THE USE OF OXIDATION-REDUCTION POTENTIAL AS A MEANS OF CONTROLLING EFFLUENT AMMONIA CONCENTRATION IN AN EXTENDED AERATION ACTIVATED SLUDGE SYSTEM

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ABSTRACT

This study developed a strategy to control effluent ammonia from an activated sludge system, using oxidation-reduction potential. By controlling effluent ammonia concentrations, disinfection of treated wastewater is more cost effectively achieved by chloramination rather than break-point chlorination. The system under consideration was an extended aeration oxidation ditch. The study takes into account the concepts of nitrification and denitrification, as well as intrinsic characteristics of oxidation-reduction potential, while also keeping ease of operation in mind. Data were gathered by varying the rate of aeration of the basin from two extremes, while collecting samples along the timeline. Oxidation-reduction potential, dissolved oxygen concentration and ammonia concentration data were collected for evaluation. Using these data a preliminary control strategy was developed. The control strategy focused on operating the system in a continuous flow and varying aeration scenario. Two attempts to control the oxidation ditch were made. Using oxidation-reduction potential as an indicator, adjustments were made to the aerator controls in order to accommodate changes in organic loading, and maintain a constant effluent ammonia concentration. The first attempt was met with success and used to fine tune the strategy for the second attempt. The second attempt experienced more success than the first in controlling effluent ammonia concentrations, thus confirming the original hypothesis of the study.

KEYWORDS

Control, ammonia, activated sludge, oxidation-reduction potential, disinfection, oxidation ditch, continuous flow.

INTRODUCTION

Electrode Potential or Oxidation Reduction Potential (ORP), as it is commonly referred to, has proven to be an effective method of monitoring wastewater processes and in some instances has been used as a control parameter. This thesis shows that ORP can be effectively used as an ammonia control indicator for use in an extended aeration oxidation ditch process. This use of ORP as an indicator to control ammonia, led to the development of a control strategy for the extended aeration oxidation ditch under consideration.
Background

In the context of this study, ORP is a measurement of the ability of the system being observed to either accept electrons (reduce) or donate electrons (oxidize). ORP sensors measure this ability in millivolts. When positive, the measurement indicates the degree to which the system is oxidative, and when negative, indicates the degree to which it is reductive. When an activated sludge system experiences high organic loading, oxygen is consumed and a reducing environment occurs (Rabinowitz, 1985).

Some oxidation ditch systems experience significant diurnal variation in dissolved oxygen concentration due to constant aeration rates for varying waste loads. During periods of low organic loading, DO levels may be sufficient to support complete nitrification resulting in no ammonia present in the effluent of the oxidation ditch. Conversely, anoxic or near anoxic conditions during periods of high organic loading preclude nitrification and effluent ammonia concentrations increase. Fluctuations in ammonia concentrations make disinfection difficult to achieve with a uniform chlorine dose. Ammonia is utilized in the disinfection process; the combination of chlorine and ammonia allows for the formation of chloramines, which are effective disinfectants. During periods of no effluent ammonia, it may be necessary to provide break point chlorination. One of the benefits of effective control of the ditch DO as proposed would be the ability to insure sufficient ammonia to allow for effective disinfection without the expense of breakpoint chlorination. Optimizing power used in aeration is another benefit of effective control.

Objectives

The objective of this study was to develop a control strategy for the operation of an oxidation ditch process using the measurement of the Electrode Potential (ORP) and dissolved oxygen of the mixed liquor. A strategy is needed to operate the process to maximize COD removal and nitrification and denitrification while allowing ammonia to remain in the effluent to aid in the disinfection process. These objectives were accomplished by first, conducting an intensive sampling regime, second, reviewing sampling data and planning a control strategy, and finally, attempting to control effluent ammonia concentrations from the oxidation ditch. All of these objectives were met an are documented herein.

LITERATURE REVIEW

This section summarizes the published literature related to the use of ORP as a control parameter for wastewater treatment processes. Specifically, the literature review is focused on previous efforts that relate to the use of ORP for controlling activated sludge processes and, specifically, extended aeration oxidation ditch process units.

Depending on operating conditions, some of the activated sludge systems nitrify ammonia, with a smaller number also denitrifying nitrates from the liquid. Extended aeration activated sludge systems, such as oxidation ditches, are an example of processes that are capable of both nitrification and denitrification. In general, however, oxidation ditch systems either accomplish very little nitrification or they completely nitrify the effluent.
Numerous automated and manual control strategies have been developed for the operation of activated sludge systems. Some strategies have been developed to control nitrification using only DO measurements from continuous on-line instruments (Yingst, et al., 1985; Hope, 2005; ACE System, 1983). Most of these control systems are aimed at complete nitrification by maintaining DO concentrations around 1.0 mg/L or higher. The systems, however, have not proven that they can reliably control nitrification by simply maintaining low DO concentrations. At low DO’s oxygen transfer may be enhanced (Okey, et al., 1961) and impact of low DO conditions are not always uniform (Harrison, 1972). In addition, low DO periods are significantly affected by COD mass load changes without the treatment plant operator being able to differentiate those changes through DO readings only (Isaacs, 1997)

