EXPLOSIVES AND WATER QUALITY

by

Bill Forsyth¹, Alan Cameron² and Scott Miller³

Abstract: Water quality regulations currently in place in Canada and the USA include criteria for allowable nitrate concentrations in mine effluent. These regulations extend not only to operating mines but also to mines at the permitting stage. In some cases, mines in the permitting process must demonstrate that their proposed practices will not result in levels above the regulatory limitations.

The primary source of the nitrates are the explosives used in the mining operation. The majority of the explosives used in the mining industry contain significant amounts of ammonium nitrate, often with some calcium nitrate or sodium nitrate.

Mining companies have opted for a number of different approaches to deal with this problem, ranging from using significantly more expensive explosive products to rigorous explosive management practices. Their approach is very dependent upon specific site conditions, infrastructure, mining rate, water treatment options and explosive costs.

Key Words: explosives, water quality, ANFO, mining, environment

Introduction

Water quality impacts due to the introduction of nitrates into the system can be a significant problem for a mining operation. The major source for the nitrates are explosives used in the mining process. A majority of modern commercial explosives contain ammonium nitrate (also sodium nitrate and calcium nitrate) as an oxidizing agent. Loading practices and blasting efficiency, as well as the presence of water, control the amount of these nitrates that enter the water system.

Nitrates can be introduced into the water in the mine or at a waste rock disposal site. They come from spillage during explosive transportation or charging, leaching of the explosive in wet blastholes or undetonated explosive in the broken rock after the blast. Techniques and/or procedures will be presented that can lead to the minimization of nitrates in water discharged from a mine.

Regulatory agencies in Canada and the United States are placing a significant emphasis on compliance with effluent nitrate concentrations. Typical limitations are established at 10 mg/l as N, based on the maximum contaminant level for potable use (U.S. EPA, 1986). In some instances lower levels are set when local water, non-degradation rules are applied (Kindt, 1994). Effluent requirements may also be based on government specified toxicity test criterion.

¹ Bill Forsyth, Associate, Golder Associates Ltd., Vancouver, B.C.
² Alan Cameron, Senior Blasting Consultant, Golder Associates Ltd., Sudbury, Ontario
³ Scott Miller, Senior Project Manager, Golder Associates Inc., Denver, Colorado
Background

The impact of mining operations upon local water quality has been well documented. Collier (1964) studied the effects of coal mining on the Beaver Creek Basin, Kentucky during the period 1955-1959. Hackbart (1979) studied the effects of surface coal mining on streams and springs in the Rocky Mountains from 1972 to 1978. The British Columbia Ministry of Environment studied the effects of explosives use on water quality around the Fording Coal mine during 1979-1980.

Explosives

Modern commercial explosives generally contain a fuel and an oxidizer (some explosives have sensitizers and other additives). Oxidizing agents are typically ammonium nitrate (NH₄NO₃), calcium nitrate (Ca(NO₃)₂) and sodium nitrate (NaNO₃). Commonly used explosives can be divided into three groups, ANFO (Ammonium Nitrate and Fuel Oil), watergels/slurries and emulsions. All contain significant amounts of nitrogen, but have a different resistance to water and therefore varying degrees of capacity to introduce their nitrogen into the water system. The relative leaching rates when exposed to a large volume of water is shown in Figure 1. Even very water resistant emulsions can eventually have their nitrates leached out.

ANFO

The basic ANFO mixture (94% Ammonium nitrate, 6% fuel oil) contains 33% (by weight) of nitrogen. This nitrogen is in two very water soluble forms, ammonium (NH₄⁺) and nitrate (NO₃⁻) ions. ANFO has no water resistance (see Figure 1) therefore its nitrogen is readily soluble if exposed to water. In addition, Ammonium Nitrate is hygroscopic (i.e. absorbs any available water) and will pick up moisture from the air if left exposed. If ANFO absorbs too much water it may become de-sensitized, fail to detonate and result in explosive in the broken rock.

Watergels/Slurries

A typical watergel/slurry mixture contains 20% to 30% (by weight) of nitrogen. This nitrogen is in two very water soluble forms, ammonium (NH₄⁺) and nitrate (NO₃⁻) ions. The water resistance of a watergel/slurry mixture is good once the cross-linker has activated a gum. This gelled gum forms a relatively impermeable barrier between the oxidizing agents and any external water. The long term stability of the gelling agent is finite and the nitrogen can eventually be exposed to external water.

Emulsions

A typical emulsion mixture also contains 20% to 30% (by weight) of nitrogen. This nitrogen is in two very water soluble forms, ammonium (NH₄⁺) and nitrate (NO₃⁻) ions. The relative proportion of ion concentration is dependent upon the ratio of ammonium/calcium and sodium nitrate used in the formulation. The water in oil emulsion is very water resistant. The thin film of oil surrounding the salt solution minimizes contact with external water sources.

