DEGRÉMONT INDUSTRY

WHITE PAPER

IBIO™

Biological Treatment System for Flue Gas Desulfurization Wastewater

iBIO ™ Biological Treatment System for Flue Gas Desulfurization Wastewater

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Abstract: Wet Flue Gas Desulfurization (FGD) systems are being installed at coal-fired power plants to improve air quality by removing sulfur dioxide from flue gas emissions. The resulting FGD blowdown wastewaters are known to contain elevated levels of chlorides (4,000 – 20,000 mg/L), trace concentrations of heavy metal contaminants such as chromium, mercury, and selenium, often high levels of nitrates (10–700 mg/L), and very high levels of total dissolved solids (20,000 to 60,000 mg/L). Of particular concern in recent years is the removal of nitrogenous contaminants such as nitrates (NO_3^-) and ammonia, as well as various heavy metals, with selenium (Se) of particular concern as the Selenate (SeO_4^{2-}) form is not efficiently removed via conventional physical-chemical treatment practices.

An innovative and patent-pending biological treatment system, iBIO™ technology, developed by Degremont Technologies – IDI, provides an enhanced treatment option for the removal of residual selenium compounds from FGD wastewaters. Using fundamental microbial biochemical principles, a (1 – 2 gpm) pilot-scale iBIO™ treatment system was designed and installed at a steamed power plant of Southern Company. A description of the iBIO™ system is presented herein along with results from the pilot-scale studies that targeted the removal of nitrates, selenium and chromium from the FGD wastewater. These results were used to develop design parameters for a full-scale iBIO™ system. The FGD wastewater in this study contained significant concentrations of nitrates (10-316 mg/L), total selenium (0.5-3.7 mg/L), and total chromium (~0.02 mg/L). The results of the study demonstrated that the iBIO™ system can achieve an average effluent concentration of NO_3^- < 1.0 mg/L, total Se < 0.2 mg/L and total Cr < 0.005 mg/L. The data shows that all of the selenate species is removed by the iBIO ™ system, while trace concentrations of residual Selenite and unknown selenium compounds were found to remain in the treated effluent.

Keywords: Flue Gas Desulfurization, wastewater, iBIO™, Biological Nutrient Removal, Selenium, Selenate, Selenite, Heavy Metals

INTRODUCTION

Coal-fired power plants produce a significant portion of the electricity for the United States. Air emissions from coal-fired power plants require air pollution control systems. This has resulted in the implementation of wet scrubbers for removal of sulfur dioxide (SO_2) from stack emissions. The wet scrubbing of flue gases with lime or limestone slurries is a proven and commercially established process for decreasing SO_2 emissions. The resulting flue gas desulfurization (FGD) wastewater can contain elevated concentrations of solids, chlorides, sulfates, heavy metals, and nitrates. FGD systems have unique combinations of characteristics (such as scrubber type, absorber type, additive use, operational issues, etc.) that result in extremely varied wastewater characteristics.

Traditionally, FGD wastewater treatment has primarily consisted of physical/chemical processes for the removal of total suspended solids (TSS) and heavy metals. Due to regulation under the Clean Water Act (CWA), effluents discharged into aquatic systems may require additional treatment beyond traditional physical/chemical systems.

Biological treatment for heavy metals removal for FGD waters is an emerging technology. Suspended-growth activated sludge systems are the most commonly employed biological treatment processes for the removal of targeted organics and inorganics from various types of wastewater. Biological treatment has proven effective for removal of particular heavy metals in FGD wastewater, such as selenium, by reduction and precipitation reactions.

Infilco Degremont, Inc. (IDI) initiated a pilot scale field demonstration study in order to provide complete and effective treatment of FGD wastewater. IDI's patent pending biological treatment process, iBIO™, has the following objectives when treating the FGD blowdown water: 1) Nitrate removal – Denitrification, 2) Selenium Removal, and 3) organics and Ammonia removal.

