WHITE PAPER / **UNDERSTANDING SELENIUM AND ITS IMPACT ON OUR ENVIRONMENT**

BIOLOGICAL TREATMENT PLAYS AN IMPORTANT ROLE IN REDUCING THIS TOXIC ELEMENT TO SAFE LEVELS

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Selenium is a naturally occurring trace mineral that, in small amounts, is safe and nutritionally necessary for human life. At higher concentrations, however, it becomes toxic. As crude oil contains high concentrations of selenium, refineries must address the need to treat effluent wastewater discharge to be compliant with new environmental regulations on selenium.

The scientific community's understanding of selenium and its impact on human health and the environment has evolved dramatically throughout the past 40 years.

The U.S. Environmental Protection Agency (EPA) published its first criteria for selenium exposure in freshwater aquatic life in 1980. These criteria initially were based on water-only exposure. A revised acute criterion was published by the EPA in 1999, recognizing selenite and selenate as the forms of selenium in water-only exposure. Additional updates were published in following years as research continued to expand the understanding of selenium toxicity.

In 2016, the EPA introduced the final update of its 1999 recommended national chronic aquatic life criterion for selenium. The new criterion has specific scientific recommendations on the duration and frequency of ambient water quality pollutant concentrations.

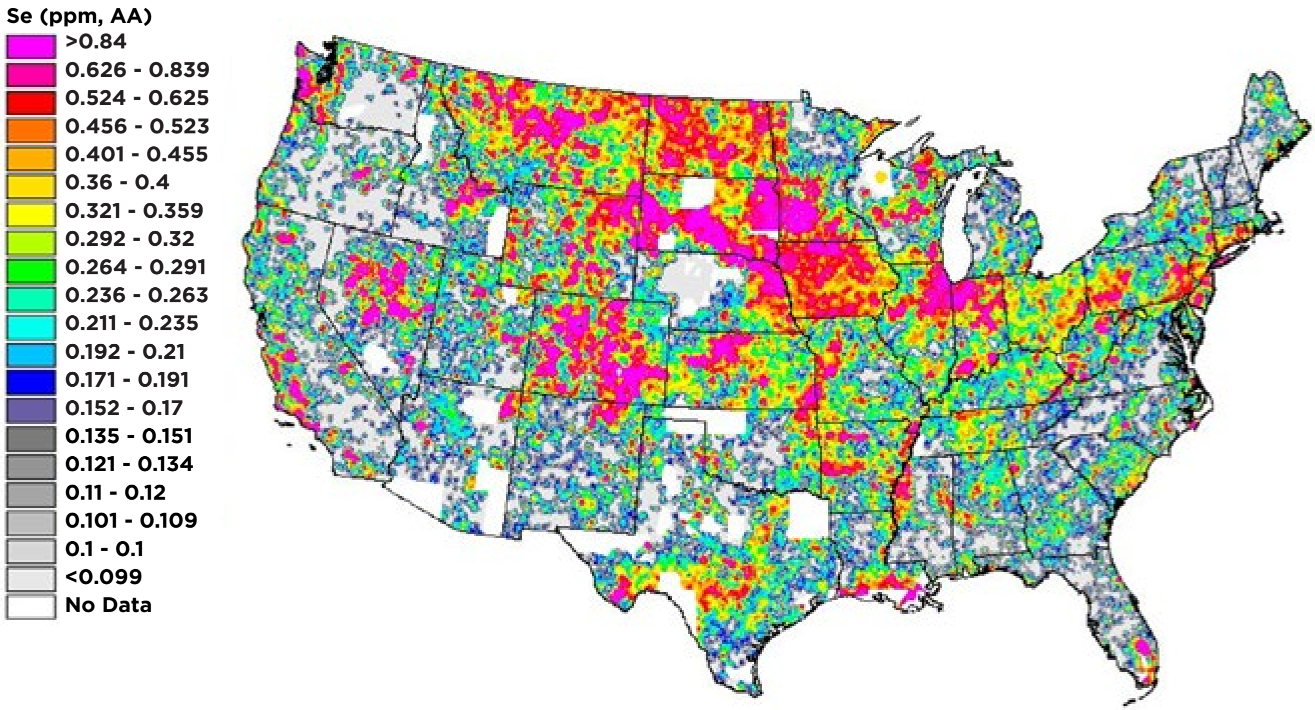
The criteria are recommendations rather than rules for water quality standards. Individual states must adapt them — particularly the water column recommendations — to address their specific environments and adjust water quality standards accordingly.

