Biological Treatment of Flue Gas Desulfurization Wastewater

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Cover Illustration: Bottle incubations of selenium reducing microorganisms promote treatment of flue gas desulfurization (FGD) effluent for surface water discharge. As the microorganisms reduce the soluble selenium oxyanions, a deep red precipitate is formed.

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Biological Treatment of Flue Gas Desulfurization Wastewater

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<tr>
<th>Term</th>
<th>Description</th>
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<tbody>
<tr>
<td>AOB</td>
<td>Ammonia-oxidizing bacteria</td>
</tr>
<tr>
<td>DFBF</td>
<td>Downflow biofilters</td>
</tr>
<tr>
<td>EA</td>
<td>Electron acceptor</td>
</tr>
<tr>
<td>EBBR</td>
<td>Expanded bed biofilm reactors</td>
</tr>
<tr>
<td>ED</td>
<td>Electron donor</td>
</tr>
<tr>
<td>ELG</td>
<td>Effluent limitation guidelines</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>FGD</td>
<td>Flue gas desulfurization</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular activated carbon</td>
</tr>
<tr>
<td>NOB</td>
<td>Nitrite-oxidizing bacteria</td>
</tr>
<tr>
<td>P/C</td>
<td>Precipitation/coprecipitation</td>
</tr>
<tr>
<td>S/S</td>
<td>Solidification and stabilization</td>
</tr>
<tr>
<td>SRT</td>
<td>Sludge retention time</td>
</tr>
<tr>
<td>SO(_x)</td>
<td>Sulfur oxide gasses</td>
</tr>
<tr>
<td>TEA</td>
<td>Terminal electron acceptors</td>
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</table>
Acknowledgments

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ABSTRACT

In order to limit and mitigate the environmental impacts associated with coal combustion, flue gas desulfurization (FGD) systems have been put into place to reduce the release of contaminants. The main constituent targeted by FGD systems is sulfur oxide gasses (SOx). While FGD systems have been able to achieve high removal rates of SOx gasses, the wastewater effluent requires treatment before release back into the environment. The release of wastewater is heavily regulated by the U.S. Environmental Protection Agency (EPA) and their effluent guideline limitations rule (ELG). The ELG rule set new limits on discharges containing constituents such as selenium, nitrogenous species, mercury, and arsenic in the effluent. This report seeks to give background on abiotic removal methods as well as highlight the most important issues when utilizing biological treatment to treat the FGD wastewater for the constituents of interest mentioned. This report also seeks to discuss the issues of foaming which can occur during biological treatment.
1. BACKGROUND

1.1 ABOUT FGD SYSTEMS

Coal-fired power plants are adding more technologies to limit the environmental impacts associated with coal combustion. Flue gas desulfurization (FGD) systems aim to reduce the release of several contaminants, though primarily sulfur oxide gases. FGD systems were first developed in the 1970s in the United States (U.S.) (Córdoba, 2015). Since then, FGD systems have been deployed to other parts of the world and a wide variety of systems have been developed.

While various FGD systems have slightly different configurations, many FGD attributes are common (Figure 1). All FGD systems are located downstream of the power plant’s boiler, where the coal is combusted and the gas flow originates, and prior to the stack, where the flue gas escapes into the environment (EPRI, 2019). In FGD systems, absorbents—whether consumable or regenerable—are inserted into the gas stream to enable removal of the contaminants of interest (Córdoba, 2015). Having contacted the contaminants and reacted with them, the absorbents are then removed from the gas stream. Under normal conditions, FGD systems often achieve >90% SO₂ removal efficiencies (Córdoba, 2015).

In the U.S., FGD is most often achieved through wet processes, as is the case worldwide (Hansen et al., 2008). In these systems, calcium is added to the water, typically as crushed or pulverized limestone (CaCO₃), prior to injection into the scrubber (Qin et al., 2014). The limestone dissolves in the water, yielding dissolved calcium and carbonate ions in a limestone slurry. This slurry is then used in an adsorber or scrubber, where the slurry is showered down upon the passing flue gas. The slurry shower reacts with the SO₂ in the incoming flue gas that lead to its initial dissolution into the aqueous phase and neutralization, often as calcium sulfate (CaSO₄(s)).

![Figure 1: Schematic depiction of the operation of a limestone-based wet FGD system adapted from Brown et al. (2012).](image-url)
Products of value, such as gypsum and plaster of Paris, can be generated through wet FGD systems. Gypsum (CaSO$_4$·2H$_2$O), which can be incorporated into drywall or used as an agricultural additive or fertilizer (Gingerich et al., 2018), can be generated if operational conditions allow. The first step is to control the pH of the gas-slurry mixture. In a range between pH 5 and 6, CaSO$_3$·2H$_2$O is the initial product (Córdoba, 2015). Providing sufficient residence time and oxidation potential allows for the desired production of CaSO$_4$·2H$_2$O. At lower pH values, Ca(HSO$_3$)$_2$(aq) is likely to form as the initial product. With lower oxidation potentials, CaSO$_3$·½H$_2$O is likely to remain a sizable fraction of the final product (Córdoba, 2015).

Along with the calcium-sulfur solids, wet FGD systems output wastewater, which might require additional treatment prior to release back into the environment. Like all industrial waste streams, FGD waste streams are influenced heavily by regulation. In the U.S., treatment of FGD wastewater is often focused on reducing SO$_2$ (Gingerich et al., 2018). However, in 2015 the U.S. Environmental Protection Agency (EPA) produced its final effluent limitation guidelines (ELG) rule$^1$. The new rule comes in response to improvements in industry practices over the last several decades. Among other limitations, the rule sets new limits on arsenic, mercury, selenium, and nitrogenous FGD wastewater discharges.

In light of the recent increase in regulation of FGD wastewater streams, this report aims to highlight the most important issues facing biological treatment of these streams. This review presents both chemical and biological treatment processes of FGD wastes. The new EPA rule helps focus attention on the contaminants it addresses: selenium, nitrogen species, mercury, arsenic. Additionally, conversations with power plant personnel have brought to attention an issue with biologically induced foaming; foaming will also be reviewed here.

1.2 **ELG RULE CONTAMINANTS**

FGD wastewater has the potential to carry both toxic compounds and nutrient pollution to receiving water bodies, leading to the 2015 EPA ELG rule. Additionally, thermoelectric power plant personnel identified foaming as a problem that can complicate the FGD biological wastewater treatment process.

