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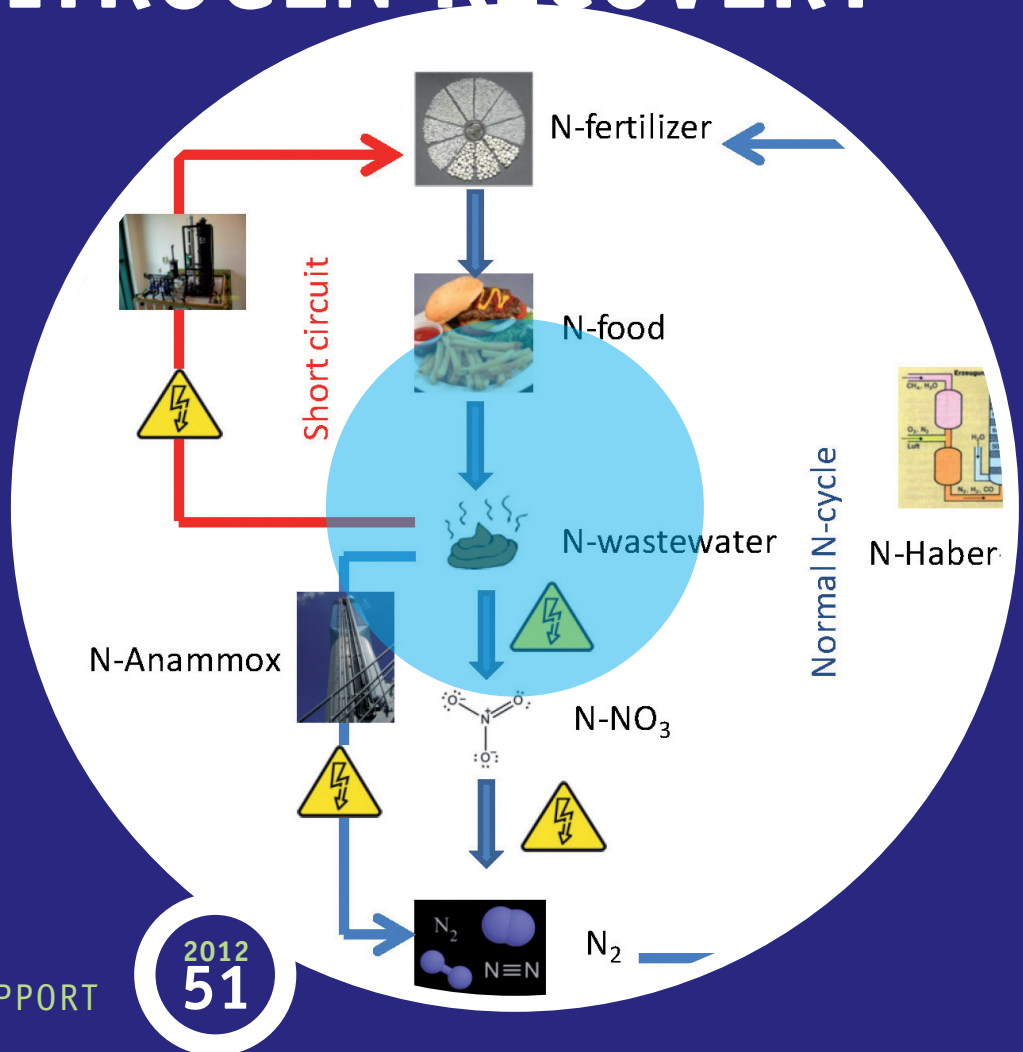# EXPLORATIVE RESEARCH ON INNOVATIVE NITROGEN RECOVERY

RAPPORT 2012 51

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EXPLORATIVE RESEARCH ON INNOVATIVE NITROGEN RECOVERY

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COLOPHON

SUMMARY

This report comprises the results of an explorative study on innovative nitrogen recovery from side streams of wastewater treatment plants (WWTPs) in the Netherlands. The main objective of the study was to identify promising new technologies for recovery of nitrogen which can be subsequently used as an artificial fertilizer. This shortcircuits the global nitrogen cycle and thereby reduces the environmental impact of the nitrogen cycle that has been distorted by human influence (eutrophication, greenhouse gases).

The amount of nitrogen that ends up in the rejection water depends on the percentage of external sludge that is treated on the WWTP. In case of large amounts of external sludge this percentage can go up to 20% (that is about 4 % of the applied artificial nitrogen fertilizer). Although this contribution is fairly small, it is still the most promising source for nitrogen recovery due to its high nitrogen concentration. In addition to WWTP sidestreams, other larger streams are identified from food industry, organic waste, etc that have sufficiently high nitrogen concentrations. The most suitable recovery products from an agricultural perspective are ammonium sulfate $(NH_4)_2SO_4$ and ammonium nitrate NH_4NO_3. Struvite $(MgNH_4PO_4.6H_2O)$ is in general also suitable, but for the Dutch situation struvite has the disadvantages of a high (12.6% w/w) P content (The Netherlands have a large P-surplus), less application potential in agriculture and current legislative restrictions for use of 'recovered' struvite as a fertilizer.

Recycling options for organic nitrogen sources (e.g. manure, compost, manure pellets) were not considered in this study. The Dutch agricultural sector (fertilizer producers, pig farms) did not participate in this study, as they prefer to wait for results of other ongoing projects in the sector that may interfere with the results of this study (nitrogen concentrates projects).

In this study five innovative techniques were selected out of nineteen possible techniques for N-recovery. The selected technologies comprise two innovative stripping techniques (AMFER, LGL), recovery of nitrogen through formation of struvite (CAFR), ARP/RCAST, which recovers ammonia under vacuum and a technique with combined biological and chemical oxidation. ARP/RCAST and LGL seem most promising because they are efficient in the phase transition and therefore need less energy. However, it is expected that these techniques still use a large amount of chemicals. The ARP/RCAST process has already been implemented in several full scale installations while LGL only functions on laboratory scale. The biological and chemical oxidation technique has financial advantages because of the low chemical use. The disadvantage of these technique is that the product cannot be designated as an artificial fertilizer, because of the presence of organics (no phase transition).

The selected technologies were compared to conventional stripping and anammox as base technologies for costs and energy consumption.

Calculations show that nitrogen recovery results in increased energy demand (based on Gross Energy Requirement (GER) values) and costs, except when cheap residues are available to substitute the chemicals and/or heat demand. The cost of conventional air stripping is about 1.9 -3.2 EUR/kg N recovered, while the cost of the Anammox process is only about 0.8 EUR/kg N recovered.

The energy demand of stripping varies from 100-150 MJ/kg N (aeration, heat, chemicals) and is significantly higher than the energy demand of nitrogen producing Haber-Bosch process combined with Anammox (60 MJ/kg N).

So in general short circuiting of the nitrogen cycle is technically possible, but energetically not very favorable. From a cost perspective the large amount of required chemicals makes the present and expected future technologies not competitive yet. Still, in special cases with the availability of residual chemicals or waste heat nitrogen recovery may be cost-effective and sustainable.

DE STOWA IN BRIEF

The Foundation for Applied Water Research (in short, STOWA) is a research platform for Dutch water controllers. STOWA participants are all ground and surface water managers in rural and urban areas, managers of domestic wastewater treatment installations and dam inspectors.

The water controllers avail themselves of STOWA's facilities for the realisation of all kinds of applied technological, scientific, administrative legal and social scientific research activities that may be of communal importance. Research programmes are developed based on requirement reports generated by the institute's participants. Research suggestions proposed by third parties such as knowledge institutes and consultants, are more than welcome. After having received such suggestions STOWA then consults its participants in order to verify the need for such proposed research.

STOWA does not conduct any research itself, instead it commissions specialised bodies to do the required research. All the studies are supervised by supervisory boards composed of staff from the various participating organisations and, where necessary, experts are brought in.

The money required for research, development, information and other services is raised by the various participating parties. At the moment, this amounts to an annual budget of some 6,5 million euro.

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EXPLORATIVE RESEARCH ON INNOVATIVE NITROGEN RECOVERY

CONTENTS

1

INTRODUCTION

Nutrients such as nitrogen, phosphorus and potassium are essential for life. In the form of fertilizer, they are extensively used. In recent years attentions for a more efficient use of nutrients and the possibilities to recover and to reuse them have increased.

The global phosphate stock is finite. The depletion of this phosphate stock will eventually result in a decrease of agricultural production. The recovery of phosphate as a reusable resource is therefore essential which is why this topic is receiving increasing attention. Although nitrogen is abundant, large quantities are "wasted", which has a major negative impact on ecosystems. The origin of nitrogen in domestic waste water is in the manure and artificial fertilizers needed for the growth of crops for human and animal consumption. Artificial fertilizers are needed for crop-specific precision nutrient application. The nitrogen in these artificial fertilizers is industrially produced with the energy-intensive Haber Bosch process. With the recovery of nitrogen from waste streams as a replacement for artificial fertilizer, the Haber-Bosch process is circumvented. Moreover, this will save the energy which is needed to remove nitrogen from waste water with current methods, which often lead to emission of greenhouse gases. Therefore, attention for the recovery of nitrogen is necessary to increase the sustainability of the nitrogen cycle.

The attention for nutrient recovery in the year 2012 is underlined by the establishment of the Nutrient Platform in 2011 in the Netherlands. Several stakeholders are involved in the Nutrient Platform such as providers and consumers of nutrients, universities, institutions and consulting agencies. This Nutrient Platform fits into a European trend on dealing with raw materials that are absent in Europe.

The pressure on the global nitrogen cycle can be decreased by recovering nitrogen into usable (inorganic) ammonium-nitrogen products and apply them directly or indirectly (after further processing) as fertilizer. Other possible advantages are lower energy consumption, less eutrophication and a reduced N_2O emission. N_2O is a strong greenhouse gas (298 times as strong as CO_2) [1]. The recovery of nitrogen from aqueous streams is still limited and is not (yet) cost effective as a result of the high energy consumption and chemicals demand of the available techniques that usually involve a stripping process. Moreover, the produced products often do not meet fertilizer specifications and regulatory or legislative conditions.

In this paper an explorative research on innovative nitrogen recovery is presented. The objectives of this research are
- Making an inventory of the nitrogen-rich side streams at waste water treatment plants;
- Determining the state of the art in nitrogen recovering techniques;
- Explore opportunities for the use of the recovered nitrogen into agriculture.

Techniques for nitrogen recovery are developing rapidly. In this report some of the most promising nitrogen recovery techniques (assumed to be fully developed in the coming 5 to 10 years) are described. An inventory of currently available techniques was made based on the knowledge available in literature and also among the advisory board involved in the project, which consisted of experts from the Dutch Waterboards and agriculture. Nonetheless, it cannot be excluded that new techniques will be developed shortly after this exploratory research.

In this study no attention will be paid to possible recycling of organic nitrogen sources (e.g. manure, compost, manure pellets). The agricultural sector (fertilizer producers, pig farms) did not participate in this study. Results of ongoing projects in the sector may interfere with the results of this study. Therefore, this project is limited to the recovery of nitrogen from side streams from waste water treatment plants and the technologies suitable for this purpose. However, the agricultural sector is involved as potential customer of the nitrogen fertilizer product.

READING GUIDE

Chapter 2 describes the nitrogen problem in general. It summarizes background information on the production process of artificial nitrogen fertilizer and the related emissions of nitrogen and greenhouse gases to the environment. Also the actual European and Dutch nitrogen policy (which is a driver for nitrogen recovery) will be discussed (Chapter 3). Chapter 4 provides information about other recoverable nitrogen rich streams in general and the suitable nitrogen-rich side streams on Dutch waste water treatment plants and their (expected future) nitrogen concentration. Chapter 5 describes which type of recovered nitrogen is allowed to be used as a fertilizer. In Chapter 6 the energy use for N production with Haber Bosch and nitrogen removal with Anammox are compared with a basis (reference) technique for N recovery (air stripping). Also, the costs of nitrogen stripping versus Anammox are compared. Chapter 7 describes the pre selection of the innovative technologies for nitrogen recovery which are evaluated in this study. In chapter 8 the selected technologies for N recovery are described in more detail. Fact sheets of the techniques are included in the enclosure part of this report. Specifications of the different technologies such as energy use and costs of the different technologies were investigated. Based on the information the different technologies are compared on outline. In the final Chapter (9) discussion and conclusions are presented.

2

THE NITROGEN PROBLEM

2.1 PRODUCTION OF NITROGEN RICH ARTIFICIAL FERTILIZER

To feed the growing population additional artificial fertilizer is needed for growing food and feed crops. Worldwide, the major part of the nitrogen is fixated by natural processes. At the same time mankind fixates a large quantity of the nitrogen for food production by means of the Haber-Bosch process where, at high pressure and temperature, ammonia is formed from nitrogen and hydrogen.

The natural nitrogen cycle is insufficient to keep up with the global population growth. Without the Haber Bosch process, which is used to produce ammonia from N_2, only about half of the current total world population can be fed [6]. The recorded increase in average fertilizer use per hectare of agricultural land and the increase in per capita meat production are responsible for the increased use of fertilizer in the previous century.

Each year about 100 million tons of nitrogen fertilizer are produced mainly in the form of anhydrous ammonia, ammonium nitrate and urea. This process consumes roughly 1- 3 % of the world annual natural gas production (about 1 % of world energy consumption).

Most of the ammonia is produced by the Haber-Bosch process in which nitrogen gas and hydrogen gas react with a catalyst under high pressure and heat (oxygen free conditions). The reaction has the following reaction equation:

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$
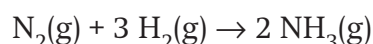
The required nitrogen is extracted from the air which contains about 78% nitrogen and 21% oxygen. The oxygen must first be removed. Therefore, the air is transported over hot cokes so that all the oxygen in the air reacts with the carbon of the cokes and CO is formed.

$$4\ N_2(g) + O_2\ (g) + 2\ C(s) \rightarrow 4\ N_2\ (g) + 2\ CO\ (g)$$
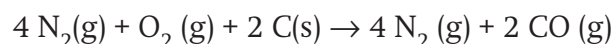
Water vapor reacts with CO tot H_2 and CO_2:

$$H_2O\ (g) + CO\ (g) \rightarrow H_2\ (g) + CO_2\ (g)$$
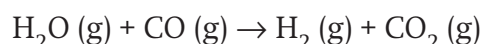
The CO_2 is then easily removed and the remaining N_2 - H_2 gas mixture is pumped to the production site. The process was developed in 1909 by Fritz Haber and Carl Bosch.

Nowadays, mostly methane from natural gas is used instead of cokes, to react with the atmospheric oxygen.

The fossil energy required to produce nitrogen-rich artificial fertilizers is between 37-45 MJ / kg N [4]. This is mainly the use of natural gas as the carbon source for the production of CO as a part of the chemical reaction. N-rich fertilizer is produced at the cost of (primary) energy, along with an additional CO_2 emission. So this CO_2 emission results from the direct primary energy use and from the CO_2 which is released as side-product from the production process (from cokes or natural gas [7]). From the perspective of sustainability it is therefore important to reduce the volume of artificially produced N-rich fertilizer. The production of the important greenhouse gas N_2O is not connected with the production of NH_3 but with NO_3 which can be a subsequent product of the fertilizer industry [7].

2.2 EMISSIONS OF NITROGEN AND RELATED EMISSIONS

Nitrogen in manure and artificial fertilizer is used in large quantities in agriculture. Because of excessive or inadequate nitrogen fertilization, only part of the nitrogen is taken up by the crops while the excess nitrogen enters the ecosystem. Too much nitrogen causes environmental problems such as oxygen depletion by reduced nitrogen and eutrophication problems due to oxidized nitrogen [3].

