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Quantifying Cyanide Inhibition of Nitrification and Developing Cost-Effective Treatment Processes

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QUANTIFYING CYANIDE INHIBITION OF NITRIFICATION AND DEVELOPING

COST-EFFECTIVE TREATMENT PROCESSES

by

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ABSTRACT

QUANTIFYING CYANIDE INHIBITION OF NITRIFICATION AND DEVELOPING
COST-EFFECTIVE TREATMENT PROCESSES

Germano M. Salazar-Benites
Old Dominion University, 2017
Director: Dr. Charles B. Bott

All wastewater treatment plants that operate multiple hearth furnaces (MHF) and
are required to nitrify must manage the inhibitory effects of free cyanide (HCN, CN⁻) in
the scrubber return flows due to inhibitory impacts on nitrifying bacteria.

HRSD Boat Harbor Treatment Plant (BHTP) a 25 MGD facility consisting of
primary and secondary treatment, employs an anoxic selector process for nitrification and
partial denitrification and operates a MHF. There is a desire to improve TN removal
performance at BHTP due to an annual mass-based bubble permit limit on a combined
discharge from seven HRSD plants, and there are no discharge limitations for ammonia
or TKN at BHTP.

Due to a limited footprint, management made the decision of dedicating one
aeration tank for sidestream treatment of incinerator scrubber water (SW) for biological
oxidation of cyanide, an approach which has been used effectively in several plants
around the US and HRSD (Daigger et al., 1998). However when this aeration tank, used
as a mainstream biological cyanide treatment process (MBCNTP), was put into service
for first time, nitrification was not achieved.

Three 22 L sequencing batch reactors (SBR's) with different configurations were
used to investigate the feasibility of sending SW to the head of the plant, dosing with

potassium cyanide (KCN) to find the maximum cyanide concentration before inhibition of nitrifying bacteria, determining the dosage rate of ferrous sulfate to form soluble Fe-CN complexes and/or insoluble Fe-CN precipitates, and to investigate if it is feasible to use one aeration tank from the BNR process as a MBCNTP.

After approximately 8 months of operation using SBRs and after performing several jar tests, it was determined that cyanide in the SW was the primary inhibitor, additionally, concentrations above 0.08 mg/L at 20 °C and concentrations above 0.26 mg/L at 28 °C were observed to have a negative impact on nitrification, when operating at 15 days total SRT, 10 days aerobic SRT.

Chemical precipitation of cyanide using ferrous sulfate could be an alternative, however trying to maintain the ideal conditions can be expensive since enough ferrous sulfate must be added to maintain the right Fe-CN ratio and enough sodium hydroxide to increase the pH to optimal conditions.

Additionally, temperatures in the MBCNTP system should be maintained below or at 40 °C to successfully degrade cyanide. Nonetheless, this parameter could be difficult to control with the new MACT 129 regulation, which basically changed the way the incinerators are operated.

ACKNOWLEDGMENTS

NOMENCLATURE

AOB – Ammonia-Oxidizing Bacteria

ATP – Atlantic Wastewater Treatment Plant

BHTP – Boat Harbor Treatment Plant

BNR – Biological Nutrient Removal

CCCSD – Central Contra Costa Sanitary District

CEL – Central Environmental Lab

CN – Free Cyanide

CN^- – Cyanide

CNCl – Cyanogen chloride

CO – Carbon dioxide

COD – Chemical Oxygen Demand

DAF – Dissolved Air Flotation

DO – Dissolved Oxygen

HCl – Hydrochloric acid

HOCN – Hydrogen cyanate

HRSD – Hampton Roads Sanitation District

HRT – Hydraulic Retention Time

HRTeff – Hydraulic detention time effective

KCN – Potassium Cyanide

LPPCP – Lower Potomac Pollution Control Plant

MACT – Maximum Achievable Control Technology

MBCNTP – Mainstream Biological Cyanide Treatment Process

MHF – Multiple Hearth Furnace

N2 – Nitrogen gas

NACWA – National Association of Clean Water Agencies

NEF – Nitrification Enhancement Facility

NH3 – Ammonia

NH4-N – Ammonia

NOB – Nitrite-Oxidizing bacteria

NO_2-N – Nitrite

NO_3-N – Nitrate

NOx – Nitrogen Oxides

OCN^- – Cyanate

PCE – Primary Clarifier Effluent

PCS – Primary Clarifier Sludge

pKa – Acid disassociation constant

RAS – Return Activated Sludge

RWI – Raw Wastewater Influent

SBCNTP – Sidestream Biological Cyanide Treatment Processes

sCOD – soluble COD

SH – Solids handling

SBR – Sequencing Batch Reactor

SCE – Secondary Clarifier Effluent

SO_2 – Sulfur dioxide

SRT – Solids retention time

SW – Scrubber Water

SW-C – Scrubber Water + centrate

TKN – Total Kjeldahl Nitrogen)

TN – Total Nitrogen

TP – Total Phosphorus

TSS – Total Suspended Solids

VIP – Virginia Initiative Plant

WAD CN^- – Weak acid dissociable Cyanide

WAS – Waste Activated Sludge

WWTPs – Wastewater Treatment Plants

YRTP – York River Wastewater Treatment Plant

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CHAPTER 1

INTRODUCTION

1.1   Background and motivation

Biological nutrient removal (BNR) processes are the preferred method for removing nitrogen and phosphorus compounds from wastewater because of reduced energy and chemical requirements of BNR treatment compared to physical–chemical treatment. However, BNR processes are known to experience various upsets due to environmental factors, such as temperature, low dissolved oxygen (DO) concentration, pH, un-ionized ammonia, and certain chemical inhibitors (USEPA, 1984). There are times when unstable BNR operations create obstacles for meeting stringent effluent limit requirements of total nitrogen (TN) and total phosphorus (TP), for wastewater treatment plants (WWTPs).

One of the biggest challenges and concerns, for all WWTPs which are making efforts to achieve nitrification and simultaneously operate a multiple hearth furnace (MHF) for the incineration of dewatered biosolids is chemical inhibition due to process chemical creation.

Incinerator flue gas, prior to being discharged into the atmosphere, is typically treated with a wet scrubber system to reduce gas temperature, aid in the separation of particulates, and remove water-soluble air contaminants, such as sulfur dioxide (SO_2), hydrochloric acid (HCl), ammonia (NH_3) and hydrogen cyanide (HCN). The water used in the wet scrubber system also known as scrubber water (SW) is collected and normally recycled back to the treatment plant headworks laden with water-soluble contaminants. Free cyanide ($HCN + CN^-$), hereinafter referred to as CN, is effectively removed from the

flue gas but is of concern because high concentrations cause inhibitory impacts on nitrification. The SW CN concentration can be as high as 30 mg/L with a typical flow of around 1 MGD. The impacts of CN on nitrification are considered only inhibitory at above 0.1 mg/L (Neufeld, 1984; Britton, 1984) and toxic for the aerobic bacteria with a CN toxicity threshold of about 200 mg/L (Fuller, 1985). Therefore, a process to treat or destroy CN must be implemented to eliminate the negative impacts on nitrification. Biological degradation of CN is the preferred method not only because it is less expensive than chemical and physical methods but also because it is environmentally friendly (Dash et al., 2009). Moreover, for WWTPs this biological degradation method is more convenient due to the variety of microorganism culture already present in the wastewater.

Sidestream biological cyanide treatment processes (SBCNTP) are typically used to minimize the impact of CN on nitrification, but these processes operate with a separate biomass requiring a formal sidestream process, including tanks, equipment, and footprint. This study was focused on the impact of CN inhibition on nitrification in WWTPs and developing cost-effective treatment processes.

1.2   Project Background

Hampton Roads Sanitation District (HRSD), a political subdivision of the Commonwealth of Virginia, owns and operates nine major wastewater treatment plants and four minor plants on the Middle Peninsula with a combined capacity of 249 MGD. The treated wastewater effluent from seven of the thirteen treatment plants is discharged into the James River Basin and five of these treatment plants operate a MHF. One of

these 5 plants is the Virginia Initiative Plant (VIP) which was designed to provide 75% reduction in phosphorus year round and 65% reduction in nitrogen on a seasonal basis. In 1992, when VIP was placed into service for the first time, plant staff noticed that twice the amount of solids retention time (SRT) was required to achieve consistent nitrification compared with the pilot study. This indicated nitrification inhibition was occurring at the facility (Waltrip et al., 1993). After conducting nitrification assays, including all recycles flows, it was demonstrated that the SW was the source of the inhibition, hence, a pilot study was conducted to consider the treatability of the VIP plant's solids-handling SW, and to develop design criteria. A CN target concentration of 1 mg/L, after treatment, was established to be less than the threshold inhibition concentration of 0.1mg/L, when diluted in the full-scale plant flow (Daigger et al., 1998).

Two existing but unused solids digestion tanks, each 18.3 m (60 ft) in diameter and 6.7 m (22 ft) deep, were used for construction of a nitrification enhancement facility (NEF). As shown on Figure 1.1, all the waste solids coming from the secondary clarifiers are mixed with the SW and centrate coming from the centrifuges (SW-C) to treat the CN.
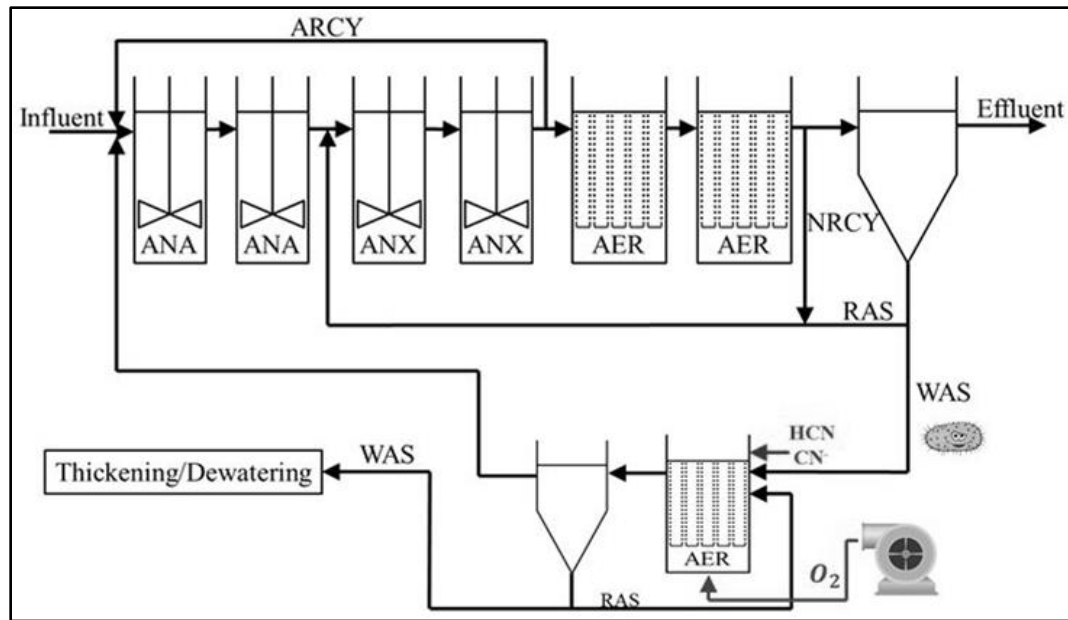
Figure 1.1 - VIP NEF System (SBCNTP)

One tank serves as an aeration basin and the second tank serves as a clarifier to have a better SRT control. Solids from the NEF clarifier can be returned back to the NEF aeration tank influent or wasted to the thickening and dewatering process. Additionally, the overflow from the NEF clarifier is piped to the headworks.

Similar to VIP NEF, in 2013, after a major upgrade, a mainstream biological cyanide treatment process (MBCNTP) was implemented at Boat Harbor Treatment Plant (BHTP) to treat CN and enhance nitrification. In this plant the footprint was limited thus the design criteria were different. It was decided that one of the six aeration tanks was to be used for CN treatment (Figure 1.2). In addition, unlike VIP NEF, return activated sludge (RAS) was the main source of microorganisms for the CN treatment; hence there will be an intermingling of mixed liquor in the main BNR process and the MBCNTP.
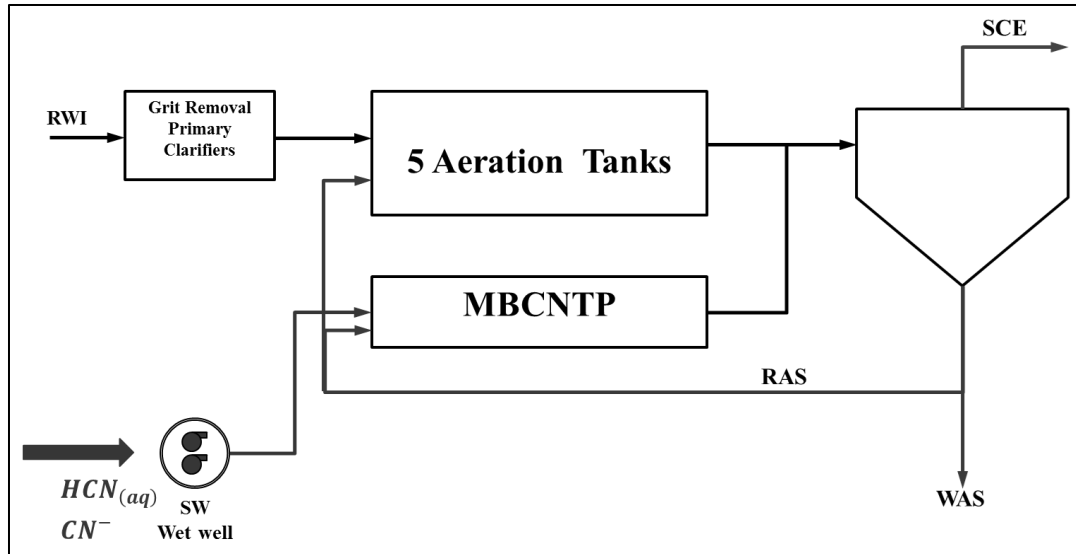
Figure 1.2 - BHTP using one aeration tank as a MBCNTP

There is adequate detention time in one aeration tank to treat CN before exiting the MBCNTP system and becoming mixed with all the other aeration effluents. However, when trying to nitrify and treat CN simultaneously for the first time, there was no success. After two months with no indication of nitrification it was decided to stop the SW-C flow going to the MBCNTP system and instead send it back to the headworks. On this configuration all 6 aeration tanks were utilized for mainstream nitrification. By doing this nitrification was finally achieved; however it was not sustainable for long term. The combination of low influent flows (lack of dilution) and high CN concentrations in the SW were causing periods of nitrification inhibition. Finally, the MBCNTP system was put back in service and within the next day, nitrification was lost.

The MBCNTP system at BHTP was expected to treat CN and enhance nitrification but, for unknown reasons, these objectives were not achieved. The only known fact was that we needed to find a feasible solution.

1.3   Research Objectives

Objective 1: Identify mechanism for the observed dramatic nitrification inhibition in the BHTP approach for managing SW, as compared to the approach used at VIP (and other HRSD facilities)

Objective 2: Quantify the impact of CN and SW on nitrification as a function of wastewater temperature, solids retention time, and other process conditions.

Objective 3: Propose a cost-effective solution in which the treatment of CN and nitrification can occur in intermingled mixed liquor.

CHAPTER 2

LITERATURE REVIEW

2.1 Biological Nitrogen Removal

Nitrification is a two-step biological process in which ammonia (NH_4-N) is oxidized to nitrite (NO_2-N) and nitrite is subsequently oxidized to nitrate (NO_3-N). This aerobic oxidation process occurs by two groups of bacteria, ammonia-oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). Both of these groups are classified as autotrophic organisms since they derive energy for growth from the oxidation of inorganic nitrogen compounds. The two groups of bacteria are distinguished from one another by their ability to oxidize only specific species of nitrogen compounds. While AOB can oxidize ammonia to nitrite it cannot complete the oxidation to nitrate, NOB is limited to the oxidation of nitrite to nitrate. (Metcalf, Eddy & AECOM, 2014).

The energy-yielding two-step oxidation of ammonia to nitrate is as follows:

Step 1:

$$2NH_4^+ + 3O_2 \xrightarrow{AOB} 2NO_2^- + 4H^+ + 2H_2O \tag{1.1}$$
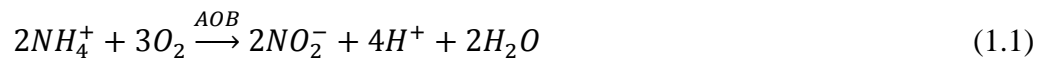
Step 2:

$$2NO_2^- + O_2 \xrightarrow{NOB} 2NO_3^- \tag{1.2}$$

Total oxidation reaction:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \tag{1.3}$$

Based on Equation 1.3, the oxygen required for the complete oxidation of ammonia to nitrate is 4.57 g O_2/g NH_4-N, where 3.43 g O_2/g NH_4-N is consumed by AOB and 1.14 g O_2/g NO_2-N by NOB representing a 75% and 25% of energy consumption respectively. Additionally, 100% alkalinity is used by AOB while oxidizing NH_4-N.

On Equation 1.4 for each gram of NH_4-N converted, 7.14 g of alkalinity as $CaCO_3$ is required (Metcalf, Eddy & AECOM, 2014).

$$NH_4^+ + 2HCO_3^- + 2O_2 \rightarrow NO_3^- + 2CO_2 + 3H_2O \tag{1.4}$$
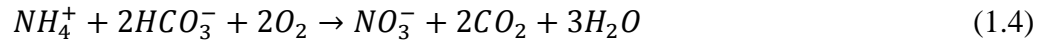
The maximal growth rate of the nitrifying bacteria (NOB, AOB) is smaller than that of heterotrophic bacteria. Consequently, if suspended growth bioreactors are operated in a way which requires the bacteria to grow rapidly, it is more than likely that the nitrifying bacteria will be washed from the system thus eliminating nitrification while the removal of organic compounds continues. (Grady et al. 2011).

After nitrification is achieved, denitrification can take place reducing the NO_3-N or NO_2-N to nitrogen gas (N_2) by denitrifying bacteria. This will occur in the absence of DO or under limited DO concentrations as oxygen is the preferred electron acceptor for denitrifying organisms. Both heterotrophs and autotrophs can carry out denitrification. In dissimilatory biological denitrification by heterotrophic bacteria, NO_3-N acts as the electron acceptor and is reduced while the organic carbon compound acts as the electron donor and is oxidized. (Metcalf, Eddy & AECOM, 2014).

The complete denitrification process from NO_3-N to N_2 can be observed in Equation 1.5 below:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \tag{1.5}$$

Additionally, on Equation 1.6, one equivalent of alkalinity is produced per equivalent of NO_3-N reduced, which equates to 3.57 g of alkalinity as $CaCO_3$ per g of NO_3-N reduced. In other words, via denitrification a 50% of alkalinity can be recovered.

$$C_{10}H_{19}O_3N + 10NO_3^- \rightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^- \tag{1.6}$$
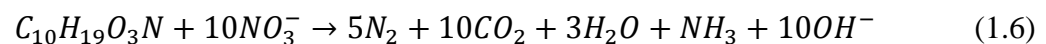
2.2 Cyanide anion (CN⁻) and Hydrogen cyanide (HCN)

Knowing the characteristics of CN⁻ and HCN helps to better understand the impact on the nitrification process, hence this section will be dedicated to CN⁻ and HCN, their toxicity, usage, important characteristics, formation, and relevant removal technologies.

2.2.1 What are CN⁻ and HCN?

CN⁻ is an anion formed from a carbon atom triple bonded to a nitrogen atom (Smith, 1999) and may be present in the environment as a gas (HCN), as a salt (KCN, NaCN) or as various cyanide complexes in solution ($[Fe(CN)_6]^{4-}$,$[Ni(CN)_4]^2$, $[Cu(CN)_4]^{2-}$, etc.), the latter form being typically formed with metallic contaminants (Dash et al., 2009). CN⁻ originates from natural sources and can also be manufactured. Annually, about 80% of the CN⁻ production is used in the manufacture of organic compounds, plastics and pharmaceuticals and a little less than 20% is used in the mining industry, especially for gold extraction (Logsdon et al., 1999).

CN⁻ and HCN can also be found, as a by-product in various industrial wastewaters, such as coking, gold mining, electroplating or incineration scrubber blowdown water (Do et al., 2008; Kim et al., 2011; Luque-Almagro et al., 2016). A better description on how CN⁻ and HCN can be found in the incineration blowdown water is discussed in section 2.4.1.

HCN in gaseous form can be a very dangerous substance and has the ability to dissolve in water, but is somewhat volatile with a Henry's constant (K_H) of 0.040 bar-mole/L (at 25 °C) and a boiling point temperature of 25.6 °C (Smith, 1999).

The acid disassociation constant (p*K*a) for CN⁻ and HCN in water is 9.24 (Benjamin, 2002), meaning that at a pH of 9.24, CN⁻ and HCN will be in equilibrium at a 50 mol% (Mudder, Botz & Smith, 2001). This can be better appreciated on Figure 2.1.
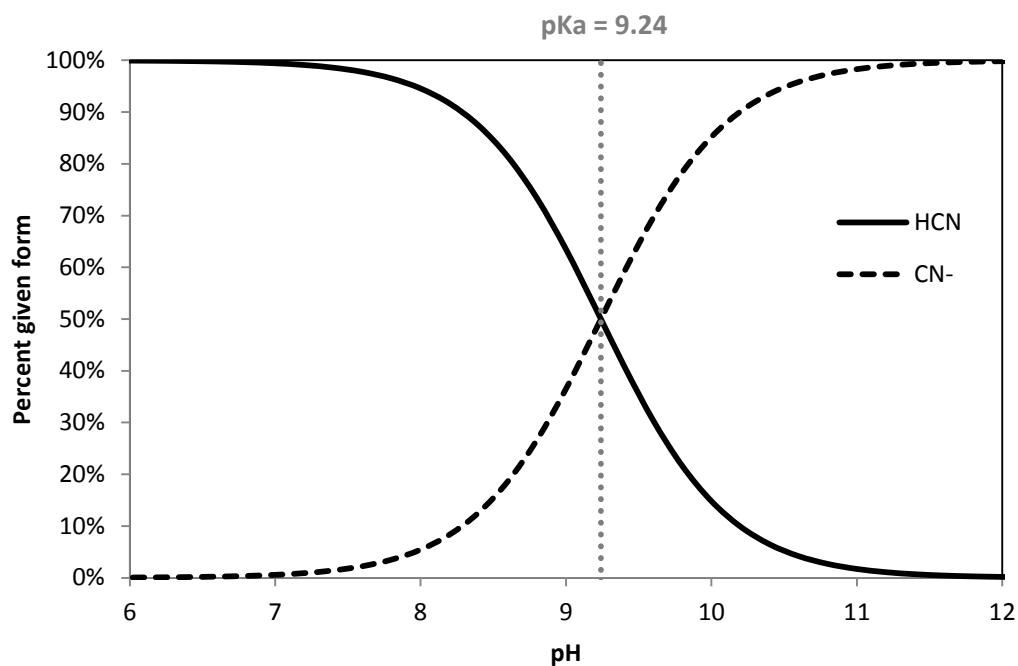
Figure 2.1 - Relationship between HCN/CN⁻ at different pH

Typically, the common pH in WWTPs it is around 7.0; hence, if CN is present, it can be said that the dominant form will be as a HCN and even more dominant in the SW-C since the pH is usually less or around 6.0. Additionally, CN⁻ can be effectively maintained in the dissolved form by increasing the pH to greater than 12.

2.2.2 CN inhibition of Nitrification

Nitrification can be affected by a number of environmental factors including, pH, DO concentration, temperature, toxicity, metals and unionized ammonia. It is important to differentiate between inhibition and toxicity. Inhibition is a temporary loss of the enzymatic activity whereas toxicity refers to a permanent loss of such activity.

Small increases in inhibitory substances can cause a dramatic reduction in nitrification (USEPA, 2010). Usually the AOB are the most sensitive nitrifying bacteria, hence, they are good indicators of the presence of toxic compounds at low concentrations, and therefore, nitrification will be lost prior the loss of the removal of organic compounds (Blum & Speece, 1991).

However, when nitrifiers are exposed to free ammonia and CN, depending on the concentration and the exposure time, NOB can be more sensitive to toxic substances than AOB allowing the oxidation of NH_4-N to NO_2-N (nitritation) but not the oxidation of NO_2-N to NO_3-N (nitratation) (USEPA, 2010).

The CN^- is an inhibitor of the enzyme cytochrome oxidase. It attaches to the iron within the protein. The binding of CN^- to this enzyme prevents transport of electrons from cytochrome to oxygen, thereby stopping aerobic cell metabolism (Mudder et al., 2001).

In order to compensate for potential inhibitory effects of CN, an increase on the SRT is necessary (Neufeld et al, 1986), additionally, the toxicity of CN tends to slightly reduce the optimum temperature for nitrification (Do et al., 2008)

2.2.3 CN Toxicity

CN toxicity depends on the stability constant of the complex in solution, i.e. the more stable the complex in solution, the lower the toxicity, HCN being the most toxic form (2.3 times more toxic than the anionic form CN^-) (Smith, 1999; Dash et al., 2009; Mudder et al., 2001).

Table 1.1 illustrates the most important soluble cyanide complexes that might be found in WWTPs based on the order of stability.

Table 1.1- Cyanide complexes found in wastewater in order of stability constant (Smith, 1999)

Cation	Formula	Name	Stability constant
Fe^{3+}	$[Fe(CN)_6]^{3-}$	ferricyanide	43.6
Hg^{2+}	$[Hg(CN)_4]^{2-}$	tetracyanomercurate	39.0
Fe^{2+}	$[Fe(CN)_6]^{4-}$	ferrocyanide	35.4
Ni^{2+}	$[Ni(CN)_4]^{2-}$	tetracyanonickelate	30.2
Cu^{2+}	$[Cu(CN)_4]^{2-}$	tetracyanocuprate	23.1
Ag^+	$[Ag(CN)_3]^{2-}$	tricyanoargenate	21.4
Zn^{2+}	$[Zn(CN)_4]^{2-}$	tetracyanozincate	19.6
Cd^{2+}	$[Cd(CN)_4]^{2-}$	tetracyanocadmium	17.9
H^+	HCN	hydrogen cyanide	9.2

On Figure 2.2 it can be observed that the cyanide complexes compounds shown in Table 1 are classified in three categories, as determined in the following analytical methods: Total Cyanide, weak acid dissociable cyanide (WAD CN^-) and free cyanide. The WAD analytical procedure measures free and weakly complexed forms of cyanide. Subtraction of the WAD cyanide value from the total cyanide value provides a measure of the essentially non-toxic and stable iron cyanide level present. (Mudder et al., 2001).
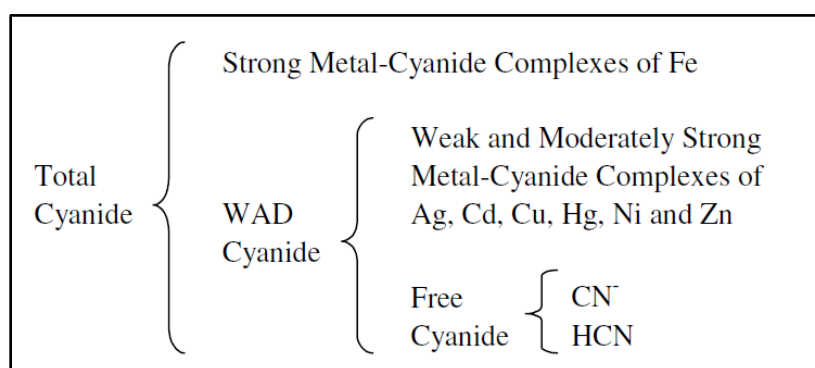
Figure 2.2 - Compounds included in Total, WAD and Free Cyanide Analysis (Mudder et al., 2001).

2.2.4 Cyanide treatment technologies

There are many different processes used for the removal of CN, however, to stay focused on the objectives of this research, only biological treatment, chemical precipitation using ferrous sulfate ($FeSO_4$) and alkaline chlorination will be discussed in detail.

2.2.4.1 Biological Treatment

Among all technologies that are used to treat CN, the preferred method is the biological treatment because it can be less expensive compared with chemical and physical treatment but much faster than natural oxidation. Furthermore, even though the biological treatment methods may have a higher capital cost, the operating cost is significantly lower (Dash et al., 2009). Also, this method is the most convenient for WWTPs because of the diversity of bacteria already present in the wastewater and the simplicity of the operation. However, it is important to mention that the biological treatment process is only effective for free cyanide and CN^- that is weakly complexed to metals. If CN^- is strongly complexed to metals, biological treatment is generally not an effective technology for cyanide removal, though these forms of cyanide are also generally nontoxic (Dash et al., 2009).