Table 1 summarizes the concentrations found in untreated FGD wastewater and the allowable treated effluent concentrations for wastewater release. Table 2 provides a summary of the treatment options for the four constituents and foaming issue covered in this report.

---

$^1$ On October 13, 2020, the U.S. EPA published a new proposed rule (EPA, 2020), relaxing some of the 2015 final rules. The new rule is to relax the 2015’s ELG rule for selenium limitation and instead implement an incentive program to give facilities more time to comply to the 2015 effluent limits. The new rule also relaxes the 2015 daily maximum release for arsenic. The public comment period for this proposed rule closed on January 21, 2020.
Table 1: Power Plant Concentrations and 2015 and 2020 ELG Rule Concentrations for Existing Sources (adapted from Gingerich et al., (2018))

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Selenium [µg/L]</td>
<td>3,130</td>
<td>23</td>
<td>70</td>
<td>12</td>
<td>29</td>
</tr>
<tr>
<td>Nitrate/nitrite as N [mg/L]</td>
<td>91.4</td>
<td>17</td>
<td>4</td>
<td>4.4</td>
<td>3</td>
</tr>
<tr>
<td>Mercury [ng/L]</td>
<td>289,000</td>
<td>788</td>
<td>103</td>
<td>356</td>
<td>34</td>
</tr>
<tr>
<td>Arsenic [µg/L]</td>
<td>507</td>
<td>11</td>
<td>18</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>TDS [mg/L] (Voluntary Incentives Program)</td>
<td>33,300</td>
<td>50</td>
<td>306</td>
<td>24</td>
<td>149</td>
</tr>
</tbody>
</table>

\* Plant average concentrations from EPA sampling activities between 2007 and 2011.

Table 2: Summary of Abiotic and Biological Treatment Options for Major FGD Problems

<table>
<thead>
<tr>
<th>Contaminant / Issue</th>
<th>Abiotic Treatment Options</th>
<th>Biological Treatment Options</th>
</tr>
</thead>
</table>
| Selenium            | • Filtration: nanofiltration, reverse osmosion  
• Ion exchange  
• Coagulation  
• Electrocoagulation  
• Photoreduction  
• Adsorption  
• Cementation | • Downflow biofilters  
• Hybrid downflow biofilters and expanded bed biofilm reactors |
| Nitrogen species    | • Air stripping  
• Vacuum distillation  
• Struvite precipitation  
• Zeolite ion exchange  
• Activated carbon adsorption and oxidative degradation  
• Breakpoint chlorination  
• Ozone oxidation with or without peroxide  
• Electrochemical oxidation | • Classical nitrification-denitrification  
• Alternative denitrification  
• Anammox |
| Mercury             | • Solidification and stabilization (S/S)  
• Thermal treatment  
• Precipitation/coprecipitation (P/C)  
• Adsorption  
• Membrane filtration | • Mercuric reductase  
• Biocyanide treatment |
| Arsenic             | • Precipitation/coprecipitation (P/C)  
• Adsorption  
• Membrane filtration  
• Ion exchange | • Phytoremediation  
• Microbial-induced precipitation or co-precipitation |
| Foaming             | • Anti-foaming agents  
• Membrane filtration | |
2. **SELENIUM**

2.1 **SELENIUM TOXICITY**

Selenium has long been known to be toxic; however, more recently discovered are its essential functions in many lifeforms. There are many micronutrients that have this property, but the concentration range in which selenium has a beneficial effect is quite narrow. The concentration between essential levels and toxic levels of selenium only differ by one order of magnitude. This means that even slightest changes in selenium concentrations can lead to harm in living organisms and possible ecological damage (Nancharaiah and Lens, 2015).

Selenium’s toxicity is dependent upon its chemical speciation. Selenium toxicity is also dependent upon bioavailability, which is further intertwined with selenium speciation. Selenium oxyanions, selenate (\(\text{SeO}_4^{2-}\)), and selenite (\(\text{SeO}_3^{2-}\)) are more soluble than other forms of selenium. As such, they often are observed to be the most toxic forms of selenium. These are also the most common forms found in FGD wastewater concentrations (EPRI, 2019).

Selenium toxicity takes on many forms in different organisms. One constant is impaired reproduction. From algae to aquatic invertebrates (Daphnia) and vertebrates to birds, cell division or other reproductive processes, e.g., more nonviable bird eggs, are harmed by increasing selenium concentrations. Aquatic invertebrates also face worsened osmoregulation and decreased feeding rates, while fish experience a slew of issues, including decreased growth rates and lower iron blood levels. Selenium toxicity is not as problematic in humans as it is for aquatic life, but selenium is detrimental to human health. Acute cases of selenosis are known to cause gastrointestinal issues, hair loss, and most frequently, nail loss (Nuttall, 2006). Rare cases of selenium-related death of toddlers have been recorded (Nuttall, 2006). Chemistry laboratories are often not familiar with measuring selenium (Nuttall, 2006), which could contribute to underreporting of selenium-related human health impacts.

2.2 **SELENIUM TREATMENT**

Selenium treatment can be challenging due to its complicated chemistry. Other wastewater constituents can affect selenium treatment processes, such as the high concentrations of many ions like sulfate, chloride, and nitrogenous species. As such, selenium removal can require multiple treatment processes to achieve the ELG compliance concentrations (EPRI, 2017). Selenium poses problems not only to FGD system wastewater, but also in a variety of other industries, such as mining and processing of the mined metal ores (Khamkhash et al., 2017). As such, treatment processes have been established for removing selenium from aqueous environments. The processes include physical, chemical, and biological processes. This section will focus on options for abiotic treatment and the following section will focus on biological selenium treatment.

2.2.1 **Filtration**

Filtration to remove selenium can be implemented successfully. Older technologies, like clay and sand filtration, have been utilized, as have more advanced (and recent) technologies, like reverse osmosis and nanofiltration (Moore and Mahmoudkhani, 2011). These technologies can be effective, but are also susceptible to issues. One issue arises because of the similarity between selenium and sulfur chemistry. High concentrations of sulfate will exhaust the filtration technologies intended to target selenium. Other issues include scaling and fouling of membranes
and waste management of streams highly concentrated with toxic selenium species, which must be managed and disposed of properly.

