

**DOKUZ EYLUL UNIVERSITY  
GRADUATE SCHOOL OF NATURAL AND APPLIED  
SCIENCES**

**TREATMENT OF REJECT WATER**

**by  
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**November, 2008  
İZMİR**

# **TREATMENT OF REJECT WATER**

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Baran EMİROĞLU**

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## M.Sc THESIS EXAMINATION RESULT FORM

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## **TREATMENT OF REJECT WATER**

### **ABSTRACT**

Sludge from primary clarifiers and final sedimentation (i.e. excess sludge) are stabilized in an anaerobic digester, and dewatered thereafter. The water flows from sludge dewatering processes (i.e. reject water or sludge liquor) on municipal wastewater treatment plants (WWTPs) are a few liters per person per day. Therefore, the hydraulic influence on the plant is not important. In contrast, the ammonium concentration in the sludge liquor can reach 2500 mg/L. Thus, the rejected nitrogen load can account for up to 25% of the nitrogen load in the raw sewage. Due to the considerable nitrogen load, reject water from dewatering of sludge could impose on the wastewater treatment process. Being returned to the inlet of a wastewater treatment plant the influent loading of the plant is significantly increased causing occasional overloading situations. Thus, separate treatment alternative is recommended as an optional solution to the problem.

Various researches works into finding innovative ways that takes advantage of ammonium rich composition of reject water, and has gained prominence in the wastewater industry over the last two decades. Currently new heights have been attained through the nitrification/denitrification step especillay for ammonium removal. In addition, there are a number of methods for treating phosphorus in reject water namely; magnesium-ammonium-phosphorus (MAP) or struvite precipitation, hydroxyapatite (HAP) precipitation and natural aging of phosphorus. However, progress at phosphorus removal has largely remained at the experimental stage, in spite of its considerable composition in reject water. Therefore, the aim of this thesis is to try to identify theoretically all the methods that have evolved over the years at treating reject water from dewatering sludge and investigate the possible strategies to handle the rejection problem, and processes for separate treatment of the sludge liquor. In this framework, characterization of the reject water taken from two different municipal WWTPs is carried out as first. Characterizaion studies were assisted to realize that important parameters such as pH, nitrogen, phosphorus,

suspended solids, coliform and heavy metals for treatability studies and use of reject water for irrigation purpose. Afterwards, treatability studies were made and struvite and hydroxyapatite precipitation methods were carried out for treatment purpose. Treatability studies stated that %25-41 of phosphate phosphorus and %28-46 of ammonium nitrogen and %76-100 magnesium were treated by struvite precipitation at optimum pH (8-9), mixing time (4 hours), perlit dose (5, 15 and 20 mg/l) and Mg-P ratio (1:1, 1.1:1). On the other hand, higher phosphate phosphorus removals were achieved by hydroxyapatite precipitation. In the hydroxyapatite precipitation studies, phosphate phosphorus treatment ratio was around %92 at optimum pH (9), 2 hours mixing time and 20 g gypsum/L were selected as optimal dose.

**Keywords:** Reject water, sludge liquor, nitrogen removal, struvite, phosphorus removal, hydroxyapatite.

## SÜZÜNTÜ SUYU ARITIMI

### ÖZ

Ön çökeltim çamuru ve son çökeltim ünitelerinden gelen fazla çamur, anaerobik çürütücüde stabilize edilir ve ardından susuzlaştırılır. Kentsel atıksu arıtma tesislerinde çamur susuzlaştırma işleminden gelen su miktarı (süzüntü suyu veya çamur suyu gibi) kişi başına günde birkaç litre mertebesindedir. Bu nedenle, tesis üzerindeki hidrolik etkisi önemli değildir. Buna karşın, çamur suyundaki amonyum konsantrasyonu 2500mg/L mertebesine ulaşabilir. Böylelikle, geri devir edilen azot yükü, ham atıksudaki azot yükünü %25 oranında arttırabilir. Bu durumda, çamur susuzlaştırma ünitesinden gelen süzüntü suyu fazla azot yükü nedeniyle atıksu arıtma işlemlerinde sorun oluşturabilir. Arıtma tesislerinin girişine süzüntü suyu gerideviri ile zaman zaman aşırı yükleme olması nedeniyle arıtma tesisine gelen yük önemli ölçüde artabilir. Bu durumda, problemin çözümü olarak mevcut sistemin haricinde ayrı yapılacak arıtma alternatifi önerilmektedir.

Süzüntü suyunda bulunan yüksek amonyum azotu konsantrasyonunun sağladığı avantajlardan yararlanarak uygun arıtma alternatifleri geliştirmek için yapılan çeşitli araştırmalar özellikle atıksu endüstrisinde son yirmi yılda önem kazanmıştır. Son zamanlarda, özellikle amonyum giderimi için, nitrifikasyon/denitrifikasyon işlemlerinde yeni gelişmeler ortaya çıkarılmıştır. Bunlara ek olarak, atıksudaki fosforun arıtımı için magnezyum-amonyum-fosfat (MAP) ya da struvite çökeltimi, hidroksiapatit (HAP) çökeltimi ve fosforun doğal giderilmesi gibi çeşitli metodlar vardır. Ancak, süzüntü suyunda yüksek miktarda fosfor olmasına rağmen, fosfor giderimine yönelik araştırmalar büyük oranda deneysel safhaya kalmıştır. Bu nedenle, bu tezin amacı, çamur susuzlaştırma işlemlerinden kaynaklanan süzüntü suyunun arıtımına ilişkin geliştirilen yöntemler hakkında teorik bilgiler vermek, süzüntü suyunun bertarafına ilişkin stratejileri incelemek ve çamur süzüntü suyunun mevcut arıtma dışında tekil olarak arıtılabileceği yöntemleri araştırmaktır. Bu çerçevede, öncelikle iki farklı kentsel atıksu arıtma tesislerinden alınan süzüntü suyu örneklerinin özellikleri (karakterizasyonu) belirlenmiştir. Karakterizasyon

çalışmaları ile pH, azot, fosfor, katı madde, koliform ve ağır metal gibi önemli kirlilik parametreleri belirlenmiş; süzüntü suyunun sulama amaçlı kullanım olanakları ve arıtılabilirliğine ilişkin değerlendirmeler yapılmıştır. Karakterizasyon çalışmalarını takiben yapılan arıtılabilirlik çalışmalarında struvit ve hidroksiapatit çökeltim metodları uygulanmıştır. Arıtılabilirlik çalışmaları, uygun pH (8 ve 9), karıştırma süresi (4 saat), perlit dozu (5-15 ve 20g/L) ve Mg-P (1:1, 1,1:1) oranında, %25-41 oranında fosfat fosforu arıtımı ve %76-100 oranında amonyum azotu gideriminin gerçekleştiğini göstermiştir. Hidroksiapatit çökeltimi ile uygun pH (9), karıştırma süresi (2 saat) ve alçıtaşı dozunda (20g/L) %92 oranında fosfat fosforu arıtımı elde edilmiştir.

**Anahtar Kelimeler:** Süzüntü suyu, çamur suyu, azot giderimi, struvit, fosfor giderimi, hidroksiapatit.



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## CHAPTER ONE

### INTRODUCTION

The water from sludge dewatering processes on wastewater treatment plants (WWTPs) are defined as reject water. In literature, it sometimes is called as sludge liquor, return liquor, sludge centrate liquor or digester supernatant. The amount of water from sludge dewatering processes on municipal wastewater treatment plants (WWTPs) are a few liters per person per day. Therefore, the increase of the hydraulic loading of a municipal wastewater treatment plant caused by the sludge dewatering process is of minor importance. However, the effluent water (i.e. reject water) from sludge digestion/dewatering process can contain up to more than 1000-2500 mg/L ammonium nitrogen as well as considerable concentrations of phosphate and chemical oxygen demand (COD) (Arnold *et al.*,2000). Since reject water has contain high concentrations of the pollutants like nitrogen, phosphorus, and organic carbon compounds, recycling of the reject water from dewatering of sludge can increase the influent loads in the WWTPs (Wett *et al.*, 1998). Thus, rejection management has become a very important at wastewater treatment over the last few decades.

As it stated above, influent nutrient load of wastewater treatment plants (WWTPs) is increased considerably when reject water is recycled to it. The reject water stream, representing typically only 2% of the volume of the influent wastewater stream, can contribute up to 25-30% of the N load of the influent to the activated sludge process. This is especially problematic in case the latter has a limited aeration/nitrification/denitrification capacity. In order to relieve the main plant, it can be decided to treat the reject water stream before recirculation. On the other hand, return liquor treatment may be beneficial when the processed nitrogen in the form of ammonium sulphate precipitated from the ammonia stripping process is used as fertilizer or as an industrial chemical (Thorndahl, 1993). Moreover, the chemical composition of sludge liquor favours the formation of the mineral magnesium-ammonium-phosphate (MAP) or struvite, which can also be used as fertilizer.

Reject water is normally treated for nitrogen and phosphorus due to their ability to over load the biological treatment process of the WWTP. Nitrogen removal in reject water has seen more advances in process technology development and implementation at full-scale levels compared to phosphorus. The conventional process of nitrification/denitrification and ammonia stripping were the earliest methods for sludge liquor treatment for ammonium removal. The conventional process (i.e. nitrification/denitrification) was carried out in different treatment reactors or by expanding the biological zone, which has turned out to be very expensive. The traditional process involves the conversion of ammonium in sludge liquor by nitrifying bacteria *nitrosomonas* and *nitrobacter* to nitrate before heterotrophic bacteria denitrify nitrate to nitrogen gas. While, that of ammonia stripping occurs when by increasing the pH of sludge liquor free ammonia occurs thus allowing it to be removed by air or steam. Currently, new heights have been attained through the nitrification/denitrification step and emerging partial nitrification/Anammox process. Studies have shown that at any given temperature pH and sludge age are the critical parameters for partial nitrification, when oxygen supply is not limiting (Pollice *et al.*, 2002). However pH control, ammonium concentration and temperature are also important to keep a stable nitrification process (Abeling and Seyfried, 1992). At full-scale level the Sequencing Batch Reactor (SBR) has proven adequate at achieving stable nitrification. The SBR operates by filling/aeration, sedimentation and withdrawal. Two types of operation of SBR are currently in practise. Ammonium removal with pH controlled nitrification in the SBR with a subsequent denitrification in the anoxic zone of the biological process (Mossakowska *et al.*, 1997, Wett *et al.*, 1998, Arnold *et al.*, 2000). The other has nitrification taking place in the SBR without pH control with denitrification taking place in the anoxic zone of the activated sludge process (Laurich and Gunner, 2003). In a parallel system from Rosen *et al.*, (1998) complete nitrification/denitrification was achieved in the SBR with the aid of about 30% raw wastewater diverted from the influent to serve as a carbon source. Another biological process that is able to achieve nitrification is the SHARON process. Four full-scale SHARON systems have been constructed at large wastewater treatment plants in Rotterdam, Utrecht, Zwolle and Beverwijk (all in the Netherlands).

On the other hand, there are a number of methods for treating phosphorus in reject water namely: magnesium-ammonium-phosphorus (MAP) or struvite precipitation, hydroxyapatite (HAP) precipitation and natural aging of phosphorus in a thermostatic room. On phosphorus removal from reject water, the focus in the seventies concentrated on the chemical crystallisation of hydroxyapatite (HAP) (Momborg and Oellerman, 1992). But this has progressed over the years to include researches into the removal and recovery of MAP through the addition of metal salts and or high pH level (Pitman, 1999). The precipitation of phosphorus in both MAP and HAP requires addition of alkaline to a pH value of 8 to 9.5 coupled with the right ratio for magnesium in MAP and calcium in HAP, respectively. Crystallization of HAP is performed with seed crystals at best with magnesia clinker, zirconium hydroxide, pumice and sand. The best results are obtained in MAP precipitation at  $\text{Mg}(\text{OH})_2$  concentration of 400 mg/l. In both cases the solubility product of MAP and HAP needs to be exceeded. However, progress at phosphorus removal has largely remained at the experimental stage, in spite of its considerable composition in reject water. Some of the reasons that have contributed to the current situation are the complexity and cost in operating chemical precipitation of phosphorus plants at full-scale level. These are due to the clogging of pipes that can lead to breakdowns and the cost involved in dewatering and drying of the precipitate.

Although phosphorus composition in reject water can be in considerable quantities research into its removal has been largely focused on removal through precipitation and more recently on its recovery. The possible uses of recovered struvite as fertilisers are addressed. At present, the researchers indicate, both fertiliser manufacturers and fertiliser trade associations are reluctant to define how struvite could fit into existing fertiliser markets, as the product has never been tested in field trials. 1960's research in the US, however, suggests that struvite can be effectively used as a slow-release fertiliser at high application rates without risk of damaging plants. Suggested uses are diverse and include ornamental plants, young trees in forestry, grass, orchards and potted plants. A recent Dutch publication suggests using struvite as a slow-release, reserve phosphorus supply for container potted plants, with

a more soluble fertiliser as the initial supply (Gaterell *et. al.*, 2000). Therefore it is assumed that struvite is indeed effectively suitable for substitution for existing fertiliser products. An estimated that 29,000 tonnes P/year could theoretically be recovered for recycling as struvite in the UK, 134,000 tonnes P/year in Western Europe, on the basis of 80% recovery of sewage works inflow phosphates and 85% of the population connected to sewage works (Gaterell *et. al.*, 2000). Although certain sewage works configurations are not readily appropriate for P-recovery (eg. trickling filter), increasing requirements for P-removal combined with pressure on sludge disposal may lead to the replacement of such installations with processes compatible with biological P-removal. This would facilitate struvite recovery, as biological nutrient removal processes offer streams with high soluble phosphate and ammonia concentrations, appropriate for struvite precipitation.

Therefore, the main objective of this study was to investigate the reject water quality (characteristics) and to evaluate the treatment performance of the chemical precipitation methods (i.e. MAP and HAP precipitation) as a separate treatment alternative. This document is structured to provide a general understanding of the reject water treatment methods and its principles, including definitions of reject water and characteristics, parameters influencing treatment performance; and particularly to give an insight for the environmentally sound management of sludge liquor. Chapter 1 summarizes the initiatives and main goals of this study. Chapter 2 reviews the literature; reject water characteristics and treatment methods. Chapter 3 explains the experimental studies including characterization and treatability studies. The results obtained from the experiments are discussed in Chapter 4. Finally, Chapter 5 contains both conclusions and the recommendations for further studies.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Reject Water Characteristics

The characteristics of reject water are different to the influent to the WWTP in terms of its concentration and composition (Arnold *et al.*, 2000). This stems from the fact that the sludge dewatering or digestion method gives different total nitrogen concentration in returned liquors (Thorndahl, 1993). According to Pitman (1999) the differences arise from the type of machine used, alkaline doses and the dewatering properties of the sludge. Nitrogen in reject water is mainly present as ammonium; since it is not removed in digestion process and therefore sludge digestion generally produce an ammonium-rich effluent (Strous *et al.*, 1997). The high ammonium content of reject water is due to the incorporation of the remainder of the non-oxidized nitrogen from the biological stage into the excess sludge. Then during anaerobic sludge digestion and dewatering process ammonium nitrogen is released into sludge liquor (Siegrist, 1996).  $\text{NH}_4\text{-N}$  loads up to 25% of the total influent  $\text{NH}_4\text{-N}$  load have been reported in reject flows, which account for only 2% of the total influent flow (Janus and van der Roest, 1997).

Pitman *et al.*, (1991) asserted that reject water can also contain considerable quantities of phosphorus in solution and fine colloidal suspension. Phosphorus concentration although considerable is most significant parameter in biological phosphorus removal (bio-P) plants where the nutrient is accumulated in the sludge. Characteristics of reject water from Hamburg's Combined Waste Water Treatment Plant (Laurich and Gunner, 2003) and Frederikshavn Sewage-Treatment works (Thorndahl, 1993) are composed of total nitrogen,  $\text{NH}_4\text{-N}$ , Total P, COD, Suspended Solids (SS) and bicarbonate. Characteristics of reject water generated from the digestion effluent from the Rotterdam's treatment plant showed high elevations of nitrogen that could potentially over load the biological stage (Hellinga *et al.*, 1998).



Typical reject water composition and concentration ranges are given in Table 2.1. The pH values of reject water are normally slightly alkaline and have a wide variability depending on whether alkaline is added to aid the dewatering process or not. Temperature ranges for reject water can be high due to the application of high temperatures during the anaerobic digestion process. Chemical Oxygen Demand (COD) removal rate at this stage of the treatment process is limited due to the relative low fraction of biodegradable substances. Additionally, carbon to nitrogen ratio (C/N) is mostly less than 1, which requires the need of an external carbon source to eliminate nitrogen.

Table 2.1 Typical reject water composition

Reject water	Range	Unit	References
N-Kj	690- 1700	mg/l	Thorndahl (1993), Wett <i>et al.</i> , (1998)
NH <sub>4</sub> -N	600- 1513	mg/l	Arnold <i>et al.</i> , (2000), Jenicek <i>et al.</i> , (2004)
P <sub>total</sub>	trace-130	mg/l	Fux <i>et al.</i> , (2003), Pitman <i>et al.</i> , (1991)
SS	<800	mg/l	Mossakowska <i>et al.</i> , (1997)
COD	700-1400	mg/l	Thorndahl (1993), Laurich and Gunner, (2003)
Temperature	25-40	°C	
pH	7-13	-	Fux <i>et al.</i> , (2003), Wett <i>et al.</i> , (1998)
Alkalinity	53-150	mmol/l	Fux <i>et al.</i> , (2003), Wett <i>et al.</i> , (1998)

## 2.2 Reject Water Treatment Methods

Methods used to treat reject waters include physicochemical methods, such as ammonia stripping, steam stripping and chemical precipitation such as struvite (MAP) and hydroxyapatite (HAP) precipitation, HAP precipitation, and biological processes, such as nitrification– denitrification in activated sludge systems, biofilm or SBRs. In this section, principles of these methods are introduced to give an insight for the reject water treatment.

