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Nitrogen compounds at mines and quarries

Sources, behaviour and removal from mine and quarry waters – Literature study

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Johannes Jermakka, Laura Wendling, Elina Sohlberg, Hanna Heinonen, Elina Merta, Jutta Laine-Ylijoki, Tommi Kaartinen & Ulla-Maija Mroueh

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Cover image: Johannes Jermakka, VTT

Abstract

Nitrogen compounds at mines and quarries
Sources, behaviour and removal from mine and quarry waters
– Literature study

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Keywords: ammonia, nitrate, mine wastewater, treatment technology, nitrogen recovery, nitrogen sources, explosives

Mining wastewaters can contain nitrogen from incomplete detonation of nitrogen rich explosives and from nitrogen containing chemicals used in enrichment processes. Nitrogen released to the wastewaters is a potential environmental risk. Nitrogen can be dangerous for aquatic organisms or more prominently cause eutrophication in receiving waterways.

Nitrogen chemistry is complex, allowing numerous chemical and biological reaction paths and compounds. Various techniques have been investigated for nitrogen removal from aqueous solutions, such as industrial and municipal wastewaters. Many of the technologies currently available are not suited for the treatment of mine wastewaters containing low levels of nitrogenous compounds, due to treatment costs or stringent operating parameters.

Although biological methods potentially offer an effective and inexpensive option for the removal of nitrogen from wastewaters, in mine applications these techniques may be limited by the temperature dependence, especially in cold regions. Zero-valent metals can be utilised for passive reduction of nitrate in aqueous solution. However, whilst no external energy is required to facilitate N reduction using zero-valent metals, pH buffering or extremely low pH conditions are required to supply adequate protons for the reduction reaction to proceed. Surface passivation due to the formation of oxide coatings on the zero-valent metal(s) results in decreased NO_3- removal and requires replacement or regeneration of the zero-valent metal.

Neither evaporation nor aeration techniques are particularly well-suited to the treatment of large volumes of wastewater containing multiple species of nitrogenous contaminants. Evaporation process may remove NO_3- to some degree, but nitrogenous compound are not the target contaminants in evaporation processes. Aeration can be used for the removal of volatile compounds such as ammonia from solution; however, aeration for ammonia removal is limited by the high pH (≥ 10.5) required for efficient ammonia removal.

Membrane technologies are similarly poorly-suited to the treatment of large volumes of mine wastewater. Due to their high cost and substantial operational requirements, membrane technologies are generally employed for the production of high-quality water. Membrane water treatment systems operate at high pressure

and require intensive continuous maintenance. In addition, wastewater pre-treatment is generally recommended to minimize membrane fouling.

Sorption techniques have been thoroughly examined for the removal of nitrogenous contaminants from aqueous solution and they offer an attractive alternative. Sorption technologies offer benefits including the relative simplicity of sorption methods, their economy in application and operation, and the low temperature dependence of sorption reactions.

Electrochemical methods can be used to convert nitrogenous compounds to a desired form facilitating nitrogen removal as nitrogen gas or as pure ammonia. Thus, these methods offer a temperature-independent alternative for biological nitrogen removal techniques. In addition, electrochemical processes can be run periodically as necessary and no chemical addition is required. Electrochemical techniques which utilize electrochemistry enhanced ammonia stripping are potentially suited for large flow rate, low concentration wastewater stream analogous to mine site wastewater. Electrochemistry enhanced ammonia stripping requires only low electrical potential for operation, and can result in an ammonia product for reuse.

A combination of sorption and electrochemical techniques is potentially most promising method for the treatment of large volumes of wastewater containing multiple nitrogenous compounds. The performance of both sorption techniques and electrochemistry enhanced ammonia stripping will be further experimentally studied for the attenuation of multiple nitrogenous compounds in mine wastewater. These techniques will be investigated both alone and in combination to assess different parameters for method optimization and to generate recommendations concerning the applicability of these techniques for the attenuation of nitrogenous contaminants in mine wastewater.

Tiivistelmä

Typpiyhdisteet kaivos- ja louhosvesissä

Päästölähteet, käyttäytyminen sekä poisto vesistä – Kirjallisuusselvitys

Tekijät: Johannes Jermakka, Laura Wendling, Elina Sohlberg, Hanna Heinonen, Elina Merta, Jutta Laine-Ylijoki, Tommi Kaartinen ja Ulla-Maija Mroueh

Asiasanat: ammoniakki, nitraatti, kaivosjätevesi, käsittelyteknologia, typen talteenotto, typen lähteet, räjähdysaineet

Kaivosten jätevedet voivat sisältää typpeä räjähdysainejäämistä sekä mahdollisista rikastusprosessin typpeä sisältävistä kemikaaleista. Typpipäästöt voivat olla vesieliöille haitallisia, mutta yleisin haitta on vastaanottavan vesistön rehevöityminen. Typen kemia on monimutkainen: se mahdollistaa lukuisia kemiallisia ja biologisia reaktiopolkuja ja -tuotteita. Typen poistoon ja talteenottoon on kehitetty runsaasti erilaisia fysikaalisia, biologisia ja kemiallisia teknologioita, mutta kaivosvesien ominaisuudet, erityisesti matala hiilipitoisuus, matala typpipitoisuus, usein matala lämpötila, pH sekä haitalliset yhdisteet tekevät monista teollisuuden ja jätevedenpuhdistamojen menetelmistä kannattamattomia.

Biologiset prosessit ovat tehokas ja edullinen typenpoistomenetelmä, mutta kaivosjätevesien matala lämpötila voi rajoittaa niiden soveltuvuutta, erityisesti pohjoisilla alueilla. Varauksettomat metallit eivät sovellu kaivosvesille, sillä ne vaativat toimiakseen erittäin matalan pH:n. Haihdutusta ja ilmastusta käytetään teollisuudessa usein ammoniakin poistoon, mutta matala konsentraatio, suuret virtaamat ja pH:n säätötarve rajoittavat niiden käyttöä kaivosvesien käsittelyssä. Membraanisuodatusta käytetään kaivoksilla tiettyihin kohteisiin, mutta typen poistoon ne eivät sovellu suuren esikäsittelytarpeensa ja korkean energiankulutuksensa vuoksi.

Selektiiviset sorptiotekniikat ovat eräs mahdollinen ratkaisu kaivosvesien käsittelyyn. Tietyt sorbentit pystyvät selektiivisesti ja regeneratiivisesti sitomaan ammoniakin myös matalasta konsentraatiosta korkeassa kokonaisionipitoisuudessa. Sorptiotekniikoiden etuja ovat mm. yksinkertainen toimintaperiaate, suhteellisen matalat käyttökustannukset ja lämpötilariippumattomuus.

Elektrokemiallisilla menetelmillä typpiyhdisteet voidaan muuttaa haluttuun muotoon ja poistaa typpikaasuna tai puhtaana ammoniakkina. Näin ollen ne tarjoavat vaihtoehdon biologisille prosesseille, joissa muokataan typen esiintymismuotoa. Elektrokemialliset menetelmät ovat lämpötilasta riippumattomia ja toimivat ilman hiiltä tai kemikaalilisäystä.

Sorptiotekniikat ja elektrokemialliset tekniikat tai niiden yhdistelmät ovat kirjallisuuskatsauksen perusteella lupaavimmat kaivosjätevesien typenkäsittelymenetelmät, jotka mahdollistavat sekä typen poiston että talteenoton. Näiden tekniikoiden kokeellista tutkimusta jatketaan MINIMAN-projektissa tämän kirjallisuusselvityksen pohjalta.

Preface

This publication presents a literature overview on nitrogen removal and recovery from mining and quarry wastewaters and recommends the most promising alternatives for further research. This publication is part of a project, Solutions for Control of Nitrogen Discharges at Mines and Quarries (MINIMAN), funded by Tekes – the Finnish Funding Agency for Innovation, aiming at a holistic understanding and technology development regarding nitrogen compounds in mining waters.

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Contents

1. Introduction

1.1 Nitrogen chemistry and environmental characteristics

Nitrogen is a colorless, odorless, tasteless, diatomic and generally inert gas at standard temperature and pressure. At atmospheric pressure, nitrogen is liquid between 63 K and 77 K. Liquids colder than this are considerably more expensive to make than liquid nitrogen.

While elemental nitrogen is not very reactive, many of nitrogen's compounds are unstable. Nitrogen has a complex chemistry with 9 oxidation states (-3 to +5), with most stable form being nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+). Nitrogen is essential in organic chemistry and is bound to carbon compounds usually in reduced forms. Nitrates and nitrites are nitrogen-oxygen chemical units which combine with various organic and inorganic compounds. Nitrate is the more stable of the two forms of nitrogen but can be reduced by microbial action to NO_2^-, which is the more toxic form. A conceptual diagram of common nitrogen pathways and forms is presented in Figure 1.

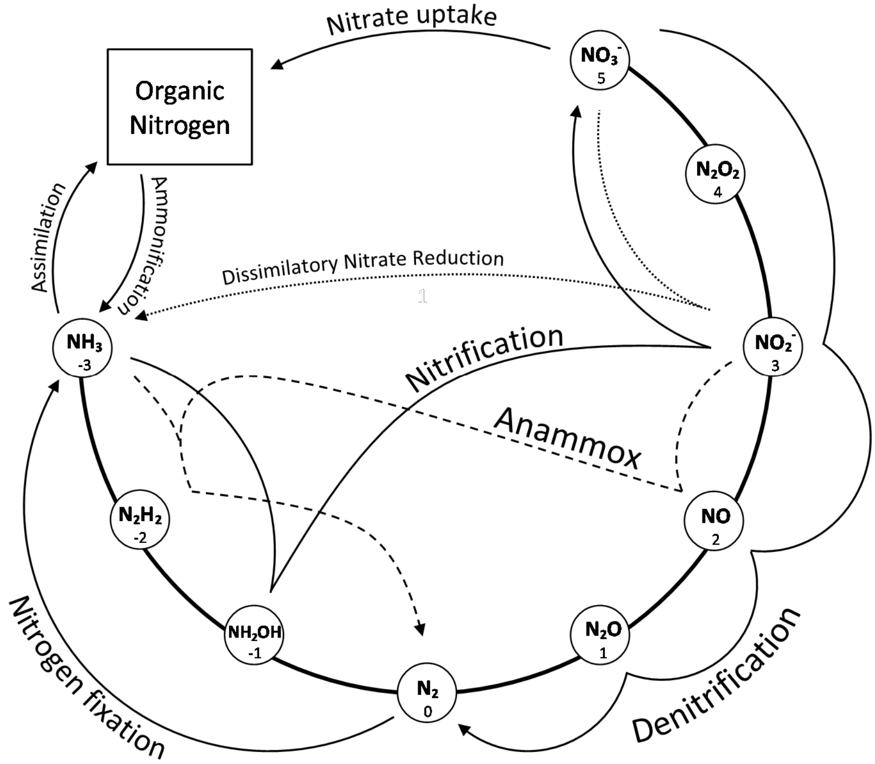

Figure 1. Common nitrogen pathways and forms (Jermakka et al. 2014).

1.1.1 Nitrate and nitrite

Nitrate and nitrite are naturally occurring ions that are part of the nitrogen cycle. The nitrate ion, NO_3^-, is the stable form of oxidised nitrogen and is not acutely toxic, while its harmfulness in drinking water has been debated and it is usually not tolerated in drinking water in raised concentrations. The nitrite ion, NO_2^-, is relatively unstable but common intermediate form in nitrogen chemistry, and it is toxic to humans. Waters containing nitrate can become toxic with nitrite by partial denitrification by bacteria e.g. during stagnation of oxygen-poor drinking-water in galvanized steel pipes or if chloramination is used to provide a residual disinfectant (WHO, 2007).

The NO_3^- ion is the conjugate base of nitric acid (HNO_3), a strong acid which is completely dissociated in solution. The NO_3^- salts of all common metals (e.g. $NaNO_3$ and KNO_3) are highly soluble in water, while the resulting free NO_3^- ion is chemically unreactive as it has little tendency to form coordination complexes with other metal ions in solution (CCME, 2003)

1.1.2 Ammonia

Ammonia nitrogen includes both the ionized form (ammonium, NH_4^+) and the unionized form (ammonia, NH_3), which have a pH dependent equilibrium at ~9.25 (at 25 °C). Ammonia is a common ion form of nitrogen derived from wastes, fertilizers, and natural processes. While ammonium is non-toxic, ammonia is highly toxic to aquatic organisms and a common cause of fish kills. The most common problems associated with NH_3 relate to elevated concentrations affecting fish growth, gill condition, organ weights, and haematocrit. (USEPA, 1998)

Ammonia is an important component of the nitrogen cycle and a large source of available nitrogen in the environment. The complexity of the nitrogen cycle, various rate determining environmental conditions for nitrification (e.g., pH, temperature), and the physical behaviour of NH_3 (e.g., volatilization, adsorption) make determining the fate of NH_3 in the environment complex. Ammonia can form explosive mixtures with air at concentrations between 16 and 27% by volume, but is generally regarded as non-flammable. Ionized ammonium salts form when NH_3 dissolves in dilute acids. Some of these salts are found in nature (water, soil, and atmosphere) (CCME, 2010; WHO, 1986).

In surface waters, both nitrification and volatilization are important competitive fate processes for ammonia. Volatilization increases with increasing wind speed, temperature, and pH. In addition, the partial pressure of NH_3 in solution increases with increasing pH, and in aqueous solutions, ammonia may form complexes with a number of metal ions. It may be sorbed onto suspended and bed sediments and to colloidal particles (CCME, 2010).

Ammonia in sediments typically results from bacterial decomposition of natural and anthropogenic organic matter that accumulates in sediment. Sediment microbiota mineralizes organic nitrogen or (less commonly) produces NH_3 by dissimilatory NO_3^- reduction. Ammonia is especially prevalent in anoxic sediments because nitrification (the oxidation of NH_3 to NO_2^- and NO_3^-) is inhibited. Ammonia generated in sediment may be toxic to benthic or surface water biota.

Ammonia may also be exchanged between sediments and overlying water. Ammonia concentrations in water vary seasonally and regionally. In natural waters, concentrations of total ammonia are generally less than 0.1 mg/L. Higher levels of ammonia are generally indicative of organic pollution (CCME, 2010).

Ammonia also exerts a biochemical oxygen demand on receiving waters (referred to as nitrogenous biological oxygen demand or NBOD) because dissolved oxygen is consumed as bacteria and other microbes oxidize NH_3 into NO_2^- and NO_3^-. The resulting dissolved oxygen reductions can decrease species diversity and even cause fish kills. Additionally, NH_3 can lead to heavy plant growth (eutrophication) due to its nutrient properties. (USEPA, 1998)

1.1.3 Cyanide

The term cyanide refers to a singularly charged anion consisting of one carbon atom and one nitrogen atom joined with a triple bond, CN^-. The most toxic form of cyanide is free cyanide, which includes the cyanide anion itself and hydrogen cyanide, HCN, either in a gaseous or aqueous state. At pH 9.3–9.5 CN^- and HCN are in equilibrium. Although HCN is highly soluble in water, its solubility decreases with increased temperature and under highly saline conditions. Both HCN gas and liquid are colorless and have the odor of bitter almonds, although not all individuals can detect the odor.

Cyanide is very reactive, forming simple salts with alkali earth cations and ionic complexes of varying strengths with numerous metal cations; the stability of these salts is dependent on the cation and on pH. The salts of sodium, potassium and calcium cyanide are quite toxic, as they are highly soluble in water, and thus readily dissolve to form free cyanide. Operations typically receive cyanide as solid or dissolved NaCN or $Ca(CN)_2$. Weak or moderately stable complexes such as those of cadmium, copper and zinc are classified as weak-acid dissociable (WAD). Although metal-cyanide complexes by themselves are much less toxic than free cyanide, their dissociation releases free cyanide as well as the metal cation which can also be toxic. Even in the neutral pH range of most surface water, WAD metal-cyanide complexes can dissociate sufficiently to be environmentally harmful if in high enough concentrations.

Cyanide forms complexes with gold, mercury, cobalt and iron that are very stable even under mildly acidic conditions. However, both ferro- and ferricyanides decompose to release free cyanide when exposed to direct ultraviolet light in aqueous solutions. This decomposition process is reversed in the dark. The stability of cyanide salts and complexes is pH dependent, and therefore, their potential environmental impacts and interactions (i.e. their acute or chronic effects, attenuation and re-release) can vary.

Metal cyanide complexes also form salt - type compounds with alkali or heavy metal cations, such as potassium ferrocyanide ($K_4Fe(CN)_6$) or copper ferrocyanide ($Cu_2[Fe(CN)_6]$), the solubility of which varies with the metal cyanide and the cation. Nearly all alkali salts of iron cyanides are very soluble, upon dissolution these double salts dissociate and the liberated metal cyanide complex can produce free cyanide. Heavy metal salts of iron cyanides form insoluble precipitates at certain pH levels.

The cyanide ion also combines with sulfur to form thiocyanate, SCN^-. Thiocyanate dissociates under weak acidic conditions, but is typically not considered to be a WAD species because it has similar complexing properties to cyanide. Thiocyanate is approximately 7 times less toxic than hydrogen cyanide but is very irritating to the lungs, as thiocyanate chemically and biologically oxidizes into carbonate, sulfate and ammonia.

The oxidation of cyanide, either by natural processes or from the treatment of effluents containing cyanide, can produce cyanate, OCN^-. Cyanate is less toxic than HCN, and readily hydrolyzes to ammonia and carbon dioxide.

1.1.4 Sources of selected nitrogen compounds – Natural sources

Natural sources of NO_3^- to surface waters can include wet and dry deposition of HNO_3 or NO_3^-, which are formed through nitrogen cycling in the atmosphere. Other natural sources of NO_3^- include igneous rocks and volcanic activity, mineralization of native soil organic nitrogen and the complete oxidation of vegetable and animal debris. This latter nitrification process is the principle source of NO_3^- in terrestrial and aquatic environments (CCME, 2003).

1.1.5 Anthropogenic sources

The main anthropogenic source of nitrogen is the Haber-Bosch in which atmospheric nitrogen is converted to ammonia. This process utilizes natural gas and has been estimated to currently use 1–2% of the yearly global fossil fuel consumption. NH_3 is used for ammonium and ammonia products, nitric acid production (Ostwald process) and subsequently nitrate and other nitrogen containing products. The largest product stream is ammonium and nitrate containing fertilizers, followed by blasting agents. The sources of nitrogen in water include agricultural fertilizers, manure, domestic sewage, industrial wastewaters, blasting agent residues and precipitation. Nitrogen concentration in natural waters is normally low, but can reach high levels from agricultural runoff, or from contamination by human or animal wastes (CCME, 2012). Consequently, in addition to natural sources, inorganic N can enter aquatic ecosystems via point and nonpoint sources derived from human activities (Table 1). Nonpoint sources generally are of greater relevance than point sources since they are larger and more difficult to control. Moreover, anthropogenic inputs of particulate N and organic N to the environment can also result in inorganic N pollution.

Table 1. Major anthropogenic sources of inorganic nitrogen in aquatic ecosystems (Camargo et al. 2007).

Point Sources	• Wastewaters from livestock farming and aquaculture operations • Municipal and industrial sewage effluents • Runoff and infiltration from waste disposal sites • Runoff from blasting sites
Nonpoint Sources	• Widespread cultivation of N_2-fixing crop species, and the subsequent N mobilization among terrestrial, aquatic and atmospheric realms • Use of animal manure and inorganic N fertilizers, and the subsequent runoff from agriculture • Runoff from burned forests and grasslands • Emissions to the atmosphere of reduced and oxidized N compounds, and the subsequent atmospheric deposition over surface waters

Nitrogen gas (N_2) is used in large quantities e.g. in enhanced oil recovery, in chemical industries as an inert gas and in liquid for as a refrigerant or in superconductors, but this fraction remains inert and is not bound as a reactive chemical.

1.1.6 Nitrate

The primary inorganic nitrates which may contaminate drinking water are KNO_3 and NH_4NO_3. Potassium nitrates are used mainly as fertilizers (85%), with the remainder used in heat transfer salts, glass and ceramics, and in matches and fireworks. Ammonium nitrates are used as fertilizers (84%) and in explosives and blasting agents (16%). (USEPA, 2010)

The detonation of ammonium nitrate fuel oil (ANFO) is often incomplete in a wet environment, leaving behind water-soluble by-products of unreacted NH_4NO_3 as NO_3^-, NO_2^- and NH_4^+ into the environment. The leaching of NO_3^- from the explosive can occur rapidly, with 25% of NO_3^- lost after a six-minute exposure and 50% after a one-hour exposure. (Brochu, 2010)

1.1.7 Ammonia

The Haber-Bosch process is the key commercial method of NH_3 production. In this process, a catalyst is used to speed up the reaction between hydrogen and nitrogen (in a 3-to-1 ratio) combined under high pressure and high temperature (approximately $600^{o}C$) to produce NH_3.

Ammonia is used in numerous applications in the refrigeration, pulp and paper, mining, food processing, refining, and animal husbandry sectors. The principal use of NH_3 is the production of nitrogenous fertilizers (ammonium nitrate, ammonium phosphate, urea, and ammonium sulphate). In the agriculture industry, anhydrous ammonia is directly applied to fields and NH_3 is injected into animal feed to increase its nutrient value. In the textile industry, NH_3 is used in the fabrication of synthetic fibres (such as nylon and rayon), and as a curing agent in leather making. The health care industry uses NH_3 in the manufacture of pharmaceuticals, vitamins, amino acids, lotions, and cosmetics. The household chemical industry uses NH_3 for the manufacturing of cleansing agents and detergents. In addition, NH_3 is used in the production of many goods including explosives, rocket fuel, beer, plastics, rubber, nitrogen oxides required for manufacturing sulphuric acid, in sugar purification, and in the treatment and transformation of metals (CCME, 2010).

Ammonia commonly enters the environment as a result of municipal, industrial, agricultural, and natural processes. Natural sources of NH_3 include the decomposition or breakdown of organic waste matter, gas exchange with the atmosphere, forest fires, animal waste, human breath, the discharge of NH_3 by biota, and nitrogen fixation processes.

Point sources of NH_3 include emissions and effluents from a wide variety of industrial plants such as iron and steel mills, fertilizer plants, oil refineries, and meat processing plants. The manufacturing of explosives and the use of explosives in mining and construction can also be significant point sources of NH_3. The largest non-industrial point sources are sewage treatment plants. Also accidental NH_3 spills can be a major anthropogenic source of NH_3. (CCME, 2010)

Non-point sources of NH_3 include agricultural, residential, municipal, and atmospheric releases. Major agricultural sources include areas with intensive farming, accidental releases or spills of NH_3-rich fertilizer, and the decomposition of livestock wastes (CCME, 2010).

1.1.8 Cyanide

Approximately 1.1 million metric tons of hydrogen cyanide is produced annually worldwide, with approximately 6% used to produce cyanide reagents for gold processing, the remaining 94% of cyanide produced is used in industrial applications including production of plastics, adhesives, fire retardants, cosmetics, pharmaceuticals, food processing and as an anti-caking additive for table and road salts. In gold processing cyanide is used as an efficient complexing agent for gold solubilisation. The amount of cyanide in solution required for gold dissolution may be as low as 350 mg/L. (International Cyanide Management Code, 2012)

Cyanide is manufactured and distributed for use in gold mining industries in a variety of physical and chemical forms, including solid briquettes, flake cyanide and liquid cyanide. Sodium cyanide is supplied as either briquettes or liquid, while calcium cyanide is supplied in flake form and also in liquid form. Although the forms of cyanide vary, once introduced into the process, the technologies used for gold recovery are the same. (International Cyanide Management Code, 2012)

1.2 Occurrence and environmental levels

1.2.1 Air

Nitrogen is released into atmosphere in three reactive forms: NH_3, NO_x and N_2O. The ammonia release is mainly related to agricultural activities (app. 85–100% of emissions) and occurs as ammonia evaporation from manure spreading to fields, animal houses, grazing animals and (degrading) plants. European NH_3 emissions were estimated at 5.1 and 3.8 million tonnes of N in 1990 and 2009, respectively, and Finnish emissions at 0.35 and 0.27 million tonnes of N in 1985 and 2000, respectively. The decrease in emissions is mainly attributed to advanced manure spreading practices adopted. Atmospheric ammonia concentrations vary locally, but levels around 2 µg/m^3 have been reported. (Sutton et al. 2011)

NO_x is the sum of nitrogen oxide (NO) and nitrogen dioxide (NO_2), which are mainly generated in high temperature oxidation of atmospheric N in combustion processes. Total NO_x emission in Europe in 2000 were estimated at 26.6 million tonnes of N the largest constituents being power generation (25.2%), road transport (22.9%), industrial production (15.4%) and shipping (11.3%). European NO_x emissions peaked in 1990, but have since dropped by one third due to improvements in legislation and technology in fuel standards and combustion technologies, respectively. (Sutton et al. 2011) Atmospheric NO_3^- concentrations range typically between 1–8 µg/m^3 with measurements between 0.1 and 40 µg/m^3 reported. (WHO 2007)

Regardless of the low reactive nitrogen concentrations measured, it has significant global effects on climate and ecosystems affecting nutrient deposition, acidification, ozone formation and atmospheric particle formation. (Sutton et al. 2011)

1.2.2 Water

Nitrogen is released into waterways through atmospheric deposition, biological nitrogen fixation, synthetic fertilizer use and commercial import of food, feed and chemicals (including municipal and industrial spot sources). Nitrogen is present mainly as particulate organic nitrogen, dissolved organic nitrogen and dissolved inorganic nitrogen (as nitrate, nitrite and ammonium). The presence of inorganic nitrogen is often a clear indication of anthropogenic nitrogen saturation as inorganic nitrogen levels are usually low in natural state waters. (Sutton et al. 2011)

European nitrogen emissions to waterways in 2010 were estimated at 10.5 million tonnes, largest contributions being from diffusion from agricultural soils (57%), direct sewage releases (22%), atmospheric nitrogen deposition onto land (9%), atmospheric nitrogen deposition onto ocean (7%), diffusion from forest soils (3%) and diffusion from livestock operations (2%). Finnish nitrogen emissions to waterways were estimated at 147 thousand tonnes with similar distribution. (Sutton et al. 2011)

The NO_3^- concentration in aerobic surface waters is normally few milligrams per litre (0–18 mg/L), with very low nitrite and ammonia concentrations. Nitrate concentrations have gradually increased in many European countries in the last few decades due to anthropogenic sources and in EU15 countries the percentage of the population exposed to NO_3^- levels in drinking-water above 50 mg/L this corresponds to nearly 10 million people and nitrate rainwater concentrations of up to 5 mg/L have been observed in industrial areas. (WHO, 2007)

EU's drinking water standard for nitrate and nitrite is 50 mg/l and 0.5 mg/l respectively, and it is based on alleged health concerns, particularly methemoglobinemia and carcinogenic effects. These health effects have been challenged by the scientific community and there has been discussion about abandoning or re-evaluating these standards. For ammonia, no drinking water limit exists as no health impacts have been detected, but an indicative value of 0.5 mg/l is mentioned.

The concentration of NO_3^- in mine effluents is site specific and varies widely from 25 to 300 mg/L, whilst the concentration of NH^{4+} may vary from 10 to 40 mg/L (CCME, 2000).

1.3 Mining and explosives

1.3.1 Use of explosives globally and in Finland

Globally, the main consumers of explosives in industrial applications include United States (31%), Socialist Asia (i.e. mainly China) (20%), Commonwealth of Independent States (14%) and Central and South America (9%). The majority of explosives are used in mining and quarrying activities coal mining being the largest sector (52% of total consumption) whereas metal mining represents ca. 29% of the total explosives consumption. Large amounts are also used in the construction sector and other industries. These applications are estimated to represent ca. 9% of the total worldwide explosives market. (IHS 2009)

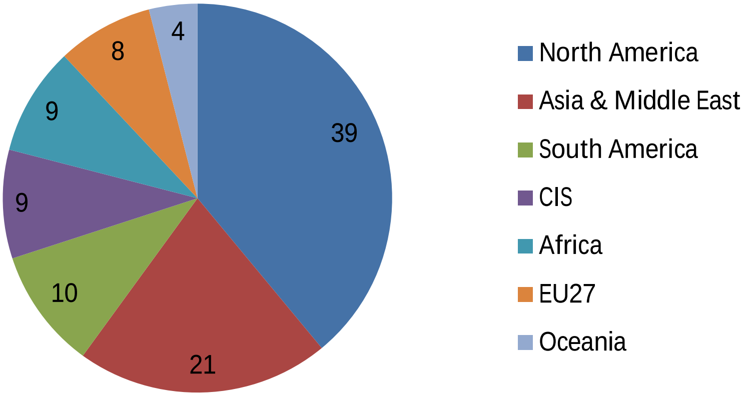

Figure 2. World consumption shares of explosives by the mining industry in 2008 (IHS 2009).

The European market of explosives market is moderate (Figure 2). Of the EU27 countries the ones using most explosives are Poland and the Czech Republic. Within EU15, the UK, Germany and Sweden are the largest consumers. (GHK 2007)

Most of the explosives market is still dominated by ammonium nitrate which is by far the most widely used blasting agent. (IHS 2009)

It was estimated by Mattila et al. (2007) that the Finnish consumption of explosives is around 12 000 t/a, corresponding ca. 0.4 kg/t rock. In open pit mining the explosives usage is around 0.2–0.3 kg/t rock whereas in underground mining the usage is higher, ca. 0.5–1.0 kg/t rock.[1] However, nowadays the total consumption is significantly higher, around 50 000 t/a (Figure 4). It is evident that the boom of the mining industry has to do with the recent rise of the explosive usage. The future usage of explosives will also depend on several other factors, such as increased share of underground mining, and growing need of crushed rock in infra and building construction.

In 2012, metallic ores were extracted at 12 mine sites and industrial minerals at 29 sites (Kokko 2013). Natural stone quarrying took place ca. 80 sites in 2010 (Uusisuo 2011). Quarrying of rock for the production of aggregates is typically local activity, and the number of enterprises (2011) on the sector exceeded 400 (Kananoja et al. 2013).

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[1] In mining the mass of explosives required to break a certain amount of rock is often called the “powder factor” (Bailey et al. 2012)

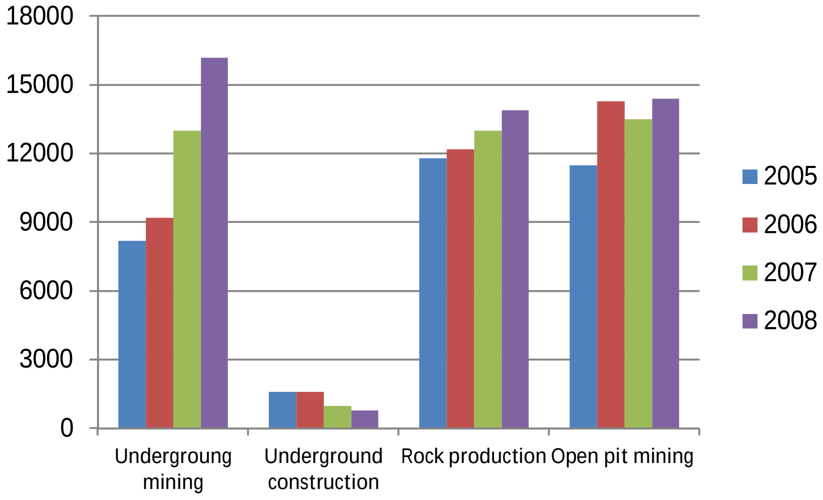

Figure 3. Extraction volumes in Finland by branch, 1000 m^3 (Infra ry and Forcit Oy 2009).

