Montana Tech Library Digital Commons @ Montana Tech

Graduate Theses & Non-Theses

Student Scholarship

Spring 2015

Nitrogen Removal in Biological Wastewater Treatment Plant

Courtney Greyn Montana Tech of

Follow this and additional works at: http://digitalcommons.mtech.edu/grad_rsch Part of the <u>Environmental Engineering Commons</u>

Recommended Citation

Greyn, Courtney, "Nitrogen Removal in Biological Wastewater Treatment Plant" (2015). *Graduate Theses & Non-Theses.* 23. http://digitalcommons.mtech.edu/grad_rsch/23

This Thesis is brought to you for free and open access by the Student Scholarship at Digital Commons @ Montana Tech. It has been accepted for inclusion in Graduate Theses & Non-Theses by an authorized administrator of Digital Commons @ Montana Tech. For more information, please contact sjuskiewicz@mtech.edu.

NITROGEN REMOVAL IN A BIOLOGICAL WASTEWATER TREATMENT PLANT

by

Courtney Greyn

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science in Environmental Engineering

Montana Tech

2015



Abstract

Wastewater treatment and disposal is an integral part of mining operations. Water must be carefully managed to prevent waterborne contaminants from entering the surrounding environment. Mining companies rely on regulatory compliance and social acceptance to continue operations. The Stillwater Mining Company operates two underground mines in southern Montana, the Stillwater Mine and the East Boulder Mine, to extract platinum group metals from the J-M Reef geological formation. The East Boulder Mine operates an on-site wastewater treatment plant to remove waterborne contaminants from the water pumped to the surface from the underground mining operations. The main contaminant of concern at the East Boulder Mine is nitrate. The nitrate is a residue of blasting operations and is highly soluble in water. This thesis research focuses on analyzing the current nitrogen removal efficiencies by the wastewater treatment operations to identify abnormalities and recommend operational adjustments to remedy atypical results.

The nitrogen removal efficiencies were investigated using weekly wastewater treatment plant samples conducted for compliance purposes. The examination of this data identified anomalies in the nitrification and denitrification treatment processes. The initial denitrification treatment was found to have increasing ammonium concentrations in the effluent. This ammonium increase is unexpected and the cause is cannot be identified with the currently available data. A second anomaly from the data analysis is the difference in treatment performance between the two Moving Bed Biofilm Reactors (MBBRs). The Moving Bed Biofilm Reactors utilize nitrification and denitrification treatment cells to remove forms of nitrogen from the wastewater. The two systems are identical, yet one MBBR averages 2.8 times greater Total Kjehdahl Nitrogen effluent concentrations than its counterpart. This finding warrants further investigation into possible differences in aeration and mixing rates in the reactors. Treatment modeling of the existing treatment system was attempted to understand these abnormalities but could not be executed with the available data.

This research identified gaps in sampling methods, monitoring capabilities, and sample analysis. These gaps could be easily remedied with relatively low costs. The additional data gained by implementing the recommendations could provide enough additional data to better troubleshoot the treatment abnormalities identified by this research.

Keywords:

Biological wastewater treatment, mine wastewater, nitrification, denitrification, fluidized bed reactor, moving bed biofilm reactor

Dedication

I wish to thank my parents for all of their love and support throughout my studies. Without their confidence in me, my educational success would not have been possible.

Acknowledgements

I wish to acknowledge and thank Dr. Bill Drury for being my thesis advisor and for taking the time to assist me with my thesis. I also wish to thank Dr. Kumar Ganesan and Dr. Butch Gerbrandt for taking the time to be on my thesis committee and advising me throughout my undergraduate and graduate studies. I would like to thank Stillwater Mining Company for providing a thesis research topic and all of their assistance along the way. I finally wish to thank Montana Tech for the financial support to continue my education which allows me to be a successful professional upon graduation.

Table of Contents

ABSTRACT		II
DEDICATION		III
ACKNOWLEDGE	MENTS	IV
TABLE OF CONTI	ENTS	v
LIST OF TABLES .		VII
LIST OF FIGURES	S	VIII
LIST OF EQUATION	ONS	x
GLOSSARY OF TE	ERMS AND ACRONYMS	XI
GLOSSARY OF SY	YMBOLS	XII
1. INTRO	DUCTION	1
2. Wast	EWATER TREATMENT PLANT OVERVIEW	5
2.1.	Wastewater Treatment Plant Design	5
2.2.	Effluent Discharge	
3. Дата	Analysis	14
3.1.	Available Data	
3.2.	Data Organization and Selection	15
3.3.	Interpretation of Nitrogen Data	
4. Treat	MENT MODELING	19
4.1.	Modeling of the Existing Moving Bed Biofilm Reactors	
4.2.	Modeling of a Fluidized Bed Reactor	21
4.3.	Stoichiometry	27
5. Discus	SSION	
6. Conci	LUSIONS	

7.	RECOMMENDATIONS	88
REFEREN	CES CITED	10
APPENDI	X A: ADDITIONAL WTP SAMPLING RESULTS4	12
APPENDI	X B: LIST OF FBR EQUATIONS	;3
APPENDI	X C: FBR CALCULATIONS	6

List of Tables

Table I: Effluent Water Quality Standards (Montana Department of Environmental Quality,	
2000)	
Table II: Weekly Sample Points and Locations	
Table III: Nitrogen Analysis Conducted14	
Table IV: 2014 Flow and Nitrogen Concentration Summary17	
Table V: FBR Nitrification Parameters (Rittmann & McCarty, 2001)	
Table VI: FBR Denitrification Parameters (Rittmann & McCarty, 2001)	
Table VII: Required Order of FBR Calculations 26	
Table VIII: Summary of FBR Modeling Results	
Table IX: Nitrification Stoichiometry Parameters 28	
Table X: Denitrification Stoichiometry Parameters	
Table XI: Summary of Stoichiometry and Observed Nitrogen Concentrations	
Table XII: Nitrification FBR Calculations 56	
Table XIII: Denitrification FBR Calculations 57	

List of Figures

Figure 1: Mine Site and East Boulder River (Google Earth)	2
Figure 2: Basic Nitrogen Cycle (Bernhard, 2010)	5
Figure 3: WTP Flow Diagram	6
Figure 4: Cloth Filter Design	8
Figure 5: MBBR Layout and Flow Path	9
Figure 6: MBBR Media Shape (not to scale)	10
Figure 7: MBBR Cells during Construction	12
Figure 8: Fully Operational MBBR 2 Cells	12
Figure 9: WTP Facility Overview (Google Earth)	13
Figure 10: TIN Concentration Trend from 2008 through 2014	15
Figure 11: TIN Concentration Trend for 2014	16
Figure 12: Average Nitrogen Concentrations	18
Figure 13: FBR Schematic	22
Figure 14: MBBR Effluent TKN Concentrations	34
Figure 15: Concentrations of Nitrogen at UTAW	42
Figure 16: Concentrations of Nitrogen at UTAW-A	43
Figure 17: Concentrations of Nitrogen at TAW-A2	44
Figure 18: Concentrations of Nitrogen at TAW-A	45
Figure 19: Concentrations of Nitrogen at TAW-A2	46
Figure 20: Concentrations of Nitrogen at TAW-A	47
Figure 21: Concentrations of Ammonia-Ammonium as Nitrogen	48
Figure 22: Concentrations of Nitrate-Nitrite as Nitrogen	49

Figure 23: Concentrations of Total Inorganic Nitrogen as Nitrogen	50
Figure 24: Concentrations of Total Kjehdahl Nitrogen as Nitrogen	51
Figure 25: Concentrations of Total Nitrogen	52

List of Equations

Equation (1)	7
Equation (2)	24
Equation (3)	24
Equation (4)	24
Equation (5)	27
Equation (6)	