### 2.2.1 Physico-Chemical Methods

The process for nitrogen elimination by either air or steam stripping in reject water involves both the application of physical and chemical methods. The chemical

part allows for the attainment of the right pH before the physical process of stripping the ammonia gas in a stripping tower or column. For the sludge water treatment, two stripping processes may be introduced, i.e. air and steam stripping.

#### *2.2.1.1 Air Stripping*

Nitrogen in reject water is mainly present as ammonium ( $\text{NH}_4^+$ ) form. By raising pH, the ammonium is converted to ammonia ( $\text{NH}_3$ ), which is readily soluble in water. When collected with a gaseous phase, the ammonia will be transferred from the water phase to the gaseous phase. The stripping process normally takes place in a stripping tower in which water and gas flow counter-currently. Packing material in the stripping tower allows for a high contact surface.

In general, ammonia stripping is a simple process used to lower the ammonia nitrogen content of a wastewater stream (USEPA, 2000). In reject water, since nitrogen is mainly present as ammonium, pH has to be raised to convert ammonium to ammonia as first (Janus and Van der Roest, 1997). When the pH is increase by the addition of lime or caustic to between 10.8 and 11.5, ammonium hydroxide is converted to ammonia gas (USEPA, 2000). At the high pH value, the equilibrium reaction shifts totally towards ammonia (Thorndahl, 1993) and this is removed by stripping. In this process, sludge flocs and precipitated  $\text{CaCO}_3$  resulting from the high pH have to be removed in a pre-sedimentation step (Siegrist, 1996).

As it stated above, stripping process takes place in a stripping tower, which comes in two types flow, i.e. cross-flow and counter-current flow. In a cross-flow tower, the solvent gas (air) enters along the entire depth of fill and flows through the packing, as the reject water flows downward (see Figure 2.1). A counter-current tower draws air through openings at the bottom, as wastewater is pumped to the top of a packed tower. Free ammonia is stripped from falling water droplets into the air stream, and then discharged to the atmosphere or collected. Packed towers as shown in Figure 2.2, usually use engineered or random plastic packings. Design criteria for packed towers include surface area provided by the packing, column height and

diameter, and air to water flow rates.

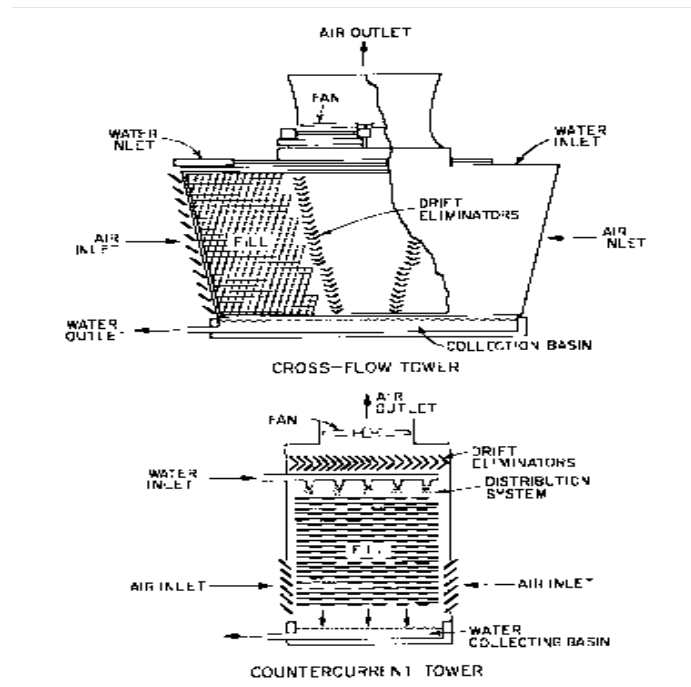


Figure 2.1 Cross-flow and counter current stripping towers (Culp, et. al, 1978)

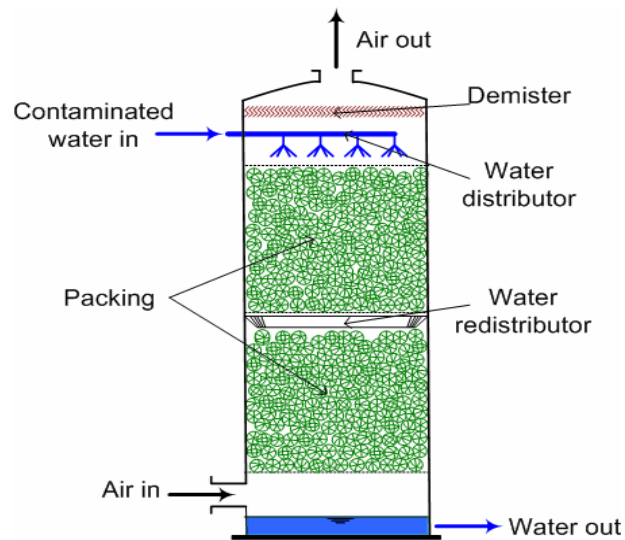


Figure 2.2 Working principle of counter current packed tower stripper (Laurich, et. al, 2003)

### 2.2.1.2 Steam Stripping

The main difference between air and steam stripping is the treatment of the ammonia rich gaseous phase. In the air stripping process, the ammonia rich air is either scrubbed with acid or combusted. In the steam stripping, aqueous ammonia is produced, which can be concentrated by reflux. Complete removal of ammonia is obtained at pH values less than 3.5 during acid scrubbing (e.g. sulphuric acid) while at catalytic combustion of temperatures greater 275°C ammonia was also completely removed (Janus and Van der Roest, 1997).

On the other hand, the sludge combustion and anaerobic digestion stages produce excess energy which is converted into steam for heating several process stages. At present, low pressure steam which could be used for steam-stripping reject water, is wasted. When the steam stripping process was compared with conventional air stripping process, the steam stripping process is found to be more economical due to low energy price of waste stream.

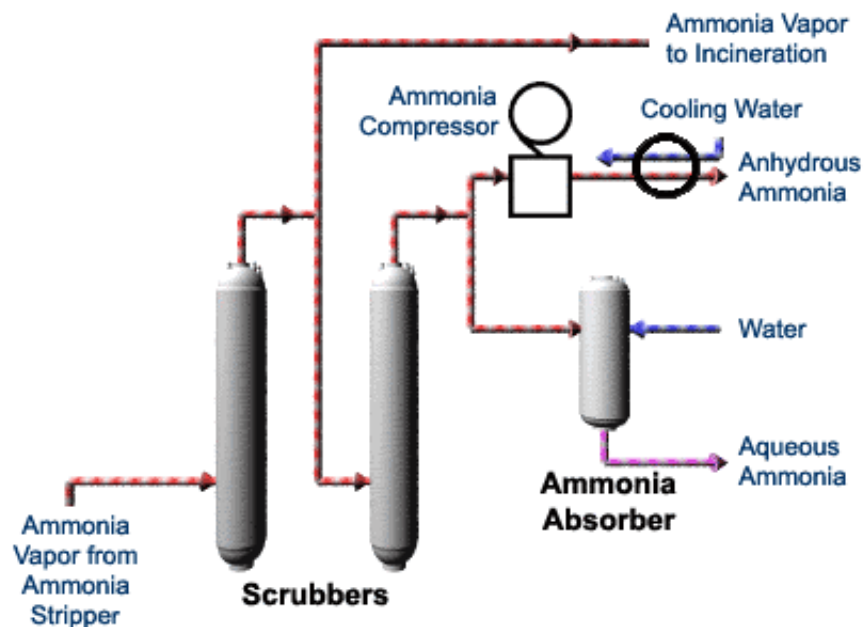


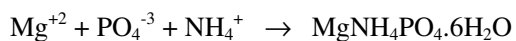
Figure 2.3 Typical steam stripping system (Chevron Corporation)

### 2.2.1.3 Chemical Precipitation

Ammonium is precipitated in the presence of phosphate and magnesium to magnesium ammonium phosphate (MAP). The product is also known as struvite. Ammonium elimination up to 85% is possible by MAP precipitation. The process is characterized by high consumption of chemicals and causes a minimum production of 17.5 kg sludge per 1 kg NH<sub>4</sub>-N, which is significant. Removal of phosphorus is performed through HAP precipitation method. Crystallization of HAP is performed with seed crystals and at best with magnesia clinker, zirconium hydroxide, pumice and sand.

The technologies for both MAP and HAP crystallization are fundamentally the same with only slight differences occurring in the parameters. The major difference is the reliance on calcium ion (Ca<sup>++</sup>) concentration for HAP crystallization and magnesium (Mg<sup>++</sup>) and ammonia (NH<sub>4</sub><sup>+</sup>) concentrations for struvite crystallization. Eventually, the products are removed as they are precipitated and these products have the tendency to clog the equipments and may cause temporal breakdown of the systems.

*2.2.1.3.1 Precipitation of Struvite/MAP.* The chemical precipitation of magnesium-ammonium-phosphate (MAP) or struvite is effective for nitrogen removal in reject water. Actually, MAP as a basic salt is soluble in acid solution. But its precipitation is much more efficient with increasing pH. Struvite precipitates (Celen and Turker, 2001) in the presence of Mg<sup>+2</sup>, NH<sub>4</sub><sup>+</sup>(N) and PO<sub>4</sub><sup>-3</sup>(P) in equal molar concentrations. Struvite formation is given in the following reaction:



Struvite precipitation is controlled by pH, degree of supersaturation, temperature and the presence of other ions such as calcium and can occur when the

concentrations of magnesium, ammonium and phosphate ions exceed the solubility product (often denoted as  $K_{sp}$ ) for struvite. The relationship between  $K_{sp}$  and pH indicates that struvite solubility decreases with increasing pH, which in turn leads to an increase in the precipitation potential of a solution.

Struvite is most likely to form in areas of increased turbulence as its solubility decreases with pH and its formation is often associated with anaerobic and post digestion processes. Struvite has been reported to foul equipment and pipework causing operational failure and downtime. For these reasons the prevention of struvite formation has become an important aspect of sludge treatment and management.

MAP precipitation described by Siegrist (1996) proceeds with the removal of SS in the digester supernatant by flocculation with a highly cationic polyelectrolyte. In a pilot study of MAP precipitation, phosphoric acid and magnesium oxide were added with an Mg: P: N ratio of 1.3:1:1, to three reactors in series each of volume  $0.5\text{m}^3$ . In the first reactor phosphoric acid is added after which the  $\text{CO}_2$  produced is stripped. Magnesium oxide is then added to the second reactor to eliminate 70% of ammonium. The pH is adjusted to 9 in the third reactor with NaOH while 85-90% of the ammonium is removed at a hydraulic load of  $0.5\text{ m}^3/\text{h}$ . Excess magnesium is necessary to lower the equilibrium concentration of ammonium, to save NaOH, and to prevent re-circulation of phosphate to the treatment plant by over dosing of phosphoric acid. The MAP slurry is directly dewatered with a decanting centrifuge to 50% dry solids.

One of the full-scale struvite treatment plants has been operated in Italy (see Fig. 2.4). The struvite crystallization process (SCP) plant is constituted of a pre-treatment and two operative sections: a stripping tank and a fluidised bed reactor (Battistoni *et al.*, 2001). The pre-treatment section is composed of an apparatus to remove suspended solids and a reservoir tank to manage the FBR (fluidised bed reactor) in continuous mode, notwithstanding how the dewatering section runs. A stripper and a connected deaeration column compose the stripping section. The anaerobic supernatant after pre-treatment is supplied from the reservoir tank and sent to the

stripper, together with the recycle flow rate from FBR. The air flow rate needed for CO<sub>2</sub> stripping is pumped from bottom using ceramic aerators, while the effluent exits from the deaeration column together with the recycle flow rate. The system stripper plus the deaeration column can work at different levels allowing different hydraulic heads and hydraulic retention times. At the bottom of the column a steel cylinder filled with gravel with decreasing size distribution to work as a filter, avoiding sand return to the pump and allowing a homogeneous distribution of the stream to the reactor. At the top of the column an expansion tank is provided in order to prevent the loss of sand from the reactor.

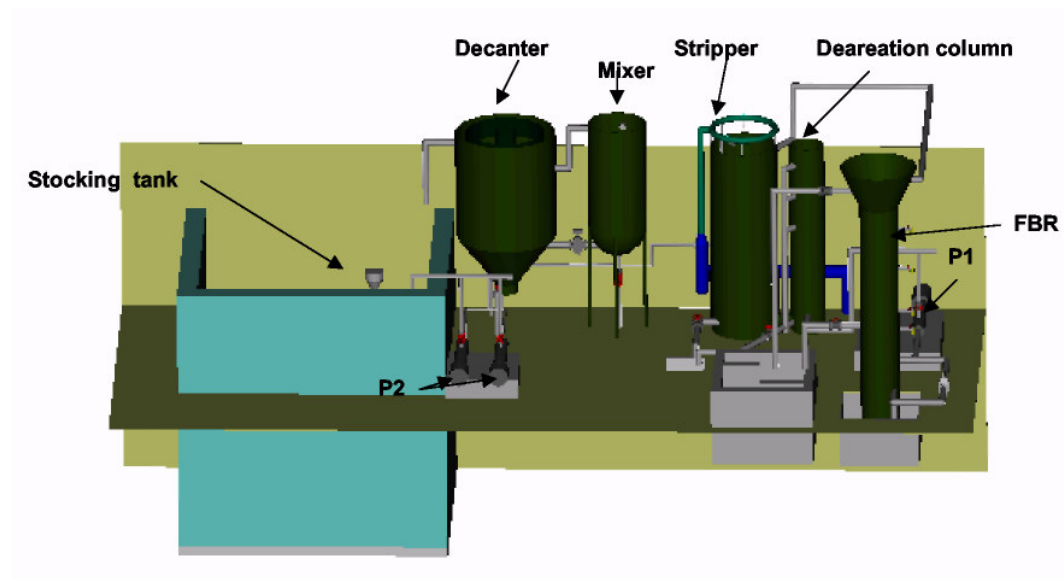


Figure 2.4 The full-scale SCP at Treviso in Italy (Battistoni, et. al, 2001)

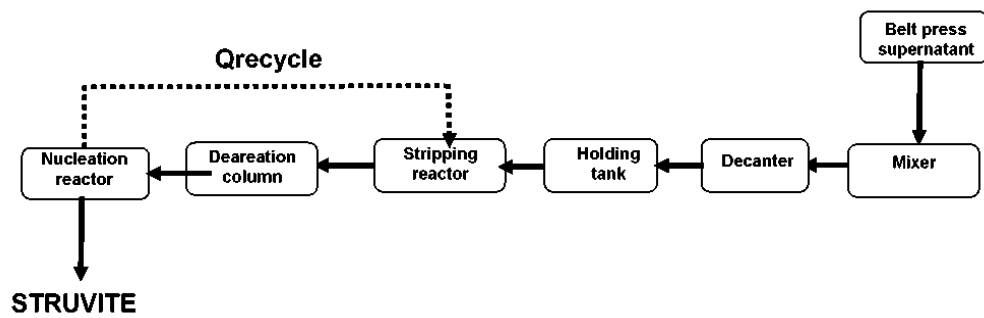


Figure 2.5 Demonstrative area of struvite crystallization in Treviso WWTP (Cecchi, et. Al, 2003)

In figure 2.6, struvite plant with a capacity of  $500 \text{ m}^3 \text{ d}^{-1}$  have been in operation at the Shimane Prefecture Lake Shinji East Clean Centre since 1998 is shown. The reactor used is a fluidised bed reactor agitated with air. The digester effluent is introduced at the bottom of the reactor. The reactants,  $\text{Mg}(\text{OH})_2$  and  $\text{NaOH}$ , are introduced at the top of the column in order to obtain a Mg/P ratio of 1 and an operating pH of 8.2-8.8. Air is injected at the bottom of the column to provide the “mixing” and the  $\text{CO}_2$  stripping.

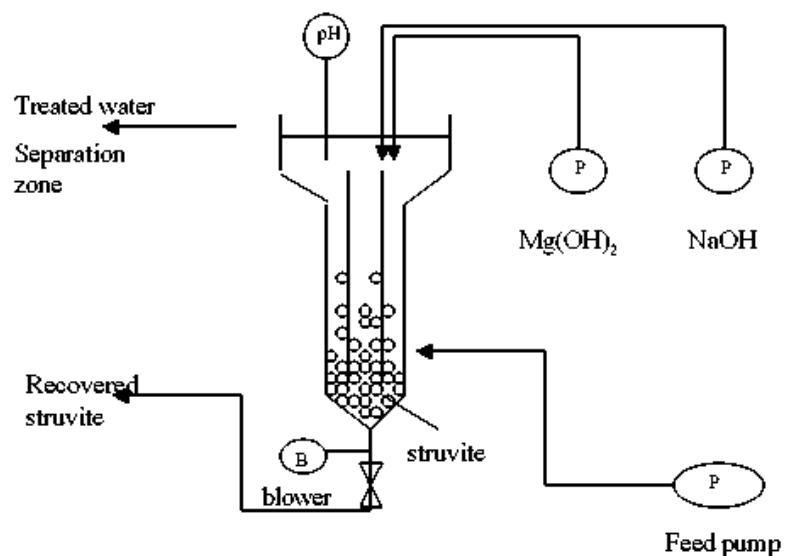


Figure 2.6 Schematic diagram of the struvite plant at the Shimane Prefecture Lake Shinji East Clean Centre (Ueno, et. al, 2001)



2.2.1.3.2 *Crystallization of hydroxyapatite (HAP)*. Crystallization of HAP for phosphorus removal from sludge liquor follows the equation below and this relies on the calcium ion concentration (Mombert and Oellermann, 1992). For chemical precipitation of HAP it has been realized from HAP molecular formula that the Ca:P ratio must be in the range of 2:1 for efficient HAP formation.



Removal of phosphate in anaerobic supernatant without the addition of chemicals has been carried out in a fluidised bed reactor (FBR) column with quartz sand as seed material for struvite crystallization (Battistoni *et al.*, 2000). Other seed crystals of good HAP precipitation characteristics are magnesia clinker, zirconium hydroxide and pumice. The use of seed crystals allows both to produce pellets and avoid sedimentation or filtration step and to operate at a lower pH. Crystallization of HAP is precipitated when the CO<sub>2</sub> is strip with air to increase the pH. The crystallization technique allows operation in the metastable state (state of delicate equilibrium) and requires a lower pH, thus obtaining phosphorus removal without addition of alkaline. At pH of 8-8.5 is sufficient to obtain a co-precipitation of HAP and MAP (Pitman *et al.*, 1991).