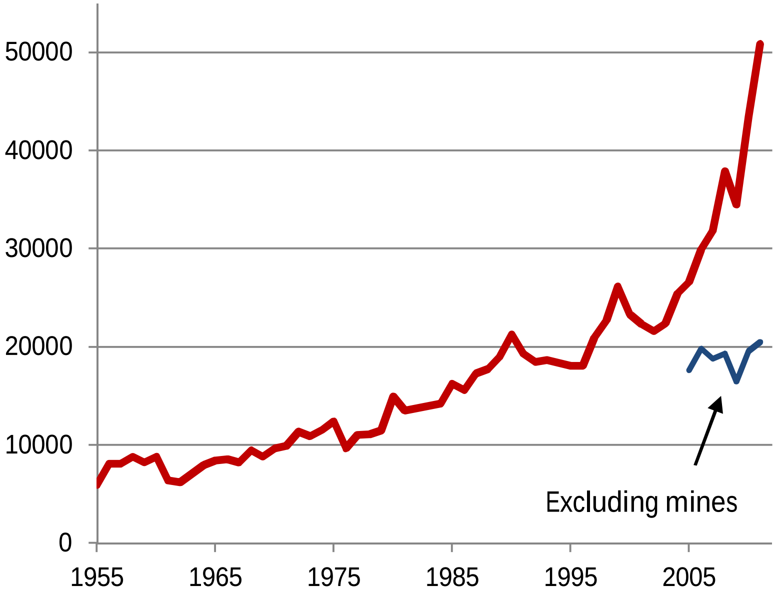

Figure 4. Use of explosives in Finland 1955–2011, tonnes (Halonen 2012).

1.3.2 Explosive classification

Explosives are chemical compounds or mixtures which release plenty of heat and gases when detonated. The reaction is initiated mechanically and by heat, typically using an explosion starter. The operation principle of starters can be either electric or non-electric, containing very sensitive speciality explosive to initiate the main reaction. (OAMK 2007; Forsberg and Åkerlund 1999)

The explosion causes shock waves that progress in rock at the speed of 3000… 7000 m/s, depending on the rock structure. During the reaction, the pressure rises to over 200 000 bar and the temperature to over 3000 K. The pressure exceeds the compression strength of the rock which results in cracking. Also the tangential tensile stress in rock and the formation of hot, high-pressure explosion gases contribute to rock breakage (Hannukainen 2009)

The established international classification, also used in Finland, divides the blasting agents as follows:

ANFO explosives contain ammonium nitrate + fuel oil. ANFOs are usually delivered to site in bags or by a mixing vehicle. Ammonium nitrate is white, hygroscopic crystalline solid at room temperature. When needed, ammonium nitrate is mixed with fuel oil to form ANFO (ammonium nitrate fuel oil). The stoichiometric composition is 94.5% ammonium nitrate and 5.5% fuel oil; however, compositions of commercial products vary by manufacturer. Ammonium nitrate is present in the mixture as prilles, i.e. as small pellets. The cons of ANFO include its poor water resistance, unsatisfactory explosion reliability in small blast holes and low density causing low explosive power per used volume. The water resistance can be somewhat improved by certain additives. The advantages of ammonium nitrate include safety compared to e.g. dynamite. Low cost has also been mentioned as a pro of ANFO. (IHS 2009; OAMK 2007; Brochu 2010; Forsyth et al. 1995)

Emulsified explosives have been developed to make explosion activities safer, more precise and more effective. Emulsified explosives entered the Finnish market in the 1980’s (Vuolio and Halonen 2010). The products are manufactured by mixing ammonium nitrate (water phase) and oil + additives (emulsifiers, energizers, sensitizers). The resulting product is an emulsion where either water or oil phase acts as a continuous phase (oil on water or water on oil), each option having different properties. The purpose of the oil phase is to maintain the oxidation reaction by generating large contact area to the oxidizer. Typically emulsified explosives contain 70–80% nitrate, 10–20% water, ca. 4% oil and 1–2% additives. The detonation velocity of emulsions can be varied by changing the shares of oil and oxidizers or by using additives (e.g. aluminium powder). Emulsified explosives usually release cleaner gases and also fewer nitrates are released to water than with traditional explosives (e.g. ANFOs). The products are also more water resistant than other explosives. The state of emulsified explosives ranges from liquid to nearly solid and they apply to a wide variety of purposes. Nowadays emulsified explosives are usually pumped straight to boreholes from specific vehicles (bulk emulsion). The main manufacturing methods are SME (Site Mixed Emulsion) and

SSE (Site Sensitised Emulsion). Emulsions are also available in cartridges. (OAMK 2007; Vihanto 2007; Golder Associates 2006)

NG explosives, so called dynamites contain easily detonating material such as nitroglycerol or nitroglycol. The power of these explosives is high and they can be used in almost all kinds of explosion projects. A suitable intermediate matter is impregnated with the explosive compound in order to make it more insensitive and easier to handle. The products are delivered in cartridges, either in tubes or in plastic packaging. NG explosives are relatively water resistant. (OAMK 2007; Forsberg and Åkerlund 1999)

Water gel explosives or slurries typically consist of a super-saturated aqueous solution of ammonium nitrate mixed with fuel, gum and cross-linking agent. A typical nitrogen content of water gel explosives is around 20–30% by weight. They present fairly good water resistance due to the gel-like consistence which forms a barrier towards water and they can be used in relatively large boreholes. Emulsified explosives have in many places largely replaced water gel explosives. (OAMK 2007; Forsyth et al. 1995; Golder Associates 2006)

The international classification does not recognize TNT-ammonium nitrate explosives such as **aniitti** which are common in Finland. The properties of these explosives are in between NG and ANFO explosives and they can be used to replace ANFO in sites where water content is high. Aniitti consists of ammonium nitrate, TNT, aluminium and additives packed in plastic or paper wraps. (OAMK 2007)

All mentioned explosives groups contain nitrogen. A rule of thumb is that around 25 % of the explosive mass is elemental nitrogen (e.g. Forcit emulsions 27%; dynamite based 20–30%). However, the water resistance of different types varies depending on the form in which nitrogen is added in the product, and therefore nitrogen is released from them at different rates. Nevertheless, in a time frame long enough, all N contained in explosives is released to the environment in some form. New raw materials for the production of non-nitrogen containing explosives have been investigated. Still, these novel explosive options are far too expensive to be used in practical operations and also the safety is not adequate compared to traditional explosives. (Forsyth et al. 1995; Halonen 2012)

In Finland there are currently two main production facilities for mining explosives, in Hanko and Vihtavuori. Both facilities are owned by Oy Forcit Ab which currently holds a market share of ca. 75% of the Finnish explosive market (Halonen 2012). Table 2 lists the product assortment of Forcit for different mining and extraction purposes. Other suppliers operating in the Finnish market include Eurenco, Maxam Suomi Oy, DNX, Orica and Sibiritfin Oy (part of Russian Nitro Sibir Corporation).

Table 2. Forcit explosive products for mining (Forcit 2011).

Application area	Product name	Classification if applicable	Effective compounds present	Applicability, requirements	State
Open pit mining	Fordyn	NG	Nitroglycol, ammonium nitrate	All mining projects in normal conditions	Plastic (formable)
	Redex	NG	Nitroglycol, ammonium nitrate, hexogene	Used as detonator for Kemiitti and Anfo products.	Cartridges
	Aniitti		Ammonium nitrate, trotyl, aluminium	Tolerates moisture	Powdery
	Kemix A	Emulsified	Ammonium nitrate, aluminium	All mining projects, can be used as detonator for Anfo and Kemiitti products. Non-water soluble	Emulsion in cartridges
	F tube cartridges	NG	Nitroglycol, diatomite	Precision mining	Powder packed in tubes
	Kemix A tubes	Emulsified	Ammonium nitrate, aluminium	As for Kemix A, where precise amount of explosive is needed	Emulsion in tubes (different sizes)
	Kemiitti 510	Emulsified	Ammonium nitrate Additives according to case specific needs	Water resistant, non-water soluble	Delivered straight to mining site, pumped into blast holes. Manufactured in specific vehicles.
	Kemiitti 610	Emulsified	Ammonium nitrate, additives according to case specific needs	Water resistant, non-water soluble	Delivered straight to mining site, pumped into blast holes. Manufactured at Forcit emulsion facilities.
	Anfo Ahti-Anfo	ANFO	Ammonium nitrate	Mass extraction in uninhabited areas, requires starter. Ahti-Anfo is rather water resistant.	Bulk explosives, dosed by pouring or by a loading equipment
Underground mining	Kemiitti 810	Emulsified	Ammonium nitrate	Water resistant, non-water soluble	Emulsion that can be pumped. Manufactured in specific vehicle on site.
	Anfos (Pito-Anfo, Anfo-800, Anfo-600)	ANFO	Ammonium nitrate, fuel oil	Mass extraction in uninhabited areas, require detonator (e.g. Redex, Fordyn, Kemix A, Aniitti, Forprime)	Bulk explosives, dosed by pouring or by a loading equipment
	Kemix A tube cartridges	Emulsified	Ammonium nitrate, aluminium	As above	As above
	Forprime		Hexogene	Used as a detonator for Anfo and Kemiitti 810. Water resistant.	
Extraction of dimension stones	K and KK tubes	NG	Nitroglycol, diatomite	Not fully water resistant. To be used with detonating cord.	Powder packed in plastic tubes
	F-cord 10 detonating cord		Pentrite		Starter covered with polypropene cord and plastic.
Open pit mining	Fordyn	NG	Nitroglycol, ammonium nitrate	All mining projects in normal conditions	Plastic (formable)

1.3.3 Usage of different explosive types in Finland

Figure 5 presents the usage of different explosive types in Finland in 2011. It is expected that in the next few decades the use of aniitti will decrease and will be replaced by emulsions (Vuolio and Halonen 2010).

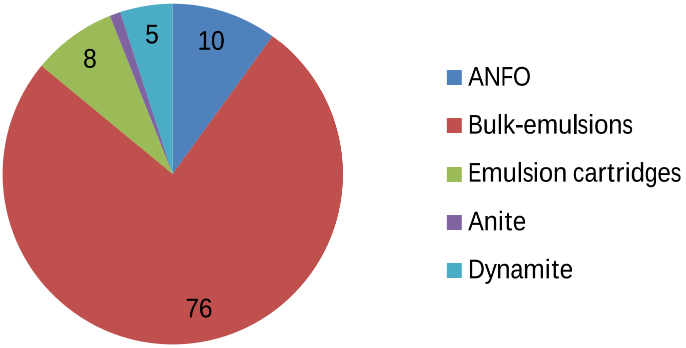

Figure 5. Shares (%) of explosive types used in Finland, 2011 (Halonen 2012).

The usage of emulsions has increased significantly during the past years. In the Nordic countries the emulsions that have been in use from the 1980’s are optimized for their droplet size. In this type of modern emulsion the oil surrounds the nitrate phase completely. A typical product type is a pumpable emulsion which does not easily enter any cracks in the rock. More “outdated” emulsion types and also water gel explosives are still in use elsewhere in the world. (Halonen 2012)

1.4 Explosion chemistry

In the detonation event, the chemical energy contained in explosive is released as kinetic energy. The energy is released in gases and transferred to the surroundings as pressure waves. The reaction is usually initiated by mechanical or heat generating factor, most commonly by a starter. The pressure wave increases the pressure, temperature and density of the surrounding explosive such that the oxidation reaction proceeds at high velocity. The reaction time and the length of reaction zone depend on the explosive used. (Vuolio and Halonen 2010)

The ideal explosive reaction of ANFO or ammonium nitrate emulsions does not release NOx. Ammonium nitrate converts to nitrogen, water and oxygen and fuel converts to carbon dioxide and water according to the following reaction equations: (Queensland 1999)

$$3NH_4NO_3 + CH_2 \rightarrow 3N_2 + 7H_2O + CO_2 \qquad (1)$$

In non-ideal conditions the reaction proceeds as follows:

$$5NH_4NO_3 + CH_2 \rightarrow 4N_2 + 2NO + 11H_2O + CO_2 \qquad (2)$$

NO reacts with atmospheric oxygen to produce nitrogen dioxide:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (3)$$

1.5 Mining and explosion practises

Metallic ores are generally situated under a layer of ordinary soil or rock, the so called waste rock or overburden. The amount of waste rock in mining projects is typically very large compared to the amount of the actual exploited ore. Waste rock is usually deposited on-site, in piles or in underground mines. Mining is done mainly as open pit or underground mining. The selection of mining method depends on e.g. the nature, location and of the deposit. Also the grade of the mineral has an impact on the selection of mining method. (ELAW 2010; Global Security 2011b) The mining method is one factor influencing the choice of explosives.

In a typical preparation of a borehole, the most sensitive and also the most expensive component, the **starter**, is placed at the bottom. Only a very small amount of starter is needed (example: 1 g). Next, the starter is covered by so called **detonator** (example: 1 kg) which is less sensitive than the starter compound but has higher explosive power (e.g. dynamite, pentrite, TNT). The **bulk explosive** (example: 1000 kg) which can be e.g. emulsion is loaded on top of the detonator. The purpose of the detonator is to get the bulk explosive to detonate; the starter initiates the reaction but does not have the power to convey the detonation throughout the bulk explosive. Emulsions are nowadays the main explosive type used as the bulk explosive in mining operations. (Halonen 2012)

The bulk explosive is made as insensitive as possible due to safety reasons whereas the detonator and starter are more sensitive. In practical operations the starter is always detonated and also the probability for detonator detonation is very high. After the detonator at least most of the bulk is detonated. The starter and the detonator typically have very low water solubility. Thus, considering effects on the water environment, the bulk explosive is the most relevant, also due to its large amount compared to starter and detonator. (Halonen 2012)

1.5.1 Open pit mining

In open pit mining the ore deposit typically extends deep in the ground and the layer of upon laying rock must be removed before actual mining. The resulting mining pit usually reaches the groundwater level and therefore requires pumping of water out of the pit. In open pit mining the typical explosive usage is ca. 1 kg/m^3 rock. It has been estimated that around 5% of the total loading can detonate incompletely and of this amount half may be left fully un-burned (2.5% of the loading). The explosion design is simpler than in underground operations and it is easier to generate an evenly distributed field of blast holes. (Halonen 2012)

In built-up areas only cartridge explosives are allowed in open pit mining. This means that explosives have been packed into paper, plastic or suitable tube by the manufacturer. The use of cartridge explosives also allows a better management of environmental effects, e.g. the explosives are not spilled in rock ruptures and dissolution to water is minimized. In uninhabited locations also bulk explosives can be used in open pit mining. (Forcit 2011)

1.5.2 Underground mining

In underground mining, a smaller amount of overburden is removed in order to access the ore deposit. First, tunnels or shafts are mined to access the deposit and allow the traffic to the mine. The main levels of the mine are usually mined at 50-200 m distances. In addition to the main levels, the venting system and a crushing station are constructed. There are different methods used in underground mining. For example in Pyhäsalmi and Kemi mines the method applied is vertical embarkment mining. In this method the rock is pre-enforced. Long-hole quarrying is used to extract rock. Afterwards the mine is filled. Other common underground mining method in Finland is the intermediate level mining. (ELAW 2010; Vuolio and Halonen 2010)

In underground mining the typical explosive usage is ca. 1.5–2.5 kg/m^3 rock. It has been estimated that up to 20% of the loaded boreholes can detonate incompletely. The main reason for the higher probability of incomplete detonation in underground blasts is the loading density. The explosion design is optimized at the targeted mineralization. In underground conditions, where loading is done from a tunnel there may be a partial overloading in some areas. This can further induce breakages in the loaded field resulting in non-ideal detonation. (Halonen 2012)

1.5.3 Quarrying operations

Quarrying operations take place in the production of aggregates, infrastructure construction projects and in the extraction of natural stones.

1.5.3.1 Production of crushed aggregates

Mineral aggregates refer to natural sand, gravel and crushed aggregates which are utilized in construction and in the maintenance of existing infrastructure as such or as processed (usually crushing and sieving). Most mineral aggregates are used in road and railway construction, bridges and asphalting. The availability of natural gravel and sand has decreased and in the meanwhile the utilization of crushed aggregates has increased. Most of the surplus blast rocks from infrastructure construction are nowadays processed to crushed aggregates. (Suomen ympäristökeskus 2010)

The rock for crushed aggregates is extracted by drilling and blasting. The amount of explosives used depends on the amount and quality of rock to be quarried. (Suomen ympäristökeskus 2010)

Infra operations still use more water soluble explosives compared to mining. In small scale quarrying projects the possible unsuccessful detonation events and incomplete explosive detonation may be reflected in the local water quality quite soon. (Halonen 2012) However, the loadings are generally quite small compared to large mining sites.

According to research by Laurila (2009) the effect of crushed aggregate production on groundwater remains usually local if the quarrying takes place above groundwater table and there is only minimal cracking in the rock. Quarrying under the groundwater table may have more significant effects, but their scale is dependent on the water flow, rock properties (conductivity, cracks etc.) and links to other aquifers. Explosives are mentioned as the single most significant risk to groundwater quality in extraction operations and also considered as a possible factor influencing the quality of nearby surface waters. Generally, the evaluation of environmental impacts of rock quarrying is more complicated compared to gravel mining as it requires extensive knowledge on the crack zones present.

Nitrogen concentrations are among the parameters most often included in the surface water monitoring requirements set to quarries. In the case locations examined by Hasari (2009) the quality of surface waters was not significantly affected by the quarrying activities even though there was usually a centralized discharge of storm waters to the environment. On the other hand, the possible quality changes are hard to evaluate as there is very limited information available on the water quality prior to quarrying operations. (Hasari 2009)

1.5.3.2 Infrastructure construction

Today underground infrastructure construction and rock engineering is common. In addition to traditional railway and road tunnels and bomb shelters various activities are placed in underground spaces at an increasing rate, such as power plants, containers for liquids and gases, water and wastewater tunnels, parking lots, sports halls, storages, data communication centres and storages for nuclear waste. The generated aggregates are often utilized on-site, especially in the construction of roads and railways. (Vuolio and Halonen 2010)

The term precision quarrying refers to quarrying where the goal is to generate a specifically designed space in rock. There the main aim is to produce smooth rock surfaces without cracking. The explosives typically used in precision quarrying include tubes as well as emulsions. (Vuolio and Halonen 2010)

1.5.3.3 Extraction of natural stones

Different methods such as drilling, wedging, sawing and blasting are used to extract different types of natural stones. The main principle is to utilize the natural cracks in rock. If blasting is used, the practices differ from those applied in ore and mineral mining as well as aggregate production. The extraction of natural stones requires accuracy with respect to the shape and size of produced blocks. In order to retain the large size and high quality of blocks the amounts of explosives utilized are relatively small compared to mining. The most typical explosives used in dimension stone extraction are tube cartridges specifically developed for natural stone extraction, combined with detonating cord (e.g. K tubes + F-cord by Forcit). (Vuolio and Halonen 2010; Aatos 2003)

According to Aatos (2003) the amounts of nitrogen containing explosives applied in natural stone extraction are so small that the resulting nitrogen emissions are negligible.

2. Explosives originated N discharges

Figure 6 summarizes the main routes for explosives originated nitrogen compounds. As pointed out by Morin and Hutt (2009), the nitrogen discharges from a specific mine site are difficult to predict at the pre-mining phase. Instead, the high levels of nitrogen may appear e.g. in the drainage after full scale mining is underway. This emphasizes the need for representative case studies on nitrogen discharges which can help in predicting nitrogen discharges at a certain site.

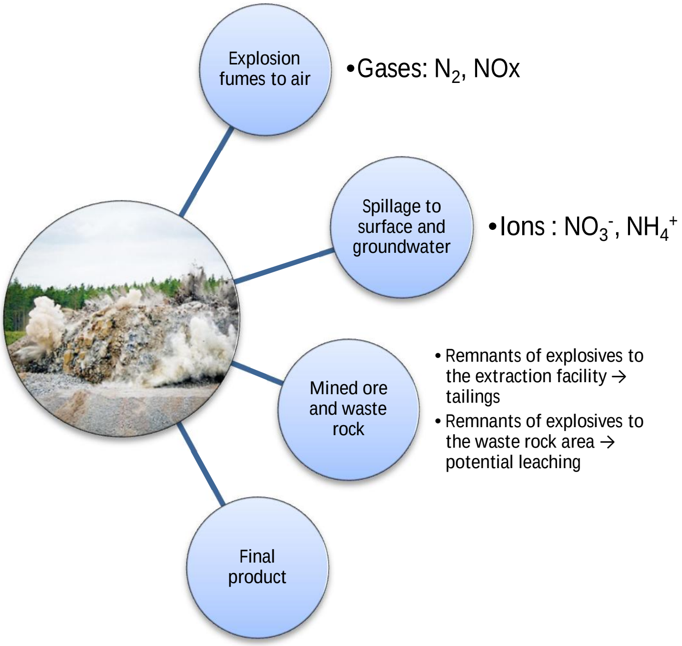

Figure 6. Routes of explosive originated nitrogen to the environment. Photo: Oy Forcit Ab.

2.1 Emissions to waterways

The potential of nitrogen to release into the water system from explosion site depend on (Forsyth et al. 1995):

1. **Explosives used**. The maximum amount of available nitrogen and its tendency to release is determined by the choice of explosive; as mentioned in the previous chapter these characteristics vary from type to type with ANFO products having the lowest water resistance.
2. **Water conditions**. The amount of water getting into contact with explosives is decisive to the transportation of nitrogen into waterways.
3. **Explosives management**. Losses and spillage of explosives may take place during filling of explosives loading equipment, actual loading of blastholes and disposal of excess product.
4. **Efficiency of the blasting operations** will control the amount of undetonated explosives and the amount nitrogen available in these. Failures may happen e.g. by poor design or execution.

Explosives management is seen by Forsyth et al. (1995) as the main factor influencing the overall rate of nitrogen spillage.

In practical blasting projects the majority of blast holes are ignited. It is, however, quite common that a blast hole is only partly detonated, due to e.g. poor design, presence of water, rock fractures etc. (Halonen 2012; Forcit 2010) In chapter 1.5 general estimates of the shares of incompletely detonated blast holes in different mining operations are given.

2.1.1 Effect of explosive type on nitrogen emissions

According to Halonen (2012), ANFO is dissolved to water within a timeframe of weeks. Emulsions may remain functional for a couple of years after which they start to decompose releasing nitrogen to waterways. Nitroglycol in NG type explosives may remain functional for years in dry conditions. It is oil like compound and very sensitive, therefore it very seldom causes nitrogen emissions to waterways. The speciality explosives that are used in starters usually do not dissolve in water.

Ammonium nitrate contained in undetonated ANFO is water soluble and therefore presents a risk for the surrounding water environment (surface as well as groundwater). Exposure of undetonated ANFO to water leads to significant nitrate losses and when >25% of nitrates is lost ANFO is no longer detonable. (Brochu 2010)

One important means of controlling ANFO originated nitrogen discharges to water is to avoid explosion work in wet conditions. Furthermore, the explosives should be stoichiometrically balanced and adequately dosed in order to ensure as complete detonation event as possible. The time between explosive loading and firing may also have quite significant effect on the dissolution of ammonium nitrate as part of fuel oil may wick away with time interfering with the balance of components. Other conditions that can increase the risk of incomplete detonation include: long explosives columns, explosive pre-compression caused by hole-to-hole shock propagation, mixing of explosives with drill cuttings (lead to reduced temperature) and use of bulk ANFO especially in wet conditions. These conditions should be avoided where possible. (Brochu 2010)

2.1.2 Share of explosive nitrogen entering the waterways: experimental studies

The share of the loaded explosive ending up in the water system in practical cases varies greatly. The shares are estimated to range from 0.1 to 8% (Golder Associates 2006). Morin and Hutt (2009) give a larger variation range for ANFO based on a number of case studies: according to them as much as 0.2 to 28% of the nitrogen contained in ANFO may leach into drainage water. The variation of N leaching at different sites may indicate the water conditions present and also that a significant amount of nitrogen may be stored at the blast site or in the blasted rock at drier conditions. In this case, this stored nitrogen might be released later on when coming into contact with water or it might release as gaseous compounds over time. (Morin and Hutt 2009)

Morin and Hutt (2008) carried out an experimental case study at an active underground metal mine in western Canada. The mine is located at ca. 1000 m elevation. The annual average rainfall is 0.51 m/a, and the average monthly temperatures range from -9 °C in January to 15 °C in July. Thus, the climatic conditions at the case mine resemble conditions in northern Finland. Freeze-thaw phenomena do not affect the geochemical processes in the underground mine, however, they affect the monthly groundwater recharge rates. There is a suitable location for water sampling: a portal where groundwater discharges.

Sporadic minor blasting and mining were started in late 2005 (first blasting campaign) and in 2006 more intensive mining activities were initiated (second blasting campaign). Before the first blasting campaign the concentrations of nitrate, nitrite, and ammonia were around or below detection limits at the sampling location receiving mine water (Station A1). After the start-up of the first blasting campaign concentrations of all nitrogenous compounds started to rice. ANFO and a proprietary powder (assumed to contain 50% ammonium nitrate) were used as explosives one batch containing ca. 12.5 kg of powder and 50 kg of ANFO which equivalents 18.3 kg N/batch. (Morin and Hutt 2008)

Monitoring of flow rate and characteristics of mine water in Station A1 and in Station A5 farther downstream were used to approximate the release the nitrogen species into mine drainage water. The concentrations of nitrate, nitrite and ammonia analysed in mine water were multiplied by flow and summed. The results showed that **the aqueous concentrations of nitrogen generally responded to blasting within a few days** and the sum at A1 was on average 28% of the nitrogen content of the explosives. The shares of nitrate-, nitrite- and ammonium-N were 51.3%, 2.9% and 45.8%, respectively. Thus, the **shares of N species in discharges resembled those present in the original explosive**. By the sampling point A5 there was around 40% loss of nitrogen and most nitrogen was found as nitrate. Consequently, there are either biological or physic-chemical processes taking place and the prediction of downstream nitrogen concentrations is more complex. It should be noted also, that some of the explosive-originated nitrogen is probably left in the blasted rock. (Morin and Hutt 2008)

In the second blasting campaign at the same mine site the nitrogen load observed at Station A1 was only 12% of the explosive originated nitrogen load. This case example shows the difficulty of estimating the nitrogen load of the mine drainage water based on explosive usage.

2.1.3 Behaviour and environmental impacts of nitrogen rich waters in ponds and in waterways

The damage caused by explosives spillage depends on environmental conditions such as soil type, depth of groundwater, presence of surface waterways, precipitation rate and vegetation. Some examples of average concentration of nitrogen and shares of nitrogen compounds in discharged mine waters are presented in Table 3.

Table 3. Examples of nitrogen in mine waters.

Mine	Ntot, mg/l	NO_3-N, %	NH_4-N, %	NO_2-N, %
Malmberg	36	95	2	3
Aitik	5	76	7	10
Garpenberg	6	79	13	8
Zinkgruvan	7	<70	30	-
Renström	9	88	10	2

Nitrate can be directly used as a nitrogen source by aquatic plants and thus increases risk for eutrophication. High concentrations of nitrate are also toxic to aquatic freshwater animals. Nitrate contaminated drinking water also is a toxicity risk for children. (Brochu 2010)

Ammonium ion (NH_4^+) is also readily soluble in water and it reaches equilibrium with ammonia (NH_3) depending on pH, temperature and ionic strength of water. The share of ammonia increases with increased pH and temperature. If available, plants prefer ammonium over nitrate as nitrogen source. Ammonia is the more toxic of the two species and presents a risk for both aquatic environment and human health. Also the fuel oil component of ANFO is a potential risk factor for the humans as well as for the nature. (Brochu 2010)

Plants can use nitrogen for biomass production only if they can get also phosphorous. If N:P ratio is less than 10:1, it can be estimated that in most cases nitrogen limits algae production and can cause eutrophication. TN:TP ratios between 10–20 are an area of uncertainty, where both nitrogen and phosphorous can be the limiting nutrient. If the ratio is > 20, algae production is usually phosphorous regulated. In order to get more information about this topic, Sara Chlot (2013) studied Kiruna and Boliden sites in Northern Sweden. Kiruna is nitrate dominated with low P concentrations, Boliden ammonium dominated with high input of P (Chlot 2013). The TN:TP ratios in macrophytes collected from recipient lakes varied between 22-8, which indicated that both the sites varied between P-limitation and N-limitation. For Kiruna this was against the predictions based on the water TN:TP ratios.

Unionized ammonia (NH_3) is very toxic to aquatic animals, particularly to fish (salmon most sensitive) and mussels, whereas ionized ammonia (NH_4^+) is nontoxic or appreciably less toxic. The toxicity of ammonium depends on several factors, including pH, temperature, dissolved oxygen concentration, ionic strength, salinity, previous acclimatization to ammonia, fluctuating or intermittent exposure, and the presence of other toxic substances (CCME 2010). From these factors pH is most important, because it, together with temperature, influence on the relative proportion of ionized and un-ionized ammonia (Figure 7). Water quality criteria within the range 0.01–0.02 mg NH_3-N/l have been proposed to protect sensitive aquatic animals. For rainbow trout the NOEC (No Effect Concentration) value of ammonia is 0.025 mg/l, and LC_{50} value (lethal concentration for 50% of test population) 0.48 mg/l (CCME 2010).

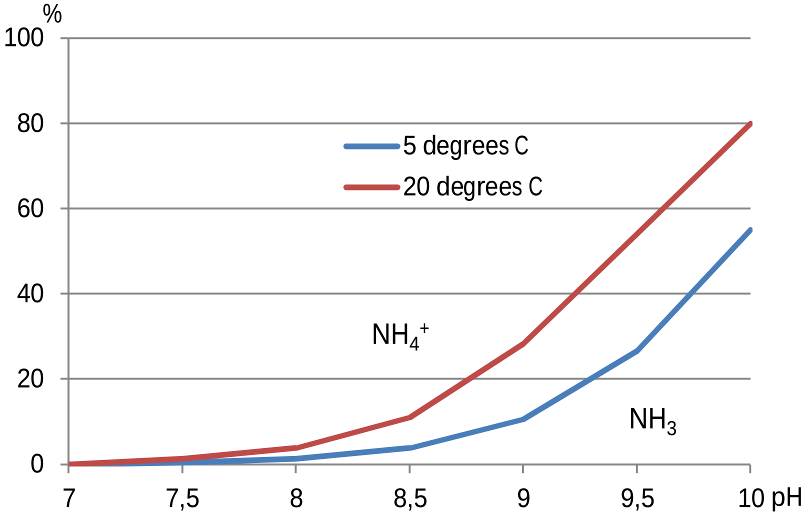

Figure 7. Dependence of ammonia : ammonium ratio on temperature and pH of water (Lindeström 2012).

In order to assess more specifically the environmental impact of nitrogen discharges in waterways, it would be important to know the fate and long-term behaviour of N species in receiving waters. Chlot et al. (2011) have developed a biogeochemical model for a clarification pond and downstream lake receiving ammonium-N rich discharge water from Boliden concentration plant in Sweden. The model can be used to increase the knowledge on the environmental factors affecting N transformations, simulate processes affecting N transport and to simulate possible measure to reduce the N load. The state variables included in the model are NH_4-N, NO_3-N, dissolved organic N, N contained in phytoplankton, N contained in macrophytes and sedimented N. The model simulates the rate of 16 nitrogen transformation processes and fairly good agreement between the measured and simulated values have been obtained.

