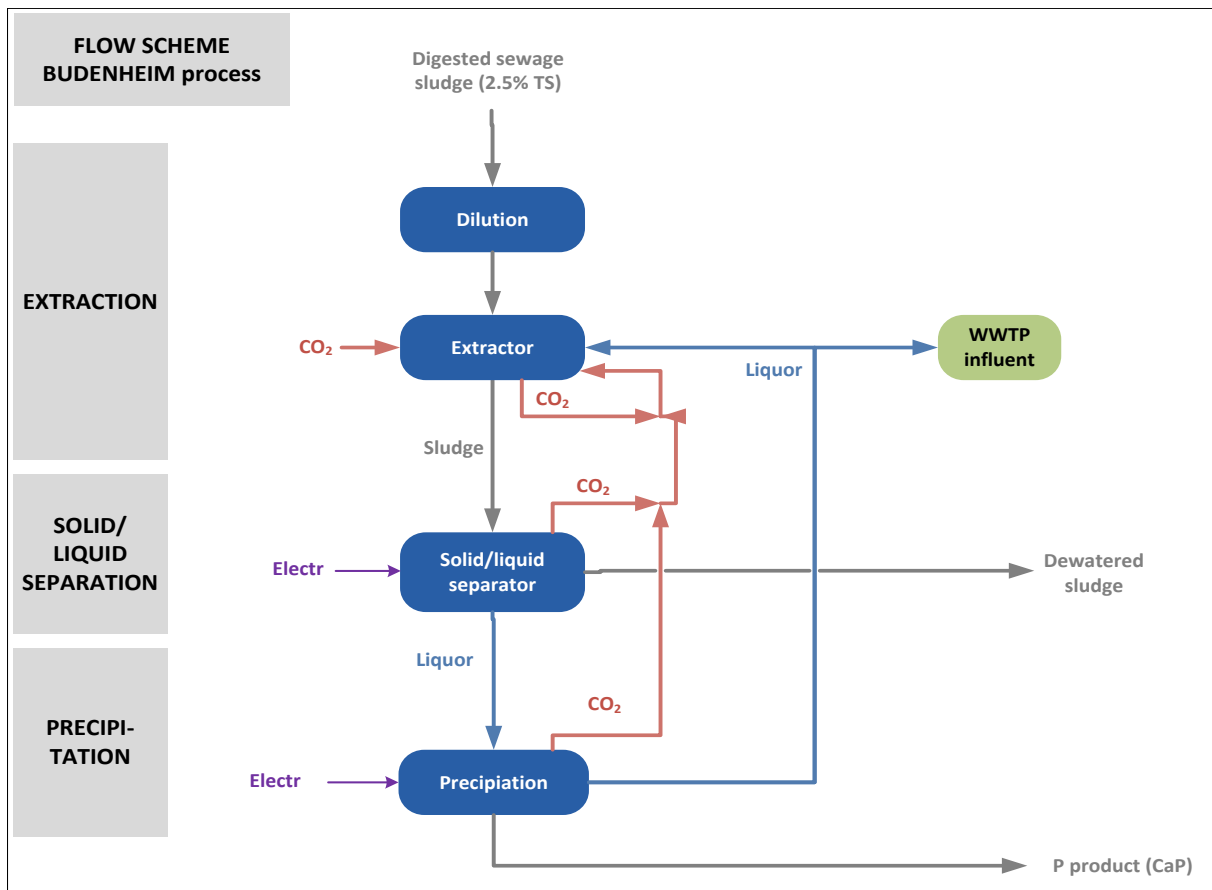


Figure 20 Flow chart of the Budenheim Process

2.7.3 Interactions

The phosphorus-extraction plant will be located between digester and dewatering at the WWTP. The digested sludge with 3,5 % TS is diluted to 0,5 – 1,0 % TS. After the CO₂-extraction the sludge is dewatered. The impact on the WWTP is as low as possible. The Budenheim plant can be seen as an additional sludge treatment step between digestion and dewatering.

2.7.4 Site specific information for Pilot, Budenheim

The P₂O₅-recovery ratio from sludge is about 50 %.The optimal parameters for the extraction according to the experimental plant tests are shown in Table 8. These values need to be verified at the pilot plant.

