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Technologies for Sidestream Nitrogen Removal

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TECHNOLOGIES FOR SIDESTREAM NITROGEN REMOVAL

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ABSTRACT AND BENEFITS

Abstract:

Liquid streams (known as “reject water” or “sidestream”) generated by the dewatering of digested solids generally contain high levels of ammonia and phosphorus. These liquids can be treated in separate or sidestream processes rather than being directly returned to the mainstream treatment process. Sidestream treatment processes can reduce overall energy and chemical costs and improve treatment reliability for biological nutrient removal facilities. Sidestream treatment processes can also be used for nutrient recovery and reuse.

This document is a compilation of a broad range of biological and physiochemical treatment processes specifically for nitrogen removal and recovery from municipal sidestreams and ammonia-rich industrial wastewaters. The benefits of these technologies are described along with design approaches and full-scale plant experiences. Reuse of recovered ammonia in the form of aqueous ammonia and ammonium salts for industrial and agricultural applications is also discussed. Future research needs in sidestream nitrogen removal and recovery are identified and summarized.

Benefits:

- Documents current sidestream management options.
- Describes treatment technologies available for sidestream nitrogen removal and their performance.
- Describes technologies available for sidestream nitrogen recovery and performance.
- Documents current practice for sidestream nitrogen removal and recovery processes.

Keywords: Ammonia, nitrogen, sidestream, centrate, filtrate, nitrification, denitrification, nitritation, denitritation, deammonification, anammox, nitrogen recovery, ammonia rich industrial wastewaters.

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LIST OF ABBREVIATIONS AND ACRONYMS

AOB	Ammonia oxidizing bacteria
ARP	Ammonia recovery process
AS	Ammonium sulfate
ATAD	Autothermal thermophilic aerobic digestion
BABE®	Biological Augmentation Batch-Enhanced (registered process tradename)
BAR	BioAugmentation Reaeration
BOD	Biochemical oxygen demand
$CaCO_3$	Calcium carbonate
CANON	Completely Autotrophic Nitrogen removal Over Nitrite
CaRRB	Centrate and RAS reaeration Basin
CaO	Calcium oxide – quicklime
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CSTR	Continuous stirred tank reactor
d	Day
DAP	Di-ammonium phosphate
DEMON®	DEamMONification (registered process tradename)
DIB	Deammonification In Biofilms
DO	Dissolved oxygen
ELAN®	ELiminatión Autótrofa de Nitrógeno (registered process tradename)
FNA	Free nitrous acid
g	Gram
GTM	Gas transfer membrane
H_2	Hydrogen (gas)
H_2S	Hydrogen sulfide
HCOOH	Formic acid
HNO_2	Nitrous acid
hr	Hour
HRT	Hydraulic retention time

IC	Internal Circulation (upflow anaerobic reactor process)
IFAS	Integrated Fixed-Film Activated Sludge (process)
ISAH	The Institute for Water Quality and Waste Management, Technical University of Hannover
kg	Kilogram
kWh	Kilowatt-hour
L	Liter
m^2	Square meter
m^3	Cubic meter
MAP	Mono-ammonium phosphate
MBBR	Moving bed biofilm reactor
MBR	Membrane bioreactor
mg	Milligram
MLE	Modified Ludzack-Ettinger (process)
mgd	Million gallons per day
N	Nitrogen
N_2	Nitrogen (gas)
NAS®	New Activated Sludge (registered process tradename)
NH_2OH	Hydroxylamine
NH_3	Ammonia
NH_4-N	Ammonium-nitrogen
NH_4Cl	Ammonium chloride
$NH_4C_2H_3O_2$	Ammonium acetate
NH_4NO_3	Ammonium nitrate
$(NH_4)_2SO_4$	Ammonium sulfate
NO	Nitric oxide
N_2O	Nitrous oxide
NO_2-N	Nitrite-nitrogen
NO_3-N	Nitrate-nitrogen
NOx-N	Nitrite/nitrate-nitrogen
NOB	Nitrite oxidizing bacteria

O_2	Oxygen (gas)
OLAND	Oxygen-Limited Autotrophic Nitrification Denitrification
ORP	Oxidation-reduction potential
P	Phosphorus
PANDA	Partial Augmented Nitritation/Denitritation with Alkalinity recovery
RAS	Return activated sludge
RBC	Rotating biological contactor
rDON	Recalcitrant dissolved organic nitrogen
R-D-N	Regeneration-Denitrification-Nitrification
Ru-Pt-Ir	Ruthinium-Platinum-Iridium
SAT	Storage and treat
SBR	Sequencing batch reactor
SCR	Selective catalytic reduction
SHARON®	Stable-reactor, High-Activity ammonia Removal Over Nitrite (registered process tradename)
SNAD	Simultaneous partial Nitrification Annamox and Denitrification
SND	Simultaneous nitrification-denitrification
SNDR	Storage Nitrification Denitrification Reactor
SRT	Solids retention time/sludge retention time
STOWA	Acronym for Foundation for Applied Water Research, the Netherlands
SVI	Sludge volume index
TCO	Thermal catalytic oxidation
TIN	Total inorganic nitrogen
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TS	Total solids
TSS	Total suspended solids
UAN	Urea ammonium nitrate
μm	Micrometer

VEAS	Vestfjorden Avløpsselskap
VSS	Volatile suspended solids
VOC	Volatile organic compound
WAS	Waste activated sludge
WEF	Water Environment Federation
WERF	Water Environment Research Foundation
WPCP	Water pollution control plant
WWTP	Wastewater treatment plant

EXECUTIVE SUMMARY

ES.1 Introduction

This report provides a review of technologies which treat nutrient-rich industrial wastewaters and recycle streams ("sidestream") generated by the dewatering of digested municipal sludges, animal manures, and source separated wastes. Of the two nutrients of interest, nitrogen (N) and phosphorus (P), this report focuses on the treatment technologies for the removal and recovery of nitrogen. Phosphorus removal and recovery have been investigated under a separate WERF project (*Towards a Renewable Future: Assessing Resource Recovery as a Viable Treatment Alternative*, NTRY1R12) and information can be found in reports including *Enabling the Future: Advancing Resource Recovery from Biosolids* (WEF, 2013).

The information in this document is up-to-date as of the time of its publication and provides an overview of the state of technologies. However, readers are encouraged to consult with the equipment suppliers and recent publications as the technologies for the removal of nitrogen from sidestream are advancing rapidly. General principles of biological and physical/chemical processes are described briefly.

ES.2 Characteristics of Sidestream

To reflect the dewatering process employed, the sidestream may also be termed as centrate, filtrate, and pressate. Reject water is also a commonly used general name for this type of plant recycle stream in Europe. The principal parameters of interest for the selection and design of sidestream treatment process for nitrogen removal include total suspended solids (TSS), organic content (e.g., chemical oxygen demand (COD)), Total Kjeldahl Nitrogen (TKN), ammonium-nitrogen (NH_4-N), alkalinity, phosphorus (TP), ortho-phosphate (ortho-P), and temperature.

The characteristics of sidestream vary significantly depending on the type of sludges processed and the technologies used for the pretreatment, digestion, and dewatering. For example, the ammonium and ortho-phosphate concentrations resulting from digestion are dependent on the feed solids concentrations to the digester and the volatile solids destruction efficiency. For conventional mesophilic anaerobic digestion of combined primary and waste activated sludges (WAS), the ammonium-nitrogen concentration is typically between 800 and 1,300 mg/L. The level of ammonium-N will be two to three times higher when sludges are pre-treated by thermal hydrolysis before digestion to enhance destruction of volatile solids and allow an increase in the total solids concentration to the digesters. The ammonia concentration in industrial wastewaters (e.g., food processing effluents) and other solids digestion processes vary and are specific to the processes from which they are derived.

Ammonia-rich municipal sidestream and certain anaerobically pretreated industrial wastewaters typically have degradable-COD-to-N ratios below 1:1, indicating that insufficient organic carbon is present to support high biological nitrogen removal efficiency via the nitrification-denitrification and nitritation-denitritation pathways described below. Therefore, an external carbon source is required by these processes. These streams also typically have insufficient bicarbonate alkalinity to support complete ammonia oxidation where no denitrification or denitritation is provided.

ES.3 Nitrification and Denitrification

The traditional method for nitrogen removal in wastewater treatment facilities is biological nitrification and denitrification. Under aerobic conditions and other conditions required to sustain the growth of the requisite bacteria, NH_4-N can be oxidized to NO_2-N ("Nitritation") by aerobic ammonia oxidizing bacteria (AOB) and then to NO_3-N ("Nitratation") by aerobic nitrite oxidizing bacteria (NOB). In the absence of dissolved oxygen, biological denitrification occurs by heterotrophic bacteria, which oxidize an organic carbon source with NO_3-N or NO_2-N as electron acceptors, reducing NO_3-N and NO_2-N to N_2 gas.

Nitrification and denitrification of sidestream ammonia-N may be conducted in separate sidestream treatment processes or integrated sidestream-mainstream processes where bioaugmentation of the mainstream plant with nitrifier-enriched mixed liquor derived from the treatment of sidestream is the primary goal. Of the separate processes, a Sequencing Batch Reactor (SBR) configuration has been most commonly applied where intermittent aeration is used to provide aerobic and anoxic periods for nitrification and denitrification, respectively. Since sidestream typically has insufficient degradable organic carbon relative to the ammonia-N concentration, an external organic carbon source is added during the anoxic periods if high nitrogen removal efficiency is required. Where the reactor is only aerated to nitrify the sidestream, an external alkalinity source will be needed if high ammonia removal efficiency is required.

Bioaugmentation configurations have proven beneficial for improving and stabilizing nitrification performance of the mainstream plant. The most common configuration for this type of operation is nitrification of the sidestream ammonia load in a Return Activated Sludge (RAS) reaeration basin. In this operation, the nitrifiers generated through sidestream ammonia removal enrich the RAS, which subsequently enhances and stabilizes nitrification in the mainstream reactors. Depending on the alkalinity balance, the RAS may have sufficient alkalinity to support near complete removal of the sidestream ammonia load.

ES.4 Nitritation and Denitritation

Nitritation-denitritation processes were developed and implemented at a full-scale in the 1990s in Europe as the first milestone towards the creation of more energy and carbon efficient nitrogen removal processes. In these processes, the nitrification-denitrification pathway is short-circuited through the restriction of nitrite oxidation to nitrate. By stopping ammonia oxidation at nitrite and reducing nitrite to nitrogen gas, the stoichiometric oxygen and carbon requirements are reduced by 25% and 40%, respectively, in comparison to requirements for nitrification-denitrification.

Suppression of NOB growth can be accomplished by several mechanisms described in this document. The most common methods to achieving stable nitritation in the relatively warm conditions of a separate biological system is operating at low Sludge Retention Times (SRT) that restrict NOB growth via the high washout rate; continuous aeration at a low dissolved oxygen (DO) concentration to exploit the higher sensitivities of NOB growth to DO; intermittent aeration and operating at a low DO concentration during each aerobic phase; and inhibiting NOB growth through exposure to free ammonia (NH_3). Each mechanism is not exclusively applied; in the processes described in this document, multiple mechanisms simultaneously play a role in restricting NOB growth and providing a stable nitritation process.

ES.5 Deammonification

Deammonification is a biological transformation of ammonia to nitrogen gas in a two-step process. In the first process, termed *partial nitritation*, a fraction of the ammonia is converted to nitrite by aerobic AOB under conditions that restrict NOB growth.

In the second step, termed *anaerobic ammonium oxidation* or *anammox*, NH_4-N is oxidized under oxygen-free conditions by slow-growing autotrophic bacteria that can use NO_2-N as the electron acceptor to produce N_2 and a small portion of NO_3-N.

Of the ammonia removed in the two-step deammonification process, approximately 89% is converted to N_2 gas and about 11% as NO_3-N, plus a minor amount of ammonia is removed as a nutrient for biomass growth. With the discovery and subsequent characterization of anammox bacteria in the 1990s, the next phase in the development of ammonia removal processes that further reduce the energy and organic carbon requirements has expanded rapidly.

The development and implementation of deammonification processes has accelerated since the first full-scale systems were commissioned in Germany and The Netherlands in 2001-2002. The technologies exploit the ability of anammox bacteria to tightly aggregate into a granulated form or readily attach to surfaces due to excessive formation of exocellular polymeric substances. The anammox bacteria also have a low biomass yield. Due to these fortuitous properties, system designers can readily achieve the high SRT required to sustain and accumulate anammox organisms in a reactor and design reactors with high specific nitrogen loading rates. The collective operating experience with all processes described in this document demonstrate that deammonification can be well controlled, provide stable sidestream ammonia removal, and provide a platform for potential implementation in mainstream facilities to reduce the energy and carbon requirements for Total Nitrogen (TN) reduction.

ES.6 Reduction of Sidestream Ammonia Through Removal in Solids Digestion Processes

Mesophilic aerobic digestion has been practiced for decades at many wastewater treatment plants with influent flows typically less than 5 mgd. During aerobic digestion, a portion of the ammonia released due to volatile solids destruction is nitrified, resulting in alkalinity destruction. To prevent a low operating pH as a result of nitrification and minimize aeration energy for volatile solids destruction, intermittent aeration can be applied to provide alternating aerobic and anoxic conditions for nitrification and denitrification or the digester can be continuously aerated at a low DO concentration to perform Simultaneous Nitrification-Denitrification (SND). The concept of nitrifying within aerobic digestion and using degradable volatile solids as a carbon source for nitrite and nitrate reduction to reduce the sidestream nitrogen load has been extended to second-stage aerobic digestion processes.

The application of second stage mesophilic aerobic digestion after autothermal thermophilic aerobic digestion (ATAD) and mesophilic anaerobic digestion has been successfully demonstrated. Up to 16% additional volatile solids destruction has been reported for second stage aerobic digesters operating at a SRT of approximately six days. Nitritation-denitritation has been identified as the primary mechanism for nitrogen removal with inorganic nitrogen removal efficiencies up to 95% being achievable; the level of residual ammonia-N may be controlled to provide the desired nitrogen content of the dewatered cake for land applications. In addition to reducing the mass of cake solids for offsite disposal and the ammonia load in the

dewatering sidestream, reduction in polymer demand and the near elimination of struvite formation in the dewatering process and piping that convey sidestream have been cited as benefits of this process. However, a higher aeration energy requirement is anticipated due to the overall higher oxygen demand in the process and a lower standard oxygen transfer efficiency in comparison to the sidestream processes described above. Site specific conditions will dictate if aerobic digestion is more economically favorable that separate sidestream treatment.

ES.7 Physiochemical Processes for Ammonia Recovery and Destruction

Technologies used in the recovery of ammonia from sidestream to generate products for industrial and agricultural applications have been demonstrated, but these processes are not as widely utilized in comparison to biological sidestream treatment systems. Of the physiochemical processes that have been applied to ammonia-rich streams, air stripping and acid absorption to produce an ammonium salt solution (ammonium sulfate or ammonium nitrate) has the most extensive application history. Removal of ammonia through steam stripping has also been practiced, but largely in industrial applications. Other mass transfer technologies such as membrane contactors and vacuum flash distillation have been developed, but their applications have been limited to industrial wastewaters.

Whether the ammonia is removed from sidestream by air or stream stripping, vacuum distillation or transfer across a membrane to an acidic solution, a prerequisite for achieving a high ammonia removal efficiency is the addition of a basic chemical to the sidestream to shift the ammonium-ammonia equilibrium to ammonia (NH_3) or the use of heat to thermally decompose the primary form of ammonia in sidestream, ammonium bicarbonate, into ammonia and carbon dioxide, which volatilize from sidestream rapidly at operating temperatures above 80-90˚C. Where an ammonium salt solution is produced, an inorganic acid is also required (sulfuric or nitric acid). The energy or chemical costs associated with these operations typically make ammonia recovery less economically favorable than the biological treatment options, even with revenue generated from the sale of the product.

Site-specific conditions such as the availability of waste steam may alter the economics of ammonia recovery to make it a viable option. Regional demand for the recovered ammonia product is also a critical factor. Although ammonium salts are readily used as a component of blended fertilizers for agricultural applications, the wastewater treatment facility may not be favorably located for reuse. The revenue is also anticipated to be below market value to ensure its consistent placement into the regional market. Due to seasonal changes in fertilizer demand, on-site or off-site storage of the recovered product is required, further increasing cost.

As an alternative to reusing the recovered ammonia, conversion of the removed ammonia to N_2 through a thermal catalytic process is technically feasible and has been demonstrated at a full-scale. This approach has been rarely applied, primarily in landfill leachate treatment applications where landfill gas is used to generate steam, which is used to increase the temperature of air stripping columns to a level that promotes thermal decomposition of ammonium bicarbonate.

Despite the unfavorable economics historically associated with conventional sidestream ammonia recovery, there has been a renewed interest in recovering ammonia due to the growth in sidestream processes for the production and recovery of magnesium ammonium phosphate hexahydrate (struvite). Struvite, which is categorized as a slow-release fertilizer, is now produced at several facilities world-wide with the product being successfully placed in regional

fertilizer markets. Due to the expanding number of plants adopting struvite production, this has increased interest in finding synergistic conditions with mainstream wastewater treatment and solids digestion processes that may make sequential struvite and ammonia recovery economically viable.

ES.8 Emerging Technologies and Research Needs

Process technologies for treatment of streams with high ammonia concentrations continue to emerge from bench and pilot-scale to full-scale implementation, as described in this document. In the biological process category, the work has focused primarily on new approaches in Deammonification reactor design and process control, with an emphasis on designing more compact processes or processes that are more readily adaptable to existing tanks in a facility. Since Deammonification processes have proven to be the most energy and carbon efficient and cost-effective group of technologies for nitrogen removal advances in nitrification-denitrification and nitritation-denitritation processes in sidestream treatment applications have been lacking. However, significant work continues in the development of operating control strategies for nitritation-denitritation in mainstream treatment processes to realize the potential improvements in energy and carbon utilization efficiencies. Research needs to more fully understand the microbiology and kinetics of the processes, particularly inhibition mechanisms, are discussed.

In the physiochemical process category, ammonia electrolysis is an emerging technology of interest. In this process, ammonia is catalytically reformed directly in the sidestream to produce hydrogen for energy production. The technical features and challenges in developing this process are discussed.

As interest in nutrient recovery has increased due to the growth in the number of facilities that produce and recover struvite for reuse, there is a growing field of research in ammonia recovery, particularly in defining holistic, facility-wide wastewater and solids treatment schemes that maximize the sidestream nutrient concentrations for sequential struvite and ammonia production.

CHAPTER 1.0

INTRODUCTION

1.1 Overview of Sidestream

Anaerobic and aerobic digestion of residuals generated at municipal wastewater treatment facilities results in the release of soluble organic nitrogen-containing compounds, ammonium and ortho-phosphate into the bulk liquid. As a result, recycle streams generated by the dewatering of the digested sludge contain elevated nutrient concentrations. Discharge of these streams to a main treatment process will result in an increased nutrient loading to the primary and secondary treatment processes. In addition, the release of ortho-phosphate and ammonium during solids digestion often results in the formation of insoluble inorganic compounds such as magnesium ammonium phosphate, also known as struvite, which can cause operational and maintenance problems in mechanical dewatering equipment and pipes that convey the recycle stream.

There has been an increasing interest in reducing nutrient loadings from the recycle streams rich in ammonium and phosphate through dedicated treatment processes since the late 1980s due to lower plant effluent discharge limits and a desire to reduce operating costs (energy, chemicals, maintenance). In addition, suspended solids return loadings and the contribution of colloidal material by some recycle streams to the facility effluent discharge require a close examination of mitigation steps that can minimize the impact of these streams on plant performance, especially granular medium filtration.

1.2 Scope of This Document

The main objective of this report is to record and disseminate the state of knowledge in the treatment of sidestream, with a specific emphasis on the recovery and removal of inorganic nitrogen. In this document, the types of recycle streams commonly found in conventional wastewater treatment plants, their characteristics, and the potential impact on the wastewater treatment facility are reviewed. Following the review of types of recycle streams and their characteristics, the focus of the remainder of the document is on biological and physiochemical treatment technologies that have been developed and implemented to separately treat the nutrient-rich streams, which are typically the primary recycle streams of concern for nutrient removal facilities. The information presented in this report is current as of the date of publication.

CHAPTER 2.0

CHARACTERISTICS OF SIDESTREAM

The focus of this study was the treatment of ammonia-rich recycle streams from the dewatering of digested sludges, digester supernatants, and certain anaerobically pretreated high strength industrial wastewaters. For the purpose of simplifying terminology, all recycle streams discussed in this chapter will be called “sidestream,” but the specific terminology that allows distinction of one type of recycle stream from another, such as "centrate" and "filtrate," will be retained as needed and used interchangeably with the general name.

The soluble nutrient concentrations in sidestreams are dependent on the process from which they originate. For example, the ammonium and ortho-phosphate concentrations resulting from digestion are dependent on the feed solids concentrations to the digester and the volatile solids destruction efficiency. If thermal hydrolysis is applied in the pre-treatment of sludge before anaerobic digestion, the total solids (TS) concentration in the feed to the digesters will be 8-11% by weight. With the higher TS concentration and enhanced volatile solids destruction efficiency in the digester associated with this advanced digestion process, the digester ammonium-N concentration will be two to three times the concentration observed in typical conventional anaerobic digesters.

The soluble constituent concentrations are also affected by the type of dewatering process used. Where belt filter presses are applied, belt washwater is typically combined with the filtrate, resulting in dilution of the constituents and a reduction in temperature, but the sidestream mass load rates are not impacted. In the case of centrate from centrifugation processes, the soluble constituent concentrations more closely reflect the concentrations in the upstream anaerobic process, accounting for some minor dilution from centrifuge washwater, which is typically discharged to the same location as centrate.

This chapter summarizes the typical characteristics of sidestreams with emphasis on characteristics of particular importance to ammonia removal processes.

2.1 Nitrogen

Sidestream from dewatering of digested sludge typically contains high ammonium concentrations ranging from less than 200 mg-N/L for aerobic digesters operated with intermittent aeration to as high as 3,000 mg-N/L in anaerobic digesters preceded by thermal hydrolysis. In the digestion of manures and source separated food wastes, concentrations above 3,000 mg/L have been reported. For conventional mesophilic anaerobic digesters, the resulting sidestream ammonia will typically range from roughly 400 mg-N/L (filtrate with belt washwater) up to 1,300 mg-N/L (centrate). In addition, soluble organic nitrogen-containing compounds are released into the bulk liquid during digestion, accounting for roughly 10% or less of the soluble TKN. The concentrations vary significantly with the types of sludge digestion or pre-treatment processes used, and the dewatering method employed. Even though the composition of sidestream constituents varies, typically about 50% of the soluble organic nitrogen in sidestream is recalcitrant dissolved organic nitrogen (rDON).

2.2 Phosphorus

The ortho-phosphate concentration in the sidestream will vary widely depending on the mainstream treatment processes and the degree of precipitation within the digesters as magnesium ammonium phosphate hexahydrate (struvite), calcium phosphate (hydroxyapatite), or iron phosphate (vivianite). The digestion of waste activated sludge from biological phosphorus removal processes has the potential to produce a very high soluble phosphate concentration in the digester and sidestream. Where a struvite crystallization and recovery technology has been implemented, this will reduce the ammonia-N load to the downstream sidestream treatment process by the stoichiometric amount required for struvite formation (N:P = 1:1 on a molar basis). For further information on struvite crystallization processes, see Tchobanoglous et al. (2014).

2.3 Alkalinity

Alkalinity concentration in a sidestream is a parameter of interest in the operation of sidestream treatment processes. Alkalinity varies, depending on the sidestream source. Anaerobic digestion and ATAD generate sidestreams with a high alkalinity concentration, primarily in the form of bicarbonate due to the retention of carbon dioxide in the digester bulk liquid to balance the positively charged ammonium ion at the typical pH range of the digesters (7.0-7.8). Therefore, the bicarbonate and ammonium-N concentrations will be equal on a molar basis. This equates to an alkalinity to ammonium-N mass ratio of 3.5:1 (kg-$CaCO_3$/kg-N).

2.4 Total Suspended Solids

Sidestreams contain non-captured solids from the dewatering process, which are primarily composed of stabilized biologically inert solids with a volatile solids content in the range of 55 to 65%. In the separate sidestream treatment processes described in this document, reduction of the TSS load and dampening load variability induced by poor or inconsistent dewatering process performance provide positive benefits for the processes. The specific benefits will be described in the technology descriptions.

2.5 Temperature

Sidestream temperature will vary depending on its source. For example, centrifugation of anaerobically-digested solids will typically generate centrate with a temperature near the digester temperature (e.g., 30-35ºC), depending on heat losses from a digested sludge holding tank and dewatering equipment. If a belt filter press is used for dewatering the same digested sludge, the temperature will typically be lower (e.g., 20-30ºC) due to the inclusion of belt washwater in the sidestream, unless the warm filtrate is collected separately from the washwater. The importance of temperature for the design of separate sidestream treatment processes will be described in the chapter sections on physiochemical and biological treatment processes.

2.6 Flow Rate

Sidestreams from digestion processes are typically less than 1 percent of the average raw influent flow on a weekly basis. However, for facilities that do not dewater digested sludge every day or operate the dewatering equipment only for a limited time in a day, the sidestream flow creates a higher instantaneous flow contribution to the primary and secondary treatment processes if discharged directly without equalization. Even though wastewater treatment

facilities normally have sufficient hydraulic capacity to receive the sidestream flow over the period of sludge dewatering, the nutrient loading associated with this sidestream flow, particularly if the sidestream load occurs during the peak diurnal nutrient loading may become significant enough to pose operational challenges. Hence, flow equalization or treating the sidestream load in a separate process to minimize the nutrient loading to the secondary process may need to be considered for a reliable operation of the wastewater treatment facility.

CHAPTER 3.0

BIOLOGICAL TREATMENT OF SIDESTREAM: AN OVERVIEW

Typically, nutrient-rich sidestreams generated by the dewatering of anaerobically digested solids are returned to the main treatment plant and treated biologically. Typical discharge points include the headworks, the inlet of primary sedimentation tanks or a location near or in the secondary treatment process (e.g., channels conveying primary effluent or RAS to the activated sludge reactors). The discharge point is determined depending on the nutrient, biochemical oxygen demand (BOD), and suspended solids loadings associated with the sidestream, and physical constraints such as the plant piping configuration and the location of the dewatering process relative to the process units associated with the main liquid treatment train.

Biological treatment in separate, dedicated reactors has been adopted at many facilities to reduce the nutrients load to the main treatment plant and limit the impact of solids digestion and dewatering on the performance of the secondary treatment process. In this section, the primary biological treatment pathways that have been employed for ammonia treatment are summarized. A description of the various types of nitrogen transformations under aerobic and anaerobic conditions is presented in Figure 3-1, which shows nitrogen used in biological synthesis or released in amino acid deamination and the primary reactions that occur during the nitrification-denitrification, nitritation-denitritation, and deammonification (partial nitritation – anaerobic ammonium oxidation) processes discussed further in Sections 3.1 through 3.3.

