

**MANAGEMENT OF NITROGEN COMPOUNDS IN MINE WASTEWATER:
COMPARING SELECTIVE ADSORPTION AND ELECTRO-OXIDATION
TO OTHER TREATMENT METHODS**

*D. Kratochvil, F. Mohamm, C. Xiao, A. Borsoi and P. Littlejohn

*BQE Water
Suite 250 – 900 Howe Street
Vancouver, BC, Canada V6Z 2M4
(*Corresponding author: dkratochvil@bqewater.com)*

ABSTRACT

Nitrogen compounds produced by cyanide destruction and/or blasting are often a cause of concern for environmental compliance and at times, for water re-use in metallurgical circuits. Natural attenuation in tailings ponds and wetlands is not always sufficient to ensure compliance and/or achievement of overall water management objectives. This paper provides a general overview of active treatment methods for nitrogen management followed by an investigation of selective adsorption combined with electro-oxidation as the potential treatment method for thiocyanate. Results from bench scale treatability study are presented. The concept of holistic assessment of nitrogen management at mine sites using Risk Adjusted Life Cycle Cost is introduced and discussed in the context of gold mining operations using sodium cyanide.

KEYWORDS

Cyanide destruction, Electro-oxidation, Nitrogen, Selective adsorption, Thiocyanate, Water management

INTRODUCTION

Unlike metals, nitrogen compounds present in mine waters originate entirely from anthropogenic sources rather than mineral deposits. Table 1 summarizes the main sources of nitrogen compounds reporting to mine wastewater.

Table 1. Anthropogenic sources of nitrogen compounds in mining effluents

Chemical Source of Nitrogen Species	Chemical Use	% of total Nitrogen in Chemical Reporting to Wastewater	Resultant Nitrogen Species in Mine Effluent
ANFO	Blasting	< 5% depending on site specific conditions	NH ₄ -N, NO ₃ -N
NaCN	Precious metals extraction Flotation activator	Up to 100%	Total-CN, CNO, NH ₄ -N, SCN
PbNO ₃	Precious metals extraction Mineral flotation	Up to 100%	NO ₃ -N
NH ₄ Cl or (NH ₄) ₂ SO ₄	Nutrients added to biological systems	Up to 100%	Mostly N-NH ₄

The best management practice related to the use of ANFO involves minimizing contact between ANFO and water, control and monitoring of blasting to reduce the occurrence of misfires, and reducing the consumption of blasting reagents for a given ore body. The most common practice for the management of NaCN is the incorporation of cyanide destruction in the metallurgical flowsheet and the use of tailings impoundments and holding ponds for natural attenuation of cyanide destruction residues such as NH₄-N and CNO. At most mine sites there is no active management of NO₃-N and SCN in wastewater.

While current practices have produced satisfactory results, new enhanced methods to manage nitrogen compounds at mines are needed due to:

- 1) Increased scrutiny over the adverse effects of nitrogen compounds released into the environment;
- 2) New effluent standards; and
- 3) The shift away from wet tailings towards dry stack systems resulting in diminished natural attenuation and dilution of nitrogen residues prior to effluent discharge or water re-use in mineral processing.

Provincial and federal guidelines exist for the nitrogen species listed in Table 1 (BC WQG, 2009; CCME, 2012). While these guidelines apply to the receiving environment, they are being used to determine acceptable end-of-pipe limits during permitting. Furthermore, Environment Canada is expected to include ammonia in the new Metal Mining Effluent Regulations (MMER) that will apply to the end of pipe discharges from all metal mines (EC, 2012). Most importantly, regardless of whether or not specific limits are applied, all mine water discharges are required to be non-toxic and all nitrogen species listed in Table 1 can contribute to mine effluent toxicity.

