Treatment of Selenium-Containing Coal Mining Wastewater with Fluidized Bed Reactor Technology

Proven Systems Provide Major Cost Advantages
and “Best-in-Class” Performance

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Introduction

In the coal mining industry today, selenium, in its many forms, is gaining attention. New regulations covering selenium discharge are either in place or being developed. It has been said that handling selenium wastes will increasingly become a limiting factor on the ability of the coal mining industry to grow. While a number of physical/chemical approaches show promise in selenium treatment, when considering optimal cost and treatment efficacy issues, biological treatment – particularly fixed-film biological treatment - is one of the most promising approaches to managing selenium-containing wastewaters. Envirogen Technologies offers a patented fixed-film fluidized bed reactor (FBR) biological treatment technology that has been proven as a 'best in class' approach for handling medium to high flow rates of selenium-containing wastewater. Envirogen FBR technology has several distinct features that make it ideally suited for the coal mining industry.

The noteworthy features of Envirogen FBR technology include its ability to consistently reduce selenium levels to less than 5 µg/L, shorter required residence times for treatment and a smaller overall footprint. Its flexibility in the choice of electron donor chemicals can translate into capital and operating cost savings with reduced solids generation. It also responds well to changes in feed flow and composition, consistently achieving discharge limit conditions. In addition, these systems can be modular, with all-weather protection where desired. These features, combined with decades of experience by Envirogen's team, allow the design and installation of FBR systems with capital costs that are a fraction of the cost of competitive fixed-film biological systems.

The selenium dilemma

Waste rock is generally the primary source of selenium in coal mining operations. When exposed to water, various selenium species will leach or migrate from the rock and enter the environment. Selenium occurs in various valence states from -2 to +6. The speciation of selenium plays a critical role in the effectiveness of any approach for removal, especially to low levels. In aqueous environments, selenium is most often found as the oxygenated anions of selenite, Se(IV) and selenate, Se(VI). Selenium in mine runoff most often occurs in the soluble form .Selenium is commonly found in mining wastewaters in concentrations ranging from 3 to >12,000 µg/L. The US National Primary Drinking Water Standard MCL is 50 µg/L for selenium. The National Fresh Water Quality Standard is 5 µg/L for selenium. The U.S. Fish and Wildlife Service has recommended that the National Fresh Water Quality Standard be lowered to 2 μg/L to protect fish, waterfowl, and endangered aquatic species. Several states have followed with enforcement actions at these same low levels. In Canada, permits may require stakeholders to monitor levels in water or biota, or to comply with Canadian Water Quality Guidelines of 1 μg/L in surface waters. Province and local regulations may vary from these requirements.

Treatment of selenium in coal mining wastewaters presents a series of challenges. It can be present in relatively dilute concentrations and in streams with variable and often high flow rates. It is present in many soluble and particulate forms, which may affect process design and treatability. The conditions of influent selenium-containing wastewaters can vary widely, with issues such as temperature, pH, total dissolved solids and other contaminants present, affecting the ability to selectively and economically remove selenium. Treatment of selenium often results in the generation of a concentrated by-product requiring disposal, and re-release from residuals can occur. Beyond these issues, the physical environment of coal mining operations offers challenges such as remoteness and harsh and/or cold weather. Currently available selenium treatment technology (Table 1) includes biological treatment and a number of physical-chemical processes – such as ion exchange, membrane filtration and adsorption – that vary widely in efficiency and cost. Most treatment options remain either too costly and/or unproven for selenium-containing waste streams for reasons that include removal levels, variability in volume and composition of influents, system sizing and logistics considerations, as well as operating requirements.

Table 1
Overview of Technologies for Removal of Selenium in Water

Physical	Chemical	Biological
Reverse osmosis	Iron co-precipitation	Algal-bacterial Se removal
Nanofiltration	Zero valent iron	Algal volatilization
Ion exchange	Cupric co-precipitation	Heterotrophic microbial reduction
Ferrihydrite adsorption	Electrocoagulation	Constructed wetlands
Activated alumina adsorption	Enhanced cementation	Phytoremediation
	Photoreduction	
	Carbohudrazide	