SBCNTPs aerobically degrade free cyanide through the activity of a diverse group of heterotrophic bacteria from the genera *Pseudomonas, Alcaligenes, Achromobacter*, etc. to form cyanate (OCN^-) and hydrogen cyanate (HOCN) (Teo & Tan, 1987; Mudder et al, 2001).

$$2CN^- + O_2 + enzymes \rightarrow 2OCN^- \qquad \qquad (Eq.\ 2.1)$$

$$2HCN + O_2 + enzymes \rightarrow 2HOCN \qquad \qquad (Eq.\ 2.2)$$

OCN^- and HOCN are chemically quite different than CN^- and HCN because they exhibit a lower toxicity to nitrifiers and have a lower tendency to form soluble metal complexes. The *pka* for OCN^- and HOCN in water is 3.66 at a 25 °C where the predominant form at a neutral pH is OCN^- (Freiser, 1992). Furthermore, the cyanate complexes are readily

hydrolyzed to bicarbonate, ammonium, ammonia and carbon dioxide (Ryu et al., 2014), via the chemical reactions as shown in eq. 2.3 and 2.4.

$$OCN^- + H^+ + 2H_2O \rightarrow HCO_3^- + NH_4^+ \tag{Eq. 2.3}$$

$$HOCN + H_2O \rightarrow NH_3 + CO_2 \tag{Eq. 2.4}$$
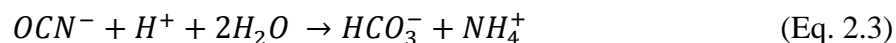
2.2.4.2   Chemical precipitation using FeSO₄

Chemical complexation of CN⁻ can be achieved using ferrous iron. The ferrous ions in solution react with CN⁻ to form the ferrocyanide complex in solution (Eq. 2.5).

$$Fe^{2+} + 6CN^- \rightarrow Fe(CN)_6^{4-} \tag{Eq. 2.5}$$

When Fe²⁺ is fed in excess with a molar ratio of 0.5:1 of Fe:CN, cyanide can be immobilized as the insoluble precipitate, Prussian blue, at an optimal pH range of 5.5 to 6.5 with a reaction time of five minutes (Adams, 1992).

$$2\,Fe^{2+} + Fe(CN)_6^{4-} \rightarrow Fe_4[Fe(CN_6)]_3 \tag{Eq. 2.6}$$
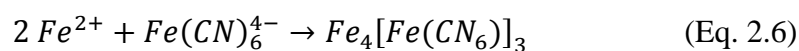
Although the chemical precipitation of CN⁻, is widely used as a polishing process and used in the mining industry, trying to maintain the pH could be difficult (Dash et al., 2009). Additionally depending on the characteristics of the wastewater, other metals like copper, mercury, nickel, silver or zinc can compete and precipitate iron-containing metal-cyanide complexes. (Mudder et al, 2001).

2.2.4.3 Alkaline chlorination

Alkaline chlorination is a chemical treatment process involving the oxidation of free and WAD forms of cyanide under alkaline conditions. This process is the oldest and most widely recognized of the cyanide destruction processes, with the first industrial applications being in the treatment of metal plating and finishing wastewaters. (Dash et al., 2009). As it can be observed on eq. 2.7 and 2.8 in the first stage of the alkaline chlorination process, free and WAD forms of cyanide are converted to cyanogen chloride (CNCl) using either a source of chlorine (Cl_2) or hypochlorite (OCl^-) (Mudder et al, 2001).

$$Cl_2 + CN^- \rightarrow CNCl + Cl^- \qquad \text{(Eq. 2.7)}$$

$$OCl^- + CN^- \rightarrow CNCl + Cl^- \qquad \text{(Eq. 2.8)}$$
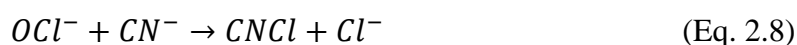
Cyanogen chloride (CNCl) is an intermediate and can volatilize from solution if the pH is less than about 8.0. With a pH in the range of 10.5 to 11.5 cyanogen chloride hydrolyses to yield cyanate (eq. 2.9)

$$CNCl + H_2O \rightarrow OCN^- + Cl^- + 2H^+ \qquad \text{(Eq. 2.9)}$$
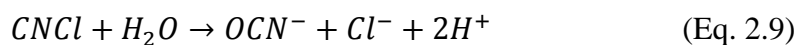
After OCN^- is formed then it can be hydrolyzed to bicarbonate, ammonium as explained in eq. 2.3.

2.3 Incineration Process

According with the latest inventory from the National Association of Clean Water Agencies (NACWA), which was revised in the year 2009, in the United States there are approximately 218 sewage sludge incinerator units at 112 facilities owned by 97 entities,

which both includes MHFs and fluidized beds (Oommen, 2010). Currently, over 80% of sewage sludge incinerators have been identified as MHF design, 15% are fluidized beds and only 3% are electric. Additionally, the majority of these units are located in the eastern United States with a significant inventory in the west coast (USEPA, 1995). MHF has been used to incinerate sewage sludge since the 1930s however; the majority of the primary and secondary municipal industrial and wastewater treatment plants were brought on-line in the U.S. between 1970 and 1990 generating large quantities of biosolids (Niessen, 2010). Most organic wastes generally can be incinerated using MHF (Vallero, 2008).

HRSD uses MHF in five WWTPs, including BHTP. The next section explores this topic in depth.

2.3.1 Multiple hearth furnace (MHF) Process Description

The number of hearths in a MHF can vary from 4 to 14 (Niessen, 2010). BHTP has two MHFs and both are configured with 8-hearths. A single MHF is typically in operation year round. When a MHF is in operation, three different zones are utilized:

- Drying zone: Where most of the moisture is evaporated from the sludge.

- Burning or combustion zone: Where all volatile gases and solids are burned.

- Cooling zone: Where the ash is cooled.
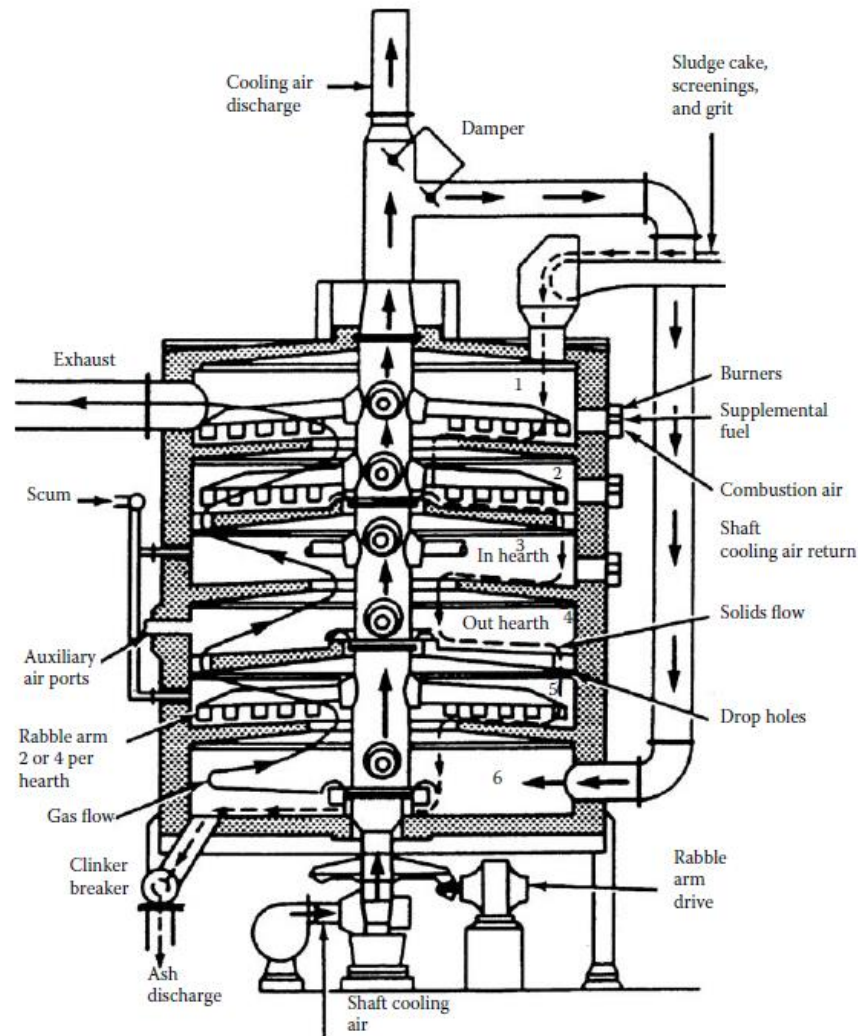
Figure 2.3 - Multiple hearth furnace (Niessen, 2010).

Figure 2.3, depicts how the sludge cake is fed to the top hearth and, with the help

of the rabble arms, mobilizes through the furnace all the way to the bottom.

Ideally, in the combustion zone, all the total hydrocarbons (THC) formed during

the incineration of the biosolids will be converted to carbon dioxide (CO_2) (Eq. 2.10).

However, due to the presence of uncontrolled variables like poor mixing between the fuel

and the air, the load, and the incineration performance in general, incomplete combustion is more likely to happen where carbon monoxide (CO) forms instead of CO_2 (Eq. 2.11) (De Nevers, 1995).

Complete Combustion:

$$THC + O_2 \rightarrow CO_{2(g)} + H_2O \qquad \text{(Eq. 2.10)}$$

Incomplete Combustion:

$$THC + O_2 \rightarrow CO_{2(g)} + H_2O + CO_{(g)} + THC \qquad \text{(Eq. 2.11)}$$
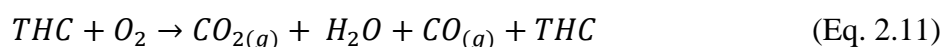
According with the new maximum achievable control technology (MACT) 129 regulations, all existing incinerators constructed on or before October 14, 2010 must meet all of the new federal plan requirements no later than March 21, 2016 (USEPA, 2015). This federal requirement applies to all HRSD WWTPs that operate an MHF.

Emission guidelines for CO, sulfur dioxide (SO_2) and nitrogen oxides (NOx) are of concern since are the parameters that will dictate how to operate the furnace. Decreasing the concentration of one parameter could increase the concentration of the others. This is the case for CO and NOx. It is well known that to achieve complete combustion, the percent of oxygen inside the system and combustion temperature should be increased, however, if the incinerator is supplied with too much oxygen (Eq. 2.12) and heat, nitrogen oxides (NOx) will be also formed at higher concentrations by the breakdown of a portion of the nitrogen compounds present in air and fuel (Dellinger et al., 1999).

Oxides of nitrogen formation:

$$N_{2(g)} + O_2 \rightarrow NO_X \qquad\qquad \text{(Eq. 2.12)}$$

In other words, increasing the percentage of oxygen to decrease the CO emissions is not the best alternative.

The presence of CN in WWTPs is mostly related with the formation of CO and NH_3, both in the gas phase (Eq. 2.13). That is why it can also be said that HCN is a product of incomplete combustion

Formation of HCN:

$$CO_{(g)} + NH_{3(g)} \rightarrow HCN_{(g)} + H_2O \qquad\qquad \text{(Eq. 2.13)}$$
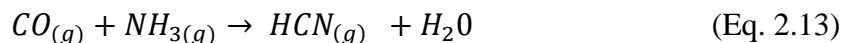
HCN will subsequently be volatilized and removed in the incinerator flue gas. The flue gas is often treated in a wet scrubber, a component of a typical air pollution control train, where a portion of the HCN formed in the MHF is absorbed into the liquid phase (SW).

2.4 Mechanisms affecting cyanide formation in WWTPs

The main reason affecting CN formation in WWTPs is the incomplete combustion in the incineration process. Additionally, the nitrogen-containing species in the biosolids which at BHTP is normally around 5% will contribute with the cyanide formation.

2.4.1 CO emissions

As described on section 2.3.1, adding more oxygen to the system to decrease the CO emissions can increase the concentration of NOx, hence to be able to decrease the CO

at a constant percent of oxygen, temperatures in the combustion zone, and in hearth 1, can be increased. The latest approach can be made in an attempt to simulate an afterburner even though the sludge cake is still being fed to hearth 1.

Typically, on the quasi afterburner operation, the sludge cake is fed on hearth two and hearth one serves as an afterburner section (Schmidt et al., 2000). Additionally sporadically high cake loading should be avoided since this will overload the air supply which will lead to have smoking conditions and excessive THC emissions (Niessen, 2010).

2.5 CN Treatment strategies in WWTPs

As mentioned in section 2.3.3.1, the biological degradation of CN using a SBCNTP (known as NEF in VIP) is the best option for WWTPs for multiple reasons; however, destroying the HCN in the MHF can also be a feasible option if operated with afterburners where the temperature can be increased (Daigger et al., 1998; Schmidt et al., 2000). Another strategy, mentioned on section 2.2.4.2, is precipitating CN^- by using FeSO4; nonetheless this method is not commonly used in WWTPs.

2.5.1 Nitrification Enhancement Facility (NEF)

The best example of an NEF is located at VIP, which has been in operation since December 1995 with a SRT of approximately 4 days. CN has successfully been treated to less than detectable levels with the exception of one particular event that occurred in April 1996 when the temperatures of the NEF system were higher than 50 °C due to a high-temperature test in the MHF. Once the test was completed and the temperatures

were below 40 °C, the NEF system recovered (Daigger et al., 1998). Temperature is an important parameter since the cyanide degrading bacteria are generally mesophilic, with optimum temperatures ranging between 20 and 40 °C (Dash et al., 2009).

2.5.2 Removal of CN at the source

Currently, thermal destruction is not an option on any of the HRSD WWTPs that operate a MHF since there are no formal afterburners. Though, a good example of this option occurs in the Lower Potomac Pollution Control Plant (LPPCP) located in Fairfax, VA. This 67 MGD WWTP operates a MHF with an afterburner. Using 800 °C (1472 °F) as a temperature on the afterburner is one of the alternatives used to destroy HCN in the flue gas stream before it reaches the flue gas scrubbers (Daigger et al., 1998). Another good example occurs in the Central Contra Costa Sanitary District (CCCSD) located in Martinez, CA, where HCN is being reduced primarily by increasing and controlling the afterburner temperature in the MHF (Schmidt et al., 2000)

2.5.3 Complexing CN^- using $FeSO_4$ in WWTPs

A recent study made by X. Yu et al (2016), suggests that there might be other contaminants present such as sulfide (S^{2-}, through precipitation) and colloids (through coagulation of Fe^{2+} hydrolysis) that will react first with the ferrous ions, i.e. and out compete CN^- compounds for removal. Moreover part of those ferrous ions will be hydrolyzed to form ferrous hydroxides (Yu, Xu, Wei & Wu, 2016).

If trying to remove CN^- by complexation/precipitation using ferrous sulfate, it should be noted that this application in WWTPs is still unclear due to the complex composition of the wastewater (in our case including the SW-C).

CHAPTER 3

MATERIALS AND METHODS

3.1 Sequencing Batch Reactors (SBR's)

Based on the research objectives previously discussed in Chapter 1, three 22 L sequencing batch reactors (SBR's) with different configurations were used to investigate the feasibility of sending SW to the head of the plant, dosing with potassium cyanide (KCN) to find the maximum CN concentration before inhibition of nitrifying bacteria, determining the dosage rate of ferrous sulfate to form soluble Fe-CN complexes and/or insoluble Fe-CN precipitates, and to investigate if it is feasible to use one aeration tank from the BNR process as a MBCNTP.

The seed biomass for the SBRs was collected directly from the fully nitrifying HRSD York River Wastewater Treatment Plant (YRTP) located in Seaford, Virginia. The three 22 Liters SBR's were operated in different configurations to simulate the following conditions:

- SBRA: BHTP using six aeration tanks without the MBCNTP

- SBR B / MBCNTP: BHTP using one aeration tank as a MBCNTP

- SBR C / NEF C: VIP NEF Configuration.

As shown on Figure 3.1, SBR A was operated using only one reactor, while SBR B and SBR C had attached two small reactors simulating their respective MBCNTP and SBCNTP (or NEF C) reactors. All SBR's were simulating a mainstream Modified Ludzack-Ettinger (MLE) process with a 12 hour hydraulic retention time (HRT) and a 15 days total SRT, 10 days aerobic SRT.
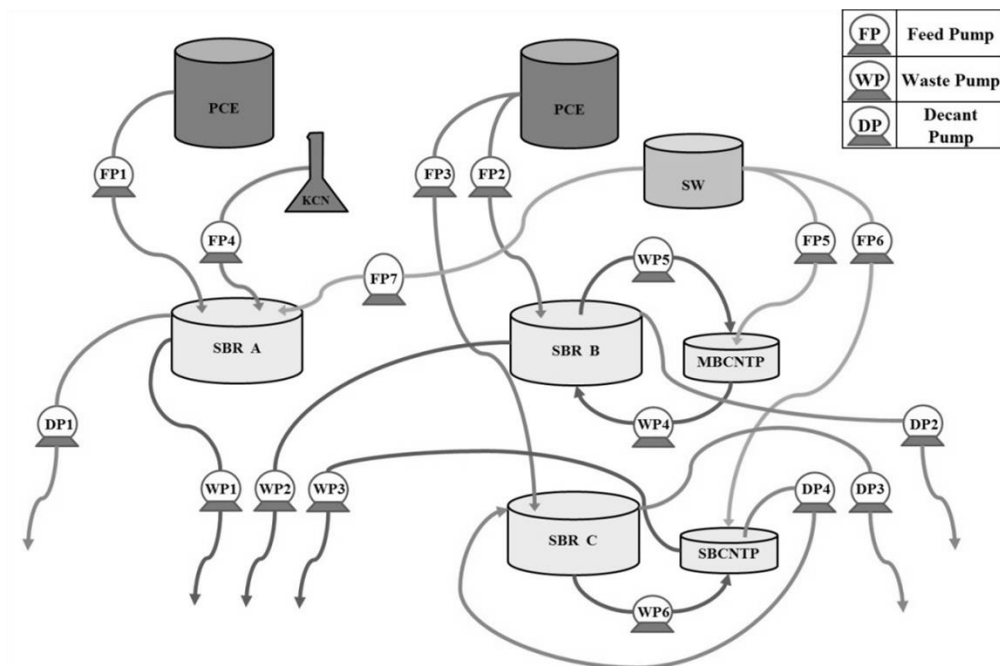
Figure 3.1 - Schematic of SBR setup

Figure 3.2 - SBR setup

3.2 Feed Collection

3.2.1 Primary Clarifier Effluent (PCE) Collection

Two 55-gallon drums containing primary clarifier effluent (PCE) were collected every Monday, Wednesday and Fridays from the HRSD Atlantic Wastewater Treatment Plant (ATP) located in Virginia Beach, Virginia. ATP doesn't use incineration, and thus the PCE would not be expected to contain any cyanide.

3.2.2 Scrubber Water + Centrate (SW-C) Collection

Three 5-gallon collapsible LDPE sample containers were collected at BHTP, at the wetwell near the Solids Handling (SH) facility every Monday, Wednesday and Friday. At this sample point SW and centrate were already mixed into a common pipe. To be able to have the most representative sample, a peristaltic pump was connected with a timer and it was collecting a sample of 100 mL every 16 minutes during week days, and 100 mL every 26 minutes during the weekends for each cubitainer. This was necessary in order to have 5 gallons of SW-C every Monday, Wednesday and Friday. Figure 3.3 and 3.4 shows the collection system for SW-C which was kept at ambient temperature.
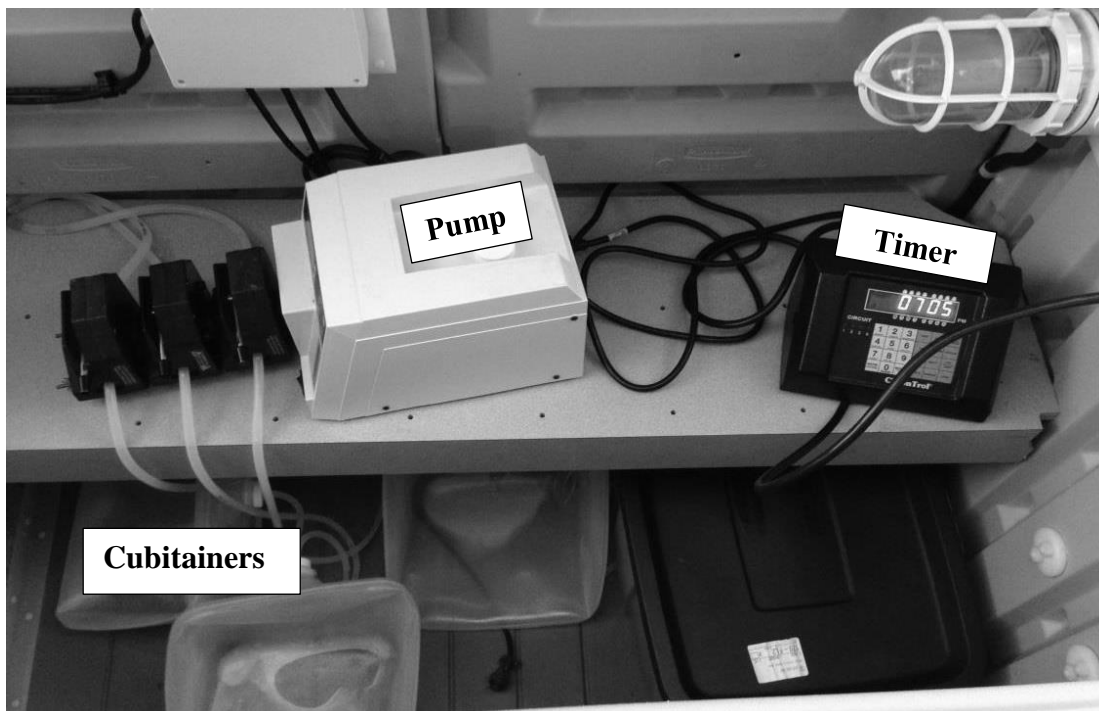
Figure 3.3 - SW-C collection system
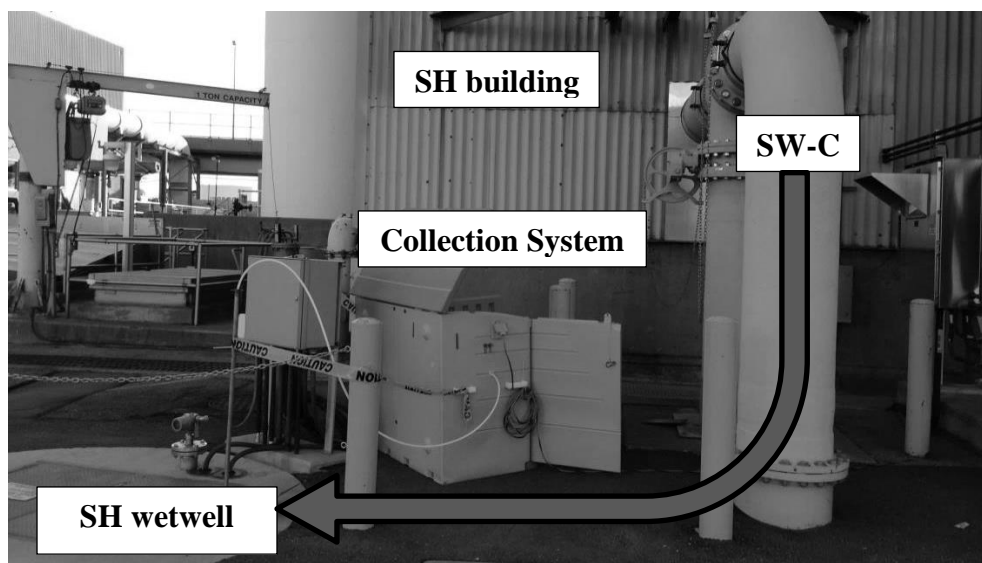
Figure 3.4 - Sample point, Collection system and SH Building view

3.2.3 KCN preparation

KCN stock solution was prepared using 1 L collapsible container. This solution was always kept with NaOH to avoid any HCN volatilization and, for safety reasons, was always kept inside the lab's fume hood. From the hood there was a small tube connected to a pump to feed the CN to SBR A.
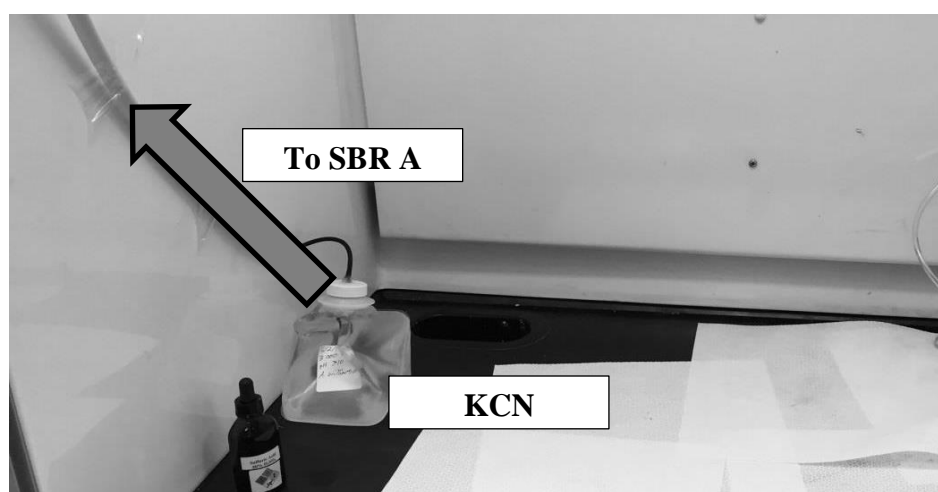
Figure 3.5 – KCN setup.

3.3 SBR's configuration

3.3.1 SBR A: BHTP using six aeration tanks without the MBCNTP.

SBR A (22L) was used to investigate three research questions which included: first, find out if CN in the SW was the primary inhibitor, second, find the feasibility of sending SW-C to the head of the plant (as a function of wastewater temperature and process SRT) and finally dosing the reactor with potassium cyanide (KCN) to find the maximum

cyanide concentration before inhibiting nitrifying bacteria. Please refer to Appendix A to learn more about the exact volumes of PCE, RAS and SW-C used on each cycle.

