

## Nitrate reduction in real mine water using zero-valent iron (ZVI) and iron waste

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### Abstract

Nitrate is present in blasting agents used by the mining industry and thus can contaminate mine water. Despite several methodologies that have been applied for the removal of nitrate, many approaches produce harmful by-products such as nitrite, and other technologies have disadvantages, such as the high energetic costs and high biomass production.

In this study, the three iron sources (ZVI) iron nanoparticles, iron powder and iron waste from a mold industry were used for the reduction of nitrates from mine water. By performing a pH and iron dosages optimization with iron powder, pH 2 showed to be the only pH capable of reducing nitrate from a range of 2 to 4. The use of 4 g/L and 20 g/L of iron nanoparticles and iron powder, respectively, reduced nitrate completely in 180 and 270 min. The iron waste tested reduced 53% and 44% for washed and unwashed iron surface of the waste, respectively, showing that the waste does not have many impurities that could affect the experiment. In spite of the surface area being determinant for choosing the load of iron and for showing the kinetics of the reaction, it proved that the type of by-product formed at the end of the chemical reduction of nitrate is not relevant. The main by-product generated was  $\text{NH}_4^+$  and  $< 7\%$  of  $\text{NO}_2^-$  was produced.

The iron waste showed to be an interesting source of iron for this environmental application. This is true not only from an economical point of view but as a greener approach since a waste is used as a raw material instead of promoting the production of other materials for mine water remediation.

Key words: nitrate, zero-valent iron, iron waste, real mine water

### Introduction

Eutrophication and Methemoglobinemia are some of the main concerns related to the existence of nitrogenous compounds in water (Rocca et al., 2007). Mine water has been polluted with nitrogenous species because the mining industry blasting agents composed of ammonium nitrate fuel oil (ANFO). Part of the detonated explosives is leached into the water, increasing the concentrations of nitrate,  $\text{NO}_3^-$ , and ammonia or ammonium,  $\text{NH}_3/\text{NH}_4^+$  (Gusek and Figuera, 2009). Around 300 mg/L of  $\text{NO}_3^-$  can be found in mine waters; nevertheless there is a lack of regulations regarding mine water discharge into water courses (Häyrynen et al., 2009).

Nitrate removal technologies include biological approaches (Koren et al., 2000), ion exchange resins (Hekmatzadeh et al., 2013), membrane processes (Häyrynen et al., 2009) and more recently electrochemical methods (Govindan et al., 2015). However, these methods still have some drawbacks like the elevated biomass production in the biological methods, high costs and membrane fouling in membrane processes. The main difficulty regarding the electrochemical approach is related to the production of by-products such as nitrite,  $\text{NO}_2^-$ , with a high toxicity associated and some ammonia,  $\text{NH}_3$ .

Iron in the metallic form,  $\text{Fe}^0$ , very well known as zero-valent iron (ZVI), can be employed for the removal of various contaminants such as metals, dyes or chlorinated compounds. Permeable reactive

barriers (PRBs) are used for *in-situ* treatments with high efficiencies for pollutants removal. ZVI can be synthesized by chemical precipitation with NaBH<sub>4</sub> or by using polyphenols from prolyphenol rich media (e.g. tea extracts), between several other methodologies. This technology is simple and effective for several applications due to high reactivity in reducing species, like NO<sub>3</sub><sup>-</sup>.

The aim of the present study was to use three types of ZVI for the NO<sub>3</sub><sup>-</sup> reduction of mine water: iron nanoparticles, iron powder and an iron waste from a mold industry. Thus, it will be ascertained if a waste can be used for the depollution of mine water contaminated with NO<sub>3</sub><sup>-</sup>.

