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ABMet: Setting the Standard for Selenium Removal

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Summary

As public awareness of environmental concerns has risen, increasingly stringent discharge regulations are being imposed. Coal-fired generating stations have become the subject of such regulations for both air and water emissions. Release of sulfur dioxide from coal-fired boilers can be mitigated through the employment of wet forced-oxidation Flue Gas Desulfurization scrubbers; however, these systems can produce a wastewater stream containing selenium, nitrate and other constituents, which necessitate further treatment prior to discharge.

Removal of selenium in its oxidized forms to concentrations of less than 10 parts per billion (ppb) has proven to be a formidable challenge for conventional physical and chemical systems. Although historically proven, natural insitu reduction of selenate/selenite in wetland systems requires a lengthy contact time and may allow the selenium to remain in the local ecosystem. A more efficient approach to natural remediation technology is the utilization of fixed-film, packed-bed bioreactors, which exploit site-specific, naturally-occurring, non-pathogenic microbes in an optimized, self-contained system. These systems have been designed to remove selenium in a two-to-sixteen hour empty bed contact time while sequestering selenium in a low-volume sludge that may be easily filtered for disposal. The self-perpetuating microbial biocatalysts require only a nominal nutrient supplement and power supply, thereby resulting in very low operating and maintenance costs. In addition to selenium and nitrate removal, other constituents and trace metals can be co-precipitated, further increasing the overall benefit and value of the system.

Three prominent United States utilities have pioneered the employment of this revolutionary treatment system at five coal-fired generating stations. This paper will discuss the fundamental concepts of biological reduction, Scanning Electron Microscope imaging of selenium nanospheres; ABMet's demonstrated removal efficiency of selenium; and the design, cycling, performance data and operating and maintenance costs of the full-scale systems.

Background

The United States Environmental Protection Agency (EPA) is required by the federal Clean Water Act to develop guidelines addressing priority constituents being discharged into public waters. While all priority constituents are potentially harmful in high enough levels, selenium in particular is controlled to very low levels, as these elements may bio-accumulate in living tissue. The current EPA National Recommended Water Quality Criteria (www.epa.gov/waterscience/criteria) are designed to assess and quantify the total recoverable selenium concentrations in a body of water and have an established chronic value of 5 ppb (µg/L) and an acute value of 20 ppb Se. States currently have the option to accept the recommended guidelines or to adopt more stringent regulations of their own.

Recent environmental publicity and litigation have encouraged the EPA to propose new guidelines for constituents such as selenium. The new EPA guidelines will have a significant impact on coal-fired power plants. Currently many of those plants abiding by the SOx restrictions (implemented by the Clean Air Act of 1990), have been retrofitted with wet Flue Gas Desulfurization (FGD) units. These FGD systems are designed to introduce an alkaline sorbant, typically consisting of lime or limestone in a spray slurry form, into the exhaust of an existing coal-fired boiler. The alkali reacts with the SO_2 gas and is collected in a liquid form as calcium sulfite or calcium sulfate slurry. The slurry is discharged to a treatment system where the gypsum (which when removed by centrifugation) can be recovered as a saleable product.

The resulting pre-treated FGD wastewater (blowdown) can contain elevated levels of mercury, nitrate and selenium as well as other metals and metalloids found in coal. Besides the extreme variability in effluent quality due to the variety of coal sources, limestone sources, and scrubber operation, FGD blowdown poses a unique set of challenges for treatment. Chloride levels can run over 25,000 ppm exacerbating scaling and corrosion issues. Temperatures in excess of 140°F and scrubber additives such as dibasic acid (DBA) both require treatment prior to discharge. Scrubber systems can go off- and on-line with the power units as the need for power and routine maintenance mandates, resulting in large fluctuations in the quantity of wastewater produced. Analytical analysis in these applications is subject to interferences from high Total Dissolved Solids (TDS), bromine, chlorides, sulfur, argon, iron, manganese, copper and zinc, as well as having the target discharge limits so close to analytical detection limits that an acceptable margin of error can mean the difference between meeting or exceeding permit levels.

Fixed-Film Biological Process Overview

Following a settling pond or clarification to remove excess suspended solids (which often exceed 5,000 ppm after gypsum removal), the blowdown can be sent to a series of fixed-film, packed-bed, anoxic bioreactors. These reactors are filled with a permanent porous substrate such as granular activated carbon (GAC) and are seeded with a naturally-occurring, beneficial, consortia of bacteria.

In the proprietary technology discussed in this paper, the bacteria used for seeding have been isolated from previously-contaminated sites and chosen specifically for use in FGD systems because of their hardiness in the extreme water chemistry as well as for their proven efficiency for selenium respiration and reduction. The bacteria form a fixed biofilm throughout the GAC substrate material (termed biomatrix), forming a

cooperative microbial community. In addition to increasing the efficiency of selenium removal, this communal structure also serves as a shelter, protecting the bacteria from chemical and physical upsets. These bacteria are facultative anaerobes, which flourish in oxygenated environments; however, when oxygen is depleted the bacteria utililize other compounds for respiration, resulting in the dissimilatory reduction of other oxianions present in the water. See Table 1.