Table 8 Optimal process parameters for the Budenheim process

Parameter	Value
Pressure [bar]	Approx.. 10
Extraction time [min]	Approx. 30
Dry matter [%]	Approx. 0.5-1
CO ₂ flow-rate [l/h]	Approx. 400

3 Conclusion

The processes included in this report can be categorized into three groups of technologies according to the type of process input and the general recovery concept (see Figure 21):

Group 1:

Phosphorus is recovered directly from the digested sludge without extraction process and without separation of supernatant and sludge phase beforehand. Therefore this process is designed for and significantly more efficient for digested sludge from wastewater treatment plants using enhanced biological phosphorus removal. This group contains only one type of process – the Airprex process. Nevertheless, this process has been applied already in different process design configurations and additional process options have been developed. The central process component is the specific airlift loop reactor.

Group 2:

Phosphorus is recovered from the supernatant of the digested sludge after liquid-solid separation, usually by centrifugation. Therefore the process input is the relatively solid-free liquid phase of digested sludge. Since no extraction process is applied, the process is designed in general for wastewater treatment plants with enhanced biological phosphorus removal. According to the different process designs, three different technologies are distinguished in this group: Crystalactor, Pearl® process and Struvia process. The central process component of these technologies are crystallisation reactors. For each of these processes a unique reactor and process concept has been developed. AirPrex® is in principle also applicable in this group. The first full-scale application in combination with thermal-hydrolysis is in preparation.

Group 3:

Phosphorus is recovered from the supernatant of the digested sludge after acidic leaching (dissolution of P) and liquid-solid separation. In contrast to the processes of group 2, these processes enable the recovery of larger amounts of phosphorus by transferring (dissolving) phosphorus fixed in the solid sludge phase into the aqueous phase. This release is achieved by applying a specific extraction process on the digested sludge. The processes belonging to this group, Gifhorn process, Stuttgarter process and Budenheim process, consist of consecutive process steps and design, type and process combinations differ. .

Additionally to the processes described in this report, the so-called Nuresys process was demonstrated in full scale for the recovery of phosphorus from sludge supernatant after solid liquid separation. In the Nuresys process phosphorus is recovered as struvite crystals in a fully stirred crystallisation reactor after pH adjustment by stripping and addition of caustic soda and magnesium dosing in form of $MgCl_2$. The process is mainly belonging to group 2 but it is principally also applicable as group-1-technology, which means that struvite is precipitated in the sludge liquor before dewatering and solid liquid separation. Presently, the companies Aquafin, Vito and Nuresys are running a project for the full scale demonstration of such an installation.

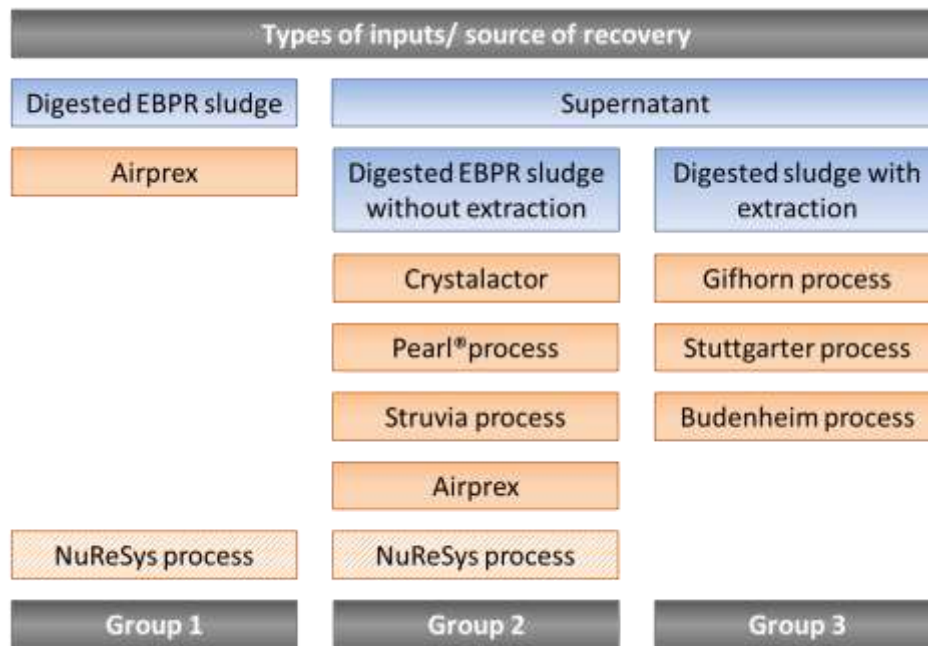


Figure 21 Classification of processes according to the source of phosphorus recovery

The Airprex process can be designed as one reactor or two-reactor layout. The process mechanisms of pH-increase by aeration and stripping, crystallisation due to dosing of magnesium chloride, sedimentation and harvesting of the mineral phosphorus product remain the same. Dewatering is done after treating the sludge in the AirPrex® reactor.

