Titre: Title:	Performance Evaluation of Pilot Scale Ozonation System for Nitrogen-Based Contaminants Removal in Mine Impacted Water
Auteur: Author:	Pascal Marcotte
Date:	2020
Type:	Mémoire ou thèse / Dissertation or Thesis
Référence: Citation:	Marcotte, P. (2020). Performance Evaluation of Pilot Scale Ozonation System for Nitrogen-Based Contaminants Removal in Mine Impacted Water [Mémoire de maîtrise, Polytechnique Montréal]. PolyPublie. https://publications.polymtl.ca/5235/

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/5235/
Directeurs de recherche: Advisors:	Carmen Mihaela Neculita, Lucie Coudert, & Éric Rosa
Programme: Program:	Génie minéral

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

et

l'Université du Québec en Abitibi-Témiscamingue

Performance evaluation of pilot scale ozonation system for nitrogen-based contaminants removal in mine impacted water

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

Génie Minéral

Avril 2020

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Ce mémoire intitulé :

Performance evaluation of pilot scale ozonation system for nitrogen-based contaminants removal in mine impacted water

présenté par **Pascal MARCOTTE**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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DEDICATION

À ma conjointe

ACKNOWLEDGEMENTS

My sincere thanks to my research director, Carmen Mihaela Neculita, who invested tremendous time and efforts in supporting me throughout this project. Her work ethic was truly inspiring for me. I look forward to further collaborations with her and her team at the Research Institute on Mines and Environment (RIME), Université du Québec en Abitibi-Témiscamingue (UQAT).

I would also like to thank the several stakeholders that were key to the successful accomplishment of this project, including Lucie Coudert, Eric Rosa, Marc Turcotte, Mathieu De Koninck, Jonathan Couture and Jean-Jacques Demers, for their constant and much appreciated review of my work. Also, special thanks to Anaël Lecompte-Charbonneau, who was instrumental during the field part of this project.

Furthermore, I would like to thank the mining partner who willingly welcomed us onto their mine site, as well as ASDR Canada Inc. who funded this project in its entirety. I could not have imagined better industrial partners to pursue my master with.

Finally, I could not thank enough my spouse, who offered unconditional support over the duration of this project.

RÉSUMÉ

La présence de contaminants azotés est commune dans les effluents miniers, leurs principales sources étant l'utilisation d'explosifs pour fracturer le socle rocheux et l'utilisation du cyanure pour l'extraction de l'or et de l'argent. En raison de leur potentiel de toxicité aiguë à faible concentration, les cyanures et dérivés des cyanures (thiocyanates, cyanates), l'azote ammoniacal et les nitrites sont les principaux contaminants azotés d'intérêt présents dans les eaux minières contaminées. Les technologies conventionnelles pour traiter ces contaminants présentent plusieurs inconvénients, notamment lorsqu'il est question d'applications en eau froide. Ce contexte nécessite le développement de technologies émergentes.

Parmi ces technologies, l'efficacité de l'ozone pour oxyder ces contaminants azotés a déjà été démontrée en laboratoire. Afin de faire progresser les connaissances à ce sujet, une évaluation des performances de cette technologie à l'échelle pilote a été entreprise. Les essais ont été divisés en deux phases: des essais paramétriques pour optimiser les conditions opératoires et des essais de longue durée pour évaluer la robustesse du procédé. La première phase du projet a été réalisée sur le surnageant du parc à résidus d'une mine d'or qui contenait 1,8 ± 0,3 mg SCN-N/L, 14,0 ± 1,2 mg CNO-N/ L et 34,9 ± 2,3 mg NH_3-N/L. Les essais de longue durée ont, quant à eux, été réalisés sur le surnageant du parc à résidus ainsi que sur l'eau provenant des opérations de maintien à sec des opérations souterraines de cette même mine. Cette eau contenait 40,1 mg NH_3-N/L, et des concentrations en thiocyanate, cyanate et cyanures totaux sous leur seuil de détection.

L'efficacité d'enlèvement du NH_3-N durant les essais paramétriques du projet n'a pas montré de différence importante entre l'utilisation d'un tube Venturi ou d'une pompe à microbulles pour injecter l'ozone dans l'eau à traiter. L'utilisation de bromure, de peroxyde d'hydrogène, de charbon actif et dioxyde de titane comme catalyseur n'a pas non plus produit de différence notable lors des essais comparatifs avec et sans catalyseur. Ces essais ont également confirmé qu'un pH de 9,5 et plus est nécessaire pour oxyder avec succès le NH_3-N avec de l'ozone.

Quatre essais de longue durée ont ensuite été réalisés. Les meilleurs taux d'enlèvement ont été obtenus en ajoutant 2 330 mg O_3/L dans le surnageant du parc à résidus, soit : 99 % pour le SCN^-, 64 % pour le CNO^- et 80 % pour le NH_3-N. Cependant, la quantité d'ozone utilisée lors de cet essai fut jusqu'à quatre fois supérieure aux valeurs stœchiométriques. Des pertes d'ozone

dans l'atmosphère et des erreurs de mesure du débit d’ozone lors de l’injection pourraient expliquer cet écart.

Les CAPEX et OPEX d'une usine d'ozonation à l'échelle commerciale ont également été estimés et comparés à une usine avec réacteurs à biofilm à lit mobile d’une capacité de 500 m^3/h déjà existante et située dans le nord du Québec, au Canada. Cette comparaison a révélé que le coût des deux technologies serait du même ordre de grandeur.

ABSTRACT

Nitrogen-based contaminants are commonly found in mine impacted water, their primary sources being the use of explosives in hard rock mining, and the use of cyanide solutions for gold and silver extraction. Due to their potential acute toxicity at low concentrations, cyanide and their derivatives (thiocyanate, cyanate), ammonia nitrogen and nitrite are the principal nitrogen-based contaminants of concern at these mine sites. Conventional water treatment processes to remove these contaminants present several disadvantages when used on mine impacted water, especially for cold-climate applications. This context calls for the development of emerging technologies.

Among these technologies, the efficiency of ozone to oxidize nitrogen-based contaminants has already been demonstrated in laboratory experiments. To further advance the general understanding of this approach, an evaluation of the performance of this technology at a pilot scale level was undertaken. Trials were divided in two phases: the parametric study to optimize operating conditions and the extended duration trials to evaluate the robustness of the process. The first phase was performed on the tailing supernatant of a gold mine which contains 1.8 ± 0.3 mg SCN-N/L, 14.0 ± 1.2 mg CNO-N/L and 34.9 ± 2.3 mg NH_3-N/L. The extended duration trials were performed on both the tailing water and water from underground dewatering operations of the same mine. This water contained 40.1 mg NH_3-N/L, and concentrations of thiocyanate, cyanate and total cyanide below detection level.

Removal efficiency results on NH_3-N during the parametric study stage of the project did not showed important difference between using a Venturi tube or a microbubble pump to inject the ozone in the water. The use of bromide, hydrogen peroxide, activated carbon and titanium dioxide as catalysts also did not yield notable difference between the trials with and without them. These trials also confirmed that a pH of 9.5 and above is required to successfully oxidize NH_3-N with ozone.

Based on the results above, four extended duration trials were then carried out. Optimal removal efficiencies were obtained by dosing 2 330 mg O_3/L in the tailing water, and are as follows: 99% for SCN^-, 64% for CNO^- and 80% for NH_3-N. However, the ozone dosing rate during this trial was four times above the stochiometric requirement. Ozone loss in the atmosphere and errors on the ozone dosing rate measurements are among the suspected explanations for this difference.

The CAPEX and OPEX of a commercial scale ozonation plant were also estimated, and compared to an existing 500 m^3/h moving bed biofilm reactor plant located in Northern Quebec, Canada. This comparison revealed that the cost of both technologies may be within the same order of magnitude.

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LIST OF SYMBOLS AND ABBREVIATIONS

AC	Activated Carbon
ANFO	Ammonium Nitrate Fuel Oil
AACE	Association for the Advancement of Cost Engineering
BATEA	Best Available Technology Economically Achievable
BOD	Biological Oxygen Demand
CAPEX	Capital Expenditure
CEC	Contaminants of Emerging Concern
COD	Chemical Oxygen Demand
CN^-	Cyanide
CN^--N	Cyanide expressed as Nitrogen
DBP	Disinfection By-Products
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
EDT	Extended Duration Trials
EPCM	Engineering, Procurement and Construction Management
HMI	Human Machine Interface
HRT	Hydraulic Retention Time
H_2O_2	Hydrogen Peroxide
H_2SO_4	Sulfuric Acid
KOH	Potassium Hydroxide
LC50	Lethal Concentration 50%
LSI	Langelier Saturation Index
M	Million
m^3	Cubic meters
MDMER	Metal and Diamond Mining Effluent Regulations
MDDELCC	Ministère du Développement Durable, de l'Environnement et de la Lutte contre les Changements Climatiques
MDDEP	Ministère du Développement Durable, de l'Environnement et des Parcs
MBBR	Moving Bed Biofilm Reactor

N/A	Not Available
NaOH	Sodium Hydroxide
NH_3	Unionized Ammonia
NH_3-N	Ammonia Nitrogen
NH_4^+	Ammonium
NO_2	Nitrite
NO_2-N	Nitrite expressed as Nitrogen
NO_3	Nitrate
NO_3-N	Nitrate expressed as Nitrogen
O_3	Ozone
OER	Objectifs Environnementaux de Rejets
OH^o	Hydroxyl Radicals
OPEX	Operational Expenditure
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PID	Proportional-Integral-Derivative
PST	Parametric Study Trials
SAD	Strong Acid Dissociable
SCN^-	Thiocyanate
SCN^--N	Thiocyanate expressed as Nitrogen
TDS	Total dissolved solids
TiO_2	Titanium Dioxide
TKN	Total Kjeldahl Nitrogen
TOTEX	Total Expenditure
TSF	Tailings Storage Facility
TSS	Total Suspended Solids
UG	Underground
USEPA	United States Environmental Protection Agency
WAD	Weak Acid Dissociable
WHO	World Health Organization

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CHAPTER 1 INTRODUCTION

1.1 Context

When operating in positive water balance environments, mining companies are generally required to discharge excess amounts of mine impacted water outside of the boundaries of their properties. In most countries with strong mining legacies, such as Canada, this water must meet strict discharge criteria prior to being released into the environment. Varying from one jurisdiction to another, these discharge criteria tend to become more stringent as new technologies emerge to quantify and treat the various contaminants found in mine water.

Among these contaminants, ammonia nitrogen (NH_3-N), nitrite (NO_2^-) and nitrate (NO_3^-) are often found in hard rock mining applications, where nitrogen-based explosives are frequently used to free the valuable commodities from the ores (Jermakka et al., 2015a). Other nitrogen-based contaminants, such as thiocyanate (SCN^-), free cyanide (CN^-), weak acid dissoluble cyanide (WAD CN^-) and cyanate (CNO^-), are also common in water from mining operations relying on cyanide solutions used to extract precious metals such as gold and silver (Mudder et al., 2001). Due to their potential toxicity on aquatic life (already highly sensitive in the Canadian cold climate), and because stricter regulations on these contaminants are expected in the future, these compounds were also identified as Contaminants of Emerging Concern (CEC) or contaminants of emerging interest for the mining industry (Neculita et al., 2018; Neculita et al., 2019; Neculita et al., 2020; Ryskie et al., 2020a).

1.2 Current Situation

Various conventional technologies are currently available to treat nitrogen-based contaminants in mine impacted water. These technologies are well documented in the scientific and technical literature, with noteworthy publications covering this subject such as Jermakka et al. (2015b), Mudder et al. (2001) and Pouw et al. (2014). However, as discussed in these previous cited publications, conventional technologies have several advantages and limits. In addition, except for the oxidation of cyanide with the INCO or the Degussa process (Botz, 2001), none of the technologies currently available to treat nitrogen-based contaminants in mine water reach unanimity among researchers and industrial stakeholders. As such, most situations need to be addressed in a case-by-case approach, a process which increases the risk and cost of mining companies seeking to manage nitrogen-based contaminants on their properties.

This context allows for the development of newer technologies for the proper management of mine water contaminated by these contaminants. Among the emerging technologies, the use of ozone, a strong oxidizing agent, to oxidize all the aforementioned nitrogen-based contaminants (in addition to other redox sensitive contaminants, such as S-based species and several metals/metalloids) into NO_3^- has previously shown promising results, in laboratory testing, with synthetic and real mine water (Ryskie et al., 2020b, Zuttah, 1999).

1.3 Proposed Approach

In the mining industry, ozonation is currently used to remove cyanide from mine impacted water (Gottschalk et al., 2010), although it is generally not used as a standalone technique because of its high operating costs (Pouw et al., 2014). This oxidation process can also remove SCN^- and CNO^- in mine water (Ryskie et al., 2020b), according to the Equation 1.1 to 1.3 (Botz et al., 2001; Carrillo et al., 2000; Khuntia et al., 2012b).

$$SCN^- + O_3 + H_2O \rightarrow SO_4^{2-} + HCN + H^+ \tag{1.1}$$

$$CN^- + O_3 \rightarrow CNO^- + O_2 \tag{1.2}$$

$$CNO^- + O_3 + 2H_2O \rightarrow NH_3 + HCO_3^- + 1.5O_2 \tag{1.3}$$

Regarding removal of NH_3-N in mine water, ozonation was investigated at a gold mine operation located in Ontario, Canada. However, the industrial scale system has not yet been installed and additional information on this project is not publicly available (Pouw et al., 2014). Laboratory studies have also been carried out by Zuttah (1999) and Ryskie et al. (2020b) on synthetic and real mine water. The ozonation of NH_3-N into NO_3^-, with NO_2^- as an intermediate product, is governed by the Equations 1.4 to 1.5 (Khuntia et al., 2012b).

$$NH_3 + 3O_3 \rightarrow NO_2^- + 3O_2 + H^+ + H_2O \tag{1.4}$$

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \tag{1.5}$$

Moreover, in the presence of catalysts, ozonation of ammonia nitrogen is expected to be governed by a different stochiometric equation (Ryskie, 2017; Zuttah, 1999), such as the one discussed by Ichikawa et al. (2014) and presented in Equation 1.6.

$$NH_3 + 3/2O_3 \rightarrow 1/2N_2 + 3/2H_2O + 3/2O_2 + H^+ \qquad (1.6)$$

According to Neculita et al. (2019), ozonation of mine water presents several advantages over other conventional technologies, including fast kinetics, oxidation of several contaminants at the same time and little to no impact on the residual salinity of the treated water and its associated toxicity. However, according to the same authors, additional research on the scaling-up and techno-economic aspects of this technology are still required. The objectives presented below aim at addressing these applied research needs.

1.4 Objectives

This project is the continuation of the research conducted during the Master thesis of Ryskie (2017), which main objective was to evaluate the efficiency of various advanced oxidation processes, including the optimization of ozone microbubbles approach, for ammonia nitrogen removal in synthetic and real mine water, in laboratory-based testing.

The general objective of the present project is to evaluate the performance of ozonation to remove nitrogen-based contaminants in mine water, at field-pilot scale. The specific objectives of this applied research project are the following:

1) Evaluate the impact of various catalysts (hydrogen peroxide, bromide, activated carbon, titanium dioxide) and injection methods (Venturi tube and microbubble pump) on the overall ozone consumption and removal efficiency of nitrogen-based contaminants during the treatment of real mine water;
2) Evaluate the impact of ozonation on the acute toxicity of treated real mine water;
3) Conduct a preliminary evaluation of the operating and capital costs of a commercial scale ozonation plant.

CHAPTER 2 LITERATURE REVIEW

2.1 Nitrogen-Based Species in the Environment

Nitrogen plays a key role in many biological and chemical reactions which are essential to sustain life on earth. With nine oxidation states (from +5 to -3), the interaction between the various nitrogenous species is very complex (Chlot, 2013). The large number of naturally occurring biological reactions in which the nitrogen molecule is involved adds to this complexity (Figure 2.1). Except for nitrogen gas, the common forms of nitrogen are ammonia (NH_3), ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-), with NO_3^- being the most stable and NO_2^- the least stable form, given conditions that are typically found in surface waters.

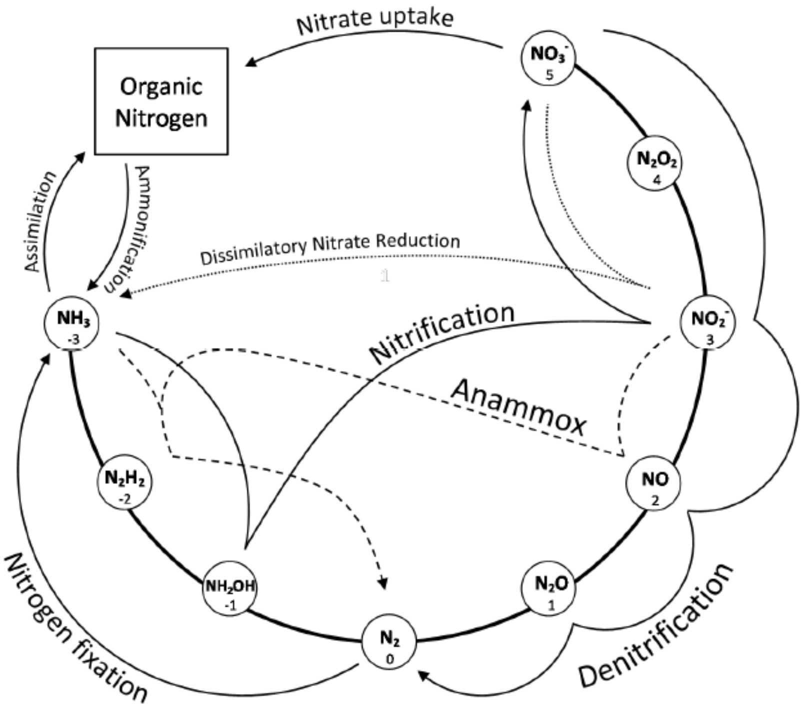

Figure 2.1 Naturally occurring biological reactions involving nitrogen (Jermakka et al., 2015a)

Ammonification, nitrification, denitrification, nitrogen fixation and anammox reactions are made possible by specific groups of bacteria. These reactions are mainly dependent on temperature, presence of macro and micro nutriments, presence of oxygen, solution pH and Eh.

Ammonia assimilation and NO_3^- uptake by phytoplankton and macrophytes are also impacted by some of these parameters (Chlot, 2013).

Apart from the biological reactions, the fate of nitrogenous species in an aqueous environment is also governed by physical processes, such as adsorption and volatilization, in the case of ammonia nitrogen. In an aqueous environment, ammonia nitrogen is present in solution either as ammonium (NH_4^+) or unionized ammonia (NH_3). The respective proportion of each form is governed by the pH and the temperature of the solution. At 25°C, the dissociation constant (pKa) of ammonia nitrogen is found at a pH of about 9.25 (Jermakka et al., 2015a). At this pH, an even proportion of the ammonium form and the unionized ammonia form is present in solution.

For the purpose of the present thesis, the ammonia nitrogen (including both ionized and unionized species, with respect to a given pH and temperature) will be referred to as NH_3-N.

2.2 Source of Nitrogen-Based Contamination in Mining Operations

Nitrogen from natural sources can be found in mine water. More specifically, naturally occurring nitrate can be introduced in mine water from the leaching of wet and dry deposition of nitric acid (HNO_3) and nitrate, the leaching of nitrate-bearing rocks, volcanic activity, mineralization and oxidation of organic matters. These sources alone can be responsible for concentrations of up to 18 mg NO_3-N/L in aerobic surface water (Jermakka et al., 2015a). As for ground water, Cloutier et al. (2016) reported averages of 0.04 mg NO_3-N/L and 0.02 mg NO_2-N/L for fractured-rock aquifers in the Abitibi-Témiscamingue region, in Quebec, Canada.

However, most of the nitrogen species found on mining sites originate from anthropogenic sources (Kratochvil et al., 2017), with the two dominant sources of these species being the leaching of undetonated explosives and the usage of nitrogen-based chemicals in the ore processing circuit (Chlot, 2013). The following sections discuss in details these two sources.

2.2.1 Nitrogen Species from Explosives Origins

In hard rock mining, the usage of explosives plays a central role in the alteration of the mechanical properties of ore bodies, enabling these bodies to be exploited in an economical way. The mass of explosives required per ton of rocks, also known as the powder factor, typically ranges from 0.2 to 1.0 kg /ton, for open-pit mining operations, and 0.5 to 2.5 kg/ton, for underground mining operations (Jermakka et al., 2015a).

Currently, all the commercially available explosives contain nitrogen, with about 25% of the mass of these explosive is elemental nitrogen (Jermakka et al., 2015a). Although there is research ongoing to develop non-nitrogen-based explosives, these novel options are, as for now, too expensive and cannot offer the same level of safety compared to conventional explosives. A list of the most frequently used explosives in the mining industry is presented in Table 2.1.

Table 2.1 Most frequently used explosives in the mining industry (Jermakka et al., 2015a)

Explosive type	Typical composition	Delivery form	Advantages	Disadvantages
ANFO explosives	- 94.5% NH_4NO_3 - 5.5% fuel oil	- Loaded bags - Mixing vehicles	- Low cost - Safer than dynamite	- Poor water resistance - Poor explosion reliability
Emulsion explosives	- 70-80% NH_4NO_3 - 10-20% water - 4% fuel oil - 1-2% additives	- Pumped straight to boreholes from vehicles	- Safer than ANFO - Release cleaner gases - Release fewer nitrate - Good water resistance	- Not specified
NG explosives (dynamites)	- Nitroglycerol - Nitroglycol	- Tubes - Plastic packages	- Relatively water resistant - High explosive power	- Easily detonated
Water gel explosives	-Super-saturated aqueous solution	- Bulk solution	- Good water resistance	- Not specified

The explosive reaction of ammonium nitrate and fuel, in ideal conditions, produces nitrogen gas, water and carbon dioxide, as presented by Equation 2.1. However, nitrogen monoxide (NO) can also be produced in non-ideal conditions, as shown by Equation 2.2. This gas then reacts with atmospheric oxygen to produce nitrogen dioxide (NO_2). Since nitrogen oxides (NO_x) can have a considerable effect on climate and ecosystems, precautions have to be taken to limit non-ideal explosive reactions (Jermakka et al., 2015a).

$$3NH_4NO_3 + CH_2 \rightarrow 3N_2 + 7H_2O + CO_2 \tag{2.1}$$

$$5NH_4NO_3 + CH_2 \rightarrow 4N_2 + 2NO + 11H_2O + CO_2 \tag{2.2}$$

When ammonium nitrate is used at a mine site, the risk of having undetonated explosives leaching by surface water is omnipresent. The actual amount of nitrogen released in the water will depend on the type of explosive used, the water balance of the site, the explosive management strategy and the efficiency of the blasting strategy (Jermakka et al., 2015a).

Different explosives have different resistance to water, thus impacting the leaching process of ammonium nitrate before ignition (see Table 2.1). However, unattended spillage or undetonated explosives, no matter what type is used, will eventually be dissolved in contact with water. This is also the case for explosive residues transported onto rock piles.

Among the factors that mining companies can have a tight control on, numerous studies have also reported the importance of explosive management to prevent nitrogen introduction in mine water (Chlot, 2013). The type of operations also influences explosive management at a mine site, with open-pit mining having simpler explosion designs compared to underground mining (Jermakka et al., 2015a).

Depending on several decisions made during the design and the operation of a mine site, as well as on the hydrology of the site, the proportion of ammonium nitrate dissolved by contact water can vary greatly. Such variance is reported in the literature, as illustrated in

Table 2.2.

Table 2.2 Proportion of total explosive undetonated according to various sources

Type of operations	**Type of explosive**	**% of total explosive undetonated**	**References**
Underground	Unspecified	Up to 20.0%	Jermakka et al. (2015a)
Unspecified	ANFO	Up to 5.0%	Kratochvil et al. (2017)
Open pit	ANFO	0.2%	Ferguson and Leask (1988)
Open pit	Water gel	2.0 to 5.0%	Ferguson and Leask (1988)
Open pit	Unspecified	15.0 to 19.0%	Chlot (2013)
Open pit	Unspecified	2.5 to 5.0%	Jermakka et al. (2015a)
Both	Unspecified	Most commonly 10.0%	Jermakka et al. (2015a)

2.2.2 Nitrogen Species from Process Origins

Apart from the mining operation, a major component of most mine sites is the metallurgical plant. Most often simply referred to as “the mill”, these plants rely on various physical, chemical and sometimes biological processes to enhance the recovery of the minerals or metals targeted (commodities). During these processes, a variety of chemicals is used, with some of them containing nitrogen species.

The most frequent nitrogen bearing chemicals used in these plants are listed below: (Jermakka et al., 2015a; Kratochvil et al., 2017):

- Cyanide salts for gold extraction;
- Nitric acid for acid washing of activated carbon;
- Nitric acid for pH adjustment;
- Ammonia solution for copper and nickel lixiviation;
- Lead nitrate for flotation processes;
- Ammonium chloride and ammonium sulfate as nutrients supplement for biological processes.

Among these chemicals, cyanide salts are the dominant source of nitrogen on mine sites, followed close by nitric acid (Kratochvil et al., 2017). Therefore, the literature is focused on cyanide salts, while public data on nitric acid consumption are scarce (Jermakka et al., 2015a).

Worldwide, 1.1 million metric tons of hydrogen cyanide is produced annually, and 6% of the production is used for gold leaching applications (Jermakka et al., 2015a). Cyanide can also be used for the recovery of silver, copper, lead and zinc (Botz, 2001). Cyanide is used in these applications because of its strong tendency to complex with metals in solutions. Once complexed, these metals are then recovered using various physical and chemical processes.

In industrial application, cyanide is typically delivered onsite as briquettes or bulk solutions of sodium cyanide (NaCN). Some sites also use flakes or bulk solutions of calcium cyanide [$Ca(CN)_2$]. For gold leaching applications, 1.5 to 2.5 kg of NaCN per ton of ore is generally used, depending on the ore composition. Once in solution, typical cyanide concentrations range from 300 to 500 mg/L (Jermakka et al., 2015a).

Up to 100% of the cyanide used in gold leaching eventually finds its way to tailing ponds and contributes to the nitrogen loading of the water present on mine sites (Kratochvil et al., 2017). However, for environmental reasons, mine tailings often go through a cyanide oxidation step, or "cyanide destruction" step in the industry jargon, before it is discharged in tailing ponds. Even in jurisdictions where natural attenuation of cyanide in tailing ponds is tolerated, like the province of Quebec in Canada, some mines will opt for a cyanide destruction step before their tailing ponds (MDDELCC, 2016).