The treatment of nitrogen-rich waste streams in waste water treatment plants (WWTPs), and manure treatment plants (like KGBI's Stichting Mestverwerking Gelderland) reduces the emissions of nitrogen (in the form of ammonia and nitrite and nitrate) to the ecosystem. It does, however, result in derived CO_2 emissions because of the energy intensive process of removing nitrogen from waste water. The nitrogen is first oxidized with energy and then with "energy-containing" organic material reduced to N_2 in the air. In addition, treatment processes could result in N_2O emissions which is a very "strong" greenhouse gas. The current view is that N_2O emissions increase under stressful and concentrated conditions which occur in wastewater treatment plants [4]. This leads to the hypothesis that the emission of N_2O from a engineered waste water treatment plant is larger than the N_2O emissions which normally would have occurred in natural processes.

2.3 NITROGEN CYCLE

From an overall global balance one can conclude that nitrogen from (artificial) manure is incorporated into biomass, eventually oxidized to NO_x and subsequently reduced to N_2 by denitrification. These are biological processes in the soil, groundwater, surface water (and in waste water treatment). Through human contribution however, the nitrogen cycle runs much faster than it would go without human interference

(Partially) closing the loop by recovering reduced nitrogen from wastewater and manure contributes to a more sustainable nitrogen cycle (less fixation and biological transformation of nitrogen) and results in a reduced energy consumption and greenhouse gas emissions. The recovered nitrogen can be reused as fertilizer. For the agricultural sector the recovery of nitrogen is especially a logistical problem. By recovering nitrogen from the liquid manure and keeping it apart from the solid manure fraction, fertilizers can be used more efficiently. This strategy also results in savings on nitrogen fertilizer (higher efficiency, cost savings) and therefore also in savings on energy and greenhouse gas emissions.

On a global scale a major part of the nitrogen input in the biosphere has its origin in natural processes (Figure 2.1). On a European and Dutch scale a major part of the nitrogen is released via human intervention (Haber Bosch, agriculture and combustion).

GLOBAL, EUROPEAN AND DUTCH REACTIVE NITROGEN (NR PRODUCTION) AND RELATIVE CONTRIBUTIONS OF NATURAL AND HUMAN CONTROLLED

PROCESSES (DATA TAKEN FROM ERISMANN ET AL, 2011 [15])
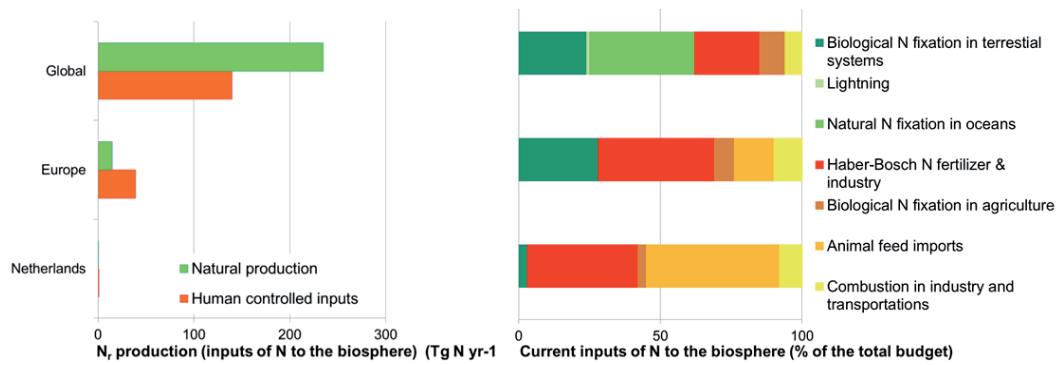
A more accurate calculation of the yearly Dutch nitrogen cycle is presented in **Figure 2.2**.

Based on budget figures in the period 1995-2000 it may be concluded that 16 % ([53+9]/398) of the synthetic fertilizer production in the Netherlands could be replaced by recovered nitrogen from wastewater provided all nitrogen entering wastewater treatment plants would be recovered (Figure 2.2.). However for an average wastewater treatment plant about 6 % of the nitrogen that enters this plant ends up in the rejection water (20 % N in sludge, 30 % degradation in digester results in 6 % N in rejectionwater). However, the sludge treatment site is often centralized with larger quantities of nitrogen (up to 20% of nitrogen in rejection water [11]) and is therefore more suitable for reuse techniques. In this perspective maximal 12 kton (62 kton * 20 %) of the nitrogen which enters the sewer can be recovered by nitrogen stripping (that is about 4 % of the applied artificial nitrogen fertilizer). Moreover other, much larger nitrogen-rich streams are available for which N recovery theoretically can be implemented (paragraph 4.2).

ANNUAL NITROGEN FLOWS IN THE NETHERLANDS IN KTON N YEAR^{-1} IN 1995-2000. THE INTERNAL N FLOW BETWEEN DIFFERENT SECTORS IS

REPRESENTED BY THE BOXES, E.G. 398 KTON N IS YEARLY PRODUCED AS SYNTETHIS FERTILIZER BY THE CHEMICAL INDUSTRY AND REFINERIES.

THIS FERTILIZER IS USED (AND THEREFORE "INPUT") BY THE AGRICULTURAL SECTOR. WWTP= WASTE WATER TREATMENT PLANT (FIGURE IS

DRAWN WITH DATA TAKEN FROM ERISMAN ET AL, 2005 [6])
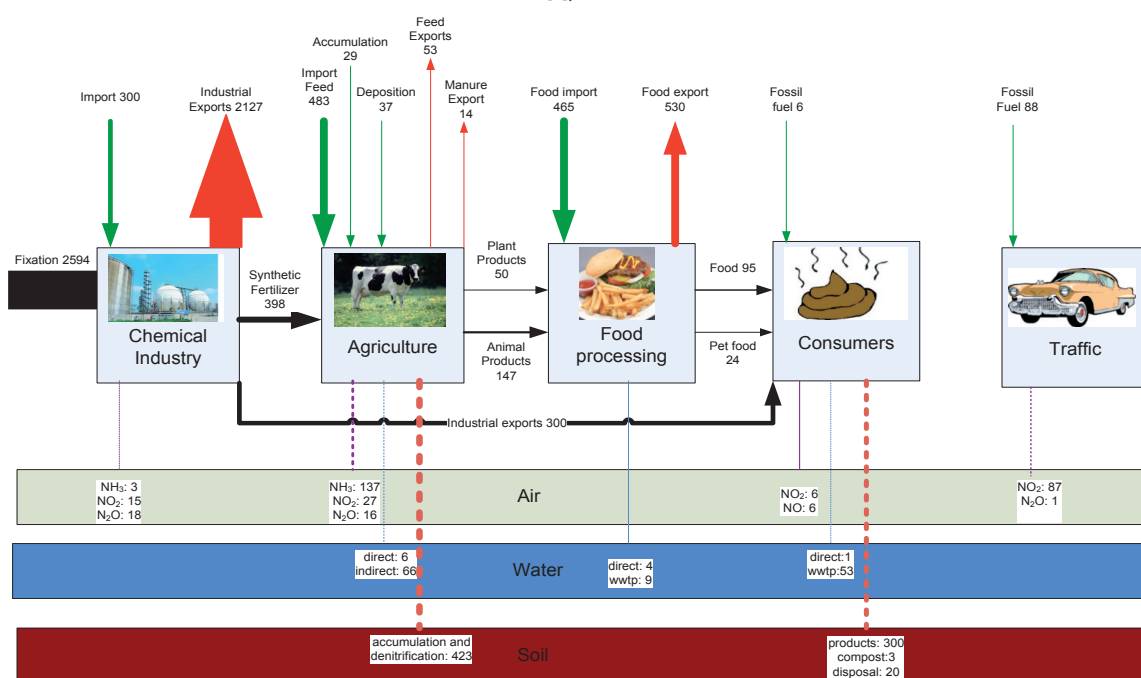
3

ACTUAL EUROPEAN AND DUTCH NITROGEN POLICY

3.1 INTRODUCTION

In the European union and in the Netherlands there are stringent regulations for the use of nitrogen containing manure. New policy will lead to a minor surplus of nitrogen. In paragraph 3.2 the EU rules are explained. At the same time the Dutch water boards have developed a new strategy for sustainable wastewater treatment: WWTP 2030 [8], which involves the recovery of nutrients and the reduction of both energy use and the emission of greenhouse gases. This will be discussed in more detail in paragraph 3.3. Moreover in the Netherlands, synergy aspects between wastewater treatment and agriculture (manure treatment) are investigated (paragraph 3.4). The recovery of nitrogen fits in these policies.

3.2 EU RULES AND DIRECTIVES FOR MANURE

In the EU the use of nitrogen containing manure products and fertilizers has been regulated in the Nitrate Guideline. The goal of the Nitrate Guideline (NG) is to protect the ground- and surface water against an overload of nitrate from agricultural sources. The maximum allowed nitrate concentration in the groundwater has been defined as 50 mg/liter. The Dutch manure policy is based on this Nitrate Guideline. Since the year 2006 there are standards for the amount of nitrogen (to prevent leaching) and phosphorus (to prevent accumulation in the soil) from animal manure, which can be applied per ha. Regarding the use of N from fertilizers the Good Agricultural Practice must be followed.

Based on the NG the maximum allowed amount of N from animal manure in the Netherlands is 170 kg/ha/year. On farms with more than 70% grassland the standard can be increased to 250 kg N/ha/year, depending on soil type (derogation). On top of that amount, an additional gift of artificial nitrogen fertilizer can be applied up to the crop specific total nitrogen gift per hectare, figure 3.1.

FIGURE 3.1   FERTILIZER REPLACEMENT BY NITROGEN FROM PROCESSED MANURE (VERDOES 27 JUNE 2012)
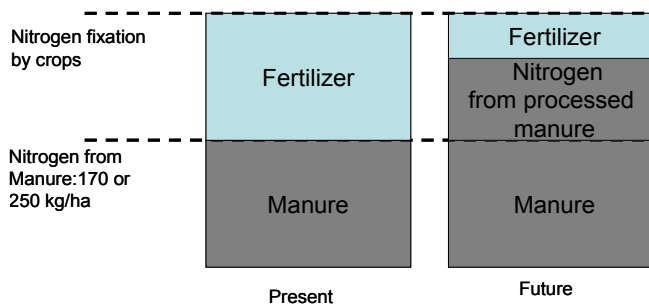
Products from manure (or other products) that contain organic matter are not considered as an artificial fertilizer by the European Fertilizer Directive. Such products remain manure (or sludge) by definition and no artificial fertilizer is substituted, so it does not contribute to a decrease in nitrogen fertilizer production by Haber Bosch.

Processing of animal manure, in addition to animal feed measures and export of manure, is considered as an opportunity to reduce the pressure on the manure market in the Netherlands. One of the options is to separate the slurry and to use the mineral concentrate, that is produced from the liquid phase by reverse osmosis, as a substitute for mineral fertilizer (as defined in the Nitrate Guideline). The agricultural sector, the ministry of Economic Affairs, Agriculture and Innovation and the ministry of Infrastructure and Environment, with consent of the European Commission, have evaluated in a number of pilot projects, the production and use of the mineral concentrate. Mineral concentrates are NK (nitrogen/potassium) concentrates. The results are compiled into a technical file that will be used for examination of the mineral concentrates by reference to the European legislation for mineral fertilizers ('EG-meststof') and the national Dutch legislation by reference to the protocol for assessment of fertilizers ('Beoordeling stoffen meststoffenwet').

The purpose of the policy is to close the mineral loops and to increase the sustainability of the agricultural production.

In September 2011 the ministry of Economic Affairs, Agriculture and Innovation, together with the farmers unions (LTO and NVV) published the outline of new manure regulations, to regulate the P overload in the country. One of the aspects is the obligatory manure treatment for agricultural farms with a surplus of manure. This obligation is planned to come into practice on 01-01-2013. At the moment (June 2012) the policy is not clear in detail yet. The surplus of the manure must be delivered at a certified manure treatment plant (percentage of treatment, depending on the density of animals in a certain region) or manure delivery contracts between manure producer and customer must be available in advance

3.3 WWTP 2030, THE WWTP AS AN ENERGY AND NUTRIENT FACTORY

The Global Water Research Coalition (GWRC) has taken the initiative in late 2008 to consider the future of urban water cycle with the objective of 'energy and climate neutral water chain in 2030'. In the GWRC subproject 'Roadmap to revamp wastewater treatment operations to measurable goals 2030' a part of the participating countries carried out a project directed to a further elaboration the communal wastewater treatment 2030 (Figure 3.2). The international initiator is the Public Utility Board (PUB) of Singapore. As a part of this the STOWA initiated the project WWTP 2030 [8]. The future trends and developments are visualized and give input for the research agenda of the STOWA and the water sector as a whole.

In the Netherlands about 12 WWTP's are reconstructed to a so called 'Energy factory', (energy reduction, production of extra biogas and reduction of sludge volume) by 2012. At the same time 5-7 WWTP's will be reconstructed to 'Nutrient factory' in which phosphate is recovered and the production/recovery of bioplastics and organic fibers is investigated.

When considering nitrogen, nowadays part of the nitrogen that comes from the sludge line is oxidized and converted to nitrogen by the Anammox bacteria. Although this is a new and efficient conversion process, still oxygen is needed to convert half of the nitrogen to nitrite.

FIGURE 3.2   NUTRIENT FACTORY SCHEME BY EXPERT GROUP **OF THE NEWATER PROJECT (NUTRIENTS, ENERGY AND WATER) [8]**
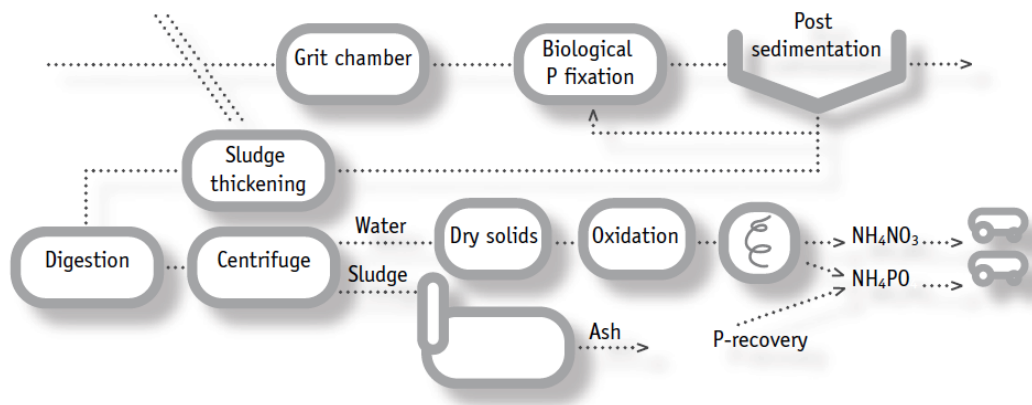
So the potential for recovery of the nitrogen from this side stream fits in the objectives of the NEWater project.

3.4 SYNERGY OF MANURE TREATMENT AND MUNICIPAL WASTEWATER TREATMENT

The manure policy gives opportunities for cooperation of the agricultural sector and the municipal sewage treatment:

• There are possibilities for municipal sewage plants to become a certified manure treatment plants;

• The products from innovative nitrogen recovery techniques can be applied in agriculture, creating a beneficial internal recycle in the overall N-cycle;

• Synergy potential for both sectors to recover N and P and to give extra value on these products;

• Other synergy opportunities: both sectors apply digestion systems; the heat and electricity generated in the CHP fed with the biogas can be reused in the different processes. This fits in the purpose of the Energy Factory;

• Scaling benefits: the same innovative systems can be applied on municipal sewage and manure.

Several projects on this subject have been carried out [4,9,10]. The recovery of nitrogen from side streams from the WWTP and from manure fits in the policy and the 2012 developments.

4

NITROGEN RICH SIDE STREAMS ON WASTE WATER TREATMENT PLANTS

4.1 INTRODUCTION

The efficient recovery of nitrogen from wastewater demands relatively high nitrogen concentrations. Techniques to efficiently recover nitrogen from wastewater usually require concentrations above 1.000 mg NH_4/l. In this chapter the suitable nitrogen rich side streams are identified, with a focus on the nitrogen rich side streams on wastewater treatment plants. Furthermore, the expected future development of these nitrogen rich streams is defined.

