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Design and Start-up of a Full-scale Biological Selenium Removal System for Flue Gas Desulfurization (FGD) Wastewater from a Power Generating Station

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Abstract

This paper describes the design, start-up and commissioning of a full-scale biological treatment system that was installed at a coal-fired power generating station to remove selenium and nitrates from a Flue Gas Desulfurization (FGD) blowdown stream. The new patented iBIO® wastewater treatment (WWT) system, which was first pilot-tested at power generating stations, is based on a suspended-growth continuously stirred-tank anaerobic reactor that has been seeded with a source of commonly available anaerobic microorganisms which were subsequently acclimated to remove selenium from the FGD wastewater. This new innovative WWT system was integrated into the existing FGD wastewater treatment units at the power generating station to provide the additional selenium removal capability from the wastewater.

This demonstrated biological selenium removal treatment system provides a robust and cost-effective alternate technology to coal-fired utilities that use FGD wet scrubbers to control their sulfur oxide (SOx) emissions with the additional need to consistently meet the more stringent lower-level selenium effluent limits.

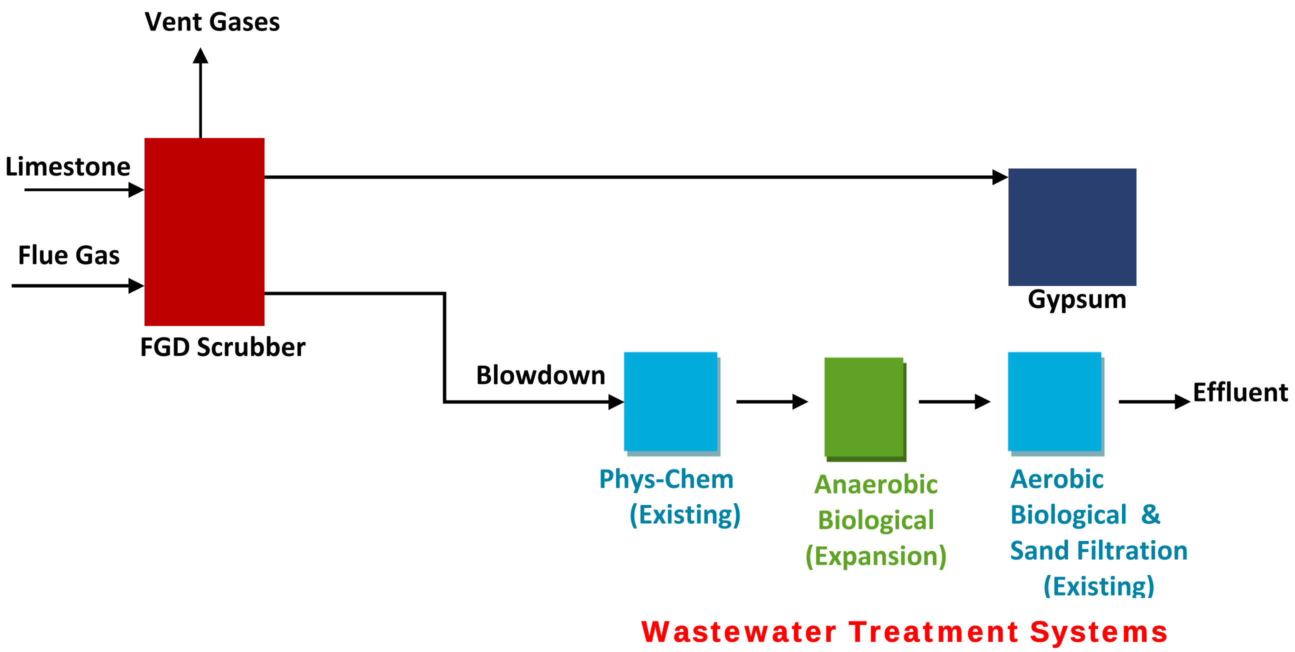
1. Introduction

Air emissions from coal-fired power plants require the installation of various types of air pollution control system technologies. One such technology is the use of wet scrubbers for the 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 to decrease SO_2 emissions. However, inherent with this treatment system is the blowdown of a slurry stream that contains elevated concentrations of suspended and dissolved solids, chlorides, sulfates, heavy metals (chromium, mercury, selenium, etc.), and nitrates. FGD systems available in the marketplace have different combinations of characteristics (such as coal type, scrubber type, additive use, operational strategies, etc.) that result in extremely varied wastewater characteristics.

This paper discusses the design and start-up of a full-scale biological wastewater treatment plant expansion implemented at a power generating station to remove nitrates and residual oxyanions (specifically, selenites and selenates) present in the wastewater after undergoing an initial physical-chemical treatment process for the removal of total suspended solids (TSS) and heavy metals from the FGD blowdown stream.

Figure 1.1 shows a schematic diagram of the FGD scrubber system and the new biological wastewater treatment plant expansion for the blowdown stream. The new biological treatment system was retrofitted into the existing wastewater treatment processes.

Figure 1.1 Schematic Diagram of a FGD Scrubber System



The new biological wastewater treatment system is a patented anaerobic activated sludge suspended-growth system developed to remove nitrates and heavy metals (specifically, oxidized ions such as selenates, selenites, chromates, vanadates, etc.).