### 2.2.2 Ion Exchange

Ion exchange is another physical method that can be used to treat selenium in wastewater (Moore and Mahmoudkhani, 2011). This method, which allows for the removal of a target ion or a target class of ions in exchange for a more desirable ion, can also fall victim to the similarities in selenium and sulfur chemistry. In waters containing both selenate and sulfate, ion exchange struggles to effectively differentiate between the two. Barium chloride (BaCl₂) can be used to first precipitate the sulfate, allowing for targeted downstream removal of selenate. Large volumes of concentrated wastes still present a waste management problem, as they do with filtration processes.

### 2.2.3 Chemical Treatment

Chemical treatment for selenium removal is possible, primarily through coagulation. Metal-based coagulants, e.g., iron or aluminum, can be added to water to alter the surface chemistry and effectively remove selenite (Moore and Mahmoudkhani, 2011). However, because selenate is less reactive, it is not amenable to coagulation-based removal. Zero-valent iron (ZVI) has been shown to be effective at both reducing selenate and selenite, leading to precipitation complex of these oxyanions within iron hydroxide compounds (Moore and Mahmoudkhani, 2011). Whether removal is accomplished via coagulation or ZVI, the costs of chemicals plus the costs of treating and disposing properly of the chemical-laden solids that are produced are important limiting factors.

### 2.2.4 Other Abiotic Methods

Other methods have also been discussed in the literature. These include electrocoagulation, photoreduction, adsorption, and cementation. While these methods might be technically feasible, they have not been demonstrated at commercial and industrial scale (Moore and Mahmoudkhani, 2011).

### 2.3 CURRENT STATE OF SELENIUM BIOLOGICAL TREATMENT

Biological processes for selenium removal have been deployed at industrial scale. Biological wastewater treatment can be achieved by suspended growth or attached growth systems. The same is true for biological treatment of FGD effluent. To date, most FGD wastewater biological treatment systems in the U.S. are attached growth systems (EPRI, 2019). Passive biological treatment systems have also been implemented. It is also important to know that while these treatment systems have been used for more than 10 years, much about the microbes and nature of selenium oxyanion reduction is unknown.

Most biological treatments for selenium removal aim to reduce selenium oxyanions (selenate and selenite) to elemental selenium (Moore and Mahmoudkhani, 2011). Reduction of either selenate or selenite is an energy-yielding reaction, and a reaction that microorganisms have the enzymatic capacity to catalyze under appropriate environmental conditions. Oxygen is likely the most important environmental factor affecting microbial reduction of selenium oxyanions. Selenium reduction in oxygen-rich environments is thermodynamically unfavorable; to encourage selenium oxyanion reduction anoxic conditions should be maintained. Other factors, like high
nitrate concentrations and high salinity, have also been documented to negatively affect microbial reduction of selenium within commercial biological FGD wastewater treatment systems (EPRI, 2019).

2.3.1 Downflow Biofilters

Downflow biofilters (DFBF) and hybrid DFBF-expanded bed biofilm reactors (EBBR) have, to date, been the most common systems that have been deployed to remove selenium from FGD wastewater (EPRI, 2019). In DFBF systems (Figure 2), biofilm is attached to a surface or medium that is stationary or fixed. Water flows top to bottom over the biofilm-colonized surface. By allowing growth of thick biofilm layers on the surface or medium, different biofilm depths can provide appropriate redox conditions for different microbiological processes to predominate. At the top layers, oxygen will be used as the electron acceptor. Deeper layers will allow for non-oxygen terminal electron acceptors (TEA), to be used, such as nitrate, sulfate, selenate, and selenite. Plant operators are careful to limit the flow of incoming water to limit the propensity of incoming water to pull bacterial cells off from the biofilm, that is, to cause “sloughing”.

![Figure 2: Downflow biofilter configuration. Black and red arrows indicate flow path of wastewater in normal DFBF operations.](image)

A main operating issue with DFBF is that flow paths through the biofilm and the surfaces or medium are inevitably obstructed. Sloughed cells and other solids clog these paths, and backwashing is intermittently required to re-open the wastewater flow channels. Not only do solids build up and require backwashing, but gases also contribute to obstructing the downward flow. Both nitrogen and hydrogen sulfide gas can become trapped under layers of solids, inhibiting fluid flow. Production of nitrogen gas is more problematic at nitrogen concentrations greater than 50 mg/L as N (EPRI, 2019).
DFBF systems have been used in industry and they have successfully removed selenium. Incoming selenium around 1,500 µg/L as total selenium has been reduced to less than 10 µg/L (EPRI, 2019).

2.3.2 Hybrid Downflow Biofilters

Hybrid DFBF-EBBR systems are not as common as DFBF systems alone, but there are several under construction, suggesting that this hybrid configuration is a viable option. Typically, the EBBR system precedes the DFBF system. In EBBR, biomass is attached to particles, and influent is shot up into the particles such that the particles become suspended. This enhanced suspension of the biofilter provides for faster kinetics and some nitrogen cycling to occur prior to the DFBF system, which helps to mitigate the sensitivity of DFBF to nitrogen gas production (EPRI, 2019).
3. **NITROGENOUS SPECIES**

3.1 **NITROGEN INPUTS’ ENVIRONMENTAL IMPACTS AND TOXICITY**

Nitrogen is one of the necessary elements for life, and decreased levels of nitrogen limit biological activity and growth. In freshwater ecosystems, additional nitrogen inputs, whether as nitrite, nitrate, or ammonia, is called nutrient pollution, and can lead to a cascade of devastating ecological impacts, namely eutrophication-to-dead zones process. This process consists of an initial blossoming of microbial and algal activity due to the extra nitrogen introduced to the environment (eutrophication, Figure 3) and is then followed by a death phase, where the blossomed organisms die. The microbial decay of the dead material consumes the oxygen in the water, leaving the environment with too little oxygen (hypoxia) to sustain any other biological activity, creating the ecological dead zones.

![Figure 3: September 2017, satellite image of algal blooms in western Lake Erie, (NASA Earth Observatory, 2017).](image)

In addition, excess nitrate (NO$_3^-$) and nitrite (NO$_2^-$) are also known to be toxic to animals, especially nitrite, which is about ten times as toxic as nitrate. Much of the attention has been devoted to ruminants, whose feed might contain excess nitrates, but humans are also susceptible to nitrate and nitrite toxicity, e.g., blue baby syndrome. The toxic effects are due to redox cycling of the nitrogen species changing the speciation of iron, such that the oxygen-carrying molecule hemoglobin is converted to methemoglobin. Young babies, lacking the enzymatic capacity to convert the methemoglobin back to hemoglobin typical of humans over six months, are more susceptible.