Glossary of Terms and Acronyms

Term	Definition
SMC	Stillwater Mining Company
WTP	Wastewater Treatment Plant
MPDES	Montana Pollutant Discharge Elimination System
DEQ	Department of Environmental Quality
MBBR	Moving Bed Biofilm Reactor
TIN	Total Inorganic Nitrogen
TKN	Total Kjehdahl Nitrogen
Nitrification	An oxic process in which bacteria oxidize the ammonia in wastewater to
	nitrite and then to nitrate
Denitrification	An anoxic process in which bacteria reduce the nitrate and nitrite ions in
	water to nitrogen gas
Ammonification	A process where decomposer bacteria convert organic nitrogen to ammonia
FBR	Fluidized Bed Reactor

Glossary of Symbols

Symbol	Definition
a	Specific surface area
aV	Total biofilm surface area
b	Endogenous-decay coefficient
b'	Overall biofilm-loss coefficient
b _{det}	Biofilm specific detachment coefficient
D	Molecular diffusion coefficient in water
D_f	Molecular diffusion coefficient of the substrate in the biofilm
d_p	Diameter of solid medium
f_d	Biodegradable fraction of biomass
f_e	Net yield of electron donor utilized for energy production
f_s	Net yield of electron donor utilized for cell synthesis
f_s^{o}	Theoretical yield of electron donor
8	Gravitational constant
J	Substrate flux
J^*	Dimensionless flux
Κ	Concentration giving one-half the maximum rate
<i>K</i> *	Compares external mass transport to the maximum internal utilization and
	transport potential
L	Thickness of the effective mass transfer boundary layer
L_{f}	Biofilm thickness
Q	Flow rate
\hat{q}	Maximum specific rate of substrate utilization
R	Overall stoichiometric reaction
R_a	Electron acceptor half-reaction
R_c	Cell half-reaction
R_d	Electron donor half-reaction
Re_m	A modified Reynolds number
S	Final concentration of the rate-limiting substrate
S^*	Dimensionless substrate concentration normalized to K
Sc	Schmidt number
S_{min}	Minimum substrate concentration
$S_{min}*$	Represents the substrate growth potential
S^o	Initial concentration of the rate-limiting substrate
S_s*	Dimensionless substrate concentration as the biofilm/liquid boundary
и	Superficial flow velocity
V	Total reactor volume
X_{f}	Active-biomass density within the biofilm
Y	True yield for cell synthesis
α	Empirical function of S _{min} *
β	Empirical function of Smin*
З	Porosity of medium bed
Θ	Hydraulic residence time
Θ_x	Solids retention time

ρ	Density
σ	Liquid shear stress
Ψ	Pore shape factor

1. Introduction

Wastewater treatment and disposal are integral parts of mining operations. Water must be carefully managed to prevent waterborne contaminants from entering the surrounding environment. Mining companies rely on regulatory compliance and social acceptance to continue operations.

The type of wastewater treatment at mining operations depends on the waterborne contaminants generated from on-site activities. A common contaminant of concern for underground mining operations is nitrate (NO_3^-). Nitrate is a residue of blasting operations. Due to it being highly soluble in water, nitrate is transported from the underground operations to the surface as water is pumped out of the mine.

The Stillwater Mining Company (SMC) operates two underground mines in southern Montana, the Stillwater Mine and the East Boulder Mine, where platinum group metals are mined from the J-M Reef geological formation (Stillwater Mining Company, 2015). The East Boulder Mine is located south of McLeod, Montana and is the basis for this research. The mine must comply with all applicable regulatory requirements including wastewater effluent discharge standards. The East Boulder Mine has been issued a Montana Pollutant Discharge Elimination System (MPDES) permit by the Montana Department of Environmental Quality (DEQ) for all wastewater discharged from the mine site to either surface water or groundwater.

The East Boulder Mine received its MPDES permit to discharge treated effluent water effective August 1, 2000 (Montana Department of Environmental Quality, 2000) and the mine began commercial production in 2002. The MPDES permit allows two available discharge outfalls for treated adit water and unaltered groundwater. One outfall discharges to the East Boulder River, which borders the mine site, and the second outfall discharges to a percolation pond where the effluent infiltrates to groundwater in an alluvial aquifer. Figure 1 shows the mine site and the adjacent East Boulder River. The red line represents the approximate site boundary and the blue line shows the East Boulder River.



Figure 1: Mine Site and East Boulder River (Google Earth)

The percolation pond outfall (Figure 1) is currently the only outfall being utilized for discharge. The East Boulder River outfall is only to be used if the percolation pond is unavailable. The MPDES permit requires that the percolation pond has a 150 percent percolation capacity based on the anticipated flow rates of treated adit water and unaltered groundwater.

The MPDES permit states discharge limits regarding flow, suspended solids, nutrients, and temperature increases. The effluent standards in the MPDES permit are shown in Table I.

Further information regarding the calculation of the limits listed in Table I is available in the

permit.

	Concentration (mg/L)		
Parameter	30-Day	Instantaneous	
	Average	Maximum	
Flow (gpm)	737.0000	1105.0000	
Total Suspended Solids (TSS)	20.0000	30.0000	
Calculated Instream Temperature Increase			
(°F)	1.0000	1.5000	
Total Ammonia as N	0.7700	1.1600	
Phosphorous, Total as P	0.1000	0.1500	
Calculated Instream Phosphorous Increase,			
Jul 15 to Oct 15, Total as P	0.0010	0.0015	
Calculated Instream Phosphorous Increase,			
Oct 16 to Jul 15, Total as P	0.0030	0.0045	
Cadmium, Total Recoverable	0.0014	0.0021	
Chromium, Total Recoverable	0.0500	0.0750	
Copper, Total Recoverable	0.0080	0.0120	
Iron, Total Recoverable	0.4300	0.6500	
Lead, Total Recoverable	0.0010	0.0015	
Manganese, Total Recoverable	0.1900	0.2800	
Nickel, Total Recoverable	0.0240	0.0360	
Zinc, Total Recoverable	0.0300	0.0450	

 Table I: Effluent Water Quality Standards (Montana Department of Environmental Quality, 2000)

Additional water quality and contaminant limits are listed in the MPDES permit as

follows:

- The effluent pH is to remain between 6 and 9 standard units.
- The total calculated nitrogen load is not to exceed a daily maximum of 30 pounds per day.
- There is to be no discharge of floating solids or visible foam in the effluent other than in trace amounts.

The most applicable standard to this research is the total calculated nitrogen load that is not to exceed a daily maximum of 30 lb/day. Compliance with this limit is verified by sampling

the wastewater treatment plant effluent weekly and by sampling on a monthly basis a series of groundwater monitoring wells located at the end of the mixing zone established for the percolation pond.

Currently, the mine is in compliance with all effluent standards. However, there have been intermittent events of increased ammonia concentrations observed in the treated effluent. Additionally, the MPDES permit is soon to be re-issued and may contain lower nitrogen limits. Nitrogen limits for the new permit have not yet been determined by the DEQ (Kenning, 2015). Another reason to analyze the WTP for its nitrogen removal capability is that nitrogen loading to the WTP may increase because of future mine operations. The objective of this thesis is to analyze the current treatment system at the East Boulder Mine to identify abnormalities which could be a cause of undesirable increases in ammonia concentrations. If causes are identified, recommendations to remedy the situation through operational adjustments will be suggested.

2. Wastewater Treatment Plant Overview

The SMC East Boulder Mine operates a biological wastewater treatment plant (WTP) on-site to treat the wastewater generated from the mining and milling operations. The current WTP design utilizes settling, nitrification, and denitrification processes to reduce nitrogen and suspended solid concentrations in the wastewater.

2.1. Wastewater Treatment Plant Design

The WTP consists of five treatment stages that reduce nitrogen concentrations to meet MPDES permit limits. The process uses the natural nitrogen cycle implemented in a bacterial wastewater treatment process. Figure 2 illustrates the basic nitrogen cycle.