Flow Through Bioreactor	Final e-Acceptor	Approximate ORP
	Oxygen	> 0 mV
	Nitrate	< 0 mV
	Nitrite	< -50 mV
	Selenate	< -100 mV
	Selenite	< -150 mV
	Sulfate	< - 200 mV

Table 1. Fixed Film Bioreactor Gradational ORP Zones

A reducing environment is required to facilitate selenium reduction. The plug-flow design of the system allows gradational zones of decreasing ORP to form in layers throughout the biomatrix. As the ORP approaches 0 mV, denitrification occurs with the nitrate being reduced to nitrogen gas and released to the atmosphere. Complete nitrate reduction is achieved in the system.

NO_3 + organic C → NO_2 + organic C → N_2 + CO_2 + H_2O

Deeper in the bioreactor bed, the ORP drops lower; dissolved selenate and/or selenite is reduced to an elemental state, precipitates out of solution and is filtered from the effluent by the biomatrix.

SeO_4 + organic C → SeO_3 + organic C → Se + CO_2 + H2O

Reduction and precipitation of selenium occurs within a two-to-sixteen hour empty bed contact time (EBCT). EBCT is the residence time of the water assuming that there is no substrate, biofilm or solids present in the bioreactor.

Periodic degassing is required to release the gasses from the bioreactor bed. This is achieved with a small-volume, high flow of stored effluent water back through the biomatrix, which releases the gasses trapped within.

Collection of the precipitated constituents is achieved by a backwash cycle, which is strong and long enough to fluidize the biomatrix. This allows the release and collection of the contaminants and spent biomass. Attrition of the GAC has been insignificant at of the full-scale facilities to date and does not contribute to the minimal sludge volume.

A proprietary molasses-based nutrient is fed into the reactors as a carbon source for the bacteria (this carbon is a food source for the bacteria, and is not to be confused with the Granular Activated Carbon substrate which serves as the permanent structure for the biofilm). The nutrient is fed into the influent line of the bioreactors utilizing a static mixer to ensure the system is evenly fed.

Bioreactor Engineering & Design

The bioreactors are designed for plug-flow, ensuring even distribution of the feed water and maximum contact with the bacteria throughout the biomatrix. The system utilizes parallel trains with each train consisting of a first- and second-stage bioreactor cell. The systems are scalable to virtually any flow size by the addition (or reduction) of trains and by

varying the volume of the individual cells. Each of the bioreactors in the first- and second-stage are identical to each other, which allows for alternate cycling and continuous operation during degas and backwash cycles.

Material selection in an FGD system is essential to the reliable, long-term operation of the plant. Elevated chloride levels in the water preclude the use of carbon steel or low alloy stainless steels due to the potential for corrosion. Process piping is non-metallic, typically fiberglass reinforced plastic (FRP) or high-density polyethylene (HDPE). Coated butterfly valves are used for most applications and pumps have 2205 duplex stainless steel wetted parts or are rubber-lined to ensure longevity.

Water is fed into the top of the bioreactors and flows evenly across the top of the biomatrix through distribution piping. The water passes down through the biomatrix and is collected via a manifold located in a gravel subfill in the bottom of the reactor. The effluent from the first-stage bioreactors is pumped into the top of the second-stage bioreactors. See Figure 1.

Periodically, the denitrification occurring within the system will cause gases to build up and form pockets within the biomatrix. These pockets can have a negative effect on the process by allowing the water flow to channel, resulting in reduced microbial contact and increasing head-loss across the bioreactors. A degassing sequence is employed in which a backwash pump pushes water at a high flow rate into the bottom of the bioreactor via a dedicated manifold. The flush duration is long enough to lift the biomatrix and allow the entrained gases to escape, but short enough to avoid wasting any water out of the bioreactor.

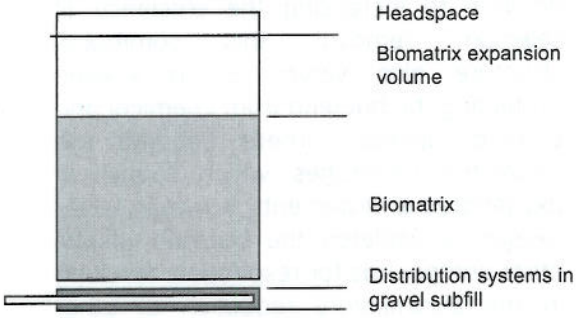


Figure 1. Simplified Bioreactor Cross-Section

Head-loss through the biomatrix is monitored across the bioreactors using level transmitters and a baseline level point. If a degas does not recover the head-loss, an accumulation of solids in the bioreactors is likely and a backwash is required.

Solids in the form of captured total suspended solids (TSS) from the wastewater, precipitated selenium, metals and excess biomass will build up over time. A high-flow backwash (similar to the degas) fluidizes the biomatrix, dislodging the trapped solids and carrying them out of the bioreactor as overflow. The biomatrix remains in the bioreactor, leaving the active bacteria population for continued operation. The resulting sludge is de-watered and disposed of.

Full-Scale Operations

Four full-scale systems treating FGD blowdown have been in operation for several years, the first being commissioned in early 2008. Each wastewater treatment system (WWTS) has utilized a slightly different philosophy in the implementation of fixed-film biological technology. These facilities cover a wide range of possible flow and constituent loadings. See Table 2.

