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Groundwater nitrate as a potential contributing source of acid and metalliferous drainage

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Abstract

Nitrate from ammonium nitrate fuel oil (ANFO) explosives used in mining/quarrying activities can be an environmental concern due to the solubility of nitrogenous contaminants and mobility over moderate timescales. In contrast, acid and metalliferous drainage (AMD), can be a long-term issue. A further concern especially relevant to closure planning is the combination of the two: elevated anthropogenic nitrate potentially leading to oxidation of pyrite in mining-affected geological units.

Lithotrophic denitrification is the microbially-catalysed oxidation of sulphide to sulphate and conversion of nitrate to nitrogen gas through the transfer of electrons from sulphide to nitrate. This produces one quarter of the acidity compared to the oxidation of pyrite by oxygen and occurs under anoxic conditions in the absence of organic carbon. The process decreases groundwater nitrate concentrations, increases sulphate concentrations, and potentially increases ferrous iron. In experimental incubations of pure quartz-pyrite mixtures with/without microbial inoculations Reid et al. (2016) indicated daily acidity production rates of 0.013 to 0.117 kg H_2SO_4/t for starting nitrate concentrations of 180 mg/L and sulphide concentrations of 1.8 wt%.

We present calculations of acidity production, groundwater flow, and alkalinity supply from two lithological units: the Brockman Iron Formation and the Mount McRae Shale (Pilbara Region, Western Australia). The former is a key host of iron ore mineralisation, while the latter is a key potential source of AMD. Groundwater in both units may potentially be impacted by anthropogenic nitrate leached from waste rock and pit walls on mine sites, including after closure.

Using published pyrite concentrations, reaction stoichiometries, and nitrate concentrations, pyrite oxidation by nitrate could produce a total acidity of the order of 0.04 to 0.15 kg H_2SO_4 /t. Our calculations show low groundwater flow rates limit nitrate supply and significantly reduce the rate of acidity release if all pyrite is oxidised. We conclude pyrite oxidation by groundwater nitrate under anoxic conditions is not likely to lead to significant subsurface plumes of AMD impacted groundwater for the stratigraphical units assessed.

Keywords: *nitrate, groundwater, AMD, denitrification*

1 Introduction

Mining activity, particularly blasting using ammonium nitrate fuel oil (ANFO) is a potential anthropogenic source of nitrate. Due to incomplete volatilisation of ANFO to N_2 gas due to poor blasting practices and/or environmental conditions, residual nitrogenous compounds, mostly nitrate and ammonium, can remain in blasted waste rock and ore. These compounds can be leached from ore stockpiles, tailings, waste rock storage facilities, and pit walls and potentially seep to groundwater.

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Nitrate is an oxidant. This raises the potential environmental concern that below the watertable acid and metalliferous drainage (AMD) may be induced by the oxidation of sulphide minerals contained within aquifer/water bearing units. This could affect the spatial extent and severity of groundwater contamination by nitrate and/or AMD-mobilised trace elements and acidity, particularly after mine closure (Figure 1).

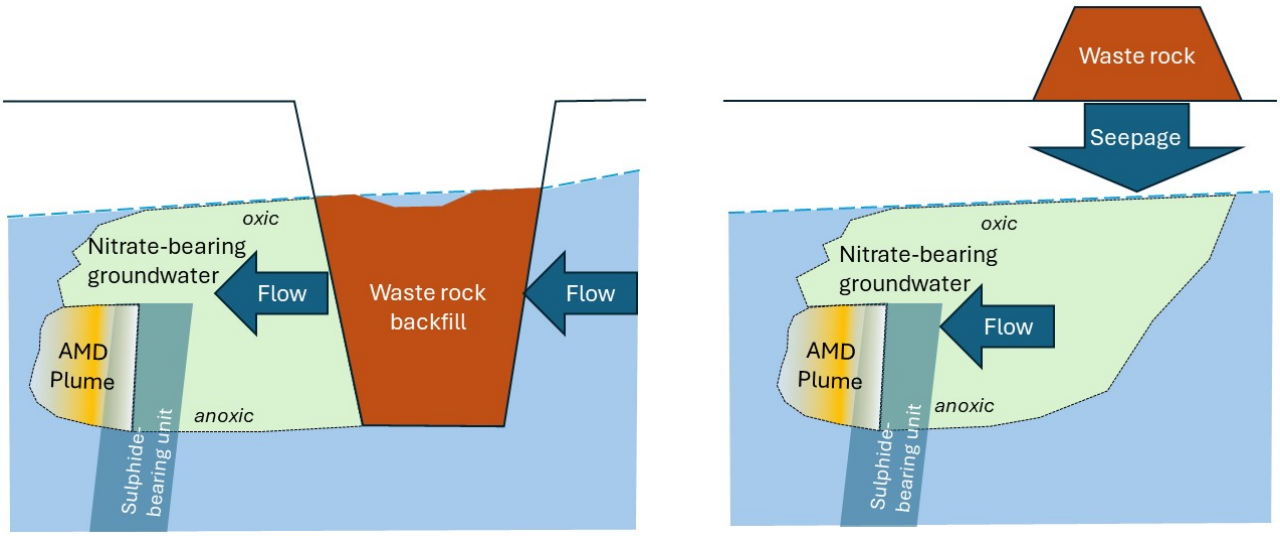


Figure 1 Conceptualisation of subsurface acid and metalliferous drainage plumes caused by oxidation of subsurface sulphides by nitrate in groundwater

The extent of the potential AMD plume and the concentration of AMD contaminants is likely to depend on factors such as the concentration of sulphide minerals in the sulphide-bearing unit, the rate of sulphide oxidation, the presence and reactivity of acid neutralising minerals, the rate of groundwater flow, the concentration of nitrate in groundwaters, and the nature and extent of attenuation mechanisms.