Given the unreliable nitrification resulting from solely DO control, there is a need for additional development in this area. Oxidation potential (ORP) is a logical parameter to add to DO to control activated sludge operation during periods of low or no apparent DO (Okey, 2001; Habertmeyer, et al., 2005; Charpentier, et al., 1989 and 1998). However, there have been some difficulties associated with the use of ORP. First, ORP values reported in the literature often do not include the type of reference electrode used. Silver-silver chloride reference electrode measurements require a conversion to be comparable to measurements made by a conventional hydrogen electrode. Lafevre, et al. (1993) and Charpentier, et al. (1989) reported the following relationship between measurements taken from these different reference electrodes:

\[ \text{EH/EHN (mV)} = \text{E Ag/AgCl (mV)} + 200 \text{ (mV)} \]

Where:
- EH/EHN: Equivalent Hydrogen Electrode Value (mV)
- E Ag/AgCl: Silver/Silver-Chloride Electrode Value (mV)

This research reports all ORP readings as silver-silver chloride reference electrode values.

A second difficulty in using ORP values reported in the literature is the relative nature of the reading. Rabinowitz (1985) reported that ORP readings varied due to heterogeneous nature of wastewater mixed liquor. Charpentier et al. (1989) reported that an acceptable variation of side-by-side instruments was ±30 mV. Other researchers (Demoulin, et al., 1997; Collivignarelli, et al., 1999) have commented that inherent factors in ORP measurement make all measurements site specific.

Finally, ORP readings may vary greatly from the surface of the floc particle to the interior of a floc particle depending on conditions external to the floc (Li, et al., 2003). Thus, ORP control systems must be calibrated to site specific and instrument specific readings.

ORP readings, coupled with DO and/or pH readings have been reported as an effective means of controlling activated sludge systems using intermittent aeration (aerobic-anoxic) to produce nitrified and denitrified effluent (Rabinowitz, 1985; Habertmeyer, et al., 2005; Charpentier, et al., 1989 and 1998; Kim, et al., 2001; Lafevre, et al., 1993; Al-Ghusain, et al., 1995; Zipper, et al., 1998; Sperandio, et al., 2004 and Demoulin, et al., 1997). Successful control programs have reported ORP ranges for nitrification-denitrification +50 mV (Ag-AgCl) to a − 250 mV (Zipper,
et al., 1998; Demoulin, et al., 1997; Al-Ghusian, et al., 1995 and Charpentier, et al., 1998). During aeration periods with ORP readings ranging from 0 mV to -50 mV, ammonia appears to be completely removed from the system. When the ORP is lower than -200 mV ammonia nitrification is not effectively occurring (Charpentier, et al., 1998). Some of the control methods depend on the “nitrate knee” being present as a means of identifying the control point where nitrate has been effectively reduced (Rabinowitz, 1985; Kim, et al., 2001; Charpentier, et al., 1989; Sperandio, et al., 2004; Al-Ghusain, et al., 1995). The nitrate knee is identified as a second inflection point during the aerator off cycle where the slope of the ORP curve begins to increase after a flattening out period as illustrated in Figure 2-1.

The country of France has used ORP as a regulatory mechanism for operation of intermittent (on/off aeration) systems. Five operating facilities have demonstrated the ability to nitrify down to about 2-3 mg/L of ammonia using ORP set points (Charpentier, et al., 1998). In this research an intermittent system was monitored and ORP was maintained within upper and lower threshold limits. Points at which ammonia and nitrates disappeared were also noted. While this research addresses ORP as a control parameter in intermittent systems, it does little to address the function of ORP in a continuously aerated system. Little literature has been found that examines of the use of ORP as a control mechanism in complete mixed activated sludge systems with continuous aeration. Okey (1983) proposed a research project to investigate such a system. However, the project was not completed.

When full nitrification is achieved, chlorine disinfection can often be less effective. White (1986) describes the interrelationship between chlorine disinfection and nitrates in water. With good mixing and the presence of sufficient ammonia, the formation of monochloramine takes place and good disinfection of the wastewater occurs. In fully nitrified effluents, the lack of ammonia allows the formation of organochloramines, which leads to increased chlorine dosages.
to achieve pathogen inactivation due to the poor disinfection properties of the organochloramines. White (1986) reports that when an ammonia concentration of 2 to 3 mg/L is present, and when mixing is sufficient, good disinfection can occur at the lowest possible chlorine dose (White, 1986; and Harp, 2000). DO control systems have been suggested for controlling a constant rate of ammonia in the effluent to aid in the disinfection process; however, the reliability of such instruments at low DO has been questioned (Stenstrom, 1980). These findings suggest that effluent ammonia control necessitates additional control parameters.

