

Chapter 6

Biological treatment technologies



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6.1 INTRODUCTION

Selenium contaminated waters are produced by various industrial activities such as mining (coal, hard rock, uranium and phosphate), refineries (metal and oil), power generation (coalfired power plants), and agriculture (irrigation waters and selenium fortification) (Chapman *et al.*, 2010). Selenium can also be present in municipal wastewater, due to inflow and infiltration of groundwater into sewers emanating from alluvium or sedimentary deposits that are high in selenium (Pontarolo *et al.*, 2017).

Background concentrations of Se in uncontaminated surface waters are generally below 1 µg/L (Seiler *et al.*, 1965), but in areas where the weathering and erosion of seleniferous soils is augmented by anthropogenic activities, environmental Se concentrations have been shown to be significantly elevated. Elevated intake of selenium, particularly in oviparous animals such as predatory fish and waterfowl, can result in teratogenic effects on entire populations in contaminated ecosystems (Janz *et al.*, 2010). The maximum permissible concentration of Se in the aquatic environment is, on average, 10 times lower than that in drinking water, at values of between 1 to 5 µg/L and 10 to 50 µg/L, respectively (Lemly, 2007). While overall, guidelines for Se in freshwater for aquatic life are very low level, they do vary by country.

An excellent review of global selenium regulations by Kumkrong *et al.* (2018) suggests Se is only regulated under Directive 98/83/EEC on the quality of water

intended for human consumption in the EU (European Union) which controls the maximum level at 10 µg/L. This same reference suggests there is little English information available relating to standards for Se in waters in Asia, though the drinking water standard in many Asian countries is set at 10 µg/L. This is despite documented negative impacts on fish and aquatic birds in locations around the world (Lemly, 2004).

The US and Canada have some of the world's most stringent aquatic water quality guidelines limiting the concentration of Se in fresh water to protect aquatic life at low levels of between 1 and 5 µg/L. Increasing public awareness in specific geographies in North America and progressively more stringent guidelines have increased demand for selenium management and treatment. Coincidentally, most full-scale treatment facilities are located in North America.

Biological treatment has been identified by the United States Environmental Protection Agency (US EPA) and others (CH2M Hill, 2010) as the best available technology (BAT) for selenium reduction to achieve ultra-low effluent selenium concentrations of less than 10 µg/L. A recent review by Golder (2020) for the North American Metals Council – Selenium Working Group (NAMC-SWG) suggests that approximately 30 full-scale selenium treatment systems with capacities between 410 m³/d and 15,260 m³/d were constructed in North America between 2007 and 2018, 70% of which rely on biological treatment. A recent review by Simm (2018) lists the limited number of vendors with full-scale experience, the high capital and operating and maintenance costs of installing these systems, and required system optimization as key issues to be addressed with biological treatment technologies.

This chapter provides an overview of currently available selenium bioremediation technologies including their advantages and disadvantages and summarizes current challenges with the technology based upon recently implemented projects. The primary focus of this review will be on technologies currently applied at full scale. Finally, a summary of fundamental and applied research needs will be identified to improve system performance and reliability.

6.2 PRINCIPLES OF SELENIUM BIOREMEDIATION IN BIOREACTOR SYSTEMS

A general overview of the principles of bioremediation in bioreactor systems is provided here for completeness. The reader is referred to Chapter 3 and the excellent review by Nancharaiyah and Lens (2015a, 2015b) for a more detailed treatise.

In industrial and municipal wastewaters, selenium is typically available in the form of the selenium oxyanions selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}). Both are toxic to living systems, although SeO_3^{2-} is potentially more toxic than SeO_4^{2-} (Nancharaiyah & Lens, 2015a, 2015b).

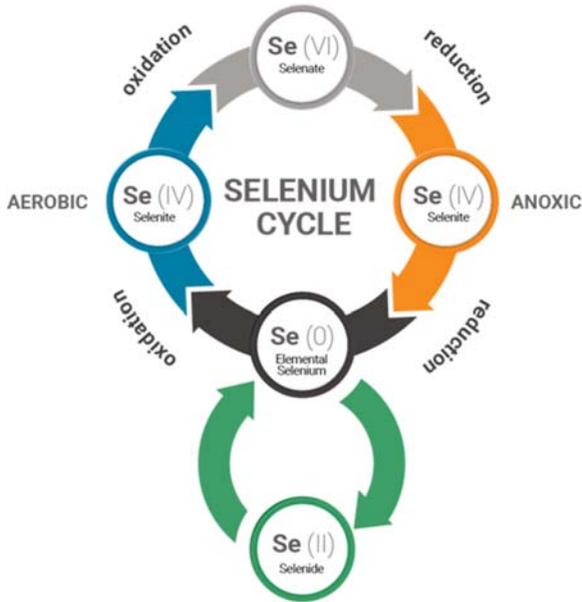


Figure 6.1 Bioconversions of Se compounds in the natural selenium cycle (Source: adapted from Simm, 2018).

Selenium bioremediation is based upon reactions carried out in nature as part of the global selenium cycle first identified by Shrift (1964). Natural bacteria and archaea readily metabolize selenium and are involved in a range of metabolic functions including assimilation, methylation, detoxification and anaerobic respiration. The reactions of primary importance in biological selenium removal systems are presented in Figure 6.1. The figure does not include all known reactions such as the aerobic conversion of Se(VI) to Se(IV) and to Se(0).

Bioremediation of selenate can occur by two processes: assimilatory and dissimilatory reduction, the latter being more common in biological treatment. In assimilatory reduction, SeO_4^{2-} is taken up and chemically reduced by bacteria and subsequently used in the synthesis of selenium-containing amino acids, such as selenomethionine and selenocysteine, both of which are classified as organo-selenium compounds (Nancharaiyah & Lens, 2015a, 2015b).

Because of the small amounts of SeO_4^{2-} required in the formation of selenomethionine and selenocysteine, assimilatory reduction is not a major process in wastewater selenium treatment. The basis of virtually all biological Se removal techniques is the dissimilatory reduction pathway in which inorganic soluble selenium oxyanions (SeO_4^{2-} and SeO_3^{2-}) are reduced to inorganic, insoluble and less toxic biogenic elemental selenium – Se^0 – with temperature,

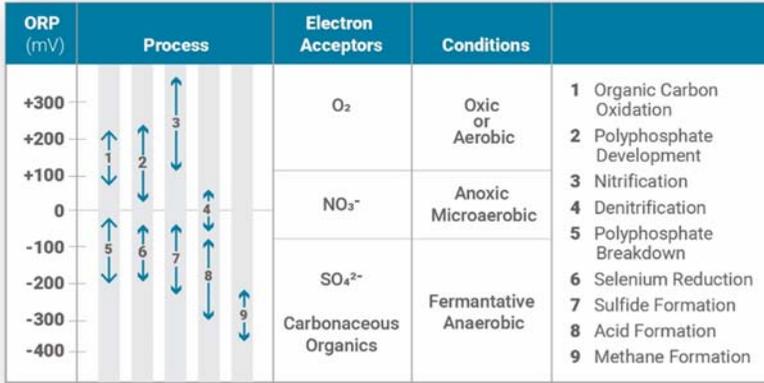


Figure 6.2 Typical ORP ranges for specific biological treatment objectives (Source: Electrical Power Research Institute, EPRI, 2009).

pH, and electron donor concentrations being among the controlling factors (Nancharaiyah & Lens, 2015a, 2015b). Elemental selenium is removed from a biological treatment system with the treatment process residuals in an active treatment process.