4.2 RECOVERABLE NITROGEN STREAMS

In addition to the nitrogen-rich streams in waste water treatment plants, and liquid manure there are other nitrogen-rich streams which are in principle suitable as a source for the recovery of nitrogen. The following flows can be distinguished (Table 4.1):

TABLE 4.1   NITROGEN RICH SIDE STREAMS IN GENERAL (MG/L N)

Stream	Unity	Value
Liquid manure fractions	mg/l	2,200- 4,800
Rejection water of waste water treatment plants with TDH, sludge treatment	mg/l	2,000
Rejection water of waste water treatment plants with sludge treatment	mg/l	500 – 1,000
Concentrated 'black water' after fermentation	mg/l	1,800
Industrial waste streams (eg from the food industry)	mg/l	*
Condensate flows released from sludge drying processes	mg/l	*
Digested manure	mg/l	2,200 – 4,800
Organic waste	mg/l	1,200

* large ranges in concentrations because of variation of sources

4.3 PRESENT AND FUTURE NITROGEN RICH SIDE STREAMS ON WASTEWATER TREATMENT PLANTS

In wastewater nitrogen is usually present as ammonium (NH_4-N) or nitrate (NO_3-N). The average nitrogen influent concentration in Dutch communal wastewater is about 50 to 60 mg/l. This concentration is too low for feasible nitrogen recovery. Nevertheless, much more concentrated side streams can be identified on a WWTP. The most promising side stream is the rejection water of the sludge dewatering process. This rejection water is produced when digested sludge is dewatered with a centrifuge or a belt filter press. In the current situation, the rejection water of the centrifuge (centrate) and the belt filter press (filtrate) is returned to the wastewater treatment plant to be treated aerobically. The average nitrogen concentration in this side stream ranges from 500 to 1,500 mg/l (Figure 4.1). In the Netherlands there are

also several WWTP's with a separate N-rich side stream treatment processes, like Sharon, Anammox of Demon. This is an efficient way of converting NH_4 to N_2. However, still oxygen is needed and NH_4 is wasted.

FIGURE 4.1   EXAMPLE LARGE WWTP WITH EXTERNAL SLUDGE AND DIGESTION
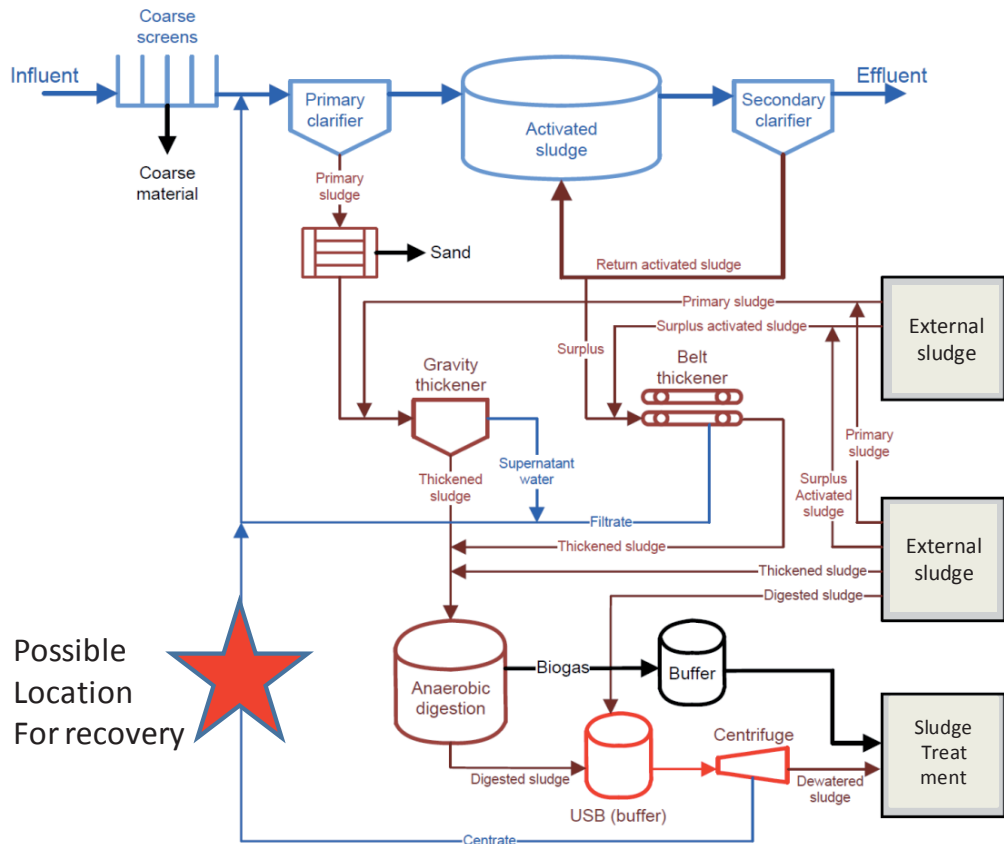
In the nearby future it is expected that the nitrogen concentrations in this side stream will increase as a result of the implementation of thermal hydrolysis processes. The thermal hydrolysis process has been developed in Europe for sterilization of (waste) streams for agricultural purposes (not allowed in the Netherlands) and in order to reduce the sludge volume and treatment costs. Pre-treating the sludge under high temperatures (140 – 170 °C) and pressure (2-10 bar) results in a lower viscosity (with a higher solids concentration in the feed as a consequence), higher biogas yield and a more efficient sludge dewatering. A higher solids concentration in the digester leads to digested sludge with a higher nitrogen concentration and a higher concentration of nitrogen in the rejection water.

In Table 4.2 the nitrogen concentrations in current and future rejection waters are presented. The expected future concentration of nitrogen is based on references of Dutch pilot projects with the thermal hydrolysis process and reference projects in other European countries

TABLE 4.2   NITROGEN CONCENTRATIONS IN REJECTION WATER (DIFFERENT SOURCES)

Source	unit	Present	Future (Thermal hydrolysis)
STOWA 2011, W03 (pilot Sustec)	mg/l N		2,000
Tauw mass balance calculations 2011 *	mg/l N	1,000	3,100 – 3,300
STOWA 2011, W03 (praktijk installatie Cambi)	mg/l N	500 – 1,500	2,500 – 3,000
STOWA 2008 – 18**	mg/l N	500 – 1,500	
Colsen presentation 2011	mg/l N		> 2,500
PCS presentation 2011 (Cambi system) ***	mg/l N	1,200	2,800 – 4,000

* Tauw 2011, Nieuwe slibeindverwerking, kansen voor slibdroging met restwarmte en slibenergiefabriek

** Slibverwerking Sluisjesdijk = 800 - 1,400 mg/l N

***Pollution Control Services (Germany)

The nitrogen concentration of the rejection water also depends on the dewatering technique. With centrifuges higher quantities of poly electrolyte (conditioning) are necessary which gives more dilution than with belt filters (of belt filter presses). From Table 4.2 it can be concluded that the current average nitrogen concentration in rejection water is about 1,000-1,500 mg/l. As a result of the implementation of thermal hydrolysis the expected nitrogen concentration in the rejection water will increase to 1,500 – 2,500 mg/l.

5

USABILITY OF RECOVERED N PRODUCTS IN AGRICULTURE

5.1 INTRODUCTION

In this chapter the potential for use of the recovered nitrogen in agriculture is discussed. First the assumptions and requirements are presented after which potential products are compared and discussed.

5.2 REQUIREMENTS AND ASSUMPTIONS

The requirements for the product to be a fertilizer are presented in Table 5.1.

TABLE 5.1 R   EQUIREMENTS FOR PRODUCTS TO BE A FERTILIZER

Fertilizer	Requirement
N-fertilizer	N-content > 15 %
NK-fertilizer	$N+K_2O$ > 15 %
NP-fertilizer	$N+P_2O_5$ > 18 %
PK-fertilizer	$K_2O+P_2O_5$ > 18 %
NPK-fertilizer	$N+K_2O+P_2O_5$ > 15 %

Moreover for admission as EU-fertilizer there are additional requirements (EU-directive 2003/2003). The products must be:

- produced by an industrial process
- free of organic nutrients from vegetable or animal origin are allowed
- free of impurities

APPLICATION FOR THE STATUS OF EU-FERTILIZER ACCORDING TO EU-DIRECTIVE 2003/2003:

Depending on the availability of data on chemical compositions, impurities, analytical methods and agricultural efficiency, the application procedure will take at least 3 month (if all information is available) but can take more than five years when information is missing or when agricultural field trials are needed. All EU member states must agree to amend the EU-directive.

5.3 THEORETICAL POTENTIAL PRODUCTS

In Table 5.2 several products which can be product with nitrogen recovery techniques are compared.

TABLE 5.2   **COMPARISON OF POTENTIAL PRODUCTS**

Name	Ammonium sulphate solution	Ammonium nitrate solution 30%	Ammonium struvite	Aqua ammonia 30%	Ammonium chloride	Ammonium lactate	Ammonium citrate
Formula	$(NH_4)_2SO_4$	NH_4NO_3	$MgNH_4PO_4.6H_2O$	NH_3 / NH_4OH	NH_4CL	$CH_3CH(OH)CO_2NH_4$	$(NH_4)C_6H_6O_7$
N-content (%)	7.4	10.5	5.7	24.7	26.0	13.1	6.7
Mineral content complies with EU-directive 2003/2003 ?	No	No	Yes (NP-fert.)	Yes	Yes	No	No
Pure substance complies with EU-directive 2003/2003 ?	Yes	Yes	No	Yes (?)	Yes	No	No
Food additive ?	No	No	No	No	Yes E510	Yes E328	Yes E330
Organic substance ?	No	No	No	No	No	Yes	Yes
Danger ?	No	No, but...	No	Yes	No	No	No
Problem / risk ?	8,5% S		12% P = 28%	Toxic gas	66% Cl		
Perspective ?	Yes	Yes	Yes, but...	Not fertilizer	Yes, but...	Not fertilizer	Not fertilizer

The usability of the products in Table 5.2 is discussed below:

1. **Ammoniumsulfate solution 28/35 %**

   Actual nitrogen content too low (2003/2003) and because of high sulphur content limited application rate of around 1 tonne per hectare. Is nevertheless recognized as fertilizer replacement in the Netherlands (independent of N-content!).

2. **Ammoniumnitrate solution 30 %**

   Actual nitrogen content too low (2003/2003), but an exemption for use as fertilizer replacement should not be very hard to get if pure. Ammonium nitrate is an explosive compound when dry. Possible impurities: organic matter, organic nitrogen.

3. **Ammoniumstruvite**

   Although the combined nitrogen and phosphate content is sufficient for recognition as NP-fertilizer (2003/2003), ammonium struvite is not yet recognized as EU-fertilizer or fertilizer replacement in the Netherlands. A request for admission as EU-fertilizer might be successful if the composition proves to be constant and pure (no impurities as potassium struvite, calcium phosphate, organic matter). The fertilizer industry has a preference for potassium struvite because of environmental issues (nitrogen oxide emissions from their installations).

4. **Aqua ammonia 30 %**

   This potentially dangerous product requires special precautions during storage and transport as to avoid toxic ammonia gas escaping. It is no longer allowed to inject ammonia solution into the soil in the Netherlands. Limited or no perspective for use in agriculture.

5. **Ammoniumchloride**

   Is a recognized fertilizer, but with limited possibilities for use because of its high chloride content. It is a food additive when pure (sal ammoniac).

6. **and 7. Ammoniumlactate and ammoniumcitrate**

These ammonium salts of the organic lactic and citric acids do not comply with 2003/2003 because of too low nitrogen contents and their organic nature. When pure, there might be other preferred applications (pharmaceuticals, feed for heterotrophic algae). Both compounds are recognized food additives.

5.4 CONCLUSIONS SUITABLE PRODUCTS

Ammonia in water is no longer used as a fertilizer in the Netherlands. NH_4Cl has a limited suitability for use as fertilizer because chloride can have a negative effect on certain crops. Struvite contains phosphate. There is a P surplus in the Netherlands and almost no P-fertilizer will be used anymore. Direct application in the Netherlands is not promising, but it is suitable for export (although pasteurization may be required resulting in a removal of ammonia). ICL Amsterdam will build a reprocessing plant for struvite when sufficiently large loads are available. Struvite is then incorporated in the production processes of different P and N fertilizers (also for export).

The products which contain organic matter are not considered to be artificial fertilizer. The organic matter remains in the product and the product remains manure (not fertilizer). With the presence of organic matter only manure is substituted, so it does not contribute to decreased N fertilizer production by Haber Bosch. If the organic matter has another origin than manure, it will take a long time to be licensed as fertilizer (if it ever happens, e.g. sewage sludge).

Only a product which is free of organic components, pathogens and has a nitrogen efficiency comparable to chemical fertilizer, can compete with currently commercially available fertilizers. This is possible (only) if a phase transition takes place (such as stripping). The N content in most actual recovery products is too low for recognition as chemical fertilizer, but after being recognized as exception to the rule, products may also be used as fertilizer replacement (eg ammonium sulfate from the air scrubbers in the composting facility of GMB, Zutphen, The Netherlands). Actually, only ammonium sulfate and ammonium nitrate are promising for direct application as N fertilizer. Ammonium nitrate is more valuable than ammonium sulfate because it contains more nitrogen and no anions such as chloride or sulfate which limit applicability. The addition of nitric acid instead of sulfuric acid in order to produce ammonium nitrate in place of ammonium sulfate may be an option for all the different recovery techniques to increase the nitrogen content.

The suitability of the nitrogen products is summarized as follows
- ammonium sulfate/ Ammonium nitrate (undergoes a phase transition and can compete with fertilizer) à suitable
- ammonium struvite (will probably be considered as a fertilizer in near future, demand in Germany and France) à suitable
- aqua ammonia, potentially dangerous and not allowed anymore in agriculture à not suitable
- ammonium chloride (contains chloride which has a negative effect on agriculture) à not suitable
- ammonium lactate and ammonium citrate (contain organics and are therefore not identified as fertilizer) à not suitable as fertilizer (outside scope of study)

In addition, some ammonium concentrates may also be used for flue gas cleaning by the DeNOx production of incinerators. However, this is outside the scope of this study.

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6

COMPARISON OF A REFERENCE N RECOVERY TECHNIQUE WITH CONVENTIONAL N REMOVAL AND HABER BOSCH

6.1 INTRODUCTION

In figure 6.1 the N-cycle for fertilizer and wastewater is presented, including the short circuit created with N-recovery.