In general, there are three challenges associated with nitrogen compounds in mining effluents including:

- 1) Specific limits applicable for various nitrogen species and for TSS
- 2) Effluent toxicity
- 3) Adverse effects on receiving environment other than toxicity

Dealing with effluent toxicity caused by nitrogen species can be further complicated by the transformation of one nitrogen species into another. Reactions (1) and (2) provide examples of these transformations:





The kinetics of these reactions depends on pH, temperature and the presence of a catalyst. Thiocyanate and cyanate are much less toxic than ammonia. However, if reactions (1) and (2) occur, then effluent may be rendered toxic despite the fact that low ammonia concentrations are measured at the end-of-pipe at the time of sample collection. Finally, even if effluents are not acutely or chronically toxic, nitrogen species present in them may still create adverse effects on the receiving environment through eutrophication, algae blooms, and changes in composition of aquatic species (CCME, 2012). Such adverse effects are evaluated by regulatory agencies and representatives of local communities during permitting and the risks associated with these effects may cause delays and increased costs in bringing new mines into production.

REMOVAL OF NITROGEN COMPOUNDS FROM MINE WASTEWATER

There are two categories of water treatment methods for the removal of nitrogen compounds from mining effluents including biological and non-biological systems.

Biological Treatment

Applied in either passive or active mode, biological treatment methods rely on series of transformations catalyzed by specific families of bacteria. Since every bioreactor contains a mixed microbial culture, treated effluents often contain not only the products of the targeted transformations but also by-products generated by side reactions that may become sources of toxicity or impacts on the receiving environment. Table 2 summarizes the three general types of biological processes involved in the transformation of nitrogen species.

Table 2. Biological treatment processes and potential by-products

Type of Treatment	Biological Process	Nitrogen Species Targeted for removal	Examples of bacteria catalyzing transformations	Target Product	Potential other products generated by treatment & sources of effluent toxicity or impacts
Oxidation	Sulphur oxidation	SCN ⁻	<i>Acidithiobacillia</i>	Sulphate	Thiosalts
Oxidation	Nitrification	NH ₄ -N	<i>Nitrosomonas</i> <i>Nitrobacter</i>	NO ₃ -N	NO ₂ -N, P
Reduction	Denitrification	NO ₃ -N	<i>Pseudomonas</i>	N ₂	NO ₂ -N, NH ₄ -N, P, BOD, H ₂ S, Organo-Se

Agnico Eagle operates a large multi-stage biological treatment system combining sulphur oxidation and nitrification to remove and convert SCN⁻, CNO⁻ and NH₃ to NO₃⁻ at the La Ronde Mine in Abitibi, QC. The biological approach was selected for La Ronde because no non-biological treatment option was available at that time to deal simultaneously with all of the nitrogen species present in the mine water (Laporte & Letourneau, 2015). While the treatment is successful, the experience from La Ronde clearly shows some of the complexities and weaknesses of the biological treatment method including: sensitivity of bacteria to trace metals, need to heat wastewater, very long start-up period including recovery from any upsets, inter-stage complexities where the conditions in one stage influence downstream stages, necessity for phosphorus removal to avoid eutrophication in downstream environment, and large footprint. The final product of treatment is nitrate which in itself can be toxic (CCME, 2012).

Teck Resources operates a large multi-stage biological treatment system for the removal of NO₃-N and selenium at the West Line Creek in the Elk Valley in Southeastern BC. Denitrification requires the addition of an organic under anoxic conditions. Experience from West Line indicates that the risks of effluent toxicity caused by treatment by-products or upsets in the treatment process are very real (Teck, 2015).

Table 3 summarizes the advantages and limitations of biological treatment systems for the removal of nitrogen compounds from mining effluents.

Table 3. Pros/cons of biological treatment for nitrogen compounds in mining effluents

Pros	<ul style="list-style-type: none"> • Able to deal with all nitrogen species (in a multi-stage system) • Proven on industrial scale (municipal/high BOD/COD streams)
Cons	<ul style="list-style-type: none"> • Sensitive to changes in flow and mass load • Sensitivity of bacteria to metals toxicity • Prolonged start-up and re-start periods • Risks of causing effluent toxicity through by-products • Sensitive to temperature • Risk of increasing TSS over MMER limit • Significant volume and mass of biosolids by-products

Non-biological Treatment

Non-biological treatment relies on strong chemical oxidants often in the presence of chemical catalysts, hydrolysis, and volatilization to remove nitrogen from mine water. Table 4 summarizes non-biological treatment systems for the nitrogen species of concern.