In FGD systems, nitrate and nitrite are the nitrogenous species that are mainly regulated for these systems, but the following section describes the abiotic treatment available for ammonia.

3.2 **NITROGEN TREATMENT**

Increases in inputs of nutrients to the environment were recognized by the mid-1950s (Barnard, 2014). The negative effects of water contamination, including nutrient pollution, led to stricter regulation in the early 1970s. In the ensuing decades, considerable effort has been made to develop reliable treatment methods for nitrogen, among other species of concern. Many
industries, including municipal wastewater treatment plants, have adopted primarily biological methods to remove nitrogen species from waste streams (Barnard, 2014). Numerous physicochemical alternatives exist, such as ammonia air stripping, vacuum distillation, precipitation and adsorption on charcoal; selected ion exchange; breakpoint chlorination; chloramine removal by activated carbon; chemical nitrate reduction; and advanced oxidation to convert ammonia and organic nitrogen to nitrogen gas (Capodaglio et al., 2015). Many of these abiotic processes are sensitive to pH. These abiotic processes will be considered, and the biological processes will be addressed in the subsequent section.

3.2.1 Air Stripping

Air stripping can be applied to concentrated wastewaters (Capodaglio et al., 2015). Lime or another caustic substance is used to raise the pH to around 11, at which point ammonia gas is produced. Ammonia is then absorbed into sulfuric acid to produce ammonium sulfate. This process has been applied to municipal solid waste and landfill leachate.

3.2.2 Vacuum Membrane Distillation

Another option for concentrated ammonia wastes is vacuum membrane distillation. This process is also pH- and temperature-sensitive. Solubility of ammonia decreases as temperature goes up, but increasing pH favors the dissolution of ammonia. Membrane distillation consists of both membrane separation and an evaporation or condensation process. The membrane is typically a hydrophobic and microporous physical barrier, which separates a warmer feed solution from a cooler permeate chamber that can have either a liquid or gas phase present. Because the membrane is hydrophobic, liquid cannot enter the micropores of the membrane due to surface tension forces. A vapor pressure gradient is formed due to the concentration and temperature difference between the feed and permeate side. The vapor pressure gradient allows for vapor molecules of more volatile compounds to migrate through the membrane to the permeate side. In vacuum membrane distillation, the volatile molecules can be removed from the membrane module via a vacuum. Vacuum distillation has been experimentally shown to have enhanced ammonia removal at higher temperatures and high pH levels (El-Bourawi et al., 2007).

3.2.3 Struvite Precipitation

Struvite precipitation can be used to produce solid magnesium ammonium phosphate (struvite) from ammonia (Capodaglio et al., 2015). Struvite is formed when sodium hydroxide and magnesium chloride are added to the supernatant of a sludge digester, known as concentrate liquor. The mixture is then fed into the fluidized reactor where struvite particles are able to aggregate into larger particles. The large particles fall to the bottom of the reactor where they are collected. This process is also governed by pH and temperature. Some work has shown that, for landfill leachate treatment, the optimal pH is 9.5. One of the most important constraints of pursuing struvite precipitation is the cost of the added magnesium. Research has explored the possibility of adding lower-cost magnesium sources. Struvite precipitation has been applied to a wide variety of wastes, including those from tanneries, coke plants, and landfills. Produced struvite can theoretically be used as a fertilizer.
3.2.4 **Ion Exchange**

Ion exchange using zeolites has received attention for its ability to remove both ammonia and nitrate (Capodaglio et al., 2015). When a natural zeolite such as clinoptilolite is used, ammonium removal occurs because of cationic ion-exchange with calcium ions. The structural pores in the zeolite also leads to ammonium removal by adsorption. Ion exchange is temperature sensitive but unaffected by pH within the range of 4 to 8. Outside of that range, performance is poor. Either natural zeolites or synthetic zeolites primarily consist of abundant and relatively inexpensive elements (aluminum and silicon). As with other ion exchange processes, regeneration of exchange capacity is required and can be achieved using solutions rich in calcium ions. The small volume of ammonia-rich eluent can then be subjected to one of the other abiotic treatment processes. Synthetic resins have been developed to apply ion exchange to nitrate removal, achieving greater than 90% removal. Research has explored the applicability of both ammonia and nitrate removal via ion exchange to municipal wastewaters.

3.2.5 **Oxidative Processes**

A variety of oxidative processes for nitrogen removal are also possible (Capodaglio et al., 2015). Activated carbon can be used to adsorb ammonia gas, but is less effective at treating ammonia dissolved in water. Other options for aqueous phase ammonia adsorption exist, as do applications of activated carbon for removal of other nitrogenous compounds, like chloramines. Chloramines, e.g., monochloramine and dichloramine, are formed when chlorine species react with ammonia. Chloramines can have human health impacts, especially di- and trichloramines, and they affect the taste and odor of water. As a result, mechanisms for removal of chloramines have been sought. Though typically an adsorbent, activated carbon can also serve as the catalyst for oxidative degradation of chloramines.

Chlorine can also be used to directly oxidize the ammonia in a process known as breakpoint chlorination (Capodaglio et al., 2015). This is mostly used as a polishing step in which chlorine is added in excess of the amount needed to produce free chlorine. With free chlorine present, the chloramines produced when the initial chlorine reacts with ammonia are oxidized to dinitrogen and chloride ions. The pH must be monitored to ensure that acids do not build up and that the pH remains below 8, above which the kinetics are much slower.

Advanced oxidative processes include use of ozone with or without peroxide and electrochemical oxidation (Capodaglio et al., 2015). Ozone reacts with ammonia to form nitrate, but the short half-life of ozone in water can limit the effectiveness of applying ozone alone. Combining the ozone with another oxidant, such as peroxide, might provide a more effective treatment (Kuo et al., 1997). Producing smaller ozone bubbles could also enhance the effect of ozone, as has been shown with microbubbles of ozone (Khuntia et al., 2013). At higher pH, the microbubbles have a more pronounced effect. In any case, nitrate is the product and would likely need to be treated thereafter.

