Phosphorus recovery from wastewater and sludge: Concept for different regional conditions

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Vorwort

Die Ressourcen der Erde werden heute genutzt wie in keinem Zeitalter zuvor, obwohl sie oftmals nur begrenzt zur Verfügung stehen. Phosphor ist weltweit nur begrenzt vorhanden, aber essentiell für das Pflanzwachstum und damit für die Sicherung der Ernährung.

Über menschliche Ausscheidungen gelangt der wertvolle Stoff Phosphor ins Abwasser und landet schließlich im Klärschlamm und Gewässer. Vor diesem Hintergrund werden Verfahren zur Rückgewinnung von Phosphor aus häuslichem Abwasser seit mindestens 10 Jahren intensiv beforscht.

Die vorliegende Arbeit bietet eine systematische Übersicht der Phosphorrückgewinnung und Recyclingrouten. Die verschiedenen Konzepte und Fallstudien aus der Praxis für unterschiedliche regionale Bedingungen könnten eine Inspiration für die zukünftige Phosphorrückgewinnung geben und damit Möglichkeiten zur nachhaltigen Entwicklung in der Abwasserbehandlung aufzeigen.

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Zuerst möchte ich meinem Betreuer, Herrn Prof. Dr.-Ing. Matthias Barjenbruch, ganz herzlich für das Vertrauen, die gute Zusammenarbeit und die Unterstützung meiner Arbeit in den vergangenen Jahren danken. Sein professionelles Vorbild im Bereich der Siedlungswasserwirtschaft hat diese Arbeit geprägt, und dafür bin ich ihm sehr dankbar.

Weiterhin möchte ich meinem betrieblichen Betreuer, Herrn Dr. Christian Kabbe, vom Kompetenzzentrum Wasser Berlin gGmbH (KWB) herzlich danken. Er gab mir die Möglichkeit, am KWB bei unterschiedlichen spannenden Projekten der Phosphorrückgewinnung und Schlammbehandlung mitzuwirken und ließ mir zudem die notwendigen Freiräume zur Erstellung dieser Dissertation. Er hat auch viele wertvolle Anregungen für die schriftliche Ausarbeitung dieser Dissertation gegeben.

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Den vielen Kolleginnen und Kollegen am KWB danke ich ganz herzlich für die sehr angenehme und offene Atmosphäre und den guten Zusammenhalt, die meine Arbeit in den

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Kuangxin Zhou

Zusammenfassung

Phosphor ist eine essentielle, aber begrenzte Ressource. Technologien zur Phosphorrückgewinnung wurden in den vergangenen Jahren weiter entwickelt und zum Teil großtechnisch umgesetzt, wodurch kommunales Abwasser und Klärschlamm als eine vielversprechende sekundäre Phosphorquelle angesehen werden kann. Deutschland ist bei Phosphor nahezu vollständig vom Import abhängig. Die neue, 2017 beschlossene Klärschlammverordnung verpflichtet zur Rückgewinnung von Phosphor aus Klärschlamm großer Anlagen nach einer Übergangsfrist. China ist der größte Phosphatproduzent (Bergbau und Verarbeitung) und Konsument weltweit mit großen mineralischen Phosphorvorkommen. Verschiedene Rahmenbedingungen erfordern unterschiedliche Ansätze zur Phosphorrückgewinnung. Diese Arbeit konzentriert sich auf unterschiedliche regionale Optionen zum Phosphorrecycling in der Landwirtschaft und Rückgewinnung aus Klärschlamm als Struvit und Düngemittelindustrieabwasser.

Die landwirtschaftliche Nutzung von Klärschlamm ist in mehreren Ländern gesetzlich eingeschränkt oder sogar verboten. Zum Beispiel verlangt in Deutschland die neue Regelung der Düngemittelverordnung, dass ab dem Jahr 2017 synthetische Polymere bei der Herstellung von Düngemitteln nur noch eingesetzt werden dürfen, soweit diese sich mindestens um 20 % innerhalb von zwei Jahren abbauen. Vor diesem Hintergrund wurde in dieser Studie die großtechnische Anwendbarkeit der stärkebasierten biologisch abbaubaren Polymere in der Schlammeindickung und Entwässerung untersucht. Ergebnisse zeigen, dass die Substitution von 20-30% des Polyacrylamid-basierten Polymers eine ähnliche Trockensubstanz bei der Schlammentwässerung erreicht.

Die Phosphorrückgewinnung durch Struvit-Fällung ist bereits sowohl technisch als auch wirtschaftlich machbar. Dies belegen die mehr als 40 großtechnischen Anlagen weltweit. Bei der Auslegung und Umsetzung dieser Verfahren sollten auch die Umweltauswirkungen berücksichtigt werden. Eine Ökobilanz wurde in dieser Studie durchgeführt. Sie vergleicht zwei Generationen des AirPrex® Reaktors auf der Kläranlage Waßmannsdorf und der Kläranlage Amsterdam West. Die Ergebnisse zeigen, dass der neue Reaktor energieeffizienter ist, weniger Treibhausgasemissionen generiert und ein geringeres Eutrophierungspotential hat. Diese Verbesserungen resultieren vor allem aus optimierter Struvitfällung und –ernte und zeigen, dass sich die Technologie vor allem im Betrieb und nicht nur im Labor oder Technikum weiterentwickeln lässt.

Die Phosphorrückgewinnung aus dem kommunalen Abwasser in China ist eingeschränkt durch niedrige Phosphatkonzentration im kommunalen Klärschlamm und die unsachgemäße Schlammentsorgung. Die Rückgewinnung aus industriellen Abwässern mit höherer Phosphatkonzentration zeigt ein höheres Potential aufgrund eines leichten Marktzugangs und der Vorteile für den Betreiber. Deshalb wurde das Potential der Phosphorrückgewinnung in Düngermittelindustrieabwasser im Rahmen einer Machbarkeitsstudie untersucht. Die Ergebnisse des Laborversuchs zeigen, dass mit einem neuen Konzept durch Mischung von Phosphat-Abwasser und Ammonium-Abwasser aus Düngemittelproduktionsanlagen, etwa 95% Orthophosphat und 30% Ammonium-Stickstoff entfernet werden können. Die wirtschaftliche Machbarkeit der Phosphorrückgewinnung als Struvit an dieser Anlage ist ebenfalls bewiesen.

Obwohl die technische Machbarkeit der Phosphorrückgewinnung bereits gezeigt werden konnte, sollte die Gesetzgebung und die nationale Politik mit der technologischen Entwicklung Schritt halten. Es sollten mehr Anstrengungen unternommen werden, um nicht nur ein einziges Element rückzugewinnen, sondern sowohl die Ressourcen- als auch die Energieeffizienz in Kläranlagen zu verbessern.

Abstract

Phosphorus (P) is an essential but limited resource. In recent years, technologies for phosphorus recovery have been developed further and some of them have been implemented on a large scale, making municipal wastewater and sludge promising secondary phosphorus sources. Germany is almost completely dependent on phosphorus imports. The newly adopted sewage sludge ordinance in 2017 requires, after a transitional period, the recovery of phosphorus from sewage sludge in large WWTP plants. China has abundant phosphate rock deposits and is the world's largest producer (mining and processing) and consumer of phosphate rock. Different frameworks require different approaches to the recovery of phosphorus. This paper focuses on different regional options for phosphorus recycling in agriculture and recovery from sewage sludge via struvite and wastewater from the fertilizer industry.

The agricultural use of sewage sludge is restricted by legislation or even prohibited in several countries. In Germany, for example, a new and more stringent regulation of German fertilizer ordinance, effective from 2017, requires the degradation of 20% of synthetic additives such as polymeric substances within two years. Against this background, the general feasibility of applying starch-based biodegradable polymers in full-scale thickening and centrifugation was demonstrated in this study. Results show that a substitution of 20-30% of the polyacrylamide-based polymer was capable of achieving similar total solids of the dewatered sludge.

P-recovery through struvite is already both technically and economically feasible. This has been proved by more than 40 large-scale plants worldwide. However, when designing and implement these P-recovery technologies, the environmental effects need to be considered. Therefore, a comparative environmental life cycle assessment of phosphorus recovery with different generations of the Airprex® reactors at WWTP Wassmannsdorf and Amsterdam West was carried out in this study. Results show that the new reactor is more energy efficient and has a lower greenhouse gas (GHG) footprint and eutrophication potential. These improvements are mainly due to optimized struvite precipitation and harvesting, and show that technology can be developed further, especially in plant operation and not only in the laboratory or pilot plant.

P-recovery from municipal wastewater in China is limited to the low P concentration in sludge and improper sludge disposal. The recovery from industrial wastewater with a high concentration of phosphorus shows higher potential due to easier market access and benefits to its operators. For this reason, the potential of P-recovery from fertilizer industry wastewater was investigated in this study. The results of the lab experiment show that about 95% orthophosphate and 30% ammonium nitrogen can be recovered using a new treatment where of phosphate and ammonia wastewater from fertilizer plants are mixed. The economic feasibility of phosphorus recovery via struvite has also been proved at this plant.

Although the full-scale P-recovery techniques have proved to be technologically feasible, legislation and national policies need to keep up with the development of technology. More efforts are required taken to recover not only one single element, but also to improve both the energy and resource efficiency in WWTPs.

We may be able to substitute nuclear power for coal power, and plastics for wood, and yeast for meat, and friendliness for isolation—but for phosphorus there is neither substitution nor replacement.

Isaac Asimov, 1959

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List of Abbreviations

AAO	Anaerobic-Anoxic-Oxic
AD	Anaerobic Sludge Digestion
AMS	Amsterdam West
AOAO	Anoxic-Aerobic-Anoxic-Aerobic
Bio-P	Biological Phosphorus Elimination
CED	Cumulative Energy Demand
CHP	Combined Heat and Power
COD	Chemical Oxygen Demand
DAP	Diammonium Phosphate
DM	Dry Matter
DS	Dry Solids
EBPR	Enhanced Biological Phosphorus Removal
FEP	Freshwater Eutrophication Potential
GHG	Greenhouse Gas Footprint
GWP	Global Warming Potential
HAP	Hydroxyapatite
HRT	Hydraulic Retention Time
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LOI	Loss on Ignition
MAP	Monoammonium Phosphate
MEP	Marine Eutrophication Potential
Mg	Magnesium
NPK	Nitrogen (N), Phosphorus (P) and Potassium (K)
OPD	Optimal Polymer Doses
OSP	Ordinary Superphosphate
P	Phosphorus
PAM	Polyacrylamide

XX

SBR	Sequencing Batch Reactor	XXI
SRT	Sludge Retention Time	
SS	Suspended Solids	
SSA	Sewage Sludge Ash	
TN	Total Nitrogen	
TOC	Total Organic Carbon	
TP	Total Phosphorus	
TS	Total Solids	
TSP	Triple Superphosphate	
TSS	Total Suspended Solids	
WMD	Wassmannsdorf	
WWTP	Wastewater Treatment Plant	

Chapter 1: Current state and full-scale applications of phosphorus recovery and recycling from wastewater in different regions

Graphical abstract

Highlights

- Overview of recently developed and promising technologies for phosphorus recovery from wastewater was reviewed
- Comparison of different P-recovery methods with Life Cycle Assessment (LCA) was given
- Current distribution of P-recovery plants in different continents was analyzed
- Future-oriented P-recovery options and trends was proposed

1.1 Introduction and objective of this thesis

Phosphorus (P) is a limited and non-replaceable resource for all life processes (Asimov, 1959). In the living cell phosphorus plays a decisive role in the cell membrane, the storage and retrieval system for genetic information, DNA and RNA, as well as in the energy system, ATP. Furthermore, in vertebrate animals phosphorus is an important component in sinew, cartilage, bone, and enamel (Butusov & Jernelöv, 2013). Phosphorus (P) is also essential for crop growth and food production, and most of the phosphorus applied to agricultural land comes from phosphate rock, which is a non-renewable resource.

The largest and least expensive source of phosphorus is obtained by mining and concentrating phosphate rock from the numerous phosphate deposits of the world. The currently explored and economically feasible global reserves may be depleted within only a few generations (Childers et al., 2011). Mined phosphate rock is global principally used for agricultural fertilizer (80%), the remainder being used for animal feed additions (5%) and industrial applications (15%) including detergents and metal treatment (Smit et al., 2009). The most important mineral phosphate fertilizers are Ordinary Superphosphate (OSP), Triple Superphosphate (TSP), Monoammonium Phosphate (MAP) and Diammonium Phosphate (DAP). The use efficiency of phosphate is quite low. Only about 20% of the phosphorus used in agriculture reaches the food we consume, most of the remainder is lost in inefficient steps along the phosphorus cycle e.g. crops harvesting, food production etc. (Alexander et al., 2017; Cordell et al., 2011).

The phosphate rock is mined and then processed into fertilizers and transported around the world for plant growth. Once the crops are harvested, the phosphorus they contain will be transported worldwide and no longer recycled locally via the decomposition of plant matter (SCUUWE, 2013). When the crops have been eaten by humans the phosphorus is excreted and in the EU the P intakes is from about 1,800 mg/d (Spain) to about 2,700 mg/d (Germany) and in women from about 1,500 mg/d (Spain) to about 2,100 mg/d (Germany) (Flynn et al., 2009). In Germany, per capita loading of phosphorus in municipal wastewater treatment is 1.8 g phosphorus per day (DWA-A-131, 2016). However, the phosphorus is no longer returned to the soil, but transported in to the sewage. Depending on the level and the efficiency of the wastewater treatment plants, most of the phosphorus ends up in the sewage sludge. Other phosphorus may end up in water systems may causing widespread pollution in lakes, rivers and coastal areas, algal blooms, and dead zones in the oceans. In Germany, 91.8% of the P entering the WWTPs are transferred into sludge (DWA, 2016) by biological accumulation in sludge using Enhanced Biological Phosphorus Removal (EBPR) or by chemical precipitation e.g. with iron or aluminum salt. The other 10% of P ends up in rivers, lakes and oceans.

With increasing industrialization and urbanization, the dependence on mined phosphate and the creation of a water-based disposal system for human waste the traditional natural cycle of phosphorus was broken (Kabbe, 2013a). Key to "closing the loop" on current phosphorus losses is the recovery of phosphorus from human and animal wastes, which should be used as a readily available phosphorus resource rather than treated as waste (Cordell et al., 2009).
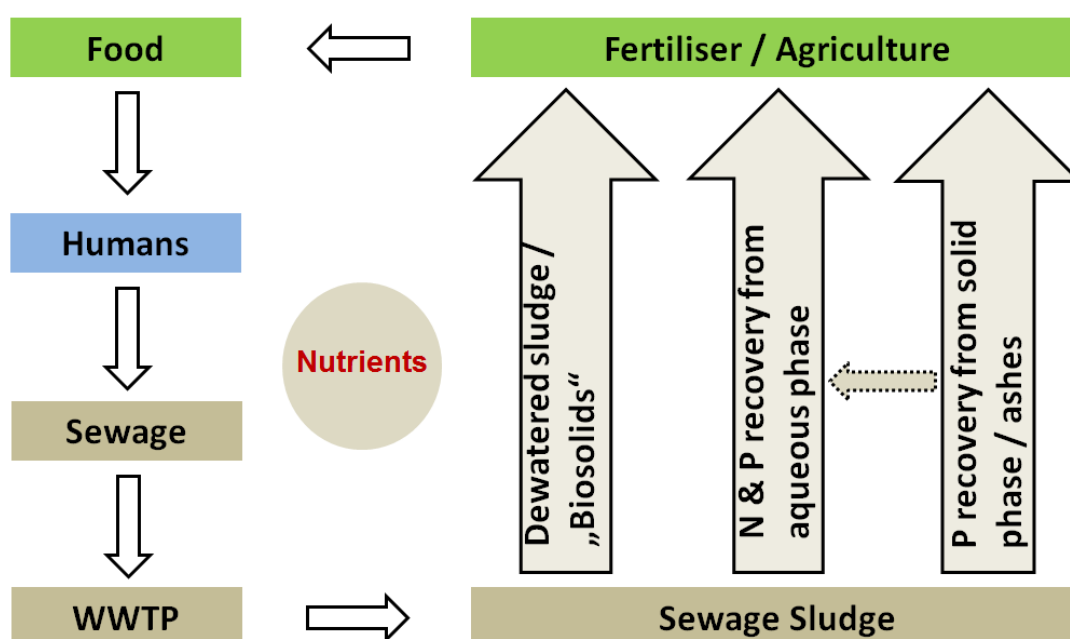
Figure 1: The three principle routes for P recovery and recycling from the wastewater stream as a nutrient (Kabbe, 2013b)

As shown in Figure 1, most of the phosphorus entering a WWTP ends up in the sewage sludge. Three principle and complementary routes for closing the phosphorus cycle by recovery from sewage sludge appear to be reasonable. Traditional sludge directly applied to arable land as bio-solid is considered one of the most economical ways for P recycling. But due to the increased concern for heavy metals, organic contaminants and pathogens, this option is controversially debated by the public and authorities. Therefore, different technologies of P recovery have been developed from the aqueous and solid phase of sludge. The details of these technologies will be discussed in Chapter 1.3.

Although various technologies of P recovery have been developed and tested in pilot plants or on an industrial scale and some of them are even economically feasible under current conditions, there is still no "one solution fits all" for different regions with different infrastructures, legal, social and economic structures. The objective of this thesis is to explore the promising relevant paths of P recovery and recycling for different regional conditions. Four case studies have been conducted to support sustainability of phosphorus on a global scale. Figure 2 provides a brief overview of this research.
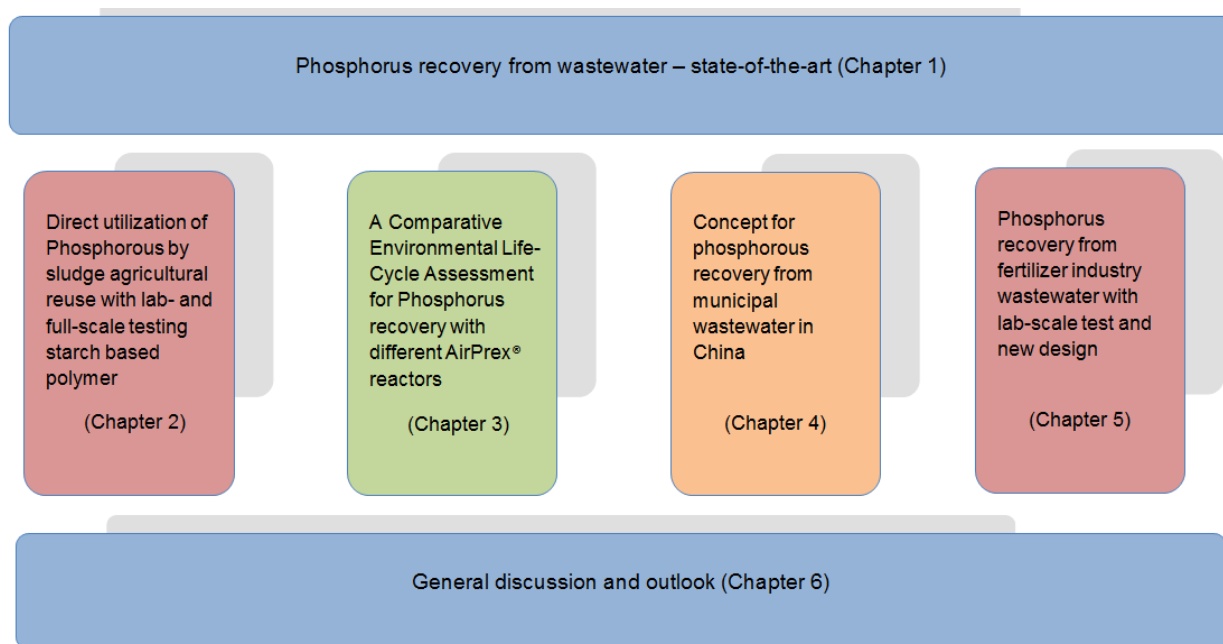
Figure 2: Overview of the research with different options for P recovery (Red box indicates experimental work, Green box indicates modelling work and Orange box indicates case research work)

Chapter 1 of this thesis gives an overview of global phosphorus security and recently developed and promising technologies for phosphorus recovery from wastewater and sludge. Full-scale implications of phosphorus recovery and recycling from wastewater and case studies in different regions are summarized.

The simplest method of phosphorus recovery from sludge is the direct use of sludge as a fertilizer in agriculture. Agricultural reuse of dewatered sludge can remain an adequate way of valorization for small and mid-size wastewater treatment plants in some countries. When the agricultural use of dewatered sludge is planned, synthetic flocculants based on non-biodegradable polyacrylamide (PAM) may have a negative impact on the environment due to toxicity and non-biodegradability. **Chapter 2** of this thesis describes the feasibility of applying starch-based "green" polymers in full-scale dewatering devices at three WWTPs in Germany. The successive approach through screening, lab-scale and pilot-scale trials paved the way for full-scale trials in order to test starch-based polymers.

P-recovery through struvite is already both technically and economically feasible. This has been proved by more than 40 large-scale plants worldwide. However, when designing and implement these P-recovery technologies, the environmental effects need to be considered. In **Chapter 3** a Life Cycle Assessment (LCA) is carried out in order to compare the environmental impact of phosphorus recovery with the one-reactor AirPrex® configuration at WWTP Berlin Wassmannsdorf and the three-reactor AirPrex® configuration at WWTP Amsterdam West. The full-scale operational data in both plants e.g. demand for electricity, chemicals, product yield and side effects were used to accomplish the assessment. The

cumulative energy demand and related environmental impacts (e.g. greenhouse gas emissions, freshwater eutrophication potential, marine eutrophication potential) were selected as environmental indicators for the LCA.

China is the second-largest economy and one of the largest water markets in the world. Considering the urbanization process in current China, the treatment capacity of WWTPs is expected to continue to grow in the next decades. In **Chapter 4** the feasibility of phosphorus recovery in the Chinese municipal wastewater and phosphate industry will be investigated. Based upon existing phosphorus recovery technologies and the current wastewater infrastructure in China, five options for phosphorus recovery from sewage sludge, sludge water, sludge ash and the fertilizer industry are analyzed according to the specific conditions in China.

According to the investigation results in Chapter 4, phosphorus recovery from phosphate industrial wastewater shows a higher potential in China. In **Chapter 5**, a new approach for the treatment of wastewater from the fertilizer industry with high phosphate and fluoride concentration is researched. A Jar test is conducted with synthetic and real wastewater to demonstrate the feasibility of the crystallization and precipitation process. The feasibility of a full scale plant using this new concept at a Chinese fertilizer plant will be further discussed in details.

The last part, **Chapter 6** gives a brief summary of the main findings in this study and presents an outlook to the future and recommendations for further research.

Different frameworks require different approaches to the recovery of phosphorus. The overall objectives of this study are firstly, to provide a systematic overview of phosphorus recovery and recycling methods and then through a series of case studies under different regional conditions to provide inspiration for the future P-recovery.

1.2 Global phosphorus security

Phosphorus deficiency is often the limiting factor of plant growth (De Vries, 1998). Thus, phosphorus is a critical element in food security: a shortage of phosphorus in any agro system results in low agricultural productivity that, in many cases, may cause undernourishment and, in extreme cases, famine (Ragnarsdóttir et al., 2011; Sanchez & Swaminathan, 2005). By 2050, the world's population is estimated to reach 9.1 billion, and in order to feed the growing population, agricultural production would need to increase by 70% overall and 100% in developing countries (FAO, 2009).
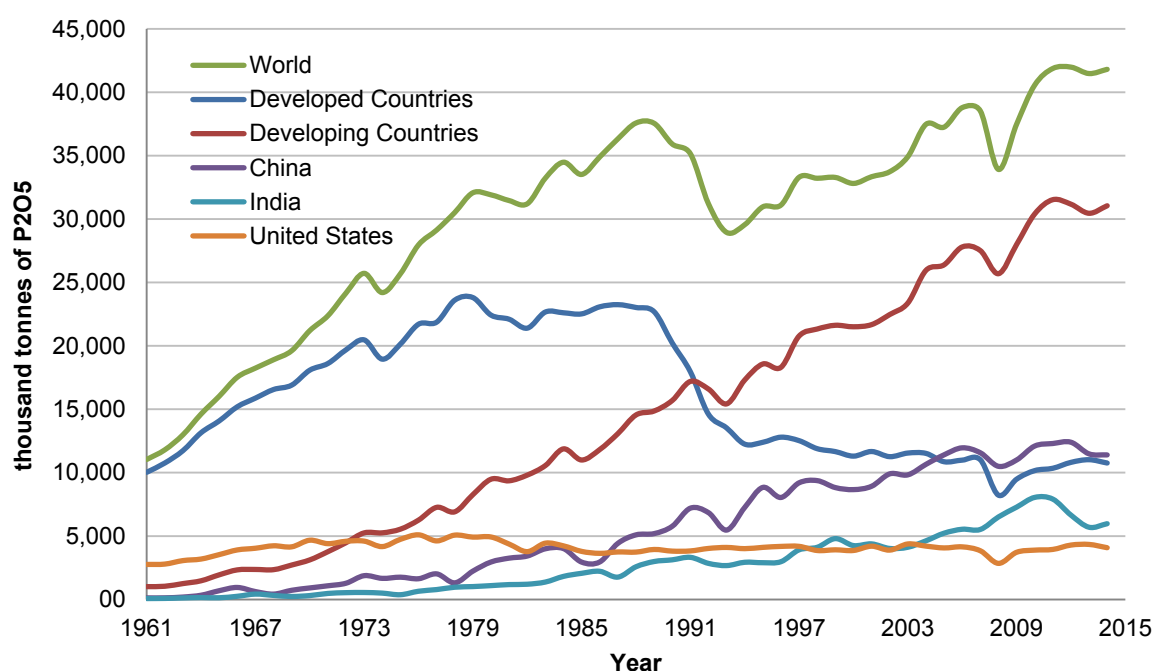
Figure 3: Trends in phosphorus consumption in different regions and the top 3 consumption countries from 1962 to 2014 (IFA, 2017)

Figure 3 gives an overview of global phosphorus consumption, in developed and developing countries from 1961 to 2014. Industrial nations have experienced decreasing demands since the 1980s. This is primarily due to an accumulation of residual phosphorus, which was not taken up by annual crops, but rather, is bound to soil particles and is available for subsequent crops. In Germany, the fertilization is regarded as in line with good agricultural practice if the phosphate (P_2O_5) surplus is less than 20 kg/ha per year (on average over the last 6 years) (UBA, 2015). The decrease is also reflective of the increasing use of livestock manures from concentrated feeding operations (Roland W. Scholz, 2014). In contrast, there is increasing demand for phosphorus in many developing countries. According to the IFA data (IFA, 2017), in 1961 fertilizer consumption of developing countries accounted for 9% of the global total and this increased to 74% by 2014. China contributed about 27% to the world fertilizer consumption in 2014. The top three fertilizer consumers (China, India and United States) accounted for 51% of the world consumption in 2014. Some countries such as China are now promoting phosphorus use efficiency and thus may flatten or decrease future

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demand projections (Fan et al., 2011; Zhang et al., 2011). A specific dip in 2008 was related to the global or regional economic booms or crashes, which caused an increase in world energy prices and directly affected P prices, production and consumption rates. World consumption of P_2O_5 contained in all uses is expected to increase incrementally to 48.9 million tons in 2020 from 44.5 million tons in 2016 (USGS, 2017).

Table 1: Global phosphorus production in 2015 and 2016 and current reserves in thousand metric tons (USGS, 2017)

	Mine production		Percent of Production	Reserves	Percent of Reserves
	2015	2016	2016		
United States	27,400	27,800	10.7%	1,100,000	1.6%
Algeria	1,400	1,500	0.6%	2,200,000	3.2%
Australia	2,500	2,500	1.0%	1,100,000	1.6%
Brazil	6,100	6,500	2.5%	320,000	0.5%
China	120,000	138,000	52.9%	3,100,000	4.6%
Egypt	5,500	5,500	2.1%	1,200,000	1.8%
India	1,500	1,500	0.6%	65,000	0.1%
Israel	3,540	3,500	1.3%	130,000	0.2%
Jordan	8,340	8,300	3.2%	1,200,000	1.8%
Kazakhstan	1,840	1,800	0.7%	260,000	0.4%
Mexico	1,680	1,700	0.7%	30,000	0.0%
Morocco and Western Sahara	29,000	30,000	11.5%	50,000,000	73.5%
Peru	3,880	4,000	1.5%	820,000	1.2%
Russia	11,600	11,600	4.4%	1,300,000	1.9%
Saudi Arabia	4,000	4,000	1.5%	680,000	1.0%
Senegal	1,240	1,250	0.5%	50,000	0.1%
South Africa	1,980	1,700	0.7%	1,500,000	2.2%
Syria	750	—	—	1,800,000	2.6%
Togo	1,100	900	0.3%	30,000	0.0%
Tunisia	2,800	3,500	1.3%	100,000	0.1%
Vietnam	2,500	2,800	1.1%	30,000	0.0%
Other countries	2,470	2,410	0.9%	810,000	1.2%
World total (rounded)	241,000	261,000	100%	68,000,000	100%

According to statistics from the U.S. Geological Survey (USGS, 2017), the world's reserves are 68 billion tons of phosphorus rock. If the world's P rock consumption of 261 million tons (44.5 million tons P_2O_5) in 2016 (USGS, 2017) continues, the world profitable phosphate ore may run out within 260 years. Table 1 shows the annual phosphate rock production for the

most important countries worldwide in 2015 and 2016 and the P rock reserves in these countries.

The main reserves include those held by four countries: China, Saudia Arabia, Iraq and Morocco. It can be seen that Morocco and the Western Sahara (73.5%) and China (4.6%) have an estimated amount of 78.1% of the world's remaining phosphate reserves. Large parts of the world, including Europe, India and Australia, are almost totally dependent on the imports of phosphate from other countries. Unless additional sources of phosphorus can be accessed or society can significantly increase phosphorus recycling, future global phosphorus security will be increasingly reliant on some single countries (Cooper et al., 2011). North Africa, especially Morocco and Western Sahara is the most important exporter in the world. The largest areas of growth are predicted for Africa and the Middle East. In Morocco, work will continue on the expansion of phosphate rock mines and processing facilities, which is expected to double phosphate rock production capacity by 2020 (USGS, 2017). The largest sedimentary deposits are found in northern Africa, China, the Middle East, and the United States. Significant igneous occurrences are found in Brazil, Canada, Finland, Russia, and South Africa. Large phosphate resources have been identified on the continental shelves and on seamounts in the Atlantic Ocean and the Pacific Ocean. World resources of phosphate rock are more than 300 billion tons (USGS, 2017).

1.3 Routes and potentials of phosphorus recovery from municipal wastewater

In the municipal wastewater treatment plants in Germany, an average of approx. 11% of the incoming phosphorus load is removed with primary sludge and 28% of the incoming phosphorus load are incorporated into the biomass and removed (DWA-A-131, 2016). Approx. another 50% of the incoming phosphorus has to be removed by biological or chemical-physical P removal processes or combined processes (Cornel & Schaum, 2009). Thus, the main hot spots for P recovery in WWTPs are from sewage sludge.
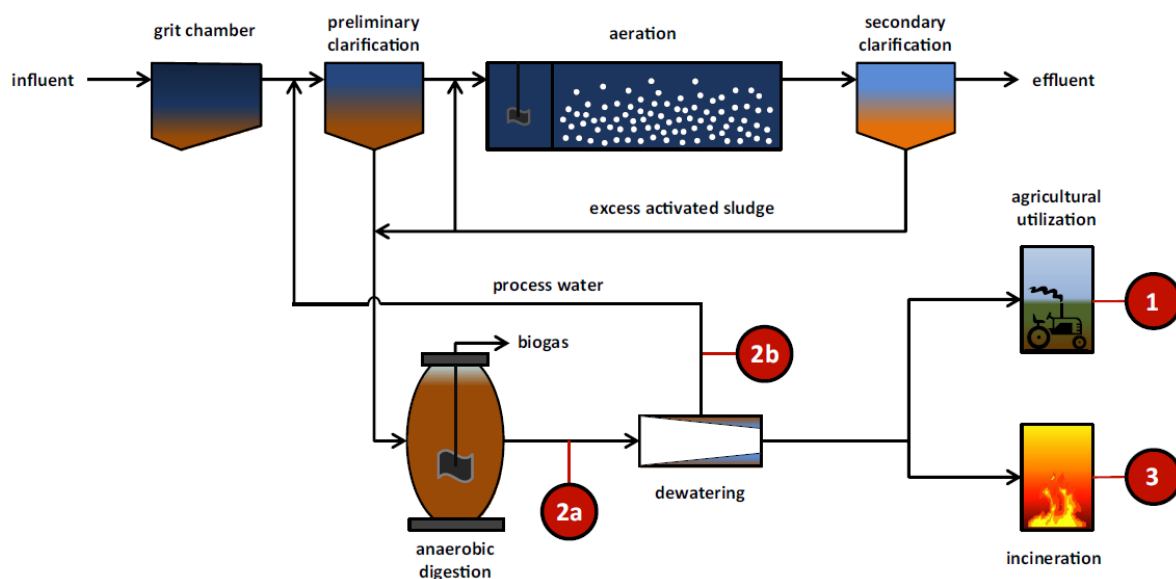
Figure 4: Hot spots for P recovery in WWTP (Kabbe et al., 2015). 1. Direct agricultural utilization of dewatered sludge; 2a. Undrained sludge after anaerobic digestion; 2b. Sludge liquor after dewatering; 3. Ash after incineration

At municipal wastewater treatment plants phosphate can be extracted and recovered or recovered mainly from three locations (Figure 4).

1. The first is direct land utilization of sewage sludge with 40-90% of the P recovery potential compared to the incoming WWTP phosphorus load. The plant availability of phosphorus in sewage sludge and the contaminants contained in sludge should be considered.
2. The second option is from sludge, including the aqueous sludge phase prior to dewatering (5-20% P load) and from sludge liquor after dewatering (≤25% P load). With forced P dissolution, e.g. chemical or thermal treatment, the maximal recovery rate can reach 50%.
3. The third option is from mono-incineration ash with the highest P recovery potential for more than 80% of the influent P load.

Over the past years, numerous technologies have been developed to recover phosphorus (P) from waste streams to close the nutrient cycles (Kraus et al., 2016b). Figure 5 gives an overview of the promising approaches and their state of maturity. These alternative routes for

phosphorus recovery are supposed to provide products or raw materials suitable for reuse in the nutrient cycle.
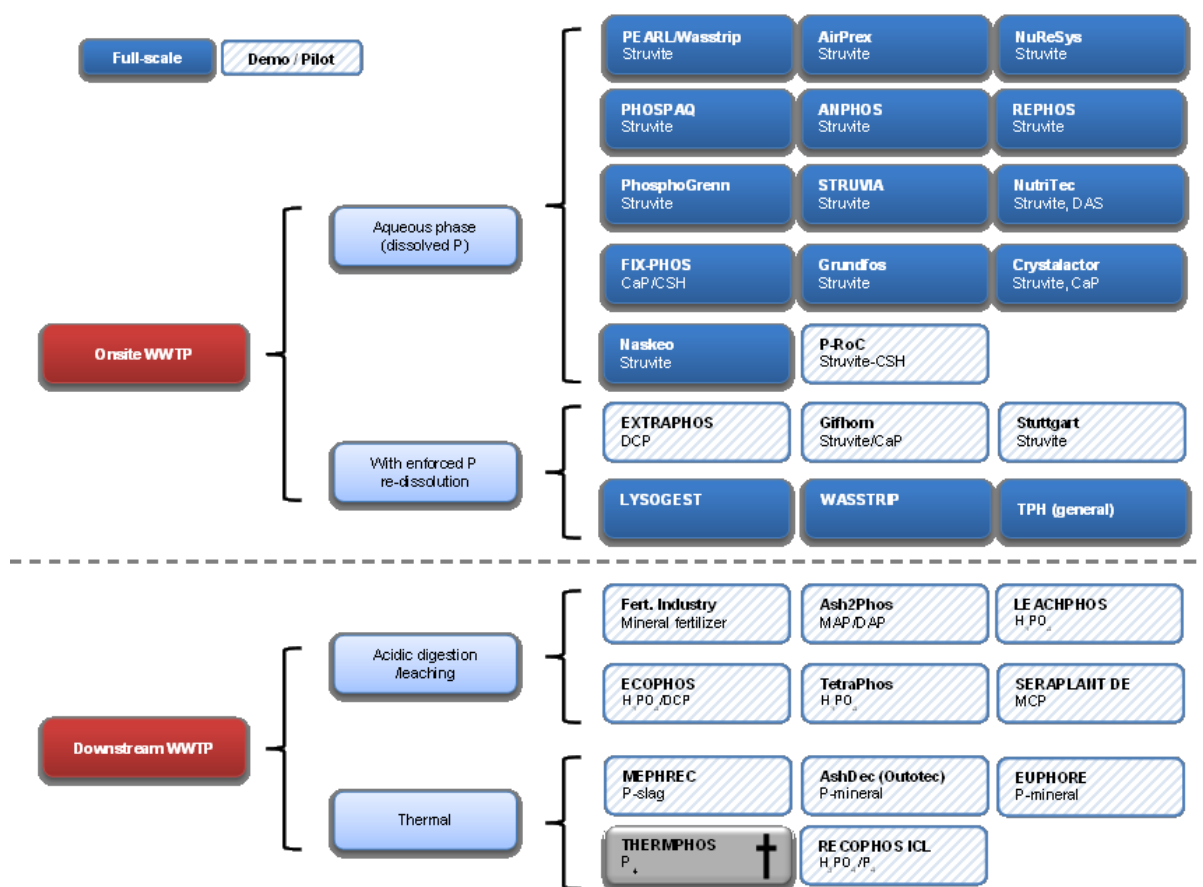
Figure 5: Most visible phosphate recovery technologies applied in Europe with indication of their state of maturity and product (Kabbe & Kraus, 2017b)

Currently the full scale plants are focused mainly on the recovery of phosphate from sludge and its liquid phase in the form of struvite or calcium phosphate. The struvite recovery process e.g. AirPrex[®], PEARL[®], NuReSys[®], Struvia[TM] offers the benefit of improved sludge dewatering and has even led to substantial savings in operational costs for sludge handling. Other technologies with forced P re-dissolution, such as the ExtraPhos[®] process and Gifhorn[®] process are able to recover more dissolved phosphate from WWTPs and the technology is also suitable for chemical-P removal plants. Recovery technology using chemical leaching or thermal treatment of sludge ash provides the best opportunity for maximum phosphorus recovery. The challenge with this approach is the separation of remobilized heavy metals from phosphorus and the disposal of the waste contaminated acid. Until now there is no technology available on an industrial scale in Europe, apart from the EcoPhos[®] plant currently under construction in Dunkerque in France and TetraPhos[®] tendered for implementation in Hamburg, Germany.

1.3.1 Potentials of P-recycling through bio-solids valorization in agriculture

In the past, phosphorus was traditionally returned to the soil and recycled in agriculture. The land utilization of sewage sludge in agriculture can significantly reduce the sludge disposal costs as well as provide a large part of the nitrogen and phosphorus. Sewage sludge as a soil improver has also obvious benefits due to improving soil structure and water retention qualities etc. With industrialization, the urban sewage systems do not only transport domestic wastewater, but also industrial effluents and storm-water runoff from roads and other paved areas. Thus sewage sludge may contain organic waste material, heavy metals, pharmaceuticals, pathogenic bacteria, viruses, worms and protozoa (Fijalkowski et al.; Kirchmann et al., 2017). Some of these substances can be phytotoxic and/or toxic to humans and/or animals. Depending on legislation, rules, attitudes and risk perceptions, the use of sewage sludge in agriculture varies between countries.
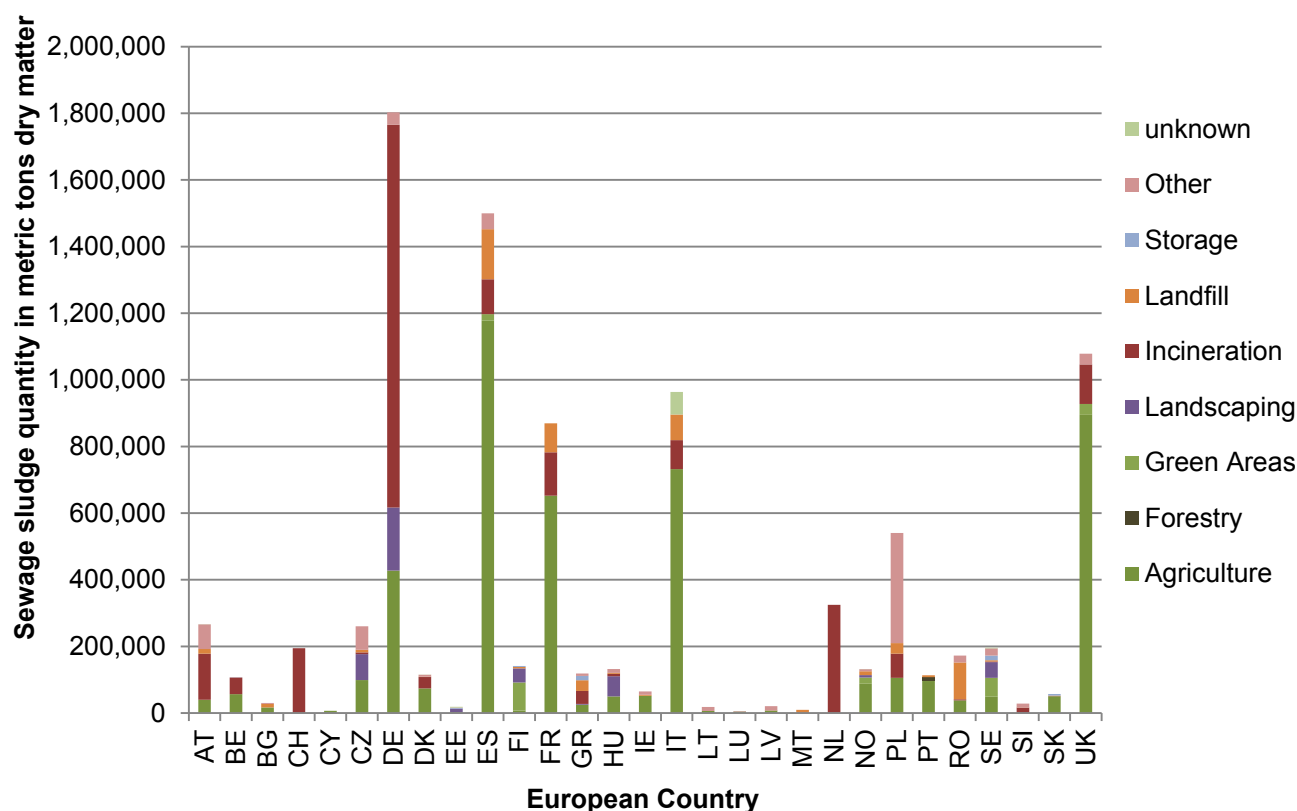
Figure 6: Disposal and recycling routes for sewage sludge in European countries (BAFU, 2013; Destatis, 2016; EurEau, 2016; Eurostat, 2016)

Since 1986, land application of sewage sludge within the European Union has been governed by Council Directive No. 86/278/EEC (Directive, 1986). As shown in Figure 6, in total 9,286,571 tons of dry sludge was generated in the 29 European countries (EU27, Norway and Switzerland) and about 51% of the sewage sludge was directly applied in agriculture. Land application is widely used in Luxemburg, France, Spain, Italy and the UK. The sludge produced in the Netherlands is banned from land application and therefore

exported or incinerated since 1995. In Greece, Malta and Romania, landfilling is the dominant disposal option. In Germany, about 23.7% (428,000 tons dry matter) of the accumulated sludge was utilized in agriculture in 2015 (Destatis, 2016).

The agricultural application on land may still play an important role for some countries within a certain period. The proportion of agricultural use of sludge in the US was always relatively high totaling 60~66% in 2015 (Yu, 2011). China has a long history of the sludge agriculture application. Currently, more than 80% of sludge is disposed by improper dumping in China (Yang et al., 2015). According to the overall situation of China, "thickening-anaerobic digestion-dewatering-land application" may be the priority technical route of sludge treatment and disposal (Yang et al., 2015). In India, the problems associated with wastewater arise from its lack of treatment. An estimated 38,354 million liters per day sewage is generated in major cities of India, but the sewage treatment capacity is only of 11,786 million liters per day (Kaur et al., 2012). Integrated management of wastewater through sewage fed aquaculture for resource recovery and reuse of treated effluent is being recognized as a suitable route for Indian (Kumar et al., 2014). Australia currently produces approximately 300,000 dry tonnes of biosolids annually (AWA, 2017). Approximately 55% is applied to agricultural land and around 30% is disposed of in landfill or stockpiled. The remaining 15% is used in composting (AWA, 2017).

In total, P recycling through the use of biosolids in agriculture varies from country to country due to differing national regulations. Yet, it can still be considered as one of the main recycling routes for phosphorus worldwide.

1.3.2 Potentials of P-recovery from sludge water

With this option, less than 25% of phosphorus loading can be recovered from the supernatant of the digested sludge either before or after sludge dewatering. In the Pearl®, NuReSys® and Struvia™ processes, phosphorus is recovered in the form of struvite crystals (magnesium ammonium phosphate) through crystallization from the aqueous sludge phase after dewatering. The crystallization of struvite directly from digested sludge can recovery 5-20% of phosphorus loading, e.g. by the AirPrex® process, and offers an additional benefit of improved sludge dewatering.