The simulations of the case waterway show that denitrification rates are on average five times higher than ammonia volatilisation rate and ca. three times higher than permanent sedimentation of N. The transformation rates in the clarification pond were considerably higher than in the lake. In the lake ammonia volatilisation was relatively insignificant. Thus, **denitrification seems to be the major removal process for N both in the pond and in the downstream lake.**

According to model simulation, increased flow and increased temperature increased the transformation rates. Based on both measured concentrations and modelling, N transformation rates were highest when the temperature exceeded 5 ^{o}C, which was the situation from late May until the end of September. Also the residence time of the mine water in recipient is an important factor influencing the N removal capacity (Chlot 2013). After calibration the model can be utilised in other waterways receiving high ammonia loads from mining. (Chlot et al. 2011)

From the extraction processes the residues of the process are transported to the tailings ponds. Often, the residues are acidic due to the nature of the extractive process. The conditions in the tailings pond are often reducing which enhance the denitrification process. High ammonia and ammonium concentrations may therefore be present. (Bosman 2009)

2.2 Emissions to air

When a batch of ANFO is detonated, a cloud of reaction gases is released. For 1 kg ANFO, ca. 1000 litres of gas is produced. The composition of reaction gases based on a laboratory experiment is reported in Table 4.

Table 4. Combustion product of ANFO, obtained from detonation in calorimeter (according to Martel et al. 2004 in Brochu 2010).

Combustion product	**Volume of gas, l/kg ANFO**
H_2O	588
N_2	230
CO_2	67.6
CO	13.2
H_2	4.2
N_2O	9.9
CH_4	0.13
C_2H_6	0.07

In ideal conditions the reaction gases contain mainly H_2O, N_2 and CO_2. However, in most practical cases the conditions are non-ideal and other more toxic gases such as CO, NO and NO_2 are generated. Commercial explosives usually generate 6 to 31 litres of CO per kg of explosive. Oxygen balance of the explosive product controls the CO and NO production. Excess amount of fuel or negative oxygen balance lead to increased CO production but on the other hand in the decreased NO formation. Similarly, less fuel or positive oxygen balance decrease the formation of CO and increase NO generation. Getting into contact with air, NO oxidises to NO_2 which is significantly more toxic than CO or NO. After the detonation event, the turbulent air flows rapidly mix the gaseous products to the atmosphere. However, a part of NO and CO may remain in the expanded rock for a long time. There is also a potential for the formed NO_2 to adsorb on surfaces and dissolve in water. (Harris et al. 2003)

The computational volume of gas produced in an ideal detonation of different Forcit products has been determined by Cheetah 2.0 programme (Table 5). The values reflect a situation where all substances react fully to equilibrium. In actual detonation event the combustion does not necessary follow the ideal reaction scheme. (Forcit 2010)

Table 5. Computational properties of Forcit products by Cheetah 2.0 programme (Forcit 2010).

Product	**Produced gas V, l/kg**	**H_2O g/kg**	**N_2 g/kg**	**CO_2 g/kg**	**NO g/kg**	**NO_2 g/kg**	**CO g/kg**
Anfo	1050	485	330	182	0.56	0.01	0.05
Aniitti	960	412	311	206	1.45	0.06	0.02
Fordyn	960	380	270	305	1.79	0.28	0.003
Kemiitti 510	860	387	216	237	0.87	0.07	0.005
Kemiitti 800	1000	567	261	119	0.0001	0	29
Kemix	1020	556	282	118	0.0001	0	40
Kemix A	960	515	270	72	0.0001	0	51
Sea-Kemiitti	870	411	246	39	0.0001	0	68
Kemiitti 810	1010	560	278	142	0.0006	0	16

As shown in Table 5 the different explosive products generate quite similar gas volumes. The amount of CO_2 varies the most, being largest in Fordyn which is a NG type explosive. Fordyn and Aniitti produce the most NOx emissions.

The visible orange-red post-blast clouds, often referred to as yellow or orange smoke, consist mainly of NO_2. Other reaction products may also occur, such as phthalates, aliphatic hydrocarbons or benzene. Gaseous reaction products may cause adverse health effect to the mine workers. (Brochu 2010) The generation of NOx compounds usually indicates the occurrence of improper or incomplete detonation reaction (Rowland et al. 2001).

The causes of non-ideal explosion event and thus explosion fume generation can be classified as follows (Queensland 1999):

1. Chemical design of explosives blends and precursors (small range of optimal sensitivity, limited condition of stability, insufficient resistance to present conditions, fume generation not considered as a qualification criteria)
2. Conformance of explosives and precursors to specification (products out of specification)
3. Blast design (mismatch in explosives – rock mass properties, selected product not suitable for prevailing conditions, impropriate initiation design, ignorance of blast dynamics)
4. Adverse impact of blast dynamics to detonation performance (desensitation of explosives by dynamic shock, decoupling of explosives column, inappropriate burden relief and inappropriate confinement due to e.g. poor ground conditions)
5. Site practises (inappropriate sensitising of explosive, contamination of explosive)
6. Blasting personnel, designers (lack of know-how on fume causes and prevention techniques, inconsistency in defining dry and wet conditions, and following product application guidelines)

To sum up, the reasons for fume generation are somewhat similar to those causing discharges to water.

The water resistance of explosive is a factor affecting not only the emissions to water but also the generation of explosion fumes. In addition to water exposure, there are other parameters that may favour the production of excessive NOx emissions. Sapko et al. (2002) identified admixture of drill cuttings, loss of fuel oil in ANFO from wicking, ammonium nitrate dissolution with water, degree of explosive confinement, ANFO density and critical diameter as critical parameters increasing NOx production in laboratory conditions. Several additives were found to decrease the formation of NOx in ANFO, emulsion and ANFO/emulsion blends. Such additives included aluminium powder, coal dust, urea and excess fuel oil in ANFO. Borehole liners could be one option to reduce the wicking of fuel oil, AN dissolution and thus excessive NOx emissions. Test detonations were conducted in closed chamber in seamless steel pipes and galvanized steel pipes. (Sapko et al. 2002)

Monitoring of blast fumes is often carried out to record the exposure of personnel and possible fumes entering the surrounding areas. Monitoring also provides data for the validation of fume diffusion models. Monitors can be (Martin 2012)

- exposure monitors which personnel carry with them,
- fixed location monitors
- in-cloud monitors (balloons) or
- environmental monitors

According a study by Forsberg and Åkerlund (1999) the amount of nitrogen compounds dissolving from the reaction gases to mine water is negligible. Therefore, the main source of nitrogen in mine water is the undetonated explosive.

2.3 Remnants in waste rock and ore

The nitrogen contained in explosive residuals is transported from the quarrying site to the environment as dissolved in rain and drainage water as well as in waste rock stones and raw ore conveyed to the enrichment process.

Waste rock is the excess mineral non-ore overburden material which is removed in order to extract ore. Typically, waste rock is stored in piles at the mine area. The size of waste rock blocks generated in blasting is determined by blast hole spacing, amount of explosives and the characteristics of the rock material. (McLemore et al. 2009)

Waste rock is generally dumbed as relatively dry material. Over time the piles have a tendency to increase gradually in water content through infiltration and water flow. Rock piles also go through physical and chemical weathering processes. Weathering is a set of physical and chemical changes which lead to disintegration of rock which further gives rise to the reduction of rock grain size, changes in cohesion or cementation properties and in mineralogical composition. (McLemore et al. 2009)

2.3.1 Amount of explosive residuals in waste rock

In a waste rock pile the majority, 60–70%, of the nitrogen is initially contained in rocks. Eventually, nitrogen will end up in soil and waterways. However, the shares of nitrogen in water and in blast stones at different time frames depend on several factors, such as the characteristics of blast stones. The pile construction, precipitation and particle size have an effect on the dissolution rate. (Hannukainen 2009)

2.3.1.1 Nordic projects

In Kaira project (Mattila et al. 2007), explosive remnants were measured from the blast stones at three Finnish mines: Siilinjärvi (Kemiitti 110 water gel), Pahtavaara (ANFO) and Kemi (Kemiitti 810 emulsified). The results showed that blast stones carried 2%, 6% and 18% of the explosives used at Siilinjärvi, Pahtavaara and Kemi mines, respectively. When taking into account the loss to water (nitrogen content of mine water) the total explosive losses were 5%, 15–19% and 30%. The results show that shares of explosives ending up in the blast stones and to mine water vary greatly by the local conditions and explosive used. However, the losses to the environment can be considered as significant.

Sjölund (1997) investigated the amount of nitrogenous explosive residuals in blast stone materials at different quarrying sites (mine, tunnel construction, and aggregate production) and used three different leaching test methods to find out the ratio of explosive nitrogen remaining in the materials. The largest scale test was the so-called container test where the size of test containers was 10 m^3 (ca. 12 t material).

The results of the underground operations (mine and tunnel construction) showed N_{tot} contents between 15 and 72 g Ntot/t rock, representing 5–20% of the loaded explosive nitrogen. The nitrogen contents of rock material from above ground operations (aggregate production) were significantly lower: 1 g Ntot/t rock (1% of the loaded explosive nitrogen). This contrast is expected to be due to differences loading and detonation conditions. The difference of underground and above ground operations is in line with the variations in the amount of explosives used presented in Chapter 1.5. The leaching nitrogen was mainly in nitrate form; however, quite large concentrations of ammonium occurred as well. In this study, the explosive type did not seem to have influence on the amount of Ntot found in rock materials. (Sjölund 1997)

Considering the time frame of nitrogen leakage, the container test showed that most nitrogen was leaching out in the early phase of the test (at L/S ratio 0.05, meaning 50 l water/t rock). This indicates that large nitrogen emissions may take place from the material within months…one year. (Sjölund 1997)

2.3.1.2 The Diavik diamond mine project

Bailey et al. (2011) have monitored the behaviour of explosive residuals at Diavik diamond mine where ANFO emulsion explosives are used to blast the ore and waste rock in the open pit and underground mining operations. Waste rock is stored on site and consists of granite and pegmatite with intrusions of diabase. Waste rock is categorised in three groups with different contents of sulphur (Types I, II and III). Three large-scale waste rock test piles (60 m x 50 m x 15 m) containing waste rock with different percentages of sulphur were constructed. Each pile is underlain by HDPE geomembrane to catch the drainage water. The waters draining from the piles has been analysed for their $SO_4{}^{2-}$, NO_3-N, NO_2-N, NH_3-N, ClO_4 - and Cl^- concentrations. In addition, four HDPE lysimeters (Ø 2 m x 2 m) were filled up and surrounded by waste rock in order to study the upper 2 m of the active zone of the waste rock pile. Two of the lysimeters were filled with Type I waste rock and two other with Type III waste rock. Furthermore, leaching tests were carried out on recently detonated waste rock at laboratory scale (100 g material in 1 l of Milli-Q water). (Bailey et al. 2011 and 2012)

In the laboratory leaching tests the observed NH_3-N concentration was below detection limit whereas N_{tot} concentrations averaged 4.6 mg N/kg waste rock. Most nitrogen was present as NO_3-N. In the lysimeters test the concentrations of nitrogen species decreased significantly after the first pore volume of water had passed through the lysimeters. Most nitrogen in the leachate was also in this case found as NO_3-N (maximum concentrations ranging from 480 to 2400 mg/l and from 600 to 640 mg/l in type I and type III lysimeters, respectively). (Bailey et al. 2012)

The residual nitrogen in the lysimeters was determined by using a mass balance approach by taking the total mass of released N in effluent (NH_3-N + NO_2-N + NO_3-N = N_{tot}) and the total N in the explosives used to blast the mass of waste rock (N_{used}). The N released to the effluent ranged from 2.0 to 12% of the N_{used}. In the laboratory leaching tests the corresponding N loss averaged 5.4% of N_{used}. Assuming that most of the explosive residuals were leaching out of the lysimeters over time, the above mentioned percentages can be used as an estimate of the amount of un-detonated explosive remaining in the waste rock after blasting. (Bailey et al. 2012)

The variations in concentrations and the gradual loss of blasting residuals indicate the heterogeneity of the piles and the role of different flow paths. The temperature rise due to ambient temperature increase, larger proportions of the pile contribute to flow and increased concentrations of blasting residuals are observed in drainage. During the summer period, the concentration increase of nitrite indicates the nitrification. However, denitrification was not occurring significantly, due to the low content of organic C present in the waste rock piles. (Bailey et al. 2011 and 2012)

2.3.1.3 Other projects

Miller et al. (1999) investigated the behaviour of several constituents (cations, anions, TDS, pH) in closed cyanide heap leaching piles. They used lab-scale column experiments (15 kg of material in 75 cm/14 cm columns, pore volume estimated to be 4.5 l) where material was leached with deionized water for 42 days. The water soluble anions nitrate and chloride eluted rapidly as expected. When the first pore volume of water had passed through the column, the concentration of nitrate had already dropped drastically. According to the authors, the column test could be used as a tool to predict the quality of drainage water. However, the hydrologic characteristics of heaps in field conditions may differ from those present in lab columns. Also, the precipitation is uneven over time and will depend on the meteorology of the case area thus resulting in both saturated and unsaturated conditions in the heap. These factors probably affect the properties of drainage water in field conditions. (Miller et al. 1999)

Based on the experimental studies presented above, it can be expected that the **ammonium and nitrate species attached to waste rock release within a relatively short period of time when the rock material comes into contact with water**.

2.3.2 Weathering phenomena in waste rock piles

Physical processes taking place in waste rock piles and causing weathering include (McLemore et al. 2009):

- Freeze/thaw and related frost-action effect
- Thermal expansion and contraction of rock
- Crushing of rock fragments due to gravitation forces
- Abrasion, pressure release on rock by erosion of overlying materials
- Growth of plants and living organisms in rock
- Crystallization of mineral phases may break up the rock

Chemical weathering includes both geochemical and biogeochemical reactions causing changes to the texture, structure, and composition of rock fragments. Relevant chemical weathering processes include (McLemore et al. 2009):

- Redox reactions, e.g. acid generating oxidation of pyrite
- Short-term acid-base reactions, e.g. dissolution of carbonates, precipitation of salts
- Solubility controlled precipitation of long-lived mineral species, e.g. goethite, sulphates
- Longer-term acid-base reactions, e.g. hydrolysis of alumina-silicates
- Soil diagenesis reactions driven by atmospheric oxygen and dissolved CO_2

The main acid causing weathering in typical environment is carbonic acid formed by the dissolution of atmospheric CO_2. Also the anthropogenic emissions of sulphur and nitrogen can lower the pH of rainwater. However, the pH of the waste rock pile is lowered much more if there is acid generation potential in the deposited rocks. Examples of such rock are pyrite containing rocks. The oxidation pyrites generates sulphates resulting in acidification of the pile (acid rock drainage, ARD). Pyrite dissolution is classified as short-term acid-base reaction. The acid causes oxidation of minerals present in the pile. (McLemore et al. 2009)

2.3.3 Amount of explosive residuals in raw ore

In addition to waste rock, explosive residuals also attach to raw ore which is transferred to the enrichment facility. It has been estimated in a Swedish mine (LKAB Kiruna, using emulsified explosive) that as much as 15 to 19% of the loaded explosives would end up in the raw ore. The analysed nitrogen contents of different ore grades ranged from 6.50 mg Ntot/kg ore to 34.70 mg Ntot/kg ore. The sample preparation included grinding of materials (particle size < 3 mm), extraction of nitrogen to deionized water (15–25 g sample, shaking 2 h) which is then made acidic by 0.1 M H_2SO_4 and filtered (0.45 µm). Nitrogen analysis was carried out by FIA instrument. Mass balance calculations showed that ca. 43% of the nitrogen brought up to the enrichment facility within raw ore ends up in tailings and the rest eventually to process water. (Forsberg and Åkerlund 1999)

2.3.4 Behaviour of explosive residuals in ore processing

Forsberg and Åkerlund (1999) analysed the effects of different ore handling processes on the explosives originated nitrogen residuals found in ore. The analysis was based on processes applied at the LKAB mine in Kiruna producing mainly iron ore pellets to the steel industry. The enrichment in LKAB is based on mechanical processes (grinding, flotation, pelletization).

In dry screening and crushing processes emulsion explosive residuals are expected to partly decompose releasing ammonium nitrate. At this stage, all the nitrogen contained in residuals most probably remains in the ground ore and waste fractions (tailings). However, there may be changes in the distribution of nitrogen between ore and waste material. The grinding process is expected to cause further decomposition of emulsion. When the ground materials come in contact with water, they release ammonium and nitrate to the process water. Simultaneously, the nitrogen content of the solid phase decreases. It is suspected that the flotation chemicals can promote the decomposition of emulsion. The production of iron ore pellets consists of filtering and pressing of water from the enrichment slurry, mixing of binding chemicals, rolling of material to pellets and sintering of pellets in a band oven. The heat of the oven may contribute to the formation of nitrous oxides as well as nitrogen containing salts. It is stated by Forsberg and Åkerlund (1999) that the effect of microbiological activities in the ore processing are probably negligible. However, in the pond system microbiological alteration of nitrogen probably takes place. (Forsberg and Åkerlund 1999)

The sampling of ore and waste material at LKAB in different process phases supported the hypothesis made: the **total nitrogen content (mg/kg ore or waste rock) of materials decreases as the process proceeds.** Nitrogen contents of waste material were somewhat higher than those of ore. One possible explanation to this distribution may be the different material densities: waste material has more surface area /kg where explosives residuals could attach. (Forsberg and Åkerlund 1999)

2.4 Options for reducing explosive originated nitrogen discharges

In many cases the most cost and environmentally effective ways to reduce environmental load are to minimise transport of contaminants from the primary source, and to make the reduction measures as near the primary source as possible. It has been estimated that the shift to emulsified explosives and improvement of the explosion practices has led to about 10% reduction in nitrogen discharges (Lindeström 2012). The LKAB Kiruna mine has been able to reduce the share of undetonated explosives from 20% in the year 2000 to current 12–13% by focusing on explosion management.

The nitrogen response plan of Snap Lake underground diamond mine (De Beers 2013) presents several measures introduced at the mine to improve blasting practices. The nitrogen discharges of the mine have increased nitrogen concentrations in a nearby lake, and in 2012, measured concentrations were above the CCME Aquatic Effects Monitoring Program (AEMP) benchmark of 2.93 milligrams as nitrogen per litre (mg-N/L) (De Beers 2013). The measures include (De Beers 2013):

- A re-design of the blasting round based on the characteristics of the rock enabled reduction of drill holes from 50 to 43 holes per round and resulted in a 15% reduction in the emulsion use.
- Better education of the crews on proper loading and blasting techniques and minimizing the overuse of the emulsion combined with the longer col-

lar lengths (90 cm instead of former 30 cm) resulted in about 7% reduction in emulsion use.

- Use of fixed quantity loaders which enable pumping of pre-determined quantity to drill holes, and thus prevent spills.
- Collection of the emulsion spillages from the underground work area and use in surface blasting
- Prevention of spills in all stages:
    - by location of the explosive magazines underground close to working areas, and better control of the explosives handling at the storage area.
    - by unloading of the containers and loading of the onsite transfer trucks inside a storage building with a concrete floor and cover-all structure
    - by contained steel structure and elevated thresholds on the doorways of emulsion plant as well as
    - by regular maintenance of all the equipment and storage bins to reduce spills
- Tight quality control of the emulsion manufacture
- Monitoring of conformance of the prevention practice
- Review of blasting practices, explosives loading and storage by an external blasting expert.

3. Process originated N sources

The main process originated sources of nitrogen in mine waters and wastes include:

- cyanide used in gold extraction
- pH regulating agents (nitric acid HNO_3)
- use of ammonia as lixiviant in copper and nickel hydrometallurgy
- use of nitric acid in acid washing of activated carbon used in gold recovery

In addition to these, cyanide is also used at mines as a depressant for sphalerite, pyrite and some copper sulphides in flotation processes.

Table 6 shows examples of essential bulk supplies used at Finnish metal mines.

Table 6. Examples of bulk supplies used at Finnish metal mines.

Mine	**Chemicals**
Kemi mine	ferrosilicon, grinding balls, grinding bars, flocculants
Kittilä mine	copper sulphate, sodium cyanide, K-amyl xantate, nitric acid, MIBC (foaming agent), sodium hydroxide, Aerophine 3418, sodium metabisulphate, activated carbon, calk, grinding balls
Pyhäsalmi mine	sodium isobutylxantate, calsium oxide, zinc sulphate, copper sulphate, sulphuric acid, Sylvapine (foaming agent), sodium cyanide, nitric acid, acetic acid, grindin balls
Talvivaara mine	nulphuric acid, sulphur, sodium hydroxide, liquid nitrogen, calk, calsium carbonate, propane, flocculants
Sastamala enrichment plant	sodium isobutylxantate, Aerophine 3418A, Danafloat 245, Flopan AN 905 SH, Dowfroth (foaming agent), grinding balls, grinding bars
Sotkamo mine	sodium ethylxantate, Montanol (foaming agent), copper sulphate, aluminium sulphate, CMC

Of all the supplies shown in Table 6 only sodium cyanide (NaCN) and nitric acid (HNO_3) contain nitrogen compounds and are also used in significant amounts at selected mine sites.

3.1 Cyanide

Gold is one of the noble metals and as such it is not soluble in water. A complexant, such as cyanide, which stabilizes the gold species in solution, and an oxidant such as oxygen are required to dissolve gold. Alternative complexing agents for gold, such as chloride, bromide, thiourea, and thiosulfate form less stable complexes and thus require more aggressive conditions and oxidants to dissolve the gold. These reagents present risks to health and the environment, and are more expensive. This explains the dominance of cyanide as the primary reagent for the leaching of gold from ores since its introduction in the later part of the 19th century. (International Cyanide Management Code 2012)

3.1.1 Cyanide leaching process

When gold is leached in an aqueous cyanide solution it forms a gold-cyanide complex by oxidizing with an oxidant such as dissolved oxygen and cyanide complexation. The gold-cyanide complex is very stable and the cyanide requirement is only slightly in excess of the stoichiometric requirement. However, in practice the amount of cyanide used needed is influenced by the presence of other cyanide consumers, and the need to increase the rate of leaching. (International Cyanide Management Code 2012)

Typical cyanide concentrations used in gold leaching range from 300 to 500 mg/l (0.03 to 0.05% as NaCN) depending on the mineralogy of the ore. Gold is recovered by means of either heap leaching or agitated pulp leaching. Heap leaching of gold is not practiced in Europe. (International Cyanide Management Code 2012) The pH of the slurry is raised to pH 10-11 using lime, at the head of the leach circuit to ensure that when cyanide is added, toxic hydrogen cyanide gas is not generated and the cyanide is kept in solution to dissolve the gold. The slurry may also be subject to other preconditioning such as pre-oxidation at the head of the circuit before cyanide is added. (International Cyanide Management Code 2012)

Normal commercial operation is estimated to result in consumption of 1.5–2.5 kg/t of sodium cyanide (Hourn 2009).

3.1.2 Cyanide destruction and decomposition products

The mining waste directive (2006/21/EC) lays down requirements for safe management of wastes from the extractive industries. Among these requirements concentrations of cyanide and cyanide compounds in tailings ponds from certain extractive industries should be reduced to the lowest possible levels, using best available techniques. In more detail, the directive states that the concentration of weak acid dissociable cyanide (WAD cyanides) at the point of discharge of the tailings from the processing plant into the pond does not exceed 50 ppm as from 1 May 2008, 25 ppm as from 1 May 2013, 10 ppm as from 1 May 2018 and 10 ppm at waste facilities which are granted a permit after 1 May 2008.

The requirements of the directive mean in practice that cyanide used in gold leaching has to be destructed from the tailings slurry before discharge to the tailings pond. All sites within the EU and the Turkish Ovacik mine destroy the cyanide in the tailings prior to discharge into the tailings pond (European Commission, 2009).

Laiva and Kittilä are the two Finnish gold mines using cyanide in the leaching of gold. They both apply the patented INCO-process to destruct cyanide from tailings slurries before discharge to the tailings ponds. Therefore the INCO-process is the only cyanide destruction process described in more detail here.

In the INCO process free and weakly complexed metal cyanides (i.e. WAD cyanides) are oxidized to cyanate by sulphur dioxide and air in the presence of a soluble copper catalyst according to following simplified equations (Mudder et al. 2001):

$$CN^- + SO_2 + O_2 + H_2O \xrightarrow{Cu-catalyst} OCN^- + SO_4^{2-} + 2H^+ \quad (4)$$

$$M(CN)_4^{2-} + 4SO_2 + 4O_2 + 4H_2O \xrightarrow{Cu-catalyst} 4OCN^- + 8H^+ + 4SO_4^{2-} + M^{+2} \quad (5)$$

Iron cyanide removal is done by reduction of ferric iron to the ferrous state:

$$2Fe(CN)_6^{3-} + SO_2 + 2H_2O \rightarrow 2Fe(CN)_6^{4-} + 4H^+ + SO_4^{2-} \quad (6)$$

The ferrous cyanide complex can be then removed through precipitation with copper, nickel or zinc:

$$2M^{2+} + Fe(CN)_6^{4-} \rightarrow M_2Fe(CN)_6 \ (solid) \quad (7)$$

The oxidation of thiocyanate and the hydrolysis of cyanate occur according to the following reactions:

$$SCN^- + 4SO_2 + 4O_2 + 5H_2O \rightarrow OCN^- + 10H^+ + 5SO_4^{2-} \quad (8)$$

$$OCN^- + H^+ + 2H_2O \rightarrow HCO_3^- + NH_4^+ \quad (9)$$

Oxidation of thiocyanate is usually limited to 10-20% in the INCO-process (Mudder et al. 2001). Based on what has been written above, nitrogen containing direct outputs from INCO-process include cyanate (OCN^-) and thiocyanate (SCN^-) in the liquid phase and possibly the metal-ferrous cyanide complexes ($M_2Fe(CN)_6$) in the solid phase, the solubility of which varies depending on the cation. Heavy metal salts of iron cyanides form insoluble precipitates.

The proportions of cyanide degradation products cannot be generalized because they obviously depend very much on the tailings slurry's composition and the destruction process used. Regarding slurry disposal, in oxic conditions both thiocyanate and cyanate degrade relatively fast to yield ammonium, bicarbonate and sulfate. In anoxic conditions the degradation of cyanate has been found to be quite slow and degradation of thiocyanate non-existent (Bucknam et al. 2012).

3.1.3 Examples of cyanide usage

The Boliden base metal mineral processing plant received a total of 1.58 million tonnes of ore from five different mines during 2001 in order to produce copper, lead and zinc concentrates. Coarse gold is also extracted using shaking tables. Depending on the ore type part of the tailings produced (approx. 50%) are further processed in the gold leaching plant.

At Boliden concentration plant in northern Sweden sodium cyanide (NaCN) is used in the gold extraction process. The yearly amount of nitrogen contained in NaCN is some 150 tonnes. It has been reported that this amount of nitrogen corresponds closely to the total nitrogen discharged to the receiving waters from the site (Frandsen et al. 2009). The gold leaching plant generated 0.8 million tonnes of tailings in 2001 (European Commission, 2009) which roughly equals the amount of ore processed at the gold extraction process. This combined with nitrogen contained in NaCN gives an estimation of NaCN usage of 525 t/a. These give a usage of 0.7 kg NaCN and 0.19 kg N per tonne of ore.

At Kittilä gold mine in northern Finland some 200 t of sodium cyanide is used annually to leach around 50 000 t of gold containing ore in a CIL-process (carbon in leach). Nitrogen contained in NaCN amounts to 57 t N/a. These give a usage of 4 kg NaCN and 1.1 kg N per tonne of ore.

3.2 Nitric acid

Nitric acid is used at gold mines in the gold recovery process to acid wash the used activated carbon. Other applications include use of nitric acid in filter washing (e.g. Pyhäsalmi mine) and as pH-regulating agent.

Generalized estimations for the use of nitric acid cannot be made based on existing public data. Pyhäsalmi mine has been reported to use 150 g/t of Nitric acid in filter washing (European Commission, 2009). Kittilä mine has reported nitric acid usage amounting to 22 tons of N contained in HNO_3 used in the gold recovery process.

3.3 Other nitrogen sources

In addition to explosives and extraction process, nitrogen found in mine waters may originate from the bedrock where the ore is extracted. Blasting disturbs and may liberate elemental nitrogen present in soil or geological formations. Coming into contact with water and air nitrogen containing minerals can form nitrate which dissolves in water. Once excavated, this so-called geological nitrogen may also contribute to nitrification also in waste rock areas. Hence, geological nitrogen can be found in waste rock drainage water as well as in mine water. (Bosman 2009) In most cases, the distinction between geological nitrogen and explosives originated nitrogen may be very challenging.

4. Review of legislation and environmental permits

4.1 Finnish legislation on mining

Mining is generally regulated in Finland by the mining law 621/2011 which came into force 1.7.2011 replacing the old law from 1965. The processing and granting of mining permits was simultaneously transferred from the Ministry of employment and the economy (TEM) to the Finnish Safety and Chemicals Agency (Tukes). The mining law regulates the exploration and beneficiation of deposits containing mine minerals (specified in the law). The environmental issues of quarrying and crushing are regulated in a specific decree (800/2010).

Considering protection of the **water environment and usage of water**, regulations are given in Environmental and Water legislation (Environmental Protection Act 527/2014 and Environmental Protection Decree 713/2014; Water act 587/2011; Act on Water Resources Management 1299/2004; Nature Conservation Act 1096/1996) and decrees (e.g. Decree on Substances Dangerous and Harmful to the Aquatic Environment 1022/2006 and 868/2010).

The **solid wastes** generated in mining and quarrying are covered in Decree on Mining Wastes 190/2013; Waste Act 646/2011 and Waste Decree 179/2012; Decree on Landfills 331/2013.

The **safety issues** of mining are covered by the law on dam safety (494/2009), the law on detonation and quarrying safety (644/2011), decree on the handling and storage of hazardous chemicals (59/1999) and the law on the handling safety of hazardous chemicals and explosives (390/2005).

The legislation on explosives is mainly focusing on the safe handling and usage of explosives. Today the environmental aspects are still in minor role in explosive legislation but this is expected to change in the future.

The emissions to air, the air quality, noise, and soil are mainly regulated in Environmental Protection Act (527/2014) and specific decrees (e.g. Decree on Air Quality 38/2011) given based on Environmental Protection Act.

The REACH regulations touch the mining industry as a user of chemicals and as a producer of ores and enrichments. The minerals, ores and ore enrichments are not in the scope of REACH if they have not been chemically modified. Examples of such products are enrichments produced by gravitation, flotation and magnetic enrichment processes. On the other hand, leaching processes, precipitation and sintering are considered as chemical modification and thus covered by REACH. (Kauppila et al. 2011)

4.2 Finnish legislation on nitrogen in the water environment

Nitrogen is currently topical in the Finnish mining sector as there are several mines in the phase of environmental impact assessment and environmental permit handling (consideration). Simultaneously, many old mines are in the process of getting updates for their environmental permits. In both cases the authorities might be considering limit values for nitrogen emissions to waterways.

In the Council of State decision 1172/1999 on the protection of inland waters in order to protect living conditions of fish there are mandatory and indicative nitrogen limit values for so called salmon and roach waters. The limit values are given for nitrite, unionised ammonia (NH_3), and total ammonium (NH_4).

The Council of State decision decision 366/1994 regulates the quality and monitoring of raw water used to produce potable water. The act gives limit values for nitrate, ammonium and total nitrogen for three water quality categories (A1, A2, A3) requiring different levels of water treatment.

Furthermore, the decree 461/2000 (and its change 442/2014) relating to the quality and monitoring of water intended for human consumption gives limit values 50 mg/l and 11.0 mg/l for NO_3^{2-} and NO_3-N, respectively. The maximum allowed nitrite concentration for water leaving the water works is 0.10 mg/l and the sum [nitrate]/50 + [nitrite]/3 may not exceed value 1. For NH_4^+ and NH_4-N the values 0.50 mg/l and 0.40 mg/l are given as indicator parameters. The requirements follow mainly the ones given in European directive 98/83/EC on the quality of water intended for human consumption.