EXPERIMENTAL

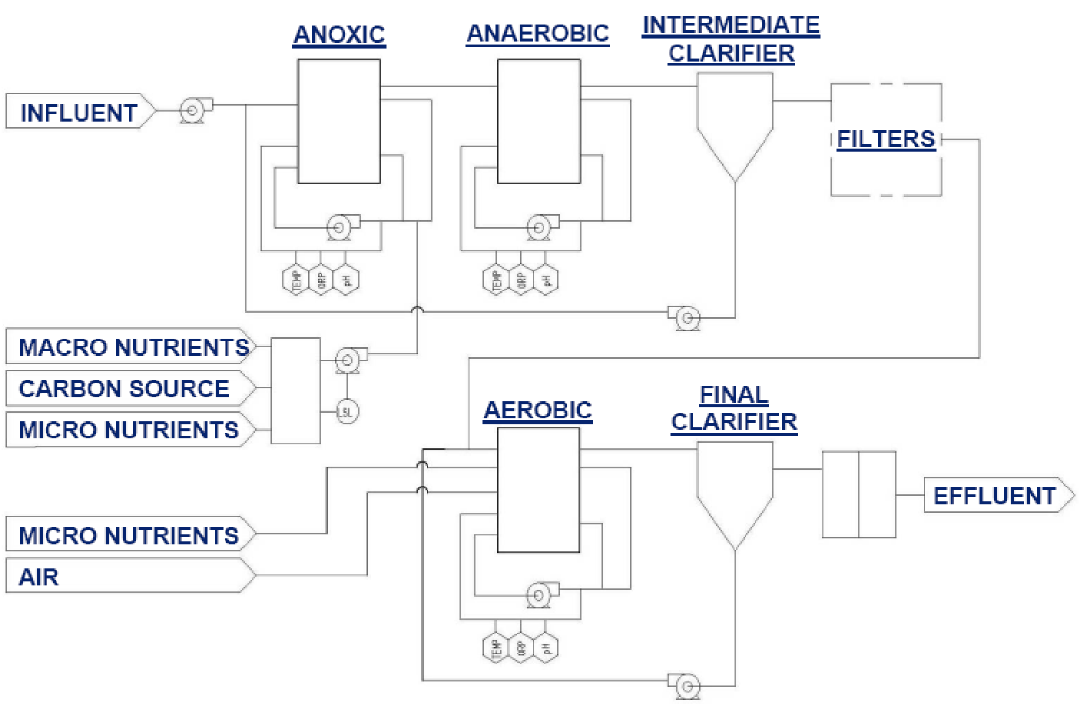
IDI's iBIO™ biological FGD wastewater treatment system is an activated sludge suspended-growth system. The biological treatment system consists of a series of reactors designed for biological removal of nitrate, heavy metals, ammonia, and organics from the FGD wastewater before discharge.

The overall treatment process consists of the following steps:

- Urea, micro-nutrients and carbon source addition.
- The removal of nitrate in the anoxic reactor.
- Sedimentation, thickening, and clarification of anaerobic/anoxic activated sludge.
- The removal of selenium, chromium by sulfate reducing microorganisms in the anaerobic reactor.
- Return activated sludge from the anaerobic/clarifier to anoxic reactor.
- Intermediate filtration before aerobic reactor.
- Removal of total organic carbon (TOC) and ammonia in the aerobic reactor.
- Waste activated sludge from the anaerobic/anoxic and aerobic clarifiers.
- Sedimentation, thickening and final clarification of aerobic activated sludge before final filtration.
- Effluent filtration before final discharge.

The biological treatment process flow diagram is presented in Figure 1.

Figure 1. Biological treatment- Process Flow Diagram



Equalization Tank (100 gallon)

An equalization tank is provided to balance the wastewater quality and flow either from the pilot physical-chemical treatment process or the scrubber pond effluent. A constant flow will enhance plant performance. The tank is equipped with an influent pump.

Anoxic Reactor (1000 gallon)

The influent through the equalization tank is loaded into the anoxic reactor. In the anoxic reactor, nitrates are removed through de-nitrification processes via microorganisms. Selenate, selenite, and sulfate are also reduced in this process. Macro- and micro-nutrients and a carbon source (sugar) are added to the anoxic reactor to allow for the biological remediation of constituents in this FGD wastewater.

Anaerobic Reactor (1000 gallon)

The wastewater leaves the anoxic reactor and flows by gravity into the anaerobic reactor that favors sulfate reducing bacteria (SRB) that can transform constituents such as selenate, senenite, and sulfate to less dissolved forms.

Anaerobic Clarifier (325 gallon)

The effluent from the anaerobic reactor flows into a clarifier, where mixed liquor suspended solids (MLSS) are settled out. Part of settled sludge is recycled back to the head of the anoxic reactor as return activated sludge (RAS) and part of sludge is removed as waste activated sludge (WAS).

Aerobic Treatment (500 gallon)

After leaving the anaerobic clarifier, the wastewater flows into the aerobic reactor. In this reactor, aerobic organisms can degrade and decrease the residual organic carbon compounds and ammonia prior to discharge.