The optimization of effluent ammonia for disinfection purposes is another factor that is not explicitly addressed in the literature reviewed. Most articles focus on the use of ORP to control intermittent aerobic and anoxic systems for maximum nitrification and denitrification results (Rabinowitz, 1985; Habertmeyer, et al., 2005; Charpentier, et al., 1989 and 1998; Kim, et al., 2001; Lafevre, et al., 1993; Al-Ghusain, et al., 1995; Zipper, et al., 1998; Sperandio, et al., 2004 and Demoulin, et al., 1997). These studies are useful for their expressed purposes, but they do not allow for a fine tuning of nitrification and a controlled constant effluent ammonia concentration, which constitutes the objective of this study.

Nitrification occurs as ammonia is oxidized to form nitrite and subsequently nitrate compounds. The equations for these reactions are as follows:

\[
\begin{align*}
2\text{NH}_4^+ + 3\text{O}_2 & \rightarrow 2\text{NO}_2^- + 4\text{H}^+ + 2\text{H}_2\text{O} \\
2\text{NO}_2^- + \text{O}_2 & \rightarrow 2\text{NO}_3^- 
\end{align*}
\]

From these equations it can be observed that oxygen is the oxidizing agent and ammonia is the reducing agent. Because oxygen is typically the limiting agent in this reaction of an activated sludge system, regulating the amount of oxygen added and the intensity of its addition can be reasonably assumed to drive nitrification. This is a major assumption that will be validated in this study.

Sufficient oxygen must be supplied through aeration equipment for this reaction to occur. Since oxygen is also needed for carbonaceous waste oxidation, oxygen must be supplied to meet this need, too. When evaluating the electrode potential (ORP measurement) where these two reactions cease to occur, the following relationship is important:

\[
\text{EP}_N > \text{EP}_C
\]

where:

\[
\begin{align*}
\text{EP}_N: & \text{ Electrode Potential – Nitrogenous Removal} \\
\text{EP}_C: & \text{ Electrode Potential – Carbonaceous Removal}
\end{align*}
\]

This would indicate that if the supply of oxygen is sufficient to meet the requirements for ammonia nitrification, most if not all of the carbonaceous oxygen demand will also be met. Therefore, if a control mechanism is developed to attain a set point for effluent ammonia, the goal of organic carbon removal will also be achieved. Theory follows the logic that nitrogenous oxygen demand takes a back seat to its carbonaceous counterpart.

This project will combine the use of DO, ORP, and aeration rates to control a low speed turbine aerator oxidation ditch process to achieve an effluent ammonia concentration of between 2 – 3 mg/L.
The treatment process should remain a complete mixed system with some aeration on continuously to maintain mixing. Initial investigation will provide for evaluation and operation of in-situ DO and ORP meters and will calibrate their readings relative to varying aeration setting. Frequent ammonia testing will be conducted during this process to calibrate ammonia and ORP conditions. After calibration, a control strategy will be devised and tested.

Denitrification is a process that is also observed in this study; however it is of less emphasis than nitrification. Denitrification is the process by which nitrogen in nitrate (NO$_3^-$) is reduced to nitrogen gas (N$_2$). The reaction can be observed below:

$$5(CH_2O) + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 7H_2O + 2N_2$$

where (CH$_2$O) represents a fragment of some arbitrary carbohydrate.

Denitrification observed in the study as nitrate concentrations decrease. Because the presence of oxygen creates highly oxidizing conditions, and due to the fact that nitrogen is reduced during denitrification, conditions must be anoxic for denitrification to occur. Complete denitrification forces the system into anaerobic conditions.

**MATERIALS AND METHODS**

This chapter details the materials and methods used to gather ORP, DO, BOD removal, nitrification, and denitrification data during the operation of an extended aeration oxidation ditch treating municipal wastewater. The study relied on several different lab procedures and a variety of instrumentation to collect and process the data. Furthermore, a description of the oxidation ditch and influent conditions are provided.

**Oxidation Ditch**

Wastewater treated by CDSD is primarily domestic in origin. There are no significant industrial users and only limited numbers of commercial sewer connections. Average per capita water discharge from metered water readings is about 63 gpcd based on winter water averages. Annual average sewer flow to the WWTP from domestic sources is about 102 gpcd indicating significant Inflow and Infiltration (I & I) additions to the WWTP.

The extended aeration oxidation ditch at the Central Davis Sewer District (CDSD) wastewater plant was constructed in 1990. The process is carried out in two separate carrousel-configuration reaction basins. The carrousels are folded in on themselves at the mid-point. There is an aerator-mixer at each end of the carrousel, i.e., two aerator per basin. In an ideal oxidation ditch configuration, the aerator-mixers enhance oxygen entrainment in the wastewater. This increases the oxygen supply for microbial processes in the basin and the portion of the oxidation ditch that operates under aerobic conditions. The ideal configuration provides for effective BOD/COD removal and nitrification in the aerobic zones of the basin and a sufficient anaerobic volume to promote denitrification as well. It would also provide enough constant mixing to keep sludge in suspension. The CDSD oxidation ditch has a maximum hydraulic design capacity of 13.1 mgd
with a maximum daily flow of about 8 mgd. This capacity is based on current wastewater average pollutant concentrations and was determined by stress testing of the facility. The secondary wastewater at CDSD is split evenly between the two extended aeration oxidation ditch carrousels. The average month hydraulic residence time for each basin is 9 hours whereas the design solids retention time for the basins is 20 days. Each basin has a maximum volume of 1.54 million gallons.