The different nitrogen limit values in the Finnish legislation are summarized in Table 7.

Table 7. Finnish legislation on nitrogen in different waters.

Regulation number	Description	Limit values given	Notes
1172/1999	Quality requirements for fish waters	NO_2: 0.01 mg/l NO_2: 0.03 mg/l NH_3: 0.025 mg/l NH_3: 0.005 mg/l NH_4: 1.0 mg/l NH_4: 0.2 mg/l NH_4: 0.04 mg/l	Salmon waters, indicative Roach waters, indicative Salmon and roach waters, mandatory Salmon and roach waters, indicate Salmon and roach waters, mandatory Roach waters, indicative Salmon waters, indicative Fulfilled if 95 % of the results comply with the requirements.
366/1994	Quality requirements for raw water used in the production of potable water	NO_3: 25 mg/l NO_3: 50 mg/l NO_3: 50 mg/l NO_3: 50 mg/l Kjeldahl-N: 1.0 mg/l Kjeldahl-N: 2.0 mg/l Kjeldahl-N: 3.0 mg/l NH_4: 0.05 mg/l NH_4: 1.0 mg/l NH_4: 1.5 mg/l NH_4: 2.0 mg/ NH4: 4.0 mg/	Treatment level A1, indicative Treatment level A1, mandatory Treatment level A2, mandatory Treatment level A3, mandatory Treatment level A1, indicative Treatment level A2, indicative Treatment level A3, indicative Treatment level A1, indicative Treatment level A2, indicative Treatment level A2, mandatory Treatment level A3, indicative Treatment level A3, mandatory Fulfilled if 95 % of the results comply with the requirements (as a general rule).
461/2000 (change 442/2014)	Quality requirements and monitoring schemes for potable water	NO_3: 50 mg/l NO_3-N: 11.0 mg/l NO_2: 0.5 mg/l NO_2-N: 0.15 mg/l NO_2: 0.10 mg/l $[NO_3]/50 + [NO_2]/3 < 1$ NH_4: 0.50 mg/l NH_4-N: 0.50 mg/l	Mandatory Mandatory Mandatory Mandatory Mandatory, water leaving the waterworks Mandatory Indicative Indicative Requirements apply to water at the point of use.

The quality requirements for raw waters utilized for potable water production (366/1994) as well as the quality requirements set to protect aquatic life (fish) (1172/1999) must be considered when setting environmental permit requirements for different operations. The goal is to prevent the deterioration of the quality of the water environment below the required level. On the other hand, wherever the quality requirements are currently not met, the objective is to enhance the status of the water environment.

However, in practise, these water quality requirements are very seldom used in the reasoning of environmental permit requirements. The argumentation for the requirements to reduce nitrogen load is usually based on the overall negative impacts of nutrient load (eutrophication etc.). (Kaloinen 2004)

In the Decree on Substances Dangerous and Harmful to the Aquatic Environment 1022/2006 (national implementation of water framework directive 2000/60/EY and directive on substances harmful to the water environment 2006/11/EY), the substances causing eutrophication and specifically nitrates and phosphates are listed as substances that must not be released to groundwater. Water framework directive mentions nitrates and phosphates in the suggestive list of the most important polluting substances.

The IPPC directive (integrated pollution prevention and control) 2008/1/EC applies to industrial processes including also production and processing of metals as well as mineral industry. Annex III of the directive contains an indicative list of the main polluting substances to be taken into account, when relevant, for fixing emission limit values. The list mentions eutrophication causing substances, especially nitrates and phosphates, within the group of water pollutants and oxides of nitrogen and other nitrogen compounds within the group of air pollutants.

4.3 Permits in mining activities

Establishing a mine requires a **mining permit**, which can be granted for a fixed period or until further notice. The mining permit gives a right to beneficiate minerals and by-products in a certain area. The permit requires a collateral to be deposited for the mine closure and aftercare. All mining permits also include a requirement for annual reporting to the authorities. Prior to the construction of a mine and production start-up, a **mining safety permit** is also needed. Both permits are granted by Tukes (Finnish Safety and Chemicals Agency). Before granting the permits, the authority consults the municipalities, ELY Centre (Centre for Economic Development, Transport and the Environment), regional council and other relevant stakeholders. (Kokko 2013)

Additionally, an **environmental permit** and usually a **water management permit** are needed. These permits are granted by the regional state administrative agencies (AVI). The environmental permit usually also includes a requirement of a collateral. The AVI request a statement on the planned activity from the relevant municipalities and from the ELY centre. Other involved parties whose rights or interests may be concerned are to be given an opportunity to comment the permit.

Compliance with the environmental permit is supervised by the ELY centre. The permit authority, AVI, decides on the use of administrative coercive measures based on the Environmental Protection Act 527/2014. (Kokko 2013)

Like every construction project, a mining project requires a **construction permit** or at least an operation permit which are granted by the local construction authority. On the regional level, the land utilization is governed by regional planning in regional councils. (Uusisuo 2011)

4.3.1 Permit requirements on water management

Nowadays the Finnish environmental permits for mines usually give requirements on the discharge water quality (treated water to the environment) or the annual load of certain pollutants. The pollutants covered by the permits include solids, residue of ignition, metals (arsenic, nickel, copper, and antimony), WAD cyanide in gold mines and pH. Sometimes also on the effluent flow rate is regulated in the permit (related to the flow rate of the receiving waterways). (Kainua 2010)

Some permits include requirements on the quality of explosives used; the nitrogen contained in explosives should have low water solubility. Also, requirements have been given to minimize the amounts of undetonated explosives in waste rock and ore. Some permits have obliged the mine to make further surveys on how to reduce the nitrogen load to the environment. (Kainua 2010)

4.4 International legislation on nitrogen in mining waters

Environmental legislation related to mining and nitrogen in mine waters was reviewed in some example countries. In general, the regulation specifically targeting nitrogen emissions from mining is very limited in the countries in question.

4.4.1 Sweden

The status of the mining sector in Sweden is comparable to Finland: the interest in opening new mines has increased during the past few years as the metal prices have increased. In 2006, there were 15 operational mines. The main products include iron, copper, zinc, lead, silver and gold. (Swedish EPA 2011)

Mining operations in Sweden are regulated by both mineral and environmental legislations. The minerals act (SFS 1991:45) with its related ordinances regulates the exploration and extraction activities. The permits for exploration and exploitation of a deposit are granted by the Mineral Inspector. (Swedish EPA 2011)

The Environmental Code SFS 1998:808 which is the main environmental law in Sweden gives regulation on environmental permits of mining. The exploitation of minerals requires permits for “Environmental Hazardous Activity” and Water Operations. Environmental impact assessment precedes the permit process. (Michanek 2008)

A major issue in the mine permitting process is the handling of mining waste. The management of waste from extractive industries is further regulated in Swedish law SFS 2008:722.

The basis for water related requirements in environmental permits are the quality standards for groundwater and surface water. The quality standards for groundwater include classification of waters to five usability classes based on seven parameters: alkalinity, nitrogen, heavy metals, redox potential, chloride, pesticides/herbicides and groundwater level. In class 1 groundwater the concentration of NO_3-N is < 0.5 mg/l. The NO_3-N guideline value for groundwater used as drinking water is 1 mg/l and the limit value 10 mg/l. (Naturvårdsverket 2012)

Swedish EPA regulation SFS 2001:554 gives for protection of fishes and mussels in fresh water given limit values (threshold values) for ammonia and ammonium and indicative values for ammonia, ammonium and nitrate (see Table 5, quality requirements for fish waters). The values are based on EU Fresh water fish directive on the quality of fresh waters needing protection or improvement in order to support fish life and the EU Shellfish directive on the quality required of shellfish waters. The regulation concerns certain types of fish waters designated by Swedish EPA and mussel water designated in Västra Götaland region by "länsstyrelsen". The point of compliance for the emissions is not specified in the regulation.

Umeå Tingsrätt, miljödomstolen has made a Court decision concerning LKAB Kiruna's nitrogen emissions. The decision was complained by LKAB but the changes applied by the company were not approved. In the decision it has been specified that the point of the compliance is the discharge from the clarification basin ("utloppet från klarningsmagasinet") to the recipient. According to the Court decision a control of the ammonia-nitrogen concentration is to be done once a month. The ammonia-nitrogen concentration is to be calculated based on the analysed concentration of ammonium-nitrogen (NH_4 – N) and pH. According to the Court decision from "Miljödomstolen" it is adequately shown that a reduction of ammonium-nitrogen emissions cannot be achieved by available technology.

In the quality standards for lakes and waterways the following aspects are included: pH, alkalinity, nutrients (nitrogen, phosphorus), TOC, COD, metals, light conditions, plankton algae, fish, water vegetation and bottom fauna. If nitrogen is the limiting substance in the waterway in question, the authorities must set the appropriate limit values for nitrogen concentration.

The Swedish mine association SveMin (Lindeström 2012) has compiled a report about the nitrogen emissions from mines. This report is available from internet and will be continuously updated.

4.4.2 The United States

The United States produced ca. 6% of the world's nonfuel nonferrous mineral in 2010 and the total value of all nonfuel mineral production in 2010 increased to $66.4 billion, which was a 13% increase compared with that of 2009. US is the leading producer of beryllium, soda ash and sulphur (NMA 2012; USGS 2010)

Environmental issues of mining (hardrock mining, non-metals mining and coal mining) in the US are regulated by US-EPA. The sector is covered in several EPA program as mining generates wastes, wastewater and air emissions. (US-EPA 2010)

The Clean Water Act (CWA, i.e. The Federal Water Pollution Control Act, 33 U.S.C.§§ 1251) requires that all point source discharges from mining have aNPDES permit (National Pollutant Discharge Elimination System), according to section 402 of the CWA. In addition, the construction of tailings ponds and treatment of waste from mining and minerals processing is regulated by CWA (section 404). Section 402 regulates any discharges from tailings ponds to waterways. Section 303 includes guidelines for the establishments of water quality standards. (US-EPA 2010)

EPA Regional offices have the authority to regulate mining activities through NPDES permits. Mining permits are issued by various state agencies but the Office of Water has a right to review the permit with respect to water quality criteria. (US-EPA 2010)

Section 303 of CWA: Water quality standards

All states have to establish water quality standards for waterways which take into account the use of water by different stakeholders (e.g. water supply, wildlife, recreation, agriculture, industry). The standards must be reviewed at least every three years. States may use EPA's gold book criteria or develop their own levels based on guidance provided in the Water Quality Standards Handbook. The NPDES permits must be set to attain or maintain the established water quality standards.

Section 402 of CWA: Requirement of permits (NPDES)

The discharges must have an appropriate NPDES permit before beginning to discharge. The permits usually include limitations aiming to meet the water quality criteria in the receiving waterways (see Section 303) as well as applicable technology-based requirements. Water quality-based limits are applicable where technology-based limits are not sufficiently stringent to maintain the quality of receiving waters. The pollutants are defined in the act very broadly to include any material that may be discharged to water as a result of any mining activity. Usually the permit must include numeric end-of-pipe limit values. The discharges are classified as mine drainage, process water, storm water or unclassified. The mine drainages and process water are subject to effluent guidelines restriction set in CFR section 440 whereas storm water can be treated according to general storm water permits. The technology-based requirements for mining operations are described in a national rule (see section 440) which includes limit values for mine drainage and for mill discharges. (US-EPA 1997)

Section 404 of CWA: Discharges of dredged or fill materials

The section regulates discharges from dredged material (materials different excavation activities) and from fill material.

4.4.3 Canada

Canada is one of the leading countries in the mining industry. In Canada the value of mineral production in 2011 was ca. $50 billion. Potash, coal and iron ore were the leading minerals, measured by the value of production. In 2008 the mining sector employed over 350 000 persons and there were about 200 mines in operation (excluding clay, peat, stone and gravel quarries). (NRCAN 2012; Federal, Provincial and Territorial Social Licence Task Group 2010)

Mining activities in Canada are regulated by provincial, territorial and federal environmental laws, depending on the location and nature of the project. Some governments (e.g. Ontario) have specific environmental laws for the mining industry whereas others have general environmental legislation which is also applied to mining. (Farrell et al. 2010)

The environmental regulations relevant to mining in Canada are given in the Fisheries Act (including Metal Mining Effluent Regulations, MMER), Canadian Environmental Protection Act, Migratory Birds Convention Act, Species at Risk Act, and Canada Wildlife Act. The regulations related to water emissions from mining activities are given in MMER which came fully into force on December 6, 2002. (Dunn 2011)

MMER contains the conditions for discharging harmful substances from metal mines to fish waters. MMER applies to mines where the effluent flow rate exceeds 50 m^3/d. The substances identified in this regulation include As, Cu, CN, Pb, Ni, Zn, TSS, 226Ra. The concentration of these in substances may not exceed limits given in MMER. Furthermore, the pH of the effluents must be 6-9.5 and cause no acutely lethal effects. MMER also includes requirements for tailings impoundment areas, testing programme for effluent water, environmental effects monitoring, emergency response plan and reporting. In the effluent characterization (4 times/a) there are among other things requirement to measure NH_3 and NO_3 concentrations. (Dunn 2011)

Environment Canada gathers regularly a summary report on the performance of Canadian metal mines with respect to selected requirements described in MMER based on annual reports issued by the mining companies. In 2010, there were 105 mines subject to the regulations. (Environment Canada 2010)

In addition to actual environmental regulations given in the Metal Mining Effluent Regulations (MMER) under the Fisheries Act, Environmental Canada with the support of stakeholders has developed a supportive “Environmental Code of Practice for Metal Mines”. The Code of practice identifies and promotes the best practices addressing all phases of the mining life cycle and covers a broad range of environmental aspects (air, water, waste, biodiversity). It includes several specific recommendations related to water and tailings management in the planning and construction phase, operation phase as well as for the mine closure phase. However, the code does not have regulatory status. (Environment Canada 2009)

4.4.4 Australia

Mining is an important industrial sector in Australia, contributing around 8% to the GDP and 40% to the Australian exports. Australia is one of the top five producers for many key mineral commodities. (Minerals Council of Australia 2010.)

The Australian federal system operates in three levels: Australian Government, six state governments and two territories and the local government sector. The main federal environmental legislation in Australia is the Environment Protection and Biodiversity Conservation Act (EPBC Act), commissioned 1999. Mineral and petroleum resources are owned either by the Australian or state/territory governments. Different levels of the federal system have different roles regarding the exploitation of the resources. The Australian government determines policies on national level. Onshore mineral exploration and mining is governed by state/territory legislation which issue mineral exploration and mining licences. State and territory level is also responsible for the regulation related to environmental issues. These also collect royalties on the produced minerals. (Penney et al. 2007)

Prior to exploration the mining companies need to get works approval for earth construction as well as an exploration licence which include environmental assessment and public consultation where necessary. To begin the actual extraction activities the mine company must go through a mining approval process where more detailed environmental assessment is carried out. (Penney et al. 2007)

According to EPBC Act the Australian Government is responsible for the regulation of the environmental impact assessment having significant impact on the environment (e.g. involve world and national heritage properties). State and territory governments are responsible for assessing potential environmental impacts and the process for is generally consistent across all states and territories. The level of EIA depends on the environmental significance and complexity of the proposed project. After the EIA process the relevant authority issues an environmental approval which is generally also linked to an environmental management system of the mine. (Penney et al. 2007)

An extensive series of Best Practice booklets have been published by Environment Australia covering different aspects of environmental management in mining, e.g. mine waste and water management and cyanide management. The booklets give practical advice to the mining industry but do not carry any legislative status. (Environment Australia 2002)

4.4.5 South Africa

South Africa is a notable producer of minerals and metals. The country is estimated to have fifth-largest mining sector in the world, in terms of GDP value. The country’s most prominent mineral reserves include manganese, platinum group metals, gold, diamonds, chromite ore and vanadium, among others. It is estimated that mining sector creates altogether 1 million jobs and account for ca. 18% of the country’s GDP value. In 2005, there were some 1113 operating mines in the country. Mining is carried out in open cast, underground, alluvial, offshore, dune and artisanal mining. (Kearney 2012; UN 2010)

The environmental issues of mining have developed significantly during the past years. Development has taken place in legislation as well as in the sustainability policies and reporting within companies. One driver for the change has been the Johannesburg Plan of Implementation (JPOI) by UN’s World Summit on Sustainable Development which set three targets for the mining sector. These include the optimisation of social and economic benefits from mining, the effective long-term management of environmental, social and health impacts (including dealing with the legacy of old mining sites), the extension of participation in mining, the strengthening of governance and institutions, effective beneficiation and on-going research and technological innovation. (UN 2010)

General regulations on all minerals related issues in South Africa are given in Minerals and Petroleum Resources Development Act 28 of 2002 (MPRDA). The act and subsequent regulations require that mines prepare comprehensive Environmental Management Plan (EMP) using current best environmental management practises. Public participation is required during the preparation of the plan. The act also requires that the post closure situation is addressed and appropriate financial allowance is made for the post closure environmental and water management. Mines cannot receive mining authorisation without an approved EMP. (Mey and van Niekerk 2009)

Water related legislation in South Africa is mainly contained in the National Water Act 36 of 1998 (NWA). The policy behind the act is integrated water quality management which takes different land uses, surface and groundwater resources and different water uses into account. The law requires integrated water resource development plans taking all quantity and quality aspects into account. The act also includes the possibility to implement waste discharge charges which would apply both diffuse and point sources thus also influencing mines. However, the system is still under development. Regulation 704 issued in accordance with §26 of the NWA contains guidelines for mine water protection. This regulation contains conditions on the separation of clean and polluted water systems; ensuring mine infrastructure is outside of flooding areas; what mine materials can be used and where and pollution control. (Mey and van Niekerk 2009; Cessford 2004)

The authorisation processes of mining activities are governed by three government departments: the Department of Mineral Resources (DMR), the Department of Environmental Affairs (DEA) and the Department of Water Affairs (DWA). The mining companies apply for the mining right from DMR. After the mining right, the right-owner goes through DEA and DWA in order to get an environmental authorisation and a water use licence. The permit process may take up to two years and the company may not start operations before acquiring the three approvals. (Sikhakhane 2012)

South Africa has established legislation concerning environmental impact assessment (National Environmental Management Act, No 107 of 1998 as amended in 2003 and 2004). There is a screening and scoping process prior to the actual EIA in order to see if and how extensive an assessment is required. Reconnaissance, exploration, production and mining are defined as operations requiring EIA. Mining projects are included in the list of activities which trigger EIA. In impact assessment, national or strategically significant projects are handled at national level. However, most impact assessments are dealt with by provincial authorities. (DBSA 2007)

5. Treatment alternatives

A selection of technologies have been developed and used for nitrogen removal or capture. Usually, a separate approach is required for ammonia and nitrate removal.

For NH_4^+ removal from water, steam stripping is a commonly used treatment technology and has been identified by the US Environmental Protection Agency as the best practice treatment options for ammonia in water (USEPA, 2000). No best available technology has been identified for NH_4^+ or NO_3^- removal from mine wastewaters in the Europen Union (Zaitsev et al., 2008). The US EPA report that granular activated carbon treatment in combination with packed tower aeration is effective for the removal of CN^- from water to result in concentrations <200 ppb (USEPA, 2012).

Nirate removal from water can be particularly problematic. As a result, numerous treatment technologies have been examined for NO_3^- attenuation. The most frequently used treatment technologies for NO_3^- removal or reduction in aqueous solution are chemical denitrification using zero-valent Fe (Fe^0) or Mg (Mg^0), ion exchange, reverse osmosis, electrodialysis, catalytic denitrification and biological denitrification (Bhatnagar and Sillanpää, 2011). Each of these technologies has characteristic strengths and limitations and all available technologies involve substantial operational costs (Table 8). Ion exchange, reverse osmosis and electrodialysis have been identified as best available NO_3^- removal technologies by the USEPA, whilst the World Health Organization (WHO) recommends biological denitrification and ion exchange for treatment of NO_3^--contaminated water (Bhatnagar and Sillanpää, 2011). Cost-effective technologies for the removal of NO_3^- from water which do not generate a NO_3^--concentrated waste stream have yet to be identified.

Table 8. Comparison of existing nitrate-N removal technologies (modified from Bhatnagar and Sillanpää, 2011).

Technology	General characteristics
Ion Exchange	- Requires waste brine disposal - pH and temperature effects are not important - Post-treatment is required due to corrosivity of product water - Up to *ca.* 90% efficiency - Moderate operational cost
Reverse Osmosis	- Requires high TDS disposal - pH and temperature effects are not important - Post-treatment is required due to corrosivity of product water
Adsorption	- May require disposal of saturated/spent sorbent - pH and temperature effects are important - Post-treatment is often not required - Removal efficiency varies with sorbent used - Moderate operational cost
Chemical methods	- No waste disposal is required - pH and temperature effects are important - Post-treatment is required due to generation of by-products - Maximum reported efficiency *ca.* 60-70% - High operational cost
Electrochemical methods	- No waste disposal is required - pH effects may influence effectiveness - Temperature effects are not important - Post-treatment may be required - High removal efficiency - Moderate operational cost
Biological methods	- Requires biomass waste disposal - pH and temperature effects are important - Post-treatment is required due to microorganisms - >99% efficiency can be achieved - Moderate operational cost

5.1 Biological methods

Because biological nitrogen removal is proven effective and inexpensive it has been used widely in favour of physicochemical processes (Young-Ho, 2006). Biological nitrogen removal is achieved by microbial processes converting nitrogen compounds to nitrogen gas. Ammonium in wastewaters can be converted to NO_2^- or NO_3^- via aerobic nitrification process or anaerobic anammox process, which converts NH_4^+ straight to nitrogen gas (Figure 8). After aerobic nitrification NO_3^- is converted to nitrogen gas via denitrification pathway.

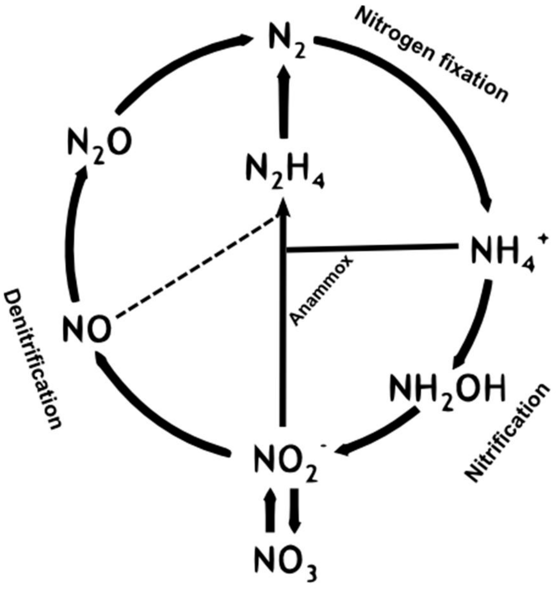

Figure 8. Microbial nitrogen cycle (modified from Kartal et al., 2011b). Dashed line represents an alternative anammox pathway that produces NO as intermediate. In this pathway first nitrite is reduced to NO and then hydrazine is formed by reducing NO and oxidizing ammonia.

Various biological nitrogen removal technologies have been developed to remove nitrogen from different kinds of wastewaters (Peng and Zhu, 2006). Nitrogen can be removed through traditional nitrification-denitrification process or anaerobic NH_4^+ oxidation (anammox) process. Novel biological nitrogen removal process is for example completely autotrophic nitrogen removal over NO_2^- (CANON). One option is also a partial nitrification process called SHARON (single reactor high NH_4^+ removal over NO_2^-) where NH_4^+ is converted to NO_2^- instead of NO_3^-. Nitrite can be then converted to nitrogen gas via anammox or denitrification pathway. In addition to biological reactors also more natural nitrogen removal systems like wetlands are used to treat wastewaters.

5.1.1 Anammox

For a long time the oxidation of NH_3 was believed to be restricted to oxic environments and traditional method for nitrogen removal has been combination of nitrification and denitrification (Figure 8). But in the early 1990s bacteria capable of anaerobic NH_4^+ oxidation (anammox bacteria) were discovered in wastewater sludge and it was found that they have unique metabolic ability to combine NH_4^+

and NO_2^- to form nitrogen gas (Mulder et al., 1995). The biological nature of the new process was verified by van de Graaf (1995). Anammox bacteria use NH_4^+ as their energy source and NO_2^- as electron acceptor (Figure 8, Equation 10). It was discovered that anaerobic NH_4^+ oxidation is an autotrophic process that releases more energy than aerobic nitrification so it is more favourable for microbes than aerobic nitrification (Jetten et al., 1999). Anammox bacteria use bicarbonate as the carbon source (Paredes et al., 2007). Hydroxylamine and hydrazine were identified as important intermediates (Jetten et al., 1999). Anammox pathway has opened new and more cost efficient possibilities for nitrogen removal from wastewaters (Paredes et al., 2007).

$$NH_4^+ + NO_2^- \rightleftarrows N_2 + 2\,H_2O \tag{10}$$

Anammox bacteria derive a fair amount of energy from the conversion of NH_4^+ and NO_2^- to nitrogen gas. However the metabolic activity of anammox seems low. Ammonium is oxidized with activities ranging between 15 and 80 nmol/mg of protein which is less than the activity of aerobic NH_4^+ oxidizing bacteria (Kartal et al., 2011a). Also the growth rates and doubling times of anammox bacteria are low, about 11 days (Strous et al., 1998) and this may be due to low metabolic activity. Anammox bacteria use NH_4^+ with high affinity (K_s <5 µM) whereas aerobic nitrifiers are less efficient (K_s 5–2600 µM). Nitrite is needed for the anammox process but concentrations above 20 mM inhibit the reaction. Nitrite is produced to the ecosystem via nitrification, denitrification or dissimilatory NO_2^- reduction (DNRA). In ecosystems with limited organic electron donors, anammox bacteria may be able to produce their own NO_2^- and NH_3.

Anammox bacteria produce hydroxylamine (NH_2OH) as an intermediate when converting NH_4^+ to nitrogen gas and hydroxylamine is converted to hydrazine (N_2H_4) (Kartal et al., 2011a). This is a unique process that has not been seen in any other bacteria. Genome sequence analysis has also indicated an alternative pathway that produces NO as intermediate instead of hydroxylamine (Strous et al., 2006b). In this pathway first NO_2^- is reduced to NO and then hydrazine is formed by reducing NO and oxidizing NH_3. Finally hydrazine is oxidized and converted to nitrogen gas.

Oxygen inhibits anammox reaction when oxygen concentration is 2 µM or more (Jetten et al., 2001). The temperature range for anammox bacteria is 20–43°C with optimum temperature at 40°C (Jetten et al., 1999). In applications growth at 15°C and 18°C have been achieved (Dosta et al., 2008; van de Vossenberg et al. 2008). One research also found anammox activity in arctic ice (Rysgaard and Glud, 2004). The anammox process functions well at pH 6.7–8.3 with optimum pH at pH 8. Anammox reaction has compounds that inhibit the reaction (Kartal et al., 2011b). Nitrite is the most important inhibitor and NO_2^- concentrations should be taken under consideration when starting anammox reactor. Nitrite concentrations above 20 mM have been verified to inhibit anammox reaction. A concentration in which NO_2^- inhibits the process varied depending on the reactor size and properties. In smaller reactors already values as low as 5 mg per litre were toxic. Anammox bacteria can grow at freshwater and marine conditions and they can adapt on higher salt concentrations if salt stress is gradually increased. In fully anaerobic conditions extreme low levels of salt (0.3 mM) inhibits the anammox reaction irreversibly. Also organic compounds can inhibit the anammox process. Methanol for example is toxic at levels up to as low as 0.5 mM.

At the present anammox process is limited to few types of wastewaters with high concentration of NH_4^+ (Zhang et al., 2008). The use of anammox technology for the treatment of low NH_4^+ wastewater has not been efficient because of biomass washout. It has been reported that nitritation/anammox technology is not feasible for treating wastewater with NH4-N concentration <100 mg/L (Mulder, 2003). Some methods have been suggested to concentrating NH_4^+ for biological nitrogen removal. Ek et al. (2006) investigated various methods for concentrating of nutrients from urine and reject from digestion of sludge. In their work they compare various methods including ion exchange, reverse osmosis, evaporation, precipitation and distillation. Häyrynen et al. (2009) used nanofiltration and reverse osmosis to concentrate NH_4^+ and NO_3^- from mine water. In the study reverse osmosis proved to be efficient method for concentrating NH_4^+ for downstream treatment in biological reactors.

Anammox bacteria have been mainly investigated in wastewater treatment plants, enrichment cultures and aquatic environments (Kuenen, 2008). Dalsgaard et al. (2005) studied anammox in sediments water columns and showed that anammox was responsible of 67% of total N_2 formation in oxygen limiting conditions. Also molecular studies have demonstrated the significance of anammox activity in the Black Sea. It was estimated that anammox contributes at least 30% of the total nitrogen turn over. This proves that anammox process is significant process in nature for NH_4^+ oxidation. Anammox bacteria abundance has also been reported for lacustrine water columns and sediments (Dale et al., 2009), deep ocean surface sediments (Hong et al., 2011) and Peruvian oxygen minimum zone (Hamersley et al., 2007). Recently it was found that anammox bacteria are also widespread in terrestrial environments (Humbert et al., 2010; Hu et al., 2011). Anammox bacteria have been found in paddy soils (Zhu et al., 2011) and from contaminated aquifers (Smits et al., 2009) and wetlands (Humbert et al., 2012).

The isolation of anammox bacteria pure cultures has been difficult and no pure cultures has been isolated with traditional isolation methods (Jetten et al., 2001). Strous et al. (1998) used density gradient centrifugation technique to isolate anammox bacteria from sequencing batch reactor treating wastewater and achieved cultures that were 99.6% pure. The DNA from this isolate was purified and based on 16S rDNA sequences anammox bacteria were found to be planctomycete-like organisms. Later isolate was named *Candidatus Brocadia anammoxidans*. Later another species *Kuenenia stuttgartiensis* was found in wastewater treatment reactors (Kuenen, 2008). Now more than eight species of anammox bacteria have been identified based on 16S ribosomal RNA gene sequences.

Anammox bacteria propagate by budding instead of binary fission and they have unusual cell envelope structure that contains unique membrane lipids called ladderanes (Kartal et al., 2011b). In anammox bacteria the anammox reaction takes place in a unique cytoplasmic membrane-bound organelle called anammoxosome (Jetten et al., 2001). The anammoxisome is completely surrounded by compartment containing nucleoid and ribosomes. The exact function of anammoxosome is under investigation but one function could be the generation of membrane potential internally across the anammoxosome membrane. Anammox bacteria are very slow-growing microbes with doubling times of 10–20 days and low biomass yield. They are not restricted to energy conservation via anammox pathway but can use other electron acceptors including iron and manganese oxides and formate as electron donor.

Anaerobic NH_4^+ removal with anammox process always consists of partial nitritation followed by anammox (Kartal et al., 2011b). Both processes can take place in same reactor or in separate reactors placed in series.

In one reactor systems oxygen is both substrate for aerobic NH_3 oxidizing bacteria and toxic for anammox bacteria. This process is also known as CANON (completely autotrophic nitrogen removal over NO_2^-) (Sliecers et al., 2003). There should be truly anoxic conditions for anammox bacteria to function. To obtain both oxic and anoxic conditions one option is use continuous operation system in which oxygen levels are governed in gradients in biofilm systems. Another option is time-depended aeration in which oxygen levels change in time. Third option is physical transportation of the biomass between oxic and anoxic zones. There are many reactor types that can be used for one-reactor nitritation-anammox systems. Options are granular sludge systems (for example sequencing batch reactor) and systems with carrier materials. The requirements for an efficient reactor are high sludge retention time and substantial mixing.