The first time SW-C was fed into SBR A it was done without making any dilutions. The second time, when trying to find out if CN in the SW-C was the primary inhibitor, before each profile, CN was measured with a dip strip and dilutions using PCE were made accordingly based on the desired concentration target for SBR A. When dosing with KCN, instead of feeding SW-C, the entire volume was replaced with PCE to keep the same HRT and just a small, but concentrated amount of KCN, was added. Figure 3.6 illustrates the SBR A cycle.
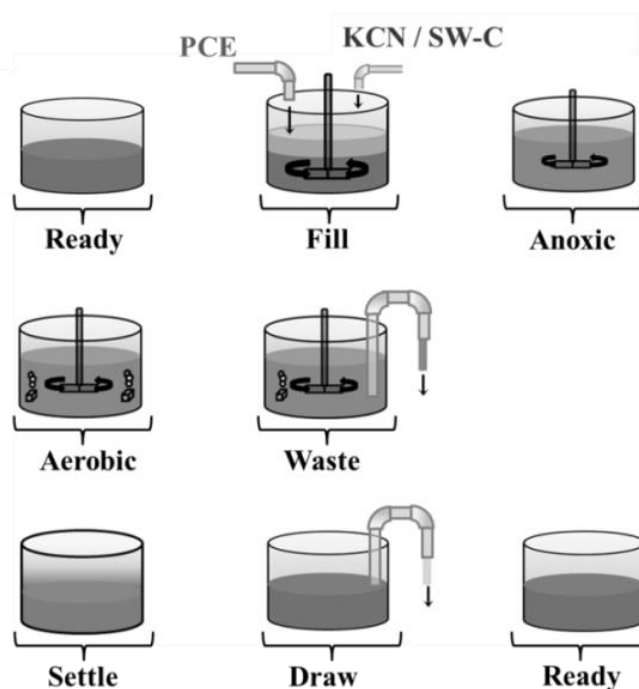
Figure 3.6 - SBR A Cycle

SBR A was operating four 6-hour cycles per day. On figure 3.7 it can be observed a typical cycle on SBR A. The anoxic period was 1.5 hours, the aerobic period 3.5 hours and the settling period lasted for 1 hour.
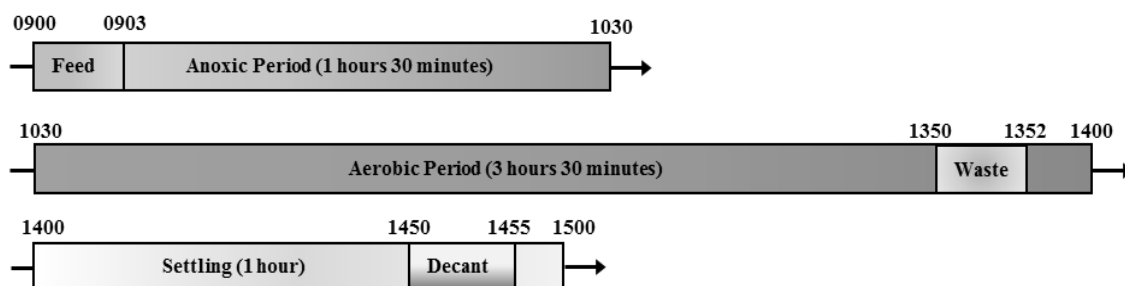
Figure 3.7 - SBR A cycle description

3.3.2 SBR B/ MBCNTP: BHTP using one aeration tank as a MBCNTP

SBR B / MBCNTP: Two tanks (19.22 L and 2.78 L) were used to simulate BHTP using one aeration tank to treat CN. To accomplish this, SW-C was only fed into the small reactor (simulating one aeration tank as MBCNTP) and PCE was fed into the larger reactor (simulating the remaining 5 aeration tanks). As it can be observed in Figure 3.8, before each cycle, all SW-C was mixed with RAS coming from SBR B and was continuously aerated until exiting the reactor. Additionally, MBCNTP and SBR B mixed liquor was combined before the settling period. This was attempted to simulate better BHTP configuration as shown in figure 1.2. As it can be observed in figure 3.9, ten minutes before the settling period was complete, SBR B was decanted for five minutes. Before sending the corresponding mixed liquor volume from SBR B to the MBCNTP

reactor, the mixer on SBR B was turned on for 2 minutes. This was done to obtain the same initial concentration of mixed liquor on SBR B and MBCNTP before every cycle.
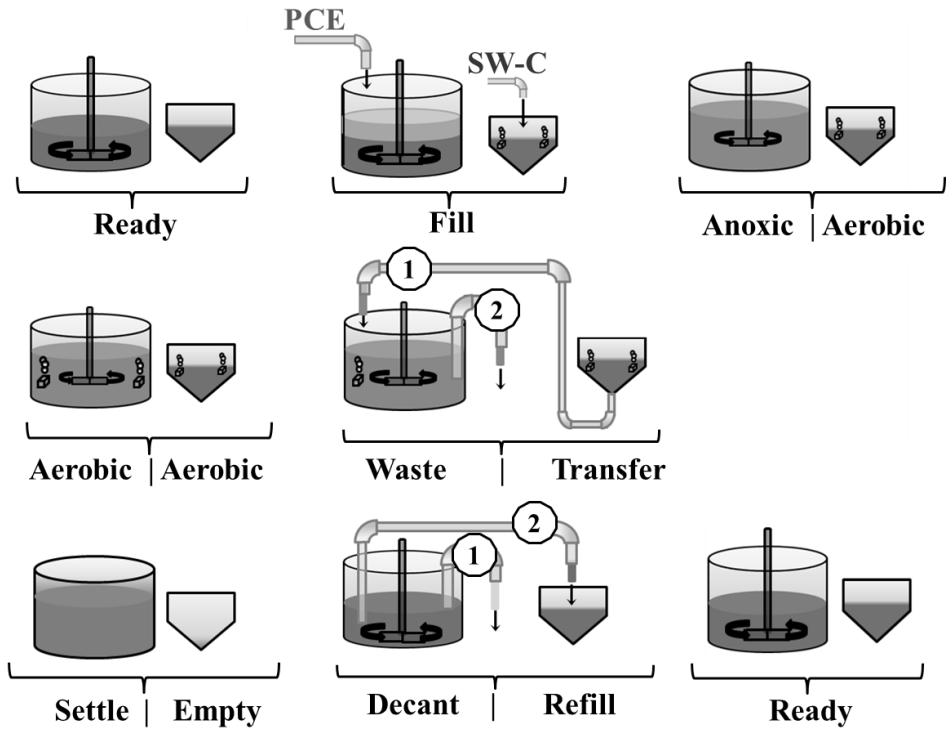
Figure 3.8 - SBR B/ MBCNTP Cycle
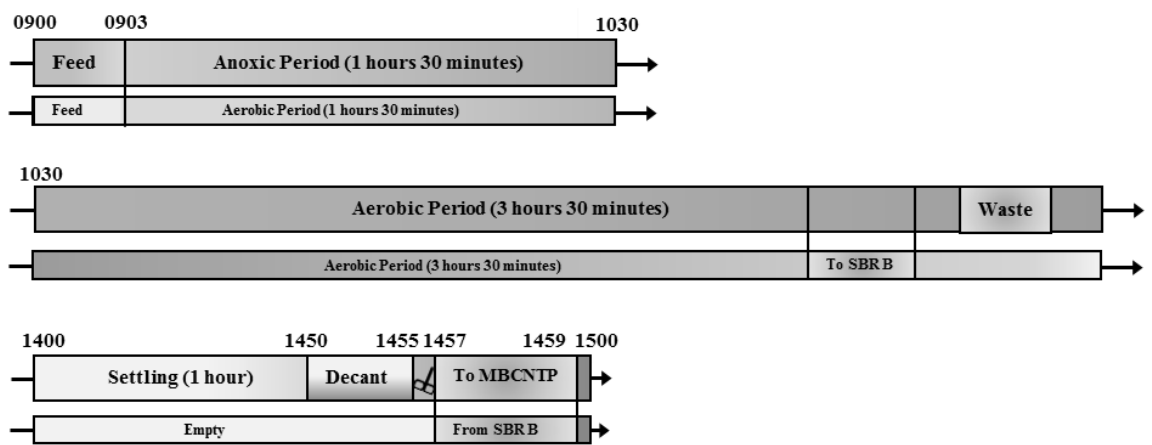
Figure 3.9 - SBR B/ MBCNTP cycle description

The first time SW-C was fed to the MBCNTP it utilized a 100% RAS configuration. In other words, the RAS volume used in the MBCNTP was the same as the other aeration tanks since usually at BHTP the same RAS flow is sent to each aeration tank. This was representing 1/6 of the total RAS flow. Temperatures on SBR B and MBCNTP were maintained at 20 °C.

When simulating 50% RAS configuration, the RAS flow used in the MBCNTP was simulating 50% of the regular RAS flow going to each aeration tank. In other words, if the total RAS flow is represented by the letter *Y*, and each RAS flow going to each aeration tank is represented by the letter *X*, then to represent a 50% configuration the total flow going to the MBCNTP will be *X/2*. This can be observed in Equation 3.1.

$$Y = 5X + \frac{X}{2} \qquad\qquad (3.1)$$

Temperatures in SBR B and MBCNTP were mainly maintained at 20 °C except when the temperature influence was studied. To better understand the impact of temperatures on CN removal, worst case scenarios were simulated. SBR B was maintained at 28 °C while temperatures on the MBCNTP were controlled and monitored, increasing them on each cycle. (See section 3.4 - Temperature Control for more details).

3.3.3 SBR C/ NEF C

SBR C / NEF C: Two tanks (22 L and 3.7L) were simulating the VIP NEF process and also served as the control. As it can be observed in Figures 3.10 – 3.11, first NEF C was wasted and second all of the SBR C's waste was sent to the NEF C where SW-C was treated, followed by a settling period. Initially 0.458 L of the settled solids was wasted but then, depending on the mixed liquor concentration, waste was corrected to maintain

the same SRT of 15 days. A total of 2.292 L were returned to the NEF C influent. The overflow from the NEF C was always sent to the SBR C before each cycle began.

This configuration was the same throughout the study but at some point temperatures on the SBR C and NEF C were increased, at the same time, from 20 °C to 28 °C (but always kept in the same water bath).
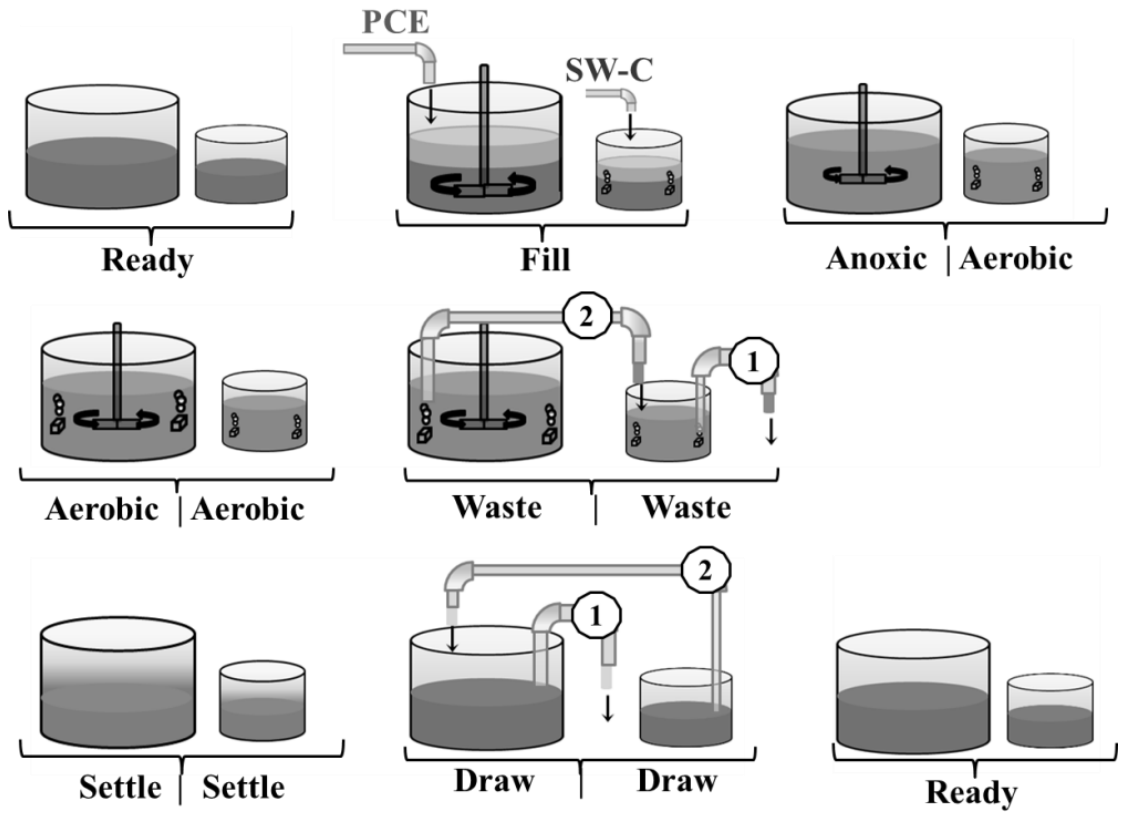
Figure 3.10 - SBR C/ NEF C cycle
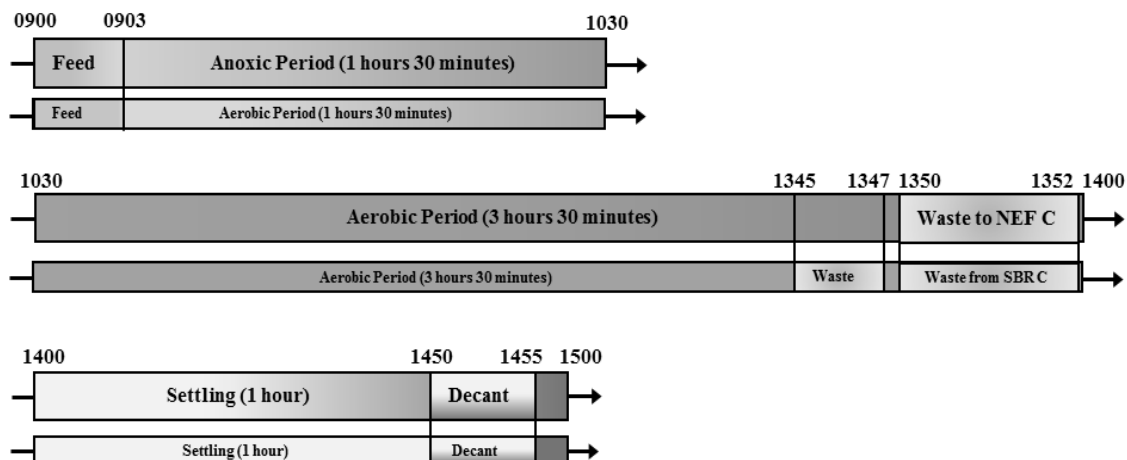
Figure 3.11 - SBR C/NEF C sequence schedule.

3.4 Temperature Control

3.4.1 SBRs temperature control

In an attempt to simulate ambient temperatures and summer temperatures, all SBRs were exposed to two different temperatures; 20 ± 0.5 °C and 28 ± 0.5 °C. This was achieved by using a Finnex Deluxe Titanium Heating Tube unit heater inside the water bath, connected to a Ranco ETC-111000 control unit.

3.4.2 MBCNTP temperature control.

MBCNTP reactor was controlled at different temperatures in a range of 20 ± 0.5 °C to 49 ± 0.5 °C. As shown on Figure 3.12, when temperatures were kept at 20 ± 0.5 °C, MBCNTP reactor was kept in the same water bath as the other SBR's.
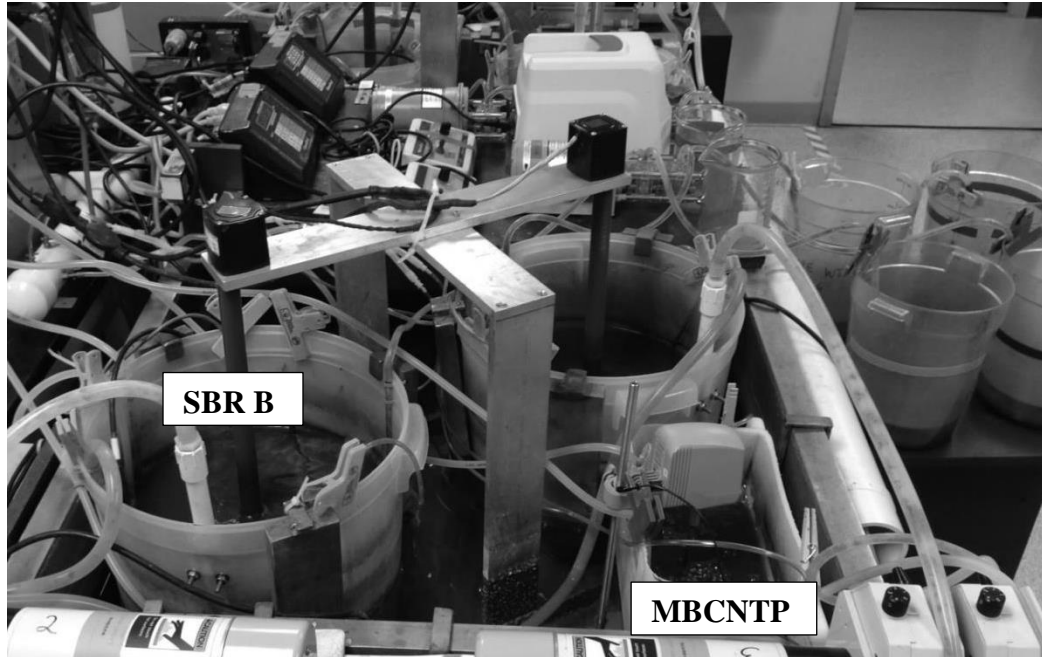
Figure 3.12 - SBR B and MBCNTP reactor sharing the same water bath.

When trying to simulate higher temperatures, MBCNTP reactor was relocated using its own water bath. On Figure 3.13 it can be observed that the MBCNTP tank was submerged in its own water bath, however, to minimize heat loss this water bath was then insulated (Figure 3.14).
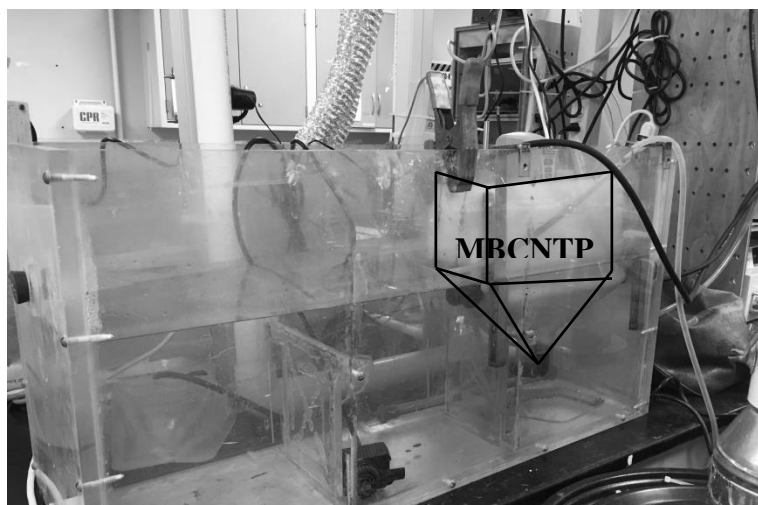
Figure 3.13 - MBCNTP waterbath before insulation.

Figure 3 14 - MBCNTP water bath after insulation.

The desired temperature on MBCNTP reactor was achieved by maintaining the temperature 2 °C higher in the waterbath. This was possible using an Ariston electric mini tank heater. Additionally, in order to have a better simulation of higher temperatures of the SW in BHTP, the SW-C cubitainers were placed into a separate water bath (Figure 3.15) using a Finnex Deluxe Titanium Heating Tube unit heater, connected to Ranco

ETC-111000 control unit. The main goal on this configuration was to achieve and maintain the desired target temperature as soon as SW-C was mixed with the RAS flow.

Figure 3.15 - NEF in the waterbath.

3.5 SRT Control

The SRT of the SBR's were maintained at 15 days SRT using a Garret configuration by wasting mixed liquor at the end of the aeration period just prior to the settling period. To monitor this, the wasted mixed liquor was collected in wasting buckets to be measured by volume on Mondays, Wednesday, and Fridays. During sampling events, the TSS concentration of the volume in the wasting buckets was assumed to be equivalent to the measured mixed liquor TSS concentration from the previous profiles. Based on the mass balance of the solids in the system and leaving the system, the additional solids that need to be added back or taken out of the system was calculated in order to maintain the

desired SRT every Monday, Wednesday, and Friday. To prevent any mixed liquor addition into SBR C, the wasting pump rate was changed for SBR C and NEF C (matching pump rates).

3.6 Dissolved oxygen control

During the aeration period, all SBR DO concentrations were automatically controlled between 2.0 and 3.0 mg/L by using two ceramic air stones with ON/OFF solenoid valves. When the DO levels dropped below 2.0 mg/L, the solenoid valve would turn on and let air flow through until the concentration of 3.0 mg/L was met. During the aeration period continuous mixing using a flat paddle mixer was performed. DO in the reactors was measured using conventional galvanic membrane probes (Royce Technologies, College Station, TX). DO data was logged every 20 seconds into a Telog system with data accessed through an online portal.

3.7 pH control

A pH probe was installed on each SBR and controlled automatically above 6.6 by adding sodium carbonate. When the pH dropped below 6.6 a peristaltic pump would turn on to add alkalinity until the pH was 6.8. The pH was monitored using Foxboro probes and the data was logged every two minutes through a Telog system for monitoring purposes.

3.8 Sampling

Samples were collected three times per week, which included: COD, sCOD, TSS, TKN and TP on the PCE, TSS on the mixed liquor, and TSS and TKN on the Effluent. Twice per week nutrient analysis (NH_3-N, NO_3-N, NO_2-N), sCOD, and WAD CN^- samples were collected over a single reactor cycle to monitor nitrification/denitrification and to determine CN removal.

3.8.1 Nutrient Analysis

Samples for nutrient analysis were taken in 15 mL aliquots and immediately vacuum filtered using Pall Metricel® 0.45 μm membrane filters and stored at 4°C until analysis. These nutrients were analyzed by Hach tubes (Loveland, CO) and through a Hach DR2800 spectrophotometer.

3.8.2 Ammonia

Ammonia analysis was performed using Hach Test'N Tube Plus (TNT Plus) 830, 831 and 832. The range for each tube was as follows:

Hach TNT Plus 830 - Ultra low range (0.015 – 2.0 mg/L NH_3-N)

Hach TNT Plus 831 - Low range (1.0 – 12.0 mg/L NH_3-N)

Hach TNT Plus 832 - High range (2.0– 47.0 mg/L NH_3-N)

These kits used the salicylate method (method 10205) for analysis where ammonium ions react with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside act as a catalyst to form indophenols. Indophenol blue detected at 690 nm is the

colorimetric indicator formed by this process, which was directly proportional to the ammonia nitrogen present in the sample.

3.8.3 Nitrite

Nitrite analysis was performed using NitriVer3 test kit or the Hach TNT Plus 840. The range for each tube was as follows:

Hach NitriVer3 – Low range (0.0 – 0.5 mg/L NO_2^--N)

Hach TNT Plus 840 – High range (0.6 – 6.0 mg/L NO_2^--N)

The NitriVer3 test kit uses the Diazotization Method, 10019, where the nitrite in the sample reacts with sulfamic acid to form an intermediate diazonium salt. This salt combined with chromotropic acid forms a pink color which is directly proportional to the amount of nitrite present. The measurement wavelength is 507 nm for spectrophotometers or 520 nm for colorimeters.

The TNT Plus 840 kit uses the Diazotization Method, 10237, where the nitrite in the sample reacts with a primary aromatic amine in acidic solution to form a diazonium salt. This couples with an aromatic compound to form a colored complex that is directly proportional to the amount of nitrite present in the sample when measured at 515 nm.

3.8.4 Nitrate

Nitrate analysis was performed using the Hach TNT Plus 835. The range for the tube was as follows.

Hach TNT Plus 835 - Low range (0.23 – 13.5 mg/L NO_3^--N)

The TNT Plus 835 kit use the dimethylphenol method (10206), where nitrate ions in a solution containing sulfuric and phosphoric acids and react with 2, 6-dimethylphenol to form 4-nitro-2, 6-dimethylphenol. These results were measured at 345 nm.

Before performing any nitrate test, to prevent any interference, nitrite concentration was verified. When any of the samples contained more than 2.0 mg/L of NO_2^-N, approximately 50 mg of sulfamic acid was added to a 5.0 mL sample. After 10 minutes, the sample was ready to perform the method described above.

3.8.5 WAD Cyanide Method

This method is to determine the weak acid dissociable (WAD) and free cyanide in samples of drinking water and domestic and industrial wastewaters. The cyanide is released by digesting and acidifying cyanide complexes, converting them to hydrocyanic acid (HCN). The cyanide ion is trapped in a 1.0 M sodium hydroxide absorbing solution which is diluted to 0.25 M solution during the distillation. By means of flow injection analysis, the distillate is converted to cyanogen chloride, CNCl, by reaction with chloramine-T, pyridine and barbituric acid, to give a red-colored complex. The absorbance of this complex is measured at 570 nm by measuring the peak area resulting from the sample.

3.8.6 Total CN Method

Total CN is defined as all of the cyanide groups in cyanide compounds that can be determined as the cyanide ion, CN^-. The cyanide is released by digesting and acidifying cyanide complexes, converting them to hydrocyanic acid (HCN). The cyanide ion is

trapped in a sodium hydroxide absorbing solution. By means of flow injection analysis, the distillate is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at pH lower than 8. The CNCl then forms a red-blue dye by reacting with pyridine-barbituric acid. The color is read at 570nm.

3.9   Jar testing

The main purpose of performing different jar tests (Figure 3.16) was to determine the dosage rate of ferrous sulfate and to find optimal conditions to form soluble Fe-CN complexes and/or insoluble Fe-CN precipitates for the removal of cyanide.

Figure 3.16 - Jar test setup.

When the DO was controlled, the target concentration was achieved by using either air or nitrogen gas (N_2). If the DO concentration was below the target, air was added to increase it and if the DO concentration was above the target, N_2 was added to decrease it (Figure 3.17).

Furthermore, the pH was controlled by using NaOH to increase it or H_2SO_4 to decrease it. Each jar test was performed by first, placing SW-C or KCN (at the desired concentration) in a beaker and then while adding ferrous sulfate a rapid mix of 1 minute was achieved, followed by 30 minutes of slow mixing to allow flocculation to commence and 30 minutes for settling. At the end of the settling period a sample from the supernatant was taken and sent to HRSD Central Environmental Lab (CEL) to test Total CN and WAD CN$^-$.

Figure 3.17 - Jar test when adding air and N_2.

3.9.1 Precipitating CN⁻ using alkalinity from the RWI

For the jar test, an approach of BHTP feeding ferrous sulfate at the SW wet well, before going to the headworks, was simulated. The idea was that after feeding ferrous sulfate, the alkalinity from the raw wastewater influent (RWI) was going to create optimal conditions for the precipitation of CN^- and subsequently remove it on the primary tanks. It should be noted that in the actual jar test PCE was used instead of RWI since it was conveniently already at the lab (feeding the SBRs) and both should have the same alkalinity.

3.9.2 Combining chemical precipitation and biological oxidation of CN

This option was simulating BHTP by feeding ferrous sulfate at the wet well before going to the MBCNTP system. Alkalinity, as sodium hydroxide, was used to increase the pH before mixing the SW-C with the RAS in the MBCNTP. The idea was to possibly reduce the CN^- concentration by precipitation before entering into the MBCNTP system or before biological oxidation occurred.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Influent characteristics

Steady state was established within two months of SBR operation and full nitrification/denitrification was verified before any reactor was exposed to CN. Table 4.1 summarizes the influent characteristics and standard deviation for all SBRs. All influent data collected throughout the operation of the SBRs were compiled and plotted vs time and can be seen in Figures 4.1 – 4.6.

Table 4.1 - Influent wastewater characteristics.