Table 4. Non-biological treatment processes and products

Type of Treatment	Treatment Process	Nitrogen Containing Species Targeted for removal	Target Product	Potential by-products as sources of effluent toxicity
Oxidation	- SO ₂ /Air - Peroxide - Caro's acid	WAD CN	CNO ⁻	NH ₄ -N, Cu, Cu(NH ₃) ₄
Oxidation	Chlorination	WAD CN, CNO ⁻ , NH ₄ -N, SCN ⁻	N ₂ Sulphate	Chloramines, NO ₃ -N
Oxidation	Ion exchange combined with electro-oxidation	WAD CN, CNO ⁻ , NH ₄ -N, SCN ⁻	N ₂	None
Volatization	Gas stripping under alkaline conditions	NH ₄ -N	NH ₃	None
Volatization	Ion exchange combined with gas stripping	NH ₄ -N	NH ₃	None

As outlined in the table, only chlorination and electro-oxidation can transform all of the nitrogen compounds commonly present in mining effluents to nitrogen gas. The remaining oxidation processes oxidize only carbon contained in the nitrogen bearing compounds leaving nitrogen in the form of NH₄-N and SCN⁻. Volatization can be applied to remove N-NH₄ by de-protonation of NH₄⁺ at pH > 11 and subsequent air stripping of NH₃. However, since the solubility of NH₃ in water is very high, large volumes of air and high power consumption are required to strip NH₃ from wastewater. SCN⁻ is not removed by conventional CN⁻ destruction processes and cannot be removed by volatization. As such, SCN⁻ is one of the most recalcitrant nitrogen compounds present in mine water and often subject to accumulation in process water.

Prior to selecting any treatment process, the risks of forming undesirable by-products needs to be evaluated. Table 4 shows that only volatization and electro-oxidation combined with ion exchange do not introduce any new potential risks of effluent toxicity.

THIOCYANATE REMOVAL BY ION EXCHANGE & ELECTRO-OXIDATION

As discussed above, thiocyanate is one of the most recalcitrant nitrogen compounds as it passes through cyanide destruction treatment virtually untouched and is relatively stable and not subject to either volatilization or rapid hydrolysis. Thus SCN^- reports to mine effluents and/or builds up in process water. Figure 1 shows a schematic block diagram of a treatment process that combines selective ion exchange to remove SCN^- with electro-oxidation of SCN^- to CN^- for re-use.

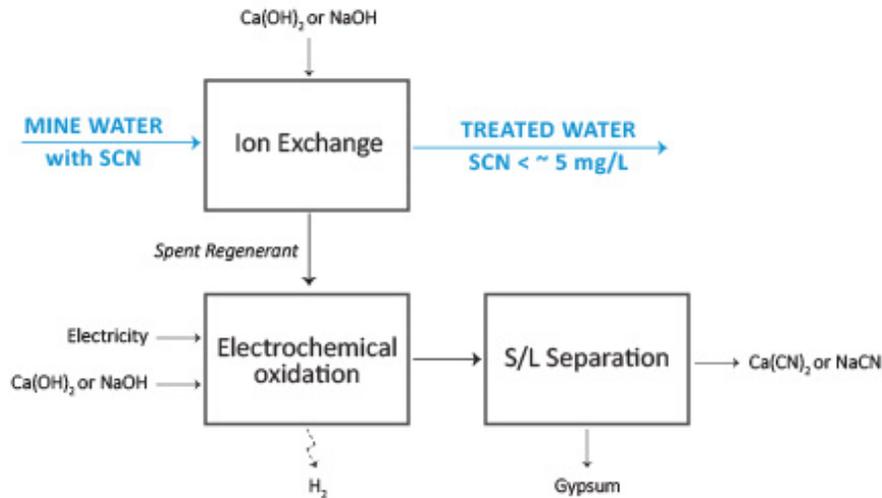
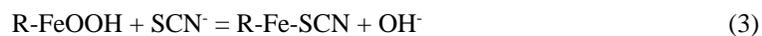
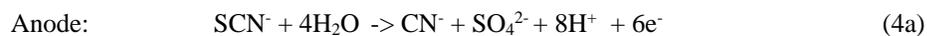


Figure 1. Thiocyanate removal process combining selective IX with electro-oxidation