Selenate can be reduced to selenite and both selenate and selenite can be reduced to elemental selenium or alkyl selenides. Selenate reduction is associated with energy production in bacteria whereas selenite reduction can be associated with either energy production or selenite detoxification. Although reduction of SeO₄²⁻ to elemental selenium was shown to be an environmentally significant process, only a few SeO₃²⁻ respiring bacteria have been isolated (Nancharaiyah & Lens, 2015a, 2015b). Certain SeO₄²⁻ reducing bacteria have been shown to perform dissimilatory SeO₃²⁻ reduction as well.

Elemental selenium can be reduced further microbiologically to soluble selenide, which in combination with metal ions forms insoluble metal selenides. Selenide can also be emitted as the volatile and highly reactive H₂Se gas, but this is spontaneously and rapidly oxidized to elemental selenium in the presence of oxygen. Organo-selenium and methylated selenium species also contain selenide.

Oxidation of elemental selenium and selenide back to selenite or selenate by selenium oxidizing bacteria completes the selenium cycle. In general, the oxidation rates are 3 to 4 orders of magnitude lower than those in the reductive part of the selenium cycle.

Numerous microorganisms capable of reducing selenium oxyanions to Se⁰ have been found in biological wastewater treatment processes such as activated sludge, denitrifying sludge, as well as sulfate-reducing and methanogenic sludge (Soda et al., 2011). Nancharaiyah and Lens (2015a, 2015b) have indicated that not only

are selenate reducing bacteria phylogenetically diverse, but they are capable of coupling growth to a wide range of electron acceptors.

Nitrates compete as an electron acceptor with selenate and selenite reduction. Therefore, nitrates need to be essentially removed for complete reduction of selenium. The presence and/or absence of specific electron acceptors is typically reflected in the bulk solution oxidation-reduction potential (ORP). [Figure 6.2](#) suggests selenate and selenite reduction take place at ORP values of between -50 mV and -200 mV. Sulfate can also begin to compete with the selenium oxyanions as an electron donor, but at the lower end of the optimal ORP range for selenium reduction.

6.3 HISTORY AND CURRENT PRACTICE OF SELENIUM BIOREMEDIATION

Selenium bioremediation technologies include active, passive, and *in situ* technologies with most biological treatment processes relying on the anaerobic-anoxic reduction processes described in Section 6.2.

The North American Metals Council – Selenium Working Group (NAMC-SWG) has commissioned several state-of-the-art reviews of selenium removal technology over the last 10 years ([CH2M Hill, 2010, 2013](#); [Golder, 2020](#)). The NAMC-SWG comprises professionals from industry and consulting engaged in sharing and commissioning technical research on issues pertaining to ecological and human health effects, regulation, and water treatment of selenium in the context of industrial discharges. The [Golder \(2020\)](#) study indicated that 30 full-scale selenium treatment systems were installed predominantly in North America between 2007 and 2018 with design flows between 410 m³/d and $15,260$ m³/d with biological systems accounting for 70% of the systems surveyed.

Several promising selenium treatment technologies have been studied but have not been implemented extensively at full scale for selenium removal. These include upflow anaerobic sludge blanket (UASB), the hydrogen-based hollow fibre biofilm reactor (MBfR), anaerobic membrane bioreactor (MBR), and the hybrid electro-biochemical reactor. These process concepts will be presented here but will not be discussed in detail.

Implementation of suspended growth systems for selenium bioremediation at full-scale are not widespread. The iBIO[®] process developed by Degremont is a suspended growth system that has been applied on wet flue gas desulfurization (WFGD) wastewaters and is discussed in Section 6.5. There are very few studies on the use of activated sludge for treatment of selenium wastewaters ([Mal et al., 2017](#)). These authors have also suggested the effect of alternating aerobic – anoxic or anaerobic conditions on selenite bioreduction, whereas the fate of biogenic selenium nanoparticles in the activated sludge wastewater treatment system are unknown.

Passive treatment options which include wetlands, biochemical reactors (BCRs), gravel bed reactors, and submerged rock fills (SRFs) are receiving increased attention particularly by the North American mining industry. This is primarily a result of the high capital and operation and maintenance (O&M) costs associated with active treatment.

Full-scale biological selenium treatment practice is currently dominated by attached growth biofilm reactors, particularly packed beds, fluidized bed reactors (FBRs), and a combination of expanded bed biofilm reactors (EBBRs)-packed bed reactors. These reactor types dominate in the power and mining industries. The reason for this is partly historical as indicated below.

There are four primary vendors in the active treatment market in North America: Suez, Frontier, Envirogen, and Veolia (Simm, 2018). These four vendors supply the packed bed, expanded bed-packed bed, fluidized bed, and moving bed biofilm reactor (MBBR) processes for biological selenium removal, respectively. The key project milestones in the development of biological selenium removal at full scale in North America between 1999 and 2018 are presented in Figure 6.3.

The ABMet[®] process was developed in the late 1990s by Applied Biosciences out of Utah (USA). ABMet[®] is a packed bed fixed film process for selenium reduction. The process was employed at Kennecott Copper in 2000 and then at the Landusky Mine in Montana in 2002. In 2006, Applied Biosciences was acquired by Zenon (which eventually was acquired by GE). Zenon applied for a patent for an apparatus and method of treating flue gas desulfurization (FGD) blowdown or similar liquids in July 2006 (US Patent No. US 7,790,034 B2). GE Water & Process Technologies, a unit of General Electric Company, completed its acquisition of Zenon that same year. The Zenon patent included the ABMet[®] process and indicated it could be operated in either an upflow or downflow configuration. GE Water & Process Technologies was subsequently purchased by Suez in 2017.

The first ABMet[®] projects for FGD blowdown commenced at Duke Energy's Roxboro and Mayo Power Generating Stations in 2006 and 2007, respectively. Interestingly, the original design for the Roxboro system was based upon an upflow configuration which was changed to a downflow configuration during the planning process (Kennedy, personal communications). The ABMet[®] installations at Roxboro and Mayo were both reinforced concrete constructions with equal volume for the first and second stage reactors and using first stage effluent for system backwash. These were followed by ABMet[®] facilities at Bellows Creek and Allen stations (planned with downflow filters and similar configuration to Roxboro and Mayo), American Electrical Power's Mountaineer Station (planned with downflow filters and similar configuration to the previous reactors but adding ORP and pH monitoring and using second stage effluent for backwash), and finally the most recent upgrade at Roxboro station which was similar to Mountaineer in many respects, but used a fiberglass tank construction (Kennedy, personal communications).