Apart from the P recovery as such, the biggest driver for struvite processes is the reduction of operational and maintenance costs for the WWTPs with enhanced biological P removal and anaerobic digestion. The growing use of digestion of sludge may results unintended struvite crystallization in their sludge train of the WWTP. P recovery from sludge liquids can help to prevent scaling in pipes and to reduce the return P load for biological wastewater treatment. It also supports the WWTP performance to meet the P discharge standard.
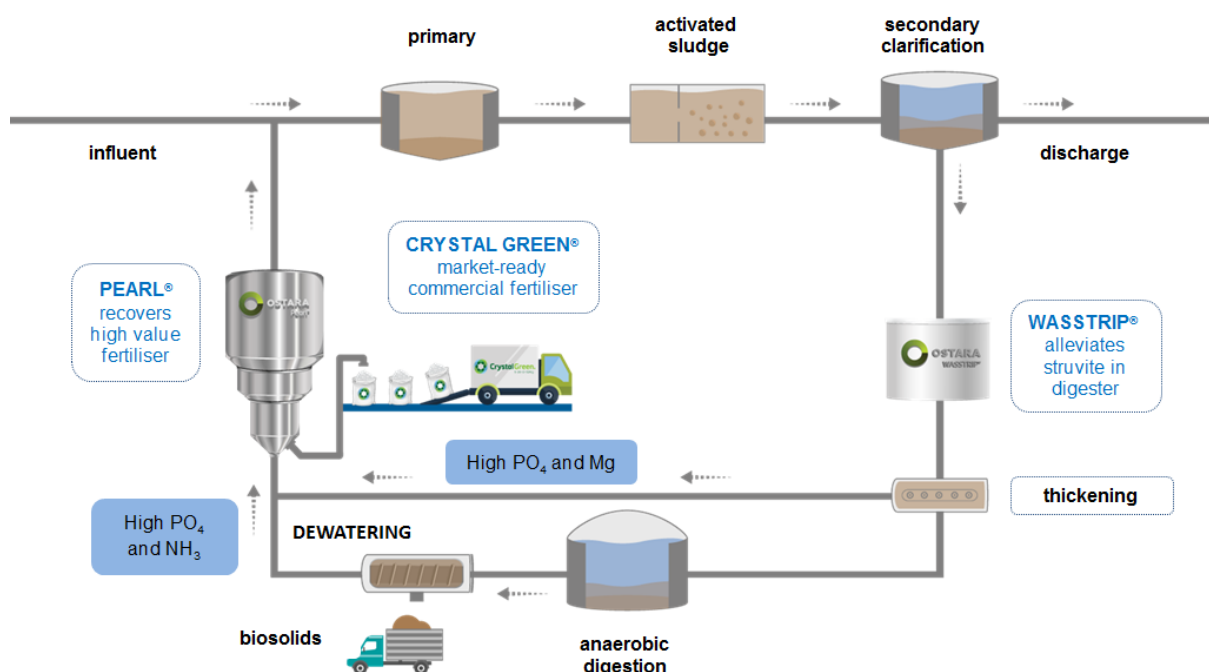
Figure 7: P-recovery from sludge water with combination of PEARL® and WASSTRIP® Process (Ostara, 2017b)

As the example in Figure 7 shows, Pearl® is designed by Ostara to prevent unwanted struvite incrustation after sludge dewatering in EBPR WWTPs. There are currently 14 operational Pearl® systems worldwide (Ostara, 2017a). The crystallization reactor is installed directly after the dewatering unit and treats the sludge liquor. Struvite is precipitated by dosing $MgCl_2$ at the bottom of the reactor and increasing pH with NaOH dosing. Internal recirculation in the PEARL® reactor assures proper mixing and good crystal growth, while the specially designed reactor shape guarantees uniform crystal size and optimum hydraulic conditions (P-REX-Factscheets, 2015). The product (Crystal Green®) reaches the desired size from 0.9 mm to 4.5 mm, with a purity of 99.6% (Ostara, 2017c). In the WASSTRIP® process the waste activated sludge or waste activated sludge of the wastewater treatment is sent to an anaerobic reactor, which is designed to rapidly trigger the release mechanism of PAOs by optimizing conditions for P release. The waste activated sludge is then sent to a thickening device and the liquid with enhanced orthophosphate and magnesium concentrations is then fed into the PEARL® reactor. In combination with the WASSTRIP® process for P release prior to digestion, P recovery can be significantly increased above 40% of the total influent while improving sludge dewaterability and digestor capacity (Ostara, 2017b). The operational data of the PEARL® and WASSTRIP® processes are from the company of Ostara.
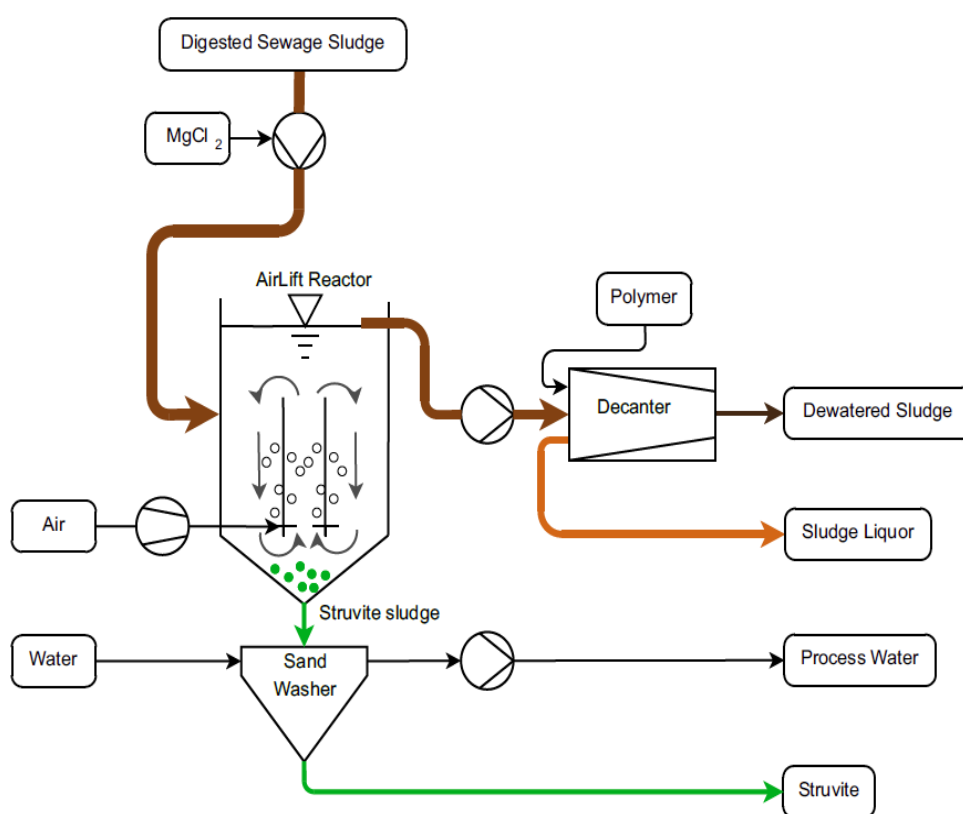
Figure 8: P-recovery from sludge with AirPrex® process (P-REX-Factscheets, 2015)

Another widely used process to recover dissolved P within the sludge directly after digestion is the AirPrex® process. The process mechanism is shown in Figure 8. In the AirPrex® reactor, CO_2 is stripped from the digested sludge by aeration to increase the pH of the sludge. With aeration it also forms a fluidized bed within the reactor and therefore sets the retention time for growing struvite crystals. After dosing of magnesium chloride, mineral phosphorus product struvite is crystallized and precipitated into the bottom of the reactor. In this process struvite is crystallized within the wet sludge and can therefore prevent the down-stream struvite scaling and at the same time improve the sludge dewaterability by 3-6 % and reduce the polymer by up to 30% for sludge dewatering (Forstner, 2015; Heinzmann & Lengemann, 2011).

Struvite process limitations:

Although struvite process from sludge water can provide environmental and economic benefits, there are limitations in application and recovery rate. Struvite recovery is only applicable to plants with an EBPR system, which can create a high concentration of recoverable orthophosphate. The struvite process is more suitable for the sludge water with more than 100 mg/l of dissolved P (Stemann et al., 2014). There are still many plants using chemical phosphorus elimination (e.g. with iron salts) or a combination of Bio-P and chemical P-removal processes. Based on the available data, in the UK and Germany EBPR is used across 23% and 16% of the total number of plants in those countries respectively (Wiseman,

14

2015). Currently, without sludge extraction, the recovery rate of phosphorus can reach 5-25 % compared to the influent phosphorus.

At present, some WWTPs are also interested in creating energy neutral or energy positive wastewater treatment plants. One of the current projects, POWERSTEP (www.powerstep.eu), uses chemical methods to remove carbon and phosphates to maximize the conversion of incoming carbon into the sludge stream. In such an "energy factory" process, EBPR process cannot be applied since the phosphorus is removed by a chemical process, which is contrary to the struvite process.

1.3.3 Potentials of P-recovery from sludge solids

In many WWTPs in Europe, phosphate removal is achieved by using chemical precipitation. At this point, an enforced phosphorus dissolution process, such as the ExtraPhos® process, Stuttgart process or Gifhorn® process is able to recover phosphate where chemical precipitation has been applied. With forced P dissolution, e.g. leaching the sludge with hard acids, the recovery potential can reach 50% of the total P load in the WWTP. The challenge of sludge leaching is to separate heavy metals, which are also re-mobilized by acid. A high phosphorus recovery rate means higher dosage of chemicals and/or energy demand (Remy et al., 2015). A promising approach without chemicals is the EXTRAPHOS® process from the company Budenheim, using carbon dioxide as solvent to dissolve phosphorus under pressure.
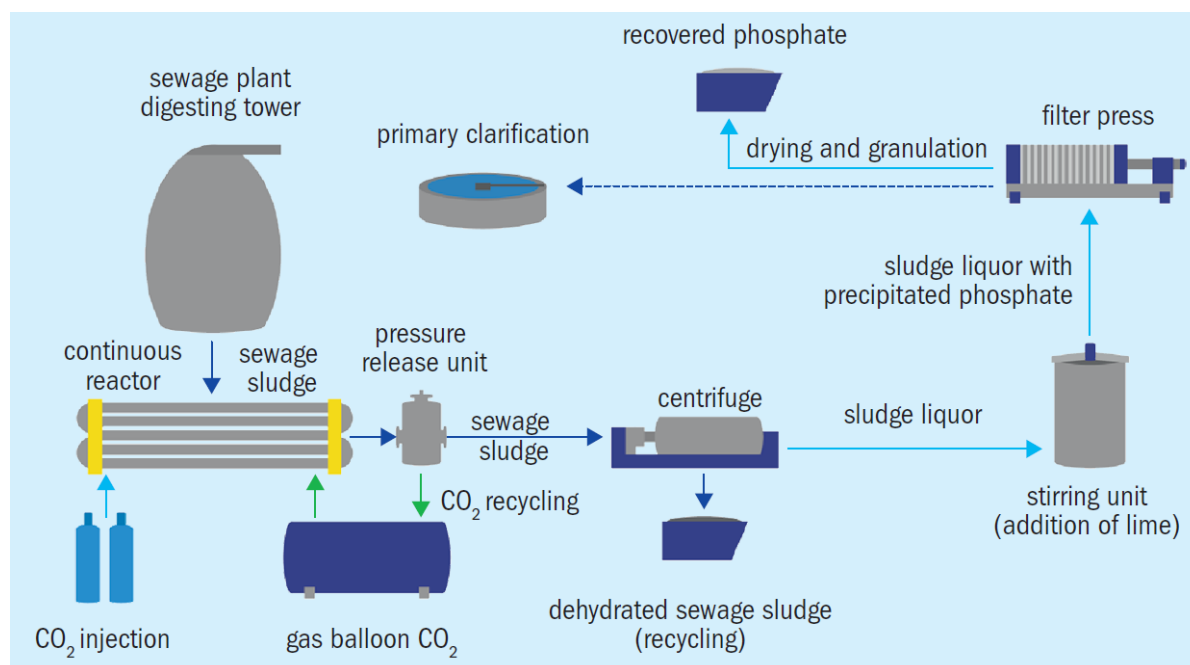
Figure 9: Process flow of ExtraPhos® process (Budenheim, 2017)

As shown, in the ExtraPhos® process in Figure 9, phosphorus is extracted from the sewage sludge particles as phosphate ions adding carbon dioxide, which leads to a drop in pH value in the sludge (Budenheim, 2017). Sludge solids are then removed by adding coagulants and

dewatering using a centrifuge, while the carbon dioxide recovered following degassing is recycled for reuse. The mobilized phosphorus is precipitated with lime (calcium hydroxide) to generate dicalcium phosphate (DCP), which is separated out and can be used as a fertilizer in agriculture, closing the loop for phosphorus. The advantage of this method is that it works without additional chemicals (except lime) or the use of thermal energy (Schnee, 2016).

1.3.4 Potentials of P-recovery from sewage sludge ash

The sludge incineration process destroys all pathogens, organic pollutants and nitrogen and the resulting ash provides the best opportunity for maximum phosphorus recovery (>80% of P load). However, this waste stream also contains heavy metals that are not degraded in the incineration process and are present in concentrations higher than their allowed limits, restricting their use in agriculture. The direct use of sludge ash is also limited to bioavailability due to low P-solubility (Krüger & Adam, 2015a). In this route the incinerated ash of sludge solids is treated with thermo-chemical and wet chemistry technologies (e.g. AshDec®, Mephrec® and LeachPhos®). Using acid or caustic digestion of these ashes can produce P products with high P-availability suitable for animal feed or fertilizers, or as elemental P. The challenge with this approach is the separation of remobilized heavy metals from phosphorus (Schaum et al., 2008) and the disposal of the waste contaminated acid. However, these technologies are based on the existing infrastructure or require high capital investment on mono-incinerators.

One of the promising technologies is the Ecophos® process, which was originally developed by the phosphate industry to process low-grade P input material into a high-quality P product.
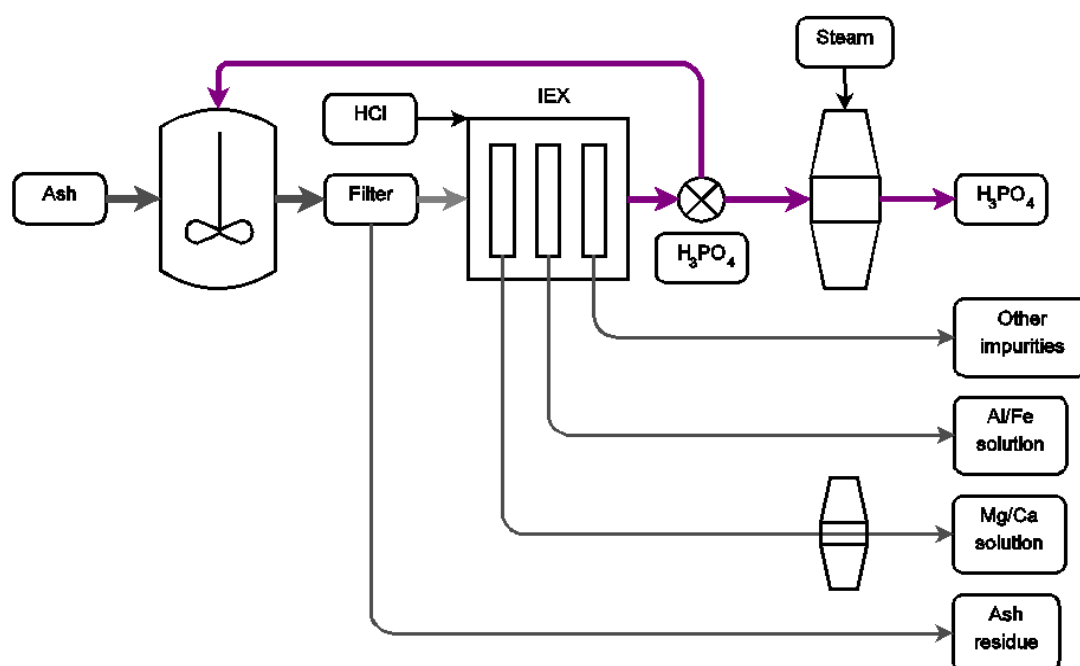
Figure 10: Process flow of Ecophos® process (P-REX-Factscheets, 2015)

The Ecophos® process is based on the digestion of ash into a large excess of H_3PO_4 (Figure 10), which is recycled from the product side. After digestion, insoluble residues are removed via filtration and disposed as inert material. The liquid solution contains a high amount of H_3PO_4 and dissolved impurities from the ash (Remy et al., 2015). This solution is purified by a multi-stage ion exchange (IEX) process, thus removing divalent salts (Mg, Ca), metals (Fe, Al), and other impurities such as heavy metals (Ruiter, 2014). After purification of the solution, a part of the H_3PO_4 is recycled back to the ash digestion, whereas another part is recovered as H_3PO_4 product and is further concentrated using steam. More than 95% of P can be extracted and recovered as phosphoric acid. The final product is a H_3PO_4 solution with high concentration (62% technical grades) and low impurities (Ruiter, 2015).

A similar approach with the application of different ion exchangers is applied by the company Remondis. With the TetraPhos® process, the sewage sludge ash is dissolved in phosphoric acid and a number of final products were produced including RePacid® phosphoric acid for the production of phosphates (inc. fertilizers), gypsum for the building supplies trade, and iron and aluminum salts which can be returned to the sewage treatment plant to be used as a precipitating agent to treat wastewater and eliminate phosphorus.

1.3.5 Comparison of different P-recovery methods with Life Cycle Assessment

Within the P-REX project, different pathways and processes for P recovery from sewage sludge have been assessed according to their environmental and economic impact (Remy et al., 2015). Process data of the different P recovery technologies had to be transferred from pilot or full-scale installations to a defined reference system to overcome potential bias due to site-specific conditions. The reference system is defined as the sludge treatment line of a wastewater treatment plant (WWTP) for 1 million inhabitant equivalents, reflecting the annual operation of a typical large-scale WWTP in Germany.

Figure 11 shows an important LCA indicator, reflecting the relation between P recovery rate and total cumulative energy demand of fossil fuels for the different P recovery pathways. It indicates that struvite recovery directly from sludge or sludge liquor is energetically beneficial due to higher dewaterability and lower return load. But the struvite process has only a limited P recovery rate (5-25%) and is only applicable in Bio-P plants.
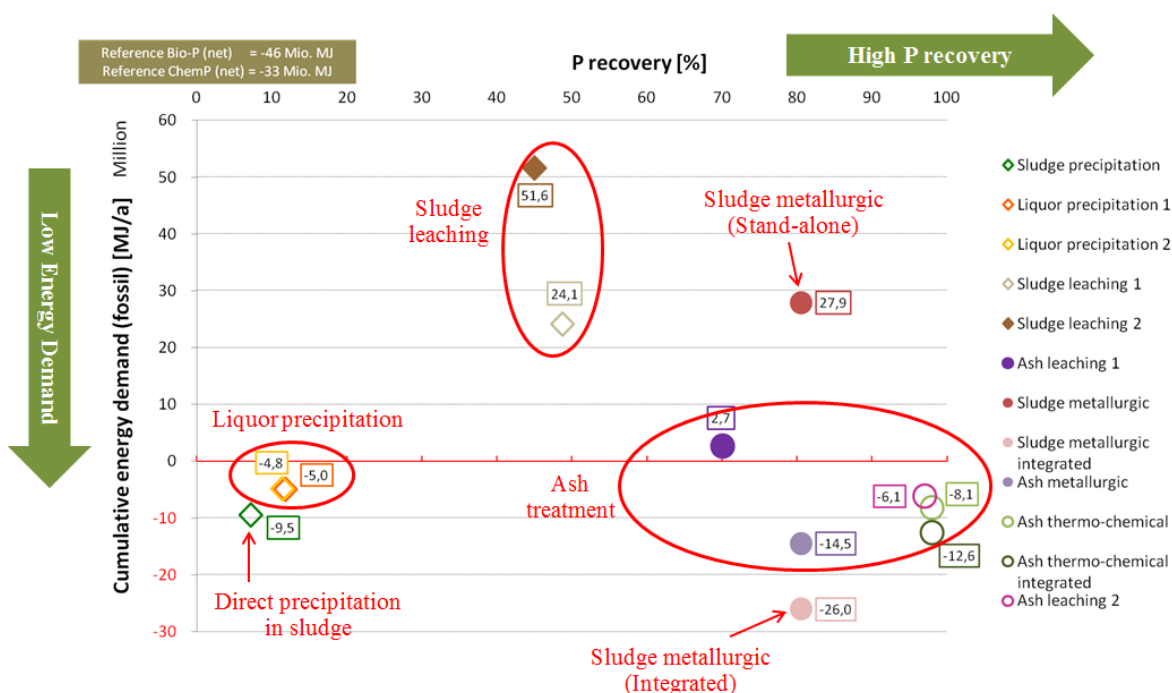
Figure 11: Net energy demand for different P recovery pathways (Remy et al., 2015)

The sludge leaching process has a higher P yield of about 50% of P load, but is also requires more chemicals and has a high energy and greenhouse gas footprint (GHG). The ash processes can recover up to 97% with a reasonable energy or GHG footprint, but it depends on the process (ash leaching, thermo-chemical, metallurgic) and the potential integration of thermal processes into existing incineration facilities for efficient heat management. The trade-off between different technologies depends on the goals of maximum P recovery and maximum energy recovery from sludge with a low carbon footprint. The struvite recovery technology is limited to dissolved orthophosphate in sludge water. It does not compete against other processes of phosphorus recovery from ash.

1.3.6 Combined energy and nutrient recovery
Compared to the single technology option for recovery of phosphorus from the municipal plant, the next generation of competitive technologies may provide the synergetic recovery of phosphate, nitrogen and carbon (Kabbe & Kraus, 2017a).
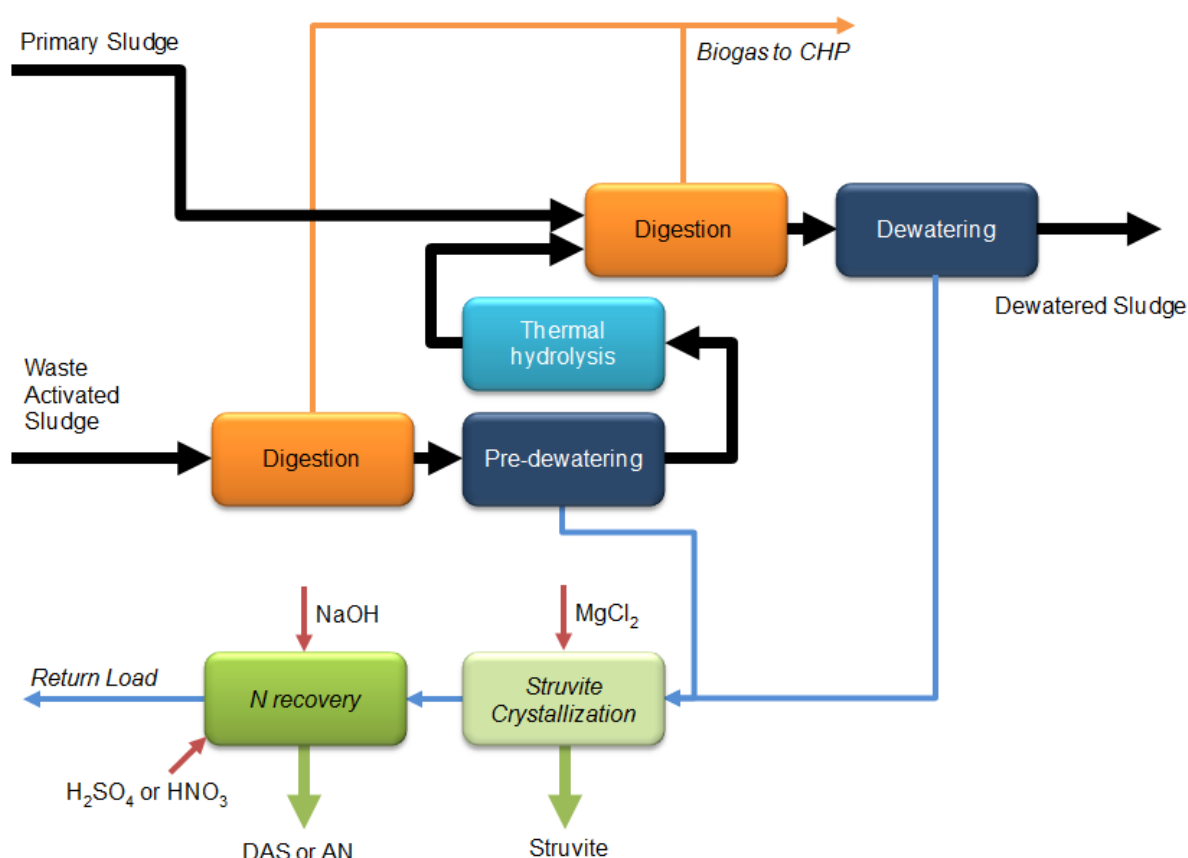
Figure 12: Combined energy and nutrient recovery (Kabbe & Kraus, 2017b)

As shown in Figure 12, one option to improve the yield of recovered struvite is a combination with thermal (i.e. CAMBI) or chemical (i.e. PONDUS) hydrolysis for the disintegration of waste activated sludge. The biogas production in the subsequent digester can be increased with sludge disintegration and, at the same time, insoluble or hardly soluble polyphosphates are transformed into soluble ortho-phosphate, which is available for struvite crystallization in the sludge water. After the struvite crystallization the ammonia in the sludge liquid is stripped by increasing pH and temperature. The stripped ammonia is mixed with sulfuric acid and recovered as liquid ammoniumsulphate.

An excellent example of future energy and nutrient recovery factory is WWTP Amersfoort in the Netherlands which combined Ostara's WASSTRIP® and PEARL® processes together with the LYSOTHERM® thermal sludge process (Kraus & Kabbe, 2017). Another example is currently underway at Steinhof WWTP in Braunschweig, Germany. Commissioning is expected for 2018. The plant will be the first full-scale enhanced carbon, phosphorus and nitrogen recovery facility in Europe. It combines thermal hydrolysis for enhanced sludge disintegration with struvite recovery and ammonia stripping. The recovered struvite and ammonium sulphate will be utilized locally (Kabbe & Kraus, 2017a).

1.4 Implementation of phosphorus recovery

1.4.1 Full scale techniques and global application

P-recovery has been widely studied and a number of full scale installations for recovery are already in operation or under construction. Figure 13 shows the distribution of plants with P-recovery processes from wastewater in different continents. Due to the rapid development of phosphorus recovery, the data may not cover all the plants worldwide. The current phosphorus recovery plants are mainly operated in three continents: Europe, North America and Asia. The major reason seems to be a low or lack number of phosphate rock reserves in these regions. In Europe, about 90% of the phosphate used is imported (van Dijk et al., 2016). Japan has even no economically viable phosphate rock reserves, being almost entirely dependent on imported phosphorus (Ohtake & Okano, 2015). To ensure the food security, the developed countries with hardly any or no P reserves take the lead in recovering and recycling phosphorus.
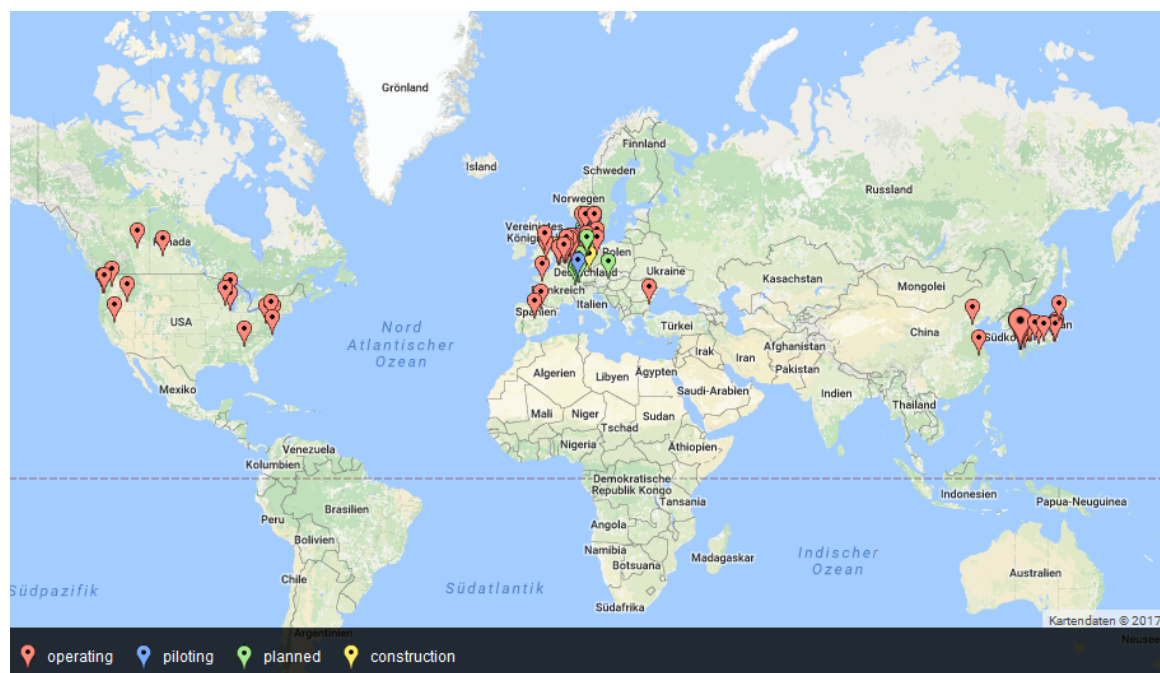
Figure 13: Distribution of plants with P-recovery process from wastewater worldwide (Kabbe, 2017)

From a technical aspect, precipitation of struvite from phosphate-rich sewage sludge water is becoming a well-established technology with more than 40 full-scale installations world-wide (Kabbe & Kraus, 2017b). There are approx. 10,000 tones/a of struvite currently produced in Europe are likely to double in the coming five years (Kabbe & Kraus, 2017a). AirPrex[®], NuReSys[®], PEARL[®] are the most applied technologies among the struvite processes. The recovery from ash is still rare in industrial scale plants. In Europe, there are some full-scale plants under construction using of recovery from ash. i.e. through the EcoPhos process or directly as secondary P sources in the fertilizer industry. In Japan, some recovery plants are in full-scale in special industries.

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1.4.2 Case studies for Europe-wide implementation

In 2014, The European Commission added phosphate rock to the list of 20 Critical Raw Materials which are economically important and are subject to a "high supply risk" (EU-Commission, 2014). In May 2017, the European Commission (JRC) circulated a draft for "nutrient recovery rules" (outline for possible CMC – Component Material Category – criteria under the revised EU Fertilizers Regulation) for struvite (widened to recovered phosphate salts), biochars and pyrolysis products and ashes – STRUBIAS (Huygens et al., 2017). The phosphorus challenge in Europe was not only taken up by the governments, but also different stakeholders and platforms, such as the European Sustainable Phosphorus Platform (ESPP), the Netherlands Nutrient Platform, German Phosphorus Platform (DPP) and Baltic Sea Action Group (BSAG) etc. They contribute to define a long-term vision for phosphorus sustainability in Europe.

According to the phosphorus flows analysis for EU-27 and its Member States (van Dijk et al., 2016), sewage sludge is apart from manure, the second most relevant P recovery and recycling renewable waste stream in Europe with a potential of 182,000 tons of phosphorus per year. About 90% of the phosphate used in the EU is imported from Morocco, Tunisia and Russia. It is estimated that, 20-30% of the EU's demands for phosphate fertilizers could potentially be met by undertaking recycling in line with a circular economy approach. Therefore, various technologies were developed in Europe and have been applied in European countries. Table 2 gives an overview of phosphorus recovery facilities operating or under construction in Europe.

Table 2: Overview of phosphorus recovery facilities operating or under construction in Europe (Kabbe & Kraus, 2017a) (modified)

Technology	Location and operator	Operational since	Recovered product
Onsite wastewater treatment plants			
AirPrex®	MG-Neuwerk (DE), Niersverband Wassmannsdorf (DE), Berliner Wasserbetriebe Echten (NL), Drents Overijsselse Delta Amsterdam-West (NL), Waternet Uelzen (DE), SE Uelzen Salzgitter Nord (DE), ASG Wolfsburg (DE), SE Wolfsburg	2009 2010 2013 2014 2015 2015 2016	Struvite
ANPHOS	Land van Cuijk (NL), Aa en Maas	2011	Struvite
EloPhos®	Lingen (DE), SE Lingen	2016	Struvite
EXTRAPHOS (Budenheim)	MZ-Mombach (DE), Wirtschaftsbetrieb Mainz	2017 (pilot)	DCP
Gifhorn	Gifhorn (DE), ASG	2007	Struvite/CaP
NASKEO	Castres (FR)	2015	Struvite
NuReSys®	Harelbeke (BE), Agristo 2x Niewkuerke (BE), Clarebout Potatoes Waasten (BE), Clarebout Potatoes Geel (BE), Genzyme Leuven (BE), Aquafin Schiphol Airport (NL), Evides Land van Cuijk (NL), Logisticon Apeldoorn (NL), Vallei & Veluwe Braunschweig Steinhof (DE), SE|BS / AVB	2008 2009/12 2012 2014 2013 2014 (pilot) 2015 2016 2018/19	Struvite
PEARL® (OSTARA)	Slough (UK), Thames Water Amersfoort (NL), Vallei & Veluwe Madrid (ES), Canal de Isabel II	2013 2015 2016	Struvite (Crystal Green®)
PHORWater	Calahorra (ES), El Cidacos	2015 (demo)	Struvite
PHOSPAQ™	Olburgen (NL), Waterstromen Lomm (NL), Waterstromen Nottingham (UK), Severn Trent Water Tilburg (NL), Waterchap de Dommel	2006 2008 2014 2016	Struvite
PhosphoGREEN (SUEZ)	Aaby (DK), Aarhus Water Marselisborg (DK), Aarhus Water Herning (DK), Herning Water	2013 2018 2016	Struvite
REPHOS® (delivered by NuReSys)	Altentreptow (DE), Remondis Aqua (dairy)	2006	Struvite
STRUVIA™	Helsingør Southcoast (DK)	2015	Struvite
Stuttgart	Offenburg (DE), AZV Mobile Pilot – MSE Mobile Schlammentwässerungs GmbH	2011 (demo) 2015	Struvite (after acid leaching)
Downstream wastewater treatment plants and ash treatment			
EcoPhos	Varna (BG), DecaPhos Dunkerque (FR), EcoPhos	2016 2017	H_3PO_4/DCP/ MCP
Fertilizer industry	Various companies already apply or consider use of secondary P sources	tested and intended	Commercial fertilizer
MEPHREC	Nürnberg (DE), SUN	2016 (demo)	P-slag
TetraPhos®	Hamburg (DE), Hamburg Wasser/Remondis Aqua	2015 (pilot) 2019 (full scale)	H_3PO_4

- **National regulations for P recovery in Europe:**

Some European countries have implemented national regulation to promote phosphorus recovery from the wastewater path and other relevant waste streams with rich phosphorus. A new waste regulation entered into force in January 2016 in Switzerland, making phosphorus recovery from sewage sludge and meat and bone meal obligatory within a 10 year transition phase.

In Germany, a new sewage sludge ordinance was passed by the German cabinet on 18th January 2017 (BMUB, 2017; Bundestag, 2017). This ordinance will make phosphorus recovery from sewage sludge obligatory for all German WWTPs larger than 50,000 person equivalents (e.p.) (approx. 500 WWTPs). They will have to recover the phosphorus if the sludge contains more than 2% phosphorus/DM (dry matter) or recover it from sewage sludge incineration ash. These 500 larger sewage works represent about 2/3 of the total phosphorus removed from German wastewater and transferred into sludge. Larger sewage plants with more than 100,000 p.e. have a transition period of 12 years. WWTPs between 50,000 and 100,000 p.e. will have a transition phase of 15 years. If the phosphorus in sludge is less than 2%, co-incineration can be authorized. Land application of sludge will only be allowed for WWTPs of < 50,000 person equivalents.

Following the legislative developments in Switzerland and Germany, Austria is now also opting for mandatory P recovery from municipal sewage sludge. The draft Federal Waste Plan 2017 (BMLFU, 2017) includes a ban of direct land application or composting for sewage sludge generated at Wastewater Treatment Plants with capacities of 20,000 p.e. or above within a transition phase of 10 years. Alternatively, these WWTPs will have to recover the P from sludge onsite targeting P contents below 20 g P / kg dry solids or have to deliver their sludge to sludge mono-incinerators. The P is then to be recovered from the sewage sludge ashes obtained. This regulation will cover 90% of the P contained in municipal wastewater in Austrian.

- **Regional study in the Netherlands**

The Netherlands is among the pioneer countries in the field of phosphorus recovery from sludge in full-scale plants at municipal level. Agricultural spreading of sewage sludge has not been allowed in the Netherlands since 1995 (Stark, 2004). One of the consequences of this situation is a 100% incineration of sludge (part of them export to Germany) in the Netherlands (Eurostat, 2016).

Within the wastewater sector, P will partly be recovered as struvite at the WWTPs (e.g. WWTP Amsterdam West, WWTP Amersfoort, WWTP Land van Cuijk, WWTP Apeldoorn etc.), but, more importantly sludge ash from mono-incineration will be used as input in order to replace rock phosphate. Acronym for Foundation for Applied Water Research (STOWA) (Notenboom et al., 2013) quantified that, based on the amount of sludge in 2010, about 11 600 t/a P can be recovered from Dutch sludge annually if all sludge in the Netherlands to mono-incinerators. An EcoPhos plant is currently under construction for phosphorus recovery

from Dutch sewage sludge incineration ash (60,000 tons/year) in cooperation with SNB (Slibverwerking Noord-Brabant) and HVC Group.

- **Regional study in Germany**

Approximately two-thirds of sewage sludge in Germany is now incinerated, with similar quantities going to sewage sludge mono-incineration and to co-incineration. 23.7% of sludge is still applied to agricultural land (Destatis, 2016), but that figure can be expected to decline in the future by implementation of new sewage sludge ordinance. According to the new sludge regulation with P-recovery, the P recovery from mono-incineration ash can been considered as the main route for Germany (Kraus et al., 2016a). Some large plants are planning to construct new mono-incineration plants, e.g. Berlin Wassmannsdorf. German sewage sludge ash (SSA) contains up to 19,000 t/a P which equals approximately 13% of the phosphorus applied in German agriculture in the form of phosphate rock based mineral fertilizers (Krüger & Adam, 2015b).

1.4.3 Case studies for implementation in North America

In North America, the dependence of phosphorus imports is not as high as in Europe. Table 3 gives information on currently operating or under construction full-scale recovery plants. All the plants in North America use the struvite process with PEARL® and Multiform™ technology.

Table 3: Overview of phosphorus recovery facilities operating or under construction in North America (Kabbe & Kraus, 2017a) (modified)

Country	Technology	Location and operator	Operational since	Recovered material or product
		Onsite wastewater treatment plants		
USA	Multiform™	Yakima, WA Boise, ID Massey, MD, Jones Family Farms (dairy) Green Bay, WI	n.a.	Struvite
USA	PEARL® (OSTARA)	Tigard, OR, Clean Water Services Suffolk, VA, Hampton Roads Sanit. District York, PA, City of York Hillsboro, OR Clean Water Services Madison, WI, Madison Metro. Sew. Distr. Burford, GA, Gwinnett County Stickney, IL, Metro. Water Recl. Chicago Reno, NV, Cities of Reno and Sparks Winchester, VA, F. Winchester Service A.	2009 2010 2010 2012 2014 2015 2016 2016 2016	Struvite (Crystal Green®)
Canada	PEARL® (OSTARA)	Edmonton, AB, EPCOR Water Services Saskatoon, SK, City of Saskatoon	2015 2013	
USA	AirPrex®	Liverpool, OH, Medina County	2017/2018	Struvite

There are about nine PEARL® plants operating or being completed in the USA and two in Canada in Edmonton and Saskatoon. The world's largest nutrient recycling facility based on wastewater is currently also located in America. The world´s largest struvite recovery installation at Stickney Water Reclamation Plant in Chicago, USA (2.3 million p.e.), started operation in 2016 with the PEARL® 10k reactor that produces 10,000 tons of struvite per year (Ostara, 2016). The Liverpool Wastewater Treatment Plant by the Medina County Sanitary Engineers in Ohio, USA, selected to install the AirPrex® process in the fourth quarter of 2017 (CNP, 2017a).

It is predicted that, the recovery of P as struvite in WWTPs will continuously grow in North America, mainly driven by the savings on maintenance costs and prevention of scaling and blocking of pipes.

1.4.4 Case studies for implementation in Asia

Most of the P-recovery plants in Asia are located in Japan. China has only two plants based on recovery from the liquid phase. Table 4 gives the details of these plants.

Table 4: Overview of phosphorus recovery facilities operating in Asia (Kabbe & Kraus, 2017a; Ohtake & Okano, 2015) (modified)

Country	Technology	Location and operator	Operational since	Recovered material or product
Onsite wastewater treatment plants				
Japan	Hitachi-Zosen (Unitika)	Matsue (JP) Senboku (JP), Senboku City	1998 2009	Struvite HAP
Japan	J-Oil	Yokohama (JP), J-Oil Mills Co.		HAP
Japan	JSA	Kawasaki (JP), Japan Synthetic Alcohol Co.	1998	HAP
Japan	KURITA	Fukuoka (JP), 3 plants	1997	Struvite
Japan	Kyowa Hakko	Hofu (JP), Kyowa Hakko Bio Corp.	2006	HAP
Japan	Swing	Kobe (JP), Swing Corp.	2012	Struvite
China	AirPrex®	Tianjin (CN), Tianjin CEPG	2016	Struvite
China	Crystalactor®	Nanjing (CN), Royal Haskoning DHV	2010	Struvite
Downstream wastewater treatment plants and ash treatment				
Japan	METAWATER	Gifu (JP) Tottori (JP)	2010 2013	HAP
Japan	Nippon PA	Chiba (JP), Nippon Phosphoric Acid	2009	H_3PO_4

The sustainable supply of P is critical in Japan, not only due to agricultural production but also industrial manufacturing (Ohtake & Okano, 2015). Approximately 44% of the total P imported into Japan is associated with food, animal feed, and mineral resources such as iron ore and coal. Phosphate rock accounts for only 15% of the total P imports from abroad (Matsubae-Yokoyama et al., 2009). P recycling has been implemented in several WWTPs (e.g. Matsue, Senbuko) and blackwater treatment plants (e.g. Senboku city) in Japan. Full-scale P recovery plants based on incinerated sludge ash are also operated at Gifu and Tottori with the production of calcium hydroxyapatite.

There are two plants with struvite recovery in China. One plant which use the with AirePrex® process in municipal wastewater treatment plant in Tianjin. Another plant uses Crystalactor technology for struvite recovery with from a chemical company producing caprolactan in Nanjing. Growing urbanization in China has caused a rising trend in domestic wastewater and sewage sludge discharges. According to the case studies research (Zhou et al., 2017), most of the P-recovery options are limited to the current infrastructure and P content in sludge. The recovery from industrial wastewater with high concentration of P shows higher potential than in municipal WWTPs due to easier market access and benefits to its operators.

1.5 Conclusion

In this review a variety of different approaches are described for the recovery of phosphorus from sludge water, solid sludge and sludge ash. The struvite recovery is state of the art for P recovery and recycling from sludge and sludge water. The additional benefits for WWTP operators play an important role in P-recovery. But this process is still limited to Bio-P plants and the recovery rate can reach a maximum of 50%. P recovery from ash has a higher recovery potential with about 80-90%. But this option requires a highly developed infrastructure. If the sewage sludge is incinerated or planned to be incinerated separately (obligatory in Switzerland, the Netherlands, Austria, Germany), the P recovery from ash seems to be the main method for these countries. In the future, a combination of phosphorus recovery with energy and resource efficiency (e.g. WWTP Amersfoort and WWTP Steinhof) will be a promising route for the further development of the technology.

The P-recovery plants are mainly located on three continents: Europe (Belgium, Denmark, Germany, Italy, the Netherlands and Spain), North America (USA, Canada), Asia (Japan, China). The most appropriate way of P recovery and recycling may differ from region to region under different national conditions. Therefore, there is no "one solution fits all" for the recovery of phosphorus. The decision for the most suitable technology depends on the existing infrastructures, economic feasibility, legislations and national policies.

