UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

April 12, 2017

THE ADMINISTRATOR

Mr. Harry M. Johnson
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Richmond, Virginia 23129-4074

Mr. Major Clark
Mr. Kevin Bromberg
U.S. Small Business Administration
Office of Advocacy
409 3rd Street, SW, 7th Floor
Washington, D.C. 20416

Re: Petitions for Agency Reconsideration and Stay of Effluent Guidelines for the Steam Electric Point Source Category

Dear Mr. Johnson, Mr. Clark and Mr. Bromberg:

This letter concerns petitions from the Utility Water Action Group dated March 24, 2017, and the U.S. Small Business Administration dated April 5, 2017, to the U.S. Environmental Protection Agency requesting reconsideration and an administrative stay of provisions of the EPA's final rule titled "Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category," 80 FR 67838 (November 3, 2015).

After considering your petitions, I have decided that it is appropriate and in the public interest to reconsider the rule. The EPA is acting promptly to issue an administrative stay of the compliance dates in the rule that have not yet passed pending judicial review, pursuant to Section 705 of the Administrative Procedure Act. This stay will be effective upon publication in the Federal Register. The EPA also intends to request that the U.S. Court of Appeals for the Fifth Circuit stay the pending litigation on the rule for 120 days (until September 12, 2017), by which time the agency intends to inform the Court of the portions of the rule, if any, that it seeks to have remanded to the agency for further rulemaking, after careful consideration of the merits in your petitions. Also, because an administrative stay lasts only during the pendency of judicial review, the EPA intends to conduct notice and comment rulemaking during the reconsideration period to stay or amend the compliance deadlines for the rule. This letter does not address the merits of, or suggest a concession of error on, any issue raised in the petitions.

As part of the reconsideration process, should the EPA conduct a rulemaking to amend the rule or any part of it, the EPA expects to provide an opportunity for notice and comment.

If you have questions regarding the reconsideration process, please contact Sarah Greenwalt at (202) 564-1722. If you have any questions or wish to discuss the litigation, please have your counsel direct inquiries to Jessica O'Donnell at (202) 305-0851.

Respectfully yours,

E. Scott Pruitt

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April 12, 2017

By U.S. Mail and E-mail

Docket No. EPA-HQ-OW-2009-0819

The Honorable E. Scott Pruitt
Administrator
United States Environmental Protection Agency
William Jefferson Clinton Building
1200 Pennsylvania Avenue, N. W.
Mail Code: 1101A
Washington, DC 20460

Supplemental Information in Support of the Utility Water Act Group's Petition for Rulemaking to Reconsider and Administratively Stay the Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category; Final Rule, 80 Fed. Reg. 67,838 (Nov. 3, 2015)

Dear Administrator Pruitt:

Enclosed please find a study by the Electric Power Research Institute entitled *Biological Treatment of Flue Gas Desulfurization Wastewater at a Power Plant Burning Powder River Basin Coal.* We are submitting this study in support of the Utility Water Act Group's Petition for Rulemaking to Reconsider and Administratively Stay the Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category; Final Rule, 80 Fed. Reg. 67,838 (Nov. 3, 2015).

As discussed in our Petition, this study examined the performance of a biological treatment pilot system for flue gas desulfurization wastewater (FGDW) installed at a power plant burning 100% Powder River Basin (PRB) coal. See Petition, pp. 48-49. The results of the study support UWAG's contention that the model FGDW biological treatment used by EPA as a basis for limits within the ELG rule is not demonstrated for FGDW generated by plants burning subbituminous coals such as PRB. The enclosed study, to our knowledge, is the only study of biological treatment at a facility burning 100% PRB coal. The study shows

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the pilot was unsuccessful in attaining consistent compliance with the rule's monthly average selenium limit for FGDW. For most of the pilot study—despite significant adjustments to ordinary operations, including a 50/50 dilution of the FGDW prior to treatment—the pilot results indicate a failure to meet the selenium limit.

A copy of this study has also been electronically mailed to the Office of Water Docket Center for filing in Docket No. EPA-HQ-OW-2009-0819.

Additionally, we will be submitting a supplemental filing in support of our Petition tomorrow.

Please contact me if you have any questions about the study or the Petition.