Aerobic Clarifier (325 gallon)

The wastewater from aerobic reactor then passes into an aerobic clarifier, where the solids are settled out. Part of settled sludge is recycled back to the head of the aerobic reactor as return activated sludge (RAS) and part of sludge is removed as waste activated sludge (WAS).

Effluent Filtration

The clarified water then flows by gravity through sand filters where suspended solids concentrations can be decreased before final discharge.

RESULTS AND DISCUSSION

Composite sampling of equalization tank was performed to determine the chemical composition of pre-treated scrubber wastewaters. Analyses included pH, ammonia (NH_3), Nitrate (NO_3^-), Nitrite (NO_2^-), TSS, COD, TOC, total and dissolved selenium, and chromium. These analyses were performed throughout this study

Influent Characteristics

FGD wastewater samples from the scrubber pond effluent (from recycle line back to scrubber) were collected three times per week during this study. Constituents measured in the scrubber pond effluent wastewaters are shown in **Table 1.** Constituent loadings (lbs/day) to the pilot-scale biological treatment system varied throughout this study and these data are presented as averages and minimum and maximum concentrations in Table 1. The flow rate ranged from 0.4 gpm to 2.0 gpm with an average of 1.1 gpm.

Denitrification

The purpose of the anoxic reactor (Reactor A) is to denitrify nitrites and nitrates (NO_x) and convert them to diatomic nitrogen gas (N_2). Sugar was added as a supplemental organic carbon source to enhance denitrification performance of the system. Application rates of sugar were critical to the performance of these systems, and indicate that these systems require appropriate and consistent amendments of sugar to maintain the performance of these systems.

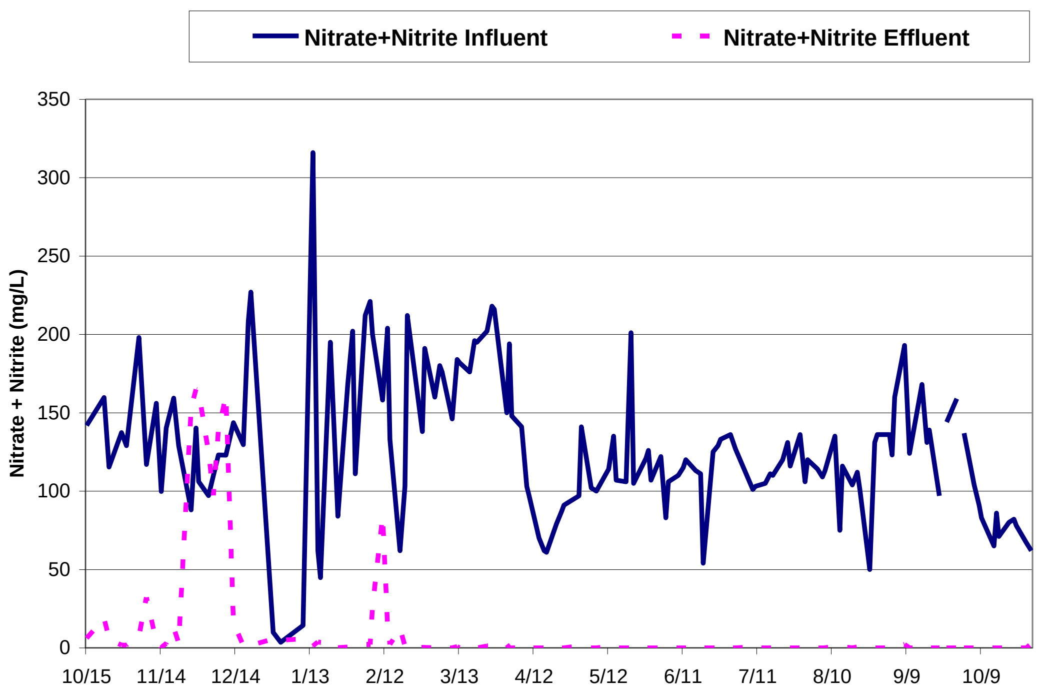
Table 1. Influent Characteristics

Parameter	Units	Avg	Max	Min
pH		6.70	7.51	5.90
Ammonia	mg/L	1.85	10.30	0.30
Nitrate	mg/L	140	316	3.60
Nitrite	mg/L	0.9	3.4	0.06
TSS	mg/L	42	77	18
COD (Total)	mg/L	149	395	35
TOC	mg/L	17	116	1.16
Selenium (Total)	mg/L	1.01	3.49	0.12
Selenium (Dissolved)	mg/L	0.72	1.43	0.09
Chromium (Total)	mg/L	0.07	0.41	0.01
Chromium (Dissolved)	mg/L	0.02	0.17	0.01

The evaluation of the anoxic reactor is based on the removal of nitrite and nitrate concentrations from influent FGD waters. The removal of nitrite and nitrate concentrations was compared to system parameters including: Food to Microorganism ratio (F/M), temperature, pH and Carbon to Nitrogen (C/N) ratio.