Biological Treatment of Selenium-Containing Wastewaters

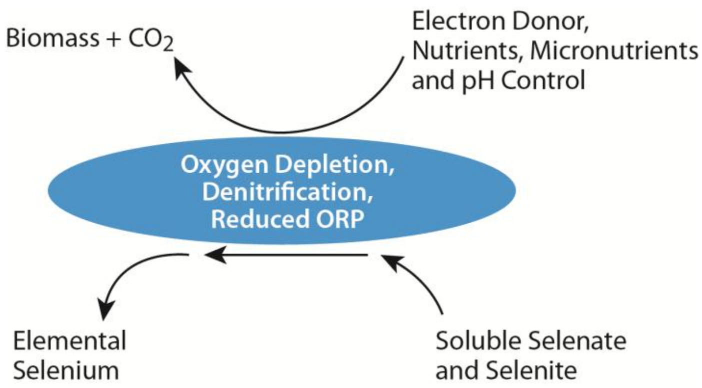
Biological treatment of selenium-containing wastewaters has been an area of significant interest in the coal mining community recently. In general, biological treatment offers a low cost alternative to more expensive physical and chemical treatment methods and is effective in cold climates. Additionally, it has the proven ability to meet regulatory selenium limits.

Biological systems catalyze the reduction of selenium. Selenate can be reduced to selenite, and both selenate and selenite can be reduced to elemental selenium.

$$SeO_4^{2-} + \text{organic carbon} \rightarrow SeO_3^{2-} + \text{organic carbon} \rightarrow Se_0 + CO_2 + H_2O$$

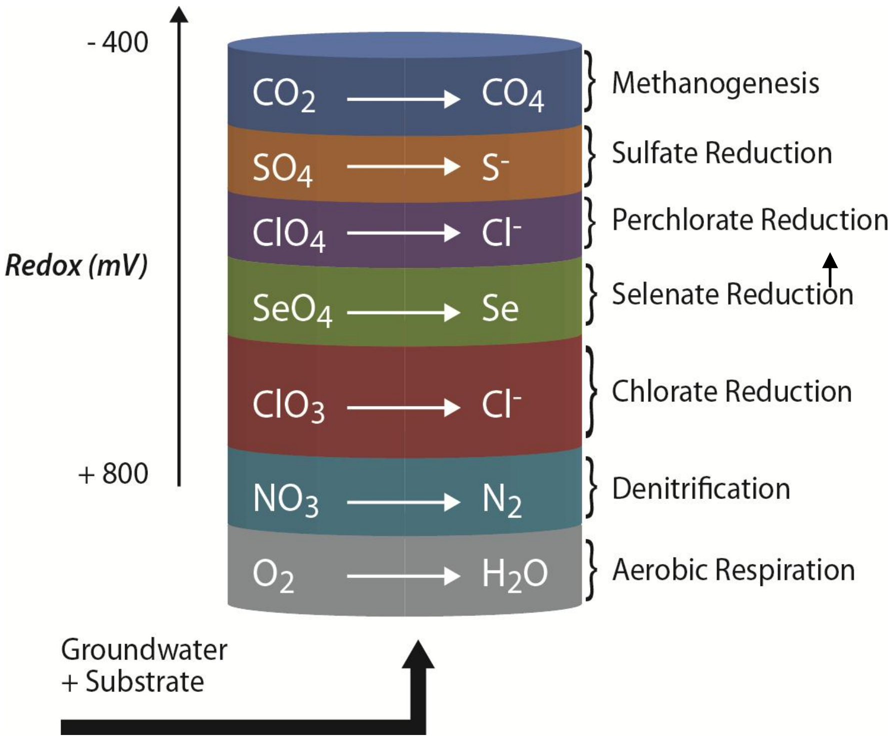
These reactions are desirable because elemental selenium is virtually insoluble and therefore can be removed from the environment through conventional liquid/solids separation and disposal. In biological treatment, the conversion of selenium anions to elemental selenium is accomplished via biologically catalyzed reduction. Selenium-reducing bacteria (Figure 1) are considered heterotrophic. They utilize organic carbon as their electron donor and selenate/selenite as their electron acceptors. Commonly used electron donor materials include methanol, acetate, citric acid and molasses. New ‘designer’ electron donors, generally composed of complex carbohydrates and organic process by-products that have been proven effective for selenium reduction and precipitation, are also available.

Figure 1: Selenium Reduction & Precipitation



One of the major issues in biological treatment of selenium is the presence of other anions in the influent streams. Both oxygen and nitrate are more favorable electron acceptors than oxidized forms of selenium. Figure 2 shows common anions and their order of biological reduction based on ORP. The order use of electron acceptors follows the more energetically favorable reactions first. Also, reduction enzyme systems appear to have evolved such that reduction enzymes are generally inhibited by electron acceptors that are more energetically favorable, particularly if the microorganism contains more than one reduction system.