In this paper we present a brief review of nitrate concentrations in groundwater, the process of nitrate-induced oxidation under anoxic conditions, and published rates of the sulphide oxidation reaction. We supplement this with calculations of acidity production, groundwater flow, and alkalinity supply in the Brockman Iron Formation and the Mount McRae Shale geological units. The former is a key host of iron ore mineralisation in the Pilbara region of Western Australia, while the latter is a key potential source of AMD in the same area. Therefore, groundwater in both units may potentially be impacted by anthropogenic nitrate leached from waste rock and pit walls on mine sites, including after closure.

The development of conceptual models to communicate the risks of AMD derived from nitrate-induced oxidation of sulphides (e.g. Figure 1) is critical for understanding potential risks. Some models suggest that in some situations nitrate concentrations can decrease 20–30% per year (Navarro-Valdivia et al. 2023). Hence, understanding the source hazard is critical for understanding the risk using a source-pathway-receptor analysis.

1.1 Nitrate in groundwater

Nitrate concentrations in groundwater within arid to semi-arid regions of Australia can be high, due to the influence of near-surface biological fixation by cyanobacteria in soil crusts, termite mound bacteria, and fixation of atmospheric nitrogen by Acacia plant species with their symbiotic microorganisms (Reid et al. 2016). High rainfall events can flush this nitrate to the groundwater table through recharge processes. In the Pilbara region of Western Australia, measured groundwater concentrations can reach several tens of mg/L (Figure 2). Gemson et al. (2022) cited nitrate concentrations as high as 239 mg/L in non-mining areas of Central Australia while Gray et al. (2018) measured 50–100 mg/L in the northern Yilgarn Craton in Western Australia (dashed outline on Figure 2).

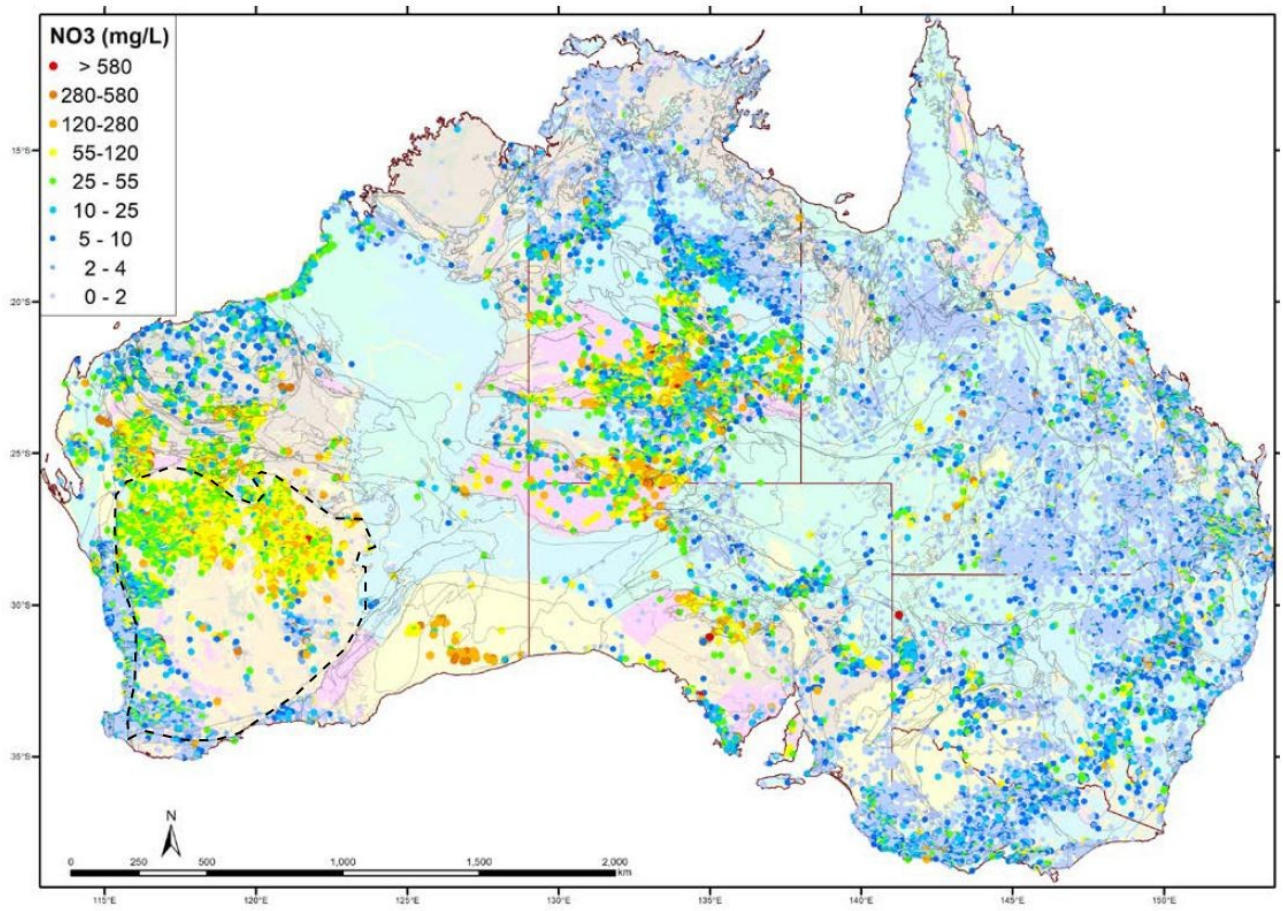


Figure 2 Nitrate distribution in shallow groundwaters for Australia (Source: Gray et al. 2019)

Nitrate concentrations due to mining influence can range from 6.6–266 mg/L (Gemson et al. 2022). In our experience in the Pilbara region of Western Australia, pervasive elevated nitrate concentrations of 10–100 s of mg/L in groundwater in the vicinity of mine pits and waste rock dumps is consistent with leaching of ANFO explosive residue from pit walls and waste rock.