Electrochemical oxidation can convert ammonia all the way to nitrogen gas (Capodaglio et al., 2015). The process can be direct or indirect. Direct oxidation would occur on an anode, where electrons would pass from the ammonia to the electrode. Indirect oxidation would occur on the cathode side and involve production of radical species, e.g., hydroxyl radicals, that would then oxidize the ammonia. To date, electrochemical oxidation has been limited by the expense of the
electrodes themselves and insufficient performance. Ongoing research is attempting to address these limitations.

3.3 CURENT STATE OF NITROGEN BIOLOGICAL TREATMENT

Abiotic nitrogen removal processes exist, but biological removal is often preferred (McCarty, 2018). Several different biological processes have been developed to remove nitrogen from wastewaters. Some of these technologies, e.g., anammox, are quite young and are still not widely used in the U.S. The classical approach, alternative denitrification, and anammox all depend upon cycling of nitrogen under oxic and then anoxic conditions. This cycling allows for ammonia present in the influent to be transformed (oxidized) to nitrite and potentially nitrate. The transformation of ammonia to nitrate is referred to as nitrification (Madigan et al., 2019). Under anoxic conditions, the nitrate or nitrite is then reduced to dinitrogen, a gas that, when created, leaves the system. As is discussed below, the different biological nitrogen removal approaches require varying degrees of operational control.

3.3.1 Classical Denitrification

In classical denitrification (Figure 4), full nitrification occurs in the presence of oxygen in the first reactor. The nitrate is then passed to a second anoxic reactor where one or more organisms partakes in reduction of the nitrate to nitrogen gas. In theory, classical denitrification can achieve complete removal of ammonia in influent (Madigan et al., 2019). The problematic features of this system include redundant cycling beyond nitrite to nitrate in the first reactor. The second reactor then requires that the nitrate be reduced back to nitrite before producing dinitrogen. This redundancy has negative consequences. More biomass is required to achieve these reactions, so more carbon (C) source must be added in both tanks to enable biological activity (for use as a C source in the first reactor and C source and electron donor (ED) in the second reactor). This also leads to the production of more sludge, which must then be treated and discarded.

![Figure 4: Classical denitrification (Madigan et al., 2019).](image)

3.3.2 Advanced Denitrification

In advanced denitrification (Figure 5), the first reactor is controlled so as to limit oxidation of nitrite to nitrate. This requires an elevated temperature (30 to 40°C) and slightly alkaline pH (7.5 to 8.5). These conditions favor ammonia-oxidizing bacteria (AOB) over nitrite-oxidizing bacteria (NOB) (Madigan et al., 2019). To help limit the potential for nitrite oxidation, a shorter sludge
retention time (SRT) is employed in the first reactor. And in the second reactor, with one step of the process not needed (nitrate reduction to nitrite), less carbon input is required, and less sludge is produced. Complete transformation of input ammonia to nitrogen gas is still expected (Madigan et al., 2019).

Figure 5: Advanced treatment - denitrification (Madigan et al., 2019).

3.3.3 Anammox

The last of the established mechanisms for biological nitrogen removal is anammox, which stands for anaerobic ammonia oxidation. This process (Figure 6) relies on a unique bacterium that combines two nitrogen species for its growth – ammonia as an ED and nitrite as an electron acceptor (EA) (Madigan et al., 2019). The first reactor, with its ammonia influent, is slightly oxic, allowing for partial aerobic oxidation of the ammonia to nitrite (Barnard, 2014). The ammonia and nitrite are then passed to the second anoxic reactor where the annamox bacteria can consume both in their production of dinitrogen. Since this is an autotrophic process, in which CO$_2$ is used as the C source, no organic C is added to the second reactor. One of the primary concerns with this process is that only 90% of the incoming nitrogen is expected to be released as nitrogen gas; the rest leaves as non-metabolized ammonia and nitrite (Madigan et al., 2019).

Figure 6: Advanced treatment- anammox (Madigan et al., 2019).
4. **MERCURY**

4.1 **MERCURY’S ENVIRONMENTAL IMPACTS AND TOXICITY**

Mercury is rated as one of the three most harmful environmental contaminants today (Rice et al., 2014). The primary concern with mercury is human consumption from contaminated food sources, especially fish. Mercury bioaccumulates within aquatic ecosystems, which can result in top predators accumulating particularly high mercury content. Humans that eat fish are, thus, cautioned against consuming certain fishes that have been shown to have high mercury concentrations. Mercury, primarily a neurotoxin, is of particular concern to developing organisms, including humans (Rice et al., 2014). Only a few microliters of the most toxic form, dimethylmercury \((\text{CH}_3)_2\text{Hg}\), can lead to death of adult humans.

Mercury is a naturally occurring element. It exists in subterranean rock formations, including in coal seams. Volcanic activity releases mercury, as does mining and combustion of coal. Human activities have led to considerably more release of mercury into the environment (Rice et al., 2014), creating increased concerns about human mercury consumption. Atmospheric release of mercury is thought to contribute the majority of mercury into the environment. Precipitation events deposit atmospheric mercury into surface waters, where microbial activity produces the methyl-mercury that can then enter aquatic organisms and bioaccumulate (Fernandes Azevedo et al., 2012).

4.2 **MERCURY TREATMENT**

Several established treatment methods for mercury-contaminated sludges or wastewaters exist. They include solidification and stabilization (S/S), thermal treatment, and precipitation/coprecipitation (P/C).

4.2.1 **Solidification and Stabilization**

S/S has been used at full scale to encapsulate mercury-contaminated soils or sludges. The process typically consists of either solidifying mercury, or stabilizing mercury. Solidification involves physically binding or enclosing mercury within a solid mass and can be achieved via microencapsulation or macroencapsulation (Figure 7). In the former, the waste is mixed with an encasing material prior to solidification. And in the latter, the encasing agent is spread over the waste, producing a solid block of encapsulated waste (EPA, 2015b).
Biological Treatment of FGD Wastewater

Figure 7: Polyethylene microencapsulation (Randall and Chattopadhyay, 2004).

Stabilization involves inducing reactions to render mercury immobile and requires that the waste be mixed with another regent (Figure 8). Unlike solidification, the goal of stabilization is to identify compounds with high affinity for binding mercury. Sulfates, phosphates, and a variety of polymers, including Portland cement, can be used. Along with the chemical reagent used to bind the mercury, pH can be adjusted to improve the binding and stabilization kinetics. Leaching of mercury is more likely to occur at lower pH, so effort is made to ensure that the pH remains basic.