1980	First published aquatic life criteria for selenium in freshwater
1987	Addressed toxicity observed in ecosystems below existing criteria
1998	Updated acute criteria and found fish tissue was more accurate than water column
2004	Draft chronic whole-body fish tissue criterion was published
2009	Fish-tissue criteria revised, and diet is found to be primary selenium exposure
2016	Chronic criterion for selenium is published with revisions from 2014 and 2015 draft

Summary of selenium criteria changes defined by the EPA from 1980-2016

CRITERION VERSION	CHRONIC					SHORT-TERM
	Egg-Ovary[1] [mg/kg dw]	**Whole Body**[1] [mg/kg dw]	**Muscle**[1] [mg/kg dw]	**Water Lentic**[1] [µg/L]	**Water Lotic**[1] [µg/L]	**Water**[1] [µg/L]
2016 Selenium Criterion	15.1	8.5	11.3	1.5 (30 days)	3.1 (30 days)	Intermittent exposure equation
1991 Selenium Criterion	N/A	N/A	N/A	15.1 (4 days)	15.1 (4 days)	Acute equation based on water column concentration

Comparison of 2016 Selenium Criterion to 1991 Criterion



Map of Soil Selenium Content in the U.S. (U.S. Department of the Interior, U.S. Geological Survey, Mineral Resources)

OIL AND GAS REFINING: A MAJOR SOURCE OF SELENIUM

Crude oil from certain geological formations, such as marine shales, can be rich in selenium, making refinery wastewater effluents a major source of loading within aquatic environments. Selenium concentration in crude oil varies by petroleum basin. Currently, there is no way to control the amount of selenium entering a refinery without changing crude sources.

Selenium associated with crude oil production primarily is organically bound. Because selenium is isomorphous with sulfur, it accompanies this element during downstream crude oil refining processes. Most of the selenium and sulfur contained in crude oil is in the sour water streams. While ammonia and hydrogen sulfide are removed from sour water by steam stripping, selenium removal by this method is not effective and results in most of the element leaving in the stripper bottoms. The selenium found in stripped sour water predominantly takes the form of hydrogen selenide or hydrogen selenocyanate at acidic-to-neutral pH.

Crude preparation operations, including the initial crude dewatering and desalting processing steps that precede refining, are a secondary source of selenium. These operations predominantly produce selenite and, to a lesser degree, selenate, depending on the level of oxidation during crude washing. The selenium found in crude dewatering and crude desalting is a significantly smaller source compared to stripped sour water.

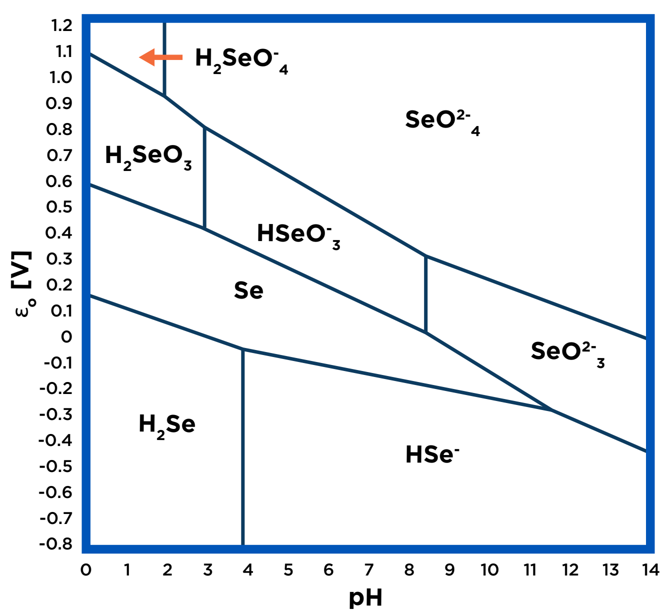
CHALLENGES ASSOCIATED WITH SOURCE CONTROL OF SELENIUM

Selenium removal can be accomplished at various locations throughout the wastewater treatment process. Source control of selenocyanate in the stripped sour water stream can be accomplished using heavy metals precipitation or through oxidation and adsorption technologies. These upstream treatment approaches, however, raise several concerns.