Characteristic	Average (mg/L)	Std. Dev (mg/L)
NH_4-N	42.6	5.9
TKN	45.5	5.9
OP	9.7	5.9
TP	10.0	5.9
COD	392.9	5.9
sCOD	172.7	5.9
TSS	61.4	5.9
Volatile Fraction	89 %	5.9 %
TVSS	54.3	5.9
COD/TKN	8.8	6.0
COD/TP	41.3	6.0
WAD CN$^-$ (SW-C)	8.3	3.6
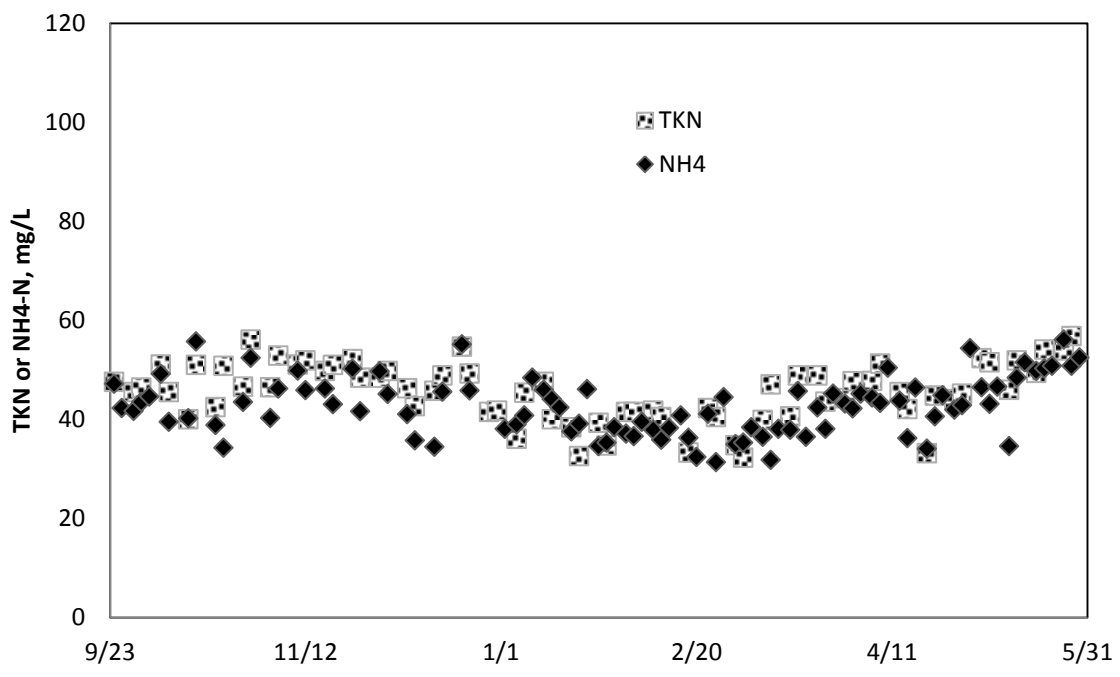
Figure 4.1 - Influent TKN - NH$_4$-N.
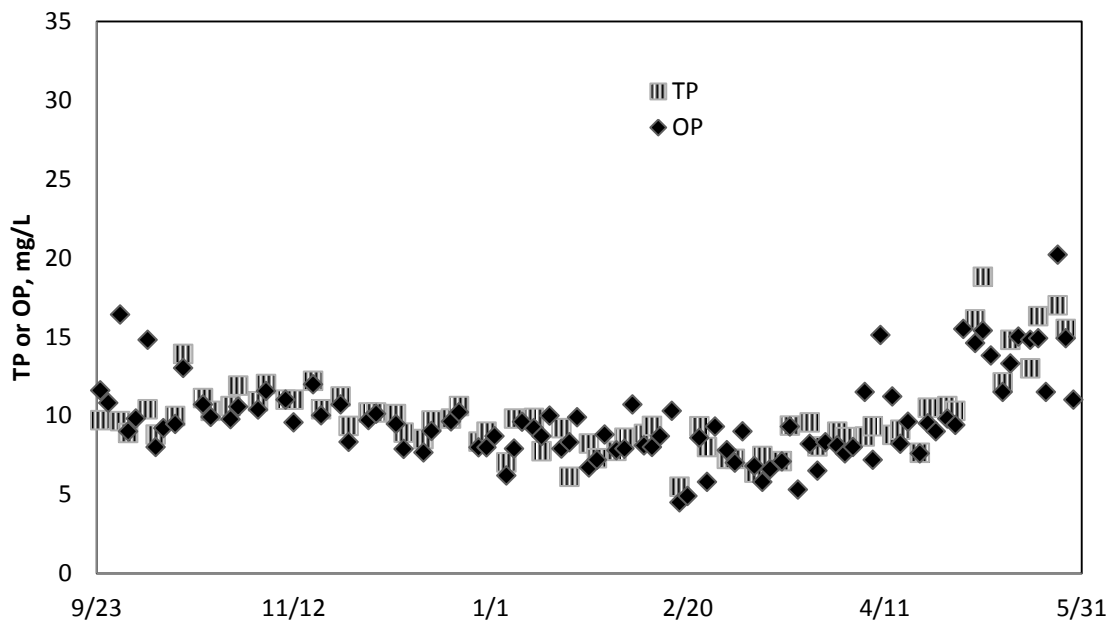
Figure 4.2 - Influent TP- OP.
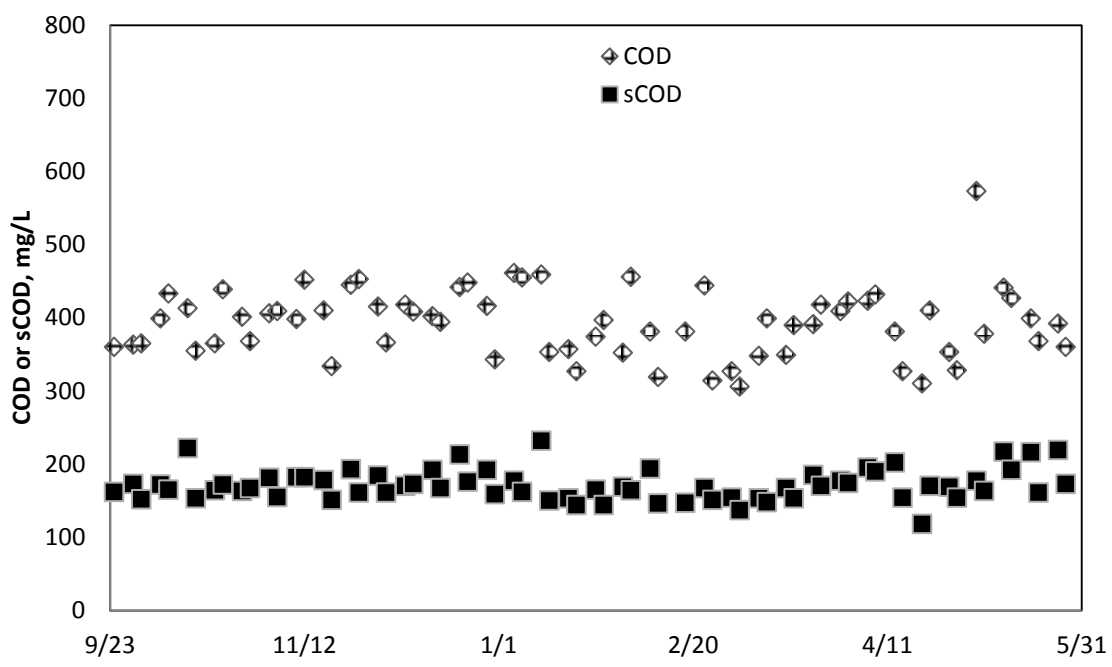
Figure 4.3 - Influent COD – sCOD.
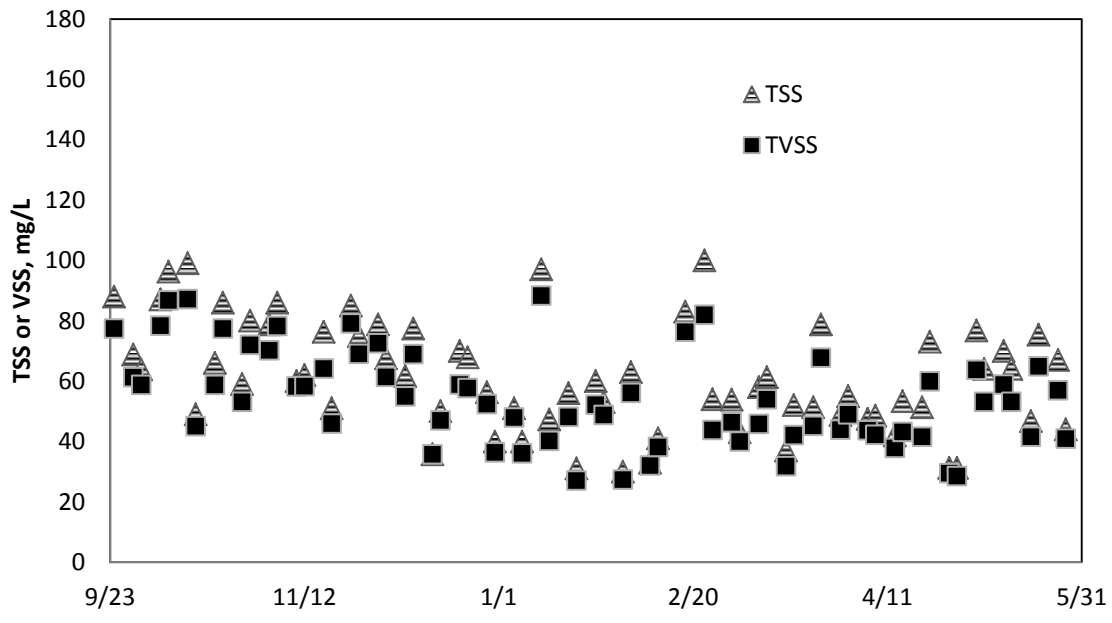
Figure 4.4 - Influent TSS - VSS.
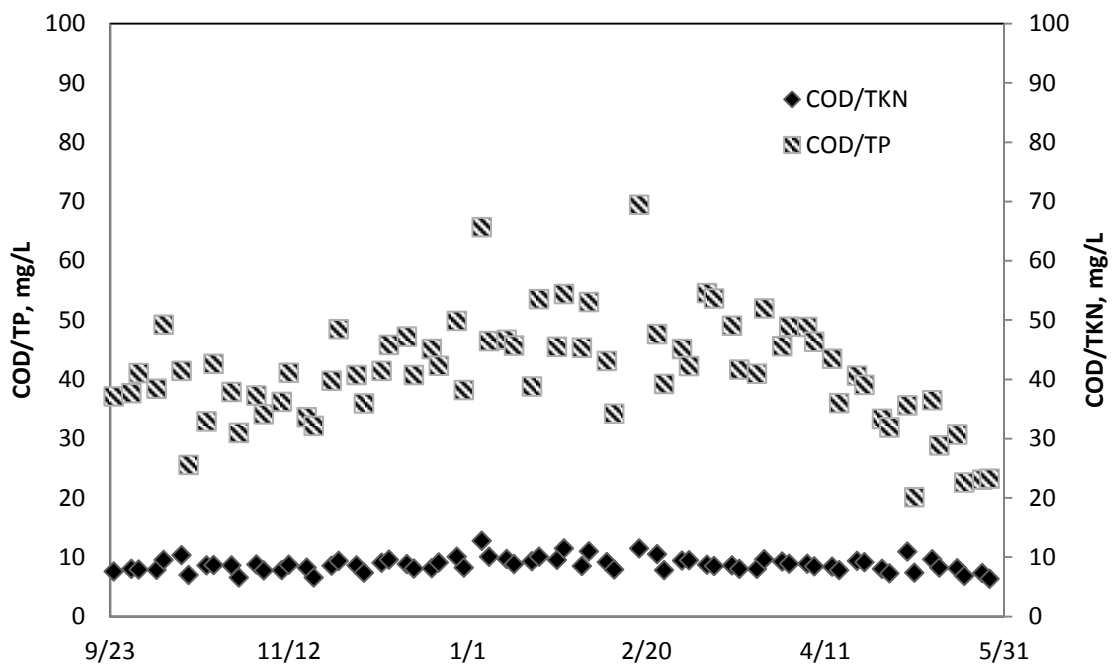
Figure 4.5 - Influent COD/TP - COD/TKN.
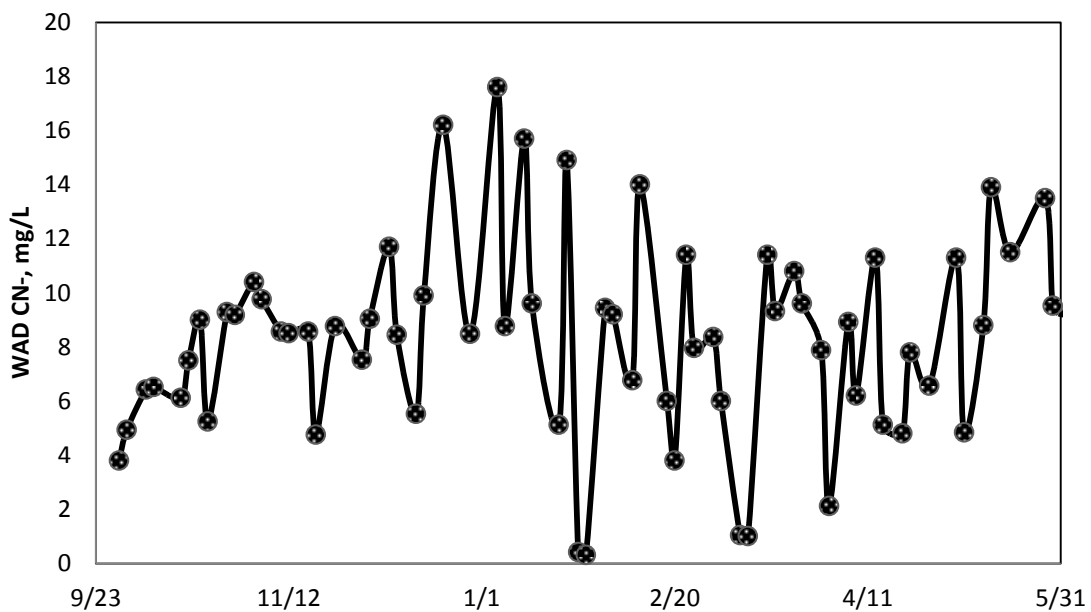
Figure 4.6 - Influent WAD CN⁻ (SW-C).

4.2 Operation

All SBRs started with the same operating conditions. As observed in Figure 4.7, the MLSS/MLVSS concentration in all SBRs was around the same, but as soon as the reactors were exposed to SW-C for the first time (September 29, 2014) the MLSS/MLVSS started to change. The best explanation for this behavior is that all SBRs were maintained at the same SRT; however, later on, the SBRs were not exposed to the same operating conditions (different CN concentration, different reactor configurations, temperatures, etc.). MLSS concentration for SBR C was constantly higher than in any of the other reactors, as this was required to maintain the 15 days SRT.
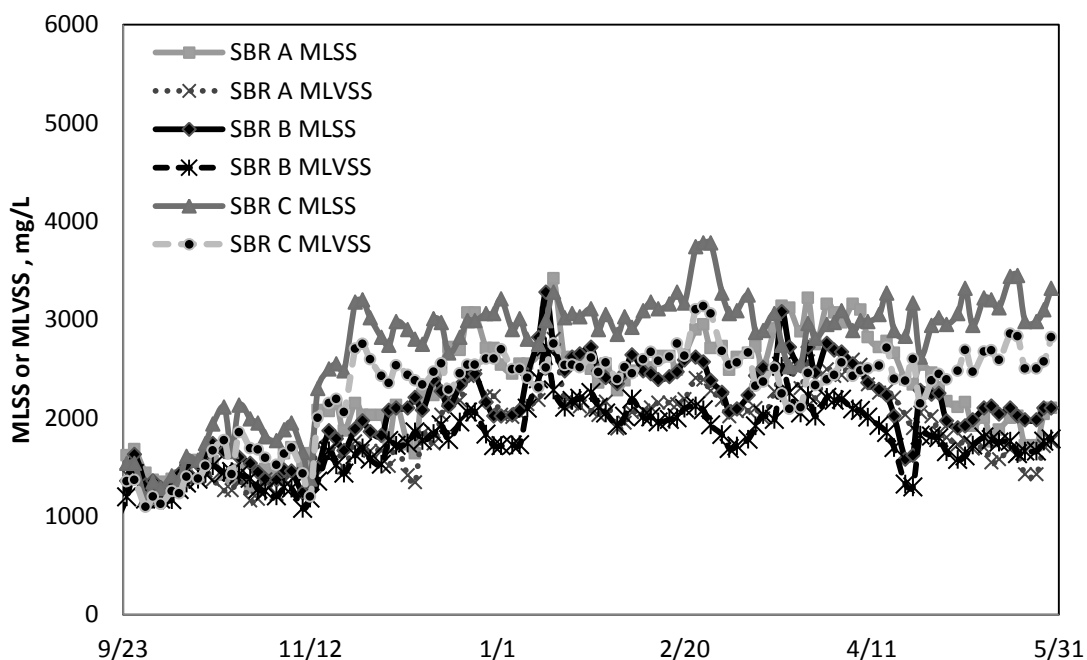
Figure 4.7 - MLSS and MLVSS through course of study.
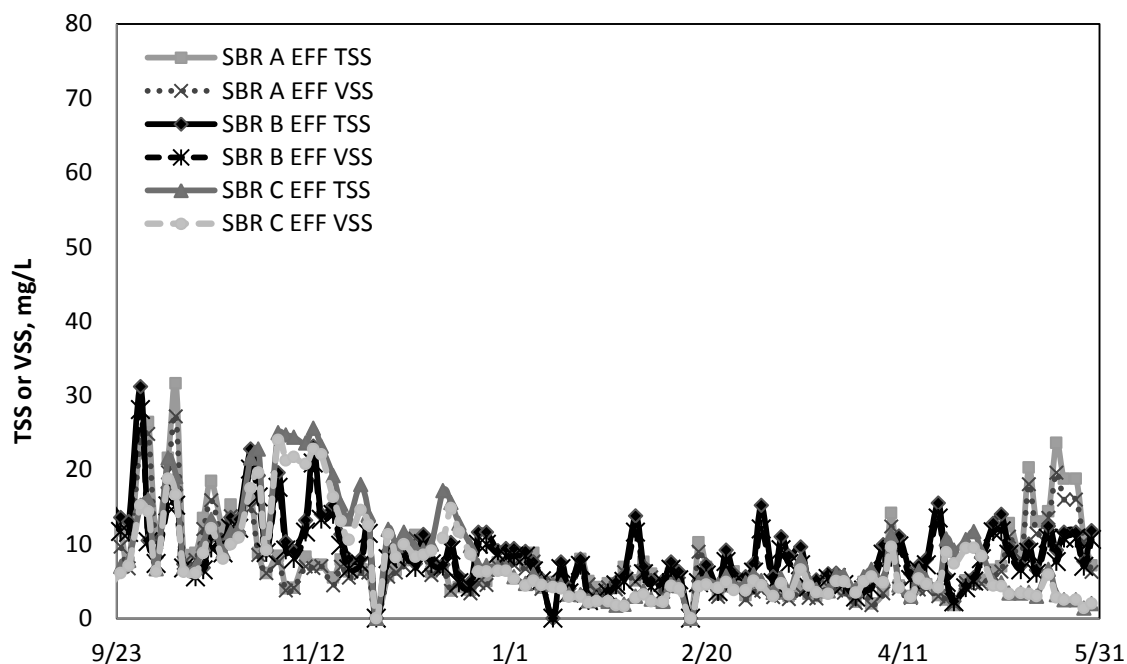
Figure 4.8 – Effluent TSS and VSS through course of study.

As shown in Figure 4.9, the SRT from all SBRs were well maintained at 15 days from September to December 2014. Nonetheless, on December 22, 2014 as soon as the configuration on SBR B / MBCNTP was switched from 100 % to a 50 % RAS, the SRT started to vary from 10 to 20 days SRT being difficult to maintain it at 15 days SRT. One possible reason of why this happened was because initially the SBR /MBCNTP was design for 100% RAS configuration but later on was decided to switched to 50%. By doing this, more solids were kept in SBR B since at the beginning of each cycle only half of the solids were transferred to the MBCNTP.
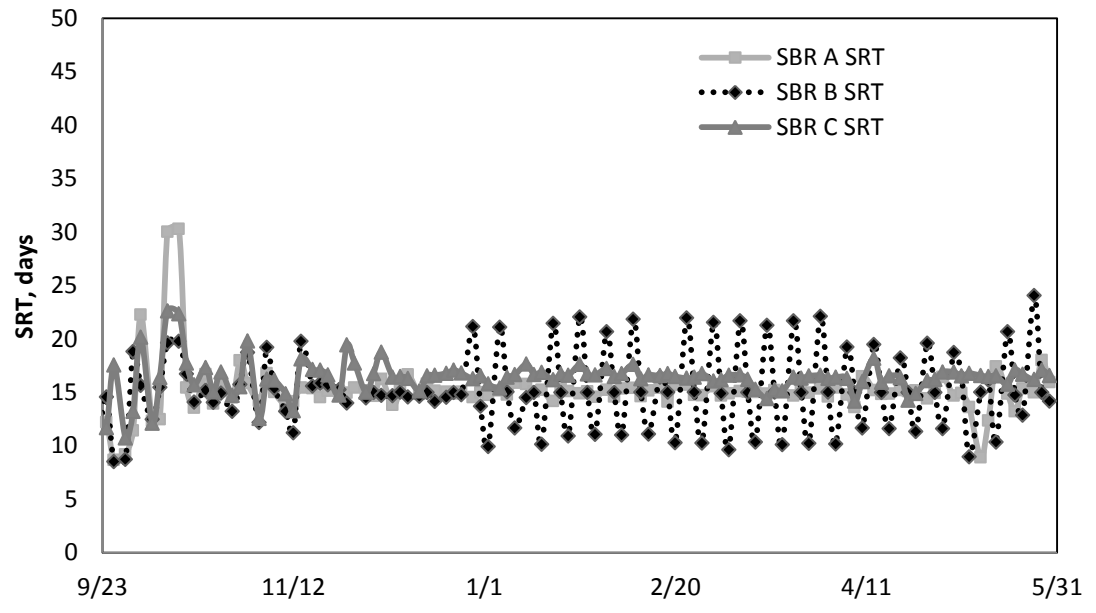
Figure 4.9 - SRT through course of study.
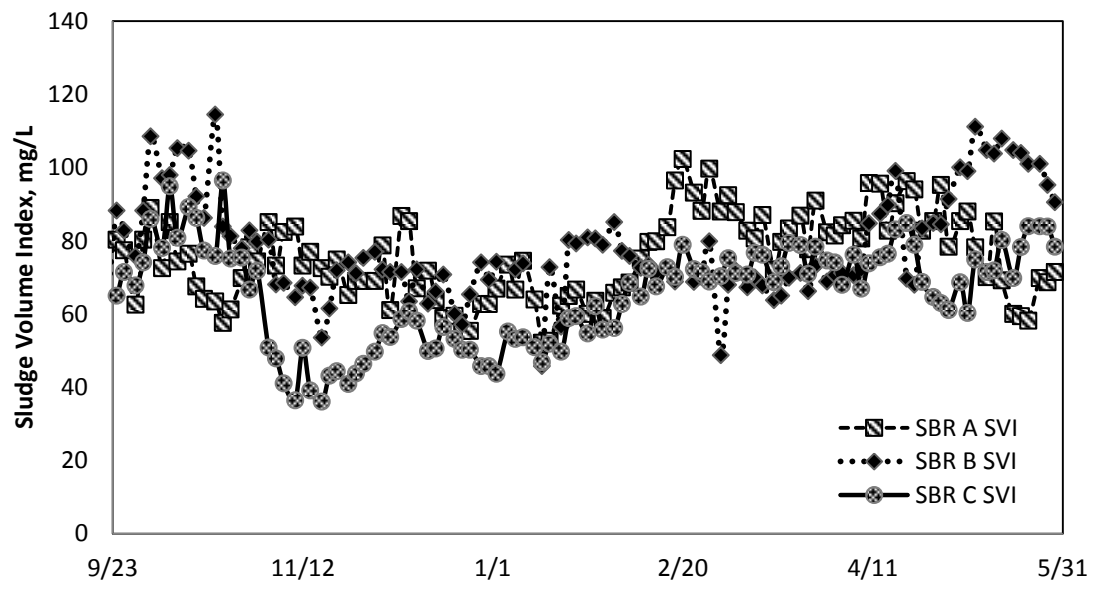
Figure 4.10 - Sludge Volume Index through course of study.

4.3 SBR Results

4.3.1 SBR A

Every time a nitrogen profile was performed, WAD CN⁻ samples were taken to determine if the target CN concentration in the reactor was achieved. Figure 4.11 showcases the four CN samples points selected for SBR A. Point 1 represented the CN concentration of the KCN stock solution or influent SW-C. Point 2 represented the CN concentration after being mixed with the PCE and RAS in the anoxic zone. Point 3 represented the CN concentration at the aeration tank effluent. Finally, Point 4 represented the CN concentration at the secondary clarifier effluent (SCE).
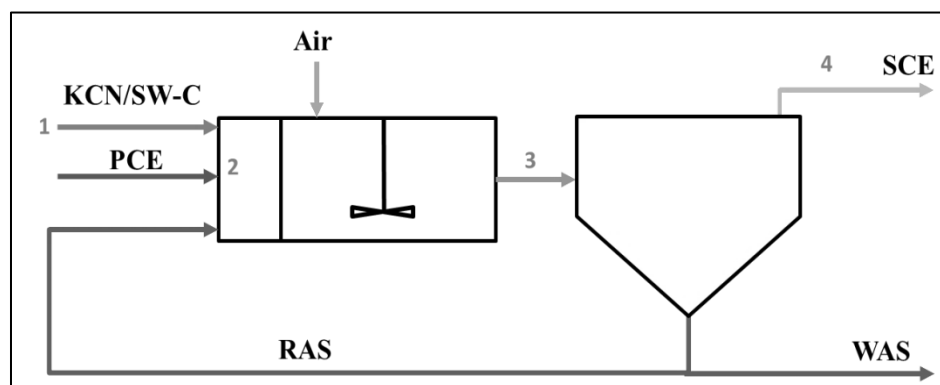
Figure 4.11 – WAD CN⁻ sample points for SBR A.

4.3.1.1 SBR A exposed to SW-C

Figure 4.12 displays the performance of SBR A reactor prior to being exposed to SW for the first time. The diamonds symbols on the uppermost graph represent the WAD CN⁻ concentration on different sample points (1, 2, 3 & 4). These sample points are the same

points as shown on figure 4.11. The solid dark line represents the threshold concentration of 0.10 mg/L CN⁻ (Neufeld, 1984; Britton, 1984), meaning that if a cyanide sample on point 2 (representing the aeration tank influent) is above the line, this will potentially inhibit the nitrification process. The lower graph represents the nitrogen profile in the anoxic, aerobic and settling zone. All samples for WAD CN⁻ and nitrogen species were taken on the same cycle.

On figure 4.12 can be noted that SBR A was fully nitrifying on September 25th, 2014.
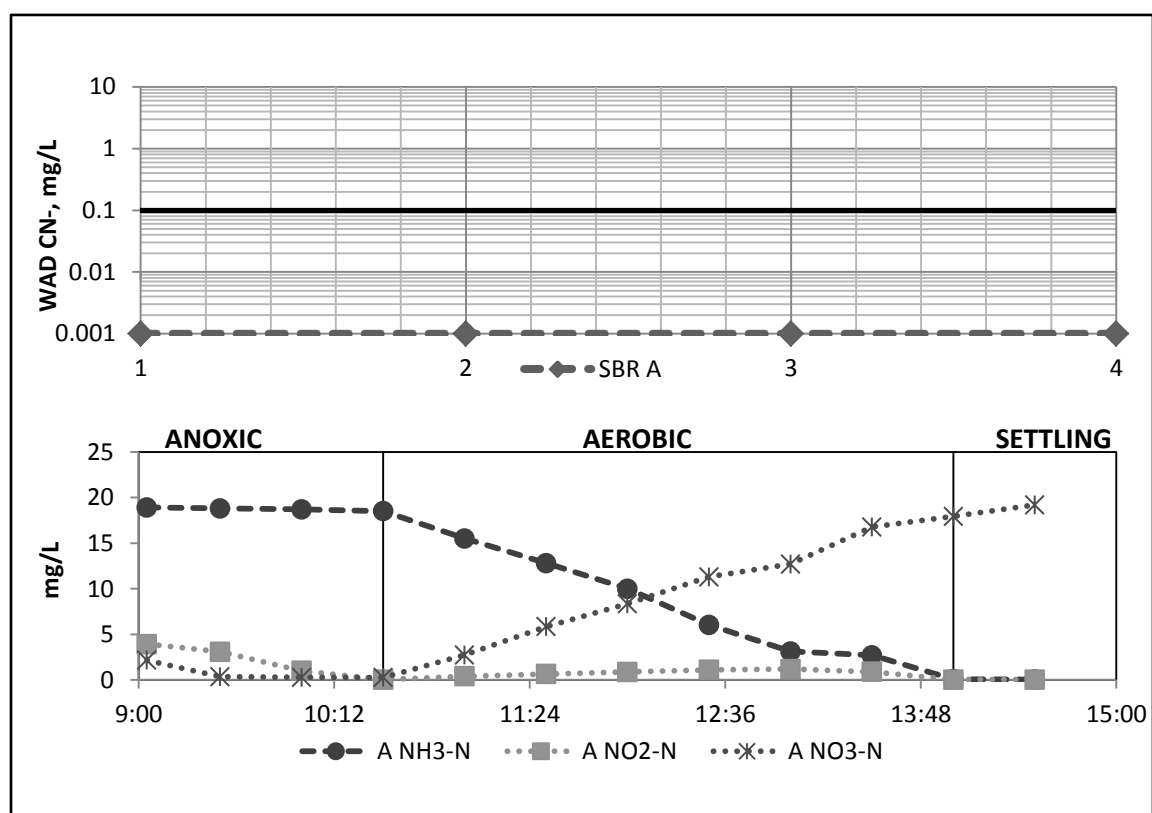
Figure 4.12 – WAD CN⁻ and Nitrogen profile without SW-C (9/25/14).

