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Solutions for control of nitrogen discharges at mines and quarries

Miniman project final report

VTT

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Abstract

Solutions for control of nitrogen discharges at mines and quarries

Miniman project final report

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Keywords: mines, quarries, explosives, nitrate, ammonium, water treatment technologies

The growth of Finnish extractive industry increases the need to study and monitor different environmental impacts and to integrate the environmental issues more tightly into the overall framework of the activities. Nitrogen released from explosives or from mining processes and ending up in the water system can have negative environmental effects. The MINIMAN project, financed by the Tekes Green Mining Programme and the industry aimed at comprehensive understanding on the nitrogen issue in the extractive industry. The project collected essential data on nitrogen compounds present in the environments of mines and quarries, and developed technologies for the treatment of nitrogen containing mine water.

Based on a technology review, selective sorption, electrochemically assisted membrane separation and biological treatment were selected to be studied and developed in the project. Denitrification and nitrification studies on synthetic mine wastewater in laboratory scale revealed that denitrification was possible at low pH (2.5) and temperatures as low as 7°C. Nitrification was more pH sensitive. Both processes tolerated metals (Fe, Ni, Co and As). In the adsorption tests with zeolite, complete ammonium removal from real mine wastewater was achieved with a hydraulic retention time of 2 minutes, with complete regeneration. In addition, a novel electropervaporative nitrogen capture technology was developed. Further larger scale testing and development of all technologies is required to ensure their feasibility in a real mining site.

A follow-up period in lysimeters showed that the explosives originated nitrogen content of left over stones from natural stone quarrying is relatively low and ca. half of the nitrogen is leached within the first weeks after detonation. The main sources of nitrogen are process and dewatering waters, irrespective of the scale of extractive activity. The total potential nitrogen load to the environment depends on the scale and type of the activity as well as the type of explosives used. In addition to factors related to the activity itself, the overall nitrogen management should take into account the background concentrations and sensitivity of the local ecosystem.

Tiivistelmä

Kaivannaistoiminnan typpipäästöjen hallinta

Miniman-hankkeen loppuraportti

Tekijät: Johannes Jermakka, Elina Merta, Ulla-Maija Mroueh, Helena Arkkola, Sini Eskonniemi, Laura Wendling, Jutta Laine-Ylijoki, Elina Sohlberg, Hanna Heinonen, Tommi Kaartinen (VTT); Jaakko Puhakka, Minna Peltola, Stefano Papirio, Aino-Maija Lakaniemi, Gang Zou, Anna Ylinen, Francesco di Capua (TUT); Raisa Neitola, Henrik Gustafsson, Tero Korhonen, Teemu Karlsson, Tommi Kauppila, Janita Laakso, Pekka Mörsky (GTK)

Asiasanat: kaivokset, louhimot, räjähdysaine, nitraatti, ammonium, vesienkäsittelyteknologiat

Suomen kaivannaisteollisuuden kasvu lisää tarvetta tutkia ja seurata erilaisia ympäristövaikutuksia sekä tiedostaa ympäristöasiat yhä paremmin osana toimintaa. Räjähdysaineista tai kaivosprosessista ympäristöön vapautuvalla typellä voi olla negatiivisia ympäristövaikutuksia. Tekesin Green Mining -ohjelman ja teollisuuden rahoittamassa MINIMAN-projektissa pyrittiin luomaan kattava näkemys kaivannaistoiminnan typpikysymyksestä. Projektissa kerättiin tietoa kaivosten ja louhimojen ympäristöissä esiintyvistä typpiyhdisteistä ja kehitettiin teknologioita typpipitoisten vesien käsittelyyn.

Teknologiaselvityksen perusteella projektin teknologiakehityksen kohteiksi valittiin selektiivinen sorptio, elektrokemiallisesti avustettu membraanierotus sekä biologinen käsittely. Denitrifikaatio- ja nitrifikaatiokokeet synteettisellä kaivosjätevedellä laboratoriomittakaavassa osoittivat, että denitrifikaatio oli mahdollista matalassa pH:ssa (2,5) ja lämpötilassa (7 °C). Nitrifikaatio oli herkempi pH:n vaihteluille. Molemmat prosessit sietivät metalleja (Fe, Ni, Co and As). Adsorptiokokeissa zeoliitin havaittiin poistavan tehokkaasti ammoniumtyppeä 2 min hydraulisella viipymällä, ja materiaali saatiin regeneroitua täydellisesti. Projektissa kehitettiin lisäksi uudenlainen elektropervaporatiivinen menetelmä typen talteen ottamiseksi. Suuremman mittakaavan testausta ja kehitystyötä tarvitaan, jotta voidaan varmistua teknologioiden soveltuvuudesta kaivosympäristöön.

Lysimetrikokeiden perusteella luonnonkivilouhimon sivukivien räjähdysaineista peräisin olevan typen pitoisuus on melko matala, ja noin puolet typestä huuhtoutuu räjäytyksen jälkeen jo muutamassa viikossa. Riippumatta kaivannaistoiminnan mittakaavasta prosessi- ja kuivatusvedet ovat pääasiallisia typen lähteitä. Ympäristöön kohdistuvan kokonaistyppikuorman suuruus riippuu toiminnan mittakaavasta ja luonteesta sekä myös käytettävien räjähdysaineiden ominaisuuksista. Itse kaivostoimintaan liittyvien tekijöiden lisäksi typen hallinnassa tulisi ottaa huomioon ympäristön taustapitoisuudet sekä paikallisen ekosysteemin herkkyys.

Preface

This publication presents an overview and conclusions of the project “Solutions for Control of Nitrogen Discharges at Mines and Quarries” (MINIMAN), aiming at a holistic understanding and technology development regarding nitrogen compounds in mining waters.

The MINIMAN-project was co-funded by Tekes – the Finnish Funding Agency for Innovation, Ekokem-Palvelu Oy, Kemira Oyj, Outotec Finland Oyj, Yara Suomi Oy, Agnico-Eagle Finland Oy, FQM Kevitsa Mining Oy, Outokumpu Chrome Oy, Nordic Mines Oy, Nordkalk Oy Ab, Kiviteollisuusliitto ry / The Finnish Natural Stone Association, BK-Automation Ky, Infra ry, VTT Technical Research Centre of Finland Ltd (VTT), GTK Geological Survey of Finland (GTK) and Tampere University of Technology (TUT).

The steering group consisted of the following persons: Mika Martikainen, Kemira Oyj, chairman (until 15.3.2013), Juha Saari, Kemira Oy, Chairman (15.3.2013–2.10.2013); Anita Alajoutsijärvi, Agnico-Eagle Finland Oy, vice-chair (until 2.10.2013); Chairman (from 2.10.2013); Jussi Ruotsalainen, Kemira Oyj (from 2.10.2013); Anita Salo, BK-Automation Ky; Jan Österbacka, Ekokem-Palvelu Oy; Eija Ehrukainen, Infra ry; Ulla Syrjälä, Kevitsa Mining Oy; Olavi Selonen, Kiviteollisuusliitto ry; Juha Koskela, Nordic Mines Oy (until 3.10.2012), Riina Mäkelä Nordic Mines Oy (from 15.3.2013); Tua Welin, Nordkalk Oy Ab; Samuli Nikula, Outokumpu Chrome Oy; Antti Salokannel, Outotec Finland Oy; Jouni Torssonen, Yara Suomi Oy; Kari Keskinen, TEKES; Harry Sandström, Spinverse Oy; Juhani Itkonen, Pohjois-Suomen AVI; Eva Häkkä-Rönnholm, VTT (until 3.10.2012), Olli Salmi, VTT (from 3.10.2012); Pekka Mörsky, GTK and Jaakko Puhakka, TUT.

The project work was conducted at three research institutions. At VTT the research was supervised by Principal Scientist Ulla-Maija Mroueh and the working group included Research Scientist Johannes Jermakka, Research Scientist Hanna Heinonen, Senior Scientist Jutta Laine-Ylijoki, Research Scientist Elina Merta, Research Scientist Helena Arkkola, Senior Research Technician Sini Eskonniemi, Research Scientist Elina Sohlberg, Senior Scientist Minna Vikman, and Senior Scientist Laura Wendling. At Tampere University of Technology the research was supervised by Professor Jaakko Puhakka and the working group included Postdoctoral researcher Minna Peltola, Postdoctoral researcher Stefano Papirio, Postdoctoral researcher Aino-Maija Lakaniemi, PhD candidate Gang Zou, M.Sc. student Anna

Ylinen and M.Sc. student Francesco di Capua. At GTK Geological Survey of Finland the research was supervised by Senior Scientist Pekka Mörsky and the working group included Senior Scientist Raisa Neitola, Research Scientist Henrik Gustafsson and Research Scientist Tero Korhonen, Geologist Teemu Karlsson, Chief Scientist Tommi Kauppila and Research Scientist Janita Laakso.

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1. Introduction

In early 2010s, the Finnish mining industry was in a period of rapid growth. The increased extraction of mineral resources places added pressure on the environmental issues. Explosive usage has been shown to release significant concentrations of nitrogenous compounds to the environment. In addition, certain mineral processing activities can generate significant nitrogenous contamination. The tightening environmental permit requirements for nitrogen compounds in mine waters increase the need for water treatment. In addition, high nitrogen content in waste rock may affect its classification and thus its further utilization.

The MINIMAN project sought to gather essential data on nitrogenous compounds present in the environments of mines and quarries, and to develop treatment technologies to allow the Finnish extractive industry to increase the use of explosives in a sustainable manner. Furthermore, by collecting and creating new knowledge the project aimed at a more holistic view on the nitrogen issue in mining and other extractive industries.

1.1 Project background

The excessive release of nutrients from municipalities and industrial activities to the environment can cause eutrophication in the receiving waterways. Nitrate ion is the primary source of nitrogen for aquatic plants, thus inducing eutrophication but elevated levels may also be toxic to aquatic animals.

The spreading of nitrogenous compounds into water and their incorporation into mineral materials is a common challenge in the extractive industries. Most minerals and rocks contain relatively low concentrations of nitrogenous compounds. However, typical explosives and leaching processes, especially cyanide leaching, used in mining activities can release a range of nitrogen-containing compounds of environmental concern. The rate of explosive-originated nitrogen discharges depends e.g. on the hydrological conditions present at the site. In the Nordic conditions, the seasonal variations in precipitation and temperature may play a significant role in the nitrogen loading. Different sources report variable percentages (1–6%; 12–28%; Morin and Hutt 2009) for nitrogen that is released from explosives to the environment. Once in environment, the nitrogen can convert to different species (nitrate, nitrite, ammonium, nitrogen gas), depending on the redox conditions and biological activities.

Nitrogen emissions are getting more attention in the environmental permit requirements for mines increasing the need for water treatment. The water treatment technologies currently utilized at mines are necessarily not optimized to remove nitrogen. Thus, development of water treatment technologies for nitrogen removal is needed. ‘Nitrogen smudging’ (contamination by explosive originated nitrogen compounds) of otherwise mineralogically and chemically inert waste rocks of good technical quality hinders the utilization of these product streams. This is an important economic and environmental issue at several quarries and mines.

1.1.1 Overview of different sectors within extractive industry

The extractive industry covers different sectors utilizing natural mineral resources. The impact assessment report on the Finnish Mineral Cluster (Hernesniemi et al. 2011) defines the extractive industry to include mining, aggregate production and natural stone quarrying.

Mining includes the extraction of metallic ores as well as industrial minerals. Mines produce concentrates to be further processed in relevant industries. The processing of concentrates to metals and industrial mineral products mainly takes place in Finland. In 2012 metallic ores were extracted at 12 mine sites and industrial minerals at ca. 30 sites. The boom of the mining sector relates specifically to the extraction of metallic ores. The basic legislative framework of mines includes the Mining act and the Environmental protection act. The Mining act covers also the production of industrial stones (soap stone and mineral wool) and extraction of gem stones. Altogether sites under the Mining act numbered 46 (TEM 2013). (Finland’s Mineral Strategy 2010; Kananoja et al. 2013; Hernesniemi et al. 2011)

Aggregates include natural sand and gravel as well as crushed rock which fulfil certain quality specifications. These materials can be further processed to different products, e.g. concrete or asphalt. Aggregate production is the largest sector in the Finnish extractive industry, measured either by revenue, production rate or the amounts of personnel. Typically aggregate production is local activity, and the number of enterprises (2011) on the sector exceeds 400. Aggregate production is mainly regulated by the Land extraction act, the Environmental protection act and the Water act if relevant. (Kananoja et al. 2013; Hernesniemi et al. 2011)

In natural stone quarrying large stone blocks are extracted from the bedrock. The sector further mechanically processes the material into products, such as raw construction stones (blocks) or boards. Natural stone products are used in building claddings, indoor decoration (floors, staircases, fireplaces) and in environmental construction projects. Finnish bedrock contains several rock types, e.g. granites, slates and soap stone that are suitable for natural stone quarrying. In natural stone quarrying the amount of left over stone is high due to the high product quality requirements. Around 200 companies operate within the Finnish natural stone industry. Natural stone quarrying is mainly regulated by the Land extraction act and the Environmental protection act. However, soap stone, limestone and marble quarrying fall in the scope of the Mining act. (Kananoja et al. 2013; Finland's Mineral Strategy 2010)

1.2 Project targets

The target of MINIMAN project was to create holistic solutions for nitrogen control in extraction activities. The project generated new know-how on the behaviour of N compounds at mines and quarries to facilitate better understanding of the nitrogen discharge issue. Advanced technologies were developed for the removal of nitrogen compounds from mine waters with the specific focus on the characteristics of mine water.

The subsequent objectives of the project were to help the extractive industry to enhance their operational preconditions and to generate new possibilities for service and technology businesses.

1.3 Project realization

1.3.1 Project partners and their responsibilities

The project work was realized in cooperation of VTT, GTK and TUT. VTT coordinated the project, studied general aspects of nitrogen management and carried out research tasks related to chemical characterization of materials as well as development of water treatment technologies utilizing physical-chemical methods.

GTK investigated and compared the sources and balances of explosives-originated nitrogen compounds at mines and quarries of different sizes. Furthermore, GTK also focused on the 'nitrogen smudging' problem of waste rocks and studied the intensity, evolution and chemical characteristics of their nitrogen contamination and participated in the development of water treatment methods.

TUT was responsible for developing nitrification and denitrification bioprocesses for treating nitrogen containing waste streams from the extractive industry.

1.3.2 Dissemination and networking

In addition to the final report at hand, the results of the project have been or will be published or presented in a number of media. Appendix A gives a detailed list of publications.

Several visiting researchers participated in the MINIMAN project work. Senior Scientist Laura Wendling from CSIRO, Australia worked at VTT in 04–10/2012 contributing on the planning of experimental sorption studies and on the literature review on water technologies. TUT hosted international researchers Stefano Papirio, Francesco di Capua, Zou Gang, Emre Oguz Koroglu and Mehmet Cakmakci, who participated in the nitrification/denitrification studies.

Research Scientist Johannes Jermakka from VTT worked as an exchange researcher in the University of Queensland in 03–06/2013 concentrating on the electrochemical removal of nitrogen.

Other international contacts of the project include research collaboration with the University of Luleå aiming at the exploitation of synergies with the research programme “Smart Mine of the Future” (SMIFU). Meetings in Espoo (05/2012) and in Kiruna (02/2013) were organized to facilitate exchange of experiences and networking.

2. Nitrogen sources and behaviour in mining

Nitrogen is a common element in the nature, constituting the majority of earth's atmosphere as well as playing a key role in all organic compounds as one of the three macronutrients. Nitrogen has a complex chemistry with a wide range of stable oxidation states (-3 to +5) (see Figure 1). It is part of numerous organic and inorganic compounds and reactions.

Nitrate, NO_3^-, is the natural stable and non-reactive degradation end product of nitrogen in the environment. It is present in all natural waters in low quantities. Increased concentrations in aquatic systems cause eutrophication, but are not directly harmful to organisms. Nitrite, NO_2^-, is a harmful unstable precursor to nitrate but is usually present in very minute concentrations.

Ammonia, NH_3, is the reduced form of nitrogen in the nature, an important component of natural nitrogen cycle and the main source of biologically available nitrogen. Ammonia and its ion form ammonium, NH_4^+, have a pH determined equilibrium in aquatic systems with ammonia dominating under high pH. Ammonia is very toxic to aquatic organisms and thus the levels of ammonia are very low in natural waters.

This section gives a brief overview on nitrogen emissions in mining. For more information, see the MINIMAN literature report "Nitrogen compounds at mines and quarries. Sources, behaviour and removal from mine and quarry waters" (Jermakka et al. 2015).

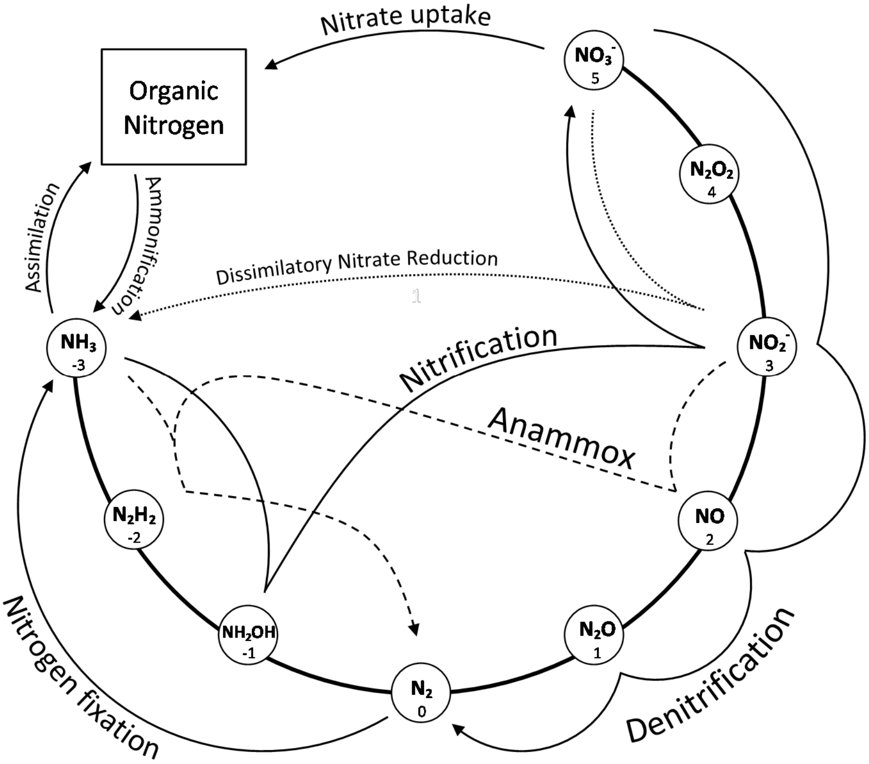


Figure 1. Common nitrogen pathways and forms (Jermakka et al. 2014).

2.1 Nitrogen released in mining

Nitrogen is extensively used in mining explosives. Explosives are chemical compounds or mixtures which release large quantities of heat and gases when detonated. The reaction is initiated mechanically and by heat, typically using an explosion starter. (OAMK 2007; Forsberg and Åkerlund 1999)

While several types of explosives are available for mining activities, all contain nitrogen in some form. A rule of thumb is that around 25% of the explosive mass is elemental nitrogen. 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. However, in a time frame long enough, all N contained in explosives is released to the environment in some form. (Forsyth et al. 1995; Halonen 2012)

Today the total consumption of explosives in Finland is around 50 000 t/a, and the usage has approximately doubled in the past decade. It is evident that the boom of the mining industry has to do with the recent rise. 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 open pit mining the specific explosives usage (/tonne of rock) is somewhat lower than in underground mining.

The main source for nitrogen emissions in mining are explosive residues due to incomplete detonation and leaching, accounting for approximately 2–10% of the total explosive usage. Other sources for nitrogen emissions to waterways and atmosphere can be cyanide used in the ore processing and nitrogen present in the waste rock or ore itself.

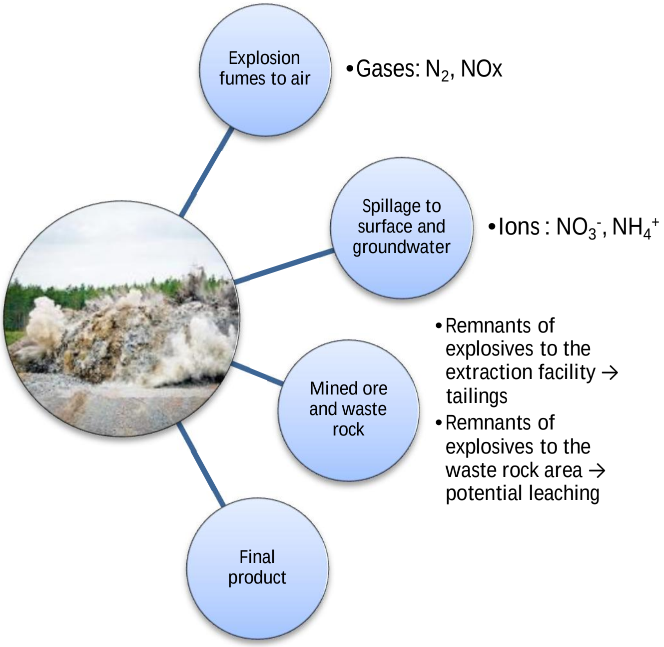


Figure 2. Routes of explosive originated nitrogen to the environment. Photo: Oy Forcit Ab.

The potential of nitrogen to release into the water system from explosion site depend on the type of explosives used, local water conditions, explosives management and overall efficiency of the blasting operations. (Forsyth et al. 1995) 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)

The reaction gases released to air after detonation contain nitrogen as NO_2. Other reaction products may also occur, such as phthalates, aliphatic hydrocarbons or benzene. (Brochu 2010) The generation of NOx compounds usually indicates the occurrence of improper or incomplete detonation reaction (Rowland et al. 2001). The reasons for fume generation are somewhat similar to those causing discharges to water.

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.

2.2 Nitrogen in mining in comparison with other nitrogen flows

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 were 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.

3. Technologies for nitrogen removal and recovery from mine wastewaters

Nitrogen removal from wastewaters is a common procedure in industrial and municipal wastewater treatment with a number of full scale and experimental technologies available. However, many of the currently available technologies 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 needed for the treatment of mine wastewaters with a range of physico-chemical characteristics. This section gives a brief overview on the technologies investigated in the MINIMAN-project. For more detailed information, see the MINIMAN literature report “Nitrogen compounds at mines and quarries. Sources, behaviour and removal from mine and quarry waters” and the related article. (Jermakka et al. 2015, Jermakka et al. 2014)

3.1 Biological methods

Biological methods are widely used in wastewater treatment and potentially offer an effective and inexpensive alternative for the removal of nitrogen from mining wastewaters. A distinct advantage of biological methods utilizing the natural nitrogen cycle 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.

Biological nitrification and denitrification are commonly performed in municipal wastewater treatment for nitrogen removal. The conventional treatment systems are not readily suited for mine wastewaters as they are based on an activated sludge process with high organic carbon substrate input and are sensitive to temperature and toxicity changes.

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 include the relatively high land area requirement for the 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. Constructed wetlands are commonly used worldwide in mine wastewater treatment but there are limitations in their applicability in subarctic or arctic conditions.

Nitrification and denitrification can be more efficiently maintained in "controlled engineered systems" such as bioreactors. As a consequence of the increasing interest in applying these biological processes for mine wastewater and acid mine drainage treatment, many different bioreactor configurations have been designed. Fluidized-bed reactors are surely a promising alternative biofilm process for biological wastewater treatment thanks to their advantages such as: 1) efficient biomass retention; 2) higher mass transfers and reaction rates; 3) large surface area for biofilm formation; 4) enhanced contact between biomass and substrates; 5) great resistance to inhibitors (i.e. heavy metals commonly present in mining effluents).

Anammox is a quite recent process used for nitrogen removal from wastewaters. It is based on autotrophic granular bacteria that utilize nitrate to oxidize ammonia into nitrogen. The technology potentially offers numerous advantages for wastewater treatment when applied at a large scale due to its low energy and no external carbon requirements. Further advantages of the Anammox process 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. The Anammox method is still fairly new, has a long start-up time and is sensitive to temperature, pH and toxicity and is thus not suitable for subarctic conditions. Anammox could however become suitable for selected mine wastewaters as the technology matures and can be proofed for different streams.

In summary, numerous processes and treatment methods are available for biological nitrogen removal from wastewaters. Based on the particular water characteristics and environmental conditions, one process can be preferred to other ones in order to enhance the removal efficiencies.

3.2 Physico-chemical methods

In addition to biological processes, physical-chemical treatment processes have been proposed to remove nitrogen from mine waters. The chemical processes are regarded as less sensitive to changes in temperature and effluent quality which are important assets when dealing with water streams from mines.

Air stripping is the most common ammonia removal method in the industry. The solution pH is risen to >10, the temperature is increased and the liquid is contacted with an air stream to move the ammonia into the gas stream. While broadly used in small high concentration volumes, it is not feasible for large streams due to pH and temperature requirements.

Water soluble nitrate and ammonia can be separated by membrane filtration, using nanofiltration or reverse osmosis membranes. Nanofiltration can remove ions partially (25–60%) and reverse osmosis almost completely (>96%). Membrane filtration is used for the treatment of sulphate and metals containing mine process water in Finland but high energy demand, potential fouling problems and need for pretreatment limit the feasibility of the technology for removal of low concentrations of nitrogen from mine wastewaters (e.g. Häyrynen et al. 2008).

Electro-oxidation and electro-denitrification are methods of nitrogen removal using an electrochemical cell-reactor. The electro-oxidation of ammonia is a full scale technology based on indirect oxidation in a high chloride content water, where the chloride ion forms hypochlorite at the anode, oxidizing ammonia directly into nitrogen gas. This electro-oxidation can be linked with cathodic electro-denitrification at the anode, reducing nitrate into nitrogen gas and ammonia. Full scale applications of the method have been developed for industrial use and include trademarks Elonita and AmmEl. Electrochemical oxidation technologies can be feasible for selected mine wastewater streams with high chloride and ammonia concentrations. For bulk mine wastewater, a concentration step is required.

Electrochemistry can be linked with membrane technologies. Electrodialysis removes cations and anions through ion exchange membranes. A commercial electrodialysis application is DesEl, that can be used for mining wastewaters, but is potentially not feasible for lean streams. A novel technology developed and tested in the MINIMAN project is an electropervaporative ammonia capture, which combines electro-denitrification and local ammonia stripping at the cathode.

Bio-electrochemical systems, including microbial fuel cells and microbial electrolysis cells, as well as electro-coagulation methods show potential for future applications for nitrogen removal, but both technologies are still in early laboratory phase and not applicable in short term.

Sorption technologies offer a wide range of methods for ion or particle removal from water streams. For nitrogen removal from mine wastewater, a selective sorbent is required as mine wastewater typically has high ion content and methods targeting all ions and particles are not feasible. There are a wide variety of sorption materials available, including low cost industrial by-products such as ashes, slags and waste rocks, activated carbon and non-activated carbon-based materials, and mineral ion exchange materials, especially zeolite. For mine wastewater treatment, zeolite is identified as the most promising sorption material as it is a natural mined mineral with a specific affinity for ammonium.

3.3 Technologies selected for further study

Based on the technological survey, two physico-chemical technologies were selected for laboratory development in MINIMAN project by VTT and GTK: a novel electropervaporative ammonium capture technology and sorption technologies, focusing on zeolite sorption of real mine wastewater. A compilation of physico-chemical technologies and their suitability is presented in Table 1.

