Barrier system for the treatment of nitrogen effluents from the Malmberget iron mine

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ABSTRACT
At the Malmberget iron mine in northern Sweden, nitrogen from undetonated explosives is discharged from the mine with process water. After passing through a settling pond, excess process water is discharged to the Linaälv River via a spillway. Because of the risk for eutrophication in rivers and coastal areas downstream, it is necessary to decrease the N levels in the effluent waters. This study presents the results from laboratory column experiments under water – saturated conditions, conducted at room temperature and 5°C, which will be used in the design of a pilot-scale barrier system. The columns were filled with a reactive substrate consisting of sawdust and activated sewage sludge. The results of the room temperature experiments demonstrated that nitrate removal efficiency was >95% for flow rates < 341 liters d⁻¹ m⁻³ reactive mixture. However, at flow rates of ~700 liters d⁻¹ m⁻³ reactive mixture, nitrate removal efficiency decreased to ~64%. Tracer experiments indicated an increasing degree of channeling in the columns as flow rate increased, thus leading to a reduction in removal efficiency. Apparent denitrification rates were estimated to 2.8 - 9.3 g N d⁻¹ m⁻³ and 2.2 g N d⁻¹ m⁻³ at room temperature and 5°C, respectively.

INTRODUCTION
While acid mine drainage is a well – known environmental issue associated with mining activities, eutrophication from nitrogen releases is an environmental issue that is often overlooked. Ammonium nitrate is the most commonly-used explosive in the mining industry; undetonated ammonium nitrate is readily soluble in water and quickly enters into the mine water and process water at a mine site. The nitrogen in these waters is primarily in the form of nitrate (NO₃⁻) and ammonium (NH₄⁺), which is eventually discharged to the environment. In the cold climate of northern Sweden, aquatic ecosystems are often nutrient – limited, and this nitrogen loading could lead to eutrophication in water bodies downstream from the mines site.

At the Malmberget iron mine in northern Sweden (67°N, 21°E), operated by LKAB, thousands of tons of ammonium nitrate – based explosives are used each year. Nitrogen from undetonated explosives enters into the process water; after passing through a settling pond, excess process water is discharged to the Linaälv River via a spillway. In 2007, approximately 8 million cubic meters of water with an average nitrate concentration of 37 mg N L⁻¹ (13 samples) were discharged to the Linaälv River (see Fig. 1; LKAB, internal data), for a total annual load of 279 tons N (i.e. nitrogen concentration x discharge). Average ammonium concentrations were 2 mg L⁻¹ N (5 samples). Considering all its combined operations, LKAB

released 415 tons of nitrogen to surface water bodies in 2007, which was primarily derived from the use of 17,300 tons of explosives at its mines (LKAB, 2007).

Figure 1. Discharge from the settling pond to Linaälv River via a spillway, as well as nitrate – nitrogen and ammonium – nitrogen concentrations in the discharge water. The spring flood occurs towards the end of April; nitrate concentrations in the discharge water are diluted during this event.

Because of the risk for eutrophication in rivers and coastal areas downstream, it is necessary to decrease the N levels in the effluent waters. One potential method for N removal is through denitrification, where nitrate in solution is reduced to a gaseous form:

\[ 4\text{NO}_3^- + 5\text{CH}_2\text{O} + 4\text{H}^+ \rightarrow 2\text{N}_2(g) + 5\text{CO}_2(g) + 7\text{H}_2\text{O} \] (1)

In other studies, permeable reactive barriers have been successfully used in the remediation of nitrate–contaminated groundwater by exploiting denitrification (Blowes et al., 1994; Roberson and Cherry, 1995). In this study, denitrification is studied in laboratory column experiments, with the aim of using the experimental results in the design of a pilot-scale barrier system for the treatment of nitrate–contaminated surface water.