Another option is two-reactor system where nitritation and anammox process take place in an aerated and nonaerated reactor (Peng and Zhu, 2006) (Figure 9). First step of this process that takes place in the first aerobic reactor is called the SHARON (Single reactor high rate NH_4^+ removal over NO_2^-) process where NH_4^+ is converted to NO_2^-. In this oxic reactor the growth of NO_2^- oxidizing bacteria must be prevented because otherwise NO_3^- is produced rather than NO_2^- and NO_3^- is costly to remove. Nitrite is then converted to nitrogen gas in the second anerobic anammox reactor. In oxic reactor about 55 % of the NH_4^+ needs to be converted to NO_2^- to provide sufficient amount of NO_2^- to the anammox process (Manipura et al., 2005).

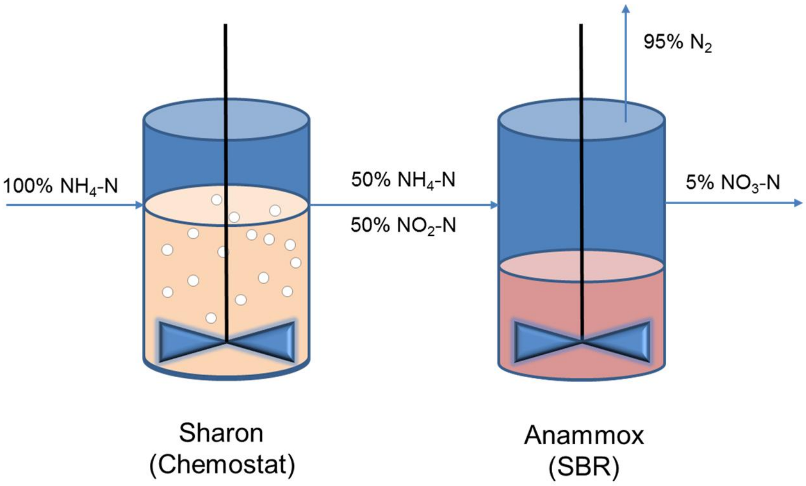

Figure 9. Sharon-Anammox process (ASM News, 2001).

Usually metal refinery wastewater contains nitrogen as a result of the use of nitrogenous compounds during production processes (Manipura et al., 2005). Usually low pH and high NH_4^+ and NO_3^- concentration are typical characteristics for mineral and metal processing wastewaters. In Finland tough pH in Outokumpu chrome mine in Kemi was 7.1–8.9 in year 2011 so pH is not a problem for biological nitrogen removal because the anammox process functions well at pH 6.7–8.3 (Kartal et al., 2011b).

Anammox process has been widely used to treat wastewaters with high NH_4^+ concentrations (Pathak et al., 2007a). In Finnish mines the NH_4^+ and NO_2^- levels are quite low. In Outokumpu chome mine NH_4^+ concentration was 265–735 µg/L and NO_2^- concentration 234–6417 µg/L in the year 2011. Very few studies have been made of application of the anammox process in low NH_4^+ wastewaters but these conditions are common in natural environments. Pathak et al. (2007a) treated low NH_4^+ wastewater (2.3 mg/L) with anammox process combined with denitrification and noticed that nitrogen removal efficiency was 60%. The main problem is how to stimulate the growth of anammox bacteria under low NH_4^+ concentrations and low temperature. One option is the development of thick biofilms or using alternative materials suitable for their growth (Hao et al., 2002). The immobilized microbial consortium (IMC) is one method. Pathak et al. (2007b) used laboratory scale bioreactors containing IMC in treating low NH_4^+ wastewater (2.5 mg/L) in 20^oC temperature. The removal rate of nitrogen in these reactors was 80–92% and anammox bacteria were detected in the bioreactor.

Temperature is one of the key factors affecting nitrogen removal process in bioreactors (Karkman et al., 2011). In Finland outside temperatures are quite low especially in wintertime and rarely optimal temperature range ($20–43^oC$) for anammox bacteria is achieved. However, anammox activity has been also reported in lower temperatures, even at -1°C (Rysgaard and Glud, 2004).

Advantages of anammox process over nitrification and denitrification is that anammox does not need any additional carbon source (Manipura et al., 2005). However microbes that are responsible of the anammox reaction are extremely slow growing and this affects the nitrogen removal rate. Metal toxicity for anammox process still remains a question and suitability of anammox for mine and metal industry or other inorganic wastewater treatment needs to be determined (Manipura et al., 2005).

5.1.2 Wetlands

Physico-chemical processes within wetlands are highly variable and are affected by numerous environmental and meteorological factors. In particular, biogeochemical N cycling within wetland systems is complex; involving conversions between different N chemical species as well as transfers between various storage compartments. Removal of N from influent water within wetlands is governed primarily by microbial nitrification and denitrification; plant uptake and NH_3 volatilisation are considerably less significant mechanisms of N attenuation (Green et al., 1997; Bastviken et al., 2003; Aguirre et al., 2005). Nitrification is the process whereby NH_4-N is converted to NO_3-N, and denitrification involves NO_3^- coversion to nitrogen gas (N_2(g)). Potential barriers to N removal in wetland systems include lack of available oxygen for nitrification and/or carbon for denitrification.

Ammonia can be found in both the non-ionised and ionised form in wetlands, depending on the pH and temperature. Ionised ammonia (NH_4^+) is the most common species and the one preferred by most wetland plants and bacteria as the non-ionised form of ammoniacal N (NH_3) is toxic to many species even at low concentrations.

In general, wetlands with adequate oxygen supply exhibit effective nitrification, or biological coversion of NH_3-N to NO_3-N. The *Nitrosomonas* spp. and *Nitrobacterer* spp. bacteria responsible for nitrification reactions are strict aerobes, thus the nitrification process requires free dissolved oxygen. For example, nearly complete (97-99%) removal of NH_4-N was observed in a wetland where influent concentrations were 20–40 mg/L, provided that available oxygen was not limiting (Bezbaruah and Zhang, 2003); however, NH_4^+-N concentration increased where oxygen was limited, possibly due to mineralization of organic N. Bezbaruah and Zhang (2003) observed NH_4-N oxidation or use by aerobic bacteria in the early section of the wetland as indicated by decreasing NH_4-N concentration and a corresponding increase in NO_3-N concentration.

Wetlands operated under saturated conditions generally exhibit effective denitrification, which occurs when facultative anaerobic bacteria use NO_3-N as their primary oxygen source under oxygen-depleted conditions (e.g. dissolved oxygen <0.2–0.5 mg/L), thereby reducing NO_3-N to N_2 (g) Denitrifying bacteria are heterotrophic and may require an external organic C source for growth if organic C in influent wastewater is low. Denitrification rates decrease as water temperature declines and can be inhibited in the presence of excess dissolved oxygen.

Nitrification and denitrification capacities of wetlands vary according to the microbial communities and the substrate supporting them, though nitrification and denitrification processes are generally more active in shallow wetlands (Aguirre et al., 2005). Sediments are regarded as the main site of microbial denitrification in wetlands due to the anaerobic environment and the presence of organic C (Bastviken et al., 2003) but microorganisms also attach to surfaces of wetland vegetation. Nitrogen removal can be enhanced by submerged plants as they offer surfaces for both nitrifying and denitrifying bacteria which form biofilms on the plant shoots (Bastviken et al., 2003). Bastviken et al. (2003), observed more than three times higher nitrification potential per biofilm area for twigs within wetlands than sediments, though denitrification potential per biofilm area was greater in the sediments. Microbial colonisation density of plant roots and biofilm structure vary as a function of vegetation type and the morphology of plant root sections (Munch et al., 2007).

Carbon cycling within wetlands will influence N cycling to some extent as organic carbon provides an energy source for denitrification and some N may be associated with dissolved organic carbon (DOC). In particular, organic N entering wetlands is typically associated with particulate material. Plant detritus and other naturally-occurring organic materials within a wetland may also be a source of organic N. Decomposition and N mineralization within a wetland will convert much of the influent organic N to NH_3-N. Within a wetland, DOC undergoes biological degradation and results in carbon dioxide emission due to respiration and biomass growth. Wetland attenuation of DOC, though having considerable ecological impact, has not been studied in detail. Dissolved organic carbon can sorb to wetland substrate or may flocculate and precipitate from solution. The DOC can also form complexes with metals and hydrophobic organic molecules.

Readily decomposed vegetative organic matter provides a major source of energy and C for microbes. Investigations by Baptista et al. (2003) showed that microorganisms fulfil a critical role in the cycling and transformation of both nutrients and energy in a wetland. This indicates that wetland performance optimisation can occur through a fundamental understanding of the microbial populations that perform the removal of organic matter. Microbial populations in wetlands with plants have been shown to differ from those in wetlands without plants, though both wetlands with and without plants contain sulfate reducing bacteria and methanogens (Baptista et al., 2003). In wetlands, microbial density is enhanced in the presence of plants and is affected by plant morphology (Gagnon et al., 2007).

Research indicates that direct nutrient uptake by macrophytes accounts for only a small proportion of nutrient removal from influent water by a wetland system. Direct nutrient removal via plant uptake is not considered permanent unless the plants are regularly harvested (Healy et al., 2007; Tanner, 2001); however, wetland plants can exert substantial indirect influences on nutrient biogeochemistry. Release of oxygen from plant roots into the rhizosphere (zone around the roots) can alter biogeochemical cycles via changes to the oxidative status of the water

(Batty, 2003). Plant root exudates may act as a carbon source for other chemical processes such as denitrification, and can potentially enhance the removal of nutrients. Submerged macrophytes are also known to release compounds which may affect the growth of other vegetation (Sundaravadivel and Vigneswaran, 2001).

The presence of wetland vegetation may also affect physical processes in wetlands via the reduction of wind velocity near the water surface as well as slowing the velocity of flowing water within a wetland. Reduction of vertical mixing and water velocity enhances sedimentation of suspended solids, and can lessen the risk of erosion whilst stabilising the substrate surface (Brix, 1997; Batty, 2003; Browning and Greenway, 2003). In temperate climates wetland vegetation can also provide insulation during winter.

Natural wetlands are naturally occurring land areas with saturated water. Main wetland types are different kinds of swamps, marshes, bogs and fens. The function of most natural wetlands is not treatment of human made wastewaters. Natural wetlands' capacity for improvement of water quality has led to the utilisation of artificially constructed wetlands for water treatment. Constructed wetland system seeks to emulate the properties of natural wetlands in an environment, which can be controlled and manipulated. Constructed wetlands are designed specifically to suit the local environmental conditions as well as the quantity and characteristics of the water to be treated. They range from small, single-house use to treatment of effluent from whole communities, to filters for entire catchments and are designed to simulate the natural processes of wetlands. Although the quality and quantity of water to be treated can vary substantially, all treatment wetlands generally have in common growing plants and surface or subsurface water (Knight, 1997).

Constructed wetlands are most commonly used to treat the following types of water:

- Municipal wastewater, for example polishing of treated sewage effluent (Berzero et al., 2003; Garcia et al., 2005);
- Landfill leachate including removal of metals, organic compounds and ammonia nitrogen (Barr and Robinson, 1999; Aluko and Sridhar, 2005; Nivala et al., 2007);
- Industrial wastewater, such as removal of metals and nutrients from metallurgic wastewater (Maine et al., 2006) and removal of nutrients and organics from tannery wastewater (Kucuk et al., 2003; Calheiros et al., 2007);
- Mine drainage, for example neutralisation of acidic drainage and/or attenuation of metals (Mitsch and Wise, 1998; Drury, 1999; Batty and Younger, 2004);
- Agricultural runoff (Headley et al., 2001; Jordan et al., 2003; Tanner et al., 2005; Borin and Tocchetto, 2007);
- Agricultural wastewater such as swine (Chen et al., 2008), dairy (Nguyen, 2000; Dunne et al., 2005; Healy et al., 2007), livestock (Knight et al., 2000), and winery wastewaters (Grismar et al., 2003);

- Stormwater (Koob et al., 1999; Walker and Hurl, 2002; Birch et al., 2004; Terzakis et al., 2008); and,
- Polluted surface water in rivers and lakes (Cheng et al., 2002; Wu et al., 2007).

The simplest types of wetlands are free water surface flow (FWSF) wetlands which consist of a densely vegetated substrate bed with a shallow water column sitting above the surface of the substrate (Figure 10). The water surface is generally exposed to the atmosphere and meteorological conditions. Plants grow in the substrate bed and emerge above the surface of the water column (Bastian and Hammer, 1993; Brix, 1994; Sundaravadivel and Vigneswaran, 2001).

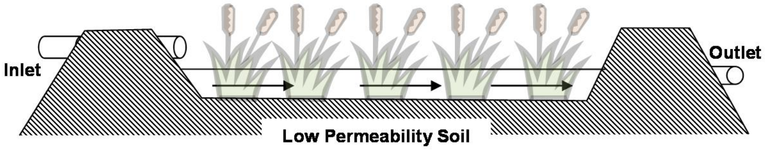

Figure 10. Conceptual diagram of a free-water surface flow wetland.

Free-water surface flow wetland systems have been established on various substrates including gravel, mine spoil, clay, and peat, and are generally designed to recycle at least a portion of the water treated. The FWSF wetlands are prevalent in the United States, particularly in areas where large volumes of wastewater are to be treated, and are frequently used as a polishing step for nutrient removal. Subsurface flow wetland systems are used more frequently than free-water surface flow systems in both Europe and Australia (Wood, 1995).

In subsurface flow wetland systems the water level is sustained below the surface of the substrate (Figure 11 and Figure 12). Subsurface flow wetland substrate media can vary, although gravel is commonly used due to its high proportion of void space. Subsurface flow systems can be maintained with horizontal or vertical flow (Brix, 1994). In subsurface horizontal flow (HF) wetlands, the substrate is completely saturated with a continuous flow of influent water (Figure 12).

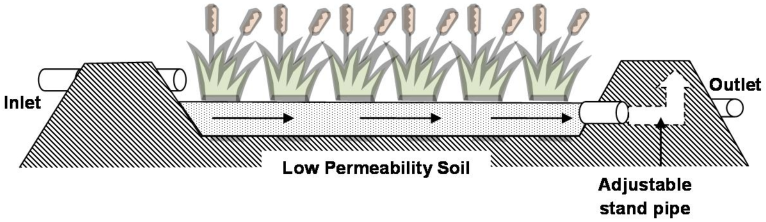

Figure 11. Conceptual diagram of a subsurface horizontal water flow wetland.

Interest in subsurface HF wetland systems was widespread from the early stages of development because these constructed wetlands offered low construction and operational costs (Cooper, 1999). For example, the use of subsurface HF wetland systems has become increasingly popular for the treatment of municipal wastewater in small communities in Spain, especially in areas where sanitation programs were previously lacking (Garcia et al., 2005). Pre-treatment of wastewater is an important consideration as whilst tertiary treatment subsurface HF wetland systems can generate well-nitrified effluents, secondary treatment subsurface HF wetland systems cannot. Limited nitrification in secondary treatment subsurface HF wetland systems led to interest in vertical flow systems (Cooper, 1999).

Subsurface vertical flow (VF), or infiltration, wetland systems (Figure 12) were initially developed to overcome the inefficiency of horizontal systems for nutrient removal (Brix, 1994; Sundaravadivel and Vigneswaran, 2001). Low nutrient removal efficiency in continuously-loaded VF wetland systems resulted in the development of VF systems with intermittent water loading to enhance oxygen supply (Felde and Kunst, 1997; Laber et al., 1997). Following this development, VF wetlands now generally operate with either intermittent flow of influent water or include pipes positioned within the substrate to promote aeration.

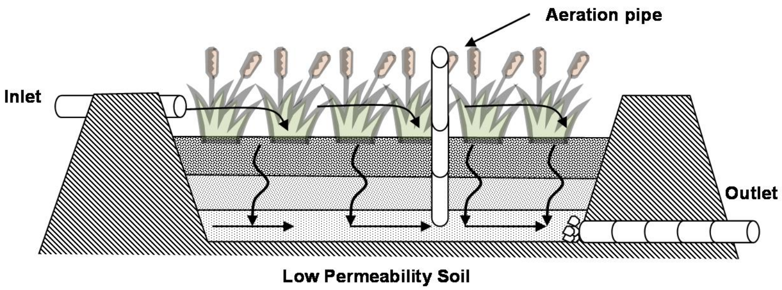

Figure 12. Conceptual diagram of a subsurface vertical water flow wetland.

Vertical flow systems can be designed as a single stage or with multiple stages, where one VF stage is unsaturated and loaded intermittently and another stage is saturated, and has an external carbon source added to increase denitrification (Laber et al., 1997). Single stage systems may recirculate effluent to enhance denitrification.

Hybrid wetland systems employ a combination of surface and subsurface systems incorporating either or both vertical and horizontal flow beds. A benefit of hybrid systems is that VF and HF can be combined to complement the advantages and disadvantages of each. Vertical flow systems are considered effective for nitrification, as they have a high oxygen transfer rate which leads to good removal of biological oxygen demand (BOD) and chemical oxygen demand (COD). They are also able to remove some bacteria. Vertical flow wetland systems are not effective for the removal of suspended solids and can become clogged, whereas subsurface HF wetland systems exhibit effective removal of suspended solids and bacteria, as well as denitrification (Cooper, 1999).

Table 9 provides a general summary of the physical, chemical and biological processes which occur during the removal of various pollutants from water within wetland systems.

Table 9. Constructed wetland pollutant removal mechanisms.

Pollutant	Removal mechanism		
	Physical	Chemical	Biological
Carbonaceous organic matter (BOD)	Sedimentation		Microbial degradation (aerobic and anaerobic)
Nitrogen	Adsorption	Nitrification Denitrification Ammonia volatilisation	Plant uptake Microbial uptake
Phosphorus	Adsorption Filtration Sedimentation	Precipitation	Plant uptake Microbial uptake
Pathogens	Sedimentation Filtration	UV radiation	Natural die-off Excretion of antibiotics from macrophytes roots Predation
Metals	Sedimentation Adsorption	Precipitation	Plant uptake Microbial uptake
Organic molecules	Adsorption Sedimentation	Volatilisation Photolysis Hydrolysis	Plant uptake Microbial degradation
Suspended Solids	Sedimentation Filtration		

Source: Kadlec and Knight, 1996; Wood and McAtamney, 1996; Reddy and Dangelo, 1997; DLWC, 1998; Sundaravadivel and Vigneswaran, 2001; Rodgers and Castle, 2008.

Passive treatment systems and especially constructed wetlands have been used extensively in the last decades to treat mine discharges of varying pH and chemical composition (Batty and Younger, 2004). Wetlands are alternative to the costly chemical treatments. Vegetation is an important component of the wetlands and they are able to grow in elevated metal concentrations, high acidity and low nutrient content.

Temperature in cold climate areas can be a potential barrier for nitrification and denitrification (Werker et al., 2002). Nitrification rates appear to become inhibited for water temperatures around 10°C and rates drop rapidly to zero below approximately 6°C. Denitrification has been observed at temperatures as low as 5°C. Subsurface flow constructed wetlands have an advantage in colder climates because treatment occurs below the ground surface, and bacterial communities are thereby insulated somewhat from the frigid air. Another factor effecting nitrification is the oxygen levels in surface waters in wetlands. Aeration has improved nitrogen removal efficiency in constructed wetlands (Bezbaruah and Zhang, 2003).

Demin and Dudeney (2003) studied the nitrification efficiency in wetlands treating mine water in England. Ammonia concentrations in the mine effluents varied from 2.3–5 mg/L and 75% of the ammonia was removed in summer time and 50% in the winter time. The conditions in the mine were favourable to nitrification and the mine waters were fully aerated.

5.1.3 Autotrophic denitrification with elemental sulphur

Elemental sulphur is an attractive source of energy for autotrophic biological nitrification due to its low cost (Soares, 2002). In addition elemental sulphur is non-toxic, water soluble under normal conditions and readily available as mined mineral or as a by-product of fuel processing and SO_2 control systems. In the process elemental sulphur is converted into sulphate. The use of sulphur in wastewater treatment was first discovered in 1970s (Batchelor, 1978). Later sulphate was used with limestone and this process is called the SLAD method (sulphur-limestone autotrophic denitrification) (Le Cloirec & Martin, 1988). In this process limestone serves as a source of inorganic carbon for bacterial synthesis and acts as pH buffering agent. The sulphur-limestone process was further developed in a field system. The system consisted of four unit operations in series: vacuum-deaeration, NO_3^- removal in a sulphur-limestone filter, aeration and soil infiltration. Optimum sulphur: limestone ratio where nitrogen removal is most efficient is 3:1. The SLAD process may be a replacement for heterotrophic denitrification in pond systems such as constructed wetlands or stabilization ponds because no organic carbon source is needed in the SLAD process and also microbes capable of autotrophic denitrifiacation exist widely in the natural environments (Zhang and Lampe, 1999). This means that SLAD process has lower costs and less sludge production which minimizes handling of the sludge.

Some microbes such as *Thiobacillus denitrificans* and *Thiomicrospira denitrificans* use autotrophic denitrification with elemental sulphur as the energy source (Zhang and Lampe, 1999) (see Equation 11). In this process NO_3^- or NO_2^- is reduced to nitrogen gas. Energy for this process is derived from inorganic oxidation-reduction reactions with various reduced sulphur compounds used as the electron donor. Inorganic carbon compounds (CO_2, HCO_3^-) are used as carbon source. Optimum growth temperature for *Thiobacillus denitrificans* is +28–32°C. Besides autotrophic denitrifiers also nondenitrifying bacteria have been found to be part of the SLAD process.

$$55\,S + 20\,CO_2 + 50\,NO_3^- + 38\,H_2O + 4NH_4^+ \rightarrow 25N_2 + 4C_5H_7O_2N + 55SO_4^{2-} + 64H^+ \tag{11}$$

Zhang and Lampe (1999) studied SLAD process in laboratory scale batch reactors treating NO_3^- contaminated surface water or wastewater. Process was operated under anaerobic or aerobic conditions. Autotrophic denitrification occurred under aerobic and anaerobic conditions and also at both high and low NO_3^- conditions. Nitrate removal efficiency, sulphate production and biomass accumulation were usually higher under aerobic conditions. In aerobic conditions NO_3^- removal was

84–94% depending on the sample source (soil, sediment, sludge) and in anaerobic conditions NO_3^- removal efficiency was 72–90%.

5.2 Electrochemical

Electrochemical methods have been developed for nitrogen removal mainly to overcome problems encountered with biological nitrification-denitrification such as dependence on pH and organic carbon, sensitivity to toxins, temperature and change of parameters as well as start-up delay (Lacasa et al., 2012).

In electro-oxidation, organic pollutants or inorganic ions are oxidised at the anode. In direct oxidation (or anodic oxidation) hydroxyl radicals are formed from water at the anode surface, reacting directly with substances that are oxidised. In indirect oxidation, most commonly chloride ions in the water from hypochlorite intermediates that then oxidize pollutants through breakpoint chlorination reactions. Different electrode materials and settings have been extensively studied also for nitrogen removal. Electrochemical nitrogen removal is based on reduction of NO_3^- and NO_2^- to ammonia on the cathode followed by oxidation of ammonia to gaseous nitrogen at the anode.

Electrochemical methods include also other methods. In electro-flocculation/electro-coagulation, phosphorus and nitrogen are bound into iron or aluminium sludge, produced from sacrificial iron or aluminium electrodes (Robinson, 1999; Mahvi et al., 2011). In electro-chemical metal recovery metal ions are captured into solid metal electrodes (Chen and Yung-Tse, 2007). In electroflotation, water splitting produces hydrogen and oxygen for flotation purposes, the size of the bubbles is very small and thus the method has advantages over regular bubbling (Chen and Yung-Tse, 2007). Electrodialysis is a membrane technology allowing ions to be concentrated or removed to different streams through cation and anion selective membranes using electrical force as a driving agent (Ippersiel et al., 2012). In microbial fuel cells biological activity is directly linked to cathodes and anodes separated by a selective membrane and connected by an electrical circuit (Lefebvre et al., 2011; Cusick and Logan, 2012; Fischer et al., 2011). Characteristics of different electrochemical treatment methods are presented in Table 10.

Table 10. Electrochemical nitrogen removal methods.

Technology	General characteristics	Pros and cons	Suitability
Electro-oxidation	Non-specific oxidation/reduction for removal of organics and nitrogen as N_2.	+ Easy operation + No COD or T requirements - High N and Cl^- requirements - pH and conductivity requirements - Mg^{2+}/Ca^{2+} and SO_4^{2-} problems - Chloride by-products - High energy consumption	**Potential.** Can be inefficient and energy-intensive for raw mine waste water. Good for high N-concentration brine clean from other ions.
Electro-coagulation	Coagulation of ions with cations from a dissolving electrode	+ Low sludge production - Analogous to chemical precipitation - Low ammonia removal	Poor
Electrochemically assisted stripping	Electrochemical pH control and ammonia concentration at a surface electrode to capture ammonia	+ Lower energy demand + Recovered product - Nitrate removal - Experimental stage	**Good.** Needs more research and testing.
Electrodialysis	Electrochemical ion exchange into a brine	+ Removes all ions - High electricity demand - Precipitation problems	Poor
Elonita	Commercial electro-oxidation for mine waste waters	+ Ready technology - High N and Cl^- requirements - Mg^{2+}/Ca^{2+} and SO_4^{2-} problems - Chloride by-products - High energy consumption	**Poor/Potential.** Requires pre-treatment or combined treatment.
AmmEL	Zeolite ion-exchange – brine treated with electro-oxidation	+ Ready technology + Designed for cold mine waters - Little information available - High N concentrations	Potential
DesEL	Capacitive deionization charge barrier ion exchange – brine treated with electro-oxidation	+ Good removal potential - High ionic content is a problem - Reject treatment	Poor/Potential

Electro-oxidation as well as biological technologies aim at nitrogen removal as gaseous nitrogen (N_2) and flocculation technologies aim at removal as solid precipitates. Recovery of nitrogen as NO_3^- or NH_3 has been studied especially in electrodialysis (Ippersiel et al., 2012), membrane contactor (Ahn et al., 2011; Ashrafizadeh and Khorasani, 2010), and stripping (Gross et al., 2012) processes.

5.2.1 Forms and reactions of nitrogen

Nitrogen has a wide variety of oxidation states with stable compounds (-3 to +5) and nitrogen chemistry is generally complex. Figure 13 presents the classical nitrogen cycle and Figure 14 shows the oxidation state diagram. Most common forms of nitrogen in wastewater are NH_4^+ and NO_3^-. Ammonium (NH_4^+) originates typically from organic N and evaporates as ammonia (NH_3) in alkaline conditions. Nitrates and nitrites are typically products of nitrification and are pollutants in air (referred usually as NO_x-emissions) and water (Rosca et al., 2009).

Nitrogen electrochemistry is complicated and involves many reactions and mid-products not mentioned here. For more extensive review on the complicated nitrogen chemistry and pathways, please consult references Rosca et al. (2009), Mook et al. (2012), Gendel and Lahav (2012) or Lacasa et al. (2011a). A simplified representation of the most relevant pathways is shown in Figure 15.

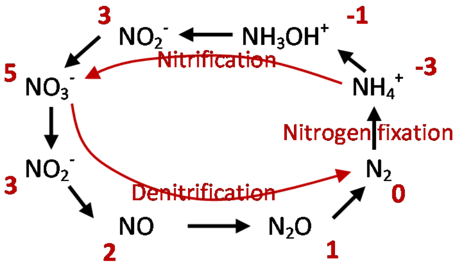

Figure 13. Simplified scheme of the classical nitrogen cycle. Red numbers indicate oxidation states of nitrogen. (Modified from Rosca et al., 2009.)

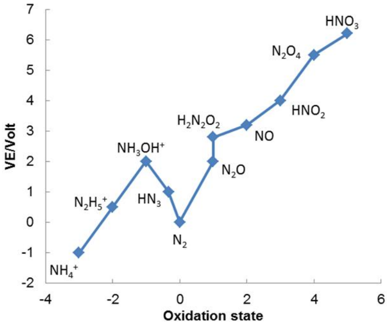

Figure 14. Oxidation state diagram of nitrogen compounds in acidic solution. VE is the volt equivalent – the standard potential for the conversion to N_2 times the nitrogen oxidation state. (Modified from Rosca et al., 2009.)

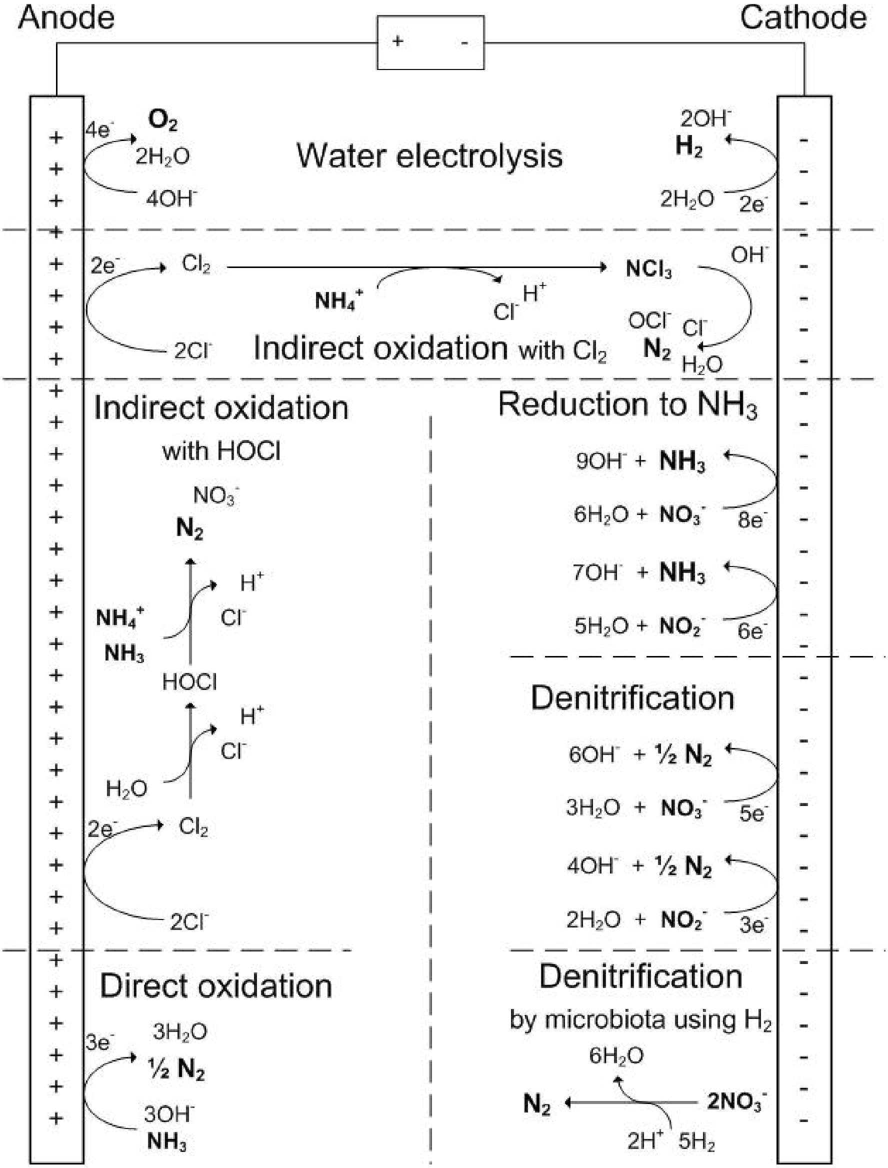

Figure 15. Simplified presentation of variety of anodic and cathodic reactions related to nitrogen electrochemistry (Rosca et al. 2009, Mook et al. 2012, Gendel and Lahav 2012, Lacasa et al. 2011a, Vanlangendonck et al. 2005, Kim et al. 2005).