The sum of nitrite and nitrate concentrations from effluent samples of the anoxic reactor ranged from 0.3 mg/L during periods of normal operation to 242 mg/L during periods of non-normal operation or upset conditions as shown in **Figure 1.**

Figure 1 Nitrite and Nitrate Removal



Lower removals of nitrite and nitrate were due to process upsets. Process upsets consisted of inadequate loading of sugar due to freezing problems associated with the delivery system. Process upsets in a biological system are highly detrimental due to the recovery time of the affected bacteria and may require 3-4 weeks before performance is consistently achieved after re-establishing normal operating conditions. During periods of normal operation, the anoxic reactor was successful in decreasing nitrate concentration from ~200 mg/L down to < 1 mg/L (>99.5% removal). A description of the various process upsets is provided below.

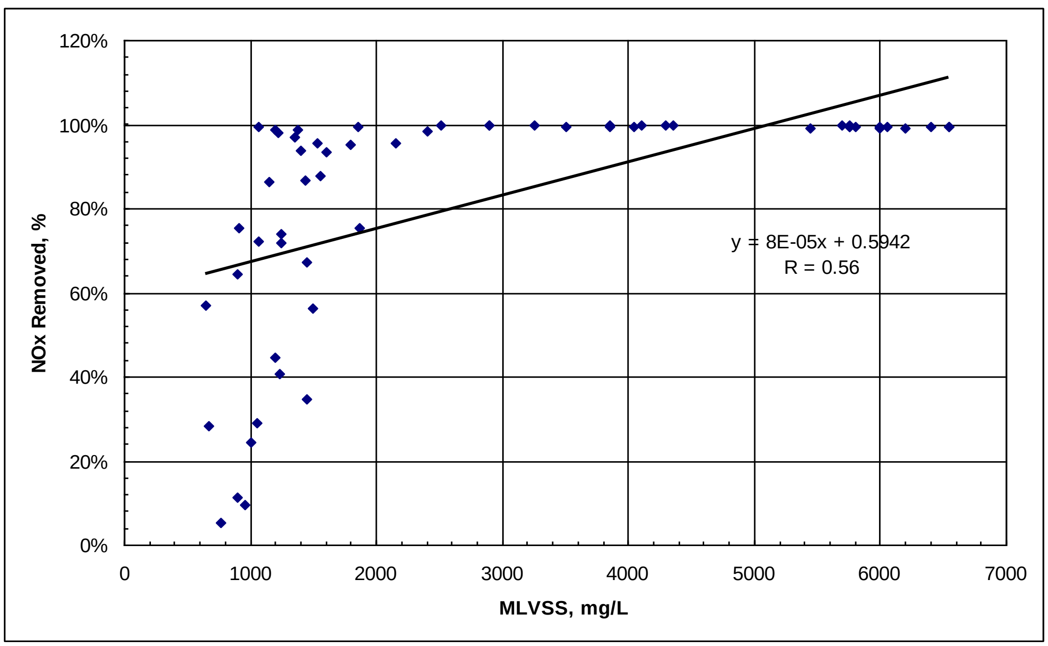
Impact of the Active Population of Denitrifying Bacteria on Denitrification

The impact of the active population of denitrifying bacteria, MLVSS, on nitrate removal was reviewed. As the MLVSS concentration in the reactor increased, the percentage of nitrate removal in the reactor also increased. **Table 2** and **Figure 2** illustrate that at MLVSS concentrations above 3000 mg/L, nitrate and nitrate removals exceed 99.5%.