In-situ DO and ORP probes were installed in the two oxidation ditch basins at two locations illustrated in Figure 3-1. Location 1 in Figure 3-1 is referred to as the 'weir' location due to its proximity to the outfall weir and location 2 is referred to as the 'anoxic' location due to its proximity to the most probable anoxic region of the channel. For the data collection process and in parts of the appendix, sampling locations are referred to as ‘anoxic’ and ‘weir.’ In the remainder of this report they will be referred to as ‘Location 1’ and ‘Location 2’ according to Figure 3-1.

The average daily flow for the first seven months of 2005 to the CDSD oxidation ditches was 3.5 mgd. In 2004 the average annual influent and effluent concentrations, measured twice per week, for measured pollutants are shown in Table 3-1.

![Figure 3-1. Oxidation ditch configuration and sampling locations](image)
Table 3-1 Influent and Effluent Parameters of the CDSD Oxidation Ditch

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent Concentration</th>
<th>Effluent Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₅</td>
<td>156 (mg/L)</td>
<td>2-5 (mg/L)</td>
</tr>
<tr>
<td>TSS</td>
<td>232 (mg/L)</td>
<td>2 (mg/L)</td>
</tr>
<tr>
<td>COD</td>
<td>390 (mg/L)</td>
<td>22 (mg/L)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>21.6 (mg/L)</td>
<td>2.1 (mg/L) (Ranges from &lt;0.5 to 2.1)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>6.3 (mg/L)</td>
<td>5.3 (mg/L) (Ranges from 1.2 to 19)</td>
</tr>
</tbody>
</table>

Data Collection

Data were gathered to better understand the sensitivity of ammonia levels in the oxidation ditch to change in oxygen delivery. Some general assumptions regarding the ditches are that the mixed-liquor in the oxidation ditch is well-mixed and that DO and ORP measurements taken along the walls of the basin apply to the entire flow along that interval of the basin. Another assumption is that scum build-up on the probe has a negligible affect on the probe readings. Rapid responses in DO readings associated with changes in aerator setting take place seemed to confirm the negligible impact of scum on the probe.

Monitoring was conducted during eight discrete intensive testing periods of one day each. On these days, grab samples were used to evaluate the effluent for nitrate and ammonia. Ammonia tests were run on each grab sample. Nitrate tests were run on only two of the six intensive sampling days. At the time of each grab sample, ORP and DO readings were recorded at both the Location 1 and Location 2.

During testing on these days, aerator controls were manipulated to represent a large swing in the oxidation-reduction potential of the wastewater. Grab samples were collected frequently enough to observe depict the effects of changing aerator conditions on the ammonia content of the ditch. Both aerators have two-speed motors with the 'Low' speed setting at about 52 HP and a 'High' speed setting at about 75 HP. The three settings for each motor provide five (5) combinations for delivering oxygen to the oxidation ditch other than the Off setting (Table 3-2).

Table 3-2 Aerator Setting Combinations

<table>
<thead>
<tr>
<th>Aerator 1</th>
<th>Aerator 2</th>
<th>Total Hp</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>0</td>
<td>52</td>
</tr>
<tr>
<td>75</td>
<td>0</td>
<td>75</td>
</tr>
</tbody>
</table>
Steady-state system operation with one aerator on low produces an effluent ammonia concentration that varies between 5 to 15 mg/L. One aerator on high and the other on low results in an approximate discharge ammonia concentration is 0 to 3 mg/L. With both aerators on high there is no measurable ammonia in the effluent (Myers, 2005).

For the purposes of the study only two setting combinations were used to achieve the resultant maximum swing in ORP. This maximum swing is the most dramatic change in ORP that can be realized by setting aerator setting combinations at the lowest possible setting (besides switching both aerators off) and then changing to the highest aerator setting combination possible. These setting combinations were:

- Combination 1 (52 HP): Aerator 1 – Off; Aerator 2 - Low.
- Combination 2 (150 HP): Aerator 1 – High; Aerator 2 - High,

These two configurations were used to examine the change in DO, ORP, Ammonia, and Nitrate over the widest range of aerator horsepower available. In real time control of the oxidation ditch, any combination of aeration setting combinations could be utilized.

On half of the testing days, the aerators were set for Combination 1 and left in place at least overnight (sometimes longer) so that the conditions in the basin could reach steady-state. Early the following morning (usually between 6:30 and 7:30 a.m.) the aerator settings were changed to Combination 2 (both aerators on high) and changes in the basin were measured. Combination 2 (both aerators on High) was left on overnight on the other testing days, then changed to Combination 1 early on the testing day to measure the changes in the basin from High to low aeration.