There are currently various approaches commercially available for cyanide destruction (Botz, 2001). For tailings applications, the INCO [SO_2 / Air] process is generally preferred (Equation 2.3). For water applications, such as the supernatant of a tailings storage facility (TSF), the Degussa [H_2O_2 / Cu catalyzer] process is generally preferred (Equation 2.4).

$$SO_2 + O_2 + H_2O + CN^- \xrightarrow{Cu^{2+} Catalyst} CNO^- + SO_4^{2-} + 2H^+ \qquad (2.3)$$

$$H_2O_2 + CN^- \xrightarrow{Cu^{2+} Catalyst} OCN^- + H_2O \qquad (2.4)$$

In both cases, CNO^- is formed which is fairly unstable and readily hydrolyzes to NH_3-N and carbon dioxide at low pH (Zuttah, 1999). Thus, although these destruction processes reduce the concentration of cyanide in the tailing ponds, they ultimately form NH_3-N, a contaminant that has to be managed later on.

When processing ore containing sulfide minerals in considerable concentrations, more commonly pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$), free cyanide can also react with sulfide to form thiocyanates, SCN^-, according to the Equation 2.5 (Botz et al., 2001).

$$S^{2-} + CN^- + H_2O + \frac{1}{2} O_2 \rightarrow SCN^- + 2OH^- \qquad (2.5)$$

At a mine site, SCN^- concentration in solution can range from a few mg/L to over 1 g/L, depending on the ore sulfur content (Botz et al., 2001). Since SCN^- can be toxic to aquatic life, it requires careful management. Furthermore, traditional cyanide destruction processes do not effectively remove SCN^- (Kratochvil et al., 2017). For example, Mudder et al. (2001) reported that between 10 and 20% of the SCN^- is treated by the INCO process. It has also been reported in the literature that CNO^- and SCN^- degrade relatively fast and form NH_3-N in oxic TSF, but this degradation is slower under anoxic conditions (Jermakka et al., 2015a).

2.3 Canadian Regulation on Nitrogenous Species in Mine Water

2.3.1 Federal Regulations

Mining companies operating in Canada have to comply with the Metal and Diamond Mining Effluent Regulations (MDMER) published by the Canadian Minister of Justice, which was last amended on June 25, 2019 (MDMER, 2018). This document sets, among other things, the maximum authorized concentrations of some contaminants in mine water, as well as the type and frequency of sampling required for environmental monitoring. Among the nitrogenous species discussed in this document, total cyanide has to be analyses at least once a week and shall not exceed 0.5 mg/L on a monthly mean, and 1 mg/L on a grab sample. Still according to this document, nitrate and ammonia nitrogen analysis on a mine final effluent has to be performed and reported every quarter. Under the new amendment, the maximum authorized monthly mean concentration of unionized ammonia is 0.5 mg N/L, while the maximum grab sample concentration is 1.0 mg N/L.

Nitrite, cyanate and thiocyanate are not mentioned in the MDMER. However, this document enforces both acute and sublethal toxicity testing. Acute toxicity testing on rainbow trout (*Oncorhynchus mykiss*) and water fleas (*Daphnia magna*) must be performed once a month, while sublethal toxicity testing on rainbow trout, Fathead Minnows (*Pimephales promelas*), little water fleas (*Ceriodaphia dubia*), freshwater macrophyte (*Lemna minor*), and green algae (*Pseudokirchneriella subcapitata*) is to be performed twice a year. If a lethality is confirmed with these tests, remedial measures must be implemented. Thus, although not all the nitrogenous species are specifically targeted by the MDMER, if any of these species is found in lethal concentrations in a mine water, their presence will trigger a series of actions.

2.3.2 Provincial Regulations

Within Canada, each provinces and territories also have a role to play in the protection of the environment. This applies to the regulation of mine water. For example, in Quebec, mine operators have to comply with the “Directive 019 sur l’Industrie Minière” (MDDEP, 2012).

This document also calls for daily, weekly, monthly and yearly sampling of mine water to determine the concentration of deleterious substances, as well as acute toxicity testing on rainbow trout and *D. magna* once a month. Except for total cyanide, none of the other nitrogenous species have a set maximum concentration in this Directive 019, thus acute toxicity is the parameter governing to acceptable levels for these contaminants.

In addition to the Directive 019, Quebec also relies on "Objectifs Environnementaux de Rejets" (OER) (MDDEP, 2007) to regulate mining effluents. With a case by case approach evaluating the impact of effluent water quality on downstream watercourses, these objectives can include a variety of nitrogenous species, and are (by definition) more stringent than the Directive 019. Similar legislative documents are present throughout Canada, such as the Ontario regulation 560/94 Effluent Monitoring and Effluent Limits – Metal Mining Sector and their Provincial Water Quality Objectives (Government of Ontario, 2017). Within each jurisdiction, maximum authorized concentrations and objectives for nitrogenous species in mine water varies.

2.3.3 Using *D. magna* as an indicator

It is commonly known that *D. magna* is generally more sensitive to acutely lethal environments than rainbow trout (Lilius et al., 1994; Neculita et al., 2008). In addition, although mine operators must test both aquatic species due to regulatory requirements, research sometime relies on *D. magna* only as a representative indicator for acute toxicity. To be noted that, acute toxicity on *D. magna* is not only faster than on rainbow trout, but also requires considerably less volume of water (Government of Canada, 2000, 2007).

More recently, the relevance of *D. magna* as an indicator of acute lethality on Canadian mine water has been challenged, since *Daphnia pulex*, a specie commonly found in Canadian lakes and rivers, shows more sensitivity during toxicity testing than *D. magna* (Foudhaili et al., 2020). Widely distributed in the northern hemisphere, *Daphnia galeata* is also more sensitive to some metals than *D. magna* (Cui et al., 2018). Finally, rainbow trout are known to be more sensitivity to NH_3-N than *D. magna* (Laliberte, 2015).

2.4 Toxicity of Nitrogen-Based Contaminants on Aquatic Life

All nitrogenous species discussed in this thesis may have negative impacts on the environment when discharged from a mine site. However, the concentration at which these contaminants become problematic varies from one species to another. In addition, concentrations of multiple contaminants may be non-lethal when tested separately, but lethal when combined, adding to the complexity of this field of study (Zuttah, 1999). Also, toxicity of aqueous compounds may be dependent on water quality parameters such as alkalinity and hardness. In this section, the toxicity of the most common nitrogenous species found in mine water is discussed.

Nitrate: In solution, NO_3^- is not considered acutely toxic. However, if the formation of NO_2^- through partial denitrification occurs, NO_2^- can be quite toxic (Jermakka et al., 2015a), as discussed below. In presence of chlorine (Cl_2), NO_3^- can form chloramination products, which also has the potential to cause toxicity events (Jermakka et al., 2015a). Furthermore, if found in solution with other nutrients such as phosphorus and potassium, NO_3^- can lead to the eutrophication of receiving bodies of water. This process considerably reduces the amount of dissolved oxygen available to aquatic life and can lead to toxic conditions (Chlot, 2013).

Nitrite: Various water parameters can influence the toxicity of NO_2^- on aquatic life, including pH, temperature, oxygen concentration, as well as concentration of chloride, bromide, bicarbonate, NO_3^-, calcium, magnesium, sodium and potassium (Kroupova et al., 2005). Among those, the concentration of chloride in solution is considered one of the most important parameters because NO_2^- actively competes with the uptake of chloride across the fish gills. Physiological disorder from NO_2^- toxicity includes problems with ion regulatory, respiratory and cardiovascular processes (Kroupova et al., 2005). Due to the important role of chloride in the NO_2^- toxicity potential, it is also not uncommon to set guidelines for this contaminant as a function of the chloride level found in solution. A leading example of guidelines, applicable for the British Columbia Province, Canada, is presented in Table 2.3.

Table 2.3 Water quality guidelines for nitrite in British Columbia (Nordin et al., 2009)

Chloride in mg/L	Maximum Nitrite in mg N/L	30-days Average Nitrite in mg N/L
Less than 2	0.06	0.02
2 to 4	0.12	0.04
4 to 6	0.18	0.06
6 to 8	0.24	0.08
8 to 10	0.30	0.10
Greater than 10	0.60	0.20

NH_3-N: As already mentioned, ionized ammonia is considered non-toxic, while unionized ammonia can be highly toxic (Jermakka et al., 2015a). Thus, the toxicity of NH_3-N is dependent on the solution pH and temperature. The water chemistry and the presence of other contaminants also play a central role in the toxicity of NH_3-N (Jermakka et al., 2015a).

One of the most coherent guidelines currently available on this topic is the National Criteria for Ammonia in Fresh Water published by the United States Environmental Protection Agency (USEPA, 2013). From these guidelines, a concentration of unionized ammonia over 0.0674 mg N/L would breach the 1-hour acute toxicity guidelines, and a concentration of 0.00753 mg N/L would breach the chronic guidelines. These concentrations are orders of magnitude lower than what is considered acceptable in Canada (MDMER, 2018). Although Canadian regulations allows for a maximum of 0.5 mg N/L of unionized ammonia in mine water, these waters are toxic to aquatic life before even reaching this threshold.

Cyanide: All types of cyanide can be toxic at certain concentrations. However, at a given concentration, free cyanides are known to be more toxic than weak cyanide complexes (weak acid dissociable – WAD) (Botz, 2001). Strong cyanide complexes (strong acid dissociable – SAD) are also known to be the least toxic species. In addition, HCN is considered the primary toxic agent to an aquatic environment because of its readily absorption by living organisms. Thus, pH variation in the solution, which impacts the dissociation state of free cyanide, also impacts considerably its degree of toxicity. Lower pH favours the formation of HCN and increases the toxicity of the sample. Low dissolved oxygen has also been identified in the literature as a factor increasing the cyanide toxicity. Once absorbed in a living organism by inhalation, ingestion or skin contact, HCN inactivates enzymes within mitochondria, which leads to a rapid asphyxiation of the organism (Mudder et al., 2001).

Mudder et al. (2001) offers a good summary of the various toxicity studies done with free cyanide on aquatic organisms, as well as the main conclusions drawn from these studies. In his review, the authors identified that fish are the most sensitive organisms to cyanide concentration. Levels as low as 10 µg/L of free cyanide can affect fish reproduction, increase mortality and pathology, impair swimming abilities and alter growth patterns.

Thiocyanate: According to Jermakka et al. (2015), SCN^- is about 7 times less toxic than hydrogen cyanide to aquatic life. Moreover, from Mudder et al. (2001), acute toxicity of SCN^- (96-hour LC50) to fish has been reported in the literature for values between 50 to 200 mg/L. The noteworthy decrease of SCN^- toxicity above hardness values of 150 mg $CaCO_3$/L is also documented (Mudder et al., 2001). As for acute toxicity of SCN^- on *D. magna*, low pH and high temperature conditions yielding the highest levels of toxicity (Watson & Maly, 1987).

Cyanate: Several studies indicate that CNO^- are more toxic to fish than SCN^- (Mudder et al., 2001). In addition, levels of toxicity decrease at high pH and high temperature. Based on the available literature, the impact of hardness on toxicity levels is controversial. Some authors found a drastic decrease of toxicity at high hardness levels (Speyer & Raymond, 1984), while others observed a slight increase of toxicity at these same conditions (Vaughan et al., 1985).

In this section, a rather qualitative summary on toxicity of nitrogen-based contaminants on aquatic life is presented. For a more quantitative evaluation,

2.5 Conventional Treatment of Ammonia Nitrogen in Mine Water

Although the previous section of this document highlighted the problematic presence of several nitrogenous contaminants mainly in water, NH_3-N is undoubtedly one of the most complex parameters to manage on a mine site (Jermakka et al., 2015b). As a result of undetonated explosive leaching and degradation of free CN^-, CNO^- and SCN^-, relatively high level of NH_3-N (about 20 mg/L in average) are found in mine water from gold mine operations (Pouw et al., 2014). With its fate governed by biological and physical processes that are highly dependent on pH and temperature, it is not uncommon to encounter mine water with levels of NH_3-N above guidelines for acute and chronic toxicities (Pouw et al., 2014).

Both predictive models and cases studies can help determine the residual NH3-N expected in the final effluent of a future mine. As for an operating mine, detailed environmental monitoring plans should provide indications on NH_3-N levels onsite, as well as general trends on this contaminant concentration.

A compilation of acute toxicity results reported in the literature on *D. magna* and rainbow trout in presented in Table 2.4. This table focuses primarily on nitrogenous species, both also includes references on ozone and bromide toxicity.

Table 2.4 LC50 of nitrogen-based contaminants and ozone on *D. magna* and rainbow trout

Contaminants	**LC50 (48h), *D. magna* (mg/L)**	**LC50 (96h), rainbow trout (mg/L)**	**References**
Thiocyanate	57.4	-	Parkhurst et al. (1979)
	-	20.8	Heming et al. (1985)
	-	40 to 265	Speyer & Raymond (1988)
	-	94	Heming & Blumhagen (1989)
	0.55 to 33	50 to 200	Mudder et al. (2001)
Free cyanide	-	0.028 to 0.068	Kovacs & Leduc (1982)
	0.12	-	Jaafarzadeh et al. (2013)
Hexacyanocobaltate	0.50	112.9	Little et al. (2007)
Cyanate	18	-	Dauchy et al. (1980)
	-	15 to 81	Speyer & Raymond (1988)
NH_3-N	3.57	-	Gersich & Hopkins (1986)
	-	32.4 to 207	Wicks et al. (2002)
Unionised NH_3-N	-	0.16 to 1.1	Thurston & Russo (1983)
	-	0.32	Scott & Ingles (1987)
	-	0.14	Buhl & Hamilton (2000)
Nitrite	-	0.62 to 1.28	Russo et al. (1974)
	-	0.56 to 17.4	Russo et al. (1981)
	-	2.6	Buhl & Hamilton (2000)
Nitrate	-	7343	Buhl & Hamilton (2000)
	1656	-	Scott & Crunkilton (2000)
	2047	3638	Government of Canada (2012)
	-	3578 to 8472	Baker et al. (2017)
Ozone	-	0.0093	Wedemeyer et al. (1979)
	0.011	-	Leynen et al. (1998)
Bromide	<0.038	0.068	Fisher et al. (1998)

In addition, for both active and future mines, it is the responsibility of the mining companies to implement mitigation measures according to the local regulations if the NH_3-N levels are such that toxicity events can occur. Mitigation measures may include the identification and reduction of NH_3-N sources on the mine site, as well as the construction of water treatment facilities. The technology used within these plants is the topic of the current section. Water treatment technology for NH_3-N in mine water can be grouped into three categories: physical, biological and chemical treatment. A brief adaptation of Jermakka et al. (2015b) for each category is presented in the following.

Physical treatment: Physical treatment includes air stripping (for high concentrations), membrane technologies and sorption. The stripping consists of raising the pH to levels where most of the NH_3-N is under its unionized form, and then promoting the transfer of ammonia from the liquid phase to the gas phase by contacting the solution with large volumes of atmospheric air. A variation of this approach consists of snow making in cold climates. The membrane-based technologies rely basically on nanofiltration and reverse osmosis membranes to produce permeates with a low concentration of NH_3-N and a concentrate with higher concentration of this contaminant. The concentrate then needs to be treated by a different approach. NH_3-N can also adsorb on material such as natural zeolite, clinoptilolite, and activated carbon, and thus be removed by adsorption.

Biological treatment: Biological treatment (passive and active) includes lagoons, wetlands, nitrification, denitrification (by autotroph or heterotroph bacteria) and anammox. Lagoons and wetlands treatments rely on naturally occurring microorganisms within the ecosystem to perform one or several of the biological processes above-mentioned. A passive treatment technology (lagoons and wetlands), due to the low amount of maintenance and monitoring required, are nonetheless generally engineered to promote such processes. Mine operators can also rely on active biological water treatment plants to accomplish these processes. Such plants are designed to maintain optimal conditions for favorable groups of microorganisms, with the aid of mixing apparatus, aerators, chemicals injections, etc.

Chemical treatment: Chemical treatment includes precipitation, classical and advanced oxidation processes, catalytic denitrification and electrochemical processes. In the presence of magnesium and phosphorus, NH_3-N can also form a precipitate called struvite, which can be valorized as a fertilizer. Once formed, a solid-liquid separation step is required to remove nitrogen from the water. NH_3-N can also be oxidized to NO_3^- by various chemical and electrochemical processes. NO_3^- is then left as is, or reduced to nitrogen gas by biological denitrification, catalytic denitrification or electro-denitrification.

Removal mechanisms, particularities, advantages and disadvantages of these technologies are well documented in the literature, with several reviews available including Pouw et al. (2014) and Jermakka et al. (2015b). However, some of the emerging technologies to treat NH_3-N are not well documented. This is especially the case for ozonation of NH_3-N in mine water.

2.6 Ozonation of Ammonia Nitrogen in Mine Water

In the mining industry, ozonation is currently used to remove cyanide from mine impacted water (Gottschalk et al., 2010). This technology can oxidize free CN^-, WAD CN^-, SCN^-, as well as precipitate SAD CN^- (Pouw et al., 2014). However, ozonation is generally not used as a standalone technique for cyanide removal because of its high operating costs (Pouw et al., 2014). Ozone can also be used on mine water to oxidize Mn(II) and As (III) (Pouw et al., 2014), as well as regenerate free CN^- from SCN^- (Botz et al., 2001). As for NH_3-N removal in mine water, ozonation was investigated at a gold mine operation located in Ontario, Canada, but the industrial scale system has not yet been installed, and additional information on this project is not publicly available (Pouw et al., 2014).

At a laboratory scale, Zuttah (1999) investigated the impact of various parameters on the oxidation of NH_3-N in mine water by ozonation. With a semi-batch apparatus, and using both synthetic and real mine water, this study tested the impact of pH, temperature, porosity of the ozone diffuser, dosing rate of ozone, initial concentration of NH_3-N and concentration of carbonate and bicarbonate. Using a similar semi-batch system, but this time with the addition of a microbubbles generating apparatus, Ryskie et al. (2020b) also investigated the impact of the parameters studied by Zuttah (1999), on both synthetic and real mine water. In addition, this last study used a laboratory pilot unit to perform tests under a continuous regime, an approach that is not often used in ozonation trials (Gottschalk et al., 2010). With this pilot unit, a 99%+ efficiency on NH_3-N removal and a residual concentration below 1 mg N/L when treating a real mine water was reported. However, the dosing rate applied during this trial was reported as 44.6 g O_3/g N-NH_3, or 3.25 times the stochiometric ratio or 13.7 g O_3/ g N-NH_3 reported in the literature (Zuttah, 1999). Poor mass transfer efficiency was identified in this study as the most likely reason for the high-dosing rate requirements, and additional trials using a more suitable liquid/gas contacting device was recommended.

A summary of the previous findings as based on the research work performed by Zuttah (1999) and Ryskie et al. (2020b) is presented in Table 2.5. This table also presents the studies of Hoigne and Bader (1978) and Khuntia et al. (2012b), both conducted with synthetic contaminated water. From this compilation, comparison of the impact observed by these authors for several parameters can be made, including:

pH: All studies found an increase in the ozonation efficiency up to pH 9. However, results above this value diverge. While Zuttah (1999) observed increased efficiency up to pH 11, Ryskie et al. (2020b) and Hoigne and Bader (1978) observed optimal results between pH 9 and 10.

Bromide concentration: According to the results obtained by Zuttah (1999), Khuntia et al. (2012b) and Ryskie (2017), the addition of bromide ions in the system increases the ozonation efficiency. In addition, each study reported observations that were unique to their work, or at least, not reported by the other authors. Zuttah (1999) observed an ozone to NH_3-N ratio below the stochiometric requirements when bromide is added to the mine water. Khuntia et al. (2012b) observed the removal of NO_3^- during the ozonation process in presence of bromide. Ryskie (2017) noted the absence of a drop in pH when bromide is added to the system.

Carbonate concentration: Similar results were found by Hoigne and Bader (1978) and Zuttah (1999) when adding a carbonate source to the ozonated water. Both studies noted an increased efficiency at low pH (< 9), and an inhibitory effect at strong alkaline pH. In contradiction with these two studies, Khuntia et al. (2012b) observed a decrease in the efficiency of ozonation in presence of carbonate at low pH (< 8), and no impact on the ozonation efficiency above pH 8.

Ozone bubble size: Both Zuttah (1999) and Ryskie (2017) confirmed that smaller ozone bubble sizes yield better ozonation efficiency. According to these studies, enhanced mass transfer is likely the potential cause for these findings.

Table 2.5 Ozonation trials for NH_3-N removal by various authors

Parameters tested	**Type of water**	**Laboratory apparatus**	**Results**	**NH_3-N in raw water (mg N/L)**	**Maximum removal efficiency**	**Maximum O_3 utilization efficiency***	**References**
pH	Synthetic Water	Batch system	Optimum observed between pH 9 to 10.	24	N/A	N/A	Hoigne and Bader (1978)
	Synthetic Water	Semi-batch system	Optimum observed at pH 9, but no test we performed above this value.	100	≈ 90%	48%	Khuntia et al. (2012b)
	Synthetic Water	Semi-batch system	Sharp increase of the ozonation efficiency up to pH 11.	40	95%	56%	Zuttah (1999)
	Synthetic Water	Semi-batch system	Ozonation at pH 9 yield better results than pH 7 or 11.	40 to 45	93%	48%	Ryskie et al. (2020b)
	Mine Water	Semi-batch system	Better results observed at pH 11 than 8.	58	≈ 99%	43%	Zuttah (1999)
Carbonate concentration	Synthetic Water	Batch system	The presence of carbonate increases the yield at a low pH but decreases it at pH above 9.	24	N/A	N/A	Hoigne and Bader (1978)
	Synthetic Water	Semi-batch system	Inhibition of NH_3-N ozonation efficiency at pH below 8.	100	N/A	N/A	Khuntia et al. (2012b)
	Synthetic Water	Semi-batch system	At pH 8, presence of carbonate increases the ozonation efficiency. At pH 11, the opposite phenomenon is observed.	20	N/A	N/A	Zuttah (1999)

Table 2.5 Ozonation trials for NH_3-N removal by various authors (*Continued*)

Variables tested	**Type of water**	**Laboratory apparatus**	**Results**	**NH_3-N in raw water (mg N/L)**	**Maximum removal efficiency**	**Maximum O_3 utilization efficiency***	**References**
Bromide concentration	Synthetic Water	Semi-batch system	One test performed at 75 mg Br/L. The presence of bromide increases the ozonation efficiency and enable the removal of NO_3^-.	100	≈ 90%	54%	Khuntia et al. (2012b)
	Synthetic Water	Semi-batch system	Lowest concentration tested was 40 mg Br/L and resulted in a considerable increase of the ozonation efficiency.	41	99.8%	85%	Zuttah (1999)
	Synthetic Water	Semi-batch system	Increased ozonation efficiency observed with 500 and 1000 mg Br/L. Not a considerable difference between the two dosages, however. pH of the solution did not drop during the trials, in opposition with the trials performed without Br.	40 to 45	100%	73%	Ryskie (2017)
	Mine Water	Semi-batch system	Lowest concentration tested was 10 mg Br/L and resulted in a considerable increase of the ozonation efficiency.	60	99.8%	201%	Zuttah (1999)
Temperature	Synthetic Water	Semi-batch system	Oxidation of NH_3-N is reduced at lower temperature.	20	N/A	N/A	Zuttah (1999)

Table 2.5 Ozonation trials for ammonia removal by various authors (*Continued*)

Variables tested	**Type of water**	**Laboratory apparatus**	**Results**	**NH_3-N in raw water (mg N/L)**	**Maximum removal efficiency**	**Maximum O_3 utilization efficiency***	**References**
Ozone bubble size	Synthetic Water	Semi-batch system	Smaller bubble size increases the ozonation efficiency.	39	83%	104%	Zuttah (1999)
	Synthetic Water	Semi-batch system	Sharp increase of the ozonation efficiency with microbubbles apparatus compared to coarse bubbling column.	40 to 45	48.1%	87%	Ryskie (2017)
Water quality variation	Mine Water	Semi-batch system	Pronounced variation in the ozonation efficiency observed between the 5 samples tested. Presence of SCN^-, total CN^- and CNO^- can greatly impact the consumption of ozone.	22-43	99.3%	39%	Ryskie et al. (2020b)
NH_3-N initial concentration	Mine Water	Semi-batch system	Higher NH_3-N concentration in the feed water increases the ozonation efficiency.	30 to 100	99.2%	52%	Zuttah (1999)
Other	Mine Water	Continuous system	Demonstration of a continuous treatment at 1.11 L/min for 10 hours.	22	99.1%	45%	Ryskie et al. (2020b)

* See Section 3.6 for more details

2.7 Ozone Fundamentals

Ozone Safety

Ozone can be highly toxic to living beings, depending on its form and the type of exposure. This exposure can take place under three circumstances: (1) ozone as a gas, (2) ozone dissolved in water, and (3) by-products of ozone reactions (Gottschalk et al., 2010).

Ozone as a gas is highly toxic, with its principal routes of entry being by inhalation, skin or eye contact. Named after the Greek word "ozein", which means "to smell", ozone has a very distinctive odour, most often described as the odour of electricity, or as the odour of an electrical spark. With an odour threshold of 0.02 ppm (Gottschalk et al., 2010), one can generally smell ozone before being exposed to dangerous levels. However, odour desensibilization will occur over time. Eye irritation may be experienced with concentrations above 0.1 ppm. Few tens of ppm can cause headaches, coughing, dryness of the throat and irritation of the nose after only a short duration of exposure. Inhalation of 50 ppm of ozone over a period of 30 minutes can be fatal (Gottschalk et al., 2010). Also, symptoms of chronic exposure to ozone can include asthma, allergies and other respiratory disorders. Furthermore, ozone gas is suspected to be carcinogenic.

Workplace exposure limits generally consider both the concentration of ozone and the duration of the exposure. To name just a few, the Occupational Safety and Health Administration (OSHA) set the legal airborne Permissible Exposure Limit (PEL) to 0.1 ppm over an 8-hour workshift, while the United States Environmental Protection Agency as its National Ambient Air Quality Standard at 0.08ppm of ozone over an 8-hour average. Also, the OSHA's PEL for 15 minutes of short-term exposure to ozone is set at 0.3 ppm.

With a density of 2.144 g/L, ozone is heavier than air, thus accumulation of this gas is expected at the bottom of reactors, or near floors of treatment facilities. For safety reasons, water treatment plant relying on ozonation should always have an ambient air ozone monitor coupled with an automatic shutdown of the ozone generator.

As for dissolved ozone in water, there is currently no workplace exposure limits, nor health hazard data available on this topic (Gottschalk et al., 2010). However, ozone is known to be toxic for aquatic life, with LC50 values such as (Langlais et al., 1991):

- 0.06 mg/L for 24h on bluegills (*Lepomis macrochius*);
- 0.0093 mg/L for 96h on rainbow trout (*Oncorhynchus mykiss*);
- 0.38 mg/L on white perch (*Morone americana*).

Also found as dissolved compounds, ozonation by-products, which are often referred as disinfection by-products (DBP), can be a concern for aquatic and human health. The formation of these compounds can be complex and is highly dependent on the water chemistry as well as the operating condition of the ozonation process. Bromate, brominated organohalogen, iodate and chlorate are examples of potential DBP from ozonation (Gottschalk et al., 2010).