For SBR A fed with SW, rapid loss of nitrification was observed at 20 °C at a 15 day SRT. According with Figure 4.13, WAD CN⁻ concentration of 2.90 mg/L (Point 1) in the SW-C was enough to inhibit the nitrification process with a concentration of 0.2 mg/L WAD CN⁻ (Point 2) in the reactor. This behavior was expected since it is higher than the expected threshold concentration.
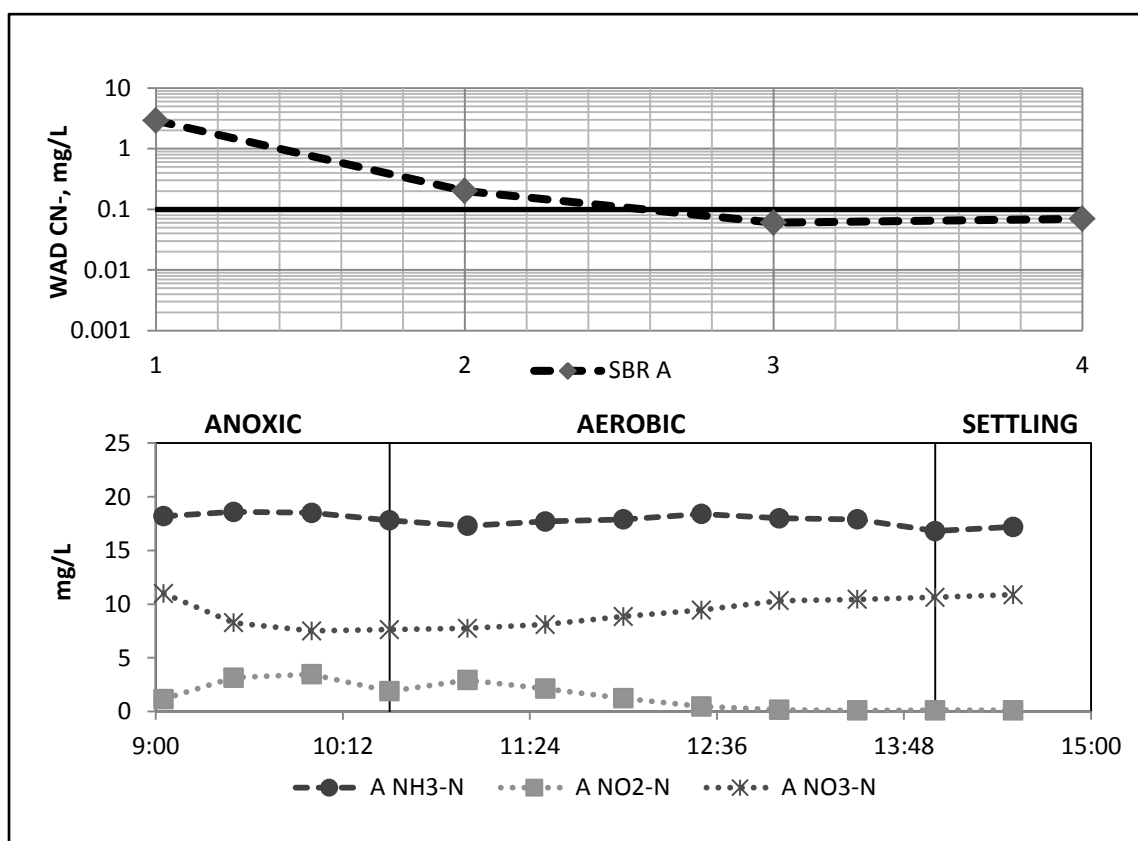
Figure 4.13 – WAD CN⁻ and Nitrogen profile without SW-C (9/29/14).

As anticipated, once SW-C feed was stopped and replaced with PCE, full nitrification was recovered. This confirmed that CN is only an inhibitor and not toxic for nitrifying bacteria, as perceived on Figure 4.14.
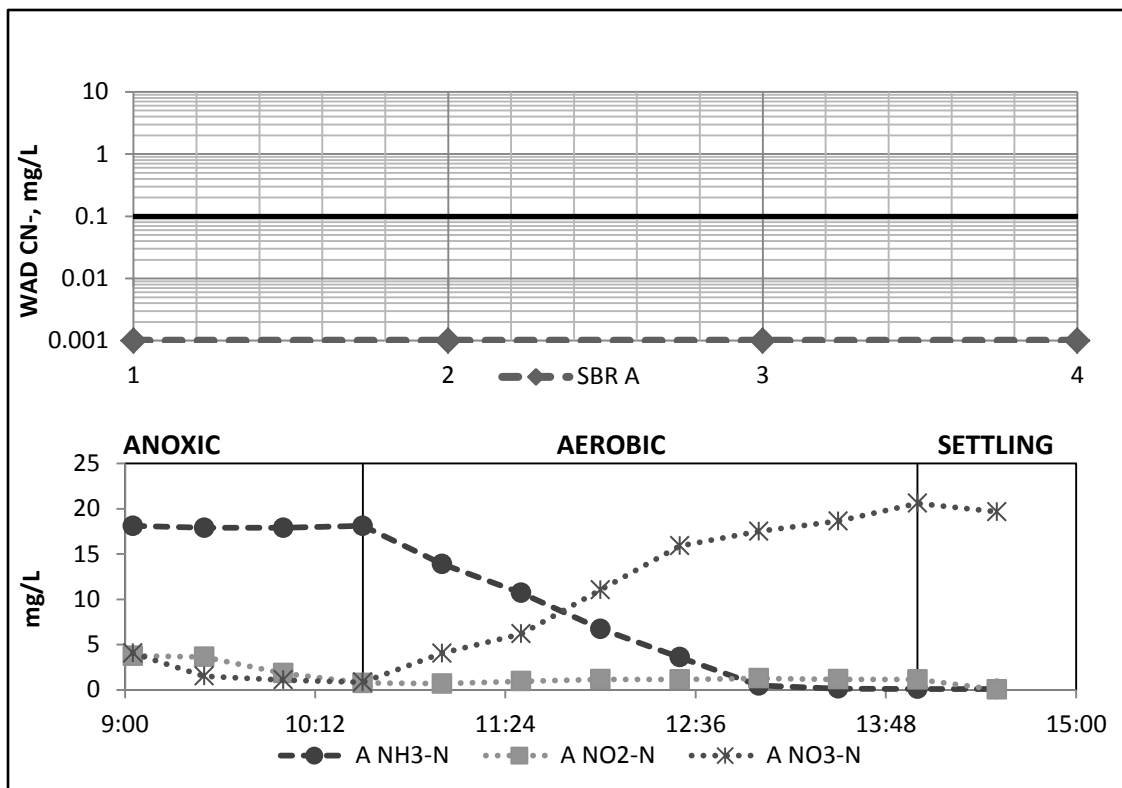
Figure 4.14 – WAD CN⁻ and nitrogen profile recovery (10/08/14).

Figure 4.15 was plotted to show the expected influent CN concentration at the influent of any aeration tank if all aeration tanks were in service and operated to nitrify. The CN concentration at the influent of the aeration tanks depends on the influent flows coming in to the plant, the RAS flow coming from the secondary clarifiers, and the SW-C CN concentration. This also depends on the degree to which the aeration tank is configured to represent more plug flow or complete mix conditions, with more complete mix providing a lower expected aeration tank CN concentration. Simulation of these processes in SBR provides a worst case in terms of potential CN inhibition, because a SBR, which is fed SW-C and CN in a single fast pulse input, simulates in time a perfect

plug flow aeration tank in space. That was the case here. The higher the influent flow, the more diluted the CN concentration will be at the aeration influent. For most MHF (one unit in service) SW-C flow is about 1 MGD, while plant flow could vary over a large range, as plant flow increases, generally MHF solids load should increase and then CN load may or may not increase depending on how the MHF is being operated.

In order to achieve a CN concentration below 0.1 mg/L, very low concentrations of CN in the SW-C must be maintained at all times. At BHTP the average SW-C flow is around 1.33 MGD, less than 3 mg/L of CN are required when having flows of 20 MGD coming in and less than 1 mg/L when having flows of 10 MGD. As shown in Table 4.1, the average WAD CN$^-$ concentration of the SW-C collected in the collapsible containers, that were used for the SBRs was 8.3 +/- 3.6 mg/L. However, the WAD CN$^-$ concentration from a grab sample at BHTP could be as high as 30 mg/L, in other words, sending the SW-C to the head of the plant, like simulated on SBR A, is not a feasible solution due to the fluctuation of the CN concentrations in the SW-C.
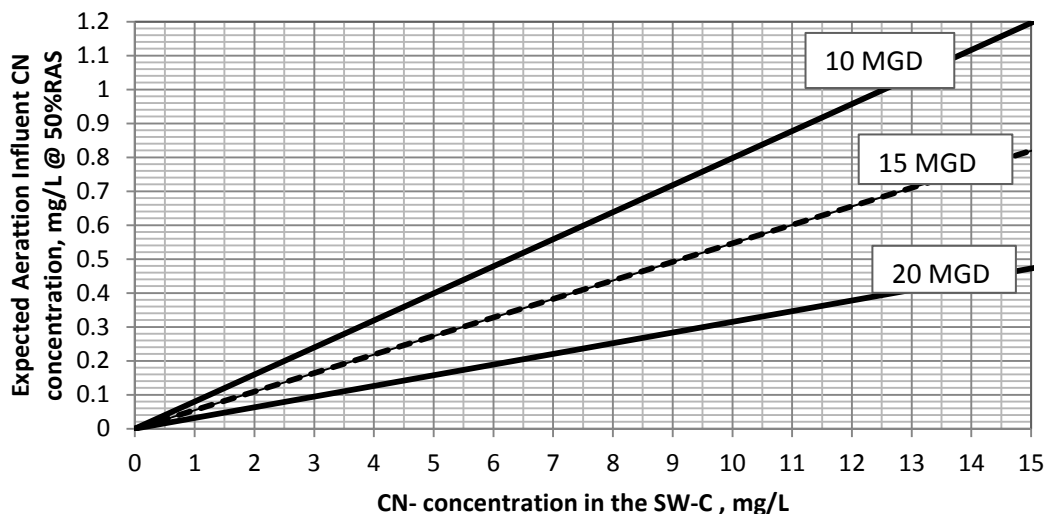
Figure 4.15 - Expected CN concentration in the aeration tanks with no separate SW treatment (assuming 1.33 MGD SW-C flow in all cases)

4.3.1.2 SBR A exposed to KCN targeting different concentrations of CN (20 °C)

To be able to confirm the literature value of 0.1mg/L CN (Neufeld, 1984; Britton, 1984) concentrations of 0.02, 0.04, 0.08, 0.09 mg/L and 0.1 mg/L as CN, using KCN as the CN source, were targeted in the SBR A reactor at the beginning of the cycle at 20 °C. On Figure 4.16, the different nitrification rates can be observed on the aeration zone (from 10:30 to 14:00) at 15 days SRT. It was found that CN concentrations began inhibiting the nitrifying activity at values above 0.08mg/L. It can also be observed that the nitrification rate was not affected when the reactor was exposed to 0.02 or 0.04 mg/L of CN, however, when it was exposed to 0.08 mg/L an evident decrease on the nitrification rate was noticed and ammonia had not been completely oxidized by the end of the aerobic period showing 20% of the initial ammonia concentration.
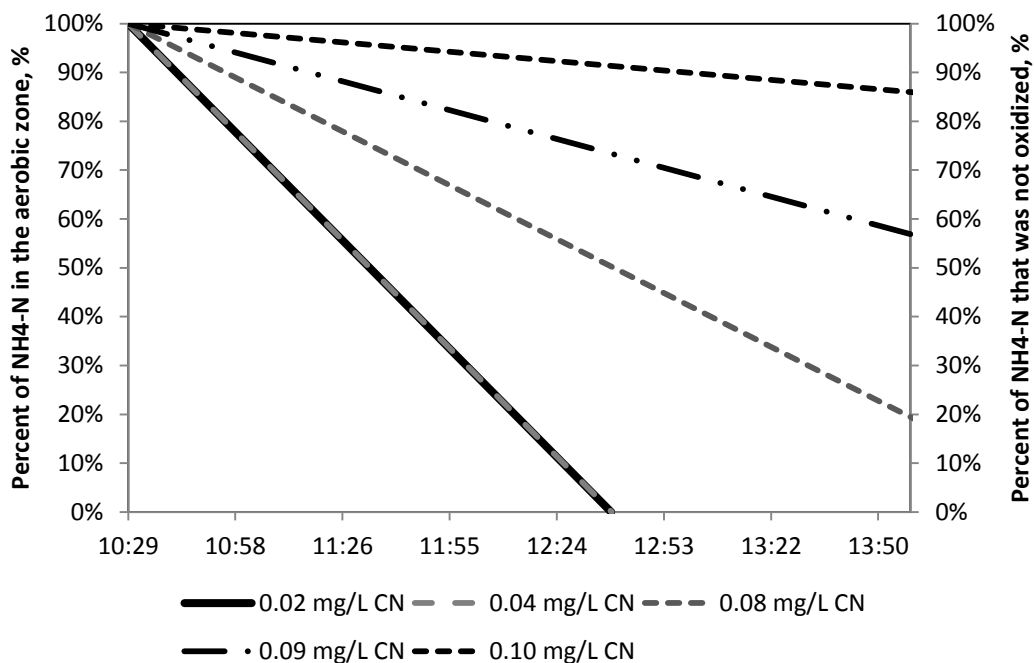
Figure 4.16 - SBR A nitrification rates at different CN concentrations using KCN.

These results reveal that at 0.08mg/L (HCN, CN⁻) is when CN inhibition will commence affecting the nitrification rate.

4.3.1.3 SBRA exposed to SW-C targeting different concentrations of CN (20 °C)

To identify if CN in the SW-C was the primary inhibitor of nitrification, the same approach of targeting different concentrations in the SBR A reactor was tested but this time instead of using KCN, SW-C was utilized.

When comparing Figure 4.17 (using SW-C) and Figure 4.15 (using KCN), it is revealed that both behaviors are almost identical. It can be claimed that the CN form present in the SW-C is as free CN. Moreover, it is clear that CN in the SW-C is the

primary inhibitor. Furthermore it can be stated that when exposing the nitrifiers to SW-C, at 0.10 mg/L of CN (20 °C AND 15 days SRT) the nitrification rate will be affected oxidizing only 20% of the initial ammonia concentration.
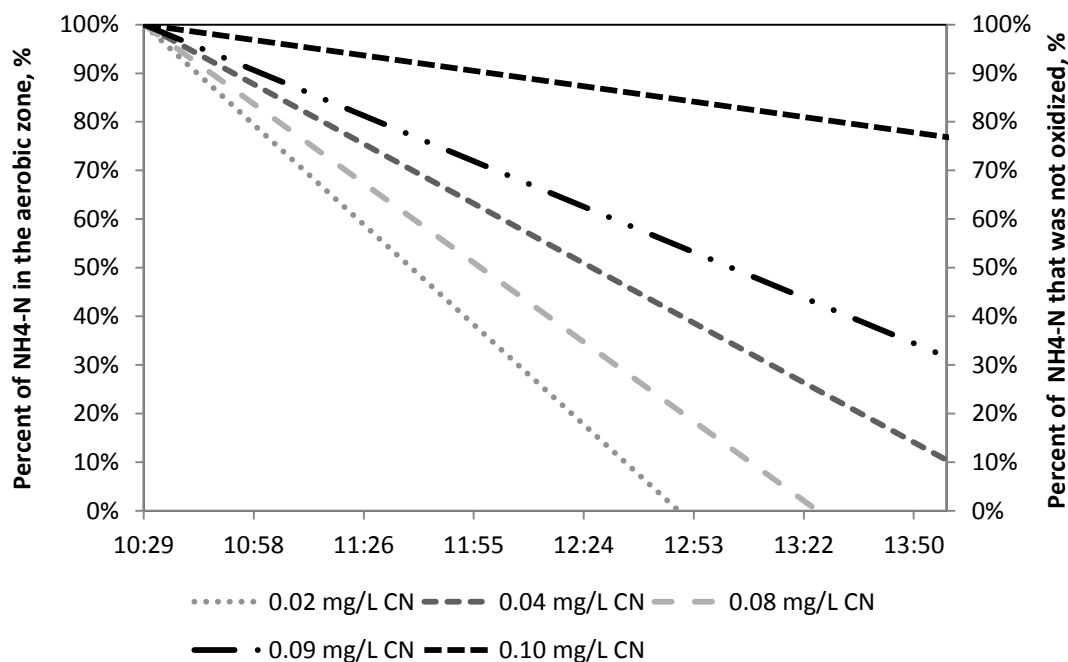
Figure 4.17 - SBR A nitrification rates at different CN concentrations using SW-C.

4.3.1.4 Nitrite Accumulation on SBR A

Something interesting happened to SBR A between March, 23rd and April 16th, 2014 while the reactor was being prepared for the next study. In an attempt to keep active the cyanide degrading bacteria, it was decided to keep feeding KCN at the beginning of each reactor cycle, targeting a concentration of 0.05 mg/L CN$^-$. Figure 4.18 shows how

the nitrite started to accumulate at the sample that represented the SCE. This was suggesting that the NOB population was becoming inhibited; however, within a few days of operation the nitrite went back to its normal low concentration. This behavior suggests that in some cases bacteria are capable to acquire some resistance when exposed to steady toxic inputs. In this case the NOB population was able to recover after being exposed to a constant concentration causing a less deleterious effect with time.
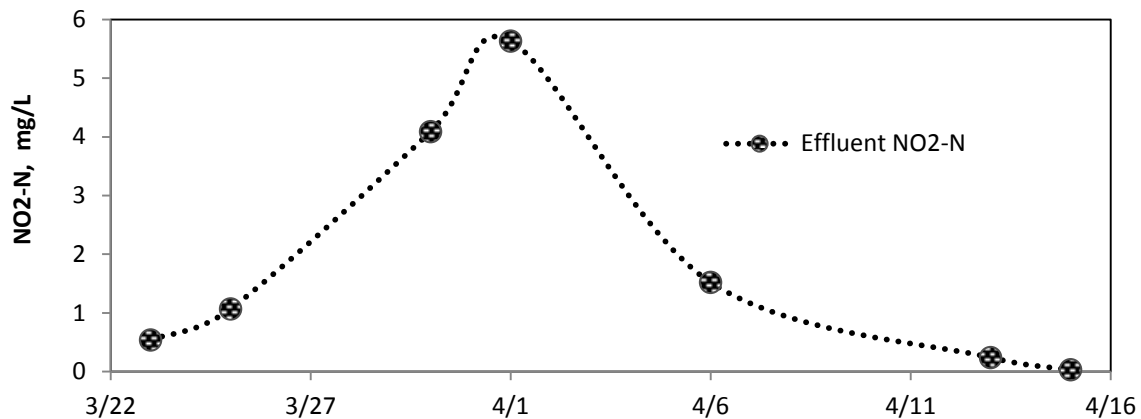
Figure 4.18 – Nitrite at SCE when SBR A was kept at a constant concentration of 0.05 mg/L CN

4.3.1.5 SBR A exposed to KCN targeting different concentrations of CN at warmer temperatures (28 °C)

To determine the effect of CN inhibition at warmer temperatures (28 °C), KCN was used because in previous tests it was proven that KCN has the same effect as SW-C on nitrification, and it was easier to control the targeted concentration in the reactor. Figure 4.19 shows that at warmer temperatures (28 °C), while keeping the same SRT of 15 days, the effect of CN was not critical when exposed to 0.1 mg/L. One possible reason is that since AOB and NOB are more active at higher temperatures, the effect of CN is less tangible, allowing complete nitrification even when exposed at concentrations of 0.22 mg/L. Another possibility is that the cyanide degrading bacteria are operating with faster kinetics and CN is removed more quickly in the aeration cycle allowing nitrification to proceed. When SBR A was exposed to concentrations greater than 0.26 mg/L of CN, complete nitrification was not achieved at the end of the aerobic zone, oxidizing only a 15% of the initial ammonia concentration when exposed to 0.28 mg/L.
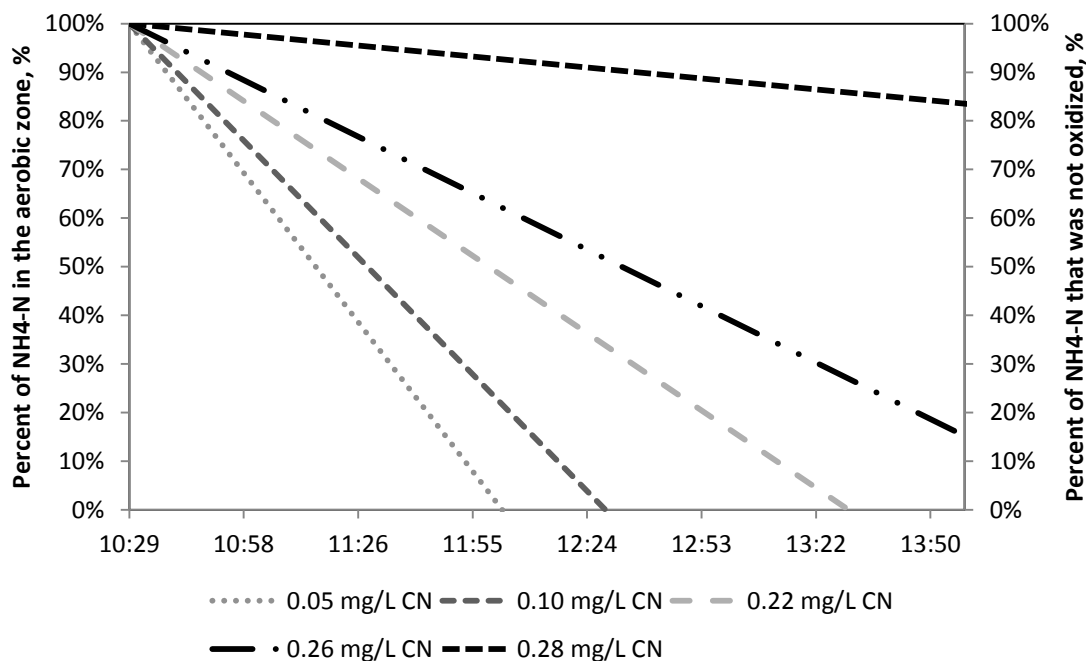
Figure 4.19 - SBR A exposed to KCN targeting different concentrations of CN at warmer temperatures (28 °C).

4.3.2 SBR B / MBCNTP: BHTP using one aeration tank as a MBCNTP Results

Besides a nitrogen profile, WAD CN⁻ samples were taken to monitor its removal. Figure 4.20 showcases the four WAD CN⁻ samples points selected for SBR B / MBCNTP. Point 1 represented the WAD CN⁻ concentration of the influent SW-C. Point 2 represented the WAD CN⁻ concentration at the SBR B influent. Point 3 represented the WAD CN⁻ concentration at the MBCNTP effluent. Finally, Point 4 represented the WAD CN⁻ concentration at the secondary clarifier effluent (SCE).
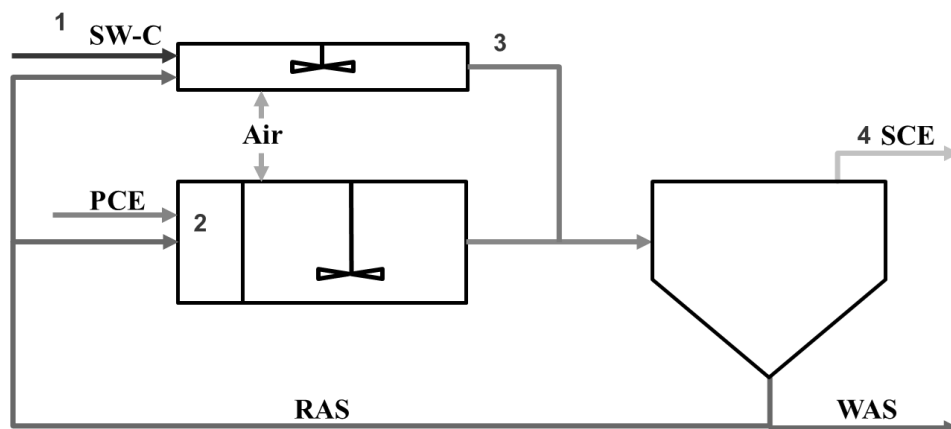
Figure 4.20 CN- Sample point for SBR B / MBCNTP