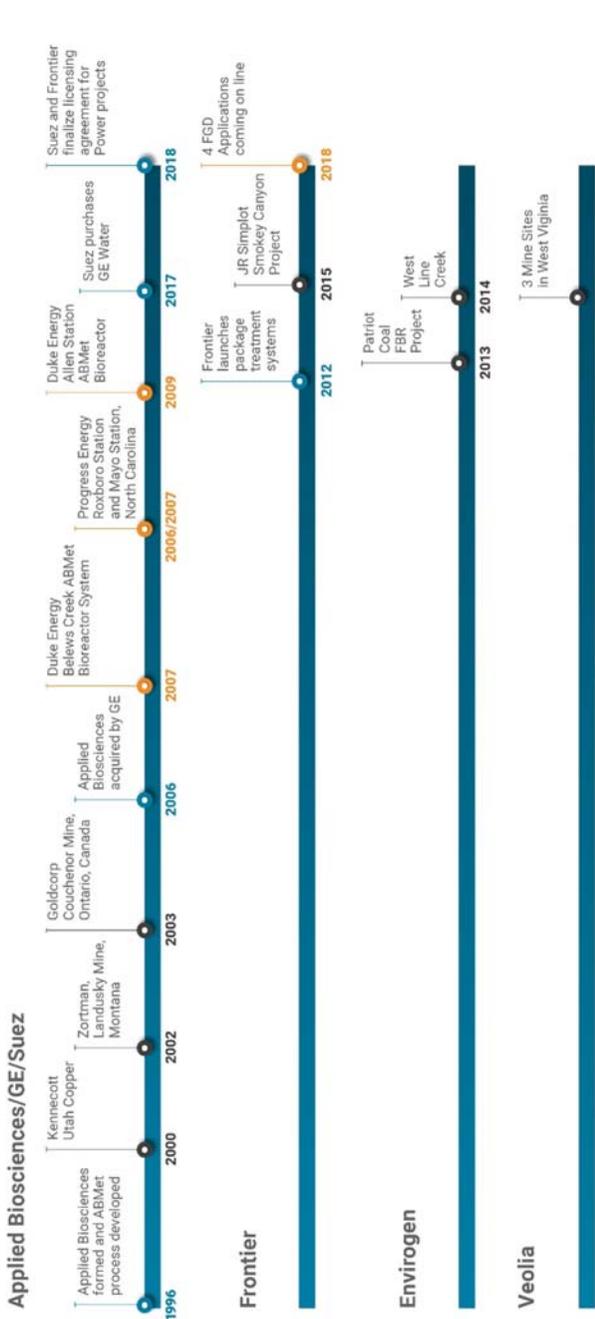


Figure 6.3 Key project milestones in the development of biological selenium treatment at full scale in North America (Simm, 2018).

In 2012, one of the original founders of Applied Biosciences left GE Water & Process and started Frontier Water Systems which specializes in modular biological selenium treatment systems. The Frontier system is based upon a two-stage reactor process with the first stage operated in an upflow mode and the second stage operated as a downflow packed bed. Evoqua acquired a majority stake in Frontier Water Systems in 2019.

The key features of each of the major fixed film processes used for selenium bioremediation are discussed in the following section.

6.4 ATTACHED BIOFILM REACTORS

Attached growth reactors rely on biochemical transformations performed by a biofilm on a surface. Fundamentally, attached growth systems are applied to wastewater where the parameters of primary interest are relatively dilute and variable in concentration. The most widely used processes are packed bed, combined expanded bed-packed bed reactors, and fluidized bed bioreactors. Moving bed biofilm reactors (MBBRs) have been used for selenium bioremediation at full scale, but to a lesser degree to date.

6.4.1 Packed bed reactor

Interest in packed bed reactors stems from the high biomass concentrations that can be achieved relative to suspended growth processes for the same solids retention time (SRT). This results in shorter hydraulic retention time (HRT) and more compact system designs. The primary components of a packed bed reactor include the reactor vessel, support media for biofilm growth, influent distribution system and effluent withdrawal system. Some of the advantages and disadvantages of the packed bed reactor system are summarized in [Table 6.2](#).

The ABMet[®] packed bed reactor system provided by Suez has been used for simultaneous nitrate and selenium removal since 2000. ABMet[®] stands for advanced biological metals removal process. A simplified schematic of an ABMet[®] process flowsheet is presented in [Figure 6.4](#).

There were 12 ABMet[®] plants installed around the world as of September 2018. A summary of full-scale ABMet[®] plants is presented in [Table 6.1](#). Most ABMet[®] applications are in the power industry treating blowdown from flue gas desulfurization (FGD) systems.

Suez has completed more than 20 pilots of the ABMet[®] on FGD blowdown in addition to the full-scale facilities presented in [Table 6.1](#) (this is as of September 2018).

A typical ABMet[®] process flowsheet includes pre-treatment, nutrient addition, two-stage ABMet[®] tanks with intermediate break tank between stages 1 and 2, backwash tank, backwash pumps and effluent storage tank. The process flowsheet can include post-treatment operations depending upon the application and effluent requirements. The need for pre-treatment will depend upon influent

Table 6.2 Advantages and disadvantages of ABMet[®] process.

| Advantages | Potential Disadvantages |
|---|--|
| <ul style="list-style-type: none"> • Longest track record and most full-scale selenium treatment applications (as of September 2018). • May not need downstream solids removal depending on effluent Se requirements. • Longer HRT and lower ORP conditions (less than -350 mV) could potentially provide more complete Se reduction. • Likely most cost-effective approach to large custom-built systems. | <ul style="list-style-type: none"> • Low tolerance for influent TSS levels >50 mg/L. • Long HRT and larger bioreactors than other technologies. • Potential short-circuiting from solids channelling and gas accumulation. • Lower tolerance for higher influent nitrate loadings than other technologies (example FBR). |

the biofilm, and/or remove gases entrained in the media. Backwashing is used to remove accumulated solids and slough biomass from the system in a controlled manner on a periodic basis. The backwash flow rates are typically 4 to 5 times the design forward flow rate for 10- to 20-minute durations to remove TSS and biomass and lift and separate the media. Backwash solids are directed to the backwash tank for settling. Settled solids are directed to further thickening and ultimate dewatering. The backwash supernatant is directed back to the head end of the process. Backwashing is application dependent but is typically done every 2 to 6 weeks.

Degassing operations are typically done once per day to once per week. Degassing requires flow to be stopped to the treatment unit, followed by a back pulse of water supplied by the backwash system at a flow rate in the order of $163\text{--}570$ L/m²/min and a duration of approximately 1 to 10 minutes (EPRI, 2019). Degassing typically is required when there is reduced flow through the bed, a higher head loss, or by a routine schedule established by operational experience.

The ABMet[®] system includes a provision for nutrient addition upstream of both the first and second stage reactors. The original systems used molasses as a carbon source. However, later systems (Site 8 in Table 6.1) use alternative carbon sources such as acetate.

The key design criteria for packed bed reactors in addition to influent TSS are temperature, influent nitrate-nitrogen and empty bed contact time (EBCT). Influent temperature is a key design consideration particularly for industrial applications (potentially too hot for power or too cold for mining applications). Empty bed contact time (EBCT) is defined as the time required for the influent flow to displace the equivalent volume of media in the reactor. The design EBCT for each packed bed reactor currently deployed for FGD wastewater is between 4 and 8 hours or 8 to 16 hours total, respectively, as two reactors in series are used (EPRI, 2019).