2.2.1.3.3 *Agricultural Use of Struvite*. Advanced biological treatment processes including nutrient removal and using anaerobic sludge digestion are facing very frequently scaling problems in discharge pipes and in the dewatering process. The deposited hard material causes serious operational problems. The deposited substance is usually a mineral – magnesium ammonium phosphate (MAP) known as struvite. So far many attempts have been made to control the process of self-deposition and recover MAP as fertiliser, which can be used directly for agricultural purposes. While only slightly soluble in water and soil solutions, MAP was found to be a highly effective source of phosphorus, nitrogen and magnesium for plants through both foliar (leaf fertilizer) and soil application (Lunt *et al.*, 1964) The main

difficulties are connected with precipitation in a form suitable to be easily separated from the liquid.

Different configurations for recovering phosphates as struvite (magnesium ammonium phosphate) from municipal sewage, and the economic and environmental feasibility of using this recovered raw material (with or without further chemical processing) were studied in UK fertiliser markets. Economic modelling and simplified Life Cycle Analysis are applied to compare production-distribution costs and environmental impacts with those of triple super phosphate fertiliser or di-ammonium phosphate fertiliser. According to the Gaterell et al., (2000), 29,000 tonnes P/year could theoretically be recovered for recycling as struvite in the UK, 134,000 tonnes P/year in Western Europe, on the basis of 80% recovery of sewage works inflow phosphates and 85% of the population connected to sewage works. Although certain sewage works configurations are not readily appropriate for P-recovery (eg. trickling filter), increasing requirements for P-removal combined with pressure on sludge disposal may lead to the replacement of such installations with processes compatible with biological P-removal. This would facilitate struvite recovery, as biological nutrient removal processes offer streams with high soluble phosphate and ammonia concentrations, appropriate for struvite precipitation.

For struvite recovery, it is assumed that magnesium will have to be added at the sewage works to bring concentrations up to the stoichiometry with phosphorus necessary for struvite precipitation. Capital costs, which are a significant element of the recovery costs, are calculated using a 6%/year discount rate. Because of the high level of capital costs compared to recovery operating costs, the economics of recovery will be very dependent on the struvite recovery rate (ratio of sewage works inflow phosphate recovered); and rates from 13% - 80% are considered.

Costs and environmental impacts take into account estimates, based on crop areas and average distances, of transport requirements to move fertilisers from import arrival ports to the field, and to move struvite from the sewage works to the field. The costs and environmental impact related to the use of recovered struvite therefore

depend on the supply/demand ratio: if supply is significantly lower than demand (struvite only replaces existing fertilisers a small part of the potential markets) then transport distances will be lower and thus so will costs and environmental impact.

Total production and distribution costs for struvite and enhanced struvite thus compare to at-the-farm prices (market price plus delivery) for existing fertilisers as follows. The highest price range for recovered struvite/enhanced struvite assumes very low recovery efficiency in the sewage works (13%), application in small-medium sewage works (50,000 p.e.) and a high supply/demand ratio (longer transport distances). The lowest price range assumes 80% recovery efficiency in 250,000 pe sewage works and a lower supply/demand ratio.

At a 49% rate for the efficiency of struvite recovery in sewage works, recovered struvite offers an at-the-farm cost equal to that of di-ammonium phosphate (see Table 2.2.).

Table 2.2: Total average cost, at the farm (UK£ per tonne P<sub>2</sub>O<sub>5</sub>)

triple super phosphate	190-200
di-ammonium phosphate	227-238
phosphate mineral rock	183-195
recovered struvite	146-1195
recovered "enhanced struvite"	217-865

One may conclude that, if high recovery efficiencies can be achieved in sewage works and recovered products can be used substitute existing fertiliser products and to meet regional demand, then struvite based products could be cost effective. In particular, the substitution of struvite for di-ammonium phosphate fertiliser looks especially attractive economically provided that these conditions are met.

Under these conditions, recovered struvite based products perform well compared to existing fertiliser products in terms of environmental burden. The authors also note that certain crops require magnesium, which is present in struvite and so, for such

applications, struvite will offer additional economic and environmental advantages by avoiding the need for a magnesium fertiliser.

#### *2.2.1.4 Adsorption*

Ammonium uptake by the natural minerals was studied using both pure ammonium solutions and synthetic human urine. The ammonium uptake varied with grain size, ion concentration and contact time. 70-80% uptake was achieved with clinoptilolite and 50-60% with wollastonite.

In experiments with synthetic urine and zeolite, nitrogen adsorption was combined with magnesium oxide induced struvite precipitation, either following it or simultaneously. 60mg of magnesium oxide was added to 25ml of synthetic urine (taking the pH to 9 - 9.5) and 0.5g of natural zeolite was used. With a contact time of 5-10 minutes, 64-67% of nitrogen was removed (to struvite or by adsorption) with clinoptilolite and 64-75% with wollastonite. (Lind *et al.*, 2000). The authors indicate that these high nitrogen removal rates are possible because most of the urea will be transformed to ammonium at pH above 9.

### **2.2.2 Biological Methods**

#### *2.2.2.1 The Airlift Reactor Process*

Airlift reactor has been used for a nitrification/denitrification process for ammonium removal. Pilot-scale three phase fluidised bed airlift reactor is used to treat the reject water by Janus and Roest (1997). The airlift reactor is a three phase fluidised bed system in which biological active material is adhered to carrier material. The reactor consists of two concentric tubes. Air is introduced in the bottom of the inner tube (riser) to supply oxygen for biological oxidation. Air is introduced from bottom of the inner tube (riser) to supply oxygen for biological oxidation. In the riser, air, water and carrier material are mixed in an up flow. The down flow takes place in an outer tube. The carrier material is completely in suspension, because its settling velocity is

lower than the flow velocity of the water phase. At the top of the reactor the three phases are separated in the settler. Sludge is recycled to an anoxic zone, where methanol is dosed for denitrification.

It was found out during the research period that denitrification in the reactor could not be achieved. Thus, if removal of total nitrogen is to be achieved, a separate denitrification reactor is needed. Also, in the airlift reactor the biomass concentration could be up to 20 times higher compared to the activated sludge process. With a height of 8 m for the pilot plant the maximum nitrogen load at 90% nitrification was 2.8 kg N/ (m<sup>3</sup>/d).

#### *2.2.2.2 SBR Process Without pH Control*

Sequencing batch reactors (SBRs) and chemostat continuous reactors are the generally preferred reactors to develop the classical nitrification/denitrification process and could be chosen to develop a partial nitrification via nitrite. In a SBR the nitrification via nitrite could be achieved working with high ammonium concentration and an appropriate pH range. A detailed description of the full-scale storage and treatment (SAT)/SBR method, for reject water treatment in Hamburg's CWWTP is given by Laurich and Gunner (2003). The basic set-up of the reactor is shown in Fig. 2.7. In this process SBR was a preferred option at the plant to manage the 25% additional nitrogen load reject water puts on the biological stage. The objective was to increase the purification rate and ensure optimal economic efficiency. When the process was tested at the Hamburgs-Köhlbrandhöft WWTP the pH value was maintained at a level guaranteeing optimum nitrification results. In that case up to 50% of the ammonium load supply can be oxidized before the pH value deteriorates owing to the fully utilized acid capacity, which limits further nitrification. The nitrification reaction produces 2 moles of hydrogen ion for every mole of ammonium oxidised. At the same time the high hydrogen ion concentration reduces the pH, which hampers the bacteria performing the nitrification reaction.

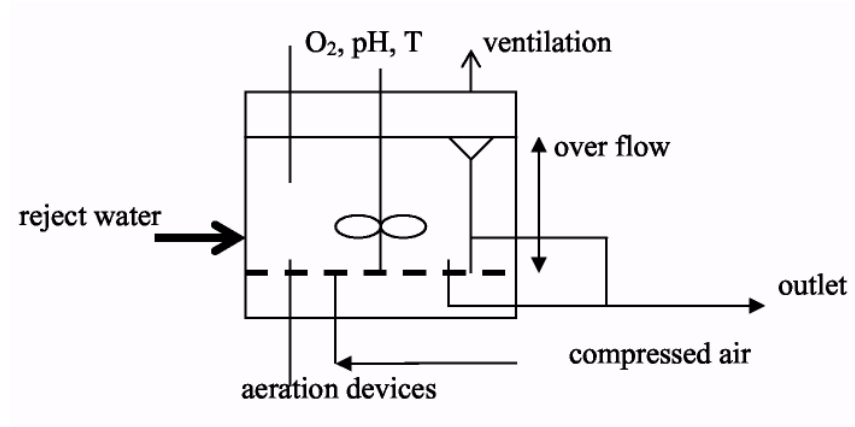


Figure 2.7 A modified set up of the test reactor (Laurich and Gunner, 2003)

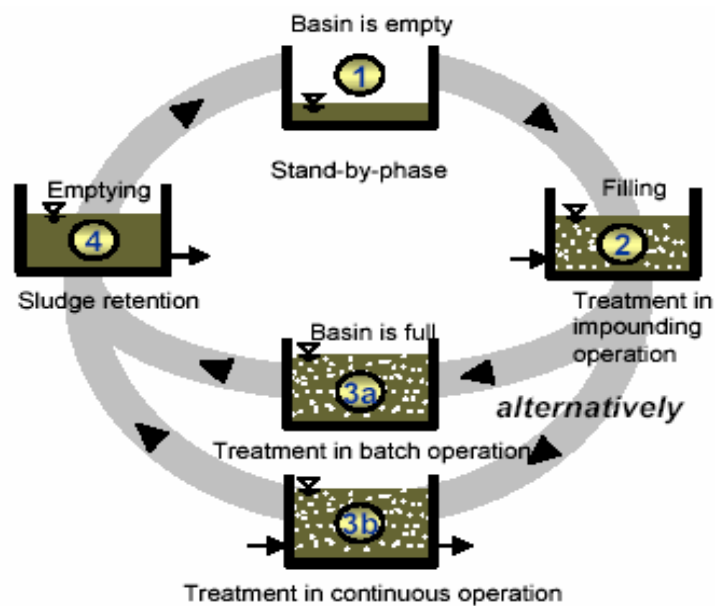


Figure 2.8 Schematic operation of the store and treat process (Laurich, 2003)

To monitor the elimination of ammonium and production of nitrate online measurements of the nitrification process is needed. The store and treat process operates (see Fig. 2.8) on the same basis as the SBR with only nitritation in a single reactor. The difference is in the name and the fact that it is also used for quantity management. The store and treat process was effective at the plant due to the

increased ammonium concentration and temperature of the sludge liquor, which permit a high growth rate of nitrifying bacteria. At the beginning of a cycle, the basin is almost empty with activated sludge retained from the last cycle left inside. This retained sludge makes up of approximately 10-20% of storage capacity. At the onset of storage the sludge liquor influent mixes with the activated sludge and nitrification starts with aeration. This stage is termed impounding operation.

When the basin is filled to capacity, treatment can be continued in continuous operation until the basin is emptied. The continuous flow of sludge liquor influent pushes back the treated basin content, which is then evacuated at the overflow. In this phase activated sludge is also discharged continuously as part of the overflow. The sludge liquor is allowed to settle before basin emptying starts, to ensure that the activated sludge sinks to the bottom so that activated sludge for the next cycle can be retained in the system. While the basin is fully emptied aeration can be reduced to the level necessary to keep nitrifiers active.

#### *2.2.2.3 Sequence Batch Reactor (SBR) Process With pH Control*

The Sequence Batch Reactor (SBR) can also be operated with pH control to increase the pH during nitrification when hydrogen ions are produced. The description of the process is achieved by Wett *et al* (1998), Arnold *et al.*, (2000), and Mossakowska *et al.*, (1997). At the WWTP Strass, which serves up 200,000 p.e. SBR-strategy seemed an appropriate operational scheme, as time control was simpler and more flexible than volume or flow control respectively. Defined amounts of primary sludge may be added to serve as a carbon source through a pump piped to the SBR. In order to increase dewater ability the sludge is conditioned by lime, which causes the high alkalinity of the reject-water with pH of 11.9 to 12.8. Choosing a flow rate that is below the nitrification capacity of the system and aerating the reactor the high pH is managed. The toxic ammonia concentrations of the reject-water require a reliable control of the SBR-influent and the low hydraulic load enables such a control.

There were two possibilities that controlled the interactions between influent and process behaviour:

- a) The process runs at highest rate and the influent is controlled by the process capacity(constant process at controlled flow rates).
- b) The influent is set on a fixed rate below the process capacity and the process itself is controlled (constant flow at a controlled process).

The time control schedules were operated 3 cycles per day (Fig. 2.9). The total cycling time was 8 hours. The operation is divided into four phases 320 minutes of aeration, 30 minutes of stirring, 100 minutes settling and 30 minutes drawing off. This does not include the fact that the reactor is not aerated during the whole aeration phase. The programmed time frame just determines the periods when aeration is possible and provides a maximum ratio of aerobic to anoxic conditions of exactly 2 to 1. The actual operation of the aerator is exclusively based on the pH-online measurement.

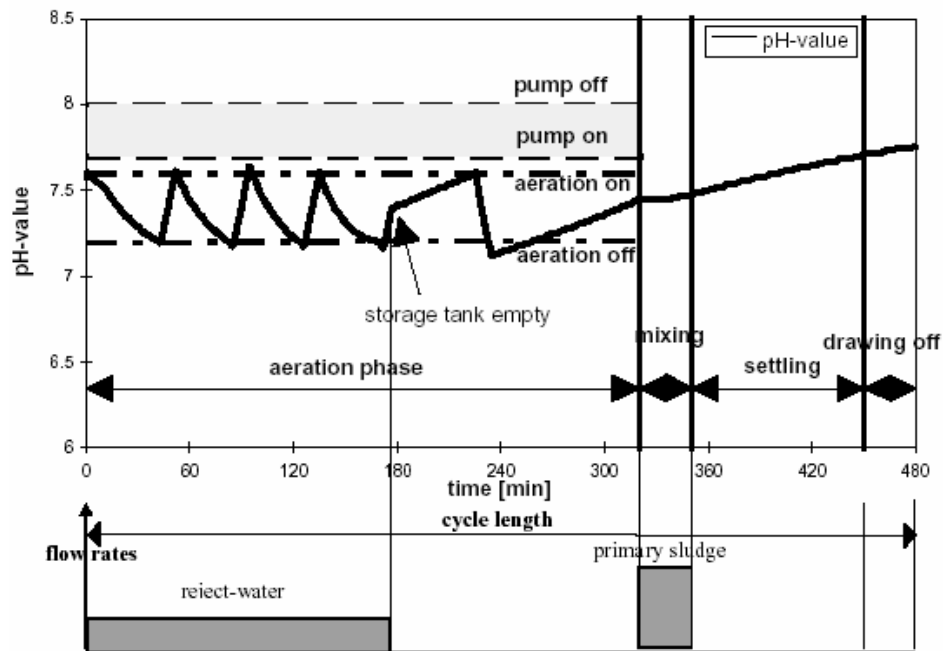


Figure 2.9 Scheme of pH control operation (Wett *et al.*, 1998)



The pH-control process shown in Fig. 2.9 had a 2-setpoint switch, programmed to control the aerator. During the aeration phase reject-water is pumped at a fixed flow rate from the storage tank into the aerated reactor. Due to nitrification the pH-value decreases despite the alkalinity, which comes from the reject-water until the lowest set point of pH 7.2 are reached. Then the aeration is switched off. Under anoxic condition the denitrification process starts. Denitrification and continued reject-water flow recovers alkalinity. When the next set point of pH 7.6 is reached, then aeration starts again. This control mechanism proceeds to the end of the aeration phase. If the storage tank becomes empty during the aeration phase, then short aerated intervals will alternate with anoxic phases until reject-water is available again or the aeration phase ends (time control).

It was found out during the operation of the plant that substrates and inhibitors limit nitrogen removal. Substrate limitation was due to the high sludge retention time, which in this case was much higher than the necessary (SRT in the full scale experiment was approximately 50 days). Autotrophic biomass is determined by growth and lyses but not by sludge removal, therefore the amount of active biomass is in balance with substrate supply. Inhibition by ammonia was due to the high concentration of about 1 mg/l in the reactor ( $\text{NH}_4^+$  concentration of 100 to 150mg/l at a relatively high pH-value) only 30% of the nitrite was oxidised to nitrate in average. Hence in this case inhibition is welcome to save energy cost.

The process performance of the SBR depends on pH measurements and not on ammonium or nitrate. pH is balanced in the reactor is by altering nitrification and denitrification processes with suitable aeration; first to reduce alkalinity then recover slight alkalinity to a stable pH for the effective operation of the process. Denitrification took place in the pre-denitrification zone of the activated sludge process where there was a ready source of biodegradable organic matter coming from a connecting brewery factory serving as carbon source (Wet *et al.*, 1998).

#### 2.2.2.4 Partial Nitrification/Anammox Process

Partial nitrification preceding Anammox seemed an interesting reject water treatment option as found in a laboratory study to be low cost, very efficient and without need for process control (Jetten *et al.*, 2001). The process of partial nitrification/Anammox process was tested on a pilot scale and is described in detail by Fux *et al.*, (2002). For the nitrification aspect two steps are essential. Firstly the nitrite oxidisers must be continuously suppressed, and secondly the nitrite/ammonium ratio produced must be about 1.3. If too much nitrite is produced, additional supernatant can be added directly to the Anammox reactor to satisfy the stoichiometry. Because nitrite can completely inhibit the Anammox process at concentrations higher than  $100 \text{ g NO}_2\text{-N/ m}^3$  (Strous *et al.*, 1999).