**Methods**

Samples were taken from a phosphate mine located in the center of Finland. The water was analyzed on site regarding pH (intelliCAL™ pH101 probe), redox potential (intelliCAL™ REDOX MTC101 probe) and electrical conductivity (intelliCAL™ CDC401 probe); all measured with a Hach HQ40d handheld device. Other parameters were measured in a commercial laboratory, Ramboll Analytics (Table 1). Three types of ZVI were used for NO<sub>3</sub><sup>-</sup> reduction: commercial iron nanoparticles used as a slurry (Nanofer Star product; Fe<sup>n</sup>) from NanoIron, s.r.o.; iron powder, -325 mesh (Fe<sup>p</sup>) and iron waste from a mold industry (Fe<sup>w</sup>). Parameters such as pH and ZVI dosage were optimized using Fe<sup>p</sup> as a first approach. Thus, the experiments were performed in a 500 mL closed reactor under stirring conditions with an incubator shaker (IKA KS 4000 I control) where mine water was previously degassed with N<sub>2</sub>. Initial pH ranges tested were 2, 3 and 4, and Fe<sup>p</sup> was tested in different dosages (0.8 g – 8 g), during 3 h of reaction time, where samples were taken during time and filtered (cellulose acetate membrane, 0.2 μm). The other two types of ZVI were used as a final step for comparison purposes.

The three sources of iron were analyzed for their BET surface area (Brunauer-Emmett-Teller specific surface area) by a Micromeritics, Gemini V device. Iron nanoparticles were observed by transmission electron microscopy (TEM), with a HT7700 120 kV High-Contrast/High-Resolution Digital TEM. The nanoparticles were sonicated for 30 min after the addition of ethanol and 1-butanol before being placed in the TEM grid.

**Table 1** Parameters analyzed in the mine water (October 2014). Values measured in mg/L and redox potential was corrected to the SHE. EC: electrical conductivity.

Parameter	Result	Parameter	Result	Parameter	Result
pH <sub>field</sub>	7.80	Mg <sup>2+</sup>	19	Hg	< 0.0001
EC (μS/cm)	1057	Ca <sup>2+</sup>	100	Co	0.00077
Redox (mV)	427	K <sup>+</sup>	65	Cr	< 0.001
Fe <sub>Total</sub>	0.036	Na <sup>+</sup>	76	Cu	< 0.001
N <sub>Total</sub>	36	Cl	30	Pb	< 0.0005
NH <sub>4</sub> <sup>+</sup>	0.00645	F	1.10	Mn	0.015
NO <sub>3</sub> <sup>-</sup>	160	Al	< 0.01	Ni	< 0.001
NO <sub>2</sub> <sup>-</sup>	0.067	As	< 0.001	Si	5.60
PO <sub>4</sub> <sup>3-</sup>	0.030	Ba	0.091	Zn	< 0.005
SO <sub>4</sub> <sup>2-</sup>	200	Cs	< 0.001	U	0.0068

**pH optimization**

An initial pH range of 2 – 4 was chosen to react with Fe<sup>p</sup>, since it has been proven that acidic cleaning of the ZVI surface avoids an oxide layer to be formed around the metallic Fe<sup>0</sup>-core. When the pH increases, the oxide coating formed is no longer dissolved and the shell of oxides will remain on the surface of ZVI, decreasing the efficiency of the chemical reduction (Huang and Zhang, 2004; Yang and Lee, 2005). After the pH adjustment, this parameter was not controlled any more. The pH showed to be a critical parameter, since the reduction of NO<sub>3</sub><sup>-</sup> requires very acid conditions of pH 2 (Figure 1) in order to obtain a decrease of NO<sub>3</sub><sup>-</sup> from 160 mg/L to 86.5 mg/L during the firsts 5 min of reaction. After 180 min, the efficiency of NO<sub>3</sub><sup>-</sup>-reduction reached 0.4 mg/L (99.7% of reduction). However, at the initial pH values of 3 and 4, the effect of pH on the NO<sub>3</sub><sup>-</sup>-reduction was almost negligible. This

result might possibly be associated with the fast increase of pH during the reaction, due to the production of OH<sup>-</sup>-ions (Eq. 1), also promoting the formation of FeO in the surface of the ZVI (Choe et al., 2004; Yang and Lee, 2005), since the pH increased up to 7.3 and 9.0 when the initial one was at 3 and 4, respectively.