The biological treatment system uses anaerobic microorganisms commonly available from industrial and municipal wastewater treatment plants and requires a carbon source to conduct their microbial activities.

This treatment system was designed to handle contaminant fluctuations from the FGD physical-chemical wastewater treatment system. Pilot-scale demonstrations of this process were previously described by Stover et. al. (Reference 1, IWC 07-49) and Teng et. al. (Reference 2). Figure 1.2 and Table 1.1 show a schematic diagram and equipment list, respectively, of the complete biological treatment process which includes the "anoxic/anaerobic" section as well as the "aerobic" polishing treatment system.

Figure 1.2 Schematic Diagram of the Complete Biological Treatment System for Selenium Removal

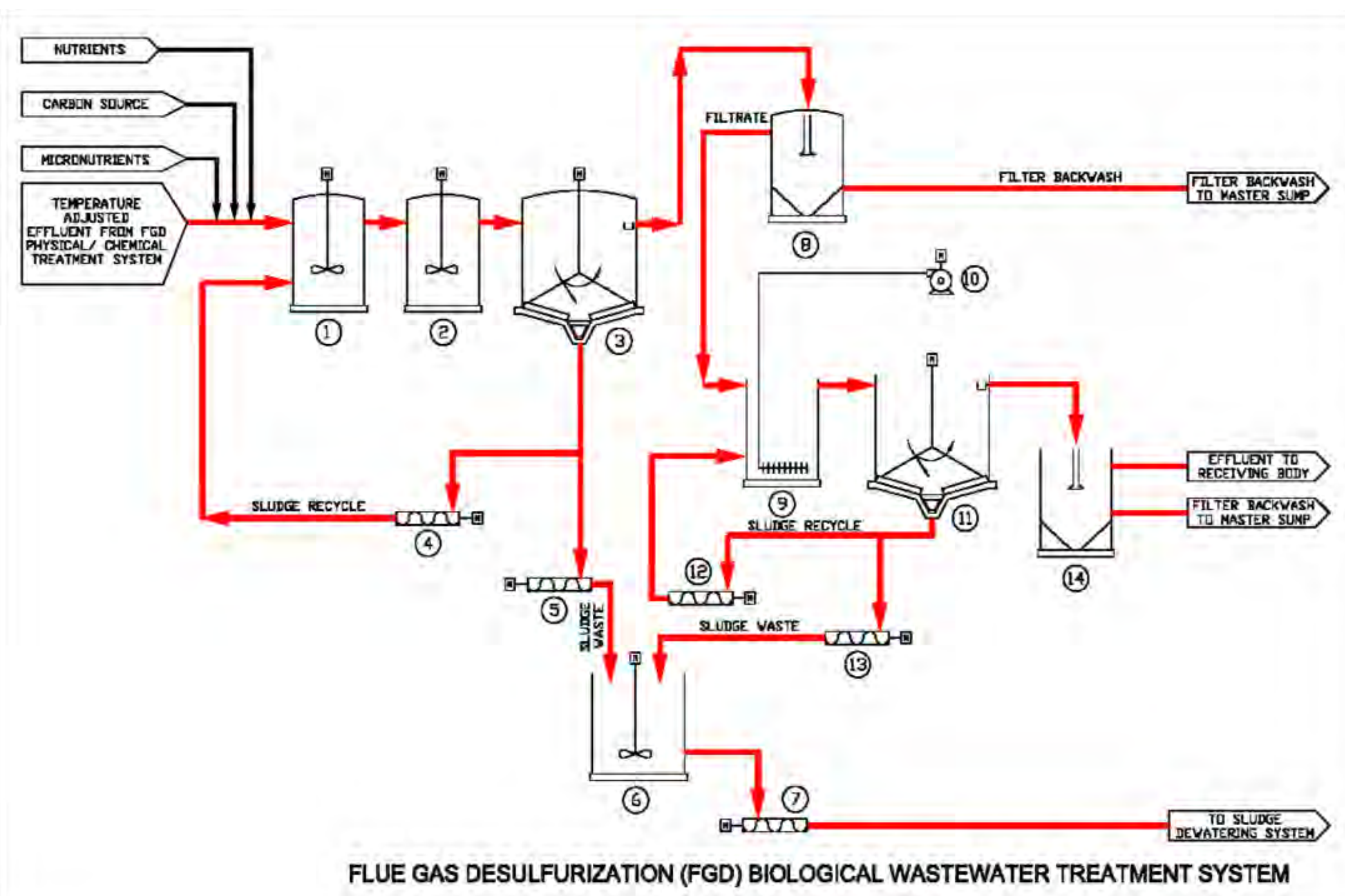
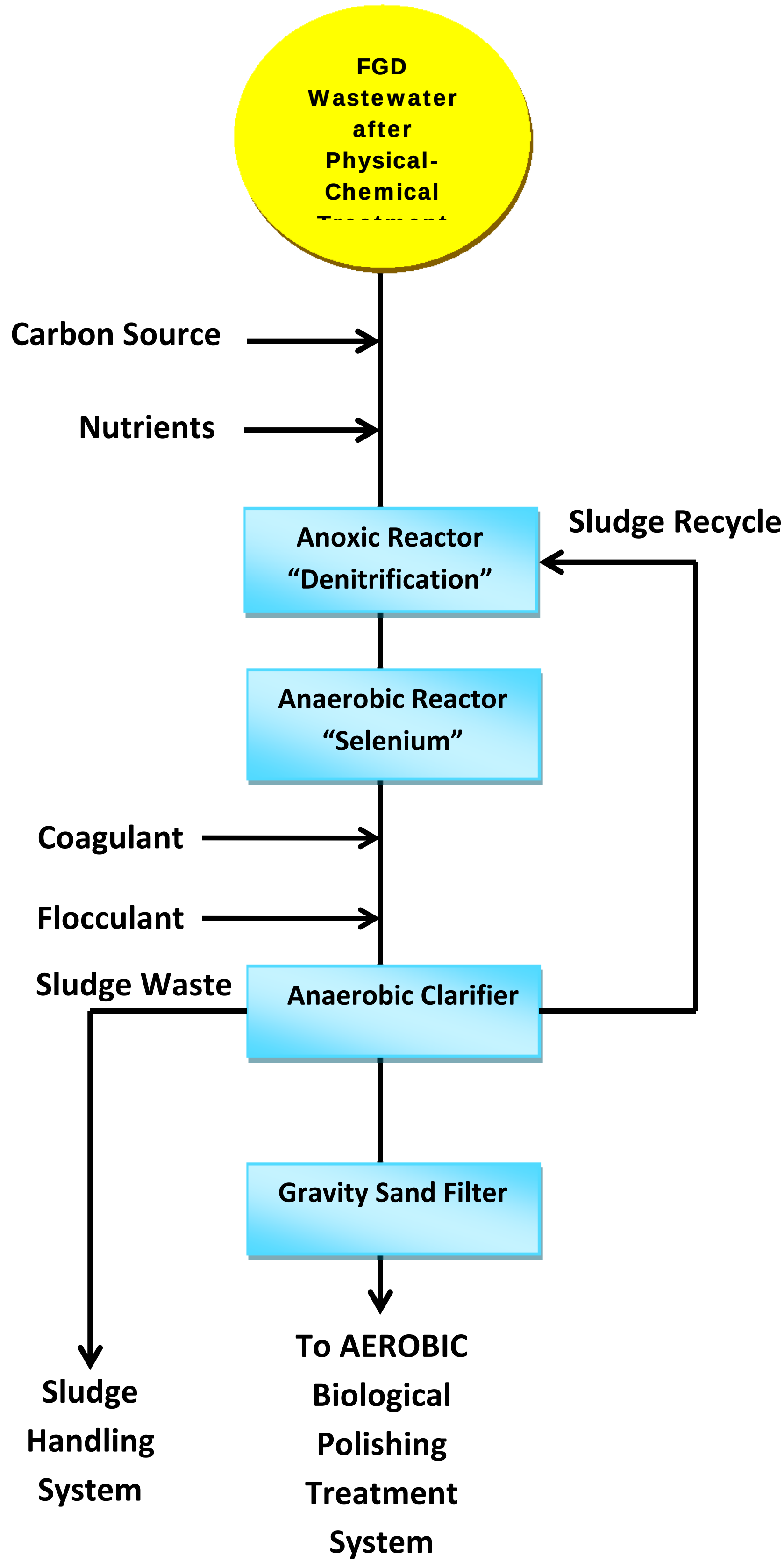