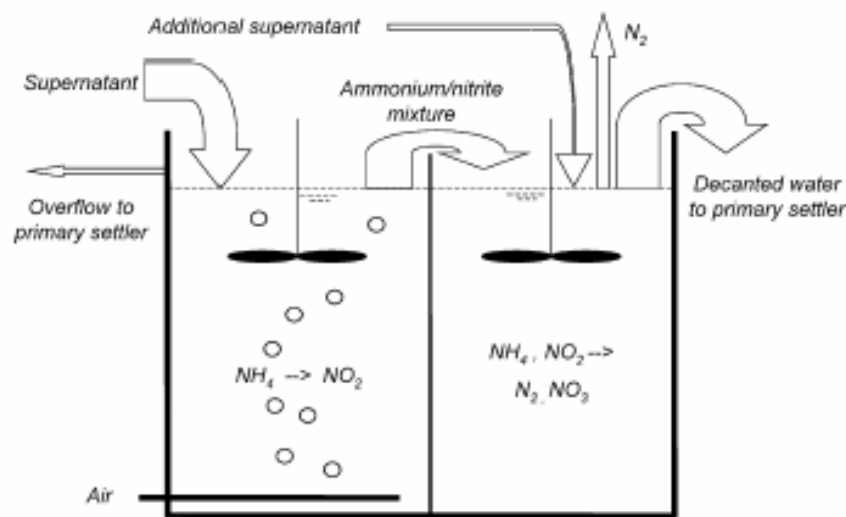


Figure 2.10 Reactor configuration for partial nitritation (left) and anaerobic ammonium oxidation (right) (Fux *et al.*, 2002)

Nitritation was performed in a continuously stirred tank reactor (Fig. 2.10) without sludge retention with normal activated sludge. Sludge residence time equals the hydraulic residence time. The reactor was inoculated with  $1 \text{ m}^3$  of activated sludge (approx.  $10 \text{ kg TSS m}^3$ ) from the WWTP. At  $24.8 \text{ }^\circ\text{C}$  it was possible to compete the nitrite oxidisers so an appropriate nitrite/ammonium mixture for the Anammox process was reached within one month.

The reactor temperature, the ammonium concentration in the digester effluent and the growth rate of the ammonium oxidisers, determines the volume of the nitrification reactor. No pH adjustments were made in the nitrification reactor. Anaerobic ammonium oxidation takes place in a sequencing batch reactor. The Anammox reactor was inoculated with excess sludge (about 1000 g TSS) from the WWTP. The SBR operated by first filling, mixing then settling. Influent to the Anammox is provided from the partial nitrification stage where the remaining ammonium and nitrite produced including the nitrification biomass. The pH in the reactor is controlled at about 7.52 by addition of a 2M HCL solution or CO<sub>2</sub> sparging. Temperature in both reactors is kept constant with the aid of heat exchanges at around 31.1°C. The whole operation cycle is 120 minutes with 90 minutes of reaction time and by the fortieth minute (Fig. 2.11) all the nitrite was used up, while the ammonium stayed constant for the remaining period of the cycle. Ammonium removal from the reactors is 92% at 2.4 kg N/m<sup>3</sup>.d).

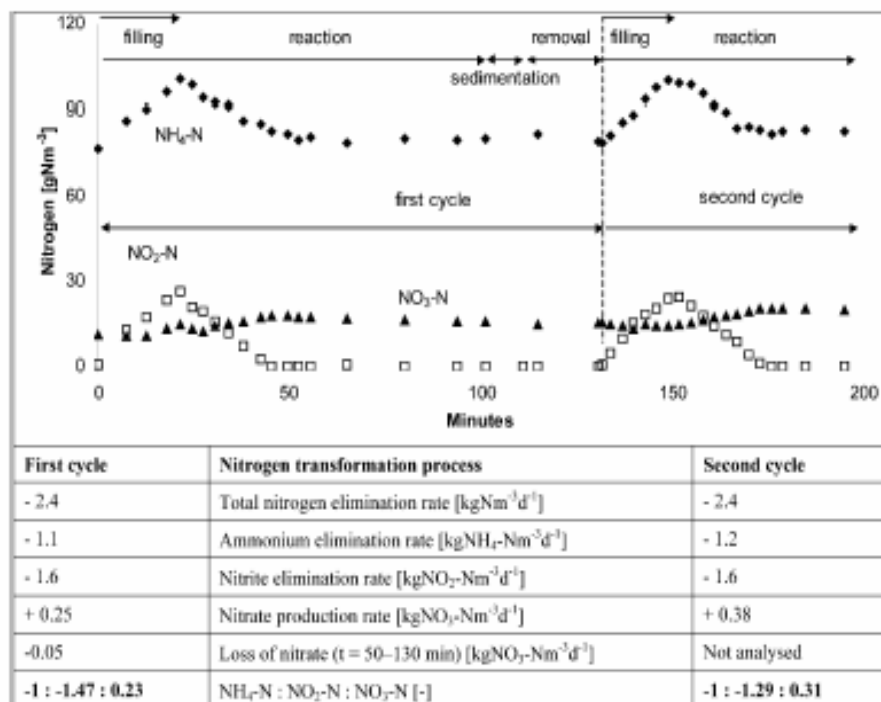


Figure 2.11 Concentration profiles of soluble nitrogen compounds and degradation rates in the Anammox reactor (Fux *et al.*, 2002)

The first full-scale anammox reactor in the world was started in Rotterdam (NL) (Fig. 2.12). The reactor was scaled-up directly from laboratory-scale to full-scale and treats up to 750 kg-N/d. In the initial phase of the startup, anammox conversions could not be identified by traditional methods, but quantitative PCR proved to be a reliable indicator for growth of the anammox population, indicating an anammox doubling time of 10–12 days. The experience gained during this first startup in combination with the availability of seed sludge from this reactor, will lead to a faster startup of anammox reactors in the future. The anammox reactor type employed in Rotterdam was compared to other reactor types for the anammox process. Reactors with a high specific surface area like the granular sludge reactor employed in Rotterdam provide the highest volumetric loading rates. Mass transfer of nitrite into the biofilm is limiting the conversion of those reactor types that have a lower specific surface area. Now the first full-scale commercial anammox reactor is in operation, a consistent and descriptive nomenclature is suggested for reactors in which the anammox process is employed.



Figure 2.12 The first full scale anammox reactor, Rotterdam, the Netherlands. It works at design load and removes over 500 kg N/day. (the anammox online resource-<http://www.anammox.com/application.html>)

#### 2.2.2.5 *Oxygen Limited Autotrophic Nitrification Denitrification (OLAND)/Anammox Process*

In two membranes assisted bioreactors (MBR) Wyffels *et al.*, (2004) performed a study on the performance of the Anammox process. In the first stage pre-filtered reject water from dewatering sludge is cooled to room temperature to feed the OLAND process. The OLAND step is the same as the partial nitrification step which precedes the Anammox reaction. Cooling the reject water means that at WWTPs where the pre-sedimentation sludge is added to sludge liquor from the dewatered anaerobic sludge, which reduces the temperature of reject water can be operated with this process.

Reject water from the Deurne-Schijnpoort WWTP in Belgium was used to fill the 1.5 l reactor volume. Effluent was removed from the reactor by creating a membrane under pressure with suction pumps. Internal hollow fibre membranes for micro filtration with a pore size of 0.6  $\mu\text{m}$  were used to completely retain the suspended biomass. Complete biomass retention ensures no wash out of nitrifying bacteria into the Anammox stage. Sludge liquor was added to the first MBR after which biomass free intermediary liquor was collected and fed to the second MBR. The first reactor is inoculated with available nitrifying sludge, whereas the second reactor is inoculated with bio film sludge from a RBC showing high autotrophic nitrogen removal capacity.

In the partial nitrification step oxygen supplied was below 0.2mg DO L<sup>-1</sup> resulting in a sustained nitrite accumulation. The pH was controlled at 7.9 by adding a base. The use of a membrane ensured longer SRT therefore higher loading rates. Total HRT in both reactors was approximately two and half days. During the Anammox process nitrite is completely removed whereas ammonium is oxidised to about 82%.

#### *2.2.2.6 Completely Autotrophic Removal of Nitrogen Over Nitrite (CANON)/Anammox Process*

Slieker *et al.*, (2003) carried out a study to evaluate the process performance of the CANON-Anammox process in the elimination of nitrogen with the airlift reactor. The experiment was carried out in two phases all in a single reactor. Firstly the airlift reactor was kept anoxic with a seed biomass consisting of anaerobic ammonium-oxidizing bacterial from an existing Anammox SBR. It was kept anoxic to grow and maintain a stable consortium of bacteria capable of Anammox. During this phase biomass trapped from the effluent was returned manually to the reactor.

After the initial period, limited amounts of air were carefully introduced to support activity and growth of aerobic ammonia oxidizers. The biomass with aerobic ammonia-oxidizing bacteria was obtained from an oxygen-limited ammonia-

oxidizing SBR. The goal was to achieve simultaneous aerobic/anaerobic ammonia oxidation. At this stage the biomass in the effluent was not returned to the reactor. Due to the possible influence of the biomass on the Anammox process, since any slight accumulation of sludge from the influent reactor could negatively affect the Anammox process. The reason for the negative effect is that, the net production of Anammox cells is low and accumulation of the influent biomass would dilute the Anammox process significantly (Van Dongen *et al.*, 2001).

The 1.8L gas-lift reactor used was supplied with synthetic wastewater with no biomass retention in the reactor. Synthetic wastewater was added at the top of the reactor. Gas was sparged from the bottom of the reactor at a maximum gas flow of 200 ml/ min for fluidisation of the biomass. The compressed air comprised 95% Ar and 5% of CO<sub>2</sub> supplied for sparging and maintaining a constant anoxic pH at 7. When oxygen-limited conditions were needed, Ar, CO<sub>2</sub> mixed with air, or solely air was used. Oxygen concentration was controlled by manual variation of the air supplied. Very good nitrogen conversion and elimination rates were obtained using the gas-lift reactor at 8.9 kg N/ (m<sup>3</sup>.d) for the Anammox process and 1.5 kg N/(m<sup>3</sup>.d) for the CANON stage. Limitations found during the study were the oxygen transfer from gas to liquid and the amount of biomass needed. However the CANON-Anammox proved to be suitable for treating reject water with high nitrogen concentration with no carbon addition and limited oxygen supply in a single reactor. It remains to be seen how the gas lift will perform with real wastewater, but this could be difficult run on long-term basis due to the slow growth of the bacteria. Moreover when the two processes run in the same reactor maintaining a constant ratio for nitrite to ammonium may present problems.

### 2.2.2.7 *The Single Reactor High Activity Ammonia Removal Over Nitrite (SHARON) Process*

The SHARON process described in detailed by Hellinga *et al.*, (1998) is a novel treatment process developed in the mid 90s. It was the first successful technique at which nitrification/denitrification with nitrite as intermediate under stable process conditions were achieved. The process distinguishes itself from other biological reject water treatment methods by the complete absence of sludge retention. The SHARON process was developed to treat reject water of high ammonium concentration by taking advantage of its specific temperature and composition all in a single reactor. Following is a description of the process. The completely stirred reactor was operated in cycles of 2 hours, 80 minutes aerobic and 40 minutes anoxic. Hydraulic residence time (HRT) was used to control sludge residence time (SRT) since there was no sludge retention, this allowed nitrite oxidisers to be washed out while ammonium oxidisers are retained in the reactor.

Since nitrification involves the production of hydrogen ions, at 50% production these were neutralised by stripping CO<sub>2</sub> formed from the bicarbonate present in the sludge digestion effluent. Alternating nitrification/denitrification further enhanced the control of pH. Methanol as COD source was used for the denitrification process because it 40-50% lower in cost than NaOH addition. The dependency of nitrification rate on temperature was very high at 30 to 40°C, which was most appropriate considering the temperature of effluent anaerobic digester was also high.

At these very high temperatures NO<sub>2</sub> oxidising bacteria grow slower than ammonium oxidisers, thus preventing nitrite oxidation. Thus, in a system without sludge retention and SRT=HRT it is possible to limit the SRT in a way that ammonium is oxidised rather than nitrite (Hellinga *et al.*, 1998). However at a full-scale operation plant in Rotterdam Dokhaven WWTP, nitritation stability was difficult to achieve since the seeding material had an aerobic retention time greater than one day therefore allowing the growth of nitrite oxidisers (Van Kempen *et al.*, 2001).



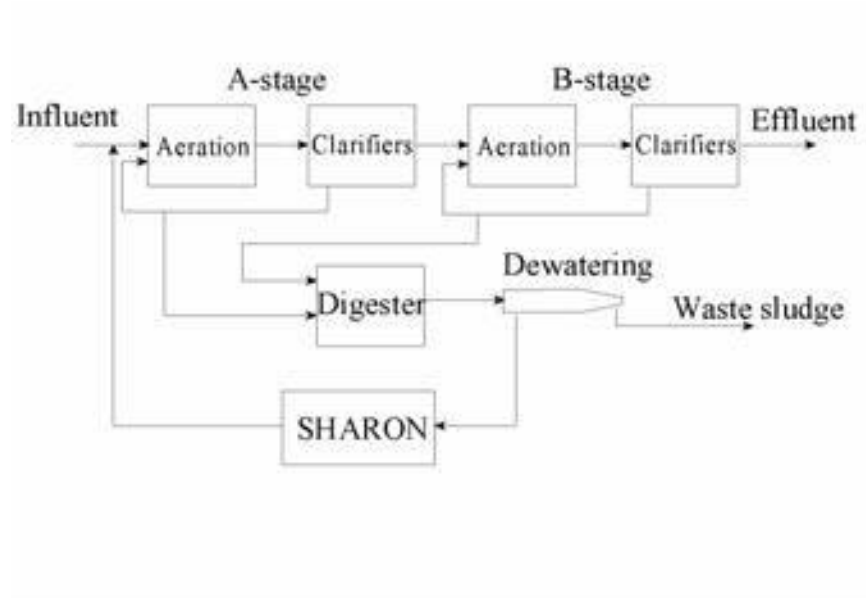


Figure 2.13 Sharon process scheme (Department of environmental protection, 2002)

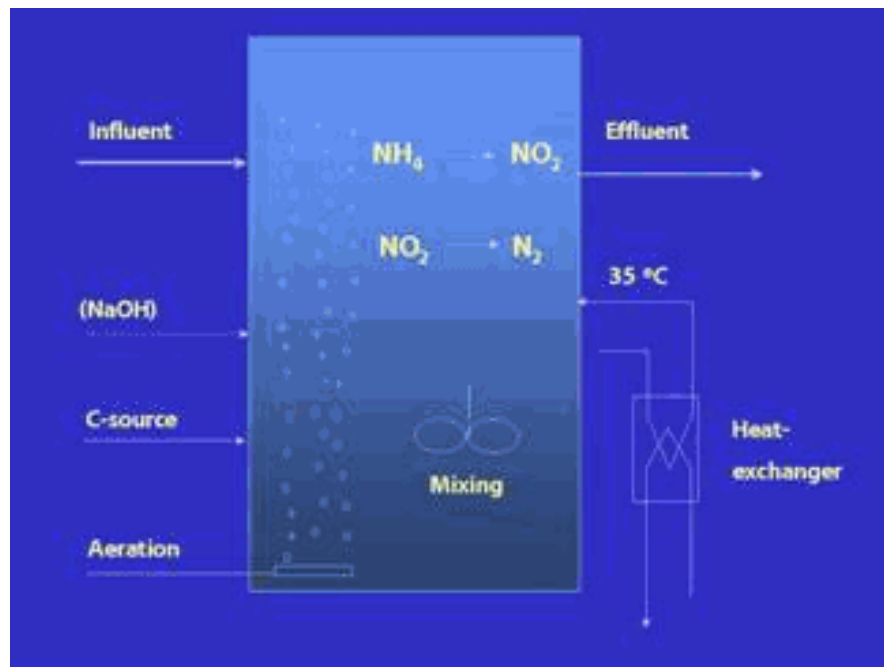


Figure 2.14 Sharon reactor scheme (Department of environmental protection, 2002)



Figure 2.15 The SHARON plant in Utrecht (Grontmij Water & Reststoffen, 2004)

#### 2.2.2.8 The SHARON-Anammox Process

The SHARON process, which operates by partial nitrification of ammonium under high temperature without sludge retention is used in combination with the Anammox process (van Dongen *et al.*, 2001). SHARON-Anammox processes a CSRT and SBR of a 2-stage reactor configuration. The Anammox process works under oxygen limitation without addition of a carbon source, for ammonium to be oxidized to nitrogen gas with nitrite as electron acceptor. The pilot scale study was influenced by the conclusions of Strous *et al.*, (1997), which investigated digester effluents with the Anammox process. The results showed that compounds in the digester effluent did not negatively affect the Anammox sludge. The pH(7.0-8.5) and temperature (30-37 °C) optimum for the process were well within the range of the values expected for digested effluents. The potential process configuration and expected removal efficiency is shown in Fig.2.16. The combination of the Anammox process and partial nitrification (SHARON) process has been tested on a laboratory scale and found to have 83% ammonium removal efficiency (Jetten *et al.*, 1997). The SHARON reactor is operated without pH control with a total nitrogen load of about 1.2 kg N/ (m<sup>3</sup>.d) and operated to the nitrite step.

The ammonium present in the digester sludge was converted at 53%, which is consisted with results from Jetten *et al.*, (1999) on the ammonium concentration needed for the Anammox process. This achievement ensured a right ammonium-nitrite mixture suitable for the Anammox stage. The effluent of the SHARON reactor is used an influent for the Anammox sequencing batch reactor.