1.2 Anoxic sulphide oxidation

Nitrogen is an important element in reactions in living organisms and (after carbon, hydrogen, and oxygen) is a major component of living cells. The incorporation of nitrogen in organic matter gives rise to a complex cycling of nitrogen between different forms. The nitrogen biogeochemical cycle 'fixes' atmospheric nitrogen, mostly through the metabolism of microbes living in the soil. Nitrate is naturally formed by the decomposition of organic matter and increased by anthropogenic sources such as fertilisers and ANFO explosive residue.

Denitrification is the microbially induced reduction of nitrate to gaseous nitrogen (Schwientek et al. 2008). Denitrification has long been recognised as being associated with the decomposition of organic matter, in which organic carbon is the electron donor (Appelo & Postma 2010). This is known as 'heterotrophic denitrification' (Ayraud et al. 2006). Nitrate may also be reduced by chemolithoautotrophic bacteria using sulphide as an electron donor in carbon-poor sedimentary environments (Ayraud et al. 2006; Jørgensen et al. 2009; Appelo & Postma 2010; Yang et al. 2012; Vaclovkova et al. 2014; Schwientek et al. 2008). This process is called 'lithotrophic denitrification' and occurs under anoxic conditions (Bosch & Meckenstock 2012). In the process of oxidising sulphide, nitrate is reduced to nitrogen gas with a change in nitrogen oxidation state from N(5+) to N(0).

Denitrifying bacteria are ubiquitous in the subsurface (Rivett et al. 2008). Therefore, the critical limiting factors for lithotrophic denitrification are anoxic conditions and the presence of a suitable electron donor, sulphide in this case.

Gray et al. (2018) reviewed groundwater chemistry from bailed samples collected across the Yilgarn craton. They observed that deep groundwater, where the sulphide weathering front is many tens or hundreds of metres below surface, was accompanied by depletion in the concentration of sulphate, bicarbonate, and nitrate, i.e. oxidants other than O_2. The groundwater pH was circumneutral in most cases. For this discussion, the focus is on nitrate as an oxidant in this setting. This deep, anoxic sulphide weathering converts the sulphides to higher sulphur-metal ratios (e.g. pyrrhotite FeS to pyrite FeS_2). Gray et al. (2018) developed models of sulphide oxidation based on observed hydrochemical signatures in the vicinity of the Jaguar, Mt Gibson, and other Yilgarn massive sulphide deposits.

Sulphide (pyrite and sphalerite) weathering by adding dissolved nitrate under anoxic conditions was modelled by Gray et al. (2018). Zn sulphides have higher thermodynamic stability and pyrite weathers first (Figure 3). This results in groundwater characterised by an increase in sulphate concentration and a decrease in nitrate. Depending on redox potential, the ferrous iron released from the weathering of sulphides might oxidise to ferric iron and precipitate as iron oxyhydroxides. These secondary iron precipitates would also be expected to reduce base-metal concentrations in solution due to adsorption and co-precipitation (Gray et al. 2018). This is illustrated in Figure 3 by the reduction in goethite precipitation in favour of ferrite-Zn as the reaction progresses.

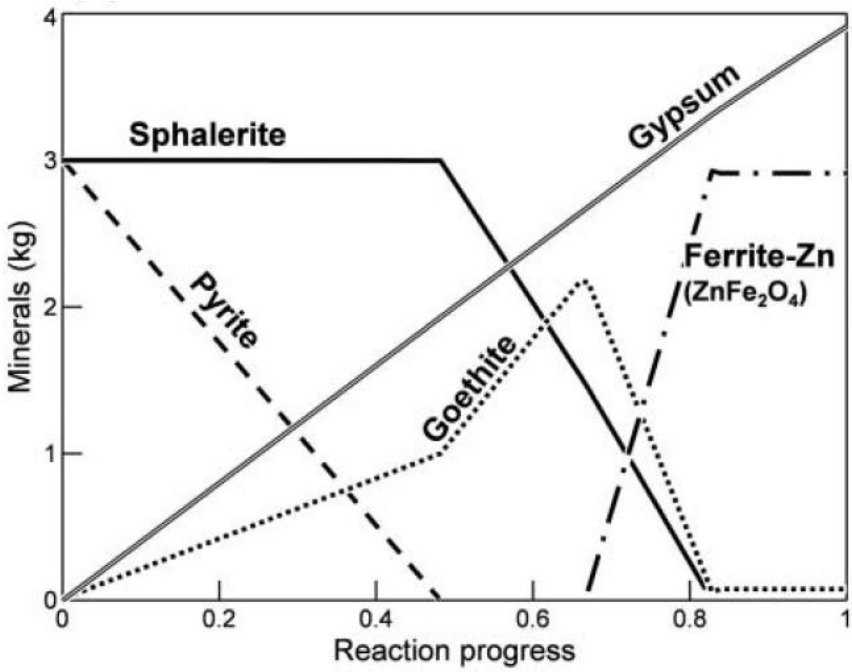


Figure 3 Model results of pyrite and sphalerite weathering under anoxic conditions in the presence of nitrate (Source: Gray et al. 2018)