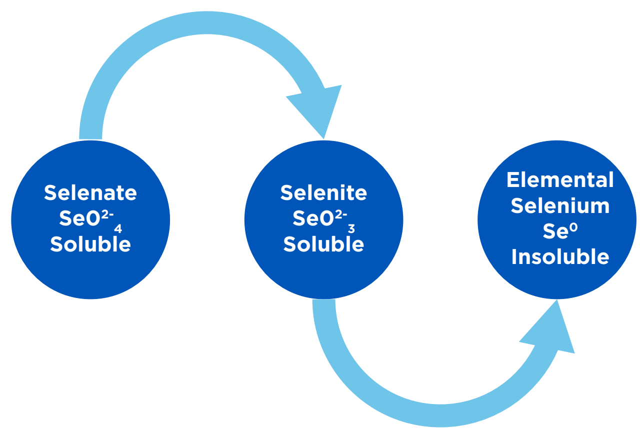
First, in full-scale systems, it is difficult to control a chemical oxidation reaction to stop at selenite formation. If the oxidation reaction proceeds, it forms selenate, which can be challenging to remove by chemical adsorption in iron coprecipitation systems. Second, it takes large and often cost-prohibitive amounts of chemicals to remove selenocyanate from stripped sour water. Assuming the oxidation reaction can be controlled to produce mostly selenite, a high quantity of iron is needed for selenium precipitation because of the presence of high chemical oxygen demand (COD) in the stripped sour water. The sludge production from this precipitation is also high, increasing disposal costs. Finally, this form of heavy metals precipitation typically achieves effluent concentrations of 50 µg/L selenium, which is significantly greater than regulatory limits of 5 µg/L.

ADVANTAGES OF BIOLOGICAL TREATMENT

Biological treatment of combined refinery wastewater offers a simpler, more cost-effective option for selenium removal. The objective of biological selenium treatment is to reduce soluble selenium to particulate, elemental selenium that can be removed from the effluent wastewater and incorporated into the biomass. Biological treatment is a favored selenium removal technology because of its proven ability to remove selenium to low levels (e.g., less than 5 µg/L). Typically, refinery biological treatment systems are designed for dissolved hydrocarbon treatment, including biochemical oxygen demand (BOD) and COD removal, as well as ammonia removal (oxidation of ammonia to nitrate). Following aerobic biological treatment, most selenium in refinery wastewater is selenite and selenate, soluble forms of selenium. Anoxic biological reactors are used for selenium removal, reducing selenite and selenate to elemental selenium. Common types of biological treatment systems for selenium are attached growth or fixed-film biological systems comprised of either a biofilm or a layer of microorganisms that grows on the surface of a solid-phase media. Water is passed through this media at a velocity high enough to suspend (or fluidize) the media, creating a reactor configuration for attached growth.



Selenium Pourbaix Diagram



INTEGRATING A SELENIUM TREATMENT SYSTEM INTO AN EXISTING WASTEWATER FACILITY

The biological reduction of selenium depends on the upstream biological systems' success in removing nitrates and oxygen from the wastewater, as well as providing the appropriate organic carbon dosing needed for the system to operate as intended.

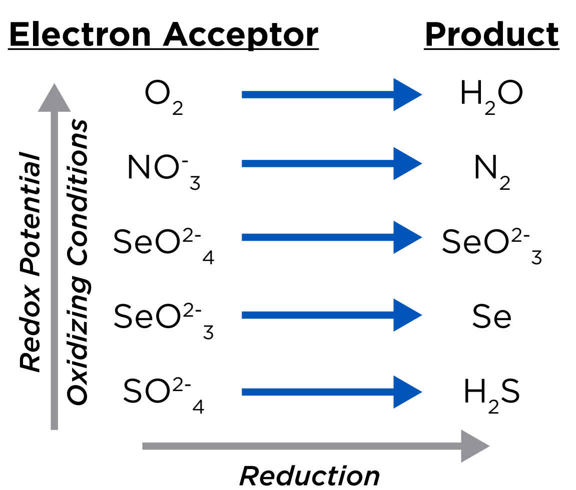
Nitrate removal is an anoxic biological process that reduces nitrate to nitrogen gas. Depending on discharge permit requirements, a refinery's biological treatment systems may or may not be configured for nitrate removal. Biochemical energetics favor nitrates and oxygen as electron acceptors over selenium. Nitrates that are not removed in upstream treatment must be accounted for in the design of the selenium removal system. If denitrification occurs in the selenium treatment system, nitrogen gas bubbles might cause floating sludge that must be filtered in the downstream effluent. A refinery can add a denitrification step in its biological treatment system to increase the reliability of a biological selenium removal system by converting its aerobic system to total nitrogen removal (aerobic and anaerobic).