Figure 8: Sulfur polymer stabilization/solidification process (Randall and Chattopadhyay, 2004).

4.2.2 Thermal Treatment

Thermal treatment has been used at full scale to volatilize mercury present in soil and other wastes. The volatilized mercury is then condensed and treated using another strategy, such as stabilization. Prior to treatment with high heat, extraneous material is removed from the waste and the waste is dewatered. The boiling point of elemental mercury is 350°C at 1 atm of
pressure, and thermal treatment ranges between 320°C and 700°C. Off-gas streams are collected and passed through sulfur-impregnated carbon to produce manageable compounds. Thermal treatment is more appropriate with sandy soils than silty or clay soils and at moisture contents no higher than 25%.

4.2.3 Precipitation/Coprecipitation

P/C is another full-scale treatment technology that can often achieve significant reduction of mercury concentrations in groundwater and wastewater. P/C consists of adding chemical reagents to water and mixing in order to precipitate a solid matrix that is then separated from the water. Typically, prior to addition of the reagent, the pH of the water is adjusted to the point where the desired solid species’ solubility is minimized. In sulfide precipitation, the most common type of precipitation, the pH is adjusted to the range of 7 to 9. Sodium sulfide is then added to the water with the goal of producing mercuric sulfide. Care must be taken to not overload the water with sulfide; in the presence of excess sulfide, soluble mercury-sulfide species can be formed. Coprecipitation is used with lignin derivatives that can produce a lignin-mercury colloid. This process can be enhanced further with addition of a chemical coagulant, such as ferric chloride. Settling, clarification, or filtration follows the P/C process to enable separation of the formed solids from the aqueous phase. In some cases, multiple precipitation steps are required and/or activated carbon treatment. P/C can reliably drop mercury concentrations to less than 2 µg/L. The solid waste produced by P/C is often treated via S/S, as discussed above.

4.2.4 Adsorption

Adsorption has been applied at scale for mercury treatment of waters most often alongside other treatment technologies and is often used as a polishing step. In adsorption, water is passed over a medium or through an adsorbent that pulls the mercury out of solution. The mercury accumulates onto the surface of the adsorbent until the adsorbent is saturated. For many adsorbents, the binding of mercury is reversible, and at saturation, the rates of both adsorption and desorption of mercury are equal. Granular activated carbon (GAC) is the most common adsorbent used for mercury. As with other technologies, pH is controlled to ensure optimal adsorption. The optimal pH for mercury adsorption onto GAC is between 4 and 5. Other water characteristics can complicate adsorption because other constituents can compete with mercury or cause the GAC to be prematurely saturated. For this reason, filtration and disinfection to remove solids may precede adsorption.

When using adsorbents, the goal is to limit the potential to clog the pores/surfaces of the adsorbent. Once they are saturated with mercury, adsorbents can often be regenerated. GAC is regenerated by heating to high temperatures. Spent adsorbents/media no longer able to adequately bind mercury require treatment prior to disposal. Adsorption can help reduce mercury water concentrations to less than 2 µg/L. This is important to note because the EPA limits mercury are less than 1 µg/L.

4.2.5 Filtration

Membrane filtration was, as of 2007, less widely used for full-scale mercury treatment, but it has been deployed at full scale for treatment of other contaminants. Membrane filtration separates influent into two effluent streams—one, the permeate, that has passed through the semi-
permeable barrier that contains a lower concentration of the contaminant and another, the concentrate or reject stream, that did not pass through the membrane and contains a comparatively small volume of water and high concentration of the contaminant. The reject stream can either be recycled back into the influent stream for a second pass through the membrane or another technology to further concentrate the contaminant, perhaps via dewatering. Depending on the mercury concentration in the permeate, additional mercury treatment technologies might be required. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are all examples of common membrane filtration processes. The difference among these processes is the pore size of the membrane. Ultrafiltration has been applied in mercury treatment systems, alongside P/C. Similar to adsorption, membrane filtration is sensitive to suspended solids, organic compounds, and colloids, among other contaminants, because of their potential to foul membranes. Membrane filtration is expected to be able to help reduce mercury concentrations below 2 µg/L.

4.3 CURRENT STATE OF MERCURY BIOLOGICAL TREATMENT

Biological treatment of mercury is not common, but two processes are known to reduce mercury content of waters. One is specifically designed to treat for mercury, while the other has been developed to treat cyanide in mining wastewaters, but also reduces heavy metal concentrations, including mercury.

4.3.1 Mercury-Specific Biological Removal

In the mercury-specific process, aerobic microorganisms transform dissolved ionic mercury ($\text{Hg}^{2+}$) to insoluble elemental mercury. Many microorganisms have the capacity to produce mercuric reductase enzymes, including common bacteria like *Pseudomonas*, that can carry out the reduction. The elemental mercury thus becomes associated with the microbial biomass, which can be settled out in a subsequent clarifier or, in a fixed growth system, stay associated with the media-attached microorganisms. To enable this biological process, appropriate microbial growth conditions must be maintained. Sucrose, salts, and yeast extract are commonly provided to encourage microbial growth, and pH between 6.5 and 7.5 is maintained using sodium hydroxide or phosphoric acid. The biological treatment effluent is treated via adsorption with GAC to remove any remaining mercury, while the residual solids, containing higher mercury concentrations, is likely subjected to additional mercury treatment technologies.

4.3.2 Biocyanide

The biocyanide treatment process has only been applied at pilot scale and features aerobic and anaerobic biological processes. The mechanisms of mercury removal are unclear, but the goal is production of insoluble mercury species, e.g., mercuric sulfide, in the anaerobic reactor. This is achieved by encouraging microbial growth via anaerobic metabolism, including sulfate reduction. The produced sulfide can then react with mercury to generate the desired low-solubility products. Documentation provided in the literature proposing this method is not specific (EPA, 2015b), so this mechanism is speculative.
5. ARSENIC

5.1 ARSENIC’S ENVIRONMENTAL IMPACTS AND TOXICITY

Arsenic is, along with mercury and lead, considered to be one of the three most toxic substances still being released into the environment (Rice et al., 2014). It can cause severe toxicity from both acute and chronic exposures. Arsenic damages cellular energy-harvesting pathways and leads to oxidative stress. In the long-term, arsenic is carcinogenic. Exposure to arsenic comes primarily from drinking water, but also from inhalation and consumption. The U.S. EPA lowered the maximum contaminant level of arsenic from 50 µg/L to 10 µg/L in 2006. In some parts of the world, most notoriously Bangladesh and West Bengal, India, aquifers are contaminated with arsenic at levels up to 3 mg/L (Ratnaike, 2003).

