

Full Scale Operation of GE ABMet® Biological Technology for the Removal of Selenium from FGD Wastewaters

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Summary: To reduce sulfur dioxide emissions from the flue gasses produced while burning coal, Wet Flue-Gas Desulfurization (WFGD) systems are being employed at coal-fired power plants across the globe. These WFGD systems transfer sulfur and other compounds released during coal combustion from a gaseous phase to a liquid phase and then collectively contains them in a wastewater stream. These same facilities may also utilize Dibasic Acid (DBA) to increase WFGD efficiency. Treatment of the resulting wastewater in order to comply with increasingly stringent discharge limits presents itself as a formidable challenge. The untreated waste stream concentrations of soluble selenate can reach over 10 ppm as well as contain elevated levels of mercury, arsenic and other solublized heavy metals, all of which require removal prior to environmental discharge. Two power plants at Duke Energy and Progress Energy in North Carolina have employed ABMet® biological technology for the removal of these contaminants from WFGD blowdown. This paper will discuss the fundamentals of the biological reduction process; its demonstrated removal efficiency of selenium, nitrate, and other trace metals; the design and commissioning of the first two facilities; as well as the data compiled during the initial months of full-scale operation with an emphasis on the Progress Energy Roxboro Station.

BACKGROUND

In 2002, the state of North Carolina adopted the Clean Smokestacks Act requiring power companies within the state to reduce their smog and haze-forming emissions by approximately 75% over the following decade. As part of this legislation, a 73 percent cut in sulfur dioxide (SO₂) emissions from 2002 levels is required by 2013¹. In order to achieve this target, Progress Energy and Duke Energy have both retro-fitted Wet Flue-Gas Desulfurization technologies into some of their coal-fired generating facilities.

Progress Energy's largest coal generating facility, the 2,443 MW, four-unit Roxboro Station² is the second of Progress' stations to be retro-fitted with WFGD scrubbers under the new act. Located just outside of Roxboro, NC and about 75 miles north of Raleigh, NC, Roxboro is the tenth largest coal-fired station in North America, and the largest in North Carolina. In order to meet the standards of the act, Progress Energy turned to Babcock & Wilcox to provide their WFGD technology to achieve over 97% SO₂ removal. At full design capacity, the WFGD scrubbers are expected to produce 1,400 gpm of blowdown flow.

Roxboro Station is located on the shore of Hyco Lake which is used to supply cooling water and WFGD make-up water to the plant. Hyco Lake also receives all of the plant's water discharges, including the new blowdown from the scrubbers. The lake is home to a large fish population and is a very popular recreational destination in the summer months for anglers and cottagers. Special care needed to be taken to ensure that harmful levels of contaminants such as selenium, nitrate and other trace metals were eliminated from an environment that

could affect the local fish and animal populations.

While all of these contaminants are potentially harmful in high enough levels, selenium and mercury in particular must be controlled to very low levels as these elements can bio-accumulate in living tissue. Long-term exposure to elevated concentrations can cause serious health issues over several years.

WET FLUE-GAS DESULFURIZATION

Wet Flue-Gas Desulfurization scrubbers, such as those from Babcock & Wilcox at Roxboro, remove SO₂ from the flue gas by passing the flue gas through a large chamber (spray or absorber tower).

WFGD systems utilize a limestone reagent mixed with water to form a slurry. As the gas travels through the tower, it is scrubbed with a spray made of the limestone mixture. Multiple levels of sprayers are utilized to obtain the most efficient contact between the limestone and the flue gas. As the flue gas contacts the spray, the limestone (calcium carbonate - CaCO₃) in the limestone reacts with the SO₂, removing the majority of the SO₂ from the flue-gas before it exits the top of the stack. The rest of the slurry collects in the bottom of the tower where it is mixed and aerated in order to oxidize the bisulfite ions and produce calcium sulfate dehydrate (CaSO₄•2H₂O), or gypsum, which then precipitates out of solution.

The slurry in the bottom of the tower is constantly recirculated back through the sprayers. A portion of the slurry mixture containing the precipitated gypsum is bled

off of the bottom of the tower (blowdown). This blowdown is sent to a pair of Hydroclones to remove the bulk of the precipitated gypsum from the stream. The removed gypsum is then sent through vacuum belt filters to produce a dry cake for sale to a wallboard manufacturer.