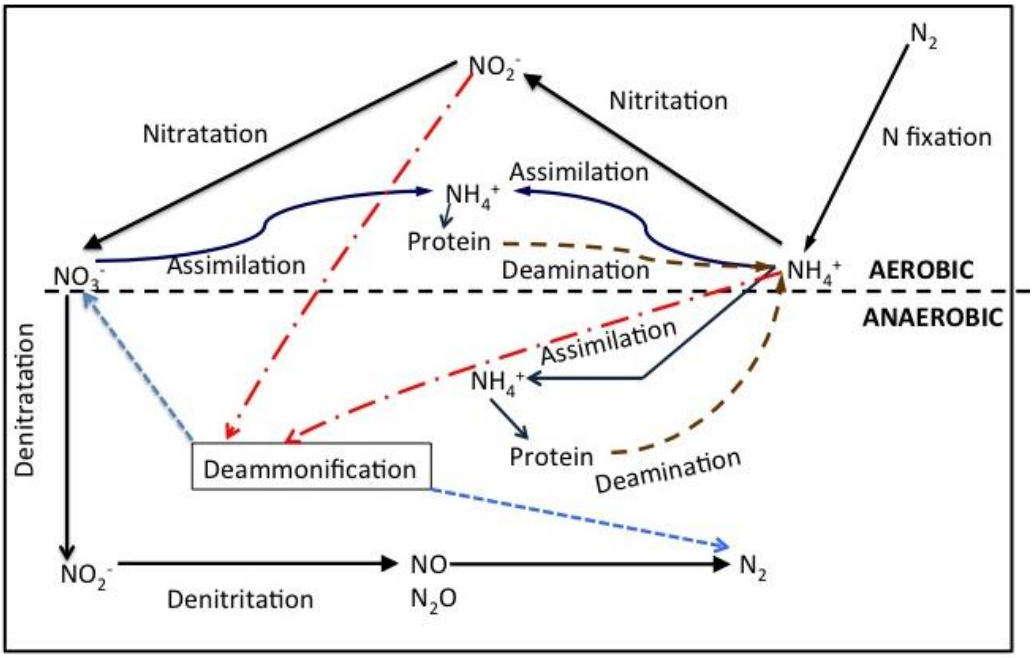

Figure 3-1. Nitrogen Transformations in Aerobic and Anaerobic Environments.
Dashed red line indicates reactants for deammonification, and dashed blue line shows products of deammonification.

3.1 Nitrification and Denitrification

The traditional method for biological nitrogen removal in wastewater treatment is biological nitrification and denitrification, which is shown in the Nitrogen Cycle in Figure 3-1. Under aerobic conditions, NH_4-N can be oxidized to NO_2-N ("Nitritation") by aerobic ammonia oxidizing bacteria (AOB) and then to NO_3-N ("Nitratation") by aerobic nitrite oxidizing bacteria (NOB) according to the basic reaction stoichiometries shown in Equations 3-1 and 3-2.

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \qquad \text{(Equation 3-1)}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad \text{(Equation 3-2)}$$

When cell mass synthesis is included, the overall stoichiometric reaction from complete oxidation to nitrate shown in Equation 3-3 is obtained (Tchobanoglous et al., 2014).

$$\begin{aligned} &NH_4HCO_3 + 0.9852NaHCO_3 + 0.0991CO_2 + 1.8675O_2 \rightarrow \\ &\quad 0.01982C_5H_7NO_2 + 0.9852NaNO_3 + 2.9232H_2O + 1.9852CO_2 \end{aligned} \qquad \text{(Equation 3-3)}$$

In the absence of dissolved oxygen, biological denitrification occurs by heterotrophic bacteria, which oxidizes a carbon source with NO_3-N or NO_2-N as electron acceptors and reduces the oxidized nitrogen to N_2 gas. An example of biological denitrification with acetate oxidation and including heterotrophic biomass growth is shown as follows:

$$\begin{aligned} &NO_3^- + H^+ + 0.33\,NH_4^+ + 1.45\,CH_3COO^- \\ &\qquad \rightarrow 0.5\,N_2 + 0.33\,C_5H_7O_2N + 1.60\,H_2O + 1.12\,HCO_3^- + 0.12\,CO_2 \end{aligned}$$

(Equation 3-4)

Based on the above reaction, 6.6 g acetate COD is needed per g of NO_3-N denitrified.

In summary, the oxygen and carbon requirements for nitrification and denitrification are illustrated in Figure 3-2.

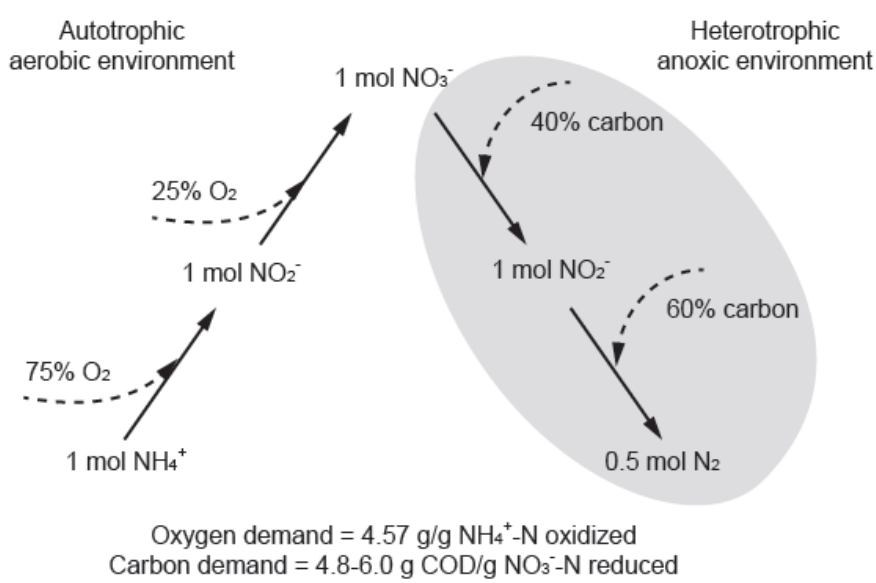

Figure 3-2. Oxygen and Carbon Requirements for Nitrification-Denitrification.

Two moles of bicarbonate are required to neutralize the acidity generated per mole of ammonium oxidized during nitrification (when including cell growth, 1.98 moles of bicarbonate are required for acid neutralization and 0.098 moles of inorganic carbon are required for autotrophic cell growth). If nitrate is completely denitrified, 50% of the alkalinity destroyed during nitrification is recovered, resulting in a net alkalinity reduction of 1 mole of bicarbonate per mole of ammonium-N nitrified and denitrified (3.57 grams of $CaCO_3$ per gram of ammonium-N).

For sidestreams derived from anaerobic digestion and ATAD processes, the alkalinity is primarily in the form of bicarbonate and is typically equal to the ammonium concentration on a molar basis, providing only one half of the alkalinity required for complete nitrification. The remaining alkalinity demand can be satisfied through the addition of an external alkalinity source (e.g., caustic soda), dilution of the sidestream into another stream with sufficient alkalinity (e.g., Return Activated Sludge) or by generating alkalinity via denitrification. In the absence of sufficient alkalinity, a stoichiometric amount of the sidestream ammonium-N will be oxidized to a mixture of nitrite and nitrate in accordance with the available alkalinity.

The role of inorganic carbon in nitrifier growth is often ignored in mainstream nitrification processes where bicarbonate and CO_2 are readily available due to the degradation of abundant organic carbon compounds in the plant influent. However, for sidestream biological treatment processes, the residual inorganic carbon concentrations in the reactor must be carefully considered when selecting the reactor operating conditions that provide optimum performance. Bicarbonate and CO_2 exist in equilibrium at concentrations dictated by the reactor bulk liquid temperature, pH, and ionic strength. As the reactor pH decreases below 7, the $CO_{2,aq}$ concentration increases and is removed from the reactor via air stripping. Therefore, under increasingly acidic conditions in a sidestream biological reactor, a restricted nitrifier growth rate may occur due to an inorganic carbon limitation.

Depending on the COD source (e.g., methanol, glycerol, volatile fatty acids), the observed sludge yield is typically in the range of 0.28 to 0.4 grams of volatile suspended solids (VSS) per gram of COD consumed, resulting in a COD to nitrate-N ratio of 4.8 to 6.6 grams/gram. In a typical high strength sidestream, the ratio of degradable COD to TKN is less than 1, indicating insufficient degradable COD is available for a sidestream treatment system where a high denitrification efficiency is desired. COD supplementation with commercially available organic carbon sources is an option; however, the use of COD sources within the facility (e.g., primary sludge; endogenous decay of secondary mixed liquor solids) is desired since the purchase of a commercial COD source increases operating cost.

For nitrification-denitrification sidestream treatment processes where a high Total Inorganic Nitrogen (TIN) removal efficiency is desired, the addition of a COD source to the sidestream reactor provides the organic substrate required for denitrification and generates the alkalinity required to sustain high nitrification efficiency. However, the addition of a COD source may not eliminate the need for an external alkalinity source. For example, if ferric or ferrous chloride is added to the digesters to control struvite formation or to the sidestream to control struvite formation in the pipe or channel conveying sidestream, a reduction in sidestream alkalinity will occur due to the acidity associated with these chemicals. Therefore, in subsequent sidestream treatment, the need for supplemental alkalinity may not be eliminated through COD supplementation and a high denitrification efficiency.

Process configurations designed to completely oxidize sidestream ammonium to nitrate or nitrify and denitrify the sidestream ammonium via nitrate are described in Chapter 4.0.

3.2 Nitritation and Denitritation

Reducing the aeration power and chemical requirements for sidestream treatment has been the primary driver in the development of advanced biological treatment processes. As illustrated in Figure 3-3, short-circuiting the nitrification-denitrification pathway through the restriction of nitrite oxidation to nitrate, reduces the stoichiometric oxygen and carbon requirements by 25% and 40%, respectively, in comparison to requirements for nitrification-denitrification.

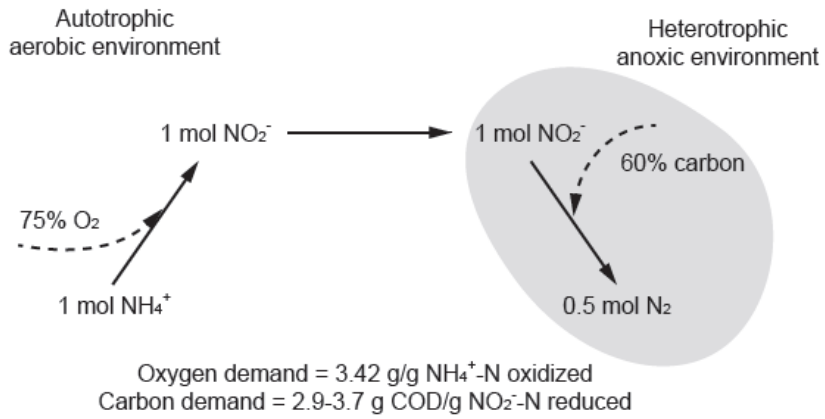

Figure 3-3. Oxygen and Carbon Requirements for Nitritation-Denitritation.

Alkalinity destruction during the complete oxidation of ammonium to nitrate occurs during the nitritation step. Therefore, the alkalinity demand for a nitritation process is identical to a process performing complete nitrification, excluding the inorganic carbon requirement for biomass growth. The alkalinity requirement for complete ammonium removal must be provided through an external alkalinity source or alkalinity generation through nitrite reduction.

Suppression of NOB growth can be accomplished by several mechanisms and the mechanism responsible for successful operation of nitritation-denitritation processes for sidestream treatment vary with the type of process and its operating conditions. The inhibition mechanisms are summarized in Table 3-1 with brief summaries and literature references.

Four primary approaches have been applied for inducing nitrite accumulation. First, the aerobic SRT can be controlled to a low value, typically less than 2-3 days, which exploits the difference between the AOB and NOB net growth rates at temperatures above 20ºC. The operating condition allows AOB to grow, but NOB growth is effectively restricted because of the high washout rate. Second, transient anoxia with a low DO concentration has been proven highly effective in restricting NOB growth. Nitric oxide accumulation induced by intermittent aeration and a delayed response in NOB activity upon the return of aerobic conditions are believed to play roles in suppressing aerobic nitrite oxidation. Third, continuous aeration at a low DO concentration has been successfully applied, which exploits the sensitivity of NOB to low DO concentration in the upper mesophilic temperature range. Inhibition of NOB growth by hydroxylamine, which has been shown to accumulate as a result of low DO conditions (Yang and Alleman, 1992), may also be providing further suppression of NOB activity. Finally, NOB growth can be restricted through free ammonia exposure (Anthonisen et al., 1976). These four primary mechanisms are not necessarily exclusive. In the case of intermittent aeration at a low DO concentration in a separate sidestream process, free ammonia inhibition is also believed to contribute to NOB suppression since the processes retain a sufficiently high residual ammonium concentration at the operating pH.

Table 3-1. Reported Mechanisms or Conditions that Restrict Aerobic Nitrite Oxidation.
Adapted from Stinson et al., 2013.

Growth Conditions and Inhibitors	Value	References and Comments
Low Aerobic Solids Retention Time at Operating Temperatures > 20˚C	< 2 days	Hellinga et al., 1998
Free Ammonia (NH_4^+) (mg N/L)	0.04 - 0.08 0.02 to 0.7 4 - 10 10 - 150	Blackburne et al., 2007 Nitrospira more sensitive to low free ammonia than Nitrobacter (Nitrobacter not inhibited until FA in range of 50 mg/l NH_3-N in Blackburne 2007 paper as opposed to range proposed by Philips et al., 2002 Vadivelu et al., 2007 – partial inhibition of NOB Anthonisen et al., 1976 – partial to complete inhibition of both AOB & NOB
Free Nitrous Acid (HNO_2) (mg N/L)	0.01 – 1.0 0.01 - 0.02 0.02 – 2.8	Blackburne et al., 2007- (Nitrobacter and Nitrospira are both highly inhibited by free nitrous acid. Nitrospira more sensitive to low concentrations of free nitrous acid than nitrobacter, demonstrating inhibition at concentrations of as low as 0.01 mg/l HNO_2-N. Vadivelu et al., 2006 – anabolic activity was inhibited. Anthonisen et al., 1976 – complete inhibition of both AOB & NOB
Hydrazine (N_2H_4) (mg N/L)	1 (Only described for Nitrobacter)	Produced by Brocadia Anammoxidans. Currently under evaluation in pure culture of Nitrospira.
Hydroxylamine (NH_2OH) (mg N/L)	0.2 mg/l	Free hydroxylamine is an intra-cellular intermediate in AOBs and is thought to accumulate extra-cellularly from AOB cells, due to low DO concentrations (Yang and Alleman, 1992). Extra-cellular free hydroxylamine is very effective in bringing about nitrite accumulation with about 15% nitrite accumulation observed at a free hydroxylamine concentration of 0.2mg-NH_2OH-N/L (Blackburne et al. 2004). However, hydroxylamine seems to react with nitrite, which results in a lack of control over the actual degree of inhibition (Stuven et al., 1992; Blackburne et al., 2004). Therefore, the benefits of free hydroxylamine inhibition are as yet uncertain but currently under investigation in pure cultures of Nitrospira.
Nitric Oxide (NO) (mg N/L)	0.007-0.448	Starkenburg et al., 2008 reversible NOB inhibition but also stimulates Anammox growth
Formic Acid (HCOOH)	>100mg/l	Eilersen et al., 1994 –At concentrations >100mg/l complete NOB inhibition with no adverse effect on AOBs. Used in some fine bubble aeration system as a diffuser cleaning fluid so infrastructure may already exist in some plants. Oxidized during the aerobic period by OHOs. Similar in cost to some supplemental carbon sources and so may be considered viable as an intermittent chemical for NOB inhibition
Salinity	>10 g/l > 5 g/l	Peng et al., 2004a, Cui et al., 2006 Ye et al., 2009
Aeration Duration limitation using real time pH, DO and ORP control and / or Blower Frequency	DO > 2 mg/l	Peng et al., 2004b, Yang et al., 2007, Guo et al. 2010, Gao et al. 2009, Wu et al. 2011, Gu et al., 2012, Lemaire et al., 2008, Zeng et al., 2009
Transient anoxia	Low DO (0.3 mg/l) Variations every 1.5 to 12 hours resulted in significant NOB inhibition	Kornaros, et al. 2010 Blackburne et al. 2008a, 2008b
Transient anoxia	High DO > 1.5 mg/l	Al-Omari et. al. 2012 Regmi et al. 2012 Applicable to mainstream processes at lower operating temperature and substrate concentrations

Once NOB suppression is achieved through one or more of the mechanisms discussed above, the accumulation of nitrite in the reactor may enhance NOB suppression further through free nitrous acid inhibition (see references in Table 3-1), depending on the nitrite concentration and pH. The AOB are also susceptible to free nitrous acid inhibition, but at a higher acid concentration than required for the inhibition of NOB growth. Depending on the sidestream treatment objectives, the inclusion of denitritation in the treatment process may be required to limit the risk of free nitrous acid inhibition of AOB through nitrite reduction and provide the desired level of inorganic nitrogen removal, particularly for very high strength sidestreams.

Despite a reduction in the organic carbon requirement, the amount of degradable organic carbon in a typical sidestream is insufficient to allow complete denitritation. An external organic carbon source or a carbon source from within the plant such as primary solids is required. In the absence of sufficient denitritation, the addition of an external alkalinity source may be required if a high ammonia removal efficiency is desired, being mindful of the potential risk to the process if nitrite is allowed to accumulate to levels where free nitrous acid inhibition of the AOB may occur. Where a high residual nitrite concentration is present in the sidestream reactor effluent, the effluent can be discharged to an anoxic zone in the mainstream secondary process to prevent further oxidation of the nitrite to nitrate and to minimize the organic carbon demand. For facilities that employ primary sedimentation, the sidestream reactor effluent may be discharged to the headworks where the nitrite will be reduced in the primary sedimentation tanks.

Process configurations designed for Nitritation-Denitritation are provided in Chapter 5.0. Included in this chapter are processes that generate a mixture of nitrite and nitrate during aeration.

3.3 Deammonification

In the 1990s, the discovery of autotrophic bacteria capable of oxidizing ammonia under oxygen-free conditions led to the development of "deammonification" processes that provide conditions that support the growth and enrichment of these unique organisms. As described in this section, implementation of a deammonification process can provide further reduction in aeration energy and chemical demand for sidestream inorganic nitrogen removal in comparison to nitrification-denitrification and nitritation-denitritation.

Deammonification is a biological transformation of ammonia to nitrogen gas in a two-step process as illustrated in Figure 3-4. In the first process, termed *partial nitritation*, a fraction of the ammonia is converted to nitrite by aerobic AOB. Reaction conditions are controlled such that NOB growth is suppressed. Mechanisms for NOB growth suppression are discussed in Chapter 5.0.

In the second step, termed anaerobic[1] ammonium oxidation or anammox, NH_4-N is oxidized under oxygen-free conditions by autotrophic bacteria that can use NO_2-N as the electron acceptor. Of the ammonia removed in the two-step Deammonification process, approximately 89% of the inorganic nitrogen (NH_4-N + NO_2-N) is converted to N_2 gas and about 11% as NO_3-N, plus a minor amount of ammonia is removed as a nutrient for biomass growth.

[1] The term "anaerobic" typically refers to an environment with zero dissolved oxygen, nitrate, or nitrite. In this case, nitrite is present, which is sometimes called "anoxic." We retain the term "anaerobic" as it is commonly used in the literature.

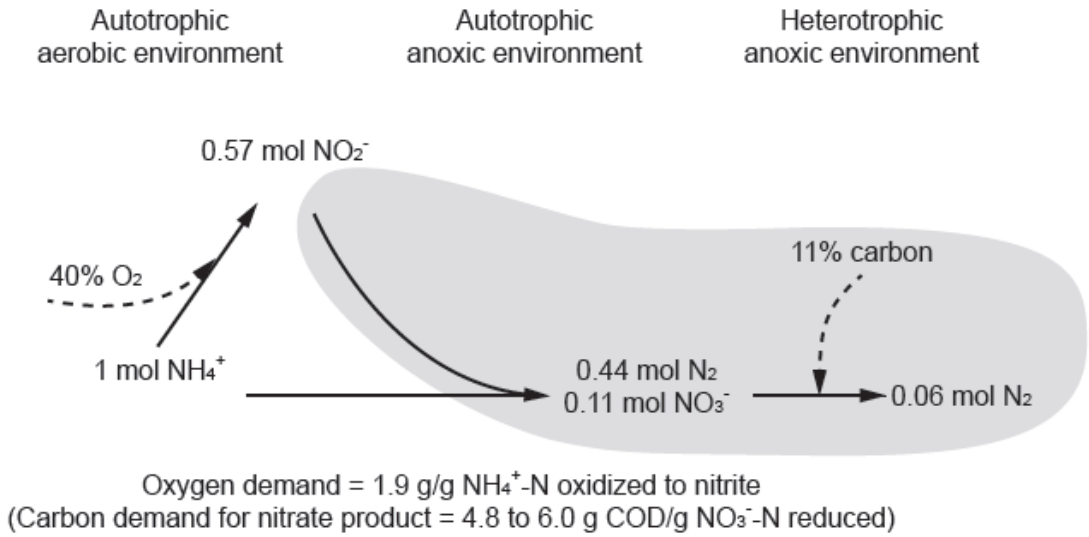

Figure 3-4. Oxygen and Carbon Requirements for Deammonification.

Examining the reaction stoichiometry in further detail, in the anammox process the energy yielding reaction is NH_4-N oxidation by NO_2-N instead of heterotrophic denitritation described above in the nitritation-denitritation process, and the uptake of CO_2 and nutrients by the autotrophic anammox bacteria for biomass growth. The energy reaction is as follows:

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O \qquad \text{(Equation 3-5)}$$

The anabolic reaction for biomass growth is as follows (Schmidt et al., 2002 and van Niftrik et al., 2004):

$$CO_2 + 2NO_2^- + H_2O \rightarrow CH_2O + 2NO_3^- \qquad \text{(Equation 3-6)}$$

The overall stoichiometric reaction, accounting for cell synthesis (Strous et al., 1998):

$$1.0NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 0.066CH_2O_{0.5}N_{0.15} + 2.03H_2O \qquad \text{(Equation 3-7)}$$

Equation 3-7 indicates that the removal of 1.0 mole of NH_4-N requires 1.32 moles of NO_2-N and produces 0.26 moles of NO_3-N. The amount of NO_3-N produced accounts for 11.2% of the NH_4-N and NO_2-N metabolized. Research has found that some species of anammox bacteria are able to reduce NO_3-N with acetate, formate and propionate (Gueven et al., 2005, Kartal et al., 2007, and Winkler et al. 2012).

As illustrated in Figure 3-4 and shown in Equation 3-7, inorganic nitrogen removal in the deammonification process is accomplished without an organic carbon source. Since ammonia is partially converted to nitrite to provide both ammonia and nitrite for the subsequent anammox reaction, aeration energy is reduced in comparison to nitritation-heterotrophic denitritation.

A detailed discussion of anammox bacteria is useful so the growth characteristics and ubiquitous nature of these unique and valuable organisms are understood, particularly in defining the conditions that promote their growth and stable performance. The anaerobic biological

oxidation of NH_4-N was named the "Anammox" by Mulder et al. (1995) in the first report of observations on anaerobic oxidation of ammonia. Subsequent research by Van de Graaf et al. (1995) confirmed that the NH_4-N oxidation was accomplished with NO_2-N under anaerobic conditions and was biologically mediated. The bacteria responsible for the reaction was called the anammox bacteria and was first identified by Strous et al. (1999a) as being an autotrophic bacterium under the order *Planctomycetales* in the phylogenetic tree for bacteria.

Since then the anammox bacteria has been found to be abundant on the earth and frequently observed in biological wastewater treatment, and in marine and fresh water sediments (Kuenen, 2008; Van Hulle et al., 2010). The discovery of the anammox bacteria helped to explain the cause of the "missing nitrogen" that some scientist have reported in the past when doing nitrogen mass balances on water bodies (Ward et al., 2011). The nitrogen cycle (Figure 3-1) now incorporates the anammox process.

Investigations on anammox bacteria using molecular tools has resulted in finding nine species within five genera as members of the bacteria order Planctomycetales (Ward et al., 2011). They are preceded by the name Candidatus, which is used when a species or genus is well characterized but not studied in pure culture. These are *Candidatus* "*Kuenenia*," *Candidatus* "*Brocadia*," *Candidatus* "*Scalindua*," *Candidatus* "*Jettenia*," and *Candidatus* "*Anammoxogloubus.*" The anammox bacteria found in wastewater treatment applications are species within *Candidatus* "*Kuenenia"* and *Candidatus "Brocadia"* (Kuenen, 2008). Anammox bacteria enrichments develop a deep red color (Jetten et al., 1999) and are found in dense granular flocs in systems with a stable operation (Strous et al. 1999b). The floc characteristics provide an advantage for separating and maintaining them in treatment systems.

Most of the information on anammox bacteria kinetics has been obtained from operations at 30-35ºC which correspond to the typical sidestream temperatures from the dewatering of anaerobically digested sludge. Anammox growth at temperatures near 4ºC and at 43ºC has been observed with the lower temperature growth based on observations of anammox activity in Arctic environments (Ward at al., 2011). Anammox bacteria growth has been sustained in reactors at 15ºC (Ward et al., 2011) and 18ºC (Winkler et al., 2012).

Anammox bacteria have much slower growth rates compared to ammonia oxidizing bacteria (AOB) but also very slow decay rates. The growth rate of both these bacteria is much lower than heterotrophic bacteria. At 30ºC the solids retention time (SRT) for the anammox bacteria needs to be 5-10 times longer than that for AOB (Jetten et al., 2001, Schmid et al., 2003 and Van de Star et al., 2008). Nitrite is a key growth substrate for anammox bacteria, but is also inhibitory to their growth. However, in comparison to AOB, the anammox bacteria have a much higher affinity for ammonia and nitrite as indicated by their very low half velocity coefficients of 0.07 to 0.10 mg/L (Strous et al., 1999b; Jetten et al., 2001) compared to about 0.50 mg/L for AOB.

The biomass yield for anammox bacteria is in the same range as that for AOB and much lower than for heterotrophic bacteria, as is typical for autotrophic bacteria with their energy needs for CO_2 fixation (Strous et al., 1999b; Schmid et al., 2003).

Nitrite accumulation in a deammonification reactor can lead to process inhibition or failure at high enough levels. The level of NO_2-N that can be tolerated varies as reported by several researchers, but the cumulative information on nitrite toxicity suggests that the inhibition is a function of concentration, exposure time, and the type of anammox species in the reactor

(Van Hulle et al., 2010). However, the reversible or irreversible nature of the inhibition has not been clearly defined. A safe operation is with NO_2-N concentrations at 5.0 mg/L or less has been reported for suspended growth sequencing batch reactors (Wett et al., 2010), while data from fixed film and granulated sludge processes indicate higher concentrations can be tolerated, presumably due to the protection provided by the diffusional effects in the biofilm or granule (Abma et al., 2010; Christensson et al., 2013). Strous et al. (1997) found that DO inhibition also occurs but is reversible such that an intermittently aerated reactor for nitritation and deammonification is possible.

Deammonification processes that have been implemented at a full-scale are presented in Chapter 6.0.