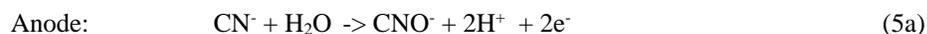
In this process, SCN^- is selectively captured from mine water by a Weak Base Anion (WBA) resin doped with iron. The effluent target concentration of $< 5 \text{ mg/L}$ of SCN^- was selected as it represents the equivalent of $\sim 1 \text{ mg/L}$ of $\text{NH}_4\text{-N}$ residual concentration in final effluent. The interaction of iron with SCN^- is the source of resin selectivity as indicated by reaction (3):



When the resin's capacity to adsorb SCN^- is reached, it is regenerated with either caustic or lime, producing a small volume of concentrated SCN^- solution. This solution is then processed through an electrocell where the conversion of SCN^- to CN^- proceeds according to reactions (4a) and (4b).



Since the electro-oxidation process is not 100% efficient, it is expected that at least some CNO^- will be produced by reactions (5a) and (5b) respectively.



The combination of reactions (4a) and (4b) shows that the conversion of SCN^- to CN^- by the electro-oxidation process generates 2 mol of H^+ per mole of SCN^- oxidized. Similarly, the combination of reactions (5a) and (5b) indicate that the oxidation of CN^- to CNO^- produces no net pH change in the electrolyte. It follows that the anodic current efficiency with respect to reactions (4a) and (5a) can be monitored by measuring acid generation and sulphate concentration in the electrolyte provided that oxygen evolution

reaction is avoided. Table 5 shows the composition of mine water used for evaluating the technical feasibility of the combined ion exchange-electro-reduction process.

Table 5. Tested mine water composition

Constituent	SCN ⁻	SO ₄ ²⁻	Cl ⁻	NH ₄ -N	Ca	Na	pH
Concentration (mg/L)	70	1,280	1,000	65	590	937	7.5

Figure 2 shows the breakthrough curve for SCN obtained using down-flow IX column at the resin loading rate of 10 BV/hr.

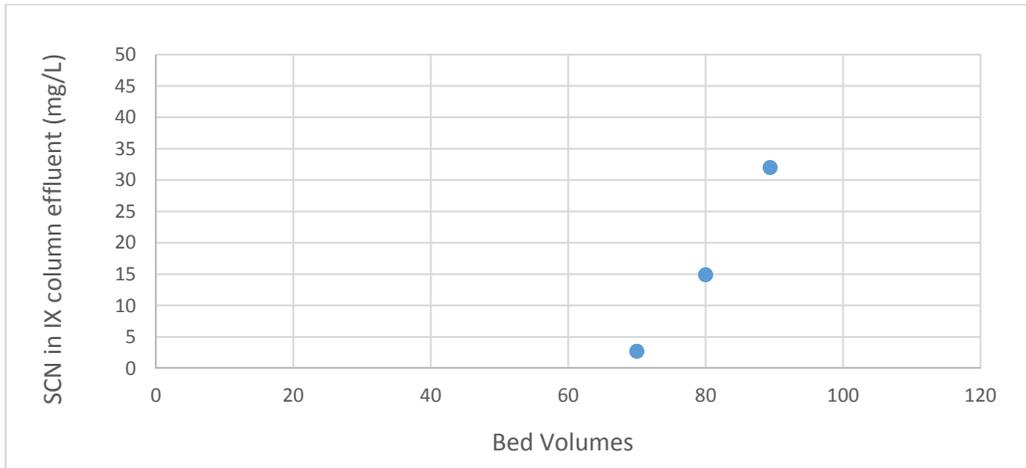


Figure 2. SCN removal from mine water using IX resin

Figure 3 shows the SCN elution curve obtained using co-current IX resin regeneration with 20 g/L NaOH solution passing through the column at the rate of 1.5 BV/hr.