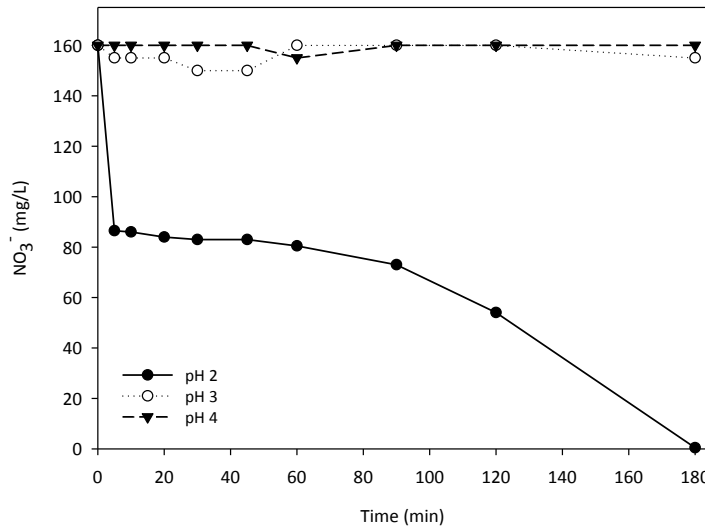
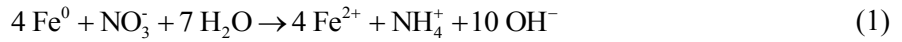


Figure 1 Influence of pH in nitrate reduction in mine water (4 g/L of Fe<sup>0</sup>, pH range tested: 2, 3 and 4).

### Optimization of the ZVI dosage

Dosages of 2, 4, 10 and 20 g/L of Fe<sup>0</sup> were used for the NO<sub>3</sub><sup>-</sup>-reduction in mine water for 270 min (Figure 2). The use of higher dosages of ZVI in an acid medium at pH 2 showed to have lower NO<sub>3</sub><sup>-</sup>-concentrations at the end of the reduction reaction. An almost complete reduction (99.9% of NO<sub>3</sub><sup>-</sup>-reduction) was obtained with 10 g/L after 180 min and 20 g/L after 270 min. On the contrary, with 2 g/L, less ZVI was accessible for the chemical reduction, leading to 34.0 mg/L of NO<sub>3</sub><sup>-</sup> (78.8% of NO<sub>3</sub><sup>-</sup>-reduction).

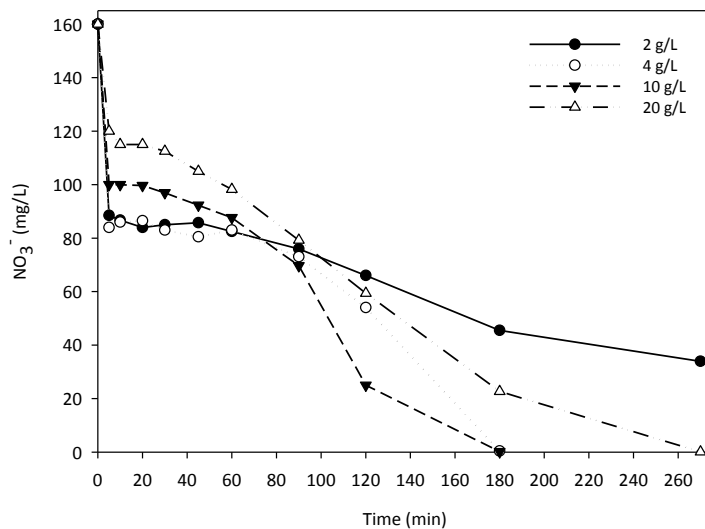


Figure 2 Influence of the Fe<sup>0</sup> dosage in mine water at pH 2.