3.4 Nitrified Sidestream for Reduction of Facility Odors

In anaerobic sewers, hydrogen sulfide and other reduced sulfur compounds are generated, which cause health risks, corrosion, and odor in the collection system and in the headworks and primary sedimentation process in the wastewater treatment facility. Hydrogen sulfide is commonly 80% of the total reduced sulfur in raw wastewater entering a wastewater treatment facility. In a unique application of separate sidestream treatment, sidestream can be nitrified, either completely or partially to nitrate, nitrite or a mixture of nitrite and nitrate in a separate biological process, and discharged to the headworks or immediately outside the plant boundary into the collection system to reduce odors associated with these compounds.

The positive benefits of using nitrate salts for odor control in the collection system and the headworks have been demonstrated. When introduced into anaerobic sewer networks, nitrate provides an electron acceptor for autotrophic denitrifying sulfur oxidizing bacteria. If dosed at a quantity beyond the sulfur oxidation requirement, nitrate continues to prevent anaerobic conditions. However, nitrate will continue to be depleted by heterotrophic denitrifying bacteria, and potential exists for the return of anaerobic conditions further downstream.

The principal reactions involved in the oxidation of hydrogen sulfide are presented below:

Sulfide oxidation to sulfur; nitrate reduction to dinitrogen:

$$5S^{2-} + 2NO_3^- + 12H^+ \rightarrow 5S + N_2\uparrow + 6H_2O \qquad N/S = 0.18 \qquad \text{(Equation 3-8)}$$

Sulfide oxidation to sulfur; nitrate reduction to nitrite:

$$S^{2-} + NO_3^- + 2H^+ \rightarrow S + NO_2^- + H_2O \qquad N/S = 0.44 \qquad \text{(Equation 3-9)}$$

Sulfide oxidation to sulfate; nitrate reduction to dinitrogen:

$$5S^{2-} + 8NO_3- + 8H^+ \rightarrow 5SO_4^{2-} + 4N_2\uparrow + 4H_2O \qquad N/S = 0.70 \qquad \text{(Equation 3-10)}$$

Sulfide oxidation to sulfate; nitrate reduction to nitrite:

$$S^{2-} + 4NO_3^- \rightarrow SO_4^{2-} + 4NO_2^- \qquad N/S = 1.75 \qquad \text{(Equation 3-11)}$$

Reaction rates and stoichiometries have been reported. For example, measured Nitrogen/Sulfur (N/S) ratios between 0.4-1.0 g-N/g-S were reported by Mathioudakis and Aivasidis (2009) for sewage samples from collection systems in Greece, suggesting a mixture of sulfur and sulfate is produced. Sulfide oxidation rates increased with temperature and electron acceptor oxidative power. Oxidation rates of 2.4-3.7 g-S/m^3•hr and 1.4-2.4 g-S/m^3•hr with nitrate and nitrite as the electron acceptor, respectively, were reported in the same study. At 25ºC and pH 7, a sulfur oxidation rate of 0.48 g-S/m^3-hr was reported by Yang et al. (2005) with "fresh" sewage from a 30-km collection system in Denmark. The residence time in the collection system was also found to have an impact on the oxidation rate and sulfate and thiosulfate were not found suggesting that sulfide was being oxidized only to elemental sulfur.

The most notable example where nitrified sidestream was used for odor control in a wastewater treatment facility is the 91st Avenue wastewater treatment plant (WWTP) in Phoenix, Arizona. Both nitrite and nitrate were tested to determine their impact on hydrogen sulfide emission rates. Using the change in sulfide concentration and the hydraulic residence time in headworks and primary clarification, the calculated sulfide oxidation rate was 1.2 g-S/m^3•hr at 27.2ºC and an effective reduction in odors was noted.

From the studies referenced above, the following conditions influence biological sulfur oxidation:

- The degree of oxidation, i.e., to elemental sulfur vs. sulfate.
- Wastewater "freshness" and the length of the collection system.
- Amount of sulfur oxidizing bacteria present.
- Temperature and pH.

This information suggests that full-scale trials are required with nitrite or nitrate salts to assess the oxidation kinetic rates and effectiveness in reducing odors under the wastewater conditions specific to the facility. If proven effective, a mass balance is required to determine if partial or near-complete nitrification of the sidestream is required. If high nitrification efficiency is needed to maximize the NOx-N mass load, the addition of an external alkalinity source will be needed since a typical anaerobic digester recycle stream only contains 50% of the alkalinity required for complete ammonia oxidation. The addition of an alkalinity source will increase operating cost and erode any economic advantage this odor control scheme may present over other odor control options such as covers and ventilation of foul air to odor control units or stacks.

CHAPTER 4.0

NITRIFICATION AND DENITRIFICATION PROCESSES

This chapter discusses nitrification - denitrification processes used for sidestream treatment. The selection of one type of process over another is dependent on the type of mainstream secondary process, its operating conditions, plant effluent quality objectives, and economic considerations.

4.1 Sequencing Batch Reactor

The most commonly practiced separate sidestream treatment reactor configuration is the SBR (see Figure 4-1). Similar to a SBR designed for mainstream treatment, the sidestream SBR is designed with mechanical mixing to provide mixed anoxic periods for denitrification. The SBR may be batch-fed at the beginning of the React period of each SBR cycle or continuously fed during this period. Intermittent aeration is applied either through control of the blowers via in situ pH measurements (blower is turned on at the high pH setpoint and turned off at the low setpoint) or by turning the blowers on and off at specific times.

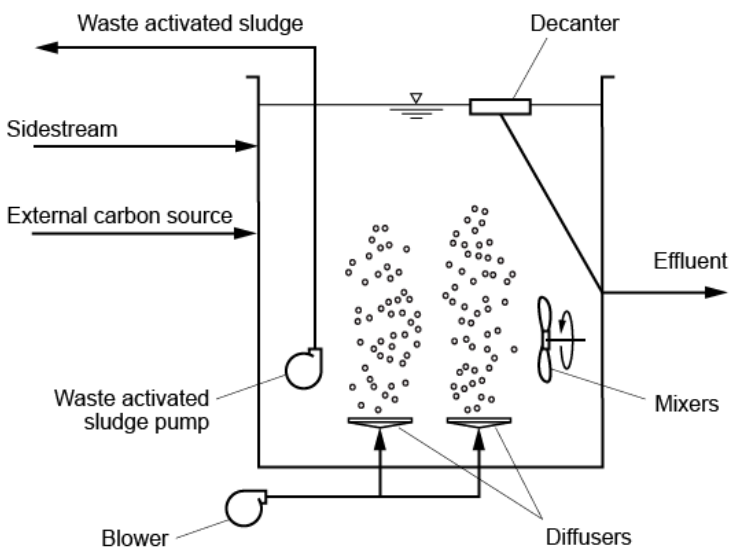

Figure 4-1. Sequencing Batch Reactor (SBR).
From Tchobanoglous et al., 2014.

If the treatment objective of the sidestream SBR is primarily high ammonium removal efficiency and the nitrate in the treated sidestream will be denitrified in the mainstream secondary process or in the collection system, headworks and primary sedimentation tanks to reduce odorous emissions, the React period will be aerobic and an external alkalinity source must be provided to sustain nitrification. If high TIN removal efficiency is the goal of sidestream treatment, a COD source is added to the SBR during the anoxic periods to remove nitrite and nitrate and generate alkalinity required to sustain nitrification. In this operating mode, the typical total aerobic time is 66% of the React period, with the remainder being the total anoxic time. At

the end of the React period, the suspended solids are settled (Settle period), treated sidestream is decanted to the mainstream plant (Decant period), and waste sludge is pumped to the solids processing train.

In nitrification SBR systems in the United Kingdom, sludge settling characteristics were found to improve with the implementation of an anoxic selector using a general guideline of 100 mg-BOD/g-MLSS as an organic load and a hydraulic retention time around 45-60 minutes. The source of poor settling is believed to be filamentous bacteria growing on sidestream volatile fatty acids under a low food-to-microorganism ratio. The anoxic selector zone may be external to or within the SBR, depending on the process configuration, and it receives a MLSS internal recycle flow and the sidestream during the Fill/React phase of the SBR cycle, overflowing to the main SBR zone.

4.2 Membrane Bioreactor (MBR)

Flat-sheet and hollow-fiber MBRs have been applied in the treatment of a wide range of industrial and municipal wastewaters, including streams with a high membrane fouling potential such as landfill leachate. However, full-scale application of membrane bioreactors for separate nitrification-denitrification of sidestream has been limited.

Separate sidestream reactors, which typically operate at elevated temperatures, would unlikely benefit from a membrane process since the reactor volume is typically dictated by the aeration design rather than the SRT. For sidestream processes where solids concentration or SRT become the limiting design parameter for the reactor volume, a membrane separation step may prove beneficial in minimizing process footprint. The implementation of membranes where existing tanks may be used as reactors may also prove to be economically favorable depending on site conditions.

Energy consumption associated with solids-liquid separation is anticipated to be higher than reactor systems that use gravity clarification. In addition, the membrane fouling potential in a sidestream treatment environment is considered high due to colloidal and inert fibrous materials and the potential formation of inorganic foulants. Sidestream screening would likely be required, but this may also be beneficial for other processes, so this pretreatment step may not be considered a disadvantage.

The most notable examples of MBR systems treating anaerobic digester sidestreams are at the Kohlfurth and Dormagen WWTPs in Germany. At Kohlfurth, two unused sludge thickeners were converted to nitrification and denitrification reactors in series (total volume of approximately 400 m^3). A dual-line membrane system was installed, each line containing two Kubota EK-400 module packages. Although initially intended for conventional nitrification-denitrification, conversion of the two tanks to partial nitritation and anammox reactors in series is a long-term goal. Similarly, at Dormagen, an existing grit chamber was converted to nitrification and denitrification stages in series. A dual-line membrane system was installed, each line consisting of two Kubota EK-150 modules. No performance data and membrane cleaning frequencies were readily available.

4.3 InNitri® or Short SRT Process

In the InNitri® or Short SRT process (Figure 4-2), flocculated nitrifier-enriched mixed liquor solids are developed in a sidestream reactor and waste solids from the reactor are sent to the mainstream secondary process to bioaugment the mainstream mixed liquor with nitrifying organisms. The InNitri sidestream treatment reactor is functionally identical to the SBR process described above, except the InNitri reactor was conceived as a dual-zone, completely mixed Modified Ludzack-Ettinger (MLE) configuration with gravity clarification. A COD source is fed to the anoxic zone to enhance denitrification and generate alkalinity for nitrification. Due to incomplete denitrification achieved in the MLE configuration, the addition of an alkalinity source is required since a high nitrification efficiency is anticipated. If the primary performance goal of the InNitri reactor is nitrification, the reactor configuration can be reduced to a Ludzack-Ettinger configuration where the sidestream COD is used to partially denitrify the RAS nitrate loading, thereby incrementally reducing the downstream external alkalinity requirement. Regardless of the reactor configuration, sidestream equalization is desirable for facilities that only dewater digested sludge a few hours per day or do not dewater sludge on weekends.

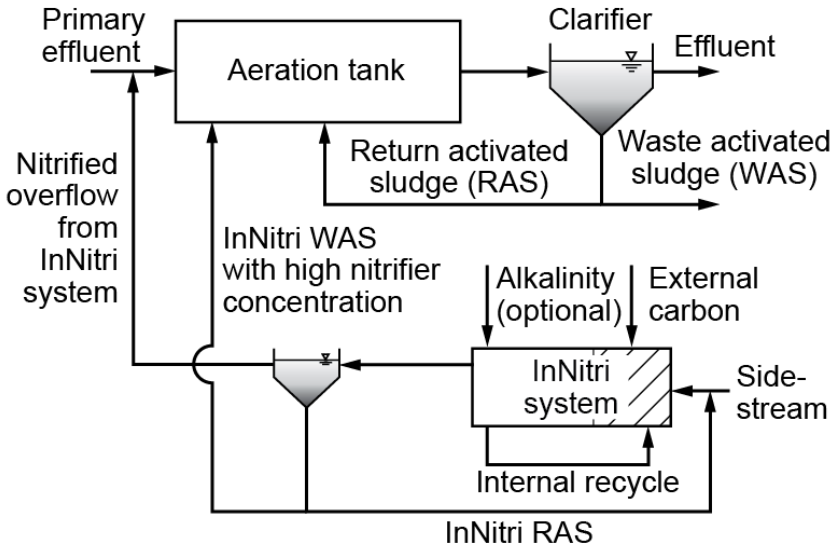

Figure 4-2. InNitri™ Process.
From Tchobanoglous et al., 2014.

Due to the temperature of the high-strength sidestream and biological heat generation, the InNitri process operating temperature will be elevated and will reach a peak temperature during the summer operating period. Depending on the geographical location of the facility, the addition of a cooler dilution water source such as primary effluent is included in the design to prevent reactor temperature for exceeding 38-40ºC. To maximize the amount of nitrifier mass sent to the mainstream secondary process for bioaugmentation, the InNitri sidestream reactor is operated at an aerobic SRT in the range of three to five days, which provides stable sidestream performance, but limits nitrifier loss through decay.

The first InNitri process is in operation at the City of Richmond, VA, wastewater treatment plant (U.S.).

4.4 Integrated Sidestream-Mainstream Treatment: Nitrification and Denitrification of Sidestream Nitrogen in a RAS Reaeration Tank

Bioaugmentation of the mainstream process may be enhanced beyond the level achieved by the InNitri or Short SRT concept by fully nitrifying sidestream ammonia in a mainstream RAS reaeration tank. In this integrated sidestream-mainstream arrangement, a portion or all of the mainstream RAS and the sidestream are fed to the RAS reaeration tank. Examples of the integrated sidestream-mainstream treatment processes are described in this section.

4.4.1 BAR and R-D-N Process

Developed independently in the United States and the Czech Republic, the BioAugmentation Reaeration (BAR) and Regeneration-Denitrification-Nitrification (R-D-N) processes (Figure 4-3) consist of nitrifying high strength sidestream in a plug-flow RAS reaeration tank. Addition of RAS flow dilutes the sidestream ammonium-N and other constituents by 50- to 100-fold, depending on the RAS flow rate (or portion of the RAS diverted to the reaeration tank), creating a mixed liquor environment for nitrification of the sidestream ammonium-N load that is essentially identical to that in the mainstream activated sludge reactors, thus providing maximum bioaugmentation of the mainstream process.

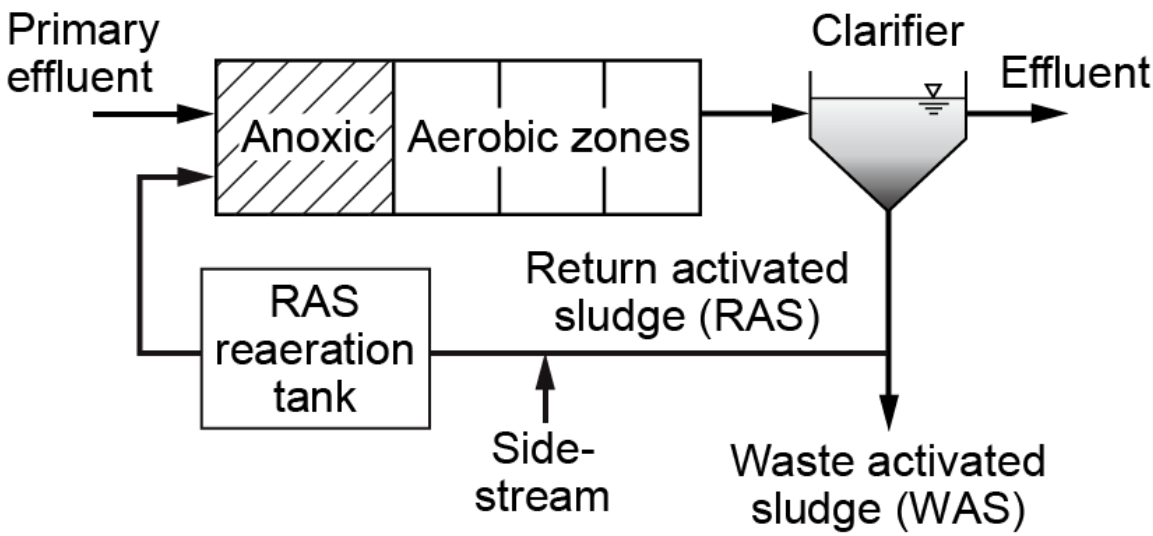

Figure 4-3. BAR and R-D-N Process.
From Tchobanoglous et al., 2014.

In a basic configuration, the RAS reaeration time is a plug-flow aerobic tank with a volume or contact time that provides the desired nitrification efficiency at the design condition (e.g., RAS flow, wastewater temperature). Typically, a process model is used to determine the reaeration tank volume required to provide the desired ammonium removal performance due to the complex calculations required for the integrated sidestream-mainstream configuration. Based on the performance of existing full-scale systems, the aerobic hydraulic retention time (HRT) of the reaeration tank will be approximately two hours. A pre-anoxic zone has been included in some tank designs with a 0.5 to 1-hour HRT to provide partial denitrification of the RAS nitrate load. A post-anoxic zone with a 0.5 to 1-hour HRT can also be provided at the end of the tank to

promote additional denitrification. Internal recycle within the reaeration tank provides little benefit in terms of nitrification and denitrification performance and has not been implemented in practice. The minimum value for the aerobic SRT for the combined sidestream-mainstream configuration (reaeration tank included in the SRT calculation) is dependent on the treatment objectives for the plant effluent, particularly during the winter operating period, and can also be estimated through process modeling.

Mixing is required for the anoxic zones to maintain the solids in suspension. Ideally, mechanical mixers are used, but for large plants coarse bubble aeration has proven to be a cost-effective method of providing mixing, eliminating the equipment cost and maintenance requirements associated with the mixers. A reduction in denitrification performance was found, in comparison to mechanical mixing, but the reduced performance was acceptable from a cost-benefit perspective.

The addition of a supplemental COD source to promote denitrification in the reaeration tank has not been practiced in facilities with existing BAR/R-D-N RAS reaeration tanks due to the treatment objectives of the mainstream secondary process. In the case where a low nitrate concentration is required in the RAS before being pumped back to the mainstream secondary reactors, the addition of a carbon source to a post-anoxic zone has been practiced under the process name, ScanDeNi® (described in Section 4.4.2). For facilities where a supplemental carbon source is required to meet the plant effluent treatment objective, the addition of a COD source to the reaeration tank may be advantageous compared to addition points in the mainstream secondary process, depending on the configuration of the process.

The addition of an alkalinity source to the reaeration tank is not commonly practiced. An alkalinity balance indicates that for typical raw influents, sufficient alkalinity is present in the RAS to sustain complete nitrification of the sidestream ammonium-N load (total alkalinity required minus the alkalinity in the raw sidestream) and maintain a residual alkalinity above 50 mg/L as $CaCO_3$. The pH of the reaeration tank mixed liquor is typically in the range of 6.0 to 6.5. Despite this condition being below the optimum pH for nitrification, an ammonium-N concentration less than 1 mg/L at the end of the reaeration tank is commonly observed.

RAS reaeration tank volume requirement and performance and the performance of the overall integrated sidestream-mainstream system are typically evaluated through process modeling. The impact of pH on the nitrification rate in the RAS reaeration tank should be accounted for in the model. System designers commonly reduce the nitrifier maximum specific growth rates by 30-40% to account for the pH effect, based on the performance of full-scale BAR/R-D-N systems.

A total of 21 BAR/R-D-N systems have been implemented in the Czech Republic. At least four facilities have been constructed in the U.S. (Appleton, WI; Blue Lake, MN; San Buenaventura, CA; Lincoln, NE) with at least two facilities in design or construction (Harrisburg, PA; Iowa City, IA). The configurations at these facilities vary depending on the treatment objectives. For example, at Harrisburg, PA, the entire RAS flow will be diverted through the reaeration tank, while at the Theresa Street Wastewater Treatment Facility in Lincoln, NE, RAS reaeration is only applied to one of the three secondary processes that operate in parallel (East, Central and West systems) and only a portion of the RAS is diverted to the reaeration tank (also referred to as the “Prenitrification Basin”). Nitrifier-enriched RAS is wasted from the reaeration tank and diverted to the other two secondary systems to provide bioaugmentation.

4.4.2 ScanDeNi® Process

Developed and implemented at several plants in Sweden, the ScanDeNi® process is a variation of the BAR/R-D-N process (Figure 4-4). The design of the RAS reaeration tank includes a post-anoxic zone and the addition of a supplemental COD source. Complete RAS denitrification was required at each facility where ScanDeNi® reaeration tanks were implemented since the RAS is pumped to the anaerobic zone of a secondary process designed to perform biological phosphorus removal.

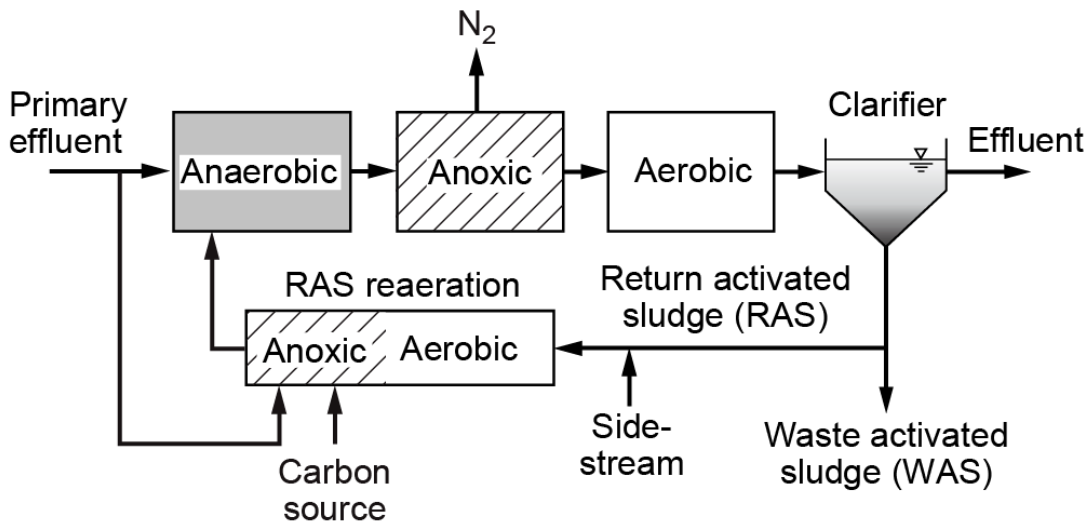

Figure 4-4. ScanDeNi® Process.
From Tchobanoglous et al., 2014.

Similar to BAR/R-D-N, no internal recycle within the reaeration tank is provided. The aerobic and anoxic volumes required to achieve the desired nitrification and denitrification efficiencies are estimated through advanced process modeling at the design sidestream loading and sidestream-mainstream operating conditions. Since internal recycle is not provided, a low average pH in the aerated zones will occur, leading to a 30-40% reduction in the nitrifier maximum specific growth rate. In general, the aerobic HRT will be approximately two hours, similar to BAR/R-D-N reaeration tanks. The design HRT of the anoxic zone will be impacted by the selected COD source since the denitrification rates will vary with the source. For most sources, a 1-hour HRT will be sufficient.

4.4.3 CaRRB Process

The CaRRB (Centrate and RAS Reaeration Basin) process was developed in a collaborative effort between the Metro Wastewater Reclamation District (Denver, CO, U.S.) and Carollo Engineers (Walnut Creek, CA, U.S.) to achieve specific treatment objectives at the North and South Secondary Complexes at the 220-mgd Robert W. Hite Treatment Facility in Denver. Closely related to the BAR/R-D-N and biological augmentation batch-enhanced (BABE®) processes, the CaRRB tank receives sidestream and a portion of the RAS flow and is aerated. The RAS to sidestream (centrate) flow ratio varies from approximately 20:1 to 30:1 due to variations in centrate flow and operating conditions within the integrated CaRRB-mainstream configuration. Unlike the other bioaugmentation processes, the intention is to only partially nitrify the centrate ammonia load to nitrate without the addition of supplement alkalinity. The

nitrate load from the CaRRB tank is subsequently denitrified in the anoxic zones of the mainstream MLE and A^2O processes. To limit the effect of residual DO on denitrification, the swing zone at the end of the CaRRB tank is typically mixed and un-aerated. By denitrifying the treated centrate nitrate load, the internal mixed liquor recirculation flows within the mainstream processes required to achieve the desired plant effluent quality have been effectively reduced.

Implementation of a pH-controlled aeration strategy has proven effective in stabilizing performance of the CaRRB reactors and the overall ammonia removal efficiency of the integrated sidestream-mainstream configuration. In this control scheme, the air flow rate is adjusted based on pH measurements at the end of the reactor. When the pH attains 6.5, which has been established as the minimum value for operation, the air flow is adjusted to moderate the nitrification rate to prevent further reduction in pH.

Four-tank and three-tank CaRRB systems are in operation at the North and South Secondary Complexes, respectively (tanks operated in parallel). However, the long-term plan is to convert two of the CaRRB tanks in the North plant to anaerobic RAS reactors using gravity thickener overflow as a source of carbon to induce biological phosphorus removal. The District is also looking at the option of converting one or more of the CaRRB tanks to a deammonification process to reduce energy consumption and enhance the carbon-to-nitrogen ratio in the mainstream processes.

4.5 Trickling Filters

The use of trickling filters for sidestream treatment has been rarely practiced. In the limited number of full-scale applications, an existing trickling filter previously used for primary effluent treatment was dedicated to pretreating high strength sidestream to reduce the ammonium loading to mainstream secondary process. Due to the low BOD-to-ammonium-N ratio in high strength sidestream, treatment of sidestream in a trickling filter resembles tertiary nitrification in a mainstream process. However, if applied to a trickling filter with plastic cross-flow media at a typical packing depth at a loading of 1.5 grams of ammonium-N per m^2 of packing surface area per day, the hydraulic loading is well below an acceptable packing wetting rate of 1 liter per m^2 of filter cross-sectional area per second. Therefore, a high recirculation rate is required or a dilution water source is combined with the sidestream (e.g., plant effluent). If using a dilution water source, the operating temperature will be reduced, resulting in a lower nitrification rate.

Treatment of sidestream in a trickling filter will primarily result in nitrification. Therefore, an alkalinity source would be needed if a high nitrification efficiency is required. The alkalinity source could be provided in part by the dilution water source if this option is selected to increase the hydraulic loading on the filter. The bioaugmentation of the mainstream secondary process with nitrifying biofilm sloughed off of the filter media is possible based on observations from full-scale trickling filter/low-SRT activated sludge systems. This practice would require the filter effluent to be pumped directly the mainstream secondary process rather than sending to the primary sedimentation tanks, where the nitrifying solids would be removed.

4.6 Moving Bed Biofilm Reactors

Moving Bed Biofilm Reactors (MBBR) have been rarely used for treatment of high strength sidestreams where the goal is nitrification-denitrification. As discussed in Chapter 6.0, MBBRs with various types of support media have been applied in full-scale facilities for deammonification. Operating experience with these processes indicates that nitritation is readily

achieved through restriction of the operating DO concentration or the implementation of intermittent aeration, which leads to a reduction in the aeration energy requirement. Due to restriction of nitrite oxidation within the biofilm, the transition to a deammonification process was the next step in the development of a lower energy process. Because of the success in developing deammonification MBBR processes, full nitrification or nitrification-denitrification is typically not a desired operating condition if a MBBR system is implemented for sidestream treatment.

4.7 Submerged Attached Growth Reactors

Although the application of upflow submerged attached growth systems such as Biofor® and Biostyr® for sidestream treatment is technically feasible, this approach has not been attempted in full-scale applications, likely due to the potential fouling of the media, sidestream filtration requirements, high liquid recirculation rates, and equipment costs.