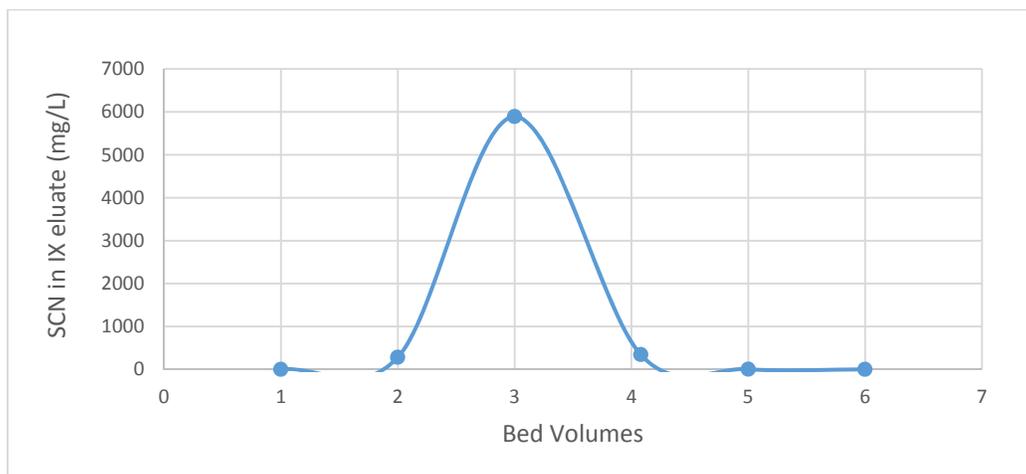


Figure 3. SCN elution from IX resin

As these figures indicate, the IX process removes SCN⁻ from the mine water down to concentrations below 5 ppm while concentrating SCN⁻ in the spent regenerant solution by a factor of 35 (70 BV load/2BV regeneration), i.e. from the IX feed concentration of 70 mg/L to 2,450 mg/L.

Next, Figures 4 and 5 show the results of the electro-oxidation process carried out in batch mode at pH 11 using the concentrated SCN^- solution. Figure 4 compares the consumption of NaOH recorded during the batch test to the theoretical rate of H^+ production if 100% of the current passing through the electrocell was consumed by reactions (4a) and (4b).

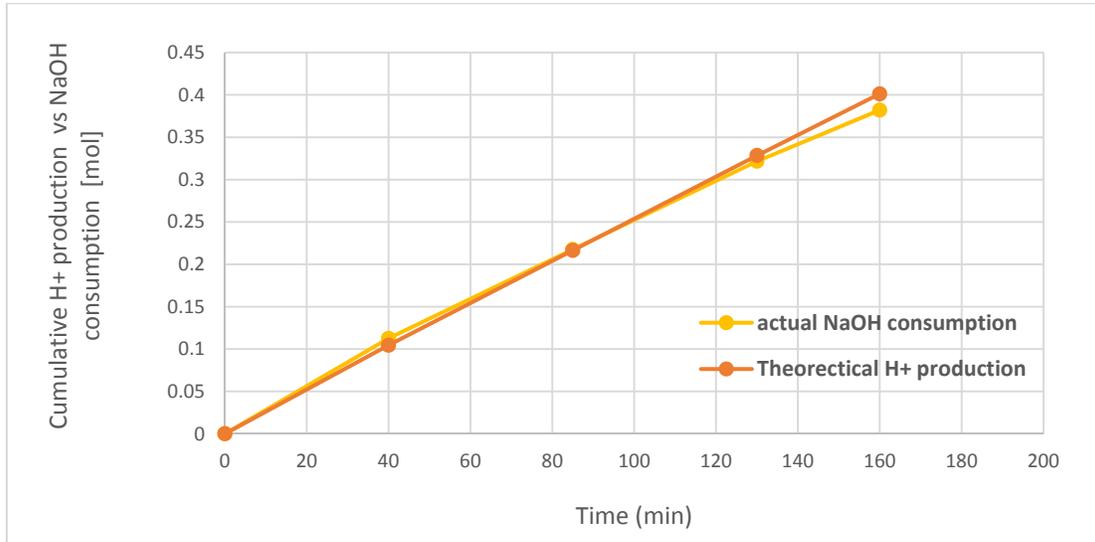


Figure 4. Caustic consumption during electro-oxidation of SCN^-

Figure 5 compared the increase in sulphate concentration measured in the electrolyte during the test to the theoretical increase in sulphate concentration if 100% of the anodic current was consumed by reaction (4a). The sulphate concentrations in Figure 5 are normalized by the initial molar concentration of SCN^- in the electrolyte in order to highlight the extent of SCN^- conversion to SO_4^{2-} .