	Flow	# of Trains
Plant 1	2.02 MGD	4
Plant 2	0.25 MGD	2
Plant 3	0.86 MGD	8
Plant 4	0.59 MGD	6
Plant 5	0.86 MGD	6

Table 2. Plant Capacities

The first two plants require reduction in levels of selenium, arsenic and mercury, while the second two employ biological treatment only for selenium removal, using other upstream processes for all other constituents of concern.

These specific systems were designed to handle chloride levels up to 20,000 ppm, suspended solids up to 100 ppm, nitrate-N loading less than 100 ppm.

Plants 1 and 2 send the blowdown (post-gypsum recovery) to large, lined settling ponds for solids removal, temperature reduction and equalization prior to biological treatment. These ponds have capacities of several months and are designed to only require solids removal approximately every 10 years at design condition. Plant 2 is also adding a sulfide-based reagent chemical for mercury reduction into the settling pond prior to the biological treatment system.

Of significant note is the behavior of the feed water temperature coming out of the settling pond at both plants. Due to the size of the ponds, the water generally cools to ambient temperature. This results in a major feed-water temperature swing throughout the year. Summer water temperatures at both Plant 1 and Plant 2 can approach 95°F. Winter temperatures have been observed as low as 42°F for several weeks at a time. Despite the variation, effluent results have remained consistent throughout the year with average performance values remaining stable. See Tables 3 and 4.

	Bio Influent	Bio Effluent	% Bio Removal
Tot Se	1,812.9	13.7	99.2%
Diss Se	1,807.5	11.8	99.3%

Table 3. Plant 1 One-Year Avg. Full-Scale Data (ug/L) and % Removal Rates

	Bio Influent	Bio Effluent	% Bio Removal
Tot Se	727.1	12.9	98.2%
Diss Se	700.9	11.3	98.4%

Table 4. Plant 2 Four-Month Avg. Full-Scale Data (ug/L) and % Removal Rates

Plants 3 and 4 direct the blowdown (post-hydrocyclone) through conventional physical/chemical processes prior to biological selenium removal. These processes begin with gypsum desaturation by adding hydrated lime, which elevates the pH to between 8.5 and 9.2. Ferric chloride is added to facilitate iron hydroxide co-precipitation of dissolved metals, followed by coagulation and clarification.

	Bio Influent	Bio Effluent	% Bio Removal
Tot Se	214.4	9.2	95.7%
Se (IV)	57.1	0.8	98.6%
Se (VI)	181.8	1.3	99.3%

Table 5. Plant 3 One-Year Avg. Full-Scale Data (ug/L) and % Removal Rates

	Bio	Bio	% Bio
Tot Se	334.1	7.1	97.9%
Se (IV)	7.0	1.5	78.4%
Se (VI)	257.8	4.4	98.3%

Table 6. Plant 4 One-Year Avg. Full-Scale Data (ug/L) and % Removal Rates

All four plants have consistently met their discharge requirements during the operation of the fixed-film WWTS. As with most scrubber systems, the majority of the selenium concentration is present in the form of selenate. While many other technologies struggle with the removal of selenium in the Se (VI) state, the fixed-film biological plug-flow system removes both Se (IV) and Se (VI) efficiently. See Graphs 1, 2 & 3. It should be noted that this data, while from a single station, coincides with performance from the three other full-scale operating units, as well as data generated from pilots conducted at five other FGD-scrubbed sites.

Operating and Maintenance Costs

Costs for a fixed-film biological treatment system are minimal in comparison to other available technologies. Electrical consumption is low. Operation and maintenance costs for these facilities range from $0.35 to $0.46 per 1,000 gallons of water treated. For a 0.6 MGD biological treatment system described earlier in this paper, operating costs are approximately $400,000 USD per year for direct labor, routine maintenance, and nutrient.

Fixed-Film Bioreactor Re-start after Cycling Event

Plant 4 is a five-unit FGD-scrubbed generating plant. It is designated as a cycling facility, indicating that load will vary from hour-to-hour and day-to-day based on demand. During the fall of 2009, mild weather that reduced industrial demand and the availability of other generating capacity on the grid both created a situation causing the station to be off-line for an extended period of time. During this outage period, the WWTS did not receive scrubber purge water for 48 consecutive days.

The WWTS operators initially were unaware that they would be experiencing an extended outage. As such, the pumps were simply turned off instead of the system being prepared for long-term shut-down. After several days, it became apparent that the outage would continue for an undetermined length of time. Process water was periodically drained from process vessels to run through the bioreactors. This procedure was conducted every four days, and lasted approximately two hours. Rather than allowing the biomatrix to become dormant, nutrient was dosed into the system during this procedure. The process water cycle also allowed for the flushing of accumulated biological waste products and prevented the ORPs from dropping to levels below negative 400 mV. Process water was used primarily because it was readily available, but also in an effort to maintain higher TDS levels. As the outage extended, it became necessary to begin using service water (filtered river water) to maintain the periodic flow to the bioreactors. During the outage the bioreactors reached ambient temperatures of between 55 and 60 °F.

When the station went back on-line, the WWTS was started up just as if it had gone through a one-day shutdown. Pumps were turned on and the automatic control system resumed. An accelerated backwash schedule of one-cell-per-day was the only change to standard operating procedures. One week after restarting the system, the selenium

concentration in the first scheduled effluent sample was less than 2 ppb. Weekly samples for the remainder of the month never exceeded selenium concentrations of 3.5 ppb.