### Fe<sup>n</sup> and Fe<sup>w</sup> as alternative metallic iron sources

Fe<sup>n</sup> morphology was observed by TEM (Figure 3a), where the nanoparticles showed to be rearranged in chains with spherical clusters, with a diameter range of 73.2 – 169.0 nm. The average diameter of Fe<sup>n</sup> was 119.4 nm, but despite the high aggregation of the nanoparticles, several studies seem to indicate that it does not decrease their reactivity as the high porosity is not affected (Hwang et al., 2011). Fe<sup>n</sup> proved to have a higher surface area (27.7 m<sup>2</sup>/g) when compared with Fe<sup>p</sup> (0.3 m<sup>2</sup>/g). Thus, the dosage used for the NO<sub>3</sub><sup>-</sup>-reduction at pH 2 for 180 min with Fe<sup>n</sup> was lower (2 and 4 g/L) than the one used with Fe<sup>p</sup> (Figure 3b). Using 2 g/L and 4 g/L of Fe<sup>n</sup> is enough to obtain concentrations of NO<sub>3</sub><sup>-</sup> of 73.0 mg/L and 2.60 mg/L, respectively, in 90 min. At 180 min, all NO<sub>3</sub><sup>-</sup> was completely reduced with 2 and 4 g/L of Fe<sup>n</sup>.

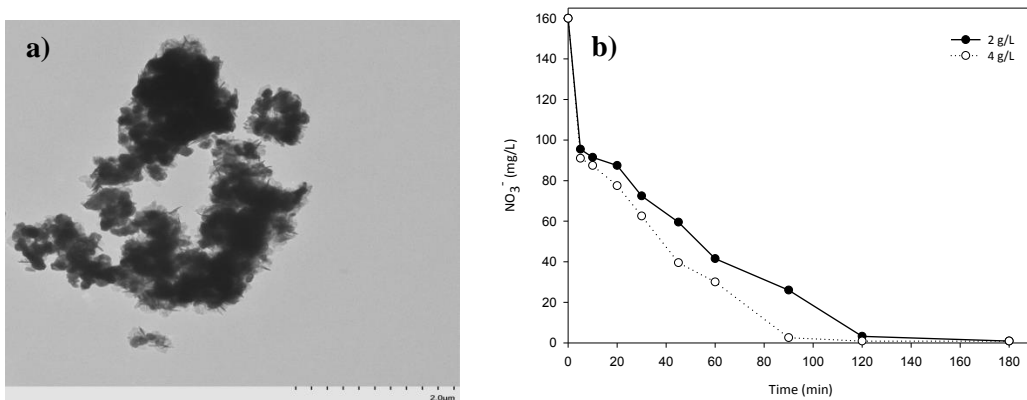


Figure 3 Iron nanoparticles, Fe<sup>n</sup>: a) TEM image; b) NO<sub>3</sub><sup>-</sup> reduction with Fe<sup>n</sup> (2 and 4 g/L, pH 2).

The same reaction was performed with Fe<sup>w</sup>; this time with higher dosages of ZVI due to the low surface area ( $\approx 0$  m<sup>2</sup>/g): 4, 10 and 20 g/L at pH 2 for 48 h, both with washed and unwashed Fe<sup>w</sup> (Figure 4). After 1440 min (24 h) reaction time, 20 g/L was the best dosage of unwashed Fe<sup>w</sup> achieved 95.0 mg/L of NO<sub>3</sub><sup>-</sup>. Similar results were obtained at 2880 min (48 h), with 93.5 mg/L of NO<sub>3</sub><sup>-</sup> (41.6% of reduction), indicating that the reaction kinetic is slower compared to Fe<sup>n</sup> or Fe<sup>p</sup>. By doing a surface washing with oxalic acid (0.2 M), the surface of the Fe<sup>w</sup> did not appear to have major impurities that prejudiced the chemical reduction since the value obtained with the surface washing, was 75.3 mg/L of NO<sub>3</sub><sup>-</sup>, representing a 52.9% reduction (11.3% of difference).