Sincerely,

Harry M. Johnson, III

Enclosure

cc by hand delivery and e-mail:
Mr. Michael H. Shapiro

cc by e-mail:
Jessica O'Donnell, Esq.
Kevin S. Minoli, Esq.
EPA Docket Center

ELECTRIC POWER
RESEARCH INSTITUTE

Biological Treatment of Flue Gas Desulfurization Wastewater at a Power Plant Burning Powder River Basin Coal

Pilot Demonstration with the ABMet Technology

2017 TECHNICAL REPORT

Biological Treatment of Flue Gas Desulfurization Wastewater at a Power Plant Burning Powder River Basin Coal

Pilot Demonstration with the ABMet Technology

3002006089

Final Report, March 2017

EPRI Project Manager
J. Preece

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The following organizations, under contract to the Electric Power Research Institute (EPRI), prepared this report:

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This publication is a corporate document that should be cited in the literature in the following manner:

Biological Treatment of Flue Gas Desulfurization Wastewater at a Power Plant Burning Powder River Basin Coal: Pilot Demonstration with the ABMet Technology. EPRI, Palo Alto, CA: 2017. 3002006089.

PRODUCT DESCRIPTION

This report documents a pilot demonstration conducted to evaluate treatment of wet flue gas desulfurization (FGD) wastewater at a power plant burning Powder River Basin (PRB) coal. FGD wastewater at PRB sites tends to have very high concentrations of total dissolved solids (TDS), calcium, magnesium, sulfate, nitrate, selenium, and various metals. The low chlorine content of PRB coal enables high cycles of concentration in the FGD absorber because absorber cycles are generally limited on chloride concentration due to specific metallurgy requirements. The resulting wastewater is typically challenging to treat due to the high TDS and high hardness scaling potential.

Background

The U.S. Environmental Protection Agency's (EPA's) revision of effluent limitations guidelines (ELGs) in 2015 has resulted in new requirements for FGD wastewater. Under the rule, EPA established limits based on physical/chemical (P/C) and biological treatment technologies with numeric limits on total arsenic, total mercury, total selenium, and nitrate/nitrite as nitrogen. Limited data are currently available on the treatment of FGD wastewater from PRB coal plants using biological treatment technologies.

Objectives

A pilot system was operated to evaluate and study processes in treating FGD wastewater, using pilot effluent water quality targets associated with the monthly average limits from the U.S. EPA 2015 ELGs. Target concentrations for arsenic, mercury, selenium, and nitrate/nitrite as nitrogen from the pilot system treated effluent were established as 50% of the 2015 ELG monthly average limits to account for initial blending with service water. Analytical and field data were collected to study performance of biological treatment systems on FGD wastewater at a PRB coal site.

Approach

For this demonstration, GE Water & Process Technologies (GE) provided and operated a pilot treatment system consisting of a membrane bioreactor (MBR) process, for nitrification and denitrification, and the Advanced Biological Metals Removal (ABMet) system for denitrification and selenium reduction. The pilot systems were evaluated using a small continuous portion of effluent from the host plant's full-scale P/C treatment system. After initial evaluations of the P/C effluent, GE determined the scaling potential was too high and would create issues in the small pilot equipment. GE also determined that the TDS was too high to support efficient bacteria growth and performance for reducing ammonia, nitrates, and selenium to the demonstration targets. The result of the initial evaluation was a decision to blend the P/C treatment effluent with plant service water (untreated water from Lake Michigan) in equal proportion, and send the combined stream to the pilot system.

Results

The ABMet pilot was initially operated with a total empty bed contact time (EBCT) of 18.8 hours vs. GE's commercial system target of 8 hours. Upon achieving acclimation, GE increased the flow rate through the treatment system to more closely simulate full-scale conditions. After the initial change, the total EBCT for the ABMet pilot was 12.4 hours and remained unchanged due to performance degradation that followed. The pilot system met the effluent targets for the first 3.5 weeks but performance quickly degraded after the flow rate was increased. It is suspected that inhibitory compounds affecting bacteria performance may be present in the FGD wastewater; however, despite various attempts to reduce inhibitory compounds, no resolution was achieved. The ABMet system produced effluent selenium concentrations three times higher than the 6 µg/L target (between 15 and 21 µg/L total selenium). A combination of factors may have resulted in the loss of selenium reduction performance, including:

- Oxidants – Data are limited on specific oxidation compounds present in FGD wastewater and how they may impact biological treatment. Surrogate data on ORP, COD, and BOD were monitored, but do not provide sufficient clarity or causality.
- Non-biodegradable organics – Based on data collected during the test (COD and nitrogen-compound concentrations), it is plausible that organic species were present that are potentially inhibitory to the ABMet bacteria.
- Nitrogen species removal (ammonia, nitrate, nitrite, and organic nitrogen) – This was the first known test using MBR for pretreatment of FGD wastewater and the first known test using a separate denitrification step before ABMet.
- Sulfate-reducing bacteria (SRB) – SRB are known to exist at ABMet conditions due to low ORP conditions and are evident by the presence of sulfide production. It is plausible that the high concentration of sulfates in the site's FGD wastewater, along with the nutrients used, encouraged SRB to suppress selenium-reducing bacteria growth.