The most relevant process mechanism for group-2-technologies is the controlled crystal growth in the separated sludge water leading to high quality products of specific size, easily dewaterable and of high purity. The reactor design of these processes can be summarized as following:

- Crystalactor: Cylindrical, up-flow-fluidized bed with large crystallization surface, mainly on surface of sand seedings (in principle also other seedings possible), classification according to particle size in the fluidized bed, operational conditions lead to low super-saturation (meta-stable region), recycle flow for dilution
- Pearl® process: Up-flow, fluidized bed reactor with zones of increasing diameter, self-seeding systems (struvite prills are the seedings themselves), classification according to changes in diameter, operational conditions lead to low super-saturation (meta-stable region), recycle flow for dilution
- Struvia process: Continous stirred tank reactor with integrated solid/liquid separation by calming zone and lamellar packing (Turboflo™) or with additional lamella settler (Turbomix®). In the latter case, part of the struvite harvested from the bottom of the settler is recycled into the mixing reactor in order to reduce the amount of nucleation and to obtain crystals with larger particle sizes.

The implementation of struvite recovery from the sludge water (no matter if done prior or after dewatering) does not reduce the efficiency of technologies aiming to recover the phosphorus from the solid phase of the sludge, as done with acid leaching or thermo-chemical treatment of sludge ash. It has to be understood as complementary phosphorus recovery.

All technologies belonging to group 3 contain an initial sludge treatment step – the dissolution of P from the solid into the aqueous phase - to increase the concentration of dissolved phosphorus in the aqueous phase. In both cases the Gifhorn process and the Stuttgarter process, extraction is done by dosage of sulfuric acid, in the case of the Gifhorn process achieving a pH of 4. The Stuttgarter Process was operated at a range of pH values – between pH 3 and 5. In the later phases of experiments the pH was adjusted between pH 4 and 5 for economical reason. The Budenheim process applies an extraction by adding CO₂ at increased pressure which leads to a pH decrease down to pH 4 to 5.

The dewatering by centrifugation or filter press is included in the process chain of these concepts. The concepts of the Gifhorn process and the Stuttgarter process include a specific process to control the co-precipitation of heavy metals with the fertilizer product. The Gifhorn process includes the precipitation of heavy metals as sulfides by dosing of NaS prior dewatering. The Stuttgarter process prevents heavy metal precipitation by adding citric acid as complexation agent.

All the different process components are summarized in Figure 22.

	Extraction process	Metall elimination process	Precipitation process
Airprex	x	x	Air-lift reactor
Crystalactor®	x	x	Up-flow reactor
Pearl®	x	x	Up-flow reactor
Struvia (Turbomix®/ Turboflo™)	x	x	Continuous stirred tank reactor+laminar packing/ settler
Gifhorn	Dosing of H ₂ SO ₄	NaS precipitation	Precipitation and centrifugation
Stuttgarter	Dosing of H ₂ SO ₄	Complexation with citric acid	Precipitation and sedimentation
Budenheim	CO ₂ extraction	x	Precipitation

Figure 22 Type of general process components

According to the different process components, several chemicals are consumed. All processes include a precipitation step and hence require the dosing of a cation – calcium or magnesium. The three processes with an extraction process apply an acidic pH. For the pH increase before precipitation or crystallisation, dosing of caustic soda is required. Processes without acidic treatment need a slight adjustment of pH but not necessarily – depending on the properties of the sludge.

A summary of types of chemicals applied in the processes is given in Figure 23.

	Extraction process	Metall elimination process	Precipitation process
Airprex	x	x	MgCl ₂ (33%), NaOH (30%) or CaCl ₂
Crystalactor®	x	x	Mg(OH) ₂ , NaOH or MgCl ₂ Up-flow reactor
Pearl®	x	x	MgCl ₂ (33%), NaOH
Struvia (Turbomix®/ Turboflo™)	x	x	MgCl ₂ (33%) or
Gifhorn	H ₂ SO ₄ (96%)	NaS (15%)	Mg(OH) ₂ (53%), NaOH (50%)
Stuttgarter	H ₂ SO ₄ (78%)	Citric acid (50%)	MgO (92%), NaOH (22%)
Budenheim	CO ₂	x	Lime

Figure 23 Summary of types of chemicals used for the different concepts

By adding of magnesium components and increasing the pH most of the processes precipitate or crystalize magnesium ammonium phosphate (MAP, struvite). The product of the concepts AirPrex®, Crystalactor, Pearl® and Struvia is a nearly pure struvite. The processes Crystalactor and Struvia are designed to produce calcium phosphate as an alternative product. The product of the Gifhorn and Stuttgarter process contain mainly struvite but also calcium and iron phosphates. The latest configuration of the Stuttgarter Process produces nearly pure struvite. The Budenheim process is designed for the precipitation of a calcium phosphate.