Figure 2: Redox Profile of Biological Reduction



From a practical standpoint, these relationships are critical. The presence of either oxygen or nitrate will limit selenium reduction. Even in anoxic biological systems, the presence of nitrates is an important consideration in system design and the selection of microorganisms and electron donors. Many coal mining wastewaters contain high levels of nitrate that will be preferentially reduced before selenium, and must be removed before effective selenium reduction will occur. Sufficient electron donor material is required to reduce both nitrate and selenium. The FBR process offers the potential benefit of denitrification and selenium reduction in a single step.

Active, fixed-film biological treatment systems have received significant attention from researchers and the coal mining community because of their potential to work with a broad range of selenium concentrations in wastewaters – including very dilute streams – and for their ability to reduce selenium to very low levels. These outcomes are due to the fact that the heterotrophic bacteria are retained in the bioreactor for relatively long periods of time, improving the chance that they will come in contact with the contaminants and the ability of these systems to control reaction conditions more precisely. Additionally, because of the tendency of the microbes to attach to the solid media and to form dense biomass films, these reactors can have high biomass concentrations. This is especially the case with the Envirogen FBR technology.

Today, there are two different types of active, fixed-film systems that have received significant field testing with selenium-containing coal mining wastewaters – the fixed-film downflow filter (also known as a 'packed bed reactor' – PBR) and the fluidized bed reactor (FBR). In evaluating active, fixed-film bioreactor technology, the following issues are salient in choosing one of these approaches:

- Treatment efficacy/efficiency
- Hydraulic residence times
- System footprint
- Flexibility in handling variable & high flow rates
- Flexibility with electron donor material
- Ability to handle solids & metals
- Recovery from upsets
- Track record of technology
- Cost of capital
- Cost of operation
- Ease of operation

The remainder of this paper will present information related to Envirogen Technologies' fluidized bed reactor technology – and where applicable, compare and contrast technical and operating features with packed bed reactor technology.

Envirogen Fluidized Bed Reactor Technology

Proven technology with critical advantages for the coal industry

Envirogen's FBR is an active, fixed-film bioreactor that fosters the growth of microorganisms on a hydraulically fluidized bed of fine media. In this type of reactor, a fluid is passed through a granular solid material at velocities sufficient to suspend or fluidize the solid media.

In Envirogen FBR systems, media types include sand and activated carbon media that are manufactured to exacting specifications for hardness, shape, size, uniformity, density and impurity levels. The small fluidized media in the FBR provide an extremely large active surface area upon which microorganisms can grow while treating contaminants. A large biomass inventory is produced while maintaining thin films, reducing mass transfer limitations and offering high volumetric efficiency.

Envirogen manufactures both aerobic and anoxic FBR systems. Aerobic systems utilize air or oxygen for removal of organics. Anoxic FBR systems are the technology of choice for inorganic contaminants such as perchlorate, nitrate and selenium. Other distinguishing features of Envirogen FBRs include patented biomass control systems that are key to retaining media and steady-state operation and plug flow; custom molded parts; proprietary design of internal vessel components and proprietary and patented controls for chemical feed systems.