Ozonation Reaction Mechanisms

Ozonation reactions follow two different mechanisms: direct and indirect (Hoigne & Bader, 1978). The pathways for these two mechanisms are presented in Figure 2.2. In a direct reaction, the ozone itself reacts with the compound. In an indirect reaction, the hydroxyl radicals, formed from the decomposition of ozone in water, react with the compounds.

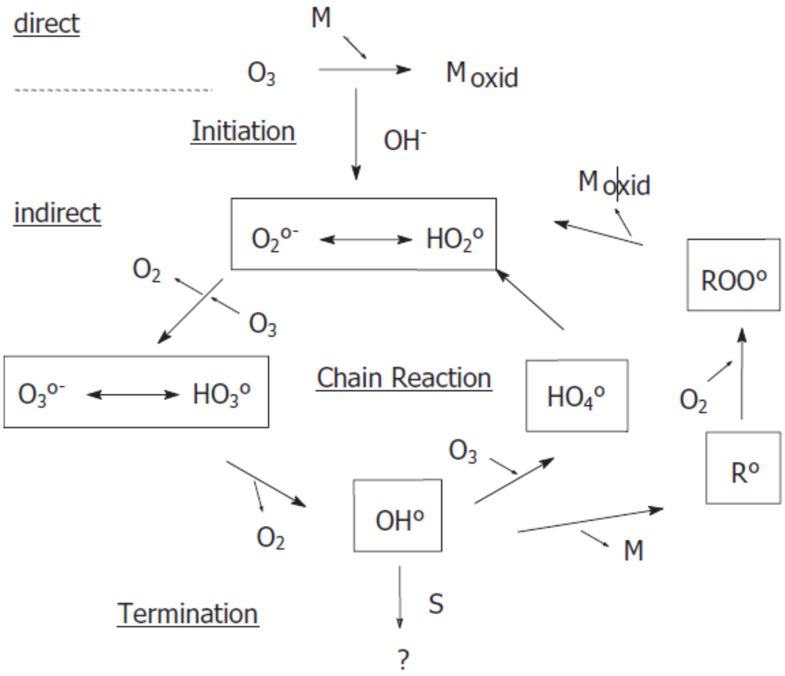

Figure 2.2 Representation of direct and indirect ozonation reactions with S as Scavenger, R as Reaction Product and M as Micropollutant (Gottschalk et al., 2010)

Hydroxyl radicals (OH^o) are highly unstable, unselective and react immediately to obtain their missing electron. As presented in Figure 2.2, the formation of hydroxyl radicals from ozone involves three steps: initiation, chain propagation and termination. The overall reaction is presented in Equation 2.6 (Gottschalk et al., 2010).

$$3O_3 + OH^- + H^+ \rightarrow\ 2OH^{\circ} + 4O_2 \tag{2.6}$$

Ozone Reactions with NH_3-N

The reaction rate of direct oxidation of NH_3-N is orders of magnitude lower than the reaction rate of indirect oxidation (Gottschalk et al., 2010). In addition, ozone generally does not oxidize ammonium but can oxidize unionized ammonia (Hoigne & Bader, 1978). For these reasons, ozonation of NH_3-N yield better results at pH > 9 (Khuntia et al., 2012b; Ryskie et al., 2020b; Zuttah, 1999), i.e. when the indirect pathway dominates (Gottschalk et al., 2010), and the equilibrium between ammonium and unionized ammonia favours the unionized form.

In contact with ozone, unionized ammonia will first oxidize to NO_2^-, then to NO_3^-, as shown in Equations 2.7 and 2.8, respectively (Khuntia et al., 2012b).

$$NH_3 + 3O_3\ \rightarrow\ NO_2^- + 3O_2 + H^+ + H_2O \tag{2.7}$$

$$NO_2^- + O_3 \rightarrow\ NO_3^- + O_2 \tag{2.8}$$

These equations can be rearranged to get the overall reaction presented in Equation 2.9.

$$NH_3 + 4O_3 \rightarrow H^+ + NO_3^- + H_2O + 4O_2 \tag{2.9}$$

From Equation 2.8, one could expect the formation of NO_2^- during the ozonation of unionized ammonia. However, it has been demonstrated that this compound is rapidly oxidized to NO_3^-, which results in no measurable buildup of NO_2^- once the treatment is completed (Hoigne &

Bader, 1978; Zuttah, 1999). As for any residual ozone in the water, it ultimately self-decomposes in oxygen (Khuntia et al., 2012b). Thus, following a complete oxidation, only NO_3^- is present in the treated water.

Key Operational Parameters

The efficiency obtained from an ozonation system is dependent on a wide range of parameters. To obtain satisfactory performance, the operator of such system requires a good understanding of these parameters and their impact on the overall treatment performance. The main parameters to identify and monitor for an ozonation system are the following (Gottschalk et al., 2010; Ryskie et al., 2020b; Zuttah, 1999):

- Type of water to treat (distilled water, surface water, ground water, wastewater, mine water, etc.);
- Average, minimum and maximum flowrates required for the application;
- Initial and final concentration of the oxidizable compounds;
- Temperature and pH of the water to treat, as well as variation of such parameters within the process;
- Concentration of initiators, scavengers and promoters in the water to treat;
- Other water quality parameters, including:
    - Total suspended solids (TSS);
    - Total dissolved solids (TDS);
    - Dissolved inorganic carbon (DIC);
    - Dissolved organic carbon (DOC);
    - Chemical oxygen demand (COD);
    - Biological oxygen demand (BOD).

<u>Type of water to treat</u>: Since the water quality can change drastically from one industry to another, and from one region to another, it is of the foremost importance to consider the type of water at hand before planning for its treatment. It is for this very reason that often, books, studies and reports discussing water treatment technologies will specify for which type of water these technologies are relevant. Mine water treatment is no exception to the rule, with published documentation such as “Study to Identify the Best Available Technologies Economically Achievable for Management and Control of Effluent Quality from Mines” (Pouw et al., 2014)

and "Potential Technologies for the Removal and Recovery of Nitrogen Compounds From Mine and Quarry Waters in Subarctic Conditions" (Jermakka et al., 2015b).

Ozonation applications can be grouped in four different types: (1) disinfection, (2) oxidation of organic compounds, (3) oxidation of inorganic compounds and (4) removal of particles (Gottschalk et al., 2010). Each of these applications can be applied to a variety of industries. Among these industries, municipal applications such as disinfection of drinking water and wastewater treatment are by far the most dominant ones (Loeb et al., 2012). To emphasize differences from one type of water to another, typical ozone dosing rates for various types of water are presented in

Table 2.6. Caution is advised when interpreting this table, as dosing rates for mine water treatment presented in this table may be overestimated due to suboptimal laboratory conditions, including poor ozone mass transfer rates, excessive removal efficiency and presence of other oxidizable compounds.

Table 2.6 Typical ozone dosing rate (mg O_3/L) for different types of industries

Type of water	Application	Dosing rate	Reference
Drinking water	Micro flocculation	0.5 – 2.0	Gottschalk et al. (2010)
Drinking water	Disinfection	1.0 – 3.5	Jackson & Pathapati (2015)
Drinking water	Disinfection	1.3 – 3.0	Mundy et al. (2018)
Municipal wastewater	Disinfection	1.5 – 5.0	Jackson & Pathapati (2015)
Municipal wastewater	Disinfection	5 – 20	Gottschalk et al. (2010)
Municipal wastewater	Disinfection	10-15	Loeb et al. (2012)
Municipal wastewater	COD removal	30-100	Gottschalk et al. (2010)
Pulp and paper wastewater	COD removal	68-172	Gottschalk et al. (2010)
Landfill leachate	COD removal	500-2000	Gottschalk et al. (2010)
Mine water (synthetic water)	Total CN removal	490*	Nava et al. (2003)
Mine water (real solution)	NH_3-N removal	1440-1920*	Zuttah (1999)
Mine water (real effluent)	NH_3-N removal	1130-5400*	Ryskie et al. (2020b)

*Results from laboratory trials only

Flowrate requirements: Flowrate, more specifically minimum, nominal and maximum flowrates, are also important factors impacting the overall performance of ozonation systems.

Table 2.7 presents a sample of flowrates found in the Canadian mining industry. As illustrated in this table, a wide range of flowrate is observed even within this sector.

With ozonation plants known to be both Capital Expenditure (CAPEX) and Operational Expenditure (OPEX) intensive, it is not expected that this technology could be applied for the upper range of this spectrum, especially with dosing rates such as the ones reported for mine water in

Table 2.6. Indeed, the world's largest drinking water plants (as of 2012) using ozonation is the Los Angeles Aqueduct Filtration Plant, and this plant relies on a few mg/L of ozone to aid the coagulation of 95 000 m^3/h (Loeb et al., 2012).

Table 2.7 Effluent flowrates of various mining subsectors (Pouw et al., 2014)

Subsector	**Minimum (m^3/h) ***	**Average (m^3/h) ***	**Maximum (m^3/h) ***	**Median (m^3/h) ***
Uranium	18 - 38	211 - 350	476 - 800	159 - 300
Precious Metals	2 - 10	179 - 330	1 200 - 1 563	94 - 230
Base Metals	1 - 7	487 - 870	5 100 - 8010	76 - 560
Coal	72 - 144	576 - 29 750	1 080 - 55 692	576 - 32 760
Iron Ore	0.2 - 31	2 000 - 6 400	20 000 - 140 600	490 - 26 800

*Ranges are from the various methods employed by Pouw et al. (2014) to generate the data

Concentration of the contaminant of concern: As stated by Gottschalk et al. (2010), the initial and final concentrations of the targeted contaminant in an ozonation process is a key factor influencing its design. From the data collected by Pouw et al. (2014) on Canadian operations, NH_3-N concentration in untreated effluent varies from one mining subsector to another, as illustrated in Table 2.8. Also, the final concentration to reach after treatment is driven by the toxicity of NH_3-N and is primarily a function of the pH and temperature of the effluent.

Table 2.8 NH_3-N concentration in untreated mine water (Pouw et al., 2014)

Subsector	**Minimum (mg N/L) ***	**Average (mg N/L) ***	**Maximum (mg N/L) ***	**95th percentile (mg N/L) ***
Uranium	3.3	4.8	25	7.2
Precious Metals	2.2	20.03	45	42.5
Base Metals	0.01	2.1	22	11
Diamond	0.05	0.17	0.32	0.35

In addition, the ozonation of NH_3-N can be approximated to a first order reaction (Hoigne & Bader, 1978). Thus, the concentration of NH_3-N in the system has a direct effect on the reaction rate and speed of the reaction. Therefore, it is not surprising that laboratory trials have revealed that the higher the NH_3-N concentrations in the feed, the faster the reaction is obtained (Ryskie, 2017; Zuttah, 1999). Additionally, it is recommended to set the residual NH_3-N treatment goal as high as possible to prevent excessive use of ozone (Zuttah, 1999).

<u>Concentration of other compounds</u>: Both ozone and the hydroxyl radicals are strong oxidants. However, these oxidants are also known to be unselective (Gottschalk et al., 2010). Thus, the presence of other oxidizable compounds in the water can have a detrimental impact on the removal efficiency of the contaminant of concern. This was highlighted in the work of Ryskie et al. (2020b) on ozonation of NH_3-N in real mine water.

According to Ryskie et al. (2020b), the removal of several compounds, including total CN^-, SCN^-, and CNO^-, was observed when trying to achieve the NH_3-N removal. The presence of these compounds can be explained by the usage of CN^- solutions for gold leaching at some of the mines where the water samples were collected. Moreover, these species not only consume a large amount of the injected ozone, but also generate additional NH_3-N when oxidized. As a result, poor NH_3-N removal efficiency was observed for some samples, including one trial with a reported dosing rate of 242 g O_3/g NH_3-N and an NH_3-N removal efficiency of only 28%.

The study also demonstrates the chronologic order in which each contaminant is removed, with the SCN^- reaching low residual concentrations first, then total CN^-, CNO^-, and finally NH_3-N. This order suggests that each of the reactions is limiting the overall oxidation process. On the contrary, both studies of Zuttah (1999) and Ryskie et al. (2020) observed concentrations of NO_2^- below detection limits well before complete oxidation of NH_3-N, which suggests that the oxidation of NO_2^- to NO_3^- is not a limiting step. Beside nitrogenous and cyanide species, a large variety of organic and inorganic compounds can also be oxidized by ozone. Thus, every oxidizable compound must be considered when designing an ozonation process. Moreover, instead of analyzing for each individual species, lumped parameters such as COD and BOD can be used to provide general indications on the expected ozone consumption of an application (Gottschalk et al., 2010).

Impact of the temperature: Variation in the water temperature can impact the ozonation process in several ways. As the temperature rises, the solubility of ozone in water decreases, which leads to a lower mass transfer. However, an increase in temperature also increases the oxidation reaction rate. Based on the Van’t Hoff rule, the reaction rate will double every time the temperature is increased by 10 °C (Gottschalk et al., 2010).

According to the study of Zuttah (1999) on synthetic mine water at 10 °C and 22 °C, the overall impact of a temperature rise on NH_3-N ozonation is positive. Indeed, lower residual NH_3-N was found on the sample at 22 °C. However, the study also mentions the need for additional work and larger temperature ranges to determine with more precision the impact of temperature on NH_3-N ozonation.

Ryskie (2017) also mentions the impact of temperature. Although this study did not attempt ozonation at low temperature, an important increase in the temperature during his semi-batch trials was observed. The temperature in some of these trials reached 35 °C, at which point the author reportedly had to stop the trials. Based on these observations, the author recommended maintaining the temperature below 30 °C during such trials. Ryskie (2017) also performed continuous trials, during which he observed a stabilization of the temperature around 25 °C.

From these two authors, one could conclude that, depending on the type of equipment used, a compromise between lower mass transfer and higher reactor rate can be achieved.

Impact of the pH: The pH value is undoubtedly one of the most important parameters to monitor during the ozonation process. This can be seen by the rich literature on the subject (Gottschalk et al., 2010; Hoigne & Bader, 1978; Khuntia et al., 2012b; Ryskie et al., 2020b; Zuttah, 1999). This parameter not only governs the type of ozonation mechanisms, namely direct and indirect, but also influences the equilibrium concentration of dissociated and non-dissociated species, the formation of radicals from collapsed microbubbles, as well as the scavenger reactions with inorganic carbon. At higher pH, hydroxide ions catalyze the decomposition of ozone, thus favouring the indirect ozonation mechanisms, as illustrated in Figure 2.2. Therefore, lower pH values favour the direct reaction of molecular ozone. According to Hoigne and Bader (1978), such mechanisms are dominant at pH < 9.

As discussed in Section 2.6, ozonation of NH_3-N yields better results at pH >9. Indeed, during semi-batch trials, Hoigne and Bader (1978) identified a pH between 9 and 10 to be optimal for NH_3-N ozonation. With similar laboratory apparatus, Zuttah (1999), Khuntia et al. (2012b) and Ryskie et al. (2020b) also observed considerable increase in their process efficiency at pH >9. According to these authors, this enhanced efficiency is explained by: (1) a much higher reaction rate during indirect ozonation of NH_3-N compared to the direct mechanism and (2) an equilibrium constant favouring the presence of unionized ammonia over ammonium at higher pH. Indeed, ozone cannot oxidize the ammonium form, but can oxidize the unionized ammonia form (Hoigne & Bader,1978). However, when treating water with high dissolved inorganic carbon levels, the positive impact of hydroxide concentrations can be counteracted by a stronger scavenging potential of carbonate over bicarbonate (Gottschalk et al., 2010). This is yet another example of the impact of pH on ozonation process by changing the equilibrium concentration of dissociated and non-dissociated species.

From Equation 2.9, the ozonation of unionized ammonia is a net producer of hydrogen ions, which leads to a reduction of pH within the process. This phenomenon was observed by Ryskie et al. (2020b) when a semi-batch trial was performed, without adjusting the pH, and showed a drop in pH from 11 to 7 over a 60-minute period. This result highlights the need to incorporate pH adjustment equipment when designing an ozonation process for NH_3-N removal.

<u>Concentration of initiators, scavengers and promoters</u>: As discussed previously, indirect ozonation of NH_3-N has a higher reaction rate than the direct mechanism. However, the decomposition of ozone leading to the indirect reaction can be influenced by various aqueous species, as shown in Table 2.9.

Table 2.9 Aqueous species influencing the decomposition of ozone (Gottschalk et al., 2010)

Initiator	**Promoter**	**Scavenger**
OH^-	Humic acid	HCO_3^- / CO_3^{2-}, PO_4^{3-}
H_2O_2 / HO_2^-	*aryl*-R	Humic acid, *alkyl*-R
Fe^{2+}	Primary and secondary alcohols	*tert*-butyl alcohol (TBA)

Amongst the scavenging species, carbonate and bicarbonate ions received by far the most attention in the literature (Gottschalk et al., 2010; Hoigne & Bader, 1978; Khuntia et al., 2012b; Ryskie, 2017; Zuttah, 1999). According to Gottschalk et al. (2010), these species play an important role in scavenging the hydroxyl radicals, and only a few µmoles can decrease the decomposition of ozone by a factor of ten. On the other hand, carbonate and bicarbonate do not react with ozone by itself. Still according to this author, the reaction rate constants indicate that carbonate is a much stronger scavenger than bicarbonate. Thus, with a pK_a (HCO_3^- / CO_3^{2-}) of 10.3, pH plays a major role on the scavenging potential of inorganic carbon.

As for hydrogen peroxide (H_2O_2), its role on ozonation process does appear to make unanimity in the scientific community. Although some qualify it as an initiator (Gottschalk et al., 2010), others qualify it as a scavenger (Hoigne & Bader, 1978). Ryskie (2017) also reported lower NH_3-N removal efficiency when adding H_2O_2 to its ozonation semi-batch trials. Zuttah (1999) also attempted to perform the peroxone process but obtained identical removal efficiency after 30 minutes using this approach compared to the simple ozonation approach.

Dissolved metals, such as Fe(II), Mn(II) and Co(II) can also be used in what is called “homogenous catalytic ozonation”. This type of catalytic reaction is different from the “heterogenous catalytic ozonation”, in which solid compounds, such as activated carbon or metal oxides (TiO_2, Al_2O_3, Fe_2O_3, MnO_2) are used as catalysts. Ferrous iron ions and their role in ozonation process could be of particular interest in the treatment of acid mine drainage, since concentration of several grams per litre of dissolved ferrous iron in such water is common. Such ferrous iron could then be oxidized to ferric iron, which has the potential to precipitate as ferric hydroxide at a lower pH than its ferrous counterpart.

In respect to NH_3-N ozonation, bromide is also reported in the literature as a catalyst (Haag et al., 1984; Khuntia et al., 2012b; Ryskie, 2017; Zuttah, 1999). Laboratory trials demonstrated that concentration of bromide above 40 mg/L can greatly reduce the reaction time in semi-batch trials (Zuttah, 1999). According to the author, an addition of 1000 mg/L of NaBr in a semi-batch trial enabled the complete oxidation of NH_3-N by ozone at a pH of 7, whereas ozonation without added bromide yielded insignificant removal efficiency. Furthermore, this author observed a reduction in the molar ratio of ozone to NH_3-N well below the stoichiometric ratio of 4:1 when bromide is present in high concentrations in the water. Indeed, a molar ratio as low as 2:1 was observed, which leads to the suggestion of the following reaction presented in Equation 2.10.

$$NH_3 + 2O_3 \xrightarrow{Br^-} NO_3^- + O_2 + H_2O + H^+ \qquad (2.10)$$

Using a similar approach to Zuttah (1999), Ryskie (2017) also observed the catalytic impact of bromide on NH_3-N ozonation. Furthermore, the pH during semi-batch trials in the study of Ryskie (2017) remained constant without the addition of an alkaline agent, in contradiction with what was observed from NH_3-N ozonation without bromide addition. This result tends to indicate that bromide is involved in a series of complex by-reactions. This is also illustrated by the conversion of NO_3^-, formed by the oxidation of NH_3-N, into nitrogen gas when bromide is present in the water (Khuntia et al., 2012b).

The faster reaction rates observed by Zuttah (1999) and Ryskie (2017) were also observed by Khuntia et al. (2012b) when performing similar semi-batch trials. This author, however, kept the molar ratio of NH_3-N to bromide below 18:1, thus much lower than the stochiometric ratio of 2:3. The intent of the author was to prevent the formation of bromate (BrO_3^-), a compound deemed carcinogenic and with a maximum permissible concentration in drinking water set by the World Health Organization (WHO) at 25 µg/L. This contaminant, formed from the reaction between ozone and bromide, can be particularly problematic when treating water with naturally high levels of bromide, such as seawater (Khuntia et al., 2012a). However, when NH_3-N is present in the water, formation of bromate does not occur (Khuntia et al., 2012b).

<u>Other water quality parameters</u>: Other parameters, often lumped into groups such as TSS, TDS, DIC, DOC, COD and BOD, can impact the ozonation process. Suspended solids can adsorb on the surface of ozone bubbles and reduce the mass transfer rates (Khuntia et al., 2012a). Inorganic salts, which are known to play a role in the promotion and scavenging effect of ozone

decomposition, also contribute to the ionic strength of the water. An increase in the ionic strength then leads to a decrease in the coalescence of bubbles, thus increasing the interfacial surface area and the overall mass transfer rate (Gottschalk et al., 2010).

As discussed previously, carbonate and bicarbonate play a central role in the decomposition of ozone. Thus, any variation in the dissolved inorganic carbon will impact the ozonation process. The DOC can also be involved in the promotion and scavenging of the decomposition of ozone. The case of humic acids is particularly interesting, since these molecules can act either as promoters or scavengers, depending on their concentrations (Gottschalk et al., 2010).

As COD and BOD are two parameters indicating the presence of oxidable compounds in the water, variation of these parameters will also impact the ozone consumption rate.

Microbubbles Principles

Several technologies are currently available to enable the dissolution of a gas in a liquid. The injection of fine bubbles directly in the receiving fluid is an approach frequently used in many applications, including ozonation process. Early testing from Zuttah (1999) revealed a strong relationship between the size of the ozone bubbles and the overall efficiency of the NH_3-N oxidation. In his study, an increase in the overall efficiency when smaller bubbles were produced was observed. These findings are coherent with the well-known fact that with smaller bubbles, a higher mass transfer rate can be achieved (Gottschalk et al., 2010).

There is currently no generally accepted nomenclature for classification of bubbles based on their diameter (Khuntia et al., 2012a), as showed in Table 2.10. In this document, mention of bubbles sizes is based on the definitions offered by Agarwal et al. (2011) and Khuntia et al. (2012a). In a laboratory setting, photographic techniques can be employed to determine the size of bubbles with diameters down to 1 µm (Khuntia et al., 2012a). This approach involves taking digital photos of the test column and comparing the size of the bubbles with a measuring tape of known scale (Baawain et al., 2007). Moreover, laser diffraction particle size analyzers are often been employed to determine the size of micro- and nanobubbles (Agarwal et al., 2011). This technique relies on the relationship between the scattering intensity and the size of the bubbles. Other techniques reported for the determination of bubbles size include pore electrical resistance, phase doppler anemometry, dynamic light scattering, X-ray particles tracking velocimetry and scanning electron microscopy (Agarwal et al., 2011; Khuntia et al., 2012a).

Table 2.10 Bubble classification based on their diameter

Bubble Classification	**Min. Diameter (mm)**	**Max. Diameter (mm)**	**Reference**
Nanobubbles	-	<0.0002	Agarwal et al. (2011)
Micro-nanobubbles	0.0002	0.01	Khuntia et al. (2012a)
Microbubbles	0.01	0.05	Agarwal et al. (2011)
Microbubbles	0.01	0.2	Gottschalk et al. (2010)
Fine bubbles	1	3	Gottschalk et al. (2010)
Macrobubbles	2	5	Khuntia et al. (2012a)
Coarse	> 3	-	Gottschalk et al. (2010)

Consistently with the findings of Zuttah (1999), Ryskie (2017) also found a considerable increase in the NH_3-N removal when using microbubble generating apparatus instead of coarse bubble diffusers. As these microbubbles rise in a water column, they gradually decrease in size, due to the dissolution of the gas inside them, to a point when they eventually collapse in on themselves (Khuntia et al., 2012a). Although there is currently a lack in understanding of this mechanism (Khuntia et al., 2012a), the collapsing of microbubbles is known to produce hydroxyl radicals. The generation of these radicals originates from the high internal pressure at the final stage of the microbubble collapse, since this pressure is inversely proportional to the bubble diameter (Agarwal et al., 2011).

According to Agarwal et al. (2011), the pH has a great impact on the generation of hydroxyl radicals when microbubbles collapse, with lower pH enhancing the generation of these radicals. However, ozonation of NH_3-N is more effective at a high pH, when the indirect ozonation pathway dominates. Thus, the generation of hydroxyl radicals from the collapsing of microbubbles may not play a considerable role in the oxidation of NH_3-N at high pH. If this is the case, the enhanced efficiency observed by Zuttah (1999) and Ryskie (2017) when using smaller bubbles could be primarily due to the enhancement of the overall mass transfer of their laboratory apparatus.

CHAPTER 3 MATERIALS AND METHODS

3.1 Site Description

The study was carried out at a gold-mining operation located in the Abitibi Gold Belt, Canada. For confidentiality reasons, the property of the mining partner will be referred as Mine A in this document. A simplified water balance diagram of Mine A is presented in Figure 3.1.

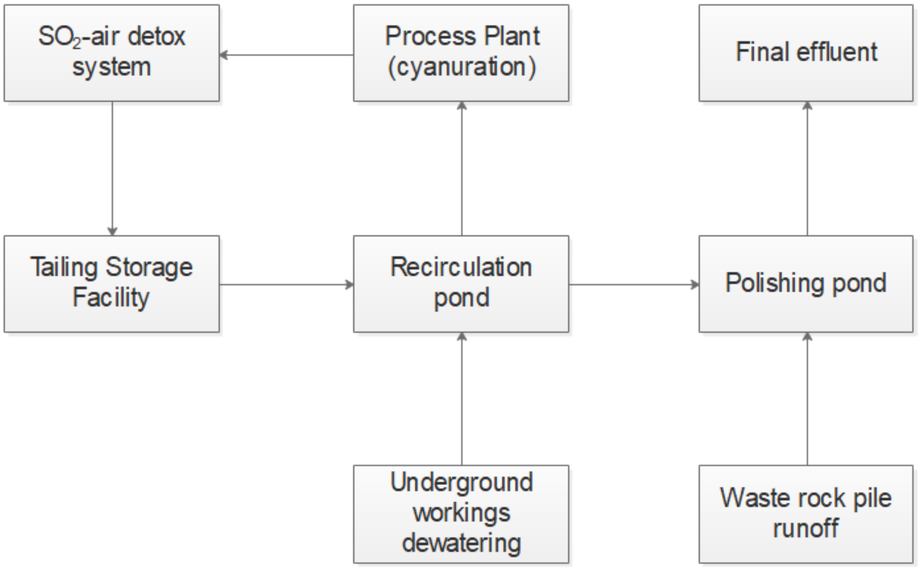

Figure 3.1 Simplified bloc diagram of water flow on Mine A

At this mining operation, free CN^- is added within the process plant to enhance gold recovery. Cyanide containing tailings are then oxidized within a SO_2-air system, converting the WAD CN^- into CNO^-. The SAD CN^- are also precipitated as insoluble copper-iron-cyanide complexes (Botz, 2001). The tailings are then stored within the TSF. The supernatant of the TSF then flows towards the recirculation pond, where a blending with water from the underground workings occurs. This water is then recirculated to meet the process plant requirements. Excess water flows towards the polishing pond, where a blending with site runoff water occurs. Finally, excess water within the polishing pond flows towards the final effluent, at which point the water quality must meet all discharge criteria of Directive 019 (MDDEP, 2012).