Pilot studies with a submerged media reactor consisting of sand (3-mm nominal diameter) and operated with intermittent aeration in downflow and upflow modes, indicated that nitritation can be readily achieved. Therefore, similar to MBBRs, since the nitritation-denitritation operating mode can be readily achieved, resulting in reduced aeration and carbon requirements, there is limited value in attempting to operate submerged attached growth reactors in a full nitrification or nitrification-denitrification mode.

4.8 Rotating Biological Contactors

Similar to MBBRs and submerged fixed media reactors, the application of rotating biological contactors for nitrification or nitrification-denitrification of high strength sidestreams is technically feasible. However, the full-scale application of rotating biological contactors for the treatment of landfill leachate resulted in the unintentional development of a biofilm that performs deammonification. Considering the advantages of this operating mode, the operation of rotating biological contactors to achieve full nitrification or nitrification-denitrification of the sidestream is unattractive.

4.9 Summary and Conclusions

Nitrification and denitrification of sidestream ammonia in separate, integrated sidestream-mainstream and mainstream processes have historically been the most common approaches for treating nutrient-rich sidestream. Of the options for separate sidestream treatment, SBRs have been most commonly applied. Despite the development of nitritation-denitritation and deammonification processes for sidestream treatment to reduce energy and organic carbon requirements, the use of nitrification and denitrification remains attractive where bioaugmentation of the mainstream plant with nitrifiers grown on sidestream ammonia is believed to be improving and stabilizing nitrification performance of the mainstream secondary process. Where odor control in the collection system near the facility, the headworks, and primary treatment process is of particular importance, nitrification of sidestream ammonia in a separate reactor without denitrification may be the most attractive option to provide nitrate for reduction of odorous emissions. Ultimately, the specific site conditions, plant effluent quality, objectives, and economics associated with treating sidestream separately, dictate selection of the sidestream treatment option in the mainstream secondary process or in an integrated sidestream-mainstream configuration.

CHAPTER 5.0

NITRITATION AND DENITRITATION PROCESSES

As the first milestone in the development of more energy and carbon-efficient sidestream treatment processes, nitritation-denitritation processes were implemented at a full-scale in the 1990s in Europe. In this chapter, separate and integrated sidestream-mainstream processes and those that produce a mixture of nitrite and nitrate during the ammonium oxidation step are described.

5.1 SHARON® Process

The SHARON (Stable-reactor, High-Activity Ammonia Removal Over Nitrite) process was developed in the 1990s at the Delft University of Technology in The Netherlands (Hellinga et al., 1998). The technology exploits the difference in the maximum specific growth rates of the AOB and NOB populations at the warm sidestream treatment operating temperatures. By closely controlling the aerobic SRT, AOB growth occurs, but NOB growth is effectively restricted due to the high washout rate.

A basic SHARON process consists of a covered single or dual-tank, continuous stirred tank reactor (CSTR). If one tank with a single zone is used, intermittent aeration is applied in order to accommodate nitritation and denitritation. However, the majority of the full-scale SHARON systems consists of two separate tanks or zones for nitritation and denitritation to provide optimum control and performance, as illustrated in Figure 5-1. In a typical SHARON reactor, the tanks or zones are in an anoxic-aerobic configuration to allow the utilization of the sidestream degradable organic carbon for denitritation. An internal recycle flow of approximately 10-12 times the sidestream flow is used to recirculate mixed liquor from the aerobic zone to the anoxic zone to provide nitrite for denitritation, typically accomplished with a wall pump to minimize power consumption.

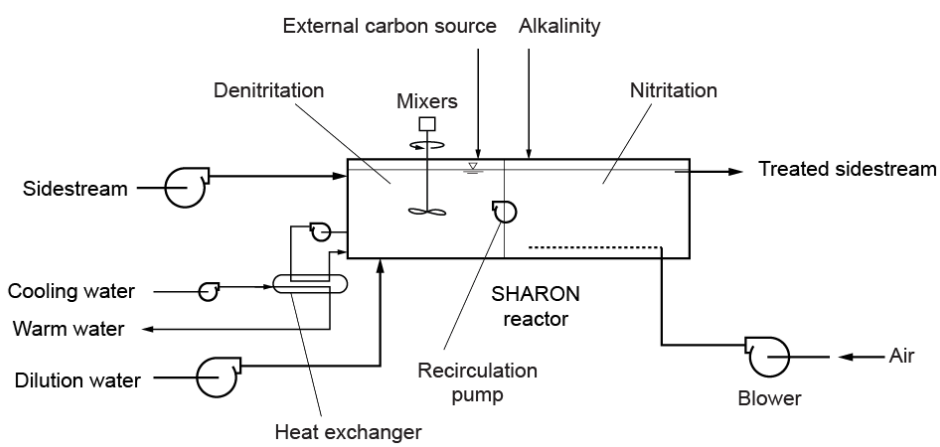

Figure 5-1. SHARON Process Flow Schematic Diagram.

The process is designed for an operating temperature in the range of 30-38ºC, an aerobic SRT of 1.5 days and an anoxic SRT of 0.75 days at the maximum sidestream flow rate. Since the SHARON reactor is a flow-through chemostat with no solids retention, the design SRT equals the design HRT. At flow rates below the maximum rate, intermittent aeration is applied to the aerobic zone to maintain the target aerobic SRT. Methanol is commonly used as the carbon source for denitritation, but carbon source selection is affected by local or regional market conditions and may be dictated by the operator's preference for a non-hazardous, non-flammable source.

Biological heat is typically removed by countercurrent heat exchangers via a mixed liquor recirculation loop and a cooling water source such as plant effluent to maintain the reactor temperature in the desired range. Dilution water (e.g., primary effluent, plant effluent) is used in the treatment of highly concentrated sidestreams to lower the reactor inlet ammonium concentration to 1,500 mg-N/L or less. Where dilution water is added, the diluted sidestream flow becomes the basis for calculating the aerobic and anoxic zone volume requirements.

Twelve SHARON facilities were built between 1997 and 2011 as shown in the facilities list in Table 5-1.

Table 5-1. SHARON Facilities List.

Facility	Year	N Load (lb-N/day)
Utrecht (NL)	1997	1,980
Rotterdam (NL)*	1999	1,870
Zwolle (NL)	2003	900
Beverwijk (NL)	2003	2,640
The Hague-Houtrust (NL)	2005	2,860
Groningen-Garmerwolde (NL)	2004	5,280
Geneva (CH)	2009	4,180
MVPC Shell Green, Manchester (GB)	2010	3,520
Seine Grèsillion, Paris (FR)	2010	7,700
Wards Island WPCP, New York City (US)	2010	12,540
Whitlingham (GB)	2011	3,300
Linkoping (SE)	2011	1,980

*SHARON tank at Rotterdam was converted to partial nitritation for a two-stage deammonification process in 2002.

5.2 Sequencing Batch Reactor

Stable nitritation-denitritation in SBRs has been demonstrated at a full-scale by operating at an SRT in the range of 5-10 days with intermittent aeration and DO concentration of 1 mg/L or less during the aerobic phases. The blower on/off cycle can be controlled by reactor pH measurements or by defining specific aerobic and anoxic time periods in the process control system. With the pH-controlled aeration approach, the air blower turns on to initiate an aerobic

phase when the reactor pH reaches the defined upper setpoint and the air flow is modulated to control the DO concentration around 1 mg/L or less. As alkalinity is destroyed through nitritation, the pH decreases to the lower pH setpoint, which turns off the blower, initiating the anoxic phase. Due to the alkalinity generated by denitritation, the pH increases to the high pH setpoint, initiating the next aeration phase. A pH interval of 0.4 units has been used in practice.

The effectiveness of operating a SBR at a low DO concentration to achieve stable nitritation has also been demonstrated in full-scale systems where continuous aeration was employed during the Fill and React phases at a DO concentration around 1 mg/L and a pH near neutral. In this particular case, the accumulation of a high nitrite concentration at a near neutral pH may be providing sufficient free nitrous acid (FNA) to further inhibit NOB growth (Anthonisen et al., 1976).

Since sidestream has insufficient organic carbon to achieve a high denitritation efficiency, a commercially available carbon source or a plant carbon source such as primary sludge is added during the anoxic phases. The denitritation rate is dependent on the type of organic carbon employed, the reactor pH, and the nitrite concentration. A reduction in the denitritation rate was observed at a high nitrite concentration under acidic conditions. Nitrite was found to directly inhibit nitric oxide reductase, resulting in the accumulation of nitric oxide and the inhibition of heterotrophic denitritation. Acidic conditions are believed to accelerate the inhibitory effect. These observations suggest that preventing nitrite accumulation to high concentrations by optimizing carbon addition and the aeration cycle times may be beneficial for performance.

Continuously feeding sidestream to the SBR during the React phase has been shown to stabilize process performance and has become accepted practice in full-scale systems treating typical high strength sidestreams. However, in sidestreams such as those derived from anaerobic digestion where thermal hydrolysis is employed for sludge pretreatment, the degradable-COD-to-N mass ratio can approach 1. For these sidestreams, an intermittent feeding strategy where sidestream is only fed to the SBR during the anoxic phases may be beneficial to optimize carbon utilization for denitritation and minimize the external organic carbon requirement.

Similar to other separate sidestream biological processes, dilution water may be required to maintain the reactor temperature below 38-40ºC. Although a minimum operating temperature required to sustain nitritation is not clearly defined, in practice the temperature will generally remain above 20ºC in a SBR performing at a high inorganic nitrogen removal efficiency due to biological heat generation.

Ammonium-N and total inorganic nitrogen removal efficiencies greater than 90% and 85%, respectively, can be realized at a design loading rate in the range of 0.4-0.6 kg-N/m^3•d.

A sidestream SBR can serve the dual purpose of flow equalization and treatment. In an approach called Storage and Treat (SAT), SBRs are used to dampen the hydraulic load sent to the mainstream process and partially nitrify the sidestream nitrogen load. In full-scale facilities where this approach was implemented, no external carbon or alkalinity source is added to the SBRs due to the treatment objectives of the facilities and to minimize operating cost. At one facility operating a dual-tank SBR system, approximately 35% of the sidestream ammonium was oxidized to a 3:1 mixture of nitrite and nitrate, which are denitrified in the pre-anoxic zones in the mainstream secondary process. Operational flexibility was included in the design by allowing continuous overflow from a tank if the other tank is in the Settle or Decant phase so as to not

interrupt sludge dewatering operations. At another facility operating a single SBR, approximately 50% of the ammonium is oxidized. Nitrite and nitrate are removed in the pre-anoxic zones of the mainstream secondary process to avoid nitrite oxidation to nitrate.

5.3 PANDA Process

The Partial Augmented Nitritation/Denitritation with Alkalinity recovery (PANDA) process was developed by aqua consult Ingenieur GmbH in collaboration with the Institute for Water Quality and Waste Management (ISAH) at the technical university of Hannover. The process applied at a full-scale at the Rheda-Wiedenbrück WWTP (Germany) consists of two suspended growth systems in series. Each system is comprised of a nitritation stage, denitritation stage, and a gravity clarifier. A supplemental carbon source (acetic acid) is added to the denitritation stage in both systems to enhance nitrogen removal and generate alkalinity. Clarified effluent is recirculated to the nitritation stage to provide alkalinity. SRT control is applied in each system to limit nitrate formation. Inhibition of NOB growth by free ammonia may also be contributing to stable nitritation. Overall, the PANDA configuration provides an inorganic nitrogen removal efficiency greater than 90%. In the latest development of the technology, modification of the denitritation stage to anammox is planned under a new process name, PANDA+. The application of PANDA at the Weißenfels WWTP in Germany has also been reported.

5.4 Integrated Mainstream-Sidestream Treatment Processes for Single-Stage Secondary Plants

Similar to the integrated sidestream-mainstream treatment processes described in Section 4.4 where the sidestream ammonia is fully oxidized to nitrate, integrated sidestream-mainstream treatment processes have been developed where a portion of the mainstream RAS and the sidestream are fed to a reactor which is controlled under conditions that limit oxidation of nitrite to nitrate. The AOB-enriched mixed liquor from this sidestream treatment reactor is sent to the mainstream treatment process to enhance nitrification. Examples of integrated sidestream-mainstream processes are described in this section.

5.4.1 Biological Augmentation Batch-Enhanced (BABE®) Process

The BABE process was developed by Delft University of Technology in collaboration with DHV (Royal HaskoningDHV, the Netherlands) for the purpose of growing flocculated, nitrifier-enriched, mixed liquor solids in a sidestream reactor to bioaugment the mainstream secondary plant. In the BABE process, the reactor is integrated with the mainstream process through the addition of a portion of the mainstream RAS. The RAS “slipstream” flow is adjusted to provide a design operating temperature of approximately 25ºC; therefore, the portion of the mainstream RAS fed to the BABE reactor may be adjusted to account for seasonal wastewater temperature changes and climatic changes that impact heat loss from the BABE reactor. Although the BABE patent describes the RAS flow to BABE as being 1-25% of the total RAS flow, the actual RAS flow to the reactor is in the lower end of this range as dictated by the preferred operating temperature of 25ºC.

The BABE reactor was originally conceived and demonstrated at a full-scale as an SBR. During the React period of the cycle, intermittent aeration is provided to nitrify and denitrify the sidestream nitrogen load. A mixture of nitrite and nitrate is produced during the aerobic periods,

with nitrite as the dominate product. Free ammonia inhibition, possibly in combination with intermittent aeration, is likely responsible for the restriction of NOB growth. A supplemental COD source such as methanol is added to enhance nitrogen removal and generate alkalinity to support nitrification. At the end of the React period, the mixed liquor solids are settled and waste sludge is pumped to the mainstream secondary process, along with the treated sidestream. High solids capture efficiency during the Settle phase is not critical since the decanted effluent and waste sludge from the BABE reactor are sent to the mainstream secondary process. The operating SRT is kept as low as possible to limit the reactor volume and the decay of the nitrifiers grown in the reactor.

The BABE process was first evaluated at a full-scale at the Garmerwolde WWTP (The Netherlands) through a Foundation for Applied Water Research, the Netherlands (STOWA) commissioned study. A permanent full-scale system was installed at the ‘s-Hertogenbosch WWTP (the Netherlands) in late 2005.

5.4.2 AT-3 Process

The AT-3 Process is named for Aeration Tank #3 at the 26th Ward Water Pollution Control Plant (WPCP) in Brooklyn, New York. As the facility had been operating below its design capacity, one of three four-pass plug-flow aeration tanks was dedicated to sidestream treatment where sidestream and a portion of the mainstream RAS are blended in a flow ratio of 1:0.5 to 1:1. The reactor is configured with alternating aerobic and anoxic zones and caustic soda is added at multiple locations along the length of the tank to sustain nitrification. An internal recycle is applied from the fourth pass to the first pass of the tank to provide NOx-N at the point of sidestream addition (~ 100% of the sidestream flow). Nitrifier-enriched mixed liquor from the tank is combined with the remainder of the mainstream RAS to bioaugment the mainstream secondary process. Free ammonia inhibition and a low secondary process SRT (~ 2-3 days) collectively limit NOB growth and nitrite accumulation is observed throughout AT-3 and the two four-pass plug-flow aeration tanks treating primary tank effluent, reducing the organic carbon requirement for nitrogen removal. As the SRT of the integrated sidestream-mainstream configuration increases beyond three days, NOB growth gradually increases, resulting in a mixture of nitrite and nitrate throughout the process.

To enhance nitrogen removal and reduce caustic soda addition, the AT-3 process at the 26th Ward facility was upgraded with supplemental carbon addition (glycerol) in 2012. The AT-3 process configuration is also currently in use at the Hunts Point and Bowery Bay WPCPs in New York City.

5.5 Integrated Sidestream-Mainstream Process for Multi-Stage Mainstream Secondary Plants

In-situ bioaugmentation of low SRT, high-rate carbon removal systems with waste sludge from downstream nitrification processes has been documented. The primary motivation for these bioaugmentation flow schemes is to induce the carbon removal system to partially nitrify and denitrify, thereby effectively using raw influent organic carbon for denitrification and reducing the nitrogen load to the downstream nitrification plant. For a two-stage plant consisting of carbon removal followed by nitrification-denitrification, a multi-purpose integrated sidestream-mainstream process has been proposed where waste sludge from the nitrifying plant is blended with sidestream in a separate reactor and the nitrifier-enriched waste sludge from the reactor is

fed to the carbon removal plant to enhance bioaugmentation (Bailey et al., 2008). The sidestream reactor can be designed as a SBR and operated at a low SRT to minimize nitrifier decay. Intermittent aeration and the addition an external organic carbon source can be included in the design to provide inorganic nitrogen removal and generate alkalinity.

Alternatively, the reactor could be designed as a RAS reaeration tank where a portion of RAS from the carbon removal plant is blended with sidestream and nitrification plant waste sludge, with either alternating aerobic and anoxic zones or a post-anoxic zone with internal reactor mixed liquor recirculation to allow denitrification with an external organic carbon source. If the facility would benefit most from stabilizing the nitrification plant performance during the winter operating period, the sidestream reactor could function similar to a BABE process where RAS from the nitrification plant is added to the reactor and reactor waste sludge is sent to the nitrification plant.

A demonstration of this integrated sidestream-mainstream process was conducted at the Salzburg wastewater treatment plant (Austria) which operates a two-stage secondary process and a separate sidestream nitritation-denitritation SBR (Wett et al., 2010). Waste sludge from the second stage nitrification-denitrification plant was pumped to the SBR and waste sludge from the SBR was sent to the high rate carbon removal stage. Despite the application of intermittent aeration at a low DO concentration, increasing the amount of nitrification plant waste sludge to the SBR effectively increased nitrate production in the SBR and lowered the reactor temperature. The bioaugmentation effect on the mainstream carbon removal stage was evaluated and quantified.

5.6 Summary

The development of processes in the late 1990s and early 2000s that result in nitrite accumulation in separate sidestream and integrated sidestream-mainstream configurations was a major step forward in the achievement of reduced energy and carbon requirements for nitrogen removal. As discussed in Chapter 3.0, our understanding of how nitratation can be prohibited has provided a foundation for the development of the next generation of energy- and carbon-efficient technologies based on deammonification.

CHAPTER 6.0

DEAMMONIFICATION PROCESSES

The development and implementation of deammonification processes has accelerated since the first full-scale systems were commissioned in Germany and The Netherlands in 2001-2002. The technologies exploit the ability of anammox bacteria to tightly aggregate into a granulated form or readily attach to surfaces due to excessive formation of exocellular polymeric substances. The anammox bacteria also have a low biomass yield. Due to these fortuitous properties, system designers can readily achieve the high SRT required to sustain and accumulate anammox organisms in a reactor and design reactors with high specific nitrogen loading rates.

In the initial development of deammonification processes, CANON (Completely Autotrophic Nitrogen removal Over Nitrite) and OLAND (Oxygen-Limited Autotrophic Nitrification Denitrification) were the general process names for single-sludge deammonification processes. However, those names soon fell out of use as specific trademarked process names became the norm for processes implemented at a full-scale.

Irrespective of the mode of operation (suspended growth, biofilm on support media, granular sludge), the essential requirement for the successful operation of deammonification process is the availability of nitrite for the anammox bacteria. Increased abundance of NOBs, which compete with anammox bacteria for NO_2^-, has been cited as a cause of instability in a single-stage deammonification system. Based on a comparison of parallel full-scale reactors, it was suggested that an infrequent and short-term increase in O_2 supply (e.g., for maintenance of aerators) that exceeds prompt depletion of oxygen by AOB may have caused increased NOB abundance.

Long startup periods and lack of operational reliability have frequently been reported as major shortcomings of deammonification technology. Transfer of sufficient seed sludge has proven to accelerate the startup period down to about 50 days. Seeding with anammox bacteria greatly accelerates the start up of a new deammonification process application (Strous et al., 1998) who found that a critical bacteria concentration is necessary to realize good anammox activity. A possible reason is that for small anammox flocs the ammonia oxidation intermediate hydrazine diffuses quickly to the bulk liquid. The addition of hydroxylamine or hydrazine was found to accelerate anammox bacteria activity (Van Hulle et al., 2010). The slow decay rate of anammox allows the seed to remain active during storage and transportation.

Several technical solutions have been developed to grow and support anammox bacteria. Table 6-1 shows a list of over 100 full-scale deammonification installations. Many different deammonification processes are commercially available and others are in a development stage. These processes differ in terms of the method to grow and retain the anammox bacteria, number of stages, the configuration of the process, and control strategies implemented. Configurations include granular sludge reactors, suspended growth SBRs, moving bed biofilm reactors, and rotating biological contactors. Deammonification has demonstrated ammonia reduction of 90-95% and total nitrogen reduction of 80-85%.

Table 6-1. Installations and Performance of Deammonification Technologies.
Data as of June 2015.

Process	Year	Installations	Country	N load, lb N/d[a]	Comment
Activated carbon		Emscherbruch	Germany		Landfill
ANAMMOX®	2002	WSHD, Rotterdam	The Netherlands	1,100	Reject water, two stage SHARON®/ANAMMOX®
ANAMMOX®	2004	Industry Water Lichtenvoorde, Lichtenvoorde	The Netherlands	700	Tannery, two stage CIRCOX®/ANAMMOX®
ANAMMOX®	2006	Waterstromen Steenderen, Olburgen	The Netherlands	2,600	One step, potato industry
ANAMMOX®	2006	Mie, semiconductor plant	Japan	500	Two stage biofilm CSTR/ANAMMOX®
ANAMMOX®	2008	ARA Niederglatt, Niederglatt	Switzerland	100	One step
ANAMMOX®	2009	Meihua I, Tongliao	China	24,300	One step, MSG
ANAMMOX®	2009	Angel Yeast, Binzhou	China	2,200	One step, yeast
ANAMMOX®	2010	Meihua II, Tongliao	China	19,800	One step, MSG
ANAMMOX®	2010	Waterschap Groot Salland, Zwolle	The Netherlands	1,300	One step, reject water
ANAMMOX®	2011	Xinjiang Meihua Amino Acid , Wulumuq	China	23,600	One step, MSG
ANAMMOX®	2011	Starch processing facility	China	15,000[b]	Starch processing
ANAMMOX®	2011	Shandong Xiangrui, Shangdong	China	13,400	One step, corn starch, MSG
ANAMMOX®	2011	Rendac, Son	The Netherlands	12,600	One step, meat processing
ANAMMOX®	2011	Severn Trent , Minworth	United Kingdom	8,800	One step, reject water
ANAMMOX®	2011	Jiangsu Hangguang Bio-engineering, Yixing	China	4,800	One step, sweetener
ANAMMOX®	2011	Confidential client,	Poland	3,200	One step
ANAMMOX®	2011	Kuaijishan Shaoxing Winery, Shaoxing	China	2,000	One Step, winery
ANAMMOX®	2012	Winery	China	2,600[b]	Winery
ANAMMOX®	2012	Ningxia Eppen Biotech	China	22,200	One step, MSG
ANAMMOX®	2012	Zhejiang Guyuelongshan Winery	China	2,300	One step, winery
ANAMMOX®	2012	Stoke Bardolph	United Kingdom	6,600[b]	Reject water
ANAMMOX®	2012	Tilburg	The Netherlands	4,400[b]	Reject water
ANAMMOX®	2013	Energy Cons. Env. Protection	China	1,670	One step, solids waste dig.
ANAMMOX®	2013	Kuaijishan Shaoxing Winery II, Shaoxing	China	1,100	One step, winery
ANAMMOX®	Design/ Construct	Vion	The Netherlands	1,800[b]	Meat processing
ANAMMOX®	Design/ Construct	Meat processing facility	Brasil	880[b]	Meat processing
ANITA™Mox	2010	Sjölunda WWTP, Malmö	Sweden	440	Reject water, K3, Anox™K5; Biofilmchip™M
ANITA™Mox	2012	Sundet WWTP, Växjö	Sweden	950	Reject water, Anox™K5
ANITA™Mox	2012	Holbæk WWTP	Denmark	260	Reject water, landfill, K3
ANITA™Mox	2013	Grindsted	Denmark	110	Reject water
ANITA™Mox	2013	James River	VA, USA	560	Reject water
ANITA™Mox	2015	South Durham	NC, USA	670	Reject Water
ANITA™Mox	2015	John E. Egan WRP, Chicago	IL, USA	2070	Reject Water

Process	Year	Installations	Country	N load, lb N/d[a]	Comment
ANITA™Mox	2014	Confidential	Poland	750	Industrial sidestream after AnMBR
ANITA™Mox	2015	Lorcana WWTP	Switzerland	660	Reject Water
ANITA™Mox	2015	Arla Foods	UK	660	Industrial sidestream after UASB
Cleargreen™	Design/ Construct	Burgos	Spain	4,200[b]	Reject water
Cleargreen™	Design/ Construct	Ourense	Spain	1,300[b]	Reject water
DeAmmon®	2001	Hattingen WWTP	Germany	260	Reject water, single (40%)
DeAmmon®	2007	Himmerfjärden WWTP Stockholm	Sweden	1,500	Reject water, dual (32%)
DeAmmon®	2009	Dailan XiaJiaHe	China	4,900[b]	
DEMON®	2004	Strass	Austria	1,100	Reject water
DEMON®	2007	Glarnerland	Switzerland	550	Reject water
DEMON®	2007	Plettenberg	Germany	180	Reject water
DEMON®	2008	Heidelberg	Germany	1,300	
DEMON®	2008	Thun	Switzerland	880	Reject water
DEMON®	2008	Gengenbach	Germany	110	Reject water
DEMON®	2009	Apeldoorn	Netherlands	3,700	
DEMON®	2009	Etappi Oy	Findland	2,100	Biogas production
DEMON®	2009	Balingen	Germany	420	
DEMON®	2010	Limmattal	Switzerland	550	
DEMON®	2010	Lahr	Germany	520	Reject water
DEMON®	2010	Zalaegerszeg	Hungry	350	
DEMON®	2010	Erpfendorf	Germany	260	Reject water
DEMON®	2010	Lavant	Austria	60	Landfill
DEMON®	2011	Alltech	Serbia	5,300	Yast
DEMON®	2011	Kokkola	Findland	1,300	Reject water
DEMON®	2011	Nieuwegein	The Netherlands	990	Reject water
DEMON®	2011	Neumarkt	Germany	700	Reject water
DEMON®	2011	Rickenbach	Germany	110	Dairy
DEMON®	2012	Kecskemet	Turkey	2,900	Reject water
DEMON®	2012	Etappi Oy II	Finland	2,000	Biogas production
DEMON®	2012	Amersfoort	The Netherlands	1,400	Reject water
DEMON®	2012	Pustertal	Italy	1,100	Reject water
DEMON®	2012	Maszewo	Poland	1,100	Biogas
DEMON®	2012	Lavis	Italy	1,100	Landfill
DEMON®	2012	Helsinki	Findland	880	Reject water
DEMON®	2012	York River	VA, USA	490	Reject water
DEMON®	2012	Bickenbach	Germany	220	Reject water
DEMON®	2013	Budapest	Hungary	5,000	Reject water
DEMON®	2013	Biogas Plant	FL, USA	1,600	Biogas production
DEMON®	2013	Leoben	Austria	1,400	Co-digestion reject water
DEMON®	2013	Poole	United Kingdom	880	Reject water
DEMON®	2013	Zell am See	Austria	660	Co-digestion reject water
DEMON®	2013	Moerdijk	The Netherlands	3,500	Reject water
DEMON®	2013	Echten	The Netherlands	880	Reject water