Approximately three moles of nitrate are required to oxidise one mole of pyrite under anoxic and reducing conditions (Gray et al. 2018) (Equation 1):

$$2FeS_{2(s)} + 5.6NO_3^- + 1.2H_2O \Rightarrow 2Fe^{2+} + 2.8N_2 + 4SO_4^{2-} + 1.2OH^- \quad (1)$$

Higher oxidation potential will oxidise the ferrous iron leading to hydrolisation and precipitation of ferric iron species leading to the net reaction (Gray et al. 2018) (Equation 2):

$$4FeS_{2(s)} + 12NO_3^- + 4H_2O \Rightarrow 4FeOOH_{(s)} + 6N_2 + 8SO_4^{2-} + 4H^+ \quad (2)$$

The acidity released by anoxic sulphide oxidation by nitrate is four times less than sulphide oxidation by oxygen under oxidising conditions (Appelo & Postma 2010; Donn et al. 2016; Reid et al. 2016). Based on data from groundwater sampling in the Yilgarn craton in southwest Western Australia, dissolved nitrate was found to be the main sulphide oxidiser and resulted in sulphate enrichment and nitrate depletion, but pH remained near-neutral (> 6) in groundwater near massive sulphide mineralisation (Gray et al. 2018).

In summary, sulphide oxidation by nitrate results in the following changes in groundwater quality (Schwientek et al. 2008; Gray et al. 2018):

- decrease of nitrate concentration
- increase in sulphate concentration
- potential increase in ferrous iron concentration, as described by Jørgensen et al. (2009), although this will depend on the redox conditions.

Weathering of sulphides will release metals like Cu, Pb, Zn, and Ni into solution. However, the effects on groundwater quality may not be significant, as these metals are readily adsorbed to clays and/or Fe oxides (e.g. goethite) in the regolith (Equation 2).

1.3 Oxidation rate

Published oxidation rates generally focus on pyrite as it is the most common sulphide mineral. Biogeochemical pyrite oxidation by denitrification proceeds slowly. Experimental incubations of sediment indicated rates of sulphate production through oxidation by nitrate under anoxic conditions were three to five times slower than under oxic conditions (Hayakawa et al. 2013). Gray et al. (2018) noted that the Yilgarn environments in their study are characterised by slow groundwater flow (less than 1 m per 1,000 years). This led to the conclusion of slow rates of sulphide oxidation by nitrate (Gray et al. 2018). A conclusion also noted by Schwientek et al. (2008).

Reid et al. (2016) diluted pyrite and pyrrhotite with pure quartz to investigate abiotic and biological oxidation rates under oxic and anoxic conditions. Anoxic biotic inoculated flasks showed nitrate dependent oxidation of sulphide. While complexities in experimental design caused significant differences between some experimental duplicates, the following findings were noted:

- Sulphide oxidation by nitrate occurred in anoxic biotic inoculated flasks. The starting concentration of nitrate was about 180 mg/L as NO_3 and decreased to ~30 mg/L after 70 days of incubation for some flasks.
- Nitrate dependent pyrite oxidation produces less acidity than oxic pyrite oxidation.
- Sulphate production under anoxic conditions varied from 3 to 27 µM/day although oxygen was not successfully excluded from all flasks. This corresponds to estimated pyrite oxidation rate of 0.07 to 0.56 µM/hour.

Bosch & Meckenstock (2012) reviewed five published experiments, in which conditions varied widely, including differences in initial nitrate concentrations (concentration values were not provided), nitrate loading rates, cell densities, and pyrite crystal size (including finely-ground ‘nanoparticle’ pyrite). These studies showed a range of denitrification rates within a ‘strikingly narrow range’ (Table 1). These rates were considered ‘modest’ in comparison to aerobic pyrite oxidation (Bosch & Meckenstock 2012) and appear generally consistent with the range of rates found by Reid et al. (2016) noted previously.

Bosch & Meckenstock (2012) indicated the experiments reviewed could not present clear evidence for production of ferric oxide, which should be one of the reaction products based on Equation 2. They considered attack of the pyrite bonds by ferric iron as the likely initial step in a multi-step oxidation process. They considered the high oxidation rate of pyrite nanoparticles to be a special case attributed to high surface area and enhanced surface reactivity.