Furthermore, TUT investigated denitrification and nitrification processes of mining water with the specific focus on the parameters relevant in real mine environment, such as toxicity effects, temperature and acidity. Fluidized-bed reactors (FBRs) were used as they have been observed being effective in mining water treatment.

Table 1. 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

4. Results of water treatment studies

4.1 Biological treatment

The use of biological processes has gained increasing interest. Microorganisms are intimately involved in metal and nitrogen biogeochemistry with a variety of processes that can be used in environmental biotechnology applications. Denitrification and nitrification are the bioprocesses used for nitrate and ammonium removal from waters, respectively.

Denitrification uses nitrate as electron acceptor and simple organic compounds as electron donors (Dahab and Lee 1988; Gayle et al. 1989). Mine waters require organic compound supplementation for denitrification (Borden et al. 2012). Among the simple electron donors, ethanol has resulted in higher denitrification rates, reaction completeness and microbial growth (Christensson et al. 1994; dos Santos et al. 2004). The denitrification reaction with ethanol is expressed by the following equation 1:

$$12NO_3^- + 5CH_3CH_2OH \rightarrow 6N_2 + 10CO_2 + 9H_2O + 12OH^- \qquad (1)$$

Nitrogen gas is produced with OH^- ions that have the potential of neutralizing acidic pH. Incomplete nitrate reduction results in nitrite accumulation, see equation 2:

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \qquad (2)$$

In this case, nitrite still represents nitrogen pollution.

Nitrification is carried out by several species of autotrophic microorganisms capable to oxidize ammonium to nitrate via nitrite. The overall reaction is expressed by the following equation 3:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \qquad (3)$$

Oxygen is needed in order to maintain the reaction. Moreover, enough alkalinity is required in the water to balance the acid produced by nitrification. Nitrate can be reduced to nitrogen gas through biological denitrification as mentioned above.

Denitrification and nitrification of mine waters can be affected by acidity and significant concentrations of heavy metals such as Fe, Cu, Ni, Co and As. Depending on metal concentration, heavy metals have different effects on microbial processes. They can be either essential as trace nutrients or toxic by altering enzyme conformation and blocking important functional groups (Gikas 2007; Giller et al. 2009). Moreover, over long-term exposure, microorganisms may develop metal resistance, tolerating high metal concentrations (Bruins et al. 2000; Gadd 2010; Holtan-Hartwig et al. 2002).

In the present work, four fluidized-bed reactors (FBRs) and numerous batch bioassays were performed to study denitrification and nitrification. FBRs have been observed to be very efficient for mining water treatment due to the great resistance to inhibitors and the potential of recycling the produced pH-buffered water. The main goal of this work was to maintain denitrification and nitrification by simulating real mining conditions (e.g. low pH's and high metal concentrations). In particular, the research on denitrification aimed at: 1) delineating the effects of temperature, pH and hydraulic retention time (HRT) on denitrification in two FBRs; 2) evaluating FBR capacity of treating acidic wastewater; 3) optimizing the ethanol/nitrate ratio for denitrification; 4) assessing the effects of iron, copper, nickel and cobalt on denitrifying microorganisms in batch bioassays; 5) evaluating Ni impact over long period in the FBRs under acidic and neutral conditions.

Nitrifying cultures were enriched in FBR and then used in batch tests for evaluating As effects on nitrification. Arsenic speciation was monitored during nitrification. For both denitrifying and nitrifying applications, the enriched microbial cultures were identified using a polymerase chain reaction – denaturing gradient gel electrophoresis (PCR-DGGE) approach.

4.1.1 Denitrifying applications

4.1.1.1 Batch bioassays

Batch experiments were performed to assess the effect of acidic pH, iron, copper, nickel and cobalt concentration on the bacterial activity at room temperature (22°C) in serum bottles of 117 mL. The pH of the solution was adjusted to the desired value using HCl. A stoichiometric ethanol/nitrate ratio (0.42:1 mol/mol and initial nitrate concentration of 200 mg/L) was used in the experiments aimed at evaluating the effect of the feed pH. Denitrification was monitored by measuring ethanol, nitrate, nitrite and pH (Figure 3) from samples taken every 1.5 h interval for a total duration of 9 h.

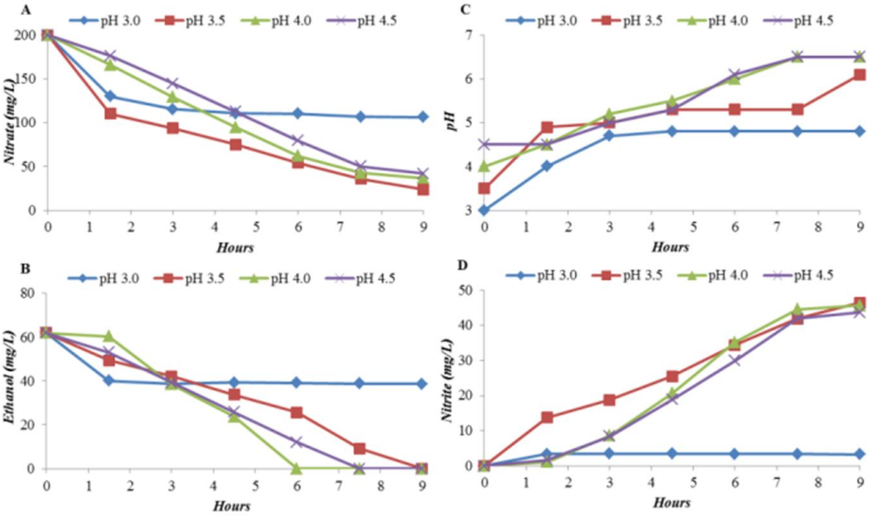


Figure 3. Effect of pH on nitrate (A) and ethanol (B) removals, pH (C) and nitrite (D) accumulation in batch assays.

Figure 3 shows that nitrate and ethanol removals and nitrite accumulation were similar at initial pH's of 3.5–4.5 and were inhibited at initial pH of 3. Accounting for the initial rapid pH increase in the first 3 h, the actual inhibitory pH for denitrification was 4.8.

The impact of iron, copper, nickel and cobalt on denitrification was studied at different initial metal concentrations at pH 7 (Figure 4, Figure 5). 200 mg/L of nitrate and 123 mg/L of ethanol (double stoichiometric amount) were added to the bottles. pH was maintained stable by using a phosphate buffer solution. In order to allow metal oxidation and reach a constant dissolved metal concentration, the bottles were stored for 24 h and placed at 7–8°C to avoid any change in ethanol and nitrate concentrations. Afterwards, 10 mL of activated carbon/biofilm was added to the bottles and N_2 was used to get rid of oxygen in the solutions. Granular activated carbon covered by the denitrifying biofilm was collected from the operating FBR3 (see Section 4.1.1.2 for further information of the FBR). Samples for nitrate, nitrite, ethanol and soluble metals were taken at predetermined time intervals for a total duration of 24 h.

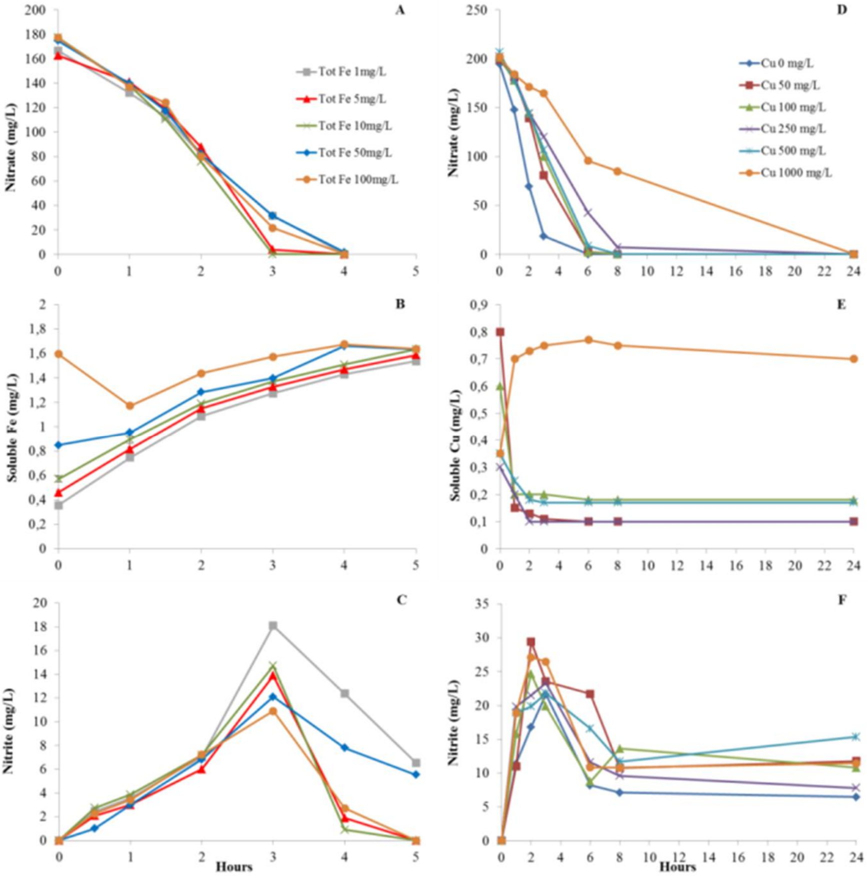


Figure 4. Evolution of nitrate (A,D), soluble Fe and Cu (B,E) and nitrite (C,F,) in iron and copper toxicity tests.

During the preliminary period, 98–99% of iron precipitated at pH 7 resulting in low and stable dissolved Fe concentrations ranging between 0.4–1.6 mg Fe_{TOT}/L. Iron supplementation stimulated denitrification increasing nitrate removal rate. This confirms the reports present in the literature that demonstrate the enhancement of denitrification in the presence of iron (Devlin et al. 2000; Nielsen and Nielsen 1998). In the present work, nitrate remained below the detection limit after 4 h in the bottles. Nitrite accumulated in the solution until 3 h followed by a sharp decrease after 4 h.

Unlike iron, Cu exhibited a higher toxicity on denitrifiers at all tested Cu concentrations. Added concentrations of 50, 100, 250 and 500 mg/L resulted all in an average dissolved Cu concentration of 0.15 mg/L. Nitrate removal rate was lower than in absence of copper, averagely resulting in 50% inhibition in the first 6 h. Denitrification was further inhibited at the highest soluble Cu concentration of 0.7

mg/L (1000 mg/L Cu added). After 8 h, nitrate removal only reached 57.2%, whereas nitrate was below the detection limit in 24 h. These results confirm the work of Ochoa-Herrera et al. (2011) that found a half maximum inhibitory concentration (IC50) of 0.95 mg/L Cu in biological wastewater treatment systems. Nitrite remained in solution and averagely ranged around 10 mg/L in all the bottles.

Figure 5 shows the fates and effects of nickel and cobalt on denitrification in batch environments. After the injection of microbial cultures in the bottles, Ni concentrations decreased from 1.2, 2.2, 5.4, 10.9, 50.0, 100.0 to 0.47, 0.62, 1.53, 3.52, 26.4, 75.2 mg/L, respectively, after 7 h. In the same period, Co concentrations clearly decreased from 0.5, 5.3, 20.2, 50.7, 86.6 to 0.23, 3.23, 10.49, 13.08, 25.90 mg/L, respectively. After 6 h, 90% of nitrate was removed at initial Ni concentrations lower than 50 mg/L, whereas nitrate removal only reached 35% in the bottle with 100 mg/L of soluble Ni. Nitrite accumulated until 5 h but then it sharply decreased at 6 h. On the contrary, in Co toxicity tests, soluble Co concentrations did not affect denitrification. Previous results reported that Co stimulated both microbial growth and COD removal in activated sludge at Co concentrations ranging from 0 to 50 mg/L and that 160 mg/L Co repressed microbial activity completely (Gikas 2007).

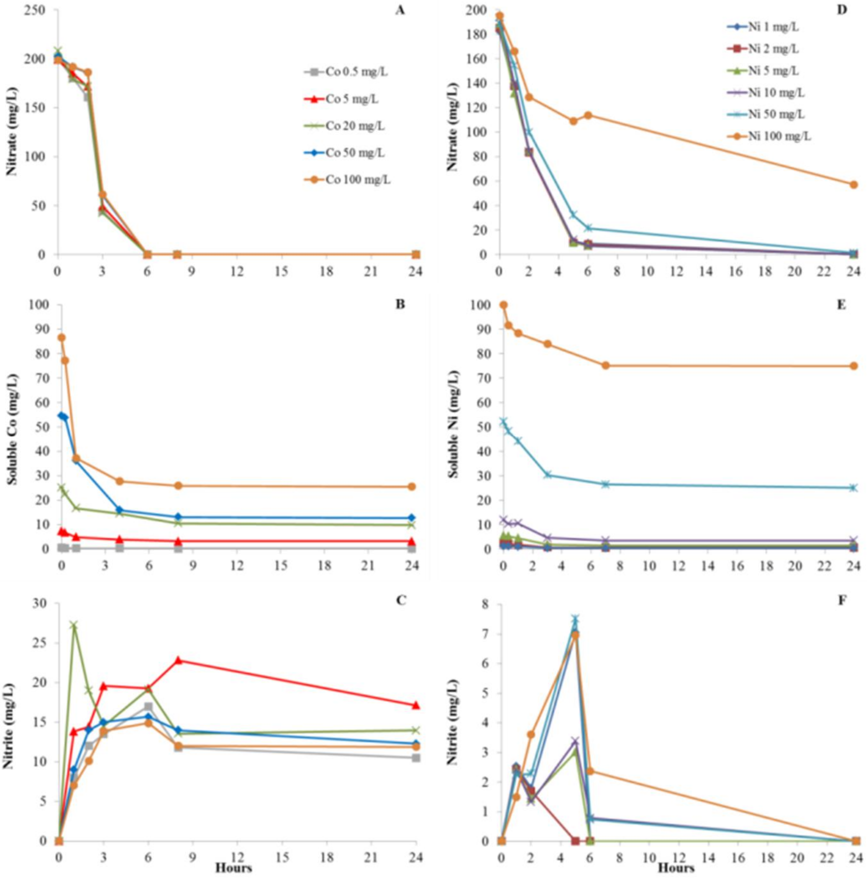


Figure 5. Nitrate (A,D), Co and Ni (B,E) and nitrite (C,F) profiles in cobalt and nickel toxicity tests.

Ethanol, fed two times in excess to nitrate, was consumed during the first 5 h in Fe, Cu, Ni and Co toxicity tests (data not shown).

4.1.1.2 Fluidized-bed reactors

Three laboratory-scale glass FBRs (volume 1.1 L) (Figure 6) were used to enrich and maintain denitrifying bacterial cultures as reported by Papirio et al. (2014a). Reactor 1 (FBR1) was operated at 7–8°C, and FBR2 and FBR3 were operated at 22 ± 2°C. FBR1 and FBR2 were used for studying process performance, while FBR3 was used for biomass enrichment for batch assays. Granular activated carbon (volume = 200 mL, particle size = 0.5–1 mm) was used as biomass carrier. The recirculation was adjusted to maintain the carrier fluidization at 25% by using a flow rate of 800 mL/min. FBRs were seeded with 240 mL of activated sludge (2.53 g VSS/L) from municipal wastewater treatment plant in Helsinki, Finland.

After seeding, a medium containing ethanol, nitrate and nutrients (Table 2) was flushed with nitrogen and fed to the FBRs.

Figure 6. Laboratory-scale fluidized bed reactor operated at 7–8 °C.

Table 2. Composition of the FBR nutrient solution.

Compound	Concentration (mg/L)
KH_2PO_4	50
$CaCl_2 \cdot 2H_2O$	20
$MgCl_2 \cdot 6H_2O$	150
$Na_2MoO_4 \cdot 2H_2O$	0.1
$MnCl_2 \cdot 4H_2O$	1.75
$CoCl_2 \cdot 6H_2O$	0.05

Removal of nitrate from the synthetic medium was investigated during three different experimental phases in FBR1 and FBR2 operated for 860 days under different operational conditions.

In the first experimental period (days 0–415), FBRs were studied with the aim to evaluate the effects of temperature, acidic pH, HRT and ethanol/nitrate ratio on denitrification and FBR performance. Figure 7 (B–C) shows FBR ethanol and nitrate removals and the pH evolution at 7–8°C and 22°C. Both reactors showed high removal efficiencies as effluent nitrate and ethanol mostly remained below their detection limits.

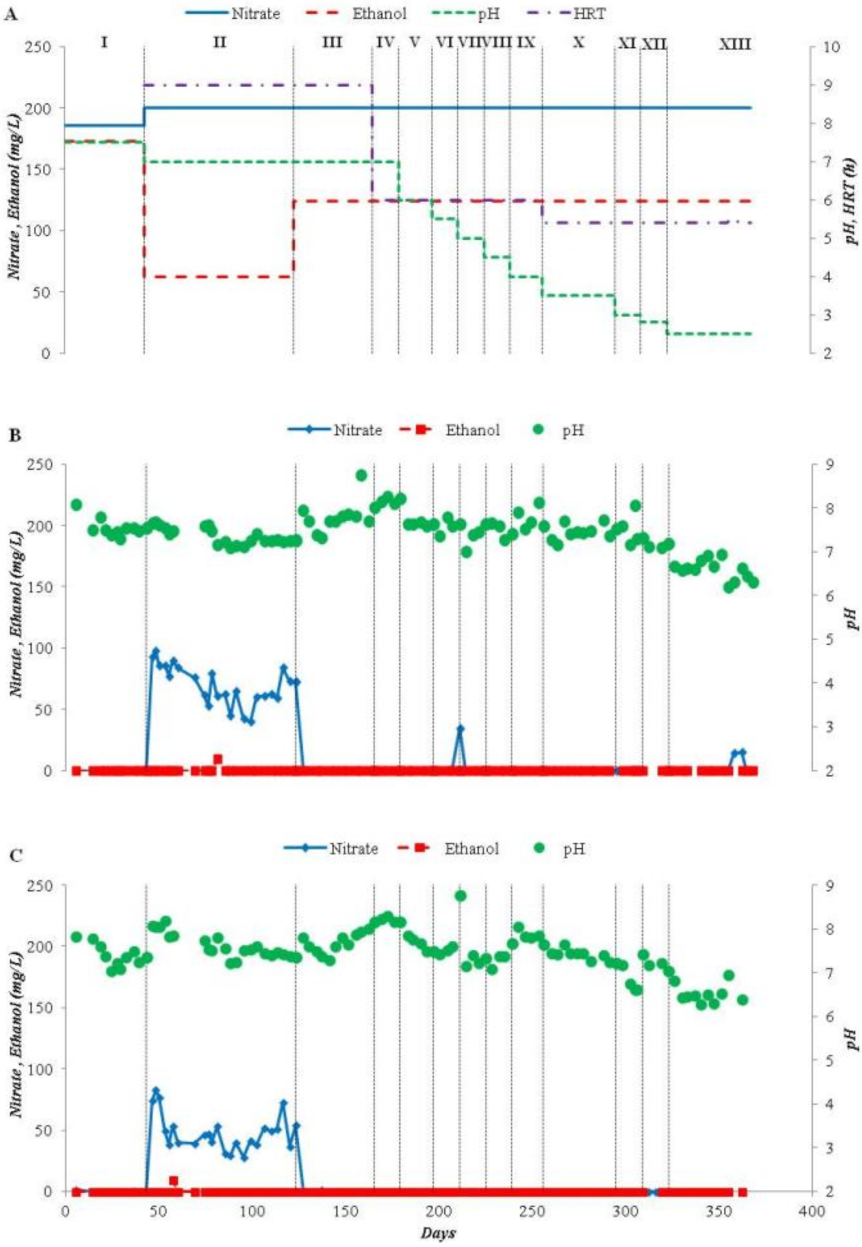


Figure 7. The effects of pH and HRT on denitrification in FBRs at 7–8°C (B) and 22°C (C).

From day 43 to 126, the FBRs were operated at a 9h HRT and a stoichiometric ethanol/nitrate ratio (0.42 mol/mol). This decreased the denitrification efficiencies.

The average nitrate concentration in the effluent increased to 69 and 49 mg/L at 7–8 and 22°C, respectively, accompanied by nitrite accumulation in both FBRs (Figure 8). Ethanol was completely oxidized although nitrate removal was incomplete.

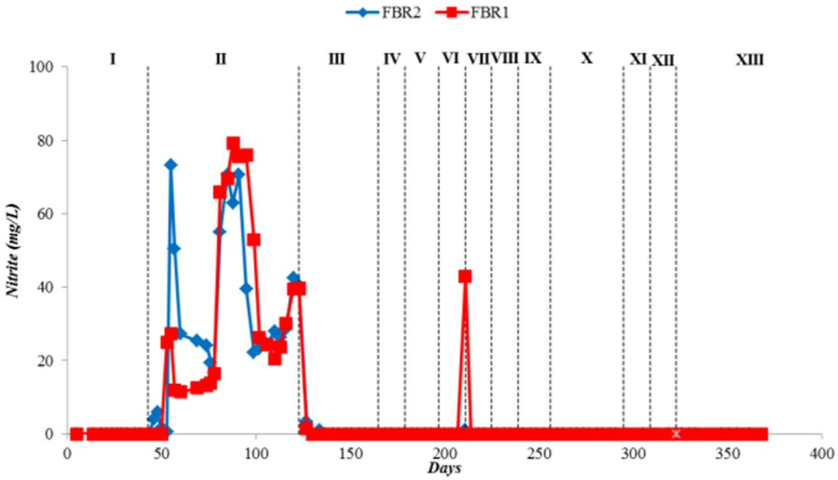


Figure 8. Nitrite accumulation if FBR1 (7–8°C) and FBR2 (22°C).

After increasing the feed ethanol/nitrate ratio to 0.83, nitrate was again removed. The present work demonstrated that the ethanol/nitrate ratio is the most critical parameter to control. The excess of ethanol over nitrate was needed for complete denitrification. When ethanol was fed to the system with an ethanol/nitrate ratio of 0.83 (mol/mol), 200 mg/L of nitrate were removed in FBR1 and FBR2 even with a feed pH of 2.5 and a 5.4 h HRT. Ethanol and nitrate remained below the detection limits and the production of alkalinity neutralized the acidic feed. The potential of the FBR technology for neutralizing acidic pH through biological alkalinity production and internal recycling was here demonstrated.

Over long-term continuous operation at 7–8 and 22°C, the FBRs performed similarly with the exception of days 43–126 when FBR2 responded faster to the feed and hydraulic condition changes. Temperature was demonstrated not to affect denitrification. Zaitsev et al. (2008) operated a denitrifying fixed-bed biofilm reactor at 5°C. Contrarily to this work, they reported unstable denitrification (30–70% of nitrate removal) during the first six months, most likely due to slow growth of methylotrophic denitrifying bacteria at 5°C. On the other hand, Martin et al. (2009) reported removal of 200 mg/L of nitrate in contaminated groundwater at a temperature of 6°C by ethanol injection.

During the second experimental period (days 416–567), Ni, a common metal in mining environments, was added twice to the feed solutions of both FBR1 and FBR2, first as $NiSO_4 \cdot 6H_2O$ and then as $NiCl_2 \cdot 6H_2O$, in concentration of 5.5 mg/L.

The first Ni injection was performed during days 416–460. Samples for Ni^{2+} analysis were taken three times a week. Biofilm coated-activated carbon was sampled once to measure the amount of Ni entrapped as reported by Zou et al. (2014). Figure 9 shows the nitrate and nitrite profiles in the FBR solutions from day 403 of operation.

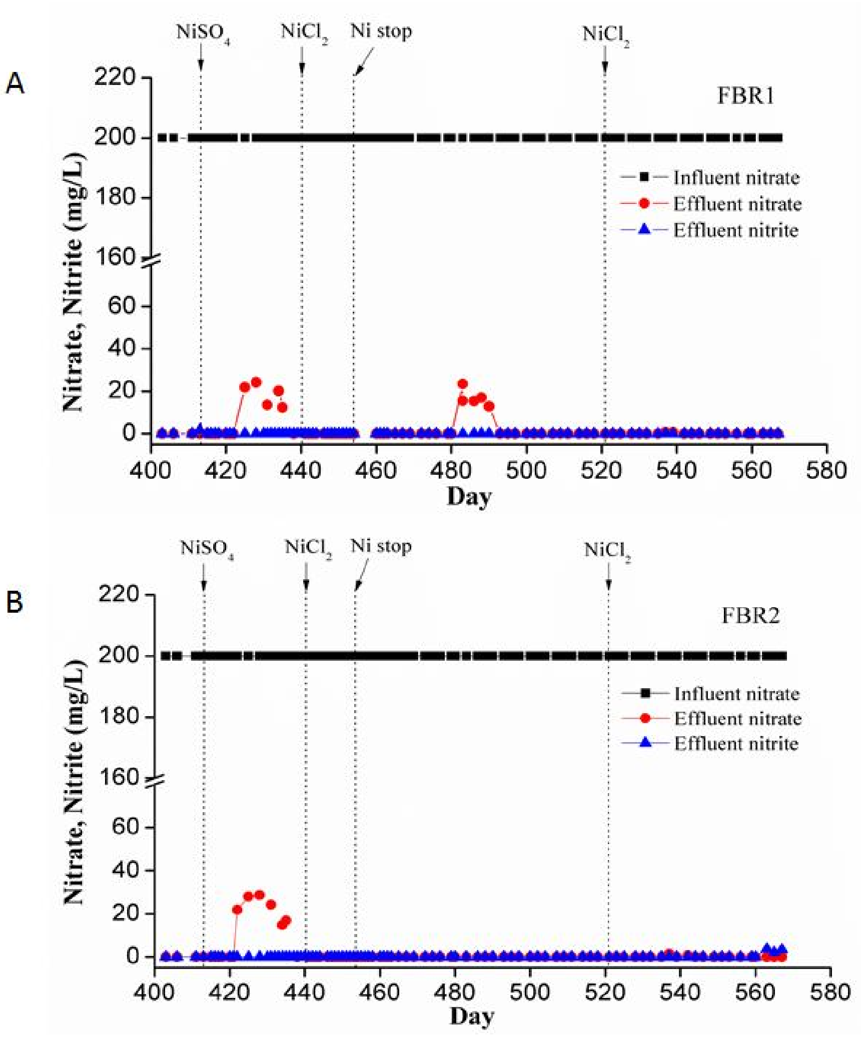


Figure 9. Nitrate and nitrite in FBR1 (A) and FBR2 (B) in presence of 5.5 mg/L Ni.

Effluent nitrate concentration first increased up to 25 mg/L on day 425 in both reactors, followed by decrease after 2 weeks. No nitrite accumulated during Ni injection period. The effluent pH gradually decreased to 5.6 and 5.4 on day 460 in FBR1 and FBR2 (Figure 10), respectively. On day 460, Ni injection was stopped. Nitrate and nitrite remained below the detection limits. In FBR1, pH rapidly increased to 6.2 again, whereas in FBR2 pH still decreased until the lowest value of 5.2 on day 490 (Fig. 7B). Finally, from day 502 on, in FBR2 pH increased until 6.5 on day 534.