Process	Year	Installations	Country	N load, lb N/d[a]	Comment
DEMON®	2013	Nieuwveer	The Netherlands	2,320	Reject water
DEMON®	2013	Bruchsal	Germany	400	Reject water
DEMON®	2013	Eisenhüttenstadt	Germany	350	Reject water
DEMON®	2013	Bern	Switzerland	3,080	Reject water
DEMON®	2013	Changsa	China	2,640	Reject water
DEMON®	2013	Palencia	Spain	330	Reject water
DEMON®	2014	Odense	Denmark	870	Reject water
DEMON®	2014	Vigo	Spain	3,390	Reject water (Cambi)
DEMON®	2014	WMG, Groningen	The Netherlands	1,360	Landfill, reject water
DEMON®	2014	Attero, Tilburg	The Netherlands	2,400	Landfill, reject water
DEMON®	2014	Marselisborg	Denmark	680	Reject water
DEMON®	2014	Land van Cuijck	The Netherlands	740	Landfill, reject water
DEMON®	2014	Velsen	The Netherlands	620	Landfill, reject water
DEMON®	2014	Sindelfingen	Germany	440	Reject water
DEMON®	2014	Rottenburg	Germany	200	Reject water
DEMON®	2014	Krakow	Poland	550	Reject water
DEMON®	2014	Solothurn	Switzerland	700	Reject water
DEMON®	2014	Reedy Creek	Fl, USA	910	Reject water
DEMON®	2014	Alexandria,	VA, USA	4,000	Reject water
DEMON®	Design/ Construct	Blue Plains, DC Water	DC, USA	27,000	Reject water (Cambi)
DEMON®	Design/ Construct	Guelph	Canada	920	Reject water
ELAN	2014	Guillarei	Spain	170	Reject water
MBBR	2011	Oslo/Bekkelaget	Norway	1,600[b]	Reject water
NAS®	2004	Kruiningen	The Netherlands	720	Potato industry, retrofitted from conventional N/DN, 4 stages + settler
NAS®	2009	Bergen op Zoom	The Netherlands	1,600	Potato industry, retrofitted from conventional N/DN, 3 stages + settler
NAS®	2010	Budrio	Italy	760	Potato industry, 3 stages + MBR
NAS®	Design/ Construct	Boxtel	The Netherlands	2,000[b]	Potato industry, 3 stages, last stage as MBR
NAS®	Design/ Construct	Salamanca	Spain	700[b]	Reject water
RBC	1985/1991	Pitsea	United Kingdom	900	Landfill
RBC	2010	Sneek	The Netherlands	0.9[b]	Digested black water
RBC	2011	Schwalmstadt-Treysa[b]	Germany		Reject water
RBC	2012	Sneek	The Netherlands	12[b]	Digested black water
RBC	1994/1998	Mechernich	Germany	48	Landfill
RBC	1997	Kölliken	Switzerland	13	Landfill
SBR (eawag)[c]	2007	Zürich	Switzerland	2,800	Reject water
SBR (eawag)[c]	2008	St. Gallen	Switzerland	470	Reject water
SBR (eawag)[c]	2008	Niederglatt	Switzerland	120	Reject water
SBR (eawag)[c]	2012	Pfannenstiel	Switzerland	170[b]	Reject water
SBR	2004	Gütersloh	Germany	580[b]	Reject water
SBR	2011	Ingolstadt	Germany	790[b]	Reject water
SBR	Design/ Construct	Dendermonde	Belgium	660[b]	Reject water

Process	Year	Installations	Country	N load, lb N/d[a]	Comment
SNAD	2006	Tianwaitian	Taiwan	425	Landfill
SNAD		Bali landfill	Taiwan	1,100	Landfill
SNAD		Keelung landfill	Taiwan	400	Landfill
TERRAMOX®	2008	Fulda Gläserzell	Germany	880	Reject water, two stage
TERRAMOX®	2010	Landshut	Germany	750	Reject water, two stage
TERRAMOX®	2011	Klaranlage Rheda	Germany	1,500	Reject water, one stage
TERRAMOX®	2012	KA North Potsdam	Germany	350	Reject water, two stage
TERRAMOX®	2012	KA Rinteln	Germany	180	Reject water, SBR

[a.] Loading rate is based on the maximum design loading.
[b.] Loading information from Lackner et al. (2014).
[c.] SBR process developed through support of the Swiss Federal Institute for Aquatic Science and Technology (eawag)

6.1 ANAMMOX® Granulated Sludge Reactor

The ANAMMOX® upflow granulation reactor was developed through a collaborative effort between Delft University of Technology and Paques BV (the Netherlands) and was implemented as the second stage in two-stage system composed of partial nitritation followed anammox (Section 6.1.1). A single reactor ANAMMOX® system design soon followed and is now the standard design provided by Paques for a grass-roots system (Section 6.1.2).

A startup period of two to three years was required for the first ANAMMOX® system due to the low growth rate of the anammox bacteria, unavailability of concentrated seed sludge, and a general lack of knowledge regarding the operating conditions that affect performance. After the first reactor attained the full loading rate and demonstrated good performance, the reactor served as a source of anammox seed for the startup of reactors at other facilities, dramatically reducing the time required to attain full sidestream loads.

6.1.1 Two-Step SHARON®-ANAMMOX® Process

Deammonification was first accomplished in a two-stage system consisting of partial nitritation followed by the anammox reaction as illustrated in Figure 6-1. In the first stage, a SHARON-type low SRT reactor can be operated without alkalinity addition to convert approximately 50% of the sidestream ammonium to nitrite. The molar ammonium-to-nitrite ratio of 1:1 in the first stage effluent is near the ideal stoichiometric molar ratio of 1:1.32 required by the anammox bacteria in the second stage. The addition of alkalinity to the reactor would allow greater conversion of ammonium to nitrite and, consequently, potentially higher inorganic nitrogen removal in the anammox stage. However, alkalinity control would be needed to prevent too much ammonia conversion to nitrite, which would put the molar ratio outside the narrow range needed.

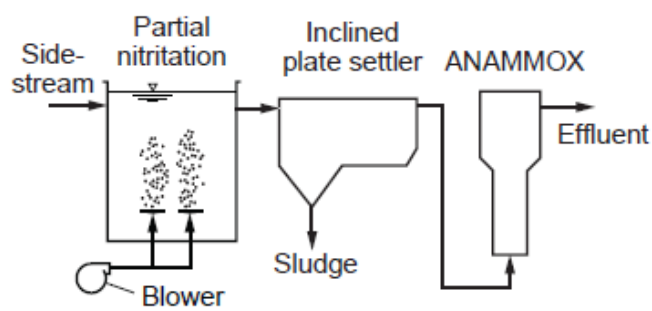

Figure 6-1. Flow Scheme for the Two-Stage SHARON-ANAMMOX Deammonification Process.
From Tchobanoglous et al., 2014.

In the two-stage deammonification process, the second stage ANAMMOX® reactor design is based on the Paques' Internal Circulation (IC) upflow anaerobic reactor used in treating high-strength industrial wastewaters. In this tank design, the propensity of the anammox bacteria to form dense granules with settling velocities greater than 100 m/h is being exploited. Under the high upflow superficial velocity induced with this reactor design, the hydrodynamic conditions provide the selective pressure for the development of a thick granulated biomass, achieving a sludge concentration as high as 5-7 wt% in the sludge bed in the lower section of the reactor. Flocculated particles with lower densities and settling velocities are washed out the reactor. The diameter of the anammox granules has been reported to be in the range of 0.2 to 2.7 mm, with a mean diameter of 1.4 mm. A photograph of granulated anammox bacteria is shown in Figure 6-2.

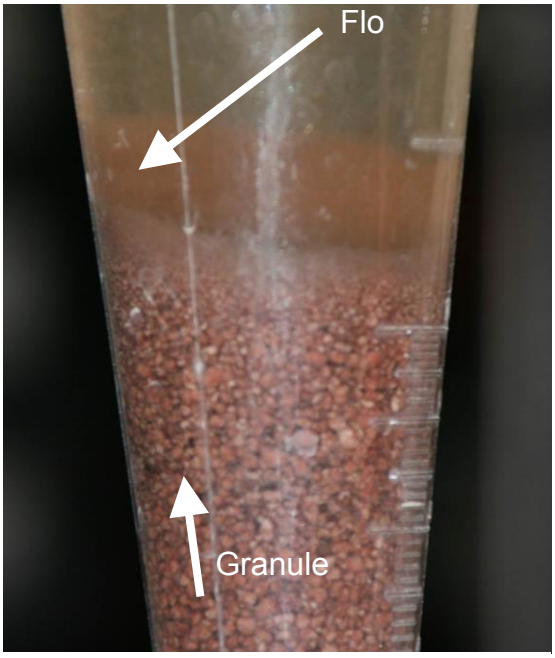

Figure 6-2. Anammox Granules from a Paques ANAMMOX® Reactor.

Reactor mixing and the desired liquid upflow velocity are accomplished via a gas lift mechanism, where nitrogen generated by the anammox reaction is used to induce liquid recirculation from the top to the bottom of the reactor. The recirculation flow is combined with the influent at the base of the reactor. The height of the sludge bed is controlled through sludge wastage to prevent its encroachment on gas collection troughs located approximately at mid-depth.

Solids separation between the partial nitritation reactor and the ANAMMOX® reactor is preferred to prevent the accumulation of inert solids in the ANAMMOX® reactor sludge bed. Inclined plate settlers have been used successfully for this function.

Design loadings for the second-stage ANAMMOX® reactors have ranged from 3-7 kg-N/m^3•d (ammonium plus nitrite), but loading rates as high as 10 kg-N/m^3•d have shown little effect on the nitrogen removal efficiency, which has been reported to be in the range of 90-95%. As discussed above, improvement in the nitrogen removal efficiency can be accomplished by slightly increasing the conversion of ammonium to nitrite in the first stage via alkalinity addition. The reactors typically operate in the range of 35-40ºC with no measurable impact on performance as the reactor approaches the upper temperature.

The geometry of the second stage ANAMMOX® reactors is dictated by the hydrodynamic conditions (superficial upflow velocity) required to maintain a fluidized and well-granulated sludge bed and prevent the accumulation of flocculated solids. The influent flow and the internal recycle flow induced by the gas-lift mechanism are the critical design parameters that dictate the diameter and height of the reactor. Since a high upflow liquid velocity is required, the reactor will tend to be relatively narrow with liquid depths around 20-m.

The overall volume of the two-stage SHARON-ANAMMOX system is dictated by the sidestream flow rate. For example, for a conventional high strength sidestream with a flow rate of 500 m^3/d and an ammonium concentration of 1,000 mg-N/L (1 kg/m^3), a conceptual-level design total volume would be:

$$[500\ m^3/d \times 1.5\ d] + [(500\ m^3/d \times 1\ kg/m^3) \div 7\ kg/m^3 \bullet d] = 821\ m^3 \qquad \text{(Equation 6-1)}$$

[SHARON reactor] [ANAMMOX reactor]

When based on the total system volume, the volumetric ammonium loading rate is:

$$500\ m^3/d \times 1\ kg/m^3 \div 821\ m^3 = 0.6\ kg\text{-}N/m^3 \bullet d \qquad \text{(Equation 6-2)}$$

6.1.2 Single-Step ANAMMOX® Process

A high-rate, single-stage deammonification reactor was developed by Paques BV, where AOB and anammox bacteria can be induced to grow synergistically in the same granulated biomass. The AOB population exists on or near the surface of the granules and the anammox bacteria grow inside the granules.

As illustrated in Figure 6-3, the single-stage ANAMMOX® reactor was initially developed with an air lift aeration and mixing design where air is continuously applied to the bases of multiple riser tubes, resulting in upward liquid-solids movement through the risers and downward movement of liquid-solids outside the risers after gas disengagement. The hydrodynamic conditions created by this arrangement favor the development of a thick well-granulated fluidized biomass. After the first single-stage systems were brought into service and could serve as a seed source for startup of new reactors, the riser tubes were not necessary and have been eliminated from process design. A proprietary gas-liquid-solids separator(s) located in the upper section of the reactor provides separation of the liquid-solids from the exhaust air and a settling zone for the granulated solids.

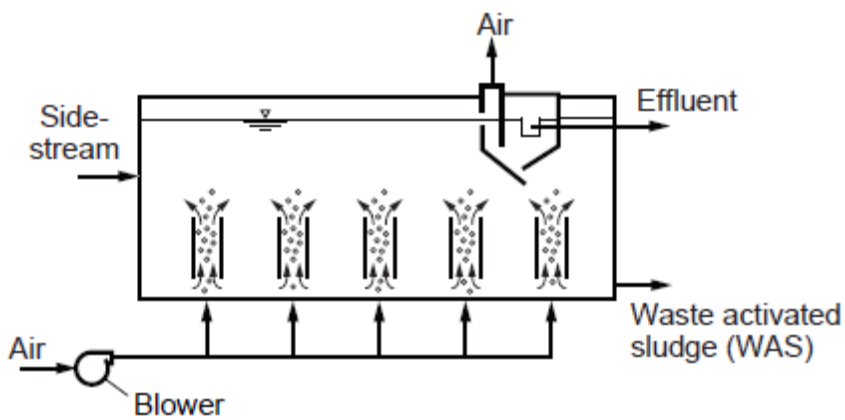

Figure 6-3. Single-Stage ANAMMOX® Process for Deammonification.
From Tchobanoglous et al., 2014.

The single-stage ANAMMOX® reactor has a design loading up to 2 kg-N/m^3•d and ammonium removal efficiencies in the range of 90-95% have been reported (Abma et al. 2010). The granulated sludge is allowed to accumulate to concentrations in the range of 10 to 15 g/L. Unlike the ANAMMOX® reactor in two-stage systems, the single-stage ANAMMOX® reactor can be of rectangular or circular geometry with a lower sidewater depth. Current reactors have heights in the range of 8-10 meters. Due to the higher design loading rates, flexibility in design, reduced space requirements and simpler operation, the single-stage ANAMMOX® systems have supplanted the two-stage configuration for new installations.

Similar to the ANAMMOX® reactor in two-stage systems, screening the sidestream may be required to remove larger inert debris. Providing a suspended solids removal process may also be required to reduce solids that have a sufficient settling velocity that may result in their accumulation in the ANAMMOX® reactor. A settling velocity of 0.8 m/hr is typically the limit. Column settling tests are conducted on the raw sidestream for this assessment.

The influent (municipal sidestream, anaerobically pretreated industrial wastewater) may have to be treated in an aerobic process prior to ANAMMOX® to oxidize sulfide, which has been identified as inhibitory to anammox bacteria at a concentration around 1-2 mg-S/L. This biological pretreatment step which is not a requirement for other deammonification technologies described in Chapter 6.0. This may be due to the lower specific loading rates (kg-contaminants/m^3•d) and higher hydraulic retention times associated with these processes which results in sufficient oxidation of sulfide to non-inhibitory concentrations. Atypical influents with a COD-to-N ratio approaching 1 may also require biological pretreatment. Such an influent ratio has been observed with sidestreams generated from anaerobic digestion processes preceded by thermal hydrolysis. this case, excessive heterotrophic growth would occur in ANAMMOX®, potentially destabilizing the process; hence, a low-SRT aerobic pretreatment step would reduce the COD-to-N ratio (and oxidize sulfide) to a desired level.

6.2 Sequencing Batch Reactor

As shown in Table 6-1, sequencing batch reactors are the most common deammonification processes at a full-scale. Of this type of process, the DEMON SBR is the majority of these systems.

6.2.1 DEMON®

Developed through a collaborative effort between the University of Innsbruck and the Achental-Inntal-Zillertal Wastewater Treatment Association (Austria), the DEMON® (DEamMONification) process consists of single or multiple SBRs operated with intermittent aeration during the Fill/React phase and a peak DO concentration of 0.3 mg/L during the aerobic phase of each aeration cycle (Wett, 2007).

The duration of the aerobic and anoxic periods is controlled by pH or time. When using pH to turn the blowers on and off, a pH interval of 0.01 or 0.02 units has been successfully applied; however, most full-scale systems use a time-based control system. With pH based control, the pH decreases during the aerobic phase from the high to the low pH setpoint due to alkalinity consumed during the oxidation of ammonium to nitrite. At the low pH setpoint, aeration is turned off and the pH begins to increase due to acidity consumed during the anammox reaction. Heterotrophic denitrification of a portion of the nitrate produced by the anammox reaction and alkalinity of the influent also contribute to the increase in pH.

As discussed in Section 3.3, anammox bacteria are irreversibly inhibited by nitrite with the loss of activity defined by the nitrite concentration and exposure time. To minimize the impact of nitrite on anammox activity, the pH interval between the high and low setpoints is 0.01 or 0.02 units resulting in an aeration cycle consisting of an un-aerated phase of five to seven minutes and an aerated phase of 10-15 minutes. With this aeration cycle, a peak nitrite concentration of around 2 mg/L is produced during the aerobic phase, decreasing to near zero

during the subsequent unaerated phase. When this aeration cycle is combined with a low operating DO setpoint of 0.3 mg/L, NOB growth is effectively restricted.

Anammox bacteria exist in DEMON in the form of dense granules with the AOB, heterotrophs and inert suspended solids remaining in a flocculated form. In an advancement of the DEMON process, the DEMON waste sludge is pumped through one or more hydrocyclones, which are operated at a pressure drop of approximately 2 bar. Due to the higher specific gravity of the anammox granules relative to the flocculated mass, the granules separate from the waste sludge to the bottom of the hydrocyclones and are returned to the SBR at a capture efficiency > 95%. This waste sludge processing step increases the SRT of the anammox bacteria to > 50 days (Wett et al., 2010). The SRT of the flocculated solids are maintained around 10 days to ensure sufficient AOB mass is in the SBR, further suppress NOB growth and limit the accumulation of heterotrophic biomass and flocculated inert solids in the mixed liquor. A photograph of a DEMON hydrocyclone is shown in Figure 6-4.

Figure 6-4. Hydrocyclone to Separate Anammox Granules from the DEMON Waste Sludge.

A DEMON SBR is typically designed with a volumetric ammonium loading rate near 0.7 kg/m^3•d, but good performance at a peak volumetric loading rate of 1.2 kg/m^3•d has been successfully demonstrated. Ammonium and total inorganic nitrogen removal efficiencies of 90-95% and 80-85%, respectively, have been reported for full-scale systems at loading rates ranging from 0.3-0.6 kg-N/m^3•d. An optimized total power consumption of 1.16 kWh/kg-N-removed (aeration and mixing) was reported for a reactor at its design loading rate (Wett, 2007).

Pretreatment of the sidestream to remove denser particulate matter is recommended. If heavy inert solids are allowed in the SBR, they will likely be retained in the system by the hydrocyclones, eventually accumulating to unacceptable levels in the SBR. Solids capture can be combined with flow equalization, which is a requirement for an SBR system or where biosolids dewatering is not continuous.

The first DEMON SBR required a startup period of two to three years in which an anammox enrichment program was used to grow sufficient anammox mass to seed the full-scale reactor. In the startup of other DEMON reactors, seed sludge from an existing full-scale reactor is added to the new reactor at a loading of 1 kg of total suspended solids per cubic meter of reactor volume. With this seed mass, stable treatment of the entire sidestream load can be achieved in one to three months, depending on the sidestream load.

6.2.2 Miscellaneous

Deammonification SBRs have been developed independently of DEMON at a full-scale. The most well-known of these processes was developed through the support of the Swiss Federal Institute of Aquatic Science and Technology (Eawag). Operational in five facilities in Switzerland since 2007, the SBR is a suspended growth process that is continuously aerated at a

DO less than 0.1 mg/L during the Fill period to perform simultaneous nitritation-anammox. The influent loading rate is controlled based on on-line ammonia measurements. The design loading rates vary from 0.23 to 0.71 kg-N/m^3•d.

As shown in Table 6-1, other SBR systems have been independently developed in the Netherlands, Belgium, Germany, and Spain. The operating strategies vary. For example, at the Ingolstadt WWTP (Germany), the SBR is intermittently fed and aerated with a DO control range of 0.8-1.0 mg/L. In contrast, the SBR at the Gütersloh WWTP (Germany) operates at approximately one cycle per day with aeration controlled by on-line ammonia and pH measurements. A DO concentration less than 0.5 mg/L is maintained in the process. Despite these various in control and operation and differences in specific loading rates, all of these systems have achieved deammonification.

Other SBR types have been developed, but are either in construction or in planning and design phase. These specific technologies will be briefly described later in this chapter.

Similar to the DEMON system, influent pretreatment to reduce the suspended solids load and dampening its variability will be beneficial for these SBR processes.

6.3 Moving-Bed Biofilm Reactor

Unexplained nitrogen losses were discovered across rotating biological contactors treating landfill leachate (Siegrist et al., 1998; Knox, 1991). The establishment and proliferation of anammox bacteria within the biofilms was subsequently found to be responsible for 70-90% of the nitrogen removal. Based on these findings, moving-bed biofilm reactor configurations were proposed for deammonification and studied in bench and pilot-scale systems using primarily the Kaldnes K1 plastic media for biofilm support (Seyfried, et al., 2001). Based on these studies and subsequent work, full-scale MBBR systems were developed with different types of support media.

As illustrated in Figure 6-5, AOB and anammox bacteria are established within the biofilm. As shown in the photograph to the right, the biofilm is primarily located on the interstitial surface of the support media.

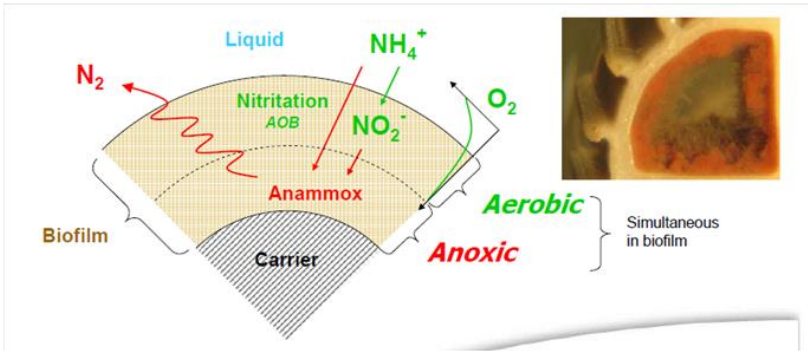

Figure 6-5. Deammonification in a Biofilm.
Courtesy AnoxKaldnes/Veolia.

6.3.1 DeAmmon®

The first deammonification MBBR system was designed and installed by Purac/Läckeby AB (Sweden) in Germany in 2001 in collaboration with the University of Hannover and the Ruhr River Association (Ruhrverband). Initially referred to as the Deammonification In Biofilms (DIB) process, the process tradename DeAmmon® was soon adopted. The process consists of a single- or dual-train reactor system with three stages per reactor. The stages are operated in series, but piping flexibility is provided to allow parallel operation. AnoxKaldnes K1 media (500 m^2 of active area per m^3) has been typically used to support biofilm growth and is added to each stage at a fill volume of 40-50%. To retain the media within each stage, screens are provided between stages. Internal recirculation from the third to the first stage may be required for very high strength streams to limit the ammonia concentration in the first stage.

Aeration is provided through medium to coarse bubble stainless steel diffusers and each zone is intermittently aerated to support the partial nitritation and anammox reactions. Aeration and anoxic times are adjusted to limit nitrite accumulation in the bulk liquid and restrict the growth of aerobic nitrite oxidizing bacteria. Aeration and anoxic times of 20-50 minutes and 10- 20 minutes, respectively, have been reported (Plaza et al., 2011; Thöle, 2007). A DO concentration of 3 mg/L during the aeration periods is considered appropriate for design and operation, but higher concentrations are avoided to prevent the potential for NOB growth and limit the time for DO depletion during the un-aerated phases. Mechanical mixers are provided to ensure well mixed conditions during non-aerated periods. Reactor pH is not controlled. On-line conductivity measurements were found to be a low-cost, effective tool for monitoring performance and making adjustments to the process operating conditions, e.g., duration of the aeration periods. An optimized energy consumption rate of 2.3 kWh/kg-N-removed was reported (Christensson et al., 2011).

The total media surface area requirement is based on the temperature-dependent specific surface deammonification rate assumed for the design condition. A maximum deammonification rate of 2 g-N/m^2•d at 28ºC and an average rate of 1.5 g-N/m^2•d at 27ºC were reported for a full-scale DeAmmon system using the AnoxKaldnes K1 media (Plaza et al., 2011). An inorganic nitrogen removal efficiency in the range of 70 to 85% has been reported over a temperature range of 25-30ºC (Plaza et al. 2011). Substantial deterioration in performance was observed at temperatures below 20˚C (Thöle, 2007). A design loading of approximately 0.6 kg-N/m^3-total-reactor-volume per day can be assumed with the K1 media at a fill volume of 40%.

Startup of a DeAmmon® system follows a strategy based on the observation that the establishment of heterotrophic growth on the media through the addition of an external organic carbon source in the early phase of the startup period enhances the initial appearance and proliferation of the anammox bacteria within the biofilm. Primary effluent was useful as carbon source and a source of dilution water to prevent high ammonium and nitrite concentrations in the reactor stages. As anammox activity increases, the dilution water and carbon source is reduced and eventually eliminated.

Removal of large inert solids from the sidestream through screening, gravity separation, or both may be required to prevent these materials from accumulating in the MBBR.

6.3.2 ANITA™Mox

A single-stage deammonification MBBR system under the trade name ANITA™Mox was developed by AnoxKaldnes/Veolia. Unlike DeAmmon, the ANITA™Mox reactor is continuously aerated and the dissolved oxygen concentration is controlled in the range of 0.5-1.5 mg/L. The DO set point is adjusted based on online reactor ammonium and nitrate concentration measurements to ensure NOB growth is being restricted. Due to the mixing energy provided by continuous aeration, mechanical mixing is not required. The reported energy consumption for the single-stage MBBR is 1.6-1.9 kWh/kg-N-removed (Christensson et al., 2011).

Studies conducted with different types of polypropylene media of various geometries and specific surface areas (Figure 6-6) showed that the MBBR volumetric removal rate could be increased through the use of media with a higher specific surface area (Lemaire, et. al., 2011). Using an AnoxKaldnes media under the trade name, BiofilmChip™M, which has an active surface area of 1,200 m^2/m^3, a volumetric ammonium-N removal rate up to 1.2 kg-N/m^3•d was demonstrated with a 40% media fill volume and a MBBR temperature range of 27-30ºC (Christensson et al., 2011). The corresponding specific surface area ammonium removal rate was approximately 3 g-N/m^2•d. However, due to the mixing energy required to maintain a well-mixed reactor when the BiofilmChip™M media is fully loaded, the K5 media with an active surface area of 800 m^2/m^3 was adopted in the design of the full-scale facilities at a 50% fill volume. Ammonium-N and total inorganic nitrogen removal efficiencies of approximately 90% and 80%, respectively, have been reported.

Figure 6-6. AnoxKaldnes Media Evaluated for ANITA™Mox.
BiofilmChip™M (1,200 m^2/m^3) – left; K3 (500 m^2/m^3) – middle; Anox™ K5 (800 m^2/m^3) – right.
Christensson, et. al., 2011.