Analytical issues with total and dissolved selenium measurements were identified during the project. In some samples, values for total selenium reported low, giving false indications of water quality. Suggested studies to evaluate analytical interferences are presented. Following data validation, the analytical results show that the pilot did not meet the effluent targets for 13 weeks, and the ABMet system was never operated at full-scale conditions.

Applications, Value, and Use

The methods used in this study may provide value for similar biological treatment technology evaluations. Due to site-specific conditions, each site should conduct its own evaluations.

Keywords

Flue gas desulfurization
Wastewater treatment
Selenium removal
ABMet
Effluent Limitation Guidelines
Biological treatment

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EXECUTIVE SUMMARY

Deliverable Number: **3002006089**

Product Type: Technical Report

Product Title: Biological Treatment of Flue Gas Desulfurization Wastewater at a Power Plant Burning Powder River Basin Coal: Pilot Demonstration with the ABMet Technology

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PRIMARY AUDIENCE: Power plant operators, chemists, and engineers and environmental managers

KEY RESEARCH QUESTION

The main objectives of the pilot system were to evaluate and study processes in treating FGD wastewater, using pilot effluent water quality targets associated with the monthly average limits from the U.S. Environmental Protection Agency (EPA) 2015 effluent limitations guidelines (ELGs). This project investigated selenium removal using EPA's selected best available technology (BAT) in order to help plants consistently meet ELG limits, and specifically for plants burning Powder River Basin (PRB) coals.

RESEARCH OVERVIEW

Effluent from the host site's full-scale physical/chemical treatment system was collected and blended with service water (originating from Lake Michigan and untreated) at a 1:1 ratio and supplied to a pilot system designed and operated by GE Water & Process Technologies. Prior to beginning the pilot evaluation, GE determined that dilution of the full-scale physical/chemical treatment system effluent is required in order to minimize the potential negative impacts of scaling, high TDS concentrations, and toxicity in the processes. The pilot system consisted of a membrane biological reactor (MBR) process with two anoxic zones, an aerobic zone with GE's ZeeWeed 500D membranes, and a final anoxic stage. The MBR process was designed mainly to reduce nitrate/nitrite concentrations prior to the Advanced Biological Metals Removal (ABMet) process. The pilot ABMet system consisted of two attached growth, packed-bed biofilters in series, each containing granular activated carbon (GAC) media. Laboratory analyses were conducted on many sample streams in the pilot process, and data were analyzed with process operating data collected throughout the pilot evaluation.

KEY FINDINGS

- The pilot test did not consistently demonstrate that the MBR/ABMet combination of technologies adequately treats selenium to meet the 2015 ELGs limits.
- 100% dilution of FGD wastewater from the effluent of the host site's full-scale physical/chemical treatment system was required for the MBR/ABMet pilot system.
- Complete denitrification (reduction of nitrate nitrogen to nitrogen gas) was achievable in the pretreatment MBR.
- Selenium, present mainly in dissolved form, was significantly reduced by the pretreatment MBR (approximately 75% on average for the entire demonstration).
- Analytical issues with total and dissolved selenium measurements were identified during the project.
- Following data validation, the analytical results show that the pilot did not meet the effluent targets for 13 weeks, and the ABMet system was never operated at full-scale conditions.

EXECUTIVE SUMMARY

WHY THIS MATTERS

This study provided the opportunity for EPRI and its members to evaluate selenium removal in an especially challenging FGD wastewater at a power plant burning PRB coal. The results, learnings, and analytical data from the study will continue to support ongoing research related to biological treatment of FGD wastewater.

HOW TO APPLY RESULTS

Due to site-specific conditions that do not translate to every application, each site should conduct its own evaluations related to FGD wastewater treatment. The methods used in this project may provide guidance for users to apply similar approaches when evaluating biological treatment technologies.