FIGURE 6.1   PROCESS SCHEME OF THE CYCLE OF N FERTILIZER OF THE WASTEWATER CHAIN AND THE SHORT CIRCUIT OF N-RECOVERY
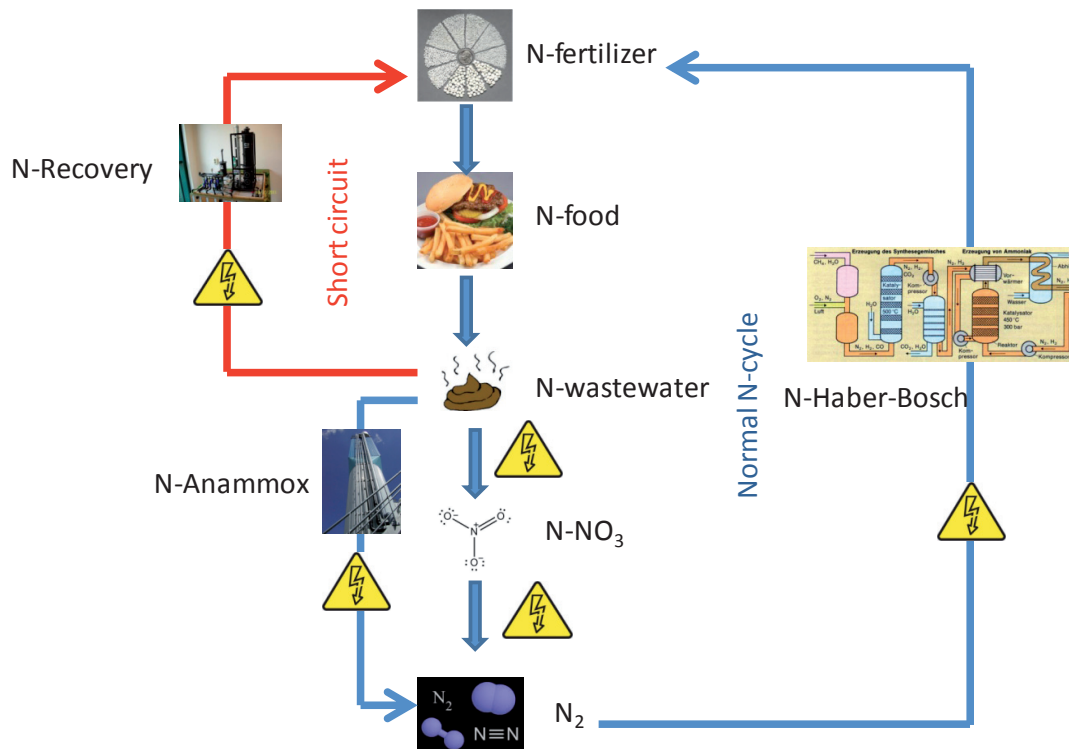
Nitrogen in fertilizer is used for crop growth, which in turn is consumed by live stock and humans and subsequently ends up into the wastewater. This nitrogen is not suitable to use as a fertilizer. In WWTP's normally this nitrogen is oxidized to nitrate (NO_3^-) in the process called biological nitrification. Nitrate is subsequently reduced (biological denitrification) to dinitrogen gas (N_2) which is emitted to the atmosphere. The biological Anammox process is a more efficient way to convert N in wastewater to N_2, and is presently applied for concentrated side streams at WWTPs. As the focus of this study is to recover N from these wastestreams,

Anammox technology is chosen as reference. With the Haber-Bosch process N_2 from the atmosphere is reduced again to N-fertilizer, thereby recycling N_2 over the atmosphere. For Anammox and Haber-Bosch energy is required. It therefore seems more efficient to directly recover N-fertilizer from the waste water. In this chapter the energy demand of a reference technique for nitrogen recovery is compared with the energy demand of Anammox as an actual nitrogen removal technique and the technique for artificial N production (Haber Bosch).

Moreover an indication is given of the costs of recovery installations compared to Anammox, depending on the scale of the installation and the N concentration in the rejection water.

By doing so, insight in the overall sustainability and cost effectiveness of nitrogen recovery is provided, which can guide further innovation .

6.2 REFERENCE CASE ANAMMOX-HABER/BOSCH

In this study the specifications of a reference rejection water stream of a large municipal waste-water treatment plant under construction (in 2012 12,000 ton ds/year sludge treatment) with TDH (thermal hydrolysis) are used. The rejection water flow was 17 m³/h and the NH_3 concentration was calculated to be 2,161 mg/l (Table 6.1).

| TABLE 6.1 | ASSUMPTIONS FOR THE REFERENCE NITROGEN-RICH STREAM |

	Unit	Value
Filtrate flow	m³/h	17
NH_3-N concentration	mg/l N	2,161
NH_3-N load per day	kg/d N	877

For energy calculations the running costs, e.g. for aeration, are considered (energy use for building materials and engines are neglected). The conversion of electricity into primary energy is based on an average European electricity mix (efficiency of 0.31) according to UCPTE (1994). In Table 6.2 the energy demand per kg nitrogen of the Haber Bosch and the Anammox process are presented.

| TABLE 6.2 | ENERGY DEMAND (MJ PER KG NITROGEN) OF HABER BOSCH AND ANAMMOX PROCESS [11] |

Aspect	Electricity	Other	Total UCPTE***
	MJ / kg N	MJ / kg N	MJ / kg N
Haber Bosch	0	37-45	37-45*
1-step anammox	13	0	13
Total	13	37-45	**50-58**

* both energy and the use of CH_4 in the chemical process

*** Union for the Co-ordination of Transmission of Electricity" (UCTE), see also: https://www.entsoe.eu/home/

So the total energy demand for the production of N-fertilizer and the removal of $N-NH_4$ from nitrogen rich wastewater with Anammox is about 50-60 MJ/kg N.

The consumed primary energy for production of consumed chemicals is included in the energy comparison. The energy consumption for the production of a certain chemical is defined as the GER (Gross Energy Requirement) value. The GER value includes the total primary energy use of the production process of the specific chemical (from the extraction of the raw materials until the end product leaves the door of the factory. In Table 6.3 the GER values of several chemicals which are used in ammonium stripping processes are described.

TABLE 6.3   GER VALUES OF CHEMICALS WHICH ARE USED IN AMMONIUM RECOVERY TECHNIQUES(STOWA 2012-06 [16])

Formula	Name (EcoInvent)	GERvalue MJ/kg
H_2SO_4	Sulphuric acid, liquid, at plant/RER U	2.12
NaOH*	Sodium hydroxide, 50% in H_2O, production mix	23.3
CaO	Quicklime, milled, loose, at plant	5.82
$(NH_4)2HPO_4$	Diammoniumphosphate	23.1

* STOWA 2010-30 [4]

In Table 6.4 a rough estimation of the investment and annual costs of the Anammox process are presented. These costs are based on the assumptions in table 6.1 and Tauw's experience with budget estimations of Anammox installations in recent projects.

TABLE 6.4   INVESTMENT AND YEARLY COSTS OF ANAMMOX

Aspect	Unit	Value	Source
NH_3-N load	kg/d N	877	
Investment costs	EUR	1,673,000	Estimation Tauw
Yearly costs	EUR	241,000	Estimation Tauw
Costs per kg N	EUR / kg N removed	0.8	

The costs of H_2SO_4 NaOH and CaO are estimated to be €0.18, €0.25 and €0.35 per kg, respectively [13, 14]

6.3 DESIGN REFERENCE NITROGEN STRIPPER

6.3.1 INTRODUCTION

In this paragraph the design of the reference nitrogen stripper is described. In paragraph 6.3.2 the process of stripping is explained. In the next paragraph the energy demand of the stripping process is calculated. In paragraph 6.3.4 the costs of the strip process are calculated, for details see appendix 1.

6.3.2 DESCRIPTION OF THE STRIPPING PROCESS

Ammonium can be stripped from ammonium rich side streams (e.g. rejection water) by means of air stripping. This is a well-known technique. In order to strip ammonium a high pH is required (pH 10 to 12). Usually NaOH or $Ca(OH)_2$ are added as alkali to realize this pH increase.

In the air stripping process (Figure 6.2) the rejection water is led through a stripping column in reverse flow through an air stream. The ammonia is transferred to the air stream which is led to an absorber. The adsorbed substance contains acid (H_2SO_4 or HNO_3) in which the ammonia dissolves and ammonium salts are formed. The ammonium salts are drained from the absorber while the ammonia free air can be recycled to the stripper.

Ammonium can also be stripped by adding steam to an ammonium rich solution. This results in a concentrated ammonium solution which can be used as fertilizer or as DeNOx agent to reduce the nitrous oxide emission in off gases.

FIGURE 6.2   PROCESS SCHEME OF AIR (AND STEAM) STRIPPING PROCESS
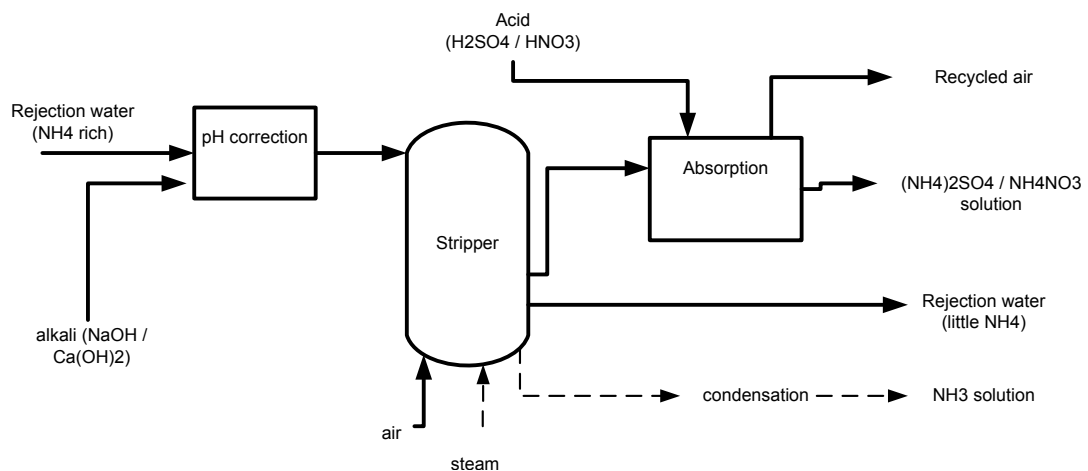
The energy demand and costs of this technique were investigated to get more insight in the energy demand and costs of ammonia stripping versus removal of nitrogen with Anammox. The operational energy demand and the costs of the nitrogen stripper are based on a budget estimation of a manufacturer of these systems (RVT Process equipment).

6.3.3 ENERGY DEMAND OF THE NITROGEN STRIPPER

The energy demand of an NH_3 stripper relates not only to the direct electricity and heat use but also to the energy demand for the production of the necessary chemicals such as H_2SO_4 (2.12 MJ/kg), NaOH (22.8 MJ/kg) or CaO (5.82 MJ/kg).

Furthermore, variations in relation to the intensity of the aeration step, the temperature and the dosage of chemicals are possible. Based on information from different sources (literature and manufacturers of strippers) the electrical, thermal and chemical use were calculated per kg of N-removed. Table 6.5 provides an overview of the energy consumption of the different aspects of the ammonium stripping process.

Table 6.5 shows that the energy use strongly relates to the electrical or thermal energy which is necessary. In the process described by Maurer a lot of electrical energy is used. By increasing the aeration, volatilization of CO2 is enhanced, which results in a reduction of alkali but increase of electricity use. The temperature of the N-rich water stream is another important parameter. A higher temperature results in a larger amount of volatilized ammonium but also an increased thermal energy use. The choice of chemicals also has a large impact on the energy use. Compared to caustic soda (NaOH) Calcium oxide (CaO) represents a relative low energy use (NaOH is however preferred by manufacturers in order to avoid scaling problems).

TABLE 6.5   ELECTRICAL, THERMAL AND CHEMICAL ENERGY USE OF AMMONIUM STRIPPING (MJ / KG N)

Source	Type Air / steam	Electrical* MJ/kg N	Thermal MJ/kg N	Chemicals CaO MJ/kg N	NaOH MJ/kg N	H$_2$SO$_4$ MJ/kg N	Total UCPTE MJ/kg N
M. Maurer, 2003 [11] en STOWA 2010 – 30 [4]	Air	84		14		15	113
Sustec (Envimac), 2012 [14]	Air	8	33		47	7	95
Sustec (Envimac), 2012 [14]	Steam	4	105		47		156
RVT, 2012	Air (T rejection water 50 °C)	3	n.a.		n.a.	9	n.a.
Range		**3 - 84**	**0 – 105 ****	**14**	**47**	**9 - 15**	**95 - 156**

* calculated for primary energy use

** depending on the temperature of the influent and the difference between air stripping / steam stripping

The stoichiometric ratio's of CaO, NaOH and H$_2$SO$_4$ which corresponds to table 6.5 are presented in table 6.6. Because of the combination of effects of air flow, heat input and dosage ratio's the literature values can be quite confusing. The total input of air, heat and chemicals should be taken into account.

TABLE 6.6   STOICHIOMETRIC RATIO'S

Source	Type Air/steam	Chemicals (kg/kg N) CaO	NaOH	H$_2$SO$_4$
M. Maurer, 2003 [11] en STOWA 2010 – 30 [4]	Air	2.4		7
Sustec (Envimac), 2012 [14]	Air		2*	3.5
Sustec (Envimac), 2012 [14]	Steam		2*	
RVT, 2012	Air (T rejection water 50 °C)		n.a.	4.1

* Sustec [14] claims: 0.7 mol NaOH/mol NH3-N. This is based on manure residue with a concentration range of > 2,000 mg/l N. Argumentation is based on the fact that NaOH is necessary to reduce carbonate. So the higher the N concentration, the lower the stoichiometric ratio kg NaOH/kg N. From literature values up to 2.5 mol NaOH/mol N with another concentration range and energy input are reported (Maurer [11]).

The range of total energy demand of ammonia stripping is 95-156 MJ/kg N. It becomes clear that the availability of waste heat, electricity or chemicals will result in a significant reduction of energy use, see paragraph 6.4.

6.3.4 COSTS OF THE NITROGEN STRIPPER

In table 6.7 the investment costs and yearly costs of the nitrogen stripper are calculated. A range is provided for the chemical costs per kg of N-recovered (based in table 6.5 and 6.6). Furthermore it is assumed that sufficient excess heat is available to heat the filtrate to a temperature of 50 °C.

COSTS OF NH$_3$ STRIPPER

Aspect	Unit	Value	Source
NH$_3$-N load	kg/d N	877	
Ammonia stripper	EUR	480,000	RVT Process Equipment
Storage tanks chemicals	EUR	150,000	RVT Process Equipment
Other works (concrete, etc)	EUR	300,000	Estimation Tauw
Total building costs	EUR	930,000	
Total investment costs*	EUR	1,581,000	
Yearly costs (excl chemicals)	**EUR**	**228,000**	Estimation Tauw
	EUR / kg N removed	0.8	
Chemical costs	**EUR / kg N removed**	**1.2 – 2.6**	Estimation Tauw
Total costs per kg N	EUR / kg N removed	1.9 – 3.2	

* Including a factor 1,7 (engineering, taxes, design, risk, profit, etc)

6.4 COMPARISON ENERGY DEMAND AND COSTS

The costs of a reference ammonium stripper are compared to Anammox. These costs are presented in table 6.8. As can be seen in table 6.8 reference air stripping is less favorable than Anammox. Independent of the scale, the costs of air stripping will always be higher than the cost of Anammox because the investment costs are more or less similar.

TABLE 6.8 COMPARISON OF COSTS OF THE REFERENCE STRIPPER AND ANAMMOX (INCLUDING ENERGY REQUIREMENT AND CHEMICALS)

		Anammox	**Reference Air stripping**
Investment costs	EUR	1,673,000	1,581,000
Yearly costs (incl. chemicals)	EUR/j	241,000	543,000 – 908,000
Gaining's fertilizer	EUR/j	-	- 29,000
Costs per kg N	EUR/kg N	0.8	1.9 – 3.2

* based on assumed gaining's of € 30 per ton of (NH$_4$)$_2$SO$_4$ [14]

The gaining's of recovered nitrogen are very limited. The most important contribution to the costs are the used chemicals to make the phase transfer. This is necessary to create a product that is applicable as an artificial fertilizer (see figure 3.1). So the cost comparison is mostly independent of scale effects. When waste heat and/or chemicals can be used, nitrogen stripping in some cases can be competitive. This also depends on the profit that can be acquired for the produced nitrogen products, but presently this is low

Table 6.9 provides the energy demand of Haber Bosch and Anammox versus ammonium stripping.

TABLE 6.9 ENERGY DEMAND OF HABER BOSCH AND ANAMMOX VERSUS AMMONIUM STRIPPING

Aspect	Total UCPTE
	MJ/kg N
Haber Bosch	37 - 45
1-step Anammox	13
Haber Bosch+ Anammox	50 - 58
Stripping to (NH$_4$)$_2$SO$_4$	97 - 156*

* see table 6.5

From table 6.9 it can be concluded that the energy demand of the combination Haber Bosch and Anammox is significantly lower than nitrogen stripping. In any case reduction of the use of chemicals, heat and/or electricity is an important objective for innovative techniques to compete in the future with other side stream techniques like Anammox and to make nitrogen recovery more realistic.