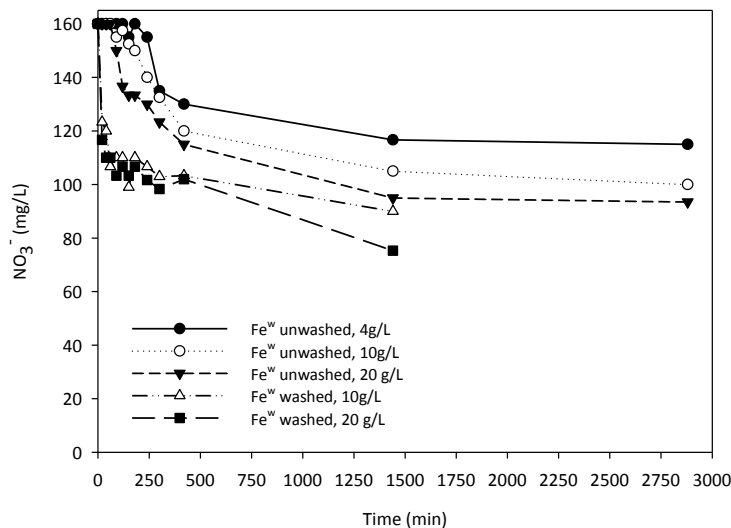
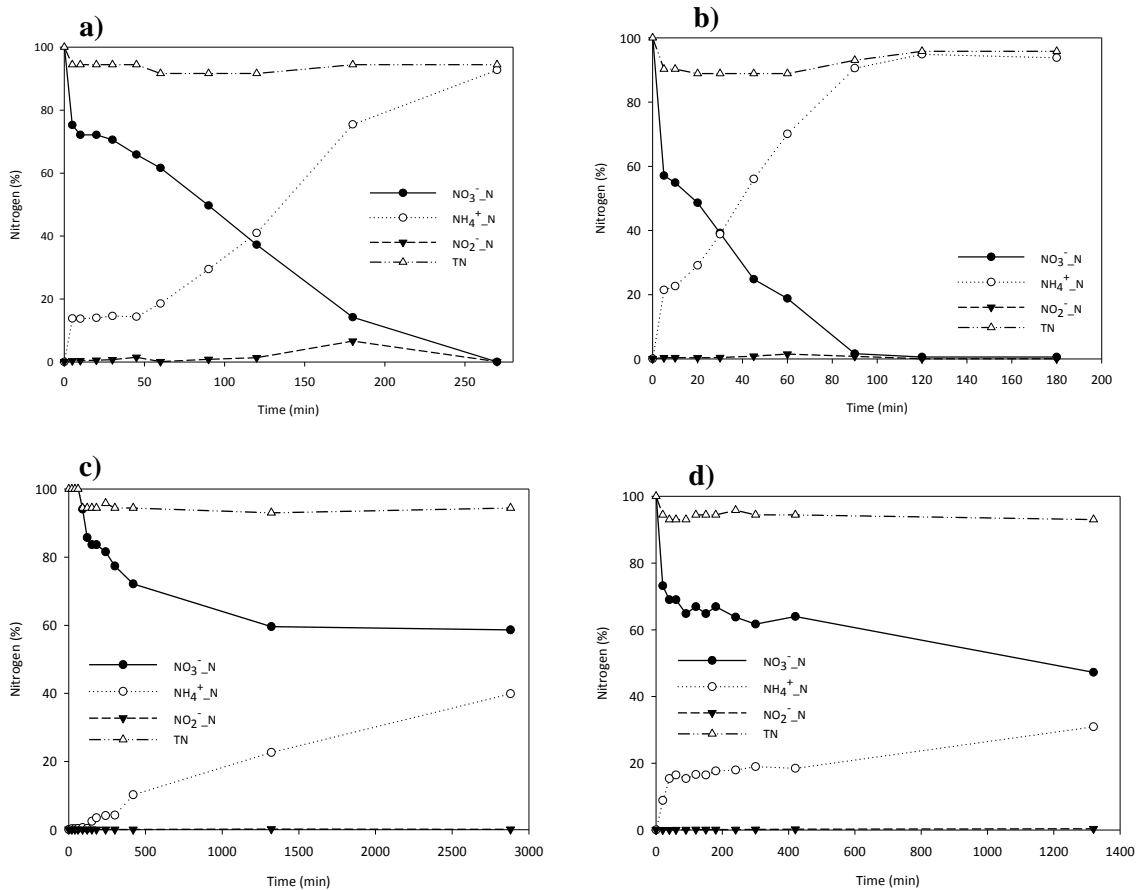


Figure 4 Use of iron waste (Fe<sup>w</sup>) on NO<sub>3</sub><sup>-</sup> reduction in different dosages at pH 2.