There was an initial concern that the cycling nature of Plant 4 would have an adverse impact on both the physical/chemical and biological portions of the WWTS; however, frequent short-term shutdowns of WWTS due to a lack of purge water had no noticeable impact on system performance. The long-term unplanned outage demonstrated the resiliency of the bioreactor system to be rapidly brought back on-line with minimal effort. An understanding of the biological technology by an experienced staff provided for a seamless cycling of the system.

SEM Imaging of Selenium Nanospheres

To demonstrate the formation of elemental selenium nanospheres in the fixed-film biological process, SEM imaging was performed on bacteria samples supplemented with 200 ppm of selenium were grown at GE's Global Research Center in Schenectedy, NY. Microbial samples were collected on polycarbonate membranes and then fixed with 2% gluteraldehyde in 0.1M sodium cacodylate buffer. The preserved samples were dehydrated in ethanol, critical point dried, platinum coated and then imaged in the Zeiss Supra FE Scanning Electron Microscope (SEM). Images were generated using 5kV and 15kV energy beams with the Scanning Electron 2 detector.

Using a Scanning Electron Microscope, Backscattered Electrons (BSE) imaging showed a contrast of chemical composition where selenium appears as bright white spheres. Energy Dispersive Spectroscopy (EDS) analysis showed selenium as bright particles vs. gray rods of bacteria. See Figures 3 & 4.

The resulting images depict late-exponential-phase gram-negative rods with elemental selenium nanospheres (Se(0)). The formation of extracellular, insoluble selenium nanospheres is a dissimilatory bi-product of anaerobic cellular respiration and can be seen adjacent to the cell walls both singularly and in clusters. See Figures 4 & 5. Dr. Ronald Oremland proposes that these nanospheres are composed of inter-connecting three-dimensional nets of selenium, in which both the chain and ring structural aspects are maintained. These red amorphous nanospheres are believed to be more structurally stable than chemically derived morphology. Oremland also noted that extracellular nanosphere accumulation was far more common than intracellular elemental accumulation in anaerobic selenium respiring organisms.

Conclusions

As more and more coal-fired utilities implement wet FGD scrubbers as a method to control SOx emissions, the need for advanced wastewater treatment is becoming a necessity. Regulating bodies are continuously implementing tighter discharge criteria requiring new and advanced technology. Historic physical and chemical treatment processes have not proven themselves capable of consistently removing selenium and heavy metals from complex waters to the low levels achieved by biological reduction. Successful long-term operation coupled with consistent low-level selenium removal demonstrates that the fixed-film, packed-bed WWTS is a proven technology both in function and design.