Seeding the ANITA™Mox MBBR with a small fraction of media (2-3% of the media volume) with well-established anammox activity was found to significantly reduce the startup time from eight to ten months to four months. Feeding a new MBBR effluent from a fully active MBBR was also found to reduce the startup time to four to five months.

Screens are required for media retention and sidestream pretreatment to remove larger inert debris is recommended to limit accumulation of these materials in the MBBR. Medium to coarse bubble stainless steel air diffusers are used for aeration.

Aerobic pretreatment of the sidestream before ANITA™Mox may be required depending on the COD-to-N ratio of the influent.

6.3.3 TERRAMOX® Process

The TERRAMOX® process (also referred to as Terra-N® and Terrana®) was developed by E&P Anlagenbau GmbH (Germany) in collaboration with Clariant/SÜD-Chemie AG (Germany) where bentonite is used as the support media for biofilm growth. The process is designed as two-stage CSTRs with separate gravity clarification or as a SBR. The SÜD-Chemie product, TERRANA 510, was selected for this application. TERRANA 510 is a fine, grey powder manufactured by thermal activation of calcium bentonite (calcium montmorillonite), which is an aluminum silicate (58% SiO_2/18% Al_2O_3) containing small amounts of alkali and alkaline earth metal oxides (Fe_2O_3, CaO, MgO, Na_2O, K_2O). The product contains a wide range of particle sizes, with a mean in the range of 25 to 45 microns, and a mean surface area of 60 m^2/g. The active surface area for biofilm development is considerably less than 60 m^2/g, but no empirical data is readily available.

In a two-stage CSTR system, TERRANA 510 is added to the partial nitritation stage at a concentration of 10-12 g/L. With biomass attachment, the total suspended solids concentration is typically 15-20 g/L. In the second stage, granulation of the anammox bacteria eliminates the need for a support media. Second-stage biomass concentrations of 5-7 g/L have been reported. In a single-stage SBR, TERRANA 510 is also added at a concentration of 10-12 g/L.

Bentonite induces a very high solids settling rate and compact settled solids. A Sludge Volume Index (SVI) of 20 mL/gram has been reported. Due to high settling rates during the clarification step, loss of bentonite in the clarifier effluent is insignificant. However, bentonite will be lost with the wasted solids and must be replaced with fresh product.

Fine bubble diffusers are typically used for aeration. In a SBR design, intermittent aeration is applied and the aerobic/anoxic pattern is adjusted based on the ammonium loading to the system and the reactor performance. Aeration energy consumption of 1.5 kW-hr/kg of N-removed has been reported. Since mechanical mixing is required for the non-aerated periods and in the anammox stage of the two-stage process, the total energy per kg of N-removed will be higher.

Since the bentonite may serve to capture and retain sidestream suspended solids, a sidestream TSS limit is recommended, requiring a solids removal pretreatment step.

Many of the TERRAMOX® systems are retrofits of existing process tankage and operate at loading rates from 0.4 to 1.0 kg-N/m^3•d (Clariant/SÜD Chemie, 2012). With the SBR design, a loading rate up to 1.5 kg-N/m^3•d is possible. Inorganic nitrogen removal efficiencies in the range of 80-90% have been reported (Clariant/SÜD Chemie, 2012). Startup time for the SBR or the anammox stage of the two-stage process can be reduced to 60-90 days by seeding the reactors with anammox-enriched sludge from an existing full-scale system.

6.4 Rotating Biological Contactors

Rotating Biological Contactors (RBC) have been applied for leachate treatment in Europe where deammonification was demonstrated (Siegrist et al., 1998; Seyfried et al., 2001). The RBC systems vary in configuration and media material, but in the contactors where deammonification was providing 70-90% of the nitrogen removal across the treatment systems, the average surface specific deammonification rate was ~ 2.5 g-N/m^2•d, with peak rates up to 4.8 g-N/m^2•day. These values are consistent with the rates observed in the DeAmmon® and ANITA™Mox MBBR processes described above.

The typical bulk liquid DO concentration in the RBCs was 1 mg/L and the pH ranged from 7.3-8.8. Deammonification performance was stable at operating temperatures less than 20˚C and a nitrogen removal efficiency of 70% was reported at temperatures as low as 10˚C. No information is available on submergence depth or rotational velocity that induced deammonification performance.

RBCs have been adopted for a process train for treatment of source separated human wastes (black water) where the black water is anaerobically digested and the effluent with an ammonia-N concentration > 1,000 mg/L is subjected to deammonification with a RBC. DeSaH b.v. (the Netherlands) has installed two small deammonification RBC systems in Sneek (the Netherlands). The rotation speed is reported to be adjusted between 1 and 4 rpm to control the DO concentration between 0.6 and 0.65 mg/L and the pH control is provided through the addition of caustic soda (Lackner et al., 2014).

6.5 NAS® Process

The New Activated Sludge (NAS®) process was developed by Colsen International b.v. (the Netherlands) and was initially conceived as three and four-stages-in-series suspended growth processes with gravity clarification for treatment of anaerobically pretreated potato wastewaters. Process development focused on operating the first stage at a DO concentration in the range of 0.3 to 0.9 and providing SRT control to accumulate nitrite in the first stage, which would decrease the carbon requirement for nitrogen removal in the anoxic second stage. The third and third/fourth stages are utilized for polishing to complete ammonia, inorganic nitrogen, and COD removal. Internal mixed liquor recycles are provided; the configuration is dependent on the number of tanks in series and their functions. The growth of anammox in the second stage developed over time creating a hybrid nitritation-denitritation and deammonification process. The deammonification pathway is believed to be responsible for 70% of the nitrogen removed in the process.

In the next phase of process development, gravity sedimentation was replaced with membranes to allow higher mixed liquor solids concentrations and, hence, smaller reactor volumes. With membrane separation, the specific loading rates of the systems in design and in operation are 0.17-0.23 kg-N/m^3•d.

Colsen is adapting the NAS® technology to a single-stage SBR for treatment of municipal digester sidestream, which will have a design specific loading rate of 0.59 kg-N/m^3•d. Operating conditions and control methods were not disclosed.

6.6 SNAD Process

The occurrence of deammonification at the landfill leachate treatment facility in Tianwaitian, Taiwan, was discovered in 2008. In a collaborative effort between National Chiao Tung University (Taiwan) and Leaderman and Associates (Taiwan), the operator of the landfill leachate treatment system at Tianwaitian, the process was further characterized and the process name SNAD (Simultaneous partial Nitrification Anammox and Denitrification) was adopted.

The biological treatment system at Tianwaitian consists of two plug flow aeration tanks operated in parallel followed by gravity clarification. At an average ammonia-N loading rate of approximately 0.5 kg-N/m^3•d, deammonification was established through continuous aeration at a DO concentration in the range of 0.2 to 0.5 mg/L and under relatively warm operating

conditions (around 30˚C) and a SRT of 18 days. An ammonia removal efficiency of 80% was reported. One of the aeration basins has been retrofitted with hollow fiber membrane modules since 2008 to increase anammox retention and the SRT to improve the ammonia removal efficiency.

The SNAD process was subsequently replicated at the Keelung and Bali landfill leachate facilities in Taiwan. In a modification to the concept, spherical plastic media were added to the reactors at both facilities to determine if a hybrid biofilm – suspended growth system could provide better performance. Performance data from these facilities has not been reported.

6.7 Emerging Technologies

The applications of new deammonification processes for sidestream treatment are at various stages of implementation. The three processes selected for this section have been demonstrated on a pilot or small demonstration-scale. In two of the three cases, the processes are in design or construction at a full-scale.

6.7.1 ELAN®

The ELAN® (ELiminatión Autótrofa de Nitrógeno or autotrophic nitrogen removal) process was developed by the University of Santiago de Compostela in collaboration with Aqualia (Spain). The process is a granulated sludge SBR that is continuously aerated during the Fill/React phase of the SBR cycle. Similar to the Paques single-stage ANAMMOX® process, the nitritation and anammox reactions are occurring simultaneously within the thick granulated biomass. Since the process operates as a SBR, no liquid/solids separation module is required as in the ANAMMOX® design.

The control of the process is based on maintaining the DO concentration at approximately 1.5 mg/L and adjusting the nitrogen loading rate as needed to ensure a high and relatively stable load to the process. An average nitrogen removal rate of 0.8 kg-N/m^3•d was demonstrated in pilot-scale studies on sidestream derived from mesophilic co-digestion of treatment plant waste sludges and food industry wastes. Sludge concentrations up to 13 g/L are established in the reactor at full nitrogen loading, generating a granulated mass with a settling velocity greater than 5 m/h, a Sludge Volume Index (SVI) less than 40 mL/g-MLSS and an average granule diameter of approximately 3-mm. An inorganic nitrogen removal efficiency greater than 80% was demonstrated.

Based on the successful pilot reactor study, a full-scale dual-reactor system is in design for the Guillarei WWTP (Spain) at a specific loading rate of 0.6 kg-N/m^3•d. A second system is in design for treatment of effluent from a seafood cannery.

6.7.2 Cleargreen™

Cleargreen™ is a suspended growth deammonification SBR process developed by Degremont. A controls strategy was developed from pilot-scale studies where the SBR cycle consists of subcycles, each consisting of mixed-feed, aeration, and mixed-anoxic periods in sequence. During the aeration phase of each subcycle, the DO is controlled at approximately 0.5 mg/L. Online ammonia and nitrate measurements are used to monitor the process and make adjustments to the durations of the aerated and anoxic periods as needed to maintain performance. The intermittent feeding strategy is also believed to enhance NOB suppression by

providing peak free ammonia concentrations, particularly during the startup period when the reactor is brought into service.

Ammonia and inorganic nitrogen removal efficiencies of 96% and 86%, respectively, were demonstrated at specific loading rates up to 0.7 kg-N/m^3•d. Degremont further demonstrated that the reactors can be started up without a concentrated source of anammox bacteria, although it requires a longer startup period than a new reactor receiving seed sludge from an existing process.

Two full-scale Cleargreen™ systems are in construction at municipal treatment plants in Spain at design loading rates of 0.55 and 0.7 kg-N/m^3•d and are expected to be operational in 2015.

6.7.3 ANITA™Mox Integrated Fixed-Film Activated Sludge Process

In an advancement of the ANITA™Mox MBBR process (Section 6.3.2), Veolia modified the process into an Integrated Fixed-Film Activated Sludge (IFAS) configuration where a gravity clarifier is added and suspended solids are settled and returned to the reactor. In this configuration, the specific nitrogen removal rate (g-N/m^2-active surface area per day) increased two to four times the rate achieved in the MBBR configuration. The suspended biomass increased to the range of 2,000-4,000 mg/L and morphological examination of the suspended biomass and biofilm revealed that the majority of the AOB growth was occurring in the suspended biomass and anammox growth was remaining on the media. To limit NOB growth, the DO concentration setpoint was reduced from 0.5-1.5 mg/L to 0.2-0.6 mg/L.

With the K5 media (800 m^2/m^3) at a fill volume of 50%, nitrogen removal rates up to 3 kg-N/m^3-d were realized in the ANITA™Mox IFAS configuration. The volume in this calculation is based on the reactor volume. For comparison to the other deammonification processes, the volume of the clarifier would be added; thus, the removal rate per total system volume is less than this value.

Pending additional optimization work, the IFAS configuration may supplant the MBBR design as the preferred process if a smaller footprint requirement and lower capital and operations and maintenance costs are demonstrated.

6.8 Summary

Deammonification of high-strength dewatering return flows has been shown to be technically and economically feasible. Several technology options have been tested and commercialized to provide the appropriate environment and control to provide stable operation. Since 2001, approximately 100 full-scale deammonification units have been constructed, are being constructed, or are in design/planning phase. Some of the technologies have been in stable operation for many years; others are still emerging with few full-scale installations.

Commercial technologies use different approaches to accumulate sufficient slow-growing anammox biomass needed in the process. These processes differ in terms of the method to grow and retain the anammox bacteria, number of stages, the configuration of the process, and control strategies implemented. Configurations include granular sludge reactors, suspended growth SBRs, suspended growth reactors with gravity clarification, moving bed biofilm reactors, and rotating biological contactors. Process control strategies vary, but all require aeration control to sustain stable nitritation and limit NOB growth. Regardless of the technology, seeding a new

reactor with anammox-enriched biomass, either in suspension or in a biofilm, reduces the duration of the startup period.

As the cumulative experience with these technologies within the wastewater community continues to grow, these processes are becoming increasingly recognized as reliable processes that can provide a consistent treated effluent quality and deliver the promised energy and chemical savings.

CHAPTER 7.0

REDUCTION OF SIDESTREAM AMMONIA IN SOLIDS DIGESTION PROCESSES

Digestion processes that can reduce the inorganic nitrogen load in the dewatering sidestream are considered in this chapter. The focus is solely on the general characteristics and performances of these processes as it relates to nitrogen removal, although the impact of reducing the ammonia concentration in the dewatered biosolids on land application rates and other positive and negative consequences on plant operating and maintenance costs, solids processing and hauling, and biosolids quality certainly cannot be ignored when evaluating the viability of these processes at specific facilities. For a detailed discussion of anaerobic and aerobic digestion, readers should refer to Tchobanoglous et al. (2014).

Mesophilic aerobic digestion has been practiced for decades at many wastewater treatment plants with influent flows typically less than 5 mgd. During aerobic digestion, a portion of the ammonia released due to volatile solids destruction is nitrified, resulting in alkalinity destruction. To prevent a low operating pH as a result of nitrification and minimize aeration energy for volatile solids destruction, intermittent aeration can be applied to provide alternating aerobic and anoxic conditions for nitrification and denitrification or the digester can be continuously aerated at a low DO concentration to perform Simultaneous Nitrification-Denitrification (SND). The concept of nitrifying within aerobic digestion and using degradable volatile solids as a carbon source for nitrite and nitrate reduction to reduce the sidestream nitrogen load has been extended to second-stage aerobic digestion processes as discussed in the following sections.

7.1 Mesophilic Aerobic Digestion After Autothermal Thermophilic Aerobic Digestion (ATAD)

The use of second stage mesophilic aerobic digestion was first applied to the digestion of ATAD-digested solids. Initially, the second digestion step was developed through the aeration of tanks that store digested solids before they are dewatered to reduce odors and improve sludge dewaterability. By operating this second stage aeration process in an intermittent aeration mode, nitrification and denitrification is accomplished and additional volatile solids destruction is realized.

The most notable engineered process for this second stage mesophilic aerobic digestion step is the Storage Nitrification Denitrification Reactor (SNDR™) provided by Thermal Process Systems (USA). The SNDR is a completely mixed flow-through system with jet aeration to providing mixing and aeration. A HRT of 5-10 days has been used for existing sludge storage tanks, but a 6-day HRT is commonly used for new tank construction. Within this range of HRTs (SRTs), 10-15% additional volatile solids destruction and reduction of the inorganic nitrogen have been demonstrated. On a COD basis, the particulate COD destroyed in the SNDR process is sufficient to denitrify NOx-N to a high efficiency.

Similar to conventional single-stage aerobic digestion, intermittent aeration can be applied to provide the aerobic and anoxic periods for nitrification and denitrification or the process may be operated in SND mode. The use of Oxidation-Reduction Potential (ORP) for SND process control has proven effective. Nitritation-Denitritation is believed to be the primary nitrogen removal pathway, although sufficient particulate COD is available for denitrification or denitritation. Consequently, the aeration requirements are essentially equivalent regardless of the nitrogen removal pathway.

Although the aerobic digestion process can oxidize ammonia and removal inorganic nitrogen to high efficiencies, an elevated residual ammonia concentration of roughly 200 mg-N/L is typical to retain nutrient value if the dewatered biosolids are land applied. Thermal Process Systems have installed 38 SNDR™ systems in the U.S. and Canada.

7.2 Mesophilic Aerobic Digestion After Mesophilic Anaerobic Digestion

Volatile solids destruction and inorganic nitrogen removal have also been demonstrated in the aerobic digestion of solids from mesophilic anaerobic digesters. Commonly referred to as "Ana-Aer", sequential mesophilic anaerobic-aerobic sludge digestion has been applied at a full-scale where enhanced volatile solids destruction and inorganic nitrogen removal have been demonstrated. Four facilities worldwide have implemented this two-stage digestion process (two facilities claimed by Thermal Process Systems Inc. in the U.S.), the most notable of these plants being a facility in Austria (720,000 PE) where a four-stage aerobic digestion system with internal sludge recirculation of 300% was operated at an aerobic digester SRT (HRT) of ~ 6 days and with intermittent aeration. Approximately 16% additional volatile solids destruction is realized across the aerobic digestion process and an inorganic nitrogen removal efficiency greater than 95% via the nitritation-denitritation pathway was demonstrated (Parravicini et al., 2008). A four-stages-in-series aerobic digestion configuration with internal recycle is not a prerequisite for achieving this performance. This configuration was specific to the Austrian facility to overcome design limitations; similar performance could be accomplished in single-stage aerobic digesters in parallel with sufficient aeration, mixing and process controls.

7.3 Design and Economic Considerations

Heat generation is a consequence of all biological reactions and as substrate concentrations in a specific stream, whether it is digested sludge from ATAD or mesophilic processes or typical ammonia-rich dewatering recycle streams, the heat generated per unit stream volume increases. Therefore, an energy balance and potential inclusion of heat removal capabilities are design considerations for all of the separate biological processes described in this document, focusing primarily on the warm summer period when heat losses from the tanks are reduced. Since the degradable COD (soluble and particulate) and ammonia-N are highest in ATAD or mesophilic digested solids, the heat generation rate in the second-stage aerobic digester is anticipated to be considerably higher than the separate biological sidestream treatment processes described in Chapters 4.0, 5.0, and 6.0. The negative consequences of insufficient heat removal are an increase in aerobic digester temperature and substantial reduction in ammonia oxidation if the temperature is allowed to increase above 42˚C. This effect was experienced in the post-aerobic digestion process placed into service in late 2011 at the Spokane County Regional Water Reclamation Facility (U.S.) where the temperature of the covered aerobic digester exceeded the limit for stable nitrification, resulting in substantial reduction in inorganic nitrogen removal.

Economic considerations when comparing post-aerobic digestion to other sidestream treatment options should be examined on a plant-wide holistic basis. Post-aerobic digestion is anticipated to have higher energy costs in comparison to the other biological treatment options due to the oxygen requirement for volatile solids destruction and potentially lower standard oxygen transfer efficiency; however, this cost may be partially offset by reductions in polymer demand in the biosolids dewatering process and biosolids hauling cost, depending on site-specific conditions. The formation of struvite in the dewatering process and piping or channels that convey sidestream will also be greatly diminished since ammonia-N is reduced in the aerobic digester, which will reduce maintenance cost. Other benefits such as reduced biosolids odors should also be considered.

CHAPTER 8.0

PHYSIOCHEMICAL PROCESSES FOR AMMONIA RECOVERY AND DESTRUCTION

Ammonia-N exists in two primary forms in wastewater: ammonium (NH_4^+) and ammonia (NH_3), which is also commonly referred to as "un-ionized" or "free" ammonia. Un-ionized ammonia is a volatile compound that can be liberated from the wastewater, recovered, and concentrated in forms that allows its reuse as a fertilizer or in certain industrial applications. Un-ionized ammonia can also be combusted under certain conditions to generate power either through catalytic combustion to generate N_2 or through reforming to generate hydrogen, which can be directly combusted or fed to a fuel cell. A portion of the sidestream ammonium may be removed with an equivalent molar amount of phosphate to generate crystallized magnesium ammonium phosphate hexahydrate, or struvite, for reuse as a fertilizer. In this chapter, physiochemical processes for removal and recovery of ammonia from wastewater and the combustion of recovered ammonia are discussed. Products generated through the recovery of ammonia for reuse are discussed in Chapter 9.0.

8.1 Air Stripping and Acid Absorption

Stripping ammonia from sidestream with air involves the ammonium-ammonia equilibrium in the liquid phase, the transfer of ammonia from the sidestream to the air, and the mass transfer efficiencies associated with typical gas/liquid mass transfer equipment. Figure 8-1 illustrates the effect of temperature and pH on ammonium/ammonia equilibrium for an aqueous ammonia solution. As shown in Figure 8-1, as the temperature of the wastewater is raised, the equilibrium shifts towards ammonia-N, which result in an increased driving force for ammonia mass transfer from the liquid phase to the gas phase. Higher temperatures also increase the Henry's Law coefficient, which defines the ratio of the ammonia concentrations in the gas and liquid phases at equilibrium, and increases the ammonia diffusivities in water and air, which enhances mass transfer. Increasing the pH also dramatically shifts the chemical equilibrium from ammonium (NH_4^+) to ammonia (NH_3(aq)). At typical temperatures of digester recycle streams (30-38ºC), pH values of 11 or higher are recommended if high ammonia removal efficiency is required. Caustic soda and lime are typically used for adjusting the pH of the liquid stream before the air stripping column.

The air stripping – acid absorption technology has been used in industrial and municipal applications. Most notable in the municipal sector is the process at the VEAS facility (80 mgd) in Oslo, Norway, where ammonium nitrate has been produced since 1998 (Sagberg et al., 2006). While this technology has been rarely applied to high stream municipal sidestreams in North America, several processes have been in operation in Europe since the late 1980s with municipal digester sidestreams, manure digestion sidestreams, landfill leachate, and industrial wastewaters.

The ionic composition affects the chemical equilibrium illustrated in Figure 8-1. Ammonium exists in digester recycle streams as ammonium bicarbonate and there are other cations and anions also present in the water. Collectively, this ion mixture results in ion-ion interactions that affect the ammonium-ammonia equilibrium concentrations and, consequently,

the ammonia removal efficiency. In addition, a shift from ammonium to ammonia due to an increase in temperature would be accompanied by the shift of bicarbonate to CO_2 and release of CO_2 into the gas phase. A shift in pH through the addition of caustic soda or lime also results in reactions involving the CO_2-bicarbonate-carbonate species. Whether ammonia is generated by inducing a high temperature or pH, the CO_2-bicarbonate-carbonate reactions will affect the process conditions required to achieve the desired ammonia removal efficiency.

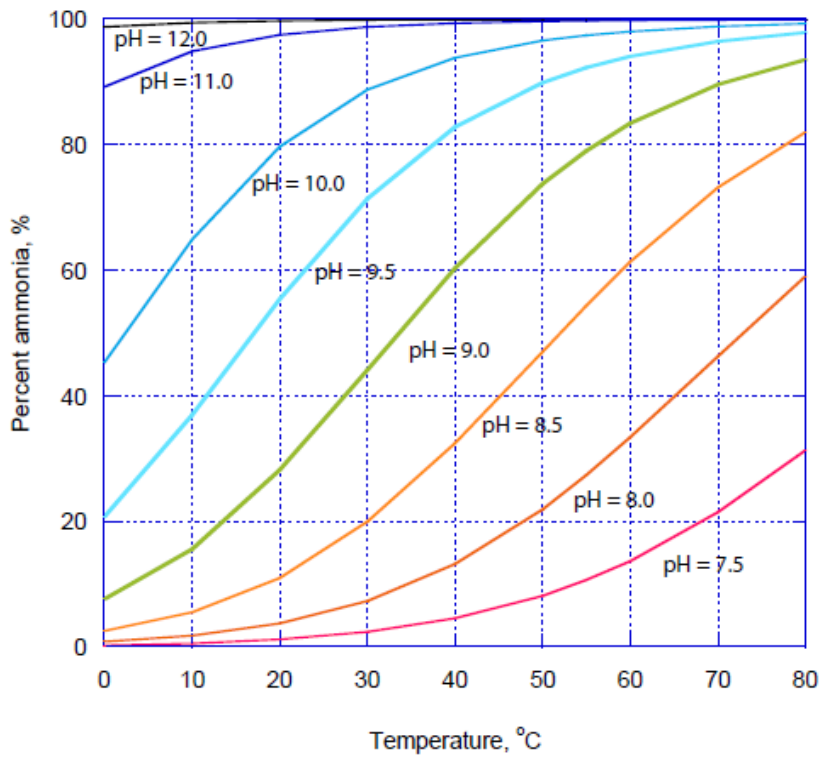

Figure 8-1. Fraction of Total Ammonium in the Form of Ammonia in Aqueous Ammonia at Various pH and Temperatures.

8.1.1 Process Configuration

The air stripping/acid absorption process consists of a stripper column and an absorber column, containing random dumped media, typically the Rauschert HiFlow media, and a closed air system where air blown through the stripper column is sent to the absorber and air from the top of the absorber flows to the inlet of the fan. A flow diagram for the process is presented in Figure 8-2. Sizing of the two columns, the fan, and product recirculation pump is based on the liquid stream flow rate, ammonia concentration, and the operating conditions in the stripper column (pH, temperature). The air stripping/acid absorption process is typically controlled by a pH setpoint and ammonium sulfate is withdrawn from the system as blowdown to maintain the driving force for ammonia into the acid solution.

In the absorber column, the acid is dosed into the product solution recirculation loop to maintain a pH setpoint that allows sufficient driving force for absorption. The product solution is continuously removed from the bottom of the column and water is continuously added to provide the desired product concentration of 35-40 wt%. The real-time measurement of the density of the product solution in the recirculation loop is also used for fine-tuning acid addition and product removal. Due to the addition of concentrated sulfuric acid (93 wt%) to the recirculated solution and the subsequent formation of ammonium sulfate, chemical heat is generated. A portion of this heat can be used to elevate the temperature of both columns. The direct addition of low pressure steam to the stripping column can also be done if higher operating temperatures are desired.

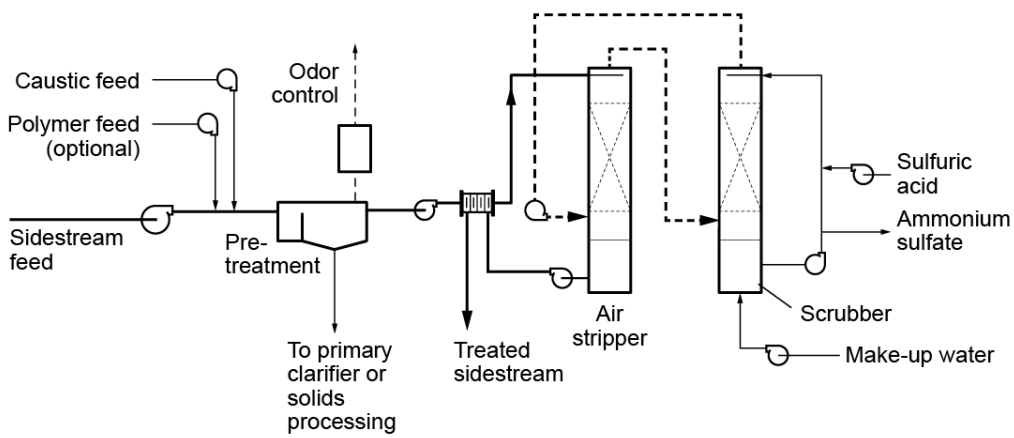

Figure 8-2. Air Stripping/Acid Absorption Process Flow Diagram.