7

PRE SELECTION OF TECHNIQUES

7.1 INTRODUCTION

In order to identify the most promising techniques for N recovery a pre selection is performed. Firstly, the selection criteria are described. Next, the possible technologies to recover N are presented. After that five of the investigated technologies were selected to be studied in more detail in chapter 8.

7.2 SELECTION CRITERIA

This paragraph describes the criteria used to select possible nitrogen recovery techniques. These criteria relate to the main objective of this research which is to select and evaluate techniques which short circuit the nitrogen cycle. In other words: using the nitrogen that is needed in agriculture as effectively as possible and preventing other nitrogen streams from being removed from the wastewater by energy intensive processes. The reused nitrogen products are intended to be used for agricultural purposes. So techniques that "accelerate" the nitrogen cycle and not short-circuit the cycle such as the microbial fuel cell (MFC) (DeAmOx, Solid Oxygen Fuel Cell (SOFC) (pilot WWTP Scheemda)) are not included in this study. Anammox is only used as a reference case. Also, techniques that produce an organic nitrogen forms, requiring further processing such as algae, duckweed and lysine are excluded.

From chapter 5 it can be concluded that concentrated solutions of $(NH_4)_2SO_4$ or NH_4NO_3 are the most promising products for use in Dutch agriculture. Because of regulations and an excess of phosphorus the demand for struvite $(MgNH_4PO_4.6H_2O)$ is limited in the Netherlands. In Germany and France however, the demand for agricultural phosphorus products is much larger.

Moreover, the following criteria apply:
- The suitable nitrogen levels are in the range of 1,000-5,000 mg/l N.
- The technique must be a modification of a known technique or truly innovative, with a time to market of maximally 5 years, and with potential to become state of the art within the next 10 years.
- It is an advantage if the technique is tested on full or pilot scale, but this not essential. An innovative technique tested on a laboratory scale is still relevant when upscaling appears feasible within the next 5 years. However, it will then be difficult to estimate the costs and energy use for a full scale application.

Finally, as the interest in nitrogen recovery rises, it can be expected that other new techniques will be proposed in the coming years that are not part of this study. In this sense, this study represents a snapshot view of current developments according to the authors and members of the supervising committee.

7.3 IDENTIFICATION OF TECHNIQUES FOR N RECOVERY FROM WASTE WATER

The next step in this research was to investigate the possible techniques for nitrogen recovery. In Table 7.1 a survey of imaginable techniques is presented. The most important criteria for this technology assessment were:

- Potential for recovery of nitrogen as a fertilizer;
- The innovation potential
- The potential for recovery of nitrogen in the waste streams described in chapter 4 of this study.

For instance, the technique ion exchange is not a new development and not realistic for the matrix. Reversed osmosis is a mature technology, but with no new developments for nitrogen recovery. A disadvantage of this technology is that the nitrogen in the concentrate is not highly concentrated. Moreover, this technology is not considered to be an innovative technology. All other techniques are evaluated in a similar way. In the table short additional information is given with a remark.

TABLE 7.1   SURVEY OF IMAGINABLE TECHNIQUES

Potential technique for N Recovery	Recovery as fertilizer	Innovative	Potential	Remark
AMFER stripping	+	+	+	convential in digestate
Anammox	-	-	-	no N recovery
ARP/CAST (vacuum distillation)	+	-	+	without ion exchange
CAFR (struvite precipitation	+	+	+	thermal recovery struvite
Capitative deionisation	?	-	-	development > 10 years
Biological/Chemical oxidation	+/-	-	+	Manure or fertilizer?
DeAmOx	-	+	-	no N recovery
Duckweed/biomass	-	+	-	out of scope
Evaporation	+	+/-	-	high energy demand
Ion exchange	+	-	-	fouling, expensive
LGL stripping (rotating discs)	+	+	+	low energy demand?
MFC (microbiol Fuel Cell)	-	+	-	energy production
Nutritec (Turbotec)	+	+	-	CAFR switched to Saniphos
Partial freezing	+	-	-	high energy demand
Reverse osmosis	+	-	-	low N content
SOFC (Solid Oxigen Fuel Cell)	-	+	-	no N recovery
Stuvite precipitation	+	-	-	low N content
WSA stripping*	+	+	-	lab scale, clogging?
ZITA proces	+	+	-	no information

* Stripping technique is part of the study by AMFER and LGL

After the selection process the next 5 techniques remain for exploration in further detail.

- Stripping with air: AMFER: conventional technique, but applied on digestate.
- Stripping rotating discs: with LGL (Liquid Gas Liquid): a process with rotating discs. The NH_3 is transported in the gas phase from rejection water to H_2SO_4.
- Vacuum distillation: ARP/CAST process – standard vacuum column (without downstream ion exchange because the N needs to be recovered instead of removed), past lab scale and will be realised as pilot;
- Struvite precipitation with struvite recycle: (CAFR), Removal of ammonia via precipitation as struvite combined with recovery of the ammonia via thermal treatment of the struvite ultimately producing an acid solution of ammonia
- Biological/Chemical oxidation: partly biological nitration followed by chemical oxidation from NO_2 to NO_3 and concentration/recovering of NH_4NO_3. Concentration of nitrogen by digestion or with excess heat

In chapter 8 the selected technologies are described in more detail which includes background information on the technology such as costs (if known), energy use, limitations and scale of application.

8

DESCRIPTION INNOVATIVE TECHNIQUES
FOR N RECOVERY

8.1 INTRODUCTION

Based on the selection criteria described in the former chapter, five techniques were selected. These are described in more detail in this chapter. Some of these techniques are still in early development. Therefore, not all techniques can be described in great detail. However, all information that is available is included in the report. The information below is partially based on data provided by the manufacturers of the different techniques that have filled in a fact sheet. Details such as removal percentages of nitrogen were not always provided in the fact sheets. These fact sheets are attached in Appendix 2. This information is provided by the manufacturers of the different techniques and is not evaluated by the authors.

8.2 AMFER

The AMFER® process (Figure 8.1 and 8.2), is based on stripping of ammonia directly from the influent (often digestate) and recovery as ammonium sulfate. This technique has been applied at a demonstration scale..

FIGURE 8.1   **AMFER® PROCESS**
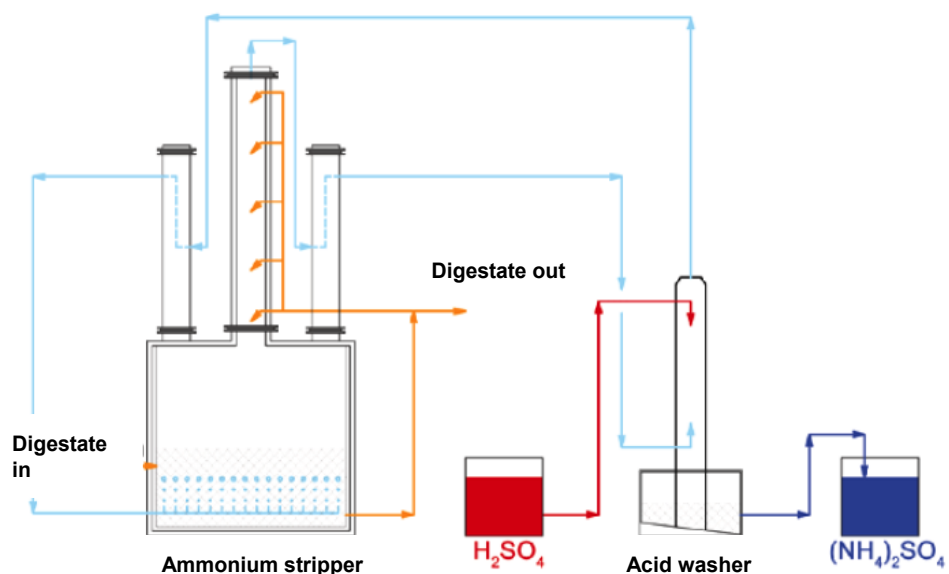
The N-containing stream (digestate, > 6 % dm) is heated to 60-70°C (with excess heat from a combined heat and power (CHP) installation on the plant). Ammonia (NH_3) is removed via a stripping process with air. As a consequence of the air-stripping, CO_2 is removed, resulting in a pH increase in the N-containing stream without the need for caustic soda. At a higher pH, stripping of ammonia becomes more efficient due to a shift in the NH_4-NH_3 equilibrium. Ammonia, which is brought into the gas phase, is retrieved by washing the gas stream in a H_2SO_4-rich solution. Ammonium sulfate (($NH_4)_2SO_4$) solution is the main product formed during the washing step. Air is led back to the stripper for reuse, recuperating a large share of the heat. The treated digestate is recycled to the digester.

FIGURE 8.2   SCHEMATIC REPRESENTATION OF THE AMFER PROCESS. THE REQUIRED AMOUNT OF NEAT SULPHURIC ACID HAS BEEN CALCULATED BASED ON STOICHIOMETRIC RATIO'S OF NITROGEN AND SULPHURIC ACID ASSUMING 100% NH_4 RECOVERY FROM STRIPPING GAS. GER H_2SO_4: 2.12 MJ/KG (STOWA 2012-06). THE AMOUNT OF NEAT AMMONIUM SULFATE FORMED PER KG N IN INFLUENT WAS CALCULATED USING THE EFFICIENCY OF 90% N REMOVAL REPORTED BY THE MANUFACTURER. A CONVERSION FACTOR OF 3.6 MJ/KWH WAS USED TO COMPUTE ELECTRIC AND THERMAL ENERGY
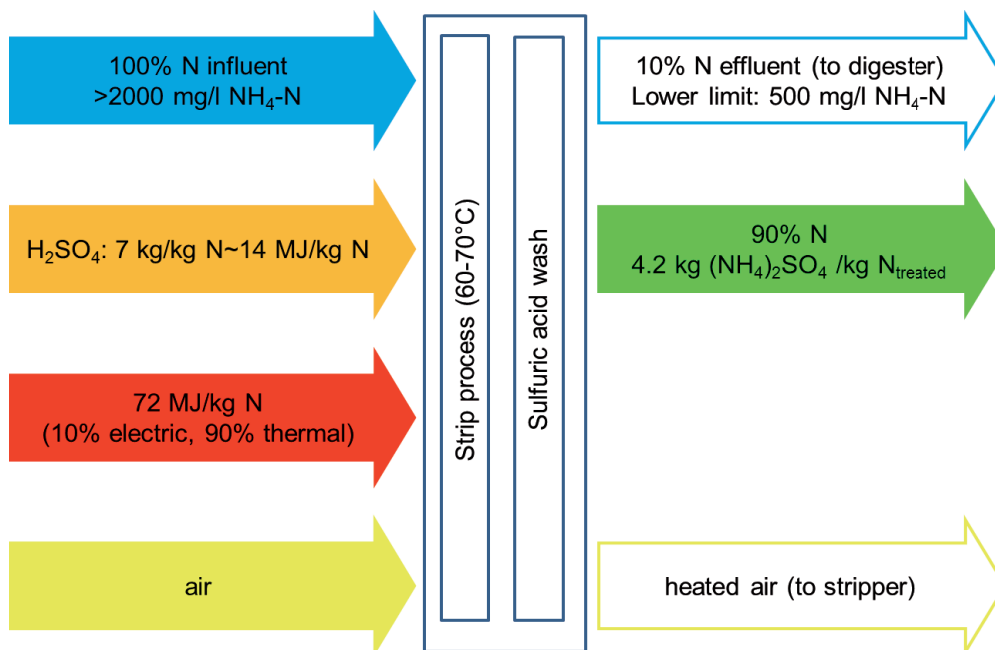
The process can also be used for treating the liquid fraction after separation of the digestate. It is expected that the process is even more efficient on the liquid fraction than on the raw digestate.

Other N-rich streams that can be treated are:
- Digestate of manure and other organic compounds (wastewater treatment and digestion).
- Rejection water of sludge digestion on WWTP.
- Pre-treatment of NH_4-rich manure before digestion.
- Treating digestate in circulation around the digester in order to lower N-toxicity and to boost biogas-production for the digestion of N-rich streams
- Industrial NH_4-rich streams

This process is also suitable for the sludge digestion side stream treatment in municipal waste water treatment plants. A demonstration plant has been operated in 2011 which treated 10 - 30 m^3/day. Full scale systems should be able to treat up to 500 m^3/day. In some cases (e.g. treatment of digestate or manure) pre-treatment will be necessary.

The influent of the AMFER should contain at least 2,000 mg/l ammonia (no upper limits). The effluent nitrogen level will be at least 500 mg/l ammonia, however at higher N concentrations the N-removal efficiency may be up to 90%, depending on the fraction of NH_4-N, the total N concentration in the liquid and the start concentration.

According to the manufacturer the effluent of this technique is ideally pre-processsed for further treatment in an ANPHOS® system (by the same manufacturer; system removes phosphates and some ammonium). The combination of AMFER® and ANPHOS® results in an effluent with an NH_4-concentration below 500 mg/l. If further polishing is desired, the effluent of the AMFER® - ANPHOS® - combination is suitable for treatment in a NAS®-system where bacteria will remove nitrogen further in combination with COD removal. This is possible because the AMFER® only removes nitrogen, the organic carbon is left as a substrate for extended biological nitrogen removal.

8.3 LIQUID- GAS- LIQUID (LGL) PROCESS

The second technique (LGL stripper) is a technology which was patented in 2010. It removes ammonia from a liquid and transfers the ammonia via the gas phase to a second liquid (an acid to be chosen by operator) in a single apparatus. The LGL stripper so far has only been tested on a laboratory scale. A test on pilot scale is planned.

The LGL process strips volatile compounds (in this case ammonia) from a liquid to another liquid. The volatile compound is transferred via the gas phase. The system is completely gas tight. Heating or intensive mixing is not required. LGL makes use of rotating discs to increase the mass transfer surface between solution and gas, and from gas to solution. A rotating disc is partially submerged in a N-rich solution, which creates a liquid film on the disc surface that is not submerged, see Figure 8.3. From this film the ammonia is transferred to the gas phase. In a second solution, which is physically separated from the N-rich solution, another rotating disc is submerged. As there is a single head space above all rotating discs, the ammonia can dissolve in the liquid biofilm on disc. More ammonia can be transferred when the second solution is acid.

FIGURE 8.3   LGL SYSTEM

26
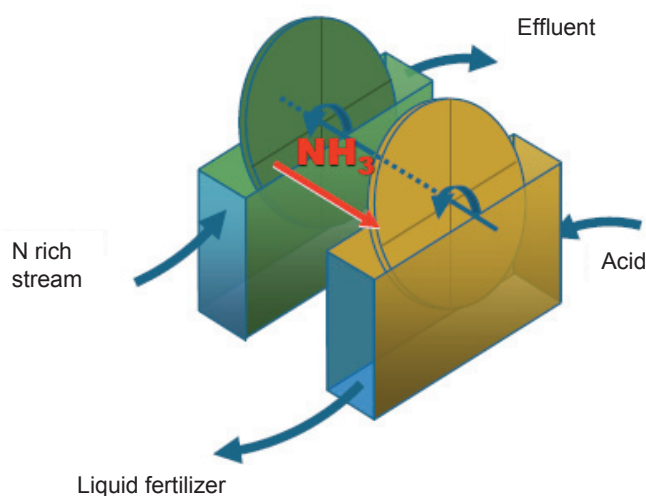
The technology is in a preliminary stage of development. Bench scale tests have been executed with a synthetic influent. The aim is to achieve 8 m^3 per day in a single module, but the techno-logy is scalable. So if a higher flow is required the stripper could be enlarged or more strippers could be installed.

In Figure 8.4 schematic representation of the LGL process is given.