### Nitrogen species analysis

During the  $\text{NO}_3^-$ -reduction reaction with the three types of iron sources, the samples were analyzed regarding the production of total nitrogen (TN) and by-products in terms of  $\text{NH}_4^+$  and  $\text{NO}_2^-$ . The  $\text{N}_2$  (g) produced was estimated by a mass balance (Figure 5). Independently of the type of iron source used, the main by-product was  $\text{NH}_4^+$ , and the  $\text{NO}_2^-$  concentrations were negligible ( $< 7\%$  of  $\text{N}_2$  content;  $< 2.4$  mg N/L of  $\text{NO}_2^-$ ). The concentrations of  $\text{N}_2$  estimated showed to be low, with a maximum of 13% (4.6 mg N/L), indicating that the production of  $\text{N}_2$  and the by-products did not depend on the typology of the iron source used. This does not comply with the studies reported by Choe et al. (2000). These authors suggest that the size of the iron source is determinant to ascertain if  $\text{N}_2$  or  $\text{NH}_4^+$  will be produced. They believe that nanoparticles and iron powder will produce,  $\text{N}_2$  (g) and  $\text{NH}_4^+$  at the end of the chemical reductions of  $\text{NO}_3^-$ , respectively. Yet, this could not be verified in the present study (Figure 5a and 5b), where practically only  $\text{NH}_4^+$  was formed with  $\text{Fe}^n$  and  $\text{Fe}^p$ , where a maximum of  $\text{N}_2$  (g) produced was around 12% for both  $\text{Fe}^n$  and  $\text{Fe}^p$  (4.4 mg N/L and 4.6 mg N/L, respectively). Similar results were observed with  $\text{Fe}^w$  unwashed (Figure 5c) or washed (Figure 5d), and once again the surface cleaning showed not to be relevant. The maximum of  $\text{N}_2$  (g) generated was 14.5% (5.2 mg N/L).



**Figure 5** Nitrogen species during  $\text{NO}_3^-$  reduction with the three iron sources at pH 2: a)  $\text{Fe}^p$  (20 g/L); b)  $\text{Fe}^n$  (4 g/L); c) unwashed  $\text{Fe}^w$  (20 g/L); d) washed  $\text{Fe}^w$  (20 g/L).

### Conclusions

Zero-valent iron was used for nitrate reduction in real mine water by comparing three types of iron sources: iron nanoparticles, iron powder and iron waste. The reduction of nitrate was possible at a very acid medium with pH 2, but no alterations on the nitrate levels were observed at pH 3 or 4 possibly due to a rapid formation of iron oxides, avoiding the contact of the metallic core ( $\text{Fe}^0$ ) with the pollutant. The dosages of iron needed for the chemical reduction were investigated, where higher loads of iron can reduce more  $\text{NO}_3^-$  from the water, depending only on the surface area of each type of iron.

Iron nanoparticles (4 g/L) with a surface area of 27.7 m<sup>2</sup>/g, were the most effective in less time, having a complete reduction of nitrate in 180 min. On the other hand, iron powder (20 g/L), with a surface area of 0.3 m<sup>2</sup>/g, had a complete nitrate reduction in 270 min. The iron waste (20 g/L) had lower efficiency results and kinetics due to the extremely low surface area around 0 m<sup>2</sup>/g. However, in two days, a maximum of 53% of reduction was obtained with washed waste particles, which brings economic benefits by using a waste as a raw material for this kind of environmental applications.

Nitrogenous species produced during the reactions were investigated, where it was concluded that the main by-product is NH<sub>4</sub><sup>+</sup> and the production of by-products is independent of the typology of the iron source used.

The nitrate reduction studied with an iron waste is a good option to be tested in an acid mine water since the optimum pH tested was pH 2. Further studies need to concentrate on reducing the reaction time as the relatively high reaction times are not yet feasible for an industrial use of this methodology.

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