Figure 2: Basic Nitrogen Cycle (Bernhard, 2010)

The following sections will detail the five treatment stages. A conceptual illustration of the WTP design and stages is located in Figure 3.



Figure 3: WTP Flow Diagram

2.1.1. Clarifier and Cloth Filters

A clarifier is the first treatment stage, in which suspended solids settle from the wastewater. All of the water collected for treatment passes through the clarifier before a portion is diverted away from treatment and sent to the recycle pond. The average flow to the clarifier ranges from 1,136 L/min to 1,533 L/min depending on the season. The highest flows occur during the late spring and summer months while the lower flows occurring during the winter months. The average flow to the clarifier in 2014 was 1,170 L/min. The clarifier is cylindrical in shape with a height of approximately 5.64 meters and a diameter of 9.30 meters. The total volume of the clarifier is 383.1 cubic meters. The hydraulic residence time of wastewater at a stage during treatment is calculated using Equation 1

$$\theta = \frac{V}{Q} \tag{1}$$

where θ is hydraulic residence time, V is volume, and Q is the flow rate. The hydraulic residence time for the clarifier is 5.46 hours at the 2014 average flow rate.

The flow from the clarifier that is not diverted to the recycle pond passes through three cloth filters in series. The pores in the cloth are 100 microns in diameter. These cloth filters further reduce the suspended solid concentrations from the wastewater. The filters are arranged as three canisters with five filters in each canister. The water flows upward from the base of the canister, passes downward through the five individual filters and exits through the bottom (Figure 4).



Figure 4: Cloth Filter Design

2.1.2. Rock Cells

The third stage of treatment is rock cells that are the initial denitrification cells in the WTP process. There are three rock cells in parallel. The cells contain rocks that are approximately 30 centimeters in diameter that serve as a biofilm substratum. The average flow to the rock cells in 2014 was 1,045 L/min. Pure methanol is added to the rock cell influent at an average rate of 132 mL/min to provide a carbon and energy source for the bacteria. The rock cells are rectangular in shape with lengths of 9.144 meters, widths of 10.973 meters, and depths of 3.51 meters. However, these cells are filled to a depth of only 2.90 meters, so the volume used for calculations was 291.0 m³ per rock cell.

2.1.3. Moving Bed Biofilm Reactors

The WTP is equipped with two Moving Bed Biofilm Reactors (MBBRs) that are each split into nitrification and denitrification cells representing the fourth and fifth treatment stages

respectively. The MBBRs are designed in parallel with three individual treatment cells in each MBBR. Treatment cells A and B are oxic nitrification cells and treatment cell C is an anoxic denitrification cell (Figure 5).



MBBR 2



Figure 5: MBBR Layout and Flow Path

Water flows through the MBBRs from A to B to C. The flow of treated water from the rock cells is split with calculated average flows of 536 L/min to MBBR 2 and 520 L/min to MBBR 3 during 2014. The MBBR design criteria were obtained from the operations manual (AnoxKaldnes, Inc, 2006) and were based on average influent NH₃-N masses of less than 9.98 kg/day and

NO_x-N (nitrate-nitrite) masses of less than 24.95 kg/day with pH ranging between 6.0 - 9.0 and temperatures ranging $5 - 15^{\circ}$ C.

The MBBR cells are filled with media to provide surface area for biofilm growth. The media are high-density polyethylene cylinders approximately 10 mm in diameter and 7 mm long. The structure of the media was designed to maximize surface area within the small dimensions to provide the greatest surface area per unit of volume. The design of the media is illustrated in Figure 6 (AnoxKaldnes, Inc, 2006). There are approximately one million individual pieces of media per cubic meter.



Figure 6: MBBR Media Shape (not to scale)

The oxic nitrification cells are aerated through grids of diffusers at the bottom of each cell. Oxygen addition provides an oxic environment that promotes the activity of *Nitrosomonas* and *Nitrobacter* bacteria which carry out the two stage nitrification process. *Nitrosomonas* oxidize ammonium (NH_4^+) to nitrite (NO_2^-) while *Nitrobacter* oxidize NO_2^- to nitrate (NO_3^-) (Rittmann & McCarty, 2001).

The nitrification cells are each 5.48 meters long, 4.42 meters wide, and with wall heights of 3.51 meters deep. The liquid depth is only 2.90 meters for a usable volume of 70.24 cubic meters each.

The anoxic denitrification cells are the fifth and final stage of treatment before the WTP effluent is discharged. These anoxic cells are continuously stirred by a single paddle located along the edge of the cell. This paddle mixes the reactor content that causes greater contact between the biofilm-covered media and the water being treated. There are a variety of bacteria which can be classified as denitrifiers including *Proteobacteria*, *Bacillus*, and *Halobacterium* (Rittmann & McCarty, 2001). These bacteria reduce NO₃⁻ to mainly N₂ gas to complete treatment. These bacteria also require a carbon and energy source like methanol be added to ensure a nutrient-rich environment. Methanol is added to the MBBR Cell C influents at an average rate of 63.5 mL/min to Cell 2C and 51 mL/min to Cell 3C.

The denitrification cells are each 9.48 meters long, 5.18 meters wide, and wall heights of 3.51 meters. The denitrification cells are also filled to a depth of 2.90 meters for a usable volume of 142.40 cubic meters.

The MBBR cells are all open to the atmosphere and are built into the ground. A photograph of the MBBR 2 during operation while MBBR 3 was under construction is shown in Figure 7 and an aerial photograph of MBBR 2 operating at full capacity is shown in Figure 8.



Figure 7: MBBR Cells during Construction



Figure 8: Fully Operational MBBR 2 Cells

2.2. Effluent Discharge

The WTP effluent travels by underground pipeline to an on-site percolation pond for discharge. Soil under the percolation pond filters the effluent before the effluent recharges the groundwater in the area. The WTP facilities are shown in Figure 9.



Figure 9: WTP Facility Overview (Google Earth)

3. Data Analysis

3.1. Available Data

A large quantity of data throughout the WTP was obtained from the Stillwater Mining Company. This data includes concentrations of nitrogen in various forms (organic and inorganic), flow rates, temperatures, dissolved oxygen levels, and nutrient additions. Most of the data were nitrogen concentrations from the various treatment stages.

SMC conducts weekly sampling of the WTP effluent to ensure compliance with their MPDES permit. These samples provided data from four locations in the treatment process. The sampling points and location descriptions are summarized in Table II and are also indicated on the WTP diagram in Figure 3.

Table II: Weekly Sample Points and Locations			
Sampling Point	Location Description		
UTAW	Flow between clarifier and cloth filters		
UTAW-A	Flow after convergence from rock cells and before distribution to MBBRs		
TAW-A2	Effluent from MBBR 2 Cell C to percolation pond		
TAW-A	Effluent from MBBR 3 Cell C to percolation pond		

The nitrogen analyses were performed by an independent laboratory. The types of nitrogen quantified during the analyses differed for the various sampling locations (Table III).

Sampling Point	NH ₃ and NH ₄ ⁺	NO ₂ ⁻ and NO ₃ ⁻	TIN	TKN	Total N
UTAW	Yes	Yes	Yes	No	No
UTAW-A	Yes	Yes	Yes	Yes	Yes
TAW-A2	Yes	Yes	Yes	Yes	Yes
TAW-A	Yes	Yes	Yes	Yes	Yes

Table III: Nitrogen Analysis Conducted

Analyses of all relevant forms of nitrogen were performed for all sampling locations other than UTAW. Analyses of non-nitrogenous analytes were also conducted on wastewater samples, but are not reported here because this thesis is focused on nitrogen treatment.

3.2. Data Organization and Selection

The weekly sampling results were provided and included additional, necessary information needed to model nitrogen treatment throughout the plant. This additional information included flow rates at the time of sampling, temperatures, dissolved oxygen concentrations, nitrogen loading rates, and methanol addition rates.