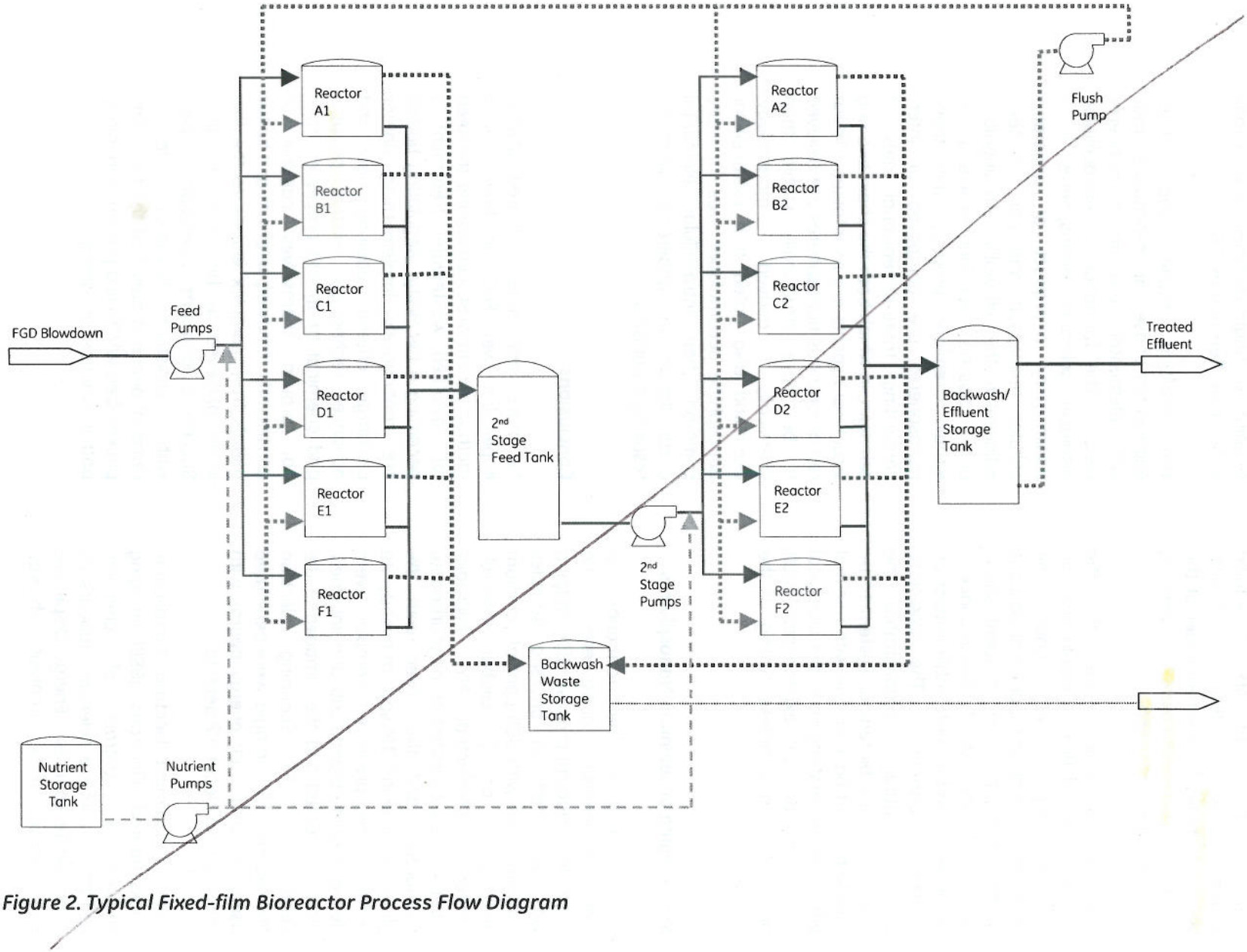
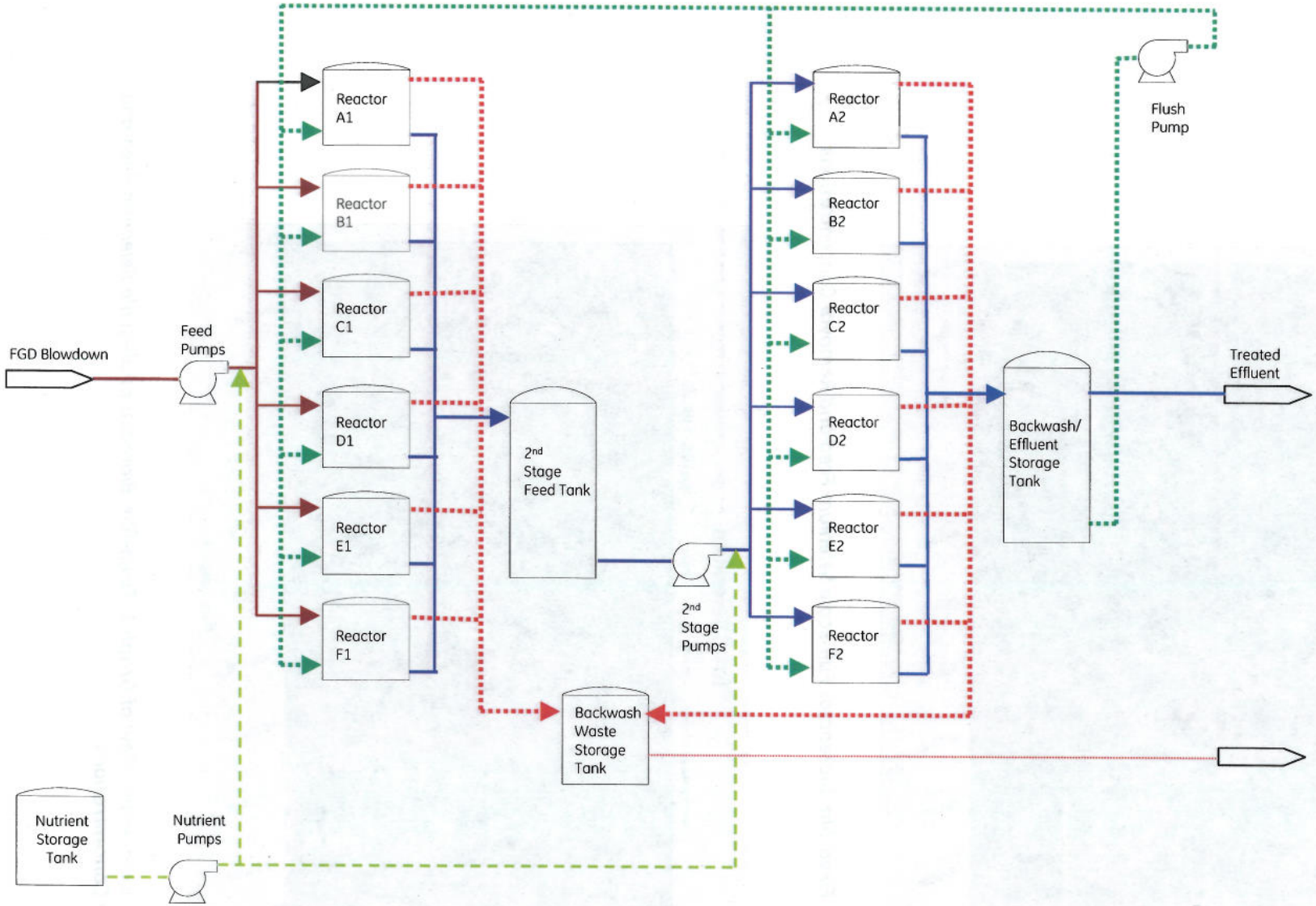