Table 2 Impact of Biomass (MLVSS) on Denitrification Performance

MLVSS	Influent NO_x	Effluent NO_x	NO_x Removed
mg/L	mg/L	mg/L	%
< 1500	147	92	41.9%
1500 - 3000	162	14	91.4%
3000-4500	183	0.7	99.6%
> 4500	128	0.6	99.4%

Figure 2 Impact of Biomass (MLVSS) on Denitrification Performance



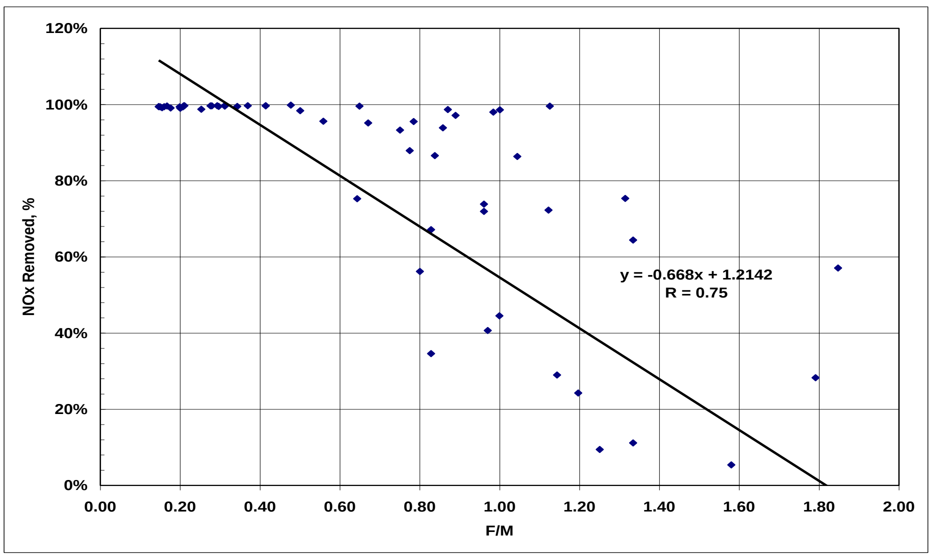
Impact of the Food to Microorganisms (F/M) Ratio on Denitrification

An evaluation of Food-to-Microorganisms (F/M) ratio shows that as the F/M ratio decreases, the percentage of nitrate/nitrite removal increases. Nitrite and nitrate removal percentages of >99.5% removal were observed when F/M ratios were below 0.5 and removal efficiencies started to decrease above the F/M ratio of 0.5. This is shown in **Table 3** and **Figure 3.**

Table 3 Impact of Food to Microorganism Ratio on Denitrification Performance

F/M (g COD/g VSS/d)	Influent NOx (mg/L)	Effluent NOx (mg/L)	NOx Removed (%)
< 0.25	128	0.6	99.4%
0.25 to 0.5	180	0.8	99.6%
0.5 to 0.75	155	8.4	92.9%
0.75 to 1.0	158	65	77.1%
> 1.0	143	103	24.7%

Figure 3 Impact of Food to Microorganisms (F/M) Ratio on Denitrification Performance

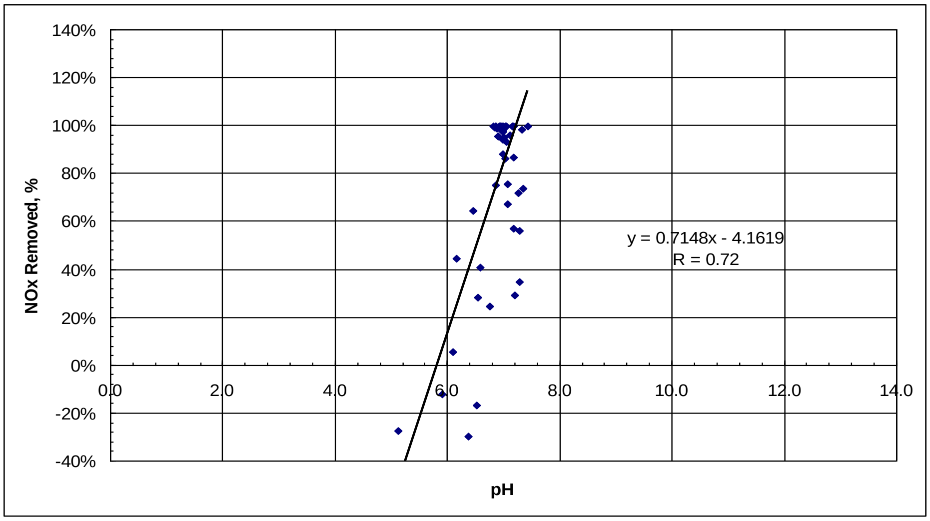


Impact of pH on Denitrification Performance

Denitrification can occur over a wide range of pH values. Denitrification is relatively insensitive to acidity; however it does decrease under low pH values. The preferred pH range for proper floc formation by facultative anaerobes is 6.5- 8.5, which is also ideal for the denitrification process. To ensure adequate enzymatic activity of facultative anaerobes, the pH in the Anoxic Reactor was maintained at ~7.0 throughout this pilot study.