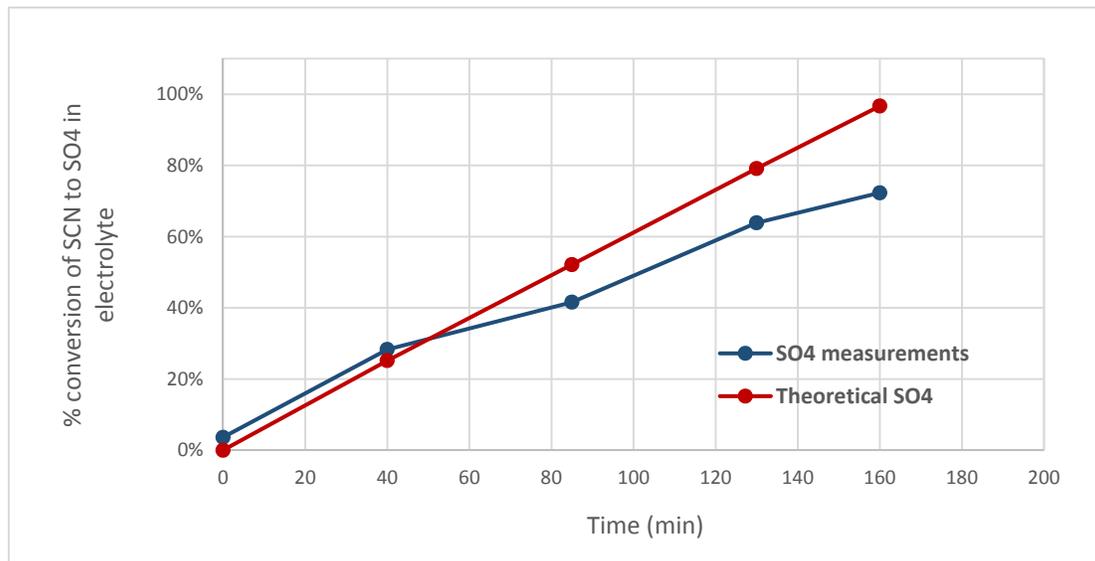


Figure 5. Sulphate production during electro-oxidation of SCN^-

It should be noted that no oxygen evolution was detected during the tests. Based on results shown in Figures 4 and 5, the anodic current efficiency associated with reaction (4a) is approximately 80% with the remaining 20% being accounted for by reaction (5a). This was confirmed by the measurement of CNO in the electrolyte at the end of the test. Overall, the results presented above indicate that the combination of ion

exchange and electro-oxidation can be used to a) remove SCN^- from mine effluents below 5 ppm, and b) recover at least 75% of N contained in SCN^- in the form of free CN^- . The work on this novel non-biological treatment is currently ongoing and several variants of the process are being investigated including the complete transformation of nitrogen contained in SCN^- to N_2 and simultaneous removal of CNO^- and SCN^- by ion exchange as shown schematically in Figure 6.

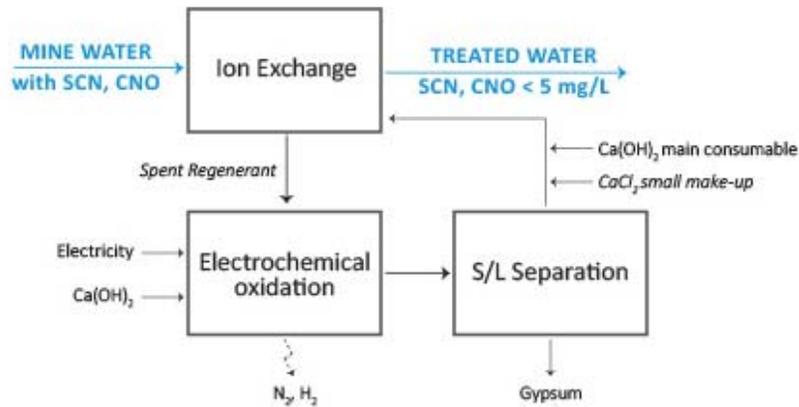


Figure 6. Process for simultaneous removal of SCN^- and CNO^- and conversion to N_2