Chapter 2: Full-scale performance of selected starch-based biodegradable polymers in sludge dewatering and recommendations for application

Graphical abstract:
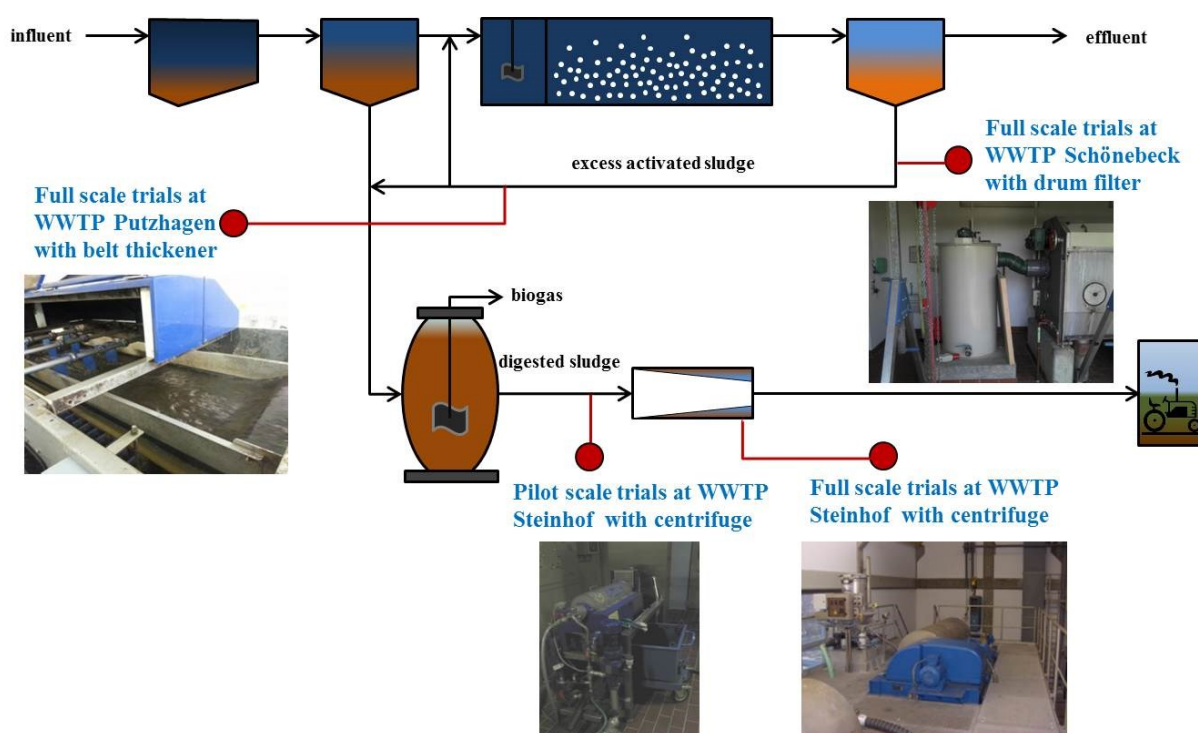
Highlights:

- A jar testing methodology was developed for the assessment of the optimal polymer dose for sewage sludge
- Comparison the dewaterability of starch-based polymers and polyacrylamide synthetic polymers in pilot and full-scale
- Evaluation of the substitution potential of synthetic polymers in WWTPs
- Recommendations for the future application of starch-based polymers was given

2.1 Sludge valorization in agriculture

Agricultural reuse of dewatered sludge can remain an adequate route for sludge valorization for small and medium sized wastewater treatment plants (WWTP) due to the direct utilization of nutrients. According to statistic data (BAFU, 2013; Destatis, 2016; EurEau, 2016; Eurostat, 2016), about 51% of the sewage sludge generated in the 28 European countries (including UK, Switzerland) is directly applied in agriculture. About 23.7% (428 000 ton dry) of the accumulated sludge in Germany was valorized in agriculture in 2015 (Destatis, 2016). When agricultural use of the dewatered sludge is planned, synthetic flocculants based on non-biodegradable polyacrylamide (PAM), may have a negative impact on the environment due to their toxicity and non-biodegradability (Khachan et al., 2011). Therefore a more stringent regulation for this valorization route has been put in force (German Fertilizer Ordinance (DüMV, 2012) which requires the degradation of 20% of the polymeric substance within two years by the year 2017 in order to increase the soil's water holding capacity. Due to uncertainty of the degradable of synthetic polymers, the regulations are still evaluated and the transition period for the application of synthetic polymers is extended until 31.12.2018 (BGBL, 2017). According to the amendment of the German Fertilizer Ordinance (BMEL, 2016), effective from 01. January 2019, the quantity of applied synthetic polymers in agricultural land should not exceed 45 kg active substance (AS) per hectare within three years. Regardless of the long term strategic decision on sludge valorization and phosphorus recycling, partial or total substitution of PAM-based polymers with biodegradable polymers is therefore an environmentally friendly alternative.

PAM-based polymers are used to improve dewatering outcomes considerably and therefore decrease the sludge volume and less energy is required for transport. However, the petroleum resources are limited and the widespread use of non-biodegradable polymers may cause serious environmental problems (Lu et al., 2009). Therefore more focus need to be put on natural polymers based on renewable input (Scott, 2000)., e.g. starch and chitosan, which are inherently biodegradable (Chiellini & Solaro, 1996) and can be considered promising candidates to meet different requirements. Starch is mainly composed of two homopolymers of D-glucose (Pareta & Edirisinghe, 2006), which form non-toxic residues after degradation. Starch-based completely biodegradable polymers (SCBP) combine the individual advantages of starch and synthetic polymers, providing promising potential for sludge dewatering.

This chapter aims at assessing the use of starch-based polymers for full-scale dewatering of municipals wastewater sludge. The successive approach through lab-scale and pilot-scale trials paved the way for full-scale trials. Varying blends of starch-based polymers and PAM-based polymers were tested in lab-scale trials with jar tests and drop-off tests. Pilot-scale trials with a centrifuge have identified the optimization and quantification of dewatering outcomes. Short term trials on a full-scale centrifuge, drum filter and belt thickener at three WWTPs in Germany with the blends demonstrated the substitution potential with different dewatering devices and showed the limits of the state of the art product.

2.2 Materials and methods

2.2.1 Study sites and sampling locations

Laboratory scale trials were conducted on the premises of WWTP Schönebeck and WWTP Putzhagen (Gütersloh) whereas pilot and full-scale trials took place at WWTP Steinhof (Braunschweig), WWTP Schönebeck and WWTP Putzhagen. Since the sludge properties as well as sludge types as well as sludge types vary significantly from one to another WWTP, the starch-based polymers were tested with three sludge types collected from different WWTPs. Table 5 summarizes the sludge types and characteristics. WWTP Steinhof is one of the very few large scale agricultural reuse sites in Germany. Sludge from WWTP Schönebeck and Putzhagen is also used in agriculture after anaerobic digestion.

Table 5: Tested sludge types and characteristics

WWTP	Sludge type	Dewatering/ thickening	Applied processes	Total Solids in %	Synthetic polymer
Ruhleben	Non-digested mixed sludge	Centrifuge	Primary sludge; Bio-P; Co-precipitation; various sludge sources	2.8 – 3.45	SUPERFLOC® C-2260
Wassmannsdorf	Digested mixed sludge	Centrifuge	Primary sludge; Bio-P, MAP-precipitation after digestion	3.4	Eurofloc DP4–60CT2
Schönebeck	Excess sludge	Drum filter	Bio-P	0.74	Eurofloc K7CZST
Steinhof	Digested excess sludge	Centrifuge	Bio-P; struvite-precipitation	2.8 – 3.5	PK1440
Putzhagen	Excess sludge	Belt thickener	Chemical P-removal	0.6-0.8	Reiflock RF1204 A

2.2.2 Testing polymers

The polymers selected for use in this study are listed in Table 6. Two starch-based polymers, Hydrex™ H0661 and H6864 (new products not yet on the market), are extracted from non-genetically modified potatoes, which were provided by Veolia Water STI. Three PAM-based polymers used for the respective WWTPs were tested as references. Blends of starch-based and PAM-based polymers were tested in order to identify the case specific substitution potential.

Table 6: List of tested polymers

Product	Molecular weight	Charge	Charge density	Origin
Hydrex™ H0661	High	Cationic	n.a.	Starch
Hydrex™ H6864	High	Cationic	High	Starch
Eurofloc K7CZST (Schönebeck)	High	Cationic	Medium	PAM
POLY SEPAR® PK1440 (Steinhof)	High	Cationic	n.a.	PAM
Reiflock RF1204 A (Putzhagen)	High	Cationic	Very High	PAM

(n.a. = not accessible)

The PAM-based polymer make up should be done according to best-practice advice and recommendations of polymer manufacturers. The synthetic polymer should mature at least 45 minutes and be consumed within 4 hours (DWA-M-366, 2013).

The H6864 and H0661 do not need any maturation time, but complete mixing should be ensured. During the pilot and full-scale trials a mixing time of 15 minutes was sufficient using an impeller mixer.

2.2.3 Jar Testing to determine optimal polymer dose (OPD)

In this study, a Jar testing titrimetric method was developed in order to determine the optimal polymer dose. The reliability and validity of this method was repeatedly confirmed by testing the original polymer demand in different WWTPs. The jar test was performed using two starch-based polymers and the combination of PAM-based polymers. The equipment used was a laboratory flocculator: solutions were observed in 4 parallel jars. The procedure of the jar test was as follows:

- For each Jar test 200 mL of sludge was filled in a 500 mL beaker and the predetermined polymer solution, approximately 60% of the total hypothetical demand, was firstly dosed.
- The mixed liquor was then stirred for 2 min at a speed of 200 rotations per minute (rpm). Stirring was continued for another 5 min at a speed of 30 rpm.
- The polymer demand was observed based on the change of the floc size as shown in the example in Figure 14 with digested sludge from WWTP Stahnsdorf in Germany. If required, another 2 ml of polymer, approximately 1 kg AS/ mega gram (Mg) total solids (TS), was added until the larger floccules appeared and the optimum polymer dose was reached.
- The polymer solutions were made with tap water as in the full-scale plant and all experiments were performed at ambient temperature (18-23°C). For all trials the

planned blend, e.g. 50:50% of the synthetic and the "green" polymer, were prepared in a mixed solution and dosed together.
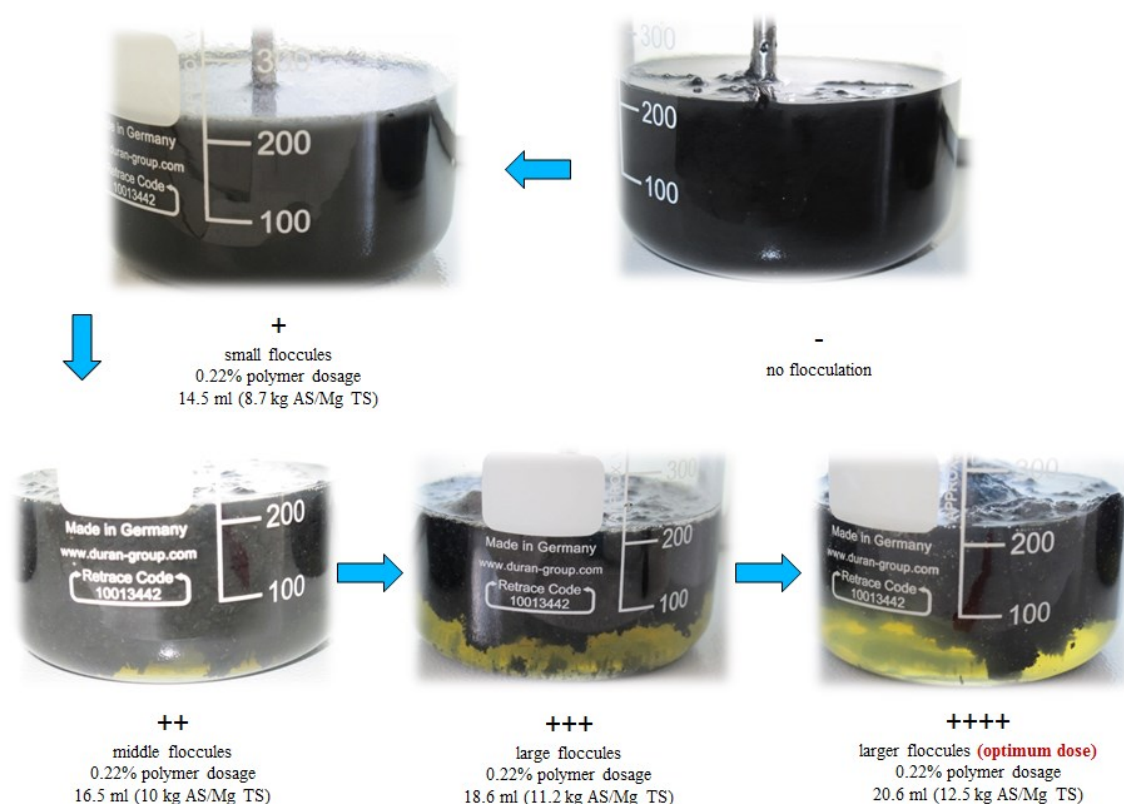
Figure 14: Sludge floccules with different polymer doses

2.2.4 Drip-off test

In order to determine the achievable dry solids (DS) and shear stability of the formed sludge, the Drip-off test was performed. For the drip-off test 200 ml sludge were dosed with the optimum polymer demand and mixed at 200 rpm for 15 seconds. Then it was filtered through a micro sieve with pore size of 100 μm. The accumulated permeate volume was documented every 5–10 seconds until the volume in the graduated cylinder was stable (Kopp, 2013).

2.2.5 Pilot-scale test

Pilot-scale trials were conducted with the polymer HYDREX H6864 in cooperation with the Institute of Sanitary and Environmental Engineering Braunschweig (ISWW). A pilot-scale centrifuge, Hiller DP15-422, with a maximum capacity of 400 l/h was used for two sludge types: mesophilic digested excess sludge and digested mixed sludge (mix of thermophilic digested primary, mesophilic digested excess sludge and thermophilic digested co-substrate). The sludge was tested with different polymer blends and compared to PAM-based polymer. Both polymers were made with a concentration of 0.2 mass%. In order to confirm the correct concentration the TS of the polymer solutions was measured for each sample.

The separation ratio was evaluated through the total suspended solids of the feed, dewatered sludge and centrate, which is defined as:

$$\text{Separation ratio} = \frac{(\text{TSS}_{\text{feed}} - \text{TSS}_{\text{centrate}}) * \text{TSS}_{\text{dewatered sludge}}}{(\text{TSS}_{\text{dewatered sludge}} - \text{TSS}_{\text{centrate}}) * \text{TSS}_{\text{feed}}} * 100 \; [\%]$$

TSS$_{\text{feed}}$: total suspended solids of feed

TSS$_{\text{dewatered sludge}}$: total suspended solids of dewatered sludge

TSS$_{\text{centrate}}$: total suspended solids of centrate

The total solids content includes both the suspended solids and dissolved salts. The total solids content is also used to determine a sludge dry weight (DS) in percent. In this paper total solids (TS) and dry matter (DS) are regarded as being equivalent

The **substitution potential** is calculated with respect to the replaced amount of the synthetic polymer considering the optimal polymer dose (OPD). The substitution potential is given in the replaced amount (kg AS/Mg TS) as well as in %.

2.2.6 Full-scale tests

At WWTP Steinhof digested mixed sludge was centrifuged using a Flottweg Dekanter Z53 with addition of the synthetic polymer PK1440 and the starch-based polymer H6864 added. The centrifuge was started and torque, differential speed and polymer dose was adapted in order to achieve a minimum separation ratio of 90 % and the highest possible TS of the dewatered sludge. The sludge flow was kept constant at 20 m^3/h and the TS value of the sludge to be dewatered was between 2.8-3.1%. Total solids (TS), loss on ignition (LOI) and total suspended solids (TSS) measurements were carried out on site as well by the laboratory of WWTP Steinhof. The subsequent pipeline was approximately 15 m long, thus a contact time of 45 – 55 s for the H6864 was achieved. The centrifuge was operated over night with the synthetic polymer PK1440 and after a stable operation was achieved the reference sample was taken in the morning. The starch-based polymer was added in increments of 10 % over the next few hours, reducing the synthetic polymer mass ratio from 70% to 50%.

At WWTP Schönebeck a drum filter was used for thickening. The starch-based polymer H6864 was tested with sludge 17 m^3/h with an average polymer demand of approximately 4.5 kg AS/Mg TS. The synthetic and the starch-based polymers were mixed once the synthetic polymer was saturated. A blend with 0.1 % AS was prepared. The blend was dosed into the sludge stream just before entering the flocculation tank. After flocculation, the sludge mixture passed to the drum filter where a stainless steel sieve was used for separation. The mesh size was 400 µm.

Full-scale trials were also performed at WWTP Gütersloh for two days. The excess sludge was treated using a Bellmer Turbodrain Compact TDC 08 belt thickener, with a sieve diameter of 0.7 mm. Excess sludge entered the process with 0.6-0.8% TS at a sludge flow of 27 m³/h; retention time on the belt was approx. 2 minutes, thickened sludge contained 4-6%

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DS. In the continuous process the cationic polymer (Reiflock RF 1204 A, 48% TS) and starch- based polymer H0661 were dosed at a flow of 1 m³/h, with 0.1% dilution (polymer solution), meaning 0.048% AS and 2.7 kg AS/Mg DS.

2.3 Results and discussion

2.3.1 Lab-scale trials at WWTP Putzhagen

The lab-scale study was performed to investigate the efficiency of different starch-based biodegradable polymers. The jar test results for excess sludge at WWTP Putzhagen are presented as an example in the following sections.
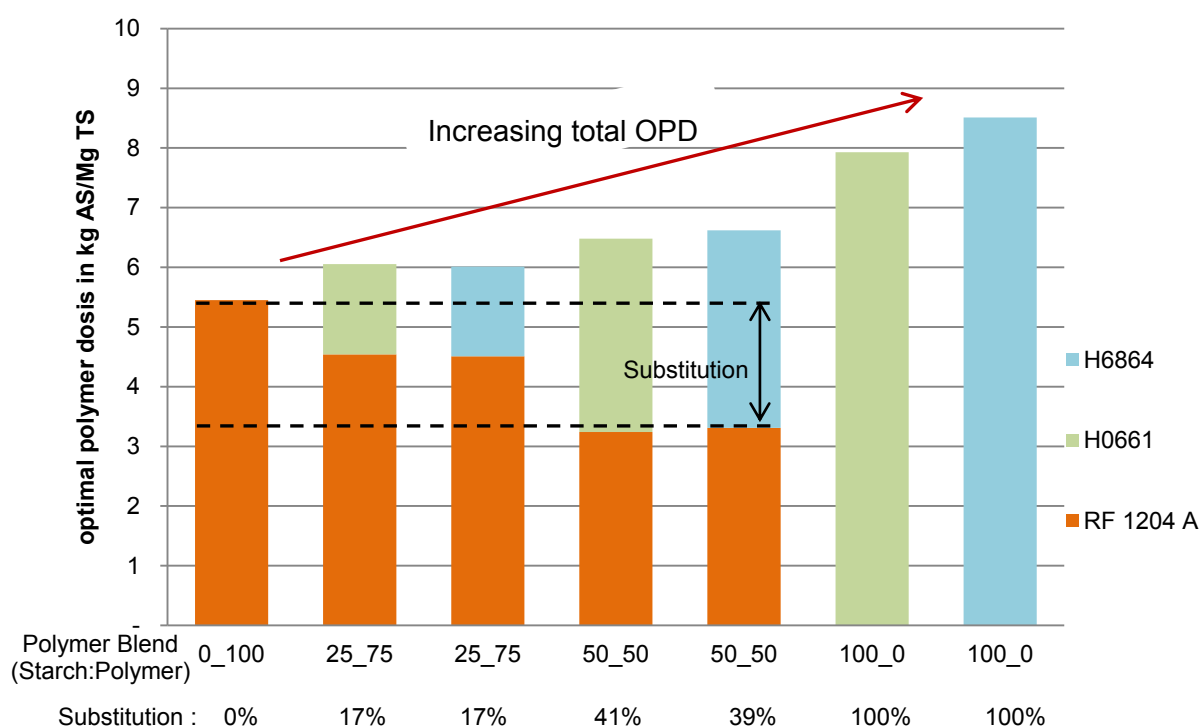
Figure 15: Jar Test results with different blends of starch-based polymer and original polymer at WWTP Putzhagen

Figure 15 shows the results of the test runs with excess sludge originating from WWTP Putzhagen. The application of the starch-based polymers H6864 and H0661 increased the optimal total polymer demand from 5.5 to 8.5 kg AS/Mg DS. The increased OPD is an undesirable effect and diminishes the positive impact of "green" polymer application. The operating costs will rise even considering an optimistic price for green polymers in the same range as for the synthetic polymers. The substitution of approximately 40% of the PAM-based polymers appears technically feasible when applying a blend of 50% starch-based polymer. H6864 and H0661 have almost the same performance on OPD, and, with the following drip-off test, the shear force stability can be tested.
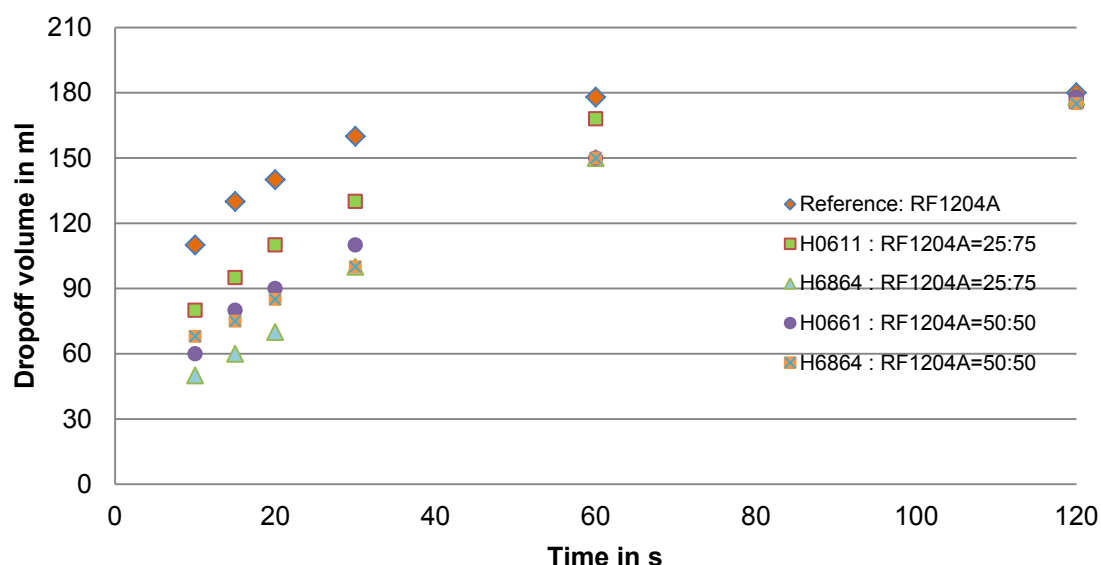
Figure 16: Results of Drip-off test at WWTP Putzhagen

Figure 16 provides the results of drip-off test with different blends of starch and PAM-based polymers. The clearly lower volume for the samples treated with blends can be explained by smaller flocs formed by the starch-based polymer. The flocs break while being mixed and transferred to the filtration unit. The small flocs block the 100 µm sieve and clogging is prevented by proper filtration. The starch-based H0661 shows a better performance with higher filtration volume than H6864. For this reason H0661 was chosen for further full-scale investigations.
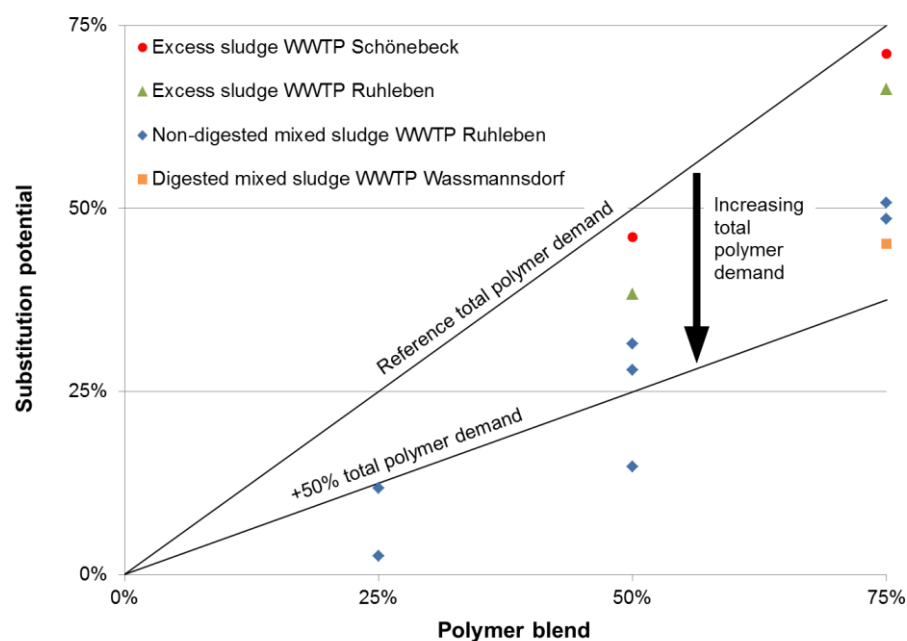
Figure 17: Substitution potential according to polymer blend and sludge type

Further laboratory scale trials were carried out to test the effect of starch-based polymer for different sludge type. Figure 17 describes the substitution potential with respect to the used polymer blend and the tested sludge types. The angle of the bisector indicates the total polymer demand for the reference. The total polymer demand with starch-based polymer blend increased for some of the sludge types, thus the substitution potential decreases. Both types of excess sludge tested at WWTP Schoenebeck and WWTP Ruheleben were more suitable for the application of the starch-based polymer than sludge from other sources.

In general, testing different sludge with varying blends of PAM-based and starch-based polymers gave a broad overview of the feasibility and applicability of starch-based polymers. Applying a blend of starch-based and PAM-based polymer can increase the total polymer demand and therefore the substitution potential has to be calculated accordingly. The flocs showed lower shear stability and are therefore less suitable for process steps requiring strong flocs, e.g. dewatering with centrifuges. In order to introduce a green polymer as an alternative or a partial substitute for PAM-based polymers, the applicability in full-scale processes has to be proved.

2.3.2 Pilot-scale trials at WWTP Steinhof

The pilot-scale centrifuge can be used to predict the full-scale dewatering results. Different dosing and mixing conditions were tested during the pilot-scale trials, and the best setup identified was dosing the starch-based polymer H6864 prior to the PAM-based polymer PK 1440. The H6864 has cationic charge that allows for surface particle neutralization resulting in flocculation. The PAM-based PK 1440 has the ability to bridge together particles suspended in the solution by an adsorption process. For each trial run the differential speeds as well as the total polymer dose were adapted balancing the TS of the dewatered sludge and the quality of the centrate, i.e. the separation ratio. The bowl speed was kept at 6000 rpm, except of the one trial run dosing 100 % of H6864. Due to the insufficient results with the starch-based polymer alone, a bowl speed of 3400 rpm was used. Apart from this particular trial run, the differential speed was kept between 1.4 – 2 rpm trying to achieve a high torque, thus increasing the DS of the dewatered sludge. For the trial run with 100 % of H6864 the differential speed was set to 5 rpm. Table 7 summarizes the operational parameters for the pilot-scale centrifuge and gives the sludge characteristics throughout the trials.

Table 7: Characteristics of digested excess sludge WWTP Steinhof for pilot trials and operation of pilot-scale centrifuge

Digested excess sludge			
DS	Loss on Ignition	pH	Temperature
%	% of TS		°C
3.0-3.4	63.5-69.4	6.6-8.7	32.5-36
Pilot centrifuge operation data				
Bowl speed	Rotational speed	Torque	Sludge throughput	Solid mass throughput
rpm	rpm	%	l/h	kg/h
~6000	1.4-2.0	22-33	280-300	7-10.4

The results of total polymer dose, DS dewatered sludge, substitution, and separation ratios of digested excess sludge are shown in Figure 18. The bars indicate the total polymer dose and the red triangles specify the achieved DS of the dewatered sludge. For each trial run the blend and the achieved substitution with regards to the reference is shown and the fraction of PAM-based and starch-based polymer are highlighted in different colors. The achieved TS of the dewatered sludge for all blends remained within a narrow range (+/- 0.7 %) and were similar to the TS achieved with the PAM-based polymer. Additionally, the total polymer dose did increase distinctively for the blend consisting of 70 % H6864. But even with this higher total polymer dose a substitution of 64 % of the PAM-based polymer was possible achieving the same DS for the dewatered sludge. The separation ratio was above 99 % indicating an optimal operation.
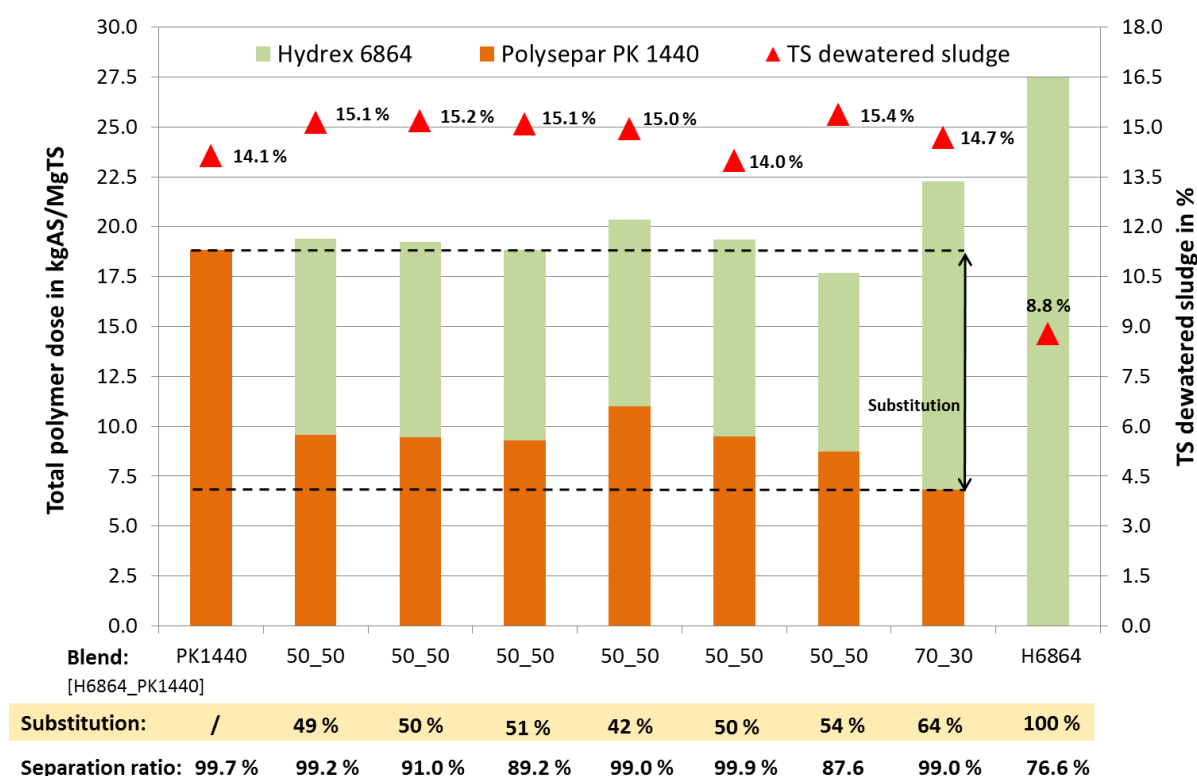
Figure 18: Results of pilot-scale trials digested excess sludge

The limitation is demonstrated by applying 100 % H6864. The total polymer demand increased and at the same time the TS of the dewatered sludge and the separation ratio dropped below an acceptable value. This confirms the outcomes of the jar tests. The flocs formed by the starch-based polymer alone do not develop a sufficient shear force stability required for centrifugation. Therefore, full-scale trials targeting a substitution of up to 50 % of the PAM-based polymer were conducted at WWTP Steinhof.

2.3.3 Full-scale trials

2.3.3.1 Full-scale trials at WWTP Steinhof with centrifuge
Full-scale trials were first conducted at WWTP Steinhof to prove the feasibility of the starch-based polymer H6864 in the centrifugation process. Table 8 shows the different operation parameters of the digested mixed sludge and centrifuge. Due to the experience gained with the pilot-scale centrifuge, the starch-based polymer was fed prior to the synthetic polymer.

Table 8: Operational parameters of sludge and centrifuge Operation data at WWTP Steinhof

Digested mixed sludge			
TS	LOI	pH	Temperature
%	% of TS		°C
2.8-3.1	70.2-72.4	7.1-7.4	32.5-36
Centrifuge operation data			
Bowl speed	Rotational speed	Torque	Sludge throughput	Solid mass throughput
rpm	rpm	%	m³/h	kg/h
~3000	1.3-3.0	28-30	20	566-614

Figure 19 illustrates the used polymer dose, TS dewatered sludge, substitution, the separation ratio as well as the achieved TS of the dewatered sludge with respect to the reference synthetic polymer PK1440.
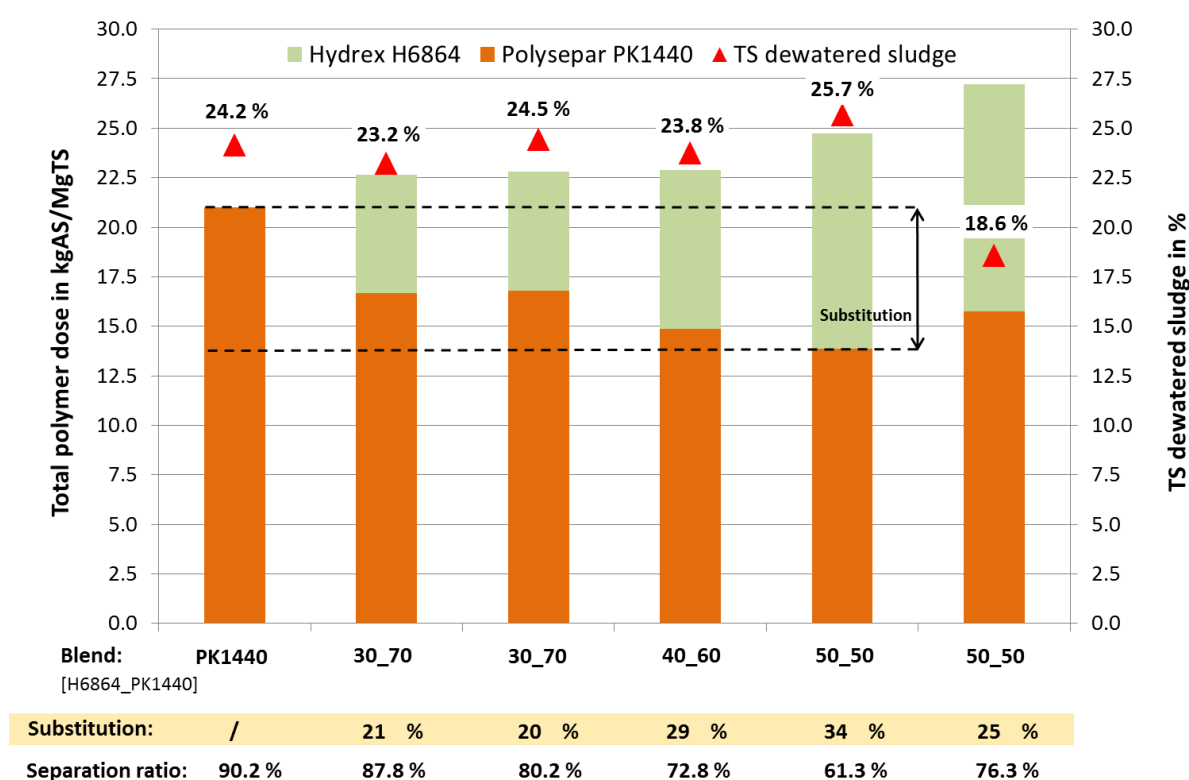
Figure 19: Results of full-scale trials digested mixed sludge at WWTP Steinhof

The achieved TS of the dewatered sludge were within an acceptable range from 23.2-25.7%. The separation ratio of blends was lower compared to the reference PK1400 alone with a separation ratio of 90.2%. For the later trials 50_50 the actual ratio differed slightly, because the dosing concentration of the H6864 was slightly lower than planned. According to the results, a substitution ratio of 34% can be achieved without decreasing of the sludge TS.

In order to increase the separation ratio to an acceptable level, further trial runs optimizing the operational set-up are required. Torque and differential speed were adapted during the tests discussed. With regards to the experience gained with the pilot-scale centrifuge, these adjustments could improve the separation ratio.

2.3.3.2 Full-scale trials at WWTP Schönebeck with drum filter

Jar tests and drip off tests were conducted to support the full-scale tests at WWTP Schönebeck using drum filter. The promising results for blends of synthetic and starch-based polymers H6864 showed a substitution of up to 67.5 % of the synthetic polymer, the shear stability still need to be confirmed in full-scale. On the other hand, flocculation with the starch-based polymers H6864 alone did not show a sufficient flocculation for excess sludge at WWTP Schönebeck. To prove the sludge flocculation in full-scale, a one mega gram blend consisting of 50 % of the starch-based polymer was first tested. After stable operation was achieved, samples were collected for detailed analysis. The result is given in Figure 20. Reference 1 and 2 with the synthetic polymer K7CZST were measured before and after the blend test with DS of thickened sludge of about 6%. During the tests with a 50% blend of H6864 and K7CZST, the sludge TS decreased to 3.7 and 3.8, which shows a lower stability of sludge flocs. Due to the low TS concentration of sludge, 100% of H6864 has not been further tested, instead, the H6864 fraction was reduced to 1/3 (33_66) and tested in full sale again. The achieved TS values of the thickened sludge for the blends with a 33% H6864 fraction were between 4.3% and 4.9%, which was still below the reference of 6%. According to the WWTP operator, a value of about 4.5% was still acceptable.
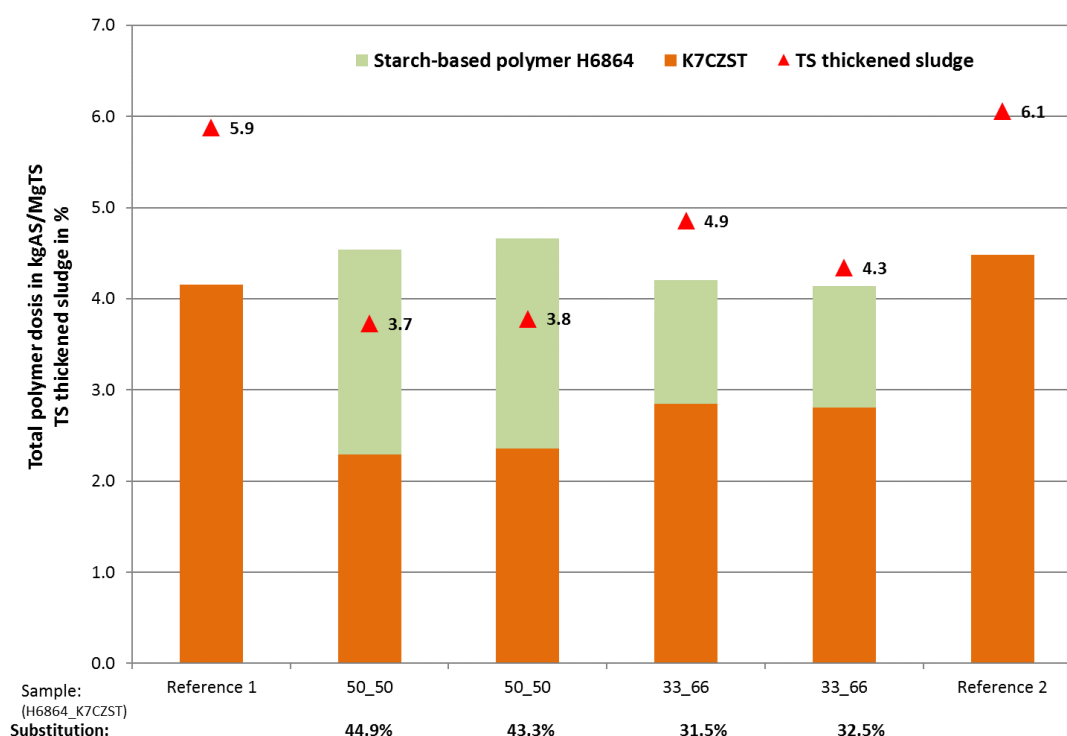
Figure 20: Results of full-scale trials with excess sludge at WWTP Schönebeck

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Full-scale tests were performed for the excess sludge using a drum filter with a blend of a starch-based polymer and a synthetic polymer. The formed flocs were shredded within the drum sieve due to insufficient shear stability. A maximum substitution of 31% was possible with an acceptable sludge TS. Due to a low shear stress on the belt filter press systems, this technology might be applicable. Further full-scale trials with a belt thickener were planned at WWTP Putzhagen.

2.3.3.3 Full-scale trials at WWTP Putzhagen (Gütersloh) with belt thickener

The results of the lab experiments are shown in Chapter 2.3.1. The starch-based polymer H0661 has a better performance with the drip-off tests. In Figure 21, different blends of H0661 and RF 1204 were tested: 25:75, 33:66, 50:50 and 66:33. According to the experience of the WWTP operator, achieving sludge TS with a ratio above 4% has shown good results for the belt thickener. As shown in Figure 9, 33% substitution of the polymer RF 1204 is an acceptable quantity limit for operators. Substituting 50% of the reference polymer RF 1204 leads to an insufficient TS below 4%. Thus, a blend of polymer and starch showed promising results for excess sludge thickening with a belt filter. The critical limit (maximum ratio) of starch is 33%. According to the experience of the WWTP operator, 25% substitution with a starch-based polymer will be a "safe" option.
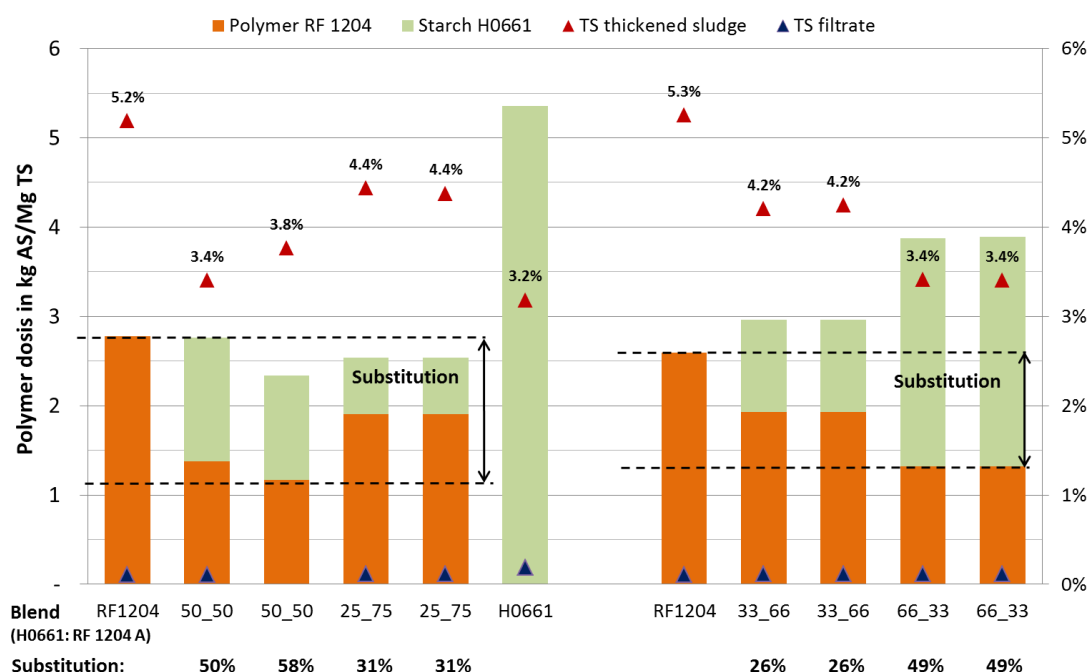
Figure 21: Results of full-scale trials with excess sludge at WWTP Putzhagen

2.4 Conclusion

The main objective of this chapter was to identify a starch-based eco-friendly polymer that demonstrates a similar performance for full-scale sludge dewatering. Based on the results of different sludge types and dewatering units, the following summary can be made:

- Non-digested excess sludge showed more suitable characteristics for the treatment with a starch-based polymer, and a 70% substitution potential can be achieved.
- A substitution of 20% - 30% of the PAM-based polymer was demonstrated achieving similar DS of the dewatered sludge with different dewatering devices.
- Optimization of operational parameters as well as machinery setup is recommended to achieve a high substitution potential.

In conclusion, a successive approach through screening, lab-scale and pilot-scale trials paved the way for full-scale trials of testing starch-based polymers. The feasibility of using a starch-based green polymer in full-scale dewatering was shown. Based on the current selected starch-based polymer product, a partial substitution of 25-30 % of the synthetic polymer can be achieved. With further development of the product, decreasing the product price and optimization of the dewatering devices in the near future, starch-based polymers have a great potential as an alternative flocculants to synthetic polymers.