Like selenium and mercury, arsenic toxicity is arsenic species dependent. In its 5+ oxidation state, arsenic is less soluble and less toxic; while at 3+ it is considerably more soluble and more toxic. A study of arsenic-contaminated groundwater in Bangladesh confirmed that over 90% of aqueous phase arsenic was Ar(III) (Gnanaprakasam et al., 2017). Under reducing, or anoxic, conditions, arsenic is more likely to be present in Ar(III). Anaerobic microbial activity can encourage the reduction of arsenic to the more toxic form (Gnanaprakasam et al., 2017). Efforts to treat waters for arsenic must consider environmental conditions and microbial activity.

5.2 ARSENIC TREATMENT

Most of the physicochemical treatment processes employed for arsenic treatment are the same as those used for mercury. These are P/C, adsorption, and membrane filtration. Ion exchange and phytoremediation could also be applied for arsenic treatment. The technologies that were discussed for mercury will only cursorily be discussed here. For more information, see the appropriate section above. A common treatment process for arsenic removal involves oxidation of As(III) to As(V), followed by P/C to produce an arsenic precipitate, and finishing with membrane filtration to remove the precipitated arsenic (EPA, 2002).

5.2.1 Precipitation/Coprecipitation

P/C is applied to arsenic treatment in much the same way it is applied to mercury. A chemical reagent is added to the wastewater and mixed. The reagent encourages precipitation or coprecipitation of the arsenic, and the solid precipitate is removed from the aqueous phase. Pretreatment often precedes P/C, which includes pH change and, even more commonly, oxidation of arsenic to transform any reduced arsenic to the less soluble As(V). Oxidants that are used to achieve this oxidation include potassium permanganate, sodium hypochlorite, or hydrogen peroxide. Ozonation or photo oxidation are also used (EPA, 2002). Iron and alum have been used to encourage precipitation of the As(V). P/C is more robust compared to the alternative treatment technologies discussed below. Successful implementation of P/C for arsenic removal can reliably reduce concentrations to below 50 µg/L. Less than 10 µg/L arsenic has been achieved, but not consistently.

5.2.2 Membrane Filtration

Membrane filtration (Figure 9) has also been used to reduce arsenic concentrations below 50 µg/L or even 10 µg/L, but it is more sensitive to other water quality concerns. Consequently, it is more commonly used in small scale operations or as a final water polishing step and/or where
arsenic is the sole contaminant of concern (EPA, 2002). Membrane filtration tends to be more expensive than other arsenic treatment technologies. This is due at least in part to the low molecular weights of typical arsenic compounds, requiring the use of finer membranes, e.g., nanofiltration or reverse osmosis. As(V) is generally larger than As(III), so pre-treatment typically includes arsenic oxidation. These processes are susceptible to membrane fouling due to a variety of other water quality constituents, as discussed above.

![Figure 9: Model of a membrane filtration system (EPA, 2002).](image)

### 5.2.3 Adsorption

Adsorption (Figure 10) is also applicable to arsenic removal. It has been used for arsenic-contaminated drinking water and groundwater, but not wastewater, where organics and suspended solids are more likely to foul the adsorbent. Greensand adsorption is one common adsorption- and oxidation-based technology. Greensand is made from glauconite, an iron-rich clay-like mineral. Potassium permanganate is added to the greensand, and a layer of manganese oxides forms on the sand. Arsenic passing through the greensand medium is first oxidized to As(V) by the potassium permanganate and then adsorbs onto the greensand. Arsenic is also removed by greensand via ion exchange, whereby arsenic ions displace other ions adsorbed onto the manganese oxide. Activated alumina and iron-based adsorbents are used for arsenic adsorption, especially for drinking water treatment. Activated carbon can be used for arsenic adsorption in drinking water, groundwater, or wastewaters. Surfactant-enabled zeolites have also been developed for arsenic adsorption. Bench-scale experiments demonstrate the potential of surfactant-enabled zeolites to treat arsenic, but no full-scale deployment is known. Pre-treatment of incoming water is needed to maintain the optimal pH for adsorption. For example, pH 6 is best to encourage arsenic adsorption on activated alumina. For any adsorption-based technology, regeneration of the surface of the saturated adsorbent is required. The process depends upon the
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exact type of adsorbent. Thermal treatment is used to regenerate activated carbon surfaces. Subsequent treatment or disposal of the concentrated arsenic waste stream will be required after adsorbent regeneration.

![Figure 10: Model of an adsorption system (EPA, 2002).](image)

5.2.4 Ion Exchange

Ion exchange has been used at full scale to treat arsenic in drinking water and groundwater. As with adsorption, care must be taken to limit organics, suspended solids, and any other constituents that could foul the ion exchange resin. This fact makes ion exchange treatment of wastewater very challenging. In ion exchange, a resin can exchange either cations or anions and is derived from materials—synthetic organics, inorganics, or natural polymers—that contain the desired category of ionic functional groups. The resins are classified as strong or weak acids or bases. Strong bases, which can exchange cations over a larger pH range, are best for arsenic, which is typically present as an anion. When applying ion exchange, the resin is packed into a column. As the contaminate water source passes through the column, arsenic anions replace the anionic functional groups, often hydroxide or chloride, adsorbed onto the resin. The resin will eventually become saturated with arsenic and other fouling agents, at which point it will need to be regenerated. Backwashing to remove the adsorbed ions and fouling agents occurs first. Then the resin can be regenerated with a concentrated solution of appropriate ions and a final rinse. To limit the frequency of regeneration, ion exchange is often achieved using multiple beds in series. The resin in the first bed will need to be regenerated most often, and subsequent beds will need regeneration much less often. Ion exchange for arsenic treatment of drinking waters and groundwater can reduce concentrations to below 50 µg/L and occasionally to less than 10 µg/L.