The difference between the process shown in Figure 6 and the one shown in Figure 1 include: N_2 gas by-product, complete recycle of IX regenerant and presence of chloride in the recycled regenerant. Preliminary results indicate that the cost of SCN^- and CNO^- removal and complete conversion to N_2 by ion exchange combined with electro-oxidation will be comparable to the cost of biological processes. However, in situations when SCN^- represents the bulk of the nitrogen load reporting to the treatment process and CN^- is recovered from SCN^- , the cost of the non-biological treatment process can be expected to be significantly lower than the cost of the three stage biological treatment involving thiocyanate oxidation, nitrification, and denitrification.

HOLISTIC ASSESSMENT OF NITROGEN MANAGEMENT IN MINING

The Risk Adjusted Life Cycle Cost (RALCC) of nitrogen control and management will vary from site to site. Nevertheless, it is useful to think about the cost of nitrogen management holistically and from the early permitting and planning stages. Table 6 provides an example of a nitrogen management cost summary for gold mines utilizing sodium cyanide and considering the recovery of cyanide from thiocyanate.

Table 6. Example of nitrogen management cost summary by chemical per kilogram of N

Chemical Source of Nitrogen Species	NaCN	ANFO
Cost of N included in the price of chemical	\$7.7/kg N	\$1.70/kg N
Cost of NaCN detox via SO ₂ /air	\$6.5/kg N	-
Cost of N transformation to N ₂ or CN ⁻	~ \$5 to \$15/kg N	~ \$5 to \$15/kg N
A: Total Cost of Nitrogen Introduced at the Mine Site	\$19 to \$29/kg N	\$7 to \$17/kg N
B: Costs associated with risks	Project specific	Project specific
C: Total risk adjusted cost of N introduced at mine site	A+B	A+B
D: Credit for value of N recovered (as CN ⁻)	\$7.7/kg N	\$0
E: Risk adjustment factor for value recovery process	Project specific	Project specific
F: Total RALCC of N management at mine site	C+E-D	C+E

Project specific unit costs: NaCN \$2,200/t, ANFO \$600/t, SO₂ \$250/t, Power \$0.10/kWh

The range of costs for N transformation to N₂ or CN⁻ shown in Table 6 is based on data available in literature (Laporte & Letourneau, 2015) and preliminary results of the bench scale tests presented in this paper. Table 6 shows that the unit cost of nitrogen introduced at gold mines (A) can vary from approximately \$20 to \$30/kg excluding any adjustments for risks. Cost adjustments for risks is important to account for the following:

- Risk of losing social license if nitrogen control either fails or is not implemented
- Technical risks associated with nitrogen control implementation
- Risk of cost escalation due to higher than expected CAPEX and OPEX of nitrogen control
- Risks of cost escalation caused by increased nitrogen mass

CONCLUSIONS

Most, if not all, nitrogen present in mine effluent comes from anthropogenic sources and as such, mines can be viewed as sources of nitrogen introduced into the surrounding environment through water and air emissions. It follows that all nitrogen brought onto mine sites during the life of mine needs to be managed carefully in order to avoid effluent toxicity or non-compliance with specific discharge limits. Furthermore, the most environmentally responsible and sustainable method of management involves the recovery of nitrogen in a re-useable form such as cyanide for recycle. If this is not possible then water treatment should be based on transforming nitrogen compounds into N₂ gas. Regardless of whether this is achieved biologically or non-biologically, multistage treatment is likely required and risks associated with long-term operation including risk of effluent toxicity through treatment by-products should be considered.

The application of biological methods relies heavily on experience from non-mining (mostly municipal) applications into mining. Transplanting this experience into mining represents a challenge and risk in itself. Non-biological methods based on the combination of electro-chemical oxidation with ion exchange is an emerging area of interest. Preliminary investigations indicate that this type of new non-biological treatment could provide more consistent effluent water quality at a comparable cost to active biological treatment systems without introducing any new risks of effluent toxicity or impact on the receiving environment. Moreover this type of approach offers the potential benefit of recovering nitrogen as cyanide that can be re-used in metallurgical processes.

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