Chapter 3: Comparative Environmental Life Cycle Assessment of phosphorus recovery with different generations of the Airprex® reactors at WWTP Waßmannsdorf and Amsterdam West

Graphical abstract

Generation I AirPrex® reactor

Generation II AirPrex® reactor

WWTP Berlin Wassmannssdorf

WWTP Amsterdam West

Highlights:

- P mass balance for both WWTPs was given
- Comparison of two different AirPrex® reactor systems was conducted
- LCA process data were taken from the full-scale phosphorus recovery plant
- Cumulative fossil energy demand was calculated
- Environmental impact (Climate change, Eutrophication) was assessed

A modified preprint version of this chapter is submitted to Springer journal "International Journal of Environmental Science and Technology" (Date of submission 09 Nov 2017): Zhou, K. *, Remy, C., Kabbe C., Barjenbruch, M. (2017): A comparative environmental life cycle assessment for phosphorus recovery at WWTP Amsterdam West and Waßmannsdorf

3.1 Phosphorus recovery with Airprex® Process

Various technologies are currently being developed to recover P by crystallization or precipitation from wastewater and sludge (Kabbe et al., 2015). The AirPrex® technology is one of the promising technologies for phosphorus recovery from sludge liquid of digested sludge. The AirPrex® technology was first developed by the "Berliner Wasserbetriebe (BWB)" after being affected by massive incrustations at their plant. The incrustations found in the centrifuges of WWTPs were later proved to consist mainly of struvite with small portions of different calcium phosphate compounds (Heinzmann & Engel, 2006). The advantages of the AirPrex® process are not only P-recovery, but also economic benefits for the WWTP operation. About 70% of the economic benefits of the AirPrex® process come from reduction of the handling costs of biosolids and polymers costs. About 20% of the savings are due to lower maintenance requirments associated with struvite and 10% is the potential revenue from fertilizer sales (Rulseh, 2015).
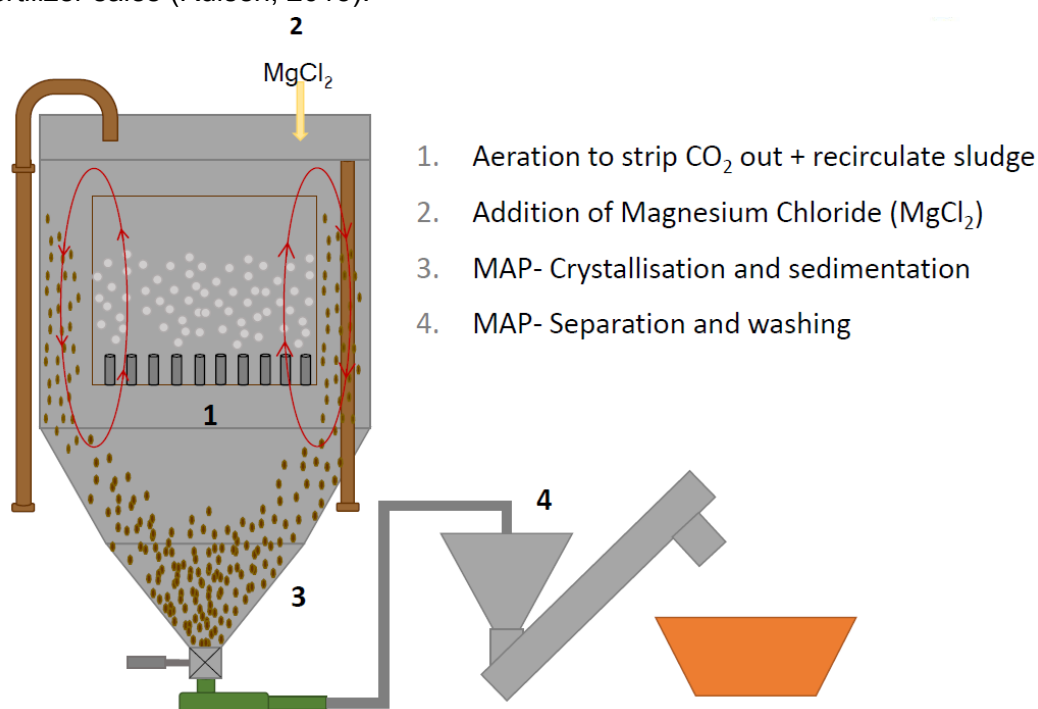
Figure 22: Principe of AirPrex® technology ©CNP (Forstner, 2015)

In the AirPrex® process, the digested sludge is led through a so-called "airlift reactor", in which air is used to create internal recycle flows (Figure 22). The aeration has two functions. First, it increases the pH value from 7 to 8 by stripping CO_2 from the digested sludge. Second, it creates a loop convection within the reactor by central air injection and the baffles is to initiate inner upflow and outer downflow of sludge. The airlift reactor sets the retention time of the growing struvite crystals, which sink to the bottom when reaching a certain size. Ammonium ions (NH_4^+) and phosphate ions (PO_4^{3-}) are present in sufficient concentrations in the digested sludge. By adding magnesium ions (Mg^{2+}, usually as magnesium chloride ($MgCl_2$), to the reactor, struvite ($NH_4MgPO_4\cdot6H_2O$) is formed. The formed Struvite crystals are suspended in the sludge until they reached a limited size, where their sink rate faster

than the circulation rate. Struvite has a density of 1.7 g/cm³ and therefore can be collected at the bottom of the reactor. It is then separated from organic residues by a sand washer. Afterwards, the crystals are atmospherically dried and the product is brought to the market or user.

The patent of the AirPrex® technology was held by Berliner Wasserbetriebe (BWB) and since 2013 the license is obtained by CNP-Technology Water and Biosolids GmbH in Hamburg, Germany. At the moment, eight full-scale plants are in operation. In these plants 80–90% of the phosphate is removed from the liquid phase of the digested sludge as struvite (CNP, 2017b). Table 9 gives an overview of the current operational plants.

Table 9: List of full-scale AirPrex® technology (CNP, 2017b)

Country	Location and Operator	Operational since	Personal equivalent	Capacity of AirPrex®	Design struvite production
			p.e.	m³/d	kg/d
Germany	MG-Neuwerk, Niersverband	2009	995,000	1500	1000
Germany	Wassmannsdorf, Berliner Wasserbetriebe	2010	1,400,000	2400	2000
Netherlands	Echten, Drents Overijsselse Delta	2013	190,000	400	500
Netherlands	Amsterdam-West, Waternet	2014	1,000,000	2500	3500
Germany	Uelzen, SE Uelzen	2015	83,000	145	n.a.
Germany	Salzgitter Nord, ASG	2015	150,000	240	n.a.
Germany	Wolfsburg, SE Wolfsburg	2016	170,000	280	n.a.
China	Tianjin, Tianjin CEPG	2016	1,000,000	1600	n.a.

(n.a. = not accessible)

The first installation of AirPrex® at WWTP Wassmannsdorf (WMD) in Berlin and the largest AirPrex® plant at WWTP Amsterdam West (AMS) were chosen for comparison in this study. The AirPrex® system in Berlin has only one big reactor, while in Amsterdam there are three separated reactors. The AirPrex® system in Amsterdam has higher struvite yield, but with higher energy demand and more materials used for the infrastructure compared to Wassmannsdorf. The objective of this study is to compare the environmental impact of the two AirPrex® reactor systems. The ultimate goal of this study is to develop an analysis that could assist decision-makers in considering environmental effects when designing new AirPrex® processes in different treatment plants.

3.2 P mass balance and AirPrex® reactor in WWTP Amsterdam West and Wassmannsdorf

3.2.1 AirPrex process in WWTP Wassmannsdorf

WWTP Wassmannsdorf currently has a daily treatment capacity of 180,000 m³ of wastewater daily during dry weather. The sludge treatment lines include three centrifuges for excess sludge thickening, six digesters each with a volume of 8,000 m³ and five centrifuges for sludge dewatering (BWB, 2017b).
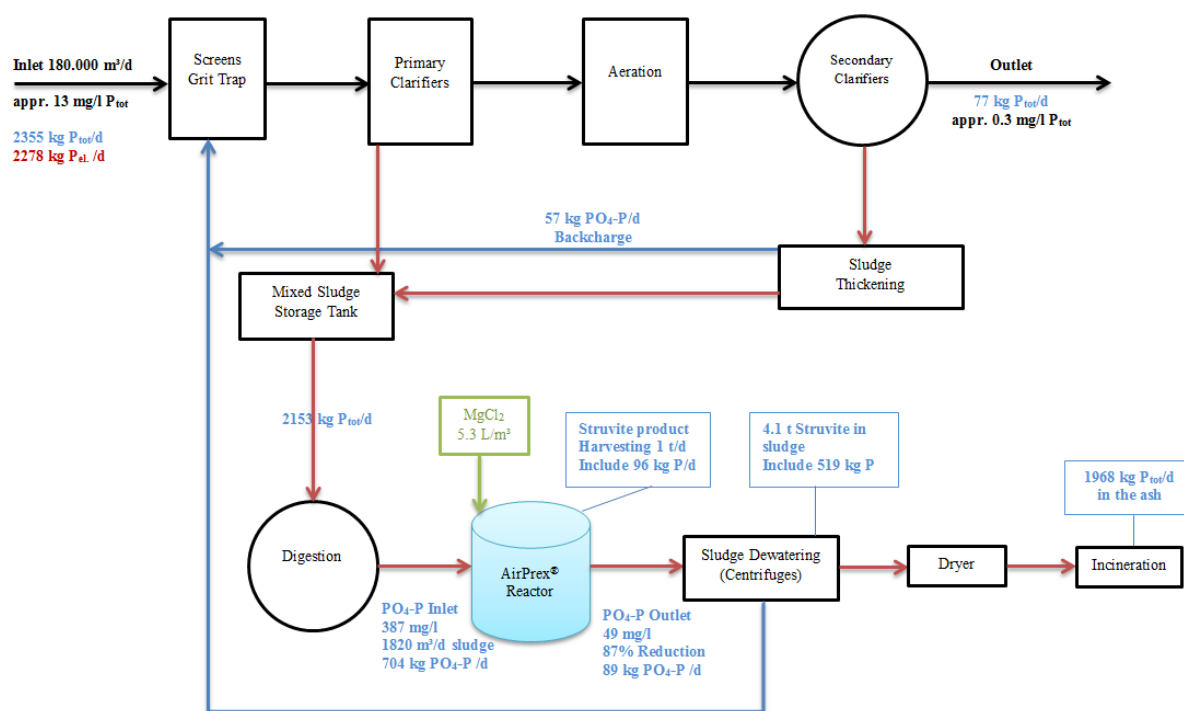
Figure 23: Process scheme and P mass balance of WWTP Wassmannsdorf (modified) (Forstner, 2015)

Figure 23 shows the process scheme and P balance of WWTP Wassmannsdorf. About 96.7% of total phosphate was eliminated from wastewater to sludge. In the AirPrex® reactor, 87% of the orthophosphate was removed from the sludge liquid phase, but the real P harvesting in struvite was only about 14% with regards to the dissolved orthophosphate in the sludge. About 74% of the produced struvite was still contained in the dewatered sludge. This part of struvite and the residual phosphorus were incinerated. In Wassamnsdorf, a part of the dewatered sludge (16% of DM) is transported to the mono-incineration plant in Berlin-Ruhleben, while the rest (50% of DM) is transported to different lignite power plants for co-incineration (Remy, 2012). In order to utilize the thermal energy of sludge completely and recover more phosphorus in accordance with the new sewage sludge ordinance, the BWB will start the construction of a mono-incineration plant in 2022 (BWB, 2017a)
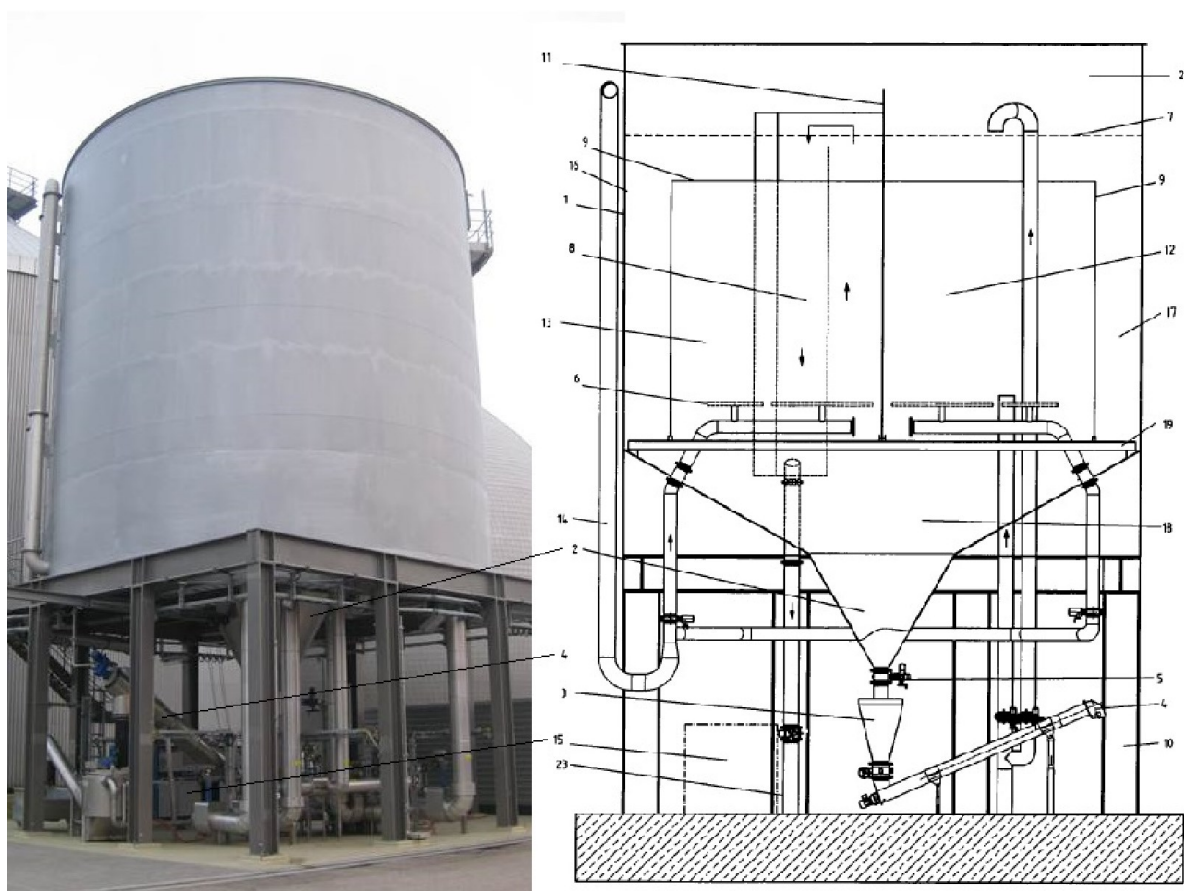
Figure 24: AirPrex® reactor at WWTP Wassmannsdorf (Wendl, 2013)

To solve the operational problem of struvite crystallization in pipes and pumps, the BWB built the first AirPrex® reactor (Figure 24) in 2009 which was put in operation in March 2010. The AirPrex® process in Berlin is a one reactor system with a volume of 800 m³. Using air stripping (2000-3000 m³/h), the CO_2 in the sludge is stripped and the pH value in the rector increases from 7.2 to 7.8-8 (Heinzmann & Lengemann, 2011). After adding 5.3 L 30% magnesium chloride solution per cubic meter sludge (Mg:P molar ratio=1.7), the dissolved orthophosphate concentration in the sludge water decreases by 87%, on average from 387 mg/l to 49 mg/l in 2016 (Lengemann, 2017). The sludge retention time in the reactor is about 10.5 hours. The energy demand for the AirPrex system is 2.2 kWh/m^3 sludge.

3.2.2 Airprex process in WWTP Amsterdam West

WWTP Amsterdam West is one of the largest WWTP of WATERNET in the Netherlands. It was opened in 2005 and has a treatment capacity of 168,000 m^3/d of dry weather influent. At the WWTP Amsterdam West (in total 1 million people equivalent), using enhanced biological phosphorus removal, massive scaling problems occurred after digestion of the primary and secondary sludge. In order to solve the operational problems, the Airprex® process was implemented in 2014, and the WWTP Amsterdam West has become one of Europe's largest production facilities of struvite. Figure 25 shows the process scheme and P balance at WWTP Amsterdam West.
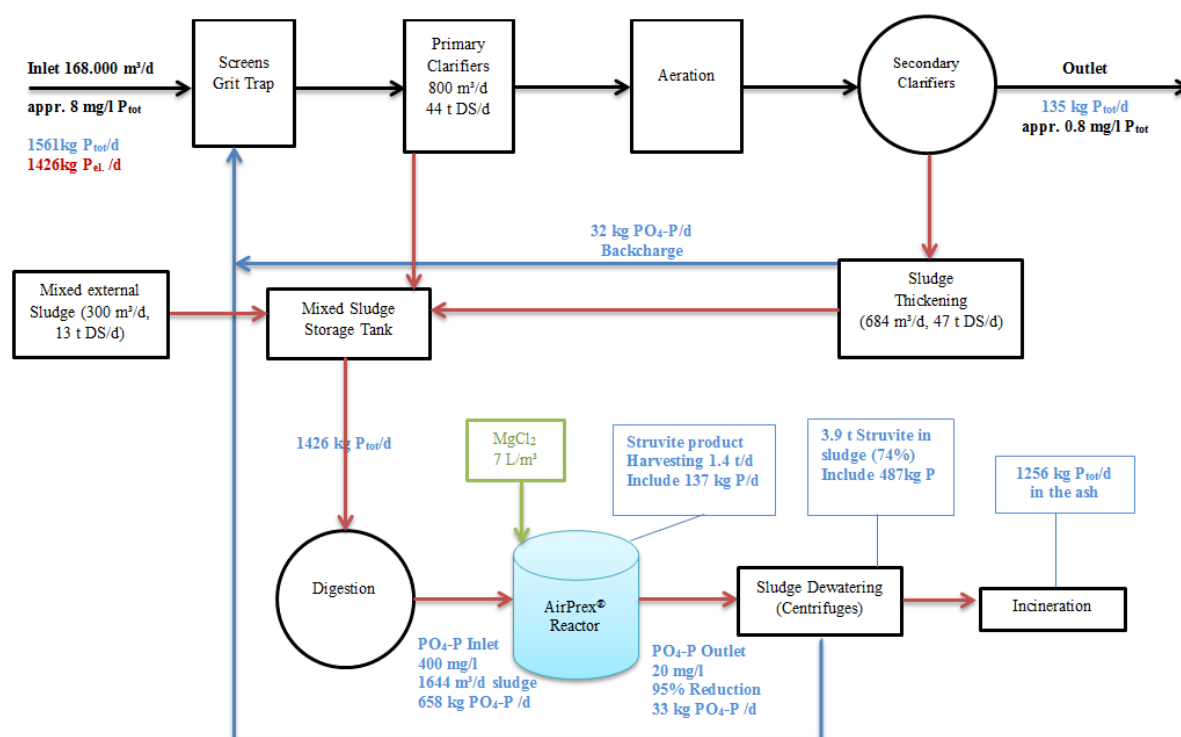
Figure 25: Process scheme and P mass balance of WWTP Amsterdam West (modified) (Forstner, 2015)

The WWTP Amsterdam West does not only process the sludge from its own treatment (approx. 91 t DS/d), but also that of the nearby WWTP Westpoort and that of some other external sources (approx. 13 t DS/d). The external sludge is collected in the Central Sludge Intake. The primary sludge is thickened by gravity thickeners and the secondary sludge by belt thickeners. After that, all sludge is treated in anaerobic digesters, where the sludge is stabilized, its volume is reduced and biogas is produced. At last, the sludge is dewatered in bowl centrifuges, after which it is transported for incineration in a waste incineration plant (Bergmans, 2011; Veltman, 2016).

Figure 26: The Airprex® reactor at WWTP Amsterdam west (Veltman, 2016)

The Airprex® process at WWTP Amsterdam West was launched in Dezember 2013. As shown in Figure 26, the Airprex® system includes three reactors. The first a volume of 500 m³ and the second reactor a volume of 250 m³ are with air stripping and magnesium chloride dosing. In total 1000 Nm³/h of air are dosed in the first two reactors. The total residence time of sludge is between 8 to 10 hours depending on the sludge flow. The third reactor is used only for struvite settling with a volume of 250 m³. Two magnesium chloride storage tanks have a volume of 50 m³ each. With the three reactor systems, the harvesting efficiency of struvite can achieve 21% with regards to the dissolved ortho-P in the digester sludge.

3.2.3 Comparison of Airprex system in WWTP Wassmannsdorf and Amsterdam West

The difference between the AirPrex® system in WWTP Wassmannsdorf (WMD) and in WWTP Amsterdam West (AMS) is described in Table 10. WWTP AMS has a higher harvesting efficiency of struvite due to the reactor design. The three separate reactor systems have a lower sludge retention time, but achieve a better separation of crystals from sludge due to a better crystallization condition in the first two reactors and an additional quiet condition for struvite precipitation in the third reactor. The WMD reactor (33 Nm³ air /m³ sludge) has more than twice the amount of air pumped into the sludge than in AMS (15 Nm³/m³), but the energy demand of WMD is lower than in AMS. This is mainly due to the sludge transport between three reactors system. Data of operational benefits show that the AirPrex® reactor installed in AMS is more efficient than the one in Berlin. AMS achieved a higher sludge dewatering improvement and polymer saving after using the AirPrex® system. By aeration and pH increase, the ammonia gas is stripped with CO_2 from liquid phase to gas phase. The AirPrex® reactor in WMD is uncovered and emits ammonia directly into the air, while the aeration reactor in AMS is closed and the exhaust gas is treated in a biofilter. However, it is to be considered that, the AirPrex® system in AMS has a higher demand for energy, magnesium chloride doses and infrastructure. For a more accurate comparison of the environmental impacts of the both reactors, Life Cycle Assessment (LCA) was used to

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evaluate the cumulative energy demand, the Greenhouse Gas emission and Eutrophication potential.

Table 10: Comparison of AirPrex® Systems in WWTP Wassmannsdorf and Amsterdam West (Lengemann, 2017; Veltman, 2016; Wendl, 2013)

WWTP			
	Unit	WWTP Wassmannsdorf	WWTP Amsterdam West
Person equivalent	p. e.	1,400,000	1,000,000
Sludge volume	m³/a	664,300	600,000
TSS	%	5.89	6
TS sludge	t/a	39,127	36,000
AirPrex reactor			
Dissolved PO_4-P Input	mg/l	387	400
Dissolved PO_4-P Output	mg/l	49	20
PO_4-P Precipitation efficiency	%	87	95
$MgCl_2$ dosing	mol Mg/mol P	1.7	1.9
Sludge hydraulic residence time in all reactors	h	10.5	9
Air pumping	m³/h	2500	1000
Energy Demand	kWh/m³	2.2	2.4
Sludge Dewatering			
TS improvement	%	2% (from 25% to 27%)	2.5% (from 21% to 23.5%)
Polymer Saving	g/kg TSS	3 (from12 to 9)	4 (from 17 to 13)
Struvite Harvesting			
Product harvesting	ton/a	360	500
Share of struvite in total solids product	%	78	80
Harvesting efficiency (P in Product/dissolved P in sludge)	%	14%	21%

A total of EUR 2.3 million was invested for the one reactor AirPrex® system in WMD (Egle, 2014) while in AMS EUR 3 million was invested for the three reactor AirPrex® system (Veltman, 2016). It is estimated that in AMS the savings of installation of AirPrex® reactor is EUR 500,000 million per year, (from that total benefits of EUR 1.2 million per year and operational costs of EUR 700,000 million per year) with return on investment (ROI) of 6 years.

3.3 Methodology and system details

3.3.1 Methodology of Life Cycle Assessment

Life Cycle Assessment is an internationally standardized method for the evaluation of the environmental burdens and resources consumed along the life cycle of products or processes (ISO-14040, 2006; ISO-14044, 2006). For assessing technical processes and systems in their potential environmental impacts, the method of Life Cycle Assessment (LCA) has been developed and applied widely within research and industry (Grahl, 2009), also in the field of wastewater and sludge treatment (Corominas et al., 2013; Remy et al., 2012; Wenzel et al., 2008).

Typical environmental effects that can be assessed using LCA include eutrophication, global warming, human health, and air acidification. LCA can be used to analyze the differences in environmental effect between multiple processes that accomplish the same task or function.

Umberto® NXT LCA is a software package providing a graphical interface for life cycle assessment. Umberto® NXT LCA is licensed and maintained by ifu Hamburg GmbH (Institut für Umweltinformatik). Umberto® NXT LCA supports environmental consultants, process engineers, and process technicians in developing comprehensive analyses of product life cycles.

Ecoinvent is a commercial database set for life cycle assessment of the Ecoinvent Association, which was originally known as the Ecoinvent Centre, the Swiss Centre for Life Cycle Inventories. The Ecoinvent database is one of the market leaders in this field. The Ecoinvent version 3 is the latest database of the provider. It contains more than 11,500 data sets and offers a lot of new and updated data sets (IFU, 2017).

3.3.2 Goal and scope definition

The purpose of this study is to quantify the life cycle environmental impacts of different reactor systems for the Airprex process. The assessment is based on a reference system, which is defined as the sludge line treating the mixed sludge of WWTP Wassmannsdorf. The following relevant side effects on the sludge treatment or the mainstream WWTP are considered:

- Demand of electricity, chemicals
- Product yield (t/a P) and quality
- Substitution of mineral fertilizer production (only P and N accounted)
- Side effects (return load, dewatering)

The function unit is chosen as sludge treatment and disposal of annual load in WMD (39127 t TS/a). The sludge treatment line can represent the view from the WWTP operator for the effect of sludge treatment. An alternative F.U. is chosen as 1 kg P product. This P-fertilizer perspective (1 kg P) gives information about the environmental impact of one kg recovered P.

The ultimate goal of this study is to develop an analysis that could assist decision-makers (engineers, owners, regulators, etc.) in considering environment effects when optimizing or designing new AirPrex® processes in the treatment plants.

3.3.3 System boundary and scope definition

The reference system consists of the WWTP Wassmannsdorf sewage sludge line with data based on previous work at KWB (Project P-REX). The boundaries include all relevant treatment steps for sewage sludge, beginning with raw sludge consisting of a mixed sewage sludge, digestion, heat and power production from biogas in a combined heat and power plant (CHP), dewatering with a decanter, transport of dewatered sludge to the mono-incineration plant, sludge mono-incineration and ash disposal. Also included as background processes are the production of fuels, chemicals, electricity and additional infrastructure demand of the two scenarios. Figure 27 shows the boundaries of this LCA study. Inventories from the Ecoinvent database are accounted as European data sets.
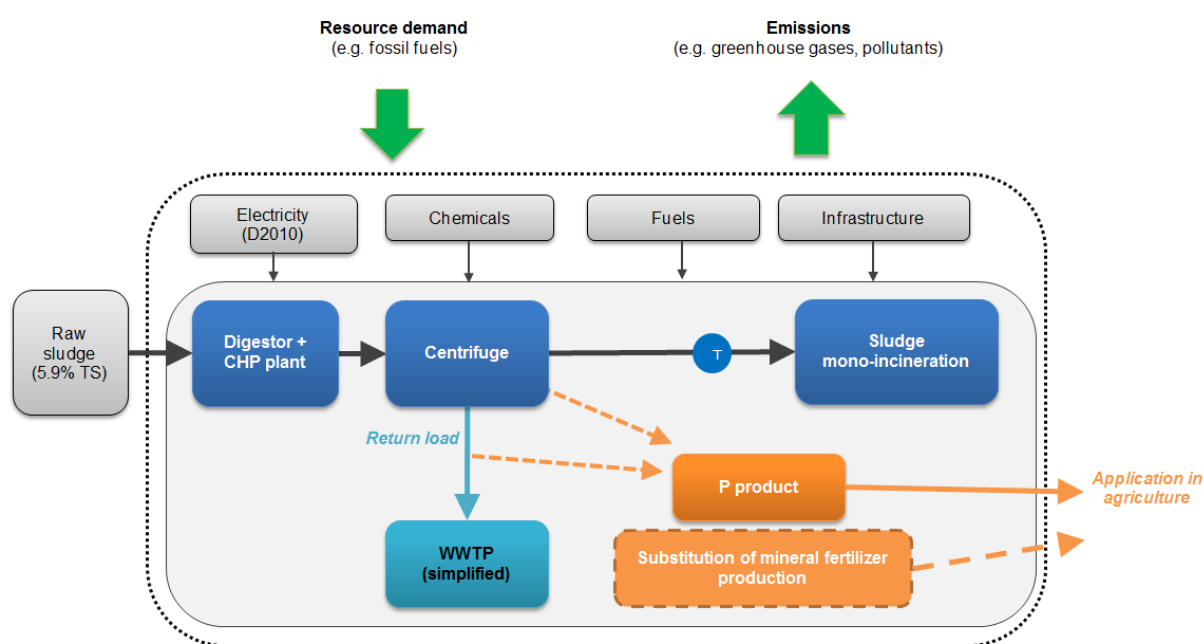
Figure 27: System Boundary of the LCA (Remy et al., 2015)

A reference system without the AirPrex® reactor is prepared to compare two different scenarios. To reduce the impact factors of different infrastructure (i.e. sludge composition, disposal route, etc.), it is assumed that, Berlin Wassmannsdorf builds a new AirPrex® system as in Amsterdam for comparison in Scenario 2.

Two scenarios and a reference system as a baseline are modelled in this LCA for comparison:

- Reference Scenario: Sludge treatment and disposal at WMD
- Scenario 1: P-recovery with 1-reactor configuration at WMD
- Scenario 2: P-recovery with 3-reactor configuration at WMD

Reference input flows:

The reference input sludge flow is defined as the mixed sludge in Wassmannsdorf, which enter the system of sludge handling. The quantity and quality of the mixed sludge in WWTP Wassmannsdorf are given or measured by the BWB staff in 2016.

Table 11: Site Specific Data for reference system at WWTP Wassmannsdorf 2016 (Lengemann, 2017)

Input mixed sludge				
	Annual Load		**Concentration**	
Parameter	**Value**	**Unit**	**Value**	**Unit**
Volume	664,300	m³/a		
Dry matter	39,127,270	kg/a	5.89	%
Organic dry matter	3,208,436	kg/a	82	% of dry matter
COD	30,816,877	kg/a	4639	mg/l
Total nitrogen	2,120,698	kg/a	54.2	mg/kg
Phosphorus	1,074,044	kg/a	27.45	mg/kg

Indicators of Life Cycle Impact Assessment:

There are different areas of protection declared in ISO 14044, but according to the goal of the LCA study only cumulative energy demand and the natural environment are considered. For the environmental impacts assessed in this study, the following indicators are relevant:

- Cumulative energy demand of fossil and nuclear origin (VDI, 2012)
- Global warming potential: CO_2 footprint including fossil CO_2, N_2O, CH_4
- Fresh Water Eutrophication Potential (FEP): P emissions into water and soil
- Marine Eutrophication Potential (MEP): N emissions into air, water and soil (Goedkoop et al., 2009)

Data Quality:

It is clear that different quality of input data results in different reliability of the output results. To collect AirPrex® operational data (energy demand, chemical demand etc.), questionnaires were sent to operators and were iteratively checked with literature and expert opinions.

The sludge input data was from Wassmannsdorf with average monthly measurements in 2016 (Lengemann, 2017). The data for the demand of electricity, heat and chemicals of each process was taken from the project *CoDiGreen* (Remy, 2012) with the operational data in 2009. Data of AirPrex® reactor (efficiency, struvite production, energy demand etc.) for the

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process model was collected from the process engineers of the WWTP Wassmannsdorf and WWTP Amsterdam West with questionnaires or emails. The data the of mono-incineration plant is based on the project P-REX (Remy et al., 2015) from the project partner Outotec.

Limitations:

- The direct comparison of the AirPrex® process in two WWTPs is difficult due to the influence of the WWTP itself and different sludge disposal routes
- The data of input sludge, treatment process and AiPrex® reactor is from different years
- The sludge dry matter improvement has different initial dry matter values, i.e. in WWTP Wassmannsdorf from 25% to 27% and in WWTP Amsterdam West from 21% to 23.5%
- The polymer savings also have a different initial demand, i.e. in WWTP Wassmannsdorf from 12 to 9 g/kg TSS and in WWTP Amsterdam West from 17 to 13 g/kg TSS

3.3.4 Life Cycle Inventory

The existing process of sludge handling and disposal at WWTP Berlin Waßmanndorf includes stabilization by anaerobic digestion, dewatering and drying, and incineration of stabilized sludge. This chapter summarizes all relevant data used for the process model of this LCA ("Life Cycle Inventory"). The process model is set up using the LCA software UMBERTO®.

Figure 28: Reference system for Life Cycle Inventory analysis (Jossa, 2014; Remy et al., 2015)

Figure 28 shows the reference system used for the Life Cycle Inventory Analysis (LCI). The LCI is carried out by using version 7.1 of *Umberto NXT LCA* by *ifu Hamburg GmbH.* The reference system is sub-divided into functional system units.

- Digester and CHP unit

The digester unit used in the system (Table 12) represents the mesophilic digester at WWTP Wassmannsdorf. The volatile suspended solid (VSS) degradation is estimated empirically to 47%, while the biogas yield and methane content of the biogas are 60.5%. The electricity demand of the digester is 4.1 kWh/m^3 Sludge, consisting of required energy for mixing and sludge pumping. The sludge is also preheated using 20 kWh/m^3 of thermal energy before it is fed to the digesters.

Table 12: Reference Data for Digester and CHP (Remy, 2012)

Digester		
Parameter	**Value**	**Unit**
VSS degradation	47	%
Biogas yield	423	NL/kg V SS$_{In}$
Biogas CH$_4$ content	60.5	Vol-% CH$_4$
Electricity demand	4.1	kWh/m^3 Sludge
Heat demand	20	kWh/m^3 Sludge
CHP		
Efficiency electric	36	%
Efficiency thermal	44	%
CH$_4$ leakage	0.75	% of Biogas
CH$_4$ to flare	0.01	% of Biogas
Electricity demand for gas purification and CHP plants	0.156	kWh/m^3 Biogas

- **AirPrex® process**

Digested sludge is pumped to the AirPrex® reactor (Scenario 1 and 2). The differences of the operational data are shown in Table 13. The harvesting efficiency of AirPrex® process describes the relation of the amount of total P that is recovered in the product and the contained dissolved ortho-P in digested sludge. With the three-reactor system in Amsterdam, there is a higher demand for electricity needed for pumping sludge to the different reactors.

Table 13: Specific Data for AirPrex® Scenarios (Lengemann, 2017; Veltman, 2016)

AirPrex			
	Unit	Scenario 1 WMD	Scenario 2 AMS
Throughput	m^3 per da	1820	1820
Retention time	h	10.5	8
PO_4-P Precipitation efficiency	%	87	95
30% $MgCl_2$ dosing	l/m^3	5.3	7
Air pumping	m^3/h	2500	1000
Energy Demand	kWh/m^3	2.2	2.4
Harvesting efficiency	%	14	21
P in recovered struvite	kg/a	34198	55243
N in recovered struvite	kg/a	15467	24985
NH_4-N emission	%	8	2

- **Dewatering Unit**

In the sludge after digestion the TS of digested sludge decreased from 5.9 to 3.4%. With the AirPrex® system the TS content of dewatered sludge was improved from 25% to 27% in Scenario 1, while in Scenario 2 has a higher improvement to 27.5% due to a lower PO_4-P content in the sludge water (Table 14).

With lower dissolved Ortho-P concentration in sludge liquid, higher TS can be achieved by dewatering (Forstner, 2015). The polymer demand is decreased from 12 to 9 g/kg TSS with the AirPrex® system. In scenario 2, the polymer demand is lower than in scenario 1 with 8 g/kg TSS. The energy demand for both scenarios is the same with 3.8 kWh/m^3 sludge.

Table 14: Specific Data for Decanter (Jossa, 2014; Veltman, 2016)

Sludge Dewatering				
	Value			Unit
	Reference	Scenario 1	Scenario 2	
Final TS	25	27	27.5	%
Decanter electricity demand	3.8	3.8	3.8	kWh/m^3 sludge
Polymer Demand	12	9	8	g/kg TSS

- **Return load and smplified WWTP**

Within the boundaries of the reference system, there is a simplified WWTP model for treatment of the return load after the dewatering unit. Calculations are mainly based on the modelling by KWB within the research project CoDiGreen and P-REX.

In the simplified WWTP (Table 15), aeration efficiency is stated as 0.5 kWh/kg O_2 and removal goals for COD, NH_4-N, TN and TP are respectively estimated at 90%, 99% (full nitrification), 80% (denitrification) and 96% (P-removal).

Table 15: Reference Data for simplified WWTP (Remy, 2012)

Simplified WWTP		
	Value	**Unit**
Energy Demand Aeration	0.5	kWh/kg O_2
Energy Demand EBPR	0.37	kWh/kg P
Energy Demand N-removal	1	kWh/kg N

The data of the return load is taken from the operational data in 2016. The AirPrex® reactor reduced 85% orthophosphate in centrat in Scenario 1 and 95% in Scenario 2. About 12-13% of ammonium nitrogen in sludge liquid is precipitated in struvite.

Table 16: Reference Data for Return Load (Lengemann, 2017)

Return Load				
	Reference	Scenario 1	Scenario 2	**Unit**
TSS	520	520	520	mg/l
NH_4-N	1286	1137	1124	mg/l
PO_4-P	387	49	19	mg/l

- **Mono-Incineration Plant**

In Wassmannsdorf, the sludge is incinerated in mono-incineration plant, different lignite power plants and cement kilns. WWTP Wassmannsdorf will build a mono-incineration plant nearby in 2022 (BWB, 2017b). For simplification, the dewatered sludge will be calculated for the mono-incineration plant with a transport distance of 5 km. For the LCA, a state of the art mono-incineration plant, based on data from the engineering company Outotec for the Zurich incinerator is modelled (Remy et al., 2015). The operational data is shown in Table 17. The thermal energy is recovered and injected in district heating, while electrical energy is produced in steam turbine.

Table 17: Reference Data for Mono Incineration (Remy et al., 2015)

	Value	**Unit**
Heating Value VSS	14	MJ/kg
Water Evaporation	-2.6	MJ/kg
Thermal Energy Conversion Efficiency	73	%
Electrical Energy Conversion Efficiency	14	%
Electricity Demand for Operation	0.23	kWh/kg TS

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- **Disposal of Ash**

Ashes from mono-incineration (0.2 kg/kg TS) are transported to landfills (100km) (Jossa, 2014; Remy et al., 2015). Disposal of mono-incinerated sewage sludge ash is modelled via a data set market for hazardous waste, for underground deposit according to Econinvent database version 3.0.2.1. The data set includes all upstream activities from cradle to grave. The used data set refers to average global data in the years 2011-2013.

- **Phosphorus and nitrogen fertilizer production**

Phosphorus fertilizer production and nitrogen fertilizer production are modelled via a data set market for phosphate and nitrogen fertilizer (Jossa, 2014; Remy et al., 2015), as P_2O_5 and N of econinvent database version 3.0.2.1. The data set includes all upstream activities from cradle to grave. The used data set refers to average global data in the years 2011-2013.

3.4 Life Cycle Impact Assessment

- **Cumulative Energy Demand (CED)**

The difference between reference scenarios and AirPrex® scenarios in energy demand per year (including fossil and nuclear) is displayed in Figure 29. Compared to the reference system, additional electricity for the AirPrex® reactor (approx. 16 million MJ) and for the magnesium chloride production (approx. 8 million MJ) is needed. The negative impact is equivalent to an energetic surplus of sludge treatment and disposal compared to the reference system. The main energy savings are savings from polymer (approx. 8 million MJ), higher electricity production in mono-incineration (approx. 14 million MJ) and heat for district heating to substitute natural gas (approx. 20 million MJ). The polymer savings and improvements in dewaterability of digested sludge enable a better energy recovery in mono-incineration and therefore obtain the saving of energy credits. Without sludge disposal, avoided production of mineral fertilizer alone cannot cover the additional efforts in energy and chemical demand.
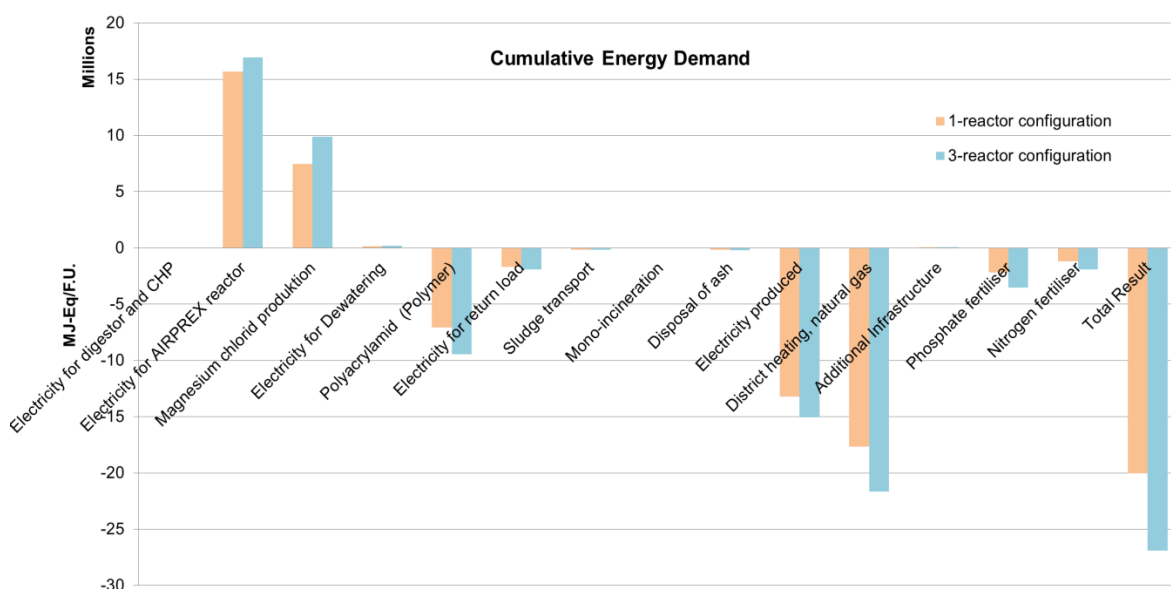
Figure 29: Total Cumulative Energy Demand of AirPrex® system with 1-reactor and 3-reactor configuration

Compared to Scenario 1 with 1-reactor configuration, Scenario 2 with 3-reactor configuration has a higher electricity demand, but also a higher benefit or surplus. In total, the net energy benefit in 1-reactor configuration is -20 million MJ/a. In Scenario 2 the total benefit is -26.9 million MJ/a, improving the energy surplus by 35%. From this point, the AirPrex® system with 3-reactor configuration has a better energy efficiency than the one with 1-reactor configuration due to the benefits of sludge disposal. It needs to be mentioned that, in Scenario 1 the 2% improvement of dewaterability is based on AMS sludge, but in Scenario 2, the improvement of dewaterability of 2.5% is based on AMS sludge with a different starting point of dry matter improvement.
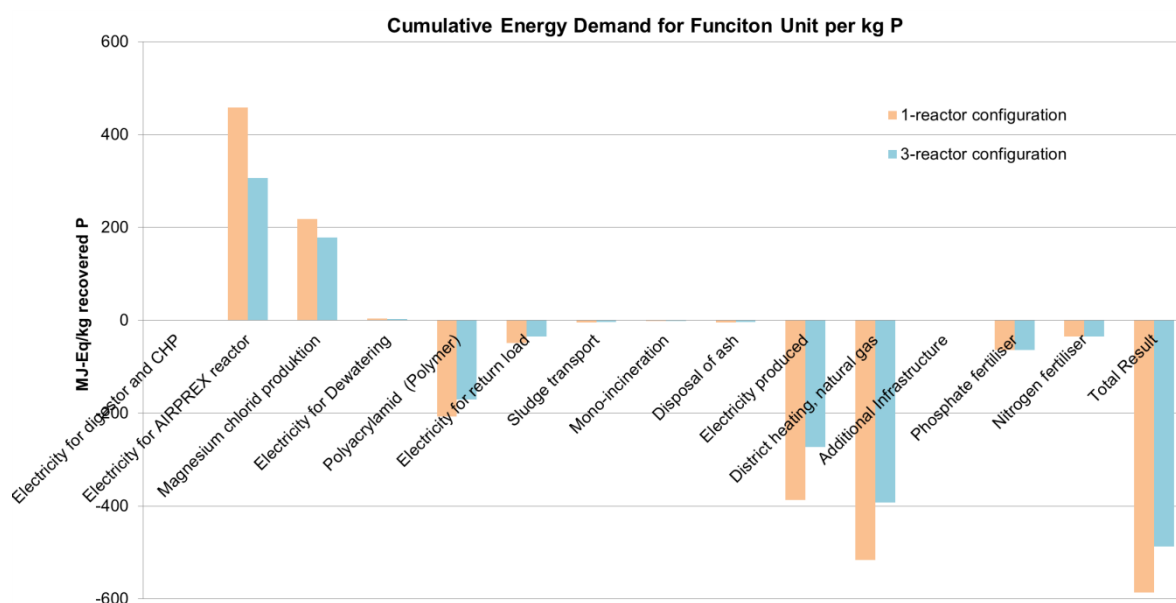
Figure 30: Total Cumulative Energy Demand for FU per kg P production

For a better understanding of the environmental impact of one kg of recovered P, the total cumulative energy demand is also calculated for the function unit per kg of produced phosphorus (Figure 30). In scenario 1 and scenario 2 the harvested P in struvite is 34198 kg/a and 55243 kg/a respectively. It can be observed that 3-reactor configuration has a lower energy and chemical demand per kg P for its AirPrex® reactor. The energy surplus is less than the one with 1-reactor configuration due to a much higher P harvested in struvite. In total, the net energy credits in 1-reactor configuration are -586 MJ/kg P and with 3-reactor configuration are -487 MJ/kg P. It is worth noting that the surplus of energy comes from sludge dewatering, polymer saving and disposal benefits, which is not directly related to the produced amount of P. Thus, considering the average demand for energy per kg P and the amount of phosphorus produced, the new reactor shows a better performance.