**Ammonia and Nitrates**

Ammonia content of grab samples was measured using a Hach DR4000 spectrophotometer. The testing process involved the centrifugation of the sample in order to ensure separation of solids from the liquid. After centrifugation, samples were tested for ammonia and nitrate within a short time frame, usually within an hour, but depending on the number of backlogged samples that needed processing. It was assumed that solid-liquid separation assured relative cessation of biological activity within the sample. Ammonia was measured using Method 8038 as described in the Hach DR4000 manual using reagents purchased from Hach. CDSD had previously determined that distillation of the sample is not needed for testing of a clear liquid. Nitrates were measured using Method 8039 as described in the Hach DR4000 manual also with reagents purchased from Hach.
During the second attempt at ammonia control outlined in Chapter 4, two online analyzers were supplied by Hach to measure ammonia and nitrates. These online analyzers were used for a period of about one day and logged continuous ammonia and nitrate measurements. The device used to measure and record ammonia concentrations is called the ‘Amtax™ compact Ammonia Analyzer.’ Nitrates were recorded using the Hach ‘Nitrax™ UV Nitrate Sensor.’ The instruments were calibrated according to Hach specifications and given time to acclimate to the conditions of the oxidation ditch.

The Amtax™ analyzer functions using a liquid-gas phase transfer methodology to measure the aqueous concentration of ammonia. Hach (year of reference & include in reference list) reports the sensor as having a range of 0.5 to 12.0 mg/L ammonia and an accuracy of ±2.5% of the measured value, or 0.2 mg/L ammonia, whichever is greater. The minimum detection of the unit is 0.5 mg/L ammonia.

The Nitrax™ sensor utilizes ultraviolet (UV) light absorption to measure aqueous concentrations of nitrate. Hach reports detection limits of 0.1 to 25.0 mg/L nitrate, with an accuracy of ±3% of the mean, or ±0.5 mg/L nitrate.

Finally, it should be noted that in the context of this report ammonia, in whatever state, is referred to as “ammonia” for the sake of convenience. This means that even if ammonium (NH₄⁺) is dominant at ambient pH levels, it is still referred to as ammonia.

**Oxidation-Reduction Potential and Dissolved Oxygen**

Data gathered during the testing process included readings from DanFoss DO probes and Stranco ORP probes installed in the oxidation ditch at Location 1 and Location 2. DO and ORP readings were recorded with every grab sample in order to establish a correlation.

In addition to the readings recorded with every grab sample, hourly DO and ORP measurements were recorded in the SCADA database. Historical SCADA (Supervisory Control And Data Acquisition) data was used to verify the relationship between ORP and DO. The SCADA system logs DO and ORP readings every half hour and then reports an average hourly value. These readings can be extracted and manipulated in any data management software package.

As mentioned in previously, supplementary Hach instrumentation was used during the second attempt to control effluent ammonia. An ORP sensor was included in the array of instruments provided by Hach. Although ORP values for this study are being considered only from the in-place Stranco probes, the Hach probe data are included in the final control attempt to illustrate the discrepancy between sensors, ORP values for this study are being considered only from the in-place Stranco sensors. Both sensors use silver-silver chloride electrodes.

**Calibration**

At the beginning of the study, the intent was to calibrate the in-place ORP sensors against known standards purchased from certified suppliers. In addition, two portable Hydrolabs with ORP sensors would be used to periodically check the in-place sensors. During the initial calibration
all three sensors were calibrated with a known +200 mV standard. Linearity of the sensors were checked +600 mV standard. All meters provided readings within 2 to 5% of the standard value. Then all three sensors were placed side by side in the oxidation ditch for a 30-minute period. At the end of the 30-minute period, significant variation existed between the readings from three readings. The process was repeated and the variations were again present. The magnitude of the reading variation was a span of 125 mV. None of the sensor readings were within ±40 mV of another sensor. Additional attempts at correlation were also unsuccessful. At a later phase of the study, a Hach ORP probe was installed next to a Stranco sensor and both recorded data for about 30 hours. While the pattern of readings was relatively consistent between sensors, the values were still distinctly different. This variation in ORP probes is consistent with experiences of Hach applications at other sites (Kiser, 2005).

For this study, sensor consistency and response to change were more important than accurate measurements. Thus, the installed sensor values were used with the understanding that the absolute value may not be accurate. As the study progressed, it was determined that the data were sufficiently accurate to support the goals of the project.

RESULTS

This chapter summarizes the data collected during the study and discusses the analysis of those data. Data for the study were collected over a period of approximately three months. Data were gathered by using two primary means. First, data were retrieved from online sensors and second, data were obtained by laboratory analysis. After being collected, data were plotted according to time sequence and in ordered pairs. Trends were analyzed and discussed, and conclusions drawn in this chapter. These trends were then used to attempt to control oxidation ditch effluent ammonia concentrations on two separate occasions. The control attempts were evaluated and found to be successful. Conclusions support the hypotheses of this work.