Since the denitrification process can produce an alkalinity source, (3.57 mg alkalinity as $CaCO_3$ is produced per mg of nitrate-nitrogen reduced to nitrogen gas) pH of the FGD wastewater can increase when nitrate concentrations are removed within the reactor. However, during the period of process upsets and/or low-influent-nitrate concentrations, a supplemental alkalinity feed system (sodium hydroxide) was initiated to maintain the anoxic reactor pH at ~7.

Figure 4 Impact of pH on Denitrification Performance



Impact of Temperature on Denitrification Performance

Nitrate removal rates were affected significantly by water temperature within the reactor. It indicates that a 10° C drop in water temperatures will decrease the kinetic rate by one-half and may also apply to microbial reaction kinetics. The impact of temperature on nitrate/nitrite removal is shown in **Table 4.4.** A significant decrease in performance was observed at lower temperatures especially when lower biomass (MLVSS) concentrations were measured in this reactor.

Table 4 Impact of Temperature on Denitrification Performance

Temperature	**Influent NOx**	**Effluent NOx**	**NOx Removed**	***SNDR $_T$**
(F)	**(mg/L)**	**(mg/L)**	**(%)**	**(g NOx /g VSS/d)**
< 65	158	94.8	45%	0.04
65 to 70	178	21.8	84%	0.05
70 to 75	141	9	90%	0.06
75 to 80	123	1	99%	0.07

*** Specific Nitrate Denitrification Rate**

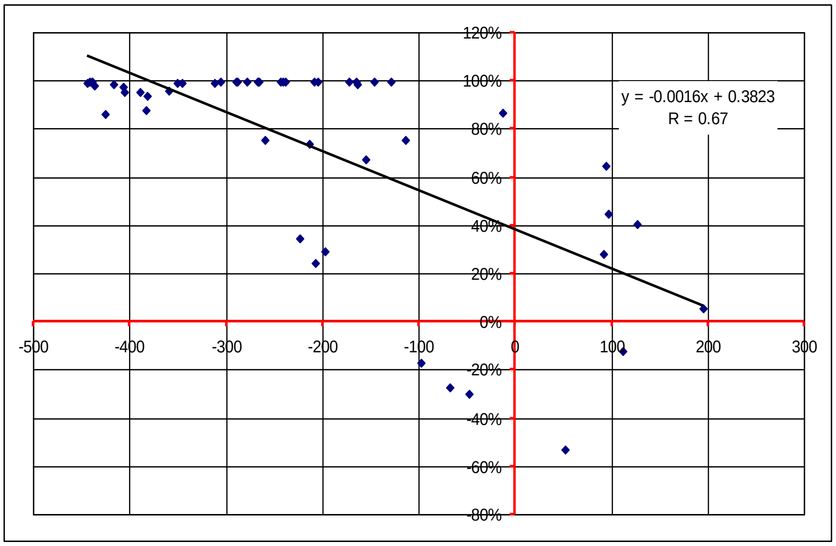
Impact of Oxidation Reduction Potential (ORP) on Denitrification

Generally, in the absence of oxygen and in the presence of nitrate/nitrite ions, bacterial degradation of carbon (e.g., sucrose) occurs when operating conditions have a redox potential <-100 millivolts (mV). Nitrate removal rates were the greatest (>96% nitrate removal) when ORP values were <-300 mV. A significant decrease in performance was observed when ORP values were measured > -150 mV as shown in **Figure 5** and **Table 5.**

Table 5 Impact of ORP on Denitrification Performance

ORP (mV)	**NOx Removed (%)**
> -100	11.84%
-100 to -200	83.55%
-200 to -300	91.43%
< -300	96.63%