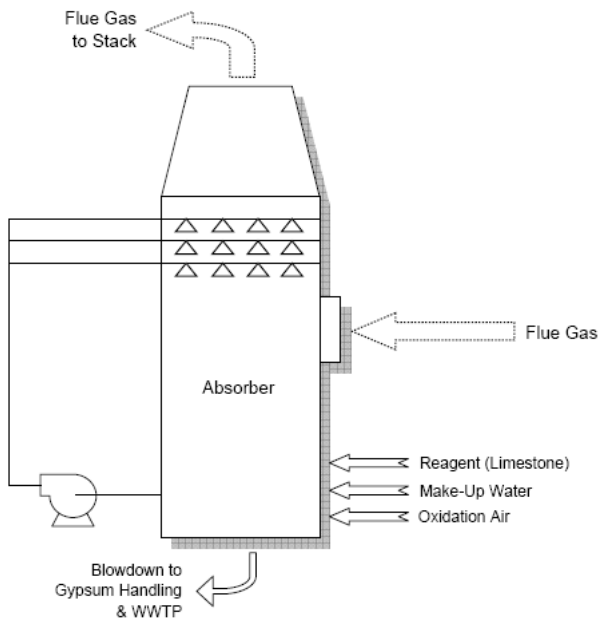


Figure 1 - Generic WFGD Schematic

After the gypsum is recovered from the blowdown, the wastewater is still laced with various contaminants which originate from the coal itself and are also captured in the WFGD process. These contaminants must undergo further treatment before they are allowed to be discharged into the environment.

TREATMENT OPTIONS

Significant concentrations of many trace elements and heavy metals pose a unique challenge to treatment, as high levels of TDS, Cl⁻, Ca⁺⁺, Mg⁺⁺ and SO₄⁼ make barrier filtration using RO or NF difficult. To add to this challenge, the majority of the

selenium present in the blowdown stream is in the form of soluble selenate (SeO₄²⁻).

Several options were considered by Progress Energy to make their blowdown suitable for discharge, such as conventional physical/chemical systems, constructed wetlands and biological treatment.

Without additional treatment processes, conventional physical/chemical systems using chemical precipitation and clarification have not been shown to consistently meet the required effluent criteria with regards to selenium in FGD applications. Progress Energy was also sensitive to consuming vast quantities of chemicals and disposing of large amounts of sludge.

Constructed wetlands were strongly considered as a potential alternative. However, this approach would have required approximately 100 acres of land for the cells, dilution of the blowdown stream in order to mitigate potential chloride toxicity, and had not demonstrated the ability to remove selenium at the high removal rates required.

Anoxic biological treatment had not yet been demonstrated in a full-scale WFGD application during the evaluation; however, it seemed to offer the best solution over the alternatives. With biological treatment, the foot-print would be <1 acre for a system of Roxboro's size, the amount of chemical required would be minimal, sludge volumes would be reduced and chloride tolerances of the microbes could handle up to 20,000 mg/l without adverse reactions.

PRETREATMENT

Even after gypsum recovery via Hydroclones, WFGD blowdown may still

contain over 4,000 mg/l of TSS, and may also still be well over maximum operating specifications of 105 °F. Both of these values need to be reduced in order to treat the blowdown biologically. Progress Energy employed the use of a 250 million gallon settling pond. The pond has a retention time of approximately 125 days and has four purposes: settle out suspended solids in the blowdown, equalize the blowdown to mitigate any fluctuations in the chemistry of the stream, cool the blowdown, and provide 30 days of blowdown storage capacity.

Solids as mostly gypsum fines will settle-out in the pond over time. With this settling, it is expected that the pond will require dredging every 10-20 years depending on solids loading and Hydroclone performance. Decant is taken from the far end of the settling pond via a floating skimmer and sent to the biological treatment system.

BIOLOGICAL PROCESS OVERVIEW

	Max	Min	Avg
Chlorides, mg/l	7,000	2,000	-
TSS, mg/l	250	20	40
Temp. °F	105	60	-
pH	6.5	5.5	-
Selenium, mg/l	3	1.2	-
TDS, mg/l	-	-	13,500

Table 1 – Design Bioreactor Influent Criteria

Following the settling pond, water is sent to a series of fixed-film, biological reactors. The bioreactors utilize a mixture of specifically selected, naturally occurring bacteria.

Many diverse species of bacteria have been proven capable of reducing dissolved selenium species (selenate and selenite) to

particulate elemental selenium in an aqueous reductive environment³ by linking the oxidation of organic substrates to the dissimilatory reduction of the selenium oxyanions⁴. The oxidized selenium compounds serve as electron receptors during the electron transport process. This effectively reduces the oxidized selenium compounds to nanospheres of granulated elemental selenium which accumulate in and around the bacterial cells. The unique physical properties of these granules cannot currently be produced by purely chemical means and exhibit a higher level of stability than other chemically-induced elemental selenium formations⁵.