The majority of wastewaters treated via packed bed reactors contain a mixture of nitrates, sulfates, and selenium oxyanions. Nitrate is typically present in the parts per million (ppm) range whereas selenium is present in the parts per billion (ppb) range. The majority of the influent nitrate-nitrogen must be reduced in order to get good selenium reduction. Nitrate reduction is typically responsible for the majority of the biomass production in the system with higher influent nitrate concentrations resulting in more biomass and more gaseous nitrogen production with the associated increase in backwash and degassing frequencies.

Packed bed reactors do not deal with high influent nitrate concentrations as well as other reactor configurations. EPRI (2019) has suggested influent nitrate concentrations in the feed water are ideally less than 25 mg/L for a packed bed. Higher influent concentrations may require pre-denitrification or an alternative process selection. Typical applied mass loading of nitrate-nitrogen is in the order of 0.32 to 3.2 kg/d/m³ of media, but additional volume may be required for reaction zones for dissolved oxygen utilization and selenium reduction (EPRI, 2019).

6.4.2 Fluidized bed reactor

A fluidized bed reactor (FBR) is one in which the biofilm grows attached to small carrier particles or media that remain suspended in the fluid. The FBRs are configured so that water flows upward through a vessel containing the media (typically sand or GAC) to promote media fluidization. The velocity of the water flowing upward is typically fixed such that the media bed is expanded by 50% to 70% of the resting volume. Most FBRs are two-phase systems containing only water and bioparticles. Three-phase systems allow for the incorporation of a gas phase. Denitrifying systems can actually be considered as two-phase systems provided the gas flow rate is relatively small compared to the liquid flow (Grady *et al.*, 1999).

The advantages and disadvantages of the FBR system for selenium removal are summarized in Table 6.3.

Table 6.3 Advantages and disadvantages of FBR process.

| Advantages | Potential Disadvantages |
|---|--|
| <ul style="list-style-type: none"> • Ability to deal with higher influent TSS than packed bed. • Ability to deal with higher influent nitrate loadings than packed bed. • Shorter retention time than packed bed and smaller reactor sizes. • Cost effective for custom built applications. | <ul style="list-style-type: none"> • Downstream solids removal required. • No full-scale track record on power applications like FGD. • Fewer full-scale operations on selenium removal than either packed bed or combined expanded bed and packed bed configuration. |

The main advantage of FBRs relative to other attached growth bioreactors is the small size of the carrier particles which provide a very large surface area for biomass growth. This high specific surface area allows for the maintenance of very high biomass concentrations resulting in shorter hydraulic retention times (HRTs), of minutes, relative to other treatment processes. Periodic deep bed cleaning of the media ensures uniform biofilm and elimination of excess biomass growth, which may cause mounding or poor fluidization of media within the system leading to poor mass transfer. This is typically accomplished via daily automated air lift sparging and periodically with a deep bed hydraulic eductor-based solids separation system or air sparging apparatus.

FBR staging should be considered if the parameters degraded at higher ORP conditions (e.g., oxygen, nitrate) are 15 to 20 times higher in concentration than the other parameters (such as selenium). Staging, in this case, would provide removal of oxygen and nitrate in the first stage, followed by treatment of selenium in the second stage. If a large reaction zone is required, sequential systems may offer a more energy-efficient alternative to a taller or wider system (EPRI, 2019).

The primary design parameters for the FBR include minimum recirculation rate, influent temperature, influent HRT, and TSS. The typical HRT in an Envirogen FBR reactor is 30 to 60 minutes for example compared to the 4 to 8 hours required for a packed bed reactor. Although it is less sensitive to influent TSS than a packed bed the FBR generally cannot tolerate TSS levels greater than 100 mg/L on average. An FBR will typically require a post-treatment solids removal process to meet a low effluent selenium concentration.

The FBR system provided by Envirogen Technologies Inc. uses fine sand and/or activated carbon as the carrier particles. Selenium-containing wastewater is pumped into the FBR in an upflow direction. A recirculation line returns flow to the suction of the influent pump. The combined influent plus recirculation flow is controlled to maintain carrier particle fluidization. The Envirogen FBR system is typically based upon a dual stage design using sand as the carrier particle in the first stage and a GAC carrier in the second stage. The bulk of the denitrification and some of the conversion of selenate to selenite occurs in the Stage 1 reactor. The remaining selenium conversion to elemental selenium occurs in Stage 2. A simple schematic of the Envirogen system is presented as [Figure 6.5](#).

There were two full-scale Envirogen FBR systems installed for biological selenium removal as of September 2018. Both systems were installed to treat mine impacted water. The first system was installed at Patriot Coal in the United States in 2013. The second system was installed at Teck Coal's West Line Creek (WLC) metallurgical coal operations in the Elk Valley of British Columbia in 2014.

[McKevitt \(2019\)](#) presented information on the West Line Creek (WLC) FBR facility at the Metal Leaching/Acid Rock Drainage Workshop in Vancouver in December 2019. The two-stage FBR system includes a ballasted sand clarifier (BSC), moving bed biofilm reactor (MBBR), and sand filtration for post

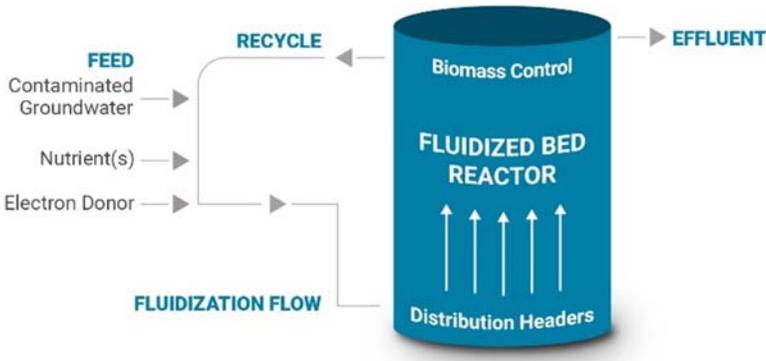


Figure 6.5 Simplified process schematic for fluidized bed reactor (Source: adapted from Simm, 2018).

treatment. The BSC and sand filtration units are required primarily for effluent solids and selenium control. This contrasts with a typical packed bed reactor system that can be operated with minimal, if any, post treatment processing depending on the effluent limits, given the packed bed acts as a filter.

Patterson (2017) presented the details of a two-stage ABMet[®] system treating mine impacted water in North Eastern British Columbia and with similar effluent TSS and selenium limits to WLC. The ABMet[®] system is able to meet these limits without post treatment downstream of the second stage packed bed.

6.4.3 Combination of expanded bed and packed bed reactor configuration

A hybrid system, using an expanded bed biofilm reactor (EBBR) and packed bed can potentially offer advantages over either of the packed bed or FBR. This system takes advantage of the high mass transfer capability of the EBBR and solids capturing and biodegradation capacity of the packed bed. An EBBR is fed from the bottom of the reactor similar to an FBR but without the recycle. The velocity of the water flowing upward is typically fixed such that the media bed is expanded by 25% to 40%. The advantages and disadvantages of the combined EBBC-packed bed system for selenium removal are summarized in Table 6.4.