Base System Design

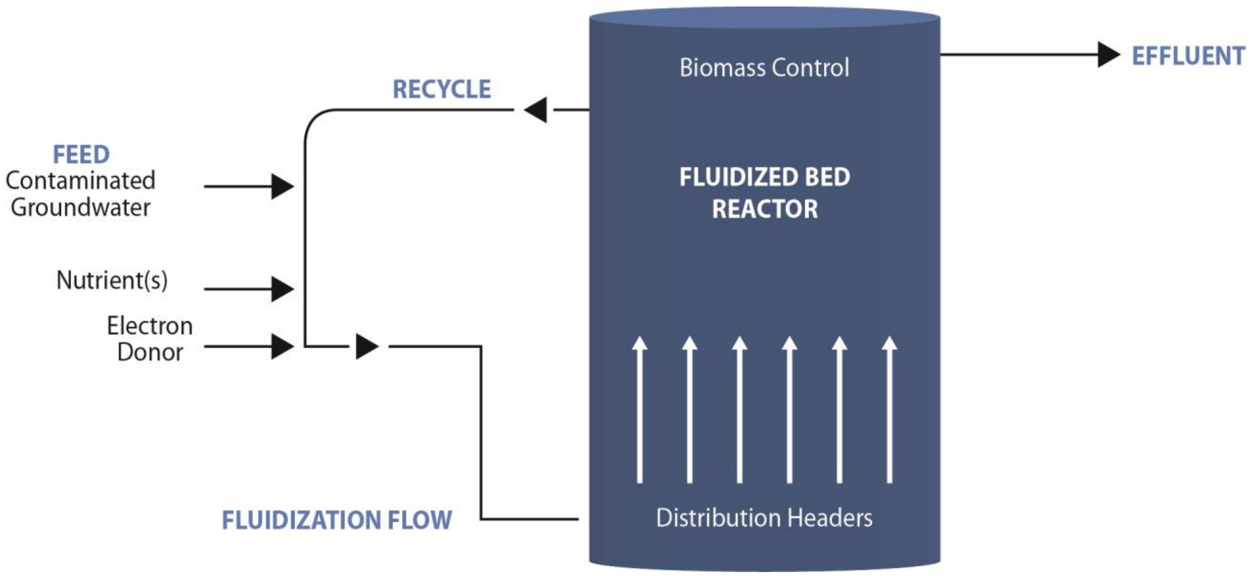
Envirogen FBR installations typically feature one or more vessels in single- or two-stage configurations, depending on influent water characteristics and discharge limits (Figure 3). A range of materials can be used for vessel construction, including stainless steel, fiberglass, lined-carbon steel or concrete. Prefabricated FBR vessels from 2- to 14-feet diameter and up to 30-feet in height are available – offering very deep beds in comparison to other fixed-film technology. This vertical orientation is one of the factors that contribute to the FBR's smaller footprint compared to packed bed reactors or other biological treatment systems. Field-fabricated concrete or metal vessels are also available for very large applications. Overall system packages are outfitted with fluidization pump(s), piping, valves, chemical feed pumps and controls that may be field assembled or pre-assembled based on client preferences. Most Envirogen FBR systems are equipped with programmable logic control and may be provided with a SCADA package, telemetry and motor controls options.

Figure 3: Envirogen FBR for Perchlorate Removal

System Operation

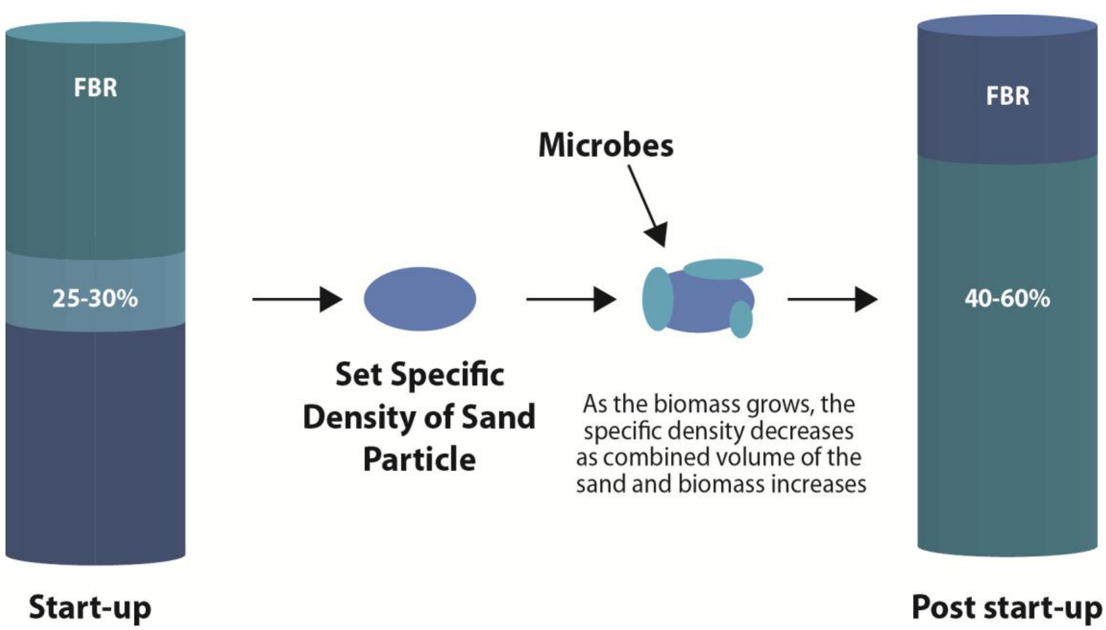
During start-up, the FBR is seeded with heterotrophic bacteria that are suited for nitrate and selenium removal (Figure 4). Electron donor materials and nutrients are pumped into the FBR to promote microbial growth.