LEARNING AND ENGAGEMENT OPPORTUNITIES

Related projects are:

- *Wet Flue Gas Desulfurization Wastewater Physical/Chemical Treatment Guidelines*. EPRI, Palo Alto, CA: 2016. 3002008515.
- *EPRI Technical Manual: Guidance for Assessing Wastewater Impacts of FGD Scrubbers*. EPRI, Palo Alto, CA: 2006. 1013313.
- *Flue Gas Desulfurization (FGD) Wastewater Characterization and Management: Preliminary Summary: 2007 Update*. EPRI, Palo Alto, CA, 2008. 1014073.
- *Case Studies to Evaluate FGD Wastewater Physical/Chemical Treatment Performance*. EPRI, Palo Alto, CA: 2013. 3002001202.
- *Flue Gas Desulfurization (FGD) Wastewater Chemical Precipitation Treatment Performance Characterization Study*. EPRI, Palo Alto, CA, 2015. 3002006251.
- *Pilot Evaluation of the ABMet Technology for Flue Gas Desulphurization Wastewater Treatment*. EPRI, Palo Alto, CA: 2014. 3002004550.

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PROGRAM: Water Management Technology, P185

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ACRONYMS AND ABBREVIATIONS

°C	degrees Celsius
°F	degrees Fahrenheit
<	less than or fewer than
µg/L	microgram per liter
µm	micrometer
µS/cm	microSiemen per centimeter
BOD	biochemical oxygen demand
COD	chemical oxygen demand
DO	dissolved oxygen
DOC	dissolved organic carbon
EBCT	empty bed contact time
ELG	Effluent Limitations Guidelines
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute, Inc.
FGD	flue gas desulfurization
GAC	granular activated carbon
GPD	gallons per day
GPM	gallons per minute
HRT	hydraulic retention time
Inf/EQ	influent equalization
MBR	membrane biological reactor
mg/L	milligram per liter
mg-N/L	milligram of nitrogen per liter
MLSS	mixed liquor suspended solids
mS/cm	microSiemen per centimeter
mV	millivolt

N	nitrogen
NA	not applicable
ng/L	nanogram per liter
NO_3/NO_2-N	nitrate/nitrite nitrogen
O&G	oil and grease
ORP	oxidation reduction potential
PAC	powdered activated carbon
P4	Pleasant Prairie Power Plant
Phys/Chem	physical/chemical
RAS	return activated sludge
Se	selenium
Se(IV)	selenite
Se(VI)	selenate
SeCN	selenocyanate
SeMe	selenomethionine
SRT	solids retention time
S.U.	standard unit
TCLP	toxicity characteristic leaching procedure
TDS	total dissolved solids
TKN	total Kjeldahl nitrogen
TMP	transmembrane pressure
TOC	total organic carbon
TSS	total suspended solids
WQBEL	water quality-based effluent limit
ZVI	zero-valent iron

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INTRODUCTION

Project Understanding

The U.S. Environmental Protection Agency (EPA) sets technology-based standards, termed effluent limitations guidelines (ELGs), by industry category based on various levels of technology performance, the most stringent of which is the Best Available Technology Economically Achievable (BAT). EPA revised the ELGs for the steam electric industry in 2015 to include BAT limits for flue gas desulfurization (FGD) wastewater.

The BAT limits set by EPA for FGD wastewater are based on physical/chemical and biological treatment technologies with numeric limits on total arsenic, total mercury, total selenium, and nitrate/nitrites as N. The ELGs also include Best Practicable Control Technology (BPT) limits for total suspended solids and oil & grease. EPA's ELG limits for FGD wastewater are shown in Table 1-1. Additionally, water quality-based effluent limits (WQBELs) in some states are necessitating removal of selenium and other trace metals from FGD wastewater.

Table 1-1
ELG Limits on FGD Wastewater

Parameter	Units of Measure	Monthly Average Limit	Daily Maximum Limit
Arsenic, total	µg/L	8	11
Mercury, total	ng/L	356	788
Selenium, total	µg/L	12	23
Nitrate/Nitrite as N	mg/L	4.4	17.0
Total Suspended Solids (TSS)	mg/L	30	100
Oil and Grease	mg/L	15	20

µg/L = microgram per liter
mg/L = milligram per liter
ng/L = nanogram per liter

The primary objective of this project was to investigate and study selenium removal using EPA's selected BAT to help plants consistently meet ELG limits, specifically for plants burning Powder River Basin (PRB) coals. The ELGs also include mercury, arsenic, and nitrate/nitrite limits; studying their removal was a secondary project goal.