ORP-DO Relationship

The relationship between ORP and DO is significant to this study. Indeed, ORP is heavily driven by dissolved oxygen content in activated sludge (Okey, et al., 1963). Other constituents, namely dissolved metals, can also affect ORP, but in the activated sludge system under consideration in this study, such constituents are of negligible proportions. Oxygenation of activated sludge increases the electron potential. (Okey, et al., 1963), attempted to model this relationship using a modified Streeter-Phelps equation. This attempt was unfortunately met with only marginal success, concluding that the ORP-DO relationship is erratic at times, especially in the low DO region. ORP and DO data were collected simultaneously at Location 2 (see Figure 3.1) of the extended aeration oxidation ditch at the Central Davis WWTP. Data were collected over a three month period of 4 hours while the plant was operating near average daily flow. Data was collected only from the basin under consideration. The relationship observed is specific to the basin and cannot be uniformly applied to other systems due to differences in aeration equipment and sensor discrepancies between the basins. The ORP-DO data are shown in Figure 4-1. The figure shows a relationship between DO and ORP in the CDSD oxidation ditch. This relationship illustrates the increase in DO as ORP increases. DO concentrations are effectively 0 mg/L until ORP reaches about a -170 mV threshold.
Figure 4-1. The ORP-DO relationship – Samples taken at Location 2

This is significant as that threshold is well above the control region established later in this chapter. The control region can be viewed in Figure 4-1. DO concentrations within this control region are negligible. This supports the assertion that in very low (≤0.1 mg/L) DO scenarios, control using DO only is impossible. This is due to sensor limitations. Thus, attempts to develop a statistically significant relationship between the DO and ORP data at very low DO concentrations were unsuccessful.

Establishing the concept that DO drives ORP is sufficient for the purposes of this study. The existence of this DO-ORP concept, combined with the known relationship between DO and Ammonia, logically indicates a relationship between ORP and Ammonia.

**ORP-Ammonia Relationship**

The relationship between ORP and ammonia suggests that general trends involving aeration and nitrification could be followed to create a sampling program. The change in ammonia concentration and ORP with oxygen supply changes was examined to investigate this relationship.

Decreasing aeration reduces the available oxygen supply and, thus, decreases DO concentration. A corresponding decrease in ORP is expected as oxygen is a driving force of ORP. Conversely, an increase in ammonia concentration would be expected because low DO and anoxic conditions will reduce the nitrification rate. Figures 4-2 and 4-3, each depicting one of the two monitoring locations, confirm this theory.
Figure 4-2. DO, ORP, and ammonia concentration change with time at Location 1. Aeration changed from combination 2 (two aerators on high) to combination 1 (one aerator on low).

Figure 4-3. DO, ORP, and ammonia concentration change with time at Location 2. Aeration changed from combination 2 (two aerators on high) to combination 1 (one aerator on low).

The data represented in Figures 4.2 and 4.3 contain samples and probe readings collected for each sampling location. The aerators were set on Combination 2 (both aerators on high) overnight to achieve a high initial DO concentration and ORP reading. The aerators were reset
to Combination 1 immediately after the first data points were collected. The DO dropped rapidly after the aeration supply was reduced. Within 30 to 40 minutes DO concentrations were below readable values. ORP however dropped at a more gradual rate with over two hours required for ORP readings beginning to stabilize at a lower value.

As evident in Figures 4-2 and 4-3, ammonia concentrations began to increase when the aeration was changed from Combination 2 to Combination 1. Nitrifying bacteria in the activated sludge floc are out competed by other more dominant species for the limited dissolved oxygen available. The increase in ammonia in the oxidation ditch is assumed to be attributed to the concentration of ammonia in the influent breaking through the system.

The rate at which ammonia increased in the system was also gradual and more consistent with the rate of ORP decline. However, once the rate of the ORP decline decreased, the ammonia increase continued at a relatively constant rate for several more hours, before again decreasing. This is assumed to be the nitrate knee discussed in the literature review.

The reverse relationship was observed when the aeration rate was increased after the basin reached an oxygen depleted state. The aerator configuration was left on aeration setting combination 1 overnight. At this settling, biological activity depletes the dissolved oxygen in the ditch and ammonia concentrations increase. Immediately after the first sample was gathered, the aerators were switched to setting combination 2 (two aerators on high). DO and ORP readings correspondingly increased and ammonia testing showed the expected depletion of ammonia as it was nitrified.

As noted in the preceding paragraph, this case generally showed the reverse of the prior experiment. There were, however, two notable exceptions. First, ORP readings rose rapidly (within 30 minutes) after the aeration was increased until a reading of about -100 mV was attained, after which the rate of increase reduced dramatically. Second, the DO concentrations increased rapidly to about 1.5 to 2.5 mg/L and then stabilized until essentially all the stored ammonia was nitrified. Then, the DO had a second period of moderate increase until about 5 mg/L. Figures 4-4 and 4-5 illustrate the Location 1 and Location 2 data for this event.
Figure 4-4. DO, ORP, and ammonia concentration change with time at Location 1. Aeration changed from combination 1 (one aerator on low) to combination 2 (two aerators on high).