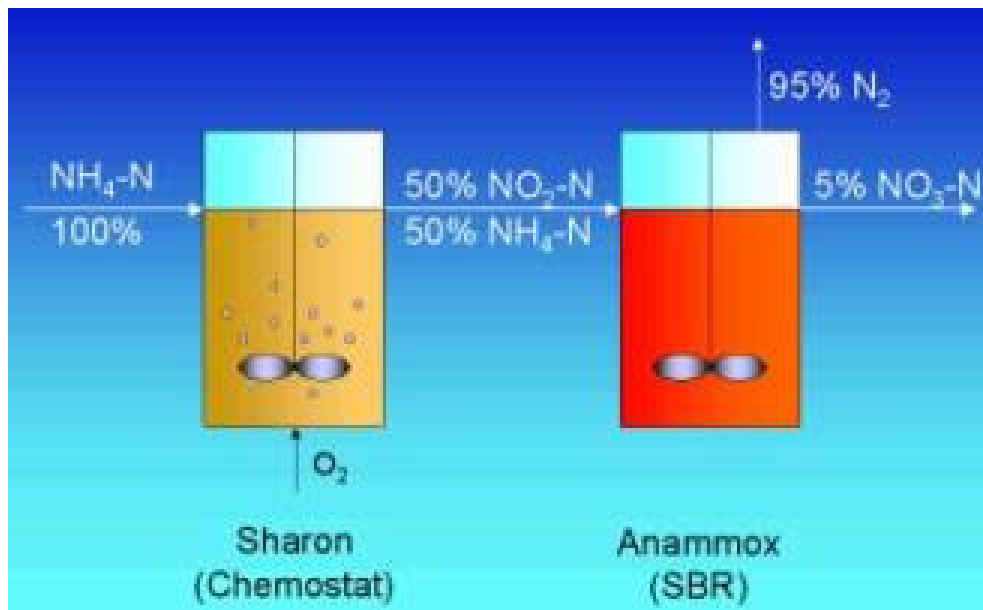


Figure 2.16 Schematic representation of the combined SHARON-Anammox process for the removal of ammonium from sludge digestion effluents (Jetten *et al.*, 2002)

In the nitrite limited Anammox reactor all nitrite was removed, the surplus ammonium remained. One limitation to the process is the fact that any slight accumulation of sludge from the influent to the Anammox reactor could negatively influence the Anammox process. To prevent the accumulation of sludge in the Anammox reactor the effluent from the SHARON should pass through a filtration mechanism before entering the Anammox reactor. This will prevent any nitrifying bacteria from entering the influent to the Anammox to cause the disruption of the Anammox process.

### 2.2.2.9 Membrane-Assisted Bioreactor(MBR)

The membrane-assisted bio-reactor (MBR) is a compact biological treatment unit which is able to treat this highly concentrated sludge reject waters. The activated sludge is coupled to a crossflow membrane filtration unit, assuring a complete retention of the biomass. In this way, nitrifying bacteria are optimally retained in the reactor. Further advantages are the possibilities to work at high biomass concentrations (concentrations up to 35 g SS/l are feasible) and at temperatures of 35 to 40°C which is often the optimum for biological processes (Van Dijk and Roncken, 1997).

The use of an MBR should enable to remove Kjeldahl nitrogen (Kj.N) from sludge reject water at high loading rates. Control of the ammonia ( $\text{NH}_3$ ) and nitrous acid ( $\text{HNO}_2$ ) concentrations then becomes crucial for the maintenance of complete nitrification. Anthonisen *et al.* (1976) worked out a nitrification-tolerance graph which indicates, as a function of pH, the levels of  $\text{NH}_4^+$ -N and of  $\text{NO}_2^-$ -N at which the nitrification ( $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ ) and the nitrification ( $\text{NO}_2^- \rightarrow \text{NO}_3^-$ ) are inhibited. There are several factors responsible for the accumulation of the nitrite ion but many authors stress the key role played by the ammonia, which may be the result of a combination of several factors, such as the initial total ( $\text{NH}_3 + \text{NH}_4^+$ ) concentration, the pH and the temperature (Abeling and Seyfried, 1992; Balmelle *et al.*, 1992; Turk and Mavinic, 1989; Verstraete *et al.*, 1977). Nitrogen removal through nitrification-denitrification can be achieved via the nitrite pathway ( $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{N}_2$ ) or the nitrate pathway ( $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2$ ). The nitrite pathway results in a 25% reduction of the oxygen requirements for nitrification and a 40% reduction of the COD requirements for denitrification (Turk and Mavinic, 1987). One of the means to favor the nitrite pathway is to inhibit the nitrite oxidizers by control of the ammonia concentration.

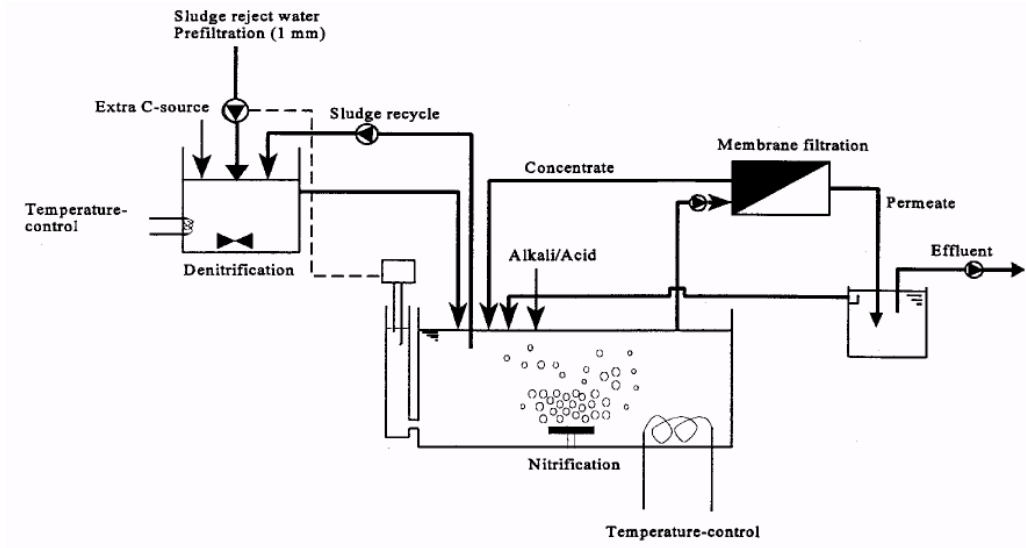


Figure 2.17 Flow sheet of the membrane-assisted bioreactor (Ghyoot, et. al, 1997)

## CHAPTER THREE –EXPERIMENTAL STUDIES

### 3.1 Experimental Procedure

The main objective of this study was to investigate the characteristics of the reject water obtained from municipal wastewater treatment plant dewatering facilities, and disposal alternatives. In this context, characterization study was achieved as first. Physical, chemical and biological properties of reject water samples were investigated. Then, the parameters exceeding the limits were determined; and finally treatability studies (i.e. chemical stabilization) were performed as a separate treatment alternative.

#### 3.1.1 Characterization Study

Characterization studies were carried out with reject water obtained from dewatering units of the municipal treatment plants. Reject water samples were taken from the outlet of the dewatering units (i.e. mechanical dewatering units - belt press) of the plants and kept at 4 °C during the experiments. The pH, temperature, salinity, chlorine, solids content (suspended solids), organic matter (COD), total nitrogen, ammonium nitrogen, nitrate nitrogen, total phosphorus, boron, sulphate, potassium, iron, magnesium, sodium, calcium, iron, manganese as well as heavy metals (Cu, Zn, Cd, Cr, Pb, Ni, Pb) were measured to determine the physical and chemical properties of the sludge samples. Besides, fecal and total coliforms were measured within the characterisation study content.

Examples are taken from two different municipal wastewater treatment plants. The first plant consists of coarse screen, fine screen, aerated grit removal chamber, anaerobic tank, aeration tank, final sedimentation tank and mechanical dewatering units, and the design capacity is 21600 m<sup>3</sup>/day wastewater (GWWTP). The second

plant is also designed according to the extended aerated activated sludge system with a capacity of 21600 m<sup>3</sup>/day wastewater (HWWTP).

As it stated in Table 3.1, the samples are taken from the inlet and outlet of the belt press. The samples from the outlet of the belt press are reject water, and they are used in the characterization and treatability studies. In addition, the samples taken from the inlet of the belt pres is used to evaluate the effect of the dewatering units.

Table 3.1 The sampling characteristics of the study (sample sources, sampling points, sampling date)

<b>Sample No</b>	<b>Unit</b>	<b>Wastewater Treatment Plant</b>	<b>Date</b>
Sample 1	Belt Pres (inlet)	HWWTP	13.03.2007
	Belt Pres(outlet)		
Sample 2	Belt Pres (inlet)	HWWTP	27.03.2007
	Belt Pres(outlet)		
Sample 3	Belt Pres (inlet)	HWWTP	29.05.2007
	Belt Pres(outlet)		
Sample 4	Belt Pres(outlet)	HWWTP	22.02.2008
Sample 5	Belt Pres(outlet)	HWWTP	18.03.2008
Sample 6	Belt Pres (inlet)	GWWTP	11.04.2007
	Belt Pres(outlet)		
Sample 7	Belt Pres (inlet)	GWWTP	10.05.2007
	Belt Pres(outlet)		

#### *3.1.1.1 Analytical Methods*

In this study, all parameters were analysed according to Standard Methods (APHA, AWWA, WEF, 1992). The methods used in the measurements are given together with the equipments used in the analysis in Table 3.2.

Table 3.2 Measurement methods and equipments used in the experimental studies

<b>Parameter</b>	<b>Method</b>	<b>Equipment</b>
pH	Glass electrode	pH meter
Temperature	Glass electrode	pH meter
Salinity	Electrical conductivity	Conductivity instrument
Chlorine	Arjantometric	Burette
Suspended solids	Gravimetric	Drying oven
Total phosphorus	Colorimetric	Spectrophotometer
Total nitrogen,	Colorimetric	Spectrophotometer
Ammonium nitrogen	Colorimetric	Spectrophotometer
Nitrate nitrogen	Colorimetric	Spectrophotometer
Phosphate phosphorus	Colorimetric	Spectrophotometer
COD	Dichromate reflux	Burette
Boron	Curcumine	Spectrophotometer
Sulphate	Gravimetric	Muffle oven
Calcium	EDTA titrimetric	Burette
Magnesium	EDTA titrimetric	Burette
Fecal coliform	Membrane filter technique	
Total coliform	Membrane filter technique	
Cadmium	Atomic absorption	Atomic abs. spectrometer
Chrome	Atomic absorption	Atomic abs. spectrometer
Copper	Atomic absorption	Atomic abs. spectrometer
Iron	Atomic absorption	Atomic abs. spectrometer
Manganese	Atomic absorption	Atomic abs. spectrometer
Nickel	Atomic absorption	Atomic abs. spectrometer
Lead	Atomic absorption	Atomic abs. spectrometer
Zinc	Atomic absorption	Atomic abs. spectrometer

*3.1.1.1.1 Total Nitrogen.* Total nitrogen analyses were made by Merck Spectroquant total nitrogen kit. Merck Spectroquant total nitrogen kit and spectrophotometer was used in the experiments.



*3.1.1.1.2 Total Phosphorus.* Total phosphorus analyses were made by Merck Spectroquant total phosphorus kit. Merck Spectroquant total phosphorus kit and spectrophotometer was used in the experiments.

*3.1.1.1.3 Chemical Oxygen Demand.* Chemical oxygen demand were made according to Standard Methods for Water and Wastewater Examination procedure 5220C by dichromate reflux method.

*3.1.1.1.4 Total Suspended Solids.* Suspended solids are known as the solids that cannot be filtered and these solids are produced by drying the non-filtered part of the water sample in 103°C drying oven for 1 hour and cooling and weighting it in desiccator. These processes are made according to 2540 B-standard methods.

*3.1.1.1.5 Total Solids.* The filtered part of the water sample was evaporated in 103°C, and the remains were weighted in the method. These processes were made according to 2540 B-standard methods.

*3.1.1.1.6 pH.* The pH value of the reject water samples were measured according to EPA Method 9045C by HANNAH HI 8314 pH meter.

*3.1.1.1.7 Chlorine.* Chloride analyses are made by applying argentometric methods. The processes are made according to 4500 chloride B-standard methods.

*3.1.1.1.8 Boron.* The method used in boron analyses is curcumine method. The processes are made according to 4500 B-B standard methods.

3.1.1.1.9 *Sulphate*. Gravimetric method is used in sulphate analyses. The processes are made according to 4500 sulphate C standard methods.

3.1.1.1.10 *Calcium*. In calcium analyses EDTA titrimetric method is used. The processes are made according to 3200 Ca-B standard methods.

3.1.1.1.11 *Magnesium*. Magnesium determination is calculated with the formula given below:

$$\text{Magnesium} = [\text{Total Hardness} - \text{Calcium} * 2,5] * 0,244$$

The calculations are made according to 3500-Mg-B standard methods.

3.1.1.1.12 *Fecal Coliform*. Fecal coliform bacterial densities were determined by the membrane filter technique according to Standard Method Procedure 9222D. The membrane filter procedure uses an enriched lactose medium and incubation temperature of 44,5 °C within 24 hours.

3.1.1.1.13 *Total Coliform*. Total coliform bacterial densities were determined by the membrane filter technique according to Standard Method Procedure 9222B. The membrane filter procedure uses an enriched lactose medium and incubation temperature of 35 °C within 24 hours.

3.1.1.1.14 *Electrical Conductivity-Salinity And Temperature*. Electrical conductivity, salinity and temperature were determined by conductimeter according to Standard Method Procedure 2510B and 2520B.

3.1.1.1.15 *Heavy Metals (Cu, Zn, Cd, Cr, Pb, Ni, Fe, Mn)*. Acid extraction procedure (EPA Method 3050B) was used in the heavy metal analyses. Cu, Zn, Cd, Cr, Pb, Ni, Fe, Mn concentrations were measured using Ati Unicam 929/1011 AA Spectrometer.

*3.1.1.1.16 Ammonium Nitrogen.* Ammonium Nitrogen analyses were made by Merck Spectroquant total nitrogen kit. Merck Spectroquant ammonium nitrogen kit and spectrophotometer were used in the experiments.

*3.1.1.1.17 Phosphate Phosphorus.* Phosphate Phosphorus analyses were made by Merck Spectroquant total nitrogen kit. Merck Spectroquant phosphate phosphorus kit and spectrophotometer were used in the experiments.

### **3.1.2 Treatment Studies**

#### *3.1.2.1 Struvite Precipitation(MAP)*

Struvite must be at optimum range of pH, mixing time, nucleus material dose and Mg-P ratio for effective precipitation (Loewenthal *et al.*, 1994). Struvite formation occurs at two stage as nucleus formation and nucleus growth. Different materials that to making crystal nucleus function are used for struvite crystal formation. These materials are phosphate rock, bone coal, magnesia clinker and sand (Battistoni *et al.*, 2000).

Since  $H^+$  ion formed during the struvite formation, solution ambience pH level will decrease. Thus, pH must be increased with an alkali chemicals like NaOH for optimum precipitation (Stranful *et al.*, 2001). Struvite has high solubility in acidic and alkali pH levels, therefore, the optimum pH range is 7-11 for struvite precipitation. (Regy *et al.*, 2001).

In this study, optimum pH, perlite (as a nucleus material) dose, mixing time (agitation time) and Mg-P ratio were determined to find the most efficient treatment. Struvite removal was performed with 100 rpm in jhar test system (see Figure 3.1). The ambience temperature was 20 °C and pH values were between 7-10 given by Adnan *et al.*, (2003). To define the optimum pH, at first, struvite precipitation was

performed at the Mg:P ratio of 1:1. After that, struvite precipitation efficiency for optimum perlite dose, mixing time and Mg-P ratio were investigated.

In this study, perlite that silica origin volcanic conglomerate was used as nucleus material for struvite formation. Perlite doses were ranged 5-20 g/L. The effect of the mixing time were also investigated. Samples were agitated throughout 2, 4, and 6 hours to determine the optimum mixing period. Struvite precipitation was performed respectively at the rate of 1,1:1-1,2:1-1,3:1-1,4:1-1,5:1-1,6:1. Mg:P rates were the molar ones and they were calculated in respect of Mg:P molcul weights and Mg-P portion in wastewater. Additional phosphorus was added as  $\text{KH}_2\text{PO}_4$  and pH adjusted by NaOH and  $\text{H}_2\text{SO}_4$ . In order to determine treatment performance,  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$ , Mg, pH were measured at reject water and at supernatant.

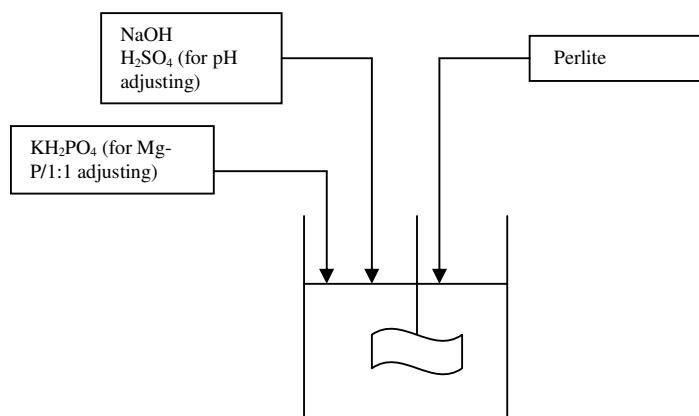


Figure 3.1 Scheme of Struvite Precipitation Experiment

### 3.1.2.2 Crystallization of Hydroxyapatite

Hydroxyapatite settling as performed with 100 rpm in jhar test system and gypsum was used as an adsorbance material (see Figure 3.2). In the experiments,

beaker having 500 ml volume were used. The wastewater samples introduced to the beakers were 250 mL, pH values were between 7-10. To define the optimum gypsum dosage, varying doses of gypsum were used (i.e., 5-10-20-30 g gypsum/L). Following to the gypsum dosage, optimum pH was determined. The pH values were changed between 7 to 10. Mixing time (2 to 6 hours) was also investigated in the experiments. Samples were taken from the supernatant and  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$  measurements were carried out to evaluate the treatment performances.