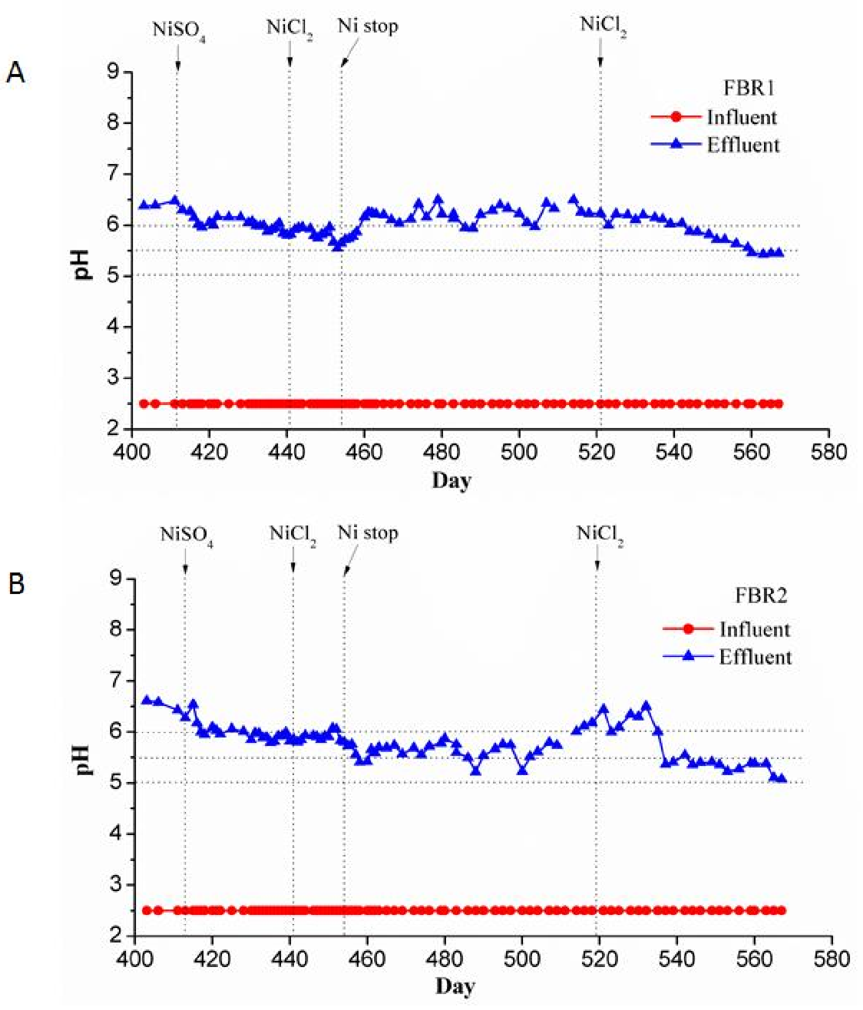


Figure 10. pH evolution in FBR1 (A) and FBR2 (B) during days 403–567.

On day 520, Ni was supplemented to the feed solution for the second time with no effects on nitrate reduction and nitrite accumulation (Figure 9). The main impact of nickel on denitrification was the effluent pH decrease both at 7–8 and 22°C (Figure

10). pH sharply decreased in FBR2, from 6.0 to 5.4 in two days, before keeping stable around 5.2, whereas only a slight pH decrease from 6.2 to 5.4 was observed in FBR1 in 47 days. This may be attributed to both nickel sulphide precipitation and nickel toxicity on denitrifiers.

Based on Ni mass balances, 31% and 23% of nickel precipitated in FBR1 and FBR2, respectively. Nickel sulphide (NiS) was the only possible Ni precipitate formed in the FBRs. Hydrogen sulphide was biologically produced by the reduction of 30 mg/L of sulphate present in the feed. NiS precipitation resulted in the production of acidity that partially repressed effluent pH increase.

The slow recovery of the process in FBR2 demonstrated that the pH decrease was also due to a partial inhibition of denitrification that resulted in less acidity consumption. Nickel possibly affected the last two steps of denitrification (NO conversion to N_2O and N_2O conversion to N_2) as also supported by Slater and Capone (1984).

Effluent Ni concentrations were as shown in Figure 11.

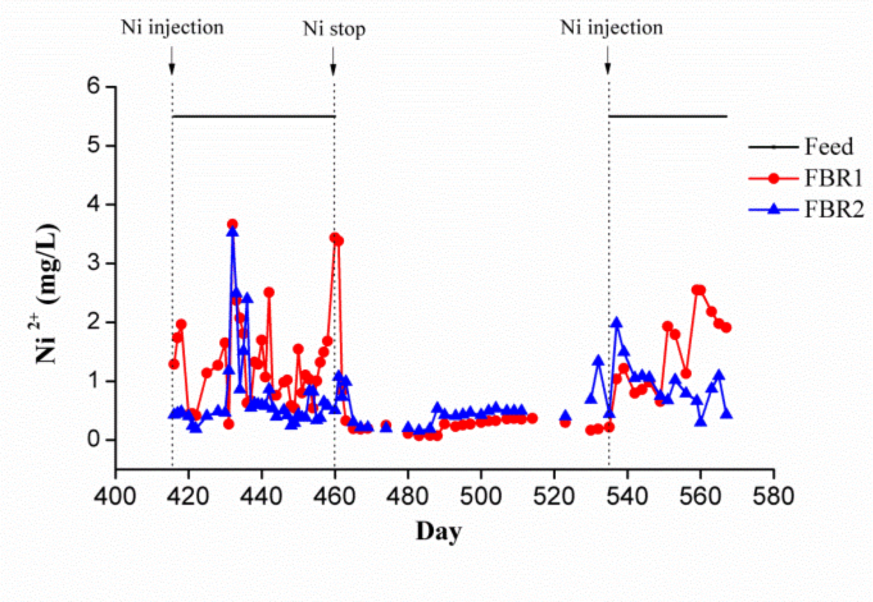


Figure 11. Feed and soluble Ni in FBR1 and FBR2 at feed pH of 2.5.

The actual soluble Ni concentrations inside FBR1 and FBR2 were on average 1.25 and 0.74 mg/L during the first injection and 1.49 and 0.92 mg/L, respectively, during the second injection. Under these conditions, nitrate and nitrite removals were not affected. FBR internal recirculation and nickel precipitation alleviated Ni effects on denitrifiers, resulting in nitrate and nitrite concentrations below the detection limits. In both FBRs, the only nitrate effects were observed when Ni was fed as sulphate from day 416 to day 446. This was likely due to activity of sulphate-reducing bacteria that competed with denitrifiers for ethanol, decreasing nitrate removal efficiencies.

The fate of Ni in FBRs was also estimated through mass balances. During days 415–460, 24% and 14% of the Ni injected was removed with the soluble effluent from FBR1 and FBR2, respectively. 38% and 37% of Ni injected was entrapped onto the biomass of FBR1 and FBR2, respectively. On average 31% and 23% of Ni precipitated as sulphide in FBR1 and FBR2, respectively. Effluent VSS concentrations were negligible resulting in non-significant Ni amounts entrapped onto the biofilm detached. The discrepancy of 7% and 26% found in FBR1 and FBR2 mass balances, respectively, was due to non-frequent sampling.

From day 633, Ni was supplemented to the FBRs at increasing concentrations at feed pH of 5.5. Initially, 10 and 20 mg/L of added Ni resulted in nitrate, nitrite and soluble Ni below the detection limits (Figure 12, Figure 13). When the feed Ni concentration was increased to 40 mg/L, soluble Ni in FBRs gradually increased up to 22 mg/L on day 686. A lower Ni concentration in the effluent indicated that nickel sulphide precipitation still occurred in both FBRs.

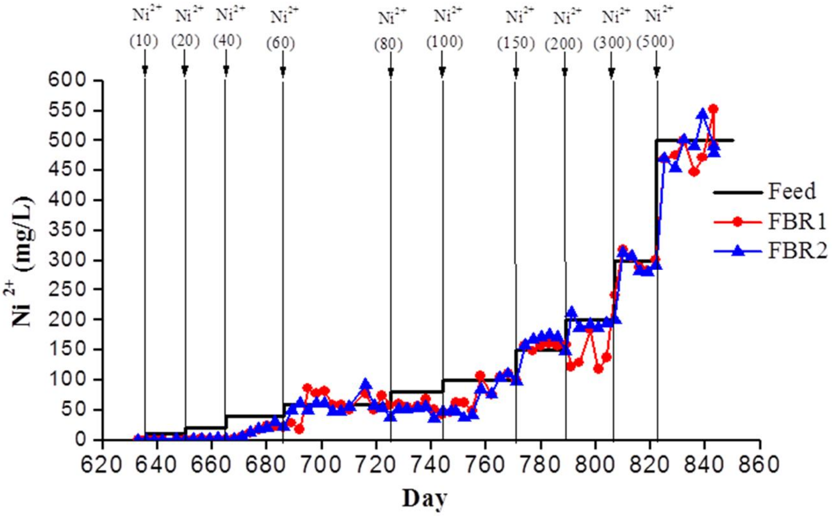


Figure 12. Feed and soluble Ni in FBR1 and FBR2 at feed pH of 5.5.

Denitrification and concomitant sulphate reduction were both maintained at feed Ni concentration up to 40 mg/L. Effluent pH was stable at approximately 7.2 in both FBRs (Figure 13C–D). When Ni was fed at 60 mg/L, nitrate and nitrite concentrations increased in both FBRs. Nitrate concentration reached 107 mg/L on day 695 and 101 mg/L on day 707 in FBR1 and FBR2, respectively (Figure 13A–B). Denitrification was partially repressed whereas sulphate reduction was completely inhibited by nickel. Nickel sulphide precipitation did not occur and Ni was removed with soluble effluent in both FBRs. However, after 34 days of adaptation to 60 mg/L Ni, denitrification recovered resulting in complete nitrate and nitrite removals in both FBRs, even at 80–500 mg/L Ni in the following experimental phases (Figure 13).

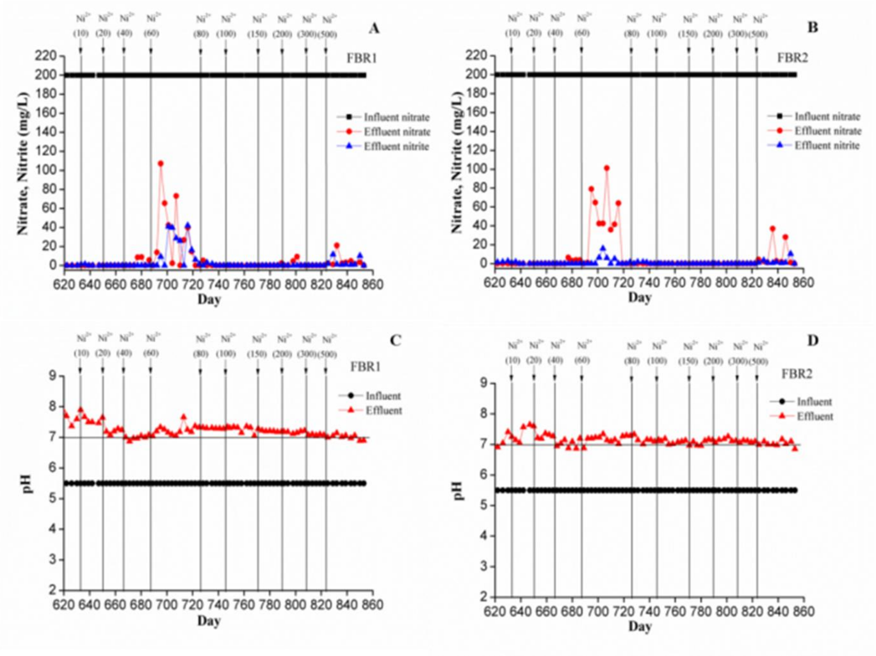


Figure 13. Effluent nitrate and nitrite (A,B) and feed and effluent pH (C,D) in FBR1 (A,C) and FBR1 (B,D).

4.1.1.3 Microbial community analysis

DGGE analysis was performed two times to reveal changes in the microbial communities at 7–8 and 22°C during the enrichment phase and operation of the FBRs (Figure 14). Dendrogram in Figure 14B shows the relationship between the bacterial sequences obtained by DGGE.

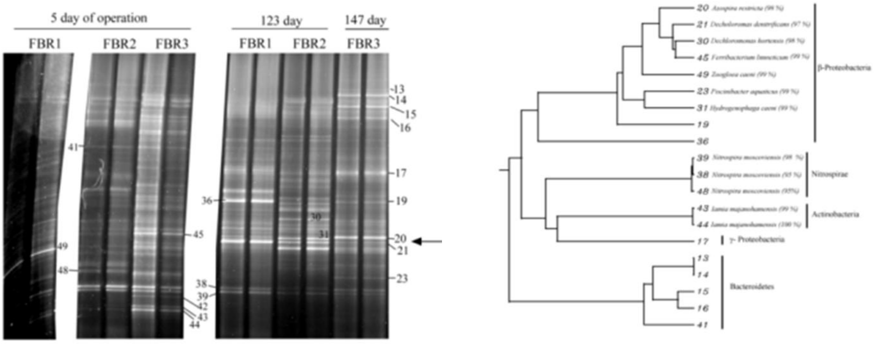


Figure 14. DGGE profiles of microbial cultures enriched on ethanol in FBRs (A); dendrogram showing the relationships between the bacterial sequences extracted from the DGGE gel.

The FBR1 and FBR2 communities significantly changed during the first 123 days of operation. One denitrifying bacterium *Dechloromonas denitrificans* (band 21) was present both at 7–8 and 22°C, indicating that this strain was mainly responsible for denitrification. Growth temperature reported for *Dechloromonas denitrificans* ranges from 5 to 36 °C (Horn et al. 2005). *Hydrogenophaga caeni* (band 31) was enriched to both FBRs, more intensively at 22°C than 7–8°C. This strain is not reported to be able for denitrification whilst it reduces nitrate to nitrite (Shao et al. 2009). *Hydrogenophaga caeni* was present at the end of period II when ethanol/nitrate ratio was decreased and nitrite accumulated.

Two bacterial strains *Nitrospira moscoviensis* and *Zoogloea caeni* found their niche in FBRs by utilizing nitrite and carbon dioxide. *Nitrospira* belonging to *N. moscoviensis* strain gains energy from oxidation of nitrite to nitrate using CO_2 as a carbon source (Hovanec et al. 1998). *Zoogloea caeni* previously isolated from activated sludge has shown to be capable for nitrate reduction to nitrogen gas but also nitrogen fixation (Chung et al. 2007).

In addition to denitrifiers, other ethanol-utilizing microorganisms were present as demonstrated by FBR performances and microbial profiling.

4.1.2 Nitrifying applications

4.1.2.1 FBR

The FBR scheme was as the one reported by Kinnunen and Puhakka (2004). An aeration unit was placed in the recirculation line and an aquarium pump was used for system aeration. The FBR was operated at room temperature (21–22°C) for 420 days using granular activated carbon as biofilm carrier (Papirio et al. 2014b). The FBR feed solution was composed by 77.8 mg/L $N\text{-}NH_4^+$, nutrients and 595 mg/L $CaCO_3$ of alkalinity (added as 1000 mg/L of $NaHCO_3$). The feed pH ranged between 7.5 and 8.0. After the initial 15 days, FBR operation was continuous by using first a 12h (days 15–84) and then a 7h HRT (days 85–420). The FBR was sampled twice a week for ammonium, pH, DO, alkalinity, nitrate and nitrite analyses.

Ammonium was completely oxidized throughout the operation and nitrite remained below the detection limit (Figure 15A). $N\text{-}NO_3\text{-}$ rapidly increased to 76.7 mg/L and nitrate production averagely remained at 85.9% during the first 84 days. From day 85 on, $N\text{-}NO_3\text{-}$ concentration strongly fluctuated with the average value of 52 mg/L and the average ammonium conversion to nitrate decreased to 66.4% during the second experimental phase (days 85–420). This discrepancy found in the nitrogen mass balance may have resulted from a simultaneous nitrification/denitrification or the presence of other nitrogen-utilizing organisms in the FBR.

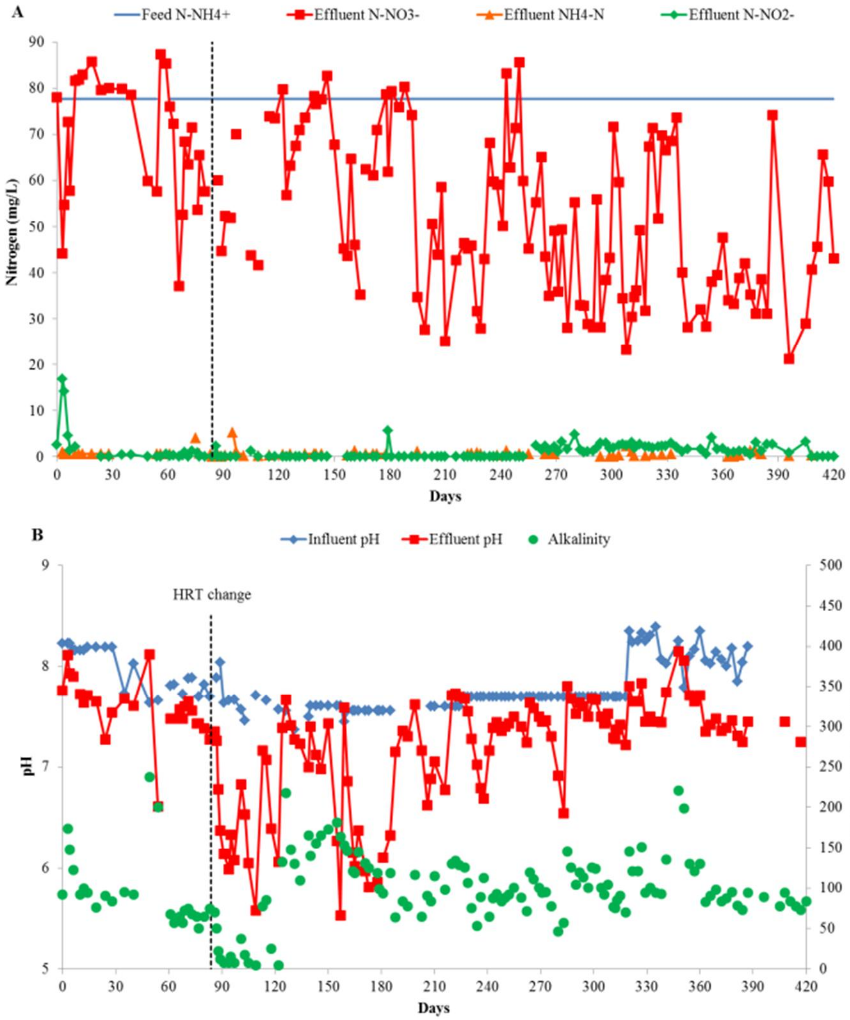


Figure 15. Ammonium, nitrate, nitrite (A), pH and alkalinity (B) profiles in the nitrifying FBR.

At a HRT of 12h, the effluent pH remained stable at 7.60 (Figure 15B). After HRT decrease, pH in the FBR solution significantly varied throughout the second experimental phase fluctuating around a mean value of 7.15. Alkalinity consumption was higher than acidity produced by nitrification.

4.1.2.2 Arsenic effects on nitrification

Arsenic is highly toxic in natural environments and it is often associated with sulfidic minerals present in gold mines. The effect of arsenic on nitrification was investigated in batch assays at initial As(III) concentrations of 0, 5, 20, 50, 100, 150 and 200 mg/L at pH 7.5 and room temperature (22°C). 5 mL of activated carbon coated with biofilm (0.49 g TSS/mL, 0.24 g VSS/mL) was taken from the nitrifying FBR and added to each bottle. A phosphate buffer (50 mM HPO_4^{2-} and 50 mM $H_2PO_4^-$) was used to maintain the pH stable. During 48 h batch assays, the bottles were monitored for arsenic (total As, As(III) and As(V)), ammonium, nitrate, nitrite, pH and dissolved oxygen (DO).

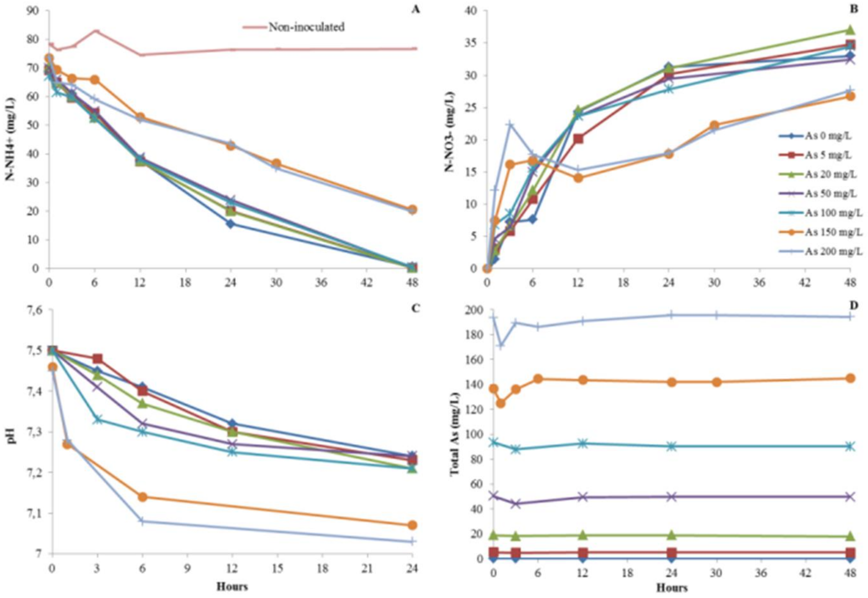


Figure 16. Evolution of ammonium (A), nitrate (B), pH (C) and total As (D) in batch bioassays.

Nitrification was not inhibited by 100 mg As_{TOT}/L. Ammonium oxidation and nitrate production were similar at initial 0–100 mg As_{TOT}/L (Figure 16). At 150 and 200 mg As_{TOT}/L, nitrification was 25% inhibited resulting in a final N-NH_4^+ concentration of 20.3 mg/L. Nitrite remained below the detection limit (data not shown). N-NO_3^- concentration was 27.3 mg/L after 48h, i.e. 21% lower than at 0–100 mg As_{TOT}/L.

The speciation of arsenic is of major importance in order to assess As toxicity and bioavailability. Figure 17 shows As(III) and As(V) concentrations at 100 and 200 mg As_{TOT}/L in the batch tests.

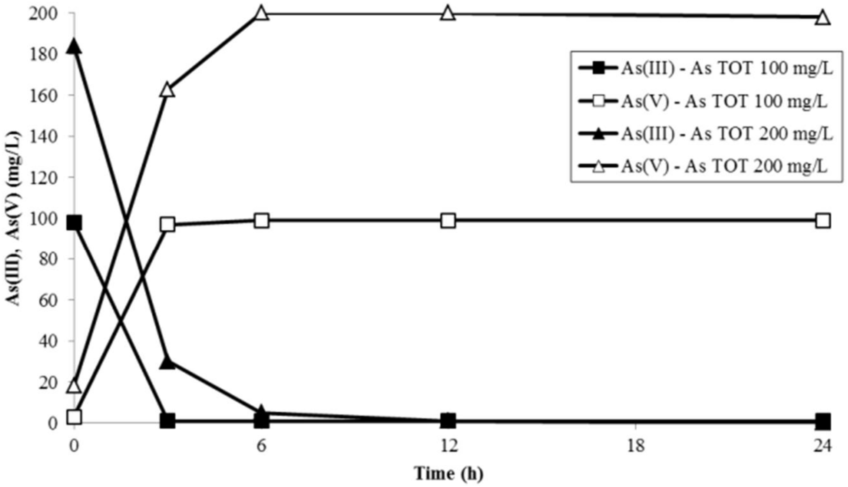


Figure 17. Liquid phase As(III) and As(V) species during nitrification in batch bio-assays.

At 100 mg As_{TOT}/L, As(III) was completely oxidized to As(V) after 3h. Differently, 5 mg/L of As(III) remained after 6h at 200 mg As_{TOT}/L. At the end of the test, As(V) was the sole As species and As(V) concentration corresponded to the initial total arsenic concentration. Ammonium oxidation and nitrate production were only repressed during the first 12h at 200 mg As_{TOT}/L, when As(III) was still present. This demonstrates that the toxic effects of As(III) were neutralized resulting in high ammonium oxidation efficiencies.

4.1.2.3 DGGE profiles

The microbial communities were studied four times during FBR operation and batch tests (Figure 18). *Ferruginibacter lapsinasis* (band 72), *Sediminibacterium salmoneum* (band 122), two aerobic heterotrophs optimally growing at 10–37°C under neutral conditions, were recognized in the activated sludge seeded to the FBR. At this stage, the quantity of nitrifying organisms was below DGGE detection. DGGE bands were too close to each other for separation and sequencing.

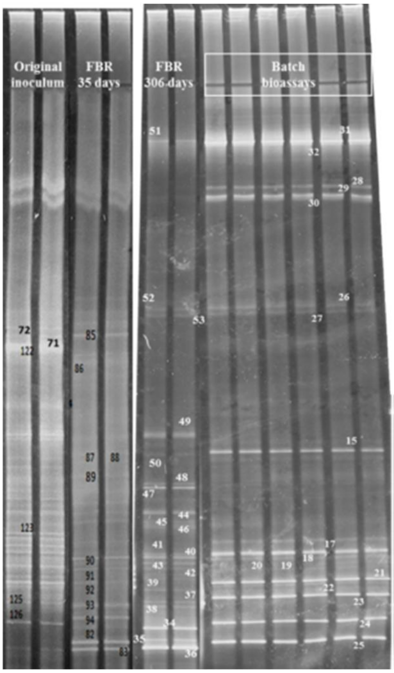


Figure 18. DGGE profiles of nitrifying microbial cultures in the original seed, FBR and batch bioassays.

After 35 days of FBR operation, *Candidatus Nitrospira defluvii* was revealed (bands 93 and 94). This bacterium is one of the most abundant nitrifiers in natural environments and wastewater treatment plants (Daims et al. 2001). FBR cultures also contained *Terrimonas lutea* (band 85), a typical activated sludge nitrate reducer under aerobic conditions, indicating that this strain was probably responsible for the reduction of part of nitrate produced by nitrification.

After 306 days of operation, two uncultured *Nitrospira* bacteria, responsible of nitrite oxidation, were seen in both FBR (bands 51 and 35–39) and batch bioassays (bands 31–32). One species of *Lysobacter* (bands 20, 23) and one *Thermomonas*, all belonging to the group of γ-Proteobacteria, were present in batch bioassays. Species of genus *Lysobacter* have been observed in a nitrifying sludge lagoon (Ducey et al. 2010). On the contrary, *Thermomonas* species reduce nitrate and nitrite in aerobic and anoxic environments (Margaert et al. 2003), possibly explaining the nitrogen loss from the mass balance in batch tests. All the microbial species demonstrated to tolerate arsenic. No arsenic oxidizers were found in the FBR cultures.

4.1.3 Conclusions

Nitrification and denitrification of simulated mining waters was evaluated in separate laboratory scale fluidized-bed reactors. Denitrification was efficiently maintained at low feed pH (2.5) and temperature as low as 7–8°C. A hydraulic retention time (HRT) of 5.4 h was reached and 890 mg/L·d of nitrate was reduced in ethanol/nitrate ratio of 0.84 mol/mol. In the nitrification process, 77.8 mg/L N-NH_4^+ was completely oxidized throughout the operation and nitrite remained below the detection limit at HRT of 7 h and feed alkalinity of 595 mg/L $CaCO_3$. Batch bioassays indicated that denitrification and nitrification process can tolerate heavy metals (Fe, Co and Ni) and As, respectively, in concentrations typical to mining waters. DGGE analyses revealed that the dominant bacteria in the denitrification FBR were *Dechloromonas denitrificans* and *Hydrogenophaga caeni*, and *Candidatus Nitrospira defluvii* and bacteria belonging to genera *Lysobacter* and *Nitrospira* were present nitrification process.