FIGURE 8.4   SCHEMATIC REPRESENTATION OF THE LGL PROCESS. THE REQUIRED AMOUNT OF SULPHURIC OR NITRIC ACID HAS BEEN CALCULATED BASED ON STOICHIOMETRIC RATIO'S OF NITROGEN AND SULPHURIC ACID ASSUMING 100% NH$_4$ RECOVERY FROM STRIPPING GAS. GER H$_2$SO$_4$: 2.12 MJ/KG (STOWA 2012-06)
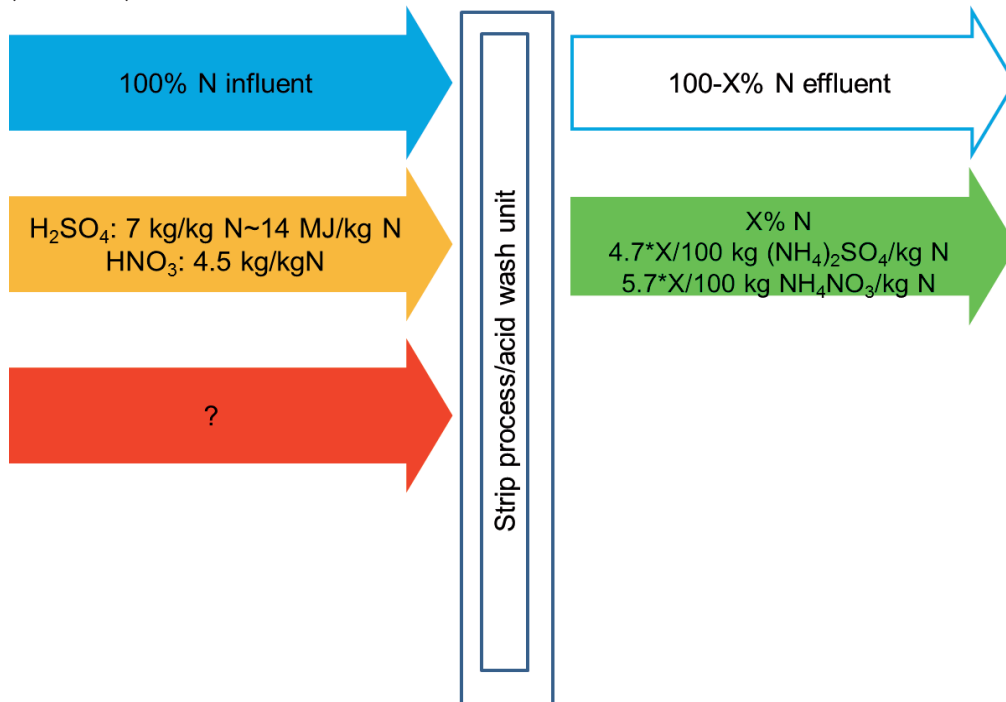

8.4 CAFR (CHEMISCHE AMMONIUM FÄLLUNG UND REZYKLIERUNG)

Although the CAFR (Chemische Ammonium Fällung und Rezyklierung) process was already patented in 1992, and piloted in the Netherlands in 1994 (Stowa 1995-13), there still do not appear to be full scale references for municipal WWTP's. The German company that introduced the technology, does not seem to actively market the technology anymore. The patent has lapsed in the Netherlands since 1997. Also in Germany the patent has lapsed. However, the authors have noticed that the CAFR technology is still often mentioned in discussions on nitrogen recovery. Furthermore, evaluation of this technology can add to the insight in possible bottlenecks for nitrogen recovery. Therefore, it was decided to include the CAFR technology in this study.

A schematic picture of the CAFR is included in Figure 8.5.

FIGURE 8.5   CAFR SYSTEM (STOWA 1995 13)
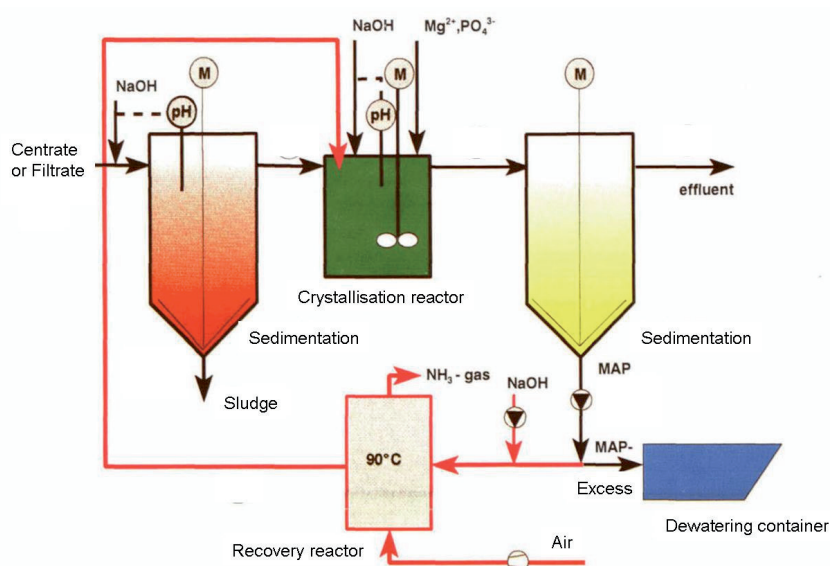
The CAFR process consists of five steps (Figure 8.6).

- Pretreatment to remove solids e.g. by means of polyelectrolyte
- Struvite formation in a crystallisation tank
- Separation of the crystallized struvite
- Thermal treatment of struvite and stripping of NH_3
- Washing the ammonia with sulfuric acid

After the pretreatment, chemicals are added to create precipitation conditions for struvite ($MgNH_4PO_4.6H_2O$). Normally, these chemicals include a magnesium salt and sometimes a base. Then the precipitated struvite is separated and brought to desired pH and temperature (80-90°C) (Stowa 1995-13). At these conditions the struvite decomposes to magnesium hydrogen phosphate and ammonia. At pH >12.75 a nearly complete decomposition is achieved. Air is blown into the decomposition reactor by a compressor. As a result, the formed ammonia is stripped from the reaction mixture and also mixing takes place. The increased pH and high temperature favor the stripping process. The ammonia-rich vapor can be processed into a concentrated solution (by condensation) or to an ammonium salt (by washing with acid). The magnesium hydrophosphate (possibly after acidification) is reused for formation of struvite, so there is a recycle of magnesium and phosphate. Recycling can result in the accumulation of various side precipitation products, such as $CaCO_3$ and $MgKPO_4$.

Chemical needed for the process are:

- NaOH for pH control during struvite precipitation at a value of 9.5. For centrate of WWTP Utrecht the pilot plant consumption was on average 5 - 10 ml/l of 20% Na(OH) solution. The amount of NaOH required for decomposition is unknown.
- Magnesium: The magnesium consumption for struvite precipitation depends a.o. on the phosphate concentration in the influent. A ratio Mg:N:P of 1:1:1 was found to be sufficient for high ammonia removal efficiencies. However, due to the accumulation of side precipitation products part of the sludge must bled which results in loss of magnesium which needs to be replenished. Also accumulation of unreactive Mg precipitates may occur, which will limit the number of times the Mg can be recycled for ammonia precipitation. To compensate for this effect, additional "fresh" magnesium needs to be added. Operational data on Mg consumption are not available.

SCHEMATIC REPRESENTATION OF THE CAFR PROCESS. THE REQUIRED AMOUNT OF NEAT SULPHURIC ACID HAS BEEN CALCULATED BASED ON STOICHIOMETRIC RATIO'S OF NITROGEN AND SULPHURIC ACID ASSUMING 100% NH_4 RECOVERY FROM STRIPPING GAS AFTER THERMAL TREATMENT OF THE STRUVITE. GER H_2SO_4: 2.12 MJ/KG (STOWA 2012-06)
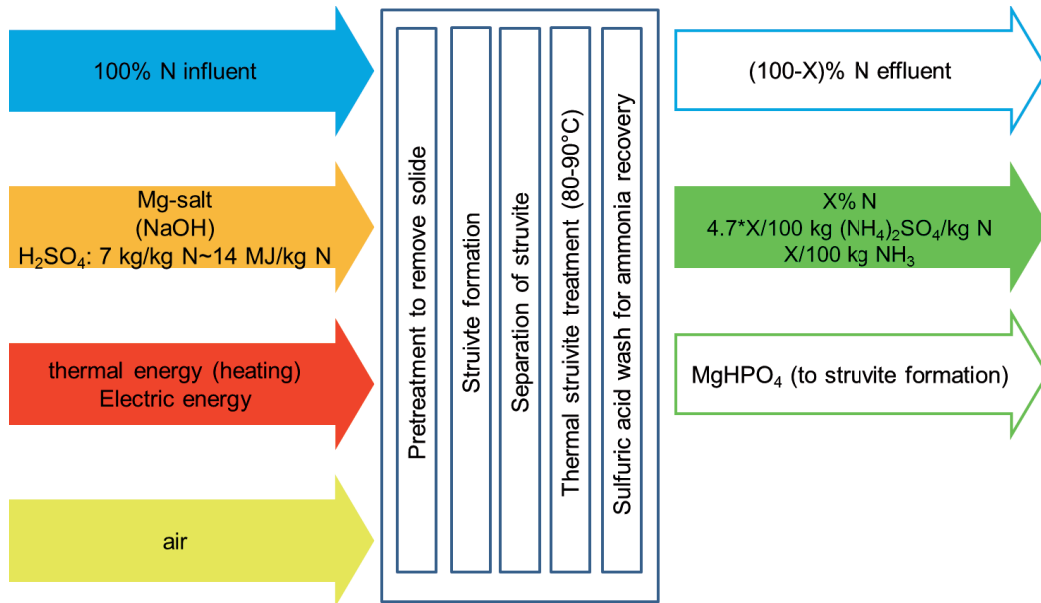
Energy is required for mixing, pumping and stripping. Energy consumption for stripping is expected to be relatively high, but operational data are not available.

Disadvantages of the CAFR process are the relatively high chemical consumption, the fairly complex process operation which is for some part due to the scaling potential of magnesium hydrophosphate which appears to be higher than for struvite (Stowa 1995-13). Also, due to formation of side products in the sludge, part of the sludge must be bled requiring additional dosing of magnesium and perhaps even phosphate. A bottleneck in the process appears to be the low stripping efficiency after decomposition. A cost estimate from 1995 amounts to 6 Euro/kg N removed (non-indexed) for a 400.000 i.e. WWTP (STOWA 1995-13). For a 100.000 i.e. WWTP the costs are doubled.

8.5 ARP/RCAST AMMONIA RECOVERY PROCESS

In the ARP (Ammonia Removal Process), N-rich wastewater is sprayed into a vacuum vessel after adjustment of the pH to pH 8-10 (via the addition of caustic) and heating to 60-70°C.

As a result dissolved ammonia is stripped at increased rates from the wastewater phase and transferred to the gas phase. The ammonia vapour is condensed in a second section and the energy released in the process is reused. At the same time the ammonia is redissolved in the condensate. In the third section of the ARP process the ammonia solution is acidified with sulphuric acid. The produced ammonium sulfate solution can then be concentrated to desired final concentration of ammonium sulfate $((NH_4)_2SO_4)$ via a standard RCAST system (Reverse Controlled Atmosphere Separation Technology) based on multi-stage vacuum assisted flash distillation.

In Figure 8.7 a schematic representation of the ARP/RCAST process is presented. The presence of magnesium, calcium and/or phosphate in the wastewater necessitates pre-treatment in e.g. a struvite reactor to remove the magnesium, calcium and phosphorous and avoid scaling. At increased pH higher concentrations of calcium, magnesium of phosphorous may precipitate. This has to be taken into account during the design of the installation (periodical cleaning of installation with acids).

The ARP system is a modular system. The flow of the wastewater is the determining factor. The actual nitrogen load is not a restricting factor (transfer rates are higher at increased concentrations). Influent concentration is at least 150 mg NH_4-N/l (no upper limit)-The effluent concentration N-NH4: minimum 50-100 mg/l. Available modules are: 5.5 m^3/day; 11 m^3/day; 19 m^3/day en 37.5 m^3/day.

FIGURE 8.7   SCHEMATIC REPRESENTATION OF THE ARP/RCAST PROCESS. THE REQUIRED AMOUNT OF NEAT SULPHURIC ACID HAS BEEN CALCULATED BASED ON STOICHIOMETRIC RATIO'S OF NITROGEN AND SULPHURIC ACID ASSUMING 100% NH$_4$ RECOVERY FROM STRIPPING GAS. GER H$_2$SO$_4$: 2.12 MJ/KG (STOWA 2012-06)
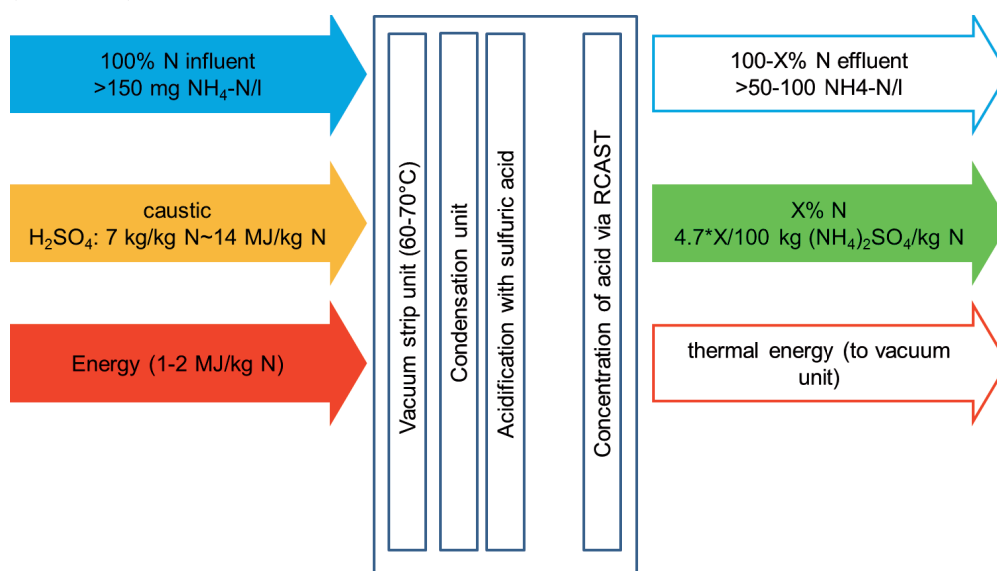

Vacuum distillation in principle takes less energy than conventional stripping. In New York this process is realized on a large scale (20 million euro's). The process in that case is cost-efficient, because alkali is present in the wastewater so that no additional alkali needs to be dosed to the plant.

8.6 BIOLOGICAL/CHEMICAL OXIDATION

This technique focuses on the conversion of ammonium in a reusable fertilizer in the form of ammonium nitrate. For this purpose, a 2-stage process has been developed (Figure 8.8). In the first step, approximately 50% of the ammonium nitrite is converted into a biological way. In the second stage, the pH is lowered and the formed nitrite is chemically oxidized to nitrate. After that an evaporation step is implemented. The final product is an aqueous concentrated solution of ammonium nitrate, having a content of 6.4 g/l ammonium nitrate.

Suitable waste streams originate from digesters (industrial and communal) with high nitrogen contents in the rejection water. The process has been studied at laboratory scale. The latest research shows that both processes could be carried out simultaneously in one reactor. At the time of writing this report the process has to be evaluated at pilot scale to validate existing mathematical models and ensure proper upscaling.