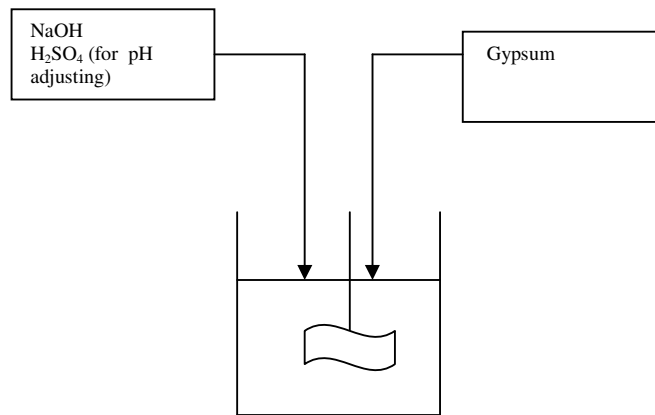


Figure 3.2 Scheme of Hydroxyapatite Precipitation Experiments

## CHAPTER FOUR – RESULTS AND DISCUSSIONS

### 4.1 Characterization Studies of the Reject Water

In the study, reject water characterization studies were made as first. The reject water samples were taken from two different municipal wastewater treatment plants. Characteristics of the reject water samples were analyzed according to the Standard Methods in Section 4. Samples from the outlet of the dewatering unit were taken and various parameters of the reject water were analyzed to determine the characteristics. Samples from inlet of the dewatering units were also analyzed to determine the performance of dewatering units.

Samples were kept in 4°C in the refrigerator and then analyzed according to the Standard Methods. In this context, pH, Temperature, Salinity, Chlorine, Suspended solids, Total phosphorus, Total nitrogen, Ammonium nitrogen, Nitrate nitrogen, COD, Boron, Sulphate, Calcium, Magnesium, Fecal coliform, Total coliform, Cadmium, Chrome, Copper, Iron, Manganese, Nickel, Lead, Zinc measurements were done and presented in Tables 4.1-4.4..

Table 4.1 Physical parameters in the reject water samples

Physical Parameters	Unit	Reject Water Samples*						
		HWWTP					GWWTP	
		S1	S2	S3	S4	S5	S6	S7
pH	-	7,1	7,2	7,1	7,6	7,5	7,2	7,2
Temperature	°C	16	16	16	16	16	16	16
Conductivity	µmhos	480	500	470	-	-	7900	9600
Salinity	-	<%0,048	<%0,05	<%0,047	-	-	0,50%	0,55%
SS	mg/L	444	59480	356	624	100	1788	172

\* reject water samples were taken from the outlet of the dewatering unit.

As can be seen from the Table 4.1, the pH values of the reject water changes between 7.1 and 7.6 (average value 7.27). These are the typical pH values for the reject water (Fux *et al.*, 2003, Wett *et al.*, 1998). The temperature was around 16°C due to laboratory studies were done during the autumn months. Electrical conductivity of the samples taken from the HWWTP was ranged between 470-500 µmhos while the samples taken from the GWWTP were higher than these values. Electrical conductivity measurements were between 7900-9600 µmhos at GWWTP. The difference between electrical conductivity levels of samples caused by the high salinity levels of the samples acquired from GWWTP. In general, SS values are dissimilar to the literature values. However, unexpected solid concentration was measured during the characterization study. Highest solid concentration in the reject water is attributed mal operation of the belt press unit of the HWWTP. So, the SS level of this sample is higher than the others.

Table 4.2 Chemical parameters in the reject water samples

Chemical Parameters	Unit	Reject Water Samples						
		HWWTP					GWWTP	
		S1	S2	S3	S4	S5	S6	S7
Chloride	mg/L	180	185	195	200	240	4700	6598
Total phosphorus	mg/L	7,85	35,9	5,3			31	41,7
Total nitrogen	mg/L	5,5	47	11			26	24
Amonium nitrogen	mg/L	4	27,7	12,77	3,72	9,3	38	15,6
Nitrate nitrogen	mg/L	2,41	9		624			
Phosphate phosphorus	mg/L				7,4	33		
COD	mg/L	120	240	1520	160	640		160
Boron	mg/L	0,6	0,50	0,53			240	1,7
Sulphate	mg/L	71		13,9	176	107	1,1	128
Calcium	mg/L	156	105	256	200	216	135	1643
Magnesium	mg/L	2,9	24	68	122	1040	842	139

Table 4.3 Heavy metals in the reject water samples

Heavy Metals	Unit	Reject Water Samples						
		HWWTP					GWWTP	
		S1	S2	S3	S4	S5	S6	S7
<b>Cd</b>	µg/L	3,176	4,292	3,162	2,152	2,684	2,773	2,513
<b>Cr</b>	µg/L	3,271	26,31	4,612	2,392	2,197	4,185	4,342
<b>Cu</b>	µg/L	5,148	18,89	17,95	11,56	19,60	11,71	11,02
<b>Fe</b>	µg/L	275,2	5808	75,52	55,33	38,32	1328	1629
<b>Mn</b>	µg/L	150,9	193,1	7,814	3,640	3,079	470,8	397,8
<b>Ni</b>	µg/L	36,3	91,27	22,78	7,025	16,19	8,846	16,99
<b>Pb</b>	µg/L	6,212	22,62	2,887	21,33	29,47	0,745	3,832
<b>Zn</b>	µg/L	401,9	569,7	204,3	111,1	210,7	69,43	30,78

As can be seen on the Table 4.2, minimum and maximum total phosphorus concentrations were measured as 5.3mg/L and 41,7mg/L, respectively. According to the literature, total phosphorus concentration can be differing from trace amounts to 130 mg/l (Fux *et al.*, 2003, Pitman *et al.*, 1991). Therefore, total phosphorus concentration of the reject water samples taken from each plant is similar to the literature values. Although higher nitrogen concentrations were reported in the literature, measured nitrogen values were lower than the literature. COD values were between 120-1520 mg/L. According to the literature, COD concentrations can be reached from 700 to 1400 mg/l (Thorndahl, 1993; Laurich and Gunner, 2003).

Table 4.4 Microbiological parameters in the reject water samples

Microbiological Parameters	Unit	Reject Water Samples				
		HWWTP			GWWTP	
		S1	S2	S3	S6	S7
<b>Fekal coliform</b>	Coliform /100ml	9600	43200	6000	14500	320000
<b>Total coliform</b>	Coliform /100ml	11200	51200			



Table 4.5 Reuse standards of wastewater for agricultural irrigation (Water Pollution Control Regulations-1991)

Parameters	Class of Irrigation Water				
	I (Very good)	II (Good)	III (Utilizable)	IV (Cautious Utilizable)	V (Harmful)
pH	6.6-8.5	6.5-8.5	6.5-8.5	6.5-9	<6 or >9
NH <sub>4</sub> (mg/L)	0-5	5-10	10-30	30-50	>50
Fecal coliform/100ml	0-2	2-20	20-100	100-1000	>1000
SS (mg/L)	20	30	45	60	>100
Chloride (mg/L)	0-142	142-249	249-426	426-710	>710
Conductivity(µmhos)	0-250	250-750	750-2000	2000-3000	>3000
Boron (mg/L)	0-0.5	0.5-1.12	1.12-2	>2	>2
Sulphate (mg/L)	0-192	192-336	336-575	575-960	>960

Table 4.6 Agricultural irrigation parameters in the reject water samples

Parameters	Unit	Samples						
		HWWTP					GWWTP	
		S1	S2	S3	S4	S5	S6	S7
pH		7,1	7,2	7,1	7,6	7,5	7,2	7,2
NH <sub>4</sub>	mg/L	4	27,7	12,77	3,72	9,3	38	15,6
Fecal	coliform/ 100ml	9600	43200	6000	14500	320000	9600	43200
SS	mg/L	444	59480	356	624	100	1788	172
Chloride	mg/L	180	185	195	200	240	4700	6598
Conductivity	µmhos	480	500	470			7900	9600
Boron	mg/L	0,6	0,50	0,53			240	1,7
Sulphate	mg/L	71		13,9	176	107	1,1	128

In this study, chloride, boron, sulphate and microbiological parameters were measured to evaluate the reuse potential of the reject water for irrigation purposes. Therefore, water acquired from HWWTP was fulfilled the standards given in the Table 4.5 for the first class (Class I) irrigation water in terms of pH, sulphate, and boron. However, certain parameters such as nitrogen, SS and coliform were higher

than the standards (Class V) thus limited the direct application on to agricultural fields. Especially very high suspended solids concentrations were measured both in HWWTP and GWWTP (see Table 4.6). Since the higher solid content can be resulted in clogging problem in the pipes it should be removed from the reject water. Similarly, higher coliforms concentrations of the reject water samples may cause health risks, thus in order to eliminate the coliforms from the reject water, treatment system should be assisted by effective disinfection. Regarding to the chlorine, reject water samples from HWWTP were classified as Class II, while higher concentrations were obtained at GWWTP (i.e. 4700 and 6598 mg/L). In addition, electrical conductivity and salinity, were highly above the limits of irrigation water, and it is obvious that use it as irrigation water may cause serious problems.

In the experiments, inlet samples from the dewatering unit were also taken to determine the performance of the unit and to evaluate the effect of the dewatering mechanisms on to pollutants. Results were presented in Tables 4.7 -4.10.

Table 4.7 Physical parameters in the inlet of dewatered unit samples

Physical Parameters	Unit	Inlet Water Samples				
		HWWTP			GWWTP	
		S1	S2	S3	S6	S7
pH	-	7	7,15	6,9	6,8	7
Temperature	°C	16	16	16	16°C	16
Conductivity	µmhos	480	700	450	7200	5000
Salinity	-	<%0.048	<%0.07	<%0.045	0,40%	0,28%
SS	mg/L	14500	8880	6216		
Solid material	%				39%	32%

As can be seen from the Tables 4.1 and 4.7, there are no significant differences in terms of temperature, salinity, pH, conductivity between belt press inlet and outlet water (reject water) except SS. In the dewatering unit, suspended solids were eliminated effectively (i.e. efficiency was around 94-96%). However, higher effluent

SS concentrations were observed in the second sampling (S2) due to the problems in dewatering unit.

Table 4.8 Chemical parameters in the inlet of dewatered unit samples

Physical Parameters	Unit	Inlet Water Samples				
		HWWTP			GWWTP	
		S1	S2	S3	S6	S7
Chloride	mg/L	180	172	163	4700	5848
Total phosphorus	mg/L	82,4	32,3	20,6	31	48,2
Total nitrogen	mg/L	222	46	15	26	32
Amonium nitrogen	mg/L	4	12,8	20,25	45	65,2
Nitrate nitrogen	mg/L	12,938	27,86			
COD	mg/L	120	400	1600	240	320
Boron	mg/L	0,6	0,53	0,6	1.1	1,5
Sulphate	mg/L	79		19,6	135	87
Calcium	mg/L	166,8	146	261	441	1800
Magnesium	mg/L	2,7	2,2	85	537	122

Table 4.9 Heavy metals in the inlet of dewatered unit samples

Heavy Metals	Unit	Inlet Water Samples				
		HWWTP			GWWTP	
		S1	S2	S3	S6	S7
<b>Cd</b>	µg/L	3,211	3,483	3,078	2,891	2,904
<b>Cr</b>	µg/L	32,35	69,23	3,762	5,429	7,261
<b>Cu</b>	µg/L	21,32	45,66	10,82	9,12	14,42
<b>Fe</b>	µg/L	1974	8225	471,4	2769	140,4
<b>Mn</b>	µg/L	141,5	250,1	111,9	537,8	272,4
<b>Ni</b>	µg/L	55,93	71,33	29,94	18,86	14,25
<b>Pb</b>	µg/L	16,89	35,19	7,032	2,216	5,04
<b>Zn</b>	µg/L	1187	1792	200,8	68,17	50,23

Table 4.10 Microbiological parameters in the inlet of dewatered unit samples

Microbiological Parameters	Unit	Inlet Water Samples				
		HWWTP			GWWTP	
		S1	S2	S3	S6	S7
<b>Fekal coliform</b>	Coliform /100ml	9600	32000	17200	260000	384000
<b>Total coliform</b>	Coliform /100ml	11200	54400			

## 4.2 Assesment of Treatability Studies

### 4.2.1 Struvite Precipitation Studies

In struvite precipitation, optimum operational parameters (i.e. pH, mixing time, perlite dose and Mg/P ratio) were determined. The pH values were changed from 7 to 10 to determine the optimal value. Mixing time were varied 2, 4 and 6 hours. Perlite was used as nucleus and thus various doses (5-10-15-20 g/L) were experienced

during the treatability study. Various Mg/P ratios were used to determine the optimum Mg-P ratio. The ratios used in the experiments were 1:1, 1,1:1, 1,2:1, 1,3:1, 1,4:1, 1,5:1 and 1,6:1. Treatability studies were replicated two times in order to get reliable results.

#### 4.2.1.1 Optimum pH

##### 1th run

In order to determine the optimum pH for struvite formation NaOH were dosed to adjust the pH from 7 to 9. In the experiments perlit dose was kept constant (15 g/L). The mixing time was determined as to be 2 hours at 100 rpm. Mg/P ratio was used as to be 1:1 thus  $\text{KH}_2\text{PO}_4$  were added into the beakers. So, phosphate phosphorus increased from 7.4 mg/L to 130 mg/L. The results obtained from the first run was summarized in Table 4.11-4.13 and schematically drawn in Figure 4.1. As can be seen from the tables and the figure, the highest treatment efficiency for nitrogen is obtained at pH 9. At pH 9, 46% of the ammonium nitrogen were eliminated. The magnesium removal was superior in struvite precipitation at pH 8. At pH 8, 88% of magnesium removal was achieved (see Figure 4.1).

Table 4.11 Optimum pH determination at pH 7 (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,65 mg/L	29%
Magnesium	122 mg/L	26,4 mg/L	78%

Table 4.12 Optimum pH determination at pH 8 (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,15 mg/L	42%
Magnesium	122 mg/L	14,6 mg/L	88%

Table 4.13 Optimum pH determination at pH 9 (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2 mg/L	46%
Magnesium	122 mg/L	19,5 mg/L	84%

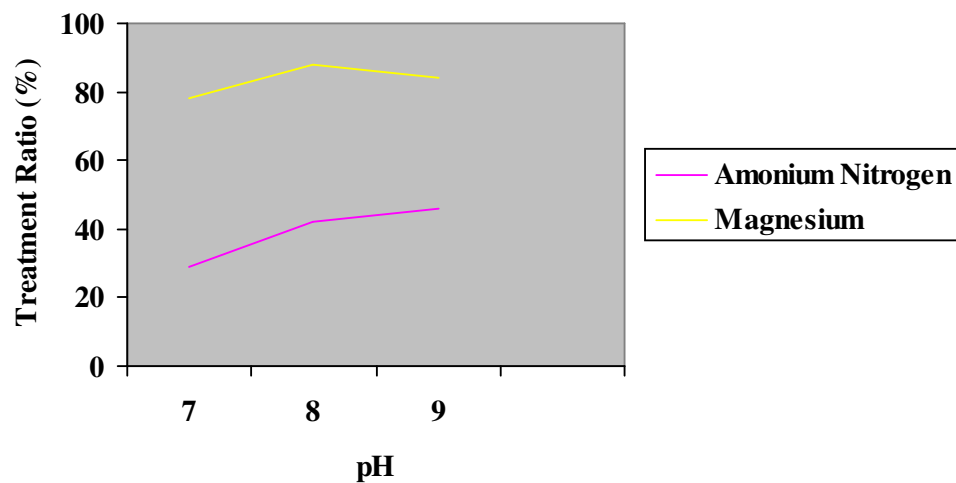


Figure 4.1 Treatment ratios at various pH levels for first run

#### 2nd run

In order to determine the optimum pH for struvite formation NaOH were dosed to adjust the pH from 7 to 10. In the experiments perlit dose was kept constant (15 g/L). The mixing time was determined as to be 4 hours at 100 rpm. Mg/P ratio was used as to be 1:1 thus  $\text{KH}_2\text{PO}_4$  were added. So, phosphate phosphorus increased from 33 mg/L to 1340 mg/L. The results obtained from the second run was summarized in Table 4.14-4.17 and schematically drawn in Figure 4.2. As can be seen from the tables and the figure, the highest treatment efficiency for nitrogen is obtained at pH 9. At pH 9, 37% of the ammonium nitrogen were eliminated. The magnesium removal was superior in struvite precipitation at pH 9 and 10. At these pH values, 95% removal was achieved (see Figure 4.2).

Table 4.14 Optimum pH determination at pH 7 ( 2nd run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	7,1 mg/L	24%
Magnesium	1040 mg/L	98 mg/L	90%

Table 4.15 Optimum pH determination at pH 8 (2nd run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	7,91 mg/L	15%
Magnesium	1040 mg/L	105 mg/L	90%

Table 4.16 Optimum pH determination at pH 9 (2 nd run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	5,91 mg/L	37%
Magnesium	1040 mg/L	61 mg/L	95%

Table 4.17 Optimum pH determination at pH 10 (2 nd run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	6,41 mg/L	31%
Magnesium	1040 mg/L	56 mg/L	95%

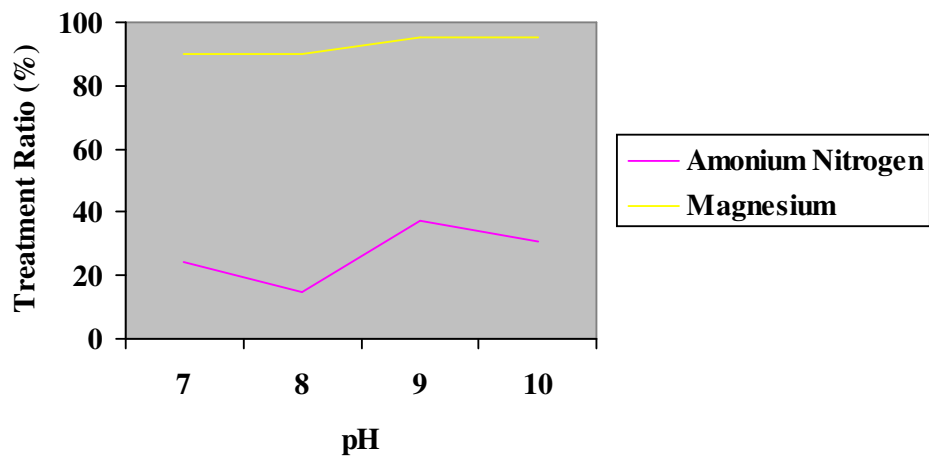


Figure 4.2 Treatment ratios at various pH levels for second run

In the experiments the highest ammonium and magnesium removals were obtained at pH 8-9 which is well-matched with the literature ( Scope Newsletter, 2001).