4.3.2.1 SBR B/ MBCNTP using 100% RAS

Figures 4.21 – 4.25 show the results of five profiles performed for SBR B when the MBCNTP reactor was operated with a 100% RAS configuration. The uppermost graph represents the WAD CN$^-$ concentration in all sample points while the lower graph represents the nitrogen profile in the anoxic, aerobic and settling zone. It can be seen that the nitrification rate was affected by CN with time. When using 100% RAS configuration nitrite lock was occurring in the main BNR process confirming once again that NOB are more sensitive to CN than AOB.
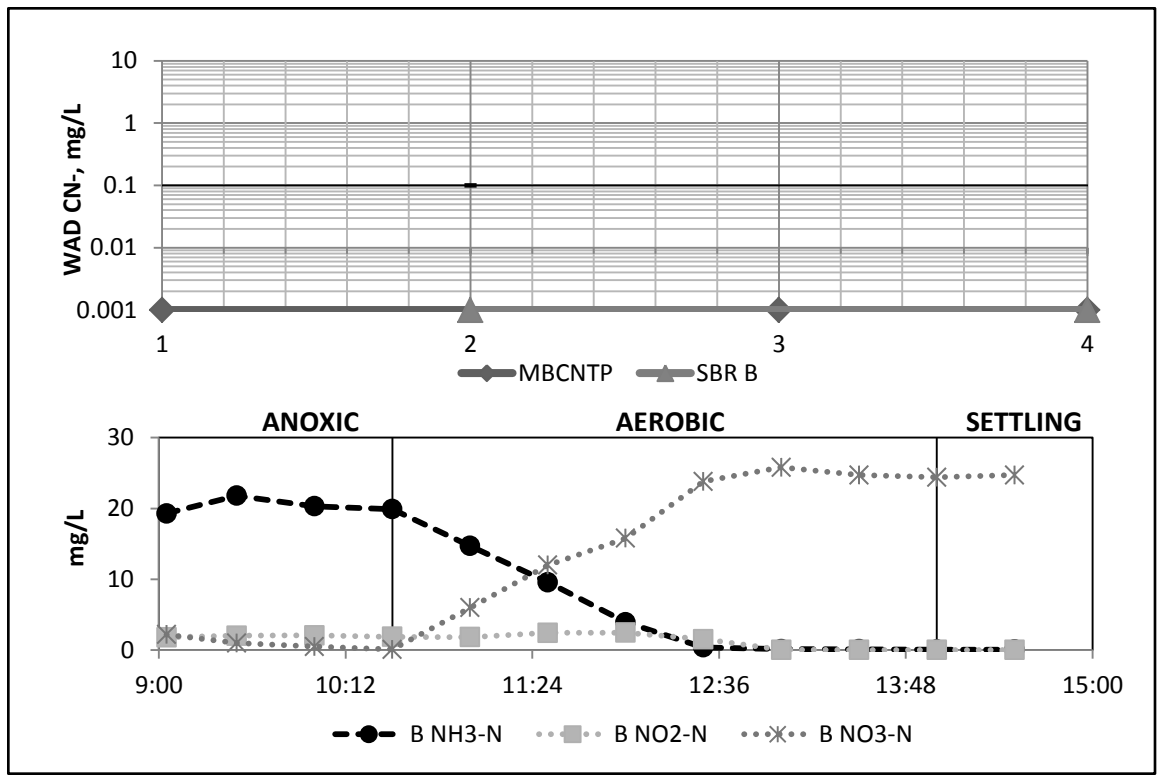
Figure 4.21 - SBR B/MBCNTP profile at 100% RAS (10/17/14)
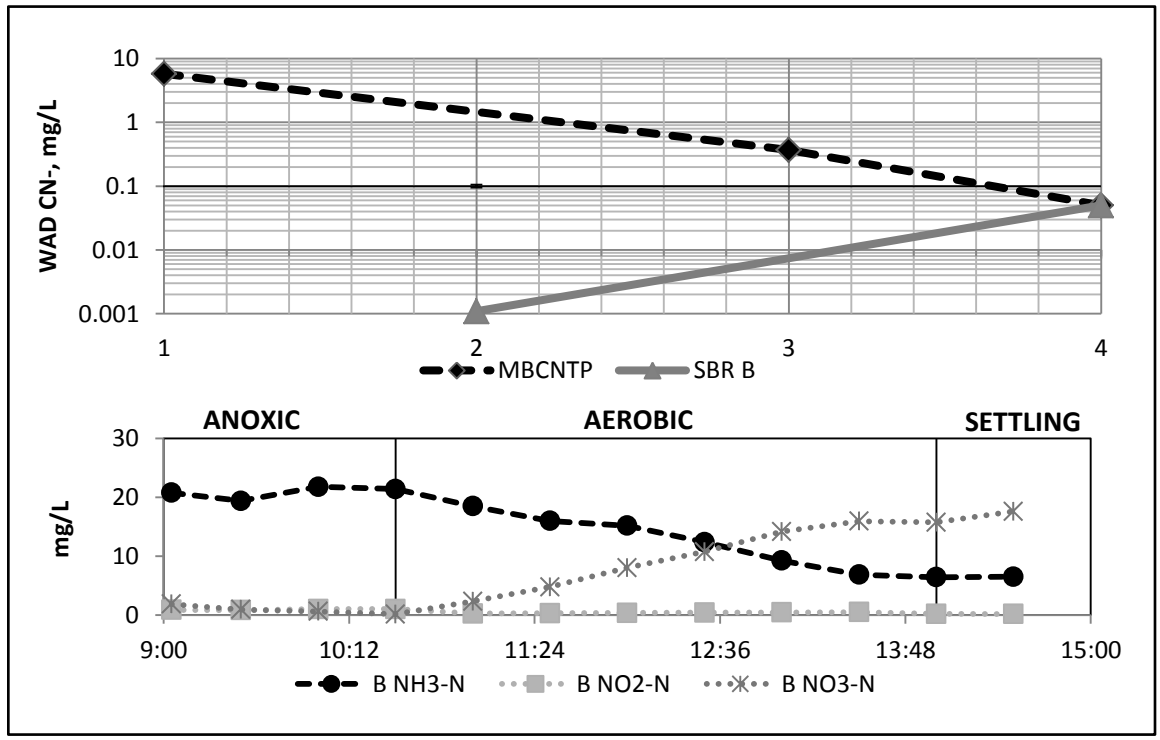
Figure 4.22 - SBR B/MBCNTP profile at 100% RAS (10/22/14)
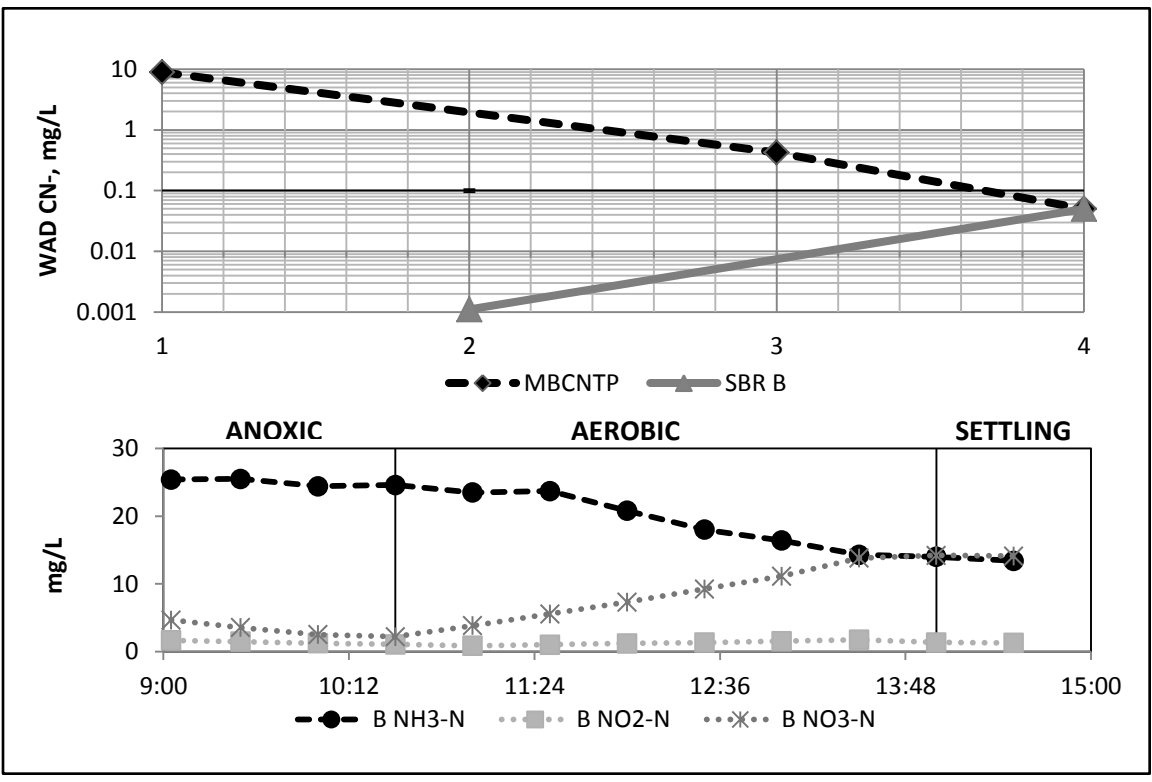
Figure 4.23 - SBR B /MBCNTP profile at a 100% RAS (10/29/14)
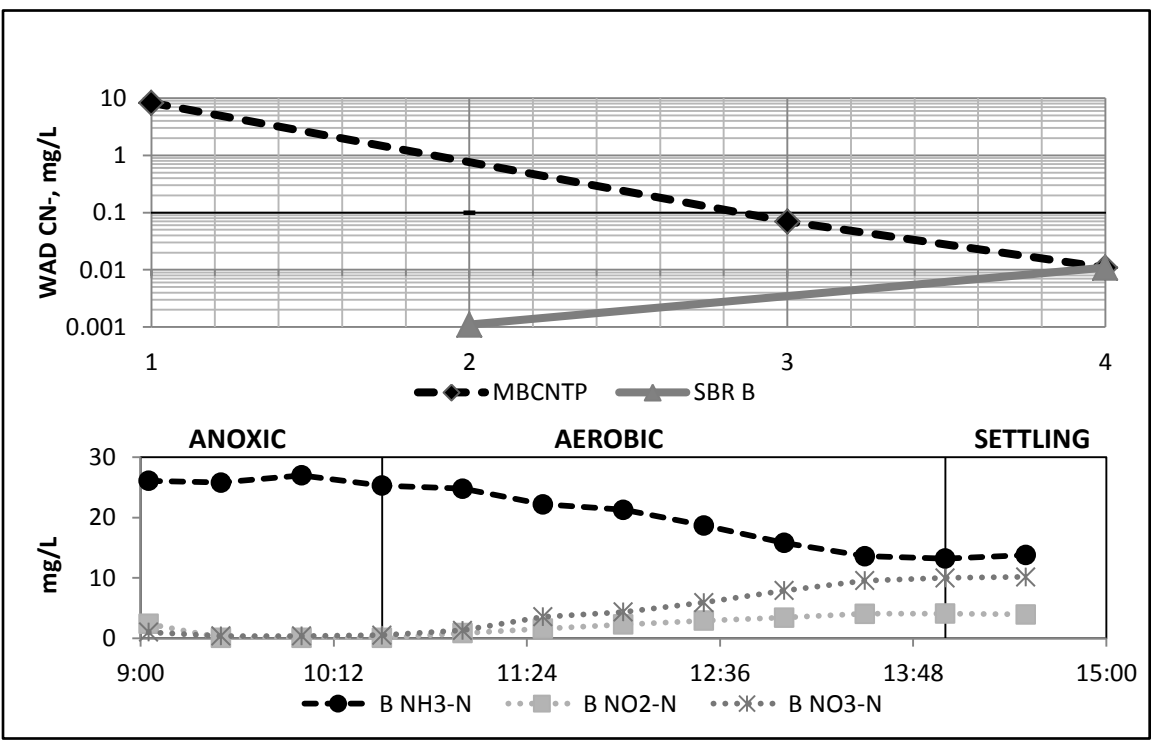
Figure 4.24 - SBR B/MBCNTP profile at a 100% RAS (11/24/14)
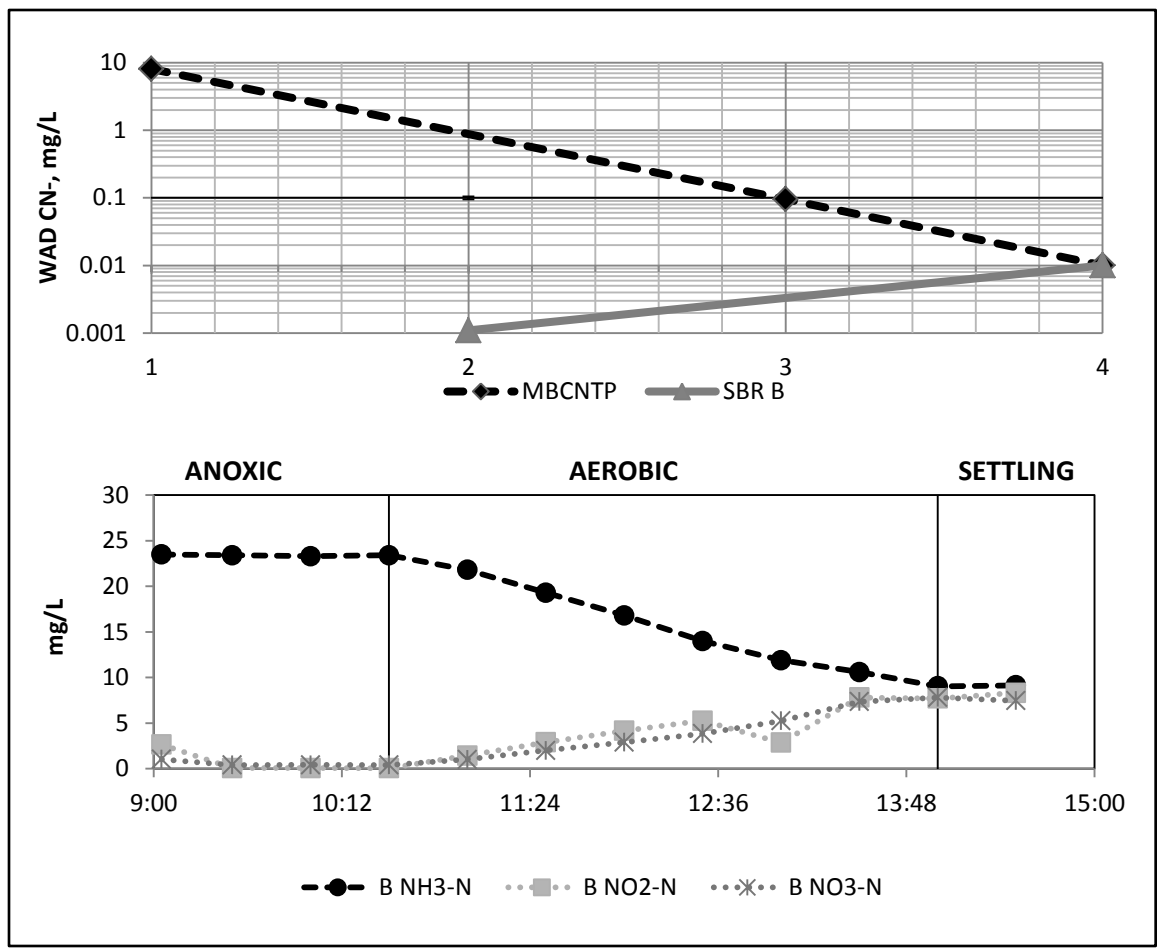
Figure 4.25 - SBR B / MBCNTP profile at 100% RAS (12/01/14)

4.3.2.2 SBR B / MBCNTP using 50% RAS

Results from SBR / MBCNTP at 50% RAS configuration can be observed in Figures 4.26 – 4.30. The uppermost graph represents the WAD CN⁻ concentration in all sample points while the lower graph represents the nitrogen profile in the anoxic, aerobic and settling zone.
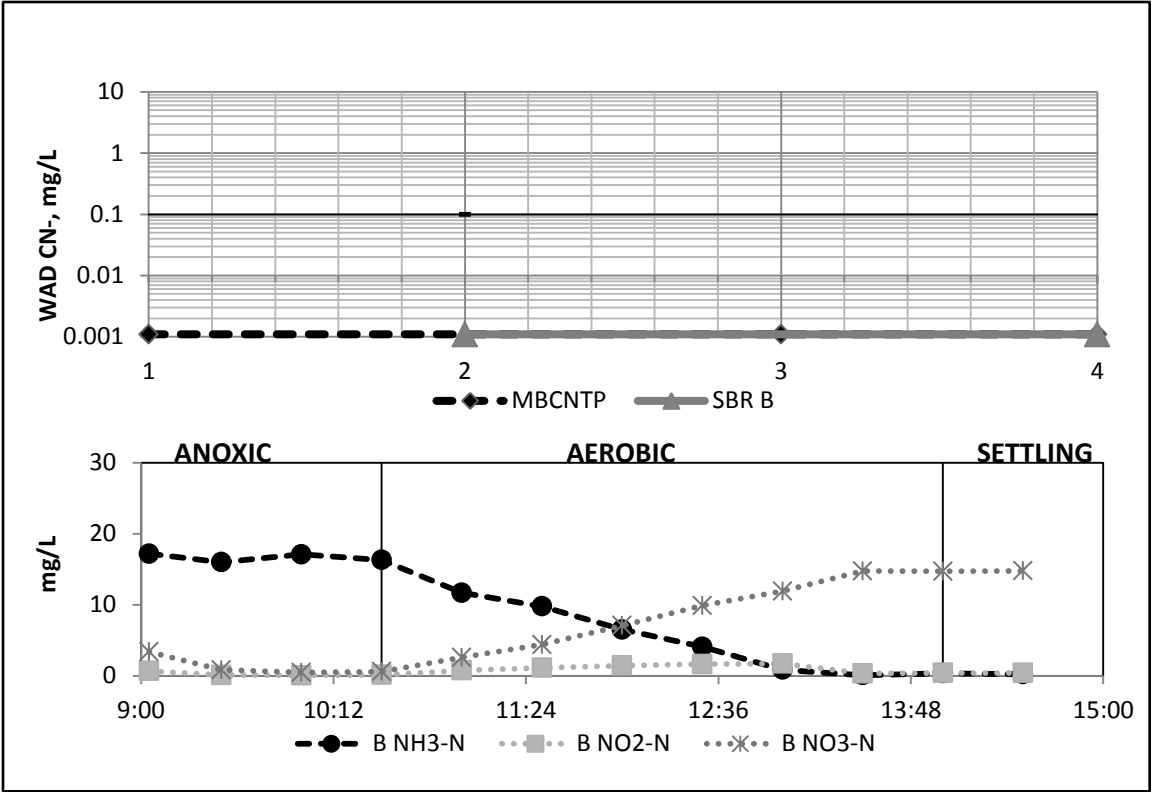
Figure 4.26 - SBR B /MBCNTP profile at 50% RAS (01/21/15)
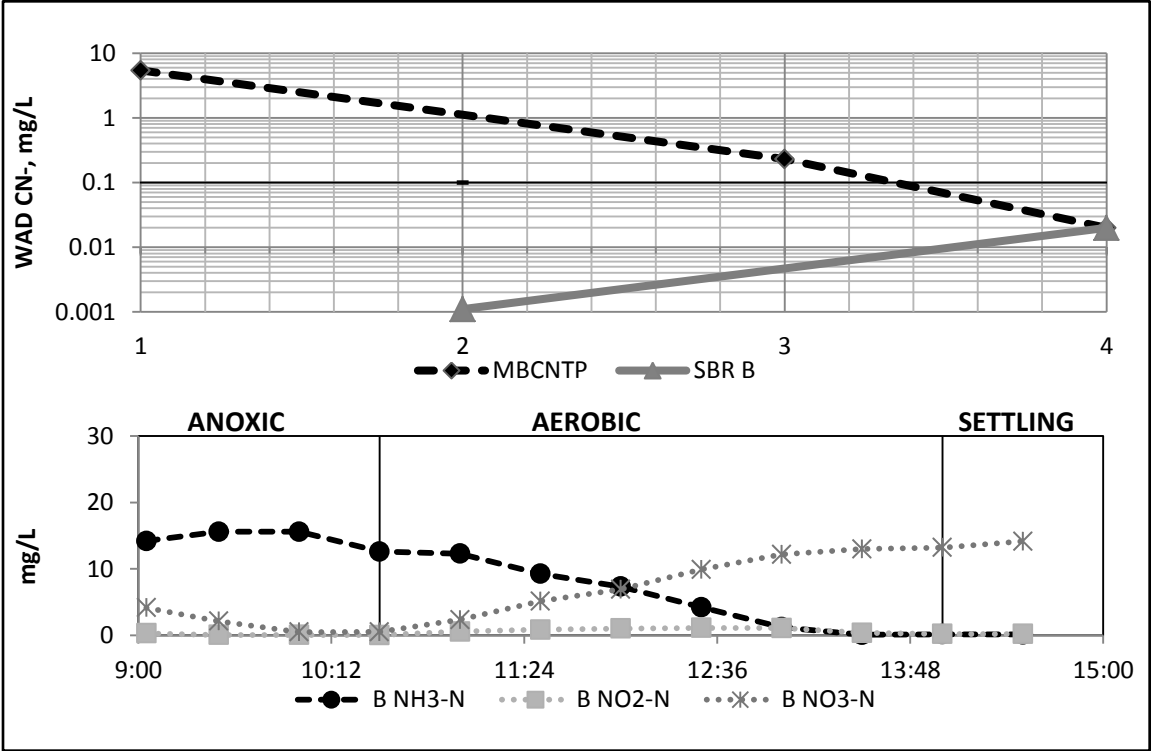
Figure 4.27 - SBR B /MBCNTP profile at 50% (01/28/15)
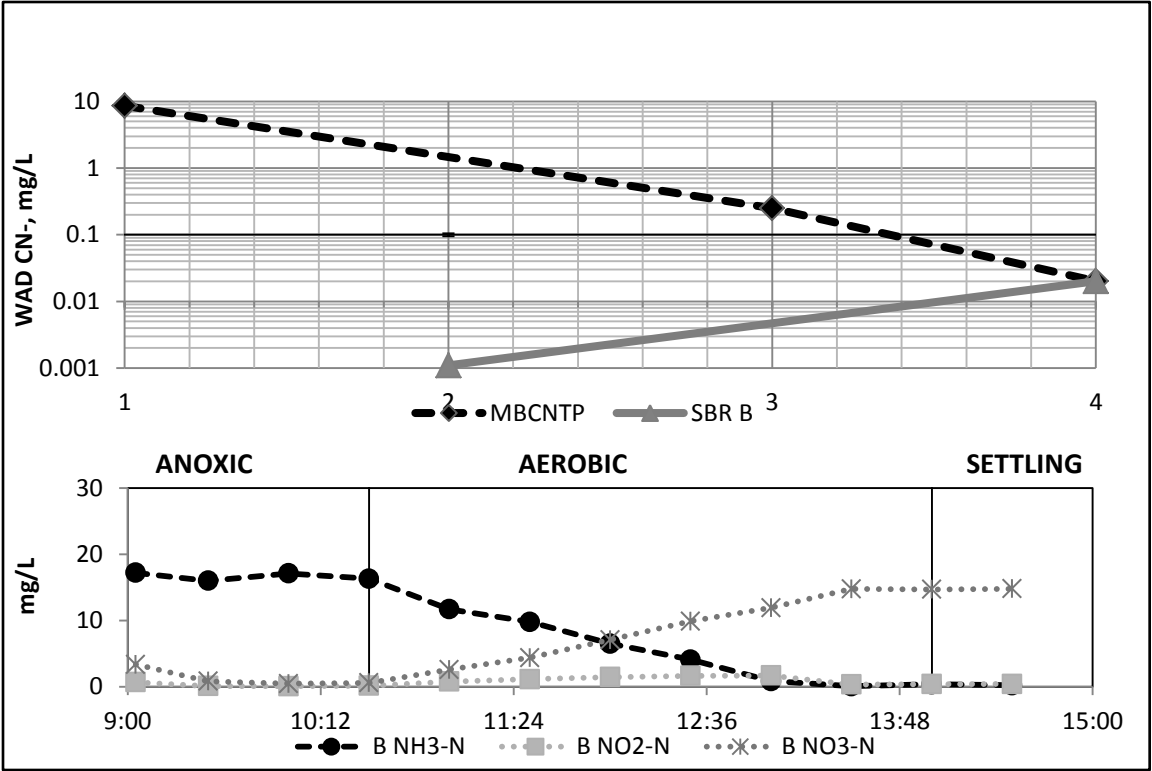
Figure 4.28 - SBR B /MBCNTP profile at 50% RAS (02/04/15)
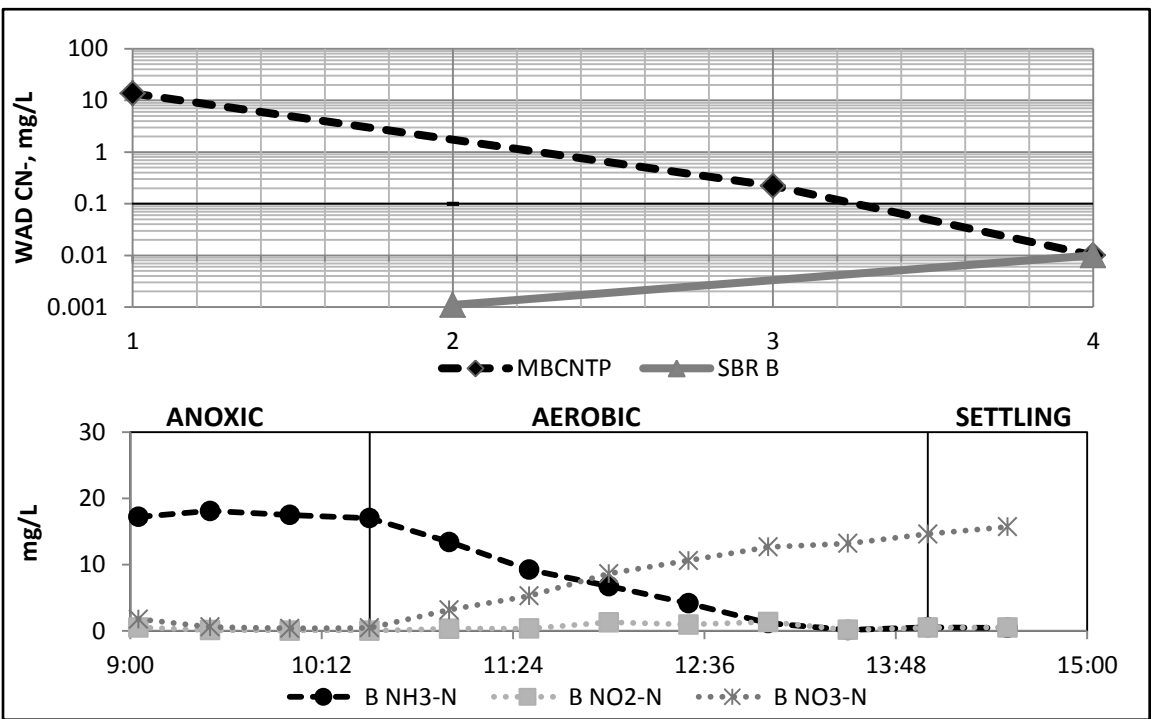
Figure 4.29 - SBR B /MBCNTP profile at 50% (02/11/15)
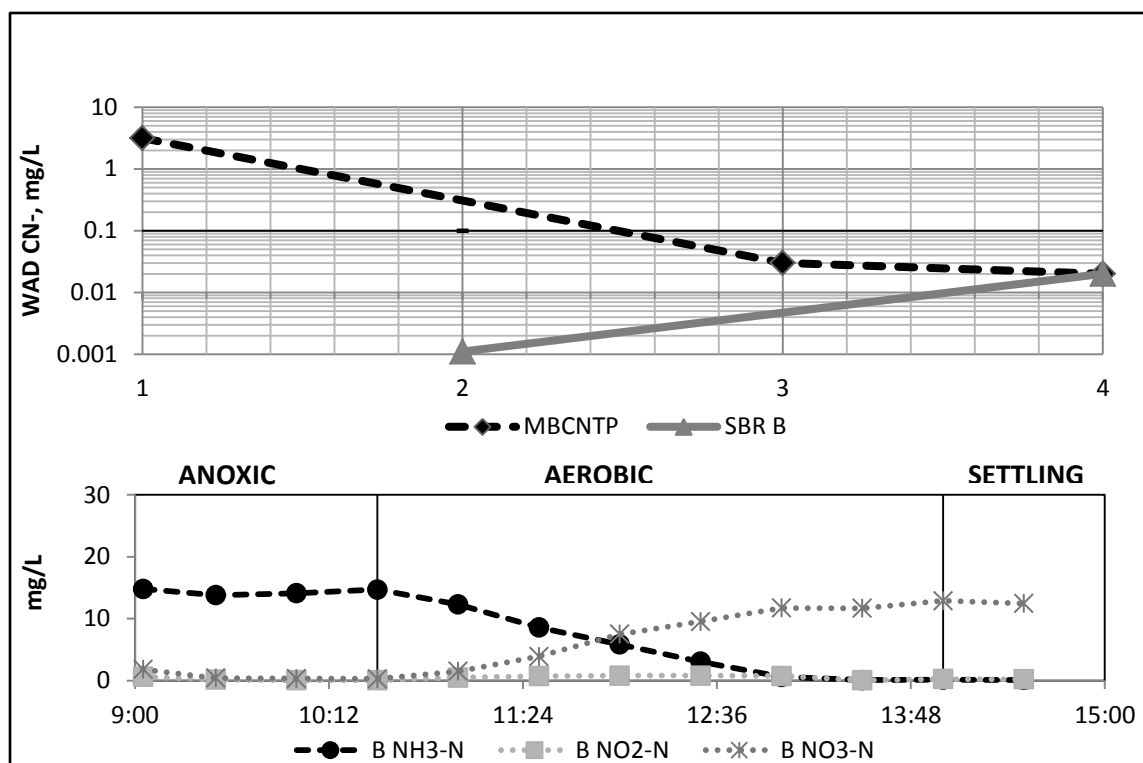
Figure 4.30 - SBR B / MBCNTP profile at a 50% RAS (02/20/15)

Results shown in Figures 4.26 to 4.30 suggest that using a 50% RAS configuration is feasible. After a month and a half of operation with this configuration there was no indication of nitrite lock and ammonia always reached complete oxidation before the end of the aerobic zone. The main reason as to why the 50% RAS configuration works better than a 100% RAS was because nitrifiers were less exposed to CN with enough biomass present to degrade it. These results suggest that this configuration should be used at BHTP.

4.3.2.3 SBR B / MBCNTP using a 50% RAS configuration with temperatures on the MBCNTP controlled

It was expected to see some effects on the cyanide removal efficiency when the temperatures where increased, since the cyanide degrading bacteria are generally mesophilic, with optimum temperatures ranging between 20 and 40 °C (Dash et al., 2009).