	Duration	Scale
Airprex	> 2 years	Full scale, several sites
Crystalactor®	> 2 years	Full scale, several sites
Pearl®	> 2 years	Full scale, several sites
Struvia (Turbomix®/ Turboflo™)	> 1 year	Pilot scale, one site
Gifhorn	Months/> 2 years	Full scale, one site
Stuttgarter	> 2 years	One demonstration site
Budenheim	> 1 year	Lab scale

Figure 24 Overview of size and duration of operation

The processes described in this report have all been operated in demonstration scale or planning of a demonstration plant is in progress. Therefore up to now, the operational experiences differ significantly for the different technologies regarding plant size and duration of operation. Figure 24 gives an overview of the duration and sizes of installations of the processes. Regarding the duration of the Gifhorn process it has to be taken into account that the general process has been operated for more

than two years but under the operational conditions optimized for phosphorus recovery only for several months. The operation of the Budenheim process in pilot scale is in preparation.

In general, it can be concluded that all processes presented here have positive impacts on the operation of the wastewater treatment plant, which are a reduced phosphorus load for the biological wastewater treatment and a reduction of the amount of sludge to be disposed. All processes which produce struvite additionally reduce the load of ammonium for the biological wastewater treatment. Furthermore all of them reduce the risk of encrustations in the sludge treatment part of the wastewater treatment plant. However, this positive effect is mainly relevant for wastewater treatment plants using enhanced biological phosphorus removal and anaerobic digestion since otherwise the re-dissolution of phosphorus during the digestion is relatively low.

The reduction of the amount of sludge to be disposed is beneficial since costs and energy for drying and for transportation decrease.

4 Annex

4.1 Experimental results obtained in the pilot study of the Struvia process

4.1.1 Influence of Mg/P and Mg/Ca ratio on removal efficiency and agglomeration of crystals

Figure 25 shows exemplary results about the soluble calcium removal according to the Mg/P molar ratio applied. For this case, when this ratio is higher than 1.5, there is no calcium removal.

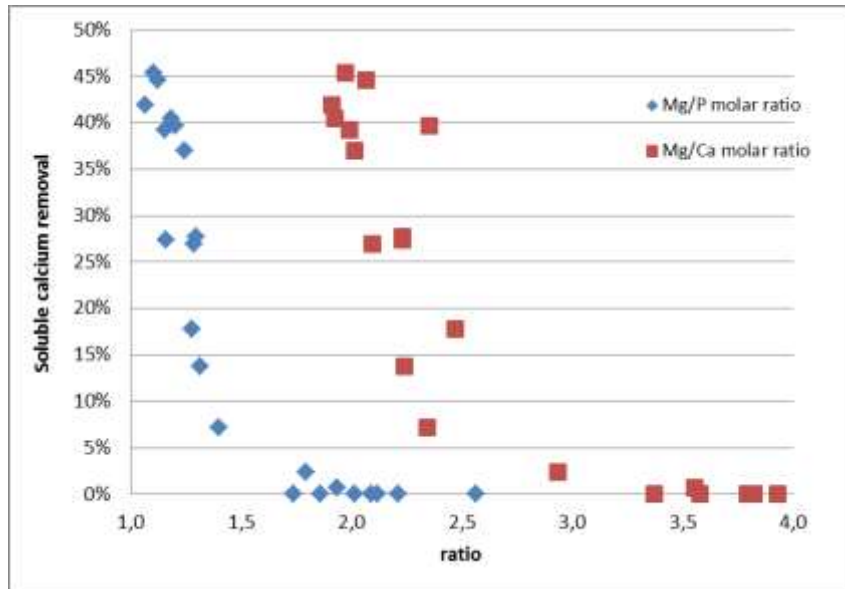


Figure 25 Example of soluble calcium removal according to the Mg/P and Mg/Ca molar ratios (Results from Struvia™ pilot unit with the industrial effluent N°4)

Figure 9 shows an example of the variation of the P-PO₄ removal according to the pH applied during the crystallisation reaction. With this effluent, we obtained a P-PO₄ removal higher than 85% when the pH is higher or equal to 8, with a P-PO₄ residual around 20 mg/l corresponding to the struvite solubility. This residual can be a little lower if the Mg/P ratio is higher.