- **Global Warming Potential (GWP)**

Global warming potential (GWP) is typically closely related to fossil energy demand, as greenhouse gases are mainly emitted from the combustion of fossil fuels (Remy et al., 2015). The CO_2 footprints in this study include fossil CO_2, N_2O, CH_4. The additional AiPrex® reactor and $MgCl_2$ production caused an increased impact of approximately 1 million and 0.5 million kg CO_2 –eq (Figure 31). The negative net impact means the equivalent CO_2 emissions are reduced in relation to the reference state. These shares are caused by the mono-incineration plant, polymer, electricity for return load, WWTP and the credits of P- and N-fertilizer. The major credits in the system come from the mono-incineration plant (heating, natural gas and electricity produced). If the sludge disposal was not considered, the net values would be positive.
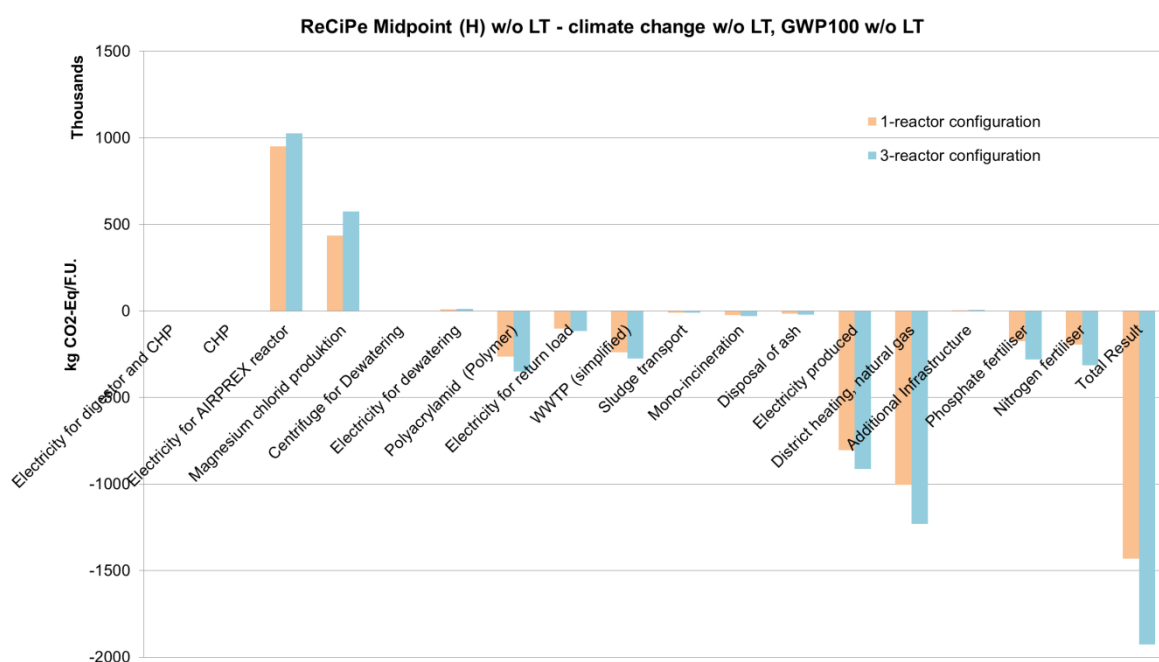
Figure 31: Global Warming Potential

In total, Scenario 2 has a net GWP of -1.9 million kg CO_2-eq and Scenario 1 has 1.4 million kg CO_2-eq. In Scenario 2 about 36% equivalent CO_2 emissions are reduced. Regarding the FU per kg produced P, net impacts are -41.8 kg CO_2-eq/kg P (Scenario 1) and -34.9 kg CO_2-eq/kg P (Scenario 2).

- **Fresh Water Eutrophication Potential (FEP)**

Freshwater eutrophication (FEP) is caused by phosphorus emissions. As shown in Figure 32, reduction in FEP is mainly related to direct reduction of P emissions from the mainstream WWTP. Other factors e.g. production of electricity for the AirPrex® reactor (P emissions caused by raw material mining), saved electricity in mono-incineration and substitution of mineral P fertilizer production (which is associated with P emissions into water) also contribute to the total results, though to a lesser degree.
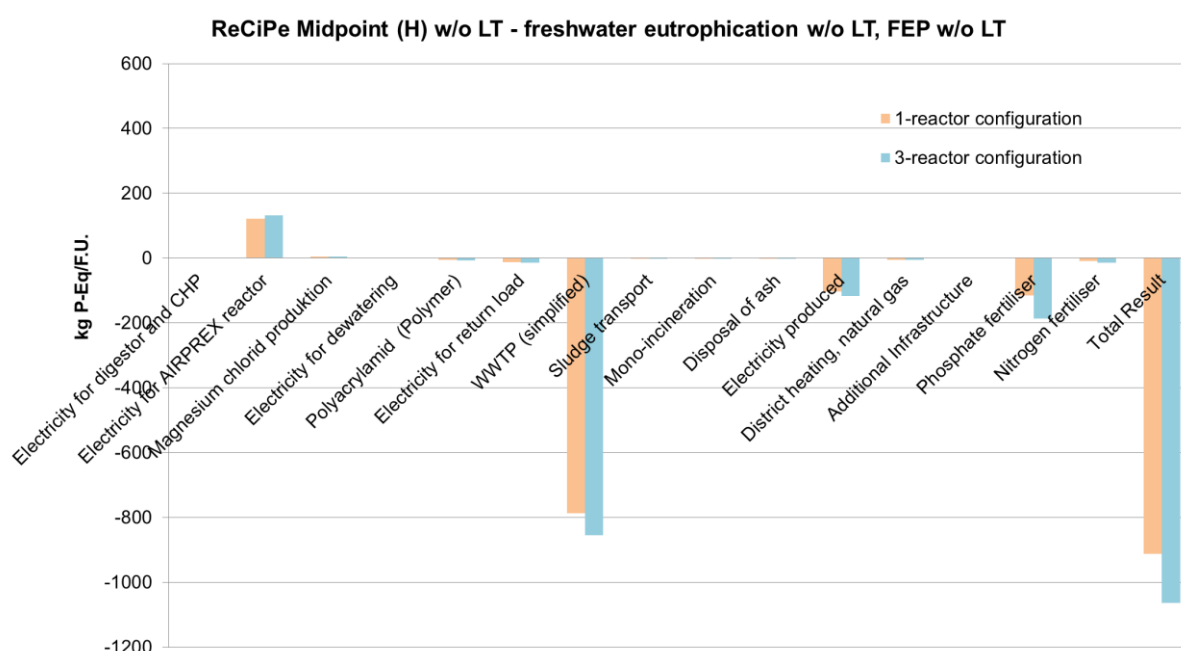
Figure 32: Freshwater Eutrophication Potential

In the model of simplified wastewater treatment plant, the removal rate of phosphorus is defined. Therefore, a higher influent concentration may cause higher emissions under this hypothetical condition. The AirPrex® system reduce the P from sludge liquid, thus reducing the considerable P return load to the mainstream WWTP and consequently its direct P emissions. Hence, totally, FEP can be reduced in AirPrex® Scenario 1 by -912 kg P-eq/a and in Scenario 2 by -1064 kg P-eq/a. Overall, Scenario 2 has a higher reduction (16.7%) of P emissions than Scenario 1 and this is mainly due to the higher P-harvesting in sludge and therefore lower residual phosphate in return loads. Regarding the FU per kg of recovered P, in Scenario 1 the FEP can be can reduced by 0.0267 kg P-eq/kg of recovered P and in Scenario 2 by -0.0193kg P-eq/ kg of recovered P.

- **Marine Eutrophication Potential (MEP)**

Marine eutrophication is caused by nitrogen emissions. As shown in Figure 33, the dominating impacts of MEP are the emission from the AirPrex® reactor and the discharge by the WWTP.
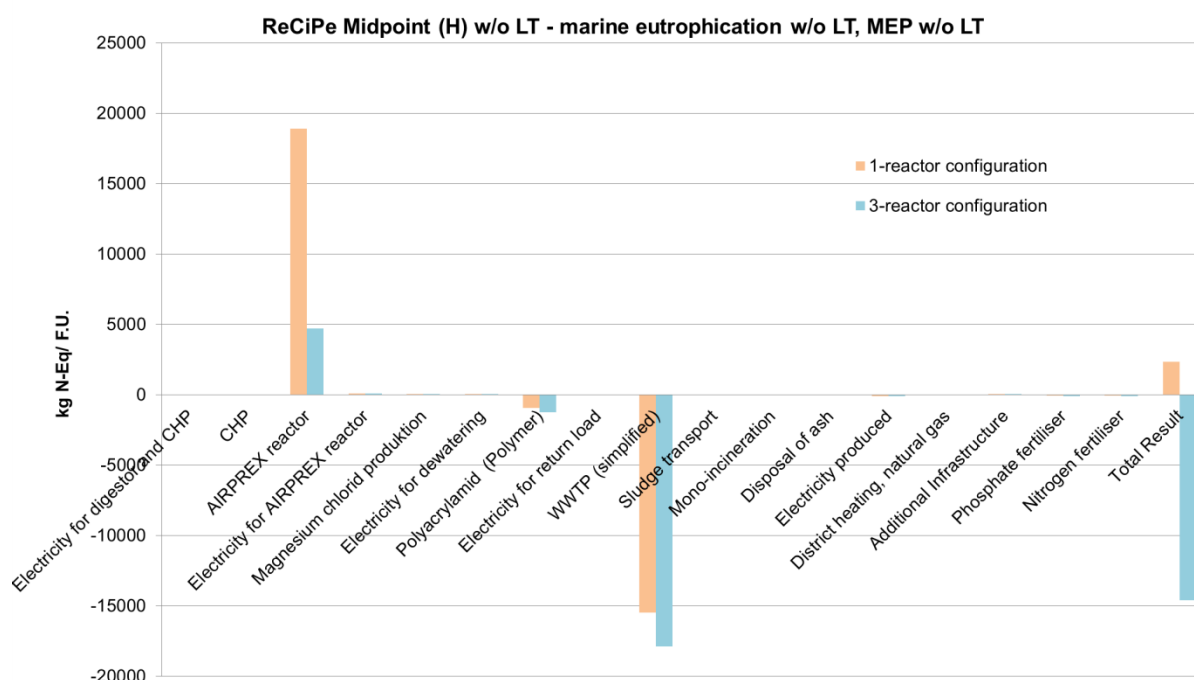
Figure 33: Marine Eutrophication Potential

The AirPrex® reactor in 1-reactor configuration is uncovered and part of in the ammonia gas in digested sludge is discharged directly into air. Calculation the ammonia concentration in the sludge before and after AirPrex®, about 8% of ammonia was emitted into the atmosphere. The aeration reactor in 3-reactor configuration is closed and the off gas is treated in a biofilter and therefore a 2% loss is taken into account. In scenario 1, the benefit of return load reduction (15481 kg N-eq per year) is offset by the ammonia emission from the AirPrex® reactor (18,908 kg N-eq per year), and finally with a total net impact of 2,357 kg N-eq per year. Scenario 2 emits 4,727 kg N-eq per year into the air and reduces 17,878 kg N-eq per year from the return load. Thus, a net redution of 14,615 kg N-eq per year is achieved in scenario 2. The net impacts per kg P are 0.069 kg N-eq/kg P and -0.264 kg N-eq/kg P. Thus, scenario 2 has improved the marine eutrophication impact significantly due to the lower ammonia gas emissions and lower nitrogen concentration in the return load.

3.5 Conclusion

In this study, LCA is used to compare 1-reactor system versus 3-reactor system of AirPrex® process and to find an orientation towards environmentally friendly reactor system. In the following, the most important findings are summarized.

Compared to the reference system, which is defined as the sludge line treating the mixed sludge at WWTP Wassmannsdorf, both AirPrex® configurations have positive energy benefits and better environmental credits for the GWP, FEP, and MEP. The most important contributors to the energy impacts in 3-reactor configuration are electricity for AirPrex® reactor (62.6%) and production of magnesium chloride (36.5%) while the main energy benefits are from the heat for district heating to substitute natural gas (40.2%), electricity production in mono-incineration (20.9%), reduced polymer demand (17.5%), the substitution of conventional N and P-fertilizer (10%) and the reduced electricity for return load (3.5%).

The AMS reactor shows better results in cumulative energy demand with 35% improvement of energy surplus, 36% reduction of global warming potential and lower eutrophication potential. The different results of both scenarios are mainly caused by the reactor design and the harvesting efficiency. The 3-reactor configuration has a better separation of crystals from the sludge due to a better crystallization condition in the first two reactors and an additional quiet condition for struvite precipitation in the third reactor. The higher the amount of struvite recovered, the more P- and N-fertilizer credits can be achieved. The TS improvement of dewatering in 3-reactor configuration has the most important impact on the CED and GWP benefits while the return load of WWTP. Ammonia gas emissions have the most important impact on the FEP and MEP.

It is suggested that, when installing a new AirPrex® reactor, the 3-reactor configuration is recommended due to a higher struvite yield and a better environmental impact. Although the investment of 3-reactor configuration is ca. 30% higher than 1-reactor configuration, the additional investment can be returned through operational savings within 1 to 2 years. In WMD, the NH_3 emissions into the air can be reduced by instilling a biofilter. At the same time, it is also important to mention that, the further development of technology, e.g. AirPrex®, can be practiced not only in the laboratory or pilot plant but also in full-scale operation.

Chapter 4: Phosphorus recovery from municipal and fertilizer wastewater: China's potential and perspective

Graphical abstract

Municipal sludge

Potentail:
• 169,000 t P/a from 3500 WWTPs

Situation:
• low P concentration in sludge
• less combined Bio-P and anaerobic digestion
• chemical P removal dominant

Sludge ash

Potential:
• 10,775 t P/a from 9 monoincineration plants

Situation:
• low P concentration in sludge ash
• high sand content

Fertiliser industry wastewater

Potential:
• 12,000 t P/a from 1861 fertiliser procution plants

Situation:
• 60 Million/a wastewater disposal
• Phosphorus losses from phosphogypsum

Highlights:

- Review of current state of wastewater treatment plants and sludge treatment in China
- Assessment of discharged and recoverable P in Chinese wastewater
- A perspective on available technologies for P recovery according to specific conditions in China are presented
- Potentials and opportunities to recover and recycle phosphorus from wastewater were assessed
- Strategies and recommendations for future P-recovery in China

4.1 The importance of phosphorus recovery in China

On one hand, China has abundant phosphate rock deposits and is the world's largest producer (mining and processing) and consumer of phosphate rock. On the other hand, China is the second-largest economy and one of the largest water markets in the world. Considering the urbanization process in current China, the treatment capacity of WWTPs is expected to continue to grow in the next decades. Thus, from a global viewpoint phosphorus recovery in this country seems to have a good prospect.

China is a big country with a large population and limited farmland area per capita with only 0.08 ha per capita compared with the world average of 0.2 ha per capita in 2012, according to the World Bank (WB, 2014). The production of sufficient food to feed the population is of vital importance for the country. In the year 2001, phosphorus was identified by the Ministry of Land and Resources of the People's Republic of China (MLR, 2012a) as one of the most important 20 minerals which, after 2010, cannot meet the development needs of the national economy.

According to statistics from the United States Geological Survey (USGS, 2015), China's phosphorus reserves are 3.7 billion Megagram (Mg), 5.52% of the global total volume. Based on current phosphate rock mine production with 100 million Mg in 2014 (USGS, 2015), Chinese phosphorus ore may run out within 37 years. It is a remarkable fact that there is only little high-grade phosphorus ore, but the country is rich in low-grade phosphorus ore. More than 80% is low grade phosphate rock and the average grade only reaches 17% of phosphorus pentoxide (P_2O_5) (Huang et al., 2014; Lu, 2004).

In Europe, phosphate rock is officially considered to be one of the 20 critical raw materials by the European Commission in 2014 (EU-Commission, 2014). The recovery of phosphorus has been repeatedly discussed due to the strong dependency on imports of more than 90% (De Ridder et al., 2012) and the food security of the growing population worldwide. Various phosphorus recovery technologies have been developed and tested on a pilot or industrial scale. Among these technical options, phosphorus is mostly recovered by precipitation or crystallization processes in the form of HAP (hydroxyapatite, $Ca_5(PO_4)_3OH$) or struvite ($MgNH_4PO_4 \cdot 6H_2O$). The recovered products can be utilized as fertilizer in the agricultural or other specific industries.

Consequently, closure of the anthropogenic phosphorus cycle through recovery and recycling of phosphorus from municipal wastewater and sludge, as well as from special industry wastewater, may help to avoid eutrophication, promote resource conservation and increase the value chain efficiency of this precious resource.

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4.2 Status of the municipal wastewater infrastructure in China

4.2.1 The development of urban sewage treatment

In 1984, the first large-scale wastewater treatment plant (WWTP), the Tianjin Jizhuangzi wastewater treatment plant was built and put into operation with a treatment capacity of 260,000 m³ (Fu et al., 2008). After 1990, with the rapid development of the economy, rapid urbanization and industrialization and the increasing environmental standards in China, the wastewater treatment infrastructure stepped into a rapid development period and improved the quantity of wastewater treatment facilities and also the effectiveness of treatment.

Figure 34: Development of urban sewage treatment from 2005 to 2013 in China (MOHURD, 2016)

Figure 34 shows the development of the treatment capacity for urban sewage and the number of facilities from 2005 to 2013. During the past years, China's sewage treatment sector has experienced rapid development. In April 2015, the General Office of the State Council issued the "National Water Pollution Prevention and Treatment Action Plan of China" (MEP, 2015) to address nationwide water protection; the objective of municipal wastewater treatment is that by the end of 2020, the city and county municipal wastewater treatment rates should reach 95% and 85% respectively.

Although China's urban wastewater treatment industry has seen much progress in terms of scale and number since the 1990s, the conditions of the municipal water networks and the treatment rate in rural areas still need to be improved. In 2013, the wastewater treatment rate of the cities, counties, towns and villages were 89%, 79%, 19%, 5% respectively (MOHURD, 2016). The majority of wastewater generated in rural areas undergoes limited treatment or is discharged to water bodies without treatment. According to the corresponding population

distribution in different areas (MOHURD, 2016), 37% of the population is connected to wastewater treatment systems in China.

4.2.2 Wastewater treatment process in China

There are three major steps in state-of-the-art wastewater treatment schemes, i.e. primary physical treatment, secondary biological treatment and tertiary treatment (or effluent polishing) to further improve the effluent quality (Halling-Sørensen & Jorgensen, 1993). Most sewage treatment plants in China are centralized with biological wastewater treatment.
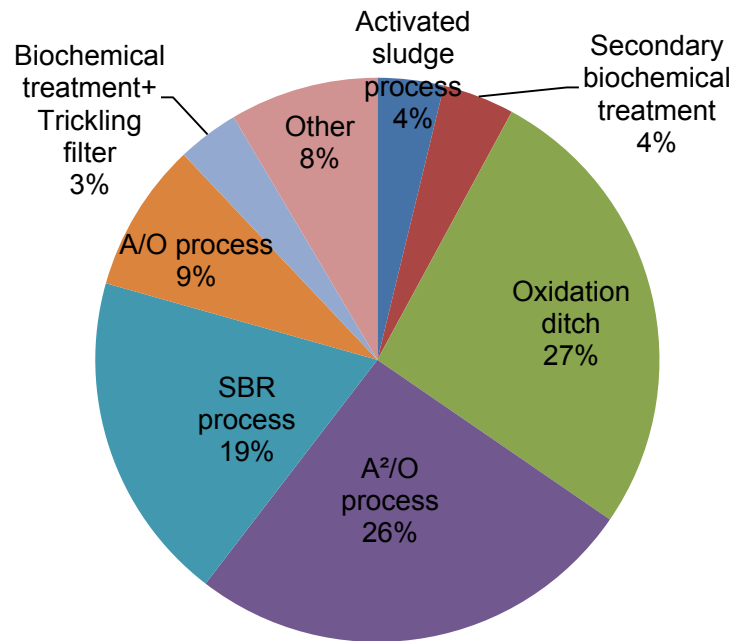
Figure 35: Variety of different processes of municipal WWTPs in China (MEP, 2014)

Figure 35 shows the variety and distribution of different processes of WWTP in China. According to the statistics of the Ministry of Environmental Protection of the People's Republic of China (MEP, 2014) for 4,136 commissioned wastewater treatment plants in 2013 (include urban sewage treatment and industry wastewater treatment plants), the most widely used technologies are the Oxidation Ditch Process with a share of 27%, the Anaerobic-Anoxic-Oxic (A^2/O) process with a share of 26% and the Sequencing Batch Reactor (SBR) process with a share of 19%.

3% of super-large-scale (>30×10^4 m^3/d) and 13% of large-scale (10-30×10^4 m^3/d) WWTPs were built in large (>1,000,000 population) and medium-sized (500,000-1,000,000 population) cities. Most of these plants apply the A^2/O process. The percentage of medium-scale (1-10×10^4 m^3/d) WWTPs was 75%. They were generally built in medium-sized and smaller (< 500,000 population) cities and commonly apply the oxidation ditch and SBR processes (Jin et al., 2014).

4.2.3 Phosphorus removal in WWTPs

Two methods are currently being used around the world to remove phosphorus from wastewater: biological and chemical phosphorus removal and combination of both. In China, influent NH_4-N ranges from 40 to 55 mg/l, and total phosphorus (TP) ranges from 4 to 9 mg/l (Jin et al., 2014). According to the "Discharge standard of pollutants for municipal wastewater treatment plant" (GB18918-2002), the primary A standard of total phosphorus concentration in WWTPs effluent built after 2005 should not exceed 0.5 mg/l. It is quite difficult to meet this requirement with biological phosphorus removal alone (Qiu & Ding, 2002). A potential reason for the low efficiency of enhanced biological phosphorus removal (EBPR) is the competition for carbon sources between denitrification and phosphorus release in sludge under an anoxic condition with respect to the sludge retention time (SRT) demand, the nitrate inhibition of phosphate release, which is not easily resolved (Chen et al., 2011; Peng et al., 2010; Qiu & Ting, 2014).

4.2.4 Sewage sludge treatment in China

In China, thickening, conditioning and dewatering are the three most applied methods for sludge treatment (Yang et al., 2015). There is no accurate official data of sludge disposal in China, rather conflicting sources with different estimates. According to (Yang et al., 2015), more than 84% of sludge is disposed by improper dumping. Regarding proper disposal, the most commonly used method is sanitary landfill (13%), followed by land application (2%), incineration (0.4%) and building materials (0.2%). Other data (Wang et al., 2015) indicates that, the most widely used disposal route was landfilling with a share of 63%, followed by compost and agricultural use with a share of 14%, incineration with a share of 2%. The disposal route for approx. 22% of sludge is unknown. Many WWTPs in China did not report clearly the treatment and final disposal of their sludge (Jin et al., 2014). In general, the majority of sludge is often processed without stabilization or drying and disposed to sanitary landfill or dumping sites.

So far, sludge digestion (AD) has not been used widely in China. Until 2010, only about 50 WWTPs adopted AD to stabilize sludge and some of them were not under stable operation or were even closed (Kong, 2012). The main problems for sludge digestion are the lack of an overall development plan on AD, the technical design parameters of sludge digestion not matching the specific local condition. On the other hand, the utilization and efficiency of sludge digestion in China is not high due to the low production of gas and the lower economic benefit. The technical reasons are the high sand content and less volatile organic compounds with 30-50% in the sludge (Dai et al., 2014). Based on the overall situation in China, thickening-anaerobic digestion-dewatering and following land application (does not include agricultural use) can be considered as the main technical route of sludge treatment and disposal in the future. This route is favorable for large-scale and medium-scale WWTPs due to the limited land resources in the city and shortage in energy supply in economically developed regions (Yang et al., 2015).

4.3 Materials and methods

Phosphorus recovery and recycling options need to be ecologically sound, socially acceptable and economically and technically feasible. Based on real operational data and samples from selected WWTPs in China and available technical solutions in the EU research and demonstration project P-REX (www.p-rex.eu), a systematic analysis of different options was conducted.

The total concentrations of phosphorus and nitrogen in sludge water, supernatants and centrates and were determined by spectrophotometry according to the respective Chinese standards (GB11893-89; HJ636-2012). Ammonia nitrogen was determined with titration according to (GB7478-87).

The sludge water samples were taken from WWTP A in China from January to May 2014. The influent and effluent of the WWTP were analysed every two days. Other supernatants and centrates were analysed every second week.

For the determination of iron (Fe) and aluminium (Al) in sludge and sludge ash, samples were digested with nitric acid/hydrochloric acid according to ASTM D3974-09 and measured in accordance with US EPA 6010/ICP-OES and US EPA 6020/ICP-MS. For the determination of phosphorus, samples were digested with sulphuric acid according to the APHA 4500P B, H.

The tested sludge and sludge ash samples were taken from incineration Sludge Treatment Facility in Hongkong from December 2014 to January 2015.

4.4 Potential and options for phosphorus recovery in China

In the year 2013, there was a total of 45.1 billion m³ (MOHURD, 2016) of municipal wastewater treated in counties and cities. The total phosphorus concentration in the WWTP influents ranged from 4 to 9 mg/l (Jin et al., 2014). Based on the average value of 6.5 mg/l, the phosphorus discharged to municipal wastewater in cities and counties added up to approximately 293,163 Mg in 2013. The quantity of this phosphorus in municipal wastewater in 2013 corresponded to 6% of the chemical fertilizer phosphorus (P) consumption of 5.3 teragram (Tg) (Li et al., 2015) in 2010 in China.

According to a statistical analysis of 98 WWTPs in China (Guo et al., 2009), the total P concentration in municipal sewage sludge varies significantly, from a low of 2.2 g/kg of sludge dry matter to 51.3 g/kg (Li et al., 2003) with a mean value of 22.2 ± 6.64 g/kg. The treatment plants with high P concentration in the sludge are mostly located in phosphate mining areas or in highly developed areas, e.g. Yunnan or Hong Kong. With the dry sludge production of 7.55 million Mg in 2013 (MOHURD, 2016) and the content mean value for phosphorus, the total phosphorus that is contained in the current Chinese sewage sludge is estimated to be 167,634 Mg/a, or in other words, 57% of the totally discharged phosphorus. This low rate of P in sludge might be due to the dilution in sanitary sewers by infiltration and inflow, which causes low phosphorus influent with average value of 6.5 mg/l.

At a municipal wastewater treatment plant, phosphorus can be recovered and recycled mainly from three locations. The first is direct land utilization of sewage sludge, the second includes the dissolved P in the aqueous sludge phase prior to dewatering and sludge liquor after dewatering and the third is the recovery from mono-incineration ash.

Plant availability and P uptake from different P products of P recycling has been tested (Achat et al., 2014; Kataki et al., 2016; Römer, 2013; Wilken et al., 2015). Products from precipitation processes Mg compounds consistently showed a better P supply in relation to comparable Ca compounds. With struvite, the same P uptake as in triple super phosphate (TSP) was reached.

The traditional land utilization of sewage sludge in agriculture is being considered as one of the most economical ways for sludge disposal, but the presence of toxic heavy metals, organic contaminants and pathogens in the sewage sludge greatly limits its direct use as a fertilizer. According to a study of heavy metals in sewage sludge all over China (Guo et al., 2014), the concentration of Cu, Zn, Cd, Hg, and Ni in alkaline soils about 2%, 6%, 6%, 3%, 4% of the samples exceeded the limits set by the "Discharge Standard of Pollutants for Municipal Wastewater treatment plants" of China (GB18918-2002). In acid soils the non-attainment rates of Cu, Pb, Zn, Cd, Hg, Cr and Ni were 7%, 1%, 10%, 27%, 20%, 2% and 12%, respectively. The main sources of the heavy metals may be derived from high-density industrial zones, non-ferrous metal ores and anthropogenic activities (Guo et al., 2014). The source control of wastewater, especially the industry wastewater, can help decrease the amount of heavy metals entering the sewers and ensure the quality of sludge. Agricultural soils are also significantly influenced by Cd, Hg and Pb derived from anthropogenic activities (Wei & Yang, 2010). The use of sewage sludge on agricultural land is strictly limited. The

amount, duration and quality of sludge applied to agriculture should meet the requirements of the "Control Standards for Pollutants in Sludges from Agricultural Use" (GB4284-84) and other existing relevant agricultural standards and regulations. Hence, cost-effective alternative strategies and technologies for phosphorus recovery for agriculture are needed.

4.5 Results and discussion

4.5.1 Option 1: Recovery from digested sludge

Dissolved phosphorus is recovered directly from the digested sludge. In the AirPrex® process, the struvite is crystallized within the wet sludge and can, therefore, prevent down-stream struvite scaling and, at the same time, improve the sludge dewater ability by 3–6 % dry matter content and save the polymer costs for sludge dewatering (Heinzmann & Lengemann, 2011).

Table 18: Anaerobic sludge digestion projects in China

Name	Wastewater Treatment process	Sludge Treatment capacity (Mg DS/d)	Disposal	year of operation	Reference
Beijing Gaobeidian	active sludge treatment process	160	-	1999	(Jiang, 2014)
Beijing Xiaohongmen	AAO process with biological phosphorus removal	160	land application	2009	(Chen, 2013; Zhang et al., 2014)
Chongqing Jiguanshi	reversed AAO process, combined biological and chemical phosphorus removal	90	co-incineration and land application	2009	(Zhang, 2009)
Dalian Xiajiahe	Constant Waterlevel SBR with biological P-removal	120	land application	2009	(Dai et al., 2008; Yang et al., 2015)
Haikou Baishamen	activated sludge and biological aerated filter, chemical phosphor removal	100	agricultural use	2005	(Pan et al., 2006; Sun et al., 2008)
Qingdao Maidao	Enhanced clarification and lamella settling with biological aerated filter (BAF)	21.8	land application	2008	(Wang et al., 2012)
Shanghai Bailonggang	AAO process with chemically enhanced primary treatment	204	land application	2011	(Jiang et al., 2013)
Wuhan Sanjintan	modified A/O process with biological phosphorus removal	40	land application	2013	(Zhu, 2009)
Zhengzhou Wangxin	AAO process with biological phosphorus removal	66	-	2009	(Li et al., 2007)
Tianjing Jizhuangzi (Tianjing Jinnan sludge treatment plant)	AAO process with deep bed filtration, combined biological and chemical P-removal	160	land application	2015	(NCME, 2013)

In Table 18 selected sewage sludge digestion projects in China are listed. These WWTPs are mostly operated with combined biological and chemical removal of phosphorus. Among

them, several plants have reported that struvite precipitation has been a problematic issue, e.g. Shanghai Bailonggang (Jiang et al., 2013), Haikou Baishamen (Pan et al., 2006). For most of these plants with anaerobic digestion, land application is the first choice for sewage disposal.

This option is designed for a significantly higher efficiency at WWTPs with biological Phosphorus elimination (Bio-P) and sludge digestion. However, for the phosphorus that is fixed within the sludge, after chemical precipitation with ferrous or ferric, aluminum, direct struvite crystallization is not a suitable option for recovery. Hence, with the current sewage and wastewater treatment facilities in China, only a few WWTPs are adapted to this option, such as Dalian Xiajiahe, Wuhan Sanjintan Beijing Xiaohongmen WWTP etc. The current limits of this option for the WWTPs in China are the shortage of combined biological phosphorus removal and anaerobic sludge digestion.

4.5.2 Option 2: Recovery from sludge water

Phosphorus is recovered from the supernatants of the digested sludge after liquid-solid separation. In the Struvia™, Pearl®, and Airprex® process, an important component of these technologies are crystallization reactors. In these processes, struvite is precipitated by dosing $MgCl_2$ and increasing the pH by adding caustic soda (NaOH) or aeration.

Table 19: Parameters of sludge water in WWTP A in China (mean value)

	Influent	Effluent	Supernatant Pre-thickener before digester	Supernatant Post-thickener after digester	Centrate after dewatering	Total returns
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Total Nitrogen	23.9	19.8	391	614	533	320
NH_4-N	19.0	15.6	325	489	398	249
Total Phosphorus	3.5	2.0	205	289	238	180

Municipal wastewater treatment plant A in southern China has a capacity of 300,000 m³/d, and the wastewater is treated with an activated sludge process and before discharge to the deep sea. After digestion, phosphate is released into the liquid phase, in which the total phosphorus increases from 205 mg/l to 289 mg/l (Table 19). Under specific conditions, this phosphate reacts with magnesium and ammonium and builds up struvite in pipes and dewatering facilities, which needs to be cleaned every one or two weeks by high pressure water in this plant. The replacement of pipelines with external mechanical cleaning is also used to cope with the scaling problem in another WWTP on the east coast of China. Mechanical treatment is preferred due to economic reasons, i.e. the low cost of manpower, compared to the chemical treatment by anti crustration agents. In the Tianjing Chennan

sludge treatment plant, P recovery from sludge water with the AirPrex® process was constructed in 2016.

Regarding the high soluble phosphorus and ammonia concentration in centrates in such plants in China, techniques are available, to recover 80–90% of the dissolved phosphorus (Niewersch et al., 2014) in sludge water. The limits of this option are that no more than 20% of a WWTP's phosphorus load can be recovered, and this only if enhanced biological P removal is applied. Furthermore, its economic viability should be considered.

4.5.3 Option 3: Recovery from sludge water with sludge extraction

Phosphorus is recovered from the supernatant of the digested sludge after acidic leaching or thermal hydrolysis pre-treatment and followed by liquid-solid separation e.g. the Gifhorn, Stuttgart and ExtraPhos® process.

Due to the additional increase of 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. Hence, with the current sewage and wastewater treatment facilities in China, Shanghai Bailonggang, Haikou Baishamen and Tianjing Jinnan WWTP, among others, are technically suitable for this option. However, it was shown that with the current reagent strategies and investment costs, the struvite recovery process was not economically feasible for WWTPs with AD and P-physicochemical removal, only in the case of Bio-P removal WWTPs with AD (Garcia-Belinchón et al., 2013).

4.5.4 Option 4: Recovery from sewage sludge ash

The P recovery from sewage sludge ash (SSA) is generally divided into two approaches: the wet-chemical (LeachPhos) and thermal processes (AshDec). Wet-chemical approaches consist of an acidic or alkaline digestion of SSA followed by a separation of P from dissolved (heavy) metals and organics. In Germany, 54.7% (Wiechmann et al., 2015) of the sludge is incinerated, but only about 3.45% (Fang et al., 2012) of sludge in China is treated by incineration. The quantity of recoverable phosphorus in sludge ash in China is not calculable due to the lack of reliable mono-incineration data.

Table 20: Analysis of selected parameters of composite sludge feed to incinerator and sludge ash in the Sludge Treatment Facility in Hong Kong, China

	Sludge				Sludge Ash			
	% Moisture Content (dried @103°C)	% P Dry Matter	% Al	% Fe	% Moisture Content (dried @ 103°)	% P Dry Matter	% Al	% Fe
Test on December 4th, 2014	69.3	0.925	0.577	3.1	0.1	2.74	2.74	10.9
Test on on January 2nd, 2015	67.2	1.12	0.78	2.85	2.1	5.25	3.8	12.7
Mean	68.25	1.023	0.679	2.975	1.1	3.995	3.27	11.8

The Sludge Treatment Facility (STF) in Hongkong is the world's largest sludge incineration facility with a capacity of 600 Mg of dry sludge per day. The facility adopts fluidized bed incineration technology to decompose sewage sludge at 850°C. In Table 20, the selected parameters of composite sludge feed to incinerator and sludge ash are presented.

SSA in the STF of Hongkong contains a phosphorus (P) concentration of around 4%, which, compared to the mean phosphorus content in Germany of 8.9% (Krüger & Adam, 2015b) is only half of the content. The concentrations of aluminum (Al) 3.3% and iron (Fe) 11.8% in Hongkong are similar to the mean value in Germany, 5.2% and 9.9% respectively (Krüger & Adam, 2014). For elementary white phosphorus P_4 production with the Thermphos process the molar ratio of Fe/P reaches about 0.6 in Hong Kong, exceeding the limit value of 0.2 (Petzet & Cornel, 2009). The high iron concentration in SSA increases the energy demand and reduces the output of P_4. Although approximately 2000 t P/a can be recovered in this plant with the current available technology, the relatively low phosphorus concentration should be considered to ensure the economic viability. The limitation of this option in China is the low P concentration in sludge ash compared to Europe.

4.5.5 Option 5: Recovery from fertilizer industry wastewater

Various industries produce wastewater that contains a high concentration of phosphorus. This includes fertilizer, semiconductor, phosphoric acid processing and swine wastewater (Hao et al., 2011). The mentioned processes (Struvia[TM], Crystallactor, Pearl[®], AirPrex[®] etc.) for sludge water are also applicable to industrial wastewater containing a significant concentration of dissolved orthophosphate.

China is not only the largest phosphorus consumer but also the largest producer. There were 1,118 phosphate fertilizer enterprises in China in 2005 (Zhang et al., 2009), and in the plants, a significant amount of wastewater containing phosphate and fluoride is generated. The use of lime as a precipitating agent for fluoride and phosphate can be considered as the most common technique for wastewater from phosphate fertilizer plants (Grzmil & Wronkowski,

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2006). But the large amount of phosphorus in the wastewater cannot be directly recycled in agriculture due to the low plant availability of fluorapatite (Manahan, 1997; Ndala et al., 2010). A controlled phosphorus recovery with separate precipitation of fluorides and phosphates in a two-stage process would be an adapted option. It was found that, by acting on precipitation pH ranging from 2.6 to 3.7, a "selective" removal of 97–98% fluoride from phosphoric acid/hydrofluoric acid mixture was possible while that of phosphate did not exceed 6–8% (Gouider et al., 2009). It can also be observed that, using calcium, fluorides were mainly separated (pH 3) in the first stage, and phosphates (pH 8) were mainly separated in the second stage amounting to approx. 85–88% and approx. 63–73%, respectively. (Grzmil & Wronkowski, 2006).

Table 21: Different streams and compositions of wastewater in a fertilizer plant in China [a]

	Wastewater flows (m^3/h)	COD (mg/l)	NH_4-N (mg/l)	F^- (mg/l)	TP (mg/l)	SS (mg/l)	pH	TN (mg/l)
Ammonia Wastewater	200	300	300	/	/	200	8	300
Phosphate fertilizer Wastewater	200	/	50	80	240	100	5	50

[a] Data came from the operator of wastewater treatment plant

Table 21 shows the different streams and compositions of wastewater in a big fertilizer plant in the east of China. The WWTP has two major types of wastewater: ammonia wastewater with 300 mg/l ammonia-nitrogen from synthetic ammonia production and phosphorus-containing wastewater with 240 mg/l total phosphorus from phosphate fertilizer production. The high concentration of both components in the wastewater provides a good possibility for producing magnesium ammonium phosphate. The excess ammonium in the wastewater, with a molar ratio (N:P) of more than 1, is also beneficial for struvite precipitation (Warmadewanthi and Liu 2009). For struvite formation in this fertilizer wastewater plant, an additional magnesium source is needed. A high calcium content in wastewater resulted in more calcium compounds rather than struvite in the precipitations (Hao et al., 2008). In this wastewater treatment plant approximately 1,800 t of struvite can be recovered annually by the technology currently available, and the product can be sold directly to customers. Unlike in Europe, China is abundant in phosphate fertilizer plants, which produce a large amount of wastewater with a high concentration of phosphate and ammonia. Wastewater treatment with P recovery can provide a promising prospect for future P recovery in an ecologicallly and economically efficient way.

4.6 Summary and perspective

Growing urbanization in China caused a rising trend in municipal wastewater and sewage sludge discharges. The contained phosphorus is not yet recycled and ends up in water bodies or landfills.

An analysis of the potential and limitations of existing P recovery technologies, taking into account their applicability to different types of WWTPs in China, shows that a huge amount of phosphorus is transferred to wastewater and sludge. However, some limitations should be taken into consideration, e.g. the existing WWTP infrastructure and sludge disposal routes.

From a long-term perspective, anaerobic digestion followed by land application can be considered as the main technical route of sludge disposal for large-scale and medium-scale WWTPs. In this way, a large part of the phosphorus will be recycled in lands, gardens or parks in China. However, the quality of biosolids for land application should be strictly controlled. On sloping land there is the risk of runoff reaching watercourses and causing water pollution. It is in this sense that a clean sludge also gives cleaner water.

For the WWTPs with struvite incrustations, the P recovery from sludge can be seen as the best option to solve this problem instead of frequent mechanical cleaning. In most cases of recovery from sludge water, dissolution of P from solid sludge into the aqueous phase is needed. In special cases, sludge with an extremely high concentration of phosphorus potentially provides positive outcomes for the recovery of phosphorus, such as in Yunnan and Hongkong.

The average concentration of phosphorus in SSA in China is lower than that in Germany due to the high sand content in sludge and a lack of separation of rain water and municipal sewage.

Therefore, the ash option is limited due to the low rate of mono-incineration and the low P concentration in SSA.

Therefore, the following suggestions for future P recovery in China are:

- Increasing wastewater collection and improved the phosphorus removal
- Promotion of sludge digestion and Bio-P and withdrawal from precipitation with iron salts
- A development strategy for a long-term perspective in sustainable P-recovery
- A legal framework governing recycling and the market for fertilizers
- Development of business models for companies utilizing P streams from wastewater
- Encouragement of research and promotion of a new treatment technology for P rich wastewater

4.7 Conclusion

There is no doubt that phosphorus is a finite resource. Most of the P recovery technical options for municipal WWTPs face strong limitations in China, therefore, more efforts should be taken to increase both energy and resource efficiency. The recovery from industrial wastewater with a high concentration of phosphorus shows a higher potential than in municipal WWTPs due to easier market access and benefits to its operators. With an expected increasing percentage of municipal sewage sludge digestion and biological phosphorus removal, P recovery as struvite and recycling as fertilizer is recommended as one of the favorable options for P recycling.

Chapter 5: Phosphorus recovery from Chinese fertilizer industry wastewater

Graphical abstract
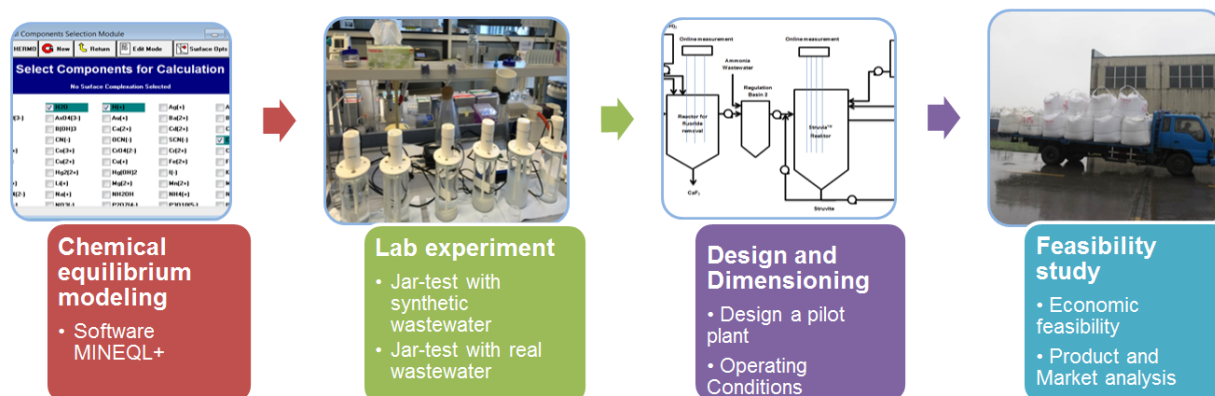
Highlights:

- A new approach for the treatment of fertilizer wastewater with P-recovery was developed
- Jar-Test with synthetic and real wastewater were conducted
- Design and dimensioning with P-recovery in a Chinese fertilizer plant
- The economic feasibility with this new concept was proved

A modified preprint version of this chapter is submitted to Elsevier Journal "Journal of Cleaner Production" (Date of submission 07 Nov 2017):

Zhou, K. *, Miehe, U., Kabbe, C., Barjenbruch, M., (2017): A new planning and design to achieve sustainable resource recovery from fertilizer wastewater

5.1 Phosphate fertilizer industry

There are large amounts of phosphate available in waste streams from e.g. agriculture, sewage treatment and from industrial side streams. Unlike Europe, China is abundant in phosphate rock deposits and is the world's largest producer of phosphate rock. China is also the largest fertilizer producing and consuming country in the world. China produced and consumed 28.1% of the world's NPK fertilizer in 2014 (IFA, 2017).

Over the past decade, domestic phosphate rock production has increased dramatically in China, from around 30 million tons in 2000, to approx. 70 million tons in 2010 and 120 million tons in 2015 (USGS, 2016). Figure 36 gives an overview of the phosphate fertilizer production in form of P_2O_5 in China and the rest of world from 1961 to 2014. China's share of phosphate production increased from 2.0% in 1961 to 20.6% in 2000 and reached 37.9% in 2014. At the same time, the make-up of Chinese phosphate fertilizer demand has changed significantly from relatively low-grade products like single super phosphate (SSP) and fused magnesium phosphate (FMP) to higher grade products such as triple super phosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) (Xiu, 2013).