By reducing the level of nitrates entering the selenium reactor, the refinery can reduce competition for electron donors and remove nitrate-level variability in carbon dosing operations to support selenium reduction. With no nitrates acting as electron acceptors in the selenium reactor, the system also will have a lower population of microorganisms to support, requiring less carbon source to support nitrate reduction, resulting in lower overall removal costs.

IMPORTANCE OF CARBON DOSING STRATEGY

Because nitrate removal is microbially favored over selenium removal, achieving the correct ratio of the carbon source to nitrates and selenium is extremely important for successful selenium reduction. If a significant amount of nitrate is present in wastewater, then a sufficient amount of organic carbon must be added to reduce the nitrates and selenium. However, a challenge for biological selenium removal is presented when nitrate and/or selenium concentrations are very low or absent. These conditions can result in little or no growth in heterotrophic bacteria, which can lead to washout or loss of the microorganisms needed to reduce selenium.

If more carbon source is added than nitrate and selenate reduction requirements, the system could promote sulfate reduction to hydrogen sulfide. Though selenate reduction is faster and can occur at higher oxidation reduction potential (ORP), sulfate-reducing bacteria can compete for electron donors and therefore waste carbon resources. Sulfate reducers also produce toxic hydrogen sulfide gas, which is a significant safety hazard.