4.2 Adsorption experiments for nitrate and ammonium

4.2.1 Introduction

Nitrogen adsorption by different media has been widely studied in the literature, and based on a wider literature review, four adsorbents were selected for the study in continuous mode. Zeolite has been reported and utilized as a cation exchange medium with a high affinity and selectivity to ammonium. Literature reports indicate that surface modification of zeolite can result in simultaneously cation/anion exchanging and treatment with the cationic surfactant hexadecyltrimethylammonium (HDTMA) has been reported to result in up to 5 mg NO_3—N/g sorption. Activated carbon is a multisorbent that can be used as a control substance. ZnCl-treatment of activated carbon has been shown to significantly increase regenerative nitrate binding of activated carbon.

Furthermore, batch mode adsorption tests were carried out on vermiculite and natural zeolite clinoptilolite both having an affinity for ammonium ions. Clinoptilolite has a cage-like structure consisting of SiO_4 and AlO_4 tetrahedra joined by shared oxygen atoms, see Figure 19. Cations, such as Na^+, balance the negative charge of the framework, and can be displaced by ammonium ions NH_4^+.

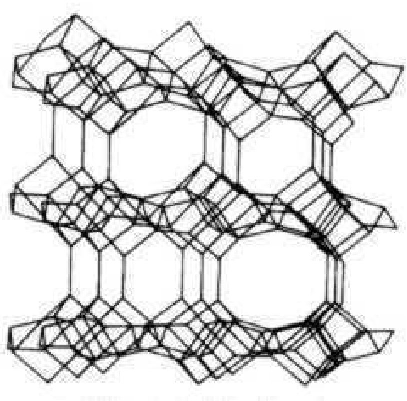


Figure 19. Clinoptilolite structure.

See Figure 20 for a model of vermiculite’s layered structure. The interlayer contains cations, such as Mg^{2+}, which can be displaced by ammonium ions NH_4^+.

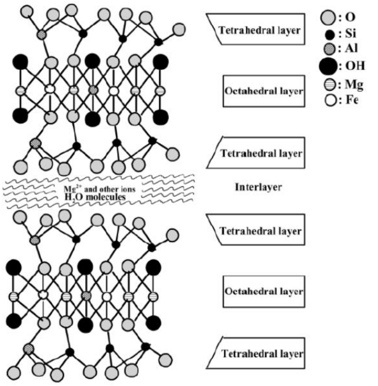


Figure 20. Vermiculite structure.

4.2.2 Batch mode adsorption tests

4.2.2.1 Materials and methods

The natural zeolite clinoptilolite was purchased from Rota mining corporation, Turkey. Its experimental chemical formula was $(Ca, K_2, Na_2, Mg)_4Al_8Si_{40}O_{96} \cdot 24H_2O$ and the mineral composition: clinoptilolite 90–95%, cristobalite 0–5% and tridymite 0–5%. The effective diameter of the pores was $4 \cdot 10^{-10}$ m and the grain size 0.7–1.6 mm. Its cation exchange capacity was reported to be 1.5–2.1 meq/g. Modified, i.e. slowly heated, vermiculite (Geosmart SPb, Russia) was used as obtained. Vermiculite has the chemical formula $(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4 H_2O$ and its CEC is 1.0–1.5 meq/g (Rama 2011).

The clinoptilolite was pretreated in 1 M NaCl (J. T. Baker) solution by shaking for 48 hours with an Edmund Bühler SM 25 mechanical shaker at 200 rpm. The NaCl solution was replaced by fresh solution twice a day. The clinoptilolite was then filtrated, washed with deionised water, filtrated again and dried in 105 °C for 24 h.

Batch mode adsorption tests were performed with the Edmund Bühler SM 25 shaker. Shake flasks containing synthetic mine water, i.e. NH_4NO_3 (Merck) solution (0.14–3.3 g/L NH_4NO_3, corresponding to 25–600 mg/L NH_4^+-N) and either 0–300 g/L clinoptilolite or 0–200 g/L vermiculite were shaken at 200 rpm for 24 h at room temperature. After filtration, the NH_4^+-N concentration of the filtrate was immediately determined with a Hach Lange DR 3900 benchtop spectrophotometer. One batch of samples was also sent to the accredited testing laboratory Nab Labs Ltd (Oulu, Finland) for analysis, in order to determine the accuracy and reliability of the Hach Lange spectrophotometer.

4.2.2.2 Results

The samples analysed by Nab Labs were also analysed twice with the Hach Lange instrument: immediately after filtering and 24 hours later, roughly at the same time the samples were analysed by Nab Labs. During these latter 24 h, the filtrate was stored at slightly above 0 °C. There were practically no difference between the two Hach Lange analysis results. The Nab Labs results show a slightly higher NH_4^+-N concentration. However, the results are well within the 10% margin of error reported by Nab Labs, see Figure 21, also showing the total amount of N in the samples, as analysed by Nab Labs.

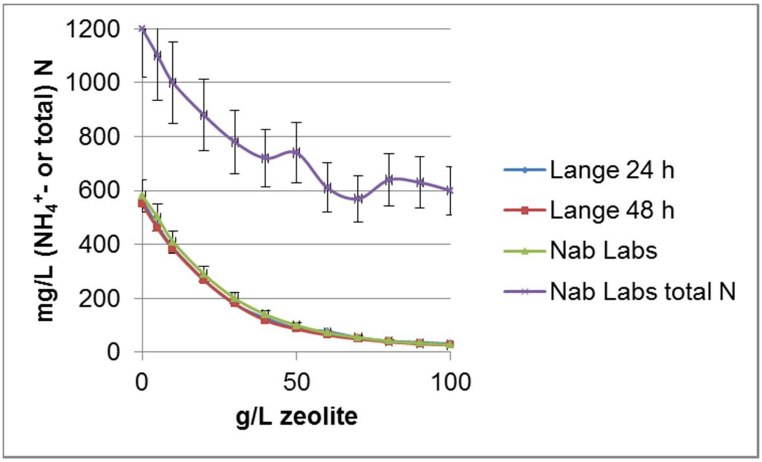


Figure 21. Comparison between analysis results by Nab Labs and Hach Lange spectrophotometer.

Because of the similarity between these results, Hach Lange spectrophotometer was used for the analysis and the results presented in Figure 22–Figure 25 were obtained using this instrument.

Figure 22 shows the adsorption behaviour of both clinoptilolite and vermiculite. Similarly shaped curves were achieved at all the ammonium concentrations tested. Clinoptilolite adsorbs most of the NH_4^+-N already at rather low adsorbent concentrations, after which there is not any significant improvement of the adsorption even though more zeolite is used. The vermiculite curves level out at higher adsorbent concentrations, still leaving more NH_4^+-N in the solution than in the case of clinoptilolite.

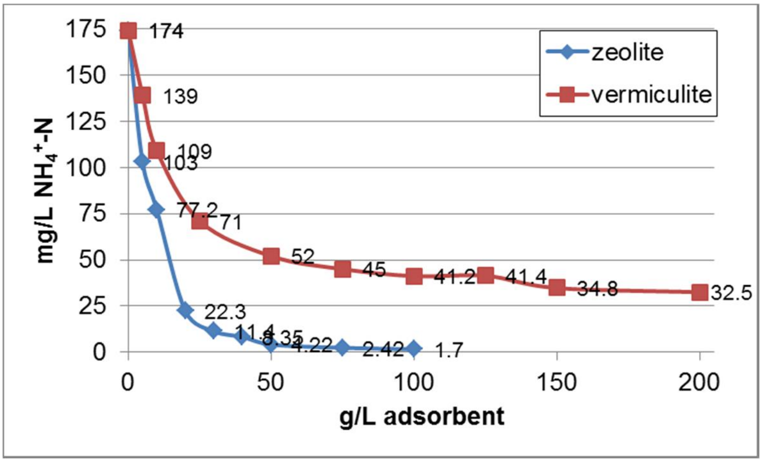


Figure 22. Typical NH_4^+-N adsorption behaviour of clinoptilolite and vermiculite.

The rise between 50 and 100 g/L adsorbent in the adsorption curve of clinoptilolite in Figure 23 is most probably the result of inefficient filtration of the solution. The lower the NH_4^+-N concentration, the more sample solution is needed for the Hach Lange analysis. Furthermore, it was not possible to dilute samples of low initial NH_4^+-N concentration as much as samples of high concentration. A part of the small zeolite particles always penetrates the filter paper, causing turbidity in the filtrate, which in turn causes Hach Lange analysis problems at low NH_4^+-N concentration.

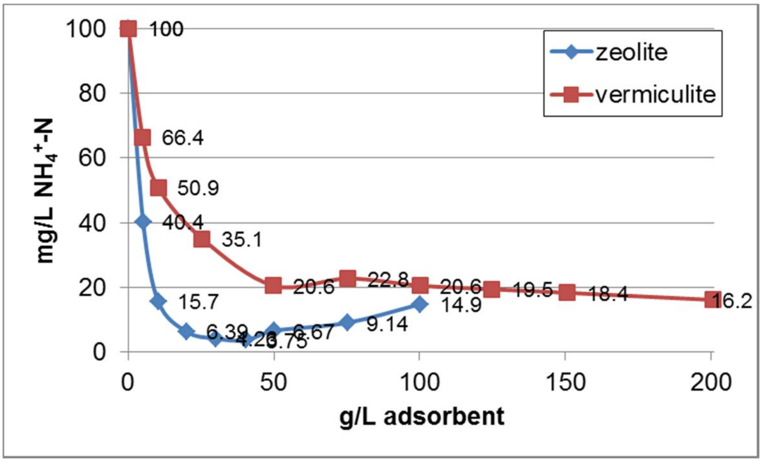


Figure 23. NH_4^+-N adsorption by clinoptilolite and vermiculite.

Zooming in on clinoptilolite's adsorption curve shows that an initial NH_4^+-N concentration of 50 mg/L is reduced to 1 mg/L by 10 g/L zeolite and to 0.2 mg/l by 20 g/L zeolite (Figure 24). In real mine water, the initial NH_4^+-N concentration would probably be lower than 50 mg/L; a report (Mattila et al. 2007) published by the Finnish Forest Research Institute mentions concentrations between 5.1 and 17.2 mg/L NH_4^+-N in mine water samples collected from 3 different mines in Finland.

Figure 24. NH_4^+-N adsorption by clinoptilolite.

An extreme case of the aforementioned analysis problems can be seen in Figure 25 where the initial NH_4^+-N concentration is slightly below 25 mg/L. The analysis of samples treated with vermiculite is not affected by turbidity even at low NH_4^+-N concentrations, since the vermiculite flakes are much bigger than the smallest zeolite particles.

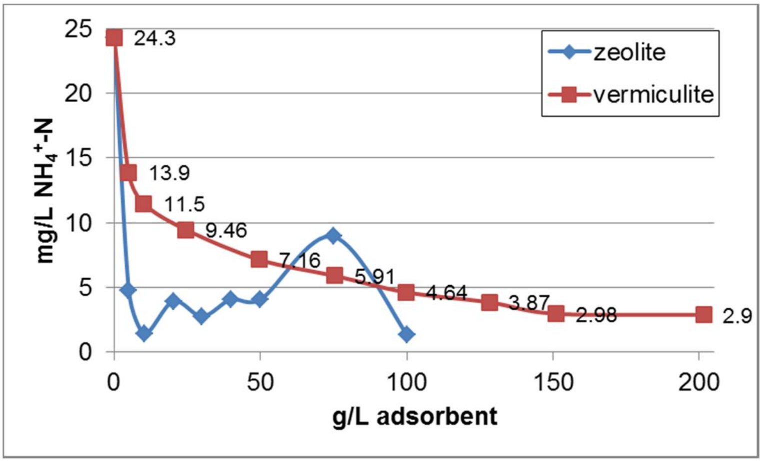


Figure 25. NH_4^+-N adsorption by clinoptilolite and vermiculite, low initial NH_4^+-N concentration.

4.2.2.3 Conclusions

Both clinoptilolite and vermiculite adsorb NH_4^+-N from synthetic mine water, according to our experimental results. Of these two materials, clinoptilolite is more efficient, removing more NH_4^+-N at lower adsorbent concentrations.

4.2.3 Continuous mode adsorption tests for nitrate and ammonium

4.2.3.1 Materials and methods

Granular activated carbon (GAC) and zeolite were used as adsorbents in continuous mode tests. The properties of zeolite are reported in 4.2.2.1. AQUACARB TM 207C 12X30 granular activated carbon was bought from Chemviron Carbon and it was manufactured from specific grades of coconut shell.

The zeolite was washed with deionised water and dried in 105 °C for 24 hours before use. Synthetic wastewater was prepared from NH_4NO_3 (Baker Analyzed). All the chemicals used were pro analysis grade.

Analyses

pH and electrical conductivity were analysed by MeterLab PHM240 pH/ION meter and by MeterLab CDM210 Conductivity meter, respectively. NH_4^+ and NO_3^- concentrations in the feed and in the effluents were analysed by Seal AQ1 Automated

Discrete Analyzer and by Hach Lange spectrophotometer and Ammonium and Nitrate cuvette tests. The AQ1 methods used for Ammonia-N and Nitrate-N + Nitrite-N were equivalent to USEPA methods 350.1 rev 2.0 and 353.2 rev. 2.0, respectively.

Treatment of GAC and zeolite

Zeolite was washed with deionized water and dried for 24 hours in 105 °C. Then, a part of the zeolite was treated with the cationic surfactant hexadecyltrimethylammonium (HDTMA). A part of GAC was treated with 1.42 mol/l $ZnCl_2$ and dried in furnace at 500 °C.

The first experimental setup

Two in-line setups were constructed and each setup consisted of two laboratory columns sizing 5 cm x 30 cm (see Figure 26). Sartorius Cellulose nitrate filters with the pore size of 8.0 µm were used in the top of the columns and Schleicher & Schuell membrane filters with the pore size of 0.45 µm in the bottom of the columns. The empty and packed columns were weighted and the masses were recorded. In order to calculate the pore volumes, also the wet columns were weighed. For the first setup, the first column was packed with untreated GAC and the other one with $ZnCl_2$-treated GAC. For the second setup, the first column was packed with untreated zeolite and the second with HDTMA-treated zeolite. The columns were set up in saturated up flow series: untreated GAC + $ZnCl_2$ treated GAC and untreated zeolite + HDTMA-treated zeolite. Valve tubing was installed between columns for sampling. A schematic description of the setup is shown in Figure 27.

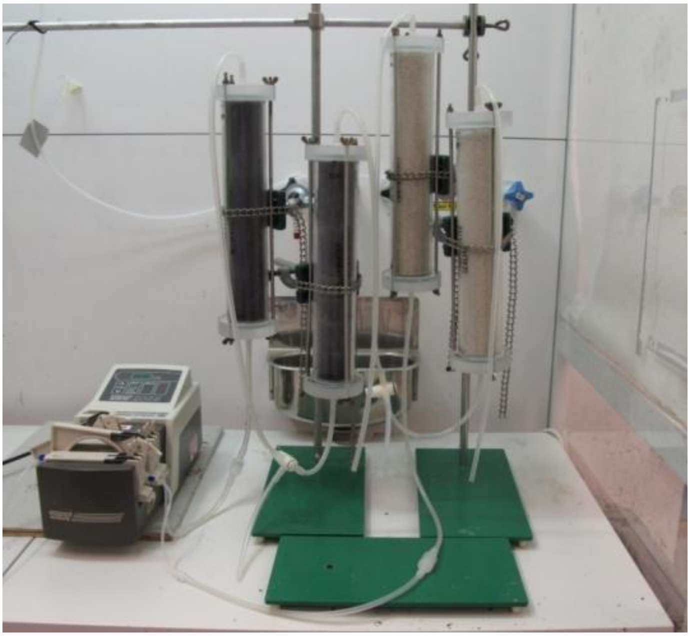


Figure 26. The first experimental setup. The GAC columns are in series on the left hand side and zeolite columns in series on the right hand side.

Synthetic wastewater was prepared by diluting 0.8 g of NH_4NO_3 in 10 litres of water. The first batch of the synthetic wastewater contained 13 mg NH_4-N/L and 33 mg NO_3^--N/L. After 180 hours and about 10 litres of water had run through each system, NH_4 and NO_3 concentrations were increased to 500 mg NH_4^+-N/L and 557 mg NO_3^--N/L, in order to obtain the breakthrough faster. All the experiments were conducted in ambient temperature, at 20 ± 2 °C. The system was run about 48 hours with distilled water before the synthetic wastewater was fed to the columns.

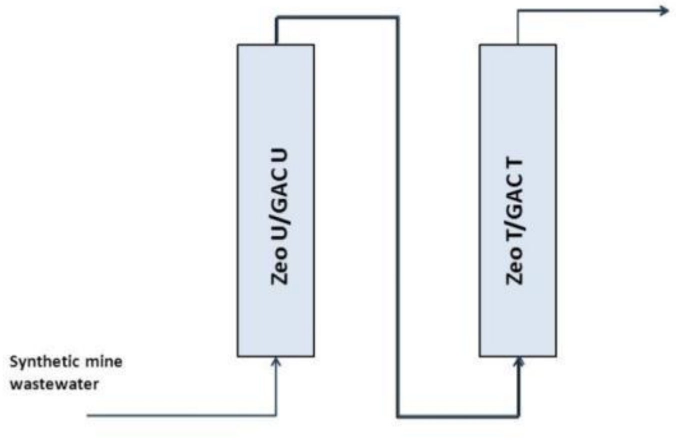


Figure 27. Schematic description of the first experiment. The first column was either untreated zeolite (Zeo U) or untreated granular activated carbon (GAC U). The second column was either HDTMA-treated zeolite (Zeo T) or $ZnCl_2$-treated granular activated carbon (GAC T).

The second experimental setup

Because of the results obtained for NH_4^+ removal by untreated zeolite and NO_3 removal by both untreated and treated GAC, the setup of the columns was changed so that there were untreated zeolite columns as the first columns in both systems and untreated GAC in the first and $ZnCl_2$-treated GAC in the second setup. The setup with untreated zeolite and untreated GAC is shown in Figure 28. Unused materials were used for these experiments. The zeolite was washed and dried and the GAC was treated with $ZnCl_2$ as described earlier. The synthetic wastewater fed to the columns contained 35–47 mg NH_4^+-N/L and 60–68 mg NO_3^--N/L.

Regeneration of GAC columns

After the breakthrough occurred, the GAC columns were regenerated with 0.05 M NaOH. The columns were regenerated in series in co-current i.e. in up-flow mode. 5 litres of 0.05 mol/l NaOH was used with the flow rate of 0.5 L/h to regenerate the GAC columns. Then, the columns were washed with approximately 5 litres of distilled water. Samples were taken between 0.5–2 hours during the regeneration and washing. The second regeneration was conducted with higher flow rate (0.67 L/h) and 6 litres of 0.05 M NaOH. 6 litres of distilled water was used for washing. In the second experimental setup, untreated GAC was regenerated alone with 6 litres of 0.1 M NaOH in counter current mode i.e. in down flow mode. After all the regenerations, other cycles were carried out.

Regeneration of zeolite columns

After the breakthrough occurred, the zeolite columns were regenerated in series in co-current mode with 7 litres of 0.5 M NaCl solution, which pH was adjusted to over 12 with NaOH. 6 litres of distilled water was used for washing. In the second setup, untreated zeolite was regenerated alone in counter current mode with 9 litres of 0.5 M NaCl and 1 litre of 1 M NaCl, which pH was adjusted to over 12 with NaOH. After both the regenerations, another cycle was carried out.

Figure 28. Second experimental setup with untreated zeolite on the left hand side (the 1st column) and untreated GAC on the right hand side (the 2nd column). The picture was taken in the beginning where the zeolite column is getting filled with water.

4.2.3.2 Results

Ammonia removal

Ammonia was adsorbed onto untreated zeolite and untreated GAC. Also $ZnCl_2$-treated GAC could adsorb some remaining ammonia after untreated GAC. Untreated GAC could adsorb only 0.06 mg NH_4^+-N /g GAC before ammonia started to leak. The total NH_4^+-N/L adsorption capacity was approximately 0.3 mg NH_4^+-N/g GAC. Untreated zeolite could adsorb NH_4^+-N effectively and its breakthrough NH_4^+-N adsorption capacity was approximately 10.9 mg NH_4^+-N/g zeolite before the zeolite columns were regenerated. The effluent NH_4^+-N concentration did not reach the influent NH_4^+-N concentration and therefore, there would have been NH_4^+-N adsorption capacity left. Thus, 10.9 mg/g cannot be considered as the total NH_4^+-N exchange capacity. NH_4^+-N concentrations after GAC and zeolite column are shown in Figure 29 until the feed concentration was increased.

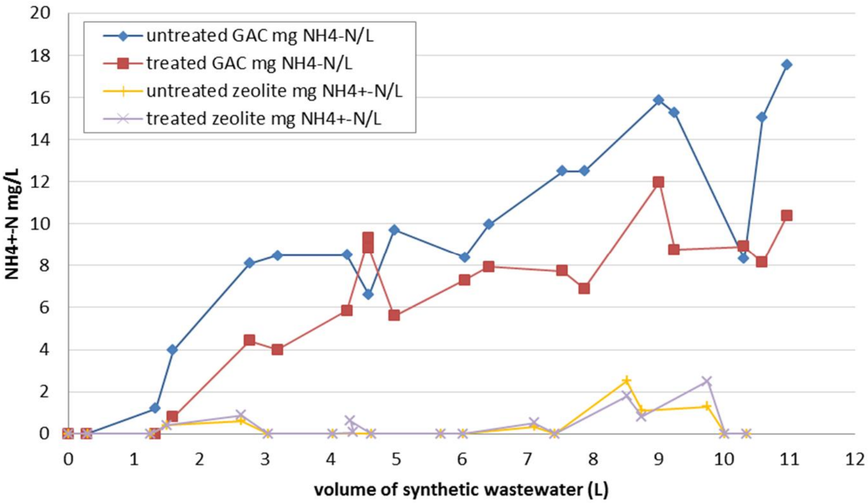


Figure 29. NH_4^+-N concentration after zeolite and GAC columns.

Nitrate removal

Both untreated and $ZnCl_2$-treated GAC could adsorb NO_3^-, with total capacities of 0.5–1.1 and 0.9–1.1 mg NO_3^- -N/g GAC, respectively. Untreated zeolite did not adsorb NO_3^-, but HDTMA-treated zeolite had total NO_3^- adsorption capacity of 1.1 mg NO_3^--N/g. Despite the similar total adsorption capacities, GAC could keep the effluent NO_3^- concentration low longer (Figure 30), while zeolite started to leak NO_3^- already after 2 litres of synthetic wastewater had flown through the columns.

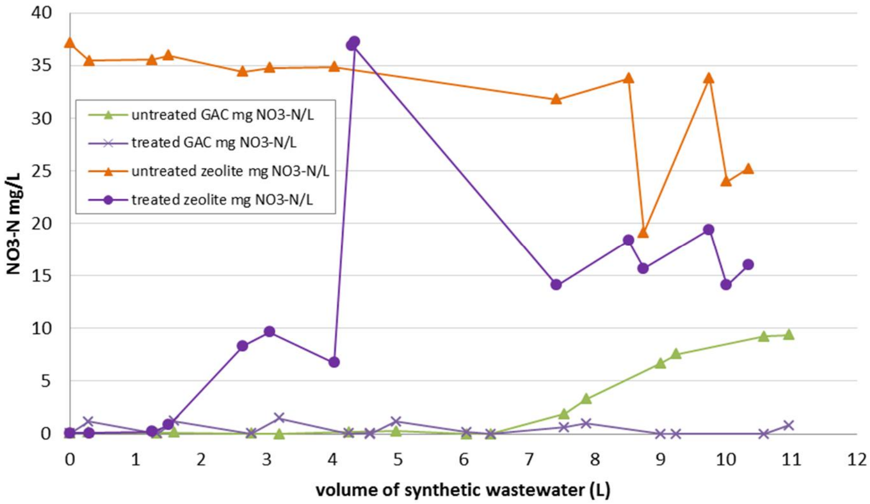


Figure 30. NO_3^- -N concentration after zeolite and GAC columns.

Regeneration of GAC columns

The GAC columns were regenerated as described before. Regeneration of GAC columns could remove the NO_3^--N adsorbed onto GAC. However, after the regeneration, GAC could not adsorb NO_3^-. When untreated GAC was regenerated alone in counter current mode, 62% of the NO_3^- was desorbed.

Regeneration of zeolite columns

Zeolite columns were regenerated in series in co-current mode as described earlier. Regeneration of untreated zeolite was successful in counter current. Approximately 92% of adsorbed NH_4^+-N was desorbed. However, 10 litres of 0.5 mol/l NaCl solution was not enough to desorb all the NH_4^+. After regeneration the NH_4^+-N concentration in the effluent was approximately 0.15 mg/L, but after 4 litres of synthetic wastewater had flown through the columns NH_4^+-N concentration decreased to < 0.04 mg/L. After the regeneration at least 15.6 litres of synthetic wastewater with NH_4^+-N concentration of 42 mg/L could be treated and the regenerated zeolite could adsorb at least 2.2 mg NH_4^+-N /g zeolite.

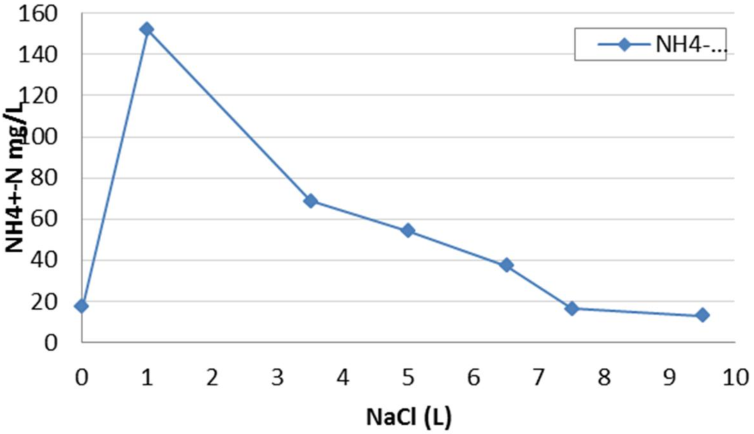


Figure 31. Effluent NH_4^+-N concentration in zeolite regeneration, when untreated zeolite was regenerated alone.

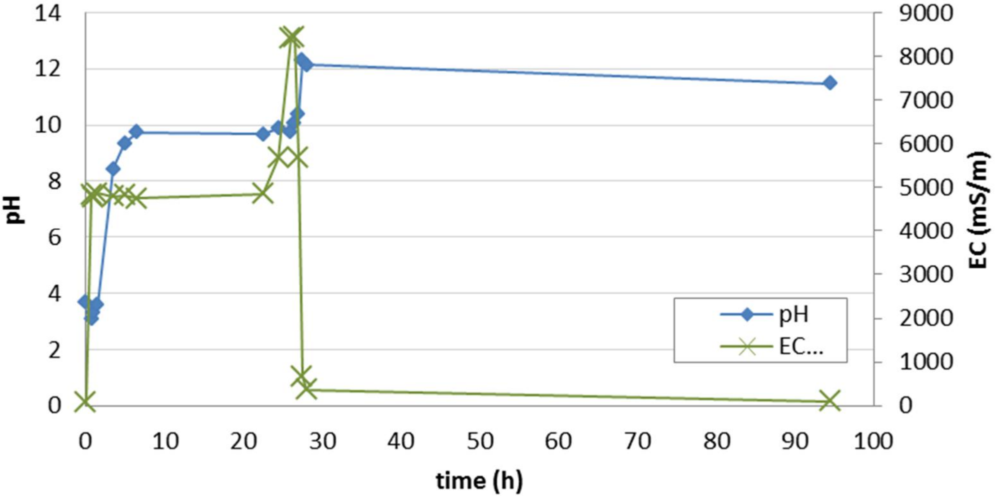


Figure 32. Effluent pH and electrical conductivity in untreated zeolite regeneration.