Figure 2. Typical Fixed-film Bioreactor Process Flow Diagram



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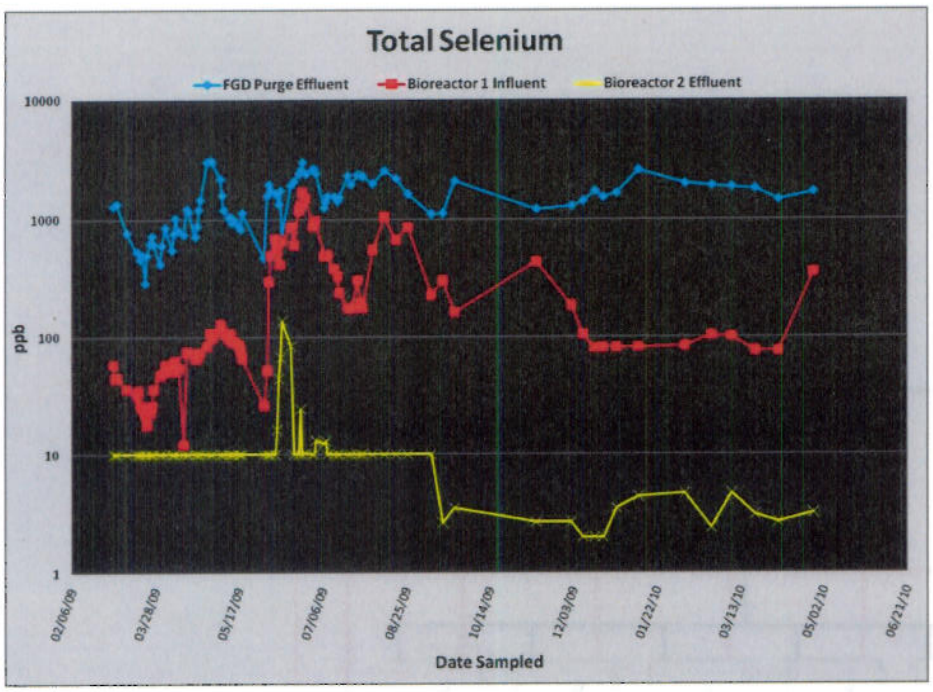
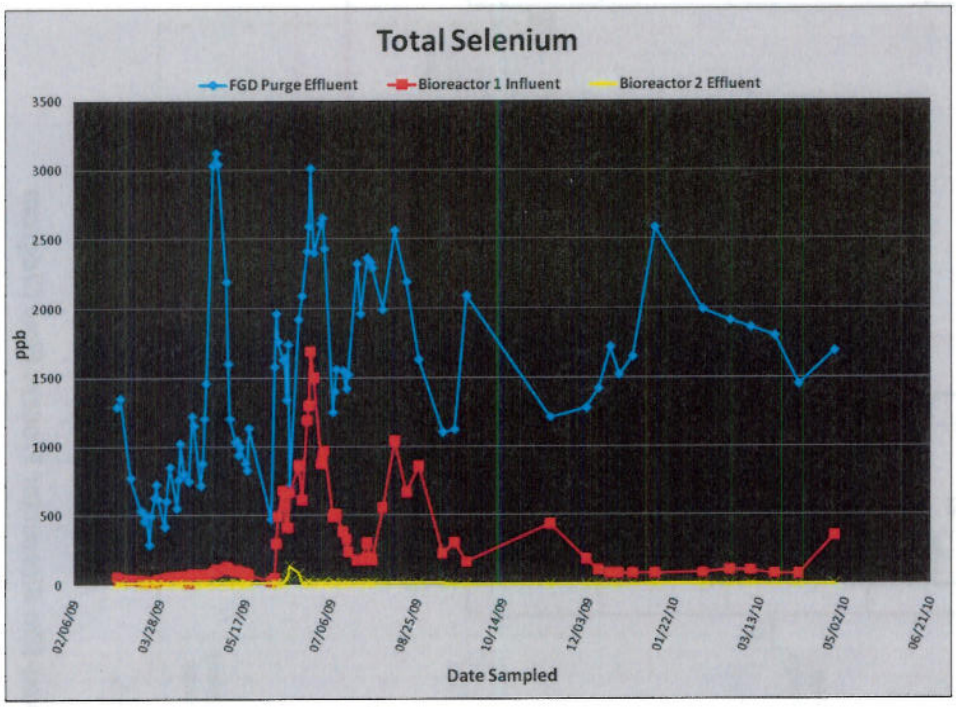
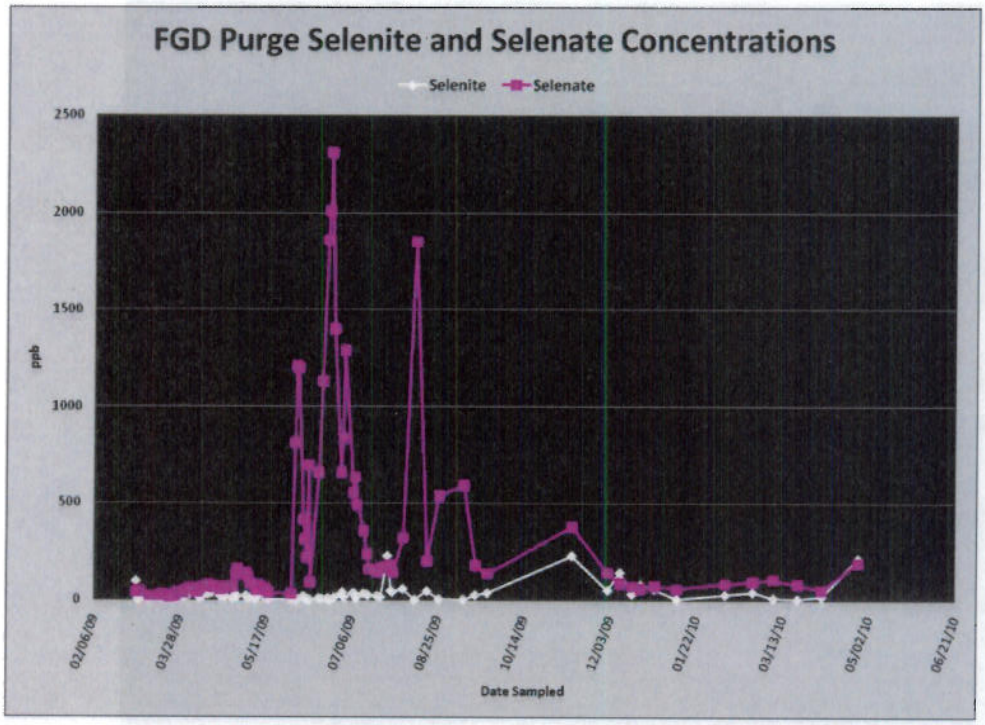