	1961	2000	2014
China's Prodution	200	6759	16576
world Prodution	10110	32744	43704
China's share	2.0%	20.6%	37.9%
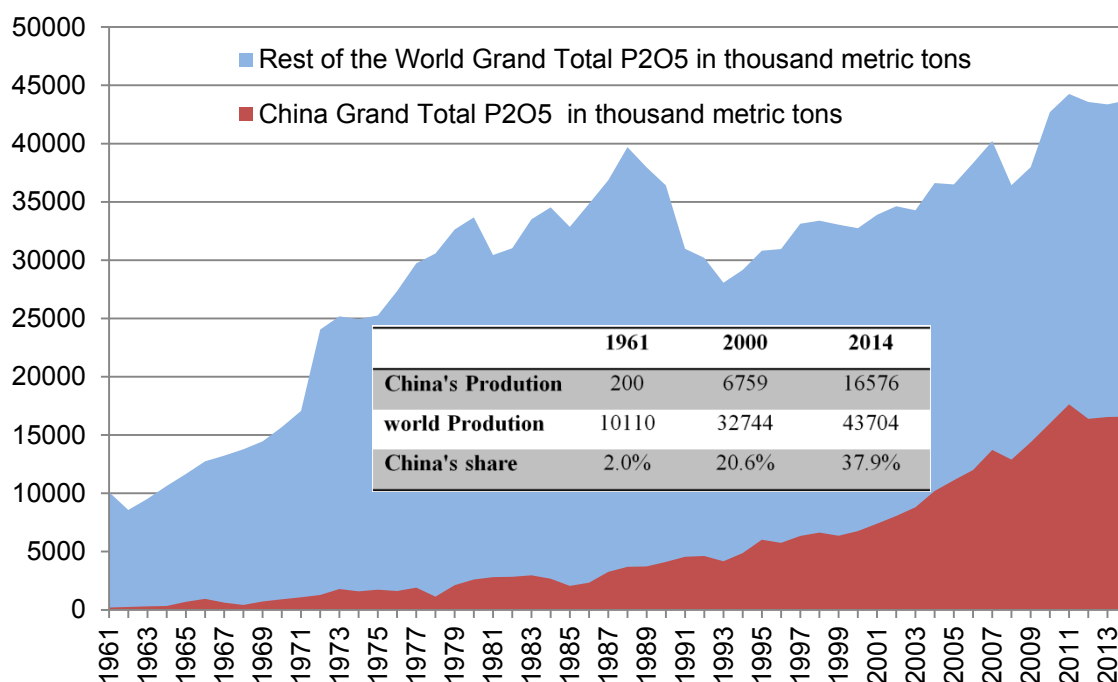
Figure 36: Phosphate fertilizer production in thousand tons P_2O_5 in China and the rest of world from 1961 to 2014 (IFA, 2017)

In 2014, a total of 16,576,000 tons P_2O_5 were produced in China. Based on the production process operated in fertilizer plant A, the plant creates 3.6 m^3 of wastewater to make fertilizer containing 1 ton of P_2O_5. It is estimated that 59,673,600 m^3 of phosphate production wastewater is produced in China per year. With a concentration of 200 mg/l phosphorus in these wastewaters, the Chinese phosphate industry wastewater contained about 12,000 tons P in 2014. This amount of P in wastewater is about 18% of the 65 000 t/a P (Adam et al., 2015) contained in German sewage sludge.

With the rapid development of the phosphate fertilizer industry in China, the quantity of industry sewage is also rapidly increasing. The new discharge standards of water pollutants for the phosphate fertilizer industry (GB15580, 2011), implemented in 2011, have put forward higher requirements for the fertilizer producers and encouraged them to develop cleaner production technologies and recover resource recovery from wastewater internally. There were 1118 phosphate fertilizer enterprises in China in 2005 (Zhang et al., 2009), and in these plants, a significant amount of wastewater containing phosphate and fluoride is generated. The use of lime as a precipitating agent for fluoride and phosphate can be considered as the most common technique for the treatment of wastewater from phosphate fertilizer plants (Grzmil & Wronkowski, 2006). But the large amount of phosphorus in the precipitate cannot be directly recycled in agriculture due to the low plant availability of fluorapatite (calcium fluorophosphate) (Manahan, 1997).

Several technologies have been developed in recent years to recovery phosphorous from wastewater, e.g. AirPrex®, Crystallactor, Pearl®, Struvia™, etc. (Kraus et al., 2016b). Unlike in Europe, most of the P recovery technical options for municipal WWTPs face strong limitations in China (Zhou et al., 2017). The recovery from phosphate industry wastewater with a high concentration of dissolved orthophosphate shows higher potential than in municipal WWTPs due to easier market access and benefits to its operators in China.

Over the years research has been conducted on industry wastewater from semiconductor and phosphoric acid processing wastewater that contains a high concentration of phosphorus. It was found that, by acting on a precipitation pH range from 2.6 to 3.7, a "selective" removal of 97–98% fluoride from phosphoric acid/hydrofluoric acid mixture was possible while that of phosphate did not exceed 6–8% (Gouider et al., 2009). It can also be observed that, using calcium, fluorides were mainly separated (pH 3) in the first stage, and phosphates (pH 8) were mainly separated in the second stage amounting to approx. 85–88% and approx. 63–73%, respectively. (Grzmil & Wronkowski, 2006). In the semiconductor industry, a selective separation of phosphate and fluoride and recovery of phosphate and ammonium as struvite were also studied (Warmadewanthi & Liu, 2009a; Warmadewanthi & Liu, 2009b). For the treatment of wastewater from semiconductor manufacturers, the presence of phosphate will compete with calcium ions and hinder the removal of fluoride (Huang & Liu, 1999). Experimental results in electronic wastewater also show the inhibitory effect of phosphate ion on fluoride removal not only through competition of calcium but also through differential reaction kinetics that calcium salt forms calcium phosphate precipitate faster than calcium fluoride under an alkaline pH (Yang et al., 2001). Consequently, higher calcium dosage is needed when dealing with fluoride-containing wastewater that contains phosphate (Huang & Liu, 1999).

The objective of this study is to identify the feasibility of phosphate recovery from fertilizer wastewater. A controlled phosphorus recovery with separate precipitation of fluorides and phosphates in a two-stage process were tested on a lab scale as an alternative option for the future fertilizer wastewater treatment process. The precipitation conditions were simulated with MINEQL+ software and the simulation results were compared with the results from the

laboratory jar test experiments. The feasibility of phosphate recovery at fertilizer production plant A is also discussed in this study.

5.2 Fertilizer wastewater characterization and treatment

5.2.1 Phosphate fertilizer wastewater

The primary products of the phosphate fertilizers industry are phosphoric acid, ammonium phosphate, and normal superphosphate. About 90% of the total world production of phosphoric acid is by the "wet process", which is based on the acidification of phosphate ores using sulfuric acid (Aly et al., 2013). A simplified process flow sheet for phosphoric acid production is shown in the Figure 37. The phosphate rock is mined, dried, crushed, and continuously fed into the reactor along with sulfuric acid. The reaction combines calcium from the phosphate rock with sulfate, forming calcium sulfate ($CaSO_4$), commonly referred to as gypsum and separated from the system by filtration. The separated crystals must be washed thoroughly to yield at least a 99% recovery of the filtrated phosphoric acid.
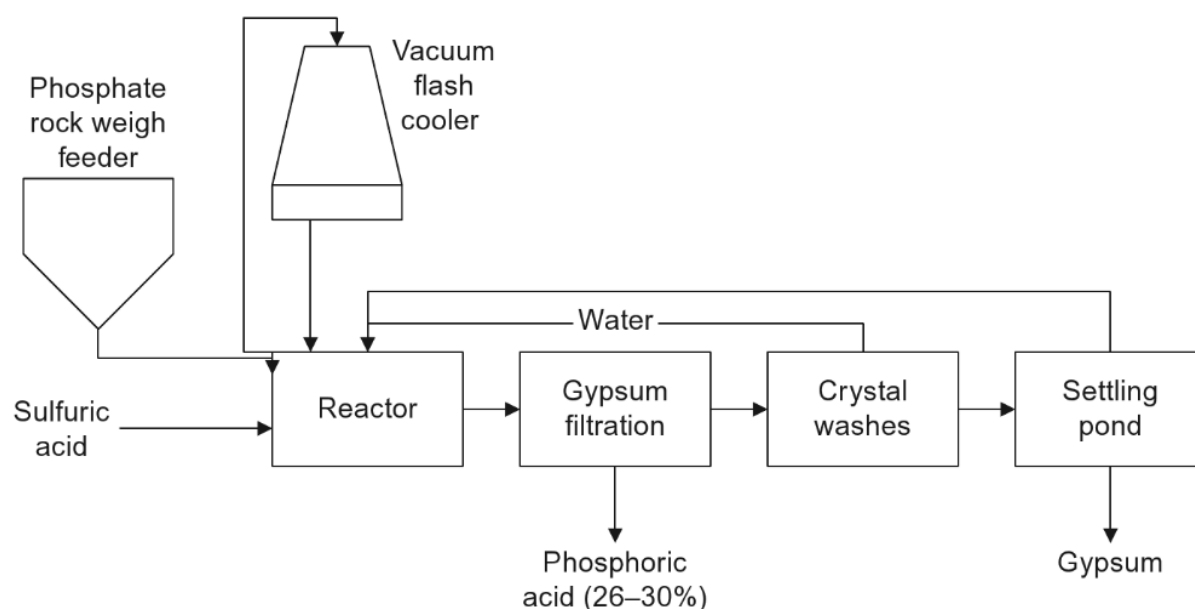
Figure 37: Process diagram for wet process dihydrate phosphoric acid plant (Cheremisinoff & Rosenfeld, 2010)

The major source of wastewater is pond water. Phosphoric acid production creates large quantities of pond water for cooling, concentration of the product and for processing and storage of the gypsum by product. Gypsum slurry water is decanted from the top of the gypsum stacks and sent to the cooling pond through collection ditches (Cheremisinoff & Rosenfeld, 2010). The wastewater is acidic and contains significant amounts of both fluoride and phosphate.

The effluent wastewater from the phosphate acid production plant was not amenable to biological treatment due to the low BOD and COD ratio and very low pH (Yapijakis & Wang, 2006). The most common method for removing phosphorus und fluoride is lime neutralization and coagulation settling using lime, aluminum, Fe salts and polyaluminumchloride (PAC).

5.2.2 Nitrogenous fertilizer wastewater

The major nitrogenous fertilizers include synthetic ammonia, ammonium nitrate, and urea. Synthetic ammonia (NH_3) is produced by reacting hydrogen with nitrogen at a molar ratio of 3:1. Nitrogen is obtained from the air, which is primarily comprised of nitrogen (78%) and oxygen (21%). Hydrogen is obtained from either the catalytic steam reforming of natural gas or naphtha, or as the byproduct from the electrolysis of brine at chlorine plants. (Cheremisinoff & Rosenfeld, 2010)
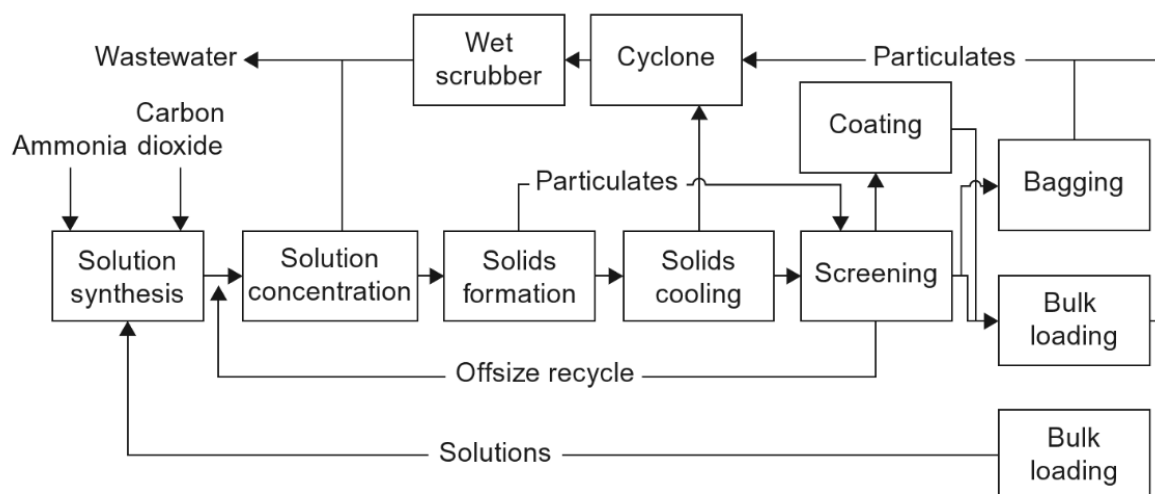
Figure 38: Process diagram for ammonium nitrate and urea manufacturing (Cheremisinoff & Rosenfeld, 2010)

The production of urea (NH_2CONH_2) is shown in Figure 38. Ammonia (NH_3) reacts with carbon dioxide (CO_2) to form ammonium carbamate ($NH_2CO_2NH_4$). The ammonium carbamate is then dehydrated to yield 70%-77% aqueous urea solution. Urea solution can be used as an ingredient of nitrogen fertilizer solutions, or it can be concentrated further to produce solid urea (Cheremisinoff & Rosenfeld, 2010).

In ammonia production, wastewater is generated from process condensate stripping. Ammonium nitrate manufacturing produces process water in the neutralization process, the evaporation unit, and air cooling equipment. The vacuum condenser in urea plants is a source of wastewater. Most scrubbing operations are also a source of wastewater. Stream generated in nitrogenous fertilizer processing may contain ammonia, chemical oxygen demand (COD), dissolved and suspended solids (SS), alkalinity, and hardness. The most common methods for removing nitrogenous compounds include: biological nitrification and denitrification, air stripping, ion exchange. In addition, carbon shortage is a problem for the treatment of such water due to the effect on the denitrification efficiency (Bao et al., 2016).

5.2.3 Wastewater influent and effluent parameters at plant A

The fertilizer plant A is an important production base of phosphate fertilizer in China. In 2013 the fertilizer plant produced 2 million tons of phosphorus composite fertilizers, 18,000 tons of industrial grade MAP, 427,500 tons of total ammonia, and 253,400 tons of urea.

The Wastewater streams at this plant include 200 m^3/h Ammonia wastewater from synthetic ammonia production, 200 m^3/h wastewater from phosphate fertilizer production and 50 m^3/h municipal wastewater. Table 22 shows the different streams and compositions of wastewater in this fertilizer plant. The two major types of wastewater: ammonia wastewater with 300 mg/l ammonia-nitrogen and phosphorus-containing wastewater with 240 mg/l total phosphorus. The orthophosphate concentration is between 160 and 200 mg/l [PO$_4$-P].

Table 22: Design parameters of wastewater quality at plant A

	Wastewater flows (m^3/h)	COD (mg/l)	NH$_4$-N (mg/l)	F- (mg/l)	TP (mg/l)	SS (mg/l)	pH	TN (mg/l)
Ammonia Wastewater	200	300	300	/	/	200	8	300
Phosphate fertilizer Wastewater	200	/	50	80	240	100	5	50
Municipal wastewater	50	400	40	/	5	200	6～9	60
Design Outlet		60	12	15	15	30	6～9	25

The high concentration of both components in the two major types of wastewater provides a good basis for producing magnesium ammonium phosphate. The excess ammonium in the wastewater, with a molar ratio (N:P) of more than 1, is also beneficial for struvite precipitation (Warmadewanthi & Liu, 2009a).

Two more phosphate rich side- streams of water from the production process in fertilizer plant A are described in Table 23: the circulating process water and gypsum stack wastewater. The process water has a low pH of about 1 to 2 and contains a dilute mixture of phosphoric, sulfuric, and fluosilicic acids. It is saturated with calcium sulfate and contains numerous other ions found in the phosphate rock used as a raw material, as well as ammonia from the solid fertilizer manufacturing process.

Table 23: Composition of process water in Chemical Plant A

Art	Wastewater flows (m^3/h)	NH$_4$-N (mg/l)	F$^-$ (mg/l)	TP (mg/l)	pH
Circulating process water	6800	300	low concentration	872-1308 (0.2%-0.3% P$_2$O$_5$)	
Gypsum stack wastewater	50	/	1000	4360 (1% P$_2$O$_5$)	<2

Phosphogypsum (PG) is a byproduct of the chemical reaction called "wet process". To make 1 ton of commercial fertilizer, the phosphate industry creates 4.5-5.5 tons (Connett, 2003) of contaminated phosphogypsum slurry (calcium sulfate). The typical ingredients of wastewater from the gypsum stack are P_2O_5, F and some heavy metal ions. The wastewater from the gypsum stack in this plant is mixed with process water, which has negative influence on the production process. Some research has been done by this plant on the separate treatment of these high-nutrient side streams.

The current Chinese standard "Discharge Standard of Water Pollutants for the Phosphate Fertilizer Industry (GB15580, 2011)" in Table 24 is applicable to the management of discharging water pollutants of existing phosphate fertilizer manufacturers or production facilities in China. The treated wastewater at plant A is discharged directly into river, which should meet the parameters marked in bold in Table 24.

Table 24: Discharge standard of water pollutants for phosphate fertilizer industry

No.	Pollutants	Direct discharge					Indirect discharge
		calcium superphosphate	calcium-magnesium phosphate	ammonium phosphate [a]	triple-superphosphate	compound fertilizer	
1	pH	6~9	6~9	6~9	6~9	**6~9**	6~9
2	COD_{Cr}	70	70	70	70	**70**	150
3	SS	30	30	30	30	**30**	100
4	Fluoride	15	15	15	15	**15**	20
5	TP	10	10	15	15	**15**	20
6	TN	15	15	20	15	**20**	60
7	Ammonia	10	10	15	10	**15**	30
8	Total arsenic	0.3	0.3	0.3	0.3	**0.3**	0.3
Benchmark effluent volume per unit product (m³/t)		0.3	0.4	0.2	0.15	**0.15**	the same with direct discharge
		12 [b]					
Units in milligrams per liter (mg/l), except pH							
a Nitrophosphate production apply the same standard with ammonium phosphate							
b suitable for fluorine production enterprises (calculated with Sodium fluorosilicate), unit in m³/t							

5.2.4 Current wastewater treatment process in plant A

The current process of phosphate and ammonia wastewater treatment is shown in Figure 39. The wastewater from the phosphate fertilizer production is mixed with municipal wastewater and treated with a two-step precipitation process, step one mainly for fluoride removal and

step two mainly for phosphorus treatment. The additional ammonia wastewater treatment is designed based on the anoxic-aerobic-anoxic-aerobic (AOAO) biological process for ammonia removal and carbon removal simultaneously. The quartz sand filter, used as advanced treatment unit, can further remove SS and COD after biological treatment. After tertiary treatment, the wastewater goes to the final pH adjustment tank together with the treated phosphorus wastewater, and if necessary, it can be pumped directly into workshop as reclaimed water. At present, the treated wastewater is discharged into the river and not used for reclamation.
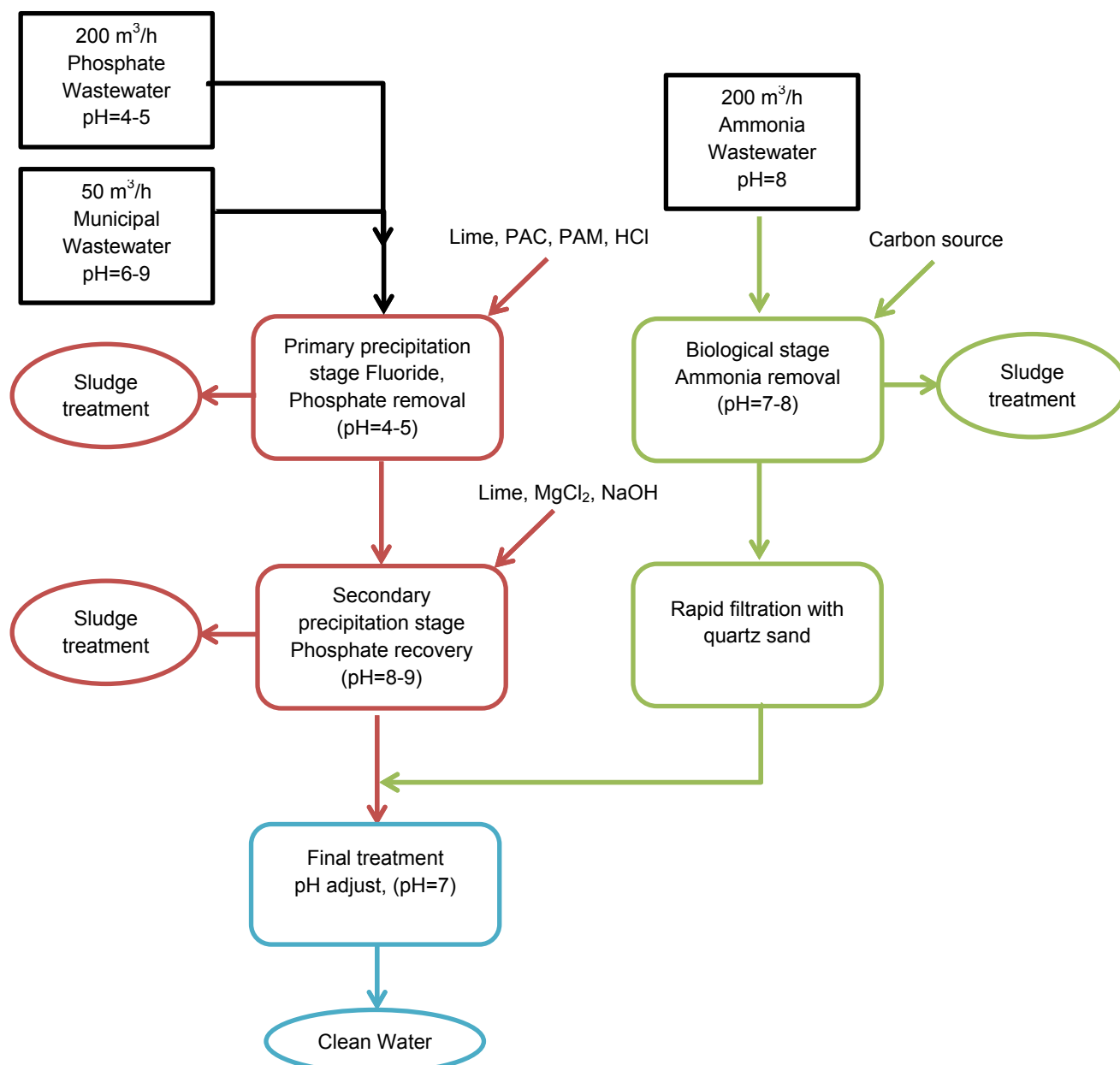
Figure 39: The current wastewater treatment scheme of plant A

5.2.5 New concept of wastewater treatment in plant A

The new concept is to apply crystallization instead of precipitation in the phosphate treatment unit with an advanced struvite crystallizer. The fluoride and phosphate can be recovered separately in form of CaF_2 and struvite as by-products. With the new concept a high purity phosphate crystal can be generated. For the struvite crystallization, the wastewater from the ammonia production can be used as a source of ammonia. About 20% - 40% of ammonia can be removed from ammonia wastewater and transferred into the product struvite. Only an additional magnesium source is needed. The municipal wastewater can be mixed into the biological process as carbon source after the crystallization stage. After biological treatment, three streams of wastewater flow to the final filtration and pH adjustment stage. The process is described in Figure 40.
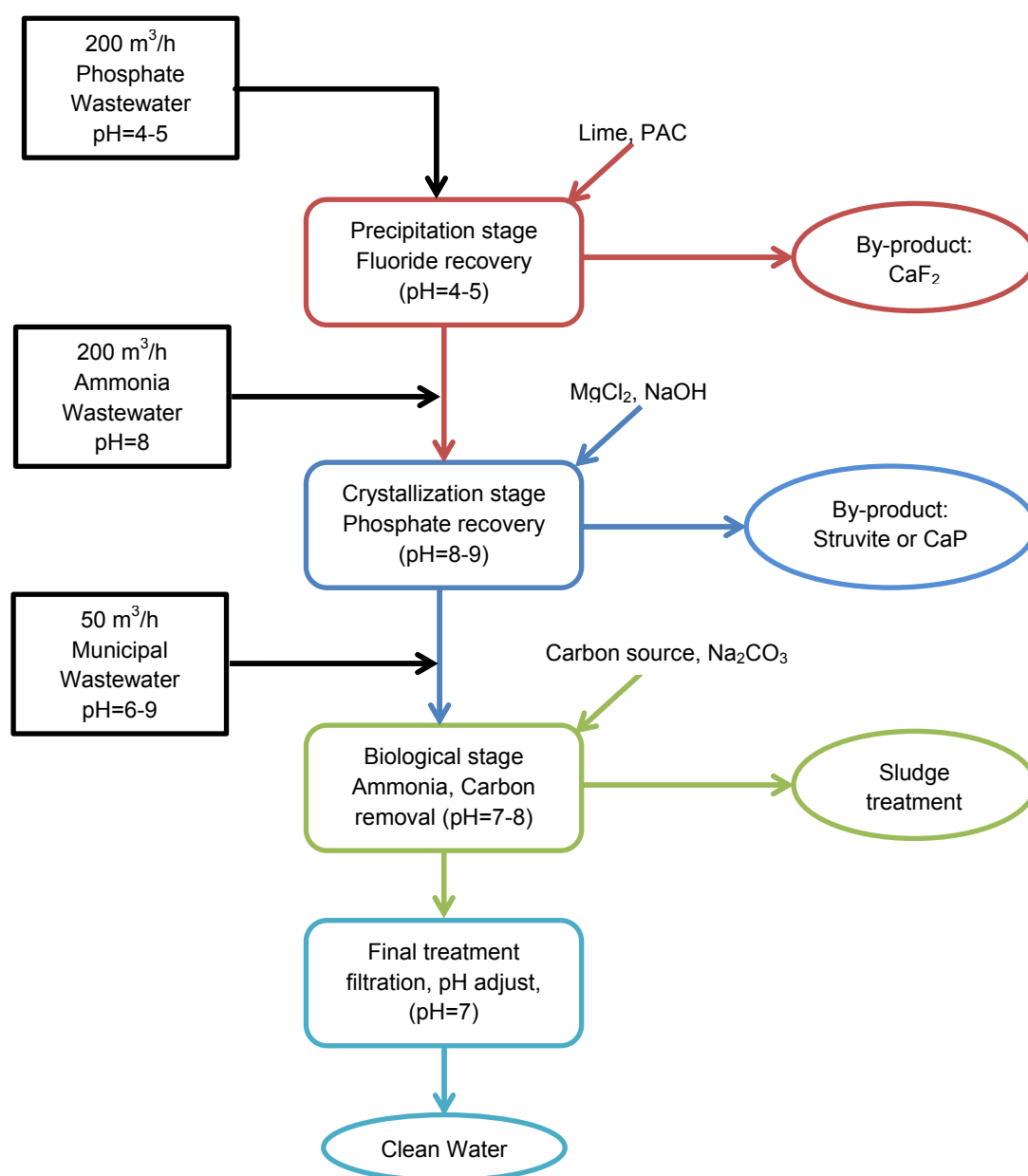
Figure 40: The new concept for treatment of wastewater in plant A

5.3 Materials and methods

5.3.1 Chemical equilibrium modelling with MINEQL+

Speciation calculations were carried out using MINEQL+ (Schecher & McAvoy, 1992) version 4.6, which is a computer program for chemical equilibrium modelling (Figure 41). Calculations were used to model calcium, fluoride and phosphate speciation at pH values 3 and 7. MINEQL + solves mass balance calculations through a NewtoneRaphson method using equilibrium constants from a thermodynamic database.
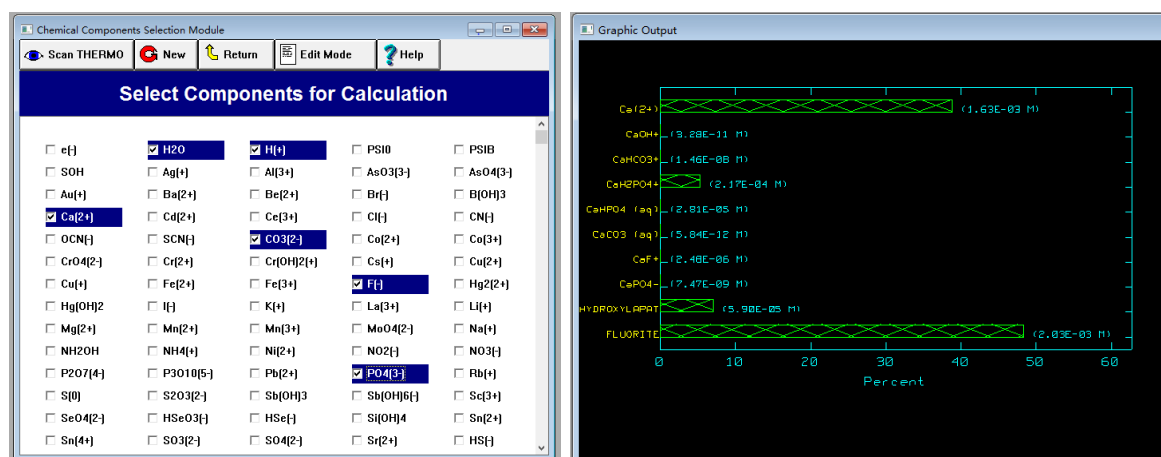
Figure 41: Software interface of MINEQL+ version 4.6

With MINEQL+ software, the effect of the $[Ca^{2+}]$ ion on the removal of fluoride ion from phosphate wastewater was investigated. Under alkaline pH, calcium phosphate forms faster than calcium fluoride (Yang et al., 2001). For a better separation of fluoride in the first stage, the modelling pH values were 3, 4, 5, 6, and 7. The initial values of phosphate and fluoride were calculated with the concentration of real phosphate wastewater. Due to different $[Ca^{2+}]$ ion additions the modelling molar ratio for calcium is shown in Table 25.

Table 25: Different molar ratio for the MINEQL+ calculation

Molar ratio $[Ca^{2+}]:[F^-]$	$[Ca^{2+}]$ [mol]	$[F^-]$ [mol]	$[PO_4^{3-}]$ [mol]
1.5:1	$6.32 \cdot 10^{-3}$	$4.21 \cdot 10^{-3}$	$6.40 \cdot 10^{-3}$
1:1	$4.21 \cdot 10^{-3}$	$4.21 \cdot 10^{-3}$	$6.40 \cdot 10^{-3}$
1.2:2	$2.526 \cdot 10^{-3}$	$4.21 \cdot 10^{-3}$	$6.40 \cdot 10^{-3}$
1:2	$2.105 \cdot 10^{-3}$	$4.21 \cdot 10^{-3}$	$6.40 \cdot 10^{-3}$

5.3.2 Laboratory jar test with synthetic and real wastewater

To demonstrate the feasibility of the crystallization and precipitation processes for fertilizer industry wastewater, jar tests were conducted at the laboratory of the Technical University of Berlin with synthetic wastewater and at the wastewater treatment plant A with real wastewater.

- **Synthetic wastewater**

The synthetic wastewater was prepared by dissolving the chemicals into distilled water at ambient temperature (25 ± 2 °C). The synthetic water sample volume was 1L for each jar test. The appropriate amount of hydrochloric acid or sodium hydroxide was added to decrease or raise the sample pH depending on the experiment. The synthetic wastewater represents major classes of ions present in real wastewater, e.g. phosphate, fluoride and ammonia. The components and concentration of synthetic wastewater is shown in Table 26.

Table 26: Components and concentration of synthetic wastewater

	F^- (mg/l)	PO_4-P (mg/l)	NH_4-N (mg/l)
Synthetic phosphate wastewater	90	170	/
Synthetic ammonia wastewater	/	/	280

Synthetic wastewater was prepared by using the following chemicals listed in Table 27. Calcium hydroxide and calcium chloride were used as sources of calcium for the pricipitation of fluoride. Calcium fluoride and magnesium ammonium phosphate powder were prepared as seeding product for the precipitation and crystillization.

Table 27: Used chemicals for the jar test experiments

Chemical name	Chemical formula	Molar weight [g/mol]
Calcium hydroxide	$Ca(OH)_2$	74.09
Sodium hydroxide 5 mol/l	NaOH	40.00
Magnesium chloride 98.5%	$MgCl_2$	95.21
Hydrochloric acid	HCL	36.46
Sodium fluoride	NaF	41.99
Trisodium phosphate	Na_3PO_4	163.94
Ammonium chloride	NH_4Cl	53.49
Calcium fluoride	CaF_2	78.07
Magnesium ammonium phosphate 98%	$MgNH_4PO_4 \cdot 6H_2O$	245.41

- **Precipitation of fluoride**

A jar test apparatus (Flocculator 200, Kemira KemWater) was used for chemical precipitation experiments. Lime was added in the first stage of treatment to precipitate only fluoride from wastewater. In the second stage of treatment, magnesium chloride and ammonia wastewater were added to recover phosphate from wastewater.

As in example shown in Figure 42, the synthetic wastewater which contained phosphate and fluoride was prepared in a 1 L test tube. The required dose of the selected solution containing the calcium (usually calcium hydroxide or calcium chloride) was added. If required,

the caustic soda solution or hydrochloric acid was immediately added increasing or decreasing the pH to the desired target value. The injected volume of the solution was recorded and it was mixed at 150 rpm for the required duration.
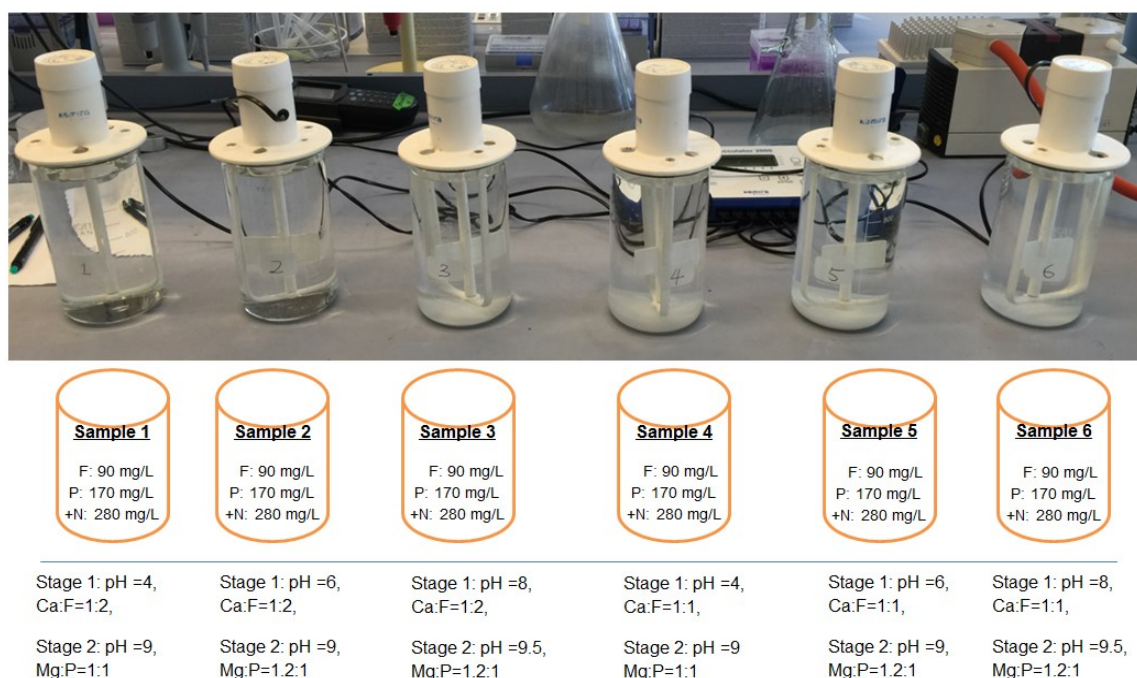
Figure 42: Jar test experiments to determine optimum operating conditions

After the fluoride precipitation experiment, the sample was mixed with ammonia wastewater in the ratio of 1:1. The required dose of magnesium chloride was added and the pH adjusted to the desired target value. The example was then mixed at 150 rpm for 1 min, slowly mixed at 50 rpm for 5 min and left to settle for 30 min.

The concentrations of fluoride, orthophosphate, ammonia, calcium and magnesium were measured using the Hach Lange (DR 5000) cuvette test LCK 323, LCK 049, LCK 302, LCK 327 and LCK 326 respectively. Due to the limitations of the local laboratory at plant A, the jar test experiment was conducted without the measuring the fluoride concentration.

- **Crystallization of struvite**

An additional experiment for the crystallization of struvite was conducted directly at plant A to evaluate the optimum operating conditions for the struvite ($MgNH_4PO_4$, $6H_2O$) crystallization. The objective of the trial was to characterize the effects associated with the variation of each of the selected parameters. One parameter only varied from one jar to another while the other parameters remained constant.

The following protocol was performed with only one parameter varying trial after trial:
I.   Fill each beaker with 1L of effluent to be treated using a test tube.
II.   Set the impellers into the solutions and start mixing with a speed of 150 rpm.
III. Add the required dose of the selected solution containing the magnesium (usually magnesium chloride).

IV. If required, add immediately the caustic soda solution increasing the pH to the desired target value. Record the injected volume of soda and keep mixing for the required duration.

V. Stop mixing, remove the impellers and allow settling for 30 minutes.

VI. Once the settling stage is completed, sample the supernatant using a syringe and filter the sample through a syringe filter of 45µm. Analyze the orthophosphate and ammonium nitrogen concentrations of the filtrate

The trials will progress while the following parameters are adjusted in the following sequence:

- **Precipitation pH:**

Tested pHs of precipitation will be within the range 8 to 10. If the trial is performed with a 6 jars bench, the selected pHs of precipitation will be 8/8.5/9/9.5/10/no pH correction.

The magnesium dose (ideally using magnesium chloride, at least at the beginning of the trials) will correspond to a molar ratio Mg/P equal to 1.2 and the reaction time will be one hour.

- **Magnesium dose:**

Under the optimum pH of precipitation (pH of precipitation selected according to the previous trials applying a variation in pH), different magnesium doses will be tested (expressed in molar ratio Mg/P): from 1 to 2. If the trial is done with a 6 jars bench, the selected molar ratios will be 0.5/0.8/1/1.2/1.5/2.

The duration of the reaction will be 1h.

- **Reaction time:**

At the optimum pH for precipitation (or selected pH of precipitation), considering the optimum Mg/P molar ratio and the optimum concentration of crystallization seeding, different durations of reaction will be tested in the range 15 min to 2 h (for instance: 15 min / 30 min / 1 h / 1 h 30 / 2h).

5.4 Results and discussion

5.4.1 MINEQL+ Results

5.4.1.1 Calcium speciation

The calculation result of calcium speciation at pH 5, $[Ca^{2+}]:[F^-]$ ratio 1:2, is presented as an example in Figure 43. The vertical axis on the graph shows the different components of calcium, while the horizontal axis represents the percentage of this component. According to the calculations, at pH 5, 90% of calcium is in the form of insoluble fluorite (CaF_2).
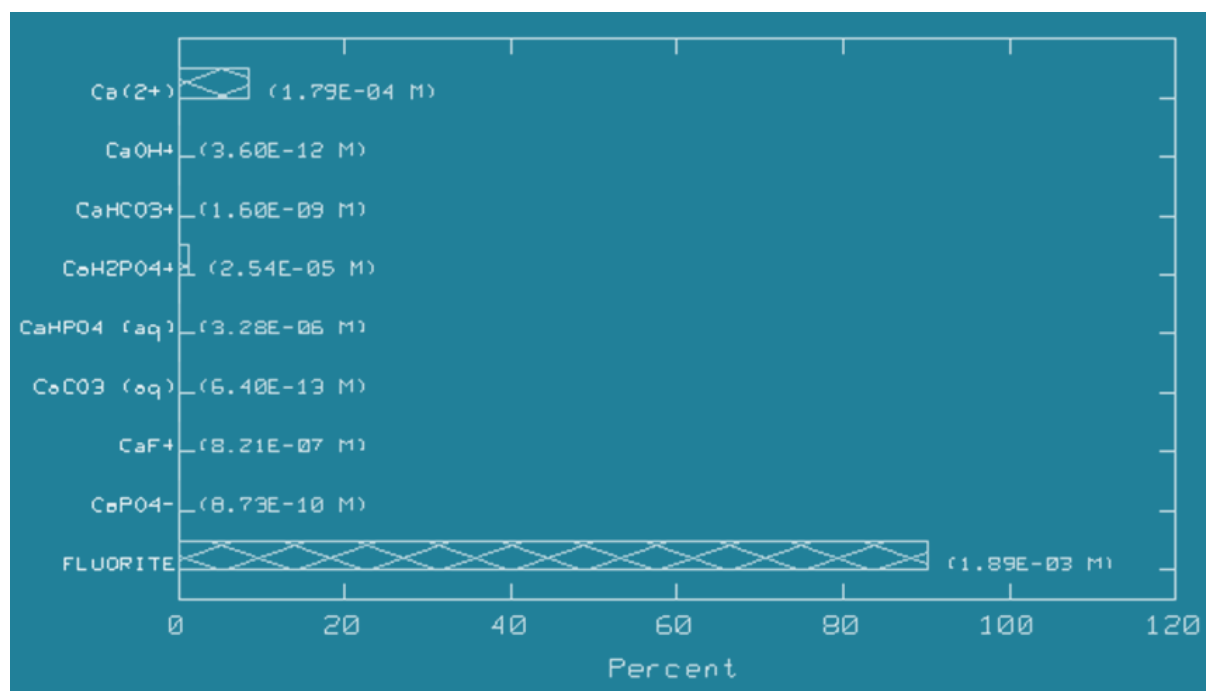
Figure 43: Calcium speciation calculation with MINEQL+ software at pH value 5, Ca:F ratio 1:2.

The effects of different pH values at 3, 4, 5, 6, 7 on the precipitation of calcium are shown in Figure 44. The MINEQL+ model predicts that with the theoretical $[Ca^{2+}]:[F^-]$ molar ratio of 1:2, under pH range 3 to 5, and 80-90% of the calcium ions are precipitated with fluoride and undissolved hydroxylapatite is not formed. Increasing the pH to 6 and 7, hydroxylapatite is formed. At pH 6, about 80% of the calcium is precipitated as calcium fluoride. At pH 7, about 70% of the calcium is present in the form of hydroxylapatite. Thus, a pH between 4 and 5 is the optional condition for fluoride precipitation under this condition, which corresponds to meet the original pH value of phosphate wastewater from plant A.
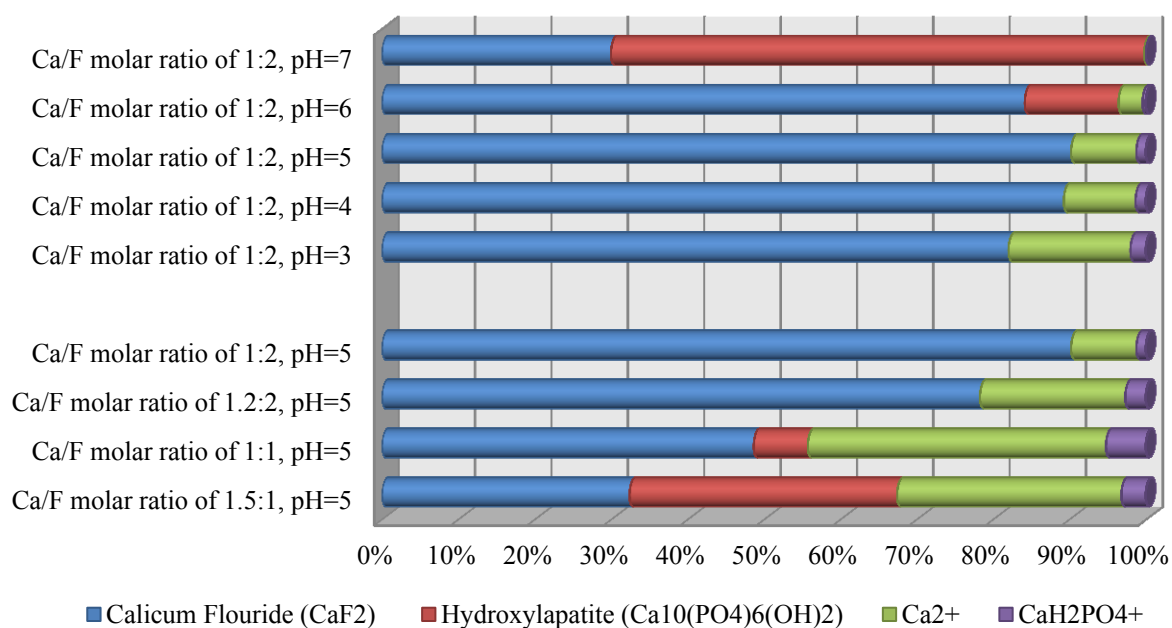
Figure 44: Modelling results of distribution of added calcium in solution under different reaction conditions

Further calculations for different molar ratios of $[Ca^{2+}]$:$[F^-]$ of 1:2, 1.2:2, 1:1, 1.5:1 under pH value 5 were carried out and are shown in Figure 44. From the model predictions, a further increase of molar ratio, $[Ca^{2+}]$:$[F^-]$, from 0.5 to 1.5, increased the molar amount of calcium fluoride formed from 1.89 mmol to 2.04 mmol. The majority of residual soluble calcium existed in the form of $[Ca^{2+}]$, $[CaH_2PO_4^+]$ and hydroxylapatite.