4.2.3.3 Discussion

Untreated zeolite had good NH_4^+-N adsorption capacity. The experiment was run until breakthrough and the adsorption capacity was 10.9 mg NH_4^+-N/g zeolite. Rahmani et al. (2004) obtained total NH_4^+-N adsorption capacity of 17.31-18.98

mg NH_4^+-N /g zeolite in a column study. The capacity until breakthrough was 9.61–11.17 mg NH_4^+-N /g zeolite, which is similar to the breakthrough capacity obtained in this experiment. The total capacity of untreated zeolite was not reached in this study i.e. the columns could still have removed NH_4^+ when the columns were regenerated. Du et al. (2005) attained 5.81–7.74 mg NH_4^+-N /g breakthrough capacity. They carried out six loading and five regeneration cycles without loss of NH_4^+ removal capacity. In addition, the NH_4^+ removal capacity increased after the first regeneration. The mineralogy of the zeolite, its particle size, relative porosity and density also have an influence on the ion exchange capacity of zeolite. Also the influent NH_4^+ concentration and the presence of other ions in the feed may affect the ion exchange capacity.

HDTMA treatment of zeolite improved the NO_3^--N adsorption from < 0.05 mg/g to 1.1 mg/g. However, the adsorption of NO_3^- by HDTMA treated zeolite was still significantly lower than NH_4^+ adsorption by untreated zeolite. Li (2003), Guan et al. (2010), Onyango et al. (2010) obtained NO_3^- adsorption capacities of 1.1 mg NO_3^--N/g, 0.8 mg NO_3--N/L, and 2.6 mg NO_3^--N/g, respectively.

Namasivayam and Sangeetha (2005) examined NO_3^- removal using $ZnCl_2$-treated GAC in a batch study and they achieved adsorption capacity of 2.3 mg NO_3^--N/L. They also examined desorption of NO_3^- and influence of other anions on NO_3^- adsorption. They found that desorption of NO_3^- from $ZnCl_2$-treated GAC was the highest at pH 11 (> 92%) and at pH 2 (> 58%). At pH 3-11 desorption was negligible. They found that from the tested anions perchlorate, chloride, and sulphate reduced NO_3- adsorption.

Higher NO_3^--N concentrations were observed for $ZnCl_2$-treated GAC in the samples taken in the afternoon compared to the samples taken in the morning, approximately 1 mg/L in the afternoon and < 0.05 in the morning (Figure 30). The temperature in the laboratory was 1–3 °C lower in the night than in the day time. It was possible that the higher temperature in the day time caused lower NO_3^- adsorption onto $ZnCl_2$ treated GAC and higher NO_3^- concentration in the effluent in the samples measured in the afternoon. Bhatnagar et al. (2008) noticed that nitrate adsorption onto $ZnCl_2$ treated GAC increased slightly by decreasing temperature. Differences between morning and afternoon samples for the effluent NO_3^--N concentrations were observed with neither the untreated GAC nor the zeolite columns.

In the first experiment, the regeneration was conducted in series. It could have been better if all the columns had been regenerated separately. HDTMA-treated zeolite was regenerated only once with NaCl-solution. Regeneration with NaOH was not examined. Because the regeneration of GAC columns was not successful, it could not be evaluated here whether the adsorption capacity decreases after generation. Cho et al. (2011) noticed that the amount of adsorbed nitrate decreased from 4.8 mg NO_3^--N /g to 3.4 mg NO_3^--N /g after four cycles of adsorption on [3-(methacryloylamino)propyl]-trimethylammonium chloride coated GAC.

4.2.3.4 Conclusions and further research

Four different sorption materials were tested for ammonia and nitrate adsorption. Untreated and hexadecyltrimethylammonium (HDTMA)-treated zeolite and untreated and $ZnCl_2$-treated granular activated carbon (GAC) were examined and tested by column experiments for their nitrate and ammonia removal capabilities as well as regeneration capabilities.

Both the GAC columns could remove NO_3^- from the synthetic wastewater, but NH_4^+ removal by both GAC columns was weak. Untreated zeolite was the best of the tested adsorbents for NH_4^+ removal and could adsorb ammonia approximately 10.9 mg NH_4^+-N /g zeolite. HDTMA-treated zeolite, untreated and $ZnCl_2$-treated GAC had similar adsorption capacities for NO_3^- adsorption, but both untreated and $ZnCl_2$-treated GAC kept NO_3^--N concentration in the effluent lower than HDTMA-treated zeolite. The NO_3^- adsorption capacities obtained for GAC and HDTMA-treated zeolite in this study were 0.5–1.1 mg NO_3^--N/g, being in similar range with literature results obtained in similar column studies. Untreated zeolite could not adsorb NO_3^-. NH_4^+ breakthrough adsorption capacities for untreated zeolite were comparable with other similar studies. However, NH_4^+ adsorption was lower in this study than results obtained by others.

The regeneration of GAC or HDTMA-treated zeolite columns was not successful. More NO_3^--N and NH_4^+-N was desorbed than was calculated to have been adsorbed onto GAC. However, after regeneration, the GAC columns could not adsorb NO_3^--N and the NO_3^--N concentration in the effluent was immediately close to the influent NO_3^- concentration. It seemed that even though NO_3^--N was removed from GAC, the adsorption sites were not active or available for NO_3^- adsorption again. When untreated GAC was regenerated alone in counter current mode, 62% of the NO_3^--N was desorbed indicating that neither counter current regeneration nor regeneration of the column alone improved the regeneration of GAC. In addition, increasing the NaOH concentration from 0.05 M to 0.1 M did not improve the regeneration. Because of the unsuccessful regeneration of GAC columns, neither untreated nor $ZnCl_2$-treated GAC was suitable for NO_3^--N removal in this study. Zeolite columns could be regenerated with 0.5–1 M NaCl-solution ($pH > 12$). Comparing different materials, only untreated zeolite proved potential for regenerative use.

Therefore the experiments were continued with zeolite only. The aim was to find the shortest retention time needed for NH_4^+ adsorption on zeolite and improve the regeneration. Real mine wastewater contains also other ions besides NH_4^+ and NO_3^-, and the other ions may decrease the adsorption capacity. Thus, adsorption of NH_4^+ from real mine wastewater was examined in subsequent testing series.

4.3 Adsorption and regeneration experiments for ammonium with zeolite

4.3.1 Introduction

In the earlier study, zeolite was identified as a potent sorption material for ammonia removal. Further column experiments were conducted to confirm its adsorption capacity, rate, regeneration capacity and effects of real mine waste water on these parameters. Additionally, one larger scale column test was carried out in order to characterize the structure of zeolite and nitrogen compounds after adsorption by MLA and XRD. The results indicate the application potential of zeolite sorption in real mine waste waters.

4.3.2 Materials and methods

4.3.2.1 Materials

Natural zeolite clinoptilolite and synthetic wastewater were prepared in a similar manner as described in 4.2.2.1. Real wastewater from Suurikuusikko gold mine (Agnico-Eagle Mines Ltd.) was used, the characteristics of which are presented in Table 3.

Table 3. Suurikuusikko mine water characteristics (dissolved ions in mg/l). Sample from open pit dewatering.

pH	7.5	Br	<0.1	Li	0.369	S	3030
EC mS/m	1050	Ca	426	Mg	2350	Sb	0.02
Redox, mV	564	Cd	<0.00002	Mn	2.11	Se	0.02
Ag	<0.00001	Cl^-	30	Mo	0.03	Si	1.47
Al	0.04	Co	0.01	Na	176	SO_4^{2-}	8490
As total	0.08	Cr	<0.0002	Ni	0.04	Sr	1.22
As^{5+}	0.08	Cu	0.01	N total	27	Th	<0.00001
As^{3+}	0.002	F	0.4	NO_2-N	0.29	Ti	<0.00001
B	0.04	Fe total	0.09	NO_3-N	5.6	TOC	5.4
Ba	0.04	Fe^{2+}	0.0206	NH_4-N	19	U	<0.00001
Be	<0.0001	Fe^{3+}	0.0694	P	0.01	V	<0.00005
Bi	<0.00002	K	152	Pb	<0.00005	Zn	0.03

The water used in the larger scale column test was collected from the neutralizing pond of Suurikuusikko gold mine and its characteristics are presented in Table 4.

Table 4. Suurikuusikko mine water characteristics (dissolved ions in mg/l). Sample from neutralizing pond.

pH	-	Br	-	Li	0.12	S	2212
EC mS/m	-	Ca	363	Mg	1470	Sb	<0.2
Redox, mV	-	Cd	<0.02	Mn	1.04	Se	-
Ag	<0.02	Cl^-	-	Mo	0.06	Si	1.06
Al	0.23	Co	<0.02	Na	125	SO_4^{2-}	-
As total	0.14	Cr	<0.02	Ni	0.05	Sr	1.05
As^{5+}	-	Cu	<0.02	N total		Th	-
As^{3+}	-	F	-	NO_2-N	-	Ti	<0.02
B	0.11	Fe total	<0.5	NO_3-N	8.65	TOC	-
Ba	0.03	Fe^{2+}	-	NH_4-N	11.1	U	-
Be	<0.01	Fe^{3+}	-	P	<0.1	V	<0.02
Bi	-	K	100	Pb	<0.05	Zn	<0.02

4.3.2.2 Analyses

Analyses of pH, electrical conductivity, NH_4^+ and NO_3^- concentrations were conducted as described in 4.2.3.1. However, the AQ1 analyser did not function properly during the experiment, resulting in bad data and final analysis was done using Hach-Lange kits only.

4.3.2.3 Experimental setup

Four separately run identical columns were constructed, with each setup consisting of a laboratory column effective volume sizing 1.9 cm x 15 cm (see Figure 33). Glass wool was used at the bottom and top of the columns to hold zeolite packing in place. The columns were packed with app. 35 g of dry zeolite. The empty and packed columns were weighted and the masses were recorded. In order to calculate the pore volumes, also the wet columns were weighed.

Figure 33. Four small columns. Zeolite packing was decreased before starting the experiment to facilitate flow.

Synthetic wastewater containing 20 mg NO_3^--N and 20 mg NH_4^+-N per litre was prepared. Two columns were run in parallel using synthetic wastewater and real mine wastewater at minimum retention time (2–5 min) to test the adsorption rate and regeneration. Two were run in parallel using synthetic wastewater and real mine wastewater with a constant, slower retention time of 30 min. All the experiments were conducted in ambient temperature, at 20 ± 2 °C. The column piping's were not designed for constant pressure and there were several flow cut-offs and leaks due to braking fittings and pipes.

4.3.2.4 Regeneration of zeolite columns

Always after the breakthrough occurred, the zeolite columns were regenerated in in co-current mode with variable amounts of 0.5 M NaCl solution, the pH of which was adjusted to over 12 with NaOH. Distilled water was used for washing.

4.3.2.5 Experimental setup for larger scale column test

The larger scale column test parameters are shown in Table 5. In this column test zeolite was sieved to the particle size fraction over 630 µm. A metallic net or screen was placed in both ends of the column in order to keep the zeolite material in place. The duration of the test was almost 20 days and nearly 1800 litres of mine wastewater was pumped through the column. The mine wastewater was stirred 100 rpm in 1m^3 container. Water was pumped with a peristaltic pump through the zeolite containing column. The ammonium and nitrate contents were measured from the column upper outlet. The ammonium contents were determined from the purified water almost daily, the nitrate contents were measured less frequently. The test equipment is shown in Figure 34.

Table 5. Column test parameters.

Column height, cm	60
Inside diameter, cm	5.5
Volume, l	5.7
Pore volume, l	0.7
Flow rate ml/min	70
Residence time, min	10
Water consumption l/hour	4.2
Water consumption l/24 hour	100.8
Zeolite in column, kg	1

Figure 34. Test equipment of the larger column test.

4.3.3 Results

4.3.3.1 Rapid wastewater filtration

Synthetic wastewater was run through an adsorption column with high flowrate. First the hydraulic residence time (HRT) was set to app. 45 minutes and filtration was continued for a week, until a rise in concentration was detected. HRT was dropped to 10 minutes for the next 24 hours after which it was further decreased to 5 minutes. 2 minutes was also tested but there were pressure problems. Breakthrough point was estimated for this case to match the point when effluent ammonium concentration exceeds 1 mg/l. The test was continued for three regeneration cycles. The results are presented in Figure 35 and Table 6.

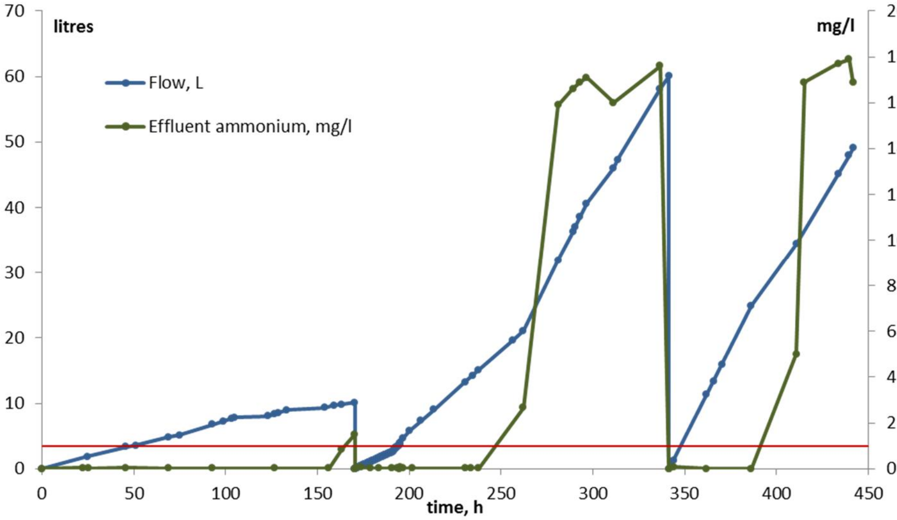


Figure 35. Short HRT cumulative flow of synthetic wastewater through column and effluent ammonia concentration. 1 mg/l breakthrough limit is marked with a red line.

Table 6. Breakpoints in rapid synthetic wastewater filtration.

Breakthrough point	**1**	**2**	**3**
Time point, h	165	247	391
Cumulative flow, L	9.9	17.3	26.8
Sorption capacity, mg/g	6.3	11.0	17.1

The sorption capacity increased with each regeneration cycle starting from 6.3 mg/g in the first run and reaching 17.1 at the third cycle. This represents the further activation of the zeolite ion exchange capacity by each activation cycle. The very short residence time was found more than adequate for full sorption – even 2 minutes contact time was enough to decrease the concentration to near zero.

Real mine wastewater was run in a parallel column. First a cycle with 45 min HRT was run (similar to the synthetic wastewater), but no signs of breakthrough appeared after 200 hours and the experiment was halted, zeolite regenerated and run continued with a 5 min HRT. The test was continued for two full regeneration cycles. The third cycle was aborted after 100 hours as no signs of breakthrough were detected. The results are presented in Figure 36 and Table 7.

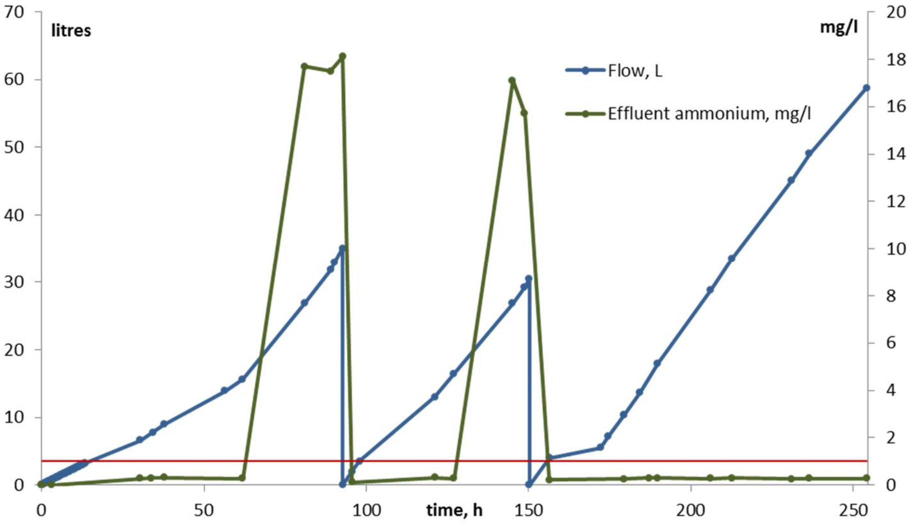


Figure 36. Short HRT cumulative flow of mine wastewater through column and effluent ammonia concentration. 1 mg/l breakthrough limit is marked with a red line.

Table 7. Breakpoints in rapid mine wastewater filtration.

Breakthrough point	1	2	3
Time point, h	63	128	>255
Cumulative flow, L	16.1	16.9	>59
Sorption capacity, mg/g	10.0	10.5	>36

The sorption remained constant for two cycles at a similar level to the second cycle of the synthetic run. The third run was not run into completion, but a high increase in sorption capacity was experienced. The very short residence time was found more than adequate for full sorption – even 2 minutes contact time was enough to decrease the concentration to near zero.

The regeneration solution usage was not minimized or optimized, and varying amounts of regeneration solution was used. This resulted in varying regeneration solution ammonia concentrations, ranging from 5 to 100 mg NH_4^+ -N/l for total regeneration solutions.

4.3.3.2 Slow wastewater filtration

Synthetic wastewater and mine wastewater were run through columns using a constant HRT averaging 31 min and 37 min respectively. The test was continued to find column breakpoints and full capacities. The experiment with mine wastewater was stopped after 700 hours when no signs of breakthrough were experienced. The results are presented in Figure 37, Figure 38 and Table 8.

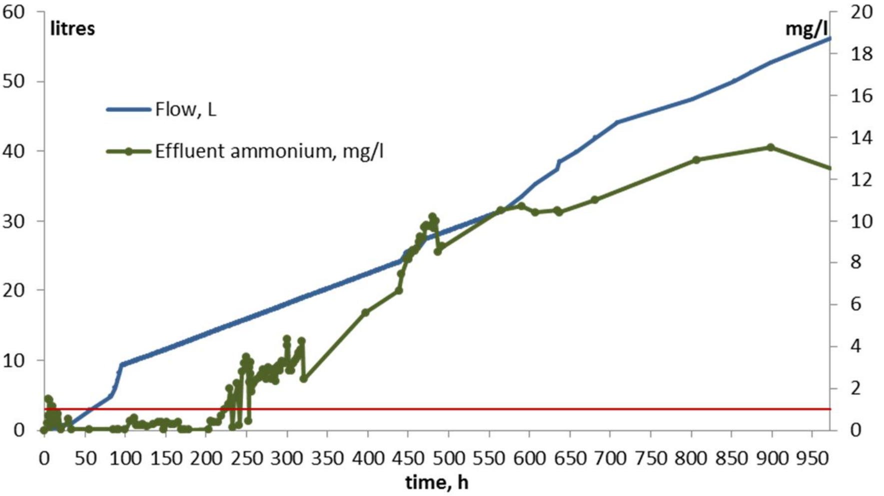


Figure 37. Long HRT cumulative flow of synthetic wastewater through column and effluent ammonia concentration. 1 mg/l breakthrough limit is marked with a red line.

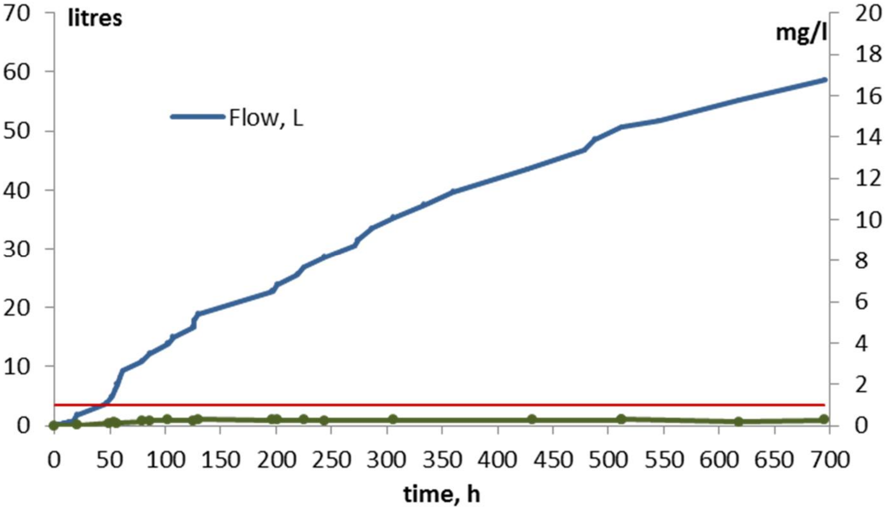


Figure 38. Long HRT cumulative flow of mine wastewater through column and effluent ammonia concentration. 1 mg/l breakthrough limit is marked with a red line.

Table 8. Breakpoints in slow wastewater filtration.

Breakthrough point	Synthetic	Mine
Time point, h	224	>700
Cumulative flow, L	14.8	>58
Sorption capacity, mg/g	9.6	>37

The breakpoint for synthetic wastewater was in line with short retention time tests. The breakpoint for mine wastewater was not reached and similar elongation of filtration capacity as seen with low HRT mine wastewater runs was experienced.

4.3.3.3 Larger scale column test

The average ammonium concentration in the purified water was 0.15 mg/l. The ammonium recoveries are presented in Table 9. According to the test results, the ammonium recovery into zeolite was 98.6% which corresponds 19.3 g. Thus, the most of the ammonium was adsorbed by zeolite and purified water was almost ammonium free. The calculated adsorption capacity was 20 mg/g zeolite.

Table 9. Ammonium contents and recoveries in the column test.

			NH_4-N	
Products	**mg/l**	**Recovery %**	**Recovery mg**	**Recovery g**
Purified water	0.15	1.4	268	0.27
Zeolite	10.95	98.6	19289	19.29
Feed NP3 water	11.10	100.0	19557	19.56

Results of XRD and MLA analysis

After column test zeolite samples were prepared for XRD and MLA investigation. MLA is a scanning electron microscope fitted with two energy-dispersive spectrometers for rapid elemental analysis and special software to automatically perform a range of quantitative mineralogical measurements and calculations. After MLA analysis one of the polished sections was selected for electron microprobe analysis (EMPA) for accurate determination of their chemical compositions. Microprobe analyses were made of the main phases of one of the samples. However, even though the microprobe was equipped with a special crystal for nitrogen analysis, the nitrogen concentrations of these analyses were invariably below the detection limit.

Based on the results of the modal mineralogy the zeolite samples can be divided roughly into three classes: Clinoptilolite, Silicon Oxide and Phlogopite. The minor minerals are Vermiculite and Montmorillonite associated with clay minerals.

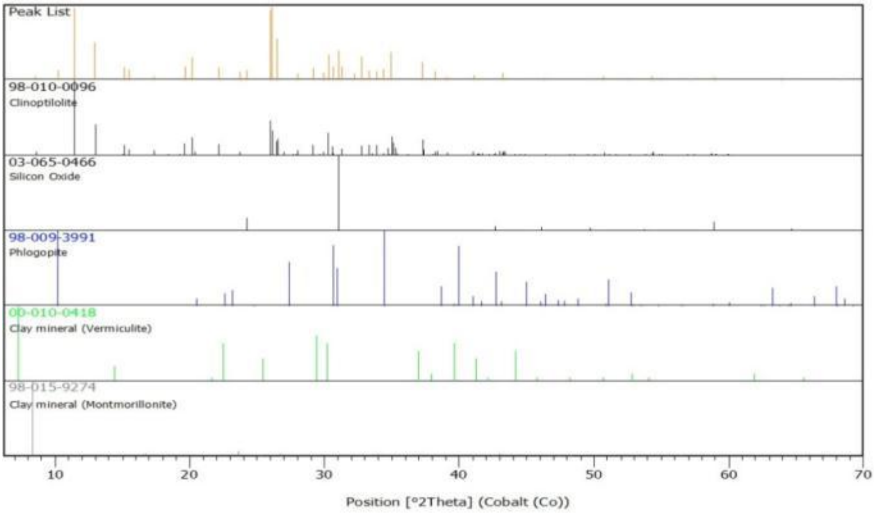


Figure 39. XRD results.

4.3.4 Discussion

The results show clearly, that zeolite effectively binds ammonia in column experiments with as low retention time as 2 minutes into a negligible concentration. The adsorption capacity averages 10 mg/g zeolite for both synthetic wastewater and real mine wastewater.

The time scale of the experiments was limited and much longer experiments with multiple regeneration cycles would be required to find the real long term ion exchange capacity and zeolite attrition and the potential long term effects of mine wastewater on these effects.

The adsorption capacity of zeolite for the mine wastewater sample did increase significantly in the last runs that never reached their breakthrough points. This happened only after a certain time period and only in mine water runs. There are several possible explanations for the phenomena. An error in the mine wastewater runs is possible: this could come from a wrong handling of the sample causing evaporation and dilution of the source feed, but no indication of such was reported. The mine wastewater can potentially form and sustain biological activity in the zeolite column potentially utilizing or converting ammonia – such reactions could include anammox and nitrification as well as organic uptake of ammonia. Mine wastewater also contains a myriad of other ions that could potentially form precipitates or reactions involving ammonia compounds or their reactions. It is also possible that the ion content and characteristics of the mine wastewater are extremely favourable for ammonia adsorption and that the true retention capacity of the columns is higher for the mine wastewater in question.

4.3.5 Conclusions and further research

Zeolite sorption and regeneration with synthetic wastewater and real mine wastewater were studied with columns using short hydraulic retention time and long hydraulic retention time. Zeolite columns were found to remove ammonia very efficiently from both mine wastewater and synthetic wastewater. The contact time required was <2 min and average sorption capacity measured was approximately 10 mg/g. For mine wastewater, much higher sorption capacities, exceeding 37 mg/g were recorded, but confirmative research would be needed to validate these results. The results showed that mine wastewater and synthetic wastewater behave similarly and the sorption capacity averages 10 mg NH_4^+-N/g zeolite.

According to these experiments, zeolite sorption seems well suited and non-problematic for mine wastewater ammonia removal. More long term experiments with multiple regeneration cycles are needed to confirm the regeneration capacity and long term effects of mine water on the process.

4.4 Electrochemical treatment

Nitrogen electrochemistry is complex and involves nine oxidation states and a spectrum of intermediate products and reactions; however, the basic chemistry revolves around inert nitrogen gas (N_2), reduced nitrogen as ammonium (NH_4^+) and oxidized nitrogen as nitrate (NO_3^-). Nitrogen from organic sources enters water as ammonium but in oxic environments is biologically oxidized into a less harmful nitrate form.

The majority of existing and researched technologies for nitrogen containing waters aim at releasing nitrogen as inert nitrogen gas through specific oxidation and reduction reactions. In MINIMAN project, a novel electrochemical method of combined nitrate and ammonium capture as ammonia, using a combination of electrochemical and membrane technology was developed.

4.4.1 Materials and methods

A poly(methyl methacrylate) electrochemical flowthrough cell reactor (see Figure 40) was constructed and utilized with an active volume of 40 ml and active membrane surface area of 70 cm^2. Materials used in the reactor configuration included a Celgard EZ2090 microporous membrane, a Nafion 424 membrane, a 70 cm^2 brass mesh and a 70 cm^2 Ru/IrO-coated Ti-mesh. Ag/AgCl reference electrode was used. Ammonia was captured in 100 ml of 0.1% H_2SO_4.