Total Inorganic Nitrogen concentrations in the clarifier effluent have trended downward from 2008 to 2014 (Figure 10).



Figure 10: TIN Concentration Trend from 2008 through 2014

Average flows and concentrations for 2014 were calculated for each of the sampling sites and forms of nitrogen analyzed from samples taken at these sites (Table IV). The averages calculated in Table IV include sampling events from January 1st through September 24th because the replacement of the media pieces for MBBR cells 3C on September 30th and 2C on October 23rd caused the remainder of the 2014 data to be atypical.

All of the following calculations were done using the January – September 24th 2014 averages because these recent data provide the most representative conditions of the WTP (Figure 11).



Figure 11: TIN Concentration Trend for 2014

	Flow	NH ₃ and NH ₄ +	NO ₂ ⁻ and NO ₃ ⁻	TIN	TKN	Total N
Sample	(L/min)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
UTAW	1,192	2.305	25.654	27.958	N/A	N/A
UTAW-A	1,063	2.925	16.949	19.874	2.149	19.100
TAW-A2	543	0.759	0.221	0.979	0.992	1.226
TAW-A	528	0.386	0.557	0.943	3.756	4.238

Table IV: 2014 Flow and Nitrogen Concentration Summary

3.3. Interpretation of Nitrogen Data

Graphs of the nitrogen concentrations throughout the WTP were used to identify trends in nitrogen conversion and the associated operating parameters. The following sections highlight the most important graphs utilized for the selection of treatment modeling.

3.3.1. Forms of Nitrogen Present

The average nitrogen concentrations (Table IV) represent all of the analyzed forms of nitrogen collected during weekly sampling events. A graphical representation of these averages is located in Figure 12. Total Inorganic Nitrogen is the sum of the NH₃ and NH₄⁺ and NO₂⁻ and NO₃⁻. The Total Kjeldahl Nitrogen (TKN) is the sum of organic nitrogen, NH₃ and NH₄⁺. Total Nitrogen is the sum of NO₂⁻ and NO₃⁻ and TKN in the system. Additional graphical representations of the sampling results for 2014 are located in Appendix A.



Figure 12: Average Nitrogen Concentrations

Ammonia-ammonium concentrations greatly increased between the influent to (UTAW) and the effluent from (UTAW-A) the rock cells (Figure 12). The difference between TKN and Total N effluent concentrations between MBBR 2 (TAW-A2) and MBBR 3 (TAW-A) is also atypical. These issues are evaluated in the Discussion.

4. Treatment Modeling

Two process modeling efforts were performed by a series of calculations in order to further our understanding of the existing MBBRs and to provide a design for an alternative nitrogen removal process. The alternative treatment process is a Fluidized Bed Reactor (FBR). Nitrogen transformation stoichiometries were determined to supplement the modeling efforts.

The series of calculations performed calculates a mass balance of nitrogen during treatment and predicts the results of chemical reactions. The existing MBBRs could not be calculated as such due to being proprietary technology. The FBR treatment process was selected to model the existing MBBRs because this treatment technology is the most similar of the available treatment modeling calculations.

4.1. Modeling of the Existing Moving Bed Biofilm Reactors

The East Boulder Mine has moving bed biofilm reactors (MBBRs), in which plastic packing pieces are suspended and moved in the water. These MBBRs remove nitrogen from mine water through nitrification followed by denitrification. There are two process trains of MBBRs. Each train consists of two nitrification reactors in series, followed by a denitrification reactor. The nitrification reactors are aerated by diffused air. The denitrification reactors are mixed but not aerated.

An attempt was made to model the MBBRs that are in use at the Mine, using the procedure for analysis of biofilm reactors developed by Rittmann and McCarty (2001). This model analysis was based on the FBR model design because an FBR is the closest treatment system to the MBBRs. Information on the existing system was used in the computations. AnoxKaldnes packing pieces used in the MBBRs have a specific area and the appropriate specific areas for the nitrification reactor and denitrification reactor were used (AnoxKaldnes, Inc, 2006). A flow rate of 530 L/min (140 gpm) per train was used in modeling, with a water temperature of 10°C. Stoichiometric and kinetic coefficients that were used were those reported in the section on the fluidized bed reactor design (Section 4.2). The influent NH_4^+ –N and NO_3^- – N concentrations were the actual average effluent concentrations from the rock cells.

The overall biofilm loss coefficient, *b*', and the mass transfer boundary layer thickness, *L*, used in modeling the existing MBBR were different than those used in modeling the proposed FBR system. Obtaining values for the overall biofilm-loss coefficient *b*' was problematic. The biofilm-loss coefficient is the sum of the endogenous decay rate *b* and the biofilm specific detachment coefficient *b_{det}*. No procedure for estimation of *b_{det}* in MBBRs like the AnoxKaldnes MBBRs could be found in the literature. A request for information on *b_{det}* was made to AnoxKaldnes by email, but no reply was received (Drury, 2015). Empirically-determined values for *b*' of 2.75 d⁻¹ for a MBBR nitrification reactor and 1.0 d⁻¹ for a denitrification reactor were found in the literature (Plattes, Henry, & Schosseler, 2008). These values are consistent with the values of up to 7.4 d⁻¹ measured in a two-phase fluidized bed reactor (Chang, Rittmann, Amar, Ehlinger, & Lesty, 1991).

The nitrification reactors model could not find a solution for any b' of 0.13 d⁻¹ or greater with an L of 1 µm. With this value for b', the value for b_{det} would be 0.05 d⁻¹ if the b for nitrifiers is its typical value of 0.08 d⁻¹ (Rittmann & McCarty, 2001). Thus, this b_{det} is too low to be realistic. This magnitude of b_{det} is what occurs in unmixed nitrification biofilm reactors when the nitrifiers are deep within a multispecies biofilm, and they are partially protected from detachment (Rittmann & McCarty, 2001). Values for b_{det} in MBBRs should be much higher because the collisions of moving packing pieces knock many bacteria off of the pieces. The model could not find a solution for the second reactor in series even with the optimistic b' of 0.1 d⁻¹. The model did no better with the denitrification reactor. The lowest effluent NO₃⁻ –N concentration that could be computed by the model, with a *b*' of 0.1 d⁻¹ and $L = 1 \mu m$, was 1.1 mg/L, which is twice the effluent concentration from the existing facility. The denitrification reactor model could not find a solution for any *b*' above 0.1 d⁻¹ and an *L* of 1 μm . A *b*' of 0.1 d⁻¹ is unrealistically low because *b* is typically 0.05 d⁻¹ and the typical value for *b_{det}* for denitrifiers in a stationary (non-MBBR system) biofilm is 0.05 d⁻¹.

The effective mass transfer boundary layer *L* is a function of the turbulence in a biofilm reactor. As with *b*', no procedure for estimation of *L* in MBBRs like these could be found. The lowest *L* utilized during modeling was 1 μ m. As mentioned above, the model produced no useable solutions with an *L* of 1 μ m. Larger values for *L* produced higher effluent concentrations.

The model will not predict accurate results if the coefficient values used are inaccurate. Values for L and b_{det} are unique to each type of MBBR, and apparently AnoxKaldnes considers such values for their reactors to be proprietary information. The stoichiometric and kinetic parameters obtained from the literature might predict a significantly slower reaction rate than what occurs in the real system which could explain why the model did not work with reasonable values for b' and L. There may be other, unidentified reasons for why the model could not predict the effluent concentrations produced by the existing system.