**MATERIAL AND METHODS**

Four column experiments have been conducted to study denitrification in a specific reactive substrate at room temperature and 5°C (mean annual temperature at Malmberget is ca. -1.5°C). Plexiglas columns (21 cm x 8 cm) were constructed for upward saturated flow. The base of each column was filled with 1 cm sand (primarily quartz), followed by 19 cm reactive substrate, and finally 1 cm sand at the top closest to the discharge point. Distilled water was pumped from below while the column was filled, to avoid the entrapment of air bubbles in the material. The reactive substrate consisted of a 4:1:1 mixture (by volume) of LECA pellets (baked clay pellets), water-saturated sawdust, and activated sewage sludge. The sewage sludge, obtained from the Uddebo sewage treatment plant in Luleå, contains an active population of denitrifying bacteria, while the sawdust provides a long-term carbon and electron source for heterotrophic denitrification. The LECA pellets (8 – 12 mm diameter) functioned as a supporting material and increased the hydraulic conductivity of the mixture. Column experiments were conducted with flow rates ranging from 150 to 750 mL day\(^{-1}\). The input solution contained 20 mg N L\(^{-1}\) (as nitrate) and 350 mg SO\(_4^{2-}\) L\(^{-1}\), which lies in the range of concentrations measured in the discharge waters from Malmberget (cf. Figure 1). It was necessary to include sulfate in the input solution, as sulfate – reducing bacteria will compete with denitrifying bacteria for labile organic compounds in the substrate.
During the course of the room temperature experiments, the columns were operated at three different flow rates: 150 mL day\(^{-1}\), 360 mL day\(^{-1}\), and 750 mL day\(^{-1}\). For a column volume of 1056 cm\(^3\), these flow rates are equivalent to 142, 341, and 710 liters d\(^{-1}\) m\(^{-3}\) reactive mixture. Different column flow rates were tested in order to determine the effect of column residence time on denitrification rates. Tracer tests with KCl (\(C_0 = 150\) mg L\(^{-1}\) Cl\(^{-}\)) were used to determine the residence time for conservative transport through the column matrix, and the computer code CXTFIT (Toride et al., 1999) was used for the calculation of pore water velocity (\(v\)) and the dispersion coefficient (\(D_e\)) in the reactive substrate from breakthrough curves. Results are presented in terms of longitudinal dispersivities (\(D_e / v\)). CXTFIT uses a least – squares routine for fitting \(v\) and \(D_e\) in the analytical solution of the advection – dispersion equation to the tracer test data. Since there was chloride present in the column pore water prior to the start of the tracer experiments (\(C_i \approx 40 – 50\) mg L\(^{-1}\) Cl\(^{-}\)), chloride concentrations in breakthrough curves are presented as \((C - C_i)/(C_0 - C_i)\).

The duplicate 5°C column experiment was started approximately 6 months after the start of the room temperature experiment, which was also conducted in duplicate. Column effluents were sampled intermittently during the experimental period, and analyzed primarily for nitrate and ammonium. On several occasions, pH, alkalinity, and hydrogen sulfide were also measured. Nitrate was determined using an ion selective electrode (Orion™ 97-07), after adjusting ionic strength and precipitating interfering agents (hydrogen sulfide, chloride, humic substances) with Orion™ interference suppression solution. Electrode readings were recalculated to concentrations using a multipoint calibration curve constructed for the relevant range of analytical results. Ammonium was determined using a Hitachi UV/vis-spectrophotometer and the phenol – hypochlorite – nitroprusside method. Chloride concentrations were determined by argentometric titration against a silver/sulfide ion selective electrode (Orion™ 96-16).