3.2 Water Sampling and Analysis Methods

Water sampling during this project was done in compliance with the "Guide d'échantillonnage à des fins d'analyses environnementales" (MDDEP, 2008). Table 3.1 presents the analytical methods used during this project. Sampling duration and frequency is discussed in more details in Section 3.5. For the field analysis, a dedicated space was established within the pilot unit container, enabling quick turnaround time on some of the critical operation parameters. This lab was equipped with a DRB200 reactor block from HACH, as well as a D3900 spectrophotometer to allow for in-situ analysis on COD and NH_3-N. For quality control purposes, the handheld YSI meter was calibrated daily with pH, ORP and conductivity standards. The turbidity meter was also calibrated with standards once a week. Field analysis for NH_3-N and COD were validated regularly using the external lab analysis. See section 4.1 for more details. During this project, the residual dissolved ozone in the pilot effluent was not monitored since it was not deemed relevant during the elaboration of the protocols.

3.3 Equipment and Chemicals

The design, construction and supply of the pilot unit was provided by ASDR Canada Inc., an industrial partner affiliated to the project. A simplified flowsheet diagram of the unit is presented in Figure 3.2, a list of the equipment used is presented in Table 3.2, while pictures of the equipment are presented in Appendix A. Furthermore, the chemical products, their strength and their origin are presented in Table 3.3.

The flowrate of each dosing pump was established during the commissioning of the pilot system by immersing the suction lines in a graduated cylinder and measuring the volume pumped per duration of time at a specific pump speed. Pump flowrate was also verified on a weekly basis during the parametric trials, as well as at the end of each extended duration trials.

Table 3.1 List of analytical methods utilized

Parameters	**Method / Equipment**
Field analysis	
pH	Handheld YSI meter
Temperature	Handheld YSI meter
ORP	Handheld YSI meter
Conductivity	Handheld YSI meter
Turbidity	Handheld turbidity meter
NH_3-N	HACH Method 10031
COD	HACH Method 10236
External lab analysis	
pH	CEAEQ: MA. 100-pH 1.1
ORP	H2Lab: M-Redox-1.0
COD	CEAEQ: MA. 315-DCO 1.1
TSS	CEAEQ: MA. 115-S.S.1.2
TDS	H2Lab: M-SOLI-1.0
Hardness	H2Lab: M-MET 3.0
Alkalinity	CEAEQ: MA. 315 – Alc-Aci 1.0
Carbonate and Bicarbonate	H2Lab: M-TIT-1.0
17+ total metals/metalloids	CEAEQ: MA. 200-Mét. 1.2
17+ dissolved metals/metalloids	CEAEQ: MA. 200-Mét. 1.2
NH_3-N	CEAEQ: MA. 300-N 2.0
NO_2-N, NO_3-N	CEAEQ: MA. 300-Ions 1.2
Total Kjeldahl Nitrogen	CEAEQ: MA. 300-NTPT 2.0
SCN	CEAEQ: MA.304-Ions 1.1
Total CN	CEAEQ: MA. 300-CN 1.2
WAD CN	CEAEQ: MA.300-CN 1.2
CNO	CEAEQ: MA.315-CNO 1.1
Thiosalts	H2Lab: M-SULF-4.0**
SO_4	CEAEQ: MA.303-Anions 1.1
Cl	CEAEQ: MA 300-Ions 1.3
Br	CEAEQ: MA. 200-Mét 1.2
Ecotoxicology	
Acute toxicity on *Daphnia magna*	Environment Canada: EC SPE1/RM/14
Acute toxicity on *Oncorhynchus mykiss*	Environment Canada: EX SPE1/RM/13

Table 3.2 Manufacturer and model of main equipment of the ASDR pilot unit

Tag	Equipment description	Manufacturer	Model
N/A	20’ repurposed container	ASDR Canada	Custom-made
DP-01	Raw Water Dosing Pump	Sera	C 409.2.140e
DP-02	NaOH/KOH Dosing Pump	Masterflex	07525-20
DP-03	H_2SO_4 Dosing Pump	Masterflex	07525-20
DP-04	NaBr Dosing Pump	Masterflex	07525-20
DP-05	H_2O_2 Dosing Pump	Prominent	BT4a
OC-01	Oxygen Concentrator	AirSep	Newlife Intensity 8
OD-01	Ozone Destructor	Absolute Ozone	AOD2002D
OG-01	Ozone Generator	Absolute Ozone	Atlas 30
PP-01	Microbubble Pump	Nikuni Co.	KTM20N
VE-01	Venturi Tube	Mazzei	¾’’ Injector, model 0584
RX-01	Ozone Contactor no.1	DT Concept	8 L, Custom-made Reactor
RX-02	Ozone Contactor no.2	DT Concept	8 L, Custom-made Reactor
RX-03	Catalytic Reactor	DT Concept	130 L Custom-made Reactor
RX-04	Flash Reactor	Mazzei	FR70-NK
RX-05	pH Adjustment Reactor	N/A	20 L pail
TK-01	Raw Water Tank	N/A	20 L pail
TK-02	NaOH/KOH Tank	N/A	20 L pail
TK-03	H_2SO_4 Tank	N/A	20 L pail
TK-04	NaBr Tank	N/A	20 L pail
TK-05	H_2O_2 Tank	N/A	20 L pail

Table 3.3 Chemical product concentration and supplier

Product ID.	Supplied concentration (% w/w)	Used concentration (% w/w)	Supplier
Oxygen gas	Produced on site	≈ 92	N/A
Ozone gas	Produced on site	≈ 10	N/A
NaOH/KOH mixture	50	5	Chemco Inc.
H_2SO_4	93	0.93	Chemco Inc.
NaBr	40	0.4	Chemco Inc.
H_2O_2	30	0.3/10	Chemco Inc.
AC & TiO_2 mixture	Solid form	15% glass media, 83% AC, 2% TiO_2	DT Concept

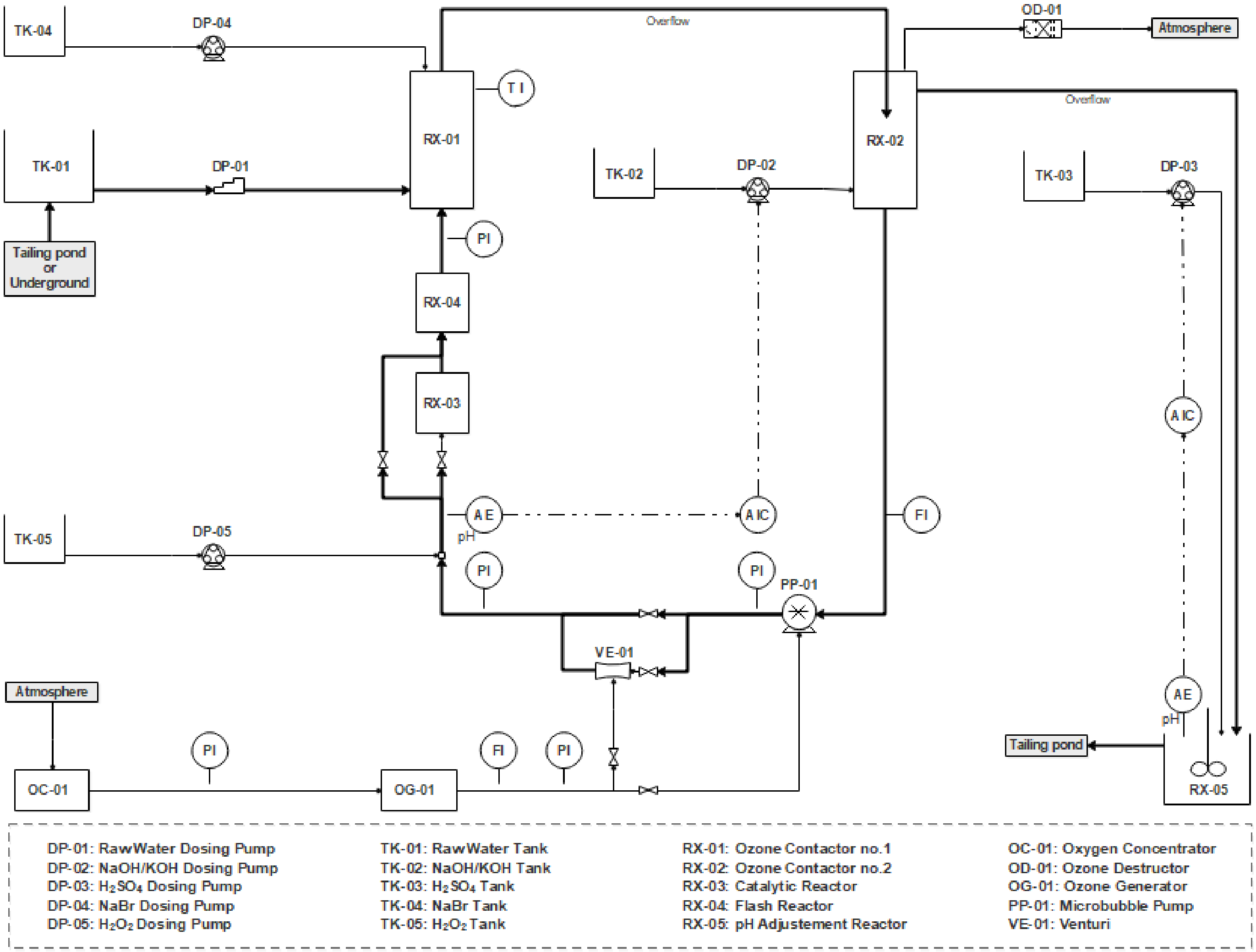

Figure 3.2 Simplified flowsheet diagram of ASDR's pilot unit, with associated instrumentation (Temperature Indicator (TI), Pressure Indicator (PI) , Analytical Element (AE), Analytical Indicator Controller (AIC) and Flow Indicator (FI)

3.4 Pilot Unit Trials

The pilot trials were carried out in two distinct steps, namely: the parametric study trials (PST) and the extended duration trials (EDT). A total of 62 PST and 4 EDT were completed. The operating parameters used during these trials are presented in Table 3.4. During the parametric study, which was carried out only on tailing supernatant water, the impact of various parameters on ozone consumption and process efficiency was investigated.

Injection Method: While maintaining consistency of all other operating parameters, two ozone injection methods were tested (PST no. 2, 3, 5, 6, 55 & 56). The first method consists of injecting the ozone directly in the microbubble pump, while the second consists of injecting the ozone in a Venturi tube located on the discharge piping of the microbubble pump. These two configurations were obtained by operating the valves on the ozone line.

Homogenous Catalysis: While maintaining consistency of all other operating parameters, various catalysts (e.g. NaBr and H_2O_2) were tested (PST no. 7, 9, 12, 13, 14 & 15). Addition of bromide ions within the recirculation loop was carried out by adjusting the speed of the NaBr Dosing Pump. The following concentrations were tested: 0, 10, 55 and 80 mg Br/L. Addition of H_2O_2 within the recirculation loop was also carried out by adjusting the speed of the H_2O_2 Dosing Pump. The following concentrations were tested: 0, 53, 92, 175 and 1 880 mg H_2O_2/L.

Heterogenous Catalysis (PST no. 17, 19, 29, 30 & 31): By operating the valves on the recirculation loop, the flow can be redirected within the Catalytic Reactor. This 130 L reactor was filled with 6 L of glass filter media, 35 L of coconut shell-based activated carbon (AC) and 1 L of titanium dioxide (TiO_2). These compounds and their respective ratio were selected by DT Concept Inc., a company specialized in catalytic ozonation.

pH: While maintaining consistency of all other operating parameters, different pH values within the recirculation loop were tested (PST no. 24, 27, 28, 39, 40, 41, 42, 48, 49, 50, 51 & 52). The modification of the pH within this loop was obtained by changing the setpoint of the Proportional-Integral-Derivative (PID) control on the NaOH/KOH Dosing Pump. Based on available data in the literature, only alkaline pH values were evaluated (Khuntia et al., 2012b; Ryskie et al., 2020b). The pH tested were the following: 7.5, 8.5, 9.5 and 10.5.

Table 3.4 Trials operating parameters

Trial No.	Date	Raw water	Flow (L/h)	Injection method	pH	Catalyst used
PST 1	2019-07-02	Tailing	16.1	Venturi tube	9.5	
PST 2	2019-07-03	Tailing	19.4	Venturi tube	9.5	
PST 3	2019-07-04	Tailing	19.4	Microbubbles pump	9.5	
PST 4	2019-07-04	Tailing	53.8	Microbubbles pump	9.5	80 mg Br/L
PST 5	2019-07-05	Tailing	21.5	Microbubbles pump	9.5	
PST 6	2019-07-05	Tailing	21.5	Venturi tube	9.5	
PST 7	2019-07-08	Tailing	21.5	Microbubbles pump	9.5	
PST 8	2019-07-08	Tailing	21.5	Microbubbles pump	9.5	
PST 9	2019-07-08	Tailing	21.5	Microbubbles pump	9.5	10 mg Br/L
PST 10	2019-07-09	Tailing	10.8	Microbubbles pump	9.5	20 mg Br/L
PST 11	2019-07-09	Tailing	16.1	Microbubbles pump	9.5	15 mg Br/L
PST 12	2019-07-09	Tailing	21.5	Microbubbles pump	9.5	
PST 13	2019-07-09	Tailing	21.5	Microbubbles pump	9.5	55 mg Br/L
PST 14	2019-07-09	Tailing	21.5	Microbubbles pump	9.5	
PST 15	2019-07-10	Tailing	21.5	Microbubbles pump	9.5	80 mg Br/L
PST 16	2019-07-10	Tailing	21.5	Microbubbles pump	9.5	92 mg H_2O_2/L
PST 17	2019-07-10	Tailing	21.5	Microbubbles pump	9.5	
PST 18	2019-07-10	Tailing	21.5	Microbubbles pump	9.5	
PST 19	2019-07-11	Tailing	21.5	Microbubbles pump	9.5	AC + TiO_2
PST 20	2019-07-11	Tailing	21.5	Microbubbles pump	9.5	
PST 21	2019-07-11	Tailing	21.5	Microbubbles pump	9.5	
PST 22	2019-07-12	Tailing	26.9	Microbubbles pump	9.5	
PST 23	2019-07-12	Tailing	32.3	Microbubbles pump	9.5	
PST 24	2019-07-15	Tailing	37.7	Microbubbles pump	9.5	
PST 25	2019-07-15	Tailing	37.7	Microbubbles pump	9.5	53 mg Br/L
PST 26	2019-07-15	Tailing	37.7	Microbubbles pump	9.5	53 mg H_2O_2/L
PST 27	2019-07-15	Tailing	37.7	Microbubbles pump	8.5	
PST 28	2019-07-15	Tailing	37.7	Microbubbles pump	10.5	
PST 29	2019-07-16	Tailing	37.7	Microbubbles pump	9.5	AC + TiO_2
PST 30	2019-07-16	Tailing	37.7	Microbubbles pump	9.5	
PST 31	2019-07-17	Tailing	37.7	Microbubbles pump	9.5	AC + TiO_2
PST 32	2019-07-17	Tailing	37.7	Microbubbles pump	9.5	
PST 33	2019-07-17	Tailing	37.7	Microbubbles pump	9.5	
PST 34	2019-07-17	Tailing	37.7	Microbubbles pump	9.5	175 mg H_2O_2/L
PST 35	2019-07-17	Tailing	37.7	Microbubbles pump	11	175 mg H_2O_2/L
PST 36	2019-07-17	Tailing	37.7	Microbubbles pump	9.5	
PST 37	2019-07-17	Tailing	37.7	Microbubbles pump	9.5	
PST 38	2019-07-17	Tailing	48.4	Microbubbles pump	9.5	
PST 39	2019-07-17	Tailing	48.4	Microbubbles pump	9.5	

Table 3.4 Trials operating parameters (continued)

Trial No.	Date	Raw water	Flow (L/h)	Injection method	pH	Catalyst used
PST 40	2019-07-17	Tailing	48.4	Microbubbles pump	8.5	
PST 41	2019-07-18	Tailing	48.4	Microbubbles pump	9.5	
PST 42	2019-07-18	Tailing	48.4	Microbubbles pump	10.5	
PST 43	2019-07-18	Tailing	80.7	Microbubbles pump	9.5	
PST 44	2019-07-18	Tailing	107.6	Microbubbles pump	9.5	
PST 45	2019-07-18	Tailing	37.7	Microbubbles pump	9.5	
EDT 1	2019-07-19	Tailing	48.4	Microbubbles pump	9.5	
PST 46	2019-07-19	Tailing	43.0	Microbubbles pump	9.5	
PST 47	2019-07-22	Tailing	37.7	Microbubbles pump	N/A	
PST 48	2019-07-22	Tailing	37.7	Microbubbles pump	8.5	
PST 49	2019-07-22	Tailing	37.7	Microbubbles pump	9.5	
PST 50	2019-07-22	Tailing	37.7	Microbubbles pump	10.5	
PST 51	2019-07-22	Tailing	37.7	Microbubbles pump	10.5	
EDT 2	2019-07-23	Tailing	32.3	Microbubbles pump	9.5	
PST 52	2019-07-24	Tailing	37.7	Microbubbles pump	9.5	
PST 53	2019-07-24	Tailing	48.4	Microbubbles pump	9.5	
PST 54	2019-07-24	Tailing	48.4	Venturi tube	9.5	
PST 55	2019-07-24	Tailing	48.4	Venturi tube	9.5	1880 mg H_2O_2/L
PST 56	2019-07-31	Tailing	43.0	Microbubbles pump	9.5	
PST 57	2019-07-31	Tailing	21.5	Microbubbles pump	9.5	
PST 58	2019-08-01	Tailing	21.5	Microbubbles pump	9.5	
PST 59	2019-08-01	Tailing	10.8	Microbubbles pump	9.5	
EDT 3	2019-08-02	Tailing	10.8	Microbubbles pump	9.5	
PST 60	2019-08-06	UG	21.5	Microbubbles pump	9.5	
PST 61	2019-08-07	UG	21.5	Microbubbles pump	9.5	
PST 62	2019-08-07	UG	10.8	Microbubbles pump	9.5	
EDT 4	2019-08-08	UG	21.5	Microbubbles pump	9.5	

For each test carried out during the parametric study trials, field analyses (see Table 3.1) were performed on the raw water. Following a stabilization period equal to or greater than four Hydraulic Retention Time (HRT) (calculated by dividing the sum of the reactors volume by the raw water pump flowrate), field analyses were performed on the treated water. Residual NH_3-N in the treated water was used as the indicator of the overall process efficiency.

Once most of the parametric study was completed, extended duration trials were performed using the most promising operational parameters. Before each test, the system was first flushed during a minimum of 12 h with raw water. Then, ozone and NaOH/KOH injections were initiated. Each test was run for a minimum of 8 h, while field analyses (Table 3.1) were carried out on both the influent and effluent at t = 0 h, 1 h, 2 h, 4 h, 6 h and 8 h. External lab analyses were also carried out on the influent and the effluent at t = 8 h. Finally, acute toxicity testing on rainbow trout and *D. magna* was carried out on all treated water, and at least once on raw water.

Four extended duration trials were performed in total (EDT no. 1 to 4). The first three trials were performed on tailing supernatant, using different ozone dosing rates (520, 780 and 2330 mg O_3/L). The last trial was performed on underground (UG) dewatering water. To adjust the ozone dosing rate for each trial, the raw water dosing pump speed was modified. Sulfuric acid at a concentration of 0.93% w/w was also added after the ozonation step to adjust the pH at around 6.5 and to potentially reduce the residual NH_3-N toxicity. Finally, a flowrate calibration of the dosing pumps was performed during each EDT.

During both the PST and the EDT, the production of ozone remained unchanged. The flowrate on the oxygen line was always set at 3 liters per minute and the pressure at 20 psi, while the potentiometer of the ozone generator was always set at 100%. Also, several weeks after the trials started and after noticing a constant deterioration of the process efficiency over time, it was assumed that the ozone generator was damaged. Thus, ozone generator “a” (OG-01a) was replaced by ozone generator “b” (OG-01b). The performance charts of each generator are presented in Appendix B. From these charts, and considering the parameters discussed above, the ozone production of OG-01a and OG-01b were expected to be respectively 24.67 and 25.15 mg O_3/h.

3.5 Data Collection

Whenever the ozonation pilot unit was in function, the operators were asked to fill the data collection log sheet presented in Appendix C. The main information captured in this log sheet was categorized in three groups, namely: 1) readings performed at the beginning of the operator's shift, 2) readings performed before any adjustment made to the pilot system, and 3) readings performed before and after adjustments, as well as every 30 minutes during a trial. This information includes:

- Date, time and operator's initials;
- Ozone dosing point (Venturi tube or microbubble pump);
- Whether or not the catalytic reactor was bypassed;
- Field analysis on the pilot influent and effluent: pH, temperature, NH_3-N, COD, ORP, conductivity and turbidity;
- Ambient temperature in the pilot container;
- Ambient ozone levels in the pilot container;
- Temperature readings in the ozone contactor No. 1;
- Online pH readings and PID control setpoints;
- Speed of the raw water pump and each chemical dosing pumps;
- Ozone generator potentiometer position;
- Speed of the recirculation pump (microbubble pump);
- Speed of the mixer in the pH adjustment reactor;
- Pressure readings on the oxygen line, the ozone line and several locations within the recirculation loop;
- Flowrate in the oxygen line and the recirculation line.

At the end of each shift, the operator was tasked with logging these results in the project database. This approach was applied during the whole duration of the field trials, which lasted from 2019-07-02 to 2019-08-08. As discussed in the previous section, water samples of the pilot's influent were also collected for external laboratory analysis (see Table 3.1) on five occasions, while water samples of the pilot's effluent were collected on four occasions.

3.6 Stochiometric Ozone Demand and Ozone Utilization Efficiency

By rearranging Equations 1.1 to 1.5, and by assuming that the contribution of the other oxidable compounds in mine water is negligible, the **stochiometric ozone demand** to obtain a given removal of nitrogen-based contaminants can be expressed as in Equation 3.1.

$$\frac{mg\ O_3}{L} = A\ (\Delta \mathrm{SCN}) + B\ (\Delta SCN + \Delta \mathrm{WAD\ CN}) + C\ (\Delta SCN + \Delta \mathrm{WAD\ CN} + \Delta \mathrm{CNO}) + D(\Delta \mathrm{SCN} + \Delta \mathrm{WAD\ CN} + \Delta \mathrm{CNO} + \Delta \mathrm{NH_3}) \quad (3.1)$$

Where:

- "Δ" represents the difference between the concentration of a species in the influent and the effluent, expressed in mg N/L;
- "A" represents the stochiometric ratio O_3:SCN-N, as per Equation 1.1, expressed in mg (3.4 mg O_3:mg SCN-N);
- "B" represents the stochiometric ratio O_3:WAD CN-N, as per Equation 1.2, expressed in mg (3.4 mg O_3:mg WAD CN-N);
- "C" represents the stochiometric ratio O_3:CNO-N, as per Equation 1.3, expressed in mg (3.4 mg O_3:mg CNO-N);
- "D" represents the stochiometric ratio O_3:NH_3-N, as per as per Equations 1.4 and 1.5, expressed in mg (13.7 mg O_3:mg NH_3-N).

Thus, by measuring the SCN^-, WAD CN^-, CNO^-, and NH_3-N concentrations in the influent and the effluent of the EDT, as well as recording the applied ozone dosing rate during these trials, the **ozone utilization efficiency** was calculated using the Equation 3.2.

$$Ozone\ Utilization\ Efficiency\ (\%) = 100 * \frac{theoritical\ stochiometric\ demand}{applied\ dosing\ rate} \quad (3.2)$$

3.7 CAPEX Estimation of Commercial Scale Units

As is the case with all emerging technologies, the cost of such technologies must be comparable to conventional technologies to be adopted. Thus, once the efficiency of a water technology is demonstrated under a specific set of constraints, a techno-economical cost estimation is required to compare with conventional technologies.

In the case of nitrogen-based contaminant treatment in mine water, such “conventional technologies” are not well defined. As presented in Section 2.5, technology selection is often site specific, with each technology boasting an array of advantages and disadvantages. This situation led to disagreements between authors on what is the Best Available Technology Economically Achievable (BATEA) for these contaminants (Jermakka et al., 2015b; Neculita et al., 2018; Pouw et al., 2014). For the purpose of this study, it was decided to consider the use of Moving Bed Biofilm Reactors (MBBR) as the BATEA, in agreement with Pouw et al. (2014) and Neculita et al. (2018). This decision was based on the existence of commercial applications of MBBR for mine water (Dale et al., 2015; Tanabene et al., 2018; Trepanier et al., 2018).

<u>Ozonation Cost</u>: Authors usually express the CAPEX of ozonation plants as a function of the ozone production capacity per period, such as lbs O_3/h or kg O_3/h (Gottschalk et al., 2010; Mundy et al., 2018). With this concept in mind, Figure 3.4 presented below was developed. To develop this figure, budgetary quotations for turnkey containerized ozone systems were requested from two water treatment plant suppliers with known expertise in the mining industry. These suppliers were asked to include in their quote the raw water pump, oxygen concentrator, oxygen compressor, oxygen holding tank, ozone generator, ozone contactor, all equipment and accessories for chemicals and ozone injection. Supplier A was tasked with providing a price for a 2 kg O_3/h system, while Supplier B was tasked with providing prices of a 10 and a 30 kg O_3/h system. Then, as per discussions with Supplier B, 100 000 CAN$ was added to each system to account for transportation and installation costs. Finally, the Equation 3.3 (Brown, 2016) was used to produce the curve shown in Figure 3.4.

$$\frac{Cost_{size2}}{Cost_{size1}} = \left(\frac{Capacity_{size2}}{Capacity_{size1}}\right)^{0.67} \tag{3.3}$$

Also, for comparison purposes, a fourth cost curve derived from the work of Mundy et al. (2018) was added to Figure 3.3. This curve is based on the actual cost of 13 ozonation plants located in the United States and designed for drinking water disinfection.