4.2. Modeling of a Fluidized Bed Reactor

Because the models attempted did not predict accurate results for modeling the existing MBBRs, a hypothetical model of a Fluidized Bed Reactor (FBR) was generated. An FBR is a reactor where small biofilm carrier particles are kept suspended by friction between the carrier particles and the water which is flowing upward. This scheme produces a large surface area to volume ratio, and large pores that will not clog. Fluidized beds require the density of the media

to be greater than the density of water. Examples of commonly used FBR media include sand, glass beads, coal, and activated-carbon particles (Rittmann & McCarty, 2001). This type of treatment is similar in function to that of the existing MBBRs in terms of small reactor volumes and low hydraulic detention times. A schematic of a typical FBR reactor is illustrated in Figure 13 (Rittmann & McCarty, 2001).



Figure 13: FBR Schematic

The FBR modeled for the situation at the East Boulder Mine requires two reactors. The first reactor is a nitrification system followed in series by a second denitrification system. The influent ammonia-ammonium concentration used in the FBR model is the 2014 average concentration at the East Boulder WTP at UTAW-A (after the rock cells). The influent nitrate-nitrite concentration used for the denitrification FBR is the 2014 average nitrate-nitrite concentration at UTAW-A plus the nitrate-nitrite produced in the nitrification FBR. The overall effluent goal for the FBR system was 1.09 mg/L of nitrate-nitrite as nitrogen. The initial effluent
goal for the FBR system was 0.50 mg/L of nitrate-nitrite as nitrogen to maintain similar concentrations as the current treatment system. This low of an effluent concentration was not kinetically possible in the FBR system, so 1.09 mg/L represents the lowest achievable effluent nitrate-nitrite as nitrogen concentrations from the FBR. To represent the worst-case conditions for microbial kinetics, the water temperatures used were the average East Boulder WTP water temperatures measured during January and February when the water average temperature of 10°C were the coldest of the year.

All of the calculations involving the FBR design follow the process, parameters, and equations presented in *Environmental Biotechnology: Principles and Applications* (Rittmann & McCarty, 2001). The parameters for the nitrification FBR are listed in Table V.

Parameter	Value	Units
Q	1.50E+06	L/d
\hat{q}	1.70	mg NH4 ⁺ -N/mg VSSa-d
Κ	0.57	mg NH4 ⁺ -N/L
b	0.07	d ⁻¹
Y	0.33	mg VSS _a /mg NH ₄ ⁺ -N
D	1.11	cm ² /d
D_f	0.89	cm ² /d
Bed Expansion	0.25	
$ ho_p$	1.04	g/cm ³
$ ho_w$	0.99	g/cm ³
Diameter	0.10	cm
З	0.46	
и	95,000.00	cm/d
X_{f}	10.00	mg/cm ³
Ψ	1.00	
a	32.40	cm ⁻¹
So	2.88	mg/L
S	0.50	mg/L

Table V: FBR Nitrification Parameters (Rittmann & McCarty, 2001)

The maximum specific rate of substrate utilization, \hat{q} , is adjusted to 10°C by Equation 2

$$\hat{q} = \hat{q}_{T^R} (1.07)^{(T-T^R)} \tag{2}$$

where T^R is any reference temperature (°C).

The endogenous-decay coefficient, b, is adjusted to 10°C by Equation 3

$$b_T = b_{T^R} (1.04)^{(T-T^R)}$$
(3)

where b_{T^R} is any reference endogenous-decay coefficient.

The molecular diffusion coefficient in water, D, is adjusted to 10°C by Equation 4

$$D_T = D_{T^R} \left[\frac{T}{T^R} \left(\frac{\mu_{T^R}}{\mu_T} \right) \right] \tag{4}$$

where D_{T^R} is any reference diffusion coefficient in water.

The molecular diffusion coefficient of the substrate in the biofilm, D_f , is 80% of the molecular diffusion coefficient in water, D (Rittmann & McCarty, 2001).

The same process was completed to obtain the denitrification parameters for the FBR model. The parameters for the denitrification FBR are listed in Table VI.

Parameter	Value	Units
Q	1.50E+06	L/d
Ŷ	3.51	mg NH4 ⁺ -N/mg VSSa-d
K	9.10	mg NH ₄ ⁺ -N/L
b	0.03	d ⁻¹
Y	0.27	mg VSS _a /mg NH ₄ ⁺ -N
D	0.96	cm ² /d
D_f	0.77	cm ² /d
Bed Expansion	0.25	
$ ho_p$	1.04	g/cm ³
$ ho_w$	0.99	g/cm ³
Diameter	0.10	cm
3	0.46	
U	95,000.00	cm/d
X_{f}	40.00	mg/cm ³
Ψ	1.00	
a	32.40	cm ⁻¹
So	19.44	mg/L
S	0.50	mg/L

Table VI: FBR Denitrification Parameters (Rittmann & McCarty, 2001)

These denitrification parameters \hat{q} , b, D, and D_f from (Rittmann & McCarty, 2001) are accurate at a temperature of 20°C, so they were adjusted so that they are accurate at 10°C by using Equations 2, 3, and 4.

The process of calculating the volume and solids retention time of an FBR is outlined in the textbook (Rittmann & McCarty, 2001) and the calculation order is listed in Table VII. The equations for the required FBR calculations are listed in Appendix B.

Calculation	Description
σ	Liquid shear stress
b _{det}	Specific biofilm-detachment loss coefficient
Θ_x	Solids retention time
b'	Overall biofilm-loss coefficient
Smin	Minimum substrate concentration
$S_{min}*$	Represents the substrate growth potential
Re_m	A modified Reynolds number
Sc	Schmidt number
L	Thickness of the effective diffusion layer
	Compares external mass transport to the maximum internal utilization and
<i>K</i> *	transport potential
<i>S</i> *	Dimensionless substrate concentration normalized to K
α	Empirical function of <i>S_{min}</i> *
β	Empirical function of <i>S_{min}</i> *
S_s*	Dimensionless substrate concentration at the biofilm/liquid boundary
J^*	Dimensionless flux
J	Substrate flux
aV	Total biofilm surface area
V	Total reactor volume
L_{f}	Biofilm thickness

Table VII: Required Order of FBR Calculation	S
--	---

The series of calculations listed in Table VII were executed first for the nitrification FBR model and then for the denitrification FBR model. A summary of the pertinent results for the two reactors is listed in Table VIII.

Table VIII: Summary of FBR Modeling Results			
Parameter	Nitrification FBR	Denitrification FBR	
$aV(m^2)$	11,130.260	1,086,718.862	
Expanded $V(m^3)$	3.435	335.407	
Unexpanded $V(m^3)$	2.748	268.326	
Θ (days)	0.002	0.224	
Θ_x (days)	36.915	15.003	
Effluent Nitrate/Nitrite $(mg/L - N)$	0.500	1.090	

Table VIII	Summarv	of FRR	Modeling	Results

The FBR modeling indicates if an FBR with nitrification and denitrification reactors in series were constructed after the rock cells at the East Boulder Mine, similar effluent concentrations would be achieved in a shorter amount of time and in smaller reactor units as the total reactor volumes are decreased by 99% for nitrification and 3% for denitrification when compared to the unexpanded FBR volumes.

4.3. Stoichiometry

Stoichiometric calculations identify the quantities of reactants and products of chemical reactions. Both the nitrification and denitrification reactions require sufficient quantities for sufficient nitrogen removal from the water. A stoichiometric analysis was completed for the nitrification and denitrification processes involved in the treatment stages.

4.3.1. Nitrification Stoichiometry

Nitrification stoichiometry was calculated to predict the concentration of nitrate formed by nitrification during the nitrification process in the first two MBBR cells. As previously stated, the purpose of nitrification is to oxidize ammonium-ammonia nitrogen to nitrite-nitrate nitrogen. The stoichiometric analysis included ammonium-ammonia as the electron donor, water as the electron acceptor, and ammonium-ammonia as the nitrogen source.