5.4.1.2 Fluoride speciation

Apart from calcium, fluoride speciation is an important indicator for the separation effect. The calculation result of fluoride speciation at pH 5, $[Ca^{2+}]$:$[F^-]$ ratio 1:2, is presented as an example in Figure 45. At pH 5, 89.8% of the fluoride has precipitated as fluorite (CaF_2). About 10% of the total fluoride is still in the form of $[F^-]$.
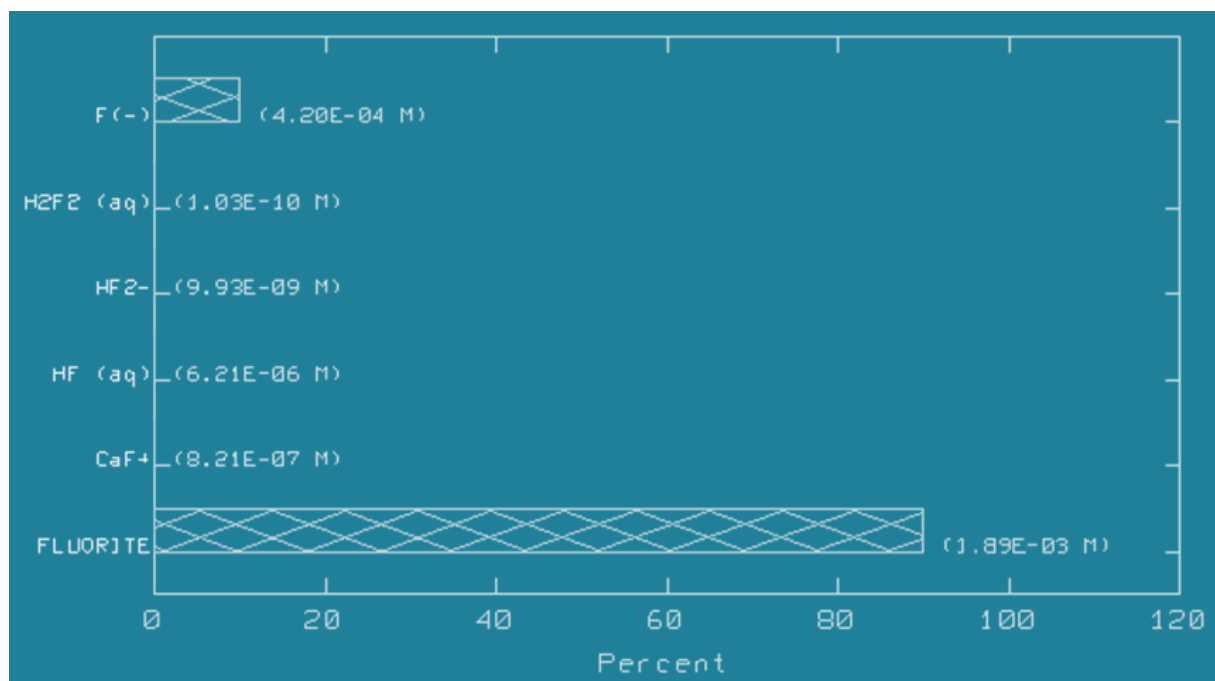
Figure 45: Fluoride speciation calculation with MINEQL+ software at pH value 5, Ca:F ratio 1:2.

The effects of different molar ratios of $[Ca^{2+}]$:$[F^-]$ of 1:2, 1.2:2, 1:1, 1.5:1 and pH values at 3, 4, 5, 6, 7 on the precipitation of fluoride are shown in Figure 46. Undissolved calcium fluoride and hydroxyapatite are the only two solids that can be precipitated under this simulation condition.

■ Proportion of fluoride in form of fluorite (CaF2)   ■ Proportion of phosphate in form of hydroxylapatite
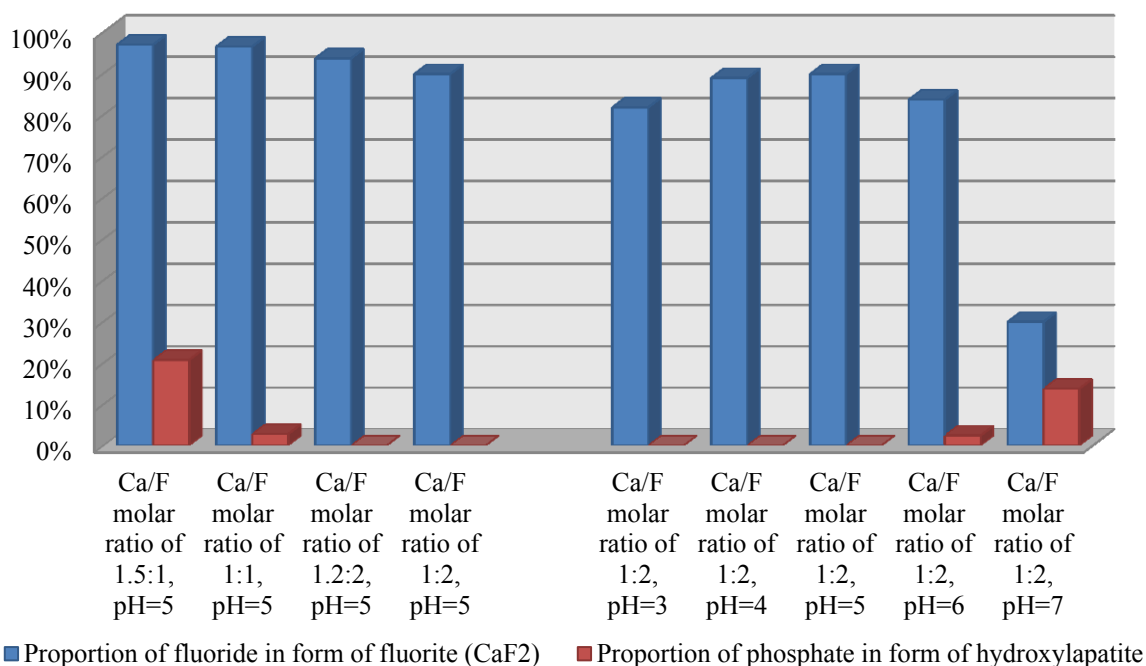
Figure 46: Modelling results of removal of fluoride in solution under different reaction conditions

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Increasing the molar ratio of $[Ca^{2+}]:[F^-]$ from 0.5 to 1.5, raised the removal efficiency of fluoride (in form of CaF_2) from 89.8% to 96.9%. At the pH value 4 and 5, the removal efficiency of fluoride was better than at pH 3, 6 and 7.

To summarize, the MINEQL+ results indicated that selective separation of fluoride and phosphate is possible with Ca^{2+} ion precipitation. According to the theoretical calculations, fluoride removal from phosphate containing wastewater was efficient at pH 4 to 5, with a molar ratio of $[Ca^{2+}]:[F^-]$ from 0.5 to 1.

5.4.2 Jar-test results with synthetic wastewater

5.4.2.1 Separation of fluoride and phosphate

- **Influence of pH and reaction time**
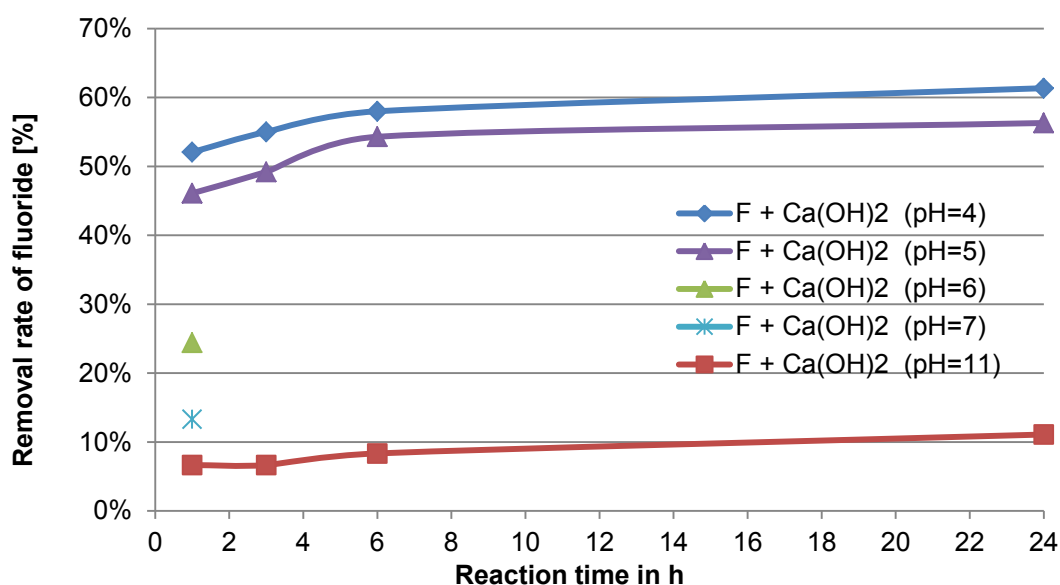
Figure 47: The influence of pH and reaction time on the fluoride removal with molar ratio ($[Ca^{2+}]:[F^-]$) of 0.5.

In Figure 47, different durations of reactions were tested ranging from 1 hour to 24 hours (for instance: 1h / 3h / 6 h / 24h) under pH 4, 5 and 11. Experimental results showed that only a limited amount (6.7% -11.1%) of fluoride was removed at pH 11. This result revealed that calcium salt tended to react preferentially with phosphate rather than with fluoride at an alkaline pH. At pH 6 and 7, the removal ratio was still quite low. It was found that, under acidic conditions (pH= 4 and 5), 46% - 61% of the fluoride was removed by calcium hydroxide as calcium fluoride at a molar ratio $[Ca^{2+}]:[F^-]$ of 0.5. The removal of fluoride is considerably lower than predicted by the MINEQL+ model. This is probably because phosphate could have an inhibitive effect on fluoride precipitation. When comparing the pH values 4 and 5, the lower pH value 4 has better removal efficiency (4 - 6%) of fluoride. The reaction time has also an effect on the removal ratio of fluoride. For a longer reaction time, a better fluoride removal was achieved. After 6 hours, the reaction time has an insignificant effect: about 2-3% fluoride removal.

- **The influence of molar ratio [Ca^{2+}]:[F$^-$]**

	Sample 1 (pH=4, Ca:F=1:2)	Sample 2 (pH=4, Ca:F=1:1)	Sample 3 (pH=4, Ca:F=2:1)	Sample 4 (pH =5, Ca:F=1:2)	Sample 5 (pH=5, Ca:F=1:1)	Sample 6 (pH=5, Ca:F=2:1)
raw wastewater (mg/L)	90	90	90	90	90	90
after add calcium hydroxide (mg/L)	35	23	22	39	25	22
Removal rate (%)	61%	75%	75%	56%	72%	76%
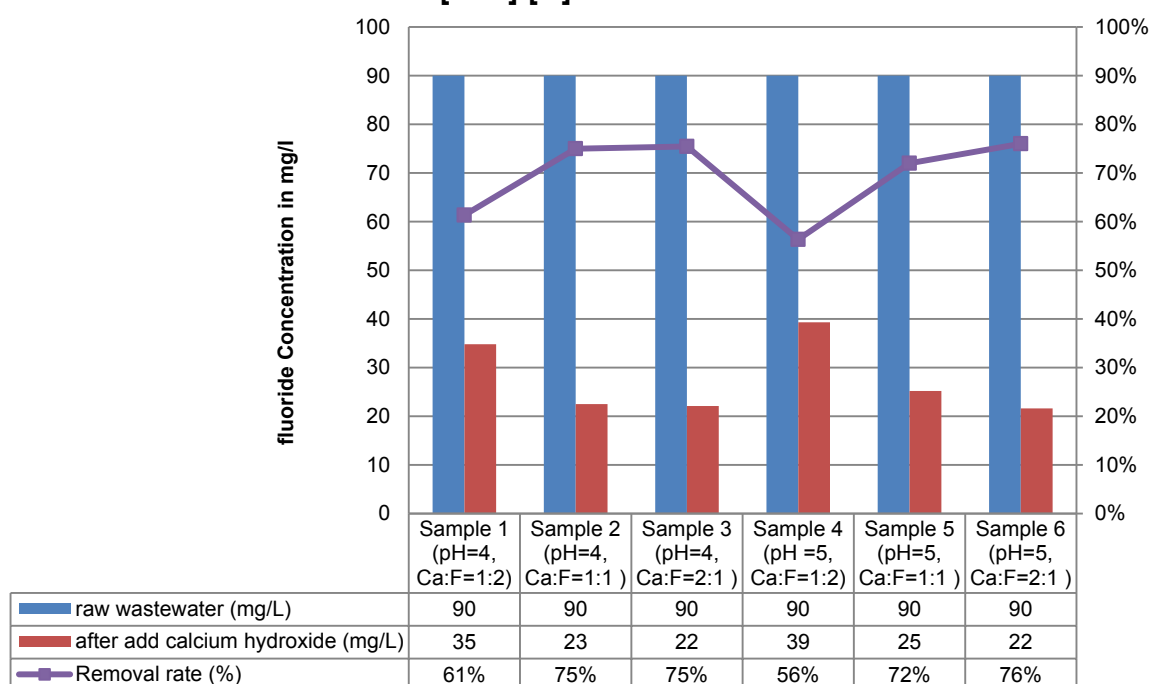
Figure 48: Experimental results of fluoride removal with different calcium doses

Under the optimum pH 4 and 5 of precipitation, different calcium doses were tested (expressed in molar ratio [Ca^{2+}]:[F$^-$]): from 0.5 to 2 (selected molar ratios 0.5/1/2) in Figure 48. From the experimental results, the increase of the molar ratio, [Ca^{2+}]:[F$^-$], from 0.5 to 1, had a significant effect on the removal efficiency after mixing for 24 hours. The removal ratio of fluoride was raised from 61% to 75% at pH 4 and at pH 5 from 56% to 72%. With further increase of the molar ratio from 1 to 2, the increment of fluoride is relatively small, less than 4%.

It was noted that under the condition with a molar ratio [Ca^{2+}]:[F$^-$] of 1:1, the fluoride concentration was below 25 mg/l. In the second stage, the phosphate wastewater was mixed with ammonia wastewater. The concentration of fluoride in wastewater was diluted from 25 mg/l to 12.5 mg/l, which can meet the discharge standard of 15 mg/l fluoride. Thus, under this condition, further treatment of fluoride is not needed.

	Sample 1 (pH=4, Ca:F=1:2)	Sample 2 (pH=4, Ca:F=1:1)	Sample 3 (pH=4, Ca:F=2:1)	Sample 4 (pH =5, Ca:F=1:2)	Sample 5 (pH=5, Ca:F=1:1)	Sample 6 (pH=5, Ca:F=2:1)
raw wastewater (mg/L)	173	173	173	173	173	173
after add calcium hydroxide (mg/L)	167	159	153	158	157	136
Removal rate (%)	3%	8%	12%	9%	9%	21%
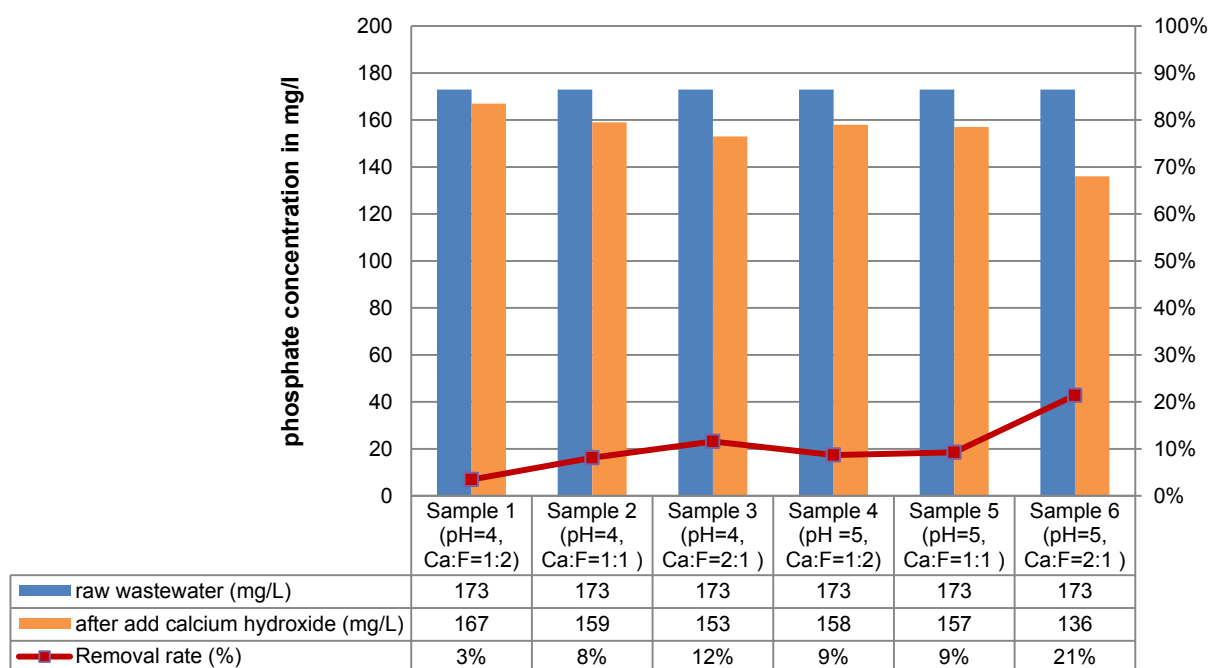
Figure 49: Experimental results of orthophosphate removal with different calcium doses

In the first stage, the goal is to remove only fluoride from wastewater and in the second stage, as much phosphate as possible can be recovered. In Figure 49, the residual phosphate in the treated effluent from the first stage reaction is presented. The overdose of calcium cased also the removal of phosphate in the first stage. This has been confirmed by the MINEQL+ results showing that about 3% of phosphate is in the form of hydroxylapatite. With a molar ratio $[Ca^{2+}]:[F^-]$ of 1:1, 8% - 9% (13-15 mg/l) of orthophosphate was removed from wastewater.

5.4.2.2 Phosphate precipitation as struvite

Struvite precipitation from wastewater is influenced by a large number of parameters such as pH of the reaction, molar ratio, interfering ions in the feed, reaction time, types of chemicals added, types of the reactor used and temperature.

- **Influence of pH**

The pH of the reaction plays a significant role during the struvite precipitation process, and not only affects the amount of struvite precipitation, but also its purity. A variety of magnesium and phosphate complex ions patterns in the reactor solution, including $MgOH^+$, $Mg(OH)_3^-$, $MgH_2PO_4^+$, $MgHPO_4$, H_3PO_4, $H_2PO_4^-$, HPO_4^{-2}, $MgPO_4^-$ can be formed when the pH of the solution is varied (Bouropoulos & Koutsoukos, 2000).
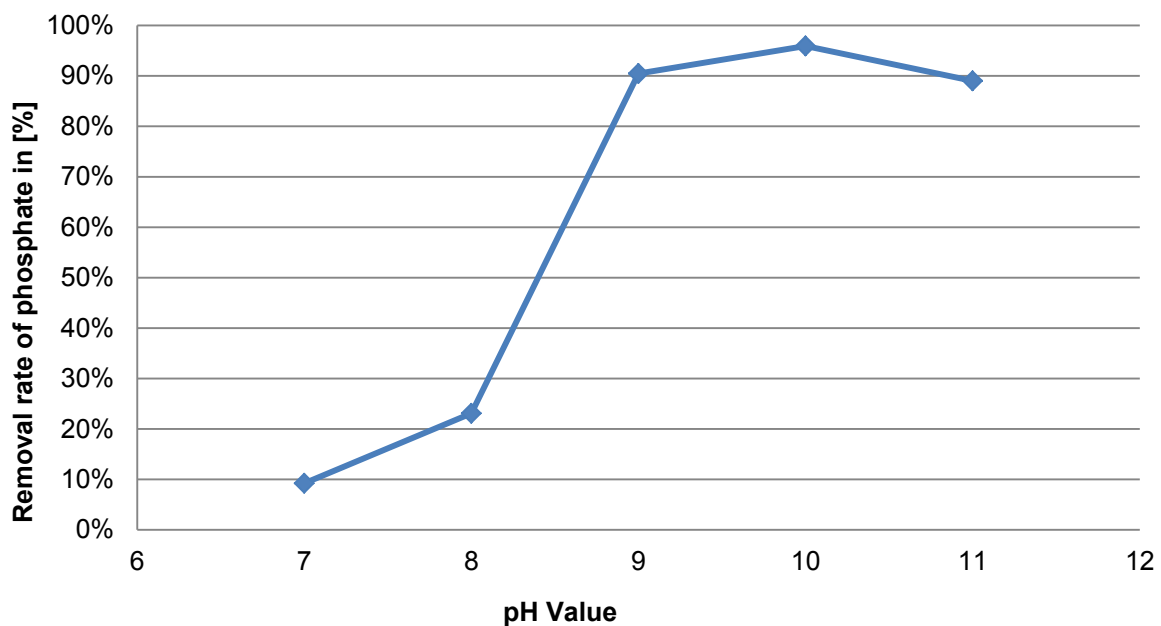
Figure 50: Experimental results of orthophosphate removal efficiency with different pH values

Based on the jar test experiment, the optimum pH for phosphate precipitation was investigated with a molar ratio Mg/P of 1. As shown in Figure 50, the optimal pH range of phosphate removal was between 9 and 10. With a pH of less than 9, the removal efficiency decreased significantly. The maximum removal efficiency of phosphate achieved was 96% at pH 10.

Figure 51 gives the removal efficiency of orthophosphate in the two stages of the reaction. In the first stage, under pH 4, only 4% of P was removed. By increasing the pH to 8, about 25% P was precipitated. It has proved that, in the first stage, a lower pH 4-5 is more suitable.

	Sample 1 (stage 1: pH =4, Ca:F=1:2, stage 2: pH =9, Mg:P=1:1)	Sample 2 (stage 1: pH =6, Ca:F=1:2, stage 2: pH =9, Mg:P=1.2:1)	Sample 3 (stage 1: pH =8, Ca:F=1:2, stage 2: pH =9.5, Mg:P=1.2:1)
raw wastewater	167	167	167
after stage 1 add Ca in [mg/l]	160.5	146	126
after stage 2 add Mg in [mg/l]	20.4	12.56	8.26
removal rate of stage 1 [%]	04%	13%	25%
removal rate of stage 2 [%]	75%	83%	87%
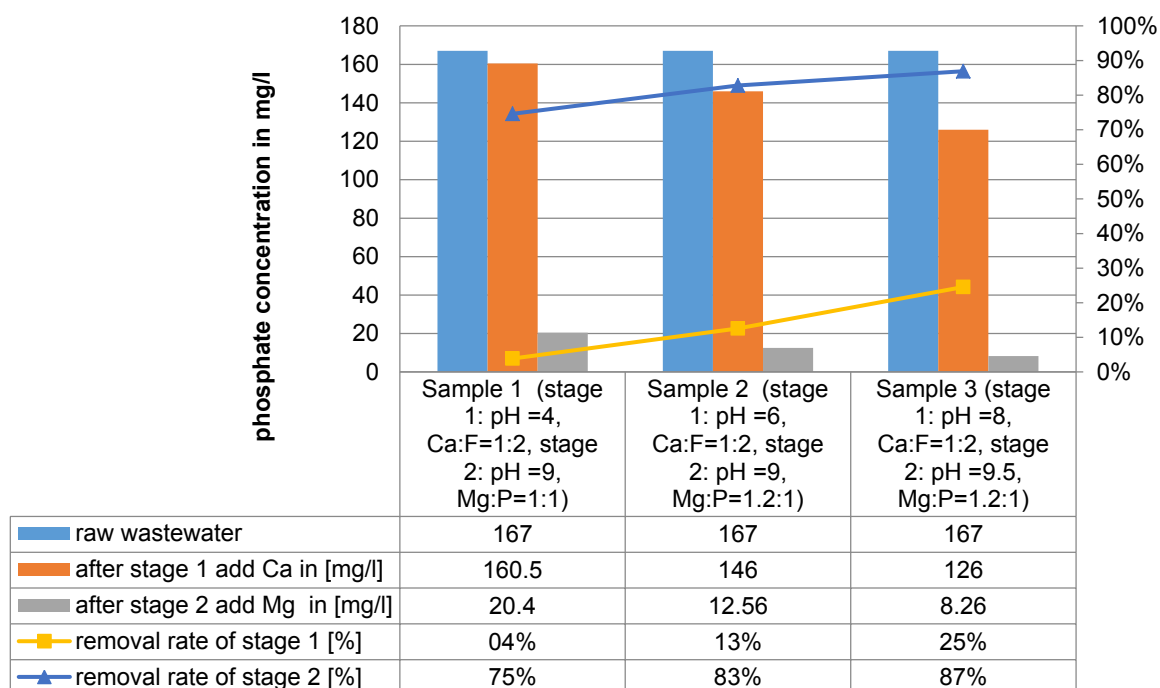
Figure 51: Orthophosphate removal in the first and second stage of reaction

In the second stage, under the optimum condition, pH with 9 and 9.5, a molar ratio of Mg/P of 1 and 1.2 was tested. In this experiment, higher pH and Mg/P ratio increased the P removal rate. The optimal condition was achieved at pH of 9.5 and Mg/P of 1.2 with 87% orthophosphate removal. The residual concentration of 8.3 mg/l is below the discharge standard of 15 mg/l.

	Sample 1 (pH 1=4, Ca:F=1:2, pH 2=9, Mg:P=1:1)	Sample 2 (pH 1=6, Ca:F=1:2, pH 2=9, Mg:P=1.2:1)	Sample 3 (pH 1=8, Ca:F=1:2, pH 2=9.5, Mg:P=1.2:1)
raw wastewater	142.4	142.4	142.4
after stage 2 add Mg in [mg/l]	107.8	113.6	107.4
removal rate of stage 2 [%]	24%	20%	25%
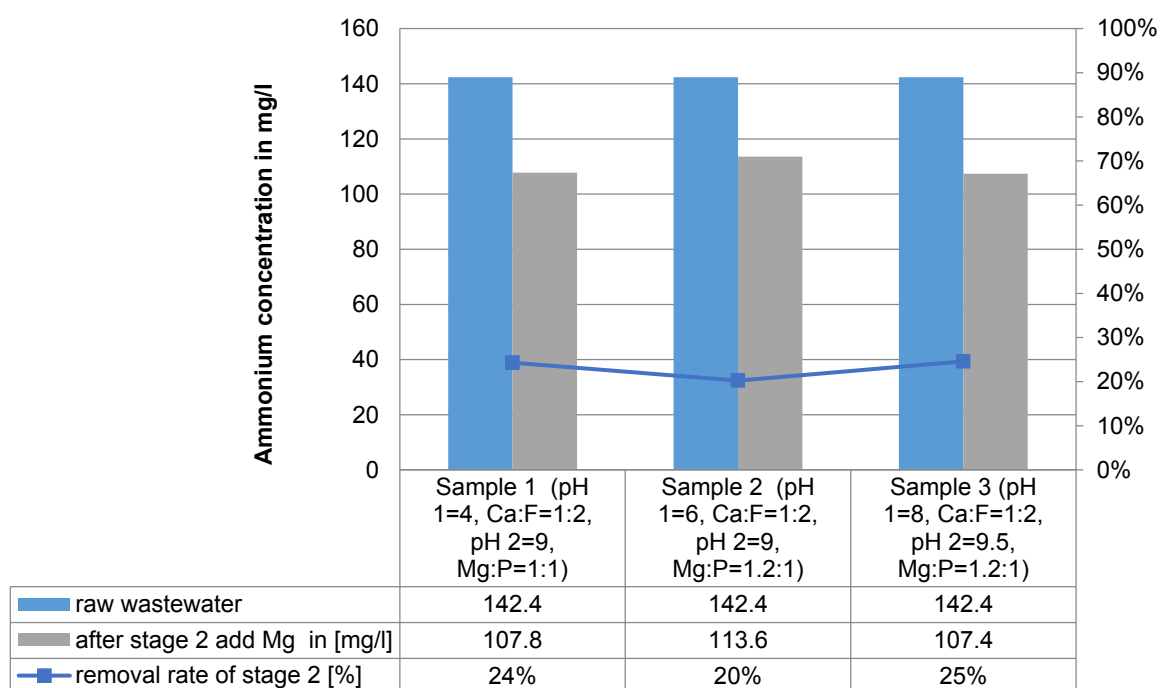
Figure 52: Ammonium nitrogen removal in the second stage of the reaction

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Figure 52 shows the removal efficiency of ammonium nitrogen by struvite precipitation. According to the calculation, the ammonium concentration is sufficient for the struvite precipitation. A similar removal rate was observed in these three samples. There were about 100 mg/l still remaining in the wastewater for the biological treatment stage.
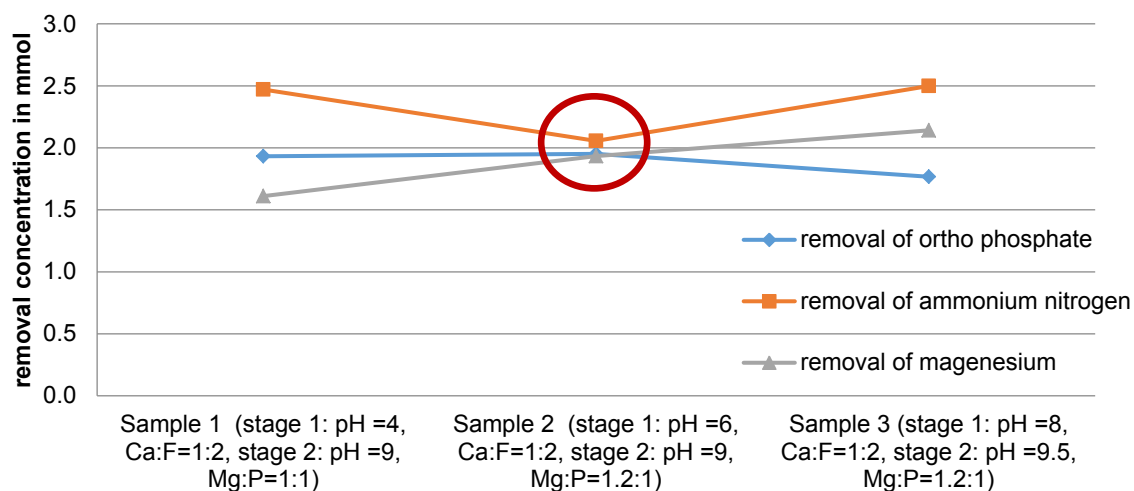
Figure 53: The removed molar concentration of orthophosphate, ammonium nitrogen and magnesium in the second stage of reaction

Figure 53 shows the removed molar concentration of orthophosphate, ammonium nitrogen and magnesium. Getting closer of these three molar ratios, a purer product can be formed. The removed molar ratio of P:N:Mg in the second example was 2.0:2.1:1.9, Which is quite close to the theoretical molar ratio of struvite Mg:N:P = 1:1:1. It can be inferred that, with a pH value of 9, Mg:P ratio of 1.2:1, a pure struvite product (magnesium ammonium phosphate) can be precipitated.

5.4.3 Jar-test results with wastewater from the fertilizer Industry

5.4.3.1 Raw wastewater concentration
Six raw wastewater samples were taken from the plant and were measured by local teams from plant A. The phosphate concentration ranges quite a lot from 65 to 220 mg/l and ammonia concentration ranges from 60 to 110 mg/l on different days. The ammonia concentration is lower than the design parameters. A possible reason might be the weather and construction work in this plant. According to the struvite solubility in water (around 200 mg/l), the struvite crystallization process is efficient for waste water containing more than 100 mg/l of soluble [PO$_4$-P] and a soluble ammonia concentration higher than 50-70 mg/l. Under this aspect, the wastewater in this plant contains enough phosphates and ammonium, which is suitable for the struvite precipitation.

5.4.3.2 Results of Jar-Test 1
The main wastewater parameters of jar test 1 are shown in Table 28.

Table 28: Characteristics of phosphate and ammonia wastewater

	pH	Conductivity	COD	NH$_3$-N	TN	PO$_4$-P
	-	ms/cm	mg/l	mg/l	mg/l	mg/l
Phosphate wastewater	5.837	1.077	11	10.6	-	93.0
Ammonia wastewater	8.397	1.613	209	110	138.4	-

- **pH regulation**

The solution pH value of the solution is one of the most important factors controlling the crystallization of struvite (Kataki et al., 2016). The phosphorus containing wastewater and ammonia wastewater were mixed in the ratio of 1:1 and the mixed wastewater had pH value of 7.8. To demine the optimum pH value for precipitation, magnesium chloride was added with a molar ratio [Mg^{2+}]/[P] equal to 1.2. The concentration of ammonia and phosphate at different pH values from 7 to 10 (8/8.5/9/9.5/10) after one hour stirring at 200 rpm and 20 minutes of precipitation, are described in Figure 54.
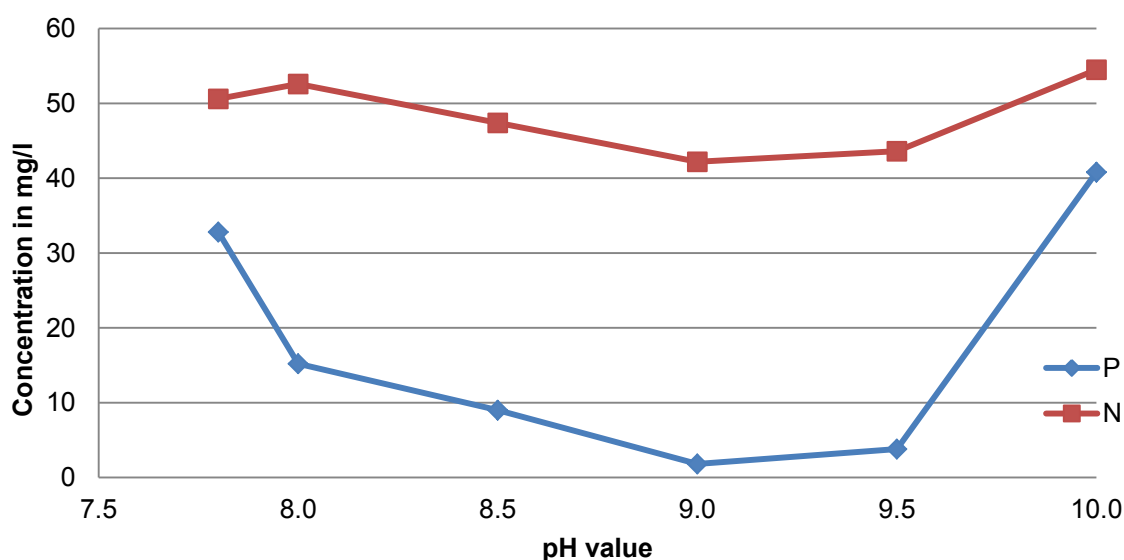
Figure 54: Effect of pH value on the precipitation of ammonium nitrogen and phosphate

The test indicated that low residual orthophosphate concentrations under 5 mg/l can be achieved at pH 9 and 9.5. The lowest concentration of orthophosphate and ammonium nitrogen was 1.8 mg/l PO$_4$-P and 42.2 mg/l NH$_4$-N at pH 9. At a pH higher than 9.5, the residual orthophosphate concentration increased significantly by 45 mg/l. So the optimum pH value for precipitation was 9.0 with the removal efficiency of 96.1%.

- **Magnesium dose**

To study the effect of [Mg^{2+}] on phosphate precipitation, different magnesium doses were tested with a molar ratio of Mg/P 1 to 2 (1/1.2/1.5/2). The duration of the reaction was 1 h with stirring at 150 rpm at the optimum pH of 9.0. After 30 minutes of precipitation, the phosphorus concentration was measured in the supernatant.

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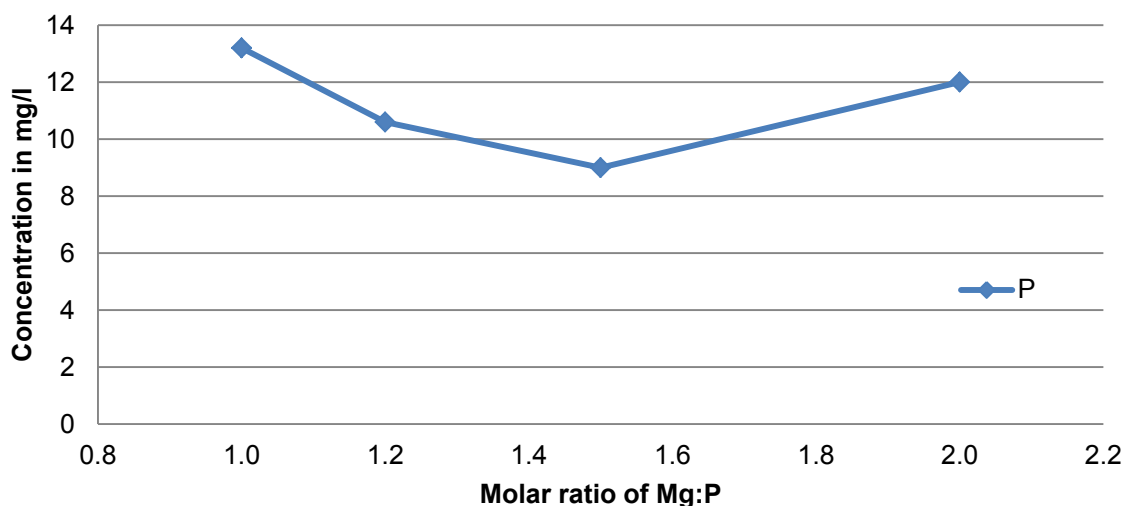
Figure 55: Effect of Mg/P molar ratio on precipitation of phosphate

It has been shown in Figure 55 that the removal efficiencies increased with the increase of the Mg/P molar ratio from 1 to 1.5. With further increase of the Mg/P molar ratio, the phosphate concentration increased in the supernatant. The lowest phosphorus concentration was 9 mg/l with a molar ratio Mg/P of 1.5. The optimum molar ratio of Mg/P is 1.5 with the removal efficiency of 81%.

▪ **Reaction time**

At the optimum pH of precipitation 9.0, considering the optimum Mg/P molar ratio 1.5, different durations of the reaction were tested ranging of 30 min to 2 h (for instance: 30 min / 1 h / 1 h 30 / 2h).
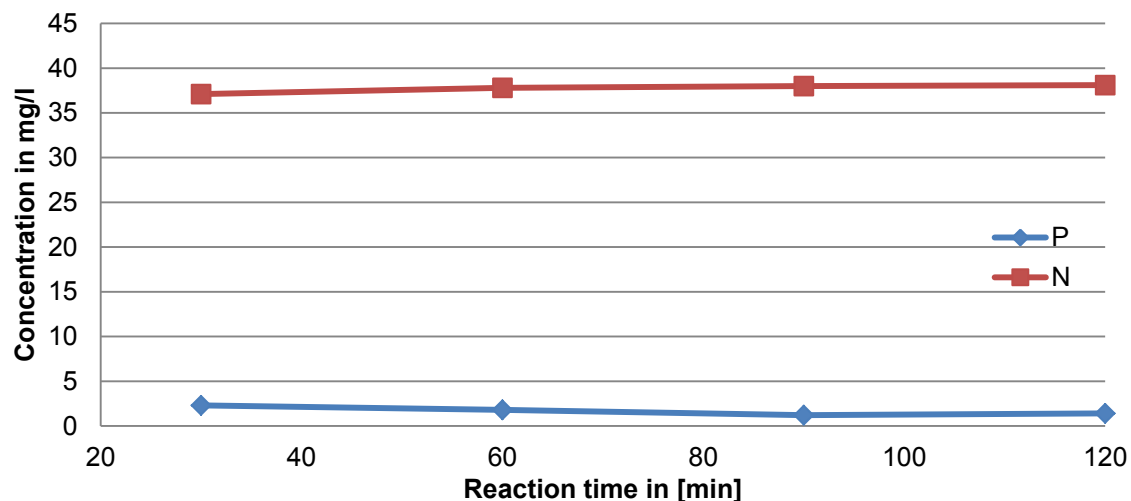
Figure 56: Efficiency of reaction time on precipitation of ammonium nitrogen and phosphate

The influence of the reaction time on the P and N removal efficiency is shown in Figure 56. No significant changes were observed by increasing the reaction time. The lowest concentration of ammonia and phosphorus was noticed in the 90 min reaction with 97% P removal.

To summarize, in jar test 1, the optimum operating conditions leading to the precipitation of the dissolved phosphate were determined. The jar tests showed a significant removal of phosphate, more than 97% P-removal was achieved at the optimum condition (pH=9, molar ratio of Mg/P 1.5; reaction time of 90 minutes). Under optimum conditions the P and N removed from the solution was 1.44 and 0.91 mmol respectively. The molar ratio of the removed P/N of 1.6 was more than the theoretical P/N molar ratio of struvite, i.e. 1. Therefore, the precipitations did not consist of pure struvite.

5.4.3.3 Results of Jar-Test 2

In this experiment, different mixing ratios of two streams of wastewater were tested. In the following Table 29 the key parameters of the wastewaters are analyzed.

Table 29: Characteristics of phosphate wastewater, ammonia wastewater and P-concentrated process water

	Water sample	pH	cond	sCOD	TOC	NH_3-N	TN	PO_4-P	TP
			ms/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
1	Phosphate wastewater	5.9	0.74	9.78	4.29	10.6	34.1	220	235
2	Ammonia wastewater	8.4	1.56	48.7	22.82	69.4	70.4	0.47	7.15

The phosphate wastewater and ammonia wastewater were mixed in the volume ratio of 1:1 and 2:1 under the optimum condition of Mg:P=1:1.2, pH= 9, reaction time of 60 min. The concentration and removal rate of orthophosphate and ammonium nitrogen is given in Figure 57.
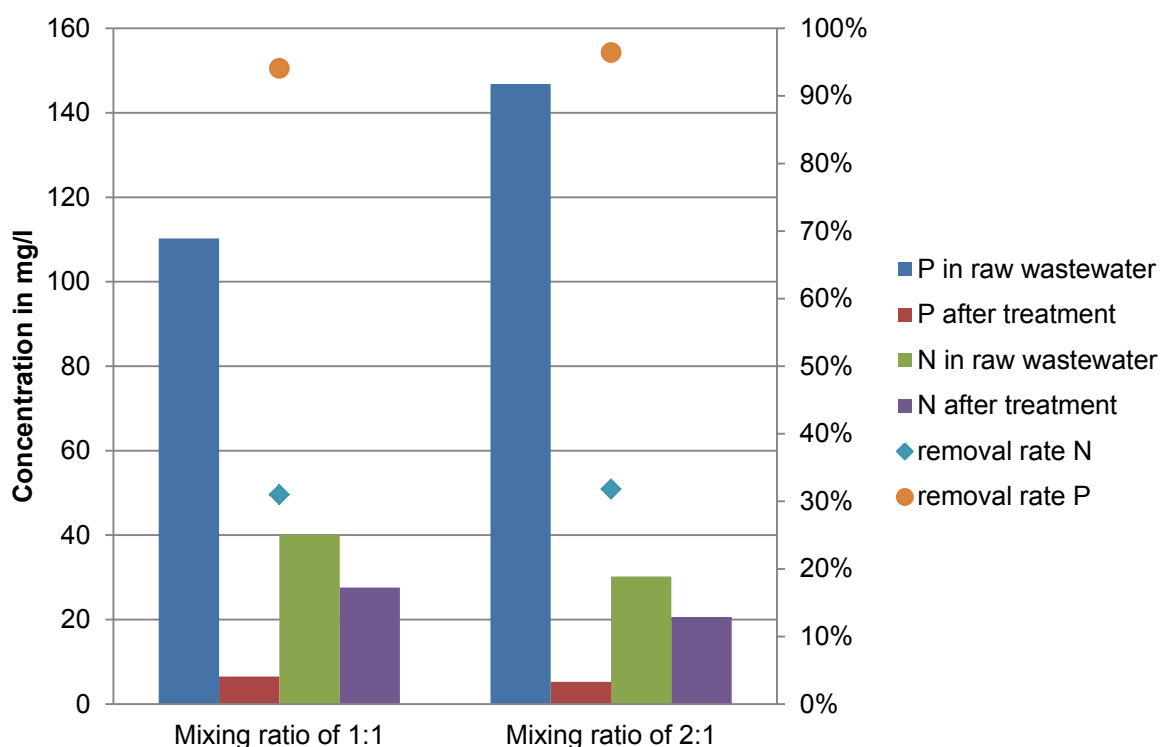
Figure 57: Results of orthophosphate and ammonium nitrogen removal with different mixing ratio of phosphate wastewater and ammonia wastewater (P wastewater: N wastewater)

With both mixing ratios of 1:1 and 2:1, a high removal rate (94% - 96%) could be achieved. Both residual phosphate concentrations were under 6.5 mg/l. It was shown that with an increase of the phosphate concentration in raw wastewater from a mixing ratio of 1:1 to 2:1, the removal rate of ammonium nitrogen was almost constant. A better removal rate of ammonium nitrogen was achieved.