Within the reactors, the bacteria are fixed to a granular activated carbon (GAC) bed. The GAC is not used for absorption, but rather as a substrate for bacterial growth. This GAC matrix creates a fixed biological film which retains the biomass and prevents it from being washed out of the reactors.

Achieving a reducing environment is critical to the success of the process. Wastewater entering the system has a positive ORP in the range of +200 to +300 mV. As wastewater travels through the bioreactors, the ORP drops across the system, causing several different reactions to occur in various locations throughout the carbon biomatrix.

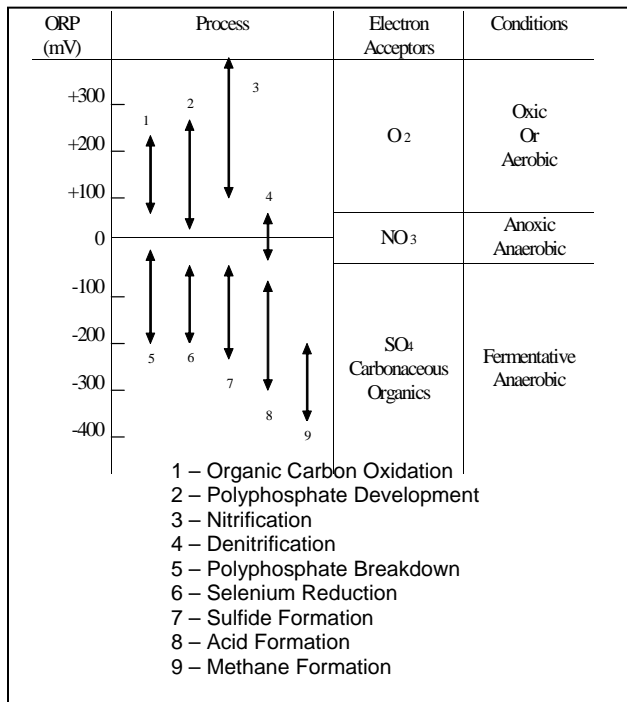
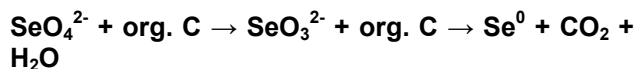


Figure 2 – Redox Profile

As the ORP approaches 0 mV, denitrification occurs as the nitrate is reduced to nitrogen gas which is then released to the atmosphere.



As the ORP drops further into the negative range, selenate and/or selenite is then reduced to an elemental state.



Further reductions in ORP will yield sulfide production within the system, which will precipitate out other trace metals such as zinc, copper, nickel, lead and others as metal sulfides. These precipitates are retained within the biomatrix much the same as the reduced selenium.



The precipitated constituents are retained within the biomatrix until the system is backflushed, leaving the effluent virtually free of these contaminants.

Controlling the ORP in the process is achieved by feeding a proprietary molasses-based nutrient blend into the reactors as a carbon source for the bacteria. The nutrient is fed into the influent line of each bioreactor through an injection quill and static mixer to ensure that the system is evenly fed. The dosage rate of the nutrient is dependant upon several factors, including feed nitrate levels, required removal rates and desired ORP range.

The bioreactors are designed for a plug-flow, ensuring even distribution of the feed water and maximum contact for the bacteria. Roxboro utilizes four parallel bioreactor trains, each with two concrete bioreactors in series. Each of the bioreactors in the first and second-stages are identical.

Material selection in this environment is important to the long-term operations of the plant. With such high levels of chlorides, carbon or regular (304, 316) series stainless steels are not appropriate due to the potential for corrosion. All process piping is non-metallic, typically PVC or HDPE depending on the line size and service. Teflon-coated butterfly valves are used for most valve applications and pumps have 2205 duplex stainless steel wetted parts. The bioreactors are lined with an HDPE sheet to ensure longevity of the concrete tanks.

Wastewater from the settling pond is pumped via two centrifugal pumps (two duty, one on-line spare) to the first-stage bioreactors. It is then fed into the top of the

bioreactors and flows evenly across the top of the GAC biomatrix through a distribution piping grid. Wastewater passes through the biomatrix and is collected via a piping collection grid located in a gravel subfill in the bottom of the reactor. The effluent from the first-stage bioreactors is pumped via a booster pump into the top of the second-stage bioreactors. Once the water flows through the second-stage bioreactor, it is sent via gravity to the ash pond discharge canal.

escape, but short enough to remain below the headspace of the bioreactor.