#### 4.2.1.2 Optimum Perlite Dose

##### 1th run

First, pH was adjusted to 8 with NaOH. The mixing time was determined as to be 2 hours at 100 rpm. Mg/P ratio was used as to be 1:1 thus  $\text{KH}_2\text{PO}_4$  were added. So, phosphate phosphorus increased from 7.4 to 130 mg/L. The results obtained from the first run was summarized in Table 4.18-4.21 and schematically drawn in Figure 4.3. As can be seen from the tables and the figure, the highest treatment efficiency for nitrogen is obtained at perlite dose of 15g/L. At 15g/L perlite dose, 46% of the ammonium nitrogen were eliminated while 90% removal was achieved for the magnesium removal for 20g/L perlite dose (see Figure 4.3).

Table 4.18 Optimum perlite dose determination at 5g/L (1 th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,65 mg/L	28%
Magnesium	122 mg/L	31,7 mg/L	69%

Table 4.19 Optimum perlite dose determination at 10g/L (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,3 mg/L	38%
Magnesium	122 mg/L	43 mg/L	65%

Table 4.20 Optimum perlite dose determination at 15g/L (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2 mg/L	46%
Magnesium	122 mg/L	16,6 mg/L	86%



Table 4.21 Optimum perlite dose determination at 20g/L (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,25 mg/L	40%
Magnesium	122 mg/L	14 mg/L	90%

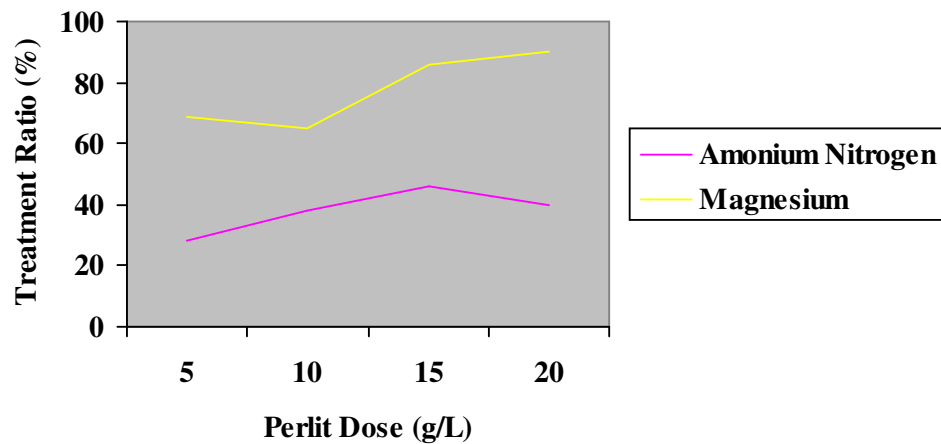


Figure 4.3 Treatment ratios at various perlite doses for first run

2nd run

First, pH was adjusted to 8 with NaOH. The mixing time was determined as to be 4 hours at 100 rpm. Mg/P ratio was used as to be 1:1 thus  $\text{KH}_2\text{PO}_4$  were added. So, phosphate phosphorus increased from 33 mg/L to 1340 mg/L. The results obtained from the second run was summarized in Table 4.22-4.25 and schematically drawn in Figure 4.4. As can be seen from the tables and the figure, the highest treatment efficiency for nitrogen is obtained at perlite dose of 10g/L. At 10g/L, 14% of the ammonium nitrogen were eliminated. The magnesium removal was superior in struvite precipitation at perlite dose of 20g/L. At this dose, 100% magnesium removal was achieved (see Figure 4.4).

Table 4.22 Optimum Perlite Dose determination at 5g/L (2nd run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	8,25 mg/L	11%
Magnesium	1040 mg/L	98 mg/L	91%

Table 4.23 Optimum Perlite Dose determination at 10g/L (2nd run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	7,97 mg/L	14%
Magnesium	1040 mg/L	98 mg/L	91%

Table 4.24 Optimum Perlite Dose determination at 20g/L (2nd run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	8,1 mg/L	13%
Magnesium	1040 mg/L	0 mg/L	100%

Table 4.25 Optimum Perlite Dose determination at 30g/L (2nd run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	8,43 mg/L	9%
Magnesium	1040 mg/L	171 mg/L	84%

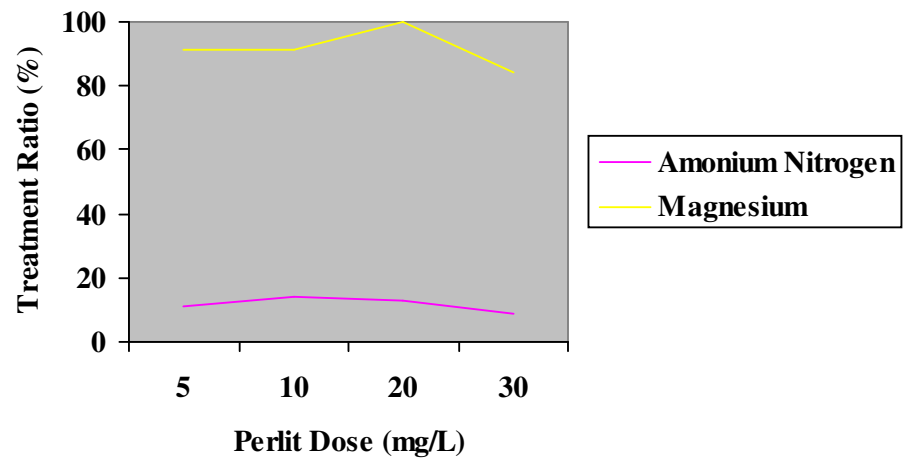


Figure 4.4 Treatment ratios at various perlite doses for second run

### 4.2.1.3 Optimum Mixing Time

#### 1th run

First, pH was adjusted to 8 with NaOH. 15g/L was chosen as perlit dose. Mg/P ratio was used as to be 1:1 thus  $\text{KH}_2\text{PO}_4$  were added. So, phosphate phosphorus increased from 7.4 to 158mg/L. The results obtained from the first run was summarized in Table 4.26-4.28 and schematically drawn in Figure 4.5. As can be seen from the tables and the figure, the highest treatment efficiency for nitrogen is obtained at mixing time of 4 hours. At mixing time of 4 hours, 36% of the ammonium nitrogen were eliminated. The magnesium removal was superior (86%) in struvite precipitation at mixing time of 4 hours (see Figure 4.5).

Table 4.26 Optimum mixing time determination at 2 hours (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,46 mg/L	34%
Magnesium	122 mg/L	29 mg/L	76%

Table 4.27 Optimum mixing time determination at 4 hours (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,4 mg/L	36%
Magnesium	122 mg/L	17,6 mg/L	86%

Table 4.28 Optimum mixing time determination at 6 hours (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	3,62 mg/L	3%
Magnesium	122 mg/L	21 mg/L	83%

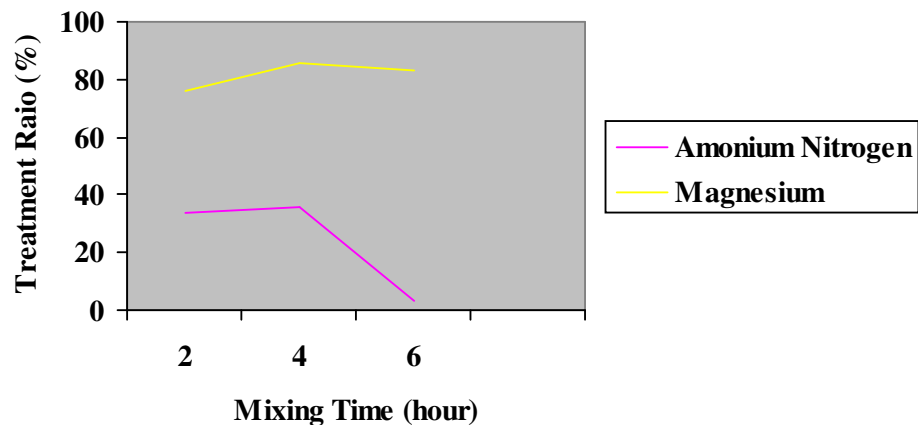


Figure 4.5 Treatment ratios at various mixing time for first run

The results were shown that optimum mixing time was 4 hours which is higher than the literature. According to the Scope Newsletter (2001), 30 minutes mixing time was enough for struvite precipitation. 90 minutes was also sufficient for phosphorus removal ( Filibeli et. al, 2007). However, for the nitrogen removal higher reaction times (i.e. 6 hours) were required. In this study, optimum mixing time was determined 4 hours for phosphate phosphorus, amonium nitrogen and magnesium removal.

#### 4.2.1.4 Optimum Mg-P Ratio

##### 1th run

First, pH was adjusted to 8 with NaOH. 15g/L was chosen as perlit dose. The mixing time was determined as to be 2 hours at 100 rpm. Mg-P rates were adjusted to 1:1, 1.1:1, 1.2:1, 1.3:1, 1.4:1, 1.5:1 and 1.6:1 with  $\text{KH}_2\text{PO}_4$ . So, after adding  $\text{KH}_2\text{PO}_4$ , phosphate phosphorus values were increased as expected. The results obtained from the first run was summarized in Table 4.29-4.35 and schematically drawn in Figure 4.6. As can be seen from the tables and the figure, the highest treatment efficiency for nitrogen is obtained at Mg-P ratio of 1.1:1. At ratio 1.1:1,

41% of the ammonium nitrogen were eliminated. 76% removal was achieved for the magnesium removal at Mg-P ratio of 1:1 (see Figure 4.6).

Table 4.29 Optimum Mg-P ratio determination at ratio of 1:1 (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,46 mg/L	34%
Magnesium	122 mg/L	29 mg/L	76%

Table 4.30 Optimum Mg-P ratio determination at ratio of 1,1:1 (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,19 mg/L	41%
Magnesium	122 mg/L	42,5 mg/L	65%

Table 4.31 Optimum Mg-P ratio determination at ratio of 1,2:1 (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,68 mg/L	28%
Magnesium	122 mg/L	37,6 mg/L	69%

Table 4.32 Optimum Mg-P ratio determination at ratio of 1,3:1 (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,59 mg/L	30%
Magnesium	122 mg/L	36 mg/L	71%

Table 4.33 Optimum Mg-P ratio determination at ratio of 1,4:1 (1th run)

Parameters	Raw reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,72 mg/L	27%
Magnesium	122 mg/L	45 mg/L	63%

Table 4.34 Optimum Mg-P ratio determination at ratio of 1,5:1 (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,41 mg/L	35%
Magnesium	122 mg/L	44 mg/L	64%

Table 4.35 Optimum Mg-P ratio determination at ratio of 1,6:1 (1th run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	3,72 mg/L	2,34 mg/L	37%
Magnesium	122 mg/L	57 mg/L	53%

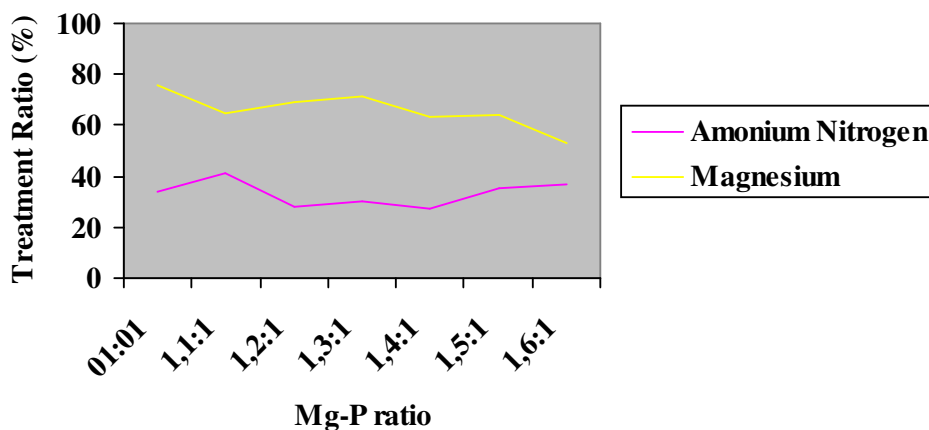


Figure 4.6 Treatment ratios at various Mg-P ratios for first run

2nd run

First, pH was adjusted to 8 with NaOH. 15g/L was chosen as perlit dose. The mixing time was determined as to be 2 hours at 100 rpm. Mg-P rates were adjusted to 1:1, 1,5:1 and 2:1 with  $\text{KH}_2\text{PO}_4$ . The results obtained from the second run was summarized in Table 4.36-4.38 and schematically drawn in Figure 4.7. As can be seen from the tables and the figure, the highest treatment efficiency for nitrogen is obtained at Mg-P ratio of 2:1. At ratio 2:1, 28% of the ammonium nitrogen were eliminated. 91% removal was achieved for the magnesium removal at Mg-P ratio of 1:1 (see Figure 4.7).

Table 4.36 Optimum Mg-P Ratio determination at ratio of 1:1 (2nd run)

Parameters	Reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	8,63 mg/L	7%
Magnesium	1040 mg/L	98 mg/L	91%

Table 4.37 Optimum Mg-P Ratio determination at ratio of 1,5:1 (2nd run)

Parameters	Raw reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	7,28 mg/L	22%
Magnesium	1040 mg/L	195 mg/L	81%

Table 4.38 Optimum Mg-P Ratio determination at ratio of 2:1 (2nd run)

Parameters	Raw reject water	Treated reject water	Treatment ratio
Amonium nitrogen	9,3 mg/L	6,65 mg/L	28%
Magnesium	1040 mg/L	122 mg/L	88%

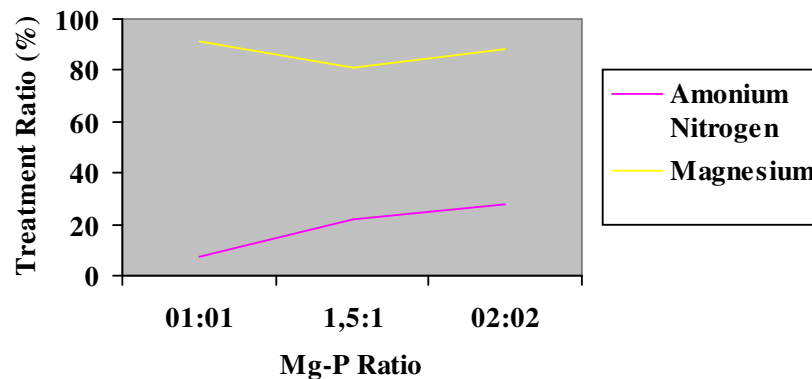


Figure 4.7 Treatment ratios at various Mg-P ratios for second run

#### 4.2.2 Hydroxyapatite Precipitation Studies

Gypsum (calcium sulphate) is used as coagulant for hydroxyapatite precipitation and optimum levels for the highest usage of phosphate phosphorus are determined as a result of analyses. The analysed optimum values are optimum pH, optimum mixing time and gypsum dose.

##### 4.2.2.1 Optimum pH

pH values used in the experiments were 7, 8, 9 and 10 for optimum pH determination. In the experiments, gypsum dose was 20 g/L, mixing timing was 2 hour. Experimental results were shown in Table 4.39 and Figure 4.8.

Table 4.39 Optimum pH determination for hydroxyapatite precipitation

pH	Reject water	Treated reject water	Treatment Ratio
7	12,3 mg PO <sub>4</sub> -P /L	7,5mg PO <sub>4</sub> -P /L	39%
8	12,3mg PO <sub>4</sub> -P /L	2,5mg PO <sub>4</sub> -P /L	80%
9	12,3mg PO <sub>4</sub> -P /L	0,7mg/ PO <sub>4</sub> -P L	94%
10	12,3mg PO <sub>4</sub> -P /L	0,8mg/ PO <sub>4</sub> -P L	93%

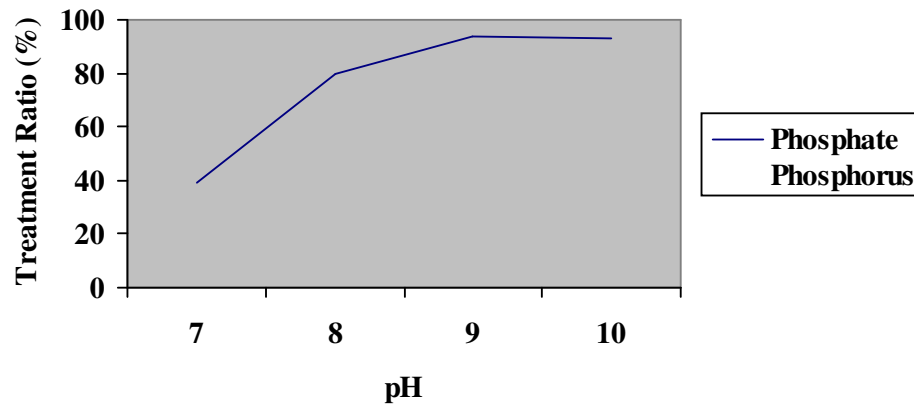


Figure 4.8 Treatment ratios at various pH levels for hydroxyapatite precipitation

As can be seen from both Table 4.39 and Figure 4.8 phosphorus removal was very low at pH 7. When pH increased to 8, treatment ratio was reached to 80%. But at pH 9 and 10, high treatment ratio was observed (93-94%). So, optimum pH was determined to prevent excess sodium hydroxide. In literature, optimum pH value was reported as 8 - 9 for the best calcium phosphate removal (Scope Newsletter, 2001).

#### 4.2.2.2 Optimum Mixing Time

In the study, for the optimum mixing time determination 2-6 hours were experienced. The results were shown in Table 4.40 and Figure 4.9. During the experiments, gypsum dose was 20g/L and pH value was 9.