Figure 4: Start-up of FBR system



Selenium-containing wastewater is pumped from a feed tank into the FBR in an upflow direction to suspend the media. As microorganisms grow on the media, the fluidized bed height expands (Figure 5).

Figure 5: Fluidization of FBR media



With time, a biofilm develops on the media surface. Nitrate and selenium reduction occur on this biofilm. Treated water from the FBR system is discharged to a downstream liquid/solids separation system where the biological solids and elemental selenium are separated. Thickened or dewatered bio-solids and elemental selenium are disposed.

One of the key features of operation is the technology used to fluidize the media bed and to uniformly distribute fluidization flow to the system. This is accomplished with the design and placement of the distribution nozzles and the sizing and arrangement of the header-lateral distributors. Uniformity of flow is critical to establishing steady-state plug flow conditions and the associated optimized performance.

Another key feature of these FBR systems is Envirogen's proprietary technology for biomass control. In all properly functioning biological systems some of the energy that is derived from the consumption of electron donor is used by the microbes for biomass growth. This results in the production of excess biomass or "yield" that must be removed from the bioreactor. In packed bed reactors this is accomplished with periodic backwash operations that remove large quantities of biomass using very high backwash rates – creating turbulence and shear to separate and wash out accumulated biomass.

In Envirogen's FBR systems biomass is removed in a steady-state manner with Envirogen's patented biomass control devices. These systems allow the FBR to operate with an optimized and consistently high biomass concentration, resulting in reliably high performance.

Limitations inherent in packed bed reactors render them incapable of handling high feed nitrate, selenium and suspended solids concentrations. This is due to problems of rapid plugging, nitrogen gas binding, channeling and high backwash requirements. With Envirogen's patented biomass controls, FBRs effectively handle feed loads that are greater than an order of magnitude higher then packed bed reactors.

Design Flexibility

The design flexibility available through utilization of the FBR with respect to vessel heights and configuration, materials of construction, modularity, Envirogen's patented bed height control, biomass control, proprietary chemical feed configurations and flexibility in electron donor selection all combine to produce improved performance, reduced capital and operating costs, and minimized excess biomass production and associated processing and disposal costs. Furthermore, this allows for the use of alternate electron donors based on considerations of availability, cost and performance.

Advantages of the Envirogen FBR technology for the coal mining industry

Extensive testing of the Envirogen FBR technology has shown that it consistently offers highly efficient removal of selenium from coal mining wastewaters at dramatically lower cost levels than competitive technologies. Three aspects of Envirogen FBR systems support this success:

- The high performance nature of FBR treatment technology
- Proprietary & patented features of Envirogen's FBR systems
- Envirogen's decades of experience with FBR in treating inorganic contaminants

The following issues highlight the Envirogen FBR systems' performance advantages for the coal mining industry:

Optimization of microorganism efficiency
One of the key advantages of FBR technology over packed bed reactors is the lack of 'channeling' that occurs in FBR systems. Packed bed reactors tend to develop preferential pathways for flow due to solids build-up in the bed and nitrogen gas binding caused by conversion of nitrate to nitrogen gas. This can cause pressure drop in the typical fixed-film system as well as short-circuiting or partial flow by-passing. These deviations from steady state plug flow conditions result in reduced performance. In the fluidized bed reactor, because of the even distribution of flow, a very high fraction of the biomass within the bioreactor is utilized – meaning increased treatment efficiency. These issues directly affect the hydraulic residence time (HRT) required and explain why the footprints for Envirogen FBR systems are so much smaller than competitive packed bed bioreactors for the treatment of nitrate and selenium.

Steady-state operation
Envirogen FBR systems are designed to be operated continuously – meaning they do not require cyclical backwash operations. Packed bed reactors require periodic backwashing to slough off excess microbial growth, to eliminate channeling and to remove nitrogen gas pockets that have built up during the running part of the packed bed reactor operating cycle. Frequency of backwashing is related to the loading of contaminants in the influent stream and requires large pumps and intermittent operation. In addition to increased energy costs, backwashing limits the flow of wastewater through the entire system since it is necessary to remove the backwashed unit from service, recover, clarify and recycle the dirty backwash suspension. Recycled backwash water adds to the feed loading and thereby limits net throughput.