Differential pressure is monitored across the bioreactors using a combination of tank-level transmitters and pressure transmitters located on the effluent piping of each bioreactor. Increases in differential pressure can be used as an indication of the accumulation of gas pockets within the beds. If a degas does not recover the differential pressure, an accumulation of solids in the bioreactors is likely and a backflush would be required. Degassing may also be done proactively to ensure optimum performance.

Solids in the form of captured TSS, precipitated metals and biomass will also build up over time. When backflushed, the steps are very similar to the degas sequence where the same dedicated flush pump pulls water from the settling pond and sends it into the bottom of the bioreactor being flushed. During a backflush, the higher flow fluidizes the bed, dislodging the trapped solids, precipitated metals and any excess biomass, and carries it out of the bioreactor as overflow while retaining the activated carbon biofilm. The spent water is sent to the lined flush pond, similar to the settling pond but much smaller. The flush pond remains undisturbed, allowing the solids to settle and the clean water to decant off of the top of the pond back into the settling pond. The flush pond is sized to hold 20 years of accumulated solids.

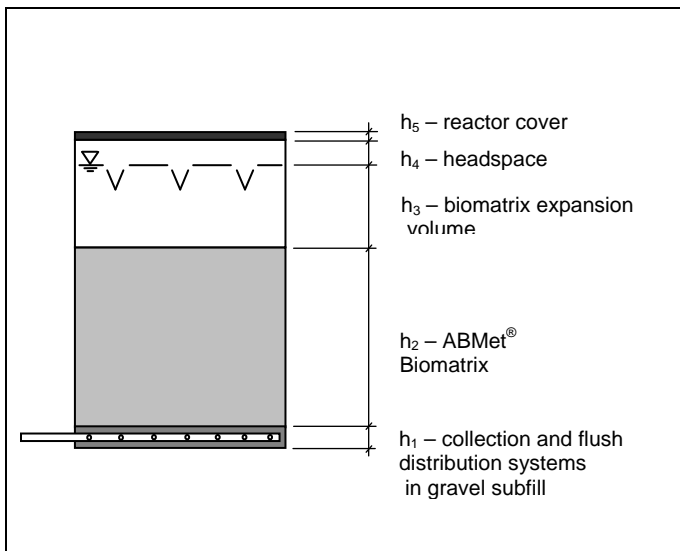


Figure 3 - Bioreactor Cross-Section

Periodically, the denitrification occurring within the system will cause nitrogen gas to build-up and form pockets within the GAC beds. These pockets can have a negative effect on the performance of the process by allowing for flow to short-circuit around them, and can increase the perceived head-loss across the bioreactors. A degassing sequence is employed in which a dedicated flush pump pulls water from the feed pond and sends it at a high flux rate into the bottom of the bioreactor via a dedicated piping distribution grid. The flush duration is long enough to loosen the media so as to allow for trapped nitrogen gas to

START-UP

The first Roxboro WFGD started-up in April 2007, followed by a second WFGD in November 2007. Blowdown from these two WFG scrubbers was stored in the settling pond while the water level came to a minimum operating height. The biological

system at Roxboro was started-up in late February 2008, which necessitated changes in the seeding process. At the time of commissioning, the settling pond temperature was just below 50 °F, lower than the design value by 10 degrees. For a two-week acclimation period, a heated recirculation loop was used to maintain the reactor temperature at over 80 °F. After acclimation, raw feed water from the settling pond was introduced without supplemental heating. Even at low temperatures, the biological system was fully acclimated to the feed and was consistently producing effluent selenium values below design requirements by week 5 of operations.

OPERATIONAL OBSERVATIONS

Through the beginning of June 2008, total selenium effluent values were consistently less than 10 µg/l with feed values averaging 1,500 µg/l coming out of the feed pond. This equates to an average removal efficiency of 99.3%. Feed values for selenium have been as expected based on the design basis. The feed TSS loading has been well below design values, indicating that the Hydroclones and the settling pond are performing above expectations. Feed TSS has averaged <10 mg/l throughout the spring of 2008. The feed pH has been well higher than expected, averaging slightly less than 7.5.

The system was not backflushed until July. The low levels of TSS in the feed water helped to slow the need for a backflush by limiting the nutrient feed's contribution to the solids in the carbon beds. Effluent selenium levels slightly increased in June, indicating that the system was in need of a backflush in order to remove the accumulated biomass and precipitated solids.