This study provided the opportunity for the Electric Power Research Institute, Inc. (EPRI) and its members to help evaluate selenium removal in an especially challenging FGD wastewater at We Energies Pleasant Prairie Power Plant (P4). The main properties of this wastewater that make treatment challenging are scaling tendency due to high sulfate and calcium concentrations; concentrations of dissolved/ionic species such as halogens, which are much higher than other FGD wastewaters from sites burning non-PRB coals; and nitrate/nitrite-nitrogen and total Kjeldahl nitrogen[1] (TKN) concentrations, both of which are also much higher than other FGD wastewaters. Hence, pretreatment for reducing suspended solids, dilution of dissolved solids and a nitrification/denitrification step were included ahead of the selenium removal unit for the P4 pilot, adding to the operational complexity of the pilot system.

P4 burns 100% subbituminous coal from the Powder River Basin, and has a low FGD blowdown rate for its power capacity (40 GPM), allowing the concentrations of ammonia, nitrates/nitrites, sulfates, arsenic, mercury, and selenium to reach very high levels. To EPRI's knowledge, this was the first time that biological treatment has been attempted on a wastewater stream from a plant that burns 100% subbituminous coal.

Pilot Objectives

The main objectives of the pilot system were to evaluate and study processes in treating FGD wastewater, with pilot effluent water quality targets equal to those listed in Table 1-2, and to validate the operating parameters for the membrane biological reactor (MBR) nitrification/denitrification pretreatment step and the Advanced Biological Metals Removal (ABMet) systems. Given the many potential changes and variations in chemistry that are inherent to FGD wastewater, the study attempted to maintain consistent selenium removal performance. When the performance changed, conditions were documented and process changes were made to recover performance.

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[1] Other than uptake for cell synthesis, a selenium treatment system does not remove TKN. Therefore, if a discharge limit for ammonia nitrogen or total nitrogen is included in the permit, a TKN removal step will be required. Because ammonia removal was part of the pilot effluent water quality objectives, the reduction/removal of TKN was monitored.

Table 1-2
Effluent Water Quality Objectives

Parameter	Effluent Target[2]	Pilot Effluent Target[3]
Selenium[1]	<12 µg/L	<6 µg/L
Mercury[1]	<356 ng/L	<178 ng/L
Arsenic[1]	<8 µg/L	<4 µg/L
Nitrate/Nitrite Nitrogen[1] (NO_3/NO_2-N)	<4.4 mg/L	<2.2 mg/L
Total Suspended Solids (TSS)	<30 mg/L	<15 mg/L
Oil and Grease (O&G)	<15 mg/L	<7.5 mg/L
Ammonia	1.9 to 30 mg/L	0.45 to 15 mg/L
Phosphorus	<0.6 mg/L	<0.3 mg/L

Notes:
[1] Regulated pollutants (2015 ELG Final Rule)
[2] 2015 ELGs BAT Monthly Average Limits
[3] 50% of the ELG BAT Monthly Average Limits to account for dilution to reduce high TDS and scale potential
< = less than/fewer than
µg/L = microgram per liter
mg/L = milligram per liter
ng/L = nanogram per liter

2

BACKGROUND

Selenium removal from wastewater is particularly challenging because of its complicated chemistry. Selenium removal typically requires multiple treatment processes, and the species of selenium can vary throughout the different unit processes that target selenium removal. Other constituents in the wastewater may also interfere with the selenium removal processes. As FGD wastewater is a highly complex wastewater (high concentrations of many ions), there are many potential constituents that can affect treatment. Examples include oxyanions like sulfate, halogens like chloride, and nutrients like nitrogen species. Additionally, variations in coal sources, coal composition, plant operations, scrubber operations and other air emission control technologies, and other factors can cause the wastewater composition to vary. Even after successful treatment of selenium, treatment system residuals and byproducts containing selenium must be managed and disposed of properly. This section describes the treatment technologies used for the pilot demonstration.