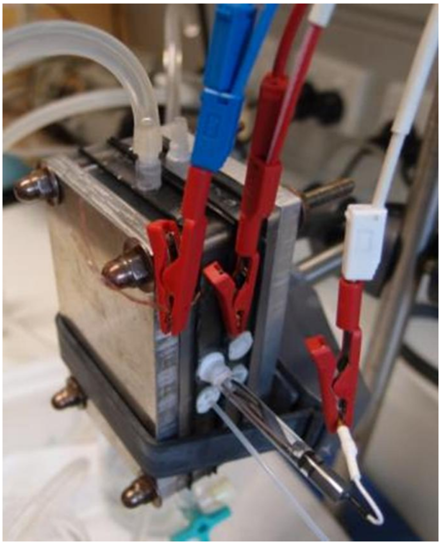


Figure 40. The acrylic 3-chamber reactor.

Model ammonia and nitrate containing wastewater were used containing Na_2SO_4, NaCl and $NaHCO_3$ as electrolytes supplemented with NH_4NO_3, $(NH_4)_2SO_4$ and $NaNO_3$ to reach desired ammonium and nitrate concentrations. Ammonia, nitrate and nitrite were measured using standardized flow injection analysis equipment and methods provided by University of Queensland Advanced Water Management Centre.

A series of 23 runs was conducted using different voltages, reaction times, ionic strengths and ionic compositions to find out the properties of the novel electrochemical method of nitrogen capture.

4.4.2 Results

The laboratory results supported the hypothesis of the functional principle of the electrochemical reactor.

The key elements affecting the reduction of nitrate were identified as the catalyst material and the voltage applied. Materials with catalytic properties include iron, steel, tin, copper and copper alloys. A step potential is required to achieve complete reduction and stepwise decrease of cathodic potential from -0.6 V to -1.5 V shows first no reduction activity, then partial reduction to nitrite and finally increasing rate of nitrate reduction.

The capture of ammonia from wastewater was validated for waters containing nitrogen in nitrate and ammonia or both forms. The key elements affecting the capture efficiency were identified as reactor configuration and especially surface parameters used, but clear correlation was seen with solution conductivity, voltage, ammonium concentration and ion composition.

The energy consumption of different setups and materials was measured and when energy price was estimated at 0.18 USD/kWh, a price range for ammonia capture for the technology was calculated. With optimal settings, a sample of 50 mg/l NH_4-N and 50 mg/l NO_3-N was treated to obtain 95% total nitrogen removal (99.7% nitrate removal) with 96% capture as ammonia utilizing 2.17 Wh of energy resulting in an energy price of 36 USD/kg N captured.

4.4.3 Conclusions

The results from the electrochemical tests were very encouraging and the technology is seen as potential for further development and possible large scale use. The technology is however still in early development stage and continuing research efforts are required to understand the complete reaction paths, kinetics, potential efficiency and feasibility in full scale real applications.

5. Behaviour and release of N from natural stone quarrying left over stone

The presence of nitrogen compounds in mining areas can have a detrimental effect to the environment. Besides environmental effects, contamination by explosive originated nitrogen compounds may be problematic due to the definition and classification of inert waste. “Nitrogen smudging” of otherwise mineralogically and chemically inert waste rocks of good technical quality may hinder the utilization of these product streams, which is an important economic and environmental issue at several quarries and mines.

The hypothesis was that nitrogen compounds gradually wash out or are released in gaseous form from the waste rock surfaces under atmospheric conditions but the rate at which this ‘ageing’ happens at small scale quarries is not well studied.

To study the ageing and the amount of nitrogen contamination on left over stone surfaces and to demonstrate the non-reactivity of the materials, a long-term field study was conducted at a selected site. The study area was a natural stone quarry located in Varpaisjärvi in Lapinlahti municipality in the Northern Savonia region (Figure 41).

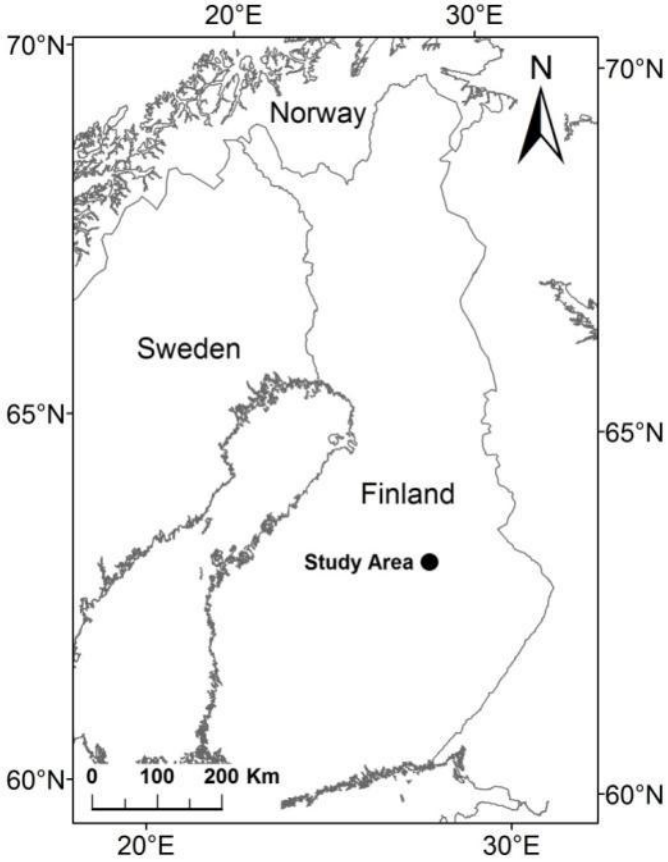


Figure 41. The target area (a natural stone quarry) was located in Varpaisjärvi in the Northern Savonia region of Finland.

5.1 Materials and methods

The main product of the target quarry is black, fine grained diabase, with average density of 3080 kg/m^3. The amount of total extraction is approximately 28500 m^3/year, of which around 24000 m^3, i.e. 73920 tons is left over stone. The use of explosives, mainly K-pipecharges by Forcit Oy, is roughly 5700 kg/year, the specific charges being around 0.2 kg/m^3 or 0.065 kg/t. According to the product information sheet (Forcit Oy 2013) the raw materials of the K-pipecharge powder explosives are nitroglycol (ethylene-glycol-dinitrate, content 17–25%), kieselguhr (diatomaceous earth), sodium nitrate and sodium chloride, packed in polypropylene pipes. The average nitrogen concentration of K-pipecharge is low compared to other explosives usually used in larger scale mining, only 4.2%. The water resistance of K-pipecharges is reasonable, but the unexploded agent dissolves gradually into water. The left over stones consist mainly of the same diabase material as the final products.

To evaluate the temporal changes in the quality of water emanating from left over stone, two ageing test units were installed at the quarry site. The test units consisted of 1 m^3 lysimeters, which were filled with left over rock material collected immediately after the excavation of a large diabase block. The rock material in both lysimeters was supposed to be identical and the purpose of setting up two units was to examine the repeatability of the test. Unit 1 contained approximately 1970 kg of rocks with 38% porosity (proportion of void space in the lysimeter), and Unit 2 contained approximately 1790 kg of rocks with 44% porosity. The test units are shown in Figure 42 and the material source in Figure 43.

The rain water flowing through the lysimeters was collected in separate 70-litre plastic tanks and analysed 9 times between 10th of October 2012 and 16th of October 2013, excluding the winter months when the test units were frozen. The sampling interval was 2 weeks during the first month and once a month during the rest of the monitoring period.

The monitored parameters included nitrogen species (NO_2, NO_3, NH_4 and total-N), Cl, pH, Ec and temperature. Chloride (Cl) is present in the rock dust and in the blasting residuals (as sodium chloride), and is considered a good indicator of the first flush of water through the test units (Bailey et al. 2013).

At the end of the observation period, the test units were filled (washed) with tap water three times (Unit 2 only once) to remove and quantify the remaining explosives-originated nitrogen and to determine the porosity and approximate weight of the rocks inside the test units.

Figure 42. The aging test units 1 (front) and 2 (behind). The rain water flowing through the units was collected in the green plastic tanks below. Photo: Lauri Solismaa / GTK.

Figure 43. The material source for the test units. Left over rock material was collected immediately after the excavation of a diabase block. Photo: Lauri Solismaa / GTK.

5.1.1 Field measurements and sampling

The untreated samples were collected into HDPE sample bottles that had been triple-rinsed with sample water. The sample bottles were sent to the laboratory in a cool box during the same day. The samples arrived to the laboratory next morning and were analysed as soon as possible, to minimize the alteration of the samples, especially the sensitive NO_2.

pH, temperature, electric conductivity, nitrite and ammonium were measured on the field. The pH was measured by the Mettler Toledo SevenGo pH-meter. The electric conductivity and temperature were measured by the WTW-electric conductivity meter Cond 340i. The nitrite and ammonium concentrations were analyzed with a portable Hach Lange DR2800 spectrophotometer using Lange cuvette tests LCK342 (0.6–6 mg/l NO_2-N) and LCK 304 (0.015–2 mg/l NH_4-N). The amount of rain water accumulated in the tanks was measured and the tanks were emptied after every sampling occasion.

Besides field measurements, the nitrogen species were also analysed in a laboratory to estimate the performance of the DR2800 spectrophotometer and to investigate the effects of transportation of the water samples to the laboratory. The results were comparable between the methods, although the portable spectrophotometer gave lower concentrations when the weather was colder.

5.1.2 Laboratory measurements

The laboratory measurements in an accredited laboratory (Labtium Oy) included total nitrogen, nitrite, nitrate and chloride. The NO_2 was measured by spectrophotometry. The anions NO_3 and Cl were measured using ion chromatography (IC) according to the standard SFS-EN-ISO 10304-1. NH_4 was measured by the Aquakem analysator (salicylate-spectrophotometric method). Total nitrogen was measured by the peroxodisulphate oxidation and Aquakem analysator (hydrazine reduction and spectrophotometric sulphanilamide method).

5.2 Results

The monitored concentrations and values followed similar trends in both test units, but the concentrations of the Test Unit 2 were somewhat lower (Table 10). At first, the electric conductivity and the concentrations e.g. of total-N and Cl were relatively high, but declined rapidly to rain water background values after the “first flush” (Figure 44, Figure 45). Cl declined more sharply and remained low for the remainder of the study. The nitrogen concentrations were more erratic, but the absence of Cl suggests that most of the nitrogen was derived from rain water / atmosphere.

The most abundant nitrogen species was NO_3. The NH_4-N concentrations were relatively high during the first flush, around 40% of the total N concentration. The field measurement values of NH_4 and NO_2 were mainly higher than those measured in laboratory, which may indicate the instability of the different nitrogen species during transport.

The total-N concentrations in rainwater have been measured by the Finnish Environment Institute (SYKE) in the closest weather station at Maaninka (about 40 km south west from Varpaisjärvi) during 2004–2012. The rainwater samples collected at the test units at Varpaisjärvi had similar total-N concentrations to Maaninka, around 0.6 mg/L. During two observation periods (30.4.2013 and 20.8.2013) the rainwater tanks were full and probably overflowed.

Table 10. Measured concentrations of NH_4-N, NO_2-N, NO_3-N, tot-N and Cl (mg/L), electric conductivity (µS/cm) and total amount of water collected in the tanks (L).

Sampling date	**NH_4-N (lab)**	**NH_4-N (field)**	**NO_2-N (lab)**	**NO_2-N (field)**	**NO_3-N**	**tot-N**	**Cl**	**eC**	**Litres**
Test Unit 1									
10.10.2012	1.09	0.43	N/A	0.09	1.27	2.5	898	1947	28
25.10.2012	0.06	0.03	0.01	0.08	1.15	0.8	55	507	48
8.11.2012	0.09	0.02	0.01	0.03	0.47	0.7	17.3	357	28
30.4.2013	0.01	0.04	0.01	0.06	N/A	0.9	3.7	199	> 70
6.6.2013	0.11	0.17	0.01	0.04	1.02	1.2	3.8	261	21
3.7.2013	0.01	0.01	0.01	0.02	N/A	0.7	3.4	399	49
20.8.2013	0.01	0.02	0.01	0.02	0.61	0.8	2.0	420	> 70
11.9.2013	0.04	0.03	0.02	0.02	0.41	0.6	1.0	313	7
16.10.2013	0.01	0.01	0.01	0.01	0.66	0.7	5.4	522	26
Test Unit 2									
Sampling date	**NH_4-N (lab)**	**NH_4-N (field)**	**NO_2-N (lab)**	**NO_2-N (field)**	**NO_3-N**	**tot-N**	**Cl**	**eC**	**Litres**
10.10.2012	0.53	0.30	N/A	0.10	1.13	1.3	574	1911	27.5
25.10.2012	0.03	0.06	0.01	0.04	0.86	0.4	43	376	48
8.11.2012	0.04	0.01	0.03	0.08	0.32	0.5	11.5	251	28
30.4.2013	0.05	0.09	0.02	0.05	0.53	0.8	6.0	112	> 70
6.6.2013	0.02	0.07	0.01	0.04	0.97	1.0	4.0	218	21
3.7.2013	0.02	0.01	0.01	0.02	N/A	0.3	2.6	218	49
20.8.2013	0.01	0.02	0.02	0.03	0.34	0.5	1.4	197	> 70
11.9.2013	0.21	0.21	0.01	0.02	0.38	0.7	0.9	181	10
16.10.2013	<0.01	0.00	0.01	0.01	0.43	0.6	4.3	287	29

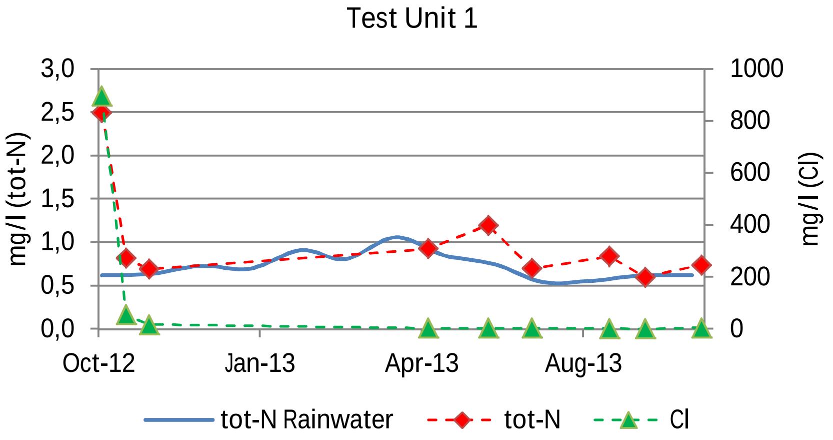


Figure 44. Total-Nitrogen and Chloride concentrations in the recharge waters of Test Unit 1 and total-N of rainwater in Maaninka (monthly averages during the years 2004–2012) measured by the Finnish Environment Institute.

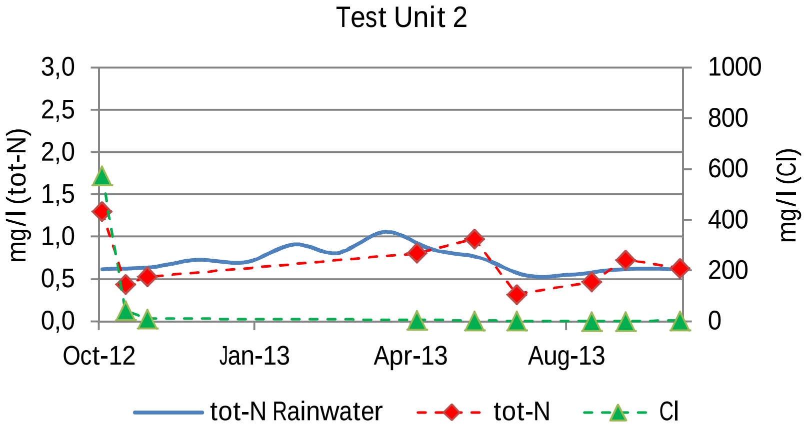


Figure 45. Total-Nitrogen and Chloride concentrations in the recharge waters of Test Unit 2 and total-N of rainwater in Maaninka (monthly averages during the years 2004–2012) measured by the Finnish Environment Institute.

The measured residual concentrations left in the lysimeters after the follow-up period are presented in Table 11. The amount of water to fill Unit 1 was 380 litres and 440 litres for Unit 2 (i.e. the porosities were 38% and 44%). The weight of rock in the units was calculated by volume and density of the diabase (in Unit 1 approximately 1970 kg and in the Unit 2 approximately 1790 kg).

Table 11. Wash water amounts and concentrations (mg/L) of tot-N, NH_4-N (field and lab), NO_2-N (field and lab), NO_3-N and Cl of the test units. Unit 1 was filled with tap water three times, Unit 2 only once. The tap water concentrations have been subtracted.

Sample	NH_4-N (lab)	NH_4-N (field)	NO_2-N (lab)	NO_2-N (field)	NO_3-N	tot-N	Cl	Water (L)
Test Unit 1								
1st wash	0.01	0.21	0.03	0.11	0.0	0.1	0.2	380
2nd wash	0.00	0.01	0.00	0.00	0.0	0.1	0.0	380
3rd wash	0.00	N/A	0.01	0.00	0.0	0.0	0.0	380
Test Unit 2								
1st wash	0.02	N/A	0.01	0.02	0.0	0.0	0.0	440

The amounts of total nitrogen released from the test units were calculated by multiplying the amounts of water (litres) by the concentrations of total nitrogen (Table 12). The nitrogen concentrations of the first flush were determined by subtracting the background value (0.6 mg/L in October) from the measured concentrations. The first flush includes the first samplings in October 2012 when the concentrations are higher than the background values of rainwater (Unit 1 10.10.2012 and 25.10.2012, Unit 2 only 10.10.2012).

The total amount of explosives-originated nitrogen leached from the Test Unit 1 was 138.8 mg i.e. 0.07 mg/kg and 32.5 mg i.e. 0.02 mg/kg for Test Unit 2. At the end of the test about half of the total nitrogen seemed to be left in the units after one year of ageing. Presumably some traces of explosives originated nitrogen was released also after the first flush, but the nitrogen concentrations were so close to the background values in rain water that assessment of the exact numbers is difficult. Also some small amounts were probably left in the stone material after the washings. Considering the uncertainty factors, the scale of the explosives originated nitrogen amount in the type of stone material used in this study is up to around 0.1 mg/kg or 0.1 g/t. Multiplying this by the annual average amount of left over stones (24 000 m^3 i.e.73 920 t) at the target quarry results in an explosives originated nitrogen load to runoff waters of around 7.4 kg/year from the waste rock pile (“worst case”).

Table 12. The amounts of total nitrogen released from the test units during first flush and washing. *NH_4-N+ NO_2-N concentrations.

Sample	tot-N (mg/L)	Water (L)	Released N (mg)
Test Unit 1			
10.10.2012	1.9	28	53.2
25.10.2012	0.2	48	9.60
1st wash	0.1	380	38
2nd wash	0.1	380	38
3rd wash	0.0	380	0
Total N			138.8
Test Unit 2			
10.10.2012	0.7	27.5	19.3
1st wash	0.03*	440	13.2
Total N			32.5

5.3 Discussion

The rock material in the test units presented a ”worst case”; real left over stone material contains more big boulders, so it has less surface area / kg (= less explosives-N / kg) than the finer material in the test units. Furthermore, because of the quarrying method not all of the left over stones have been in contact with explosives (approx. 50/50). This indicates that in practice the possible leaching from the left over stones is small.

Left over stones produced by natural stone industry seem to contain less explosives-originated nitrogen than the waste rocks produced by larger mining activities. For example waste rock at the Diavik diamond mine in Canada contains tot-N around 4.6 mg/kg (Bailey et al. 2013), and the waste rock and ore at the Kemi chromium mine around 20 mg/kg (Mattila et al. 2007).

The leaching tests conducted in this study apply for the K-pipecharge explosives used at the target quarry that contain relatively low amounts of nitrogen, about 4.2%. Different types of explosives exist for different purposes and their nitrogen contents and solubility may vary. In general the nitrogen content of different rock blasting explosives varies between 20–30% of total weight (Chlot 2011).

Lysimeters were relatively small scale compared to the size fractions of normal waste rock material, which gives uncertainty to the test setup. Also the explosive residuals are heterogeneously distributed in a waste rock material, as demonstrated by the differences between the two test units in this study.

5.4 Laboratory scale studies

During loading of the field test vessels sub-samples were taken aside from the same waste rock material and sent to VTT for laboratory scale comparison studies. At the laboratory samples were crushed to particle size below 4 mm. Up-flow percolation test CEN/TS 14405 was performed for the <4 mm material to study the leaching of N compounds.

The up-flow percolation test CEN/TS 14405 is used to simulate the leaching behaviour of a granular or powdery material in placement conditions at different time frames. In the test granular material is packed into a vertical column with diameter of 5 cm to a bed height of 30 cm. A peristaltic pump is used to pass demineralised water through the column. Liquid (the eluate) appearing at the outlet is collected in 7 fractions ranging from a liquid to solid (L/S) ratio of 0 l/kg to 10 l/kg. The eluate fractions are filtered and prepared for subsequent chemical analysis. The results are expressed in terms of accumulated leached amounts (mg/kg) as a function of L/S. Time to reach a certain liquid to solid ratio at the site of placement can be roughly estimated when annual infiltration through the material bed is known.

Figure 46 shows the evolution in leaching of N compounds from the waste rock material. In this case the tests were stopped when cumulative L/S ratio of 2 was reached. For comparison, results from the field test unit 1 are plotted alongside the laboratory results for total nitrogen.

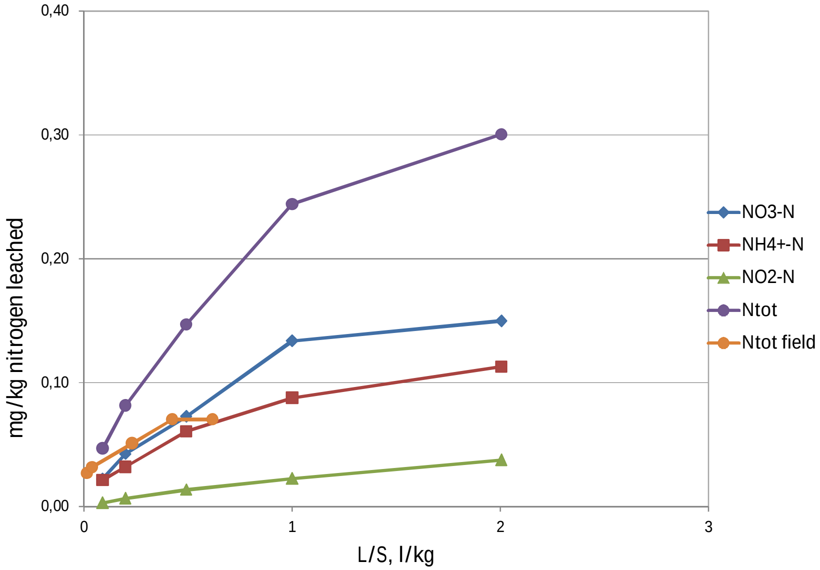


Figure 46. Leaching of N compounds from waste rock in up-flow percolation test and comparison to field test leaching.

It can be seen from Figure 46, that the leaching of total N in lab-scale is somewhat higher than in the field. They are however at the same order of magnitude.

5.5 Conclusion

Based on the observation period of more than a year the “first flush” of recharge water from the natural stone quarrying waste rock occurs quickly, during the first few weeks, after which the nitrogen drainage settles to natural rainwater levels. Based on calculations the first flush removes approximately half of the total nitrogen, mainly as NO_3 and NH_4.

Chloride, which is present in the pipecharge explosives as sodium chloride (Forcit Oy 2013), was observed to be a good indicator and representative of the first flush of recharge water, as the amount of Cl in waste rock does not increase by an external source. Nitrogen, on the other hand, had a more erratic tail, as natural rain water contains significant amounts of nitrogen species.

Calculations on the nitrogen leached out of the test units during the observation period and the remaining nitrogen detected on the rocks after the test period indicate that some explosive residuals remain within the test material. The remaining nitrogen is leached out fairly slowly, promoting also loss to the atmosphere.

The two seemingly identical units had different nitrogen concentrations, which suggest that the undetonated explosives are heterogeneously distributed in a waste rock pile.

The total amount of explosives-originated nitrogen on the waste rock material of a natural stone quarry seems to be on the scale of 0.1 mg/kg or below, which is well below the amount detected on the waste rock produced by a larger scale mine. The main reason for the difference is probably the moderate use of low nitrogen containing explosives in natural stone quarrying.

As the “nitrogen smudging” of natural stone quarrying left over stones is relatively low to begin with and enhanced by the rapid flushing by rainwater, the residues of explosives should not be considered to prevent the utilization of otherwise mineralogically inert waste rocks of good technical quality.

6. Nitrogen balances at case study areas

Most of the nitrogen load produced by the extractive industry is originated from the use of explosives. Explosives that remain unexploded after blasting are carried along with the ore, waste rock and dewatering water into different parts of the site and to receiving water systems. Despite the importance of case studies for assessing nitrogen related risks in the extractive industry, there is a deficiency of well documented ones, especially in smaller scale activities. (Morin & Hutt 2009)

In this project the nitrogen migration routes and balances were studied at two case study areas; Varpaisjärvi natural stone quarry and Kemi mine. The study included sampling of the surface waters around the sites. The sampling and field and laboratory measurements are described in Chapter 5.

6.1 Varpaisjärvi natural stone quarry

The research target was a diabase quarry located in Varpaisjärvi, in the Northern Savonia region of Finland (for more details, see Chapter 5). To evaluate the nitrogen discharge from the mine site, the surface waters around the quarry were monitored from August 2012 to November 2013. The sampling points are presented in Figure 47 and the monitored concentrations and values in Table 13.

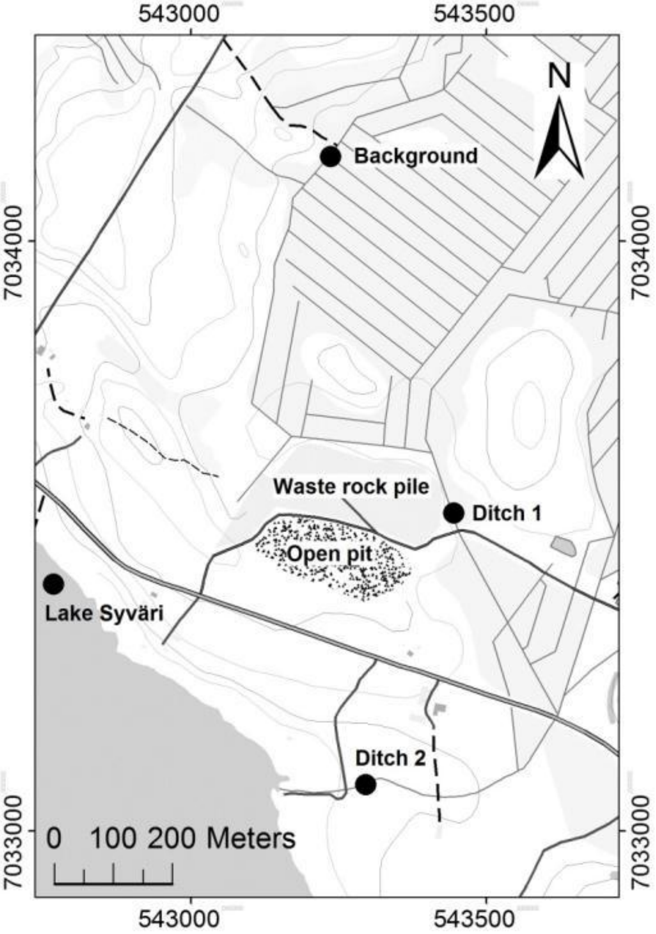


Figure 47. Surface water sampling points around the target quarry.