In electro-chemical nitrogen removal, electrical potential combined with chemicals or microbiota is used to evoke chemical reactions that convert nitrogen compounds into a wanted species for removal or capture. Most commonly the technologies aim at NO_3^- and NO_2^- reduction to NH_4^+ or N_2 at the cathode followed by the oxidation of $NH_4^+$to N_2 at the anode.

5.2.2 Electro-oxidation of NH_3/NH_4^+

Electro-oxidation or electrochemical oxidation refers to indirect and direct oxidation reactions occurring in an electrochemical reactor at the anode that acts as the final electron acceptor. The research and applications of electro-oxidation are focused on oxidation of organic matter and NH_3/NH_4^+ nitrogen species from wastewater (Anglada et al., 2009).

Ammonia can oxidize into various end products through complicated reaction pathways with varying kinetics (see Equation 12). The overall reaction from ammonia to nitrogen is presented in Equation 13). Nitrogen chemistry is complex, and in most cases only the overall reaction is known (Kim et al., 2005).

$$NH_3 \rightarrow NH_2OH_{ad} \rightarrow NOH_{ad} \rightarrow NO \rightarrow NO_2^- \rightarrow NO_3^- \qquad (12)$$

$$N_2 \hookleftarrow\hookrightarrow N_2O \rightarrow N_2$$

$$NH_3 + 3OH^- \rightarrow \tfrac{1}{2}N_2 + 3H_2O + 3e^- \qquad (13)$$

In direct oxidation of NH_4^+, NH_4^+ ions diffuse to anode surface and are partially or fully oxidized by hydroxyl radicals formed on the electrode surface from interaction with water. Direct oxidation is highly affected by solution pH, electrode material, conductivity, applied potential and concentrations of ammonia, chloride and other ions and organic material (Mook et al., 2012; Kim et al., 2005; Anglada et al., 2009). In basic conditions ammonia (NH_3) is adsorbed to the anode surface and converted mainly to N_2 gas, in neutral or acidic conditions NH_4^+ ion is oxidized by hydroxyl radicals originating from oxygen evolution, which is much less effective (Gendel and Lahav, 2012; Kim et al., 2005). Different electrode materials have different potentials for oxygen evolution and radical formation and can be selective towards certain reactions. Oxygen evolution inhibits direct oxidation and is generally an unwanted reaction and thus electrode materials with low affinity for oxygen evolution are preferred and investigated – electrode materials studied include platinum, iridium oxide, graphite, titanium oxide and boron doped diamond covered materials (Anglada et al., 2009). Conductivity and applied potential are connected and reaction rates are usually linked with currents per area where as reaction types can be limited by applied potential and good conductivity usually ensures higher efficiency. Ammonia concentration is linked with surface area and active sites on the electrode – high ammonia concentration results in higher oxidation rate of ammonia whereas low concentration promotes more oxygen evolution and other reactions (Kim et al., 2005). Organic material is oxidized at the anode simultaneously and it decreases oxidation efficiency for NH_4^+. Chlorides and other indirect oxidation promoting agents (such as iron) can dominate anode activity and direct oxidation into indirect oxidation reactions (Kim et al., 2005).

In indirect oxidation, chloride ions form active chlorine Cl_2 at the anode which then reacts as an oxidizing agent. The mechanism of indirect oxidation has been widely cited as being analogous to “breakpoint chlorination” mechanism in which the addition of active chlorine species (HOCl or OCl^-) results in stepwise formation of monochloramine and dichloramine which finally “breaks” into nitrogen gas and NO_3^- through trichloroamine when a sufficient Cl_2 to N mole ratio of 1.5 is achieved. According to this mechanism, the total soluble nitrogen concentration remains constant and no nitrogen gas is produced before the breakpoint concentration. In literature, the total stoichiometric reactions involved are the formation of chlorine (Equation 14), hypochlorite (Equation 15) and its reactions with nitrogen species (Equations 16 to 18) (Gendel and Lahav, 2012; Vanlangendonck et al., 2005).

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{14}$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- \tag{15}$$

$$HOCl + \frac{2}{3}NH_3 \rightarrow \frac{1}{3}N_2 + H_2O + H^+ + Cl^- \tag{16}$$

$$HOCl + \frac{2}{3}NH_4^+ \rightarrow \frac{1}{3}N_2 + H_2O + \frac{5}{3}H^+ + Cl^- \tag{17}$$

$$HOCl + \frac{1}{4}NH_4^+ \rightarrow \frac{1}{4}NO_3^- + \frac{1}{4}H_2O + \frac{3}{2}H^+ + Cl^- \tag{18}$$

However, contrary to this widely cited theory, electro-oxidation in practice results in gradual drop of total nitrogen concentrations starting immediately while very low chloramine concentrations are detected. It has been suggested that this is due to extreme pH and concentration conditions close to the anode and that breakpoint chlorination reactions occur rapidly at the anode producing N_2 (Kapalka et al., 2010c). Another hypothesis is that trichloramine (NCl_3) is produced directly at the anode (Equation 19) from NH_4^+, which then further reacts at the alkaline environment near the cathode to produce gaseous nitrogen (Equation 20). This hypothesis considers also other reactions in the bulk solution widely (Gendel and Lahav, 2012).

$$3Cl_2 + NH_4^+ \rightarrow NCl_3 + 3Cl^- + 4H^+ \tag{19}$$

$$2NCl_3 + 6OH^- \rightarrow N_2 + 3OCl^- + 3Cl^- + 3H_2O \tag{20}$$

Indirect oxidation is considered to be the governing method of nitrogen destruction in systems containing chloride and most applications utilize solutions containing chloride to achieve high electro-oxidation rates.

Electro-oxidation is not an NH_4^+-specific reaction, but affects potentially all species that can be oxidized, most notably organic material measured as chemical oxygen demand (COD). It has been applied as a combined method for COD and nitrogen removal for various wastewaters.

5.2.3 Electrochemical nitrate reduction and denitrification

Electrochemical NO_3^- reduction can result in at least eight end products, NO_2, NO_2^-, NO, N_2O, N_2, NH_2OH, NH_3 and NH_2NH_2 (Katsounaros et al., 2006). Most important factors in determining the reaction path are the electrocatalytic material, the cathode potential and the pH of the solution (Szpyrkowicz et al., 2006). The main cathodic reactions involved all produce hydroxide molecules lowering the pH (Equations 21 to 26) (Mook et al., 2012; Lacasa et al., 2011; Szpyrkowicz et al., 2006).

$$NO_3^- + H_2O + 2e^- \rightleftharpoons NO_2^- + 2OH^- \tag{21}$$

$$NO_3^- + 3H_2O + 5e^- \rightleftharpoons \frac{1}{2}N_2 + 6OH^- \tag{22}$$

$$NO_3^- + 6H_2O + 8e^- \rightleftharpoons NH_3 + 9OH^- \tag{23}$$

$$NO_2^- + 2H_2O + 3e^- \rightleftharpoons \frac{1}{2}N_2 + 4OH^- \tag{24}$$

$$NO_2^- + 5H_2O + 6e^- \rightleftharpoons NH_3 + 7OH^- \tag{25}$$

$$NO_2^- + 4H_2O + 4e^- \rightleftharpoons NH_2OH + 5OH^- \tag{26}$$

Nitrite (NO_2^-) is a reactive intermediate that is believed to have a central role in NO_3^- reduction reactions and it is believed to be the first intermediate usually formed from NO_3^- at the cathode. Nitrite will react with water to generate NH_3, nitrogen gas N_2 and hydroxylamine (NH_2OH) (Mook et al., 2012).

Generation of N_2, that is denitrification, has been the aim of most NO_3^-/NO_2^- reduction studies and especially different electrode materials have been extensively studied. Ammonia is usually the dominating end product when using metal electrodes such as iron and aluminium (Dash and Chaudhari, 2005) and catalysts such as gold and cobalt can further promote NH_3 generation (Szpyrkowicz et al., 2006). Electrodes studied for nitrogen gas generation include tin (over 90% N_2 yields observed), Cd (70%), Pd-Cu (50%), Pb (22%), Sn-Pt (85%), Pd-Rh (94%), Pt-Pd-Ge (60%) and Pd-Cu/graphite (70%) (see Katsounaros et al., 2006; Dortsiou et al., 2009 and references therein). Most applications do not apply special cathode materials for high nitrogen yields but combine electro-oxidation with electrochemical reduction so that reduction side products oxidize at the anode to nitrogen gas or back to NO_3^- (Mook et al., 2012).

5.2.4 Electro-coagulation

In electro-coagulation, a sacrificial anode (usually iron or aluminium) is used for producing soluble cations (Equation 27 and 28) that will act as coagulants and precipitate phosphorus and nitrogen as well as organic material from water stream. Hydrogen can be simultaneously produced at the cathode enabling fine bubbling to remove the flocculated particles (Equation 29) (electroflocculation). At acidic conditions, the pH of the effluent rises due to the metal dissolution and at alkaline conditions the pH decreases due to increased hydrogen evolution at the cathode (Chen, Y.-T., 2007).

$$Me \rightarrow Me^{x+} + xe^{-} \tag{27}$$

$$Me^{x+} + xOH^{-} \rightarrow Me(OH)_x \tag{28}$$

$$2H_2O + 2e^{-} \rightarrow H_2(g) + 2OH^{-} \tag{29}$$

Electro-coagulation is analogous to traditional coagulation with coagulation chemicals like aluminium or ferric chloride but with several advantages – no anions are added and the salinity does not increase, only about one third to half the sludge compared to chemical addition is produced and the cations are more active and the precipitation is more efficient and capable of removing a wider range of pollutants (Robinson, 1999). Particularly, the active cations form growing metal hydroxide precipitates that readily absorb NO_3^- and NH_3, a phenomenon not detected in traditional chemical coagulation (Lacasa et al., 2011b). The efficiency of nitrogen removal by electro-coagulation has been shown for various types of wastewaters (Mahvi et al., 2011; Vasudevan et al., 2010; Wei et al., 2010).

5.2.5 Stripping and membrane removal

Air stripping of ammonia is the most used method of ammonia removal in industry. In air stripping liquid pH and/or temperature are raised to increase the fraction of gaseous NH_3 in the solution after which it is contacted with air in a stripping tower or with help of membranes to move the ammonia into the gaseous phase. The NH_3 in the air can then be further treated e.g. thermally to N_2 or captured into an acidic solution for further use. Conventional air stripping can be an effective method for high strength wastewaters but becomes expensive in high volume low concentrations applications due to the high demands of air flow, pH adjustment and temperature change. Applications of stripping have been used in various wastewater treatment studies and it is potential especially in combination with a concentration step (Ippersiel et al., 2012; Gross et al., 2012; Lei et al., 2007; Zeng et al., 2006; Zhang et al., 2012).

Hydrophobic membrane contactors can be used as an alternative to stripping towers. The hydrophobic microporous membrane enables transport of volatile compounds through the membrane but blocks the movement of liquid constituents. This enables the selective stripping of volatile compounds such as NH_3 directly through the membrane into a collection gas stream, vacuum or a stripping solution. Advantages compared to air stripping include larger surface area, independent control of gas and liquid flow rates, no production of secondary pollutants, easier recovery of volatile compounds and smaller pressure loss which combined result in lower capital costs and ease of operation (Ahn et al., 2011; Ashrafizadeh and Khorasani, 2010). The method still requires pH adjustment.

In electrodialysis, cation and anion selective membranes are stacked by turns between cathode and anode and the electric field drives cations towards the cathode until they are blocked by an anion selective membrane and vice versa. The total effect is the concentration of ions into every other spacing. Electrodialysis can be used for ion removal from water or wastewater and it has been demonstrated in laboratory conditions for NH_3 capture from swine wastewater (Ippersiel et al., 2012).

Electrochemically assisted ammonia removal is a novel technology developed which combines air stripping with an electrochemical cell utilizing electric potential for pH-control and ammonia propagation onto the gas surface. This technology potentially overcomes the pH and temperature adjustments required for air stripping and the large electrical energy required for ammonia oxidation required in the electro-oxidation technology.

5.2.6 Bio-electrochemical systems (BES)

Bio-electrochemical systems (BES) or bio-electro/biofilm-electrode reactors (BER) are reactors where the oxidation of an electron donor at the anode is coupled with the reduction of an electron acceptor at the cathode and where bacteria catalyse the electrochemical reactions. Microbial fuel cells (MFCs) are BESs, that convert chemical energy in water into electrical energy, and microbial electrolysis cells (MECs) are BESs, where external electrical energy is utilized by microorganisms directly or via water splitting products such as hydrogen (Mook et al., 2012; Desloover et al., 2011).

The electrodes of BES are usually of large surface area and carbon cloths, carbon granules and graphite rods are frequently used, often in combination with steel or platinum meshes or rods to increase conductivity (Rabaey et al., 2007; Ghafari et al., 2008). The anodic and cathodic compartments are frequently separated by a cation exchange membrane, allowing the transport of positive ions to balance the electron flow, but they can also be grown without membranes (Zhao et al., 2011). Biofilms are formed on the electrode surfaces and microbes utilize the electrodes as an electron sink (anode) or an electron source (cathode) (Rabaey et al., 2007; Ghafari et al., 2008; Virdis et al., 2010, 2011, 2012). The electron transport has been the subject of intense research and while electron transfer can happen via extracellular electron shuttles, it has been demonstrated that mainly electron transfer happens via direct contact throughout the whole multilayered biofilm. The mechanism of electron transfer is not yet clear but is most likely affiliated with electron transport chain of the bacterial membrane and highly conductive pili and nanowires detected (Lefebvre et al., 2011). A simplified reaction pattern for BES is presented in Figure 16.

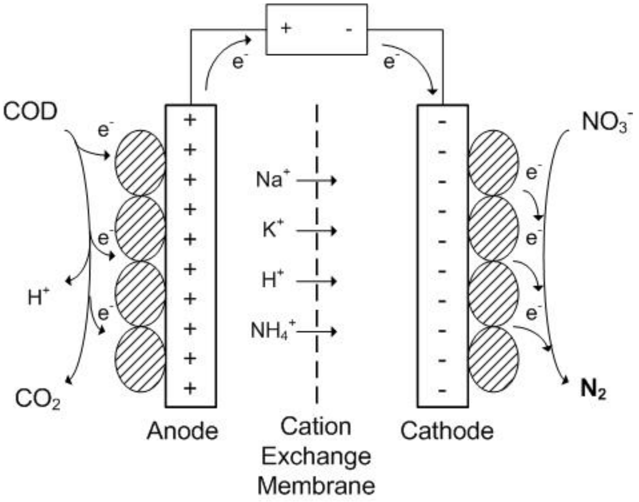

Figure 16. Simplified presentation of reactions at biologically catalysed anodes and cathodes (Desloover et al. 2011, Rabaey et al. 2007).

The BES can be used in specific reaction induction with separate liquid streams in the cathodic and anodic sides and for instance MFC-reactor has been used as an electron source for sludge treatment (Fischer et al., 2011). More recently, MFCs are designed to act as combined COD and nitrogen removal units from wastewater by combining the anodic and cathodic sections so that COD is first oxidized at the anodic side, from where the stream is directed to the cathodic side for denitrification and/or further COD removal (Virdis et al., 2008, 2009, 2010, 2011, 2012; Wrighton et al., 2010; Watanabe et al., 2002; Xu et al., 2011; Zhang et al., 2005; Zhao et al., 2011; Zhou et al., 2009). In the most advanced reactors, the cathode is combined with a biofilm filter which, with careful aeration, can function as a simultaneous nitrification-denitrification membrane achieving very high nitrogen and COD removal from municipal wastewater (Wang et al., 2011).

Bio-electrochemical systems for nitrogen removal are potentially feasible as they have many advantages such as energy self-sufficiency, no need for chemical addition and low concentration requirements for biofilms. Currently the technology is however still in its infancy and requires more research before larger scale applications.

5.2.7 Case examples

5.2.7.1 Electrochemical oxidation techniques

Electrochemical oxidation applications often apply an electronic potential with specific electrodes but studies do not necessarily specify which of the above mentioned reactions and phenomena are involved but concentrate on the complete results.

Most commonly studied technology is a combined oxidation of organic material, micropollutants and nitrogen using metallic electrodes, most often dimensionally stabile electrodes (DSA) and boron doped diamond electrodes (BDD) as they favour oxidation of organic material to oxygen evolution from water (Anglada et al, 2009).

For landfill leachates, the effectiveness of electro-oxidation for ammonia and organics removal has been widely studied. It is considered a functioning AOP-technology and pilot scale studies have confirmed the technology to be able to clean landfill effluent stream (860 mg/L COD, 780 mg/L NH_4^+, 1000 mg/L NO_3^-, 1600 mg/L Cl^-) to meet discharge requirements (160 mg/L COD, 30 mg/L NH_4^+) at an energy consumption of 35-54 kWh/m^3 (Anglada et al., 2010, 2011; Kapalka et al., 2010b; Cabeza et al., 2007a, 2007b, 2007c; Urtiaga et al., 2009). Certain chlorine by-products can be problematic in landfill effluents (Pérez et al., 2012).

Electro-oxidation has been tested for various streams such as NO_3^- rich agricultural wastewater (Georgeaud et al., 2011), swine excreta (Cho et al., 2010b), food industry wastewater (Huang et al., 2012), textile industry wastewater (Van Hege et al., 2002), kitchen waste (Lei and Maekawa, 2007; Zhu et al., 2009) and pharmaceuticals (Babu et al., 2009). There is a lot of research about the effect of different constituents for electro-oxidation such as chlorine (Lacasa et al., 2011; Ding et al., 2010; Ihara et al., 2006), anode material (Guo et al., 2009; Kapalka et al., 2010a; Katsounaros et al., 2006), conductivity and general reactor settings (Kim et al., 2005, 2006).

More specific NO_3^- removal has been also studied for various streams such as groundwater and aquaculture wastewater (Szpyrkowicz et al., 2006; Reyter et al., 2010; Saleem et al., 2011; Li et al., 2009a, 2010c). Also applications combined with traditional activated carbon process (Xie et al., 2006) and electroenzymatic processes (Cho et al., 2008) have been tested.

Generally the technology is seen as versatile and feasible for variety of streams but stream specific testing and optimization is always needed. The main barrier for utilization of electrochemical oxidation techniques is the energy consumption and efficiency.

5.2.7.2 Elonita

Elonita is a technology developed in an EU funded project 2002–2005 by Laborelec, a research centre of electrical power technology operating in Belgium. The technology was developed to remove NO_3^- and NH_3 from power plant wastewater with concentrations ranging around 200–1000 mg/L NO_3^- and 500–10 000 mg/L NH_4^+ (Labrolec, 2006).

The Elonita process consists of a cathodic chamber containing a reticulated vitreous copper doped carbon electrode and an anodic chamber containing a RuO_2-coated titanium plane electrode. The chambers are separated with a cationic membrane and a current density of 50 mA/cm^2 is applied. Water to be treated is first pretreated to remove organic constituents that lower the efficiency of the system and to potentially attain other characteristics suited for the process (see Table 11) (Vanlangendonck et al., 2005; Corbisier and Van Lierde, 2005; Corbisier et al., 2006; Labrolec, 2006; Chen et al., 2007).

Table 11. Suitable water characteristics for Elonita process.

Parameter	**Value**
Conductivity, mS/cm	3, preferably > 10
Nitrate and ammonia concentration, mg/L	at least 1000
Chloride concentration, mg/L	3000
Organic content	Low
Suspended solids	Low/None
Ca/Mg concentration	Low/None

Water is first circulated through the cathodic chamber where NO_3^- is reduced to NH_4^+ on the cathode surface. The expected reaction follows Equations 21 and 26. Solution pH is controlled with HCl if needed and the circulation is continued until NO_3^- concentration is under a desired limit. Then the water now containing mainly NH_4^+-N is pumped to the anodic chamber where the NH_4^+ is oxidized into nitrogen gas through indirect hypochlorite oxidation (see Equations 14 to 18). The total anodic reaction is expressed in Equation 30. Solution pH is controlled with NaOH if needed and the circulation is continued until ammonia concentration is under a desired limit (Vanlangendonck et al., 2005; Labrolec, 2006; Corbisier et al., 2006).

$$2NH_4^+ + 3HClO \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \qquad (30)$$

The pH, chloride concentration, electrode material and current density are important parameters in controlling the Elonita process and their effect has been studied and optimal ranges determined for both cathodic and anodic processes. Also, oxygen containing anions, especially carbonate (CO_3^{2-}), phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}) are noted to inhibit ammonia oxidation on the anodic side (Vanlangendonck et al., 2005; Chen et al., 2007).

Pilot scale runs using power plant effluent water resulted in final effluent concentrations of <20 mg/L NO_3^-, <0.2 mg/L NO_2^- and <5 mg/L NH_4^+. The NO_3^- reduction rate and NH_4^+ oxidation rates achieved were 37 g NO_3^-/h·m^2 and 41–96 g NH_3/h·m^2, respectively. By-products detected in the treated effluent included AOX-compounds (adsorbable organo-halogenated compounds), NO_x (nitrogen oxides NO, NO_2, N_2O), chlorine derivatives and gaseous ammonia (NH_3). Electric consumption was 56 kWh/m^3 treated. In 2005, the cost for a unit treating 15 kg NO_3^-/d was estimated at 724 k€ with additional chemical costs of 2.9 €/m^2 and the price of electricity (56 kWh/m^3). This was seen comparable to a biological treatment unit (Vanlangendonck et al., 2005; Labrolec, 2006; Corbisier et al., 2006).

The Elonita process is potentially feasible for mine waste waters but low nitrogen and chlorine concentrations as well as high sulphate concentration can decrease the efficiency and render the system ineffective.

5.2.7.3 AmmEL

AmmEL is a patented technology developed by the American company Enpar technologies Inc. for the removal of nitrogen compounds, specifically ammonia-based explosives, flotation reagents and cyanide destruction products from cold mine waste waters. The technology consists of a zeolite ion-exchange column that is regenerated with brine to remove NH_4^+, which is then oxidized electrochemically to nitrogen gas.

In the process the wastewater is flown through a zeolite packed ion-exchange column with a 30 min HRT in which about 90% of the NH_4^+-N is absorbed into the column. The column is regenerated after several hours with 3–4% NaCl brine solution. The brine solution is then treated in an electrochemical reactor similar in settings to the one described in the Elonita process, resulting in nitrogen gas. The regeneration ability of the brine has been suggested to be very efficient (Shelp et al., 2011; Seed et al., 2003).

The process has been tested for high strength municipal activated sludge dewatering wastewater and for clarified secondary effluent without pretreatment. A full scale installation has been constructed in 2010 in Ontario, USA, that treats 400 m^3/d of mine waste water containing 30 mg NH_3-N/L to reach concentrations below 10 mg NH_3-N/L. Capital costs are estimated to be lower than in attached growth biological system and operational costs were estimated (in 2003) at US \$2.20–2.40/kg NH_3-N (Shelp et al., 2011; Seed et al., 2003).

The zeolite ion-exchange and electrochemical destruction of ammonia has been further researched by a Chinese group who suggest combining the electro-oxidation of ammonia into the ion-exchange column and the results indicate that this method can improve the functionality of the absorption as well as remove one process step from the system (Li et al., 2010b; Lei et al., 2009; Li et al., 2009b).

The AmmEL process is designed particularly for cold mine waste waters with nitrogen and thus is potentially directly feasible for Miniman project waters. The process details are not available and more research is needed to ensure the applicability.

5.2.7.4 DesEL

The DesEL is a capacitive deionization (CDI) charge barrier technology developed by the American company Enpar technologies Inc. The technology has been developed to remove ionic compounds from water streams such as groundwater or process water (Seed et al., 2006).

In the process, treated water is flown between electrodes manufactured of powdered activated carbon with an organic binder layered with a cation selective membrane (cathode) or an anion selective membrane (anode). Electric potential forces ions through the membranes and binds them onto the electrode surface, removing them from the flow. Electrodes are regenerated by reversing the polarity of the electrodes, forcing the bound ions to the reject solution (Broséus et al., 2009; Seed et al., 2006).

The method has been tested in pilot scale for artificial wastewaters and achieved high removal efficiencies (90% TDS removal, 88–98% NO_3^- removal and 72–88% NH_4^+ removal). Further research is needed to investigate the fouling properties and long term effects of the system (Broséus et al., 2009).

The DesEL process is potential for mine waste water treatment but can be problematic in highly ionic solutions such as mine waste waters and it further requires treatment steps for the reject phase.

5.3 Sorption, precipitation and ion exchange

Sorption of nitrogenous contaminants possesses some advantages, including the relative simplicity of sorption techniques, their economy in application and operation, and the low temperature dependence of sorption reactions. Desirable attributes for a sorbent to be used in N capture include: high NO_3^- and/or NH_4^+ sorption capacity and selectivity; kinetically rapid N sorption from solution; and, a high degree of mineral stability, including resistance to degradation during both N sorption and desorption. In addition, an ideal sorbent should facilitate low-cost N separation and purification including low initial capital and ongoing operational investment requirements. In general, aggregate materials, resins, and fibres are potentially more suitable for N capture in a fixed bed or column-type configuration than finely-textured materials.

Sorption reactions typically involve surface ion or ligand exchange, and may facilitate precipitation of de novo mineral solids. Some zeolites, layered double hydroxide (LDH) or hydrotalcite minerals, and carbon-based sorbents examined in laboratory studies have demonstrated potential for large-scale application to remove nitrogenous compounds from wastewaters. Selected by-products and their derivatives, such as iron- or steel-making slags or zeolitized fly ash, may also be suitable for use.

5.3.1 Zeolites

Zeolites are a class of tectosilicate aluminosilicate minerals which may be either synthetic or naturally-occurring. In general, zeolite minerals consist of silica (SiO_4^{4-}) and alumina (AlO_4^{5-}) tetrahedra which form a framework containing exchangeable alkali and alkaline earth cations and adsorbed water. Zeolites are characterised by a high cation exchange capacity (CEC) and large void volume. The CEC of zeolite minerals can be substantially influenced by chemical and physical pre-treatment. Synthetic zeolites can be tailored to produce specific pore size distributions and are occasionally referred to as molecular sieves. Many different zeolites have been synthesized for special catalytic or ion-sieving industrial applications. Due to the rigid, porous framework, zeolite is not structurally altered by reversible cation exchange or hydration-dehydration reactions (Boettinger and Ming, 2002).

The natural zeolite mineral clinoptilolite has demonstrated highly selective NH_4^+ sorption in several studies and is widely used for NH_4^+ removal from municipal sewage effluent and wastewaters. Zeolite capacity for NH_4^+ sorption from aqueous solution varies depending on the mineralogy of the zeolite mineral, its particle size and relative porosity and density, and the pH and ionic composition of the solution. Lebedytnes et al. (2004) reported a NH_4^+ capacity of 0.64 meq/g (11.5 mg/g) for natural clinoptilolite from the Ukraine, whilst Nguyen and Tanner (1998) calculated NH_4^+ capacities of 5.7–8.3 mg/g for natural clinoptilolite and mordenite zeolites from New Zealand.

Zeolites specifically sorb large cations; the cation selectivity of clinoptilolite has been shown to decrease in the order $Cs^+>Rb^+>K^+>NH_4^+>Ba^{2+}>Sr^{2+}>Na^+>Ca^{2+}>Fe^{3+}>Al^{3+}>Mg^{2+}$ (Koon and Kaufman, 1971). In laboratory trials, clinoptilolite crushed to 0.16–0.6 mm and converted to a homoionic Na form exhibited a NH_4^+ capacity of 1.09 meq/g (19.7 mg/g), demonstrating a substantial increase in NH_4^+ sorption capacity as a result of pretreatment with NaCl (Haralambous et al., 1992). Schoeman (1986) reported sorption capacities of 21.8 and 28.0 mg/g for two different homoionic Na-clinoptilolites. In a separate study, homoionic Na-clinoptilolite exhibited slightly greater but statistically insignificant ($\alpha=0.05$) NH_4^+ sorption as compared to homoionic Ca-clinoptilolite (Ji et al., 2007). Ji et al. (2007) reported a maximum NH_4^+ sorption capacity for Ca-clinoptilolite of approximately 15 mg NH_4^+/g at pH 6. Clinoptilolite pre-conditioned with $(NH_4)_2SO_4$ and treated with NaCl to generate homoionic Na-clinoptilolite sorbed 6.7–16.0 mg NH_4^+/g in batch studies and 9.6–19.0 mg NH_4^+/g in column studies, respectively (Rahmani et al., 2004).

Ammonium sorption/ion exchange by clinoptilolite has been shown to occur rapidly. Haralambous et al. (1992) and Karadag et al. (2006) reported up to 70% of equilibrium NH_4^+ sorption within 10 min from initiation of contact. Similarly, both Booker et al. (1996) and Du et al. (2005) observed rapid sorption of NH_4^+ to zeolite within the first 10–15 minutes of contact, and an ion exchange equilibrium is attained in approximately 4 h. The NH_4^+ removal capacity of zeolites has also been shown to increase with increasing initial NH_4^+ concentration (Du et al., 2005; Karadag et al., 2006). Karadag et al. (2006) examined the effect of solution temperature on NH_4^+ sorption to clinoptilolite at 25, 40 and 55°C, and observed increasing NH_4^+ sorption to zeolite with decreasing solution temperature.

Heat and/or alkali treatment of fly ash can be used to form zeolitic materials with CEC ≥3 meq/g (Querol et al., 2001, 2002), usually referred to as zeolitized fly ash (ZFA). Alternately, pure zeolites may be synthesized from silica extracts of fly ash. Laboratory studies using an alkali-generated ZFA showed >23 mg/g NH_4^+

sorption in low ionic strength aqueous solution with substantially decreased NH_4^+ sorption as the ionic strength of the solution increased (Querol et al., 2001). Zeolitized fly ash generated by alkali (NaOH) treatment is essentially Na^+-saturated. The NH_4^+ removal capacity of ZFA may be enhanced by salt treatment to generate homoionic Ca, Mg, Al or Fe forms of ZFA. Wu et al. (2006) reported NH_4^+ removal from solutions containing ≤ 60 mg N/L by homoionic zeolites in the order $Al^{3+} > Mg^{2+} > Ca^{2+} > Na^+ > Fe^{3+}$.

The physico-chemical characteristics of ZFA are strongly influenced by the composition of the parent fly ash and the conditions under which it is zeolitized. At least half of the >140 Mt of fly generated worldwide each year is disposed of in landfills, which has the potential to cause significant environmental problems (Higgins et al., 1976; Singer and Berkgaut, 1995). Numerous studies have reported the mobilization of potentially toxic trace elements such as As, Cr, Mo, and V from fly ash (e.g.Phung et al., 1979; Quafoku et al., 1999; Vassilev and Vassileva, 2007; Wendling et al., 2012a); however, zeolitization may reduce the lability of trace elements (Querol et al., 2002). An additional potential barrier to the use of ZFA for N sorption is its fine particle size, which may limit infiltration rates. Whilst natural zeolite is massive and may be crushed or ground as desired, zeolitized fly ash is fine-textured and may require pelletization or other means to generate the desired particle size distribution.

Ammonia sorbed to zeolites can be effectively removed by treatment with alkaline salt solution (Booker et al., 1996; Du et al., 2005). At high pH, sorbed NH_4^+ is converted to NH_3 which readily diffuses from the zeolite matrix. Rahmani et al. (2004) reported 95–98% regeneration of clinoptilolite using 1.0 M NaCl, whilst clinoptilolite used as sorptive media in a column configuration to remove NH_4^+ from solution was effectively regenerated using 0.5 M NaCl adjusted to pH 11-12 with NaOH (Du et al., 2005). During NH_4^+ desorption, treatment of the clinoptilolite with NaCl resulted in the formation of a homoionic Na-zeolite and a subsequent increase in the material's NH_4^+ sorption capacity. There was no decline in the NH_4^+ removal capacity of clinoptilolite over six loading and five desorption-regeneration cycles (Du et al., 2005). Air-stripping of spent regenerant solution will remove desorbed NH_3-N and the solution can be re-used following re-adjustment of pH as needed.