Results of backflushing in July 2008 showed a full recovery of the system, with effluent levels of selenium back below 10 mg/l.

CONCLUSIONS

Overall, the biological system is performing as expected in terms of selenium reduction, and even better than expected when the start-up feed water temperature is considered. Several key points need to be taken away from this project:

- Facilities with multiple scrubbers will have staggered start-ups and subsequent increases in blowdown flow. The system needs to have the flexibility to handle all flow scenarios.
- The acceptable feed water temperature for acclimation and operations may be more forgiving than initially perceived, with the system starting operations in 50 °F water while the design minimum was originally 60 °F.
- Accurate, factory certified ORP probes are critical. Verification with hand-held ORP meters can be done, provided that a meter is selected with the right electrode material (platinum).
- Proper analytical techniques for low-level selenium need to be used.
- A comprehensive sampling protocol with quick analysis turn-around is needed during the first few months of operation in order to ensure that the system is fully optimized for the best performance.
- Changes in blowdown chemistry need to be monitored closely in order to adjust system parameters as needed.

Figure 4 - Bioreactor Process Flow Diagram

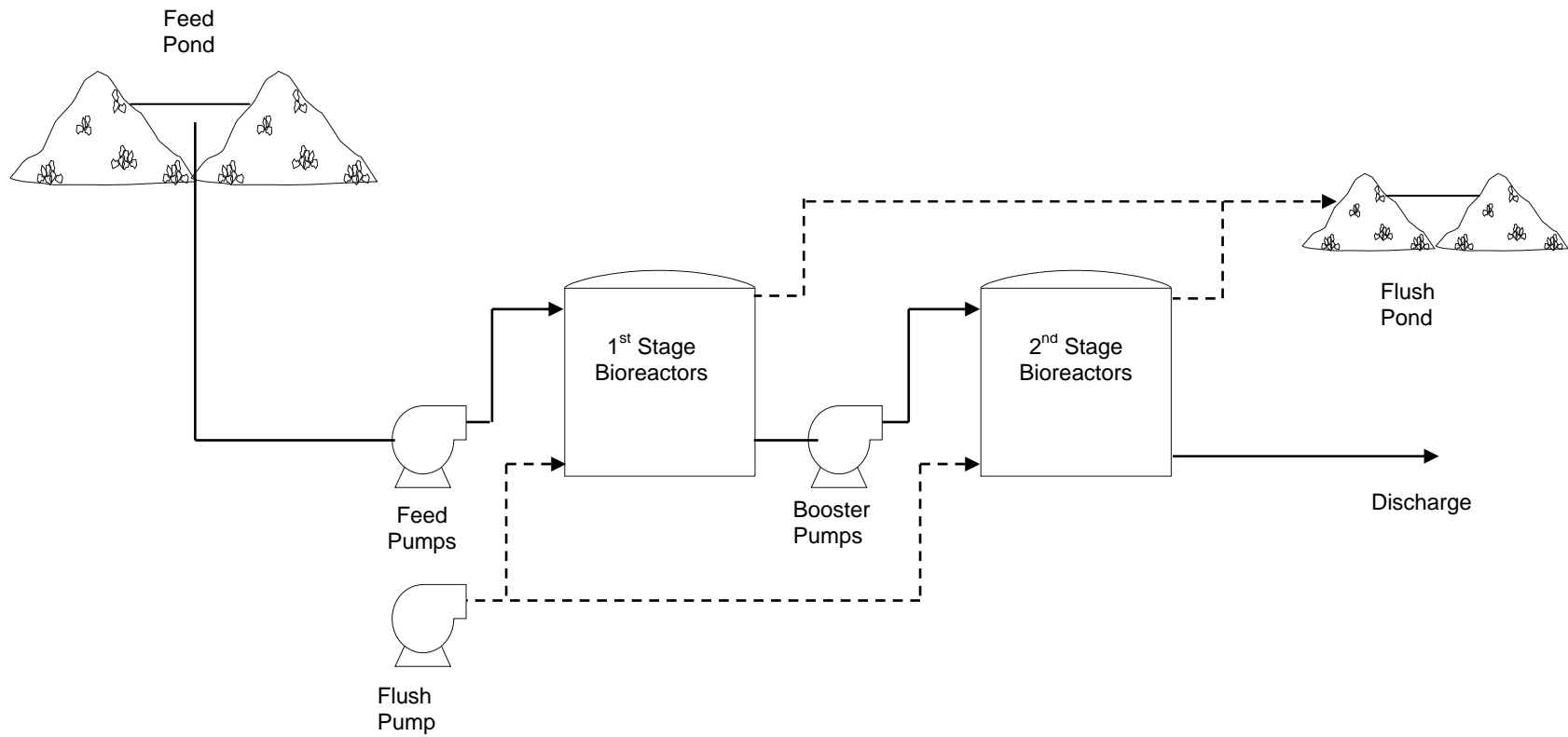
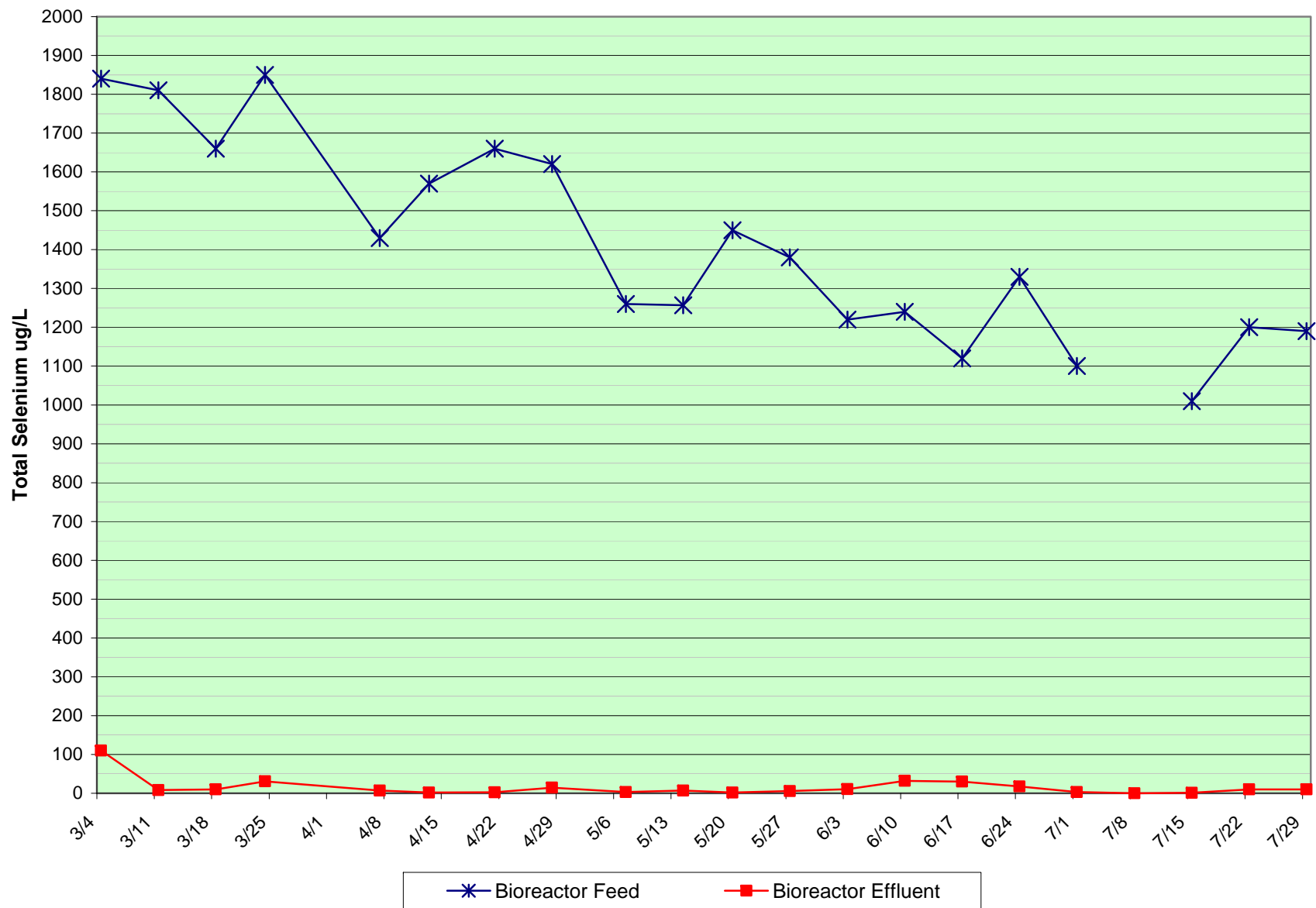


Figure 5 – Roxboro Bioreactor System



Figure 6 – Roxboro Bioreactor Selenium Analytical Data



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