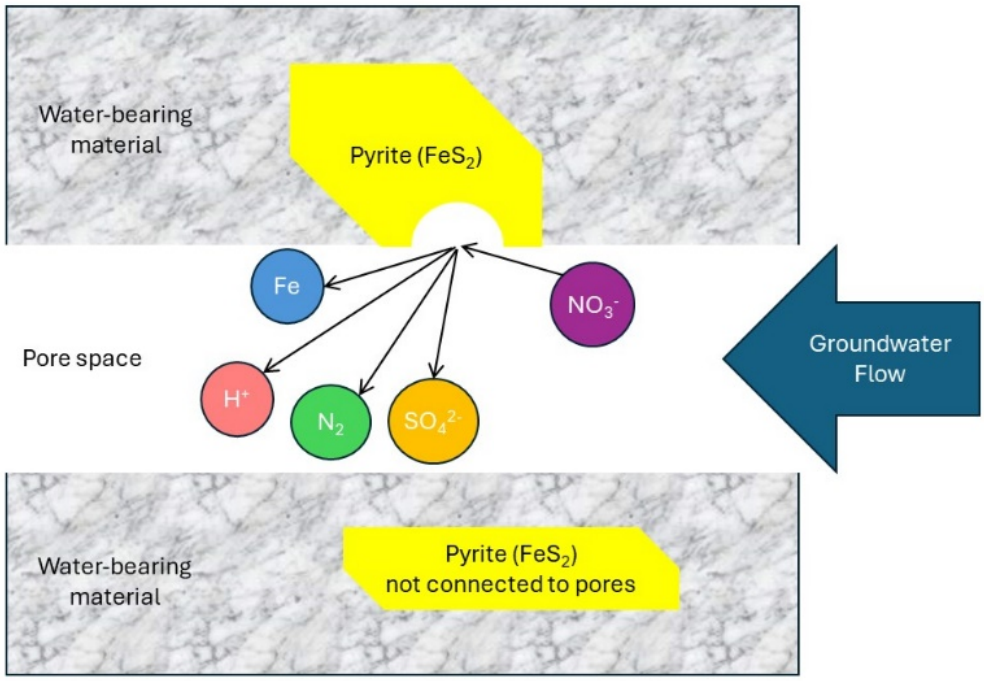
Table 1 Pyrite oxidation rates linked to lithotrophic denitrification (after Bosch & Meckenstock 2012)

Experiment type	Pyrite species	Starting NO_3 mg/L[1]	Denitrification rate µM/hour NO_3	Pyrite oxidation rate[2] µM/hour FeS_2	Reference
Batch incubation	Crystals of 25–100 µm	41–275	2.04	0.68	Torrentó et al. (2010)
Batch incubation	Nanoparticles of ~1 µm	304	38.56	12.9	Bosch et al. (2012)
Columns	Crystals of 45–200 µm amended in sediment	1,000	0.05	0.017	Jørgensen et al. (2009)
Columns	Crystals of 25–100 µm amended in sediment	7–31	4.67	1.56	Torrentó et al. (2010)
Field Study	Sedimentary pyrite deposit	250–500	0.07	0.023	Zhang et al. (2009)

Note 1 – Starting concentrations obtained from review of the respective referenced study.
Note 2 – Rate converted on basis of 3 mol NO_3 required to oxidise 1 mol FeS_2 (Equation 2).

2 Methodology

Figure 4 illustrates a conceptual model of pyrite oxidation by nitrate under anoxic conditions.



Not to scale

Figure 4 Conceptualisation of subsurface acid and metalliferous drainage generation by nitrate in groundwater

Key features of the conceptual model include:

- Pyrite is present in the geological unit which is under anoxic conditions.
- The geological unit contains negligible organic carbon. That is, carbon to support heterotrophic denitrification is not available, forcing microorganisms to utilise other electron donors, such as pyrite.

- The geological unit is sufficiently porous to allow for groundwater to flow through the unit. The porosity depends on the characteristics of the material.
- A portion of the pyrite in the geological unit is exposed in pore spaces ('pore-facing pyrite').
- Acidity can only be mobilised from those interconnected pore spaces through which groundwater flow occurs. Collectively, these pore spaces make up the effective porosity of the geological unit (Domenico & Schwartz 1997).
- Oxidation of pyrite by nitrate releases nitrogen gas (N_2), sulphate (SO_4^{2-}), iron (Fe) and acidity (H^+). The prevalent oxidising potential will control whether ferrous iron (Equation 1) or ferric iron (Equation 2) is produced .

Considering the aforementioned conceptualisation, the potential significance of pyrite oxidation by nitrate under anoxic conditions is illustrated by calculating the following parameters for two geological units frequently affected by iron ore mining in the Pilbara:

- Acidity production. Acidity per tonne of material in the Pilbara geological units under consideration was calculated using known sulphur concentrations and the formula of AMIRA (2002).
- Nitrate loading. The rate of nitrate supply to potential anoxic pyrite oxidation, depends on the groundwater flow rate and the concentration of nitrate flowing through the Brockman and Mount McRae units. Darcy flux per tonne of geological material was estimated using hydraulic conductivity values from Kalaka (2021) and credible hydraulic gradients based on experience in the Pilbara. The time to supply sufficient nitrate to oxidise the sulphide in the geological units was calculated for a range of nitrate concentrations from 1–100 mg/L as NO_3.
- Alkalinity loading. Alkalinity loading was calculated from the Darcy flux per tonne of geological material using the same hydrogeological parameters as for the nitrate loading calculation. An indicative alkalinity concentration was obtained from published sources.

3 Results and discussion

3.1 Acidity production

The production of acidity per tonne of geological unit was calculated using values for sulphur concentration and porosity. This has been done for the two Pilbara rock units:

1. Brockman Iron Formation. This banded iron formation unit hosts iron ore mineralisation. Mineralisation increases porosity and hydraulic conductivity[1] (Morris 1980; Perring & Hronsky 2019). However, since mineralisation is generally limited in extent and largely removed in existing mine pits, the oxidation of pyrite in unmineralised Brockman surrounding excavations is the focus of the calculations.
2. Mount McRae Shale. This shale unit is considered an aquitard, that is, it has a low permeability, several orders of magnitude less than the Brockman Iron Formation. However, it is associated with the highest pyrite concentrations and is generally recognised as a potential AMD source in the Pilbara. The Mount McRae Shale is also known to contain organic carbon to the extent that heat generated by sulphide oxidation under oxic conditions can lead to spontaneous combustion.