Table 1.1 Major Process Equipment List for the Complete Biological Treatment System

1	Anoxic Reactor for Denitrification
2	Anaerobic Reactor for Heavy Metals Reduction
3	Anaerobic Clarifier
4	Anaerobic Sludge Recycle Pump
5	Anaerobic Sludge Waste Pump
6	Sludge Holding Tank
7	Sludge Dewatering Pump
8	Continuous Backwash Sand Filter
9	Aerobic Reactor
10	Aerobic Reactor Aeration Blower
11	Aerobic Clarifier
12	Aerobic Clarifier Sludge Recycle Pump
13	Aerobic Clarifier Sludge Waste Pump
14	Continuous Backwash Sand Filter

Figure 1.3 shows the major components for the denitrification and selenium removal steps which consist of an Anoxic Reactor, Anaerobic Reactor, Anaerobic Clarifier and a Gravity Sand Filter.

Figure 1.3 Denitrification and Selenium Removal Major Components



2. Microbial Reactions for Nitrate and Selenium Removal by the Biological Treatment Process

Soluble selenium in FGD wastewaters is primarily present in the form of selenates (SeO_4^{2-}) and selenites (SeO_3^{2-}). Selenites, to some extent, can be removed through chemical precipitation, leaving selenates as the primary selenium species remaining in the wastewater. Biological processes have proven to be a viable and robust option for removal of selenates from wastewaters (References 1,2,4). A number of microorganisms are able to utilize the oxygen in selenate for energy and growth in a manner similar to the way denitrifying microorganisms utilize the oxygen from nitrates (NO_3^-). The selenium removal bacteria are commonly known as the “sulfur reducing bacteria” (SBR) and they only operate in a reducing environment. The selenium removal process can be represented as follows:

SeO_4^{2-} (selenates) + Carbon Source + Microorganisms ------> Se^0 (solid) + CO_2 + H_2O + Biomass

Similarly, the denitrification reaction carried out by heterotrophic bacteria known as “denitrifiers” operate in an anoxic environment and can be represented as follows:

NO_3^{1-} (nitrates) + Carbon Source + Microorganisms ----→ N_2 (gas) + H_2O + Alkalinity + Biomass