It was demonstrated that the increase of the Mg/P ratio (beyond the isoelectric point of the struvite) allows to increase the size of the MAP crystals. It seems that excess of magnesium leads to agglomeration and thus crystals or granules of several hundred micrometres (see the SEM pictures in Figure 26):

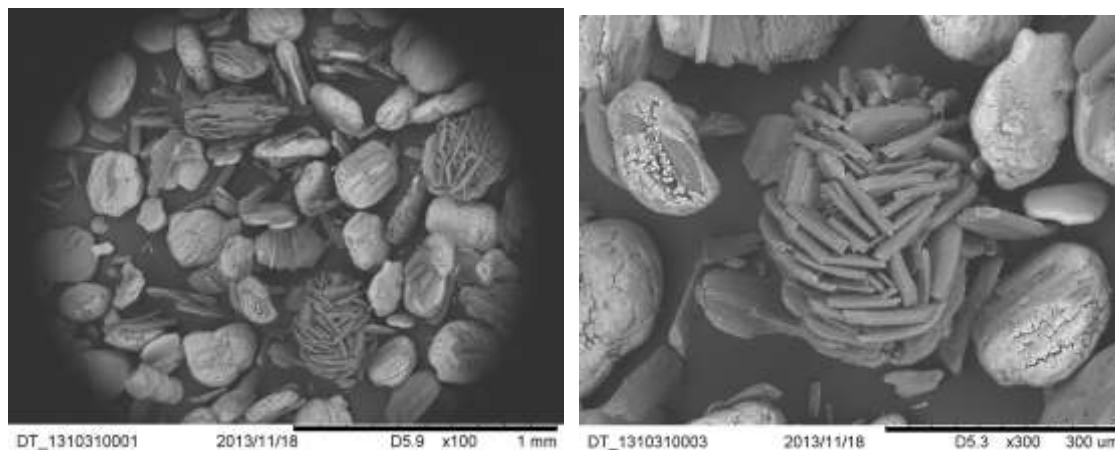


Figure 26 Struvite crystals or granules (SEM microscopy) produced with Struvia™ pilot unit

4.1.2 Results from pilot tests with different types of effluent

For treatment of Athos™ effluent alone (effluent 1) a promising soluble P-PO₄ precipitation of >80% was observed but insufficient struvite capture. The struvite crystallization was impacted by formation of fines, COD precipitation and foam formation, and the settling velocity was too low. An explanation could be linked to the high VFA (Volatile Fatty Acids, in particular acetic acid) concentration of this effluent and/or a high salinity. Two years ago, Ostara also observed a granulation problem with this effluent explaining this with the high pH.

The treatment of centrate from thickened sludge (effluent 3) mixed with the Athos™ effluent was investigated at different mixing ratios in the range of 75% to 98% thickened sludge. For these effluent mixtures a high P-PO₄ removal was observed (≥80%). It was concluded that a N:P of higher than 2 is mandatory to avoid limitation of crystal growth. The struvite capture was between 70% and 95% estimated from TSS, P-PO₄ and total P analysis. A high TSS concentration impacted the crystallization, the settling velocity and the struvite quality. The precipitation of some amorphous calcium phosphate was observed for Ca:P molar ratios higher than 0.5.

For the tests with the effluent type 4, struvite precipitation was excellent with a soluble P-PO₄ removal up to 95%. The estimated struvite capture was very high (> 95%) with a very good quality of the Turboflo™ supernatant (Turbidity < 5 FNU). A N/P molar ratio of the effluent higher than 2 is still necessary. To avoid the CaP precipitation (when Ca/P > 0.5) the Mg/P molar ratio must be increased and we obtained a struvite crystals size up to 500µm.

The centrate from digested sludge (effluent 2) has not been tested yet on the P-REX pilot for the moment but is planned for the future.

With the effluents tested on the pilot unit at Brussels North WWTP, the following energy consumption can be estimated:

- Effluent 3 composed of a mix of sludge centrate + Athos effluent: P average concentration of 150 mg/l, P average recovery rate of 80%, Energy consumption estimation: 2.5 kWh/Kg P recovered.