Figure 4-5. DO, ORP, and ammonia concentration change with time at Location 2. Aeration changed from combination 1 (one aerator on low) to combination 2 (two aerators on high).
Figures 4-4 and 4-5 show that an inversely proportionate relationship exists between ORP and ammonia. Not only is there a definite relationship, but ORP appears to more quickly respond to aeration changes. This can be attributed to a lag in the ability of the nitrifying bacteria to respond instantly to a change in their environment. DO is impossible to use to compare with ammonia as it increases to high values or decreases to unreadable levels on the DO meter.

In order to further examine the relationship between ORP and ammonia, the ordered pairs of increasing or decreasing data previously illustrated in Figures 4-2 through 4-5, were plotted against one another (see Figures 4.6 and 4.7).

![Plot of ORP and ammonia ordered pairs at Location 1.](image)

**Figure 4-6. Plot of ORP and ammonia ordered pairs at Location 1.**
Figure 4-7. Plot of ORP and ammonia ordered pairs at Location 2.

Figure 4-6 further illustrates that as oxygen is added to a formerly anoxic system, ORP increases rapidly relative to the rate at which ammonia concentrations decrease. The converse relationship occurs as aeration ceases in an oxygen-rich system. ORP drops rapidly relative to the increase in ammonia. It should be noted that the two data points, in Figure 4-6, where it appears that ORP levels rise with ammonia were probably affected by an automatic cleaning cycle experienced by the probe at that time. The dotted and dashed lines and arrows show the direction and trend of the ORP-ammonia relationship when transitioning between oxygen environments. These trend lines do not represent mathematical regressions to fit to the data, but serve only to aid in the understanding of the plot and the data set. Attempts to fit a regression line to this data were met with little success and are not shown. Sufficient for the study, is to show that these trends do exist, and can be utilized in effluent ammonia control. Figure 4-7 shows the envelope as it occurs at Location 2.

Plotting these data together illustrates a pseudo-envelope between the two trends. This envelope illustrates the region in which control of the oxidation ditch can occur. In other words, successful execution of an ammonia control strategy using ORP needs to have as its target output, a point within the envelope. This method of control is discussed further below.

**Controlling Effluent Ammonia through ORP Indication**

Controlling effluent ammonia from the oxidation ditch by using ORP measurements is the central hypothesis of this thesis. This hypothesis holds true if, in a real time scenario, the effluent ammonia can be effectively controlled by monitoring swings in ORP and manipulating
the aerators accordingly. If ORP can be kept within a specific range then a relatively constant concentration of ammonia can be achieved in the effluent. This ORP range was determined from the Figures 4-6 and 4-7. The range is used to establish high and low ORP indication thresholds used for the first effluent ammonia control attempt. These thresholds were chosen from Figures 4-6 and 4-7, and are as follows:

Upper ORP Threshold: about -185 mV
Lower ORP Threshold: about -230 mV

The upper threshold indicates there is too much oxygenation for the ammonia control to be maintained and the aeration is driving the system toward over-nitrification. The lower threshold indicates nitrification is not keeping up with the ammonia loading on the ditch and therefore the ditch is not being aerated sufficiently. The thresholds were established as follows:

When the ORP thresholds were realized, the aerator controls were changed. When the upper threshold was reached the aerators were adjusted to the next lowest HP setting. When the lower threshold was reached, the aerators were adjusted to the next highest HP setting.

**First Control Attempt**

On August 3\textsuperscript{rd} 2005, the first attempt was made at controlling the ammonia concentration of the oxidation ditch effluent. As shown in Figures 4-8 and 4-9, during the control attempt ammonia concentrations were maintained at between 0.3 and 2.2 mg/L at both sampling locations.

In Figure 4-8, the aerator settings are depicted at the times adjustments were made to the aerators. The horsepower settings denote the degree to which the system was changed during the control attempt. The settings apply to both Figure 4-8 and Figure 4-9.

It should be noted that an error occurred during the control attempt. At approximately 10:30 am the aerators were shifted to accommodate the increasing load; however, instead of being changed from the 104 HP setting to the 127 HP setting, they were erroneously changed from 104 HP to 150 HP. This mistake resulted in the over-aeration and corresponding over-nitrification of the system, and resulting loss of baseline ammonia concentration. Aside from this error, the control attempt did keep the concentration of ammonia from exceeding 3 mg/L, and kept it at or above 1 mg/L for about half of the time.
Figure 4-8. Ammonia optimization – ORP, DO, ammonia, and nitrate concentration responses at Location 1 during first control attempt.