While the biological reduction of nitrates results in gaseous nitrogen formation, the biological reduction of selenates and selenites results in the formation of elemental selenium (Se^0), which is insoluble and can be removed along with the biological solids. Microorganisms gain more energy from using the oxygen in nitrate than they do from using the oxygen in selenate, and as such, nitrates must first be reduced to near zero levels before selenate reduction will take place. Both types of microorganisms (SRB and denitrifiers) were found to be capable of reducing the oxidized selenium compounds to elemental selenium. The process configuration used in this new biological system optimizes these microbiological reactions by providing two separate reactors to allow the environmental conditions to be better established in each stage. First, the biological reduction of nitrates is conducted in the Anoxic Reactor, which is followed by a second Anaerobic Reactor for the biological reduction of selenates and selenites where more reducing (i.e., more negative Oxidation Reduction Potential (ORP)) conditions are created for the SRB microorganisms.

3. Process Design Considerations

3.1 Selenium Removal Target Concentration

The power generating station had a target to reduce the concentration of Total Selenium from 1.3 mg/L in the untreated FGD blowdown stream down to <0.21 mg/L in the effluent of the wastewater treatment system.

3.2 Integration into Existing Wastewater Treatment Facilities

The power generating station had an existing physical-chemical treatment system which included the typical precipitation of metals at an elevated pH followed by an aerobic biological treatment system which consisted of sequencing batch reactors, mainly for organics reduction. As a final polishing step, the Total Suspended Solids (TSS) of the wastewater is reduced by flowing through multimedia pressure filters.

In this project, it was possible to insert the new anaerobic biological treatment process after the existing physical-chemical treatment system to be followed by the existing aerobic treatment process to remove the residual organic carbon and ammonia nitrogen to the required permit limits. As part of the process design for the new biological treatment system, a six-month laboratory study was conducted to simulate and validate the selenium removal performance using actual FGD wastewater from the power generating station.

3.3 Carbon Source Selection

FGD wastewaters do not have sufficient amount of organic carbon to support the microbiological reactions to denitrify and reduce selenium. Therefore, an external source of organic carbon is required to be added to the anaerobic treatment system.

Molasses is known to support biological selenium reduction, but it can be difficult to handle due to its high viscosity, and can vary in composition, even from a single provider. It is suspected that the sugar fraction of molasses is primarily responsible for supporting selenium reduction, and as such, sugar (sucrose) was used in our initial pilot studies.

A commercially-available liquid carbon source (carbohydrate-based product) was also evaluated in the laboratory and was selected for this project. This liquid carbon product is non-flammable, and according to the manufacturer, has both a consistent compositional make-up and a long shelf-life. The material flows readily at temperatures as low as 16°F, with a viscosity of about 100 cp at this temperature, and therefore is easier to handle than molasses. The material is approximately 50% by weight carbohydrate, with a COD concentration of 670,000 mg/L, which is higher in concentration than sugar solutions, which have a typical maximum concentration of 25 to 35 percent by weight.

Discussion on the selection of the appropriate carbon source for this process was provided by Lau, et. al. (Reference 3, IWC 11-33, and Reference 5) which describes a pilot study conducted to confirm the applicability of the liquid carbon source.

3.4 Treatment System Robustness Considerations

Consideration was taken in the design of the biological treatment system to provide a design that was both robust and operationally flexible, while still being able to meet the stated effluent requirements. Some critical items that were incorporated are the following: (1) Equalization Tank to provide sufficient wastewater holding time to allow for minor mechanical repairs/changes, (2) instrumentation redundancies for critical parameters, such as the ORP and pH sensors, (3) bypassing loops for the anaerobic reactors and anaerobic clarifier.

3.5 Final Process Flow Diagram

The final Process Flow Diagram shown in Figure 3.1 provides the major components of the new biological treatment system installed at the power generating station for selenium removal. The design flow rate of this treatment system is 410 gpm (0.6 MGD). The major process components include:

- Chemical addition systems for the carbon source, macronutrients (urea, phosphoric acid), micronutrients, coagulant (ferric chloride) and flocculant (polymer).

- Anoxic and Anaerobic Reactors for denitrification and selenium reduction.