The chemical formula of struvite is $MgNH_4PO_4 \cdot 6\,H_2O$ with a molar ratio of Mg:N:P = 1:1:1. The removed molar ratio of P:N in the first and second jar test were 0.9:3.4, 0.7:4.6 respectively. Under this condition the precipitate in the jar test is probably not only struvite. One possible reason could be that the ammonia wastewater contains a cationic ion which can react with phosphate to precipitate, e.g. calcium, magnesium. An amorphous magnesium or calcium phosphate might be formed in the precipitation.

To identify the purity of struvite precipitated in the jar-test, the following methods can be used:
- X-ray diffraction analysis: XRD diffractograms of precipitates compared to the database model for struvite
- Morphology of struvite precipitations via scanning electron microscope (SEM), compared with the regular size
- Dissolution experiments with HCL and element analyses

The results of jar tests showed the mixing process of two streams of wastewater can remove the phosphorus and part of the nitrogen cost-effectively from wastewater. However, the purity of the precipitated product should be analyzed and the application of struvite crystallization

processes still needs to overcome a constant wastewater concentration, different operating factors such as Mg:P:N molar ratio, pH, aeration rate, reactor types, which can all have an effect on the struvite quality.

5.5 Dimensioning and design of a pilot plant

5.5.1 Process Description

Based on the jar test results, a pilot plant project was planned to be located in fertilizer plant A. The project is based on the Struvia™ unit technology, which was developed by Veolia France. The overall aim of this project is to develop a new method of wastewater treatment technology with phosphorus recovery, combined with the local fertilizer production process. The main pilot research topics in this project are crystallization processes, process reactor and control.

The process flowsheet of the pilot is shown in Figure 58. The phosphate wastewater is first treated in a reactor in order to remove fluoride. The two streams of wastewater are proportional pumped into the regulation basin 2 and then in the main crystallization process in the Struvia™ reactor. A magnesium source, usually liquid magnesium chloride with a concentration of 33% is added. If the pH is not optimal, sodium hydroxide (NaOH) with a concentration of 30% can also be added.
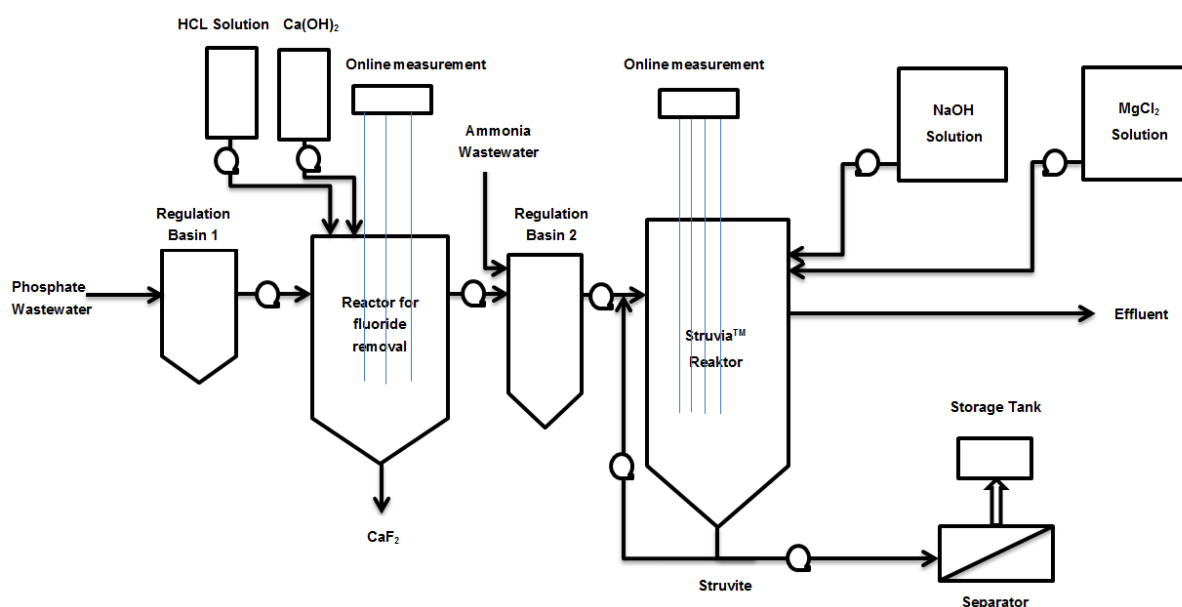
Figure 58: Flow of designed pilot system

An on-line [PO$_4$-P], [NH$_4$-N] and pH analyzer can be installed in the supernatant to check the efficiency of the chemical precipitation in real time. As an option, an on-line turbidity analysis of the supernatant allows checking the efficiency of the solid-liquid separation. Based on the results, the operational conditions (mixing velocity, Mg/P ratio, TSS) can be adapted if necessary.

The struvite crystals settle at the bottom of the Struvia™ reactor. A pump recirculates part of the crystals into the reactor and another part of the struvite is drained in a gravity draining system which allows dewatering struvite sludge. The struvite will be dried in the atmosphere for several weeks and stored in a tank for the fertilizer production.

Struvia™ Reactor

The crystallization reactor is the core of the pilot processing plant. In the Struvia™ reactor, the two steps, crystallization and liquid/solid separation, take place in the same device. The mixing zone is equipped with a vertical mixer, a draft tube and several baffles to optimize the mixing and the chemicals injections. Above the mixing zone is an integrated lamellar settler to ensure the separation of the treated effluent and the produced struvite particles. A simplified scheme of the Struvia™ reactor is given in the Figure 59.
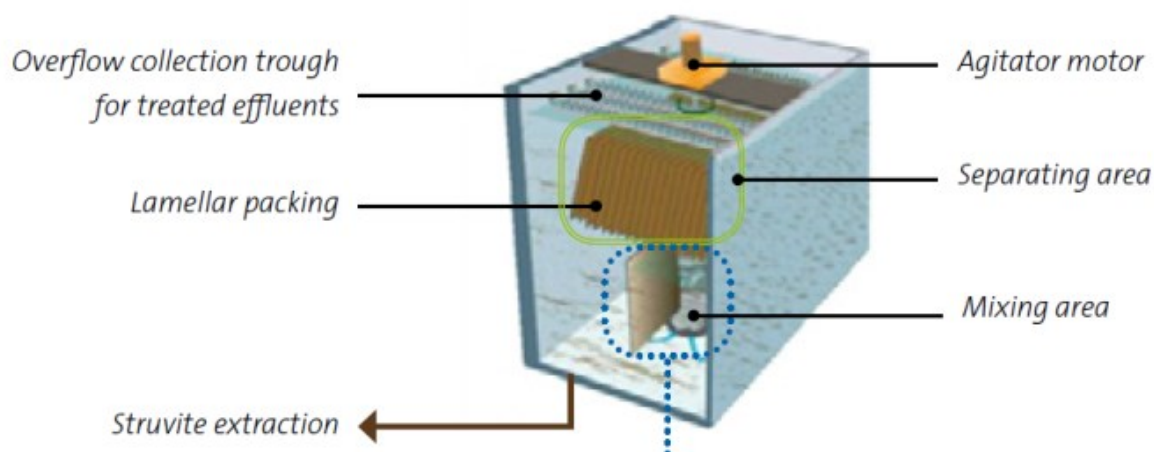
Figure 59: Simplified scheme of the Struvia™ reactor (source: Veolia)

In this pilot, the volume of the reactor in the pilot design is 1000 L with a daily treatment capacity of 60 m³. With a hydraulic retention time (HRT) from 30 to 120 minutes under optimum conditions, the removal rate of soluble $[PO_4-P]$ is about 90%.

5.5.2 Operating conditions

Based on the experience from the pilot installation of the Struvia™ process in Brussels, the following operational parameters for the pilot plant are designed and listed in Table 30 and a description of the designed parameters is given below:

Table 30: Design parameters of Struvia™ pilot plant (Stemann et al., 2014)

	Throughput of centrate [L/h]	500-2500 L/h
	pH control by	Caustis soda or lime injection
Characterisation of pilot	Type of precipitation	Struvite or CaP
	Mixing velocity	30-300 rpm
	Total reactor volume	1000 L
	Liquor specific phosphorus yield [%]	80-95%
Operational data obtained from pilot study	Energy consumption [kWh per m³ wastewater]	≤ 0.3 (~0.2)
	NaOH (30%) [kg/m³ wastewater]	0-0.6
	Molar ratio of magnesium to phosphate [-]	1-2
	Percentage of P in the product [weight %]	12-13

The mixed water from regulation basin 2 is pumped into the mixing and reaction zone. In the configuration magnesium chloride with a concentration of 33% is added. The molar ratio Mg/P applied in the Struvia^{TM} process varies from 1 to 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. The optimal pH is between 8 and 10, caustic soda or hydrochloric acid can be added to control the pH value. The struvite crystals are retained directly in the reactor. A certain concentration of struvite crystals or TSS is kept in the reactor to promote the crystals growth and avoid nucleation. According to the data of the pilot installation of the Struvia^{TM} process in Brussels, electricity is consumed by the feed pump, which is estimated to consume max. 0.1 kWh/m^3 treated flow for an industrial unit, and by the reactor mixer which consumes approximately 0.2 kWh/ m^3.

The TSS concentration of the wastewater has an impact on the struvite crystallization. Therefore, it should be less or equal to 1 g/l. In the case of fertilizer wastewater, the calcium, carbonate, soluble COD or organic compounds contained there may have a negative effect on struvite crystallization. In these cases, the operational conditions must be adapted for struvite crystallization (i.e. the Mg/P ratio applied) and/or a specific pre-treatment may be necessary.

Another option for the fertilizer industry may also be suitable: calcium phosphate precipitation instead of struvite. By adding lime, the pH of wastewater raises and at the same time provides calcium to precipitate phosphates. It is also possible to use caustic soda for pH adjustment to approx. 8 and to use pricier calcium chloride as the precipitation agent. The precipitated product Hydroxy Apatite (HAP) can be directly used as raw material for the fertilizer production.

5.5.3 Cost estimation for the pilot plant

Principally, the total cost of the pilot plant can be categorized into two main types of costs: construction costs and operation & maintenance cost.

5.5.3.1 Cost estimation for the construction of the pilot plant

The main components of the pilot plant are two equalization tanks, one fluidized bed reactor, one Struvia™ reactor and a gravity draining system. The infrastructure systems include a piping system, electrical system and site preparation etc. The estimated price for this pilot plant in a container is about 123,998 € in total and the details are summarized in the following Table 31.

Table 31: Summary of construction cost for the pilot plant

Equipment	Price	Remark
Display module pH&Temp	1,100 €	
pH (Temp)	270 €	
pH instalation	400 €	
NH_4-N online	7,500 €	
PO_4-P online	7,500 €	
Stamoclean	2,500 €	sample preparation
Flowmeter 1	1,300 €	feed for Struvia^{TM} reator
Flowmeter 2	1,200 €	recycle for Struvia^{TM} reator
Flowmeter 3	1,300 €	feed for fluoride removal reator
Pump 1, feed	3,000 €	feed
Pump 2, recycle	2,500 €	recycle
Pump 3, NaOH	2,000 €	NaOH
Pump 4, $MgCl_2$	2,000 €	$MgCL_2$
Pump 5, feed	3,000 €	feed
Pump 6, feed	3,000 €	feed
Pump 7,	2,000 €	$Ca(OH)_2$
Pump 8	2,000 €	HCL
Pumpe 9	3,000 €	feed
Engine 1	1,000 €	Reactor
Mixer	600 €	
Engine 2	1,000 €	Reactor
Mixer	600 €	
Engine 3	1,000 €	Basin 3
Mixer	600 €	
Engine 4	1,000 €	Basin 4
Mixer	600 €	
Level Control 1	100 €	Regulation tank, feed pump off at low level
Level control 2	100 €	
Switch Cabinett	12,000 €	Including frequency converter etc
Computer	2,500 €	Data storage and process control
UPS	1,000 €	Uninterrupted power supply
Regulation basin 1	500 €	100 L, PE or similar
Regulation basin 2	800 €	200 L, PE or similar
Struvia^{TM} reactor	10,000 €	500 L, stainless steel
Fluoride removal reactor	5,000 €	500 L, stainless steel
Lamella	1,500 €	
Chemical basin 1	300 €	50 L, PE or similar, NaOH
Chemical basin 2	300 €	50 L, PE or similar, HCL

Chemical basin 3	300 €	50 L, PE or similar, $MgCl_2$
Chemical basin 4	300 €	50 L, PE or similar, $Ca(OH)_2$
Programming	7,500 €	
Wiring	5,000 €	
Piping	8,000 €	PE or similar
Container	7,500 €	including heating, light
Total	**104,200 €**	
With taxes	**123,998 €**	
In Chinese CNY	**954,784 CNY**	1 EUR = 7.70 CNY, (on 1 July 2017)

5.5.3.2 Cost estimation for the operation and maintenance cost of the pilot plant

The operation and maintenance cost (O&M) is estimated based on the operation and maintenance activities of the pilot plant in one year. The main operational costs for the struvite unit are chemicals, electricity, labor and maintenance costs. The main O&M activities of this pilot plant are summarized as follows in Table 32:

Table 32: Summary of operation and maintenance cost for the pilot plant

Operational costs for Struvite pilot Unit				
	Operational data	Market Price	Costs for 50 t/d Wastewater in CNY	Cost (CNY/year)
Magnesium powder (46%)	0.75 kg $m^3_{treated flow}$ (Molar ratio Mg:P=1.2)	500-800 CNY/t	18.75 - 30	8896
Sodium Hydroxide (30% solution)	0.2 kg/ $m^3_{treated flow}$	500-600 CNY/t	5 - 6	2008
Total electricity	0.5 kWh/$m^3_{treated flow}$	0.6 CNY/kWh	15	5474
Maintenance, labor personal cost	-	-	100	36,500
Total	-	-	138.75-143.5	52,879

5.6 Economic feasibility study for the new concept of wastewater treatment

5.6.1 Recovered product

The process for phosphorus recovery from wastewater provides a solid mineral phosphorus product by precipitation or crystallization. If the phosphate rich stream is mixed with the ammonium rich supernatant, there is a good chance of producing struvite, i.e. magnesium ammonium phosphate ($MgNH_4PO_4$). If the phosphate wastewater or ammonia wastewater contains a high content of potassium or calcium, the recovery of the phosphate can be done through the formation of magnesium potassium phosphate (MKP or KMP, also K-Struvite) or Calcium phosphate (CaP, HAP, DCPD).

- ▪ B to B for selling to fertilizer plant as "ordinary fertilizers"

After having discussed the issue with the chief engineer of this fertilizer group, the company is willing to buy the recovered product for the price of "ordinary fertilizers" and use it as a raw ingredient in their product. To sell as phosphate fertilizer, the price of 1% P_2O_5 in one ton of the product is between CNY 35.0 to 40.0 (EUR 5.0-5.7). The product should not be obtained in very high purity but it should contain less than 2 percent of water. If needed, the surplus heat in the factory can be used for drying the recovered product.

- ▪ B to B for fertilizer manufacturers or distributors as "special fertilizers"

An alternative to supplying the product directly to end-users is to sell it to another slow-release fertilizer manufacturer to sell the product separately or use it as an ingredient in their products. If the recovered product can be registered by the Administration of Industry in China, the product can be sold separately as special fertilizers at a higher price.

- ▪ B to C as garden fertilizer

The product can also be sold in bulk as garden or landscapes fertilizer to costumers online. In Germany, Berliner Wasserbetriebe sold part of the "Berliner Pflanze" fertilizer from sludge in a transparent and recyclable plastic bucket (250 g net weight) at a price of 5.0 €/kg. Large part of struvite was sold for farmers at a bulk price of 20 €/t.

5.6.2 Fertilizer industry analysis in China

Over the past decade, domestic phosphate rock production has increased dramatically in China. At the same time, the five main production provinces in China, Hubei, Hunan, Sichuan, Guizhou and Yunnan, have planned to reduce the number of phosphate producers by shutting down operations under 150,000 tons and decreasing access to phosphate mining rights (MLR, 2012b). The Chinese fertilizer industry has been experiencing a trend towards fewer producers with larger herd sizes.

According to market research, there were in total 1,861 companies in fertilizer production and the ammonia industry in China in 2015 (CNCIC, 2016). The fertilizer companies, which produce water soluble fertilizers, e.g. NPK compound fertilizers, diammonium phosphate, monoammonium phosphate, monopotassium phosphate, may have high concentrations of phosphorus and ammonia in their wastewater. Based on the numbers of compound fertilizer,

NPK, MAP, DAP in China, about 447 units in the fertilizer and ammonia industry (CNCIC, 2016) may have the potential for using this new concept.

The new concept could be favored by the larger and medium-sized fertilizer producers due to a higher product yield. For small producer, the amount of recovered product is limited. In China, the top ten phosphate fertilizer producers mined for about 50% of the total phosphate production.
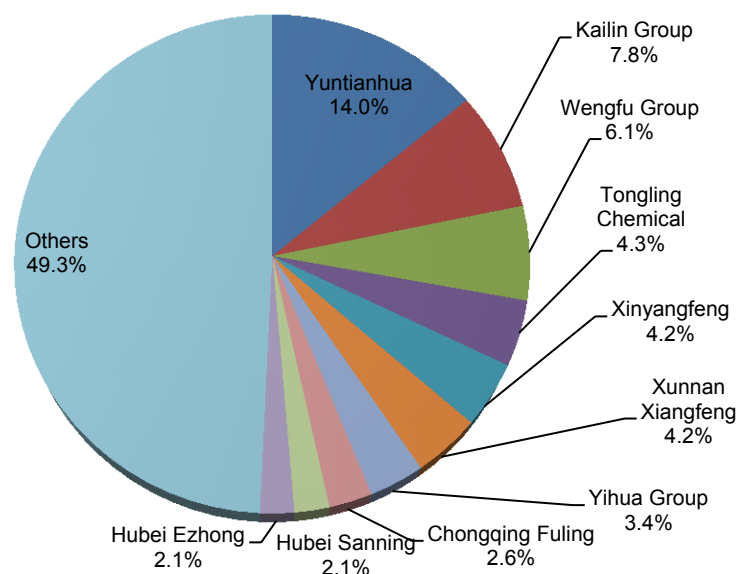
Figure 60: Top ten phosphate fertilizer producers accounted for about 50% of the total output in 2012 (Xiu, 2013)

The Top then phosphate fertilizer producers and their market share are shown in Figure 60. The new concept is ideal for new installations. It can be applied in a retrofitting or upgrading project for increasing the capacity or improving the WWTP effluent quality in these plants.

5.6.3 Commercial feasibility

In general, the cost of the full scale application with Struvia^{TM} system is directly related to the amount of wastewater, influent characteristic of wastewater and required infrastructure in the fertilizer plant. The total cost of the full scale plant can be categorized into two main types of costs: capital expenditure and operational expenditure.

5.6.3.1 Capital expenditure (CAPEX)

Table 33 shows the total capital expenditure with Struvia^{TM} process. The cost of the current asset of this plant is CNY 32,810,614 (approx. EUR 4.3 m). As shown in Figure 61, two tanks from the phosphate treatment line can be replaced by Struvia^{TM} reactor and three tanks can be removed due to lower influent ammonia concentration in the new process. It is estimated that a total of CNY 3,000,000 (EUR 0.39 m) can be saved for of infrastructure investments.

Table 33: Summary of capital expenditure with Struvia^{TM} process for the full scale application

Categories	Facility	Capacity	Cost (CNY)
CAPEX basic Scenario			32,810,614
CAPEX savings on P treatment line	Coagulation tank 2	100 m^3	-1,400,000
	Flocculation tank 2	100 m^3	
	Final Clarifier	1600 m^3	
CAPEX savings on N treatment line	Anoxic tank 2	1950 m^3	-1,600,000
	Aeration Tank 2	550 m^3	
Additional CAPEX for P recovery	Struvia^{TM} reactor	2*250 m^3	6,000,000
	P+N joint treatment capacity increase	from 200 m^3/h to 450 m^3/h	2,800,000
CAPEX P-recovery as Struvia^{TM} scenario			38,610,614
			9.79 CNY/m^3 treated
Increase of Investment			5,800,000

The additional construction and installation cost of one industry scale-design Struvia^{TM} reactor is estimated to be CNY 6,000,000 with a treatment capacity of 400 m³/h. The new ammonia treatment line should increase its capacity from 200 m³/h to 450 m³/h. The incensement of invest for such a new plant is in total about CNY 5,800,000, which is about 17% of the total investment in the basic scenario.
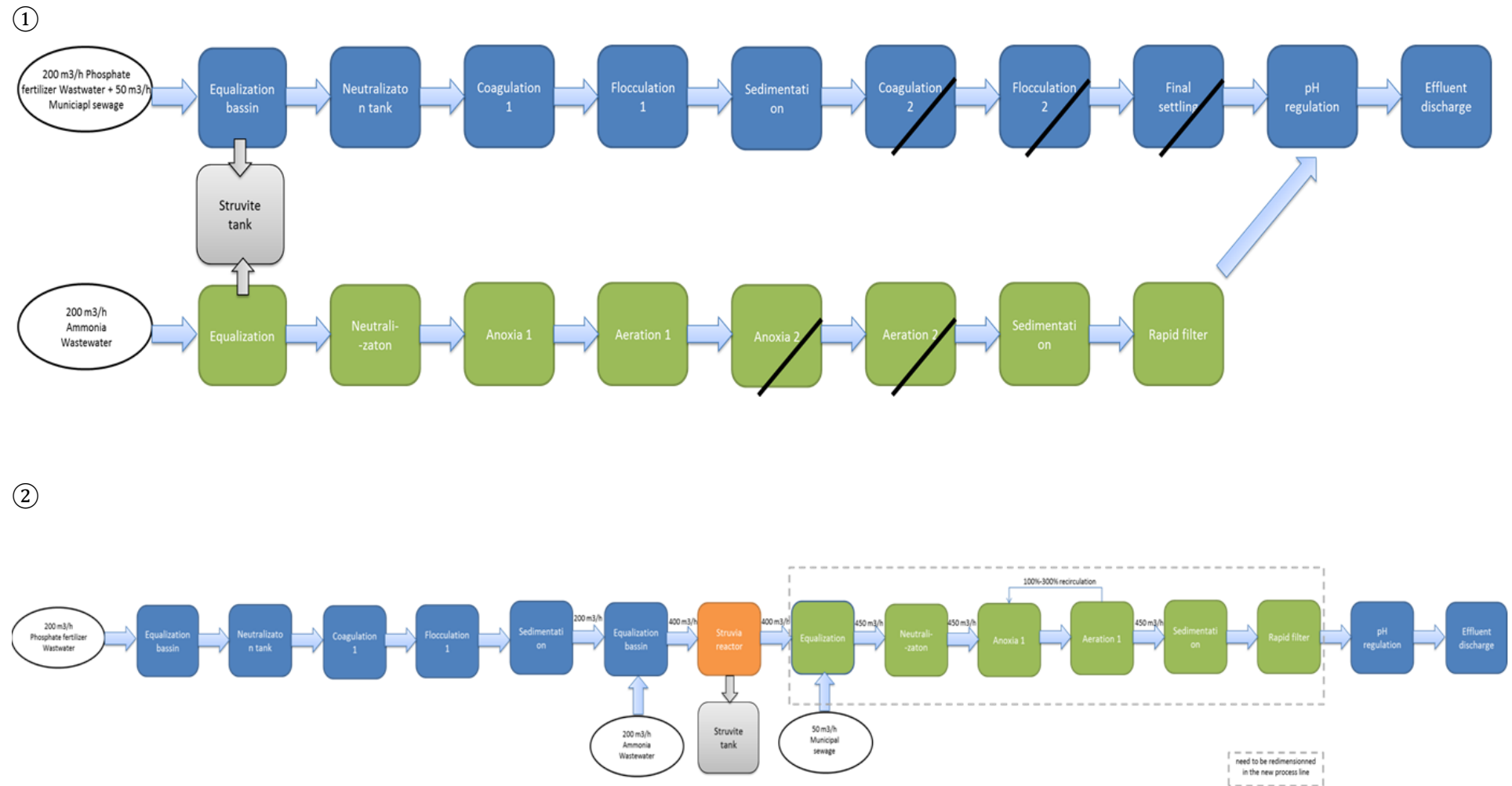
Figure 61: The current wastewater treatment process (1) and the new process with struvite recovery (2)

5.6.3.2 Operational expenditure (OPEX)

The estimated operational cost and the benefit of the recovered product and the other cost savings are estimated for Plant A in the following Table 34.

Table 34: Summary of operation cost and benefit for the full scale application

Extra Operational costs for Struvite full unit					
Categories	Operational data	Market Price	Costs for 10,800 t/d Wastewater in CNY	Cost (CNY/year)	Cost (CNY/ m^3 treated flow)
Magnesium powder (46%)	0.71 kg m^3 treated flow (Mol ratio Mg:P=1.2)	600 CNY/t	4601	1,679,292	- 0.43
Sodium Hydroxide (30% solution)	0.2 kg/ m^3 treated flow	550 CNY/t	1188	433,620	- 0.11
Total Electricity	0.25 kWh/m^3 treated flow	0.6 CNY/kWh	1620	591,300	- 0.15
Maintenance, Labor and personal	-	-	216	78,840	- 0.02
Total	-	-	7625	2,783,052	- 0.71
Benefit					
Categories	Reason	Current costs	Saving in %	Cost Save (CNY/year)	Cost (CNY/m^3 treated flow)
Power consumption	Save 30%, the second stage of phosphorus removal and the second anoxic/oxic process will be closed	1,649,160	30%	494,748	0.13
Chemical save on phosphate treatment line	The second stage of phosphorus removal can turn down: save 40% chemicals $Ca(OH)_2$, PAM(anion), HCl	11,233,282	35%	3,931,649	1.00
Chemical save on ammonia treatment line	Only one unit of anoxic/oxic is needed, more than 1/3 of ammonia is already removed by P-recovery, save 30% chemicals, NaOH, HCl, carbon source				

other costs	Administrative, Personnel, Maintenance	707,805	10%	70,781	0.02
Total benefit without struvite				**4,497,178**	1.14
Potential for additional revenue: Sale price for Struvite	0.45 kg Struvite/ m^3 treated flow	1000 CNY/t Struvite	4500 CNY/d	1,773,900	0.45
Total benefit including struvite				6,139,678	1.59
Total savings including struvite				3,488,026	**0.88**
Current operation costs				16,250,630	4.12

The estimated operational cost savings in plant A of the full scale application with a treatment capacity of 10,800 m³/d is about CNY 0.88 per m^3 treated wastewater with the sale of the struvite product and CNY 0.43 per m^3 treated wastewater without selling the product. The current operational cost of the full scale plant is CNY 4.12 per m^3 treated wastewater. This means approximately 21% percent of OPEX saving can be achieved. A total cost saving of CNY 3,488,026 (approx. EUR 0.45m) per year in this plant can be realized with this innovative method, including the product sale, power and chemical save.

The cost for the magnesium chloride that has to be added is estimated to be around CNY 600 per t magnesium chloride powder and the cost for Sodium hydroxide (30% NaOH) solution is CNY 550 per ton. To reduce this cost, waste streams from other industries containing magnesium and sodium hydroxide can be sourced.

The full-scale unit with a throughput of 100,800 m³/d wastewater requires about 0.71 kg/m³ of 46% magnesium chloride powder (Mg:P=1.2), 0.2 kg/m³ of 30% sodium hydroxide. This calculation is based on the mixed fertilizer wastewater containing 89 mg/l PO_4-P mg/l soluble phosphorus and with 80 % phosphorus removal by the Struvia[TM] Process.

Other operating costs (labor and electricity) are estimated to be:

- Labor: One person for one hour per day at a rate of CNY 100 per hour
- Electricity: 120 CNY per day (average industrial electricity price in China is estimated to be CNY 0.6 per kWh, with energy consumption 0.25 kWh per m³ wastewater)

The total OPEX of the new concept include chemicals, operating and electricity without selling struvite is estimated to be CNY 3.24 per ton of wastewater.

- **Sale price for fertilizer**

According to the calculation about 4.5 t/d of struvite can be produced in this plant. The potential selling price for CaP is lower than for struvite depending on the nutrient types and content. Based on the phosphorus content alone, a sales price of recovered product CNY 1000 per ton is possible. This would be the price if the struvite was to be used in broad-scale agriculture. However, the intention is to use struvite as a "boutique" fertilizer for specialized applications. For those applications, a much higher sales price until CNY 3000-4000 per ton

can be achieved. Based on the price of CNY 1000 per ton, the value of recovered product is estimated at CNY 0.45 per ton of wastewater treatment.

- **Saving costs for chemicals**

The phosphate compound in the fertilizer wastewater is typically treated by neutralization, coagulation, flocculation and precipitation with lime, PAC and PAM. An overall phosphate removal of 80% can be achieved by this unit and thus part of the costs can be saved. On the ammonia wastewater treatment line, about 1/3 of ammonia can be recovered in struvite. The carbon source and other chemicals can be saved. According to the overall chemical use, approximately 35% of the chemical costs for wastewater treatment can be saved, which means saving about CNY 1.08 per ton of wastewater for the costs of chemicals.

- **Environmental benefits**

It is important to highlight that the recovery of phosphorus from wastewater involves important environmental benefits because it prevents eutrophication in the receiving environment, and increases the availability of non-renewable resource phosphorus.

- **Financial outcomes with different commercial scenarios**

The financial plan of this process includes revenues from the wastewater treatment service provided and the sale of the fertilizer product. Expenditure is mainly centered on capital acquisitions of P-recovery Process Struvia^{TM} units, the actual costs of which may be less than the current estimates used in these calculations, significantly increasing profits returned.

Table 35: Different business scenarios for the application of the new technology

	Base scenario	Commercial scenario 1 :	Commercial scenario 2 :
	A plant current	Wastewater is treated at the same price, struvite is given back to the client for free	Wastewater is treated at a lower price, struvite is resold to the client at a low market price
	CNY/m^3	CNY/m^3	CNY/m^3
OPEX	4.12	3.24	3.24
CAPEX depreciation (10 years amortization)	0.83	0.98	0.98
Margin/Profit	0.99 20% of (OPEX + Depreciation)	1.72 Treatment price - OPEX - CAPEX depreciation	0.84 20% of (OPEX + Depreciation)
Treatment price for the client	5.94	5.94	5.56
Profit A Plant in CNY/a	36,441,256	63,404,883	31,048,531

Different commercial scenarios are shown in Table 35. As compared with the base scenario, scenario 1 seems to be the best option. Wastewater from the plant is treated at the same price as before and the recovered product struvite is given back to the client for free, which reveals a significant increase in annual profits of 74%.

5.7 Conclusion

In this chapter, a promising new approach for the treatment of wastewater from the fertilizer industry with phosphate recovery was developed. The major findings from this study are summarized as follows.

Based on the jar test result with synthetic wastewater, an effective two stage process fluoride removal and phosphate recovery has been found. In the first stage, it was observed that under optimum conditions, with a pH between 4 and 5, and a molar ratio $[Ca^{2+}]:[F^-]$ of 1:1, 75% removal of fluoride can be achieved. The residual concentration of fluoride can meet the discharge limits. In the second stage, 87% of orthophosphate and 25% ammonium nitrogen were precipitated under the condition of pH 9.5, with a molar ratio Mg/P of 1.2.

The jar test with real wastewater shows similar results. A significant removal of soluble phosphate, more than 97% P-removal was achieved by mixing of ammonia and phosphate wastewater under the optimum condition (pH=9, molar ratio of Mg/P 1.5; reaction time of 90 minutes). However, the purity of the precipitated product still needs be analyzed. Different operating factors with an impact on the struvite quality should be further optimized, such as Mg:P:N molar ratio, pH, reactor types.

The feasibility of building a Struvia™ pilot plant and full scale plant for the fertilizer industry is also discussed in this study. Results showed that mixing ammonia and phosphate wastewater together with the production of struvite can be cost-effective. When fully operational in this plant with this concept, the nutrient-recovery plant is expected to produce about 1,643 tons of struvite per year. The recovered struvite can be used in the agriculture, turf and ornamental markets. The operational cost savings are the highlight of this new concept: approximately 21% of OPEX savings can be achieved in plant A.

The basic advantages/benefits of this new approach are:

- Simple structures and flexibility in application, minimizing installation footprint
- Saving operational costs, reducing the phosphorus and nitrogen load for the following treatment
- Yield of struvite (TURNING WASTE INTO FERTILIZER)
- Lower demand for chemicals
- Increase of the overall energy efficiency
- Reducing emissions and improving the environment

Chapter 6: General discussion and outlook

In this research, a variety of different approaches for phosphorus recovery and recycling have been analyzed. As shown in Figure 6.1, at a municipal wastewater treatment plant, phosphorus can be recovered and recycled from different locations.

The first option is direct land utilization of sewage sludge with 40% - 90% P recovery potential with regards to the WWTP influent, mainly dependent on the plant availability of the nutrient. This option is suitable for small and medium-sized WWTPs. It is considered as one of the most economical ways for sludge disposal and phosphorus recycling, but the presence of toxic heavy metals, organic contaminants and pathogens in the sewage sludge greatly limits its direct use as a fertilizer. The regulations for the use of sewage sludge in agriculture are different from country to country. In Europe, some countries have already banned or are phasing out this traditional route, i.e. The Netherlands, Switzerland, Norway, and Belgium. In China, the quantity, duration and quality of sludge applied to agriculture should meet the requirements of relevant agricultural standards and regulations. However, many WWTPs in China exceeded the concentration limits of heavy metals in sludge due to the wastewater derived from high-density industrial zones, non-ferrous metal ores and anthropogenic activities. To ensure the quality of sludge, the source control of wastewater, especially the industry wastewater, and reduced use of chemicals in WWTPs are needed. P-recycling via agricultural application of sludge may still be the dominant route for some countries within a certain period, especially in developing countries. However, for reasons of human health, the quality of biosolids for land application should be strictly controlled.

The second option includes recovery of the dissolved P in the aqueous sludge phase prior to dewatering and sludge liquor after dewatering. The maximum recovery potential from the aqueous phase and sludge phase without or with forced P dissolution is 25% and 50% respectively. The phosphorus recovery as struvite is a mature technology, which is applied in more than 40 full-scale plants worldwide. Due to the operational benefits and easy integration within the existing infrastructure, the struvite processes will grow very fast, even without law enforcement. The limitation of this option is only applicable to plants with an EBPR system and recovery of only 25% of influent phosphorus. To overcome these limitations, a forced P re-dissolution with acidic leaching or thermal hydrolysis pretreatment of sludge can improve the P-recovery rate to 50% and is also suitable for the WWTPs with chemical P elimination. The recovered product from sludge extraction is mainly in the form of struvite, dicalciumphosphat and calciumphosphat.

The third option, P-recovery from ash provides the best opportunity for maximum phosphorus recovery. More than 80% of influent P at WWTPs can be recovered by wet-chemical or thermal processes from the mono-incineration ash. This option depends on existing mono-incineration facilities or needs high capital investment on mono-incinerators. The favored recovery product from ash tends to be H_3PO_4 and P_4. The further promotion of this option will depend on law enforcement, e.g. in countries like Switzerland and Germany.
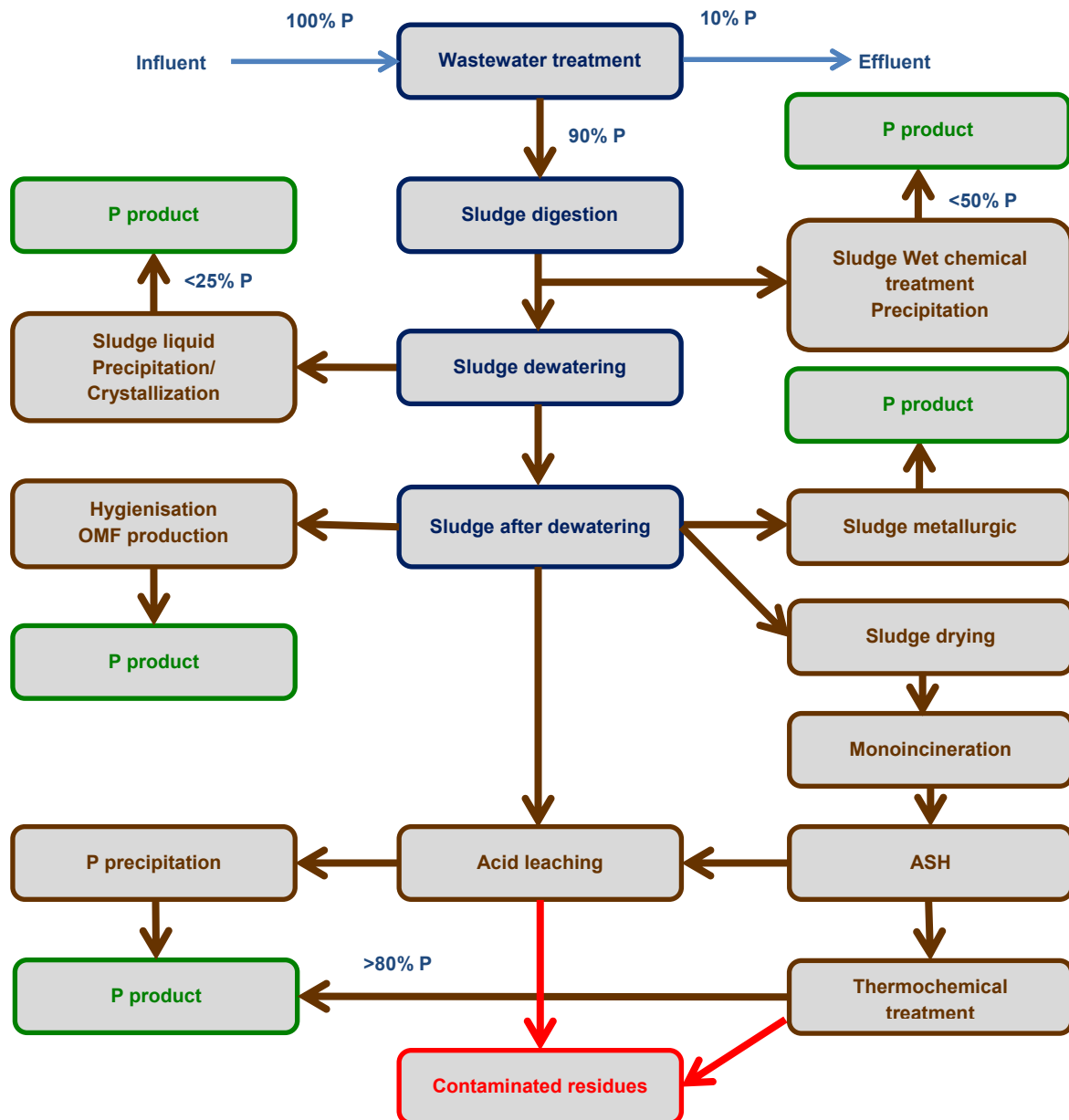
Figure 62: Possibilities of phosphorus recovery from sewage sludge (modified) (Kabbe, 2015; Schaum, 2016)

In Chapter 2, a starch-based biodegradable polymer was tested and examined to meet the regulation of German Fertilizer Ordinance for agricultural use. A more stringent regulation of German fertilizer ordinance requires the degradation of 20% of the synthetic additives like polymeric substances within two years or with limitation of amount of 45 kg active substance (AS) per hectare within three years. This chapter aimed at assessing the use of starch-based polymers for full-scale dewatering of municipal sewage sludge. The successive approach through lab-scale and pilot-scale trials paved the way for full-scale trials at three WWTPs in Germany. The general feasibility to apply starch-based "green" polymers in full-scale centrifugation was demonstrated. Depending on the sludge type and the following process step, the substitution potential was up to 70%. The substitution of 20-30% of polyacrylamide-

based polymer was demonstrated achieving similar total solids of the dewatered sludge. The optimization of operational parameters as well as machinery set up in WWTPs is recommended in order to improve the shear stability of sludge flocs and to achieve higher substitution potential. It is suggested that the starch-based biodegradable polymer has great potential as an alternative polymers to synthetic polymer in sludge dewatering.

In Chapter 3, a comparative Environmental Life Cycle Assessment of phosphorus recovery with 1-reactor system versus 3-reactor system of AirPrex® reactors at WWTP Wassmannsdorf and Amsterdam West was investigated. The reference system is defined as the sludge line treating the mixed sludge of WWTP Wassmannsdorf. Both AirPrex configurations have positive energy benefits and better environmental credits for the GWP, FEP, and MEP. The major contributors to the energy impacts in 3-reactor configuration are electricity for AirPrex reactor (62.6%) and production of magnesium chloride (36.5%) while the main energy benefits are from the heat for district heating to substitute natural gas (40.2%), electricity production in mono-incineration (20.9%), reduced polymer demand (17.5%), the substitution of conventional N and P-fertilizer (10%) and the reduced electricity for return load (3.5%).

The 3-reactor configuration shows better results in cumulative energy demand with 35% improvement of energy surplus, 36% reduction of global warming potential and less eutrophication potential. The different results of both reactors are mainly caused by the reactor design and the harvesting efficiency. It is suggested that, when installing a new AirPrex reactor, the three-reactor system is recommended due to a higher struvite harvesting and lower environmental impact and reasonable investment return. In WMD, the NH_3 emissions into the air can be reduced by instilling of a biofilter. At the same time, it is also important to realize that, the further development of technology, e.g. AirPrex®, can be practiced not only in the laboratory or pilot plant but also in full-scale operation.

In Chapter 4, an analysis of the potentials and limitations of existing P recovery technologies, taking into account their applicability to different types of WWTPs in China, shows that a huge amount of phosphorus is transferred to wastewater and sludge. China's municipal wastewater contains up to 293,163 Mg/a of phosphorus which equals approximately 5.5% of chemical phosphorus fertilizer consumed in China. However, some limitations should be taken into consideration, e.g. the existing WWTP infrastructure and sludge disposal routes. With the increasing of sludge digestion in the future, P recovery from sludge with struvite can be seen as the best option to solve the problem of struvite incrustations at WWTPS. In most cases of recovery from sludge water, dissolution of P from solid sludge into the aqueous phase is needed. In special cases, sludge with an extremely high concentration of phosphorus potentially may provide positive economic effects for the recovery of phosphorus, e.g. in Yunnan and Hong Kong. The average concentration of phosphorus in sludge and sludge ash in China is lower than that in Germany due to the high sand content in sludge and a lack of separation of rain water and municipal sewage. The recovery from industrial wastewater with a high concentration of phosphorus e.g. fertilizer industry, milk production

industry, shows a higher potential than the municipal WWTPs due to easier market access and benefits to its operators.

Unlike in Europe, phosphate rock deposits are abundant in China and the country is the world's largest producer (mining and processing) of phosphate rock. But China is also the largest fertilizer producing and consuming country in the world. The Chinese fertilizer wastewater contained about 12,000 Mg P in 2014. In Chapter 5, a promising new approach for the treatment of fertilizer industry wastewater with high phosphate and fluoride concentration was developed. According to jar test result with synthetic wastewater and real wastewater from a Chinese fertilizer plant, an effective method of soluble phosphate recovery and fluoride removal has been developed. The optimum operating conditions leading to the precipitation of the dissolved orthophosphate and ammonium nitrogen were determined. The jar tests showed a significant removal of phosphate, about 95% P-removal and 30% N-removal was achieved at the optimum condition (pH=9, molar ratio of Mg/P 1.2; reaction time of 60 minutes) with real fertilizer wastewater. Results show that the mixing of ammonia and phosphate wastewater yielding struvite can be cost-effective. The feasibility of phosphorus recovery at a Chinese fertilizer production plant has also been proven.

There is no doubt that phosphorus is a finite resource. In the past few years, the development of P-recovery technologies is quite fast, from lab-scale to full-scale plants, showing that P-recovery is technically feasible. The pioneer countries like Germany and Switzerland already make phosphorus recycling from sewage sludge obligatory. However, the economical feasibility for P-recovery from ash, the revision of the EC fertilizer regulation, EC organic farming regulation and national polices still have an influence on the implementation of the developed technologies. More efforts should be taken to increase both energy and resource efficiency. The next generation competitive technologies should not only focus upon the recovery of the single nutrient P in isolation, but rather more on combined recovery of energy and nutrients, tapping synergies etc. The integrated solution combining complementary struvite recovery processes and ash recovery processes can reach the maximum P-recovery potential from wastewater and sludge.

P-recovery plants are currently mainly located on three continents: Europe, North America and East Asia. There is no "one-fits-all" solution for phosphorus recovery for all countries. The most appropriate way of P recovery and recycling may differ from region to region under different national context. With an expected increasing percentage of municipal sewage sludge digestion and biological phosphorus removal systems, P recovery as struvite and recycling it as a next generation fertilizer is recommended as one of the favorable options for all countries. The recovery from industrial wastewater with a high concentration of phosphorus can also be promoted due to easier market access and benefits to its operators.

Based on the experience of leading countries in phosphorus recovery (Germany, The Netherland, Switzerland, and Japan etc.), the following suggestions are given and can be used as a reference for other countries.

- Building a platform or a nation-wide association among industry, academia, and government to promote sustainable P-management
- Bringing together a wide range of stakeholders, filling knowledge and information gaps between different sectors
- Developing a strategy for a long-term perspective in sustainable P-recovery and raise public awareness
- Creating value chains bridging the gap between recovery and actual recycling for a sustainable market and new business opportunities
- Creating a legal framework to govern P recycling as a level playing field for primary source and secondary (recovered) source nutrients

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