**RESULTS AND DISCUSSION**

**Hydraulic properties of column substrate**

From the breakthrough curves, the time for 50% of the input chloride concentration to be measured in the column effluent is obtained; this time is considered the column residence time (\(t_R\); Table 1; Fig. 2). For the lowest flow rate, an acceptable fit and reasonable values for substrate dispersivity were obtained (Table 1) by CXTFIT (Toride et al., 1999). At this flow rate, the dispersivity was much less than the characteristic length of the flow system (i.e. 21 cm), which is reasonable. For the medium flow rate, a reasonable fit was obtained (see Figure 2), but the substrate dispersivity was similar to the characteristic length of the flow system, which is not a reasonable result. For the high flow rate, a considerable amount of tailing occurred for column 2; i.e. effluent chloride concentrations approached the input concentration (\(C_0\)) at time > \(t_R\) more slowly than expected by the analytical solution (Fig. 2). The dispersivity was much greater than the characteristic length of the system. A satisfactory fit was not obtained at this flow rate.

The increasing dispersivity with increasing flow rate (decreasing \(t_R\)) suggests that flow channeling is occurring in the columns at the higher flow rates. Instead of plug flow, the tracer tends to follow paths of lower permeability as flow increases. With increasing flow, the effective porosity of the media decreases, indicating that less of the substrate volume is available for advective transport. This suggests that simulating the tracer test using a one region / single porosity model is inadequate for the conditions in these experiments, at least at flow rates in excess of ~150 mL d\(^{-1}\), and that a dual porosity model would be more
appropriate for simulating tracer breakthrough in the heterogeneous substrate. Although this outcome is perhaps not surprising, it demonstrates that channeling must be considered in the design and construction of a pilot – scale barrier system using the same reactive substrate as in these laboratory studies.

**Table 1**: Hydraulic parameters determined from breakthrough curves from tracer tests. $t_0$ is the residence time, calculated as the time for 50% of the input chloride concentration to be detected in the effluent. $n_e$ is effective porosity and is calculated as $(\text{flow rate} \times t_0) / (\text{column volume})$. Parentheses indicate unreasonable values.

<table>
<thead>
<tr>
<th>Flow rate (mL d$^{-1}$)</th>
<th>$t_0$ (days)</th>
<th>$n_e$</th>
<th>Dispervivity (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low flow</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Column 1</td>
<td>153</td>
<td>1.61</td>
<td>0.23</td>
</tr>
<tr>
<td><strong>Medium flow</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Column 1</td>
<td>356</td>
<td>0.72</td>
<td>0.24</td>
</tr>
<tr>
<td>Column 2</td>
<td>365</td>
<td>0.64</td>
<td>0.22</td>
</tr>
<tr>
<td><strong>High flow</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Column 1</td>
<td>745</td>
<td>0.19</td>
<td>0.14</td>
</tr>
<tr>
<td>Column 2</td>
<td>733</td>
<td>0.19</td>
<td>0.13</td>
</tr>
</tbody>
</table>

**Figure 2**: Breakthrough curves for medium flow rate (left) and high flow rate (right). See Table 1 for further results.

**Nitrogen removal**

Nitrate and ammonium concentrations in the column effluents are presented in Figures 3 and 4 for the room temperature and 5°C experiments, respectively. While the room temperature experiments have been completed, the low temperature experiments are on-going, as shown in Fig. 4. In columns 1 and 2 (Fig. 3), nitrate concentrations decrease from ~20 mg N L$^{-1}$ at the inlet to < 1 mg L$^{-1}$ at the outlet for both the low flow and medium flow rates (Table 1). At the high flow rate, nitrate concentrations at the outlet ranged from 5 to 12 mg N L$^{-1}$. In columns 3 and 4 (Fig. 4), nitrate concentrations at the outlet decreased initially to ca. 4 mg N L$^{-1}$. However, after ca. 50 days, nitrate concentrations had increased in column 3 to 11 mg L$^{-1}$.