Supplemental carbon is typically added both before and after the EBBR system to achieve reduction of nitrate and selenium. The system theory is based on having most of the denitrification and therefore gas formation occurring in the EBBR stage of the process, where it will not create short-circuiting through the reactor or require degassing. The packed bed stage of the system then does not need to be increased in size to allow for retention of this gas volume and the downtime associated with expelling this gas. Effluent solids from the EBBR are collected at the top of the packed bed. Cleaning of the EBBR may involve the use of periodic

Table 6.4 Advantages and disadvantages of combined EBBC-packed bed process.

| Advantages | Potential Disadvantages |
|---|--|
| <ul style="list-style-type: none"> • Ability to deal with higher influent TSS than packed bed. • Ability to deal with higher influent nitrate loadings than packed bed. • Shorter retention time than packed bed and smaller reactor sizes. • Cost effective for smaller capacities where modular reactor configuration can be used. • Large number of installations relative to other technologies. | <ul style="list-style-type: none"> • Cost effective capacity potentially constrained by size of largest modular unit. |

air scouring followed by a forward flush with the waste transferred along with the packed bed backwash water to solids handling.

The SeHAWK[®] system supplied by Frontier Water Systems supplies a combination of an EBBR and a packed bed system. The SeHAWK[®] system is based on a modular bioreactor design to reduce the overall capital cost. A simplified schematic of the SeHAWK[®] system is presented in Figure 6.6. Frontier had nine full-scale systems installed in mining applications and four full-scale FGD systems under construction as of September 2018 (Simm, 2018). The SeHAWK[®] systems at Duke Energy’s Marshall, Crystal River, and Miller Generating Stations were commissioned in 2019 (Kennedy & Henderson, 2020). All of the SeHAWK[®] installations as of September 2018 are located in North America.

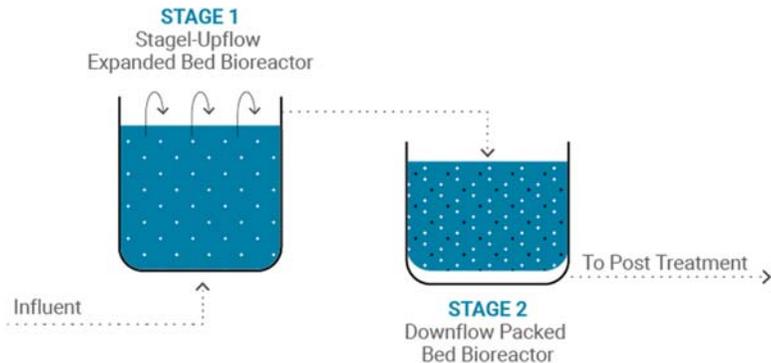


Figure 6.6 Simplified schematic of Frontier SeHawk[®] system (adapted from Pickett, 2020).

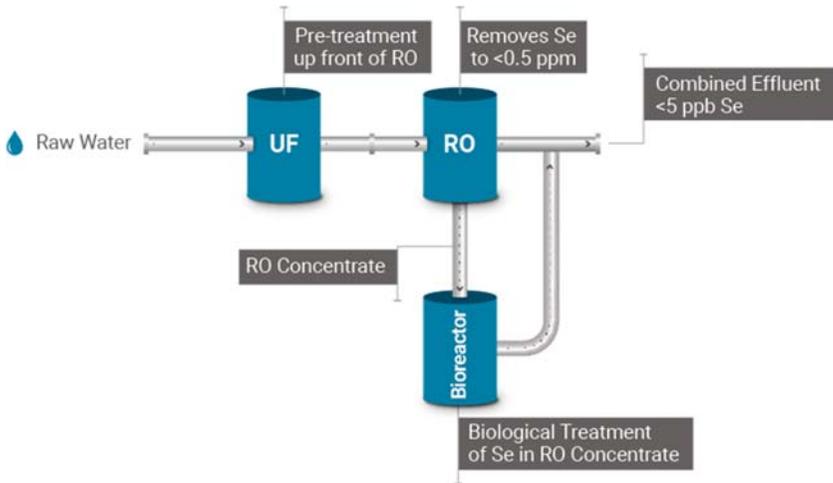


Figure 6.7 Se bioremediation with UF-RO concentration step (from [Simm, 2018](#)).

The cost effectiveness of the SeHAWK[®] system will likely be limited by available module size although Frontier continues to develop larger capacity modular units. In addition, they have employed ultrafiltration (UF) – reverse osmosis (RO) on some projects as a concentration step to reduce the size of the biological treatment step. A simplified process schematic of the UF-RO-Bioremediation configuration is presented in [Figure 6.7](#). This approach is limited by the total dissolved solids (TDS) concentration in the RO concentrate. High TDS concentrates could potentially precipitate on the bioreactor media, thus negatively impacting treatment efficacy. The approach illustrated in [Figure 6.7](#) was used for a selenium treatment system at a phosphate mine in Idaho and is described by [Witt *et al.* \(2019\)](#).

6.4.4 Moving bed biofilm reactor (MBBR)

An MBBR uses specifically designed plastic carrier elements for biofilm attachment that are neutrally buoyant (specific gravity less than/or equal to water). The carrier elements, or media, are held in suspension throughout the reactor by turbulent energy created by mechanical mixing or liquid recirculation, thereby resulting in improved mass transfer through a completely mixed regime. The medium takes up between one-third and two-thirds of the reactor volume. To allow treated water to pass through to the next treatment step while retaining the media in the reactor, a perforated plate or screen is installed on the effluent end of the reactor.

MBBRs combine the advantages of attached growth with many of the advantages of suspended growth systems. One advantage of the MBBR in selenium treatment applications is the ability to handle high influent solids levels. The completely

mixed media and continuous flow through process of an MBBR eliminates the need for backwashing to maintain throughput and performance because there is no potential for clogging or plugging. Solids separation will, however, be required following the MBBR to remove solids like reduced selenium particles. MBBR systems can suffer performance problems if precipitates form on the media hampering media neutral buoyancy. This is a particular concern with industrial applications with a high influent TDS.

Veolia is one of several suppliers of MBBR systems. Veolia had provided three MBBR systems for selenium removal in mine water treatment applications with capacities of between 757 litres/min and 3,028 litres/min, as of September 2018 (Simm, 2018). These systems have since been shut down and replaced with passive treatment systems having a lower operation and maintenance cost.

6.5 SUSPENDED GROWTH SYSTEMS

6.5.1 Biofloc systems

Suspended growth systems are distinctly different from attached growth systems in that biological growth is not supported by a substrate, but rather aggregated microorganisms are suspended freely within a water matrix, where they both naturally coagulate and flocculate into bioflocs. A method of solid-liquid separation, such as sedimentation or membrane filtration, is required to concentrate and remove the bioflocs from the treated effluent. Larger tanks are typically required for suspended growth systems relative to fixed film systems because of the higher biomass inventory carried by fixed film processes.