Table 13. Measured nitrogen and Cl concentrations (mg/L), eC (µS/cm) and pH around the Varpaisjärvi quarry.

Background

Sampling date	NH_4-N (lab)	NH_4-N (field)	NO_2-N (lab)	NO_2-N (field)	NO_3-N	tot-N	Cl	eC	pH
29.8.2012	0.02	0.03	N/A	0.05	<0.05	0.6	0.8	22	6.1
25.9.2012	0.02	0.03	0.02	0.04	<0.05	0.5	0.8	17	6.7
25.10.2012	0.02	0.07	0.03	0.06	0.23	0.5	0.8	27	6.1
30.4.2013	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6.6.2013	0.03	0.10	<0.01	0.07	<0.09	0.5	0.8	29	7.9
3.7.2013	0.01	0.09	0.05	0.07	<0.05	0.8	0.6	33	6.5
20.8.2013	0.03	0.06	0.02	0.04	0.18	1.3	<0.4	34	5.2
16.10.2013	0.01	N/A	0.03	0.04	<0.05	0.8	0.6	35	6.5

Ditch 1 (next to the left over stone pile)

Sampling date	NH_4-N (lab)	NH_4-N (field)	NO_2-N (lab)	NO_2-N (field)	NO_3-N	tot-N	Cl	eC	pH
29.8.2012	0.12	0.15	N/A	0.07	0.18	1.1	5.7	98	6.4
25.9.2012	0.16	0.11	<0.01	0.03	0.16	1.1	3.6	62	6.2
25.10.2012	0.19	0.08	<0.01	0.04	0.27	1.2	1.2	53	5.8
30.4.2013	0.15	0.22	0.05	0.08	0.20	1.1	3	32	6
6.6.2013	0.26	0.30	0.02	0.08	<0.05	1.2	35	433	7.7
3.7.2013	0.16	0.21	<0.01	0.04	<0.05	1.1	13.2	337	6.2
20.8.2013	0.09	0.13	0.03	0.05	0.32	1.5	1.5	61	4.7
16.10.2013	0.16	N/A	0.02	0.02	0.41	1.1	11.1	145	6.5

Ditch 2 (near Lake Syväri)

Sampling date	NH_4-N (lab)	NH_4-N (field)	NO_2-N (lab)	NO_2-N (field)	NO_3-N	tot-N	Cl	eC	pH
29.8.2012	0.06	0.07	N/A	0.03	0.14	1.1	3.9	77	6.1
25.9.2012	0.09	0.06	<0.01	0.08	0.09	1.1	4.8	71	6
25.10.2012	0.14	0.05	<0.01	0.04	0.27	1.2	1.8	51	5.8
30.4.2013	0.17	0.15	0.03	0.06	0.26	1.2	2	27	5.8
6.6.2013	0.20	0.20	0.02	0.06	<0.05	1.1	32	441	6.8
3.7.2013	0.19	0.31	0.06	0.08	<0.05	1.4	9.1	268	6.5
20.8.2013	0.06	0.09	0.05	0.05	0.36	1.5	1.6	65	4.7
16.10.2013	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Pit dewatering (drained to the left over stone pile)

Sampling date	NH_4-N (lab)	NH_4-N (field)	NO_2-N (lab)	NO_2-N (field)	NO_3-N	tot-N	Cl	eC	pH
3.7.2013	0.02	0.04	<0.01	0.02	<0.05	0.4	35.4	442	8.3
20.8.2013	0.01	0.09	0.04	0.07	0.63	1.0	14	354	7.1
11.9.2013	0.25	N/A	0.12	N/A	0.77	1.0	68	489	8.1
16.10.2013	8.54	N/A	0.21	0.38	10.2	19.0	137	741	7.7
20.11.2013	0.01	N/A	<0.01	N/A	1.17	1.4	19	N/A	N/A

Lake Syväri

Sampling date	NH_4-N (lab)	NH_4-N (field)	NO_2-N (lab)	NO_2-N (field)	NO_3-N	tot-N	Cl	eC	pH
3.7.2013	0.02	0.03	<0.01	0.02	<0.05	0.5	0.9	39	6.4
20.8.2013	0.01	0.02	0.02	0.01	<0.09	0.6	0.9	39	7.0

According to the results (Table 13), the average background concentration of tot-N was around 0.7 mg/l (forest trenches and rain water average), with seasonal changes from 0.5 to 1.3 mg/l. The amount of tot-N in the trench flowing through the quarry site (Ditch 1) rises on average about 0.47 mg/l compared to the background value, being 1.18 mg/l, with proportional and quantitative increase in NO_3 and NH_4. The quarry impact can also be detected as an increased amount of Cl and electric conductivity. The average amount of tot-N in pit dewatering water was 4.56 mg/l, in which the most abundant nitrogen species were NO_3 (56%) and NH_4 (39%). The measured tot-N concentrations in Lake Syväri were around 0.6 mg/l.

The average proportions of different nitrogen species in background, pit dewatering, ditch 1 and Lake Syväri samples are presented in Figure 48 (calculated with laboratory values). The average measured (laboratory) concentrations are presented in Figure 49.

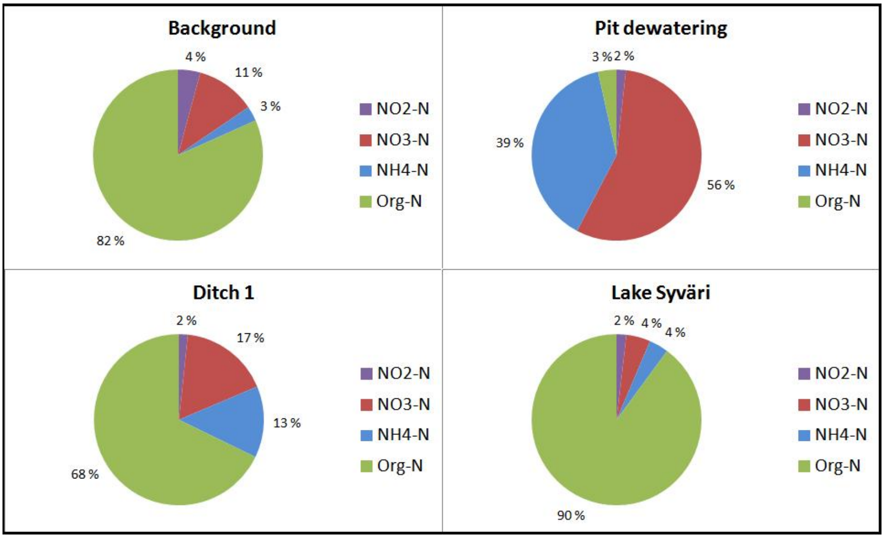


Figure 48. The average proportions of different nitrogen species in selected sample points. The amount of organic nitrogen was calculated by subtracting NO_2, NO_3 and NH_4 values from tot-N value.

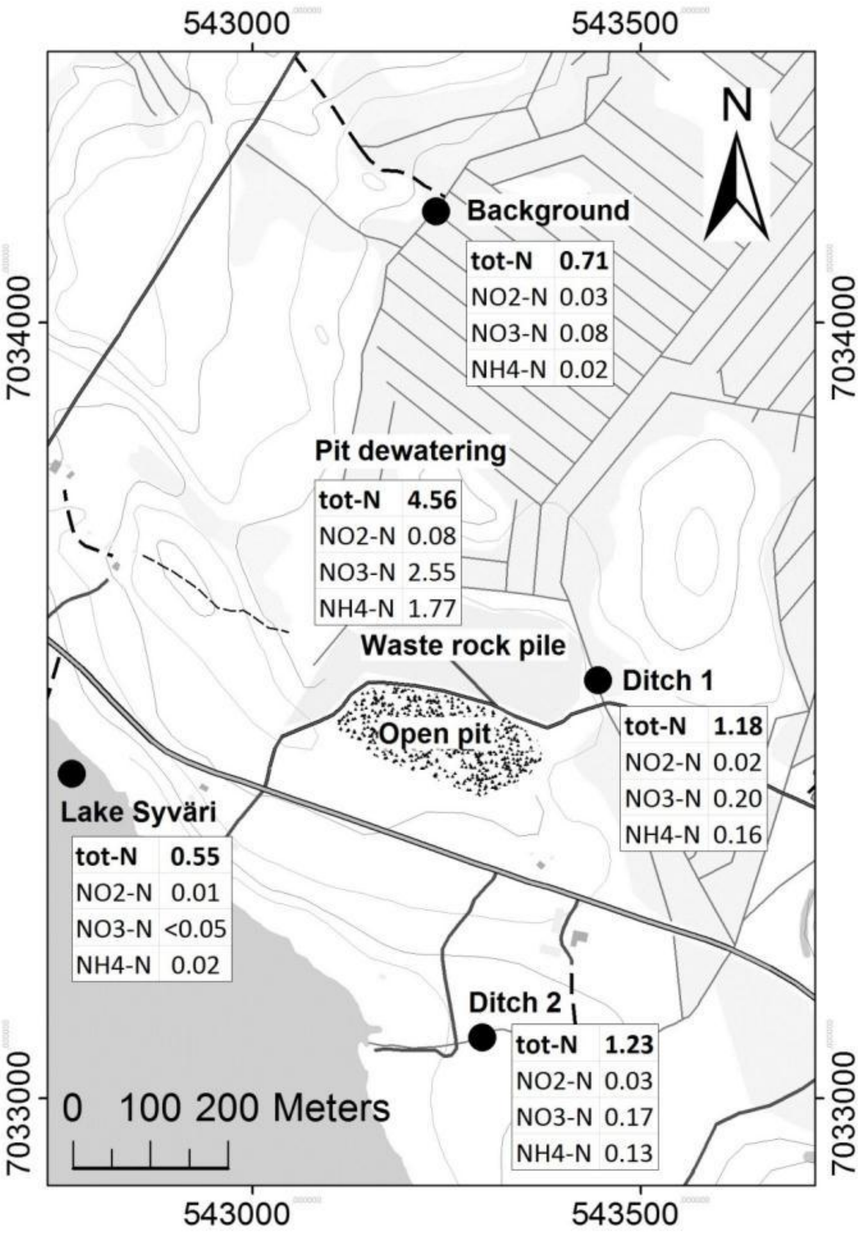


Figure 49. The average measured nitrogen concentrations (mg/L).

The average flow of the ditch was estimated to be around 4 litres / second. The estimated annual nitrogen load from the target quarry to Lake Syväri can be calculated by multiplying the flow (4 l/s) by the average input of tot-N by the quarry (0.47 mg/l), which results in a nitrogen load of around 59 kg/year.

An assessment of the nitrogen load can be made also by calculating the drainage from the waste rock pile and pit dewatering. No data exists concerning the amount of pit dewatering water, but an estimation can be made by multiplying the average annual precipitation 650 mm (Ilmatieteen laitos 2014), the pit area 24 000 m^2, and a “rule of thumb” evaporation of 50% (Mustonen 1986), which results in 7800 m^3 of water. Multiplying this amount of water with the average tot-N concentration of 3.9 mg/l (4.56 mg/l minus the average rain water concentration of 0.7 mg/l), explosives originated nitrogen load caused by dewatering can be estimated to be around 30.4 kg/year. The nitrogen load from the waste rock pile of the target quarry was estimated to be around 7.4 kg/year (Chapter 5). Combining the dewatering and waste rock pile drainages, the total estimated nitrogen load of the target quarry is around 38 kg/year.

Both estimations include obvious uncertainties, but the order of magnitude of the nitrogen load can be expected to be tens of kilograms / year. The results also suggest that pit dewatering water is the main source of explosives originated nitrogen, while emissions from the waste rock pile have a smaller role.

At the target quarry about 5 700 kg of K-pipecharges are used annually. The nitrogen concentration of average K-pipecharge explosive is 4.2%, which results in 239 kg of tot-N per year. The estimations on nitrogen load calculated above indicate that 16–25% of nitrogen used in natural stone blasting is leached into drainages.

6.2 Kemi mine

The Kemi chromium mine is located in North-West Finland, some kilometres north of the city of Kemi. The production started in 1968, first in open pit mining but gradually transferred underground during the early 2000’s. Today the mine operates fully underground and the production has been increasing. In 2013 the mine produced over 1.7 Mt of chromium ore, the total extraction being around 2.7 Mt. While moving underground, the amount of piled waste rock has been decreasing as the empty stopes are filled with barren rock. (Outokumpu Chrome Oy 2014)

The mine waters (mine area drainage, process water and mine dewatering water) are directed to a pond system, from where some water is circulated back to the mine processes and the rest is further discharged into dike Iso-Ruonanoja. The annual nitrogen load is estimated by comparing the nitrogen concentrations in background samples and the samples taken from Iso-Ruonanoja downstream from the mine area. The Kemi mine site, including the tailings area and settling ponds, water routes, background sampling point and the sample point downstream from the mine area is presented in Figure 50. (Outokumpu Chrome Oy 2013)

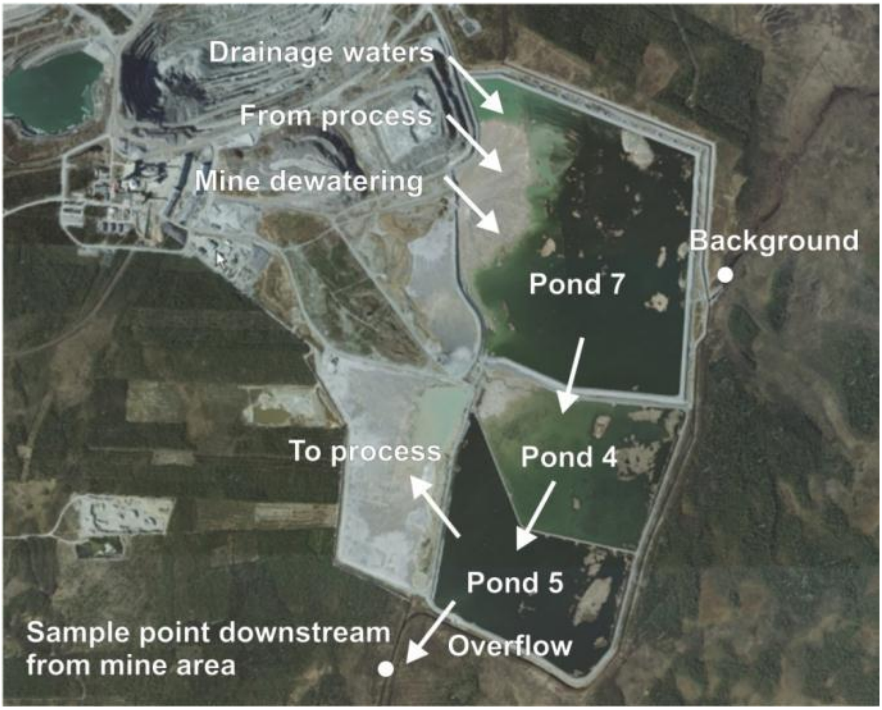


Figure 50. The Kemi mine site and water routes.

According to Mattila et al. (2007) and Tuokila (2008) the main nitrogen inputs to the pond system are the process water from the refinery and the mine dewatering. To evaluate the nitrogen balances at the pond system water samples were taken in June 2013 and additional nitrogen data was obtained from the Outokumpu Company and the Hertta database of Finland’s environmental administration. The analytical results are presented in Table 14. Figure 51 presents how the total nitrogen concentration and proportions of different nitrogen species vary from the first pond to the last in different seasons of the year. Figure 52 presents the seasonal change of nitrogen concentrations in the dike Iso-Ruonanoja, downstream from the mine.

Table 14. Measured nitrogen and Cl concentrations, eC and pH along the water system of the Kemi mine. Concentrations mg/L, eC µS/cm.

Kemi mine, 13.6.2013									
Sample	**NH_4-N (lab)**	**NH_4-N (field)**	**NO_2-N (lab)**	**NO_2-N (field)**	**NO_3-N**	**tot-N**	**Cl**	**eC**	**pH**
Dewatering	4.81	x	1.7	x	46.09	55.0	1085	3780	8.0
Enrichment plant	3.73	x	0.30	x	13.22	17.0	123	825	9.2
Pond 7	0.30	0.31	0.09	0.11	5.06	6.1	151	794	8.3
Pond 4	0.03	0.04	0.05	0.06	2.55	2.7	129	747	9.2
Pond 5	0.02	0.03	0.03	0.03	1.73	1.8	103	605	9.0
Kemi mine, 17.9.2012 (by Nablabs Oy in 2012)									
Sample	**NH_4-N (lab)**		**$NO_{2,3}$-N (lab)**			**tot-N**			
Dewatering	2.90		32.00			35.0			
Enrichment plant	1.70		5.80			7.5			
Pond 7	0.07		1.40			2.0			
Pond 4	0.06		0.26			2.8			
Pond 5	0.03		<0.005			0.9			
Kemi mine, 15.1.2013 (by Nablabs Oy in 2013)									
Sample	**NH_4-N (lab)**		**$NO_{2,3}$-N (lab)**			**tot-N**			
Pond 7	1.30		5.00			6.8			
Pond 4	0.41		1.20			1.8			
Pond 5	0.67		1.70			2.8			

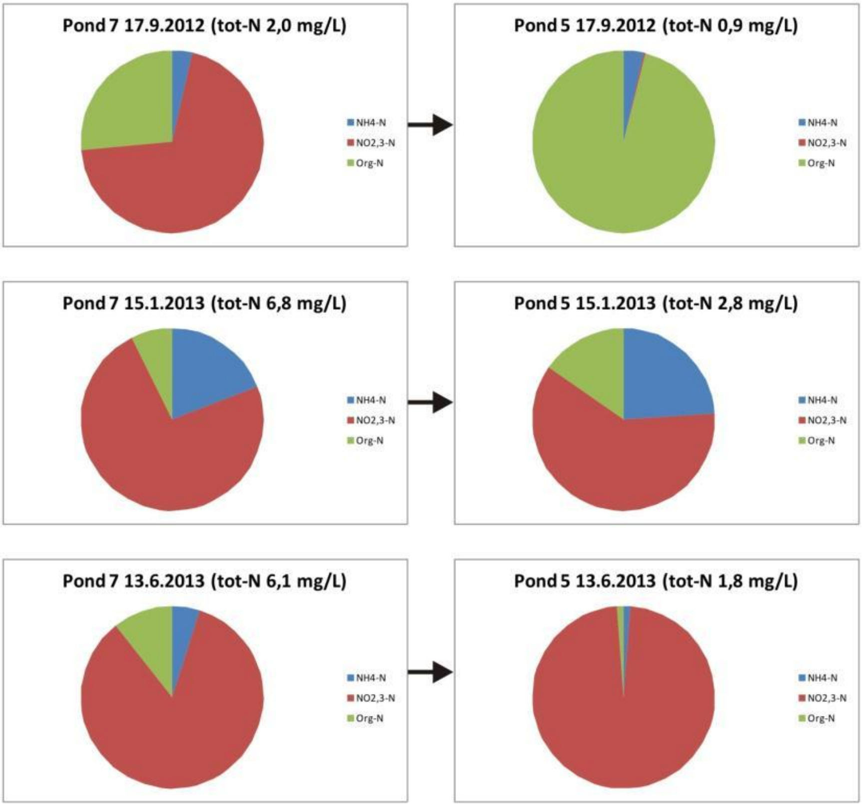


Figure 51. The total nitrogen concentration and proportions of different nitrogen species vary from the first pond to the last in different seasons of the year. The amount of organic nitrogen was calculated by subtracting NO_2, NO_3 and NH_4 values from tot-N value.

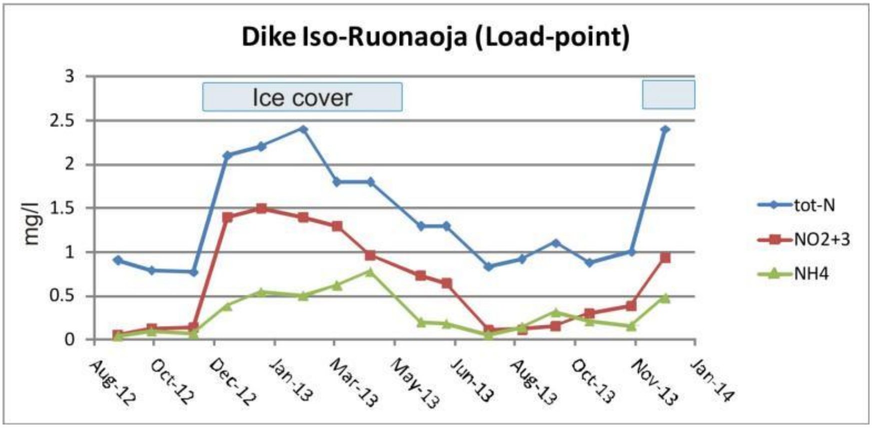


Figure 52. Seasonal variation of total nitrogen, NO_{2+3} and NH_4 concentrations in the dike Iso-Ruonanoja, downstream from the Kemi mine. Concentrations and ice cover data from Hertta database (sample place name: ISO-RUONAOJA, KAIVOS AP, samples taken and analysed by NabLabs Oy).

In general the concentrations of total nitrogen and mineral nitrogen species decrease along the watersystem from Pond 7 to Pond 5, also during winter. The seasonal data indicates that the pond system's ability to remove mineral nitrogen species (NO_2, NO_3, and NH_4) is at its highest level during late summer and autumn, from July to November, when the vegetation is full-grown. The amount of nitrogen, especially NO_{2+3} and NH_4 concentrations, increase significally during ice cover. The concentration levels begin to drop in spring when biological activity increases.

The results support the estimation of Mattila et al. (2007) that the total *in situ* removal of nitrogen in the pond system is around 58% annually. The key elements for nitrogen removal at the pond system are long retention time and rich vegetation that provides a carbon source for denitrifying processes (Mattila et al. 2007).

In general, estimations of how much nitrogen of the total nitrogen in the explosives end up into the environment vary between 0.2% and 28%, the average of underground metal mines being around 10% or higher (Morin & Hutt 2009, Kauppila et al. 2011).

Data about the use of explosives, extracted rock material, measured nitrogen concentrations and precipitation during the years 2007-2013 was obtained from the mining company and is presented in Table 15. The amount of nitrogen in the explosives mainly used (Kemiitti 810) is estimated to be 28%. The nitrogen loads to the environment have been estimated by comparing background values and concentrations after the mine (Outokumpu Chrome Oy2014).

Table 15. Data about used explosives, extracted material, measured nitrogen amounts and precipitation at the Kemi mine during 2007–2013.

Year	Explosives used (t)	Explosives-N (kg)	Extracted (t)	Explosives / extracted (kg/t)	tot-N load (kg), by Pöyry	Explosives-N to environment (%)	Precipitation (mm)
2007	679	190120	1611682	0.42	10376	5.5	710.1
2008	740	207200	1822408	0.41	10023	4.8	666.0
2009	379	106120	712780	0.53	6555	6.2	486.6
2010	898	251440	2052901	0.44	5786	2.3	545.2
2011	1120.6	313768	2264147	0.49	9457	3.0	754.5
2012	915.1	256228	1901269	0.48	21283	8.3	864.2
2013	1333.2	373296	2684182	0.50	17233	4.6	640.6

The measured nitrogen loads suggest that an average of 5% of total nitrogen in explosives ends up to the water system below the Kemi mine, ranging annually from 2.3 to 8.3%.

6.3 Conclusions

Nitrogen contamination of natural stone quarrying is relatively low (tens of kilograms per year) compared to larger mining activities (thousands of kilograms per year), which is obvious when taking into account the amounts of explosives used. For further comparison, annual nitrogen drainage from agriculture is estimated to be 8–20 kg/ha (Rekolainen 1992). Based on the relatively small nitrogen load of the natural stone quarrying the need for additional nitrogen purification is questionable.

Although some undetonated explosives are carried to the waste rock piles along with the stone material, the main sources of nitrogen loads are process and dewatering waters, irrespective of the scale of mining activity.

Type of the explosives used affects the relative amount of leached nitrogen. The calculations on nitrogen released from the target quarry in Varpaisjärvi correspond to a 16–25% loss of nitrogen from blasting explosives used commonly in natural stone extraction. At the Kemi mine the loss of nitrogen of the emulsion type explosive is probably around 10%, but the efficient pond system together with closed process water circulation reduces the amount of explosives-originated nitrogen ending up to the water system to 5%. The pond system’s efficiency has seasonal variation; natural biological processes remove inorganic nitrogen well during summer and autumn, but the amount of nitrogen, especially NO_{2+3} and NH_4 concentrations, increases significantly during ice cover and remains high until the vegetation is full-grown. If the water reservoir has to be emptied during winter or spring, the mineral nitrogen load to environment will be higher. Another important aspect regarding the annual nitrogen load to the environment seems to be the amount of precipitation; excess of water leaches more nitrogen and complicates the water management at the mine site.

7. Conclusions

The natural nitrogen cycle is of crucial importance to living organisms. Atmospheric nitrogen is converted to nitrate ions through lightning storms and nitrogen fixing bacteria. The nitrates fertilize plant growth whereby N becomes bound in compounds (amino acids, DNA and proteins) that can be consumed by animals. Over time, the nitrogen from plants and animals is returned to the soil and atmosphere. However, the excessive release of nutrients from municipalities and industrial activities to the environment can cause eutrophication in the receiving waterways. Nitrate ion is the primary source of nitrogen for aquatic plants, thus inducing eutrophication. Ammonia is toxic for aquatic animals in relatively low concentrations. Also nitrate can be toxic in elevated levels.

The concentration of nitrogen compounds in groundwater and surface water is normally low, but can reach higher levels, if it is contaminated by human activities (CCME 2012). Anthropogenic sources of nitrogen compounds in water include agricultural fertilizers, manure, domestic sewage, biowaste, industrial wastewaters from e.g. fertilizer plants, food industry, oil refineries and chemical production, as well as precipitation.

Extractive industries, including mining and quarrying operations is one of the sectors where the spreading of nitrogenous compounds into water and their incorporation into mineral materials can be a challenge. Most minerals and rocks contain very low concentrations of nitrogenous compounds. However, typical explosives and leaching processes, especially cyanide leaching, used in mining activities can produce a range of nitrogen-containing compounds of environmental concern.

Once in environment, nitrogen can convert to different species (nitrate, nitrite, ammonium, nitrogen gas), depending on the redox conditions and biological activities. In the Nordic conditions, the seasonal variations in precipitation and temperature may play a significant role in the nitrogen loading and transformations.