The decrease in nitrate concentrations during transport through the reactive substrate is probably the result of denitrification (equation 1), since ammonium is not a major reaction product; either N$_2$O or N$_2$ would be the primary reaction products, but these were not analyzed in this study. The results in both cases (Fig. 3 and 4) reveal relatively high ammonium concentrations at the start of the experiments, but these concentrations decrease steadily with time. The consistent decrease in ammonium concentration suggests that
ammonium, originally present in the sewage sludge as a product of organic matter degradation, is being flushed from the column along with mobile organic matter (data not shown). Low concentrations of ammonium are detected in the effluent from columns 1 and 2 during the entire experimental period, indicating that this ammonium is either the product of continued organic matter degradation or of dissimilatory nitrate reduction to ammonium (equation 2):

\[
\text{NO}_3^- + 2\text{CH}_2\text{O} + 2\text{H}^+ \rightarrow \text{NH}_4^+ + 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}
\]  

(2)

Nitrate reduction to ammonium is therefore a minor process compared to denitrification in the room temperature experiments. This seems to be the case in the low temperature experiments as well, but further sampling will be needed to confirm this.

![Figure 3](image.png)

**Figure 3.** Nitrate and ammonium concentrations in the effluents from the duplicate columns (1 and 2) operated at room temperature. Day 0 corresponds to change from distilled water to 20 mg L\(^{-1}\) NO\(_3^-\) input to column. Calculated residence times (\(t_R\)) in days are shown for each change in flow velocity.

**Denitrification rates**

The results of the room temperature experiments demonstrate that nitrate removal efficiency was >95% for flow rates <360 mL day\(^{-1}\) (341 liters d\(^{-1}\) m\(^{-3}\) reactive mixture). However, at flow rates of ~710 liters d\(^{-1}\) m\(^{-3}\) reactive mixture, nitrate removal efficiency decreased to ~66%. The low temperature experiments indicated a lower removal efficiency of 43 – 78%.

Apparent denitrification rates, determined as the product of the change in N concentration and flow rate, divided by the total reactive substrate volume, ranged from 2.8 - 9.3 g N d\(^{-1}\) m\(^{-3}\) for the room temperature experiments; an apparent denitrification rate of 2.2 g N d\(^{-1}\) m\(^{-3}\) was calculated for the low temperature experiment at low flow. Reaction rates can also be expressed as the difference between the input and output concentrations, divided by the column residence time. With only the input and output concentrations available, it is necessary to assume that the denitrification rates in all the experiments are zero-order with respect to nitrate concentration. Using this rate representation, apparent denitrification rates of 12 – 68 mg N L\(^{-1}\) d\(^{-1}\) and 11 mg N L\(^{-1}\) d\(^{-1}\) are calculated for the room temperature and 5°C experiments.
experiments, respectively. In a field-scale reactive barrier, Robertson et al. (2000) obtained denitrification rates of \( \sim 30 \text{ mg L}^{-1} \text{ d}^{-1} \) at 20\(^\circ\)C and \( \sim 5 \text{ mg L}^{-1} \text{ d}^{-1} \) at 2 – 5\(^\circ\)C.

Using the maximum apparent denitrification rate determined for this study, 220 m\(^3\) of reactive substrate would be needed to treat a daily discharge of 100 m\(^3\) containing 20 mg N L\(^{-1}\). Thus, considering the magnitude of the annual discharge to the Linaälv River (Fig. 1), the construction of one passive barrier system for nitrate removal from the entire effluent volume is not a realistic solution. Instead, efforts should be made to reduce N fluxes from the major point sources in Malmberget.

![Nitrate and ammonium concentrations in the effluents from the duplicate columns (3 and 4) operated at 5\(^\circ\)C. Day 0 corresponds to change from distilled water to 20 mg L\(^{-1}\) NO\(_3\^-\) input to column. Results are for slowest flow rate, with a residence time of 1.6 days.](image)

**Figure 4.** Nitrate and ammonium concentrations in the effluents from the duplicate columns (3 and 4) operated at 5\(^\circ\)C. Day 0 corresponds to change from distilled water to 20 mg L\(^{-1}\) NO\(_3\^-\) input to column. Results are for slowest flow rate, with a residence time of 1.6 days.

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**REFERENCES**