Nitrogen Cycle

The relationships between the various forms of nitrogen and changes that can occur in nature are shown in Figure 2. Explosives use can introduce nitrogen into the environment as NH₄⁺ and NO₃⁻ (from NH₄NO₃, Ca(NO₃)₂ and NaNO₃) and as N₂, NH₃, N₂O, NO and NO₂ gases formed during detonation (Pommel, 1983).
Nitrate and ammonia are generally the compounds of greatest concern for water quality degradation due to the potential human health and aquatic life impacts.

The following criteria have been established for nitrate and ammonia concentrations:

Drinking water criteria - maximum level for nitrate of 10 mg/l is based on the potential for methemoglobinemia development in infants. This condition develops when nitrate combines with hemoglobin to form methemoglobin, which does not absorb oxygen. Death can result from lack of oxygen. There are no drinking water or human health based ammonia criteria. State or Provincial criteria are frequently established as narrative or numeric standards based on antidegradation.

Aquatic life criteria - nitrate can effect aquatic life in three ways: direct toxicity (similar to impact on humans), reduction in dissolved oxygen, and cutrophication. There are no aquatic life criteria established for nitrate. The acute toxicity of ammonia is primarily due to the un-ionized free ammonia molecule (NH₃). Ammonia toxicity is related to temperature and pH of the water. Numeric or narrative ammonia standards are calculated using stream specific pH and temperature.

**Explosives Use in Mining**

Explosives use can be divided into two types, small quantity/high frequency and large quantity/low frequency. Examples of the first use would be drifting, raising and shaft sinking. Examples of the second type would be stope or bench blasting. The potential for introduction of nitrogen into the water system is dependent upon the following:

1. The specific explosives used
2. The water conditions
3. The handling and management of the explosives
4. The efficiency of the blasting operations

The specific explosive chosen will control the absolute amount of available nitrogen, the potential rate of release and the ease of release in the water system. This ranges from ANFO with a high nitrogen content and very low water resistance to film wrapped emulsions with a lower nitrogen content and a much higher water resistance.

The water conditions will determine the water volume and flow rate the explosive is exposed to in the blasthole. The amount of water available to transport the nitrogen in the mine water system will also influence the relative concentration of nitrogen.

The handling of the explosive product has the most significant influence on the quantity of nitrogen entering the water system. In the case of ANFO, losses occur as spillage during filling of explosives loading equipment, actual loading of blastholes and disposal of excess product. Wiber (1991) reports that these losses could amount to between 5% and 15% of total ANFO used. Golder Associates (1993, unpublished) found that, for a particular mine, nearly one tonne of ANFO was entering the water system per month (5.2% of total use). The losses are not limited to the use of ANFO. Pommen (1983) reports that 6% of the total nitrogen used at Fording Coal’s operations was entering the surface and ground water. The primary explosive at this site was a slurry.

The efficiency of the blasting operation will control the amount of nitrogen available from undetonated explosives. Blastholes may fail to detonate due to proximity effects such as dislodgment or
desensitization. Poor design or execution are the most common causes of “misfires”. Advanced blast monitoring routinely shows that 10% to 20% of blastholes misfire in a given blast. Inaccurate drilling can also result in severe proximity effects. The ultimate result is undetonated explosives in the muckpile and available for dissolution into the water system.

**Explosives Management**

A substantial reduction in nitrate concentration can be achieved through proper management of the source material. Education of operating personnel on the problem of nitrates in the water is the first step. Appropriate handling and loading procedures represent the most cost effective means of reducing nitrate concentrations.

**Education**

It is important that all employees are made aware of the potential magnitude and severity of the nitrate problem. Case studies have shown significant reductions in total dissolved nitrate levels after implementing employee education programs. Wiber (1991) shows a greater than 30% decrease in total ammonia as N in mine discharge water at Hemlo Gold Mines, Golden Giant Mine during the summer of 1991 (Figure 3). An education program was given as the primary reason for the decrease.

**Handling and Loading Practices**

ANFO is the most commonly used explosive in the world and the most common source of nitrates in mine water. The following practices are especially important:

- Identification of blastholes containing water and proper procedures for loading a wet blasthole. Any water in a blasthole must be removed prior to loading with ANFO.
- Adequate unloaded collar lengths must be established to reduce both “blowback” when loading pneumatically and blasthole proximity effects.
- Proper “standoff” distance and loading vessel pressure to reduce “blowback” during pneumatically loading ANFO.
- Partially used bags of ANFO must be resealed and returned to the explosive magazine.
- Loading equipment must be cleaned in an area where the water can be properly handled.

Emulsion and slurry/watergel explosives have significantly higher water resistance but must be handled with the same care and attention to realize the potential benefits. The following practices are important:

- Spills of the product must be handled correctly. Improper cleanup could result in explosives in the mine water and/or the broken rock. This rock could end up on a waste pile where the nitrates will eventually be leached from the explosive.
- Proper loading techniques must be followed when loading a bulk product into a wet blasthole. The product should be extruded into itself and not into water. Water entrapped in the explosive during loading can reduce the efficiency of the detonation and increase the amount of available nitrates.