6.5.1.1 Continuous stirred tank system

Lau *et al.* (2012) reported on 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 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. The major components of the treatment system include physical-chemical treatment (pH adjustment and coagulant-polymer addition) and denitrification and selenium removal steps which consist of an anoxic reactor, anaerobic reactor, anaerobic clarifier and a gravity sand filter. 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. The authors reported the majority of the selenium treatment took place in the physical-chemical treatment stage (removal of selenite) with only 36% removal in the anaerobic biological treatment stage.

6.5.1.2 Activated sludge systems

EPRI (2019) indicated that there is currently only one commercial activated sludge system known to be operating in the United States that is treating wet flue gas desulfurization wastewater for nitrate and selenium removal.

Mal *et al.* (2017) showed that a sequencing batch reactor (SBR) can remove both selenate and ammonium via, respectively, bioreduction and partial nitrification-denitrification, and thus offers possibilities for treating selenium and ammonium contaminated effluents. These studies were conducted using a bench-scale treatment system.

Interest is growing in the fate of selenium at municipal wastewater treatment facilities, the majority of which use suspended growth systems. This is particularly true in areas with seleniferous soils. Pontarolo *et al.* (2017) conducted a two-year-long study of a biological nutrient removal (BNR) wastewater treatment plant in Colorado with pre-anoxic, anaerobic, anoxic, and aerobic zones. They reported a 49% and 65% reduction in influent recoverable selenium without and with poly-aluminium addition. No attempt was made to optimize selenium removal through the process.

6.5.1.3 Membrane bioreactors

Membrane bioreactors (MBRs) and in particular anaerobic MBRs have been piloted for combined nitrate and selenium reduction. EPRI piloted anaerobic MBR systems for treatment of WFGD blowdown. The results of studies conducted to date are considered by EPRI to be insightful but inconclusive (EPRI, 2019). To this author's knowledge, there are currently no full-scale anaerobic MBR systems in operation for selenium bioremediation.

6.5.2 Granular sludge systems

The upflow anaerobic sludge blanket (UASB) reactor uses self-immobilized small (3 to 5 mm) compact biofilms without carrier support. The environmental conditions created in the reactor result in the development of large, dense, readily settleable particles called granules, which allow for very high biomass concentrations. Wastewater flows from the bottom of the reactor to the top at a high enough velocity (typically 1 m/h) to keep the granules suspended without washout. The upper part of the bioreactor contains a gas/liquid separator to allow produced gases to be vented. UASB reactors are typically employed for high strength wastewaters.

The Adams Avenue Agricultural Drainage Research Centre in California performed a UASB pilot for selenium removal in 2004. The study reported between 58% and more than 90% selenium removal from an influent selenium concentration of approximately 500 µg/L (CH2M Hill, 2010). A number of operational issues were identified with the pilot including short circuiting caused by accumulation of gas within the pilot reactor that became trapped in the sludge,

long acclimation period (approximately 6 months), and variability in Se removal efficiency due to temperature sensitivity.

Tan *et al.* (2018a, 2018b) demonstrated that two reactor configurations employing different biomass retention systems (biofilm in biotrickling filter (BTF) and granules in UASB) result in a diverse removal performance when treating synthetic mine wastewater contaminated with SeO_4^{2-} , SO_4^{2-} and Ni^{2+} . The Se removal efficiency of the BTF biofilm was improved by $>70\%$ in the presence of SO_4^{2-} , whereas the Se removal performance of the UASB reactor was not affected. Nickel addition initially negatively impacted selenate reduction in both processes, although both processes eventually recovered with the UASB recovering sooner.

6.6 PASSIVE AND SEMI-PASSIVE BIOREACTOR SYSTEMS

The cost of constructing full-scale active selenium treatment facilities like those described in Section 6.4 can be significant. Active biological selenium removal plant projects can cost as much as \$3,963 to \$7,926 (USD) per cubic metre of capacity to construct (Simm, 2018). The high cost of active treatment has resulted in significant interest in passive treatment technologies for selenium bioremediation particularly in the mining industry.

A passive system can be considered one that does not require a deliberate continuous nutrient feed and can operate with minimal or no electrical equipment and operator attention (Golder, 2020). Passive treatment systems are often referred to as biochemical reactors (BCRs). These systems include an organic medium such as hay, wood chips, or sawdust. Semi-passive systems differ from passive systems in that they include the controlled addition of an electron donor and essential nutrients.

The advantages of passive and semi-passive treatment systems for selenium include low capital and operating cost relative to active treatment. The disadvantages include low hydraulic loading rates and large area requirements, lack of control over organic media degradation, and potential for high levels of residual nutrients. By design, passive treatment lacks precision in process control but can provide acceptable performance in certain applications.

The need to consistently meet ultra-low effluent selenium limits has increased interest in semi-passive treatment systems where electron donor and nutrient addition are more precisely controlled. Gravel bed reactors (GBRTM) and submerged rock fills (SRFs) are two examples.

One key issue associated with both passive and semi-passive treatment is the long-term fate of reduced selenium. These systems, unlike the active systems discussed previously, do not include controlled solids wasting to remove reduced selenium from the system. These systems remove selenium from the system for the remainder of the system life. This raises concern with respect to what happens

if there is an upset and/or in cases where the conditions develop such that the selenium could/can be remobilized?

6.6.1 Constructed wetlands

Constructed wetlands are designed and constructed to use vegetation, soils, and associated microbial activity to provide treatment. Wetlands create a layer of biological detritus that through decomposition creates an anoxic/anaerobic substrate rich in organic carbon. The aquatic environment supports the growth of bacteria supporting the reduction of selenium oxyanions as an energy source. According to [Kadlec and Wallace \(2009\)](#) selenium is reduced to elemental selenium as well as organic forms such as dimethyl selenide and dimethyl diselenide. The elemental selenium is sequestered in the wetland sediment.

Constructed wetlands include surface flow wetlands, subsurface flow wetlands, and variations on surface flow wetlands such as vertical downflow wetlands. Constructed wetlands are designed to allow inflow rates and water depths to be regulated which influences hydraulic and mass loading of the system as well as the hydraulic residence time. Typical retention times can be several days or more ([CH2M Hill, 2010](#)). The area requirements for municipal and industrial wastewaters can be 4 to 405 hectares and more than 4,000 hectares for large agricultural drainage flows ([CH2M Hill, 2010](#)).

The treatment effectiveness among surface flow wetlands varies widely. [Kadlec and Wallace \(2009\)](#) reported selenium removal rates of between 0% and 96% for 10 full-scale surface flow wetland sites. Constructed wetlands have been attempted at full scale at several power plants and interest appears to have waned due to performance issues ([Kennedy, Personal Communications](#)). Some have witnessed late Winter and early Spring selenium release for instance ([Kennedy, Personal Communications](#)).

Constructed wetlands may also pose an ecological risk to wildlife by exposure to accumulated constituents. Monitoring of ecological effects may be required particularly for selenium impacts on fish and other vertebrates. Practices to exclude wildlife, such as covering, can be appropriate.