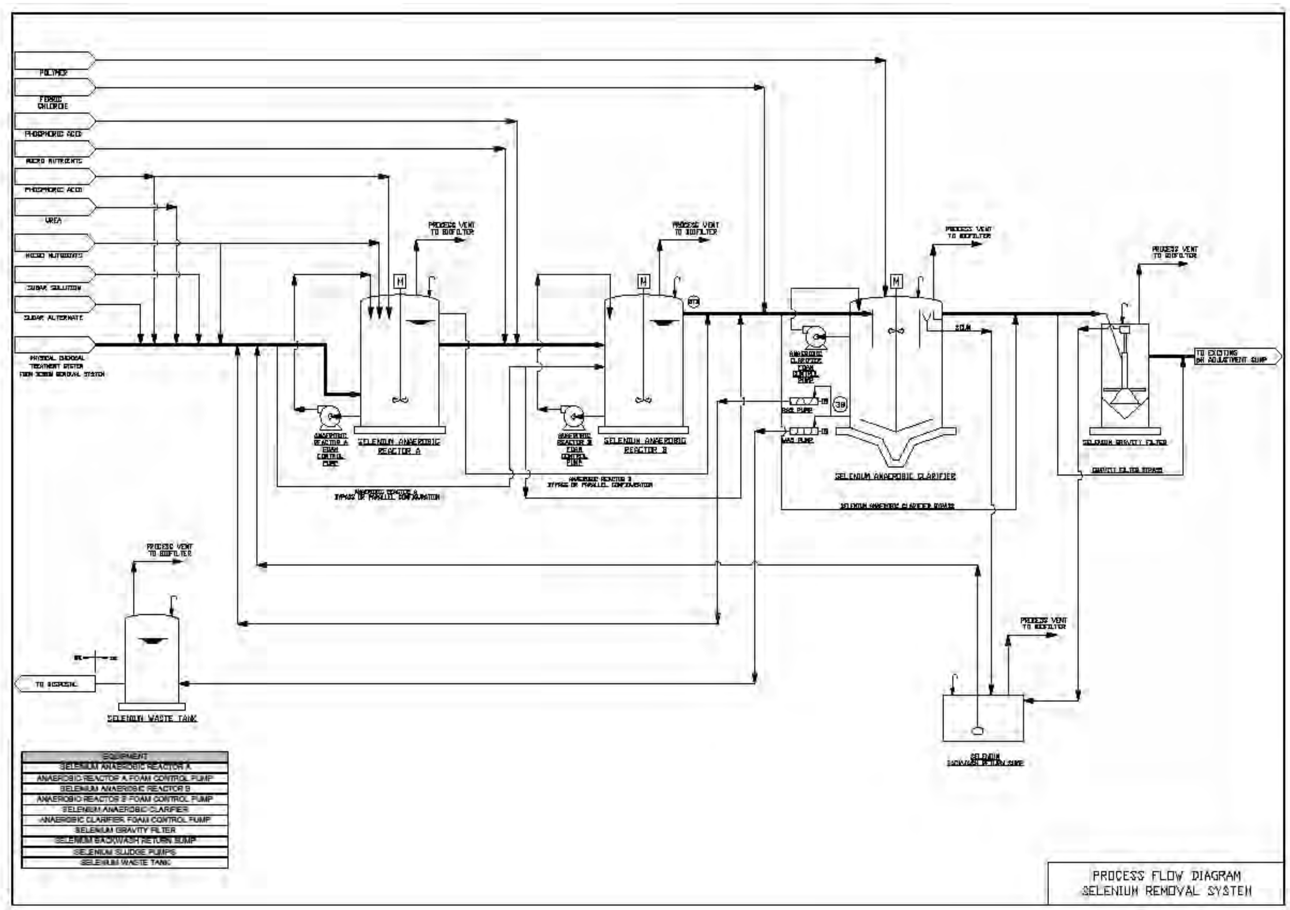
- Anaerobic Clarifier for the separation of the anaerobic biomass from the treated wastewater followed by a gravity sand filter for additional polishing of the suspended solids.

- The reactors and the clarifier vessels are equipped with a foam control system which recirculates the contents of the vessel and sprays it on top of the tank.

- The vent gases are collected and sent to a biofilter for biological conversion of sulfides into sulfates.

- A “Sludge Storage Tank” was included to maintain an on-site inventory of acclimated bacteria.

Figure 3.1 Process Flow Diagram of the Installed Selenium Treatment System



4. Full-Scale Start-Up Considerations

4.1 FGD Wastewater Characteristics

The FGD wastewater characteristics used for process design is shown in Table 4.1

Table 4.1 FGD Wastewater Characteristics Design Basis

Parameter	Concentration (mg/L)
Ammonia (NH_3-N)	8
Nitrate (NO_3-N)	10
Total Kjeldahl Nitrogen (TKN)	62
Sulfate (SO_4)	3,789
Chemical Oxygen Demand (COD)	897
C-BOD_5	53
Total Suspended Solids (TSS)	91
Total Selenium	1.3
Chloride (Cl^-)	20,000
Total Dissolved Solids (TDS)	28,907
pH	6.6

4.2 Biological Seed Acclimation

The biological treatment system utilizes anaerobic microorganisms that have been acclimated to the existing FGD wastewater. This treatment process does not require the purchase of expensive proprietary microorganisms supplied by some vendors for the specific removal of selenium compounds. This treatment process, in contrast, uses typical anaerobic microorganisms easily available and found in industrial or municipal wastewater treatment sludges, usually obtained for a minor cost to the client.

For this project, the source of the anaerobic bacteria was from anaerobic sludges of a WWT facility treating food manufacturing wastewaters. The bacteria were acclimated to the actual FGD wastewater in a separate "Biological Seed Acclimation Unit" which consisted of a 6,000 gallons anaerobic reactor followed by an anaerobic clarifier (see Figure 4.1).

The major factor in the acclimation process was the controlled increase of the chloride concentration in the mixed liquor from ~500 mg/L up to ~20,000 mg/L while maintaining the proper Oxidation Reduction Potential (ORP) in the reactor. The bacterial acclimation process was initiated ~3 months prior to the full-scale start-up date.

Figure 4.1 Biological Seed Acclimation Unit

5. Full-Scale Results

5.1 Control of the Oxidation Reduction Potential (ORP) in the Reactors

One of the critical parameters in the operation of the selenium removal reactors is the Oxidation Reduction Potential (ORP) of the mixed liquor.