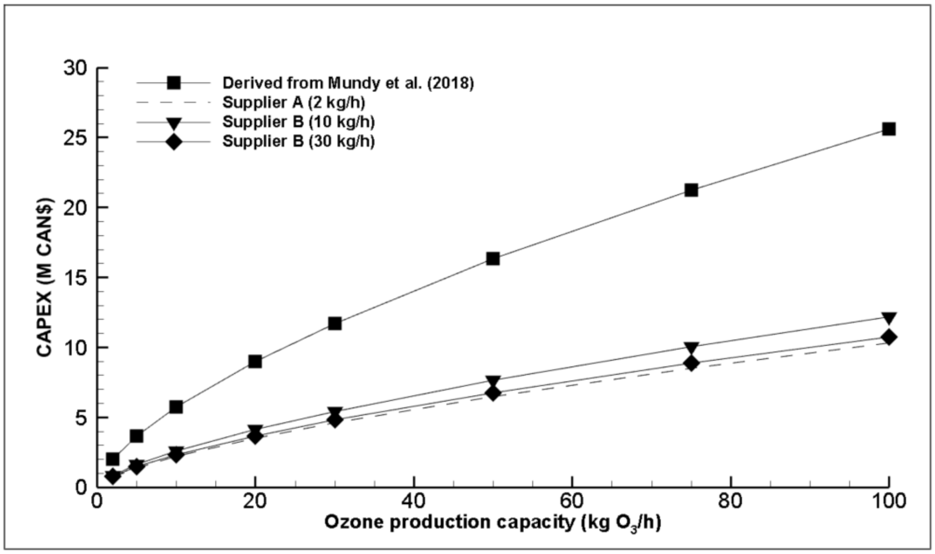

Figure 3.3 Installed CAPEX cost curves as a function of ozone production

As shown in Figure 3.3, the cost curves obtained from suppliers' data are roughly 55 to 60% lower than the curve derived from Mundy et al. (2018). The method of construction, i.e. containerized versus built onsite, might explain this difference, since building costs, utilities cost, as well as installation costs of containerized plants should be smaller than for plants that are built onsite. Also, turnkey model, compared to the traditional Engineering, Procurement and Construction Management (EPCM) model generally applied for large municipal infrastructure projects, are generally more cost effective and limit project cost overruns (Zaheer & Fallows, 2011). Additionally, the prices provided by Supplier A and Supplier B were for budgetary purposes only, which implies a certain inaccuracy on these figures. To clarify this situation, the establishment of an accuracy range was required. Given the preliminary nature of the data provided to these suppliers, and considering the limited number of engineering deliverables produced during this exercise, it was estimated that the budgetary prices provided would classify for an early Class 4, according to the Association for the Advancement of Cost Engineering (AACE) standards (Zaheer & Fallows, 2011). From these same standards, a conservative accuracy range for a Class 4 estimate is between -30% and +50%.

<u>MBBR Cost</u>: From Pouw et al. (2014), the installed CAPEX of an MBBR system to treat mine water is presented in Figure 3.4. However, this last study does not provide any indication on the nitrogen load that was assumed for the elaboration of this figure, nor included the cost of heating the water. Since nitrogen loading and water temperature have considerable impacts on the cost of an MBBR system (Boltz & Debarbadillo, 2010), comparison of the MBBR technology with other technologies using this figure alone would raise comparison issues.

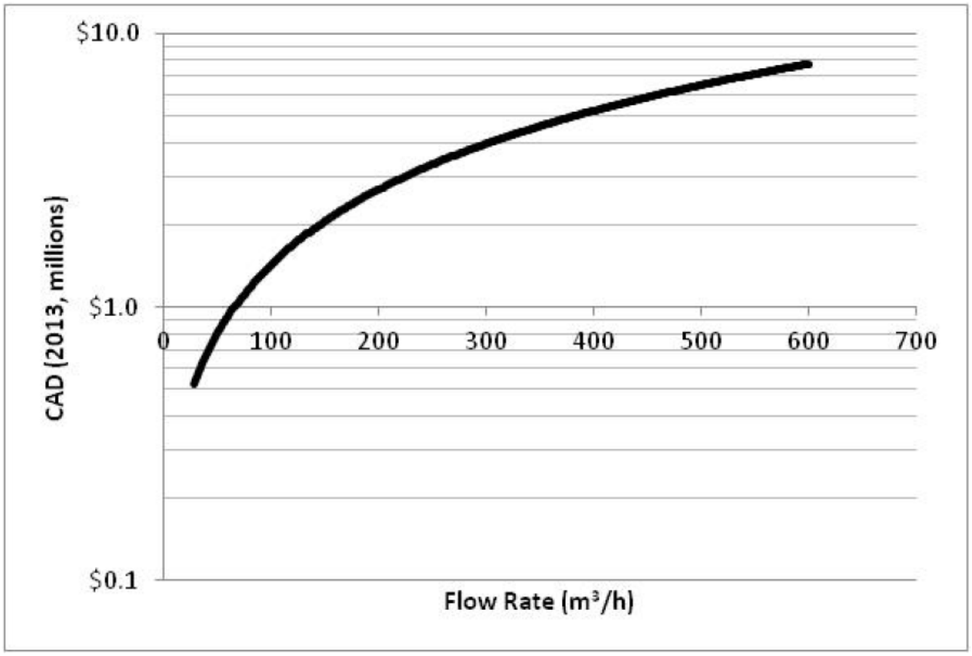

Figure 3.4 Total Installed CAPEX for a MBBR system (Pouw et al., 2014)

More recently, Trepanier et al. (2018) published a study on the topic of an MBBR plant that was built to treat the effluent of the Eleonore mine, in Quebec, Canada. Commissioned in 2017, this plant has a design flowrate of 500 m^3/h and a design loading rates of 462 kg of NH_3-N/day and 146 kg of SCN-N/day. Once converted in concentration terms, these loading rates equal to 38.5 mg NH_3-N/L and 12.2 mg SCN-N/L. Also, the removal efficiency obtained in the 8 months following commissioning of the system for NH_3-N and SCN^- were respectively 88% and 98%. From the same author, this plant cost about 40 M CAN$ to build, making it 6 times more expensive than what is shown in Figure 3.4.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Raw Water Characterization

For this project, two sources of raw mine water were used: supernatant from the TSF and water from the dewatering operations of the underground workings of an active gold mine. Characterization of the tailing water was carried out a week prior to the starting of the PST (2019-06-26), as well as three times at the end of the EDT (2019-07-19, 2019-07-23 and 2019-08-02). The UG water was also characterized at the end of an EDT (2019-08-08). Field readings, analytical results for parameters with discharge criteria in the Directive 019, as well as analytical results for nitrogen-based compounds are presented in Table 4.1. Appendix D also presents results of other water quality parameters, metals, metalloids and elements contained in these waters.

Except for the TSS concentration in the tailing water on June 26th, the water analysis performed on both sources of raw water met the Directive 019 criteria on pH, TSS, total arsenic, total copper, total iron, total lead, total nickel and total zinc. However, the Directive 019 also stipulates that mine water should not be acutely toxic to rainbow trout and *D. magna*. In that regard, and based on the information discussed in Section 2.4, NH_3-N, CNO^-, SCN^- and NO_2^- were key contaminants of concerns in the tailing water, while NH_3-N and NO_2^- were contaminants of concerns in the UG water.

It is noteworthy to add that consistent differences between field and laboratory results on NH_3-N were observed. After discussion with the analytical laboratory, it was postulated that CNO^- presence in the sample could interfere with laboratory results. Indeed, in accordance with the laboratory sampling and conservation procedures, NH_3-N samples were preserved with sulfuric acid. However, CNO^- is known to readily hydrolyze into NH_3-N, especially under acidic conditions (Mudder et al., 2001). To test this assumption, muck solutions containing 16.67 and 33 mg N/L of CNO^- were prepared, with their pH adjusted below 2 with sulfuric acid. After a 10-day period stored at 4 °C, NH_3-N concentration in each sample was analyzed and resulted in respectively 16 and 30 mg N/L. These results were deemed satisfactory to demonstrate the CNO^- interference on NH_3-N analysis. Acknowledging this interference, it was decided to exclusively use the field analysis on NH_3-N for data interpretation, since these analyses were performed only a few minutes after sampling.

Table 4.1 Raw mine water physicochemical characterization

Date	**Jun. 26**	**Jul. 19**	**Jul. 23**	**Aug. 2**	**Aug. 8**
Water (Tailing or Underground)	**Tailing**	**Tailing**	**Tailing**	**Tailing**	**UG**
Field readings					
Ammonia Nitrogen (mg N/L)	32.7	37.2	36	32.5	40.1
COD (mg/L)	204	165	162	190	77.5
Electrical Conductivity (mS/cm)	2.98	2.85	2.85	2.74	1.38
Redox Potential (mV, Ag/AgCl(s))	419	294	280	266	327
pH (units)	8.01	8.24	8.38	8.27	7.86
Temperature (°C)	22.2	21.0	19.7	23.9	19.9
Turbidity (NTU)	34.10	5.54	8.01	8.67	3.22
External lab analysis - parameters with discharge criteria in the Directive 019 (MDDEP, 2012)					
Arsenic, Dissolved (mg/L)	0.0008	0.0016	0.0016	0.0018	0.0005
Arsenic, Total (mg/L)	0.0022	0.0016	0.0017	0.0031	0.0008
Copper, Dissolved (mg/L)	0.2577	0.2553	0.2839	0.2498	0.0082
Copper, Total (mg/L)	0.2888	0.2949	0.2929	0.2888	0.0118
Hydrocarbon (C10-C50) (mg/L)	N/A	N/A	N/A	N/A	N/A
Iron, Dissolved (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01
Iron, Total (mg/L)	2.02	0.15	0.24	0.23	0.11
Lead, Dissolved (mg/L)	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003
Lead, Total (mg/L)	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003
Nickel, Dissolved (mg/L)	0.0042	0.0053	0.0040	0.0222	0.0035
Nickel, Total (mg/L)	0.0056	0.0052	0.0039	0.0234	0.0061
pH (units)	8.26	8.23	8.30	8.30	7.95
Total Cyanide (mg/L)	0.023	0.117	0.018	N/A	0.002
Total Suspended Solids (mg/L)	107	4	10	5	4
Zinc, Dissolved (mg/L)	<0.001	<0.001	0.003	<0.001	0.038
Zinc, Total (mg/L)	0.007	0.012	0.002	0.002	0.049
External lab analysis - nitrogen-based contaminants					
Ammonia Nitrogen (mg N/L)	55.1	59.7	47	44.5	44.5
Total Kjeldahl Nitrogen (mg N/L)	56.1	47.9	52.1	50.3	43.4
Cyanate (mg/L)	103	42.9	38.2	45.6	<0.01
Total Cyanide (mg/L)	0.023	0.117	0.018	N/A	0.002
WAD Cyanide (mg/L)	N/A	<0.001	<0.001	<0.001	<0.001
Free Cyanide (mg/L)	0.009	N/A	N/A	0.002	N/A
Thiocyanate (mg/L)	6.31	5.99	8.21	8.74	<0.05
Nitrate (mg N/L)	18.4	22.2	23.7	18.9	21.9
Nitrite (mg N/L)	1.20	1.10	1.12	1.33	1.20

4.2 Pilot Unit Trials – Parametric Study

The objective of the parametric study was to investigate the impact of the injection methods, the pH and the use of catalytic materials (hydrogen peroxide, bromide, activated carbon and titanium dioxide) on the treatment process performance. To compare the performance of the various trials, the mass of NH_3-N removed divided by the mass of ozone injected was used as the primary indicator. This approach was selected because NH_3-N concentrations in the influent and the effluent of the pilot could be measured directly on the field, and the ozone injection rate could be deducted based on the vendor specifications (see Appendix B). This approach allowed for timely interpretations of the results of the trials.

The first trials performed on the pilot system were planned to evaluate the impact of ozone injection methods, namely using a Venturi tube or a microbubble pump. However, it became clear after operating the pilot system for a few days that the reproducibility of the results generated were an issue, with the ratio of NH_3-N removed to ozone injected varying considerably between trials with identical operating parameters (Figure 4.1).

In this figure, the results from the trials referred as "baseline" are presented. These trials were performed using the microbubble pump as the injection method, a pH of 9.5 in the ozone contactor, and without the addition of catalytic material. In addition, the ratio of NH_3-N removed to ozone injection observed for the first six baseline trials varied between 12.8 and 22.3 mg NH_3-N/g O_3. These trials were performed at identical treatment flowrates of 21.5 L/h and HRT of 37.4 minutes. Considering these results, it was suspected that the ozone generator (OG-01a) might be the cause of the system's low reproducibility, and this generator was replaced by a second one (OG-01b) on 2019-07-14. The next 5 baseline trials were performed using this second generator. With identical treatment flowrates of 37.7 L/h and HRT of 21.3 minutes, the ratio of NH_3-N removed to ozone injected for these trials varied between 17.3 and 46.7 NH_3-N/g O_3. Thus, replacing the ozone generator had the reverse effect of acerbating the low reproducibility of the system.

Unfortunately, the sources of low reproducibility within the system could not be isolated during this project. However, the potential causes detailed below could partially explain the results.

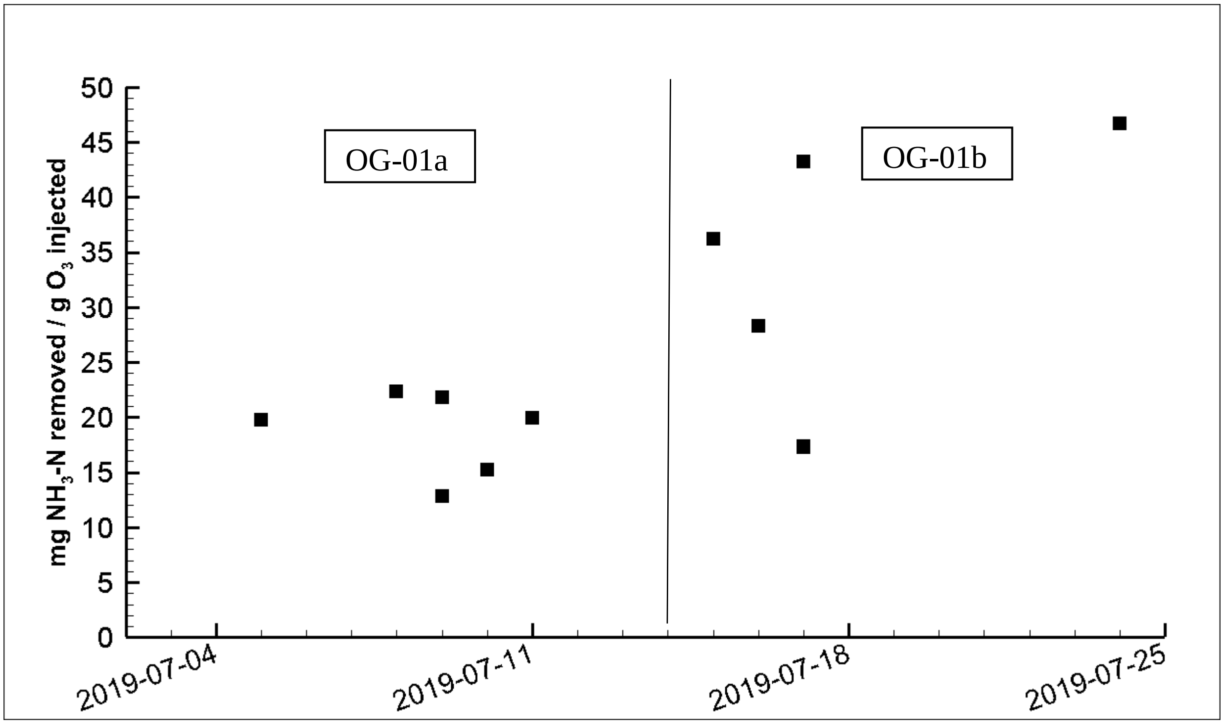

Figure 4.1 Baseline results: ammonia nitrogen removed to ozone injected ratios

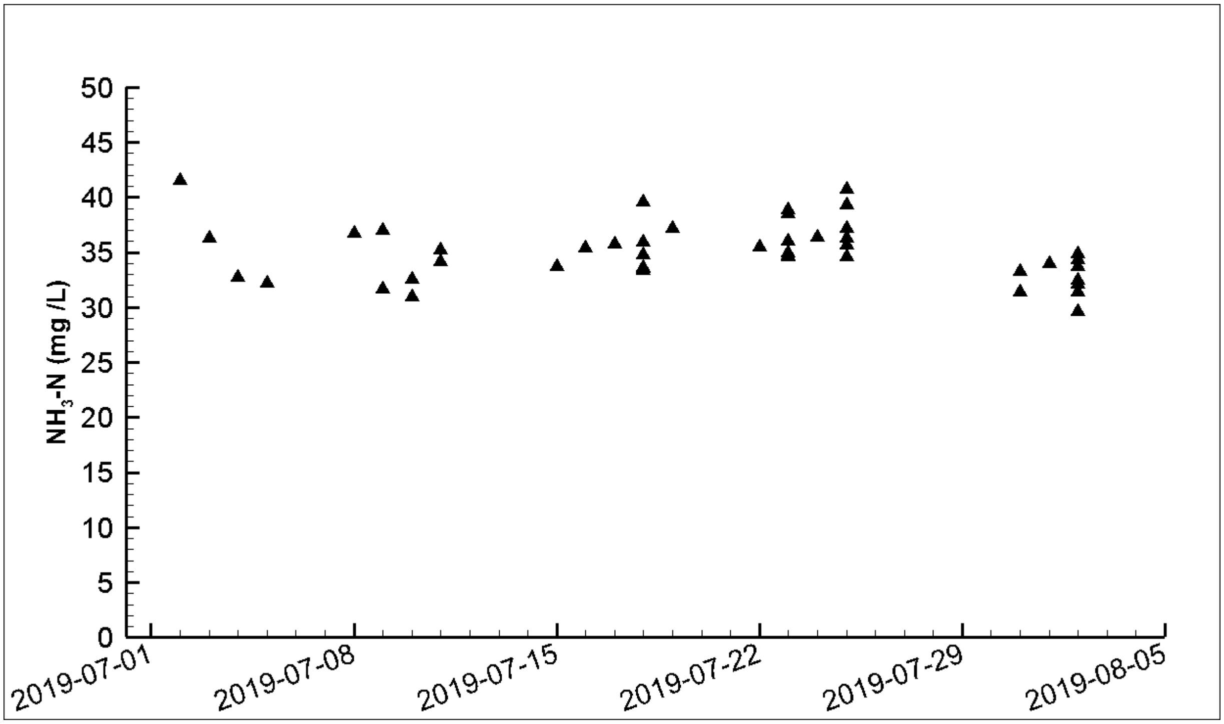

Figure 4.2 NH_3-N analysis on raw tailings water

Poor accuracy of the NH_3-N analysis: As showed in Figure 4.2, NH_3-N analysis on raw tailing water using the HACH method could vary greatly during a same day. Although some variations were expected from this field analysis, the scale of these variations (above 5 mg N/L) was considered high. With the ratio of NH_3-N removed to ozone injected relying heavily on the NH_3-N analysis, poor accuracy of the HACH method may have greatly impact the reproducibility of the system.

Variation in the influent concentration of SCN^- and CNO^-: The SCN^- and CNO^- concentrations in the tailing pond were not analyzed on a frequent basis during the PST. It is possible that these concentrations varied considerably over time, which would change the ozone requirement to treat this water.

Scaling problem and recirculation flowrate: Not long after the commissioning of the pilot plant was completed, mineral scaling[1] within the recirculation loop was observed. This scale was particularly affecting the rotameter and the microbubble pump within that recirculation loop, making flowrate readings unreliable. As such, another possible cause of the system low reproducibility could be the flowrate variability within the recirculation loop. Potential solutions to this source of error include relying on a different type of flowmeter (which is less impacted by scaling than a rotameter), the addition of a softening step prior to the ozonation step, addition of antiscalants and selection of a flowmeter that would be less susceptible to scaling issues.

Poor precision on the ozone injected: With no means of measuring the exact ozone mass rate injected, the vendor specification presented in Appendix B were used. During the entire duration of this project, it was assumed that as long as 3 L/min of O_2 at 20 psi were fed to the ozone generators, and that the potentiometers of these generators were set at 100%, the ozone injected in the system was 24.67 g O_3/L for OG-01a and 25.15 g O_3/L for OG-01b (as per appendix B). However, after discussion with the vendor, it was highlighted that the ambient air temperature and the oxygen concentration could also considerably impact the ozone production. In an email correspondence, the vendor representative mentioned that the performance charts presented in

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[1] To identify the nature of this scale, hydrochloric acid (HCl) 5% w/w was first poured on it. From the vigorous formation of bubbles (see picture in Appendix E), it was then suspected that this scale was mainly composed of calcium carbonate ($CaCO_3$). The Langelier Saturation Index (LSI) of the tailing water was also calculated. At its initial pH of 8, the tailing water has an LSI close to 0, indicating a saturated but balanced solution. However, when the pH is increased to 9.5, the LSI is around 1.5, indicating supersaturation in $CaCO_3$ and potential scale formation.

Appendix B were developed with an ambient air temperature of 20 °C. Also, 5°C increase in the ambient air temperature around the generators could result in an ozone production reduction. A potential solution to this source of error would be the addition of an online O_3 analyzer on the injection line. With this equipment, a more accurate ozone injection rate could be determined. Because the system low reproducibility made the interpretation of the PST results non-conclusive, it was decided to always perform a baseline trial before testing a new process parameter. The results of this new parameter would then be compared with its respective baseline trial, in an attempt to mitigate this low reproducibility. It was also decided that any interpretation should be supported by consistent results from at least 3 different trials. Using this approach, Table 4.2 below was developed, and the following interpretations were made.

Injection method: Results obtained from the trials to determine if ozone injection using a microbubble pump would yield better results than with a Venturi tube were inconclusive. Although the ratios of NH_3-N removed to ozone injected were higher using the Venturi tube for two sets of trials, the third set of trials showed the opposite. Also, the difference in the ratios obtained with the Venturi tube compared to the ones obtained with the microbubble pump (+13.9%, -0.4% and +5.3%) were considered small and potentially insignificant given the low reproducibility of the system. Without being able to conclude if one method was performing more than the other, it was decided to perform the next trials with the microbubble pump. This decision was justified by the ease of operation of this equipment.

pH: Consistent with the findings reported by Zuttah (1999) and Ryskie et al. (2020b), results obtained indicate that a pH of 9.5 and above improves the performance of ozonation of NH_3-N in mine water. However, results at a pH of 10.5 were considered inconclusive, for similar reasons as the one discussed in the injection method section above. Under these circumstances, it was decided to carry on the next trials at a pH of 9.5.

Homogenous catalysis with bromide: None of the trials using bromide as a catalyst produced results showing a consistent and important improvement in the process performance. Considering the range of bromide concentrations added to the system (from 0 to 80 mg/L), these results are in contradiction with Zuttah (1999) and Khuntia et al. (2012b) findings. Although the reasons behind this contradiction are still unclear, the low reproducibility of the system, as well as the water chemistry of the tailing water are suspected to have played a role in these findings.

Table 4.2 Parametric study results

Trial No.	Ozone Generator	Type of Trial	mg NH_3-N removed / g O_3	Difference with the baseline
Injection method				
PST 3	a	Baseline (Microbubble pump)	18.7	N/A
PST 2	a	Venturi tube	21.3	13.9%
PST 5	a	Baseline (Microbubble pump)	19.8	N/A
PST 6	a	Venturi tube	19.7	-0.4%
PST 55	b	Baseline (Microbubble pump)	53.6	N/A
PST 56	b	Venturi tube	56.5	5.3%
Homogenous catalysis with bromide				
PST 7	a	Baseline (0 mg Br/L)	22.3	N/A
PST 9	a	10 mg Br/L	21.2	-5.1%
PST 12	a	Baseline (0 mg Br/L)	21.8	N/A
PST 13	a	55 mg Br/L	21.6	-0.8%
PST 14	a	Baseline (0 mg Br/L)	12.8	N/A
PST 15	a	80 mg Br/L	13.3	3.4%
Homogenous catalysis with H_2O_2				
PST 14	a	Baseline (0 mg H_2O_2/L)	12.8	N/A
PST 16	a	92 mg H_2O_2/L	12.6	-1.4%
PST 24	b	Baseline (0 mg H_2O_2/L)	36.2	N/A
PST 26	b	53mg H_2O_2/L	35.3	-2.5%
PST 33	b	Baseline (0 mg H_2O_2/L)	17.4	N/A
PST 34	b	175 mg H_2O_2/L	17.3	-0.9%
PST 56	b	Baseline (0 mg H_2O_2/L)	56.5	N/A
PST 57	b	1 880 mg H_2O_2/L	52.7	-6.7%
Heterogenous catalysis with activated carbon and titanium dioxide				
PST 17	a	Baseline (no Catalytic Reactor)	15.3	N/A
PST 19	a	Catalytic Reactor	18.2	19.4%
PST 30	b	Baseline (no Catalytic Reactor)	28.3	N/A
PST 29	b	Catalytic Reactor	28.4	0%
PST 31	b	Catalytic Reactor	24.6	-13%
pH				
PST 24	b	Baseline: pH = 9.5	36.2	N/A
PST 27	b	pH = 8.5	28.9	-20.3%
PST 28	b	pH = 10.5	29.2	-19%
PST 41	b	Baseline: pH = 9.5	13.5	N/A
PST 39	b	pH = 7.53 (no pH adjustment)	0.8	-94.2%
PST 40	b	pH = 8.5	6.1	-55.1%
PST 42	b	pH = 10.5	14.3	6%
PST 50	b	Baseline: pH = 9.5	26.0	N/A
PST 48	b	pH = 7.49 (no pH adjustment)	2.7	-89.4%
PST 49	b	pH = 8.5	18.0	-30.6%
PST 51	b	pH = 10.5	26.6	2%
PST 52	b	pH = 10.5	27.0	4%

Homogenous catalysis with hydrogen peroxide: All trials performed with the addition of H_2O_2 resulted in slightly lower mass of NH_3-N removed per mass of ozone injected, compared with their baselines. However, the difference in the ratio obtained (-1.4%, -2.5%, -0.9% and -6.7%) were not judged substantial given the low reproducibility of the system. Thus, it was not possible to demonstrate the positive, nor the negative impact of the addition of H_2O_2 on the performance of the ozonation process. This conclusion is consistent with the findings reported by Zuttah (1999), in which no improvement in the NH_3-N removal efficiency after addition of H_2O_2 to the ozonation process was found. This conclusion is, however, inconsistent with the reported results of Ryskie (2017), in which H_2O_2 addition to the process, had the adverse effect of reducing the removal efficiency of NH_3-N. Given the strong reactivity of H_2O_2 with ozone, the different methodologies used to add this product within the ozonation process may account for these observations. All these tests were carried on at similar pH conditions.