6.6.2 Biochemical reactors

Biochemical reactors (BCRs) consist of a lined area that has been filled with organic substrate and can be considered as an enhancement to constructed wetlands. These systems are generally operated in a gravity downflow mode. An underdrain, overlain by gravel, is constructed at the bottom of the reactor. Water level control is installed to control the water level in the BCR. Organic substrates in the reactor include hay, manure, and woodchips. The organic media degrade over time and will ultimately need to be replaced. Anoxic/anaerobic conditions are created in the reactor and selenium reducing bacteria convert selenium oxyanions to elemental selenium. The effluent from a BCR will typically have elevated BOD

(biological oxygen demand) and will require further aerobic treatment. [CH2M Hill \(2010\)](#) present several BCR case studies with a range of selenium removal efficiencies. As indicated previously, these systems have lower capital and operation and maintenance costs than active treatment systems. However, the ability for these systems to consistently meet ultra-low selenium discharge limits is uncertain.

6.6.3 Gravel bed reactors

Gravel bed reactors (GBRTM) are referred to as a semi-passive treatment alternative ([Mancini *et al.*, 2019](#)). The GBRTM consists of an engineered bed of gravel/media through which water containing nutrients of concern is passed and treated. Electron donor(s) and nutrients are added to the water at the inlet of the GBRTM to promote the activity of selenium reducing bacteria, sequentially immobilizing the reduced selenium in the gravel bed. The top and bottom of the treatment zone are lined using synthetic membranes to prevent water loss/influx, creating hydraulic isolation from the surrounding environment. A schematic of a typical GBRTM is presented in [Figure 6.8](#).

[Mancini *et al.* \(2019\)](#) provide general performance information for two case studies treating water in an urban stream in California and mine impacted water at a coal mine in West Virginia. The influent selenium concentrations for the California and West Virginia applications were approximately 40 ppb and 30 ppb, respectively. Both systems are reported to reduce selenium to less than 5 ppb. These types of systems offer lower capital, operating and maintenance cost relative to active systems. The one concern with these types of systems is the long-term fate of sequestered selenium given there is no active control of solids wasting.

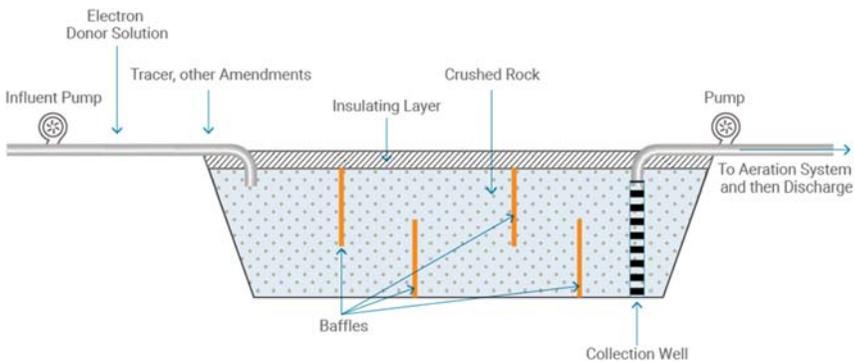


Figure 6.8 GBRTM main system components (figure from [Mancini *et al.*, 2019](#)).

6.6.4 Submerged rock fills in mining applications

Submerged Rock Fill (SRF) uses a backfilled mine pit as a bioreactor (Golder, 2020). Mine water and nutrients are injected into the backfill, then flow horizontally through the backfill, and the treated water is pumped out of the backfill for polishing treatment and discharge. Denitrification and selenium reduction occur in the backfill. The long-term fate of sequestered selenium is of concern with SRF as it is with GBRs.

One of the mining companies in British Columbia, Canada, has posted on the company website that they plan to expand their SRF for selenium bioremediation from 10 million to 20 million litres per day (Teck, 2020). The expanded facility will replace a previously planned active treatment system. The rationale for choosing the SRF over a tank based system includes: “SRFs can treat large volumes of water with less energy and with a smaller environmental footprint compared to tank-based facilities, SRFs are also quicker to build, less complex to operate, and have lower capital and operating costs”.

6.7 OTHER REACTOR TYPES

6.7.1 Fungal based bioreactors

Fungi are heterotrophic, eukaryotic and achlorophyllous organisms, which have the ability to secrete large amounts of enzymes and reductive proteins. Different fungal strains have shown their ability to degrade a wide range of environmental pollutants, from dyes to pharmaceutical compounds, heavy metals, trace organic contaminants and endocrine disrupting contaminants. Some researchers have investigated the potential of fungal based bioreactors for selenium bioremediation (Espinosa-Ortiz *et al.*, 2015, 2016; Negi *et al.*, 2020).

Espinosa-Ortiz *et al.* (2015) investigated the performance of a novel fungal bioreactor system containing pellets of *Phanerochaete chrysosporium*. The bioreactor was initially operated under batch conditions and then switched to continuous operation for 41 days. The reactor was fed with selenite at selenium and glucose loading rates of 10 mg Se L/d and 0.95 g glucose L/d, respectively. The reactor hydraulic retention time was 24 hours. The reported selenium removal at steady state was approximately 70%. The reactor was tested under fluctuating loads and showed significant resilience. Espinosa-Ortiz *et al.* (2017) also studied the simultaneous biomineralization of Se and Te by *P. chrysosporium*.

6.7.2 Electro-biochemical reactor

The electro-biochemical reactor (EBR), produced by INOTEC, is a patented high-efficiency denitrification, metals and inorganics removal technology. The system is based on the concept of providing electrons to the microbial community using electrodes and a low voltage potential (1–3 V) at low milli-Amp levels (Opara *et al.*, 2014).

INOTEC lists several selenium removal EBR projects on its website (website visited August 30, 2020). These include 17 projects (11 bench-scale tests, 5 pilots, and 1 full-scale facility). Selenium was not a target constituent for 2 of the 17 projects. The one full-scale facility on INOTEC's selenium experience list is for a gold mining project where influent selenium is reportedly reduced from 690 ppb to approximately 50 ppb. The influent nitrate at the gold mining site is reportedly approximately 180 mg/L as nitrate-nitrogen. The bioreactor HRT is listed as 24 hours.

6.7.3 Hydrogen based membrane biofilm reactor

The hydrogen-based membrane biofilm reactor (MBfR) is designed to reduce oxidized pollutants using hydrogen gas as an electron donor. Hydrogen or a mixture of hydrogen and carbon dioxide (4:1) is delivered by diffusion through the walls of non-porous hollow fibre membranes. A hydrogen oxidizing biofilm forms on the membrane outer walls and reduces electron acceptors in the bulk liquid including nitrate and selenate.

Several studies (Chung *et al.*, 2006; Lai *et al.*, 2014; Van Ginkel *et al.*, 2011a, 2011b) have reported high SeO_4^{2-} removal rates employing the MBfR technology. Studies with actual WFGD wastewater showed a high selenate reduction efficiency (Van Ginkel *et al.*, 2011a, 2011b).

The MBfR technology has been commercialized by APTwater of Sacramento (California, USA). The APTwater website references the selenium removal technology as AROSel targeting selenium, naturally occurring and from flue gas desulfurization, oil production and refining. As of August 30, 2020, the APTwater website referenced the AROSel system as "In Development".