FIGURE 8.8   SCHEMATIC REPRESENTATION OF THE BIOLOGICAL/CHEMICAL OXIDATION PROCESS
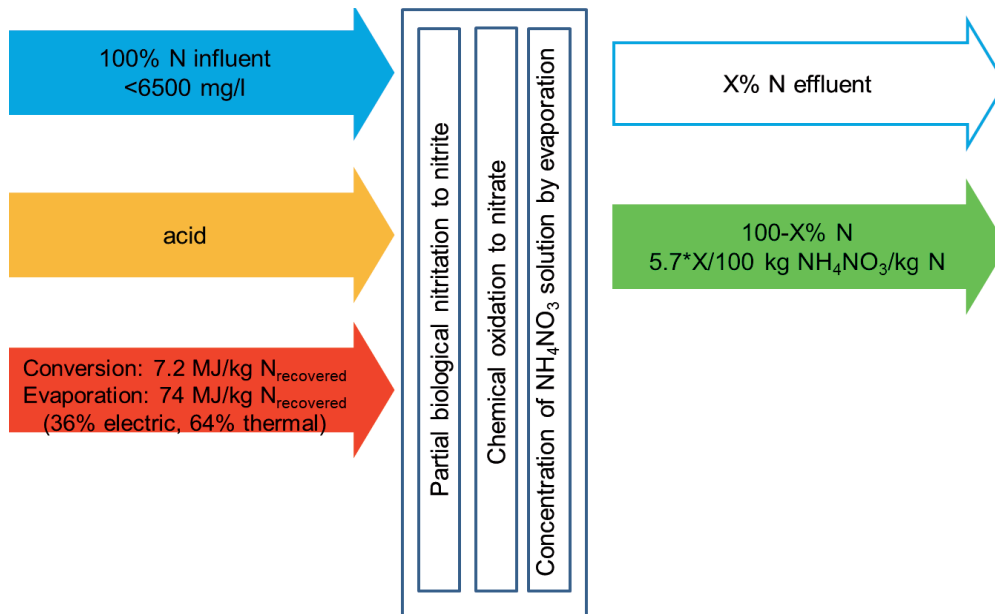
A conversion factor of 3.6 MJ/kWh was used to compute electric and thermal energy. This process needs fewer chemicals than the other processes, which is an important advantage. There are uncertainties about the necessity of the evaporation step and feasibility at lower ammonium concentrations. It is particularly suitable for liquid manure flows with high nitrogen contents. However the organic matter remains in the product and the product remains manure (no phase transition, so it is not an artificial fertilizer). This product replaces no fertilizer and will meet a lot of regulatory boundaries, see paragraph 3.2.

8.7 COMPARISON OF TECHNIQUES

After the description of the selected 5 techniques in more detail the question must be answered, with technique is best for now and in the future (best opportunities).

In the detailed exploration of the techniques, the first technique that does not fit to the criteria is the partial biological and chemical oxidation technique. The product of this technique contains residual organic substances. Because of that it is not a fertilizer and competes with manure instead of inorganic fertilizer. So it may have a positive contribution to reduce the nitrogen cycle, but does not fit in the objectives of this exploratory study. Moreover, while the organics present actually originate from wastewater, the use of this product will not be allowed as such. A lot of time will be required to get it licenced, if ever. The energy demand of this technique is high because of the evaporation process needed to produce a concentrated end product. With residual heat the process still may be sustainable. The costs are estimated (by the company involved in the future marketing of the product) on 0.7 euro/kg N. That

is relatively low compared to conventional stripping and the other techniques, presumably because of the limited use of chemicals for the processing. However, It is difficult to check if this estimation is accurate and complete. With this current claim these costs are comparable to Anammox, thus rendering this technique attractive from an economical point of view.

The second technique that fails the comparison is CAFR. The technique has been developed more than 20 years ago but did not come to maturity. The costs that are calculated in 1995 are much higher than the calculated cost of the reference stripper. The processing is complex and the cost and energy use of heating to evaporate the NH_4 are higher than used by the other techniques.

Comparison of the other techniques is difficult. The reference stripping technique and AMFER are comparable (as they are based on the same principal).

Both LGL and ARP/RCAST are expected to demand less electrical energy than the other techniques. However, the largest part of primary energy demand is caused by the used chemicals. It is not clear whether these techniques will differ from each other and from the conventional stripping technique in that respect. In any case, the use of chemicals should be intensively reduced to become cost-competitive with Anammox.

9

DISCUSSION

This explorative research on innovative nitrogen recovery focuses on the recovery of nitrogen from side streams on Dutch WWTP's. At first the nitrogen problem is defined, the nitrogen cycle which runs twice as fast compared to natural processes, with several consequences, like eutrophication, greenhouse gasses, additional energy demand. Currently, the EU and Dutch government develop policies to diminish the nitrogen emissions and turn-over.

In this respect it is obvious to investigate the possibilities to short circuit the nitrogen cycle and to convert nitrogen in WWTP side streams to artificial fertilizer (precursors). In that way the production of N fertilizer may be reduced with positive environmental consequences. A quick scan of the amount of nitrogen side streams shows that about 4% of the nitrogen in wastewater can be recovered, far less than the need for artificial fertilizer by agriculture. However, also other nitrogen streams eg. from industry can be identified, and recovery from these waste streams as well may lead to higher possible recovery quantities. In addition, nitrogen recovery from manure can solve logistic bottlenecks in agriculture, but manure is not included in this study.

With the recovery techniques a range of N-containing products can be made. Only $(NH_4)_2SO_4$ and NH_4NO_3 are considered to fulfill market and agricultural requirements. In theory, struvite can also be used as a fertilizer. However, at the moment the struvite originating from wastewater has legislative restrictions. Also, the high phosphate content makes it only suitable for export, because of the surplus of phosphate in the Dutch agricultural area.

Information about conventional ammonium strippers was gathered in order to define the investment costs and yearly costs as a reference technique. The costs of ammonium stripping were compared to the costs of Anammox to remove nitrogen in WWTP side streams. The costs of conventional air stripping are between 1.9 and 3.2 EUR/kg N, while the costs of Anammox are about 0.8 EUR/kg N (on the scale of a sludge line with thermal hydrolysis of a large Dutch WWTP). The main part of the costs are caused by the energy and use of chemicals (CaO or NaOH and H_2SO_4). It is concluded that cost reductions cannot drive nitrogen recovery for waterboards, except when cheap residues in stead of expensive chemicals or waste heat/electricity are available. The energy demand of the reference stripping varies from 100-150 MJ/kg N (aeration, heat, chemicals) and is significantly higher than the energy demand of nitrogen producing Haber-Bosch process combined with Anammox (60 MJ/kg N).

Five innovative techniques were selected out of nineteen imaginable techniques: AMFER, LGL, CAFR, ARP/RCAST and a technique with biological and chemical oxidation. Information on each technology was obtained from the manufacturers, and fact sheets were made (refer to appendix). ARP/RCAST and LGL seem most promising because they are efficient in the phase transition and need less energy. The ARP/RCAST process has been implemented in several full scale installations while LGL only functions on laboratory scale. It is expected however that these techniques still use a large amount of chemicals.

The energy demand of the Delft University of Technology and IV Water technique of biological and chemical oxidation is comparable to the GER values of the other techniques, because of the evaporation. However the technique uses far less chemicals. This results in a cheaper process. Yet this technique is not suitable to make artificial fertilizer, because no phase transition is present. This will meet a lot of stringent regulations that will be a showstopper for this technique.

So in general short circuiting of the nitrogen cycle is technically possible, but energetically not very favorable. From a cost perspective the large amount of required chemicals makes the present and expected future technologies not competitive yet. Still, in special cases with the availability of residual chemicals or waste heat nitrogen recovery may be cost-effective and sustainable.

To have a process of nitrogen recovery in the future that will be feasible for side streams on a WWTP, new techniques should reduce the use of electricity, heat and/or chemicals as much as possible to become competitive.

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CONCLUSIONS

- The amount of nitrogen that can be recovered from municipal waste water is about 4 % of the N load which is present in waste water and is far from sufficient to cover the amount of applied artificial nitrogen fertilizer. Only side streams with a relative high N content (>1.000 mg/l N) are suitable for N recovery. However, several alternative N-rich streams have been identified that might be suitable for nitrogen recovery;

- Most suitable recovery products are NH_4NO_3 and $(NH_4)_2SO_4$. Struvite $(MgNH_4PO_4.6H_2O)$ in theory is also suitable, but has the disadvantage of a high P content (large surplus in the Netherlands) and current legislative restrictions;

- In general thte energy demand of the reference stripping varies from 100-150 MJ/kg N (aeration, heat, the chemicals, including the GER values of the chemicals) and is significantly higher than the energy demand of the nitrogen producing Haber-Bosch process combined with Anammox (total 60 MJ/kg N).

- In general (reference case) it shows that nitrogen recovery is more expensive (1.9 – 3.2 EUR/kg N) than nitrogen treatment using Anammox (0.8 EUR/kg N). This is caused by the energy use and price and quantity of chemicals (NaOH or CaO and H_2SO_4).

- From the five selected techniques only two seem promising (one based on vacuum distillation and one based on stripping of nitrogen), although both techniques still need large amounts of chemicals. For that reason nitrogen recovery from waste water is not competitive yet to Anammox or other biological ways for treatment of nitrogen containing wastewater.

- Nitrogen recovery may be feasible, when residual chemicals and/or waste energy streams are provided, or new techniques with less chemical demand will be developed or perhaps when for another N-rich stream other business cases apply (e.g. logistic bottlenecks in agriculture).

11
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APPENDIX 1

DESIGN AND COST CALCULATION OF A CONVENTIONAL AIR STRIPPER

Budget quotation 1ks120727

29.05.2012
ks
Page 2 of 12

Tauw B. V., NL- 7400 AC Deventer

1. Operating conditions

1.1 Preconditions

Water flow	17 m³/h
Feed pH-level	approx. 7,0
Stripping pH-level	≥ 8,8
Feed temperature	50°C
Stripping temperature	50°C
Inlet concentration NH_4-N	2.160 mg/l
Outlet concentration NH_4-N	max. 1.080 mg/l
Efficiency	> 50 %[1]
Total suspended Solids (TSS)	unknown
TS-content	unknown

Remark:
In the past we learned, that the solid fraction out of digestion waste water is comparable unpleasant in its fouling/ blocking behaviour. Our experience with waste water from biogas plants is mainly based on pilot tests (research project in Fürstenwalde, Germany) and a stripping unit in Lithuania, which is also working with reject water from digested biomass. Please be informed that we found a tolerable TS-content of approx. **1,6 wt.%**, whereas 3,6 wt% TS caused great fouling problems. Of course, 1,6 wt.% is a benchmark, depending on the specific type and structure of the solids. But please consider, that besides hairily and fibrously components, in particular solids from digestion reject water clog the packing and other equipment. This material pollution can't be removed by chemical, but only by manual cleaning.

RVT PE will not guarantee a trouble-free operation and strongly recommends to remove solids before the stripping unit.

Installation	outdoor

auxiliary energies:	
electrical energy	220/400 V, 50 Hz
city water	without solids, for cleaning purpose
acid for scrubbing system	H_2SO_4, 96% (estimated)
acid	for cleaning purpose e. g. HCl
hot water	available
compressed air	5-7 bar, g.

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[1] As requested, we designed the system for an ammonia recovery of 50%. Please be informed, that much more efficiency would be possible with stripping technology. If required, we could realize an outlet concentration of about 40 mg/l with an air stripping plant with higher stripping and scrubbing columns and using a higher operation-pH-value (which also means a higher consumption of chemicals and more produced $(NH_4)_2SO_4$).

1.2. Expected consumption and operating values

For cleaning 17 m³/h waste water, following operating data will show up:

Water flow	17 m³/h	
Inlet concentration NH₄-N	2.160 mg/l	
Outlet concentration NH₄-N	1.000 mg/l	
Sulfuric acid, 96 %, approx.	80 kg/h	
Ammonia phosphate, 38 %, approx.	245 kg/h	
Make-up water, approx.	160 kg/h	(without loss of evaporation and cleaning)
Electricity (installation), approx.	32 kW	(Option 1: approx. 42 kW)

Note:
- pH- value of stripped water: approx. 0,2 to 0,5 below inlet pH-value.
- To determine the NaOH-consumption analysis by titration is required.
- Instead of pure sulphuric acid (technical quality of approx. 96-98 wt%), H_2SO_4 from a secondary source can be used (e.g. diluted acid of 70-80 wt%). Thus acid qualities are cheaper or even free of charge, but mustn't contain substances, which avoid the use of Ammonia sulphate solution, 38 wt.% as liquid fertilizer (e.g. no heavy metals, toxic organic, etc.).

2. Description

Waste water with an ammonia-N content of 2.160 mg/l, which is nearly free of solids is treated in an ammonia stripping plant.

The waste water is stored in a local buffer tank, which is provided by others. Our battery limit is the stripper feed pump, which feeds the waste water to the top of the stripper column.

In order to separate the ammonium ions from the solution and to dissolve ammonia physically, the pH-value of the waste water has to be alkaline. The alkalisation is done by dosing NaOH into the feed pipe. The storage tank, the diaphragm dosing pump as well as the required NaOH-pipeline between pump and stripping plant (estimated max. 15 m) are in our scope of supply.

At the battery limit the feed is provided with a temperature of 50°C.

We take it for granted, that suitable defoaming agents will be dosed on site, if it is required.

In order to clean the waste water, the stream is distributed at the top of the stripping column. Vapour-saturated air is introduced over the bottom of the column, led in counter flow to the waste water and removes the ammonia ingredients out of the liquid. The ammonia containing air leaving at the top of the column is led to the absorption column next by. The treated waste water taken from the bottom of the column is purged out by the discharge pump.

The air coming from the stripper is cleaned in the absorption column with sulfuric acid. Ammonium sulfate solution with approx. 38 % is removed from the bottom by the circulation pump. The almost ammonia-free air leaves over the top of the column and is led again into the stripping column.

The stripping column and the absorption column are working under atmospheric pressure.

The packed beds contain Hiflow-rings, size 50 mm, made of polypropylene. They are supported by a support grid made of polypropylene. The distribution of the liquid is ensured by a trough distributor which is also made of polypropylene. The stripping and the absorption tower are equipped with a mist eliminator.

The salt solution is pushed out discontinuously. The concentration of the washing liquid is observed by density determination. In order to ensure a constant pH-value fresh water is added by a control valve.

The storage tanks for NaOH, sulfuric acid and $(NH_4)_2SO_4$-salt solution are quoted as a separate price. With regard to a truck-supply/ pick-up (normally a net load of approx. 23 to) and sufficient buffer capacity during weekend, we recommend a tank volume of at least 25 m³ for H_2SO_4 and NaOH. The tank for the produced salt solution (fertilizer) should have a volume of at least 30 m³.

The packed bed and the pipes, which are in contact with caustic water, are cleaned by a rinsing circuit at the stripping column. Fresh water and hydrochloric acid are required for the cleaning step.

Remark:
The columns as well as the pipelines are made of polyprolylene. As the plant is installed outdoor, the influence of ultraviolet radiation on polypropylene is the formation of a thin corrosion film. This optic change however has no impact on the mechanical resistance.