Graph 1. Fixed-film Bioreactor Full-scale Selenium Feed and Removal Concentrations



Graph 2. Exponential View of Graph 1: Fixed-film Bioreactor Full-scale Selenium Feed and Removal Concentrations



Graph 3. FGD Purge Selenite and Selenate Concentrations

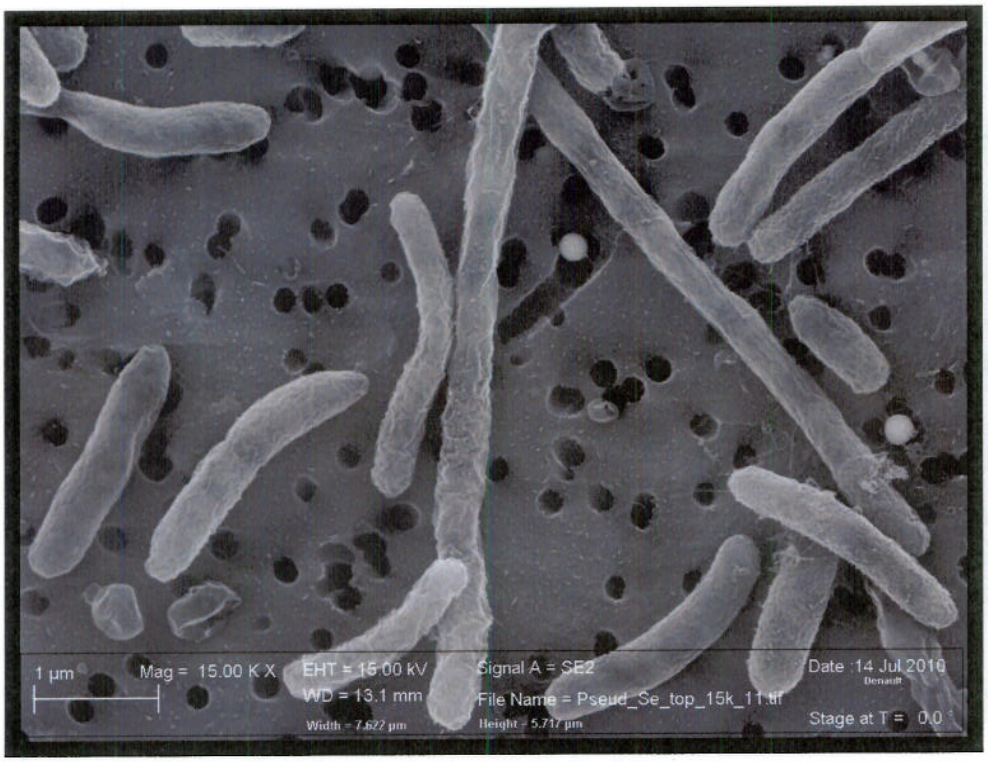
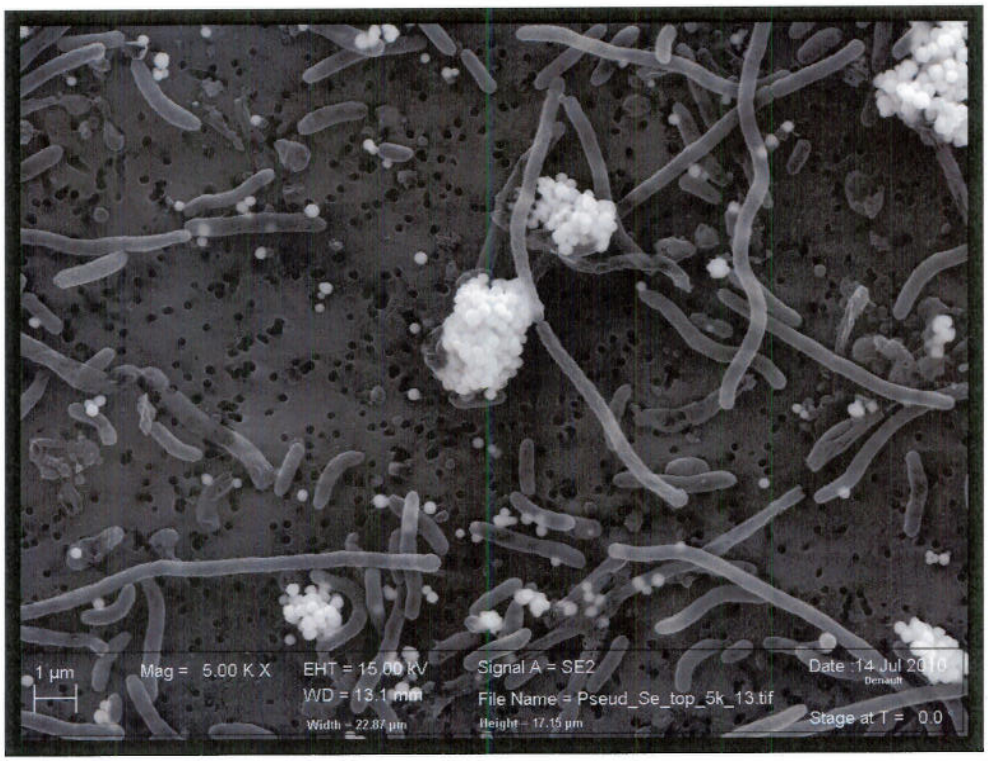