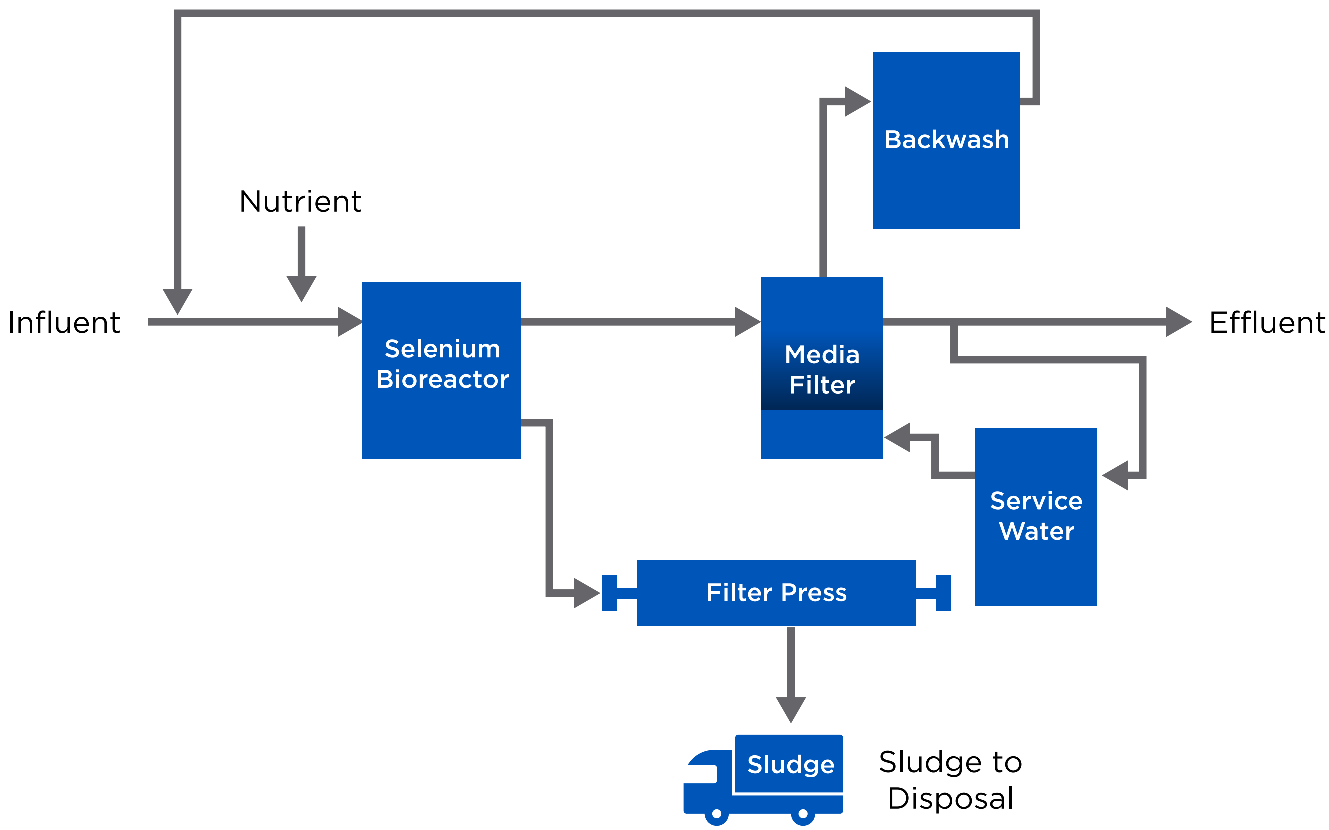


Redox Profile of Biological Reduction

ROLE OF POST-FILTRATION

Post-filtration of a biological selenium removal system's effluent stream typically is necessary to control suspended solids and particulate selenium removal. Microfiltration systems, such as sand or multimedia filtration, commonly serve this purpose.

In cases where denitrification is expected, floating sludge caused by nitrogen gas bubbles increases the need for post-filtration. Particle size analysis should be performed to determine the appropriate media for filtration. Backwash pumps, tanks and other ancillary equipment to support post-filtration must be considered when evaluating the cost and space for the system. Sludge generated from a filter backwash needs to be dewatered, and the dewatered solids need to be disposed of properly. During post-filtration, it is important that residuals not be aerated or otherwise oxidized to avoid the possibility of elemental particulate selenium reoxidizing, which forms selenite and selenate. As a result, forms of backwashing that involve air purging should not be used. Following media filtration, an aerobic process might be required downstream of the selenium-reducing bioreactor to remove any remaining BOD before discharge. Closely monitoring carbon dosing in the selenium reactor can reduce the need for BOD removal. The need for this final polishing step also depends on BOD discharge limits. Because any elemental



Fluidized Bed Reactor Process Flow Diagram

selenium present in the wastewater post-filtration will be reoxidized in the aerobic process, post-filtration also impacts the applicability of this aerobic process.

CONCLUSION

As states begin to implement the updated EPA aquatic life criterion for selenium, refineries might find that their current wastewater treatment systems are unable to meet stricter National Pollutant Discharge Elimination System (NPDES) permit limits on selenium. While selenium removal technologies exist to help refineries achieve compliance, it is important to understand the state of a refinery's wastewater treatment plant to successfully implement new selenium removal technologies. Upstream process conditions, such as nitrate concentration, can affect selenium reduction and should be considered when designing a biological selenium treatment system. Carbon dosing, post-filtration, residuals management and BOD removal are all important auxiliary processes that also should be considered when designing selenium reduction systems. Specifically, the selection of post-filtration technology depends, in large part, on the designer's understanding of the selenium's particle size and concentration, as well as the subtle yet important differences in filtration system options.

It is important to consider the impact that operational parameters can have on selenium treatment processes, as well as entire wastewater treatment systems. With years of experience in industrial wastewater treatment, Burns & McDonnell has a comprehensive understanding of the design and operation of such systems. Refineries are advised to consider the operational parameters discussed in this paper as they implement new capital projects involving selenium removal.

BIOGRAPHIES

PATRICK HIRL, PE, Ph.D., is a process technical lead and a senior project manager in the Industrial Wastewater Treatment Group at Burns & McDonnell. Pat specializes in the treatment of water and wastewater from industrial facilities, including petroleum refineries, chemical production facilities and various agricultural processing facilities. Since 1987, his professional experience has been in the research, development, process analysis and design of chemical and biological processes in water and wastewater treatment, environmental remediation, biofuels and renewable energy markets. Pat earned his Bachelor of Science degree in civil engineering and doctorate in environmental engineering from the University of Notre Dame. He also is a former nuclear power submarine officer.

BRYCE JONES is a process engineer in the Industrial Wastewater Treatment Group at Burns & McDonnell, specializing in wastewater treatment for industrial facilities. Bryce's professional experience began in 2016 and has focused on wastewater process analysis and design, field evaluations, and renewable energy markets. He earned his Bachelor of Science degree in chemical engineering magna cum laude from the University of Arkansas-Fayetteville. His academic experience includes three years of research on water quality and a pending patent on a water-borne pathogen biosensor device.

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