Zeolites used to sequester NH_4^+ may also be regenerated electrochemically via oxidation of NH_4^+. In the presence of Cl^-, formation of the oxidizing agent HClO contributes to indirect NH_4^+ oxidation as in the reaction: $2NH_4^+ + 3HClO \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^-$ (Lei et al., 2009). In the preceding reaction, the primary mechanism of NH_4^+ oxidation is indirectly oxidation by HClO formed in electrochemical processes, whilst direct oxidation at the electrode-liquid interfaces of the anode through stepwise dehydrogenation and indirect NH_4^+ oxidation by hydroxyl radicals are negligible in the presence of Cl^- (Li and Liu, 2009). In laboratory batch studies, Lei et al. (2009) observed complete regeneration of NH_4^+-saturated zeolite following electrochemical treatment using 40 mA/cm^2 in a 2 g/L NaCl regeneration solution. More than 96% of the NH_4^+ was converted to $N_2(g)$ and < 4% of the NH_4^+ remained in the regeneration solution as NO_3^-. No decrease in the NH_4^+

sorption capacity of the zeolite was observed following five cycles of sorption and regeneration (Lei et al., 2009). The NaCl electrochemical regeneration solution can be re-used multiple times.

Similarly, Li et al. (2009b) observed > 98% conversion of zeolite-sorbed NH_4^+ to $N_{2(g)}$ in an electrochemical-ion exchange reactor (EIR) system. Ammonium was sorbed to zeolite by passing an NH_4^+-rich solution through a column-type EIR filled with zeolite. A Cu/Zn cathode plate and Ti/IrO_2-Pt anode plate, each with 50 cm^2 immersed area, were set within the zeolite-packed column. Zeolite within the EIR was loaded with NH_4^+ via saturated upflow of $(NH_4)_2SO_4$. Following NH_4^+ breakthrough from the column, NaCl regeneration solution was pumped into the reactor and a current applied to the EIR electrodes. During multiple loading and regernation cycles, > 98% of the NH_4^+ bound to zeolite was converted to N_2(g) and < 2% of the NH_4^+ remained in the regeneration solution as NO_3^- (Li et al., 2009b).

Whilst NH_4^+ sorption using natural or synthetic zeolite-type materials has been widely documented, recent research suggests that surfactant-modified zeolites can be effective for NO_3^- removal from solution. Treatment of zeolite with a cationic surfactant results in the formation of a surfactant bi-layer on the mineral surface, yielding an increased anion sorption capacity. The lower surfactant layer is retained on zeolite through electrostatic interaction between the negatively-charged mineral surface and the positively-charged surfactant head groups and the upper layer of surfactant molecules is bound to the lower by hydrophobic forces between the surfactant tail groups in both layers. After treatment of zeolite with a surfactant the cation exchange sites within zeolite pores remain available for cation exchange as the surfactant only interacts with the external mineral surface. Thus, cations and anions can be simultaneously loaded on surfactant-modified zeolite.

Li et al. (1998) demonstrated that zeolites treated with the cationic surfactant hexadecyltrimethylammonium (HDTMA) were resistant to chemical and biological degradation over a wide range of pH, Eh, and soil moisture conditions. The surfactant-modified zeolite was also reported to possess ideal hydraulic properties for use in flow-through water treatment applications (Li et al., 1998). In one study, modification of a zeolite using HDTMA resulted in NO_3^- sorption corresponding to surfactant loading, with a maximum NO_3^- sorption capacity of approximately 80 mmol/kg (*ca.* 5 mg NO_3^-/g ; Li, 2003). Guan et al. (2010) also observed increased NO_3^- sorption with increasing HDTMA loading, and reported NO_3^- capacities ranging from 3 mmol/kg (0.19 mg/g) for an unmodified zeolite to 56 mmol/kg (3.5 mg/g) for zeolite with an HDTMA admicelle structure bi-layer. Following clinoptilolite surface coverage by an HDTMA bi-layer, Onyango et al. (2010) determined NO_3^- sorption maxima between 10.5 and 11.4 mg/g for different material size fractions.

Although investigations of NO_3^- sorption by surfactant-modified zeolites to date has focused on the use of bromide or chloride salts of HDTMA, use of the cationic surfactant cetylpyrdinium bromide (CPB) has also been examined. Nitrate sorption by CPB-zeolite increased with increasing CPB loading, reaching a sorption maximum of 6.6 mg NO_3^-/g CPB-zeolite where surfactant loading was sufficient to generate a bi-layer surface configuration (Zhan et al., 2011). The co-presence of SO_4^{2-}, Cl^-, or HCO_3^- at > 2 times the concentration of NO_3^- in solution resulted in

17.5%, 19.4% or 5.8% inhibition of NO_3^- sorption by CPB-zeolite, respectively (Zhan et al., 2011).

Examination of NO_3^- removal from solution by HDTMA-clinoptilolite in the presence of competing anions using equimolar binary NO_3^-/anion solutions showed NO_3^- sorption inhibition in the order $PO_4^{3-}>SO_4^{2-}>Cl^-\approx F^-$ (Onyango et al., 2010). In both binary solutions and in solution containing all four anions, Schick et al. (2010) observed decreasing HDTMA-clinoptilolite sorption selectivity in the order $NO_3^- >HCO_3^-\approx SO_4^{2-}>>Cl^-$ when all anions were present in equimolar concentrations. Li (2003) demonstrated rapid but incomplete NO_x desorption from NO_3^--saturated, HDTMA-modified zeolite by washing with deionized water. Nitrate desorption from the surfactant-modified zeolite using NaCl increased with increasing solution ionic strength. Using the same concentration of electrolyte, NO_3^- desorption from the HDTMA-modified zeolite was greater at pH 7 than at pH 4 and 10 (Li, 2003).

Nitrogen-enriched zeolite may be suitable for use as fertilizer or as a nutrient-bearing soil amendment following N sorption from aqueous solution. The primary factors influencing a material's suitability for use as a soil amendment are its chemical composition and geochemical stability or susceptibility to physical and chemical weathering processes. Nitrogen, P and K are considered primary macronutrients and are usually deficient in agronomic soils because plants require relatively large quantities of these elements for growth. In glasshouse studies, NO_3^--loaded surfactant-modified zeolite has shown potential for use as a slow-release N fertilizer. After 13 weeks growth, there was no significant difference between plant height and dry weight of corn (*Zea mays*, L.) grown in soils amended with NO_3^--saturated, HDTMA-modified zeolite as the only source of plant N and corn which was fertilized with water-soluble KNO_3 fertilizer (Li, 2003).

In Finland, Envitop Oy markets a zeolite ammonium removal by the name EnviStone.

5.3.2 Hydrotalcites

Layered double hydroxide minerals, or hydrotalcites, exhibit potential for use in the removal of anionic contaminants such as NO_3^- from wastewaters (e.g. Socias-Viciana et al., 2008; Islam and Patel, 2009; Olfs et al., 2009) and may also function as catalyst precursors for selective catalytic oxidation of ammonia to nitrogen (Chmielarz et al., 2011). In-situ formation of LDH minerals and concomitant removal of NO_3^- and/or ammonia as well as a range of co-contaminants may be feasible depending on wastewater characteristics. Layered double hydroxides comprise a class of anionic clays containing brucite ($Mg(OH)_2$)-like layers in which some of the Mg^{2+} cations have been replaced by a trivalent ion, yielding positively charged sheets. The positive charge is balanced by intercalated anions within the hydrated interlayer between adjacent sheets. The general, ideal unit call formula for LDH minerals is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$ where M^{2+} and M^{3+} are di- and trivalent ions, respectively, and A^{n-} is the interlayer anion with valence n. The value of the stoichiometric coefficient x ranges from 0.17-0.33 (Ookubo et al., 1993) and the interlayer anion may vary widely. The Mg/Al LDH mineral with CO_3^{2-} as the charge-compensating anion ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$) occurs naturally, whilst most other forms of LDH minerals must be synthesized. Layered double hydroxide minerals exhibit anion exchange properties in contrast to the more common cation exchange properties of clay minerals and are used for a variety of purposes, including as ion exchangers, catalysts, polymer additives, and as antacids.

Specific removal of anionic contaminants using various synthetic LDH minerals has been examined by numerous researchers. Carbonate contained within LDH mineral interlayers is generally difficult to exchange, and some research indicates that only LDH minerals prepared in carbonate-free solution will exhibit substantial anion exchange, typically around 3 meq/g (Miyata, 1983). Calcination at > 400°C will decompose CO_3^{2-} anions in LDH mineral interlayers leaving O^{2-} anions (Parker et al., 1995). Layered double hydroxide minerals calcined at 400–900°C will return to their original structure upon rehydration, and thus exhibit potential for use as anion sorbents. Sato et al. (1986 demonstrated near-complete attenuation of HPO_4^{2-}, SiO_3^{2-}, SO_4^{2}- and CrO_4^{2-} by calcined synthetic Mg/Al LDH but no adsorption of the anions by the Mg/Al LDH prior to calcination.

Socías-Viciana et al. (2008) prepared Mg/Al LDH with CO_3^{2-} as the interlayer anion, then calcined the mineral at 550°C, 650°C or 850°C. X-ray diffraction (XRD) analyses showed that calcination resulted in the gradual loss of adsorbed and interlayer water molecules, OH^- groups linked to the brucite-like Al sheet of the LDH mineral, and interlayer CO_3^{2-}, followed by collapse of the layer structure and formation of amorphous Mg-Al mixed oxide minerals. When the calcined LDH samples were rehydrated in KNO_3 solution the LDH minerals calcined at 550°C and 650°C recovered their initial layered structure with NO_3^- replacing CO_3^{2-} in the mineral interlayers (Socías-Viciana et al., 2008). The LDH calcined at 850°C exhibited only a partial recovery of LDH structure, likely due to the irreversible formation of spinel-like crystalline oxides at >800°C. Upon rehydration in KNO_3 solution the LDH minerals calcined at 550°C and 650°C displayed NO_3^- sorption capacities of 61.7 and 82.0 mg/g, respectively (Socías-Viciana et al., 2008).

The Mg/Al ratio of synthetic LDHs may influence their NO_3^- sorption capacity and specificity. Nitrate forms of LDHs synthesized by co-precipitation exhibited differences in NO_3^- exchangeability by counter-anions based on the mineral Mg/Al ratio (Olfs et al., 2009). Synthesized NO_3^--LDHs with a lower Mg/Al ratio (2:1) had a greater total NO_3^- sorption capacity than those with a higher (5:1) Mg/Al ratio; however, NO_3^- exchange by HCO_3^-, Cl^- and SO_4^{2-} was lower for the NO_3^--LDHs with a 5:1 Mg/Al ratio (Olfs et al., 2009). Nitrate sorbed to 2:1 Mg/Al LDHs was exchanged equally by by HCO_3^-, Cl^- and SO_4^{2-} whilst NO_3^- sorbed to 5:1 Mg/Al LDHs was exchanged by anions in the order $HCO_3^- > Cl^- > SO_4^{2-}$. Olfs et al. (2009) attributed the differences in NO_3^- sorption and exchangeability between synthetic LDH minerals with 2:1 and 5:1 ratios of Mg/Al to the greater density of positively charged sites on the 2:1 Mg:Al minerals, and differences in LDH mineral crystallinity and textural characteristics.

Frost and Musumeci (2006) demonstrated successful NO_3^- sorption by a thermally-activated Zn/Al LDH mineral. A Zn/Al LDH mineral synthesized with CO_3^{2-} in the interlayer was heated to remove CO_3^{2-}, then added to a decarbonated $NaNO_3$

solution under an $N_{2(g)}$ atmosphere. Sorption of NO_3^- from the solution over a 21-h period resulted in reformation of a Zn/Al LDH mineral containing NO_3^- as the charge-compensating anion. Spectroscopic investigations indicated that the sorbed NO_3^- was present in the reformed LDH mineral in two different forms: NO_3^- was sorbed to the brucite-like LDH mineral surface and hydrated NO_3^- was present in the mineral interlayer (Frost and Musumeci, 2006). Layered double hydroxide mineral freormation following removal of interlayer anions by heating and loss of 3-D mineral structure was attributed to a structural memory memory effect, indicating that thermal treatment of LDH minerals can be used to generate an activated mineral phase for anion sorption.

The potential exists for *in-situ* formation of LDH minerals containing NO_3^- as charge-compensating anions via manipulation of solution chemistry. Henry et al. (2012) reported the successful synthesis of LDH minerals with the basic structure $Mg_6Al_2(NO_3)_2(OH)_{16}\cdot 4H_20$ via the addition of either aqueous $NaAlO_2$ or uncarbonated Al-rich, alkaline bauxite residue liquor to $Mg(NO_3)_2$ solution under an N_2 atmosphere. Layered double hydroxides synthesized using $NaAlO_2$ exhibited sharper peaks in XRD spectra indicative of greater crystallinity than those synthesized with bauxite residue liquor due to the incorporation of inpurities from the bauxite residue liquor within the precipitated LDH, including S, V, As, and P which existed as intercalated oxyanions (Henry et al., 2012). The LDH precipitated from bauxite residue liquor and $Mg(NO_3)_2$ solution contained only 0.2% N (w/w), or 8.9 mg/g; however, examination of the LDH solid showed incorporation of *ca.* 4% (w/w) organic C as oxalate, malonate, and succinate, as well as substantial CO_3^{2-} (159.6 mg/g) and SO_4^{2-} (27.6 mg/g) and lesser quantites of PO_4^{3-} (1.6 mg/g), Cl^- (0.7 mg/g), VO_4^{3-} (0.3 mg/g), and AsO_4^{3-} (0.1 mg/g) (Henry et al., 2012). Although the quantity of NO_3^- intercalated during *in-situ* LDH formation was relatively low, the capacity for LDH precipitation as a result of alteration to solution chemistry and the resultant sequestration of a range of contaminant cations and (oxy)anions indicates potential for application of *in-situ* LDH mineral precipitation to remove a range of contaminants from mine wastewaters.

5.3.3 Carbon-based sorbents

Activated carbon filters are widely used in water and wastewater treatment for the removal of synthetic organic chemicals and naturally-occurring organic chemicals. Activated C is generated when biomass is carbonized to charcoal and then activated with steam. Some industries generate activated C through integrated processes, and a number of agricultural and industrial by-products demonstrate potential as precursors for the manufacture of biomass-derived activated C products (Dias et al., 2007; Ioannidou and Zabaniotou, 2007). In many cases, activated C derived from agricultural by-products or other waste biomass performs comparably to commercially-available activated C in terms of contaminant attenuation (e.g. Mizuta et al., 2004).

Although activated C is generally considered a universal adsorbent for aquatic pollutants, untreated activated C exhibits a greater specificity for organic nitrogenous species compared to inorganic species and demonstrated a greater capacity for NH_4^+ sorption than for NO_3^-. For example, Wendling et al. (2012a) reported substantially greater attenuation of dissolved organic N from a nutrient-rich surface water using a biomass-derived granular activated C compared to inorganic N species, and greater removal of NH_4^+ (76% of influent NH_4^+) compared to NO_3^-/ NO_2^- (11% of influent NO_x). Similarly, Öztürk and Bektaş (2004) reported a nearly 36% decrease in NO_3^- sorption to activated C in the presence of NH_4^+. Treatment of activated C with acid may enhance its anion sorption capacity via protonation of surface OH^- groups, resulting in enhanced electrostatic interaction between anions and the activated carbon surface. Afkhami et al. (2007) reported a NO_3^-sorption capacity of *ca.* 126 mg/g at pH 7.0 for activated C cloth with a surface area 2500 m^2/g that had been pre-treated with H_2SO_4.

Treatment of activated C with $ZnCl_2$ has also been shown to enhance NO_3^- recovery from aqueous solution. Studies by Namasivayam and Sangeetha (2005, 2006) treated lignocelluosic coconut coir pith fibre with $ZnCl_2$, then carbonized the Zn-treated material at 700°C and leached excess Zn salt using dilute HCl. The Zn-treated activated C exhibited significantly greater specific surface area and total pore volume then untreated activated carbon derived from coconut coir pith (Namasivayam and Sangeetha, 2005). In batch experiments, the Zn-treated activated C rapidly reached equilibrium with respect to NO_3^- in solution, sorbing > 6 mg NO_3^- /g. Optimal NO_3^- removal was obtained in solutions between pH 3 and 10 (Namasivayam and Sangeetha, 2005). In a similar study, Bhatnagar et al. (2008) documented sorption of > 10 mg NO_3^-/g by Zn-treated GAC derived from coconut fibre. Other lignocelluosic agricultural waste materials examined for NO_3^- removal from aqueous solution include sugarcane bagasse and rice hull chemically converted to weak base anion exchangers. Orlando et al. (2002) reported maximum NO_3^- sorption of 1.4 and 1.3 mg NO_3^-/g sugarcane bagasse and rice hull, respectively, following treatment with eipchlorohydrin and dimethylamine.

Chitosan beads derived from thermochemical deacetylation of crustacean chitosan have also been investigated for use as NO_3^- sorbents. Jaafari et al. (2001) showed that NO_3^- sorption by cross-linked chitosan beads was pH-dependent, and exhibited a maximum between pH 3 and 5. Chatterjee and Woo (2009) showed that NO_3^- removal from aqueous solution by chitosan beads was also temperature-dependent, with the chitosan beads exhibiting a maximum sorption capacity of *ca.* 92 mg NO_3^-/g at 30°C. Both Jaafari et al. (2001) and Chatterjee and Woo (2009) reported effective desorption of NO_3^- from the chitosan beads in pH 12 solution. Treatment of chitosan beads with $NaHSO_4$ resulted in increased NO_3^- sorption maxima of 104 mg/g at pH 5, compared to *ca.* 91 mg NO_3^-/g for untreated beads (Chatterjee and Woo, 2009). The effect of zeolite surface modification with chitosan on NO_3^- removal has also been examined. Arora et al. (2010) reported a capacity of *ca.* 46 mg NO_3^-/g zeolite after coating the mineral with a layer of chitosan followed by acid protonation of the material surface. The chitosan-modified zeolite is unlikely to be suitable for NO_3^- removal from mine wastewaters, however, as thematerial was shown to be more selective towards SO_4^{2-} and Cl^- compared to NO_3^- (Arora et al., 2010).

5.3.4 Mineral-based by-products

Previous research has shown potential for the use of by-products in nutrient attenuation schemes (e.g. McPharlin et al., 1994; López et al., 1998; Drizo et al., 2006; Pratt et al., 2007; Wendling et al., 2012b). Mineral-based by-products may be cost-effective alternative materials for use as filtration media within constructed wetlands, treatment filters such as permeable reactive barriers, drainage channels, or as sorptive media within other nutrient intervention schemes. In addition to fly ash and ZFA (section 0), several Ca- and Fe-rich mining and mineral processing by-products with potential for use in nutrient interception schemes are generated worldwide in substantial quantities, including heavy minerals processing residues, by-products from alumina refining, and iron-and steel-making slags.

Limitations to by-product re-use in water treatment schemes are largely due the potential for release of labile trace elements at concentrations which may be harmful to exposed biota, and by the potential for accumulation of naturally-occurring radioactive material (NORM) in by-products. Some by-products which effectively remove N species from nutrient-rich waters in laboratory studies may be unsuitable for environmental application due to the pH of leachates (e.g. Wendling et al., 2012c). Extensive testing of by-products including mineralogical, geochemical, radiochemical and ecotoxicological characterisation of by-products is required to assess their suitability for application within water treatment schemes.

5.4 Zero-valent metals

Biologically-based nutrient removal systems may provide economical, effective N management but generally require large land areas due to kinetically slow removal processes. Physico-chemical wastewater treatment is a kinetically rapid alternative to conventional biologically-based nutrient removal systems and requires relatively small land areas for treatment of equivalent water volumes. Extensive study has shown that zero-valent metals, such as Al^0, Fe^0, or Mg^0, show substantial potential for remediation of contaminated soils and groundwater including those containing nitroaromatic compounds and NO_3^-. Murphy (1991) demonstrated optimal selective reduction of NO_3^- relative to SO_4^{2-} by Al^0 and < 2% dissolution of Al^0 when solution pH was maintained between 9.1 and 9.3. A subsequent study of NO_3^- reduction by powdered Al^0, however, showed < 30% NO NO_3^- removal from solutions at pH < 10 and a maximum of only 62% NO_3^- removal at pH 10.2 (Luk and Au-Yeung, 2002). The relatively low NO_3^- attenuation efficiency and health concerns related to residual Al in treated water limit the applicability of Al^0 to treatment of NO_3^- -enriched waters.

Zero-valent Fe is a relatively inexpensive, non-toxic and readily available reducing agent. The reduction of NO_3^- to NH_4^+ by Fe^0 is a thermodynamically favourable reaction which proceeds as follows:

$$NO_3^- + 10H^+ + 4Fe^0 \rightarrow NH_4^+ + 3H_2O + 4Fe^{2+} \qquad (31)$$

The reaction consumes Fe^0 through corrosion ($Fe^0 \rightarrow Fe^{2+}$); thus, the exposed metallic Fe surface becomes passivated with time and the Fe^0 media must be replaced or regenerated for further NO_3^- reduction to occur. Passivated oxide layer can be removed by acidification or heat treatment. Numerous laboratory studies have documented NO_3^- reduction by Fe^0 and near-stoichoimetric recovery of N as NH_4^+ (e.g. Ginner et al., 2004; Huang et al., 1998; Siantar et al., 1996).

Disadvantages associated with the process of NO_3^- reduction by Fe^0 are the requirement for pH buffering or extremely low pH conditions to supply adequate protons for the reaction to proceed, and the production of NH_4^+. Chen et al. (2005) documented only 13% NO_3^- removal efficiency by Fe^0 in the absence of pH control, and > 92% efficiency when pH was maintained at 4.0. Several studies have documented substantially greater NO_3^- reduction under acidic conditions, whilst some research has demonstrated that efficient NO_3^- reduction by Fe^0 occurs only at pH ≤ 4, where the passive oxide layers on Fe surfaces are dissolved to maintain a fresh Fe^0 surface and the redox reaction between NO_3^- and Fe^0 proceeds continuously (Choe et al., 2004; Huang et al., 1998). The formation of surface passivating layers and decreased permeability of Fe^0 reactive barriers or filtration systems due to formation of Fe oxides are among the primary concerns for long-term sustainability of Fe^0 systems for remediation of NO_3^- -contaminated water (Westerhoff and James, 2003).

Maintenance of solution pH < 4 for efficient NO_3^- reduction by Fe^0 may be unnecessary where aqueous Fe^{2+} is added to the system to regenerate the Fe^0 reductant. Reduction of NO_3^- at near-neutral pH is enhanced via the addition of Fe^{2+} to the solution (Huang and Zhang, 2005, 2006; Huang et al., 2003). It is postulated that Fe^{2+} bound to the Fe^0 surface may enhance electron transfer from to the solid-liquid interface (Huang and Zhang, 2005). Huang and Zhang (2006) demonstrated that in the presence of NO_3^-, Fe^{2+} is sorbed to Fe^0 surfaces as an inner magnetite (Fe_3O_4) layer and a thinner outer layer of iron oxide, such as lepidocrosite (γ-FeOOH). Magnetite does not hinder electron transport from Fe^0 to the solid-water interface as it is a highly conductive metal; however, non-conductive lepidocrocite does. When Fe^{2+} is added to solution, lepidocrocite can be transformed to conductive Fe_2O_3 via the reaction (Suzuki et al., 2012):

$$2\,\gamma FeOOH + Fe^{2+} \rightarrow Fe_3O_4 + 2H^+ \tag{32}$$

Thus, NO_3^- reduction by electron transfer from Fe^0 is expected to proceed as long as sufficient Fe^{2+} remains in solution. Green rust compounds, $Fe(II)_4Fe(III)_2(OH)_{12}SO_4 \cdot xH_2O$ are also redox-active and some evidence suggests they may likewise serve as secondary reducing agents for NO_3^-(Hansen et al., 1996).

Zero-valent Mg, Mg^0, has been shown to effectively reduce NO_3^- in solution. Kumar and Chakraborty (2006) reported 83-93% NO_3^- reduction by Mg^0 within 10-20 min when initial solution pH ≤ 3, and decreasing NO_3^- removal efficiency with increasing pH. Similar to Fe^0, pH control is required for efficient NO_3^- reduction by Mg^0. Irrespective of initial solution pH, the generation of OH^- ions during NO_3^-

reduction by Mg^0 resulted in a rapid increase in solution pH to 10.8 which resulted in Mg^0 surface passivation due to $Mg(OH)_2$ precipitation (Kumar and Chakraborty, 2006).

Numerous investigations have focused on developing techniques whereby the zero-valent metal matrix and/or reaction conditions are modified to facilitate NO_3^- reduction only to N_2 (g) rather than complete NO_3^- reduction to NH_4^+. The size of zero-valent metal particles may influence reaction end-products by altering reaction kinetics. Choe et al. (2000) successfully oxidised NO_3^- in solution to N_2 (g) within 30 mins using nanoscale (1–100 nm) Fe^0 particles in laboratory-based batch tests at ambient temperature and with no pH control. In contrast, although Liou et al. (2005) reported a substantial change in first-order NO_3^- reduction rate constants using nanoscale Fe^0 and Cu/Fe^0 bimetallic particles, NH_4^+ remained the dominant reaction end product. Nanoparticulate Cu/Fe^0 also proved unsuitable for groundwater denitrification schemes as ca. 40% of the reduced NO_3^- remained in solution as NO_2^- (Liou et al., 2005). Deposition of Pd and Cu on the surface of Fe^0 particles used to attenuate NO_3^- in solution resulted in the production of various quantities of NO_2^-, NH_4^+ and N_2 (g) depending on initial solution pH, with a maximum of 30% coversion of NO_3^- to N_2 (g) (Liou et al., 2009).

Maintenance of surface reactivity and minimization of NH_4^+ production are keys to successful treatment of NO_3^- by Fe^0 -based systems. Silica minerals have been demonstrated to reduce surface passivation of Fe^0 by scavenging precipitates formed during the reaction (Oh et al., 2007). Clay minerals used in conjunction with Fe^0 may enhance the efficacy of NO_3^- attenuation by reducing surface passivation, and may also provide sorption sites for NH_4^+. Bentonite intercalated with poly hydroxo-aluminium cations, or pillared bentonite, has been shown to enhance NO_3^- removal by Fe^0 (Li et al., 2010); however, a combination of Na-bentonite and Fe^0 did not attenuate substantially more NO_3^- than Fe^0 alone.

A similar study reported 41%, 43% and 33% more NO_3^- removal from groundwater using bentonite, fuller's earth, and biotite, respectively, in combination with Fe^0, in addition to sorption of the resultant NH_4^+ by the bentonite and fuller's earth (Cho et al., 2010a). Cho et al. (2010a) documented maximum NH_4^+ sorption capacities for bentonite and fuller's earth of 5.6 and 2.1 mg/g, respectively. The use of novel composites comprised of zero-valent metals with low-cost precursor clays also demonstrates promise for attenuation of NO_3^- in water. Zhang et al. (2011) mixed nanoscale Fe^0 and hydroxo-aluminium pillared bentonite to generate Fe^0 supported on pillared clay as dispersed particles (Fe^0/PILC). Nitrate attenuation by Fe^0/PILC was enhanced compared to Fe^0 alone. The Fe^0/PILC exhibited complete removal of NO_3^- from solution within 120 min in batch experiments, but little sorption of generated NH_4^+ (Zhang et al., 2011).

Laboratory studies have shown that Fe^0 may be suitable for CN^- removal from aqueous solution via precipitation of ferrocyanide ($Fe(CN)_6^{4-}$) and ferricyanide ($Fe(CN)_6^{3-}$) Fe-cyanide complexes (Ghosh et al., 1999). Cyanide removal rates of 50–71% were obtained using Fe^0 in constant-flow column experiments (Ghosh et al., 1999). In addition, several investigations have documented the degradation of a variety of oxidized chemicals using Fe^0. In particular, studies have shown that

Fe^0 is capable of degrading munitions wastes such as trinitrotoluene (TNT), the monocyclic nitramine explosive RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and the polycyclic nitramine explosive CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) (e.g. Balakrishnan et al., 2004; Hundal et al., 1997; Oh et al., 2007; Singh et al., 1998). Nitrous oxide (N_2O) and NH_4^+ were the primary products of CL-20 degradation by Fe^0 (Balakrishnan et al., 2004), whilst Fe^0 treatment of solution containing RDX yielded three moles NH_4^+ per mole RDX degraded but no NO_3^- or NO_2^- (Hundal et al., 1997). Oh et al. (2007) reported enhanced RDX degradation in soils amended with anaerobic microorganisms and Fe^0 compared to RDX degradation by Fe^0 in sterile soil, and N_2O as the sole end-product of RDX degradation.

5.5 Aeration

Aeration is a removal method for volatile compounds, like ammonia. Desorption of ammonia from water takes place when large amounts of air is directed into liquid with high pH value. Desorption of ammonia from water by aeration is an equilibrium process. The size of the air bubbles and the depth of the air diffuser have no significant impact for the efficiency of the process. Alkaline solution with pH 10.5 or more is needed for ammonia removal level of 95% or more. However, optimal pH value of the water treatment process is case-specific. To get the maximum ammonia removal level, air flow, temperature and pH should be maximized (Srinath and Loehr, 1974). Aeration is relatively cheap technology and there are different ways to release the air into the water. Aeration usually needs high pH which is often adjusted during the aeration. Aeration can be combined with other water treatment processes such as wetlands, but its use as a sole water treatment process is limited (Patoczka and Wilson, 1984; Jamieson et al., 2003).

Air can be introduced to water in different kind of units. Sparged (bubbled) aerator feeds air into the water through perforated tubes, porous plates or diffusers. In spray aerator, water is broken up by nozzles into fine drops in the atmosphere, increasing the contact area between water and air. In cascade-type aerator, the water flows across series of weirs positioned one above the other, so that the water comes into contact with the atmosphere at each overflow (Bochkarev et al., 1994).

There are quite few studies about diffused aeration where air is simply introduced to wastewater. Lin et al. (2009) studied combining aeration and microwave radiation. Results showed that only 3 minutes radiation time with aeration raised the solution temperature to 100°C and the ammonia removal level to 80%. Higher temperature would enhance the ammonia escape from the solution, but radiation time more than 3 minutes would not be cost efficient anymore (Lin et al., 2009).

Aeration can be used also for the reduction of some dissolved metals from low oxygen content waters, like mine waters. Increasing of the dissolved oxygen in water promotes oxidation of e.g. iron, manganese and arsenic and increases the efficiency of water treatment. Aeration is applied simultaneously with addition of lime and flocculant to increase pH, oxidize metals species and precipitate metal hydroxides. Aeration can reduce chemical usage, improve oxygenating efficiency, and therefore reduce energy and chemical costs. High oxygen content waters will not benefit from aeration technologies.

5.6 Membranes

Membrane technologies, such as reverse osmosis and nanofiltration are active technologies which need maintaining. Still they require less energy than many alternative processes. The equipment is compact, modular and capable of continuous operation. Best performance of membranes is achieved in combined or integrated system (Häyrynen et al., 2009).