11. Budget price

Ammonia stripping plant,
Delivery, mounting and commissioning, as specified   480.000,-- Euro

Option 1: Storage tanks
Storage tanks for NaOH, H_2SO_4 and ASL,
incl. operator platform, discharge pump $(NH_4)_2SO4$,
measurement and control technology
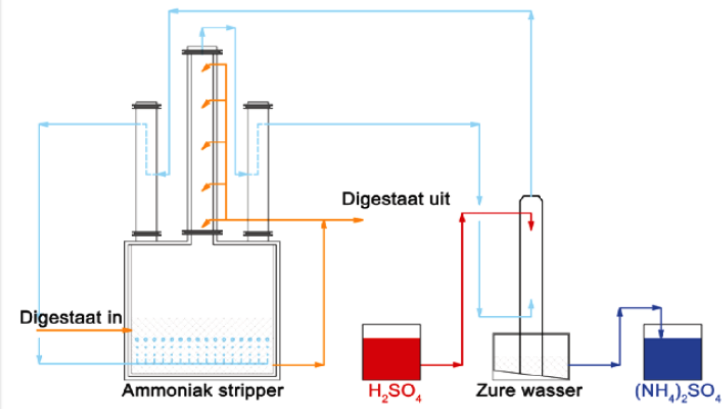Delivery, mounting and commissioning, as specified   150.000,-- Euro

Place of delivery:	free delivered NL
Delivery time:	approx. 8 months after receipt of order and technical clearance
Terms of payment:	30 % down-payment immediately upon receipt of the order confirmation
	30 % upon advice that goods are ready for shipment
	30 % upon completion of plant assembly resp. 3 months after advice that goods are ready for shipment
	10 % upon completion of stripper-plant commissioning resp. 10 months after advice that goods are ready for shipment
Payment:	30 days net
Valid:	31.08.2012

Cost estimation Air Stripper		RVT air stripper	
Capacity (kg N/d)	kg /d N	877	
N removed	%	90%	
Ammonia stripping plant (RVT)	EUR	480.000	
Storage tankts NaOH, H2SO4 and ASL	EUR	150.000	
Concrete works	EUR	300.000	
Total building costs	EUR	**930.000**	
Engineering, surtax, etc		1,7	
Total investment costs	EUR	**1.581.000**	
Yearly costs (excluding chemicals)	EUR / y	228.000	
	Eur / kg N recovered	0,8	
Chemical costs			
NaOH	kg / kg N recovered	2	7,2
H2SO4	kg / kg N recovered	3,5	7
cost H2SO4 per kg	EUR / kg N	0,09	
cost CaO per kg	EUR / kg N	0,35	
costs NaOH	EUR / kg N	0,25	
Chemical costs	EUR / kg N recovered	1,2	2,6
Yearly costs (including chemicals)	**EUR / y**	**543.000**	**908.000**
	EUR / kg N recovered	**1,9**	**3,2**

APPENDIX 2

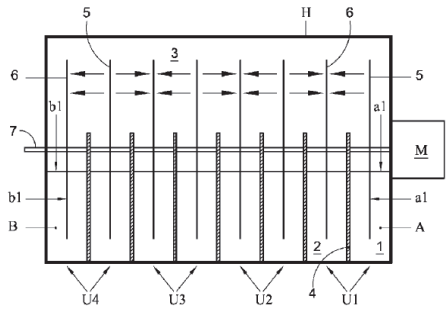# FACT SHEETS SELECTED INNOVATIVE TECHNIQUES

	AMFER
Technological basis:	The N-containing stream (digestate, > 6 % dm) is heated to 60-70°C (with excess heat from a CHP on the plant). Ammonia (NH_3) is removed via a stripping process with air. As a consequence of the air-stripping, CO_2 can be removed, resulting in a higher pH without the need for caustic soda. At a higher pH, stripping of ammonia becomes more efficient due to a shift in the NH_4-NH_3 equilibrium. Ammonia, which is brought into the gas phase, is retrieved by washing the gas stream in a H_2SO_4-rich solution. Ammonium-sulfate (($NH_4)_2SO_4$) solution is the main product formed during the washing step. Air is led back to the stripper for reuse, recuperating a large share of the heat. Treated digestate is fed to a digester in order to lower N-toxicity in the digester. Another option is further treatment until the desired specifications. The process can also be used for treating the liquid fraction after separation of the digestate. It is expected that the process is even more efficient on the liquid fraction as on the raw digestate. With this process, the stream is ideally pre-processed in order to treat in an ANPHOS® process to remove the phosphates and some ammonium. The combination of AMFER® and ANPHOS® can easily result in an effluent with a resulting NH_4-concentration < 500 mg/l. If further polishing is desired, the effluent of the AMFER® - ANPHOS® - combination is ideally suited for treatment in a NAS® -system whereas Anammox bacteria will remove nitrogen further in combination with COD removal. This is possible because the AMFER® will only remove nitrogen, the organic carbon is left as a substrate for extended biological nitrogen removal. This process is also meant for the sludge digestion side stream treatment on municipal WWTP.

Relevant parties involved in the development:	Colsen, adviesburo voor Milieutechniek BV
Stage of development:	full scale demonstration plant
Areas of application:	• Digestate of manure and other organic compounds (wastewater treatment and digestion). • Rejection water of sludge digestion on WWTP. • Pre-treatment of NH_4-rich manure before digestion. • Treating digestate in circulation around the digester in order to lower N-toxicity and to boost biogas-production for the digestion of N-rich streams • Other industrial NH_4-rich streams
Concentration range:	Start concentration > 2.000 mg/l ammonia (no upper limits!) removal till 500 mg/l ammonia; ; N-removal efficiency up to 90%, depending on the fraction of NH_4-N on total N in the liquid and the start concentration.
Limitations and boundary conditions:	.
• Limitations	• The Nitrogen must be available as ammonium • < 15 % dm and particles < 5 mm
• Pretreatment	• Grinding (in case of digestate or manure) • -
• Waste / Side stream	• Treated digestate is fed to digester • Treated liquid from digestate is fed to ANPHOS® • Treated liquid from digestate is fed to NAS® system • Treated digestate can be further polished
Scale for application:	Demonstration plant treats 10 - 30 m^3/day. Actual designs up to 500 m^3/day
Costs (excluding transport)[1]:	*For an application of 100 m^3/day, 3500 mg NH_4/l, 30°C* *(treated till 1000 mg NH_4/l)*
• Investments	• € 400.000

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1   Costs and energy calculations do not include transport of the N-containing (waste)stream and chemicals and products.

• Exploitation (including energy, labo rand chemicals)	• Electricity: 5 kWh$_{(el)}$/m³ • Heat: 45 kWh$_{(th)}$/m³ • H$_2$SO$_4$ € 1,1/m³ • (calculated with a market price of € 125/ ton for 97 % H$_2$SO$_4$) • (NH$_4$)$_2$SO$_4$ € 2,50/m³ (income due to selling of product, calculated with a revenue of € 75/ ton for 35 % (NH$_4$)$_2$SO$_4$) Total exploitation cost down to € 120/day[2], if heat is freely available the AMFER has a netto profit up to € 100/day Costs for supervision and maintenance of the installation are not taken into account; these costs are expected to be very low due to the robustness of the technology.
Energy (per kg N recovered; excluding transport):	• Electrical energy: 2 kWh/kg N • Thermal energy: 18 kWh/kg N
Products:	
• Formula	• (NH$_4$)$_2$SO$_4$ solution (target >35% w/w) • (NH$_4$)$_2$SO$_4$ solution with UREAN (higher pH and higher N content)
• Alternative products	
• Potential market	• Both formula are applied in agriculture. AMFER produced (NH$_4$)$_2$SO$_4$ has been qualified by MINELI as similar to (NH$_4$)$_2$SO$_4$ produced in gas wash facilities, which has been recognized as fertilizer and can thus be applied.
Reference projects	
References	

2   With € 0,10/kWh(el) and € 0,05/kWh(th)

	LGL stripper
Technological basis:	Transport of volatile compound (ammonia) from a liquid to another liquid. The volatile compound is transferred via the gas phase. The system as a whole is gas tight. Heating or intensive is not required.

Fig. 3A

(57) Abstract: Method and system for transferring a volatile substance from a first liquid to a second liquid. The system includes: - at least one first reservoir (1) for receiving first liquid (A); - at least one second reservoir (2) for receiving second liquid (B); - at least one airtight transfer space (3) overhead of the at least one first and at least one second reservoir (1,2); -at least a first liquid conveyor (5) for generating a film of first liquid (A) from liquid received in said first reservoir (1), and for conveying that film along said airtight transfer space (3); and -at least a second liquid conveyor (6) for generating a film of second liquid (B) from liquid received in said second reservoir (2), and for conveying that film along said airtight transfer space (3).

Relevant parties involved in the development:	DLO-WUR, Dorset
Stage of development:	**Laboratory**
Areas of application:	Wastewater, sludge, manure
Concentration range:	Applicable for all concentration ranges.
Limitations and boundary conditions:	
• Limitations	• Flow could be impaired due to wastewater/manure characteristics
• Pretreatment	• Preconcentration not necessary
• Waste/ Side stream	• Liquid wastes
Scale for application:	Aim is to achieve 8 m3 per day, but technology is scalable. So if a higher flow is required the stripper could be enlarged or more strippers could be installed
Costs (excluding transport)[3]:	
• Investments	• Unknown

3   Costs and energy calculations do not include transport of the N-containing (waste)stream and chemicals and products.

• Exploitation (including energy, laborand chemicals)	• Acid: €2-3 per m3, but depends on NH_4-content and the final saturation level of the acid • Base: €2-3 per m3, but depends on pH-level of the wastewater and buffer capacity of the wastewater.
Energy (per kg N recovered; excluding transport):	Unkown, but due the design of the stripper expected to be low.
Products:	
• Formula	• Depending on liquid 2 used $(NH_4)2SO_4$, NH_4NO_3
• Alternative products	• NH_4-low wastewater/manure
• Potential market	• Fertilizer market: alternative for artificial N-fertilizers
• Price	• Depends on the market price for artificial fertilizers which is linked to energy prices
References	Patent application

	CAFR (Chemische Ammonium Fällung und Rezyklierung)
Technological basis:	After pretreatment to remove suspended solids, chemicals (magnesium salt and sometimes a base) are added to create precipitation conditions for struvite ($MgNH_4PO_4.6H_2O$). The struvite is separated and then decomposed to magnesium hydrogen phosphate and ammonia at high pH and temperature (80-90°C). Ammonia is stripped from the reaction mixture. The ammonia-rich vapor can be processed into a concentrated solution (by condensation) or to an ammonium salt (by washing with acid). The magnesium hydro phosphate (possibly after acidification) is reused for formation of struvite, so that there is a recycle of magnesium, and phosphate.
Relevant parties involved in the development:	Nalva Umwelttechnik GmbH
Stage of development:	pilot stage
Areas of application:	Digestate
Concentration range:	~at least up to 1800 mg N/l; N-removal efficiency with decomposed struvite up to 80%
Limitations and boundary con-ditions:	
• Limitations	• Stripping efficiency ver low
• Pretreatment	• Removal of suspended solids
• Waste / Side stream	• Bleed sludge
Scale for application:	undefined
Costs (excluding transport)[4]:	
• Investments	Overall cost estimate from 1995 amounts to 6 Euro/kg N (non-indexed) removed for a 400.000 i.e. WWTP. For a 100.000 i.e. WWTP the costs are doubled.
• Exploitation (including energy, laborand chemicals)	
Energy (per kg N recovered; excluding transport):	unknown

4   Costs and energy calculations do not include transport of the N-containing (waste)stream and chemicals and products.

Products:	
• Formula	• Ammonia solution or ammonia salt
• Alternative products	
• Potential market	
• Price	
Reference projects	Pilot RWZI Utrecht.
References	1) STOWA (1995). Behandeling van stikstof rijke retourstromen op rioolwater-zuiveringsinrichtingen. Praktijkonderzoek aan het MAP/CAFR-proces bij de RWZI Utrecht. (in Dutch). STOWA report 95-013.

ARP/RCAST	
Technological basis:	The wastewater is first brought to a pH of 8-10 by adding caustic and then heated to 60-70 C. It is then sprayed into a vacuum vessel so that the dissolved ammonia is stripped out of the waste water in vapor form. This is again condensed in a second section, whereby the released energy is recycled. Simultaneously, the ammonia is again dissolved in the condensate. In a third section, the solution is acidified with sulfuric acid and evaporated in vacuum to the desired final concentration of ammonium sulphate ($(NH4)2SO4$)
Relevant parties involved in the development:	Thermo Energy ProfiNutrients
Stage of development:	This technique is already used in full scale. There are lab and pilot plants available for testing
Areas of application:	Waste water, centrate/filtrate. digestate, manure
Concentration range:	Incoming NH4-N concentration: 150 mg/l- unlimited Based NH4-N concentration: at least 50-100 mg / l
Limitations and boundary conditions:	
• Limitations	• too much magnesium, calcium, phosphate, this can cause scaling in the system. If this is the case, it is recommended to treat the waste stream for example, by a struvite installation to remove the phosphate, magnesium and calcium. When the calcium and magnesium concentrations are high they will precipitate at elevated pH. This can be taken into account in the design of the system (periodic acid cleaning for example).
• Pretreatment	• In the presence of magnesium, calcium or phosphate in the waste water it is recommended to pre treat the waste stream (for example with a struvite installation for the removal of phosphate, magnesium and calcium
• Waste / Side stream	• Residual: condensate, ammonium sulphate

Scale for application:	Depends on the nitrogen load to remove: The system is modular with regard to the flow rate of waste water. The load of nitrogen removal is almost irrelevant (at higher concentrations, the process faster).Available modules are: 5,5 m3/day; 11,5 m3/day and 19 m3/day and 37,5 m3/day.
Costs (excluding transport)[5]:	
• Investments	Depends on the nitrogen load to remove. In the order of € 560,000 to 900,000. Below a table with a price of installations for different flows and loads:

Flow	Removed N	Budget price
m3/d	kg/d	euro
5,5	22	560.000
11	44	633.000
19	76	727.000
37,5	150	939.000

• Exploitation (including energy, labo rand chemicals)	Depends on the nitrogen load to remove. Approximately 2-4 euros per kilogram removed nitrogen. These costs include the evaporation of the ammonium sulfate solution. These costs include depreciation on investment (10 years 5% interest). Proceeds from the fertilizer was not included.
Energy (per kg N recovered; excluding transport):	Depends on the nitrogen load to remove: approximately 1-2 MJ per kg N. There are currently pilot tests were done in order to concentrate the ammonium sulfate solution with the aid of RO membranes. This technique will greatly reduce the total energy demand.
Products:	
• Formula	• distilled water: H_2O. ammonium sulphate $(NH_4) 2SO_4$
• Alternative products	• Alternative products: ammonium chloride (NH_4Cl), ammonium lactate $(NH_4-C_3H_5O_3)$, ammonium $(NH_4-C_6H_7O_7)$, ammonium nitrate (NH_4NO_3)
• Potential market	• Outlets: the ammonium salts can be sold as fertilizer.
• Price	• Price: 100-400 per ton value
Reference projects	
References	Not yet in the Netherlands or in America (NewYork sanitation: This is not yet completed but is working hard to build this immense project. There is AECOM by all the necessary reports made.

5   Costs and energy calculations do not include transport of the N-containing (waste)stream and chemicals and products

	Biological/chemical oxidation
Technological basis:	In a digester organic matter is broken down into biogas and water. Nutrients such as nitrogen and phosphate are in solution. For the recovery of phosphate, various techniques are available. For nitrogen, yet often chosen for removal thereof. This technique focuses on the conversion of ammonium in a reusable fertilizer in the form of ammonium nitrate. For this purpose, a 2-stage process has been developed. In the first step, approximately 50% of the ammonium nitrite is converted into a biological way. In the second stage, the pH is lowered and the formed nitrite oxidized to nitrate. The final product is an aqueous solution of ammonium nitrate.
Relevant parties involved in the development:	Delft University of Technoloy and Consultancy IV Water
Stage of development:	Scientific (laboratory) research is completed, reporting is available. Latest developments show that both processes might be possible in one reactor. The process should now prove itself in a pilot-plant, in particular to verify the mathematical model and to be able to scale the process up to full scale installations.
Areas of application:	Industrial and municipal digesters with higher Nitrogen levels in the rejection water.
Concentration range:	Up to approximately 6,500 mg NH_4-N
Limitations and boundary conditions:	
• Limitations	• N.A.
• Pretreatment	• N.A.
• Waste / Side stream	• Because of logistical considerations the end product must be concentrated. Final product must be certified as green fertilizer
Scale for application:	undefined
Costs (excluding transport)[6]:	
• Investments	Conversion Technique: € 0.15 / kg N Evaporation final: € 0.60 / kg N (up to 30% solution) Total: € 0.75 / kg N
• Exploitation (including energy, labo rand chemicals)	Conversion Technique € 0,22 / kg N
Energy (per kg N recovered; excluding transport):	**Conversion Technique:** 7.2 MJ / kg N **Evaporation-heat:** 47 MJ / kg N (often available as low-grade waste heat from CHP plant) **Evaporation-electricity:** 27 MJ / kg N

Products:	
• Formula	• Ammonium nitrate (nitrogen fertilizer)
• Alternative products	• N.A.
• Potential market	• Fertilizer Industry / Farming / agriculture / horticulture
• Price	• € 0.75 / kg N (related to fertilizer price)
Reference projects	
References	