Perhaps more importantly, the biomass in the system requires time to regrow following a backwash, further increasing the required HRT. With higher loadings of feed nitrate, selenium and/or suspended solids, the backwashing requirements can become so excessive as to render the packed bed bioreactor ineffective or completely impractical.

Improved overall water quality

Besides selenium and nitrate, another parameter that may be of concern is soluble biological oxygen demand (BOD) or chemical oxygen demand (COD). Mine run-off waters are generally very low in BOD and COD. However, discharge from biological systems treating for these contaminants can contain excess un-reacted electron donor, resulting in soluble BOD or COD in the bioreactor effluent. This will depend on the electron donor used and the quality of the biological contacting system, both of which affect the completeness of the reactions.

For example, some grades of molasses contain a substantial fraction of non-biodegradable or difficult to degrade compounds that will exit the bioreactor as soluble BOD and COD. Allowing for flexibility in the choice of the electron donor(s) to be used, especially as this relates to two-stage operation, can allow the system operator to control treated water BOD and COD. Additionally, the plug flow characteristics of the FBR tend to result in more complete bio-reactions and lower treated water concentrations.

Smaller overall footprint

FBR systems have a smaller site footprint than other biological treatment systems. The key contributors to this feature are the vertical orientation of the FBR vessels and the efficiency of treatment (lower HRTs). Treatment efficacy is affected by a high concentration of biomass and the tall beds. This smaller footprint has a dramatic effect on construction and installation costs and schedules.

Dramatically lower hydraulic residence times

Despite having a smaller overall footprint, field studies have shown that FBR systems can achieve required performance with dramatically shorter HRTs than packed bed systems. This is due primarily to deep beds and steady-state plug flow operation. HRTs for typical FBR systems used in selenium treatment for coal mining operations are 1/3 to 1/10 those required for packed bed reactors.

Electron donor options

Envirogen offers the ability to customize electron donor materials based on decades of experience with the FBR technology. Key issues that are considered include treatment efficacy, overall water quality, operational ease of use, availability and cost. Table 3 shows a typical comparison of electron donor usage, costs and treated water quality as a function of alternate electron donors selection in a two-stage FBR system treating selenium and nitrate.

Table 3: Electron Donors Comparative Evaluation

	Molasses	MicroCg	1st stage Methanol 2nd stage MicroCg	1st stage Methanol 2nd stage Molasses
Usage L/day	4260	3135	1362 (1st stage) 627 (2nd stage)	1362 (1st stage) 852 (2nd stage)
US$/L delivered	0.373	0.528	0.396 (methanol) 0.528 (molasses)	0.396 (methanol) 0.373 (molasses)
US$/yr	580,000	604,000	317,700	312,900
FBR Effluent TSS mg/L	30	25	22.6	23.6
FBR Effluent filtered COD mg/L	100	50	20	30

Robustness of the system

Envirogen FBR systems have a proven history over the past 30 years, operating effectively over a wide range of feed flow rates and influent types. The systems are tolerant of high feed concentrations of total suspended solids (TSS) and metals. In addition, these systems have the ability to recover quickly from upsets such as power outages and loss of chemical feeds.

Modularity & extreme environment performance

In many cases, Envirogen FBR systems can be pre-fabricated for delivery to a coal mining treatment site. This contrasts with packed bed reactor systems which, because of their large size, are usually built-in-place. FBR systems may be supplied as prefabricated modules and associated equipment can be containerized in insulated and heated containers, per client requirements. This allows for ease of transportation and rapid installation – even in bad weather conditions.

Generally speaking, it is expected that biological treatment systems suffer loss of efficiency when used in cold weather environments (> 15^{o} C). Recent tests by Envirogen on selenium-containing wastewater at a coal mining site showed that the FBR system performed effectively at influent water temperatures down to 4o C.

Lower costs

One of the major advantages of employing an FBR in a selenium treatment application is a considerable cost advantage in system design and installation compared with other commercially available technologies. This is primarily due to smaller system footprints as well as the ability to manage issues such as suspended solids and waste disposal in a much more effective fashion, over a broad range of influent flow rates. A recent third-party analysis performed for the North American Mining Council showed that initial capital costs for an FBR system can be 1/3 or less the cost of a packed bed reactor system designed for similar treatment requirements.