- Effluent 4 representing an industrial effluent from Food&Bev industry: P concentration of 150-200 mg/l, average recovery rate of 90%, Energy consumption estimation: 1.7 to 2.2 kWh/kg P recovered.

4.2 Laboratory and mini-pilot study of the Struvia process

The first steps of the pilot study (1st sem. 2013) were to perform some preliminary batch laboratory tests and a mini-pilot test with a reactor volume of 5 L (see picture in Figure 27).

The following optimal conditions for struvite precipitation have been identified: pH = 8, reaction time= 30-60 min, molar Mg/P ratio=1.1-1.3. A soluble P-PO₄ removal of 80-90% has been obtained (around 10-20 mg/l of soluble P-PO₄ residual) and a soluble N-NH₄ removal around 4-5% (according to the ammonia concentration of the Athos™ effluent).



Figure 27 Struvia™ mini-pilot

Figure 27 shows the start-up phase of the Turboflo™ reactor. During a certain time period the initial formation of crystals takes place until the required particle size distribution is obtained (measured here with laser granulometry, further information is given in annex (4.1)).

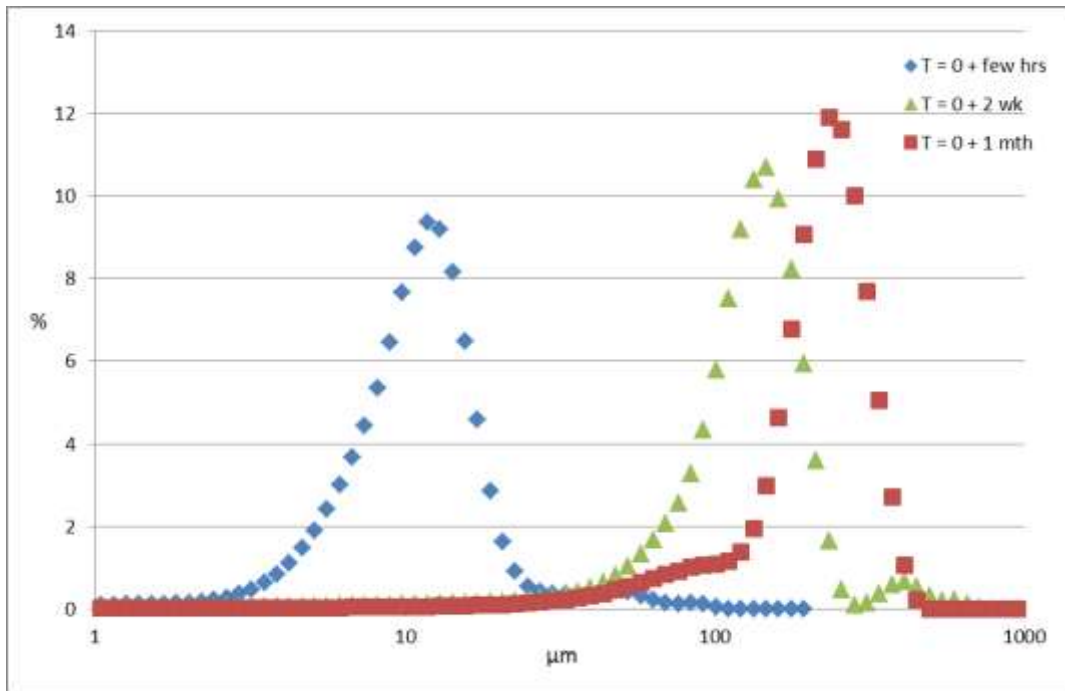


Figure 28 Laser granulometries of struvite crystals extracted (LS 230, VSM Plus Instrument)

Different magnesium sources (MgCl_2 , MgSO_4 , MgCO_3 , MgO , Mg(OH)_2), by-products containing MgCl_2 or MgO have been evaluated. The liquid magnesium chloride at 33% as potash mining by-product has been validated as the best product technically (quick reaction, low dose to apply) and economically. The magnesia (at 80%, under powder form) remains interesting for certain areas away from a potash mining activity. But this product must be finely crushed ($40\ \mu\text{m}$) and injected as a suspension (preparation needed). The Mg/P ratio must be equal to 2 to have the same P-PO_4 removal (80-90%). The advantages of the magnesia are that it is a significantly more concentrated product and that is also leads to an increase of the pH and indirectly to a saving of caustic soda.



Figure 29 Organo-mineral fertilizer product containing struvite

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