Figure 5 Impact of ORP on Denitrification Performance



***Impact of Carbon Source and C/N Ratio on Denitrification* Performance**

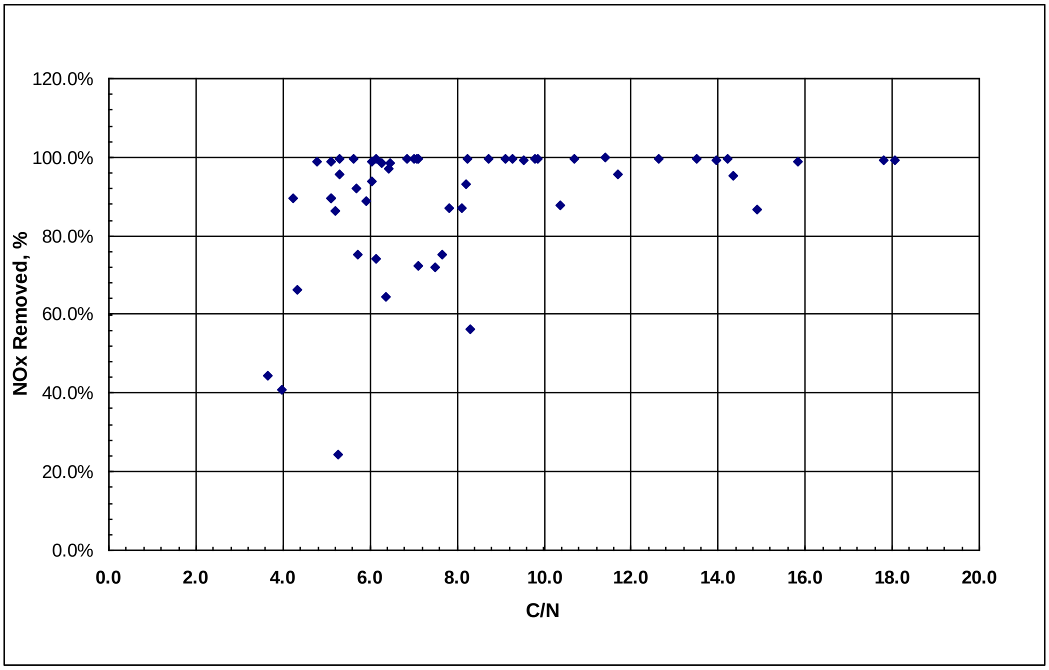
Addition of an organic carbon source (e.g., sucrose) is required for denitrification because there is insufficient biodegradable-carbon available in the FGD wastewater to support denitrification processes. The quantity of the organic carbon source, rather than the quantity of nitrite or nitrate ions, is considered to be an important factor in denitrification kinetics. The larger the quantity of degradable organic carbon sources, the higher quantity of electron acceptors such as nitrite and nitrate ions is needed to maintain microbial respiration. Theoretically, complete denitrification usually occurs when the carbonaceous biochemical oxygen demand (cBOD) to nitrite-ions-and-nitrate-ions ratio is ~ 3:1.

Sugar was chosen as the supplemental carbon source due to its low cost, and ease of application in a full-scale system. The impact of supplemental carbon on the denitrification rate was evaluated based on the chemical oxygen demand (COD) to NO_x ratio (C/N). An evaluation of the C/N ratio shows that as the C/N ratio decreases from 6:1, the percentage of nitrate/nitrite removal decreases. Results are shown in **Figure 6** and **Table 6.**

Table 6 Impact of Carbon to Nitrogen ratio on Denitrification Performance

C/N Ratio	NOx Removed (%)
< 5.0	68%
5.0 to 6.0	86%
6.0 to 7.0	92%
>7.0	94%

Figure 6 Impact of Carbon to Nitrogen Ratio on Denitrification Performance



Selenium Removal Performance

The dissolved selenium leaving the Anaerobic Reactor ranged from 0.081 mg/L to 1.25 mg/L with an average value of 0.32 mg/L, as shown in **Figure 7**. The average influent dissolved selenium concentration was 1.16 mg/L during the pilot study. These average values apply to the complete study period, including data that was taken when the pilot unit was experiencing upsets.