Table 2 presents the estimated acidity production for these two units.

[1] Ore formation is characterised by Fe enrichment and stripping of silica. During mineralisation gangue material is pseudomorphed by goethite, which is subsequently leached.

Table 2 Total potential acidity production by lithotrophic denitrification for two Pilbara rock units

Parameter	Units	Brockman Iron Formation	Mount McRae Shale
Sulphur concentration	wt%	0.05[1]	0.8[1]
Effective porosity	%	10[2]	2.5[3]
Available sulphur to generate acidity[4]	wt%	0.005	0.021
Acidity from complete oxidation of available sulphide (NO_3 as oxidant)[5]	kg H_2SO_4/t	0.04	0.15

Note 1 – Average, based on review of several thousand assay samples from several sites in the Pilbara (not published).
Note 2 – Based on porosity range of 0–10% for fractured crystalline rocks (Domenico & Schwartz 1997).
Note 3 – Based on lower end of total porosity range of 1–10% for shale (Domenico & Schwartz 1997).
Note 4 – Proportion of pyrite exposed in pores, i.e. porosity multiplied by the sulphur concentration.
Note 5 – One mole of pyrite produces one mole of acidity per Equation 2.

Table 2 overestimates acidity production for the following reasons:

- Effective porosity implies interconnection between pores in the rock mass and can be more than one order of magnitude less than total porosity (Domenico & Schwartz 1997). Shales like the Mount McRae Shale may have significant porosity, but the pores are known to lack significant interconnection. The values used in Table 2 are based on total porosity which assumes a greater volume of interconnected pore space, and hence a greater mass of sulphide, exposed to flowing groundwater.
- The mass of sulphide exposed in pores assumes that the sulphide (and pore space) is evenly distributed throughout the geological unit. Sulphide occurrence is likely to be heterogeneous and may not coincide with pore spaces. This is especially the case in Brockman Iron Formation rocks, where primary porosity (spaces between the mineral particles) is generally significantly less than secondary porosity (fractures from microscopic to macroscopic scale), and in the Mount McRae Shale, where sulphides may be preferentially located along fracture and bedding planes. Therefore, in a given volume of geological unit material, only a relatively small proportion of the total pore space may expose pyrite to potential oxidation and only a small proportion of the total pore space is likely to be interconnected and contribute to effective porosity.
- It is assumed 100% of the pyrite mass is oxidised. As Figure 4 suggests, much of the pyrite mass may be embedded in the geological unit around the pore space. Also, while oxidation may progressively remove an entire pyrite grain in some cases, low solubility oxidation products (such as goethite) may block access to the rest of the grain and limit or prevent further oxidation of the remaining pyrite mass. Therefore, it is unlikely that the total mass of pyrite oxidised will approach 100%.

Based on this, total acidity production could potentially be more than 10 times less than indicated in Table 2.

3.2 Nitrate loading

The rate of nitrate supply to potential anoxic pyrite oxidation sites, depends on the groundwater flow rate and the concentration of nitrate. Table 3 presents the time to complete oxidation of the sulphide exposed in the pore space of a unit mass of geological material, assuming that the supply of nitrate is sufficient to maintain the sulphide oxidation rates.

Table 3 Time to complete pyrite oxidation by lithotrophic denitrification for two Pilbara rock units

Parameter	Units	Brockman Iron Formation	Mount McRae Shale
Available sulphide concentration (assuming pyrite)	wt%	0.1	1.6
Laboratory pyrite oxidation rate[1]	µM/day	0.40–37[1]	0.40–37[1]
Time to oxidise pyrite (in 1 kg of rock)	days	22-2,000	88-8,200

Note 1 – From Bosch & Meckenstock (2012) excluding nanoparticle result.

Table 4 presents parameter values for calculations of nitrate supply. The range of hydraulic conductivity for the unmineralised Brockman Iron Formation is consistent with mean values for proxy geological units, the unmineralised Dales Gorge Member of the Brockman Iron Formation (1.68 m/day) and unmineralised Marra Mamba Iron Formation (2.72 m/day), reported by Kalaka (2021). As previously indicated, the Mount McRae Shale is recognised as a low permeability unit (aquitard) and the hydraulic conductivity range is several orders of magnitude less than the Brockman Iron Formation.

Table 4 Groundwater flux for two Pilbara rock units

Parameter	Units	Brockman Iron Formation	Mount McRae Shale
Hydraulic gradient	–	0.01–0.05	0.01–0.05
Hydraulic conductivity	m/day	1–3	0.0001–0.001
Area of one face of one tonne cube of geological unit[1]	m^2	0.4	0.52
Darcy flux	L/day/t	4–60	0.0005–0.026

Note 1 – Upstream face of cube of one tonne mass based on aquifer density: 3.95 for Brockman, 2.65 for McRae.

Based on Figure 5, groundwater flux in the Mount McRae Shale is too low to supply sufficient nitrate to oxidise sulphur at laboratory-determined rates. At the expected groundwater flux rates, complete pyrite oxidation would take centuries.

Based on Figure 6 groundwater flux in the Brockman Iron Formation is too low to supply sufficient nitrate to oxidise sulphur at the higher bound of laboratory-determined oxidation rates. Under conditions of K = 1 m/day and i = 0.01 with nitrate concentrations less than about 20 mg/L the nitrate loading is not sufficient to oxidise sulphur at the lower bound of laboratory-determined rates either. The field between the solid and dashed orange lines in Figure 6 is the range of hydraulic conditions within which nitrate supply may be sufficient to oxidise sulphide in the Brockman Iron Formation.