P4 Existing Full-Scale Wastewater Treatment Plant Description

The full-scale P4 wastewater treatment plant was designed to treat 75 GPM of wastewater with a total suspended solids (TSS) content of less than 1.5%. An overview of the existing physical/chemical system is provided in Figure 2-1. After equalization, wastewater flows to Reaction Tank 1 where pH is adjusted from approximately 5.6 to 8.5 S.U. by adding hydrated lime to the wastewater. Effluent from Reaction Tank 1 flows by gravity to a primary clarifier where polymer is added to aid in solids removal. Primary effluent flows to Reaction Tank 2 where METCLEAR MR2405 (commonly referred to as an organosulfide) is added for mercury precipitation. Effluent from Reaction Tank 2 flows by gravity to Reaction Tank 3 where ferric chloride is added for coagulation and for iron co-precipitation. Effluent from Reaction Tank 3 passes to a flash mix tank where polymer is added, and then to a flocculation tank, followed by a parallel plate clarifier (secondary clarifier). The plant was equipped with an upflow sand filter, but its use has been discontinued due to problems with scaling of sand, recurring fouling issues in the filters, and because it had limited effectiveness in removing mercury below the level achieved by secondary clarification alone. Optional cartridge filters can be installed after the final effluent tanks, when necessary, to filter to 0.45 microns for removal of suspended particles which may contain large amounts of mercury. Sludge is pressed in plate and frame filter presses and combined with coal combustion residuals (CCR) before being landfilled on plant property.

The average operating flow rate for the system is currently 40 GPM. Operations staff run the primary clarifier continuously when the treatment plant is in operation. The secondary clarifier mainly runs throughout the five-day work week and is shut down on weekends for cleaning (to remove scale). The two effluent discharge tanks hold approximately 10,000 gallons each and are used for storage during the weekend cleaning activities.

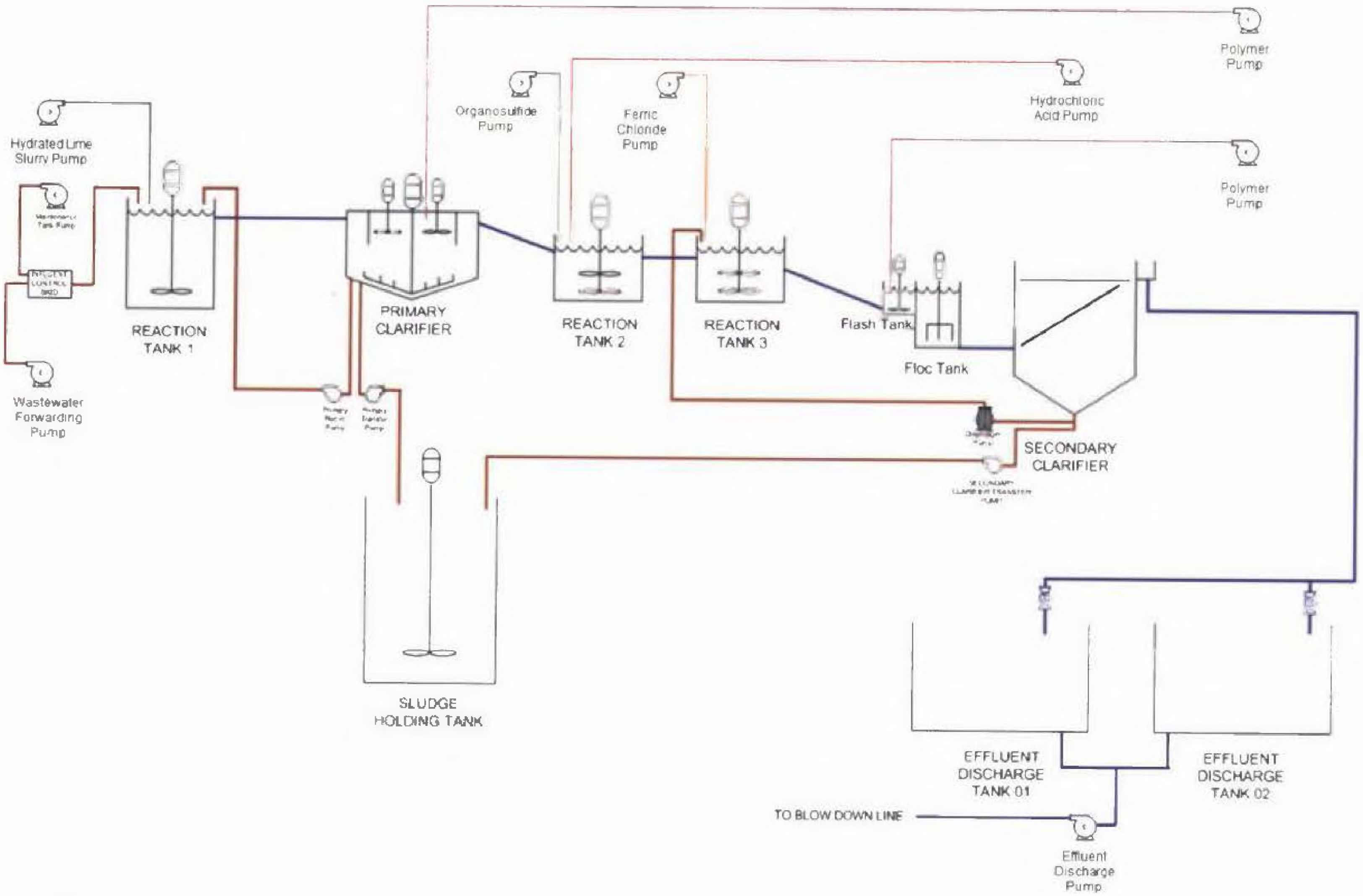

Figure 2-1
P4 FGD wastewater treatment plant process flow diagram
Courtesy of We Energies