The ORP is an analytical parameter reported in milliVolts (mV) which is obtained when the ORP sensor is placed in contact with the liquid being measured. The ORP value defines whether the reactor is in an *oxidizing* environment or a *reducing* environment. An oxidizing reactor environment (or an oxygenated environment) is indicated by a positive ORP value (ORP>0 mV); the higher the positive ORP value, the stronger is the oxidizing environment. In contrast, a reducing reactor environment (or an oxygen depleted environment), is indicated by a negative ORP value (ORP<0 mV); the more negative the ORP value, the stronger is its reducing environment. The Selenium Removal Anaerobic Reactors require a "**reducing**

environment" for the bacteria to accomplish their tasks. This ORP scale is graphically shown below in Figure 5.1.

Figure 5.1 Oxidation Reduction Potential (ORP) Chart

Positive ORP Values => Oxidizing Environment

(ORP > 0 milliVolts)

Negative ORP Values => Reducing Environment

(ORP < 0 milliVolts)

-150 mV (minimum level for selenium removal)

-200 to -300 mV (Target Operation)

-300 to -350 mV (Conservative Operation)

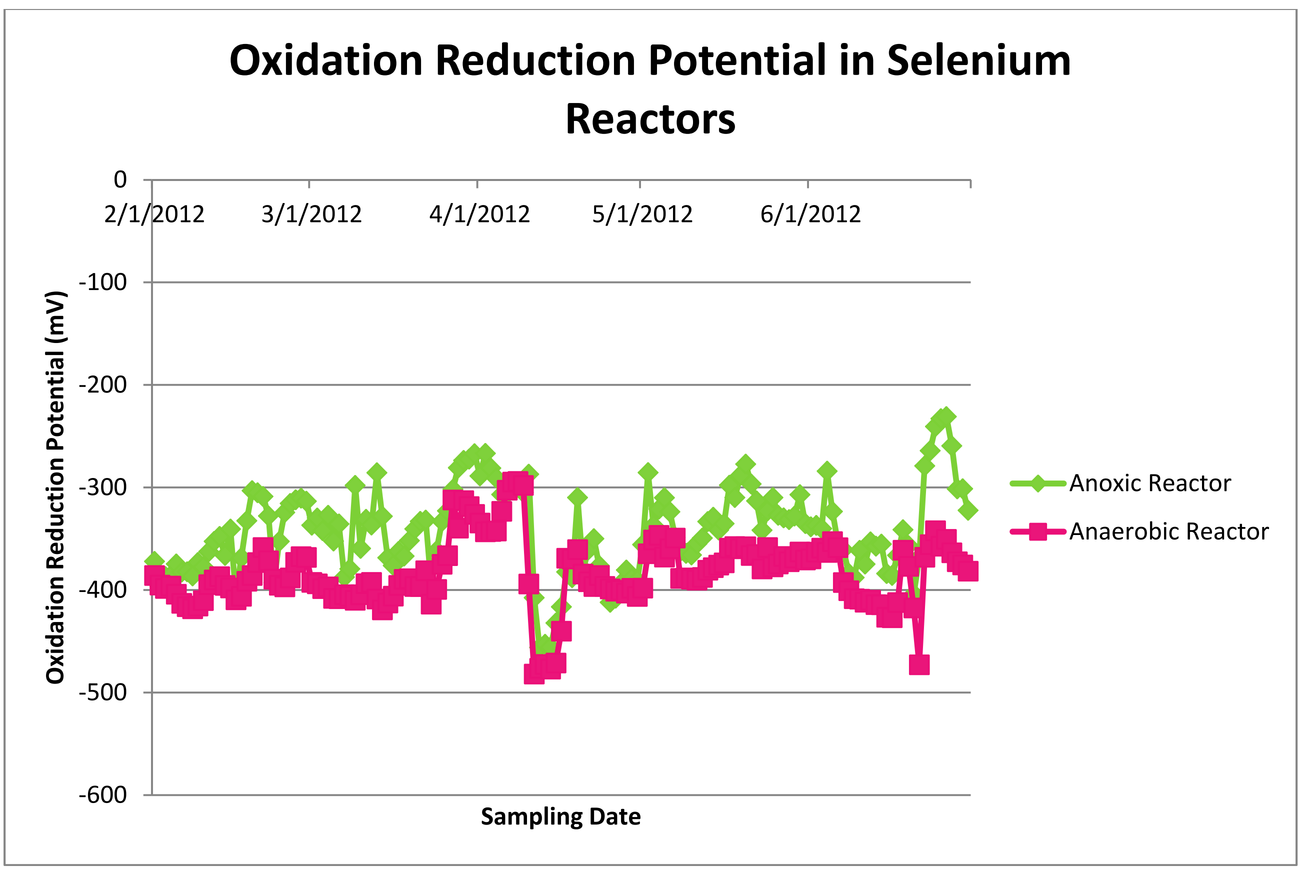
The purpose of monitoring ORP in the Selenium Anaerobic Reactors is to ensure that the oxidized species of selenium (i.e., selenates and selenites), are reduced to elemental selenium. Selenates and selenites are soluble compounds and they are not sufficiently removed in the existing physical-chemical treatment system to meet the required lower selenium effluent limit. Therefore, the wastewater is treated in the new Selenium Removal Anaerobic Reactors under a *reducing environment* where the selenate and selenite compounds are converted by the bacteria into their **insoluble elemental selenium** form. The elemental selenium precipitates out of solution and stays with the biomass as a particulate material and it leaves the treatment system via the Anaerobic Clarifier waste biomass. As a requirement prior to precipitation of the oxidized selenium compounds, the nitrates present in the wastewater must be reduced to nitrogen gas.