Table 4.40 Optimum mixing time determination for hydroxyapatite precipitation

Mixing timing	Reject water	Treated reject water	Treatment Ratio
2 hour	12,3mg PO4-P /L	0,8mg PO4-P /L	93%
4 hour	12,3mg PO4-P /L	0,8mg PO4-P /L	93%
6 hour	12,3mg PO4-P /L	0,9mg PO4-P /L	92%

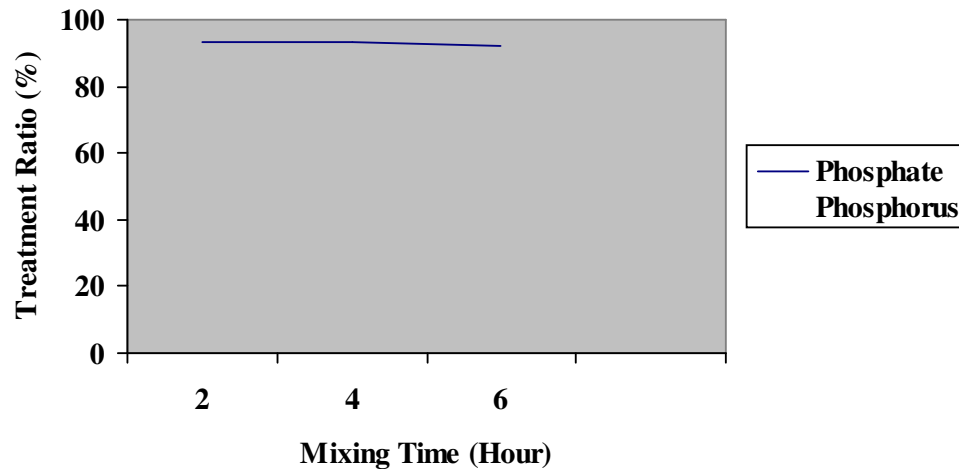


Figure 4.9 Treatment ratios at various mixing timings for hydroxyapatite precipitation

As can be seen from Figure 4.9 and Table 4.40, the optimum mixing time was applied as 2 hour.

#### 4.2.2.3 Optimum Gypsum (Calcium Sulphate) Dose

In order to determine the optimum gypsum dose various doses of gypsum were studied (5,10,20 and 30 g/L). Experimental results are shown in Table 4.41 and Figure 4.10. In the study, pH was adjusted as 9, and mixing time was used as 2 hour.

Table 4.41 Optimum gypsum dose determination for hydroxyapatite precipitation

Gypsum Dose	Reject water	Treated reject water	Treatment Ratio
5g/L	12,3mg PO4-P /L	1,2mg PO4-P /L	90%
10g/L	12,3mg PO4-P /L	1,4mg PO4-P /L	88%
20g/L	12,3mg PO4-P /L	1mg PO4-P /L	92%
30g/L	12,3mg PO4-P /L	1mg PO4-P /L	92%

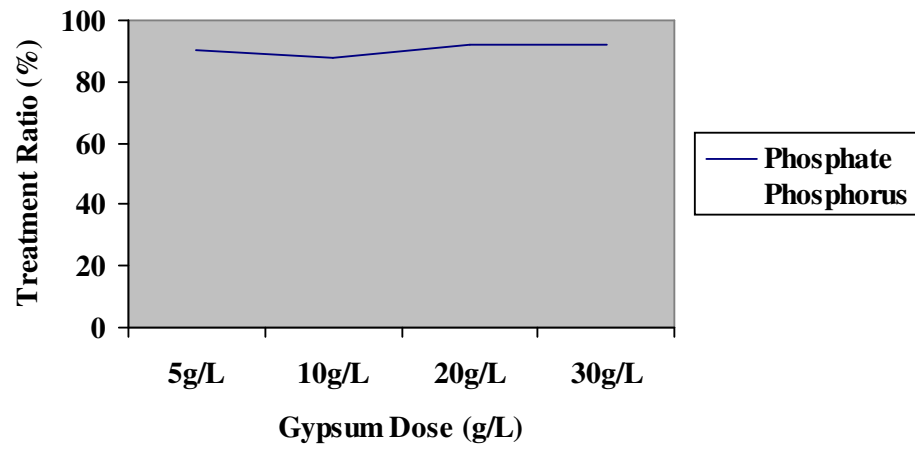


Figure 4.10 Treatment ratios at various gypsum doses for hydroxyapatite precipitation

## **CHAPTER FIVE**

### **CONCLUSIONS**

Reject water poses a great challenge to the efficient performance of the wastewater treatment process due to its ability to increase mainly the nitrogen load of the plant. This has the tendency to overload the treatment process with a return flow of just about 2% contributed to the influent. Due to the stringent effluents demands as well as protection of the environment from nutrient impacts, treatment of reject water is inevitable since reject water treatment is able to reduce effluent limits by up to 25%.

In this study, reject water characteristics were investigated and struvite precipitation (MAP) and hydroxyapatite precipitation (HAP) experiments were made for treatment of nitrogen and phosphorus in reject water. The following conclusions were obtained:

Reject water pH values were between 6.8-7.6 which are typical pH values for the reject water. Electrical conductivity of the samples taken from the GWWTP were higher (7900-9600  $\mu\text{mhos}$ ) due to high salinity levels. In general, SS values were dissimilar to the literature values. Higher solid concentrations of the reject water are attributed mal operation of the belt pres unit. Total phosphorus concentrations differing from 5,3 mg/L and 41,7 mg/L. Although higher nitrogen concentrations were reported in the literature, measured nitrogen values were lower than the literature. COD concentrations were not differed from the literature (i.e. COD concentrations were measured between 120-1520 mg/L).

Water acquired from HWWTP was fulfilled the standards for the first class (Class I) irrigation water in terms of pH, sulphate, and boron. However, certain parameters such as nitrogen, SS and coliform were higher than the standards (Class V) thus limited the direct application on to agricultural fields. Regarding to the chlorine,

reject water samples from HWWTP were classified as Class II, while higher concentrations were obtained at GWWTP (i.e. 4700 and 6598 mg/L). In addition, electrical conductivity and salinity were highly above the limits of irrigation water, and it is obvious that use it as irrigation water may cause serious problems.

- Reject water ammonium nitrogen values were between 3.5-65.2 mg/L in the samples. In struvite precipitation studies, %28-46 of ammonium nitrogen were eliminated. The optimum treatment efficiency was obtained at pH 9, perlite dose of 15 g/L, and 4 hours mixing time. In addition, optimum removal was obtained at Mg/P ratio 1.1/1.

- Reject water phosphate phosphorus values were between 7,4-33 mg/L. In struvite precipitation studies, phosphate phosphorus treatment ratios were between %25-41. The highest treatment efficiency for phosphate phosphorus were obtained at pH 8. Perlite dose was 5 g/L at this pH. Four hours of mixing were sufficient for 41% phosphate phosphorus removal. Finally, efficient Mg/P ratio was 1/1.

- Reject water magnesium values were between 2.9-1040 mg/L. In struvite precipitation studies, magnesium treatment ratios were between %76-100. The highest treatment efficiency was obtained at pH 9. 20 g/L perlite was used as nucleous material at highest magnesium removal. Four hours of mixing time was required for 86% magnesium removal. Finally, efficient Mg/P ratio was 1/1.

In hydroxyapatite precipitation studies, phosphate phosphorus treatment ratio was %92 at optimum pH, mixing time and gypsum dose.

- In struvite crystallization, phosphate rock, bone coal, magnesia clinker and sand were used as nucleous material. However, in this study, perlite was experienced and found as efficient for nucleous formation.

## REFERENCES

- Abeling, U., Seyfried, C. F. (1992). "Anaerobic-aerobic treatment of high-strength ammonium wastewater - nitrogen removal via nitrite." *Wat. Sci. Tech.* 26(5-6), 1007-1015.
- Adnan, A., D.S. Mavinic, and F.A. Koch. (2003). Pilot-scale study of phosphorus recovery through struvite crystallization – examining the process feasibility. *Journal of Environmental Engineering Science* 2:315-324.
- Anthonisen, A.C., Loehr, R.C., Prakasam, T. B., Sarinatu, E.G. (1976). "Inhibition of nitrification by ammonia and nitrous acid." *J. Wat. Pollut. Control. Fed.* 48, 835-852.
- Arnold, E., Böhm, B., Wilderer, P. A. (2000). "Application of activated sludge and bio film sequencing batch technology to treat reject water from sludge and dewatering systems: a comparison." *Wat. Sci. Tech.* 41(1), 115-122.
- Balmelle B., Nguyen K. M., Capdeville B., Cornier J. C. and Deguin A. (1992) Study of factors controlling nitrite build-up in biological processes for water nitrification. *Wat. Sci. Technol.* 26(5-6), 1017-1025.
- Battistoni, P., Pavan, P., Prisciandaro, M., Cecchi, F., Struvite Crystallization: A Feasible and Reliable Way to Fix Phosphorus in Anaerobic Supernatants, *Water Research*, 34,11,3033-3041, (2000).
- Battistoni, P., Boccadoro, R., Pavan, P., Cecchi, F. (2001). "Struvite crystallisation in sludge dewatering supernatant using air stripping: the new-full scale plant at Treviso (Italy) sewage works." *Second International Conference on the recovery of phosphorus from sewage and animal wastes. Noordwijkerhout, March 12 & 13, 2001.*  
<http://www.nhm.ac.uk/mineralogy/phos/Nordwijkerhout/Battistoni1302.doc>  
 (November 2004)
- Cecchi, F., Battistoni, P., and Boccadoro, R. (2003). Phosphate crystallisation process for P recovery applied at Treviso municipal wastewater treatment plant. Available from <http://www.nhm.ac.uk/mineralogy/phos/Treviso2003.pdf>

Chevron Corporation, [http://www.chevron.com/products/sitelets/refiningtechnology/waste\\_wtr\\_treat\\_6b.aspx](http://www.chevron.com/products/sitelets/refiningtechnology/waste_wtr_treat_6b.aspx)

Çelen, I., Türker, M. (2001). "Recovery of ammonia as struvite from anaerobic digester effluents." *Environ. Tech.* 22, 1263-1272.

Department of environmental protection, (2002). The SHARON® High-Rate Nitrogen Removal System: An Innovative Wastewater Treatment Process  
[http://www.dep.state.pa.us/dep/DEPUTATE/Watermgmt/WSM/WSM\\_TAO/InnovTech/ProjReviews/SharonHiRate.htm](http://www.dep.state.pa.us/dep/DEPUTATE/Watermgmt/WSM/WSM_TAO/InnovTech/ProjReviews/SharonHiRate.htm)

Fux, C., Boehler, M., Huber, P., Brunner, L., Siegrist, H. (2002). "Biological treatment of ammonium-rich wastewater by partial nitritation and subsequent anaerobic ammonium oxidation (anammox) in a pilot plant." *J. Biotech.* 99(3), 295-306.

Gaterell, M. R., Gay, R., Wilson, R., Gochin, R. J. and Lester J. N. (2000). An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK Fertilizer markets. *Environ. Technology* vol. 21 n° 9 pages 1067-1084.

Ghyoot, W., Vandalee, S., and Verstraete, W. (1997). Nitrogen Removal From Sludge Reject Water With A Membrane-Assisted Bioreactor. *Wat. Res.* Vol. 33, No 1, pp. 23-32, 1999.

Goto, I., Fertiliser value of recovered struvite, *Scope Newsletter*, Nr.42, Centre Europeen d'Etudes sur les Polyphosphates (CEEP), Brussel, (2001).

Hellinga, C., Schellen A. A. J. C., Mulder J. W., van Loosdrecht, M. C. M., Heijnen, J. J. (1998). "The SHARON process: an innovative method for nitrogen removal from ammonium-rich wastewater." *Wat. Sci. Tech.* 37(9), 135-142.

Janus, H. M. and van der Roest, H. F. (1997). "Don't reject the idea of treating reject water." *Wat. Sci. Tech.* 35(10), 27-34.

Jetten, M. S. M., Horn, S. J., van Loosdrecht, M. C. M. (1997). "Towards a more sustainable municipal wastewater treatment system." *Wat. Sci. Tech.* 35(9), 171-180.

- Jetten, M. S. M., Wagner, M., Fuerst, J., van Loosdrecht, M., Kuenen, G., Strous, M. (2001). "Microbiology and application of the anaerobic ammonium oxidation ('anammox') process." *Curr. Opin. Microbiol.* 12, 283-288.
- Laurich, F., Gunner, C. (2003). "The store and treat process for sludge liquor management." *Wat. Sci. Tech.* 42(12), 269-275.
- Laurich, F. (2003). "Combined quantity management and biological treatment of sludge liquor at Hamburg's WWTP." *Presentation at the 9<sup>th</sup> IWA Specialised Conference on Large WWTPs, Prague 2003.* [http://www.vscht.cz/tvp/9th\\_IWA\\_Conf/conference/Laurich.pdf](http://www.vscht.cz/tvp/9th_IWA_Conf/conference/Laurich.pdf) (November 2004)
- Lind, B.B., Ban, Z. ve Bydén, S. (2000). Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite, *Bioresource Technology*, 73, 169-174.
- Loewenthal, R.E., Kornmuller, U.R.C., Van Heerden, E.P., Modeling struvite precipitation in anaerobic treatment systems, *Water Science and Technology*, 30 107-116, (1994).
- Lunt O.R., Kofranek A.M. and Clark S.B., (1964), Availability of minerals from magnesium ammonium phosphate., *Agr. Food Chem.*, 12. 497-504
- Momberg, G. A., Oellermann, R. A. (1992). "The removal of phosphate by hydroxyapatite and struvite crystallisation in South Africa." *Wat. Sci. Tech.* 26(5-6), 987-1992.
- Mossakowska, A., Lars-Gunnar, R., Hultman, B. (1997). "Nitrification reactions in treatment of supernatant from dewatering of digested sludge." *Wat. Environ. Res.* 69(6), 1128-1133.
- Pitman, A. R., Deacon, S. L., Alexander, W. V. (1991). "The thickening and treatment of sewage sludges to minimize phosphorus release." *Wat. Res.* 25(10), 1285-1294.
- Pitman, A., R. (1999). "Management of biological nutrient removal plant sludges- Change the paradigms?" *Wat. Res.* 33 (5), 1141-1146.

- Pollice, A., Tandoi, V., Lestingi, C. (2002). "Influence of aeration and sludge retention time on ammonium oxidation to nitrite and nitrate." *Wat. Res.* 36(10), 2541-2546.
- Regy, S., Mangin, D., Klein, J.P., Lieto, J., Phosphate recovery by struvite precipitation in a stirred reactor, Centre Europeen d'Etudes des Polyphosphates, (2001).
- Scope Newsletter (2004), 'Struvite, its role in phosphorus recovery and recycling', international conference 17-18th June 2004, Cranfield University, Great Britain.
- Siegrist, H. (1996). "Nitrogen removal from digester supernatant- Comparison of chemical and biological methods." *Wat. Sci. Tech.* 34(1-2), 399-406.
- Sliker, A. O., Third, K. A., Abma, W., Kuenen, J. G., Jetten, M. S. M. (2003). "CANON and Anammox in a gas-lift reactor." *FEMS Microbiol. Letters.* 218(2), 339-344.
- Stranful, I., Scrimshaw, M.D., Lester, J.N., Conditions influencing the precipitation of magnesium ammonium phosphate, *Water Research* 35, 17, 4191-4199, (2001).
- Strous, M., van Gerven, E., Kuenen, J. G., Jetten, M. S. M. (1997). "Ammonium removal from concentrated waste streams with Anaerobic Ammonium Oxidation (Anammox) process in different reactor configurations." *Wat. Res.* 31(8), 1955-1962.
- Strous, M., Kuenen, J. G., Jetten, M. S. M. (1999). "Key physiology of anaerobic ammonium oxidation." *Appl. Environ. Microbiol.* 65, 3248-3250.
- The Anammox online resource*, April 7, 2006 from <http://www.anammox.com/application.html>
- Thorndahl, U. (1993). "Nitrogen removal from returned liquors." *J.IWEM.* (7), October: 492-496.
- Turk O. and Mavinic D. S. (1987) Selective Inhibition: A Novel concept for Removing Nitrogen from Highly Nitrogenous Wastes. *Env. Technol. Lett.* 8, 419.



- Turk O. and Mavinic D. S. (1989) Stability of nitrite build-up in an activated sludge system. *J. Water Pollut. Control Fed.* 61(8), 1440-1448.
- Ueno, Y.; Fujii, M. (2001). Three years experience of operating and selling recovered struvite from full-scale plant, *Environmental Technology* 22, S. 1373-1381
- United States Environmental Protection Agency. (2000). "Wastewater Technology Fact Sheet Ammonia Stripping." September, EPA 832-F-00-019.
- Van Dijk L. and Roncken G. C. G. (1997) Membrane bio-reactors for wastewater treatment: the state of the art and new developments. *Wat. Sci. Technol.* 35(10), 35-41.
- Van Dongen, U., Jetten, M. S. M., van Loosdrecht, M. C. M. (2001). "The SHARON- Anammox process for treatment of ammonium rich wastewater." *Wat. Sci. Tech.* 44(1), 153-160.
- Van Kempen, R., Mulder, J. W., Uijterlinde, C. A., Loosdrecht, M. C. M. (2001). "Overview: full scale experience of the SHARON<sup>®</sup> process for treatment of rejection water of digested sludge dewatering." *Wat. Sci. Tech.* 44(1), 145-152.
- Verstraete W., Vanstaen H. and Voets J. P. (1977) Adaptation to nitrification of activated sludge systems treating highly nitrogenous waters. *J. Water Pollut. Control Fed.* 49(7), 1604-1608.
- Wett, B., Rostek, R., Rauch, W., Ingerle, K. (1998). "pH-controlled reject-water-treatment." *Wat. Sci. Tech.* 37(12), 165-172.
- Wett, B., Alex, J., (2003). "Impacts of separate rejection water treatment on the overall plant performance." *Wat. Sci. Tech.* 48(4), 139-146.
- Wu, Q., Bishop, P. L., Keener, T. C., Stallard, J., Stile, L. (2001). "Sludge digestion enhancement and nutrient removal from anaerobic supernatant by Mg(OH)<sub>2</sub> application." *Wat. Sci. Tech.* 44(1), 161-166.
- Wyffels, S., Boeckx, P., Pynaert, K., Zhang, D., Cleemput, O. V., Chen, G., Verstraete, W. (2004). "Nitrogen removal from sludge reject water by a

two-stage oxygen-limited autotrophic nitrification denitrification process.” *Wat. Sci. Tech.* **49**(5-6), 57-64.

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