Heterogenous catalysis with activated carbon and TiO_2: Although this approach was not mentioned in any of the publications consulted on ozonation of NH_3-N in mine water, trials using activated carbon and TiO_2 as catalysts were also carried out. This idea originated from conversations with an ozone specialist from DT Concept Inc. Unfortunately, results from these trials were also inconclusive, with one trial showing positive results, one trial showing no change and one trial showing negative results compared to the baseline. Given the size of the catalytic reactor (130 L), trials performed using this equipment lasted several hours to allow the system to reach a steady state regime. Thus, results from these trials may have been particularly exposed to the low reproducibility of the system.

4.3 Pilot Unit Trials – Extended Duration Study

As mentioned previously, four EDT were performed during this project, at pH of 9.5, using the microbubble pump and without any catalytic material. Three of these trials were conducted on tailing water at different ozone injection rates, and one trial was performed on UG water. For each of these trials, field readings on the influent and effluent were performed regularly, and external laboratory analysis were performed once the trials were completed.

Similar to the PST approach, the NH_3-N in the effluent was used during the EDT to gauge the process performance in the field. However, for these trials, the primary objective was to determine whether the system had reached steady state before the end of the trial and to ensure that representative samples were sent to the external laboratory. The results obtained during the extended duration trials on the tailing water are shown in Figure 4.3. Hence, trials at 520 mg O_3/L, 780 mg O_3/L and 2330 mg O_3/L appear to have, respectively, reached steady state regimes at approximately 2, 4 and 6 h.

The steady state regime for the trial performed on UG water appears to have been reached at 6 h (Figure 4.4). However, the optimal removal efficiency was observed at t = 1 h, after which the system performance appears to deteriorate. This trend can also be observed to a lesser extent in the trial on tailing water at 520 mg O_3/L. Although the cause of this deterioration could not be identified, it is likely related to the low reproducibility problems described above. Indeed, given the length of the EDT, these trials were deemed particularly sensitive to reduced ozone production caused by elevated ambient air temperature, as well as scaling issues. For example, results from a fourth EDT on tailing water had to be completely discarded because the microbubble pump stopped working at t = 4 h due to scale accumulation in the pump volute.

Once each trial had reached t = 8 h, samples for external analysis were taken. Table 4.3 presents nitrogenous species results for these trials. Results of all the parameters analyzed on these waters are also presented in Appendix C.

For both the PST and EDT, temperature of the influent, effluent as well as inside the first ozone contactor of the pilot was also recorded. As discussed in section 2.7, an increase in water temperature can positively impact the ozonation process by increasing the kinetic reaction rate. However, an increase in temperature will also lower the solubility of ozone in water, thus reducing the overall mass transfer. During this project, no control over the temperature within the system was performed, for which the recorded values ranged between 22 and 46 ºC.

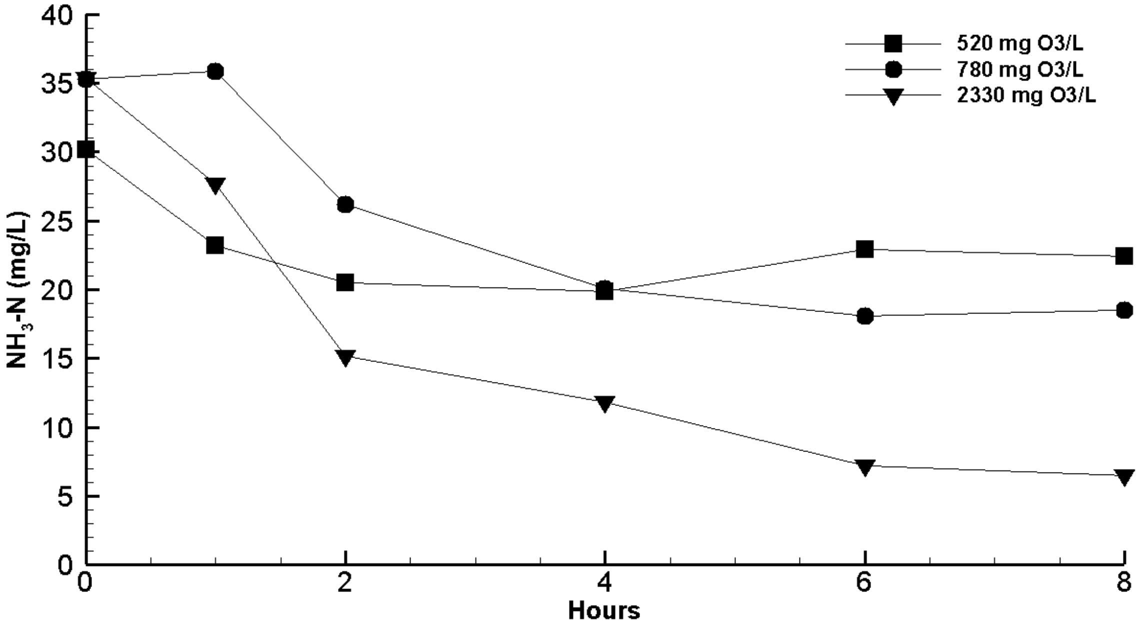

Figure 4.3 Ammonia nitrogen concentration in the pilot effluent during the extended duration trials on tailing water

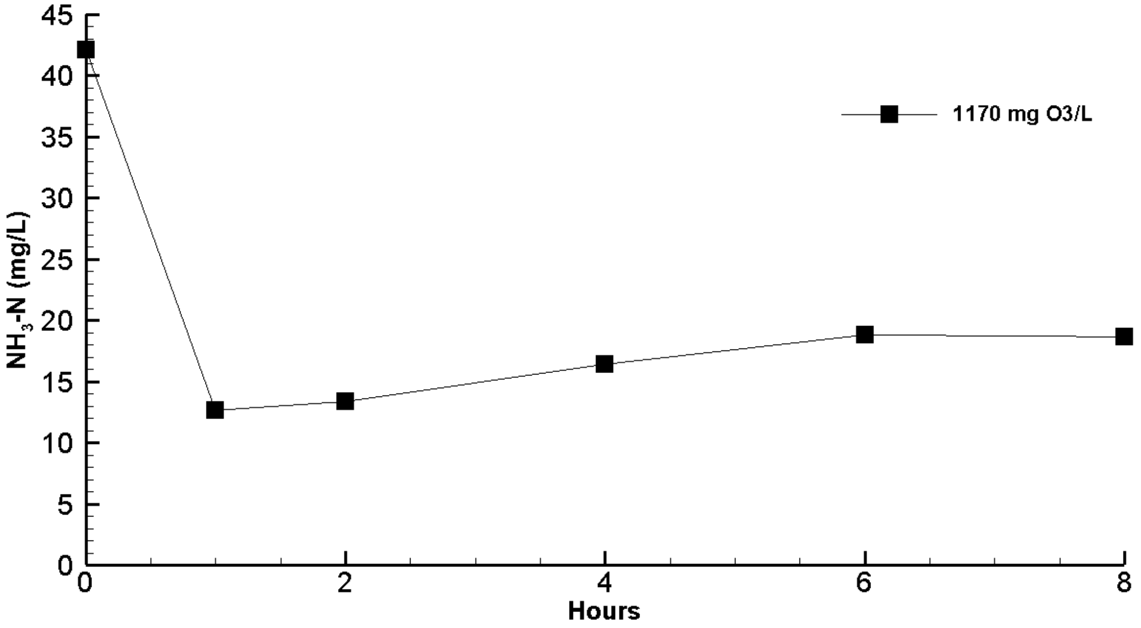

Figure 4.4 Ammonia nitrogen concentration in the pilot effluent during the extended duration trials on underground water

Table 4.3 Results of extended duration trial results for nitrogen-based contaminants removal

Parameters	**Units**	**Influent at t = 8 h**	**Effluent at t = 8 h**	**Removal Efficiency**
Trial no.1: 520 mg O_3/L on Tailing Water				
Thiocyanate	mg N/L	1.40	0.03	98%
WAD Cyanide	mg N/L	<0.001	<0.001	N/A
Cyanate	mg N/L	14.3	10.1	29%
Ammonia Nitrogen	mg N/L	37.2	22.4	40%
Nitrite	mg N/L	1.10	0.06	95%
Nitrate	mg N/L	22.2	42.6	-92%
Total Kjeldahl Nitrogen (TKN)	mg N/L	56.0	37.0	34%
Total Nitrogen	mg N/L	79.3	79.7	0%
Trial no.2: 780 mg O_3/L on Tailing Water				
Thiocyanate	mg N/L	2.00	<0.01	99%
WAD Cyanide	mg N/L	<0.001	<0.001	N/A
Cyanate	mg N/L	12.7	8.2	35%
Ammonia Nitrogen	mg N/L	36.0	18.5	49%
Nitrite	mg N/L	1.10	0.02	98%
Nitrate	mg N/L	23.7	50.6	-114%
TKN	mg N/L	52.1	29.6	43%
Total Nitrogen	mg N/L	76.9	80.2	-4%
Trial no.3: 2330 mg O_3/L on Tailing Water				
Thiocyanate	mg N/L	2.10	<0.01	99%
WAD Cyanide	mg N/L	<0.001	<0.001	N/A
Cyanate	mg N/L	15.2	5.5	64%
Ammonia Nitrogen	mg N/L	32.5	6.5	80%
Nitrite	mg N/L	1.30	0.03	98%
Nitrate	mg N/L	18.9	52.3	-177%
TKN	mg N/L	50.3	10.5	79%
Total Nitrogen	mg N/L	70.5	62.8	-11%
Trial no.4: 1170 mg O_3/L on Underground Water				
Thiocyanate	mg N/L	<0.01	<0.01	N/A
WAD Cyanide	mg N/L	<0.001	0.002	N/A
Cyanate	mg N/L	<0.003	<0.003	N/A
Ammonia Nitrogen	mg N/L	40.1	18.7	53%
Nitrite	mg N/L	1.20	<0.01	99%
Nitrate	mg N/L	21.9	43.2	-97%
TKN	mg N/L	43.4	15.6	64%
Total Nitrogen	mg N/L	66.5	58.8	12%

From Table 4.3, SCN^- and NO_2^- are the nitrogenous species on which the ozonation process was the most effective. Regardless of the ozone dosing rate, removal efficiency of 95% and above was obtained. Also, SCN^- in contact with ozone oxidizes into free CN^-, as per Equation 1.1. So, although WAD CN^- concentration in the tailing water was below detection limits, it was expected that this water would contain free CN^- once exposed to an ozonation process. However, all WAD CN^- analysis performed on the effluent of tailing water trials also resulted in below detection values, indicating that most, if not all, of the free CN^- generated by SCN^- oxidation rapidly oxidized again to CNO^-. This also suggests that the oxidation of SCN^-, free CN^- and NO_2^- were not the limiting reactions in the overall oxidation of nitrogenous species into NO_3^- (Equations 1.1 to 1.5). Although this conclusion has already been demonstrated for the oxidation of NO_2^- to NO_3^- (Ryskie, 2017; Zuttah, 1999), it was previously assumed that SCN^- and free CN^- oxidation were also limiting reactions (Ryskie, 2017). However, this author was using a semi-batch ozonation system, which would explain why different conclusions were drawn.

This observation also means that for projects in which SCN^-, free CN^- and/or NO_2^- are the only contaminants of concerns, ozone dosing rates much lower than 520 mg O_3/L could be successfully employed. This would have a substantial impact on the economic performance of these projects, as discussed in Section 4.5.

Removal efficiencies observed for CNO^- and NH_3-N were lower than for the other nitrogenous species. In addition, for the trials performed on tailing water, increases in the ozone injection rate led to increases in the removal efficiencies for these contaminants. This indicates that the removal of CNO^- and NH_3-N (Equations 1.3 and 1.4) are the limiting reactions in the overall oxidation of nitrogenous species into NO_3^-. This conclusion is somewhat consistent with the finding of Ryskie et al. (2020b), although this last study reported a semi-batch trial during which CNO^- concentrations went from 20.7 mg /L to below detection limits in only 30 minutes. In the same time, the last study reports a semi-batch trial on another mine water during which CNO^- concentration went from 35.9 mg/L to 27.1 mg/L in 90 minutes. Considering these results, the removal of CNO^- by ozone, and the resulting removal efficiencies, seems to be closely linked to the water chemistry of the treated effluent. Moreover, although the pilot system used for this project did not allow for a two stage ozonation process, information collected during this project indicates that a pre-ozonation step, under acidic conditions, could be beneficial for the overall performance of the system. Indeed, several sources consulted indicate that CNO^- readily hydrolyses to NH_3-N under acidic pH (Mudder et al., 2001; Zuttah, 1999). This information was confirmed by the results of the test discussed in Section 4.1, during which the CNO^- interference on NH_3-N readings in acidified samples was demonstrated. Thus, when dealing with effluents with elevated CNO^- and low SCN^- and free CN^-, a pre-ozonation step at a low pH could be implemented to specifically target CNO^-. A second ozonation step at a high pH would then complete the oxidation of NH_3-N towards NO_3^-.

However, according to Table 4.3, all four EDT resulted in an increased level of NO_3^- in their effluent. This observation is consistent with Equations 1.1 to 1.5, which imply that any removed nitrogen contained in SCN^-, WAD CN^-, CNO^-, NH_3-N and NO_2^- shall ultimately be found under its NO_3^- formed in the pilot effluent.

Similarly, the TKN was reduced in each trial effluent. This was expected, since TKN is the sum of organic nitrogen and NH_3-N, and any oxidation of NH_3-N towards NO_3^- reduces the TKN of the effluent. It is noteworthy to add that limited information is available on whether nitrogen contained in SCN^-, CN^- and CNO^- are included in TKN results. Based on an email correspondence with the owner of the external laboratory used during this project, these species are indeed captured during a TKN analysis. However, in a technical note, Hill Laboratories (2000) stipulate that nitrogen in free CN^- is not recovered during a TKN digestion. Since SCN^- form free CN^- during an oxidation process, one could presume that SCN^- is also not recovered during a TKN digestion. Based on this information, it is assumed in this document that TKN is then the sum of NH_3-N, CNO^- and other organic nitrogen.

As for total nitrogen, the difference between the influent and the effluent for trials 1, 2, 3 and 4 were respectively 0%, 4%, -11% and -12%. Since the final product of the ozonation process is NO_3^-, it was expected that the mass of total nitrogen within the system would be conserved, resulting in similar values of total nitrogen in the influent and effluent. This seems to be the case, if a certain allowance is given to account for the inaccuracy of the analytical results. A good example of this inaccuracy is highlighted in the effluent results of trial No. 4, where the NH_3-N concentration alone is 3.1 mg N/L, or 17%, above the TKN results.

Since the final goal of removing nitrogen-based contaminants in mine water is to reduce the toxicity of such water, acute toxicity tests were performed on both the raw water and treated water of this project. The results of these tests on rainbow trout and *D. magna* are presented in Tables 4.4 and 4.5, respectively. These results are also presented in the chronological order in which the samples were submitted.

Table 4.4 Acute toxicity testing results on rainbow trout

Concentration (%v/v)	**0**	**6,25**	**12,5**	**25**	**50**	**100**	**LC50 (95%)**
Tailing water	0%	0%	0%	0%	100%	90%	35.4
Tailing water at pH 6.5	0%	0%	0%	0%	80%	100%	40.2
Trial 1: 520 mg O_3/L	0%	0%	0%	0%	90%	100%	38
Trial 2: 780 mg O_3/L	0%	0%	0%	10%	90%	100%	35.4
Trial 3: 2330 mg O_3/L	0%	0%	40%	100%	100%	100%	13.6
UG water	N/A	N/A	N/A	N/A	N/A	N/A	N/A
UG water at pH 6.5	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Trial 4: 1170 mg O_3/L	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Table 4.5 Acute toxicity testing results on *D. magna*

Concentration (%v/v)	**0**	**6,25**	**12,5**	**25**	**50**	**100**	**LC50 (95%)**
Tailing water	0%	0%	10%	10%	100%	100%	29,4
Tailing water at pH 6.5	0%	0%	0%	100%	100%	100%	17,7
Trial 1: 520 mg O_3/L	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Trial 2: 780 mg O_3/L	10%	0%	20%	30%	90%	100%	26,3
Trial 3: 2330 mg O_3/L	0%	20%	90%	100%	100%	100%	8,22
UG water	N/A	N/A	N/A	N/A	N/A	N/A	N/A
UG water at pH 6.5	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Trial 4: 1170 mg O_3/L	N/A	N/A	N/A	N/A	N/A	N/A	N/A

As a starting point, samples of raw tailing water were submitted to the external laboratory for acute toxicity analysis. Since the toxicity of NH_3-N is known to be influenced by the pH of a sample, and considering the elevated concentration of NH_3-N in the tailing water, a second set of tailing water samples were submitted, but this time with their pH adjusted to 6.5 using 93% w/w sulfuric acid.

As shown in Tables 4.4 and 4.5, the raw tailing water failed the acute toxicity test for rainbow trout and *D. magna* when no dilution was applied. This was expected, given the high concentration of NH_3-N and CNO^- in this water. However, based on the LC50 of each sample, acidification of the tailing water to 6.5 only marginally reduced the acute toxicity on rainbow trout, and increased the acute toxicity on *D. magna*. This last result was unexpected and might be partially due to the complex chemistry of the water in the TSF. For example, lowering the sample pH may have accelerated the hydrolysis of CNO^- into NH_3-N, which in turn exacerbates the toxicity of resulting water.

Following the tailing water toxicity assessment, the acute toxicity of effluents from trials 1, 2 and 3 was also assessed. Since the pH of each of these effluents was adjusted to about 6.5 with sulfuric acid, comparison with the acute toxicity of the acidified tailing water was deemed appropriate. For the rainbow trout, the toxicity of these effluents increases with the amount of ozone injected. However, the LC50 on the acidified tailing water, the effluent at 520 mg O_3/L and the effluent at 780 mg O_3/L, respectively 40.2%, 38% and 35.4%, are quite close to one another, and perhaps fall within the imprecision range of the method. Nevertheless, with a LC50 of 13.6%, the effluent at 2330 mg O_3/L was unquestionably more toxic than the other trials. This result was unexpected, since removal efficiencies of 99%, 64%, 80% and 98% were obtained on SCN^-, CNO^-, NH_3-N and NO_2^-, respectively. Previously identified as the main contaminants of concern in this TSF water, the removal of these contaminants should have reduced the toxicity of the effluent. With a LC50 of 0.0093 mg/L on rainbow trout (Wedemeyer et al., 1979), a potential explanation could be the presence of dissolved ozone in the effluent at the time of the toxicity tests. Nevertheless, with a half life in the order of minutes (Gottschalk et al., 2010), and considering the delay of few days between sampling the water and starting the toxicity tests, it is uncertain if residual ozone could the cause of this toxicity. Another potential explanation could be the formation of ozonation by-products, also called disinfection by-products (DBP), such as formaldehydes and acetaldehydes (Park et al., 2016). Finally, the presence of residual copper, and potentially Cu complexes, in the pilot effluent could also contribute to the toxicity of the effluent. If this is the case, an additional treatment step for Cu removal might be necessary.

Regarding the acute toxicity testing on *D. magna*, results from trial 1 had to be discarded because the sample was mishandled by the external lab. Also, with a LC50 of respectively 26.3% and

8.2% for trials 2 and 3, ozonation with 780 mg O_3/L seems to have slightly improved the toxicity of the water, while ozonation with 2330 mg O_3/L clearly worsen the situation. Since these results are somewhat coherent with the ones from the rainbow trout trials, potential explanations for the toxicity of ozonated water on *D. magna* would also include residual ozone and presence of DBP. For this reason, the monitoring of dissolved ozone in future projects of that nature should be investigated. Monitoring of formaldehydes, acetaldehydes, bromate, chlorate and copper should also be considered.

Samples of UG water, acidified UG water and trial 4 effluent were also submitted for acute toxicity testing on rainbow trout and *D. magna*. However, the results from these samples, which were all shipped the same day, had to be discarded due to mishandling at the external laboratory.

Based on the results presented in this section, additional studies are required to better understand the impact of ozonation processes on the acute toxicity of mine water. Studies on ozonated effluents from more than one source of raw water would be particularly relevant. Analysis of dissolved ozone in samples before shipment, as well as before and after acute toxicity testing would also be relevant. Also, if the dissolved ozone is identified to be the cause of the observed toxicity, additional treatment steps could be implemented. If not, research on DBP and other potential sources of toxicity produced by ozonation of mine water may be required.

4.4 Stochiometric Ozone Demand and Ozone Utilization Efficiency

Using Equations 3.1 and 3.2, the stochiometric ozone demand and the ozone utilization efficiency were calculated for the four extended duration trials performed during this project. These values were also calculated for the trial from Ryskie et al. (2020b), performed using a continuous system. These results, as well as the NH_3-N removal efficiency obtained during each trial are presented in Table 4.6.

Table 4.6 Stoichiometric ozone demand, ozone utilization efficiency and NH_3-N removal efficiency results from extended duration trials

Trials	**Raw water type**	**Applied Dosing Rate (mg O_3/L)**	**Stochiometric Ozone Demand (mg O_3/L)**	**Ozone Utilisation Efficiency**	**NH_3-N removal efficiency**
No .1	Tailing	520	308	59%	40%
No. 2	Tailing	780	365	47%	49%
No. 3	Tailing	2330	573	25%	80%
No. 4	UG	1170	293	25%	53%
Ryskie et al. (2020b)	Unspecified	1145	277	24%	99%

Based on these results, none of the EDT resulted in ozone utilization efficiencies above 60%. Trials 3, 4, as well as the continuous trial performed by Ryskie et al. (2020b) present ozone utilization efficiencies of only about 25%, meaning that 75% of the ozone injected did not react with the contaminants of concern. This efficiency is quite low and indicates that further research for troubleshooting addressing and performance optimization is still required. Indeed, the ozone utilization efficiency of a commercial scale unit would have a considerable impact on the cost of such unit, as discussed in Section 4.5. Several reasons could explain these low ozone utilization efficiencies, including the following:

Presence of other oxidable species in the raw water: one of the assumptions behind Equation 3.1 is that the presence of other oxidable compounds in the treated water would have a negligible impact on the overall demand for ozone. With analysis on raw tailing and UG waters revealing low concentrations of metals, metalloids, TSS, organic nitrogen, as well as low chemical oxygen demand, this assumption seems reasonable. However, other compounds that were not analyzed, such as hydrocarbons, may have increased the ozone demand for these waters.

Loss of ozone to the atmosphere: Given the limited solubility of ozone in water, it is also expected that a portion of the ozone injected in the system as a gas will not dissolve in the treated water and will eventually be lost to the atmosphere[2]. Any ozone injected in the system that does not react with the contaminant of concern will then reduce the ozone utilization efficiency. This

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[2] For this same reason, an ozone destructor was installed on the vent of the ozone contactors of the pilot used in this study, in accordance with the industry best practices (Gottschalk et al., 2010).

source of error was also identified by both Zuttah (1999) and Ryskie et al. (2020b) as one of the main reasons behind the high ozone requirement observed in their respective studies. Indeed, although it is common for commercial systems to show ozone transfer efficiencies of 90% and above (Jackson & Pathapati, 2015), such transfer efficiencies would not be expected from laboratory and pilot units that were not specifically designed to optimize mass transfer rates.

Additional ozone requirements for higher NH_3-N removal efficiency: When strictly looking at the results presented in Table 4.6, higher removal efficiency could be associated with lower ozone utilization efficiencies. This would be consistent with the findings of Khuntia et al. (2012b), where an equal amount of ozone was required to oxide the first 99 mg/L of NH_3-N and the last 1 mg/L of NH_3-N in a 100 NH_3-N/L muck solution. However, when comparing these results with the results obtained from some of the baseline trials performed during the parametric study, this conclusion is no longer valid. Even though the lack of water analysis on these trials prevents the calculation of their exact stochiometric ozone demand and the ozone utilization efficiency, the NH_3-N removal efficiency for these trials are presented in Table 4.7. These results highlight the feasibility of obtaining removal efficiencies of 80% and above with a dosing rate of only 667 mg O_3/L.

Overestimation of the ozone dosing rate: A more likely explanation for the low ozone utilization efficiencies shown in Table 4.6 could be an overestimation of the actual amount of ozone injected in the system. As discussed in Section 4.2, the ozone mass flowrate was not directly measured in the field. It was instead estimated from the performance chart provided by the ozone generators manufacturer (see Appendix B). Also, fluctuations in the oxygen concentration fed to these generators, as well as fluctuations in the ambient air temperature, are suspected of reducing the performance of these generators, and consequently the amount of ozone injected in the system. This could explain why some of the trials performed during the PST yielded better removal efficiency than the EDT.

Table 4.7 NH_3-N removal efficiency results from some of the most successful baseline trials during the parametric study

Trials	**Raw water type**	**Applied Dosing Rate (mg O_3/L)**	**Stochiometric Ozone Demand (mg O_3/L)**	**Ozone Utilisation Efficiency**	**NH_3-N removal efficiency**
Parametric trial No. 24 (baseline)	Tailing	667	N/A	N/A	70%
Parametric trial No. 37 (baseline)	Tailing	667	N/A	N/A	79%
Parametric trial No. 54 (baseline)	Tailing	667	N/A	N/A	84%

Trials presented in Table 4.7 were performed using the same operating parameters as the extended trials, namely a pH of 9.5 in the ozone contactors, the injection of ozone via the microbubble pump and the absence of catalytic materials. Thus, given that the NH_3-N removal efficiency of trial 3 was similar to the removal efficiencies presented in Table 4.7, and assuming constant removal efficiencies for the other nitrogenous species, the stoichiometric ozone demand for the trials in this table could be approximated as equal to the stoichiometric ozone demand for trial 3, i.e. 573 mg O_3/L. This assumption would lead to an ozone utilization efficiency of 86%, which would be much closer to the industry standards in terms of mass transfer efficiency.

In summary, the presence of oxidable species in the raw water, the loss of ozone to the atmosphere, and the inaccurate measurements of ozone injection (which was already identified as a potential reason for the low reproducibility of the system) are the main causes suspected to have led to the low ozone utilization efficiency observed in this study. Future studies of similar nature should then:

- Identify and monitor additional contaminants that could increase ozone requirements, such as hydrocarbons;
- Minimize the loss of ozone to the atmosphere by using industry best practices to promote mass transfer rate within the experimental apparatus;

- Use an online ozone analyzer and a rotameter on the injection line to constantly monitor the ozone mass flowrate. Use similar apparatus on the ozone contactor vent, before the ozone destructor, to monitor ozone loss to the atmosphere.

4.5 Techno-Economical Cost Estimate for Commercial Scale Units

From the results and information gather during this project, cost estimations for the CAPEX of a commercial scale ozonation plant are presented in Figure 4.5.