Nitrification coefficients were determined after starting with an initial theoretical yield value of $f_s^o = 0.12$ (Rittmann & McCarty, 2001). This represents the portion of the electron donor, ammonium-ammonia, utilized for cell synthesis. However, f_s^o represents the theoretical yield, and a more accurate representation of the electron donor utilized for cell synthesis is represented by the net yield, f_s . The relationship between the theoretical and net yield values for cell synthesis is represented by Equation 5

$$f_s = f_s^o \left[\frac{1 + (1 - f_d)b\theta_x}{1 + b\theta_x} \right]$$
(5)

where f_s is the net yield of the electron donor.

The fraction of electron equivalents that go into energy production, f_e , is equal to $1 - f_s$. Therefore it is understood that $f_s + f_e = 1$ because it is assumed all of the electron equivalents from the electron donor that is utilized go into either cell synthesis and energy production.

Analysis of the nitrification stoichiometry required use of values obtained from the theoretical FBR model (Section 4.2) designed as an alternative to the MBBR treatment stages. Construction of the stoichiometry for the existing MBBR system was not possible because an accurate value for b_{det} , which is necessary for calculating the solids retention time Θ_x , in the MBBRs could neither be obtained nor estimated (see Section 4.1). A summary of the calculated nitrification stoichiometry parameters is listed in Table IX.

Parameter	Value
f_s^o	0.12000
f_d	0.80000
b	0.06575
b _{det}	0.02709
Θ_x	36.91588
f_s	0.05201
fe	0.94799

Table IX: Nitrification Stoichiometry Parameters

The stoichiometric parameters f_s and f_e as well as the half-reactions for ammonium being oxidized to nitrate and oxygen (O₂) being reduced to water were used to provide an overall nitrification reaction.

The overall reaction, R, is developed by Equation 6

$$R = f_e R_a + f_s R_c - R_d \tag{6}$$

where R_a is the electron acceptor half-reaction, R_c is the cell half-reaction, and R_d is the electron donor half-reaction. The half-reactions, intermediate equations, and overall nitrification reaction are listed below. $R_a: 0.25 \text{ O}_2 + \text{H}^+ + \text{e}^- \rightarrow 0.5 \text{ H}_2\text{O}$

 $f_e R_a: 0.236997 \text{ O}_2 + 0.947989 \text{ H}^+ + 0.947989 \text{ e}^- \rightarrow 0.473994 \text{ H}_2\text{O}$

 R_c : 0.05 NH₄⁺ + 0.2 CO₂ + 0.05 HCO₃⁻ + H⁺ + e⁻ → 0.05 C₅H₇O₂N + 0.45 H₂O

 $f_s R_c: 0.002601 \text{ NH}_4^+ + 0.010402 \text{ CO}_2 + 0.002601 \text{ HCO}_3^- + 0.052011 \text{ H}^+ + 0.052011 \text{ e}^- \rightarrow$

 $R_d: 0.125 \text{ NH}_4^+ + 0.375 \text{ H}_2\text{O} \rightarrow 0.125 \text{ NO}_3^- + 1.25 \text{ H}^+ + \text{e}^-$

R: 0.127601 NH₄⁺ + 0.236997 O₂ + 0.010402 CO₂ + 0.002601 HCO₃⁻ →

 $0.002601 C_5 H_7 O_2 N + 0.122399 H_2 O + 0.125 NO_3^- + 0.25 H^+$

The overall reaction, *R*, shows that 0.97962 moles of NO_3^- are produced per 1 mole of NH_4^+ consumed and that 0.02038 moles of organic nitrogen are produced per 1 mole of NH_4^+ consumed during nitrification.

4.3.2. Denitrification Stoichiometry

Denitrification stoichiometry was calculated to predict the amount of denitrification in the final two MBBR cells. As previously stated, the purpose of denitrification is to reduce nitritenitrate nitrogen to nitrogen gas (N_2) released to the atmosphere. Methanol is added to serve as the electron donor and carbon source in this denitrification process. Nitrogen-nitrate serves as the electron acceptor and nitrate serves as the nitrogen source.

Denitrification coefficients were determined after starting with a value of $f_s^o = 0.36$ (Rittmann & McCarty, 2001). The net yield, f_s , for denitrification was also calculated using Equation 5 and the denitrification FBR model parameters. The calculated denitrification stoichiometric parameters are listed in Table X.

Parameter	Value
f_s^{o}	0.36000
f_d	0.80000
b	0.03378
b _{det}	0.06607
Θ_x	15.13657
f_s	0.26257
fe	0.73743

Table X: Denitrification Stoichiometry Parameters

As with the nitrification stoichiometry, a series of calculations is required to produce the overall denitrification stoichiometry which is developed by Equation 6 and outlined below.

 R_a : 0.2 NO₃⁻ + 1.2 H⁺ + e⁻ → 0.1 N₂ + 0.6 H₂O

 $f_e R_a: 0.147487 \text{ NO}_3^- + 0.884921 \text{ H}^+ + 0.737434 \text{ e}^- \rightarrow 0.073743 \text{ N}_2 + 0.442460 \text{ H}_2\text{O}$

 R_c : 0.035714 NO₃⁻ + 0.178571 CO₂ + 1.035714 H⁺ + e⁻ →

 $0.035714 \ C_5 H_7 O_2 N + 0.392857 \ H_2 O$

 $f_s R_c: 0.009377 \text{ NO}_3^- + 0.046887 \text{ CO}_2 + 0.271943 \text{ H}^+ + 0.262566 \text{ e}^- \rightarrow$

 R_d : 0.166667 CH₃OH + 0.166667 H₂O → 0.166667 CO₂ + H⁺ + e⁻

R: 0.156864 NO₃⁻ + 0.166667 CH₃OH + 0.156864 H⁺ →

 $0.009377 C_5 H_7 O_2 N + 0.119780 CO_2 + 0.073743 N_2 + 0.378945 H_2 O_2 N_2 + 0.073743 N_2 + 0.0000 N_2 +$

From the overall reaction, R, it can be calculated that 0.47011 moles of nitrogen gas are produced per mole of NO₃⁻ consumed during denitrification.

4.3.3. Stoichiometry Summary

The stoichiometric calculations were completed using the parameters for the theoretical FBR design. Chemical concentrations from the stoichiometric calculations were compared with the existing MBBR treatment concentrations. A summary of both the calculated concentrations by stoichiometry and the measured concentrations is listed in Table XI.

Calculation	Value	Units
UTAW-A NO_3^- - N (measured)	17.0600	mg/L
NO ₃ ⁻ - N produced by nitrification (calculated)	2.2874	mg/L
Organic – N produced during nitrification (measured)	0.0476	mg/L
NO ₃ ⁻ - N available for denitrification (calculated)	19.2998	mg/L
Average NO ₃ ⁻ - N in TAW-A2 and TAW-A (measured)	0.5700	mg/L
NO ₃ ⁻ - N consumed (calculated)	18.7298	mg/L
Organic – N produced during denitrification (calculated)	1.1197	mg/L
Average TKN in TAW-A2 and TAW-A (measured)	3.2250	mg/L
Total organic – N (calculated)	1.1673	mg/L
Total organic – N (measured)	2.6800	mg/L
Organic – N difference (measured – calculated)	1.5127	mg/L

Table XI: Summary of Stoichiometry and Observed Nitrogen Concentrations

From the stoichiometric analysis, it was determined that the MBBR treatment cells produced more organic nitrogen than what was predicted by stoichiometry. As listed in Table XI, the average measured organic nitrogen from the MBBRs was 2.68 mg/L and the stoichiometry predicted a value of approximately 1.17 mg/L. Therefore the MBBRs are producing approximately 2.3 times higher concentrations of organic nitrogen than predicted.