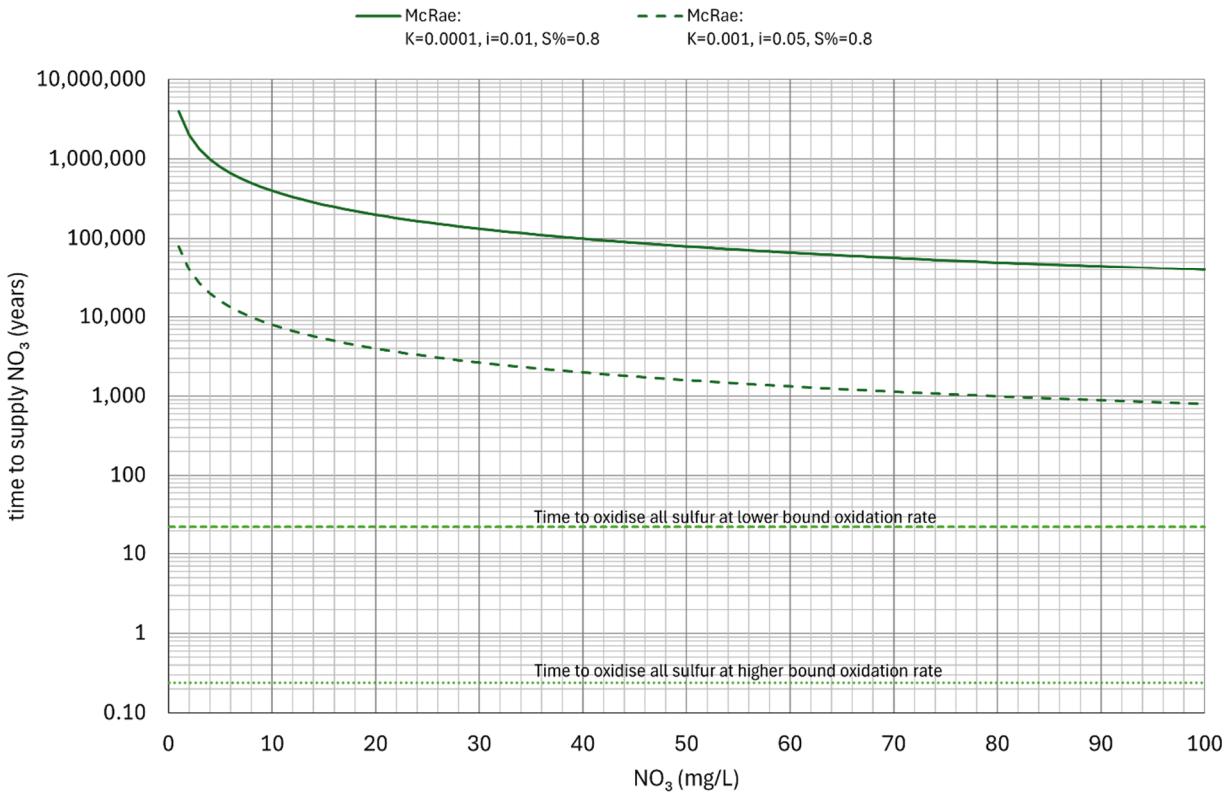


Figure 5 Calculated time to oxidise sulphur at expected Darcy flux rates in Mount McRae Shale at a range of nitrate concentrations (K = hydraulic conductivity in m/day, i = hydraulic gradient, S% = bulk sulphur concentration in wt%). Times to oxidise are from Table 3