During the start-up period, the strategy was to operate the Anaerobic Reactors at a controlled ORP value of at least -300 mV. This was a conservative ORP value with sufficient flexibility to allow the removal of selenium to meet the target effluent selenium concentration if the maximum system design value of 1.3 mg/L Total Selenium is reached in the untreated FGD wastewater. Once the WWT Operator develops sufficient expertise with this biological treatment system, an optimization process will be implemented to adjust the ORP value that will result in a more cost-effective operation.

To achieve a negative ORP value, the addition of the correct proportions of a carbon source, macronutrients (urea, phosphoric acid) and micronutrients is necessary. These chemicals are added to the Anaerobic Reactor to serve a two-fold purpose: (1) they are first needed for proper biological growth, and (2) they are needed to support the biological reaction mechanisms necessary to reduce nitrates, selenites, and selenates in the Anaerobic Reactors. Sulfate reduction to hydrogen sulfide occurs simultaneously when the oxidized selenium species are converted to elemental selenium. Thus, vent gases containing sulfides are collected and sent to a biofilter for oxidation to sulfates.

Figure 4.3 below shows the ORP level achieved in both Anaerobic Reactors during the full-scale start-up period. The data shows that the ORP was maintained between -300 mV to -400 mV, as originally planned.

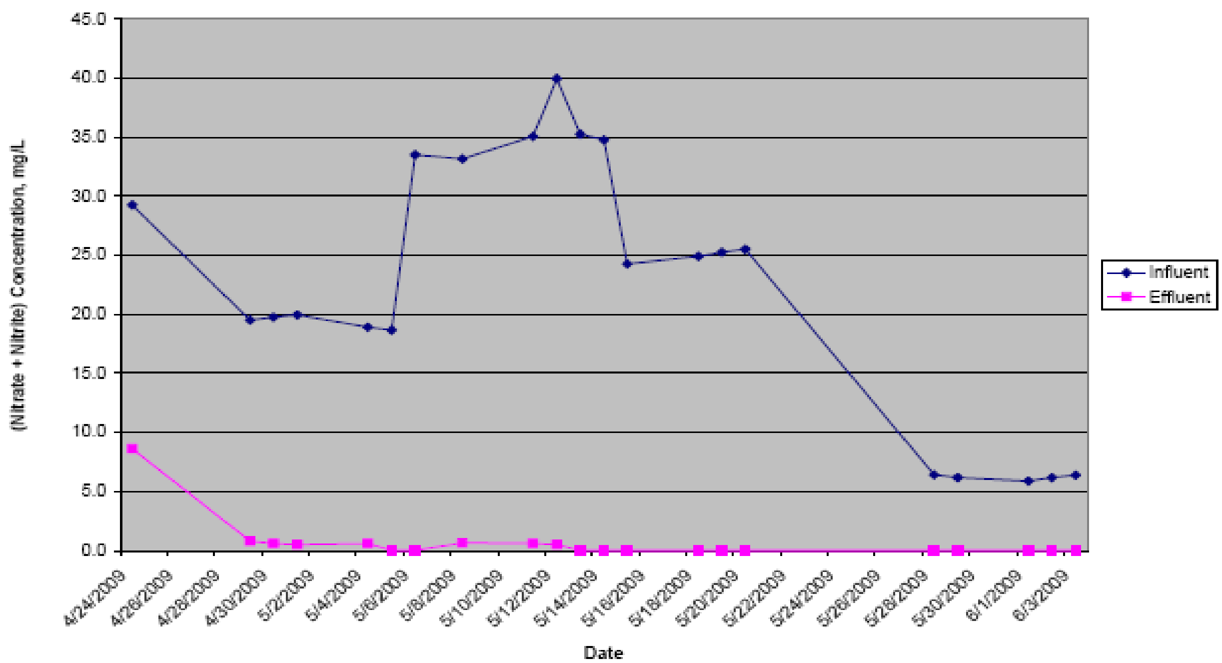
Figure 5.2 Oxidation Reduction Potential (ORP) in Selenium Anaerobic Reactors



5.2 Denitrification Performance

Currently, the FGD wastewater at this power generating station has a very low concentration of nitrates and nitrites in the wastewater (<10 mg/L). Daily analytical monitoring showed that the nitrate values were <1 mg/L in the effluent stream of the new biological treatment system indicating complete denitrification. The full-scale data confirmed the laboratory finding that was obtained when the same wastewater was tested over a six-month period. The laboratory data showed that the treatment system successfully removed the (nitrate/nitrite) concentration from ~22 mg/L (average) down to <0.2 mg/L as shown in Figure 5.3 below.