Figure 3. SEM Imaging of Anaerobic Selenium Respiring Bacteria and Selenium Nanospheres



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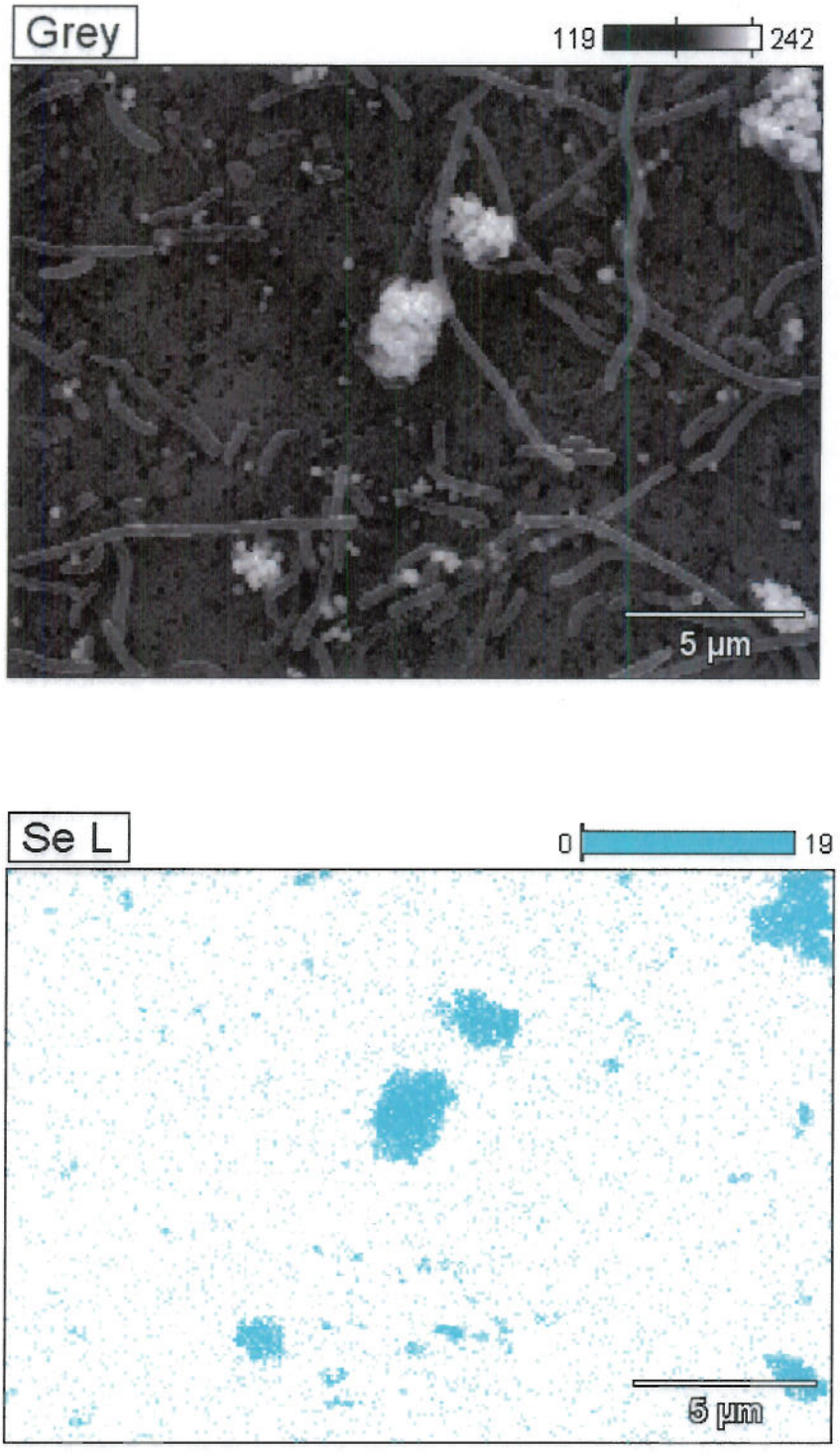

Figure 5. Elemental Analysis of Selenium Nanospheres imaged in Figure 4

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