During this test, the initial WAD CN^- concentration of the SW-C was kept at 10 mg/L. Figure 4.31 shows the concentration of WAD CN^- at the end of the MBCNTP where the main reactor (SBR B) was kept at 28 °C and the temperatures on the MBCNTP were controlled to be 38 °C, 40 °C, 43 °C, 45 °C, 47 °C, 48 °C and 49 °C. It is clear that when the temperatures on the MBCNTP reactor were increased, the CN removal efficiency was affected. In other words, it can be concluded that increasing the temperatures on MBCNTP reactor will decrease the CN removal efficiency and hence, will expose the nitrifiers to CN for longer periods. Just by looking to this graph it is difficult to determine what temperature on the MBCNTP should be avoided. However, on Figure 4.32 it can be noted that when temperatures on the MBCNTP were kept at 48 °C, the nitrite concentration on the SBR B spiked from 0.680 mg/L to 8.49 mg/L, suggesting that at 15 days SRT and at 28 °C on the main BNR reactor (SBR B) NOB population will be affected when the CN effluent concentration on the MBCNTP is higher than 0.263 mg/L. Despite the temperature in the MBCNTP, effluent CN concentrations higher than 0.263 mg/L should be avoided at 15 days SRT.
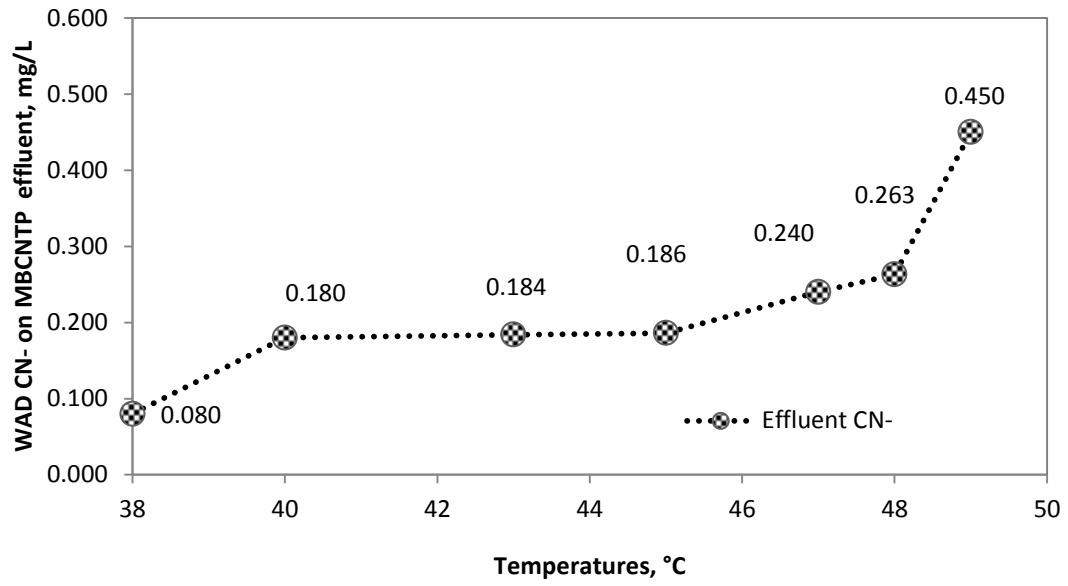
Figure 4.31 - Effects of temperatures on CN removal
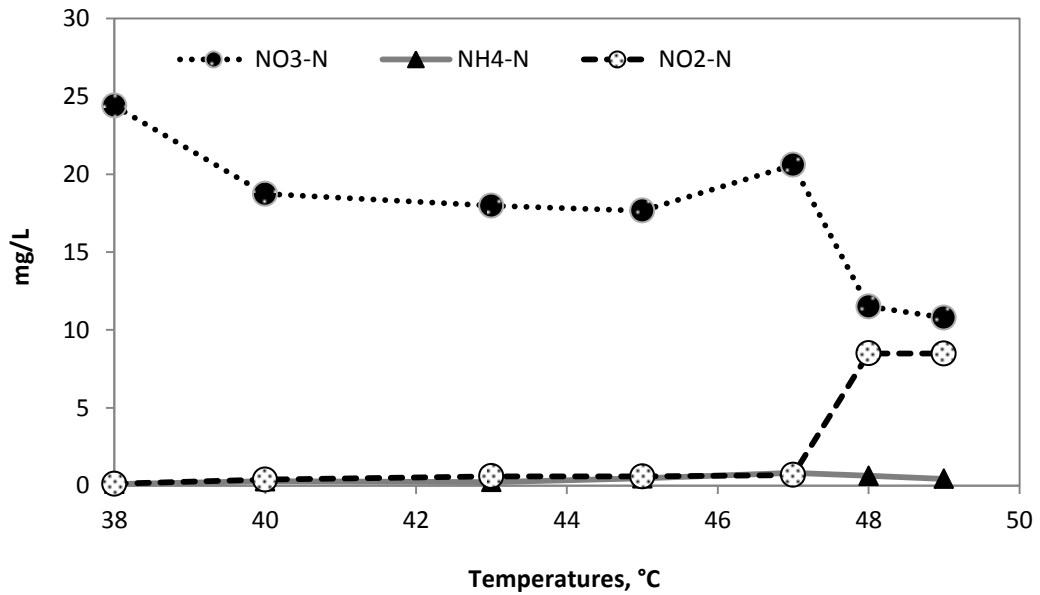
Figure 4.32 - Effluent TIN when increasing temperatures on MBCNTP

4.3.3 SBR C / NEF C: VIP NEF Results

SBR C / NEF C configuration was capable of nitrifying throughout the study. As demonstrated on Figure 4.33, low TKN values were always maintained at the end of the settling period even when the WAD CN$^-$ concentration on the SW-C was as high as 18 mg/L. The CN percent removal on the NEF C was always among 90-100%, suggesting that this option should be considered if tanks are available and space is not a limitation.
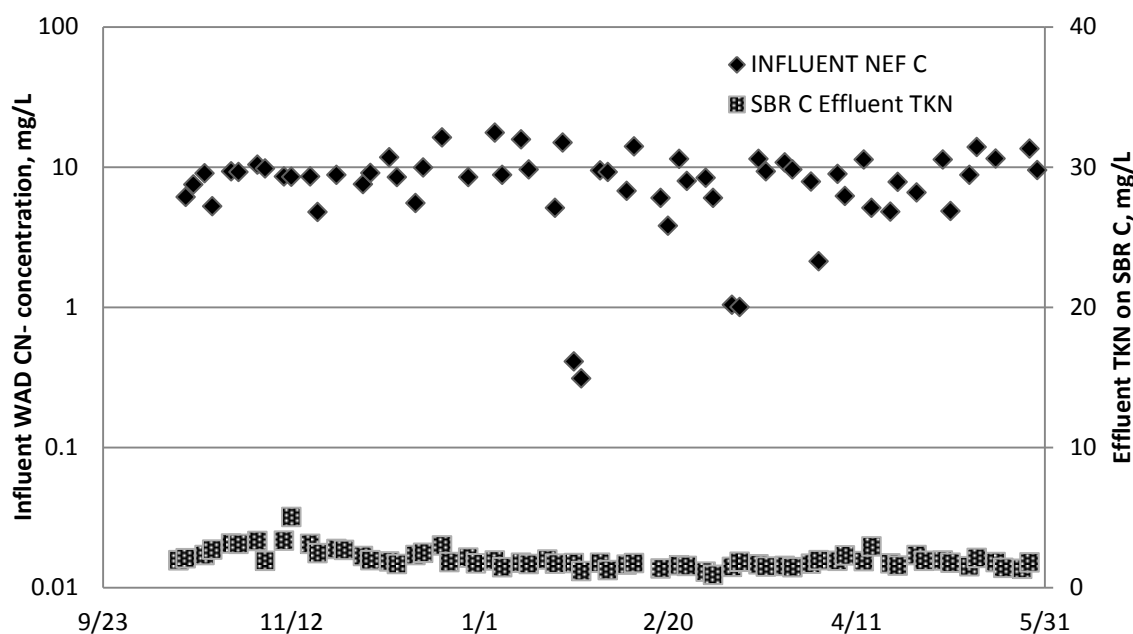
Figure 4.33 - Influent WAD CN$^-$ and effluent TKN on SBR C / NEF C reactor

4.4 Jar Test Results

Several jar tests were performed during this study to determine the ideal conditions for CN$^-$ precipitation using ferrous sulfate (FeSO$_4$); the most relevant results will be discussed in this section.

4.4.1 SW-C vs KCN with Fe^{2+} and Fe^{3+}

`   Table 4.2 describes each jar test condition. Jar test $1 - 4$ were performed using KCN, while 5 and 6 used SW-C. Ferrous sulfate was used on Jar test 1, 2 and 5 and ferric chloride was used on Jar test 3, 4 and 6. All jar tests were maintained at the same molar ratio of 0.5 using Fe^{2+} and Fe^{3+} while different pHs were tested. The pH was controlled by either using sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4). During this test DO was neither monitored nor controlled.

Table 4.2 - Jar test conditions using KCN and SW-C at different pH and Fe/CN ratio

Jar test conditions					
1	2	3	4	5	6
KCN	KCN	KCN	KCN	SW	SW
Fe^{2+}/CN^-	Fe^{2+}/CN^-	Fe^{3+}/CN^-	Fe^{3+}/CN^-	Fe^{2+}/CN^-	Fe^{3+}/CN^-
0.5	0.5	0.5	0.5	0.5	0.5
pH 5.5-6.5	pH 7	pH 5.5-6.5	pH 7	pH 5.5-6.5	pH 5.5-6.5

Figure 4.34 and table 4.3 displays that when ferric chloride was used (jar test 3, 4 and 6) the percent of CN^- removal by precipitation was lower than when using ferrous sulfate. The color of the precipitate when using ferric chloride was brown.

Additionally when comparing the precipitation of CN^- with ferrous sulfate under the same conditions, the best CN^- percent removal was obtained when the Fe/CN ratio

was kept at 0.5 and pH around 5.5-6.5. This time, the color of the precipitate was blue. When using KCN or SW-C (Jar test 1 and 5), 35.3 % and 44.1 % removal was obtained respectively. These percent removals were not ideal but gave us a clearer scheme on the conditions that should be maintained to improve the CN^- precipitation using the Fe^{2+} ion. As shown in chapter 2 (Figure 2.2), the difference between Total and WAD CN^- represents the soluble Fe-CN complexes.
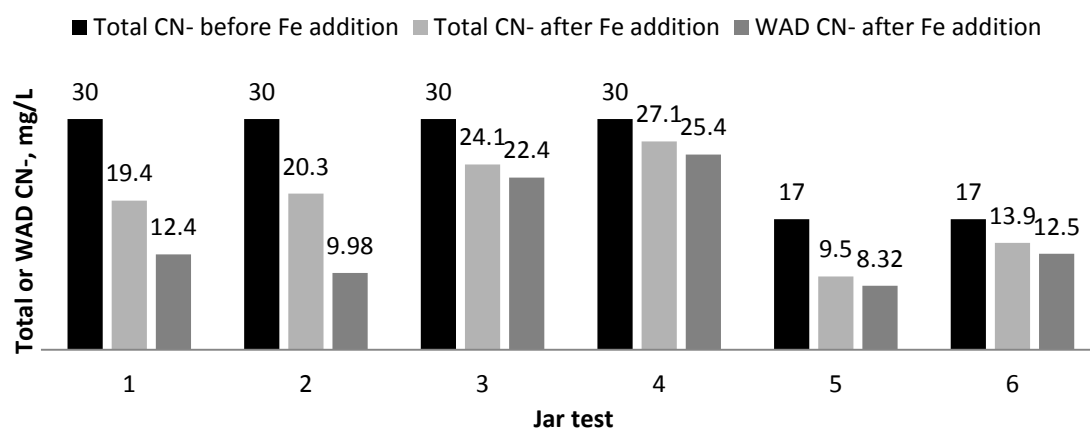
Figure 4.34 - Jar test results using Fe^{2+} and Fe^{3+} at different Fe/CN molar ratio and pH.

Table 4.3 - Jar test Results using KCN and SW-C at different pH and Fe/CN ratio

Jar test Results					
1	2	3	4	5	6
CN⁻ percent removal by precipitation					
35.3%	32.3%	19.7%	9.7%	44.1%	18.2%
% of soluble Fe-CN complexes					
23.3%	34.4%	5.7%	5.7%	7.0%	8.2%

4.4.2 SW-C plus Fe^{2+} and PCE - Alkalinity source comparison

The reason for performing this jar test was to compare the effect of the alkalinity when using NaOH or when using alkalinity from the RWI, however PCE was decided to use since it has the same alkalinity and less interference was expected. BHTP process was simulated without the use of a MBCNTP system; hence ferrous sulfate would be added into the wetwell before going to head of the plant and getting mixed with the RWI. Furthermore, on this occasion two different Fe/CN molar ratios were tested. One set was using a ratio of 0.5 and another set was using 1.0. On jar tests 1 and 2, first, ferrous sulfate was added and then pH was adjusted to 6.0 using NaOH. On jar tests 3 and 4, first, NaOH was added and then ferrous sulfate was added to maintain the desired Fe/CN ratio. The same amount of NaOH added to jar tests 1 and 2 was added to jar test 3 and 4. This amount was 0.0687 g of NaOH per liter of SW-C. On jar tests 5 and 6, first, ferrous sulfate was added and then PCE was added maintaining a SW-C/PCE ratio of 1/15 (similar to BHTP).
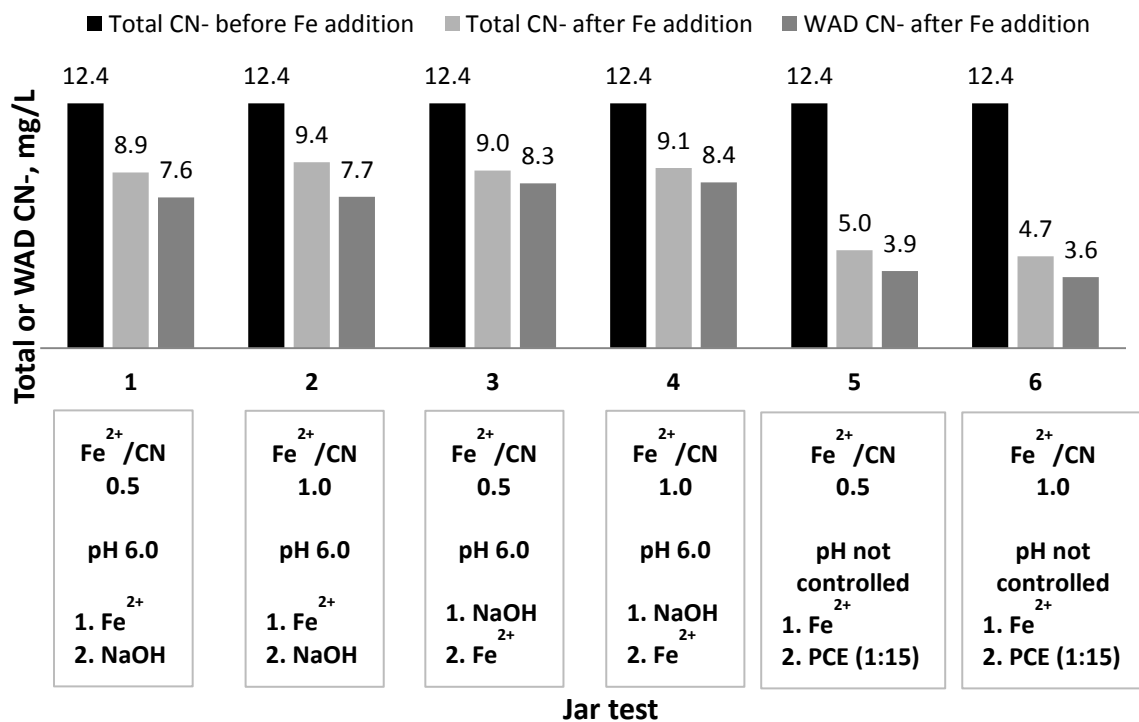
Figure 4.35 - Jar test results when using different Fe/CN ratios and using NaOH or PCE for alkalinity. pH controlled at 6 not controlled when using PCE.

In Figure 4.35 above and table 4.4 below, the results for each jar test can be observed. It is important to mention that the results for jar test 5 and 6 which includes the dilution factor 1:15 are already factored in, meaning that the actual values from the lab were 0.33 and 0.30 mg/L Total CN$^-$ respectively but values of 4.7 and 3.6 mg/L were reported..

Similar results were obtained when using NaOH either before or after the ferrous sulfate addition, indicating that the order in which the alkalinity is added is irrelevant. The best results were obtained on jar test 5 and 6 when alkalinity was used from the PCE, see table below. Only 3% was improved when increasing the Fe$^{2+/}$CN ratio from 0.5 to 1.0. However if this option is going to be pursued, the amount of ferrous sulfate needed

to precipitate CN⁻, could be expensive. Assuming 20 mg/L of CN in the SW-C with a flow of 1.33 MGD, 232 lbs/day as a Fe^{2+} will be needed to keep a Fe^{2+}/CN molar ratio.0.5. In the year 2014 the price per pound of ferrous sulfate was $1.299 per lb as Fe, indicating that the final price per month will be around $ 9,290. Using PCE for alkalinity could be a good option if the CN concentration in the SW-C can be controlled and maintained at lower concentrations.

Table 4.4 - Jar test Results using SW-C at different pH and Fe/CN ratio

Jar test Results					
1	**2**	**3**	**4**	**5**	**6**
Total CN⁻ percent removal by chemical precipitation					
28%	24%	28%	26%	60%	63%
% of soluble Fe-CN complexes					
10%	14%	5%	6%	8%	8%

4.4.3 Chemical precipitation and biological oxidation jar test

This jar test was conducted to simulate the impact of feeding ferrous sulfate at the wetwell before going to the MBCNTP system. Table 4.5 displays the operating conditions for each jar test. When a 0 is shown on the table it means that it was not utilized. For example, for jar test #1, 1L of SW-C was mixed with 1L of RAS and no non

potable water (NPW) or ferrous sulfate was used. The pH and DO recorded on this table were measured at the very end of the each test. No NaOH was added during this test, since the alkalinity from the RAS was expected to be utilized. The process that this jar test was performed was as follows; First, SW-C CN concentration was measured and it was found to be at around 10 mg/L. Another 10 mg/L of CN, using KCN, was added to increase its concentration to around 20mg/L. Afterwards, ferrous sulfate was added during a rapid mix of 5 minutes (simulating the time from the wetwell to the MBCNTP system). After the 5 minute period, SW-C was mixed with RAS, while air was supplied using an air stone. For jar tests 6 and 7, in addition to RAS, NPW was also added (0.6 L) to simulate how the MBCNTP performs when adding NPW for temperature control. After allowing 15 minutes of reaction and after 2 hours, samples were taken and preserved with NaOH before being sent to the CEL.

Table 4.5 - Jar test details

JAR TEST	SW-C	RAS	NPW	Fe/CN Ratio	pH	DO mg/L	Comments
#1	1L	1L	0	0	7.33	8.16	No Ferrous addition
#2	1L	0.75 L	0	0.5	7.03	7.9	RAS = 75% SW
#3	1L	0.75 L	0	1	6.75	7.89	RAS = 75% SW
#4	1L	1L	0	0.5	7.39	8.55	RAS = SW
#5	1L	1L	0	1	7.24	8.61	RAS = SW
#6	1L	1L	0.6 L	0	7.48	8.29	NPW=60%SW, RAS=SW
#7	1L	0.75 L	0.6 L	0	7.35	7.17	NPW=60%SW, RAS=75% SW

As shown on Figure 4.36 and 4.37 the DO after 15 minutes and after 2 hours was at around 8.0 mg/L. The reason the DO was high was because the DO was not controlled and air was just added using a pump connected with air stones. Table 4.6 and 4.7 show the results in percent of removal after 15 minutes and 2 hours. These results were already taking into account the different dilution factors used on each jar test. The best results were obtained when ferrous sulfate was added to jar test 4 and 5, however there was no a significance difference when a Fe/CN ratio of 0.5 or 1.0 was used. The percent removal by precipitation and biological oxidation was 93% and 92%, respectively.

When adding NPW (jar test 6 and 7) it can be observed that this has a negative effect on the biological oxidation of CN. Results show that when NPW was added, the percent of CN removal was 10% lower when compared to jar test 1, where NPW was not used.

As expected using less RAS volume (jar test 2 and 3) when using the same volume of SW-C, the percent removal by chemical precipitation and biological oxidation was lower. Adding NPW will decrease the detention time hence the reactor will have less time to degrade CN.
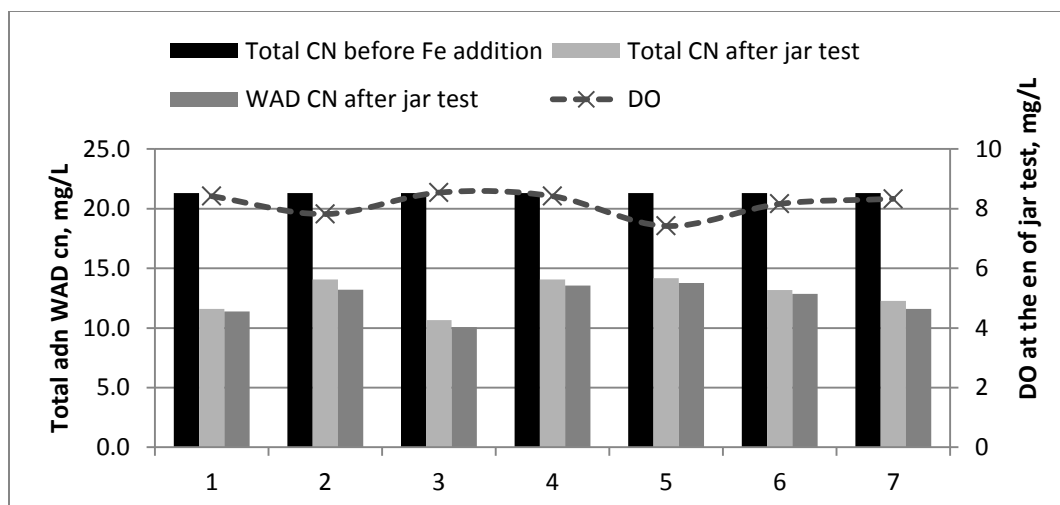
Figure 4.36 - Jar test results after 15 minutes.
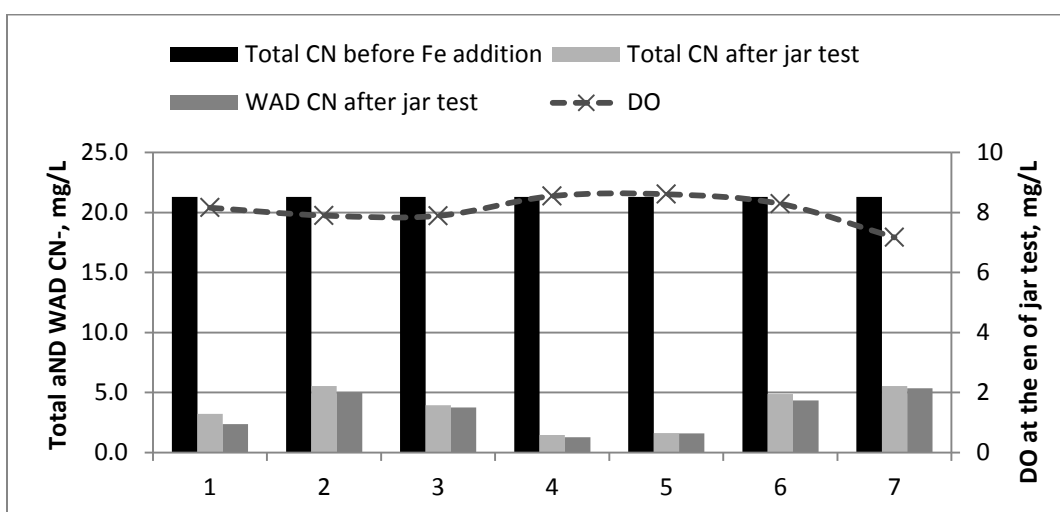
Figure 4.37 - Jar test results after 2 hours

Table 4.6 - Jar test results after 15 minutes

Jar test Results after 15 minutes						
1	**2**	**3**	**4**	**5**	**6**	**7**
Just Biological	**CN⁻ percent removal by chemical precipitation and biological oxidation.**				**Just Biological**	
46%	**34%**	**50%**	**34%**	**33%**	**38%**	**42%**
% of soluble Fe-CN complexes						
1%	**4%**	**3%**	**2%**	**2%**	**1%**	**3%**

Table 4.7 - Jar test results after 2 hours

Jar test Results after 2 hours						
1	**2**	**3**	**4**	**5**	**6**	**7**
Just Biological	**CN⁻ percent removal by chemical precipitation and biological oxidation.**				**Just Biological**	
85%	**74%**	**82%**	**93%**	**92%**	**77%**	**74%**
% of soluble Fe-CN complexes						
4%	**2%**	**1%**	**1%**	**0%**	**3%**	**1%**

4.4.4 SW-C plus Fe^{2+} jar test controlling the DO concentration

After evaluating the results in the previous section, it was determined that the overall CN percent removal was due to biological oxidation. Hence, in order to understand better the CN precipitation by using ferrous sulfate another jar test was performed. This time the SW-C was not mixed with PCE or RAS and it was only mixed with ferrous sulfate. Additionally, KCN was added to increase the CN concentration in the SW-C.

Table 4.8 shows the condition used during this jar test. As it can be observed, two different Fe^{2+}/CN ratios were used and the target pH varied from 5.5 to 7.5. Additionally, the DO was maintained between 1-2 mg/L. DO was not controlled during the settling period. Table 4.9 – 4.10 shows the DO, pH results and observations during the jar test.

Table 4.8 - Jar test conditions from SW-C plus Fe2+ jar test controlling DO concentration between 1 – 2 mg/L

JAR TEST	KCN	SW	Fe^{2+}/CN^- Ratio	Target pH	Target DO mg/L
#1	X	X	0.5	5.5	1-2 mg/L
#2	X	X	0.5	6.0	1-2 mg/L
#3	X	X	0.5	6.5	1-2 mg/L
#4	X	X	0.5	7.0	1-2 mg/L
#5	X	X	0.5	7.5	1-2 mg/L
#6	X	X	1.0	5.5	1-2 mg/L
#7	X	X	1.0	6.0	1-2 mg/L
#8	X	X	1.0	6.5	1-2 mg/L
#9	X	X	1.0	7.0	1-2 mg/L
#10	X	X	1.0	7.5	1-2 mg/L

Table 4.9 - Jar test #1 - #5 observations

	CN Test #1		CN Test #2		CN Test #3		CN Test #4		CN Test #5	
Initial	**pH**	**DO**	**pH**	**DO**	**pH**	**DO**	**pH**	**DO**	**pH**	**DO**
	3.16	1.99	3.31	1.40	3.2	1.73	2.87	1.92	2.88	2.33
After CN	4.9	0.12	4.06	1.86	4.2	0.2	3.55	2.03	3.52	2.40
After Fe	4.8	0.40	4.02	1.70	4.04	1.2	3.03	1.40	3.52	2.57
NaOH	5.49	2.21	6.01	1.40	6.53	1.4	7.12	1.20	7.6	1.18
0 min	5.47	2.20	5.84	0.40	6.5	1.6	6.98	1.32	7.48	2.06
5 min	5.34	1.81	5.74	0.07	6.51	1.54	6.96	1.25	7.51	2.04
10min	4.93	0.13	5.45	0.07	6.52	1.58	6.96	1.21	7.54	1.99
15min	4.87	0.10	5.32	0.07	6.51	1.57	6.96	1.14	7.56	1.95
20min	4.83	0.09	5.27	0.07	6.51	1.57	6.96	1.07	7.57	1.92
25min	4.8	0.08	5.22	0.07	6.5	1.58	6.96	1.01	7.57	1.90
30min	4.77	0.07	5.18	0.07	6.51	1.6	6.96	0.95	7.57	1.89
Comments	Pale Blue color. Small particles in suspension. Doesn't look like is settling at all. Settling is bad after 30 min.		Green color. Small particles in suspension when starting the settling period. Not settling quite well. At the end was partial settled. Darker green at the end.		Green-Blue color. Not settling quite well. Nitrogen was used. Starting to see more particles and slowly settling at 5 min.		A lot of small particles can be seen while on the 5 min flocculation time, but they look green at the beginning. Getting darker with time.		Using air to keep the DO between 1-2 mg/L. Yellow-green color. Small particles can be observed. Good settling at the very end comparing with other jar tests.	

Table 4.10 - Jar test #6 - #10 observations.

	CN Test #6		CN Test #7		CN Test #8		CN Test #9		CN Test #10	
Initial	**pH**	**DO**	**pH**	**DO**	**pH**	**DO**	**pH**	**DO**	**pH**	**DO**
	2.9	2.17	2.87	1.13	2.88	1.15	2.87	1.51	2.89	1.5
After CN	3.54	2.31	3.31	1.18	3.33	1.22	3.33	1.6	3.33	1.54
After Fe	3.48	1.90	3.32	1.37	3.3	1.51	3.32	1.79	3.35	1.83
NaOH	5.5	1.60	6.02	1.67	6.54	1.71	7.05	1.82	7.48	2.2
0 min	5.48	1.63	5.88	1.87	6.32	1.93	6.76	1.79	7.5	1.92
5 min	5.47	1.60	5.75	1.81	6.18	1.78	6.67	1.36	7.54	1.82
10min	5.44	1.54	5.69	1.66	6.11	1.56	6.66	1.17	7.55	1.71
15min	5.41	1.49	5.65	1.52	6.07	1.36	6.64	1.00	7.56	1.63
20min	5.39	1.41	5.62	1.39	6.03	1.21	6.58	0.90	7.57	1.55
25min	5.38	1.33	5.61	1.28	6.01	1.08	6.55	0.80	7.57	1.49
30min	5.36	1.23	5.6	0.93	5.99	0.91	6.53	0.72	7.58	1.42
Comments	Blue color was noticed before the pH was adjusted. With time the color changed to light green-blue. Not settling quite well yet at the 5 min. Small particles can be observed.		Small particles can be noticed. Green color. Looking more blue than green after ten minutes. Good settling at the very end.		When adding NaOH, DO drop to 0.4 and color was yellow. After adjusting the DO changed to green. Dark green when settling. Looks more blue than green at min 15 of settling.		When adding NaOH DO dropped to 0.33 and color was yellow-brown. Best 5 min settling so far. Dark green color at the end. Best settling so far!		Color brown-green. Good settling dark green at the end.	