8.1.2 Chemical Requirements for Ammonia Stripping

Caustic soda (sodium hydroxide) and lime have been used in practice for adjusting the pH of digestion sidestream. The two primary reactions that govern the caustic soda requirement are:

$$NH_4HCO_3 + NaOH \rightarrow NH_3 + H_2O + NaHCO_3 \qquad \text{(Equation 8-1)}$$

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad \text{(Equation 8-2)}$$

Due to the solubility of sodium carbonate, the pH-adjusted sidestream contains a significant buffering capacity, allowing the air stripping column to operate at the desired pH throughout the column depth. For wastewater treatment facilities that require alkalinity addition

to sustain nitrification, the sidestream processed by air stripping – acid absorption where caustic soda is used for pH adjustment can provide a portion or the entire alkalinity requirement for the secondary treatment system. Because the cost of caustic soda is a significant portion of the operating cost for an air stripping-acid absorption process, assuming partial or total credit for the alkalinity provided to the secondary treatment system is an important economic consideration.

Alternatively, lime (CaO) can be used for pH adjustment. The primary benefit of lime is the significantly lower cost compared to caustic soda. However, lime removes carbonate alkalinity through precipitation as calcium carbonate. If a beneficial use of the calcium carbonate cannot be found (e.g., beneficially land applied as "Farmer's Lime"), disposal of the solids may result in an additional operating cost, offsetting the cost advantage lime has over caustic soda.

The substantial loss in buffering capacity via carbonate removal results in a decreasing pH gradient through the depth of the air stripping column as ammonia is stripped from the sidestream, reducing the effectiveness of the lower section of the column. The use of lime also has the disadvantage of increasing the air stripping column fouling rate, thereby increasing the frequency at which the air stripping column is removed from service for cleaning.

8.1.3 Chemical Requirements for Absorption

Ammonia stripped from the liquid stream is absorbed into an acidic solution to generate a soluble ammonium salt. Sulfuric acid is the least expensive and most commonly used, but other types of acids could also be used such as:

- Phosphoric acid - produces mono-ammonium phosphate (MAP) or di-ammonium phosphate (DAP).
- Hydrochloric acid - produces ammonium chloride (NH_4Cl).
- Acetic acid - produces ammonium acetate ($NH_4C_2H_3O_2$).
- Nitric acid - produces ammonium nitrate (NH_4NO_3).

The selection of the acid is driven by local or regional demand for the resulting product and if revenue can be realized from its sale. However, ammonium sulfate [$(NH_4)_2SO_4$] is the dominant product of choice from air stripping/acid absorption processes currently in practice, largely driven by chemical cost and market demand.

8.1.4 Pretreatment Requirement

Sidestreams from digestion processes contains suspended solids, which can cause significant fouling in the air stripping column. During pH adjustment, carbonate and phosphate precipitates will form, although the solids mass generated by pH adjustment with caustic soda will be far less than the amount of chemical sludge generated by lime. To reduce the negative impact of the suspended solids on the air stripping column, a solids reduction step is required. If lime is used for pH adjustment, the solids removal process is essentially conventional cold lime softening, which is commonly practiced in water treatment.

Solids production from pretreatment requires processing and disposal, which increase the operating cost for the process.

8.1.5 Product Crystallization

Crystallizers have been used to produce ammonium sulfate crystal from the solution, mainly in industrial applications such as nylon industry where a large amount of ammonium sulfate is generated as a byproduct. While crystallization is viable for large industrial processes to reduce storage and shipping cost and provide a more flexible product for the fertilizer market, for small production sites such as municipal wastewater treatment plants, the cost and operational complexities of crystallization have been difficult to justify.

8.1.6 Blending AS with Biosolids

If biosolids are beneficially re-used, the 40 wt percent ammonium sulfate (AS) solution can be mixed with the dewatered solids to enhance its N and S content. However, there are several potential concerns with this approach:

- Increased solids mass will result from the blending of 40% by weight AS solution with the biosolids, thereby increasing the hauling costs.
- Land application rate: Biosolids are land applied an agronomic rate based on nitrogen content. Because the nutrient content will be higher, the acreage needed will be larger.
- Increased potential for hydrogen sulfide odors: Because the solution has a high level of sulfate, there is a potential to generate hydrogen sulfide if the mixed biosolids becomes anaerobic during storage. However, a study has shown that p-cresol, an odorous compound, was reduced when sulfate was added to the biosolids cake (unpublished).

8.1.7 Economic Considerations

As discussed in the overview of the air stripping – acid absorption process, 93% sulfuric acid is typically used in the absorption column and caustic soda or lime is used for pH adjustment of the digestion sidesteam. Because these chemicals represent a major operating cost, the future pricing trends of these chemicals is critically important information to obtain to assess the economic viability of this process, in comparison to biological treatment.

To offset the costs of the caustic soda or lime and the acid, selling the product to generate revenue will improve the economics of ammonia recovery. A discussion of the use of the AS product as a fertilizer is provided in Section 9.1.

8.2 Air Stripping with Thermal Destruction of Ammonia

As an alternative to capturing the stripped ammonia to produce ammonium sulfate, the ammonia-laden air from the air stripping column can be subjected to thermal catalytic oxidation (TCO). Air stripper/TCO has been rarely practiced. The most notable applications are landfill leachate treatment systems in Hong Kong (Organics Limited, www.organics.com).

8.2.1 Process Description

The ammonia-laden air from the stripper is subjected to thermal catalytic oxidation (air stripper/TCO; Figure 8-3) where up to 98% of the ammonia is selectively oxidized to N_2 (typically ~ 95% selectivity) with the balance of the oxidation products primarily being N_2O or NO, depending on the catalyst temperature.

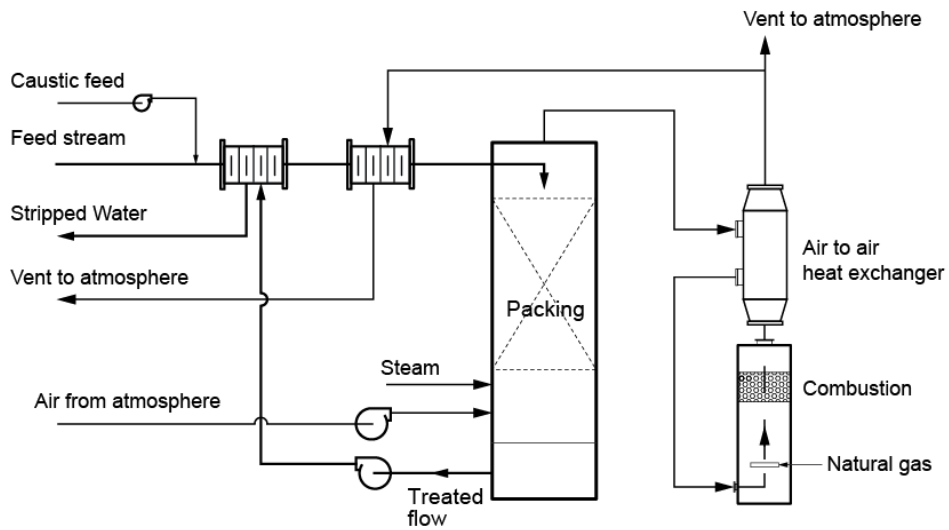

Figure 8-3. Air Stripping – Thermocatalytic Oxidation Process for Ammonia Removal and Combustion.

The air stripping column is operated similarly to the column in the air stripping/acid absorption process, only the air is single-pass ambient air that must be heated via steam injection to compensate for evaporative cooling of the column to maintain the desired temperature. The ammonia-laden air is then subjected to oxidation at temperatures in the range of 550-600ºF with a catalyst typically composed of mixtures of transition metals or transition metal oxides on silica or alumina supports and doped with a noble metal such as platinum. The reaction is exothermic (generates heat), reducing or eliminating the natural gas input to the oxidizer required to sustain the target temperature. The primary reactions of interest in this process are:

$$NH_3 + 0.75\ O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O \qquad \text{(Equation 8-3)}$$

$$NH_3 + O_2 \rightarrow 0.5\ N_2O + 1.5\ H_2O \qquad \text{(Equation 8-4)}$$

$$NH_3 + 1.25\ O_2 \rightarrow NO + 1.5\ H_2O \qquad \text{(Equation 8-5)}$$

Temperatures above 350ºC (660ºF) are avoided to limit the formation of NO2. Even when operating within the desired temperature range, a certain portion of the ammonia will convert to NO, which must be reduced by Selective Catalytic Reduction (SCR). Un-oxidized

ammonia will react with NO in the downstream SCR, but there is likely a need for supplemental addition of urea or anhydrous ammonia to maximize NO removal.

When chemical and energy costs are considered, the optimum operating temperature of the air stripping column is above 70ºC. At high operating temperatures, ammonium bicarbonate is partially or entirely decomposed into ammonia and carbon dioxide, thereby minimizing or eliminating the need for caustic soda or lime. The air flow required to strip ammonia from the sidestream is also reduced, which provides a higher ammonia concentration in the column outlet air to the TCO. Since sidestreams from anaerobic digestion contain acetate, partial volatilization of acetic acid likely occurs, although combustion in the TCO is unlikely where the catalyst and operating conditions are specifically designed for selective combustion of ammonia to N_2. Consequently, acetic acid and other low molecular weight volatile compounds would remain in the stack exhaust and increase volatile organic compound (VOC) emissions from the facility. Volatilization of reduced sulfur compounds, particularly H_2S, and volatile organic siloxanes is also expected, which may cause gradual fouling and deactivation of the TCO catalyst, depending on their concentrations.

Since the stripping column uses one-pass ambient air, the relatively dry, colder inlet air induced evaporative cooling of the filtrate. Hence, the energy required to operate the air stripping column includes sensible heat and the latent heat of water vaporization. Low pressure steam is directly injected into the air stripping column to satisfy this energy requirement. As shown in Figure 8-3, a portion of the exhaust air can be used to preheat filtrate to reduce the steam requirement, upper limit to this energy recovery step being the condensation temperature for the stack exhaust. Steam demand is also reduced by also preheating the sidestream influent with sidestream effluent from the stripping column.

The heat released by the catalyzed oxidation of ammonium to N_2 is not sufficient to increase the stripping column outlet air temperature to the desired setpoint of 600ºF in the TCO. An air-to-air heat exchanger is provided to heat the column outlet air to ~ 300ºF with exhaust air from the TCO. The heat exchanger is designed such that the temperature of the air to the inlet of the TCO is less than the setpoint (a design feature to account for potential variability in the ammonia concentration in the stripping column outlet air) and natural gas is injected and combusted at the thermal oxidizer inlet to provide TCO temperature control.

8.3 Thermoenergy Ammonia Recovery Process: Vacuum Flash Distillation

The proprietary Thermoenergy/Castion Ammonia Recovery Process (ARP) is an alternative to the air stripping and steam stripping technologies. The process is based on elevating the filtrate temperature to thermally decompose ammonium bicarbonate into ammonia and carbon dioxide and subjecting the stream to a vacuum to volatilize ammonia for recovery.

In the initial form of ARP, the process was operated at typical digester recycle stream temperatures (35ºC); therefore, the pH was increased to 11 or higher with caustic soda to achieve a high removal efficiency. After further developmental work, the process was changed to a high temperature operation (80-85ºC) to thermally decompose ammonium bicarbonate to ammonia and carbon dioxide, similar to the steam stripping process, to reduce caustic soda consumption.

The treatment train includes a pretreatment process, flow equalization tanks, vacuum distillation units (“R-CAST” units), product concentrator vacuum units (“CAST”), and chemical storage. In the pretreatment process, the filtrate is screened to ensure no large debris enters the

downstream processes. The pH is adjusted to the target for ammonia recovery and suspended solids are reduced via gravity settling or an enhanced clarification process. The pH-adjusted influent is pumped to an equalization tank from which influent is distributed to multiple R-CAST units where ammonia is removed. Each R-CAST unit consists of a cylindrical vessel with a vacuum zone and bottom liquid well. The high pH stream is recirculated from the bottom well, through a heat exchanger and to the inlet of a spray nozzle located in the top section of the vessel. The stream is dispersed through the nozzle into the vacuum zone, where a vacuum pressure is maintained with a venturi or liquid ring vacuum pump. Under this reduced pressure and elevated operating temperature, ammonia, CO_2, and water volatilize into the gas phase, along with trace amounts of volatile compounds (e.g., methane). The sprayed filtrate drops to the bottom liquid well of the vacuum vessel where it is circulated back to the spray nozzle. The batch processing continues over 5-10 minutes, typically, until the filtrate ammonia-N concentration decreases to the desired level.

The low pressure gas from each R-CAST unit is cooled in a heat exchanger and condensed to form an ammonium bicarbonate solution. The “condensate” is subsequently contacted with sulfuric acid to form an ammonium sulfate solution; carbon dioxide is liberated from the dilute product solution and vented to the atmosphere. During each batch processing period, the water mass volatilized with the ammonia far exceeds the amount needed to produce the targeted 40 wt% ammonium sulfate solution. The diluted ammonium sulfate solution is processed further with a secondary ARP system referred to as a “concentrator” or “CAST” where water is volatilized from the solution with heat addition to produce a final ammonium sulfate concentration of 40 wt%.

Despite the use of recuperative heat recovery via the preheating of the pH-adjusted influent with warm treated effluent, significant energy is consumed by the process, the majority of which is to drive water evaporation in the R-CAST units and R-CAST product concentrators. Hot water or steam serves as the energy source for the numerous heat exchangers required to run the process at the target operating temperatures.

A large ARP facility was planned for the 26th Ward plant in Brooklyn, NY, but the project was cancelled in late 2012. The facility was to process approximately 1.2 mgd of centrate at an ammonia-N concentration of 500 to 800 mg/L. Two small systems were designed and built for industrial applications. One of the processes is located at a power plant in Indonesia. The location of the second system was not disclosed.

8.4 Removal of Ammonia from Digester Sidestream by Steam Stripping

The use of steam to volatilize ammonia from water is practiced at several industrial installations, but, for municipal wastewater sidestreams, the implementation of steam stripping has been limited, with the only performance data reported from pilot or demonstration-scale studies (Teichgräber and Stein, 1994; Gopalakrishnan et al., 2000).

In the steam stripping process (Figure 8-4), low pressure steam increases the operating temperature above 90ºC resulting in the thermal decomposition of the ammonium bicarbonate into ammonia and carbon dioxide and, therefore, complete elimination of caustic or lime addition. Carbon dioxide can be removed from the filtrate in a "decarbonization" step before the ammonia stripping column by taking advantage of the higher volatility of the carbon dioxide at elevated temperatures (not shown) or the CO2 can be separated in the overhead condenser by controlling the condensate temperature at a level that limits CO2 absorption. Separation of the CO2 from the ammonia is essential since ammonium bicarbonate would simply reform in the downstream equipment. The CO2 vent contains odorous compounds, thus requiring odor abatement. From the decarbonization column, the filtrate, now at a pH of 9.5 or higher due to the liberation of CO2, enters the stripping column where ammonia is removed. The overhead from the stripping column is condensed and may be further processed by distillation (rectification) to yield an industrial grade product (20% ammonia). Sulfuric acid can also be added to the concentrated ammonia to produce ammonium sulfate if desired. Although the use of caustic soda is not a requirement for the process, the addition of some caustic to maintain a consistent pH throughout the distillation column was found to increase performance and reduce the steam requirement.

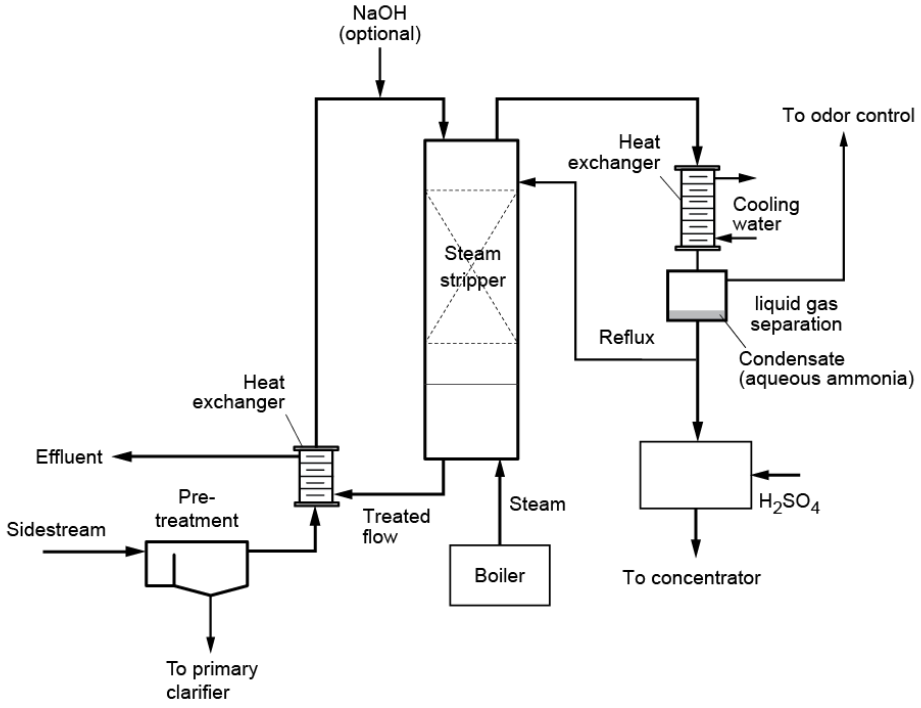

Figure 8-4. Steam Stripping Process for Removal and Recovery of Ammonia from Sidestream.

At the elevated operating temperature, volatile organic compounds will transfer into the steam as indicated by the COD content of the product (Teichgräber and Stein, 1994). The potential presence of VFA and other organic compounds in the aqueous ammonia or ammonium sulfate product would present difficulties in marketing these products if they do not conform to established product purity specifications.

Operating problems that have been encountered with steam stripping include: 1) extensive fouling (iron deposits, for example) within the heat exchanger and in the stripper due to the presence of waste constituents at elevated temperatures, 2) maintaining the required pH for effective stripping, 3) controlling the steam flow, and 4) maintaining the stripping tower temperature. Because of the importance of temperature, steam stripping should be carried out in enclosed facilities. Spiral wound heat exchangers have proven to be effective. In Europe, an acid wash is used to clean the piping, the heat exchanger, and the stripping column.

Approximately 0.15 to 0.18 kg of low pressure steam is required per kg of sidestream to achieve a stripped sidestream ammonia concentration of approximately 100 mg-N/L, if energy is recovered from the stripped sidestream to pre-heat the sidestream influent. The steam demand will be lower if CO_2 is removed from the pre-heated sidestream in a decarbonization step. Additional energy is consumed to process the low strength aqueous ammonia to a higher concentration or to produce higher strength ammonium sulfate for reuse.

8.5 Gas Transfer Membrane/Membrane Contactor

Membrana (a division of Celgard LLC) provides a gas transfer membrane (GTM) technology called Liqui-Cel, which utilizes hydrophobic hollow fiber membranes to transfer dissolved gasses such as O_2, CO_2, N_2, or ammonia from a liquid stream to either a gas or a different liquid on the other side of the membrane. Also referred to a “membrane contactor”, this membrane technology is commonly used in industrial water applications for the removal of dissolved oxygen and carbon dioxide from water. As illustrated in Figure 8-5, the Liqui-Cel membrane module consists of a bundle of hollow fibers contained in a cylindrical casing. On the “shell side” of the contactor, the wastewater flows across the fibers through a circuitous route induced by an inner baffle. In a countercurrent flow, the gas or liquid that is inducing the dissolved gasses to diffuse across the gas-filled microporous wall of the hollow fibers is pumped through the hollow fibers. In the case of ammonia-N removal, free ammonia is the species that diffuses across the membrane; therefore, similar to air stripping or the Thermoenergy ARP process, the pH of the wastewater (filtrate) must be increased over 10, preferably to 11-12, to shift the equilibrium from ammonium to ammonia in order to maximize ammonia removal. To induce the ammonia to diffuse across the hollow fiber membranes, an acidic ammonium sulfate solution is recirculated through the fibers (Figure 8-5). Also similar to air stripping and the Thermoenergy ARP process, high ammonia concentrations and temperatures are preferred since mass transfer rates are concentration and temperature dependent.

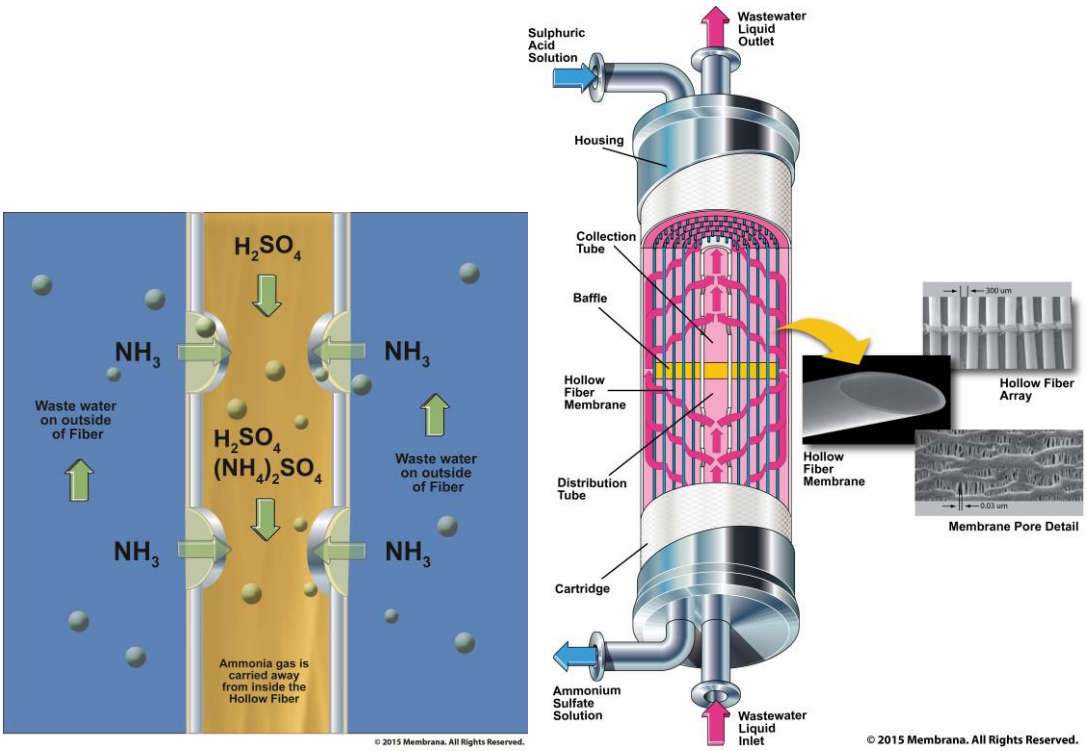

Figure 8-5. Gas Transfer Membrane for the Removal of Ammonia (Membrana Liqui-Cel Membrane Contactor).

The most significant disadvantage of GTM for wastewater applications is the pre-cleaning requirements. The feed stream should be extensively pretreated to remove suspended solids, colloidal material, and hardness to prevent the membrane from fouling with organic material and inorganic precipitates (e.g., $CaCO_3$). The minimum requirement for the feed water is pre-filtering with 10 µm, according to Membrana. However, microfiltration, perhaps even ultrafiltration, is advisable after the initial filtration step to remove colloidal materials from the filtrate.

There is at least one installation of a Liqui-Cel system for ammonia removal from a chemical industry wastewater. The system was designed and installed in 2002, treating a 44 gpm wastewater stream with an incoming ammonia concentration of 1,100 mg/L. The reported ammonia removal was 95%.

Pilot studies in Denmark were reported by du Preez et al. (2005). In this work, pig manure was processed with a thermophilic digester coupled with an ultrafiltration membrane to separate the digested manure from the liquid. The ammonia-laden permeate was then subjected to lime treatment to remove carbonate and phosphate and increase the pH. After gravity separation of the chemical precipitates, the high pH filtrate was pumped to a contact membrane provided by Microdyn-Nadir Gmbh. Similar in structure to the Liqui-Cel membrane shown in Figure 8-5, the contact membrane module was operated over a range of temperatures and pH to assess the ammonia transfer rate, with an acidic ammonium sulfate solution providing the driving force for mass transfer across the polypropylene hollow fiber membranes. Unlike Liqui-Cel, the investigators pumped the filtrate through the hollow fibers and the product solution was on the shell-side of the membrane. Removal efficiencies up to 99.9% were reported. Despite the performance of this recovery process, air stripping/acid absorption is currently preferred over

membrane contactors in these manure digestion applications due to the lower maintenance requirements. Research with membrane contactors continues in an effort to optimize the process and reduce maintenance, which is primarily membrane cleaning.

8.6 Crystallization and Recovery of Magnesium Ammonium Phosphate Hexahydrate (Struvite)

Magnesium ammonium phosphate hexahydrate, commonly known as struvite, has limited water solubility and forms encrustations in anaerobic digester outlet structures and downstream processes (dewatering equipment, pipes conveying the dewatering recycle stream) causing significant operational and maintenance problems. In recent years, phosphorus recovery processes have been developed to form struvite from sidestream and anaerobically digested sludge under controlled conditions and produce a crystallized product with sufficient purity and physical characteristics that it qualifies for reuse as a fertilizer. Although the development of these struvite crystallization processes arose from a need to address problems associated with uncontrolled struvite formation in municipal treatment plants, these processes have been adopted for phosphorus recovery from industrial wastewaters.

The basic stoichiometry of the struvite precipitation reaction is as follows:

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \bullet 6H_2O \qquad \text{(Equation 8-6)}$$

Although the primary focus of this report is on sidestream nitrogen removal, struvite crystallization processes are included in the discussion of physiochemical processes since the equation shown above indicates that for every mole of phosphorus that is recovered in the form of struvite, one mole of ammonium-N is also removed. On a mass basis, approximately 0.45 kg of ammonium-N is removed for every kilogram of phosphorus-P. Typically, magnesium is not present in municipal wastewater or in an anaerobic sludge digester at a concentration that allows struvite formation at a high level; therefore, the addition of a magnesium salt is required for high phosphorus removal efficiency and is a common feature of all of the processes that have been developed for struvite crystallization and recovery. In addition to magnesium, the pH, hydrodynamic conditions and struvite retention time within the crystallizer must be controlled to optimize phosphate removal and generate a product of sufficient size that can be separated easily from the wastewater.

As shown below, at least nine struvite crystallization technologies have been developed and implemented at a full scale. More than forty processes are in operation, design or construction, with more technologies in development at a pilot scale.

- NuReSys® Process – Two-stage complete mixed process marketed by Nutrient Recovery Systems bvba (Waregem, BE).
- ANPHOS® Process – Two-stage complete mixed process marketed by Colsen International bv (Hulst, NL).
- Cone-Shaped Reactor – Upflow fluidized bed crystallizer marketed by Multiform Harvest Inc. (Seattle, WA, US).
- Pearl® Process – Upflow fluidized bed crystallizer marketed by Ostara Nutrient Recovery Technologies, Inc. (Vancouver, BC, CA).

- PHOSPAQ™ – Aerated bioreactor and crystallizer marketed by Paques bv (Balk, NL).
- REPHOS® - Two-stage process marketed by Remondis Aqua GmbH (DE).
- Crystalactor® – Upflow fluidized bed crystallizer marketed by Royal HaskoningDHV (Amersfoort, NL).
- Airprex® Process – Two-stage aerated crystallizer marketed by Centrisys/CNP (Kenosha, WI, US) and PCS GmbH (Hamburg, DE).
- Phosnix® Process – Upflow and aerated fluidized bed crystallizer marketed by Unitika Ltd. (JP).

Descriptions of these technologies, performance information and process requirements can be found in other WERF project Towards a Renewable Future: Assessing Resource Recovery as a Viable Treatment Alternative (NTRY1R12), specifically focused on phosphorus recovery.