5.3 CURRENT STATE OF ARSENIC BIOLOGICAL TREATMENT

Microorganisms are capable of conserving energy from cycling arsenic (Wang et al., 2012). In the last few decades, improved understanding of microbial activity has encouraged attempts to implement biological treatment of arsenic. Several pilot scale and at least one full scale biological treatment processes have already been pursued (EPA, 2002). Either suspended or
attached growth microbial systems are believed to be feasible. The goal of biological treatment is to encourage precipitation or coprecipitation of arsenic. Some systems focus on encouraging microbial iron metabolism. With the production of iron oxide solids of large surface area and subsequent contact between the arsenic-contaminated water with the iron oxide-rich biological system, there is potential for arsenic coprecipitation and adsorption. Another approach is to enrich specifically for sulfate- and/or arsenic-respiring microorganisms under anaerobic conditions. The production of sulfide can lead to insoluble arsenic-sulfide complexes. The arsenic solids must be removed, often via filtration processes. As with any biological process, optimal conditions for microbial activity should be considered. Important variables include pH, nutrients, and oxygen content. High arsenic concentrations can also impair microbial activity, making this approach more amenable to low and medium-level arsenic-contaminated waters. It is also important to note that the speciation of the arsenic species affects the tolerance of the microbes. It has been shown that microbes are more tolerant of arsenate (As V) than arsenite (As III) (Wang et al., 2012). Data show that biological treatment can be used to reduce arsenic concentrations below 50 µg/L, but not all systems have consistently achieved those results (EPA, 2002).

### 5.3.1 Phytoremediation

Phytoremediation is the passive process by which plants encourage the sequestering of contaminants present in soils or groundwater. The research literature has shown that phytoremediation can be used to remove arsenic from such environments, concentrating the arsenic within the plant itself up to 250 times the environmental concentration (Chen et al., 2002). Some full and pilot scale applications for arsenic treatment have already occurred (EPA, 2002). Plant root systems must be able to make contact with the arsenic, so phytoremediation is only applicable in cases where arsenic is present in relatively shallow surface/subsurface environments. Exact concentrations of arsenic that are susceptible to phytoremediation are not known, but it is believed that very high concentrations will impair the plants’ activity and, thus, render phytoremediation impossible. After phytoremediation, plant tissues will require subsequent treatment and proper disposal, and care must be taken to avoid animal consumption of phytoremediating plants during and after the process has been implemented.
6. FOAMING

6.1 FOAMING’S IMPACTS

Foaming within the wastewater treatment refers to an abnormally high buildup of gases within a
liquid matrix, creating low density, bubble-like fluids similar to foam. This problem afflicts
numerous industries, including wastewater treatment and pulp processing (Qin et al., 2013).
Foaming can be due to increases in surfactant concentrations that lower the liquid’s surface
tension, thus enabling the entry of gas into the (waste)water column (Hansen et al., 2008). In wet
FGD systems, increased aqueous phase gas concentrations can lead to problems with the quality
of the produced gypsum or, more importantly, poor process efficiency, including reduced
absorption of SO₂ (Qin et al., 2014), and increased solids in the effluent (Qin et al., 2013).

The literature on the role of foaming in FGD systems is extremely limited. Only three reports
have included discussion of the negative impacts of foaming on FGD systems. (All three have
been cited here.) However, power plant personnel reported that foaming was one of their primary
concerns. Given the potential of microorganisms to produce surfactants that could be
contributing to lowering of surface tension (Ron and Rosenberg, 2002) and, ultimately, foaming,
the power plant personnel pointed to this problem as one with a biological origin.

6.2 DEALING WITH FOAMING

A limited body of research has accumulated on foaming in wet FGD systems. These studies
considered possible solutions to foaming problems, i.e., antifoaming agents and membrane
filtration. All the solutions thus far appear to have only been considered at the lab scale.

One study considered the potential of commercial antifoaming agents and rapeseed oil to
mitigate long-term foaming issues. The commercial antifoaming agents performed better than
rapeseed oil (Qin et al., 2013). In all cases, the antifoaming effects were ephemeral; after a short
period post-introduction of antifoaming agent where foaming did not occur, foaming resumed.
Even when the antifoaming agents reduced the production of foam, the FGD system’s SO₂
absorption efficiency remained impaired (Qin et al., 2014). Subsequent studies have looked into
other foaming contexts, outside of FGD systems. Results suggest that membrane filtration
processes, such as nanofiltration, could help reduce foaming (Razzaz et al., 2015).

6.3 CURRENT STATE OF FOAMING BIOLOGICAL TREATMENT

Power plant personnel believed that foaming was due to microbiological activity. But only one
literature source connects wet FGD foaming to microbiological activity (del Valle-Zermeño et
al., 2016). And the extent of this report’s connection is expressed in this statement: “Foaming is
caused by adipidic acids, small particles/electrolytes, and microbiology” (del Valle-Zermeño et
al., 2016). No biological treatment strategies are described here or, as far this research is
concerned, anywhere else in the literature. Further discussions with the power plant personnel
are required to better understand the justification behind their connection of foaming with
microbiological activity, along with any anecdotal evidence of either abiotic or biological
treatment strategies that have been successful in dealing with their FGD foaming issues.

It is important to note that organic anti-foaming additives can also be carbon micronutrient
sources in biological treatment systems, although they are not sufficient enough to be the main
nutrient source (EPRI, 2019).
7. **CONCLUSIONS**

While FGD systems have helped mitigate the release of environmentally detrimental SOx gasses, these systems produce wastewater that require treatment before release back into the environment. The most problematic contaminants in FGD systems are selenium, nitrogen species, mercury, and arsenic. For these contaminants, both abiotic and biological treatment strategies are feasible.

Abiotically, filtration was mentioned as a treatment strategy for these contaminants of interest, but this process is susceptible to failure via fouling. Biological treatment is known for some of these constituents, but it is also important to note that the contaminants in high concentrations can also be fatal to the microorganisms and impair their capabilities. The microorganisms that are capable of treating these contaminants also need a controlled environment in order to conduct microbial processes. The pH of the environment seems to be one of the biggest factors in biological treatment because it can impact both microbial activity and chemical speciation.

And while society has come a long way in treating wastewater, there is still a need for experts in chemistry and microbiology to work with power plant companies to enhance and progress technologies in this area. Further studies still need to be performed to understand how coal composition effects how to treat FGD wastewater. In addition, additional research will also need to be done in order to combat issues like fouling and foaming. It is imperative that research is continued in how to manage energy waste so that future generations can live in a world with clean water and resources.
8. REFERENCES


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