Figure 4-9. Ammonia optimization – ORP, flow, DO, ammonia, and nitrate concentration responses at Location 2 during first control attempt.
This error served to illustrate that over-aerating is a concern during control of the system. In comparing the way in which ammonia decreases and increases it is evident that, generally speaking, ammonia can be nitrified from the system more quickly than it can accumulate. This can be seen visually in Figures 4-10 and 4-11 as the increasing and decreasing ammonia trends of Figures 4-2 through 4-5, are plotted against one another. In the plots, ammonia is nitrified as soon as oxygen is added to the system. The decrease is relatively rapid as ammonia is essentially eliminated within four hours of high aeration. Conversely, as oxygenation ceases in the basin, ammonia remains negligible for about an hour until gradually increasing at an initially relatively constant rate, before beginning to plateau between 5-6 mg/L.

![Diagram of ammonia concentration over time](image)

**Figure 4-10.** Increasing and decreasing ammonia concentration at Location 1.
Another observation, in conjunction with the observation that ammonia can be easily lost, was that the thresholds should probably both be decreased for the next control attempt. This decision was made in order to err on the conservative side of the spectrum. The thresholds for the second attempt are as follows:

- Upper ORP Threshold: about -200 mV
- Lower ORP Threshold: about -270 mV

**Second Control Attempt**

The first attempt at controlling effluent ammonia laid the groundwork for the second and final attempt. As previously discussed, Hach representatives provided several online sensors for a day and a half of use. These sensors included an Amtax™ compact Ammonia Analyzer and a Nitrax™ UV Nitrate Sensor. Also included was a Hach ORP sensor, although the in-place ORP sensors were the sensors used for indication. The In-place DanFoss probes were used for measurement of DO. These sensors were left in position for several hours to acclimate to the oxidation ditch conditions. Data were recorded every 5 minutes and converted into hourly averages to correspond to in-place ORP data retrieved from the SCADA system. Data was collected for the Location 2 only because that location was most convenient for placement of online sensors provided by Hach.

Data were gathered from 3:00 pm on August 10th until 3:00 pm on August 11th. The control scheme for this attempt centered on the new thresholds established in the previous section.
Figure 4-12 and 4-13 are plots of the data collected during this control attempt first without and then with indication of when aeration was changed.

Figures 4-12 and 4-13 are both plots of the same data, however Figure 4-13 includes indication of changes of HP setting. This attempt was much more successful than the first attempt. The online analyzers proved to be a very valuable asset in controlling the ammonia. ORP was used as an indicator as planned, but the Amtax™ Analyzer was very useful in that ammonia could be seen instantly on the display panel. ORP swings served to forewarn an increase or decrease in ammonia, and tracking the rate of ammonia change made it possible to assess the loading swings in conjunction with ORP.

Figure 4-12. Ammonia optimization – ORP, flow, DO, ammonia, and nitrate concentration responses at Location 2 during second control attempt.
CONCLUSIONS

Through consideration of data obtained, this work has shown that ORP can effectively be used as an ammonia control mechanism for use in an extended aeration oxidation ditch process. An effective ammonia optimization control run has further supported this hypothesis. Use of an online ammonia probe can aid in and improve control of the operation. The implication for Central Davis Sewer District is that chloramination can be achieved by constant monitoring and adjustment of air supply using ORP as the ammonia control indicator. Chlorination and aeration power consumption can be optimized. This is significant because the District can save money while operating in a sustainable manner. Additionally, wear on the aerators can be minimized by using them on an as-needed basis.

Another interesting observation is that by optimizing ammonia removal, nitrate removal is also somewhat optimized. This can be observed in Figure 4-12, where nitrate concentration is also kept at or below 1 mg/L for the majority of the control attempt. This concomitant removal of nitrate with ammonia is an added bonus of ammonia control.

Figure 4-13. Ammonia optimization – ORP (in-place and Hach) and ammonia concentration responses at Location 2 during second control attempt.

The ammonia ranged from about 1 to about 3.5 mg/L as can be seen in Figures 4-12 and 4-13. This is an acceptable range for chloramination. Fine tuning could conceivably produce a tighter control of effluent ammonia. However, these results show that ORP can effectively be used as a valuable metric for indication and control of effluent ammonia concentrations of an oxidation ditch.

Flow information in Figure 4-12 (as well as Figure 4-9) shows how increasing flow into the ditch results in the need for more aggressive control. In the second control attempt it can be noted that nitrification of increasing influent ammonia contributed to the late surge in nitrate concentration.
This study shows that DO, ORP and organic loading are all related in the activated sludge process. A key finding made was that ORP is effective for control of oxygen delivery in the low DO region. DO alone is not efficient in this area.

This study shows that the reliability of ORP probes is in their response to oxidation or reduction changes in the system, and not necessarily in the value displayed. The study illustrates how system and probe specific thresholds need to be established.

Chloraminating wastewater effluent in this manner requires more attention than is given in this study. Excess formation of organochloramines is not only undesirable from a disinfection standpoint but can also be harmful to the quality of effluent receiving water. Dechloramination could be an option for protecting receiving waters where this is a concern.
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