8.7 Synergies Between Solids Processing and Nutrient Recovery

Physiochemical processes for ammonia removal are dependent on conditions that induce the diffusion of un-ionized ammonia through the laminar liquid boundary layer at the liquid-gas interface, the liquid-gas interface surface area, the difference between the actual ammonia concentration in the gaseous phase and the concentration at equilibrium under the conditions in which the process is operated, and the turbulence near or at the liquid-gas interface. Where ammonia is removed through struvite crystallization, the driving force for struvite formation is dependent on the degree of supersaturation of ammonium, phosphate, and magnesium and complex mass transfer conditions that control diffusion of the principal constituents to the surface of the developing struvite crystals, the type and size of the crystals and where these crystals are formed within a given process.

A common denominator in these processes is the dependence on concentration to drive the processes at a rate that is practical from a capital and operating cost perspective. Hence, a digester or sidestream ammonium concentration of 3,000 mg/L will provide a greater driving force or potential for recovery than 800 mg/L where a practical limit for the effluent from a physiochemical process is around 150-200 mg/L. In the case of struvite formation, a high digester ammonium concentration is commonly associated with higher pH, which creates an additional driving force for struvite formation by increasing the concentration of trivalent phosphate (PO_4^{3-}). A higher digester ammonium concentration is also associated with a higher ortho-phosphate concentration since the solids being digested contain both N and P, thereby further increasing the potential for struvite formation.

A synergistic effect between digestion and nutrient recovery can be created by operating the solids digestion process under conditions that provide high ammonium and ortho-phosphate concentrations. For example, through solids pretreatment by thermal hydrolysis, the total solids concentration fed to anaerobic digesters can be increased to 9-11%, creating digester conditions where the ammonium is greater than 2,000 mg/L, the ortho-phosphate is released in the bulk liquid in the hundreds of milligrams per liter and the pH is above 7.5. The phosphorus concentration can be driven higher if enhanced biological phosphorus removal is being performed in the secondary treatment process. Although the potential for struvite formation in the digester, biosolids dewatering process, and the pipe that conveys sidestream is a cause for

concern for plant operators, there is growing interest in process designs that take advantage of this nutrient recovery potential, while reducing the maintenance cost associated with removing struvite from equipment impaired by its formation. Readers should refer to the WERF project NTRY1R12, Towards a Renewable Future: Assessing Resource Recovery as a Viable Treatment Alternative, on phosphorus recovery technologies for detailed discussion on this topic.

8.8 Emerging Technologies and Applications

The technologies described in this report are fully developed and applied at full scale at WWTPs and other industries. The emerging technologies described in this section are still in developmental phase at a pilot-scale and require demonstration in full-scale installations.

8.8.1 Ammonia Electrolysis

The emerging science of ammonia-to-energy has led to the development of electrocatalytic processes that reform ammonia to N_2 and H_2 directly from the wastewater (Vitse et al., 2005; Bonnin et al., 2008). In its simplest form as illustrated in Figure 8-6, the electrolyzer consists of two-compartment electrolytic cell immersed in a tank. One compartment contains an anodic electrode and the second compartment contains the cathodic electrode. The anodic and cathodic are physically separated by a conductive polypropylene membrane that allow separate collection of the N_2 and H_2, but yet allows the passage of hydroxide from the cathode to the anode.

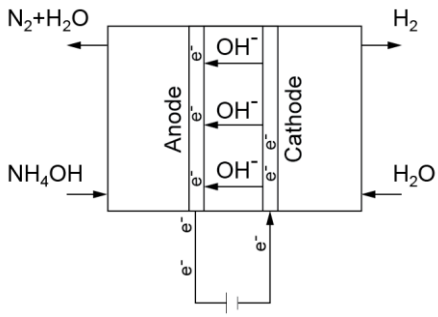

Figure 8-6. Electrolytic Conversion of Free Ammonia (NH_3) to Nitrogen and Hydrogen.

In the first compartment, the wastewater is contacted with an anodic catalyst consisting of a Ruthinium-Platinum-Iridium (Ru-Pt-Ir) composite on a support media, resulting in the following reaction.

Anodic Reaction

$$2\ NH_3(aq) + 6\ OH^-(aq) \rightarrow N_2(g) + 6\ H_2O(l) + 6\ e^-,\ E0 = -0.77V$$

(vs. standard H_2 electrode) (Equation 8-7)

At the cathode in the second compartment, water is reduced to H_2 and hydroxide according to the following reaction:

Cathodic Reaction

$$6\ H_2O(l) + 6\ e^- \rightarrow 3\ H_2(g) + 6\ OH^-(aq),\ E0 = -0.82V$$

(vs. standard H_2 electrode) (Equation 8-8)

To drive the reactions, a potential of 0.059 V is applied to the electrolytic cell. Hydroxide provided by the potassium hydroxide solution that fills the space between the anode and the membrane and the membrane and the cathode is consumed at the anode, but is replenished by production at the cathode. Overall, the energy consumed by the electrolytic process is 1.55 kWh/kg H_2. The H_2 liberated from the wastewater can be catalytically reacted with pure oxygen in a fuel cell to produce power or sent to a boiler or a combined heat and power facility and co-combusted with natural gas or digester gas to generate additional energy.

The limited data from bench-scale studies indicate that the process produces more power than it consumes, but the anticipated equipment cost for a full-scale system is likely to be considerably higher than other physical/chemical processes since the catalysts used in ammonia electrolysis contain expensive noble metals. Also, the rate of hydrogen production is dependent on the wastewater pH since ammonia is the primary reactant at the catalyst surface; therefore, caustic soda or lime addition is required. Pretreatment of the wastewater to remove solids and chemical foulants is also advisable to limit fouling of the catalyst surface and to maximize the life of the catalyst.

E3 Clean Technologies, a startup company associated with Ohio University (Athens, OH), markets ammonia electrolyzers, but to date their work has been limited to bench-scale and small demonstration-scale units. Acta S.p.A., a catalyst developer and renewable energy company based in Pisa, Italy, has also been very active in this field, but to date there have been no full-scale wastewater applications. Their work is primarily focused on the electrocatalytic conversion of gaseous anhydrous ammonia to hydrogen.

While the conceptual idea of generating hydrogen from ammonia is appealing from a sustainability viewpoint, ammonia electrolysis remains in an embryonic state of development. The technology merits future monitoring as product developers continue to improve the anode and cathode catalysts, reduce the noble metal content and look at alternative operating conditions that reduce chemical consumption (e.g., high operating temperatures to thermally decompose ammonium bicarbonate).

8.8.2 Sequential Phosphate and Ammonia Recovery

The lack of economic advantages for ammonia recovery and reuse has historically limited the adoption of physiochemical processes for sidestream treatment. However, the growth of phosphorus recovery processes to produce struvite and the number of full-scale facilities and their particular economic drivers (discussed further in Chapter 9.0) have stimulated interest in nutrient recovery, research and a general reassessment of the role of nutrient recovery for sidestream treatment.

Phosphorus recovery as struvite followed by ammonia recovery has been considered. Since struvite crystallization processes generally require an increase in sidestream pH above 8.0, along with the addition of a magnesium salt, to create conditions for optimum struvite formation, this increase in pH partially contributes to the increase in pH required for ammonia removal. The formation and removal of struvite from sidestream before further processing for ammonia recovery also reduces inorganic fouling potential in the downstream ammonia removal process equipment.

An example of sequential struvite-ammonia recovery is the dual crystallization processes proposed by EkoBalans Fenix AB (Lund, SE; www.ekobalans.se) for sidestreams from the

anaerobic digestion of municipal sludge, manures, and source separated organics. In this proposed scheme, a two-stage struvite crystallization process (air stripping to remove CO_2 and increase pH; followed by a completely stirred crystallizer) is followed by an air stripping/acid absorption process to remove ammonia and recover it as ammonium sulfate. In their particular process scheme, the acid absorber is a fluidized bed crystallizer where ammonium sulfate is formed directly in a crystallized form. The recovered struvite and ammonium sulfate in form of fine crystallized products are dewatered, dried and agglomerated along with potassium chloride to produce a pelletized fertilizer.

8.9 Conclusions

The application of physiochemical processes for ammonia recovery in municipal wastewater treatment facilities has not been widely practiced historically. Operating and maintenance costs for conventional processes such as air and steam stripping and insufficient revenue from the recovered products to compensate for these costs are primarily responsible for limiting the adoption of these processes for sidestream treatment. However, recent growth in phosphorus recovery processes and interest in “green” or “sustainable” technologies has led to renewed interest in nutrient recovery and reuse, where the focus is on understanding how wastewater treatment processes, digestion, and nutrient recovery can be linked through synergistic and holistic process designs to create a more favorable environment for nutrient recovery. Overcoming the economic barriers that have historically limited the use of physiochemical processes should be the primary challenge.

CHAPTER 9.0

BENEFICIAL USE OF RECOVERED AMMONIUM PRODUCTS

The ammonia or ammonium recovered by physiochemical processes can only be used for beneficial purposes if it is in a form that is acceptable by the intermediary that incorporates the recovered ammonia into final products (e.g., fertilizer blender) or by the end user for direct application (e.g., farmers). In this chapter, there are brief discussions on the most desirable forms of ammonium recovered in wastewater treatment plants, placement of these recovered products into regional markets and the potential for generating revenue to offset facility operating cost.

9.1 Ammonium Sulfate

The primary use of ammonium sulfate (AS) is as a fertilizer, but there is no established market for AS produced from wastewater treatment plants. However, there is an established market for AS as a by-product of various industries, primarily from the production of nylon. The product is typically marketed worldwide and produced in a crystallized form due to customer preference and to reduce shipping costs. Ammonium sulfate can be used in a direct application or it can be blended in custom fertilizer solutions. For instance, it is common to blend AS with urea ammonium nitrate (UAN) to produce a fertilizer solution that will increase the sulfur content of the solution fertilizer blend. While the use of sulfur-containing fertilizers are increasing due to the substantial reduction in atmospheric sulfur deposition in certain regions, the use of nitrate and anhydrous ammonia based fertilizers are decreasing due to security issues, ammonia volatilization, and a general shift to liquid fertilizers.

The aqueous fertilizer solution market is much larger than the AS market, as shown in Figure 9-1 for the U.S. In 2007, ammonium sulfate represented only 5% of U.S. nitrogen fertilizer consumption, while 45% was provided in the form of nitrogen solutions (AAPFCO, 2007). The use of AS has been steadily growing since the 1980s, while use of ammonium nitrate and anhydrous ammonia have been steady declining. Nitrogen fertilizer prices, which are tied to the cost of energy, have shown a dramatic increase in the last few years. These trends are all favorable for introduction of AS product from wastewater treatment facilities into the market.

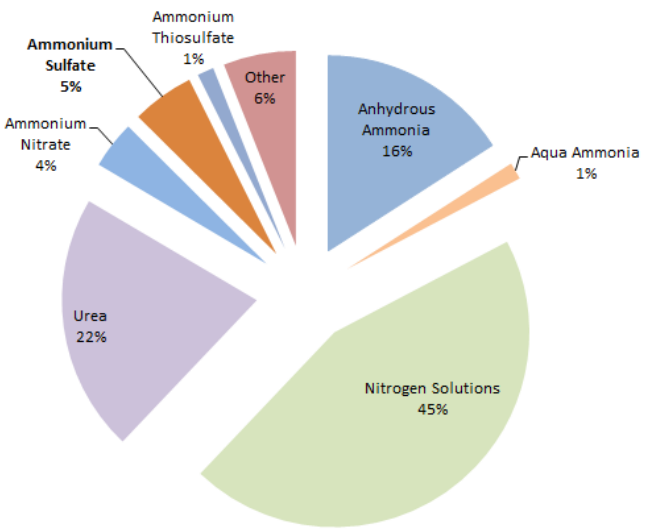

Figure 9-1. Nitrogen Fertilizer Use in the United States in 2007.
Data from AAPFCO, 2007.

Ammonium sulfate can be used throughout the year; however, the highest use (50-75% of annual usage) will typically occur in the late spring and early summer. Smaller amounts would be used in late summer and in the fall. For the remainder of the year (approximately six months), AS must be stored. Typically, a fertilizer blender/distributor will have storage capability, thus avoiding the need to install storage tanks at the wastewater treatment facility.

The ammonium sulfate supply chain contains three distinct groups: manufacturer, blender/distributor, and applier/end-user. A treatment facility would sell their product, as a manufacturer, to a blender/distributor in order for them to either incorporate into a fertilizer blend or sell it as is. The most critical issue with marketing AS for the fertilizer suppliers and farmers is its quality and consistency. The fertilizer/chemical suppliers generally will not accept the AS unless the quality and consistency is known and meets their specifications. However, product quality is anticipated to be higher than the standard specifications based on current experience with ammonium nitrate (Sagberg et al., 2006) where the products were found to have low levels of heavy metals (<1 ppm and largely attributed to the quality of the commercial grade acids used in the process) and low total organic carbon (TOC, < 50 ppm). Typically, TOC content is tightly specified and monitored to limit the liability of explosion potential with the nitrate-based product, but this would not be a factor with ammonium sulfate. The data from operating processes also indicates that the TOC in the product is likely methylamine, which is stripped from the digestion sidestream and absorbed into the product solution along with the ammonia.

9.2 Ammonium Nitrate

Ammonium nitrate is an important fertilizer used extensively throughout the world and is commercially available in both dry and liquid forms. Because ammonium nitrate can be used in explosives, the handling and purchase of dry ammonium nitrate is strictly regulated to prevent misuse. This regulation would not apply to “liquid” form, and liquid usage is increasing substantially. However, most nitric acid capacity is “captive”, i.e., manufactured for internal use, and, therefore, the price and availability are uncertain. Based on experience at the Vestfjorden Avløpsselskap (VEAS) facility in Norway, the fertilizer manufacturer would supply the nitric acid to the wastewater treatment plant and take the ammonium nitrate product; however, this arrangement results in a less cost competitive environment compared to ammonium sulfate production since the fertilizer manufacturer has more extensive control of the acid supply and purchase of the ammonium nitrate.

9.3 Aqueous Ammonia

The Thermoenergy ARP and steam stripping processes described in Chapter 8.0 can be operated to generate concentrated aqueous ammonia instead of a neutralized ammonium salt such as ammonium sulfate or ammonium nitrate. Aqueous ammonia or ammonium hydroxide is used in a wide range of industrial and agricultural applications. Selection of aqueous ammonia over the neutralized ammonium salts as the preferred product would be dictated by regional market conditions. Commercial aqueous ammonia is typically supplied at concentrations of 19.5%, 25%, or 29%. At concentrations of 25% or higher, the solution must be stored and shipped in pressure storage vessels due to the ammonia vapor pressure at these concentrations. Therefore, a concentration of 19.5% would be preferred, although it would marginally increase on-site storage volume requirements and transportation cost.

With the relatively smaller quantities potentially produced by municipal treatment plants, the most readily viable option for reuse of aqueous ammonia is at power plants where ammonia is used in the Secondary Catalytic Reaction (SCR) process for combustion exhaust air NOx reduction. Although anhydrous ammonia is preferred in this application, due to health and safety risks associated with storage of anhydrous ammonia, aqueous ammonia is often used despite the additional energy required for water vaporization.

9.4 Magnesium Ammonium Phosphate Hexahydrate (Struvite)

Struvite has been recognized as a fertilizer for over 150 years and is considered a slow-release fertilizer due to its low water solubility. The low dissolution rate into the soil limits high soluble nutrient concentrations around the root structure and the occurrence of "fertilizer burn", and minimizes the loss of nutrients due to surface runoff and groundwater percolation.

Struvite is only a minor contributor to the overall slow-release fertilizer market, dominated by slowly soluble urea-aldehyde reaction products and polymer and sulfur-coated controlled-release fertilizers. Due to high manufacturing costs, slow-release fertilizers have been predominately used in high valued-added applications in non-agricultural markets such as nurseries, greenhouses and golf courses. Struvite is currently available in a blend with potassium magnesium phosphate under the tradename of MagAmp or MagAmp®-K, typically defined as a 7% N, 40% P_2O_5, 6% K_2O fertilizer with 12% Mg. The product also appears under other labels such as Crystal Green® (5-28-0+10%mg fertilizer) which is struvite produced by Ostara Nutrient Recovery Technologies, Inc.

Demand for slow-release fertilizers has been increasing world-wide to improve fertilizer utilization efficiency and limit the release of nutrients into water bodies. Consequently, phosphorus recovered from municipal and industrial wastewater treatment facilities in the form of struvite is being viewed increasingly as an asset rather than a nutrient that must be treated and disposed. As presented briefly in Chapter 8.0, several struvite crystallization and recovery processes are in full-scale operation. Product purity reported from these facilities has been high, generally greater than 99%, with low heavy metal concentrations and coliform counts after the product is washed and decontaminated (Nawa, 2009; Baur et al., 2011; Moerman, 2011). Purity requirements and product accreditation vary by country, state or region, but the product purities have not limited their introduction into regional markets. The product is not considered an organic fertilizer as it is derived from a wastewater treatment facility.

9.5 Product Value and Revenue Generation

Revenue from the sale of recovered ammonia or ammonium salts is likely to be less than the market value. An assessment of the ammonium sulfate market in the mid-Atlantic region of the United States revealed that even for a large wastewater treatment plant, the quantity of ammonium sulfate solution would have minimal impact on the regional market price (Tsuchihashi et al., 2011). Further, the product from the treatment plant is likely to be priced at a level to ensure reliable acceptance by regional fertilizer blenders. Offsite storage and marketing fees would also be applied, reducing the value of the product further. Thus, the ammonium sulfate solution would not generate revenue corresponding to full market value. Crystallization of ammonium sulfate to produce a fine grade or granular product, both of which have specific market values, could roughly double the revenue, but when examined on a life cycle cost basis,

the capital and operations and maintenance costs associated with a crystallizer operation cannot be justified.

In contrast to ammonium sulfate where the facility generating the product is generally responsible for identifying one or more regional fertilizer blenders and directly negotiating the terms and conditions for product acceptance and revenue from its sale, different business models have emerged for struvite. Struvite technology vendors are increasingly engaged in a more active role than simply providing the equipment and design, startup, and training services. Design-build, design-build-operate, and design-build-operate-finance are emerging as procurement options allowing the utility to remove itself from the business aspect of nutrient recovery and placement of the product in the market to the extent that its finds acceptable from a risk perspective. This does not completely remove all financial risk since most of these struvite technology vendors are small companies with limited financial resources, hence any financial difficulties leading to a bankruptcy would likely impose on the municipalities the full responsibility for placement of their product in the market.

Regardless of the type of ammonium product, revenue from its sale generally does not fully offset the costs associated with the chemicals and energy required to operate the ammonium/ammonia recovery process to the extent that makes physiochemical processes widely applicable. The net operating cost for a physiochemical process (chemicals, energy, and maintenance minus product revenue) typically remains the impediment when compared to a biological process such as deammonification using a life cycle cost or present worth analysis. The economic viability of a physiochemical process is then dependent on other site factors. As an example, where metal salts usage is greatly diminished or completely eliminated for phosphorus removal by implementing a struvite crystallization process, the cost of the metal salt and the costs associated with processing and disposing of the chemical sludge are included in the economic analysis, which generally has improved the overall business case in favor of struvite production. For ammonium sulfate or nitrate production, the site or regional conditions that may lead to favorable economics are considerably more constrained. This has led to interest in finding synergies between struvite and ammonia recovery and treatment plant operating conditions that may make the overall proposition of combined nutrient recovery a more viable business case.

9.6 Conclusions

Ammonium sulfate and struvite are the most common forms of recovered ammonia among the facilities that perform nutrient recovery. While there are established markets for these products and revenue may be realized from their sale, particularly when produced at large wastewater treatment plants, the business cases that make nutrient recovery viable have been limited historically. The growth in struvite production facilities has renewed interest in N and P recovery schemes that are synergistic, particularly with certain wastewater and solids treatment processes that can elevate the ammonium and ortho-phosphate concentrations in anaerobic digesters.

CHAPTER 10.0

RESEARCH NEEDS

A variety of biological processes have been presented that carry out ammonia transformations via different pathways leading to nitrogen gas. Physical-chemical processes that capture the sidestream ammonia-N for reuse are also presented. Many of these processes are proprietary and the process owners may recognize specific opportunities for further optimization in terms of increased loadings or to reduce operating costs. Some general research needs that apply to the biological processes and odor control process using biologically produced nitrite/nitrate are presented that may help to better understand some of the biological processes to provide more efficient and reliable designs.

1. What type of organisms result in most efficient sidestream nitrification processes used for bioaugmentation? Reports on actual versus expected performance from sidestream nitrification and mainstream bioaugmentation show varying results. Results from some studies indicate that the types of nitrifying bacteria that are dominant in sidestream and mainstream processes are selected by these specific and distinct environments (Wett et al., 2010a). A better understanding of the type of nitrifying organisms associated with the sidestream nitrification reactor and mainstream performance could be beneficial. Of interest for example would be whether some processes select for archaea versus ammonia-oxidizing bacteria (AOB) and if the archaea are outcompeted in the mainstream reactor. Also of interest are the specific AOB species present.
2. Control of nitrite concentration and prevention of NOB activity is of particular interest in anammox and nitritation-denitritation processes. Of interest would be the effect of having archaea versus NOB populations. Ammonia-oxidizing archaea may be more competitive at very low DO concentration compared to NOB. No archaea have been found that oxidize nitrite to nitrate. However, a large amount of time may be needed to establish an archaea population. Methods to establish an archaea population over a bacteria NOB population in an anammox process or a nitritation process and its effect on process performance could be of interest.
3. The wide range of free ammonia-N or free nitrous acid concentrations shown in Table 3-1 that inhibit NOB shows a need for more fundamental research to better understand the inhibition levels and degree of inhibition. The type of organisms present, pH and temperature could be important factors.
4. A general range of nitrogen loadings have been observed for the anammox process leading to empirical design parameters. A better understanding of the biological kinetics and reactor populations is needed to better relate nitrogen loading to effluent ammonia-N and nitrite-N concentrations. Such research could provide a basis for process analysis using mechanistic models.
5. The use of nitrite or nitrate produced in sidestream process for sulfide odor control at a wastewater plant's headworks was presented as a potential beneficial use of sidestream treatment. The effects of pH, temperature, and bacteria population need to be better

understood to design such odor control processes that help to remove nitrogen and reduce the cost of other chemicals for odor control.

6. Much is to be learned about transient anoxic conditions that inhibit NOB development. How is the on/off time affected by the AOB and NOB populations, DO, pH, and temperature?

The developments in struvite crystallization and recovery processes have renewed interest in nutrient recovery, but considerable work is needed in identifying plant operating schemes or conditions that increase its economic viability. Specifically, the following topics require further investigation:

1. Since most struvite recovery processes require the addition of a strong base to increase the pH up to 8.5 for optimum struvite formation, is there economic justification with increasing the pH further in a second stage ammonia recovery process such as air stripping/acid absorption?
2. Is there a positive business case in the apparent synergistic relationships between enhanced biological phosphorus removal, certain solids treatment schemes such as thermal hydrolysis pretreatment which allow high total solids concentrations to anaerobic digestion, and N and P recovery? Where chlorination is used for final effluent disinfection, is there a business case for generating sodium hypochlorite at the facility to allow use of the sodium hydroxide byproduct for sequential struvite and ammonia recovery?
3. What are the specific site conditions where steam stripping becomes economically viable? Does struvite production ahead of steam stripping improve its business case?

Finally, the direct catalytic reformation of ammonia to generate hydrogen as an energy source remains a fertile ground for future research, particularly in optimizing catalyst design to reduce its cost and extend its performance life.

CHAPTER 11.0

CONCLUSIONS

Sidestream nitrogen removal has become of increased interest by plant operators to incrementally reduce the cost of nitrogen removal across the facility, reduce the plant effluent Total Nitrogen (TN), total ammonia-N, or nitrate-N concentration to meet lower discharge limits or enhance the stability of nitrification in the mainstream plant where the maximum aerobic SRT is limited. The cost-effectiveness of implementing sidestream nitrogen removal in a facility is often site-specific and dependent on the following conditions:

1. The availability of existing tanks to accommodate a retrofit to the desired sidestream treatment process.
2. Space in the facility for construction of a new sidestream treatment process.
3. Energy and chemical costs and regional construction costs.
4. Cost of separate sidestream treatment in comparison to treating the sidestream nitrogen load in the existing or an expanded mainstream plant as determined through a financial tool such as a present worth analysis.
5. Financial metrics that define the maximum payback period for investment in new facilities or retrofit of existing facilities for separate sidestream treatment.
6. Potential benefits from bioaugmentation of the mainstream plant with nitrifiers growing in a separate or integrated sidestream treatment process.
7. Non-economic considerations such as sustainability goals or metrics and public perception.

As presented in this report, biological treatment of sidestreams has been practiced more widely than physiochemical processes, largely due to the familiarity of plant operators with biological treatment and a limited number of economically viable physiochemical processes with an extensive operating and performance history. However, as ammonia-N and phosphate-P are increasingly viewed as products that can be recovered and reused as opposed to pollutants that must be “treated,” interest in physiochemical processes has increased in recent years, largely due to the expansion in crystallization technologies and product reuse opportunities for magnesium ammonium phosphate hexahydrate (struvite).

The conventional approaches of air stripping and acid absorption to generate ammonium sulfate or ammonium nitrate or steam stripping to generate these neutralized ammonium salt solutions or aqueous ammonia have not been widely adopted for municipal sidestream treatment due to operating cost (chemicals, energy), operating issues such as fouling of key process equipment, the dependence on third parties to accept the recovered product, and seasonal variations in the demand for these products. However, through the growing interest in struvite production, technology developers and process design engineers are increasingly seeking synergistic opportunities to link P and N recovery within a single process train. As the number of enhanced anaerobic digestion processes such as pretreatment of raw sludges by thermal hydrolysis has increased, the thermodynamic and economic drivers for N and P recovery have

increased since the concentrations of these nutrients are considerably higher in the digesters, dewatering processes and resulting sidestreams.

While there is a greater interest in physiochemical processes for N and P recovery, the rapid adoption of deammonification technologies has created a challenge for physiochemical ammonia recovery processes if viewed through a present worth analysis. Although the capital cost and footprint requirements may be higher for a deammonification process, the absence of a chemical requirement makes deammonification one of the lowest cost options for separate sidestream nitrogen removal. The economic advantages of deammonification are further enhanced if existing tanks can be converted for deammonification. However, site-specific conditions (e.g., space availability, availability of a low-value waste heat source, energy and chemical costs), sidestream characteristics, mainstream treatment process operating conditions, and plant discharge quality objectives will dictate the most cost-effective option for a given wastewater treatment plant. For example, an integrated configuration that provides nitrifier bioaugmentation of the mainstream plant may be the most desirable and cost-effective option for a facility, while another plant that is not limited by the aerobic SRT in their mainstream process may find a separate sidestream treatment process the most cost-effective option to meet their specific requirements.

Finally, physiochemical and biological treatment of sidestreams should not be viewed as mutually exclusive options. For example, a struvite production process may be implemented as a first stage to be followed by a biological process such as one of the deammonification technologies. The elevated pH and alkalinity of the struvite crystallizer effluent may prove beneficial to the downstream deammonification reactor where a higher residual alkalinity concentration may enhance ammonia removal.

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