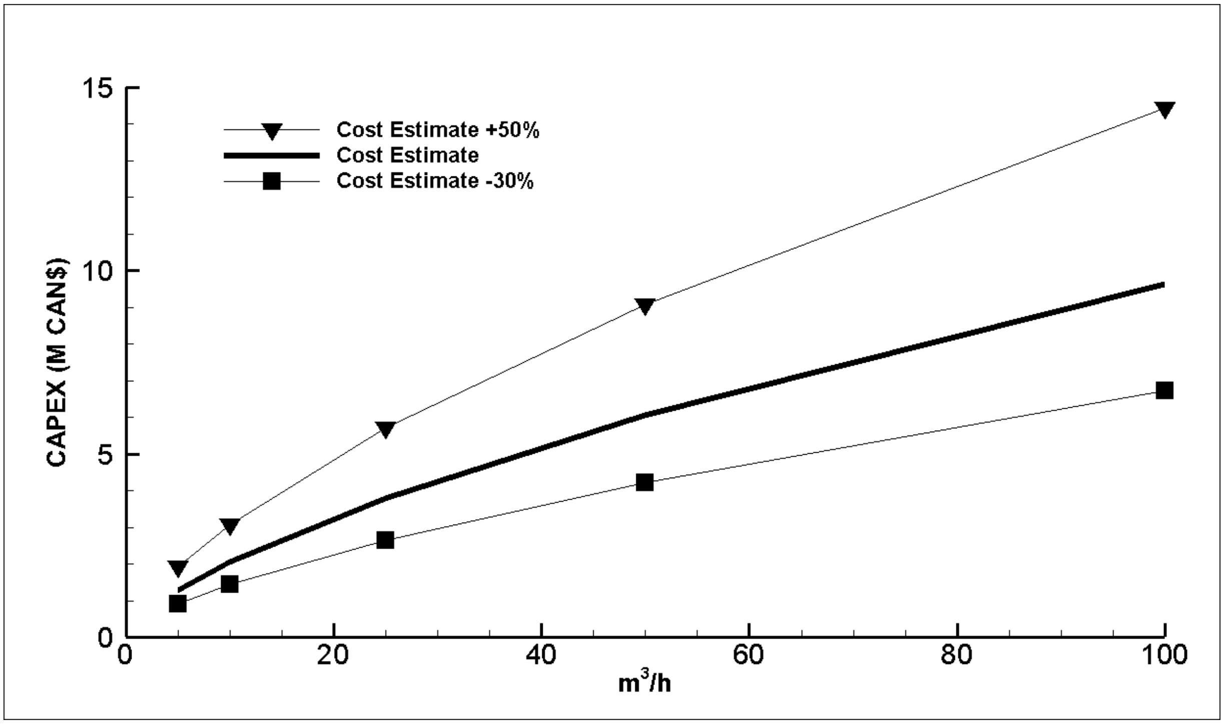

Figure 4.5 Estimated CAPEX for a commercial scale ozonation plant (extrapolation from a 10 kg/h estimate)

Also, to develop this figure, the list of assumptions below was established:

- A turnkey construction model is preferable over an EPCM model;
- A containerized plant is preferable to a plant built onsite;
- The installed CAPEX of a turnkey and containerized ozonation plant is equal to the 10 kg/h cost curve from Figure 3.3, with an accuracy range from -30% to +50%;
- The water chemistry used for this estimation is the tailing water from Mine A;

- A commercial scale ozonation plant is expected to be in operation 90% of the time, leaving 10% of downtime for maintenance and unexpected shutdowns;
- Additional research into the acute toxicity of ozonated effluents will provide a low-cost solution to overcome this challenge;
- An injection of 667 mg O_3/L is sufficient to reach the removal efficiencies obtained during the extended duration trial 3 and meet local discharge criteria;
- Although additional research into catalytic ozonation may hold the key to considerably reducing the dosing requirement for ozone when treating mine water, the results obtained during this current project were not able to confirm this information. As such, this cost estimation does not rely on catalytic ozonation.

As expected, the CAPEX of a commercial scale ozonation plant is high, especially when compared to the cost of a MBBR plant as presented in Figure 3.4. In this figure, a plant with a capacity of 200 m^3/h is expected to cost just under 3 M CAN$, compared to about 15 M CAN$ for an ozonation plant with a similar capacity. However, as previously stated in Section 3.7, Figure 3.4 does not consider the cost of equipment required to heat the water and accommodate the bacterial community within a MBBR. The nitrogen loading rate used to develop this figure is also unclear.

With Mine A located in Quebec, it is likely that the water would require heating during the winter months to enable biological treatment. Also, with about 35 mg NH_3-N/L and 2 mg SCN-N/L present in its raw tailing water, the nitrogen loading rate into an MBBR would be similar to the Eleonore mine's MBBR. Thus, a price comparison with this specific MBBR plant seems more appropriate.

To enable this comparison, the ozone dosing rate required to treat water with similar characteristics as the Eleonore mine was estimated. For this calculation, the concentration of SCN^- to be removed was estimated at 12.0 mg SCN-N/L, considering a 98% removal efficiency and a design concentration of 12.2 mg SCN-N/L in the raw water. As for NH_3-N, the concentration to be removed was estimated at 33.9 mg NH_3-N/L, considering an 88% removal efficiency and a design concentration of 38.5 mg NH_3-N/L in the raw water.

Using Equation 3.1, the stochiometric ozone demand to oxidize 12.0 mg SCN-N/L and 38.5 mg NH_3-N/L into nitrate is equal to 816 mg O_3/L. Also, assuming an ozone utilization efficiency of 80%, similar to what was observed during some of the parametric trials, the actual ozone dosing rate requirement to treat the Eleonore water is estimated at 1020 mg O_3/L.

Based on the same assumption made to develop Figure 4.5, but this time using an ozone dosing rate of 1020 mg O_3/L, a comparison between the ozone technology and the MBBR technology at the Eleonore site is presented in Figure 4.6. The cost curve of the MBBR system in this figure was produced from Equation 3.3.

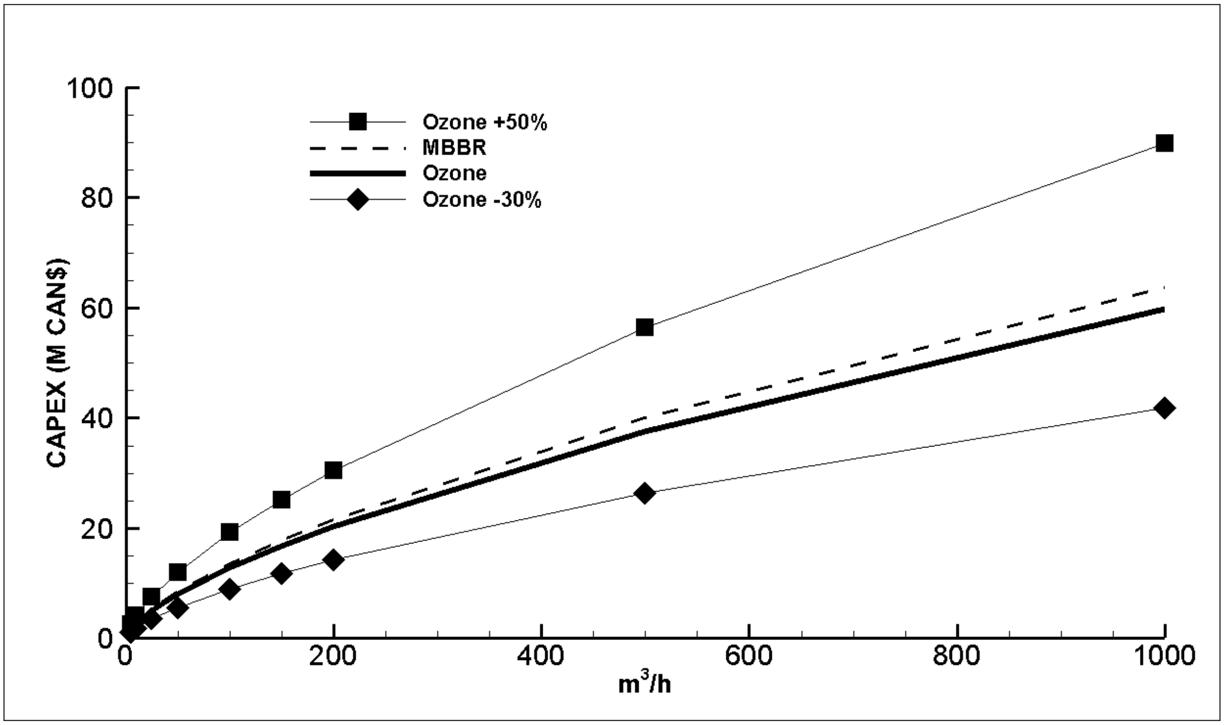

Figure 4.6 Installed CAPEX comparison between a MBBR plant and an ozone plant (using cost estimates from Supplier B)

Figure 4.6 shows that the cost of an ozonation plant is similar to the cost of a MBBR plant, for a given raw water chemistry. Of course, this is true only if the many assumptions used to develop this figure are accurate. Among these assumptions, some are more uncertain than others. The expected ozone utilization efficiency is one of them. Assumed at 80%, this value would need to be confirmed with a pilot trial. Also, it appears unrealistic to house an ozonation plant capable of processing several hundreds of m^3/h and costing tens of millions of dollars only in repurposed sea containers. For similar reasons, perhaps such plant would be built using the EPCM model instead of the turnkey model. In this case, a more conservative approach to estimate the cost of a large ozonation plant should then rely on the work of Mundy et al. (2018). Hence, Figure 4.7 was developed. This figure shows that an ozonation plant would cost almost twice as much as an MBBR plant, for a given raw water chemistry. This tends to indicate that ozonation of large flowrate or high loading rate may not be competitive compared to MBBR systems. However, other factors to consider, such as commissioning time, process resilience, manpower and chemical requirements could potentially favour an ozonation plant over a MBBR plant. This would be specifically true for small systems, where CAPEX would be smaller and of lesser importance compared to other decisional factors.

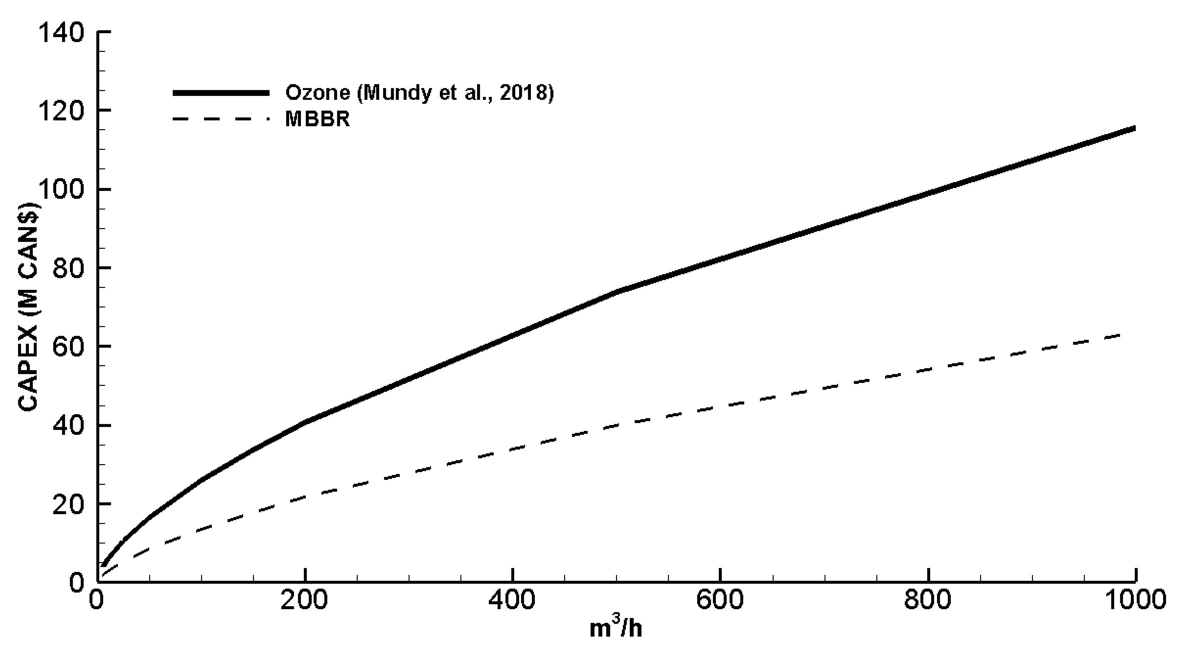

Figure 4.7 Installed CAPEX comparison between a MBBR plant and an ozone plant (using cost estimates from Mundy et al. (2018))

The OPEX of a commercial scale ozonation system was also calculated, as shown in Figure 4.8. In addition to the assumption made to develop Figure 4.5, Figure 4.8 also relies on the following assumptions:

- No pre-treatment or post-treatment is required, other than pH adjustment with NaOH/KOH and H_2SO_4;
- Dosing rate of NaOH/KOH and H_2SO_4 is equal to the what was observed during the extended duration trial 3, or about 190 mg/L and 70 mg/L respectively. This represents the worst-case scenario, since chemical consumption for trials 1 and 2 were lower;
- NaOH/KOH and H_2SO_4 used in the commercial plant will have respective concentration of 50% w/w and 93% w/w. These products will be handled in 1000 L IBC tote;
- The cost of NaOH/KOH 50% w/w and H_2SO_4 93% w/w, including transportation, is equal to 1.50 CAN$/kg and 0.75 CAN$/kg respectively, according to discussion with Chemco Inc;
- The hourly rate of the plant operator should be 75 CAN$/h, according to Supplier B;
- The manpower required to operate this plant should be 8 h per day, with some of the monitoring done via remote access to the plant's Human Machine Interface (HMI);
- The electrical consumption to produce a kg of ozone should be 10 kWh (Gottschalk et al., 2010), and the electricity cost should be 0.033 CAN$/kWh (Hydro Québec, n.d.). Electrical consumption other than for ozone production should be negligible compared to the total OPEX;
- For simplicity, the only item included in the OPEX calculation should be the manpower, the cost of NaOH/KOH and H_2SO_4, as well as the electrical cost to produce ozone.

As shown in Figure 4.8, the cost associated with the manpower is expected to be fixed and independent of the flowrate of the plant, making these charges the majority of the total OPEX up to a flowrate of about 25 m^3/h. On the other hand, the electricity required for the ozone production, as well as the volume required of NaOH/KOH and H_2SO_4 are expected to be a function of the flowrate. The costs associated with these items were estimated at 0.47 CAN$/$m^3$ and 0.34 CAN$/$m^3$, respectively. Noteworthy, this estimate was made on a Canadian context, where electricity is relatively not expensive. Higher electricity costs, which are common at mines operating on generators, are expected to increase the OPEX of this process.

The total OPEX of the system was estimated from 5.81 CAN$/$m^3$ for a 5 m^3/h ozonation plant, and down to 1.31 for a 100 m^3/h ozonation plant. According to Pouw et al. (2014), the OPEX of an MBBR system range from about 0.50 CAN$/m^3 to 8.00 CAN$/m^3, although this author does not specify the flowrates associated with these values. As for the Eleonore MBBR, OPEX values for this plant does not appear to be publicly available. Thus, if the assumptions used to develop Figure 4.8 are accurate, the OPEX of an ozonation system would be in the same order of magnitude as a MBBR system.

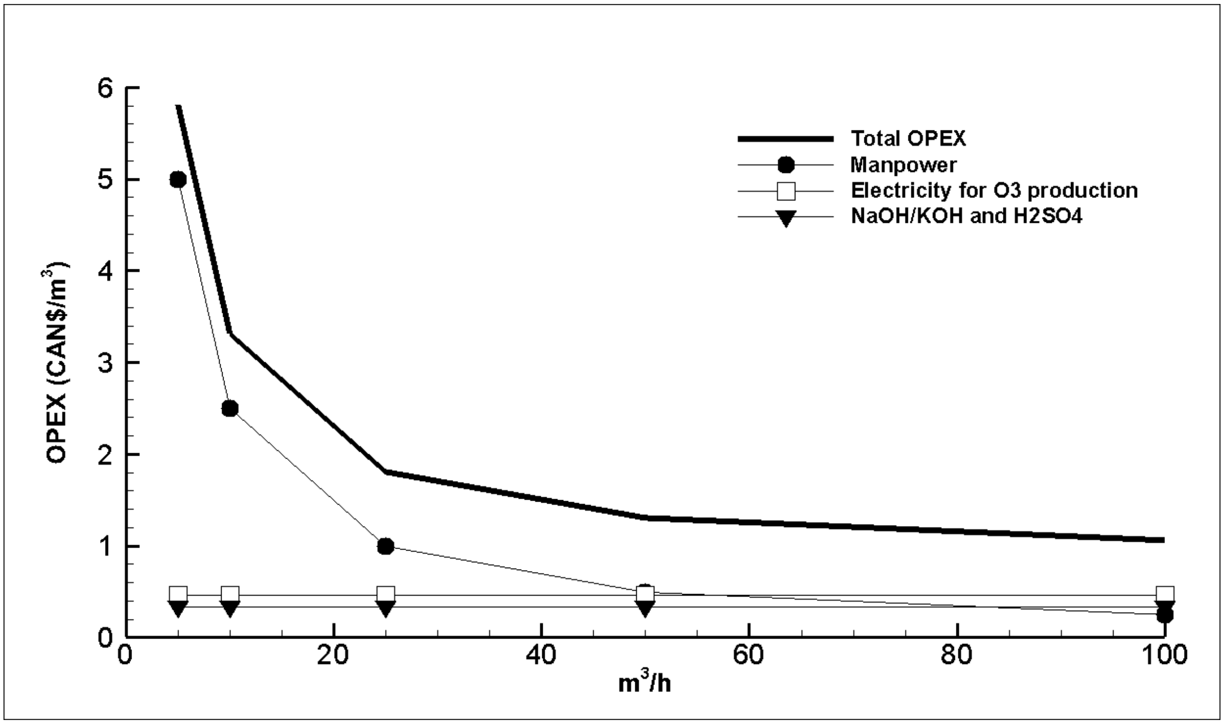

Figure 4.8 Estimated OPEX for a commercial scale ozonation plant

By combining the CAPEX and OPEX estimated in Figures 4.5 and 4.8, the Total Expenditure (TOTEX) of the system can be calculated. This value would be of particular interest to a services provider who would build a portable ozonation system and rent it to several mining clients over the course of its amortization period (from 3 to 10 years) and beyond.

Figure 4.9 also relies on the following assumptions:

- The plant is financed at an interest rate of 6%, compounded daily
- For the whole duration of its amortization period, this plant is in utilization 75% of the time. The remining 25% represent downtime between clients, during which the plant is not rented.

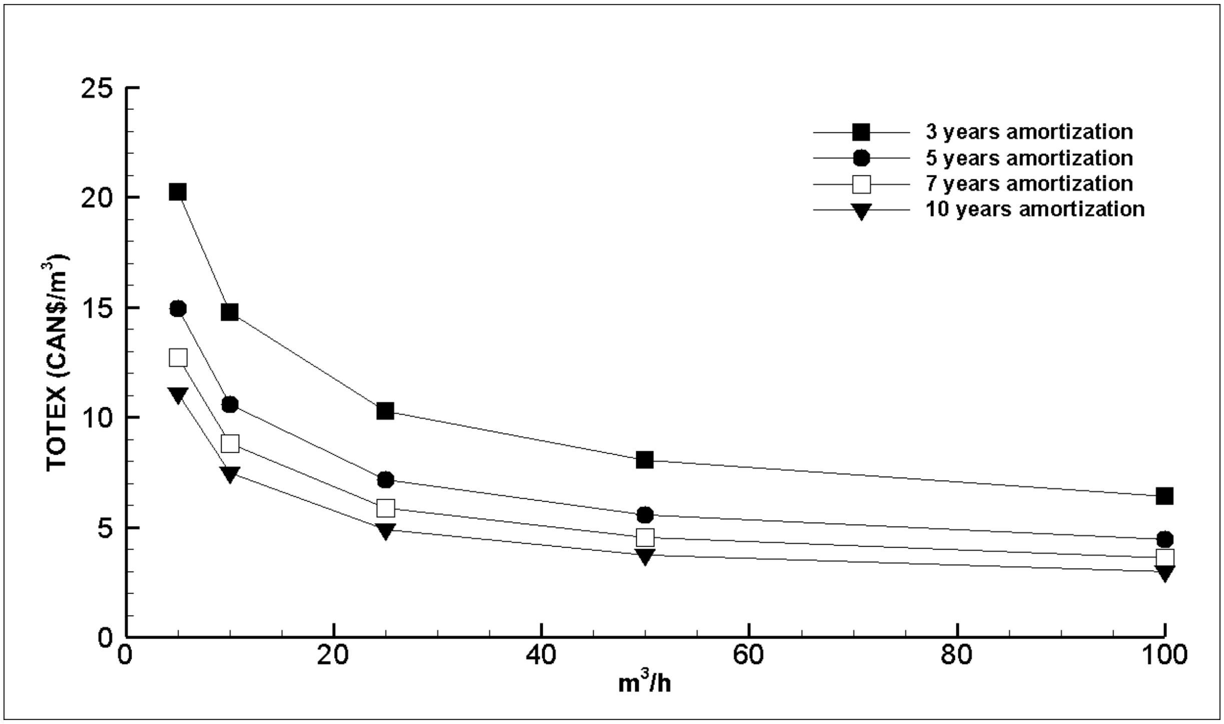

Figure 4.9 Estimated TOTEX for a commercial scale ozonation plant

When both the CAPEX and OPEX are taken into consideration, the TOTEX of an ozonation treatment could approximately range between 3 and 20 CAN$/m^3, depending on the treatment flowrate and the amortization period. Also, similar to the OPEX presented in Figure 4.8, the TOTEX somewhat plateaus at 25 m^3/h, which could indicate that this flowrate could be optimal for a commercial ozonation plant offered on a rental basis. At 667 mg O_3/L, it is estimated that 16.675 kg O_3/h would be required, which would mean an installed CAPEX between 3.5 M CAN$ and 5.7 M CAN$. For larger flowrate, more than one of these units could be mobilized.

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

Nitrogen-based contaminants, including SCN^-, free CN^-, WAD CN^-, CNO^-, NH_3-N and NO_2^-, are commonly found in mine impacted water. These contaminants are known to be acutely toxic to aquatic life, even when present in relatively low concentrations, especially due to the high sensitivity of aquatic biota in the Canadian cold climate. For these reasons, these contaminants of concern require careful management on mine sites, and often require the installation of water treatment systems to control their concentrations.

Although there are currently several water treatment technologies available to manage nitrogen-based contaminants, each of these technologies have advantages and drawbacks when applied to mine water. Indeed, wide variations in temperatures, loading rates and flowrates are typical for mine water, which make their treatment challenging for conventional systems. Recent studies and full-scale applications of MBBR seem to indicate that this technology is currently recognized as the BATEA for this particular application. Nevertheless, the MBBR technology also has several limitations when applied to mine impacted water. Notably, bacteria are highly sensitive to changes in temperature and contaminant loading rates, both common characteristics of Canadian mine water.

Acknowledging the need for development of new treatment technologies targeting nitrogenous species in mine water, several innovative approaches have been investigated recently. Among these emerging technologies, the results from recent study showed promising potential of ammonia nitrogen treatment with ozone microbubbles.

To further advance the understanding and the development of potential large-scale applications of this technology, an ozonation pilot unit was designed. Using this equipment, the main objective of this project was to evaluate the performance of ozonation to remove nitrogen-based contaminants in mine water. The specific objectives of this project also included the evaluation of various catalytic material addition (e.g. NaBr, H_2O_2, AC, TiO_2) and the injection method on ozone requirements (e.g. microbubbles pump, Venturi tube), the evaluation of the impact of ozonation on the acute toxicity of mine water, as well as the cost evaluation of a commercial scale ozonation plant.

The experimental phase was divided in two principal activities: the parametric trials and the extended duration trials. The parametric trials were short in nature, with the intent of determining the impact of the injection method (e.g. Venturi tube vs. microbubbles pump), the pH (from 7.5 to 10.5) and the use of catalytic material (e.g. NaBr, H_2O_2, AC, TiO_2) on ozone dosing rate and ammonia nitrogen removal efficiency. During these trials, the removal efficiency of the other nitrogen-based contaminants in the raw water was not systematically monitored. From these trials, similar results were obtained when using a Venturi or a microbubble pump to inject the ozone in the system. Also, the results from these trials demonstrated that a pH of 9.5 and above is required to enable the oxidation of ammonia nitrogen by ozone. This result was expected and is consistent with observations from previous authors on the topic. However, according to these same authors, some of the catalytic material used during the parametric trials should have improved the ammonia removal efficiency of the system. Nevertheless, the results obtained from these trials did not show considerable improvements when using these catalysts.

As for the extended duration trials, they were designed to confirm that the pilot system would reach a steady state regime, after which several samples of the influent and the effluent were sent to the external lab for analysis. The results from these analyses enabled the calculation of several parameters, such as the removal efficiency for the main nitrogen-based contaminants, the stochiometric ozone demand and the ozone utilization efficiency.

During the extended duration trials, SCN^- and NO_2^- were the nitrogenous species on which the ozonation process was the most effective in their removal. Regardless of the ozone dosing rate, removal efficiency of 95% and above was obtained. Removal efficiency observed for CNO^- and NH_3-N were lower than for the other nitrogenous species, with an increase in the ozone injection rate leading to increases in the removal efficiency for these contaminants. With a dosing rate of 2330 mg O_3 per litre of tailing water, removal efficiency of 64% on CNO^- and 80% on NH_3-N was observed.

From the stochiometric ozone demand calculated for each extended duration trials, ozonation utilization efficiency from 25% to 59% were observed. Several explanations were provided to explain the relatively low utilization efficiency observed, including the presence of other oxidable species in the raw water, the loss of ozone to the atmosphere, the overestimation of the ozone dosing rate.

Acute toxicity testing on rainbow trout and *D. magna* was also performed on the raw and treated water of the extended duration trials. But due to mishandling of the samples by the external lab, only the results from the trials on the tailing water are available. These results show that the raw water was acutely toxic to both rainbow trout and *D. magna.*, with LC50 (95%) values of respectively 35.4 and 29.4. The ozonation treatment aggravated this situation, with the largest dose of ozone (2330 mg O_3/L) resulting in the most toxic effluent (LC50 (95%) of 13.6 and 8.22 for rainbow trout and *D. magna*, respectively). Potential explanations such as the presence of dissolved ozone, formaldehydes, acetaldehydes, bromate, chlorate and copper in the effluent were identified.

The results obtained during the parametric and the extended duration trials were also used to develop cost estimate curves for the CAPEX and OPEX of a commercial scale ozonation plant. To produce these curves, several assumptions were made and documented. These cost estimates were then compared to available data on MBBR systems. With both the installed CAPEX and the OPEX within the same order of magnitude as an MBBR system, the use of an ozonation system to treat nitrogen-based contaminant appears competitive with the current BATEA. However, the total flowrate of the system, as well as the cost of the electricity, have considerable impact on the cost of an ozonation system. Finally, the TOTEX of a commercial scale ozonation plant was also presented.