Technology track record

Envirogen is an industry leader in the use of bioreactor technology, with over 150 systems installed in the United States. Envirogen FBRs have been used in similar reductive applications for more than 10 years in applications such as perchlorate and nitrate, where low levels (<4 ppb) are consistently achieved at high flows (6,000 gpm) and in high TDS streams. The same anoxic operating regime is used for selenium installations.

Recently, Envirogen FBR technology demonstrated the ability to achieve <5 ppb selenium over a 10-month period in treating mining leachate at a U.S.-based coal mining site. Competitive trials run at the same site indicated that Envirogen FBR systems were the ‘technology of choice’ for reliability and cost-effectiveness. Summary results for this trial are shown in Table 4.

Table 4: Operating results from 10-month coal mining trial (USA)

Constituent	Feed Concentration	Effluent Concentration
Dissolved Selenium	22 to 27 ppb Se	4.7 ppb maximum filtered Se
Nitrate - Nitrogen as N	6 to 8 mg/L	
Dissolved Oxygen	11 to 13 mg/L	
pH	7 to 9	

Full Scale System Design Summary

Parameter	Value
Flow	15,261 m^3/day (2,800 gpm)
Design Temperature	10°C
Number of Fluidized Bed Bioreactor Vessels (FBRs)	3
Size of Vessels	14 ft Diameter X 30 ft High
Design Hydraulic Residence Time	26.8 minutes

A four-month trial was also run at a Canadian coal mine – examining Envirogen FBR technology in the presence of high nitrate levels and at colder influent water temperatures. Table 5 shows results of this trial.

Table 5: Operating results from 4-month coal mining trial (Canada)

Constituent	Feed Concentration	Effluent Concentration
Dissolved Selenium	200 to 500 ppb Se	10 ppb maximum filtered Se
Nitrate - Nitrogen as N	15 to 40 mg/L	
Dissolved Oxygen	11 to 13 mg/L	
pH	7 to 8	

Full Scale System Design Summary

Parameter	Value
Flow	15,261 m³/day (2,800 gpm)
Design Temperature	4°C
Number of Fluidized Bed Bioreactor Vessels (FBRs)	6 in 2 stages
Size of Vessels	14 ft Diameter X 28 to 30 ft High
Design Hydraulic Residence Time	56.9 minutes

Envirogen Lifecycle Cost Assurance Programs

In any environmental installation the most important – and often the most expensive – contributors to a treatment program are the performance and operating costs over its 10- to 20-year life. Developed to support all FBR installations, Envirogen Lifecycle Cost Assurance Programs are designed to ensure performance, to deliver low lifecycle costs and to guarantee the life of the assets. Elements of an Envirogen Lifecycle Cost Assurance Program range from basic O&M support services or the assignment of Envirogen supervisory and management personnel to comprehensive operations programs wherein Envirogen becomes a single line item on the operating budget for the system in question. They can even include financing options for system design, construction and installation. Envirogen Lifecycle Cost Assurance Programs are typically 10 to 20 years or more, with the length generally following the anticipated life of the system in question. Guarantees are provided for system performance, operating cost components, asset life and overall lifecycle cost. In addition, Envirogen can also provide guarantees for cost elements such as utility consumption and chemical usage for the life of the contract. Through the resources and experience that Envirogen Technologies brings to design, fabrication, installation, and long-term operation, significant value can be realized via an Envirogen Lifecycle Cost Assurance Program. These include:

- Predictable and guaranteed costs for the lifetime of the asset
- Guaranteed performance, repair and maintenance costs, and regulatory compliance

- Opportunities for cost reduction through process improvements, capital improvement and energy/chemical savings
- Risk protection via performance and cost guarantees
- Improved budget management (avoid unbudgeted cost excursions)
- Cost-effective access to industry specialists
- Continual process improvements
- Better utilization of capital
- A comprehensive EH&S Program

Conclusions

With selenium regulations having an increasing presence in the coal mining industry landscape, efficient, cost-effective treatment is critical to the growth of the industry. Envirogen FBR technology offers the industry's best, most broadly applicable solution to selenium treatment in systems that are field-tested and ready for design and deployment. The design of Envirogen's FBR systems ensures that selenium removal targets can be consistently and reliably met – at costs substantially below other commercially available competitive technology. The experience of the Envirogen team with FBR technology for decades ensures that the goals for a cost-effective selenium treatment program can be met today and in the future.