Figure 4.38 shows the results from each jar test and as it can be observed the initial CN concentration (SW-C plus KCN) before ferrous sulfate addition was 34.5 mg/L.
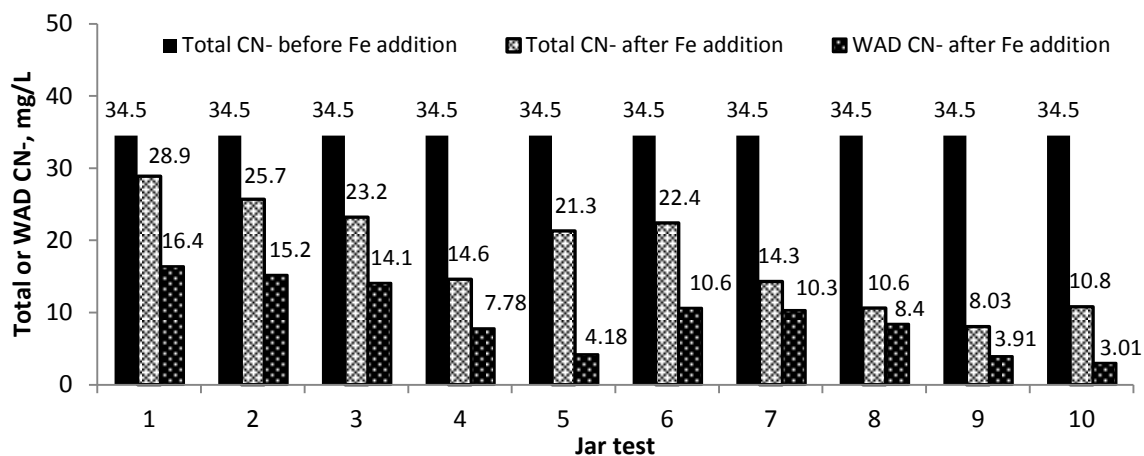
Figure 4.38 - Results from SW-C plus Fe^{2+} jar test controlling DO concentration.

The results from this jar test were plotted on Figure 4.39. These results suggest that in order to obtain a higher percent of CN removal by chemical precipitation using ferrous sulfate, the formation of soluble Fe-CN complexes must be avoided.
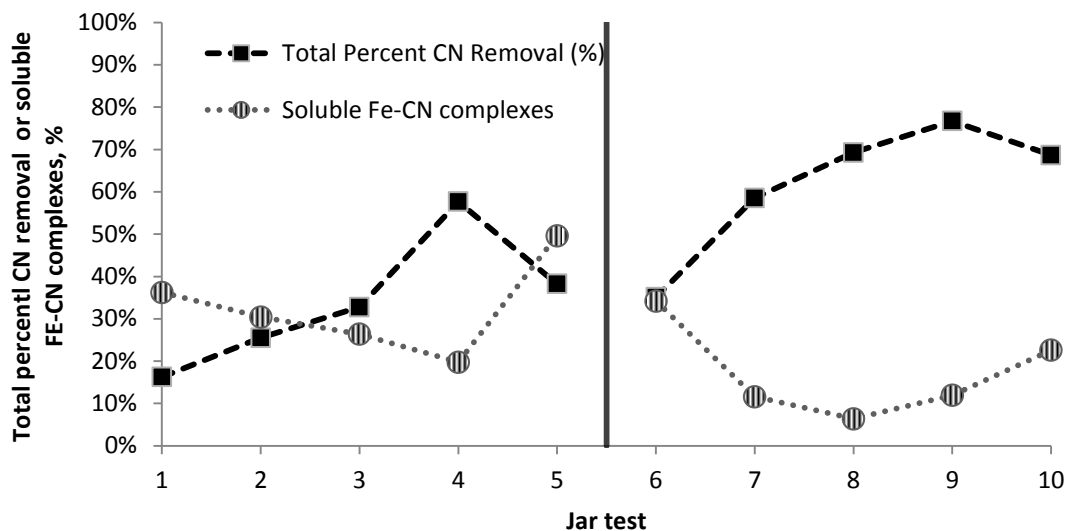
Figure 4.39 - Importance of precipitating Fe complexes for a better CN⁻ removal.

4.4.5 SW-C plus Fe²⁺ and RAS controlling the DO concentration

Previous jar tests indicated that in order to obtain the highest CN removal by precipitation, the percent of soluble Fe-CN complexes that will not precipitate should be maintained low. However to investigate the impact of chemical precipitation and biological oxidation on CN removal, different jar tests were performed. This time the targeted pH was selected from the previous jar test which was 6.5. It was known that after mixing the RAS with SW-C (previously mixed with ferrous sulfate) the pH was going to increase; however, it was not going to be enough to reach the targeted pH. A test to know how much NaOH should be added to reach a pH of 6.5 was performed prior the jar test. The final amount of NaOH that was added to 1 L was 0.0938 g and this was added prior to the ferrous sulfate addition. The targeted DO concentration was controlled again by using air or N_2. Table 4.11 shows the jar test conditions that were used. Note that for jar test 1 and 2 the DO target concentration was to be 1/3 anoxic and 2/3 aerobic (1-2 mg/L)

of the total reaction time that was 2 hours. Once again KCN was added to increase the

CN concentration in the SW-C.

Table 4.11 - Jar test conditions from SW-C plus Fe2+ jar test controlling DO concentration

JAR TEST	Group	KCN	SW	Fe^{2+}/CN^- Ratio	pH	Target DO mg/L
#1	1	X	X	0	6.5	(ANOX-1-2)
#2	1	X	X	0.75	6.5	(ANOX-1-2)
#3	2	X	X	0	6.5	1-2mg/L
#4	2	X	X	0.75	6.5	1-2mg/L
#5	3	X	X	0	6.5	2-4 mg/L
#6	3	X	X	0.75	6.5	2-4 mg/L
#7	4	X	X	0	6.5	4-6 mg/L
#8	4	X	X	0.75	6.5	4-6 mg/L

Figure 4.40 shows the total CN percent removal from this jar test separated in 4

different groups based on target DO concentration. However the first column (black

column) from each group shows the results from the jar tests that were performed without

chemical addition and the second column with the addition of ferrous sulfate and NaOH.

There was less than 10% improvement when chemical addition was added to group 1, 2

and 4 and only 2 % improvement on group 3.

■ No chemical addition   ▣ With chemical addition
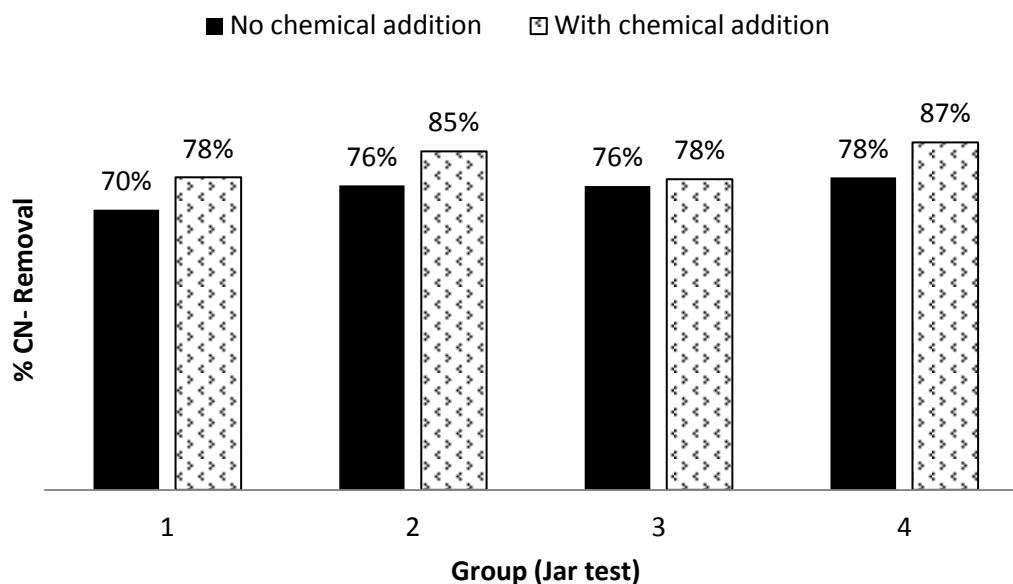
Figure 4.40 - Jar test results. Interference from RAS solids.

It appears that when combining chemical precipitation with biological oxidation, the CN percent removal takes place mainly because of the biological oxidation or it could be that the solids from the RAS interfere with the CN chemical precipitation.

During the chemical precipitation of CN using ferrous sulfate it is important to minimize the soluble Fe-CN complexes for a better percent of removal; this will depend on the pH, the Fe^{2+}/CN ratio and the DO concentration. Up to 69% percent removal was achieved with a Fe/CN of 1.0, DO among 1 and 2 mg/L and pH close to 6.5. Though, further studies needs to be performed to improve this approach.

4.5 BHTP Operation

4.5.1 MBCNTP system

On December, 2014 BHTP staff noticed an unusual increment in the chlorine demand for disinfection. By this date, BHTP was not nitrifying, however nitrite at the effluent was tested. The results indicated that nitrite was not the problem with concentrations below detection. After one month of trying to find out what could be causing the problem, management correlated the problem with the incinerator performance. After switching incinerators on December 19, 2014 the problem with the chlorine demand also started. Additionally it was noticed that high CN concentration was coming from the SW-C since the incinerators were switched. The possible reason was that perhaps the CN concentration was too high that even after passing through the aeration tanks was not enough to remove it, and hence it was reacting with sodium hypochlorite, increasing the chlorine demand. Finally, on January 13, 2015 it was decided to put the MBCNTP system in service and within the next day, the chlorine demand was alleviated. Figure 4.41 shows the daily usage of sodium hypochlorite for disinfection between November, 2014 and February 2015. The first vertical line indicates when the incinerators were switched and the second line is showing when the MBCNTP system was put in service.
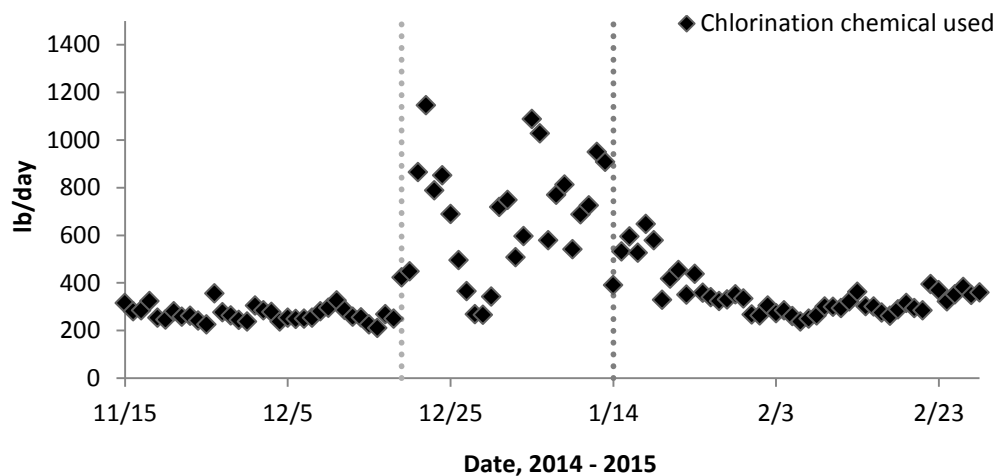
Figure 4.41 - Sudden increase on chlorine demand at BHTP.

On April, 2015, when the MBCNTP system was already in service it was determined to commence recording the influent temperatures (SW-C already mixed with RAS) and samples were taken and sent to the CEL for WAD CN$^-$.

Figure 4.42 show the results of the influent temperatures and effluent CN$^-$ concentrations in the MBCNTP system from April 16, 2015 to January 21, 2016. As observed every time the influent temperatures were higher than 40 °C the effluent WAD CN$^-$ concentration was also higher. These results suggest that temperatures in the MBCNTP system are critical and should be maintained below than 40 °C to keep effective the CN removal in the MBCNTP system.
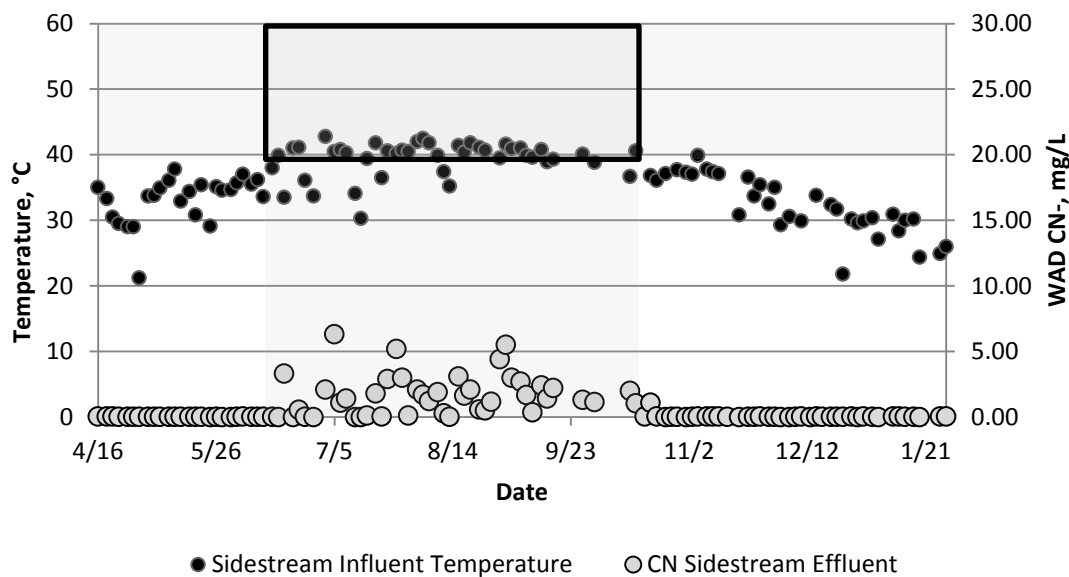
Figure 4.42 - Critical temperatures of 40 °C in the MBCNTP system

4.5.2 BHTP Overall Performance

The MBCNTP was put in service in January 13, 2014 to address the problems with the chlorine demand, but it was not until April 5, 2015 when it was decided to switch the RAS configuration from 100% to a 50% based on SBR's results. Figure 4.43 showcases the overall performance of BHTP during the year 2015. Temperatures and WAD CN⁻ effluent from the MBCNTP system were plotted in conjunction with the effluent TN, effluent NO_2-N and the caustic usage (lbs/month). It can be observed that nitrification was finally achieved in June, 2015 and even though the temperatures in the MBCNTP system were higher than 40 °C and the effluent CN⁻ concentrations were higher as well, good TN was obtained. However, in order to maintain good TN numbers during this period, considerable amounts of caustic was used. Additionally, it can be

noted that high effluent CN concentrations in the MBCNTP system let the NO_2-N to accumulate. These results suggest that BHTP can nitrify and treat CN simultaneously; however it is important to keep the temperatures below 40 °C. When temperatures are higher than 40 °C in the MBCNTP, the main BNR process can still nitrifying, but a considerable amount of caustic will be needed to maintain a low TN number.
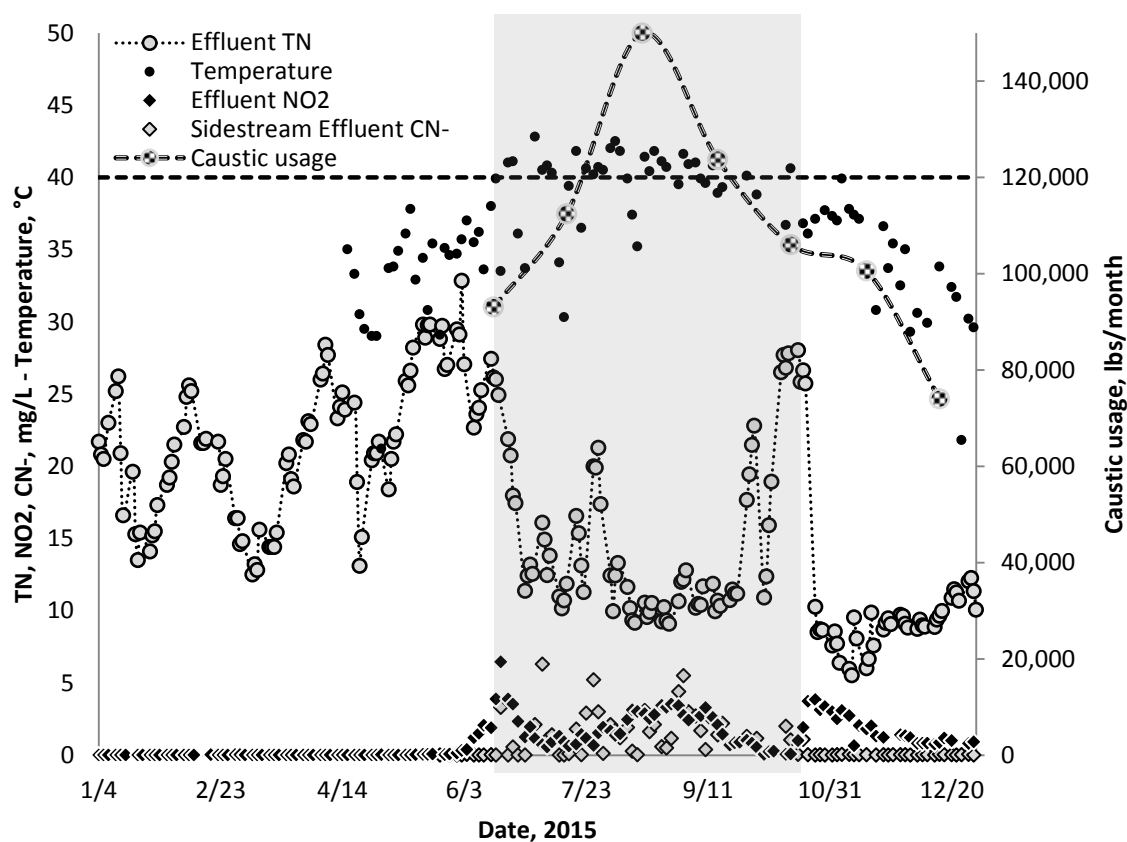
Figure 4.43 - Overall performance at BHTP in 2015 when the MBCNTP system and nitrification were working simultaneously.

4.5.3 Effect of new MACT 129 regulation.

As mentioned in section 2.3.1, emission guidelines for CO, SO_2 and NOx are the ones of concern, since these are the parameters that dictate how to operate the furnace. Table 4.12 show the limits for each parameter mentioned above.

Table 4.12 - MACT 129 Emission guidelines

Parameter	Limit*
CO	3800 ppmdv
NOx	220 ppmdv
SO$_2$	26 ppmdv

* parts per million of dry volume (corrected to 7 percent O_2)

To be able to maintain these parameters the following conditions were established at BHTP:

- Percent of oxygen inside the furnace maintained at 5%.

- Temperatures in hearth 1 were increased and maintained at 1100 °F (593 °C).

It should be noted that when the temperature in hearth 1 is controlled to be at 1100 F, the SW can be heated to higher temperatures with an increase on the MHF solids load. Burning more solids will create more gases and hence this will heat the SW to warmer temperatures since the SW it's always kept at a constant flow. In other words, the higher the MHF solids load at a constant controlled temperature, the higher the temperatures in the SW. This suggests that to be able to maintain the temperatures on the MBCNTP

below 40 °C under the new MACT 129 regulations, the MHF solids load should be maintained low especially during the warmer months.

CHAPTER 5

CONCLUSION AND ENGINEERING SIGNIFICANCE

The purpose of this project was to identify the source of nitrification inhibition at Boat Harbor Treatment Plant when the MBCNTP system was in service and additionally to propose a cost-effective solution in which the treatment of cyanide and nitrification can occur simultaneously. The results presented on this research, not only benefits BHTP, but all the WWTPs that operate an incinerator and are facing problems when trying to nitrify.

Sending the SW-C back to the headworks without experiencing problems with nitrification will always depends on the dilution factor. Low CN concentration in the SW-C or high flows coming in to the plant will protect the BNR process. However this option could be a problem if the CN concentration on the SW-C is too high, can't be controlled and it is fluctuating too much. This also depends on the degree to which the aeration tank is configured to represent more plug flow or complete mix conditions, with more complete mix providing a lower expected aeration tank CN concentration. Simulation of these processes in SBR provides a worst case in terms of potential CN inhibition, because a SBR, which is fed SW and CN in a single fast pulse input, simulates in time a perfect plug flow aeration tank in space.

Based on SBRs experiments, it was determined that cyanide in the SW-C is present as free cyanide and it was the primary inhibitor on the nitrification process. The minimum CN concentration at the aeration influent that must be maintained at all times, when the main BNR process is at 20 °C, is 0.08 mg/L. At 0.08 mg/L of CN and at 15

days total SRT, 10 days aerobic SRT, only 80% of the initial ammonia concentration will be oxidized and will become worse with time as the CN concentration increases. However, at warmer wastewater temperatures (28 °C) at the same SRT, when the nitrifiers are more active, the minimum concentration changes from 0.08 to 0.26mg/L of CN.

As observed at BHTP in the year 2013 and what was proven using the SBRs, CN is only an inhibitor and not toxic for the nitrifiers, letting the BNR process recover when CN is not present or when it is below the threshold concentration.

If an aeration tank from the BNR process is used to treat CN, the amount of RAS flow (main source of microorganisms) used to treat CN in a MBCNTP system, must be enough to degrade it, but at the same time it must be low enough so that the nitrifiers are less exposed to high concentration of CN. It was discovered that 50% RAS configuration is enough for CN treatment at BHTP.

When footprint is not a limitation and budget not an inconvenience, using a SBCNTP for the treatment of CN, should be considered. This configuration allows treating CN beyond detectable levels.

There is no doubt that ferrous sulfate works better than ferric chloride when trying to precipitate CN^- and form Prussian blue, however, trying to maintain the condition to make this happen at full scale could be expensive. An alternative that was evaluated was to use the alkalinity from the RWI. It was found that this approach could work; however, the amount of ferrous sulfate needed at BHTP to only remove 60% of the CN^- could be expensive as $ 9,290 per month if 20 mg/L is assumed to be in the SW-C. If

in the future the CN^- concentration coming from the incinerators can be reduced, this option should be considered.

During the chemical precipitation of CN^- it is important to minimize the soluble Fe-CN complexes for a better percent of removal; this will depend on the pH, the Fe^{2+}/CN ratio and the DO concentration. Up to 69% percent removal was achieved with a Fe/CN of 1.0, DO among 1 and 2 mg/L and pH close to 6.5. Though, further studies needs to be performed to improve this approach. Additionally, when combining chemical precipitation with biological oxidation, the CN percent removal takes place mainly because of the biological oxidation and it was also found that solids from the RAS might interfere with the CN chemical precipitation.

High temperatures in the MBCNTP system interfere with the biological cyanide degradation, causing a reduction in the removal efficiency. Temperatures should be maintained below or at 40 °C to successfully degrade CN. However, trying to control these temperatures with the new MACT 129 regulation could be a challenge especially during the summer. To keep the CO and NOx under permit, it was found that the percent of O_2 should be around 5% and temperatures in hearth 1 should be maintained at 1100 °F. This is ideal to maintain CN formation low, but not ideal for the MBCNTP system since SW temperatures will be higher, especially when the MHF solids load rate is high, which can be the case most of the times since currently the solids load is never controlled or managed. Use of NPW addition to alleviate temperatures in the MBCNTP could be used, however, it should be noted that, if a large volume of NPW is added, this will decrease the detention time in the reactor (SBCNTP), affecting the CN percent removal.

CN inhibition to nitrification can be alleviated with warmer wastewater temperatures in the BNR process since the nitrifiers are more active and increasing the caustic dose for alkalinity purposes has the same positive effect. Nonetheless, as mentioned above, it will be more cost-effective to maintain the temperatures below or at 40 °C on the SBCNTP during the summer than to use a considerable amount of caustic. This could be achieved by maintaining low the MHF solids load.

In different tests (SBRs and on plan site) it was recognized that NOB are more sensitive to CN than AOB, i.e.the ammonia is oxidized to nitrite but not completely oxidized to nitrate. However it is recommended to further study this inhibition mechanism to obtain more valid data to be able to control it and take advantage of it. Some current studies are focusing on the out selection of NOB and this could be the case using CN if it is better understood.

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APPENDIX A

SBR A, SBR B/MBCNTP AND SBR C/NEF C DESIGN CRITERIA

SBR A design

On this configuration, SBR A was operating only one reactor. The decant volume

per cycle was calculated to setup the J-tube location as follows.

$$\frac{Total\ Reactor\ Volume\ (22L)}{Number\ of\ Cycles\ per\ Day * HRT} = Decant\ Volume\ per\ cycle$$

$$\frac{22L}{4.0\ \frac{cycles}{day} * 0.5 day} = 11.0\ \frac{L}{cycle}$$

$Total\ Reactor\ Volume - Decant\ Volume\ per\ cycle =$

$Volume\ to\ fill\ with\ Mixed\ Liquor$ (J-tube location)

$$22L - 11L = 11\ L$$

Because 11L was also simulating an average influent flow of 15 MGD (PCE + SW-C),

the representative volume per cycle of SW-C used to simulate the average flow of 1.30

MGD was calculated as follows:

$$11L * \left(\frac{1.3MGD}{15MGD}\right) = 0.95\ L$$

Hence,　　　　SBR A mixed liquor volume: 11L (J-tube)

　　　　　　　SBR A PCE Volume: 10.05L　　　　　　**22 L**

　　　　　　　SBR A SW-C: 0.95L

All SBR's designs were based on the same principle; therefore all PCE, RAS and SW-C volumes were the same.

SBR B / MBCNTP Design

This design was more complex than a normal SBR setup, but it can be easily explained. Since 11 L were simulating the RAS flow distributed in six aeration tanks, and using a 100% RAS configuration, the mixed liquor volume in the NEF B needed, per cycle, was:

$$\frac{11L}{6} = 1.83L$$

MBCNTP mixed liquor volume: 1.83 L

MBCNTP SW-C: 0.95L

2.78 L

SBR B was simulating 5 aeration tanks, therefore the mixed liquor volume needed per cycle was:

$$11L - 1.83L = 9.17\ L$$

SBR B mixed liquor volume: 9.17L*

SBR B PCE Volume: 10.05L

19.22 L

*J-tube on SBR B was located so that it could retain 11 L of mixed liquor and, just before each cycle, a volume of 1.83 L was transferred to the NEF B before PCE or SW-C was fed into their respective reactors.

SBR C / NEF C Design

In order to have the best representation of VIP process using an NEF in lab scale,

the following assumptions were made based on average operational parameters.

$$V_{NEF_C} = V_{SBR_C} \cdot \left(\frac{SBR\ C\ time\ aerating, hr}{24\ hr}\right) \cdot \left(\frac{VIP\ NEF\ Aeration\ tank\ Volume\ (MG)}{VIP\ Aerobic\ Volume\ (MG)}\right) \cdot$$
$$\left(\frac{VIP\ WAS\ TSS}{approx\ SBR\ C\ WAS\ TSS}\right)$$

$$V_{SBR_C} = 22\ L$$

$$SBR\ C\ time\ aerating, hr = 4\ cycles\ of\ 3.5\ hrs = 14\ hours$$

$$VIP\ NEF\ Aeration\ tank\ Volume = \frac{\pi}{4} \cdot (60ft)^2 \cdot 22ft \cdot \left|\frac{7.48\ gal}{1\ ft^3}\right| \cdot \left|\frac{1\ MG}{10^6 gal}\right|$$
$$= 0.5\ MG$$

$$VIP\ Aerobic\ Volume = 4 \cdot 180ft \cdot 65ft \cdot 20ft \cdot \left|\frac{7.48\ gal}{1\ ft^3}\right| \cdot \left|\frac{1\ MG}{10^6 gal}\right| = 7.0\ MG$$

The volume needed to simulate the NEF at lab scale was:

$$V_{NEF_C} = 22L \cdot \left(\frac{14\ hrs}{24\ hrs}\right) \cdot \left(\frac{0.5\ MG}{7.0\ MG}\right) \cdot \left(\frac{approx.\ 8,000\frac{mg}{L}}{approx.\ 2,000\frac{mg}{L}}\right)$$

$$\boxed{V_{NEF_C} = 3.70\ L}$$

J-Tube location on NEF C was designed using the waste from SBR C using 12 days SRT,

but after a few days of operation, the waste from SBR C was corrected to achieve a 15

days SRT. Therefore, the waste and J-tube location from SBR C was calculated as

follows:

$$SRT = \frac{Reactor\ Volume}{Waste\ voulme}$$

$$12\ days = \frac{22L}{Waste\ volume\ /day}$$

$$Waste\frac{volume}{day} = 1.833\frac{L}{day} \cdot \left|\frac{1\ day}{4\ cycles}\right| = \frac{0.458L}{cycle}$$

$$J - Tube = Full\ volume - waste\ from\ SBR\ C - scrubber\ water$$

$$J - Tube = 3.7L - 0.458L - 0.95L$$

$$\boxed{J - Tube = 2.292L}$$

Hence,

Waste coming from SBR C: 0.458 L

Mixed liquor volume: 2.292 L (J-tube) $\rbrace$ **3.7 L**

SW-C: 0.95 L

And for SBR C,

SBR C mixed liquor volume: 11L (J-tube)

SBR C PCE Volume: 10.05 L $\rbrace$ **22 L**

Treated water coming from NEF C: 0.95 L

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