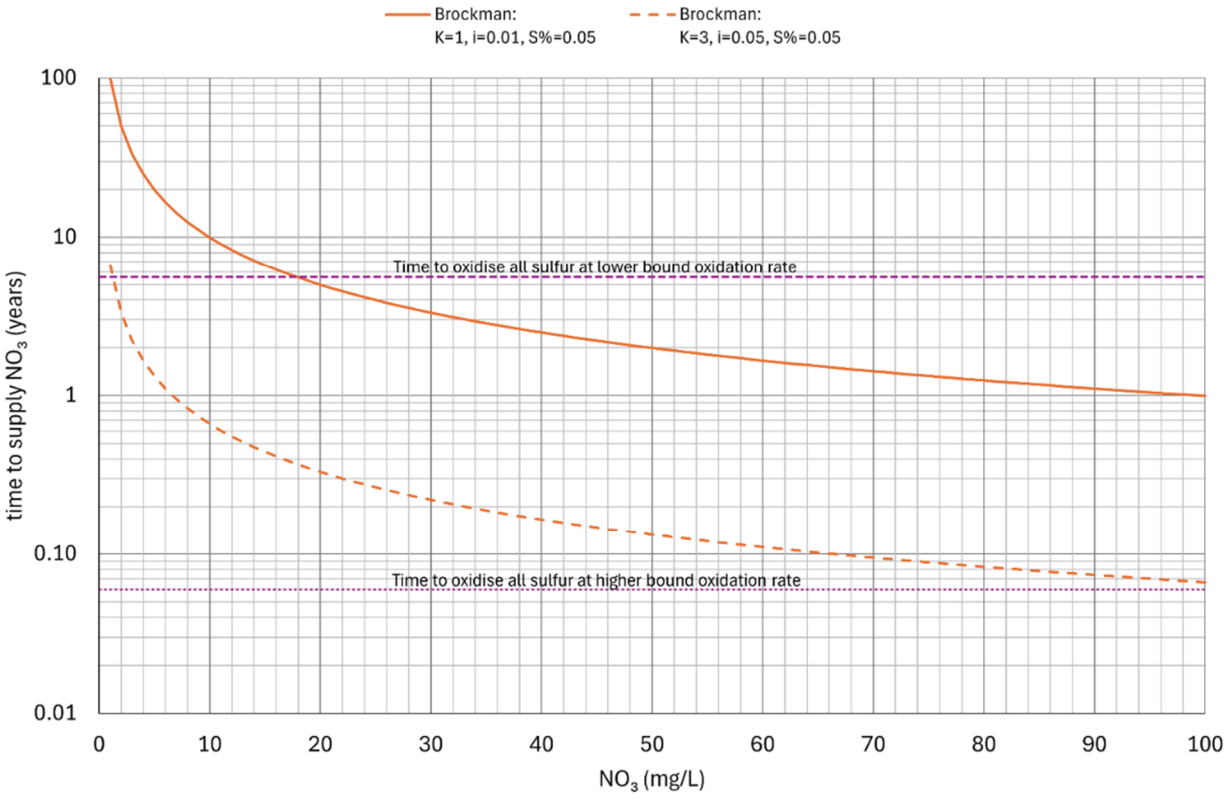


Figure 6 Calculated time to oxidise sulphur at expected Darcy flux rates in Brockman Iron Formation at a range of nitrate concentrations (K = hydraulic conductivity in m/day, i = hydraulic gradient, S% = bulk sulphur concentration in wt%). Times to oxidise are from Table 3

3.3 Alkalinity loading

Hydrochemical mapping data from Gray et al. (2019) shows alkalinity range of 60–1,500 mg/L as HCO_3 (97–2,400 mg/L as $CaCO_3$) in the Pilbara region. Our own experience suggests a similar range, with the higher end values reflective of the dolomitic Wittenoom Formation (presenting a regional aquifer in the Pilbara where sufficiently weathered). Our conservative estimate of the lower quartile of groundwater total alkalinity is ~100 mg/L as $CaCO_3$ (102 mg/L as H_2SO_4 equivalent, ~120 mg/L as HCO_3). This may underestimate the mass of alkalinity available to neutralise acidity but provides a conservative number for calculations to consider the potential risk from nitrate-induced oxidation of pyrite.

Table 5 indicates that the rate of alkalinity supply from groundwater flow through the Brockman Iron Formation and Mount McRae Shale exceeds the rate of acidity release from the nitrate supply by a factor of ~10, even at nitrate concentrations of 40 mg/L as NO_3, within the range expected on mine sites (Gemson et al. 2022). The acidity balance associated with nitrate-induced oxidation of pyrite is negative with respect to the alkalinity load associated with groundwater flow.

As previously indicated, acidity production has been conservatively overestimated by a factor of at least 10 in this assessment. The alkalinity contribution from groundwater has been conservatively underestimated. Both factors would contribute to reducing the acidity production from lithotrophic denitrification by pyrite oxidation.

Table 5 Alkalinity supply and acidity balance from groundwater during pyrite oxidation by lithotrophic denitrification in two Pilbara rock units

Parameter	Units	Brockman Iron Formation	Mount McRae Shale
Time for complete sulphide oxidation (NO_3 = 40 mg/L)[1]	Years	0.17–2.5	>1,000
Cumulative alkalinity from inflowing groundwater[2]	kg H_2SO_4/t	0.4	>0.98
Acidity from complete sulphide oxidation (per Equation 2)	kg H_2SO_4/t	0.04	0.15
Acidity balance (acidity – alkalinity)	kg H_2SO_4/t	−0.36	−0.83

Note 1 – Read from Figures 5 and 6.
Note 2 – Assuming groundwater alkalinity of 100 mg/L as $CaCO_3$ (102 mg/L H_2SO_4 equivalent), Darcy fluxes from Table 4 and time indicated in row above.

In the case of acidic groundwater flow through the geological unit (as in AMD impacted groundwater), there would be no alkalinity to offset acidity from pyrite oxidation. In this case, the acidity contribution from lithotrophic denitrification and pyrite oxidation would be of questionable relevance.

4 Conclusion

Published literature demonstrates that lithotrophic denitrification, that is, the reduction of nitrate by oxidising sulphide minerals (particularly pyrite) under anoxic conditions in the absence of organic carbon, is a natural process. It has been observed mostly in geological units with significant porosity. It has been inferred to occur in geological units in the vicinity of massive sulphide deposits over very long time periods.

Using sulphide concentrations measured in two key Pilbara geological units (Western Australia), and published reaction stoichiometries, pyrite oxidation by nitrate could potentially produce a total acidity of the order of 0.04 to 0.15 kg H_2SO_4/t if all the pyrite was oxidised.

The calculations presented in this paper indicate anoxic pyrite oxidation by nitrate is unlikely to lead to an acidic groundwater plume from rocks with similar characteristics to those assumed for the Brockman Iron Formation and Mount McRae Shale. A key mitigating factor is the low groundwater flow rate which limits nitrate supply. This reduces the rate of acidity release from pyrite oxidation. A second mitigating factor is the

alkalinity of the groundwater flowing through the rock which, under conservative assumptions, still significantly exceeds the rate of acidity release from pyrite oxidation. Although, this mitigation would not apply if the groundwater were already acidic from AMD impact.

It is concluded that pyrite oxidation by groundwater nitrate under anoxic conditions is not likely to lead to significant subsurface plumes of AMD impacted groundwater in the Pilbara.

Acknowledgement

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