Reverse osmosis and nanofiltration are both based on osmosis phenomena (Figure 17). Osmosis is defined as a spontaneous movement of liquid solvent from a dilute solution through a semipermeable membrane to a concentrated solution. In reverse osmosis process and also in nanofiltration, applied pressure forces water through semipermeable membrane against osmosis force while ions and molecules stay on the other side of semipermeable membrane. The quality of water produced by membrane processes is high compared to other common water treatment technologies, like ion-exchange (Madaeni and Koocheki, 2010; Molinari et al., 2001).

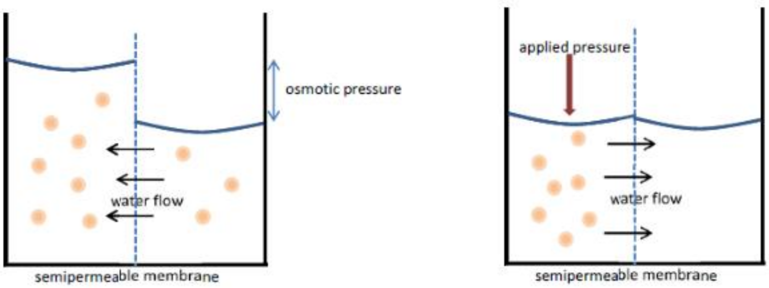

Figure 17. Osmosis process (left) and reverse osmosis process (right).

5.6.1 Reverse osmosis

Reverse osmosis is a process to separate ions, even monovalent salts, from water. It utilizes a semi-permeable membrane that is under high pressure, 30-60 bar, and impermeable to ions and molecules in the solution. The back pressure must be sufficient to overcome the natural osmotic pressure of the solution, so that water will flow from the high salt concentration side of the membrane to the dilute side. The size range of the molecules to be separated is approximately from 0.5 nm to 1.5 nm. A major application of reverse osmosis is the desalinization of brackish water (Koyuncu et al., 2001; Hutten, 2007; Malaeb and Ayoub, 2011).

Reverse osmosis is also used to concentrate and recover high value products from effluents (Kurihara et al., 2000).

Reverse osmosis is used in many application areas like semiconductors, food processing, power generation, pharmaceuticals, biotechnology, pulp and paper, mine and dairy wastewater, process and boiler water industries. The process efficiency depends on operational parameters, and membrane and feed water properties (Malaeb and Ayoub, 2011).

Commercially available membrane modules are often spiral-wound and hollow fiber modules. The membranes can be asymmetric containing one polymer layer or composite containing two or more layers. The functional groups introduced into the polymer structure control the valence and strength of the membrane charge, and the degree of adsorption of dissolved species is determined by membrane hydrophobicity, charge and roughness effect. Fouling caused by pore clogging and adsorption of solutes on the membrane surface, is the main limiting factor in reverse osmosis applications. Water pre-treatment before reverse osmosis prevents fouling and prolongs the membrane life. For future, new kind of membrane materials and coatings are studied. Cross-linked matrix of polymers and engineered nanoparticles are designed to draw in water molecules but repel contaminants including salts, organic and bacteria. This would decrease the energy consumption and prevent fouling of the membranes (Malaeb and Ayoub, 2011).

Several researchers have studied reverse osmosis to remove nitrogenous compounds. Hollow fibre polyamide membranes have shown removal efficiencies of 80–85% for NH_4^+ and NO_3^- ions at neutral pH. Cellulose acetate membranes were studied by Malaiyandi and Sastri (1981) to remove NH_4^+ and NO_3^- ions in the mining industry. At that time the removal efficiency of these ions was below 30%. Awadalla et al. (1994) have achieved removal efficiency of more than 90% for NH_4^+ in complexed form and 10–30% for pure ammonia.

Madaeni and Koocheki (2010) have studied the effect of $H_2PO_4^-$ ion for reducing NO_3^- and NO_2^- in water. They found out that the negatively charged phosphate ions bond with the polyamide surface, after the attachment of potassium ions. Large phosphorus ions form a negatively charged layer preventing other anions from getting through the membrane. Nitrate and NO_2^- removal rates were increased from 91% and 92%, respectively, to 99% with additional $H_2PO_4^-$ ions.

According to Molinari et al. (2001) up to 99% of soluble manganese could be removed with reverse osmosis, and the efficiency stayed practically equal with single pollutants and multiple pollutants. Nanofiltration removed only 15% of the soluble manganese.

5.6.2 Nanofiltration

Nanofiltration is a form of reverse osmosis. Nanofiltration is used for the separation of molecules in the range of 300–1000 kDa molecular weight and for larger ions like Ca^{2+} and Mg^{2+}. The size range for particle and molecule separation is approximately 1.2–12 nm. Nanofiltration has many advantages like low operation pressure, high flux, high retention of multivalent anion salts and organic molecules, relatively low investment and low operation and maintenance costs. Main application of nanofiltration is water treatment for drinking water as well as wastewater treatment. Nanofiltration can be also used as a pre-treatment for desalination process. The main problem in nanofiltration is fouling of the membrane which can be decreased with pre-treatment (Hilal et al., 2004).

Marttinen et al. (2002) have made laboratory scale nanofiltration experiments for leachates from two solid waste landfills. Ammonium removal with nanofiltration from different leachates was 27–50% with molecular weight cut-off membrane (200–300 g/mol). At pH 7–8 and 25°C, most of the ammoniacal N is in ionic form (e.g. NH_4^+) and can form complexes with anions and cations. These clearly larger sized NH_4^+ salt complexes are trapped to nanofiltration membrane. Temperature influences strongly the permeability of the membrane. If temperature is decreased from 25 to 5 or 10°C, permeability of the membrane can decrease 30–40% (Awadalla et al., 1994; Marttinen et al., 2002).

Häyrynen et al. (2009) studied the removal of NH_4^+ and NO_3^- from mine water by reverse osmosis and nanofiltration. Four commercial thin film composite reverse osmosis membranes and one nanofiltration membrane were studied. The removal rate of NO_3^- fluctuated from 96 to 97.4% and ammonia removal from 91.5 to 94.3%. Heavy metals, except aluminium and copper, did not enrich into concentrate.

5.6.3 Ultrafiltration and microfiltration

Ultrafiltration is used mostly for removal of large molecules and proteins from aqueous solution. The basis of ultrafiltration is the same as for nanofiltration, only the size of separated particles is different. Microfiltration is fundamentally different from ultra- and nanofiltration. In microfiltration, high pressure is not needed, because of the large pore size of membranes. Membrane pore size in microfiltration ranges from 0.1 to 10 µm. Microfiltration is mostly used in biotechnology to remove large bacteria or pathogens.

5.7 Evaporation

Thermal evaporation and distillation are not commonly used water treatment method except for the control of dissolved salts such as sodium chloride, and sodium and calcium sulphates. All other dissolved contaminants are removed coincidentally. Evaporation process may remove e.g. NO_3^- to some extent, but it is intended to remove other contaminants.

Evaporation requires large surface areas, and the larger the surface area, the higher is the rate of evaporation. Also climatic conditions such as temperature, humidity, solar radiation and wind affect to the evaporation of water. Temperature and solar radiation provide heat to enable evaporation. Wind replaces saturated air with unsaturated to evoke further evaporation. High humidity level prohibits evaporation, because air is already evaporated water in the air and air is saturated faster than with low humidity level (Gilron et al., 2003).

6. Conclusions

6.1 Mining nitrogen emissions and options for their mitigation

Nitrogen is an important chemical and nutrient, the production of which accounts to a significant portion of global energy consumption, and the use of which in fertilizers enables the global population increase into its current dimensions. Increased fixed nitrogen production and use have substantial environmental effects to local and global ecosystems, mainly through eutrophication of waterways and shallow seas.

In the environment the behaviour of N compounds is complex making the overall nitrogen management at mine sites and in their surroundings challenging. Concentrations of different N compounds fluctuate due to seasonal variations. Water conditions and temperature have an impact on e.g. water flow rates, biological activity and ammonia volatilization. The acceptable levels of N compounds in the waterways are not set constants but depend on the local environmental conditions and the sensitivity of recipients. Natural background concentrations of nutrients, the limiting nutrient (P or N) and the possible habitats of sensitive aquatic animals may be determinant factors when considering the acceptable N compound levels in the recipient and the allowed discharges for a certain industrial activity.

Nitrogen is released into air and water in mining operations, mainly through the use of ammonium nitrate explosives. The most cost-effective way of N emission mitigation is to control the emissions at their source. By implementing good blasting and explosives management practices, education and monitoring it is possible to achieve significant reductions (30–40%) in explosives originated N emissions. Furthermore, the minimization of the water streams being contaminated and the water management so that clean and contaminated streams are separated will help in reducing emissions of N as well as other pollutants. The natural degradation or reduction of nitrogen compounds can be enhanced by different means. In some cases water treatment technologies, such as reactive barrier, adsorption, electrochemical, biological or membrane techniques are needed.

The scale of nitrogen emissions from the extractive industry can be compared to other nitrogen emission sources, e.g. agricultural streams.

In Finland, the total use of explosives in 2010 is estimated at 50 000 t/a (Halonen 2012). 94% of explosives used are bulk emulsions, ANFO or emulsion cartridges with ammonium nitrate as the effective compound present (Halonen 2012). The nitrogen content of ammonium nitrate is 35 mass-% and can be assumed as the maximum mass of released nitrogen during incomplete detonation (in complete detonation, all nitrogen is theoretically transformed into nitrogen gas). The extent of incomplete detonation has been estimated at a very wide range from 0% to over 40% of explosive loading, depending on the type of operation, skill and explosives used. In Finland, explosive practices are well controlled and low leaching explosives are used. An estimation of 5% incomplete detonation for open pit mines and as high as 20% incomplete detonation for underground operations is presented, with half of this left completely un-burned (Halonen, 2012). This is partially released as NO_x and N_2O compounds in the air, partially as soluble compounds in the waterways and partially fixed in the solid waste rock and ore. As more than half of explosives used are in open pit rock production or mining, a total estimation of max. 10% of nitrogen release to the environment from all explosives used in Finland can be assumed. Taking 10% of 50 000 t of explosives and 35% of nitrogen content gives an estimate of under 2 kt N/a released into environment in Finland through mining operations. Experimentally, detonation of ANFO released app. 13 g N/kg of ANFO into atmosphere (Martel et al. 2004 in Brochu 2010) and if 35 g N/kg is estimated as total maximum release, we can estimate the gaseous fraction to be app. 40% of the release.

The total reactive nitrogen emissions to water and air in Finland are estimated in several sources. The total N-emissions to waterways was estimated as 147 kt/a in 2002 (Leap et al. 2011) and emissions to atmosphere have been estimated as 172 kt/a in 2000 (as 25, 130 and 17 kt/a NH_3-N, NO_x-N and N_2O-N, respectively) (Leap et al. 2011) and as 77.2 kt/a in 2011 (as 46.7 and 30.5 kt/a as NO_x-N and NH_3-N, respectively) (Bartnicki 2013). The 2 kt N/a released from mining in Finland accounts to approximately 0.6–0.9% of total nitrogen emission to air and water in Finland, and if 60/40 division between water/air is assumed, it covers for 0.8% and 0.5–1% of nitrogen emission into water and air, respectively.

Finnish mines consume an estimate of 500–11000 t of ammonium nitrate per year and (e.g. 500, 2000, 7000 and 11000 t NH_4NO_3/a by Pyhäsalmi, Suurikuusikko, Kevitsa and Talvivaara, respectively) (PSAVI 2011a, PSAVI 2011b, Pöyry 2012, PSY 2004). This corresponds to estimated total nitrogen emissions to air and water of 17.5-385 t N/a, if 10% nitrogen loss is assumed. The average nitrogen overflow (i.e. the “worst case” amount of leachable nitrogen) of farmland in Finland is estimated at 49 kg N/ha in 2005–2010 (TIKE 2013), and the actual annual nitrogen drainage from agriculture is estimated to be 8–20 kg/ha (Rekolainen 1992). Based on the worst case amounts of nitrogen overflow, a mine in Finland can have nitrogen emissions comparable to average emissions from 360–7860 ha farmland. A mid-sized mine, using 2000 t of NH_4NO_3 annually, if releasing 10% of applied nitrogen, has the same scale of potential nitrogen release as 1400 ha farmland.

In conclusion, a mine can have nitrogen emissions comparable to very large scale farming units. The environmental effects of such emissions depend on the receiving waterways and can be significant especially in barren subarctic environments, typical to Nordic mines.

6.2 Comparison of technologies and research opportunities

Many of the currently available technologies for the removal of nitrogenous compounds from wastewater are not suitable for the treatment of mine wastewaters containing low levels of nitrogenous compounds due to treatment costs or operating parameters. Robust, low-cost technologies with no or low temperature or pH-dependence are sought for the treatment of mine wastewaters with a range of physico-chemical characteristics.

Biological methods potentially offer an effective and inexpensive alternative to physicochemical techniques for the removal of nitrogen from wastewaters. A distinct advantage of biological methods is their minimal impact on the environment; in some applications, use of biologically-based wastewater treatment systems such as constructed wetlands can enhance biological diversity and ecological sustainability. Constructed wetlands can be an effective method for the removal of nitrogen from mine wastewaters where sufficient oxygen is available for optimal nitrification and adequate organic carbon is provided for denitrification reactions to proceed. Alternately, constructed wetlands which substitute autotrophic denitrification, in which elemental sulphur is utilized in place of organic carbon, can mitigate the need for external organic carbon addition associated with heterotrophic denitrification. Limitations to the use of constructed wetland systems for nitrogen removal from wastewaters include the relatively high land area requirement for treatment of large volumes of wastewater, and the temperature dependence of biological processes within wetlands. Temperature limitations are particularly important in cold regions, as wetland processes (e.g. nitrification) require temperatures > 10^{o}C.

Anammox technology offers numerous advantages for wastewater treatment when applied at a large scale due to its low energy and no external carbon requirements. Further advantages to use of the anammox process for nitrogen removal include the minimization of surplus sludge production and compatibility with high volumetric loading rates, resulting in reduced operational and investment costs. Anammox technology can be used in combination with systems which concentrate NH_4^+ to improve biological nitrogen removal in dilute nitrogenous wastewater steams, such as mine effluents.

Electrochemical methods have been developed for nitrogen removal primarily to overcome problems encountered with biological nitrification-denitrification, such as pH-dependence and the organic carbon requirement, as well as the sensitivity of biological systems to toxins, temperature and change of environmental parameters. Unlike biological N removal techniques, electrochemical methods do not require organic carbon and are not temperature dependent. Additional advantages to the use of electrochemical processes for N mitigation are that electrochemical processes can be run periodically as necessary and usually no chemical addition is required. Some electrochemical methods require a high chlorine concentration for indirect ammonia oxidation, and large potentials can be required for oxidation. High concentrations of ions such as Mg^{2+}, Ca^{2+} and SO_4^{2-} can be problematic as they can precipitate with changing pH or inhibit the movement and reactions of nitrogen ions. Electrochemical techniques which utilize electrochemistry enhanced ammonia stripping would potentially suit a large volume, low concentration wastewater stream analogous to mine site wastewater. Electrochemistry enhanced ammonia stripping would require only low electrical potential for operation, and would result in an ammonia product for reuse.

Zero-valent metals can be utilised for passive reduction of nitrate in aqueous solution; however, whilst no external energy is required to facilitate N reduction using zero-valent metals, pH buffering or extremely low pH conditions are required to supply adequate protons for the reduction reaction to proceed. Surface passivation due to the formation of oxide coatings on the zero-valent metal(s) used results in decreased NO_3^- removal and requires replacement of regeneration of the zero-valent metal. In addition, NO_3^- reduction generally does not stop at N_2 but proceeds to form NH_4^+. Zero-valent metals are most commonly used in passive permeable reactive barrier systems to attenuate dilute concentrations of NO_3^- in groundwater. This type of system is poorly-suited to treatment of large volumes of wastewater with moderate to high concentrations of multiple nitrogen species.

Due to their high cost and substantial operational requirements, membrane technologies are generally employed in the production of high-quality water. Membrane water treatment systems operate at high pressure and require on-going maintenance. Pre-treatment of wastewater is generally recommended to minimize membrane fouling.

Neither evaporation nor aeration methods are particularly well-suited to the treatment of large volumes of wastewater containing multiple species of nitrogenous contaminants. Thermal evaporation and distillation are not commonly used water treatment methods. Evaporation process may remove NO_3^- in some degree, but it is intended to remove other contaminants. Aeration can be used for the removal of volatile compounds such as ammonia from solution. Aeration for ammonia removal is limited by the high pH (≥ 10.5) required for efficient ammonia removal. As aeration is a relatively inexpensive treatment option, it is frequently employed in combination with other treatment techniques where applicable. For the treatment of wastewaters with circumneutral pH and containing multiple nitrogen species, aeration is unlikely to be a cost-effective treatment technique.

Advantages associated with the use of sorption techniques for the removal of nitrogenous contaminants from aqueous solution include the relative simplicity of sorption methods, their economy in application and operation, and the low temperature dependence of sorption reactions. Depending on the sorbent, solution pH may affect N removal. Numerous materials have been examined for sorption/ion exchange/precipitation of nitrogenous compounds from solution, and zeolites, layered double hydroxide minerals and carbon-based sorbents are among the materials exhibiting the most potential for large-scale application. Some industrial, mining and metallurgical by-products have also demonstrated potential for use as N sorbents; however, by-products are generally not suited to use in industrial-scale processes requiring consistent material performance and compliance with regulatory guidelines due to their inherent variability and the potential for release of chemical constituents (e.g. metals and metalloids).

Natural zeolite minerals and biomass-based activated carbon may be particularly suited to use as sorbents for N capture. Zeolite and surfactant-modified zeolite have demonstrated kinetically rapid and highly selective sorption, concomitant with a high degree of mineral stability, including resistance to degradation during both N sorption and desorption. Similarly, granular activated carbon and GAC treated with Zn rapidly removed NH_4^+ and NO_3^- from solution, respectively, in laboratory-scale trials. Both natural zeolite and biomass-based granular activated carbon are low-cost materials, with relatively low initial capital and on-going operational expenses. Layered double hydroxide minerals, whilst showing substantial promise for the use in small-scale operations, are relatively costly and less stable minerals compared to e.g. natural zeolite. The layered double hydroxide minerals which may be generated via precipitation reactions are fine-textured and not amenable to use as filtration media for large volumes of wastewater. In general, aggregate materials, such as granular zeolite and granular activated carbon, are more suitable for N capture in a fixed bed or column-type configuration than finely-textured materials.

A compilation of technologies and their suitability is presented in Table 12.

Table 12. Summary of selected technologies with demonstrated effectiveness for treatment of water containing nitrogenous compounds.

Technique	Advantages	Disadvantages	Reported removal rate or efficiency				Suitability for mine wastewater treatment
			NO_3^-/NO_2^-	NH_4^+	Org. N	CN^-	
Biological N removal methods	• >99% efficiency can be achieved • Moderate operational cost	• May require biomass waste disposal • pH and temperature effects are important • Post-treatment may be required	60–99%[1]	12–97% [1]	ND	ND	Toxicity and low temperature may limit the applicability
Reduction using zero-valent metals	• Moderate operational cost	• Surface passivation and/or reduced permeability may limit efficacy/lifespan • pH effects are critical	Fe^0: 13–92% Al^0: < 30–62% Mg^0: 83–93%	Low	10–30%	Fe^0: 50–71%	Poor due to surface passivation, requirement for strict pH control
Electrochemical methods	• No waste disposal is required • Temperature effects are not important • High removal efficiency • Moderate operational cost	• pH effects may influence effectiveness • Post-treatment may be required	98%[2]	> 97% [2]	90% [2]	ND	Good
Sorption, precipitation and ion exchange methods	• Removal efficiency varies with sorbent and but can be targeted to specific contaminants • Moderate operational cost	• May require disposal of saturated/spent sorbent or waste brine • pH and temperature effects are important • Post-treatment may be required	3.5–11 mg/g (HDTMA-zeolite) 60–82 mg/g (Mg/Al LDH) 6–10 g/mg (activated C)	6–28 mg/g (zeolite) > 70%	ND	ND	Good
Membranes	• High quality water • Monovalent ion separation	• Require maintenance • High pressure • Pretreatment recommended • High operation costs	91–99%	> 90%	ND	90–95%	Poor
Air stripping	• Relatively cheap technology	• High pH required	ND	> 95% (> pH 10.5)	ND	ND	Fair in combined technology
Combined technologies	• Can be selected and optimised to suit a particular wastewater	• Research/testing may be required to optimize treatment system for individual applications	Variable	Variable	Variable	Variable	Good

ND = not determined/no data, [1]depends on conditions in reactor/wetland, efficiency good when optimal conditions for microbial processes are achieved, [2]depends highly on the electrochemical method selected

6.3 Proposed technologies for investigation during Miniman project

A combination of sorption and electrochemical techniques is potentially most suitable for the treatment of large volumes of wastewater containing multiple nitrogenous compounds. We propose to further examine the performance of an electrochemical process, utilizing electrochemistry enhanced ammonia stripping. This type of electrochemical process would potentially suit a large volume, low concentration wastewater stream, would require only low electrical potential for operation, and would result in an ammonia product for reuse. The electrochemical nitrogen removal process could also be coupled with sorption techniques to pre-concentrate nitrogenous compounds and to reduce the volume of wastewater for electrochemical treatment.

We propose to further examine the removal of nitrogenous compounds from a mine site wastewater using the following techniques:

- electrochemistry enhanced ammonia stripping;
- zeolite/surfactant-modified zeolite sorption; and,
- granular activated carbon/Zn-treated granular activated carbon sorption.

In addition, we propose to investigate a sorption-electrochemical stripping combined technique by desorbing immobilized nitrogenous compounds from zeolite and granular activated carbon using a NaCl solution, followed by electrochemically enhanced ammonia stripping and ammonia recovery from the concentrated solution. Furthermore, denitrification and nitrification reactor processes will be studied with the special focus on the parameters relevant in real mine environment, such as toxicity effects, temperature and acidity.

6.3.1 Mine wastewater

A representative mine wastewater is required for use in this study. High concentrations of SO_4^{2-} may interfere with NO_3^- removal, depending on the technique used. The SO_4^{2-} concentration of mine wastewater is a function of the ore characteristics and ore processing methods employed. Thus, it is advisable to assess the performance of selected technologies in laboratory trials using both the selected mine wastewater (underground mine wastewater, Table 13) and a synthetic mine wastewater analogue containing little or no SO_4^{2-}.

Table 13. Characteristics of representative mine wastewater requiring treatment for removal of nitrogenous compounds.

Parameter	Open-pit mine wastewater	Underground mine wastewater	Whole of mine wastewater[1]
pH	8	8	6.6-9.1
Conductivity (mS/m)	17-540	43-378	610-1100
TSS (mg/L)	1-810	22-180	2-59
COD_{Cr} (mg/L)	ND[2]	ND	40-74
Total N (mg/L)	3-40	1.23-12	3.3-40
NH_4^+ (mg/L)	ND	ND	0.02-19
NO_3^-/NO_2^- (mg/L)	ND	ND	5.3-9.1
CN^- (µg/L)[3]	ND	ND	<10-570
Total P (µg/L)	ND	ND	8.2-120
PO_4^{3-} (µg/L)	ND	ND	2-71
SO_4^{2-} (mg/L)	72-99	58-89	4100-10 000
Cl^- (mg/L)	3-16	5	ND
Al (µg/L)	<30-2880	290-3280	30-190
Sb (µg/L)	81-1230	65-220	0-200
As (µg/L)	69-880	<15-180	15-370
Cu (µg/L)	<5-14	<15-15	5-18
Fe (µg/L)	10-10 100	620-5600	15-4120
Mg (mg/L)	ND	ND	785-1900
Mn (µg/L)	160-580	120-1180	220-13 200
Na (mg/L)	ND	ND	220-500
Ni (µg/L)	12-200	6-200	3-190
Zn (µg/L)	<10-34	<10-36	10-15

[1] Prior to discharge to site wetland system.

[2] No data.

[3] Weak acid dissociable cyanide.

6.3.2 Techniques selected for further investigation

6.3.2.1 Electrochemically-enhanced ammonia stripping

Mine wastewater sample from open pit drainage containing ammonia and nitrate from explosives will be treated in laboratory scale in an electrochemical ammonia stripping reactor. In a continuous flow reactor, a novel method combining airflow and dimensionally stabile electrodes separated by cation exchange membrane is used for 1) reducing nitrates and nitrites into ammonia and 2) stripping ammonia as ammonia gas and capturing it into an acidic collection solution. Effects of electric current, hydraulic residence time and air flow are investigated by following nitrite, nitrate and ammonia concentrations as well as pH of the reaction products and intermediate products.

6.3.2.2 Sorption techniques

Natural clinoptilolite zeolite and clinoptilolite treated with HDTMA-Br surfactant will be loaded into two separate laboratory-scale columns to be operated in series in a saturated upflow mode. Effluents from the columns will be monitored to determine the capacity of each material for NO_3^- or NH_4^+ sorption. When the zeolite system has reached its capacity, NO_3^- and NH_4^+ will be desorbed from surfactant-treated and untreated zeolite, respectively, and the solution will be reserved for electrochemically-enhanced ammonia stripping tests. Multiple sorption-desorption cycles will be employed to examine the system durability and assess on-going maintenance requirements.

In a separate trial, biomass-based granular activated carbon and Zn-treated biomass-based granular activated carbon will be loaded into two separate laboratory-scale columns. These two columns will also be operated in series in a saturated upflow mode. Effluents from the columns will be monitored to determine the capacity of each material for NO_3^- or NH_4^+ sorption. When the granular activated carbon system has reached its capacity, NO_3^- and NH_4^+ will be desorbed from Zn-treated and untreated granular activated carbon, respectively, and the solution will be reserved for electrochemically-enhanced ammonia stripping tests. As with the zeolite system, multiple cycles of sorption-desorption will be employed to examine the system durability and assess on-going maintenance requirements.

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Title	**Nitrogen compounds at mines and quarries** Sources, behaviour and removal from mine and quarry waters – Literature study
Author(s)	Johannes Jermakka, Laura Wendling, Elina Sohlberg, Hanna Heinonen, Elina Merta, Jutta Laine-Ylijoki, Tommi Kaartinen & Ulla-Maija Mroueh

Abstract

Mining wastewaters can contain nitrogen from incomplete detonation of nitrogen rich explosives and from nitrogen containing chemicals used in enrichment processes. Nitrogen released to the wastewaters is a potential environmental risk. Nitrogen can be dangerous for aquatic organisms or more prominently cause eutrophication in receiving waterways. Nitrogen chemistry is complex, allowing numerous chemical and biological reaction paths and compounds. Various techniques have been investigated for nitrogen removal from aqueous solutions, such as industrial and municipal wastewaters. Many of the technologies currently available are not suited for the treatment of mine wastewaters containing low levels of nitrogenous compounds, due to treatment costs or stringent operating parameters.

Although biological methods potentially offer an effective and inexpensive option for the removal of nitrogen from wastewaters, in mine applications these techniques may be limited by the temperature dependence, especially in cold regions. Zero-valent metals can be utilised for passive reduction of nitrate in aqueous solution. However, whilst no external energy is required to facilitate N reduction using zero-valent metals, pH buffering or extremely low pH conditions are required to supply adequate protons for the reduction reaction to proceed. Evaporation and aeration techniques are often used for ammonia removal from industrial wastewaters but their use in mine applications is limited by low concentrations, large volumes and requirement for pH control. Membrane technologies are similarly poorly-suited to the treatment of large volumes of mine wastewater. Due to their high cost and substantial operational requirements, membrane technologies are generally employed for the production of high-quality water.

Sorption techniques have been thoroughly examined for the removal of nitrogenous contaminants from aqueous solution and they offer an attractive alternative. Sorption technologies offer benefits including the relative simplicity of sorption methods, their economy in application and operation, and the low temperature dependence of sorption reactions. Electrochemical methods can be used to convert nitrogenous compounds to a desired form facilitating nitrogen removal as nitrogen gas or as pure ammonia. Thus, these methods offer a temperature-independent alternative for biological nitrogen removal techniques. In addition, electrochemical processes can be run periodically as necessary and no chemical addition is required.

Based on a literature review, a combination of sorption and electrochemical techniques is potentially most promising method for the treatment of large volumes of wastewater containing multiple nitrogenous compounds. The performance of both sorption techniques and electrochemistry enhanced ammonia stripping will be further experimentally studied for the attenuation of multiple nitrogenous compounds in mine wastewater.

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Nimeke	**Typpiyhdisteet kaivos- ja louhosvesissä** Päästölähteet, käyttäytyminen sekä poisto vesistä – Kirjallisuusselvitys
Tekijä(t)	Johannes Jermakka, Laura Wendling, Elina Sohlberg, Hanna Heinonen, Elina Merta, Jutta Laine-Ylijoki, Tommi Kaartinen & Ulla-Maija Mroueh
Tiivistelmä	Kaivosten jätevedet voivat sisältää typpeä räjähdysainejäämistä sekä mahdollisista rikastusprosessin typpeä sisältävistä kemikaaleista. Typpipäästöt voivat olla vesieliöille haitallisia, mutta yleisin haitta on vastaanottavan vesistön rehevöityminen. Typen kemia on monimutkainen: se mahdollistaa lukuisia kemiallisia ja biologisia reaktiopolkuja ja -tuotteita. Typen poistoon ja talteenottoon on kehitetty runsaasti erilaisia fysikaalisia, biologisia ja kemiallisia teknologioita, mutta kaivosvesien ominaisuudet, erityisesti matala hiilipitoisuus, matala typpipitoisuus, usein matala lämpötila, pH sekä haitalliset yhdisteet tekevät monista teollisuuden ja jätevedenpuhdistamojen menetelmistä kannattamattomia. Biologiset prosessit ovat tehokas ja edullinen typenpoistomenetelmä, mutta kaivosjätevesien matala lämpötila voi rajoittaa niiden soveltuvuutta, erityisesti pohjoisilla alueilla. Varauksettomat metallit eivät sovellu kaivosvesille, sillä ne vaativat toimiakseen erittäin matalan pH:n. Haihdutusta ja ilmastusta käytetään teollisuudessa usein ammoniakin poistoon, mutta matala konsentraatio, suuret virtaamat ja pH:n säätötarve rajoittavat niiden käyttöä kaivosvesien käsittelyssä. Membraanisuodatusta käytetään kaivoksilla tiettyihin kohteisiin, mutta typen poistoon ne eivät sovellu suuren esikäsittelytarpeensa ja korkean energiankulutuksensa vuoksi. Selektiiviset sorptiotekniikat ovat eräs mahdollinen ratkaisu kaivosvesien käsittelyyn. Tietyt sorbentit pystyvät selektiivisesti ja regeneratiivisesti sitomaan ammoniakin myös matalasta konsentraatiosta korkeassa kokonaisionipitoisuudessa. Sorptiotekniikoiden etuja ovat mm. yksinkertainen toimintaperiaate, suhteellisen matalat käyttökustannukset ja lämpötilariippumattomuus. Elektrokemiallisilla menetelmillä typpiyhdisteet voidaan muuttaa haluttuun muotoon ja poistaa typpikaasuna tai puhtaana ammoniakkina. Näin ollen ne tarjoavat vaihtoehdon biologisille prosesseille, joissa muokataan typen esiintymismuotoa. Elektrokemialliset menetelmät ovat lämpötilasta riippumattomia ja toimivat ilman hiiltä tai kemikaalilisäystä. Sorptiotekniikat ja elektrokemialliset tekniikat tai niiden yhdistelmät ovat kirjallisuuskatsauksen perusteella lupaavimmat kaivosjätevesien typenkäsittelymenetelmät, jotka mahdollistavat sekä typen poiston että talteenoton. Näiden tekniikoiden kokeellista tutkimusta jatketaan MINIMAN-projektissa tämän kirjallisuusselvityksen pohjalta.
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