Figure 5.3 Nitrate/Nitrite Removal from FGD Wastewater (Laboratory Data)



5.3 Selenium Removal Performance

The reduction of total selenium throughout the wastewater treatment process is shown in Figure 5.4 and Tables 5.1 and 5.2 below. The influent selenium concentration from the FGD blowdown ranged from 0.1 to 0.7 mg/L and the final effluent from the complete WWT system had a total selenium concentration range of 0.02 to 0.22 mg/L. The new Selenium Treatment System, when operating at steady-state conditions, does produce an effluent wastewater that meets the targeted total selenium concentration of <0.21 mg/L.

Total selenium removal across the major wastewater treatment processes is shown in Table 5.2. The physical-chemical treatment process consisting of pH elevation and coagulant/polymer addition was able to remove 51% of the total selenium. This result is expected because historical data from this power generating station indicates that the selenium species in the influent wastewater is ~90% in the selenite form. During the start-up period, the selenium removal across the Anaerobic Treatment System was 36% and across the complete WWT system was 69%. These results were obtained during the start-up period while the system is not yet stabilized at the optimized operating and performance conditions. Higher removals of selenium are expected as the system gets optimized.

Figure 5.4 Selenium Removal from FGD Wastewater

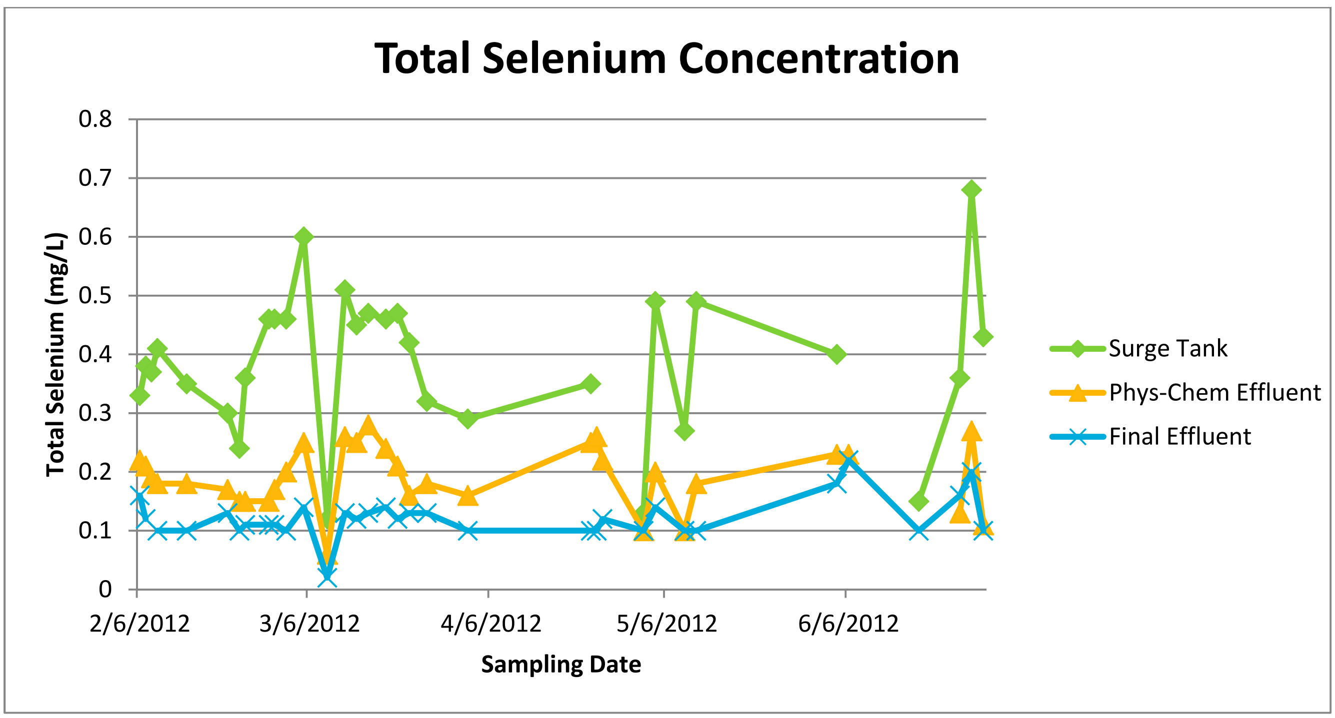


Table 5.1 Total Selenium Concentration through Wastewater Treatment

Sampling Point	Total Selenium Concentration Range (mg/L)
FGD Blowdown - Influent to WWT	0.12 - 0.68
After Physical-Chemical Treatment	0.06 - 0.28
After Anaerobic Biological Treatment	0.02 – 0.23

Table 5.2 Total Selenium Removal Across Wastewater Treatment Units

Process	Average Total Selenium Removal (%)
Physical-Chemical Treatment	51
Anaerobic Biological Treatment	36
Across All WWT Units	69

6. Conclusions

As coal-fired power generating stations face stricter effluent regulations, there is a need for advanced wastewater treatment technologies to meet the lower, stricter limits. The selenium removal anaerobic biological wastewater treatment system installed at this power generating station has demonstrated that it can meet the targeted selenium concentration of <0.21 mg/L in the effluent stream. In fact, total selenium concentrations of <0.1 mg/L were obtained on many operating days.

In summary, the application of a suspended-growth activated sludge treatment system which includes anoxic, anaerobic and aerobic reactor stages proved to be successful for the removal of selenium compounds from FGD blowdown wastewaters from a power generating station.

7. References

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8. Acknowledgements

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