Greater removal of particulate matter containing nitrogen from the MBBR effluent could significantly decrease the amount of Total Nitrogen in the MBBR effluent. If it is assumed that all the organic nitrogen is in particulate matter (principally bacterial cells), the effect of increased solids-liquid separation on Total Nitrogen can be estimated. Assuming that treatment of the MBBR effluent by sedimentation removes 50% of the particulate matter, sedimentation would remove 0.5 times 2.68 mg/L N, or 1.34 mg/L N. This would decrease Total Nitrogen concentrations from 3.76 mg/L N to 2.42 mg/L N. Assuming that treatment of the MBBR effluent by ultrafiltration removes 99.9% of the particulate matter (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012), ultrafiltration would remove 0.999 times 2.68 mg/L N, or 2.68 mg/L N. This would decrease Total Nitrogen 2.68 mg/L N.

Reverse osmosis (RO) is a process that uses a semi-permeable membrane to remove dissolved and particulate solids from water (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012). Reverse osmosis would remove all forms of nitrogen, whether they be in the dissolved or particulate phases. Therefore, the existing treatment units (rock cells and MBBRs) may not be necessary if RO was used to treat the mine water. This process has been used for a number of years at the abandoned Beal Mountain Mine (Silver Bow County, Montana) to treat water containing numerous contaminants including nitrate and nitrite (Tetra Tech, 2010). Reverse osmosis is a relatively expensive process because the membranes must be replaced periodically and RO uses a lot of electricity to pressurize water so the water goes through the semi-permeable membrane. An economic evaluation as to whether RO would be a cost-effective water treatment solution at the East Boulder Mine was outside the scope of this thesis.

It cannot be determined whether enhanced particulate nitrogen removal would meet effluent discharge requirements. The Montana DEQ has not yet decided as to what the nitrogen limits for a discharge from the East Boulder Mine should be, and a Total Maximum Daily Load Plan has not been completed for the Boulder River by the Montana DEQ. Therefore, a decision on whether or not enhanced particulate nitrogen removal is required would have to be made at a later date. The projected TN concentrations given above could be used to assist in making this decision. Laboratory and pilot-scale testing should be done before any final decision be made on the use of a particulate matter removal process.

5. Discussion

Examination of the data showed that ammonium concentrations in the rock cells effluent are greater than ammonium concentrations in the influent. The rock cells are intended to cause denitrification. The increase in ammonium concentrations across the rock cells is unexpected and cannot be explained with the available data. There is no process that could cause this increase in ammonium concentrations except for ammonification, and whether or not ammonification is occurring in the rock cells cannot be determined because TKN in the rock cell influent has not been measured. Measurement of TKN in the rock cells influent is recommended. Also, measurement of methanol concentrations in the rock cells effluent is recommended, so that the amount of denitrification occurring in the rock cells can be determined. The amount of denitrification cannot be calculated from nitrate data alone, because there may be some nitrification occurring that produces nitrate, and nitrogen gas cannot be quantified because it vaporizes from the water.

A second finding from the nitrogen analyses is that effluent TKN concentrations from MBBR 3 were higher than were the effluent TKN concentrations from MBBR 2 (Figure 14).



Figure 14: MBBR Effluent TKN Concentrations

The MBBRs receive the same influent water and are identical in size, but there was a significant difference in TKN, and therefore Total Nitrogen, effluent concentrations. The average TKN concentration at TAW-A was 2.8 times greater than the average TKN concentration at TAW-A2.

Biofilm sloughing is not a likely cause because the rate of biomass sloughing should be approximately equal between the two systems. It is possible that there is a difference(s) between the two MBBRs that is not obvious. Investigation into possible differences in aeration rates in the nitrification reactors and mixing rates within the denitrification reactors is warranted. MBBR 3 (TAW-A) may be operating relatively poorly because of such a construction or operational difference(s) and the Total Nitrogen concentration in the blended effluent could be lowered if MBBR 3 could be made to perform like its partner.

The stoichiometric analyses for the nitrification and denitrification processes did not provide any definitive conclusions. However, it was determined that the average measured organic nitrogen concentrations sampled from the MBBR effluent contained approximately 2.3 times higher concentrations of organic nitrogen than predicted by the stoichiometric analysis. The high concentration of organic nitrogen from the MBBRs is consistent with previous discussion which identified a discrepancy of TKN concentrations between MBBR 2 and MBBR 3.

6. Conclusions

The existing treatment system at the East Boulder Mine is doing a good job in removing TIN. The system was designed to remove 86% of the TIN in the MBBR influent. Data supplied by the East Boulder Mine showed that TIN removal is about 95%. It is unlikely that any modifications to the MBBRs will result in significantly better TIN removals. However, effluent samples show a relatively large concentration of TKN. Should stringent effluent limits on Total Nitrogen (TN) be placed on this facility by the DEQ in the future, the TKN may cause MPDES permit violations. If so, the existing MBBRs would need to be improved. Addition of a solids-liquid separation process following the MBBRs such as clarification would remove about half of particulate N; addition of an enhanced solids-liquid separation system like ultrafiltration would remove the vast majority of particulate N. AnoxKaldnes did recommend that a sedimentation tank follow the MBBRs: "For this project the effluent from the third MBBR will require clarification ..." (AnoxKaldnes, Inc, 2006). Another alternative would be to use reverse osmosis. This would be an expensive option, but use of reverse osmosis may allow abandonment of the rock cells and the MBBRs all together.

Analysis of the data supplied by the East Boulder Mine revealed several anomalies. One anomaly was that ammonium concentrations in the rock cells effluent are greater than ammonium concentrations in the rock cells influent. The cause of this situation could not be determined because there is no data on TKN concentrations in the Rock Cell influent, and no information on the quantity of methanol utilized.

One MBBR performs much better than the other MBBR. Total Kjeldahl Nitrogen concentrations at the TAW-A sampling location are 2.8 times higher than are TKN

concentrations at the TAW-A2. The reason for this difference could not be determined because of insufficient information.

Organic nitrogen concentrations in the MBBR effluent are greater than what is predicted by stoichiometry. The cause of this situation may be difficult to determine. It is linked to the high TKN concentrations in the TAW-A effluent. Investigation into why MBBR 3 has so much TKN in its effluent may lead to a relatively inexpensive way to significantly reduce Total Nitrogen concentrations in the combined MBBR effluent. Further investigation of the anomalies identified in this research is important to ensure the most denitrification. Achieving the greatest achievable nitrogen conversion throughout the treatment stages is a significant goal to ensure compliance with future permit limits; limits which are unknown at this time.

Replacing the existing MBBRs with a FBR would not be a practical solution to lowering effluent nitrogen concentrations. The MBBRs are removing nitrogen quite effectively and the predicted nitrogen effluent from the FBR design is approximately twice the concentration level of the existing MBBR average.

7. Recommendations

The treatment anomalies identified through this research need to be further evaluated. In order to obtain the data and information necessary for the research the following actions are recommended:

- Add sampling points after the second nitrification reactors in the MBBRs. This
 would allow better analysis of the only nitrification processes in the entire
 treatment process. It is important to analyze the concentrations of the forms of
 nitrogen present to understand the efficiency of the nitrification cells.
- Add TKN to the analyses performed on UTAW samples. By having the same nitrogen analyses conducted at all sampling points, it is possible to gain a better understanding of the nitrogen reactions occurring at all stages of treatment. It would also provide a baseline concentration of organic nitrogen entering the WTP to allow for removal efficiency calculations.
- Install temperature and dissolved oxygen sensors in the rock cells. Currently, there are no automated sensors that monitor the temperatures and dissolved oxygen concentrations in the rock cells. Installing sensors would be beneficial due to the sensitive nature of the denitrifying bacteria working in this treatment stage. Because of the increase in ammonia concentrations in the rock cell treatment, temperature and dissolved oxygen data would provide a starting point for further investigation.
- Measure methanol concentrations in the effluents of denitrification processes. Along with the addition of sampling the effluents of the MBBR nitrification

reactors, much better estimation of the amounts of denitrification would be possible.