Indications from operating mines are mixed, Wiber (1991) reported that the level of nitrates in the mine effluent at Falconbridge’s Thayer-Lindsey Project was reduced when ANFO use was discontinued (at a cost of $50/ft of advance) whereas Pommern (1983) reports continued high levels of nitrates in the mine water at Fording Coal with the use of a slurry product.
Treatment Options

Nitrate removal technologies are outlined in a paper by Kindt (1994) and can be divided into three categories. These categories are ion exchange, electrochemical ion exchange and biological denitrification (or combinations of the three). Some of these technologies have been traditionally applied in municipal waste water treatment.

For a generic project outlined in Kindt (1995) the following operating costs were given for a range of treatment options per 1000 gallons of treated water, estimated capital costs are given in brackets:

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Exchange</td>
<td>$1.28 ($400K)</td>
</tr>
<tr>
<td>Electrochemical ion exchange</td>
<td>$0.57 ($590K)</td>
</tr>
<tr>
<td>Submerged rotating biological contactor</td>
<td>$0.95 ($460K)</td>
</tr>
<tr>
<td>High rate fixed film biological filters w/intermittent backwash</td>
<td>$0.95 ($770K)</td>
</tr>
<tr>
<td>High rate fixed film biological filters w/continuous backwash</td>
<td>$0.95 ($345K)</td>
</tr>
<tr>
<td>Low rate fixed film biological reactor</td>
<td>$0.80 ($395K)</td>
</tr>
<tr>
<td>Ion exchange and electrochemical ion exchange</td>
<td>$0.52 ($485K)</td>
</tr>
<tr>
<td>Ion exchange and biological denitrification</td>
<td>$1.10 ($675K)</td>
</tr>
</tbody>
</table>

Note: all costs in US dollars. Additionally, costs assume treatment of 100 gpm at a nitrate concentration of 25 to 100 mg/l with a treatment objective of 10 or less mg/l of nitrate.

Ion exchange removal of nitrate is a proven and established commercial process. Ion exchange resins are placed either in a fixed bed or suspended in a reactor as a slurry. The untreated mine water is then contacted with resins to affect treatment. A fixed bed configuration is the most common configuration and is similar in design to a filtration system. The advantages of ion exchange is the excellent performance reliability, especially with fluctuating flow and nitrate levels. Disadvantages include relatively high capital and operating costs and disposal of backwashed brines. Additionally, clarification and filtering of the mine water may be required if the total suspended solids concentrations are above 10 mg/l.

Electrochemical ion exchange of nitrate is an emerging technology which has not been utilized in large scale operations. The principal advantage of the process is that the nitrate is completely destroyed through conversion to nitrogen gas eliminating the requirement for secondary disposal of brines or sludges. However, high operating costs due to power consumption is a significant disadvantage. As with ion exchange, clarification and filtration of the mine water may be required prior to electrochemical destruction.

Biological denitrification is a technology which utilizes anaerobic bacteria and an organic food source for biochemical reduction of nitrate to nitrogen gas. The process completely destroys nitrate through conversion to nitrogen gas eliminating the requirement for secondary disposal. The process is well established and forms an integral component of many municipal wastewater treatment plants. The process involves living organisms or bacteria, which are sensitive to fluctuations in mine water chemistry. The mine water chemistry may require pre-treatment to create an environment suitable for biological treatment.

Nitrate and nitrogen compound treatment technologies are generally feasible and potentially economically viable. However, emphasis by the mining industry should be placed on pollution prevention alternatives and treatment used only if absolutely necessary.
Summary

The need to address the potential for nitrate contamination of surface and ground water around mine sites is becoming increasingly important. The largest source of nitrates at an operating mine are explosives. Given that explosives are an integral part of the mining cycle, the most logical approach to reducing nitrate levels is proper management of their use. The approach outlined below is based upon increasing economic costs:

1. Develop and implement explosive management practices.
2. Evaluate and improve the current level of blasting efficiency.
3. Change to a more water resistant explosive product.
4. Assess treatment options.

Significant reductions in the nitrate level of mine discharge water can usually be achieved through care and attention to detail in the mining operation with little added cost to the mining operation. This may require some alteration to the bonus system used at many underground mines to reflect the importance of good house keeping and appropriate use of explosives.

References


Figure 1 - LEACHING TEST RESULTS: PERCENT OF UNDISTURBED CHARGE vs TIME

(Ref. Dyno, 1993)
Figure 2 - THE NITROGEN CYCLE

(Ref. Pommem, 1983)
Figure 3 - MINE WATER MONITORING FOR TOTAL AMMONIA AS N  