6.8 FUTURE PERSPECTIVES FOR OPTIMIZING BIOLOGICAL SELENIUM REMOVAL TECHNOLOGIES

Implementation of more stringent aquatic water quality guidelines for selenium, particularly in North America, has driven the development and commercialization of a small number of active selenium bioremediation technologies. Several private companies and members of the Electrical Power Research Institute (EPRI) in the United States have conducted numerous pilot studies of selenium bioremediation technologies. Golder's (2020) recently completed report on the state of knowledge of selenium treatment technologies concluded: "*despite numerous installations, selenium treatment technologies have not reached full maturity and should be regarded as developmental.*"

A 2018 presentation (Simm, 2018) presented at the EPRI Selenium Summit in the Netherlands summarized some of the key issues and challenges associated with biological Se removal and identified key research and development needs based upon observations at full-scale facilities. One of the primary drivers for

having this summit in Europe was to connect leading European researchers working on the fundamental science of selenium bioremediation with North American practitioners engaged in implementing selenium bioremediation projects to meet current and proposed stringent effluent selenium regulations. It is this author's opinion that the practice of selenium bioremediation is lagging the regulatory implementation. Some of the key issues and research requirements associated with selenium bioremediation are presented in this section.

6.8.1 Selenium measurement and speciation

The primary driver for ultra-low selenium limits is the protection of sensitive aquatic species and waterfowl. The concentration and speciation of selenium affects its bioaccumulation potential. It can be difficult to measure selenium speciation in complex environmental matrices like mine water and wet flue gas desulfurization (WFGD) blowdown. Being able to accurately measure influent and effluent selenium concentrations is critically important.

Based on what is known about the potential for the production of organic Se species in biological treatment systems, monitoring for their presence could be extremely beneficial in predicting the toxicity of the effluent. According to [LeBlanc *et al.* \(2018\)](#), sensitive and robust analytical methods for the measurement of Se speciation in water samples are required for such an endeavour, as environmentally relevant concentrations of organic Se may be only a small fraction of the total Se in a given sample.

6.8.2 Bioavailability of reduced selenium species in treated effluents

Waterborne inorganic selenate and selenite typically bioaccumulate 100 to 4000 times in aquatic food chains, but organic selenoamino acids can produce bioaccumulation factors in excess of 350,000 ([Tan *et al.*, 2016](#)). There have been limited studies on effluent selenium speciation and its direct impact upon the aquatic environment. However, the studies that have been conducted suggest reduced selenium species in the effluent from a selenium bioremediation facility are of potential concern.

[Amweg *et al.* \(2003\)](#) studied an algal-bacterial selenium reduction (ABSR) process for treating agricultural drainage water in the San Joaquin Valley of California. These authors used laboratory-based algal bioaccumulation tests and *in situ* microcosms with a variety of invertebrates to measure differences in Se bioavailability before and after ABSR treatment. These authors reported a 2 to 4 times increase in Se concentration in aquatic biota tissue exposed to ABSR system effluent relative to organisms exposed to untreated water. This is despite the fact the ABSR system removed approximately 80% of the total influent Se.

[LeBlanc and Wallschläger \(2016\)](#) measured organo-selenium in natural and industrial waters. These authors showed industrial biological treatment systems

designed for remediation of selenium-contaminated waters increased both the concentration of organic selenium species in the effluent, relative to influent water, and the fraction of organic selenium which increased to up to 8.7% of the total selenium in the effluent, from less than 1.1% in the influent.

Golder *et al.* (2020) reported on one biological system where environmental effects monitoring indicated an approximate 50% reduction in selenium concentration in the receiving waters. Despite this reduction, the near-stream selenium concentrations in benthic invertebrates increased approximately 7-fold compared to before treatment. The owner at this particular site attributed the increase to organo-selenium species in the effluent and ultimately implemented an effluent oxidation step to convert reduced selenium species to selenate.

The management of reduced selenium or organic selenium species in the effluent of biological selenium treatment facilities serves as a potential challenge that needs to be addressed. Research needs to be conducted on the reactor conditions leading to organo-selenium production and optimization of post treatment methods for mitigating their impact.

6.8.3 Bioprocess operations

6.8.3.1 Bioreactor sizing and design optimization

Selenium oxyanions are the dominant selenium species in selenium impacted waters requiring treatment. Nitrate and sulfate are typically present in significant concentrations (parts per million) relative to selenium oxyanions (parts per billion). As indicated in Section 6.2, significant selenium oxyanion reduction does not typically take place until the majority of nitrate has been reduced.

Contrary results on the inhibition or stimulation of selenium oxyanion reduction in the presence of NO_3^- and SO_4^{2-} have been reported. In addition, previous studies have shown both sulfate reducing bacteria and denitrifiers can reduce selenium oxyanions (Simm, 2017). Tan *et al.* (2016) have suggested optimizing bioreactor operational parameters for establishing and maintaining a microbial community with coexisting denitrifying as well as sulfate and selenate reducing bacteria is yet to be fully understood and operated at full scale.

The EPRI State of the Knowledge Document (2019) suggested: “*Even though the complex nature of selenium reduction is not fully understood, WFGD wastewater biological treatment systems have operated for more than 10 years and are demonstrating significant selenium reduction. Identifying and understanding the pathways for selenium reduction may lead to new insights into operating systems more efficiently.*”

There is a need for a biochemical model and process simulator that takes into account the interactions between nitrate, selenium oxyanions, and sulfate and that can be used to provide operational insights for both pilot and full-scale facilities (Simm, 2017). Such a model could ultimately reduce piloting requirements and be used for system sizing and design optimization.

[Boltz \(2019\)](#) is currently developing a mathematical model that is capable of describing the biochemical transformation of selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), nitrate (NO_3^-), and sulfate (SO_4^{2-}), amongst other relevant compounds, by functional bacterial groups within the system's operational environmental conditions. Model features include a description of the simulated processes, state variables, Gujer matrices, stoichiometric relationships, kinetic expressions, conversion factors, and parameter values (see Chapter 4). Preliminary model results suggest good agreement between model predictions and pilot plant observations. Additional research is required to verify the model's efficacy.

6.8.3.2 Better understanding and optimization of passive treatment designs

Reduced selenium (S^0 and selenides) is not routinely removed in passive systems and will accumulate over time. The long-term fate of these accumulations is not well understood. There is a need for research that identifies the selenium sequestration capacity of various passive systems, potential for selenium re-release and the factors controlling re-release, and best practices for environmentally sound system closure.

6.8.3.3 Optimization of selenium reduction at municipal wastewater treatment plants

Municipal wastewater treatment plants in areas with seleniferous soils are likely to have elevated influent Se and stringent effluent Se discharge limits. This is certainly the case in the western US in states like Colorado and Arizona. The work of [Pontarolo *et al.* \(2017\)](#) is instructive and there is a need for further research focused on optimization of Se removal in municipal activated sludge systems and in suspended growth systems in general.

6.8.3.4 Selenium treatment residuals handling and long-term management

Most selenium bioremediation technologies produce residuals with a high selenium concentration. In many cases, selenium laden residuals from active treatment systems are dewatered and landfilled. The long-term fate of these residuals is a concern especially the potential for re-mobilization and future environmental contamination. There is significant interest in selenium recovery technologies ([Hageman, 2015](#)) and/or encapsulation.

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