• Construct a second clarifier, or other solid-liquid separation process, as the final treatment stage. Allowing microbial mass to settle in a clarifier before discharge will decrease organic nitrogen concentrations, and, therefore, Total Nitrogen concentrations in the effluent.

The first four recommendations have fairly low costs and minimal labor involved to improve the overall understanding of the actual treatment occurring throughout the WTP. These initial recommendations could provide the additional data necessary to more easily identify the discrepancies in the WTP identified by this research. The final recommendation to increase solid-liquid separation before discharge would be the most costly but would reduce organic nitrogen and Total Nitrogen concentrations in the effluent.

References Cited

- AnoxKaldnes, Inc. (2006). Complete Treatment Moving Bed Biofilm Reactor (MBBR) for Stillwater Mining Company. Providence: AnoxKaldnes, Inc.
- Bernhard, A. (2010). *The Nitrogen Cycle: Processes, Players, and Human Impact*. Retrieved March 3, 2015, from Nature Education:

http://www.nature.com/scitable/knowledge/library/the-nitrogen-cycle-processes-playersand-human-15644632

- Chang, H., Rittmann, B., Amar, D., Ehlinger, O., & Lesty, Y. (1991). Biofilm detachment mechanisms in a liquid-fluidized bed. *Biotechnology and Bioengineering*, 499-506.
- Crittended, J., Trussell, R., Hand, D., Howe, K., & Tchobanoglous, G. (2012). *Water Treatment -Principles and Design (3rd ed.)*. New York: Wiley & Sons.

Drury, W. (2015, January). Personal Communication.

Kenning, J. (2015, February 13). Bureau Chief, Water Protection Bureau. *Montana Department* of Environmental Quality. Personal communication.

Montana Department of Environmental Quality. (2000, August 1). *Minor MPDES Permits: Stillwater Mining Co East Boulder*. Retrieved November 17, 2014, from Montana Department of Environmental Quality Web site: http://www.deq.mt.gov/wqinfo/mpdes/majorpermits.mcpx#Minors

- Plattes, M., Henry, E., & Schosseler, P. (2008). A zero-dimensional biofilm model for dynamic simulation of moving bed bioreactor systems: Model concepts, Peterson matrix, and application to a pilot-scale plant. *Biochemical Engineering Journal*, 392-398.
- Rittmann, B. E., & McCarty, P. L. (2001). *Environmental Biotechnology: Principles and Applications*. New York: McGraw-Hill.

Stillwater Mining Company. (2015). *Overview*. Retrieved February 9, 2015, from Stillwater Mining Company Web site: stillwatermining.com/aboutus.html

Tetra Tech. (2010). Engineering Evaluation/Cost Assessment - Beal Mountain Mine, Beaverhead-Deer Lodge National Forest. Bozeman: Tetra Tech.



Appendix A: Additional WTP Sampling Results

Figure 15: Concentrations of Nitrogen at UTAW



Figure 16: Concentrations of Nitrogen at UTAW-A



Figure 17: Concentrations of Nitrogen at TAW-A2



Figure 18: Concentrations of Nitrogen at TAW-A



Figure 19: Concentrations of Nitrogen at TAW-A2



Figure 20: Concentrations of Nitrogen at TAW-A



Figure 21: Concentrations of Ammonia-Ammonium as Nitrogen



Figure 22: Concentrations of Nitrate-Nitrite as Nitrogen



Figure 23: Concentrations of Total Inorganic Nitrogen as Nitrogen



Figure 24: Concentrations of Total Kjehdahl Nitrogen as Nitrogen



Figure 25: Concentrations of Total Nitrogen

Appendix B: List of FBR Equations

Note: All of the variables listed in the FBR equations are defined in the Glossary of Symbols.

$$\sigma = \frac{\left[\left(\rho_p - \rho_w\right)(1 - \varepsilon)g\right]}{a}$$

$$b_{det} = 8.42 \times 10^{-2} \sigma^{0.58}$$

$$b_{det} = 8.42 \times 10^{-2} \left(\frac{\sigma}{1 + 433.2(L_f - 0.003)}\right)^{0.58}$$

$$\theta_x = \frac{1}{b_{det}}$$

$$b^{'} = b + b_{det}$$

$$S_{min} = K \frac{b'}{Y\hat{q} - b'}$$

$$S_{min}^{*} = \frac{b'}{Y\widehat{q} - b'} = \frac{S_{min}}{K}$$

$$Re_m = \frac{2\rho d_p u}{(1-\varepsilon)\mu}$$

$$Sc = \frac{\mu}{\rho D}$$

$$L = \frac{D(Re_m)^{0.75} Sc^{0.67}}{5.7u}$$

$$K^* = \frac{D}{L} \left[\frac{K}{\widehat{q} X_f D_f} \right]^{1/2}$$

$$S^* = \frac{S}{K}$$

$$\alpha = 1.5557 - 0.4117 \tanh[\log_{10} S_{min}^*]$$

$$\beta = 0.5035 - 0.0257 \operatorname{tanh}[\log_{10} S_{min}^*]$$

$$S_{s}^{*} = S^{*} - \frac{\left(\tanh\left[\alpha \left(\frac{S_{s}^{*}}{S_{min}^{*}} - 1\right)^{\beta}\right] \right) \left(2[S_{s}^{*} - \ln(1 + S_{s}^{*})]\right)^{1/2}}{K^{*}}$$
$$J^{*} = K^{*}(S^{*} - S_{s}^{*})$$
$$J = J^{*} \left(K\hat{q}X_{f}D_{f}\right)^{1/2}$$

$$aV = \frac{Q(S^o - S)}{J_{ss}}$$

$$V = \frac{aV}{a}$$

$$L_f = \frac{JY}{X_f b'}$$

Appendix C: FBR Calculations

Table XII: Nitrification FBR Calculations			
Calculation	Value		
σ	0.6582		
b _{det}	0.0271		
Θ_x	36.9159		
<i>b</i> '	0.0928		
S_{min} (mg/L)	0.1723		
$S_{min}*$	0.3023		
Re_m	2,691,249.3978		
Sc	0.0117		
L	0.0070		
<i>K</i> *	1.1633		
S^*	0.8772		
α	1.7522		
β	0.0516		
S_s*	0.5245		
J^*	0.4100		
J	0.0322		
$aV(m^2)$	11,130.2625		
V (expanded, m ³)	3.4353		
V (unexpanded, m ³)	2.7482		
L_f (cm)	0.0114		

Table XII: Nitrification FBR Calculations

Calculation	Value
σ	0.6582
b _{det}	0.0661
Θ_x	15.1366
<i>b</i> '	0.0998
S_{min} (mg/L)	1.0725
$S_{min}*$	0.1178
Re_m	2,691,249.3978
Sc	0.0136
L	0.0066
<i>K</i> *	1.3328
<i>S</i> *	0.1198
α	1.8562
β	0.5223
S_s*	0.1179
J^*	0.0026
J	0.0025
$aV(m^2)$	1,086,718.8624
V (expanded, m ³)	335.4071
V (unexpanded, m ³)	268.3256
$L_f(\mathrm{cm})$	0.0002

Table XIII: Denitrification FBR Calculations

SIGNATURE PAGE

This is to certify that the thesis prepared by Courtney Greyn entitled "Nitrogen Removal in a Biological Wastewater Treatment Plant" has been examined and approved for acceptance by the Department of Environmental Engineering, Montana Tech of The University of Montana, on this 30th day of April, 2015.

ener

Bill Drury, PhD, Professor Department of Environmental Engineering Chair, Examination Committee

Kumar Ganesan, PhD, Professor and Department Head Department of Environmental Engineering Member, Examination Committee

echan

Butch Gerbrandt, PhD, Rrofessor Department of General Engineering Member, Examination Committee