Treating Wet Flue Gas Desulfurization Wastewater

Some technologies have been implemented full-scale at FGD wastewater treatment facilities in the United States to remove particulate (generally >0.45 µm) and/or dissolved/soluble selenium from the wastewater stream. Additional processes have been tested on a pilot scale on FGD or other selenium-containing streams. These technologies fall into two main categories:

- Physical/chemical treatment technologies, in which various configurations are possible:
  - Solids settling (is tank-based or in a settling pond; generally removes some particulate selenium, but is likely not sufficient to meet new ELG limits as much of the selenium tends to be in the soluble fraction)
  - Zero valent iron (ZVI) contact (uses complex redox and adsorption reactions to remove soluble forms of selenium)
  - Filtration (removes particulate selenium using media or ultrafiltration membranes; reverse osmosis membrane filtration can potentially remove all forms of selenium, including soluble forms)
- Biological treatment:
  - Fixed-film anaerobic/anoxic (where there are low levels of dissolved oxygen [DO]) reactor-based biological treatment; generally removes various selenium species, including selenate and selenite
  - Passive treatment by surface-flow aerobic wetlands and anaerobic subsurface, vertical flow wetlands (which are generally similar in function to fixed-film systems) have been demonstrated to remove various selenium species
  - Suspended growth anaerobic/anoxic systems (have recently been pilot tested in membrane biological reactors [MBRs] and moving bed biofilm reactors [MBBRs] to remove various selenium species using mechanisms similar to the established fixed-film systems)

The pilot system evaluated by EPRI at P4 is based on active biological treatment for selenium removal, which included anoxic/aerobic MBR for nitrogen pretreatment and the GE ABMet primarily for selenium removal, tested on P4's full-scale chemical precipitation system effluent.

Summary of Treatment Systems and Equipment

The P4 pilot included the following treatment systems:

- ZeeWeed 500D MBR Pilot
- ABMet Pilot

ZeeWeed 500D Membrane Biological Reactor

In anoxic/anaerobic biological treatment, nitrate must be removed from the wastewater in order to create conditions conducive to the biological reduction of selenate and selenite to insoluble elemental selenium. Nitrate removal occurs via denitrification where nitrate/nitrite nitrogen is ultimately reduced to nitrogen gas, but at ORP conditions higher than where reduction of senate and selenite occurs. Unfortunately, removing high concentrations of nitrate using downflow reactors, such as those in ABMet, leads to plugging caused by high bacterial solids growth and the need for more frequent backwashes. Also, because ABMet operates at low oxidation reduction potential (ORP), some ammonia-nitrogen may be formed when high nitrate is present in the influent. Additional reactors may be required to achieve the conditions needed to facilitate effective selenium reduction when high nitrate levels are present in the influent; however, site-specific evaluations must be conducted to determine the exact process suitable for treatment. Therefore, nitrate removal is key to successfully treating selenium in FGD wastewater using any of the established treatment technologies. In this P4 wastewater, the TKN concentration is also high requiring ammonia-nitrogen oxidation to nitrate-nitrogen (nitrification). Therefore, an MBR was included in the pilot system as a pretreatment nitrification/denitrification step to remove both the nitrates in the influent and nitrates generated from the nitrification process.

An MBR is a combination of suspended growth activated sludge and membranes, with the latter performing the liquid/solids separation function. The membranes provide a positive barrier resulting in permeate with negligible TSS concentration. The ZeeWeed 500 module is designed to reject particles greater than 0.04 microns. Treated water is drawn through membrane by vacuum, enters the hollow fibers of the membrane, and is then pumped out of membrane. The redox conditions in stages within the activated sludge system can be manipulated to achieve target reactions (for example, carbon oxidation, nitrification, and denitrification). Target reactions can also convert dissolved species into insoluble constituents and result in rejection by the membranes.