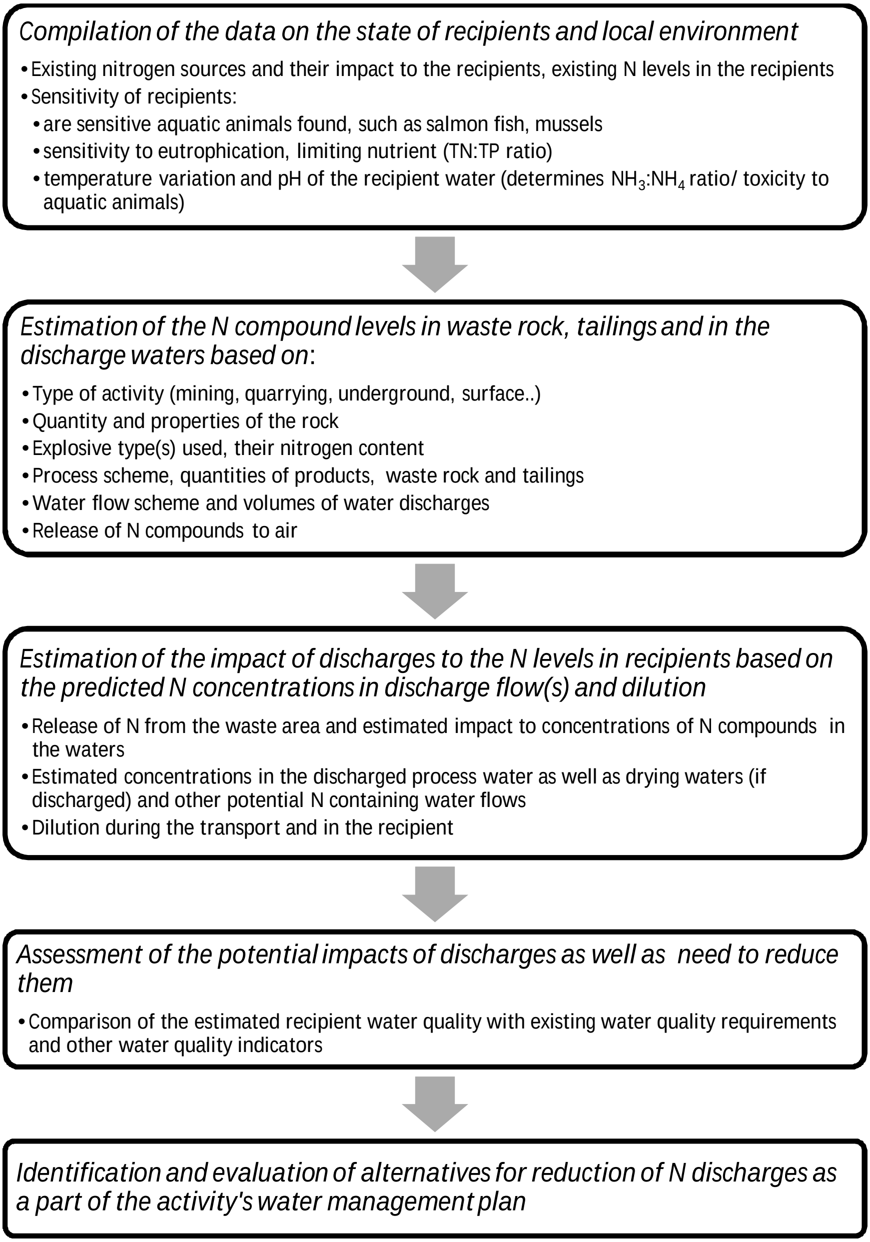
Because of the complex behaviour and sensitive environments, it is important to minimise the nitrogen discharges to the environment by using good management practices and by developing cost effective water treatment techniques.

7.1 Nitrogen management procedure

First estimation of the nitrogen balance and nitrogen load into the environment is carried out in the planning stage of the activity. The first estimate of impacts is also made, including predicted concentrations and their influence in the recipients. The information needed for the assessment includes quantities and types of explosives as well as other nitrogen containing chemicals, process, water and solid material flow schemes, background concentrations of nitrogen compounds, sensitivity of the local ecosystem to nitrogen as well as the other local nitrogen sources. Normally this data is also needed for the Environmental Impact Assessment (if the activity is subject to the EIA procedure) and environmental permissions.

In later stages the calculations should be revised based on the more exact data about the use of explosives and other nitrogen containing chemicals and the measured environmental loads.

As an example, the main stages of the nitrogen management procedure for explosive originated N compounds are described below (Figure 53, Figure 54). Typical values of the parameters needed in the estimation of the nitrogen load in blasting are given in Table 16.



Compilation of the data on the state of recipients and local environment

- Existing nitrogen sources and their impact to the recipients, existing N levels in the recipients
- Sensitivity of recipients:
  - are sensitive aquatic animals found, such as salmon fish, mussels
  - sensitivity to eutrophication, limiting nutrient (TN:TP ratio)
  - temperature variation and pH of the recipient water (determines NH_3:NH_4 ratio/ toxicity to aquatic animals)

Estimation of the N compound levels in waste rock, tailings and in the discharge waters based on:

- Type of activity (mining, quarrying, underground, surface..)
- Quantity and properties of the rock
- Explosive type(s) used, their nitrogen content
- Process scheme, quantities of products, waste rock and tailings
- Water flow scheme and volumes of water discharges
- Release of N compounds to air

Estimation of the impact of discharges to the N levels in recipients based on the predicted N concentrations in discharge flow(s) and dilution

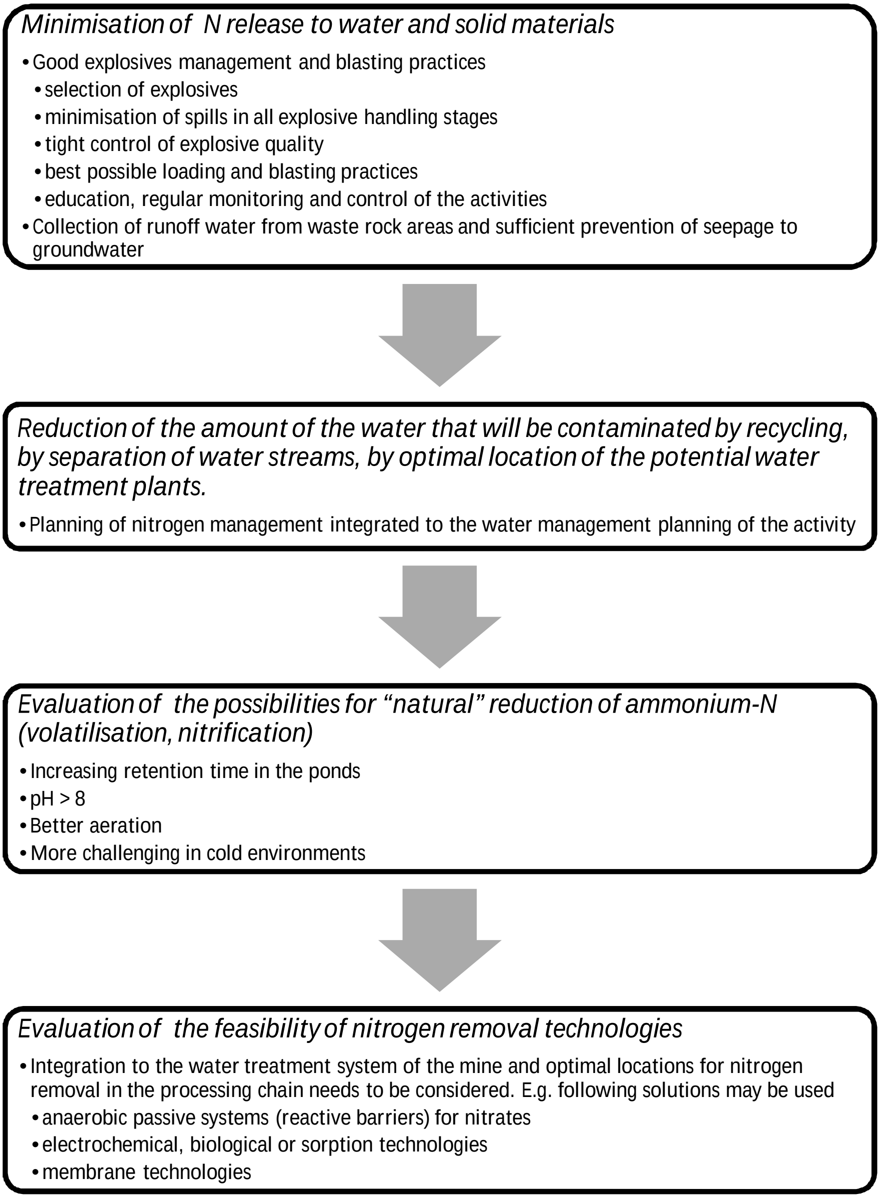
- Release of N from the waste area and estimated impact to concentrations of N compounds in the waters
- Estimated concentrations in the discharged process water as well as drying waters (if discharged) and other potential N containing water flows
- Dilution during the transport and in the recipient

Assessment of the potential impacts of discharges as well as need to reduce them

- Comparison of the estimated recipient water quality with existing water quality requirements and other water quality indicators

Identification and evaluation of alternatives for reduction of N discharges as a part of the activity's water management plan

Figure 53. Nitrogen management procedure for explosive originated nitrogen compounds.



Minimisation of N release to water and solid materials

- Good explosives management and blasting practices
  - selection of explosives
  - minimisation of spills in all explosive handling stages
  - tight control of explosive quality
  - best possible loading and blasting practices
  - education, regular monitoring and control of the activities
- Collection of runoff water from waste rock areas and sufficient prevention of seepage to groundwater

Reduction of the amount of the water that will be contaminated by recycling, by separation of water streams, by optimal location of the potential water treatment plants.

- Planning of nitrogen management integrated to the water management planning of the activity

Evaluation of the possibilities for "natural" reduction of ammonium-N (volatilisation, nitrification)

- Increasing retention time in the ponds
- pH > 8
- Better aeration
- More challenging in cold environments

Evaluation of the feasibility of nitrogen removal technologies

- Integration to the water treatment system of the mine and optimal locations for nitrogen removal in the processing chain needs to be considered. E.g. following solutions may be used
  - anaerobic passive systems (reactive barriers) for nitrates
  - electrochemical, biological or sorption technologies
  - membrane technologies

Figure 54. Identification and evaluation of alternatives for reduction of N discharges.

Table 16. Typical values of the parameters needed in the calculation of nitrogen load from blasting.

Component	**Type**	**Typical values**	**Background information**
Nitrogen content of explosives, weight %	Emulsified explosives	25–28%	Typical composition: 70–80% NH_4NO_3, 10–20% water, ca. 4% oil, 1–2% additives
	ANFO	ca. 33%	94.5%, 5.5% fuel oil
	Dynamite based cartridges	20–30%	Nitroglycerol or nitroglycol, diatomite or other impregnation material, plastic tubes
Typical explosive use	Open pit mining	1 kg/m^3 rock (0.5–1.2 kg/m^3)	
	Underground mining	1.5–2.5 kg/m^3 rock	
Non-detonated, %	Open pit mining	2.5–3%	
	Underground mining	10–20%	10–12% with specific attention to blasting, loading and storage practices
Specific densities of rock, examples (SImetric)	Crushed waste rock (most typical)	1.5–2.2 t/m^3	
	Gneiss, crushed	1.8 t/m^3	
	Gneiss, solid	2.6–2.9 t/m^3	
	Granite, crushed	1.6–1.7 t/m^3	
	Granite, solid	2.6–2.7 t/m^3	
	Pyrites	2.4–5.0 t/m^3	
	Copper ore	1.9–2.6 t/m^3	Depends on mineral composition
	Iron ore, crushed	ca 2.1–2.9 t/m^3	

7.2 Nitrogen removal technologies

Nitrogen removal from water is a common process in municipal and industrial wastewater treatment. In mining activities, no specific nitrogen removal or treatment unit, apart from cyanide destruction, has been conventionally used to treat wastewater. Thus, nitrogen is usually mitigated through wetlands treatment, dilution and natural attenuation and is usually in an oxidized nitrate form when entering the environment.

In municipal and industrial wastewater treatment nitrogen is most commonly removed by biological nitrification and denitrification, and air stripping, respectively. Neither of these technologies is, however, readily suited for subarctic mining wastewater applications due to low organics concentration, low temperature, high volume and low ammonium concentration.

A selection of other technologies for nitrogen removal from wastewater have been developed and also commercialized. These include membrane separation, wetland treatment (physical), anammox reactors and autotrophic denitrification reactors (biological), catalytic denitrification, electrochemical treatment options and sorption technologies (chemical). Based on a literature review, selective sorption and electrochemically assisted membrane separation were identified as most promising technologies for subarctic mining wastewaters, as well as biological treatment, if it could be operated on mine wastewater in cold climates.

TUT tested the denitrification and nitrification of mine wastewater in separate laboratory scale bioreactors and the inhibition of pH, temperature and metal ions. The outcomes revealed that denitrification was possible at low pH (2.5) and temperatures as low as 7°C. Nitrification was more pH sensitive as ammonium oxidation was partially inhibited already at pH 6.5. Both processes tolerated metals (Fe, Ni, Co and As) typically present in mine processing waters and acid mine drainage.

VTT and GTK tested the selective adsorption of nitrogen compounds. While tests with nitrate adsorption gave discouraging results, selective ammonium sorption using natural zeolite ion exchange worked well and complete ammonium removal from real mine wastewater was achieved with a hydraulic retention time of 2 minutes, with complete regeneration. Zeolite sorption is identified as a feasible ammonium removal method for mine wastewaters.

VTT also developed a novel electropervaporative nitrogen capture technology that can recover nitrate and ammonium nitrogen from a water stream simultaneously as pure ammonia gas. The technology is patented, but is still in a development stage for real scale applications. For simulated mine wastewater complete nitrogen removal and capture as ammonia was achieved with an energy cost of app. 40 $/kg N. Further material and technology development could potentially reduce the cost close to 1 $/kg N, which would make it an economically feasible technology for large mine wastewater streams. VTT will continue the development of the technology in continuing projects.

The technology review, testing and development showed that a wide range of technologies exist for nitrogen removal, but no direct full scale technology references were directly applicable for subarctic mine conditions, and further larger scale testing and development of novel sorption, electrochemical or biological technologies is required to ensure their feasibility in a real mining site. While nitrogen removal is not technically limited, the mining water quantity makes the cost of removal a key question in assessing the feasibility of the technologies.

7.3 Nitrogen balances and flushing

The left over stones produced by natural stone quarrying seem to be relatively nitrogen free. Based on the observation period of more than a year at the target quarry, the “first flush” of recharge water from the left over stones occurs shortly, during the first few weeks after the detonation, after which the nitrogen drainage settles to natural rainwater levels. Based on calculations the first flush removes approximately half of the total nitrogen, mainly in NO_3 and NH_4 forms.

Chloride was observed to be a good indicator and representative of the first flush of recharge water, as the amount of Cl in waste rock does not increase by an external source. Nitrogen, on the other hand, had a more erratic tail, as natural rain water contains significant amounts of nitrogen species.

Calculations on the nitrogen leached out of the test units during the observation period and the remaining nitrogen detected on the rocks after the test period indicate that some explosive residuals remain within the test material. The remaining nitrogen is leached out fairly slowly, promoting also loss to the atmosphere.

The two seemingly identical units had different nitrogen concentrations, which suggest that the undetonated explosives are heterogeneously distributed in a waste rock pile.

The total amount of explosives-originated nitrogen on the waste rock material of a natural stone quarry seems to be on the scale of 0.1 mg/kg or below, which is well below the amount detected on the waste rock produced by larger scale mining activities. The main reason for the difference is probably the moderate use of low nitrogen containing explosives in natural stone quarrying.

As the “nitrogen smudging” of natural stone quarrying left over stones is relatively low to begin with and enhanced by the rapid flushing by rainwater, the residues of explosives should not be considered to prevent the utilization of otherwise mineralogically inert waste rocks of good technical quality.

Nitrogen load of natural stone quarrying is relatively low (tens of kilograms per year) compared to larger mining activities (thousands of kilograms per year), which is obvious when taking into account the amounts of explosives used. Based on the relatively small nitrogen load of the natural stone quarrying the need for additional nitrogen purification is questionable.

Although some undetonated explosives are carried to the waste rock piles along with the stone material, the main sources of nitrogen loads are process and dewatering waters, irrespective of the scale of activity.

Type of the explosives used influences the relative amount of leached nitrogen. The calculations on nitrogen released from the target quarry in Varpaisjärvi correspond to a 16–25% loss of nitrogen from blasting explosives commonly used in natural stone extraction. At the Kemi mine the loss of nitrogen of the emulsion type explosive is probably around 10%, but the efficient pond system reduces the amount of nitrogen ending up to the water system to 5%. The pond system’s efficiency has seasonal changes; natural biological processes remove inorganic nitrogen well during summer and autumn, but the amount of nitrogen, especially NO_{2+3} and NH_4 concentrations, increases significantly during ice cover and remains high until the vegetation is full-grown. If the water reservoir has to be emptied during winter or spring, the mineral nitrogen concentrations will be higher. Another important aspect regarding the annual nitrogen load to the environment seems to be the amount of precipitation; excess of water leaches more nitrogen and complicates the water management at the mine site.

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Zou, G., Papirio, S., Ylinen, A., Di Capua, F., Lakaniemi, A.M., Puhakka, J.A. 2014. Fluid-ized-bed denitrification for mine waters. Part II: effects of Ni and Co. Biodegradation 25, 417-423.

Appendix A: List of publications

<u>Peer-reviewed articles</u>

Papirio, S., Ylinen, A., Zou, G., Peltola, M., Esposito G. & Puhakka, J.A. 2013. Fluidized-bed denitrification for mine waters. Part I: low pH and temperature operation. Biodegradation. 25:425-435

Zou, G., Papirio, S., Ylinen, A., Di Capua, F., Lakaniemi, A.M. & Puhakka, J.A. 2013. Fluidized-bed denitrification for mine waters. Part II: effects of Ni and Co. Biodegradation 25:417–423

Zou, G., Ylinen A., Di Capua, F., Papirio, S, Lakaniemi A.M. & Puhakka, J.A. 2013. Impact of heavy metals on denitrification of simulated mining wastewaters. Advanced Materials Research 825:500-503

Papirio, S., Zou, G., Ylinen, A., Di Capua, F., Pirozzi, F. & Puhakka, J.A. 2014. Effect of arsenic on nitrification of simulated mining water. Bioresource Technology 164:149–154.

Zou, G., Papirio, S., Van Hullebusch, E.D. & Puhakka, J.A. 2015. Fluidized-bed denitrification of mining water tolerates high nickel concentrations. Bioresource Technology 179:284-290.

Jermakka, J., Wendling, L., Sohlberg, E., Heinonen, H. & Vikman, M. 2014. Potential Technologies for the Removal and Recovery of Nitrogen Compounds from Mine and Quarry Waters, Critical Reviews of Environmental Science and Technology. doi: 10.1080/10643389.2014.900238

Jermakka, J., Mehta, C. & Batstone, D. Combined cathodic recovery of ammonia, nitrate and nitrite from low-organics wastewater using cathodic pervaporation (submitted)

Conference and other presentations

Arsenic and nitrogen compound discharges in mining and solutions to their removal', Annual seminar of Tekes Green Mining -program, Finlandiatalo 24.10.2012.

Ulla-Maija Mroueh, Johannes Jermakka, Elina Merta, Raisa Neitola, Teemu Karlsson, Jaakko Puhakka, Stefano Papirio and Aino-Maija Lakaniemi. 2014. Control of nitrogen discharges at mines and quarries. Poster. Annual Seminar of Tekes Green Mining Program 24.11.2014.

R. Neitola, T. Korhonen, P. Mörsky, S. Backnäs, K.Turunen, T. Karlsson, GTK; T. Kaartinen, J. Laine-Ylijoki, J. Jermakka, U-M. Mroueh, VTT; S. Ahoranta, S.Papirio, J.A. Puhakka, Tampere University of Technology. 2013. Solutions for Control of Arsenic and Nitrogen Discharges in Mining Areas and Processes. FEM, Poster presentation.

Arsenic and Nitrogen handling in Mining Areas and Processes. 2013. Euromining 2013. Green Mining Seminar, Tampere.

Teemu Karlsson, Tommi Kauppila, Kaisa Turunen, Pekka Forsman, Janita Laakso. 2014. Behaviour of explosives-originated nitrogen compounds in left-over stone of a dimension stone quarry. 11. Geokemian päivät, 5.-6.2.2014

S. Papirio, G. Zou and J.A. Puhakka. 2014. Nitrification of arsenic-containing mining waters. Biohydrometallurgy'14, Falmouth, UK.

G. Zou, S. Papirio and J.A. Puhakka. 2014. Impact of Ni^{2+} on denitrification of mining waters in fluidized-bed reactors. Sustainability through Resource Conservation and Recycling '14 (SRCR'14), Falmouth, UK.

Presentations of the project in Tekes Green Mining workshops and in collaboration meeting with the Technical University of Luleå and LKAB

Teemu Karlsson, et al. Article on behaviour of explosives-originated nitrogen compounds in left-over stone. In writing

Patent applications

Jermakka, J. Patent Application No. 20145623. Nitrate, nitrite and ammonium capture from wastewater. Filed 27.6.2014.

Additional project reports

Jermakka, J., Wendling, L., Sohlberg, E., Heinonen, H., Laine-Ylijoki, J., Merta, E., Kaartinen, T. and Mroueh, U.-M. 2015. Nitrogen compounds at mines and quarries. Sources, behaviour and removal from mine and quarry waters, Literature study. Will be published in VTT Technology Series.

Series title and number

VTT Technology 225

Title	**Solutions for control of nitrogen discharges at mines and quarries** Miniman project final report
Author(s)	Johannes Jermakka, Elina Merta, Ulla-Maija Mroueh, Helena Arkkola, Sini Eskonniemi, Laura Wendling, Jutta Laine-Ylijoki, Elina Sohlberg, Hanna Heinonen, Tommi Kaartinen, Jaakko Puhakka, Minna Peltola, Stefano Papirio, Aino-Maija Lakaniemi, Gang Zou, Anna Ylinen, Francesco di Capua, Raisa Neitola, Henrik Gustafsson, Tero Korhonen, Teemu Karlsson, Tommi Kauppila, Janita Laakso & Pekka Mörsky
Abstract	The growth of Finnish extractive industry increases the need to study and monitor different environmental impacts and to integrate the environmental issues more tightly into the overall framework of the activities. Nitrogen released from explosives or from mining processes and ending up in the water system can have negative environmental effects. The MINIMAN project, financed by the Tekes Green Mining Programme and the industry aimed at comprehensive understanding on the nitrogen issue in the extractive industry. The project collected essential data on nitrogen compounds present in the environments of mines and quarries, and developed technologies for the treatment of nitrogen containing mine water. Based on a technology review, selective sorption, electrochemically assisted membrane separation and biological treatment were selected to be studied and developed in the project. Denitrification and nitrification studies on synthetic mine wastewater in laboratory scale revealed that denitrification was possible at low pH (2.5) and temperatures as low as 7°C. Nitrification was more pH sensitive. Both processes tolerated metals (Fe, Ni, Co and As). In the adsorption tests with zeolite, complete ammonium removal from real mine wastewater was achieved with a hydraulic retention time of 2 minutes, with complete regeneration. In addition, a novel electropervaporative nitrogen capture technology was developed. Further larger scale testing and development of all technologies is required to ensure their feasibility in a real mining site. A follow-up period in lysimeters showed that the explosives originated nitrogen content of left over stones from natural stone quarrying is relatively low and ca. half of the nitrogen is leached within the first weeks after detonation. The main sources of nitrogen are process and dewatering waters, irrespective of the scale of extractive activity. The total potential nitrogen load to the environment depends on the scale and type of the activity as well as the type of explosives used. In addition to factors related to the activity itself, the overall nitrogen management should take into account the background concentrations and sensitivity of the local ecosystem.
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Date	June 2015
Language	English, Finnish abstract
Pages	110 p. + app. 3 p.
Name of the project	Solutions for Control of Nitrogen Discharges at Mines and Quarries (MINIMAN)
Commissioned by	Tekes, Ekokem-Palvelu Oy, Kemira Oyj, Outotec Finland Oyj, Yara Suomi Oy, Agnico-Eagle Finland Oy, FQM Kevitsa Mining Oy, Outokumpu Chrome Oy, Nordic Mines Oy, Nordkalk Oy Ab, The Finnish Natural Stone Association, BK-Automation Ky and Infra ry
Keywords	mines, quarries, explosives, nitrate, ammonium, water treatment technologies
Publisher	VTT Technical Research Centre of Finland Ltd P.O. Box 1000, FI-02044 VTT, Finland, Tel. 020 722 111

Julkaisun sarja ja numero

VTT Technology 225

Nimeke	**Kaivannaistoiminnan typpipäästöjen hallinta** Miniman-hankkeen loppuraportti
Tekijä(t)	Johannes Jermakka, Elina Merta, Ulla-Maija Mroueh, Helena Arkkola, Sini Eskonniemi, Laura Wendling, Jutta Laine-Ylijoki, Elina Sohlberg, Hanna Heinonen, Tommi Kaartinen, Jaakko Puhakka, Minna Peltola, Stefano Papirio, Aino-Maija Lakaniemi, Gang Zou, Anna Ylinen, Francesco di Capua, Raisa Neitola, Henrik Gustafsson, Tero Korhonen, Teemu Karlsson, Tommi Kauppila, Janita Laakso & Pekka Mörsky
Tiivistelmä	Suomen kaivannaisteollisuuden kasvu lisää tarvetta tutkia ja seurata erilaisia ympäristövaikutuksia sekä tiedostaa ympäristöasiat yhä paremmin osana toimintaa. Räjähdysaineista tai kaivosprosessista ympäristöön vapautuvalla typellä voi olla negatiivisia ympäristövaikutuksia. Tekesin Green Mining ohjelman ja teollisuuden rahoittamassa MINIMAN-projektissa pyrittiin luomaan kattava näkemys kaivannaistoiminnan typpikysymyksestä. Projektissa kerättiin tietoa kaivosten ja louhimojen ympäristöissä esiintyvistä typpiyhdisteistä ja kehitettiin teknologioita typpipitoisten vesien käsittelyyn. Teknologiaselvityksen perusteella projektin teknologiakehityksen kohteiksi valittiin selektiivinen sorptio, elektrokemiallisesti avustettu membraanierotus sekä biologinen käsittely. Denitrifikaatio- ja nitrifikaatiokokeet synteettisellä kaivosjätevedellä laboratoriomittakaavassa osoittivat, että denitrifikaatio oli mahdollista matalassa pH:ssa (2,5) ja lämpötilassa (7 °C). Nitrifikaatio oli herkempi pH:n vaihteluille. Molemmat prosessit sietivät metalleja (Fe, Ni, Co and As). Adsorptiokokeissa zeoliitin havaittiin poistavan tehokkaasti ammoniumtyppeä 2 min hydraulisella viipymällä, ja materiaali saatiin regeneroitua täydellisesti. Projektissa kehitettiin lisäksi uudenlainen elektro-pervaporatiivinen menetelmä typen talteen ottamiseksi. Suuremman mittakaavan testausta ja kehitystyötä tarvitaan, jotta voidaan varmistua teknologioiden soveltuvuudesta kaivosympäristöön. Lysimetrikokeiden perusteella luonnonkivilouhimon sivukivien räjähdysaineista peräisin olevan typen pitoisuus on melko matala, ja noin puolet typestä huuhtoutuu räjäytyksen jälkeen jo muutamassa viikossa. Riippumatta kaivannaistoiminnan mittakaavasta prosessi- ja kuivatusvedet ovat pääasiallisia typen lähteitä. Ympäristöön kohdistuvan kokonaistyppikuorman suuruus riippuu toiminnan mittakaavasta ja luonteesta sekä myös käytettävien räjähdysaineiden ominaisuuksista. Itse kaivostoimintaan liittyvien tekijöiden lisäksi typen hallinnassa tulisi ottaa huomioon ympäristön taustapitoisuudet sekä paikallisen ekosysteemin herkkyys.
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Rahoittajat	Tekes, Ekokem-Palvelu Oy, Kemira Oyj, Outotec Finland Oyj, Yara Suomi Oy, Agnico-Eagle Finland Oy, FQM Kevitsa Mining Oy, Outokumpu Chrome Oy, Nordic Mines Oy, Nordkalk Oy Ab, Kiviteollisuusliitto ry, BK-Automation Ky ja Infra ry
Avainsanat	kaivokset, louhimot, räjähdysaine, nitraatti, ammonium, vesienkäsittelyteknologiat
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Solutions for control of nitrogen discharges at mines and quarries

Miniman project final report

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