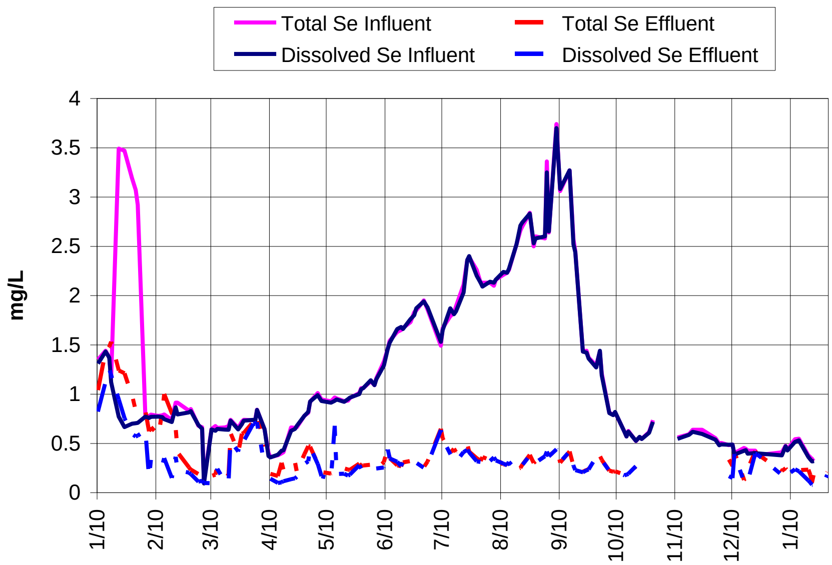
The results also show that the biological system is capable of producing an effluent dissolved selenium concentration < 0.1 mg/L when operating conditions are optimized (i.e. ORP and pH at the targeted values) and influent selenium concentration is lower than 1mg/L. When the pilot is operated under normal conditions, the effluent selenium was kept lower than 0.4mg/L consistently even when the influent selenium was as high as 3.7mg/L. The selenium speciation analysis further showed that the biological system completely removed the selenates (below detection limit) from the wastewater (**table 7**).

The variation in effluent dissolved selenium concentrations is correlated to the denitrification performance in the Anoxic Reactor. It was noted throughout the study that the presence of nitrite or nitrate ions in the Anaerobic Reactor inhibits the respiration of sulfur and selenium reducing bacteria, and hence it reduces the performance of selenium removal.

Table 7. Influent and Effluent selenium speciation

	IBIO Influent	IBIO Effluent
Total Se	390.7	227
Diss Se	375.7	61.4
Se(IV)	45.4	40.6
Se(VI)	231.7	ND
other Se	98.6	20.8

Figure 7 Total and dissolved selenium removed by the IBIO™ system

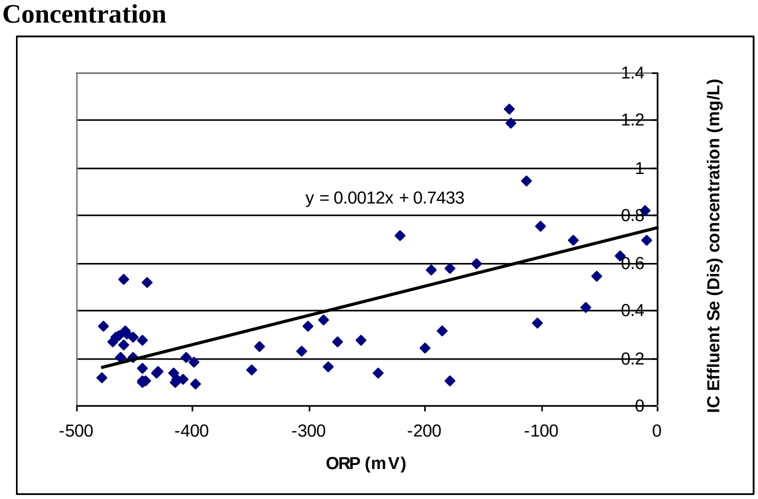


An evaluation of ORP shows that the lower ORP the reactor achieved, the lower selenium concentration in the effluent. The lowest selenium concentrations (0.097 to 0.12 mg/L) in effluent occurred when ORP is <-400mV. The correlation between ORP and intermediate clarifier effluent soluble selenium are shown in **Table 8** and **Figure 8**.

Table 8 Correlation between ORP and Intermediate Clarifier Effluent Soluble Selenium Concentration

ORP (mV)	Soluble Selenium (mg/L)
> -150	0.76
-150 to -250	0.38
-250 to -350	0.25
< - 350	0.22

Figure 8 Correlation between ORP and Intermediate Clarifier Effluent Soluble Selenium Concentration



CONCLUSIONS

The pilot plant study performed at the Yates Station demonstrated that IDI's FGD wastewater treatment provides complete and comprehensive solution to achieve NPDES discharge criteria. The iBIO™, biological treatment, can effectively remove dissolved selenium to <0.2 mg/L. Anaerobic treatment provides selenium removal at ORP values <-350 mV. Furthermore, the reduced environmentalconditions required for selenium reduction, were also found to provide the reducing conditions that precipitated other heavy metal species such as hexavalent chromium and vanadium. Aerobic biological treatment was demonstrated as a polishing process to effectively remove residual organics and ammonia-nitrogen.