Moreover, the aim of this project was to evaluate the performance of ozone as a standalone technology to treat nitrogen-based contaminants in mine water. However, combining this ozone with other technologies such as ion exchange or reverse osmosis could show some advantages. By having a pre-treatment that increases the concentration of nitrogen-based contaminants, it is likely that ozone utilization efficiency would be increased.

Nevertheless, this study progressed the knowledge on the ozonation potential for further full-scale applications to treat nitrogen-based contaminants in mine impacted water. However, additional research is still required. Since the ultimate goal of treating these contaminants is to reduce the acute toxicity of mine water (given the current Canadian and international regulations), further investigation on the effect of ozonation on this toxicity is recommended.

Also, since the ozone dosing rate substantially impact the cost of commercial scale ozonation plants, new research to improve the ozone utilization efficiency is recommended. The potential cost reduction using catalysts during the ozonation reaction shows great prospects and should be further investigated.

As a final note, valuable information was acquired during the execution of this project. Some of this information was new and unexpected, while some should have already been known, and mistakes could have been avoided. As such, a list of the major “lessons learned” is left below for those who would be interested in carrying out similar experiments in the future.

- Achieving high ozone mass transfer is key to enabling economical viability of ozonation processes. A strong emphasis on maximizing this mass transfer during the design of laboratory, pilot and full-scale apparatus is required;
- Potential interference of CNO^- when samples for NH_3-N are preserved with H_2SO_4 should be closely monitored;
- Daily analysis on SCN^-, CNO^-, free and WAD CN^- should be done on the raw water;
- Scaling formation when increasing the pH of a tailing water saturated with $CaCO_3$ can be expected. Testing apparatus should be designed accordingly, while considering the addition of a softening step, or antiscalants, upstream of the ozone contactors. Pre-treatment of the carbonate and bicarbonate could also result in increased ozone utilization efficiency, since they are known scavengers the hydroxyl radicals;
- Actual production of an ozone generator should be validated. An online ozone analyzer and a rotameter on the injection line instead could be used. At the very least, the ambient temperature and humidity should be measured next to the ozone generator and steps should be taken to reduce variations of such temperature;
- The use of an online ozone analysis on the ozone contactor vent, before the ozone destructor, to monitor ozone loss to the atmosphere would also be useful;
- The installation of a cooling system on the pilot unit could enable the stabilization of the temperature between trials, and hopefully reduce the non-reproducibility of the system;
- When testing catalytic materials on real mine water, laboratory trials should be performed first, enabling the preselection of these catalysts;

- External laboratory tasked to perform the acute toxicity testing should be carefully selected and some of the results needing to be discarded could be expected;
- Dissolved ozone must be analyzed in acute toxicity samples before shipment, as well as before and after testing. Formaldehydes, acetaldehydes, bromate, chlorate and copper in shipped sample should also be analyzed. An additional treatment step to remove one or several of these contaminants might also be required.

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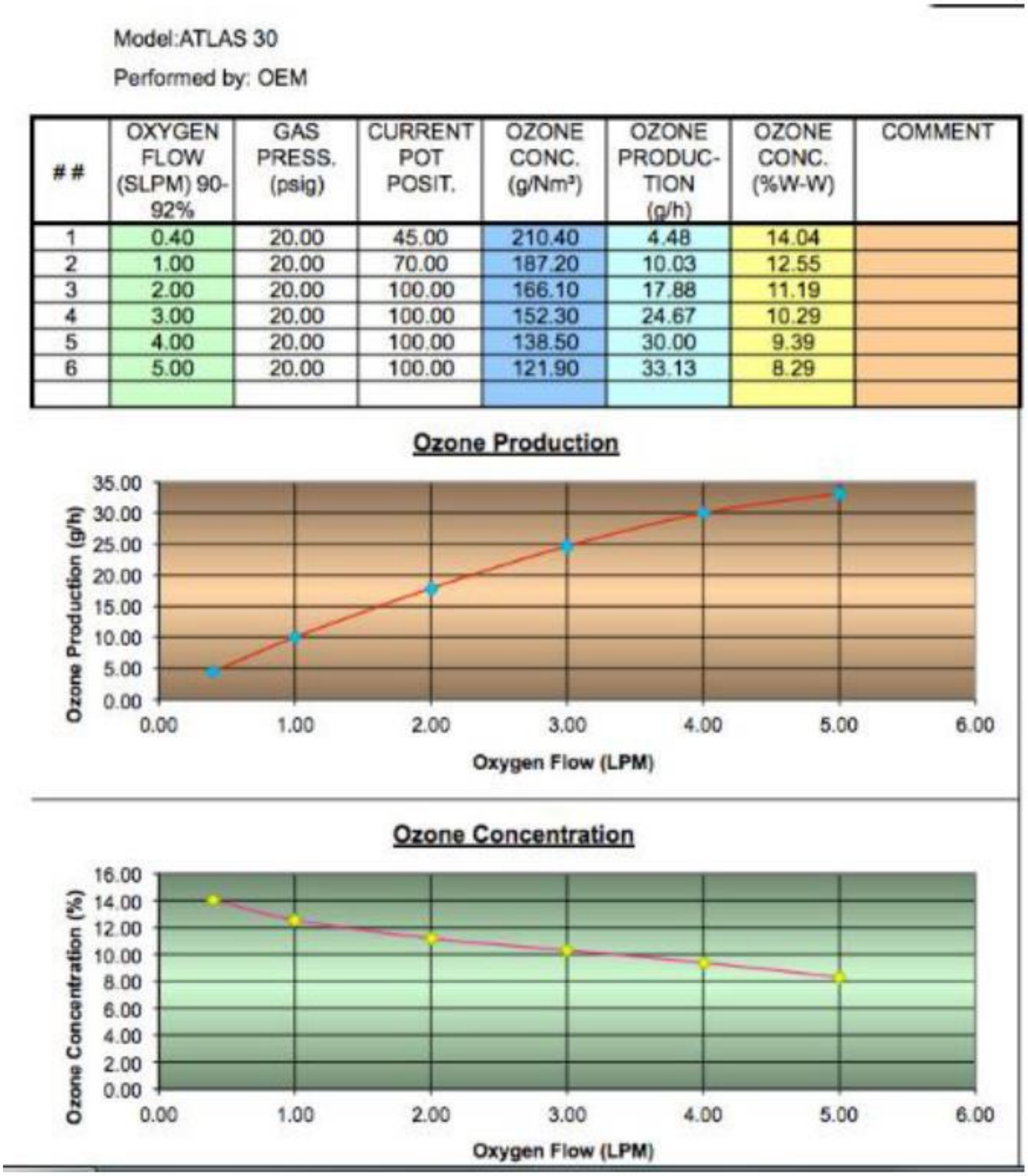
APPENDICES

1. APPENDIX A – PICTURES OF THE PILOT UNIT

Picture A : Ozone pilot skid

Picture B: 20’ repurpose container housing the ozone pilot skid

2. APPENDIX B – OZONE GENERATORS PERFORMANCE CHART

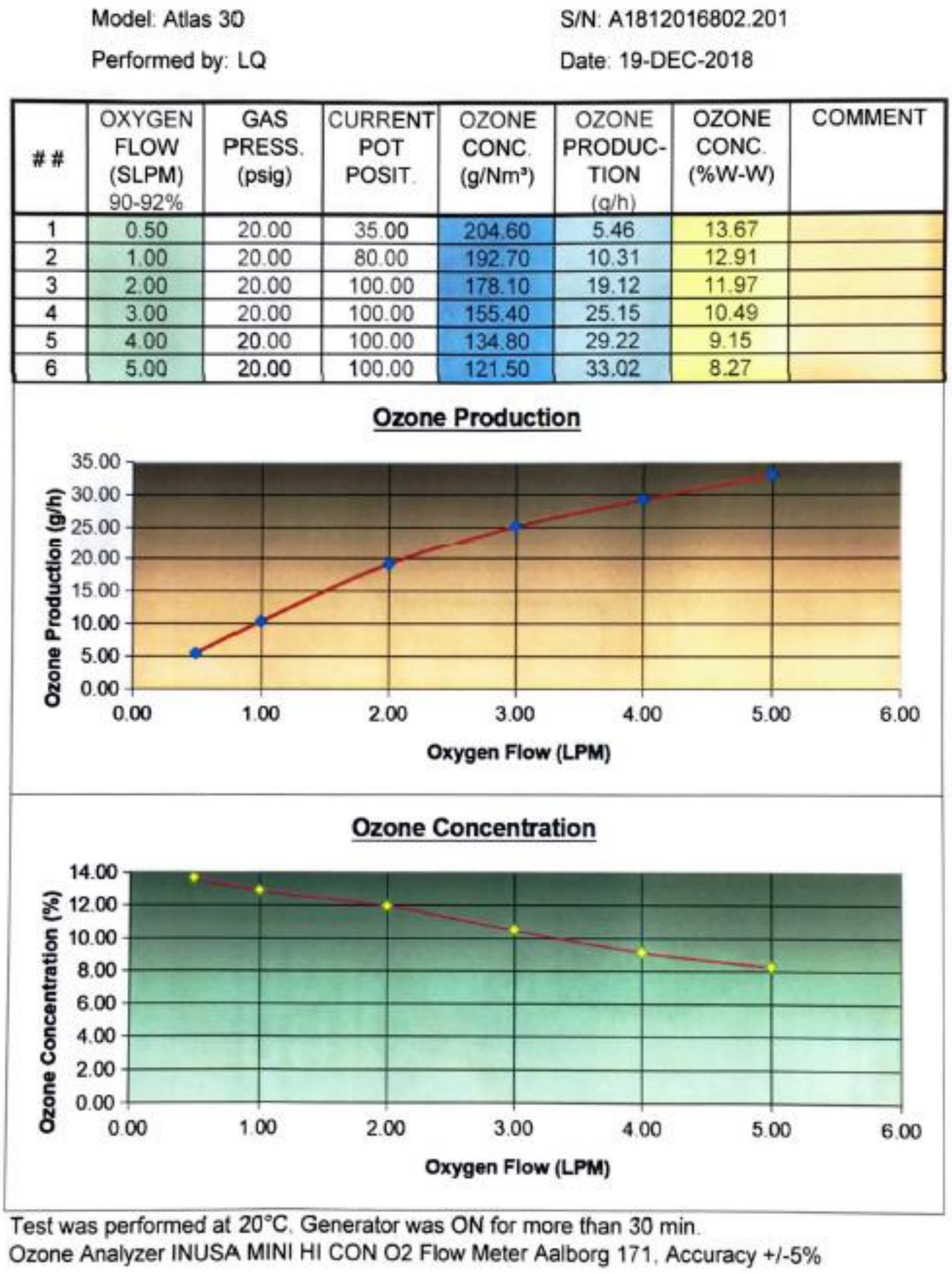


Model:ATLAS 30

Performed by: OEM

##	OXYGEN FLOW (SLPM) 90-92%	GAS PRESS. (psig)	CURRENT POT POSIT.	OZONE CONC. (g/Nm³)	OZONE PRODUC-TION (g/h)	OZONE CONC. (%W-W)	COMMENT
1	0.40	20.00	45.00	210.40	4.48	14.04	
2	1.00	20.00	70.00	187.20	10.03	12.55	
3	2.00	20.00	100.00	166.10	17.88	11.19	
4	3.00	20.00	100.00	152.30	24.67	10.29	
5	4.00	20.00	100.00	138.50	30.00	9.39	
6	5.00	20.00	100.00	121.90	33.13	8.29	

Figure A: Performance chart test of OG-01a



Model: Atlas 30

S/N: A1812016802.201

Performed by: LQ

Date: 19-DEC-2018

##	OXYGEN FLOW (SLPM) 90-92%	GAS PRESS. (psig)	CURRENT POT POSIT.	OZONE CONC. (g/Nm^3)	OZONE PRODUC-TION (g/h)	OZONE CONC. (%W-W)	COMMENT
1	0.50	20.00	35.00	204.60	5.46	13.67	
2	1.00	20.00	80.00	192.70	10.31	12.91	
3	2.00	20.00	100.00	178.10	19.12	11.97	
4	3.00	20.00	100.00	155.40	25.15	10.49	
5	4.00	20.00	100.00	134.80	29.22	9.15	
6	5.00	20.00	100.00	121.50	33.02	8.27	

Test was performed at 20°C. Generator was ON for more than 30 min.
Ozone Analyzer INUSA MINI HI CON O2 Flow Meter Aalborg 171, Accuracy +/-5%

Figure B: Performance chart of OG-01b.

3. APPENDIX C – DATA COLLECTION LOG SHEET

ASDR

Document title: Logsheet Pilot UQAT
Prepared by: Pascal Marcotte, P.Eng.
Date: 2019-08-15

▓ Reading every between + before and after adjustment
░ Reading before adjustment
Reading at the beginning of each shift

Date	▓	▓	▓	▓
Hour	▓	▓	▓	▓
Operator initials	▓	▓	▓	▓
O3 dosing point (VE-01 or PP-01)	▓	▓	▓	▓
VE-01 bypassed (Y/N)	▓	▓	▓	▓
RX-03 bypassed (Y/N)	▓	▓	▓	▓
Hydraulic retention time (min)	▓	▓	▓	▓
SP_INF pH (units)				
SP_INF Temp. (°C)				
SP_INF NH3 spectro (mg N/L)				
SP_INF COD (mg/L)				
SP_INF ORP (mV)				
SP_INF Cond. (mS/cm)				
SP_INF Turbidity (NTU)				
SP_EFF pH (units)	▓	▓	▓	▓
SP_EFF Temp. (°C)	▓	▓	▓	▓
SP_EFF NH3 spectro (mg N/L)	▓	▓	▓	▓
SP_EFF COD (mg/L)	░	░	░	░
SP_EFF ORP (mV)	░	░	░	░
SP_EFF Cond. (mS/cm)	░	░	░	░
SP_EFF Turbidity (NTU)	░	░	░	░
Ambient temp reading (°C)	▓	▓	▓	▓
TI-01 reading (°C)	▓	▓	▓	▓
AIT-01 reading (unit)	▓	▓	▓	▓
AIT-01 setpoint (unit)	▓	▓	▓	▓
AIT-02 reading (ppb)	▓	▓	▓	▓
AIT-03 reading (ppm)	▓	▓	▓	▓
AIT-04 reading (ppm)	▓	▓	▓	▓
AIT-05 reading (unit)	▓	▓	▓	▓
AIT-05 setpoint (unit)	▓	▓	▓	▓
DP-01 speed (%)	▓	▓	▓	▓
DP-02 speed (%)	▓	▓	▓	▓
DP-03 speed (%)	▓	▓	▓	▓
DP-04 speed (%)	▓	▓	▓	▓
DP-05 speed (%)	▓	▓	▓	▓
OG-01 settings (%)	▓	▓	▓	▓
PP-01 speed (%)	▓	▓	▓	▓
MX-01 speed (rpm)	▓	▓	▓	▓
PI-01 reading (psi)	▓	▓	▓	▓
PI-02 reading (psi)	▓	▓	▓	▓
PI-03 reading (psi)	▓	▓	▓	▓
PI-04 reading (psi)	▓	▓	▓	▓
PI-05 reading (psi)	▓	▓	▓	▓
PI-06 reading (psi)	▓	▓	▓	▓
FI-01 reading (L/min)	▓	▓	▓	▓
FI-02 reading (L/min)	▓	▓	▓	▓

Comments:

4. APPENDIX D – COMPLETE WATER CARACTERIZATION

Date	Jun. 26	Jul. 19	Jul. 19	Jul. 23	Jul. 23	Aug. 2	Aug. 2	Aug. 8	Aug. 8
Water (Tailing or Underground)	Tailing	Tailing	Tailing	Tailing	Tailing	Tailing	Tailing	UG	UG
Source (Raw or Treated)	Raw	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated
<u>Field readings</u>									
Ammonia Nitrogen (mg N/L)	32.7	37.2	22.4	36	18.5	32.5	6.5	40.1	18.7
Chemical oxygen demand (mg/L)	204	165	128	162	113	190	85.2	77.5	48.2
Conductivity (mS/cm)	2.98	2.85	3.32	2.85	3.35	2.74	3.68	1.38	1.66
Oxydoredox potential (mV)	419	294	304	280	299	266	262	327	313
pH (units)	8.01	8.24	6.5	8.38	6.56	8.27	7.11	7.86	6.99
Temperature (°C)	22.2	21	25.8	19.7	21.9	23.9	32.4	19.9	25.5
Turbidity (NTU)	34.1	5.54	3.45	8.01	5.11	8.67	6.64	3.22	9.86
<u>External lab analysis - parameters with discharge criteria in the Directive 019 (MDDEP, 2012)</u>									
Arsenic, Dissolved (mg/L)	0.0008	0.0016	0.0008	0.0016	0.0005	0.0018	<0.0005	0.0005	<0.0005
Arsenic, Total (mg/L)	0.0022	0.0016	0.0008	0.0017	0.0009	0.0031	0.002	0.0008	0.0006
Copper, Dissolved (mg/L)	0.2577	0.2553	0.0918	0.2839	0.1095	0.2498	0.2255	0.0082	0.0622
Copper, Total (mg/L)	0.2888	0.2949	0.1235	0.2929	0.1207	0.2888	0.2657	0.0118	0.064
Hydrocarbon (C10-C50) (mg/L)	---	---	---	---	---	---	---	---	---
Iron, Dissolved (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Iron, Total (mg/L)	2.02	0.15	0.16	0.24	0.21	0.23	0.3	0.11	0.1
Lead, Dissolved (mg/L)	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	0.007	<0.0003	<0.0003
Lead, Total (mg/L)	<0.0003	<0.0003	0.0069	<0.0003	0.0014	<0.0003	0.0071	<0.0003	0.0023
Nickel, Dissolved (mg/L)	0.0042	0.0053	0.0028	0.004	0.0011	0.0222	0.0054	0.0035	0.002
Nickel, Total (mg/L)	0.0056	0.0052	0.003	0.0039	0.0012	0.0234	0.0071	0.0061	0.0029
pH (units)	8.26	8.23	7.02	8.3	6.8	8.3	6.53	7.95	6.41
Total Cyanide (mg/L)	0.023	0.117	0.074	0.018	0.07	---	---	0.002	0.006
Total Suspended Solids (mg/L)	107	4	2	10	6	5	6	4	5
Zinc, Dissolved (mg/L)	<0.001	<0.001	0.018	0.003	0.021	<0.001	0.08	0.038	0.035
Zinc, Total (mg/L)	0.007	0.012	0.028	0.002	0.021	0.002	0.092	0.049	0.036

Date	Jun. 26	Jul. 19	Jul. 19	Jul. 23	Jul. 23	Aug. 2	Aug. 2	Aug. 8	Aug. 8
Type (Tailing or Underground)	Tailing	Tailing	Tailing	Tailing	Tailing	Tailing	Tailing	UG	UG
Source (Raw or Treated)	Raw	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated
External lab analysis - nitrogen-based contaminants									
Ammonia Nitrogen (mg N/L)	55.1	59.7	23.4	47	23.3	44.5	11.8	44.5	20.3
Total Kjeldahl Nitrogen (mg N/L)	56.1	47.9	37	52.1	29.6	50.3	10.5	43.4	15.6
Cyanate (mg CNO/L)	103	42.9	30.4	38.2	24.7	45.6	16.4	<0.01	<0.01
Total Cyanide (mg/L)	0.023	0.117	0.074	0.018	0.07	---	---	0.002	0.006
WAD Cyanide (mg/L)	---	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	0.003
Free Cyanide (mg/L)	0.009	---	---	---	---	0.002	0.002	---	---
Thiocyanate (mg/L)	6.31	5.99	0.11	8.21	<0.05	8.74	<0.05	<0.05	<0.05
Nitrate (mg N/L)	18.4	22.2	42.6	23.7	50.6	18.9	52.3	21.9	43.2
Nitrite (mg N/L)	1.2	1.1	0.06	1.12	0.02	1.33	0.03	1.2	<0.01
External lab analysis - other water quality parameters									
Dissolved solids (mg/L)	1540	1478	1712	1569	1792	1442	1740	714	870
Hardness (mg $CaCO_3$/L)	339	318	125	315	109	330	110	351	154
Alkalinity (mg $CaCO_3$/L)	94	84	22	102	11	79	60	82	50
Bicarbonate (mg $CaCO_3$/L)	94	84	22	102	11	79	60	82	50
Carbonate (mg $CaCO_3$/L)	<2	<2	<2	<2	<2	<2	<2	<2	<2
Chemical oxygen demand (mg/L)	21	14	7	19	<7	22	8	<7	<7
Oxydoredox potential (mV)	---	---	---	---	---	348	399	523	393
Ortho-Phosphate (mg P/L)	0.11	---	---	---	---	---	---	---	---
Thiosalts. Total (mg/L)	<2	<2	<2	<2	<2	<2	<2	<2	<2
Bromide (mg/L)	0.87	0.85	0.63	---	---	0.85	1.21	0.11	0.1
Chloride (mg/L)	107	106	109	114	112	116	99.9	48	48.1
Sulfate (mg/L)	950	1054	1168	1052	1225	1166	1074	382	502

Date	Jun. 26	Jul. 19	Jul. 19	Jul. 23	Jul. 23	Aug. 2	Aug. 2	Aug. 8	Aug. 8
Type (Tailing or Underground)	Tailing	Tailing	Tailing	Tailing	Tailing	Tailing	Tailing	UG	UG
Source (Raw or Treated)	Raw	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated
External lab analysis - other metals and elements									
Aluminium, Dissolved (mg/L)	0.007	0.039	0.017	0.05	0.007	0.107	0.013	<0.0005	<0.0005
Aluminium, Total (mg/L)	0.743	0.104	<0.005	0.141	0.105	0.149	0.223	0.008	<0.005
Antimony, Dissolved (mg/L)	0.0004	0.0026	0.0027	0.0026	0.0028	0.0026	0.0032	0.0007	0.0007
Antimony, Total (mg/L)	0.0026	0.0025	0.0017	0.0024	0.0025	0.0029	0.0034	0.0005	0.0004
Barium, Dissolved (mg/L)	0.0255	0.029	0.0153	0.0239	0.0159	0.0225	0.0145	0.0248	0.0099
Barium, Total (mg/L)	0.0325	0.0339	0.0131	0.0247	0.0147	0.0278	0.0234	0.0247	0.0101
Beryllium, Dissolved (mg/L)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Beryllium, Total (mg/L)	0.0008	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Bismuth, Dissolved (mg/L)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Bismuth, Total (mg/L)	0.048	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Boron, Dissolved (mg/L)	0.27	0.48	0.5	0.45	0.48	0.49	0.6	<0.01	<0.01
Boron, Total (mg/L)	0.79	0.46	0.35	0.4	0.43	0.54	0.6	<0.01	<0.01
Cadmium, Dissolved (mg/L)	0.00008	<0.00002	0.0001	<0.00002	<0.00002	<0.00002	<0.00002	<0.00002	<0.00002
Cadmium, Total (mg/L)	0.00018	<0.00002	<0.00002	<0.00002	<0.00002	0.00023	0.00037	0.00012	0.00005
Calcium, Dissolved (mg/L)	129	119	44.9	126	36.8	108	36.2	118	55.7
Calcium, Total (mg/L)	125	118	41.8	116	34.6	122	35.8	114	50.7
Chromium, Dissolved (mg/L)	<0.0006	<0.0006	<0.0006	<0.0006	<0.0006	0.0013	0.0162	0.0009	0.0034
Chromium, Total (mg/L)	0.0077	0.0014	0.0014	0.0023	0.0028	0.0167	0.0221	0.0064	0.0069
Cobalt, Dissolved (mg/L)	0.0076	0.0086	0.0084	0.0108	0.0099	0.0126	0.0076	0.0006	0.0007
Cobalt, Total (mg/L)	0.0085	0.0086	0.0084	0.0102	0.0097	0.0133	0.0084	0.0009	0.0006
Magnesium, Dissolved (mg/L)	5.65	5.61	5.37	6.04	5.65	6.32	5.11	15.1	15
Magnesium, Total (mg/L)	6.3	5.99	5.18	5.95	5.57	6.2	5.13	15.9	13.5
Manganese, Dissolved(mg/L)	0.0065	0.0033	0.004	0.0043	0.0061	0.0017	0.0053	0.1254	0.0668
Manganese, Total (mg/L)	0.0882	0.007	0.005	0.0188	0.0104	0.0099	0.0097	0.1386	0.0733

Date	Jun. 26	Jul. 19	Jul. 19	Jul. 23	Jul. 23	Aug. 2	Aug. 2	Aug. 8	Aug. 8
Type (Tailing or Underground)	Tailing	Tailing	Tailing	Tailing	Tailing	Tailing	Tailing	UG	UG
Source (Raw or Treated)	Raw	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated
External lab analysis - other metals and elements									
Mercury, Dissolved (mg/L)	---	---	---	---	---	0.00004	0.00002	---	---
Mercury, Total (mg/L)	---	---	---	---	---	0.00003	0.00007	---	---
Molybdenum, Dissolved (mg/L)	0.0273	0.0331	0.033	0.0355	0.0378	0.0481	0.0532	0.0193	0.0172
Molybdenum, Total(mg/L)	0.0301	0.0327	0.0301	0.0341	0.0357	0.0478	0.0563	0.0184	0.0167
Potassium, Dissolved (mg/L)	28.8	32.5	98.5	35.9	125	47.4	177	9.05	99.8
Potassium, Total (mg/L)	30.4	34.1	94.3	34.6	119	47.1	181	9.7	98.7
Selenium, Dissolved (mg/L)	<0.0005	0.0026	0.0012	0.0008	<0.0005	0.001	0.0011	<0.0005	<0.0005
Selenium, Total (mg/L)	<0.0005	<0.0005	0.0024	0.0013	<0.0005	0.0009	0.0044	<0.0005	<0.0005
Silica, Dissolved (mg/L)	5.98	8.94	9.33	8.93	9.17	10.8	11.9	17	17.7
Silica, Total (mg/L)	3.81	9.71	8.79	8.54	8.9	11.3	12.8	18.1	16.9
Silver, Dissolved (mg/L)	<0.0001	0.0004	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Silver, Total (mg/L)	<0.0001	0.0004	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Sodium, Dissolved (mg/L)	362	398	489	463	590	509	713	42.5	154
Sodium, Total (mg/L)	376	423	504	442	577	502	732	44.7	140
Tellurium, Dissolved (mg/L)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Tellurium, Total (mg/L)	0.0047	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Tin, Dissolved (mg/L)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Tin, Total (mg/L)	0.005	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Titanium, Dissolved (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Titanium, Total (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Uranium, Dissolved (mg/L)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Uranium, Total (mg/L)	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Vanadium, Dissolved (mg/L)	0.0007	0.0009	<0.0005	0.001	0.0008	0.0009	<0.0005	0.0011	0.0009
Vanadium, Total (mg/L)	0.0025	0.0015	0.0011	0.0012	0.0011	0.0013	0.0018	0.0016	0.0008

5. APPENDIX E – PICTURE OF BUBBLE FORMATION FROM EXPOSING MINERAL DEPOSITION TO 5% HCL