A diagram of the ZeeWeed membrane fiber and ZeeWeed 500 module is provided in Figure 2-2.

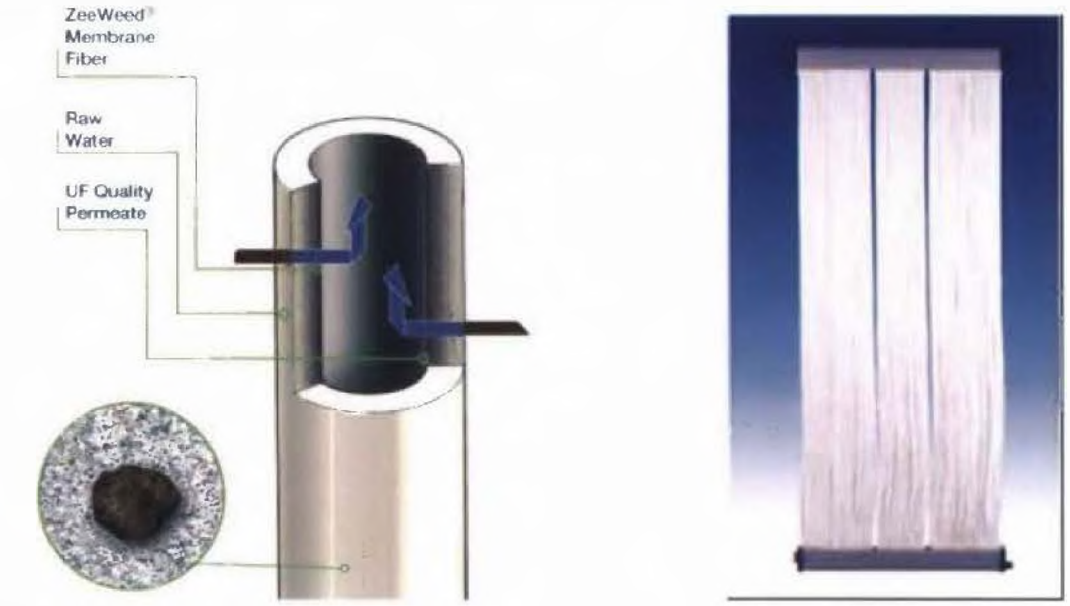

Figure 2-2
ZeeWeed membrane fiber and ZeeWeed 500 module
Courtesy of GE Water & Process Technologies

Membrane permeability is maintained through multiple approaches. During normal operation, continuous air scouring from the bottom of the module is used to remove accumulated solids, containing biological activity and biomass, on the membrane surface. Mixed liquor in the membrane tank is recirculated back to the biological reactors to maintain solids distribution throughout the system. Solids are wasted from the membrane tank based on the targeted solids retention time (SRT). Treatment of the wasted solids is generally a separate process that includes dewatering and disposal of the sludge.

Maintenance of the membranes includes backwashing, maintenance cleanings, and recovery clean-in-place (CIP) activities, all of which can be implemented on a set frequency or based on transmembrane pressure (TMP - calculated by the difference between the membrane influent and effluent pressures). Because the ZeeWeed 500 system is designed to maintain a constant flux, an increase in TMP indicates membrane fouling. Detailed descriptions of each cleaning option are as follows:

- A backwash is performed by reversing the flow through the membrane (also called "back pulse") for a short time period using permeate (clean water produced by the membrane during normal operation) from the inside of the membrane to the outside where the suspended solids are held. For this study, aeration was also used during the backwashes.
- A maintenance cleaning using aeration and chemical cleaning solutions to remove more challenging material from the membrane surface that can lead to fouling. Cleaning solutions may include sodium hypochlorite, citric acid, and other traditional products used to restore membranes. These chemicals are generally recirculated, in separate batches, through the membrane system for a length of time (on the order of 15 minutes) depending on conditions.
- The recovery CIP process is generally conducted only one or two times per year. The process is more aggressive than maintenance cleanings with higher concentrations of chemicals and longer contact times for each batch. Defining the recovery CIP process requires an understanding of treatment and membrane conditions.

ABMet

The ABMet system is an attached growth downflow carbon filter. It was developed by Applied Biosciences and is currently marketed by GE Water & Process Technologies. The ABMet system uses microbes cultured in bioreactor granular activated carbon (GAC) beds that create anoxic/anaerobic conditions for selenate and selenite reduction to insoluble elemental selenium particles. The GAC material acts as a physical media for fixed biofilm development. A diagram of the ABMet biofilter is presented in Figure 2-3.

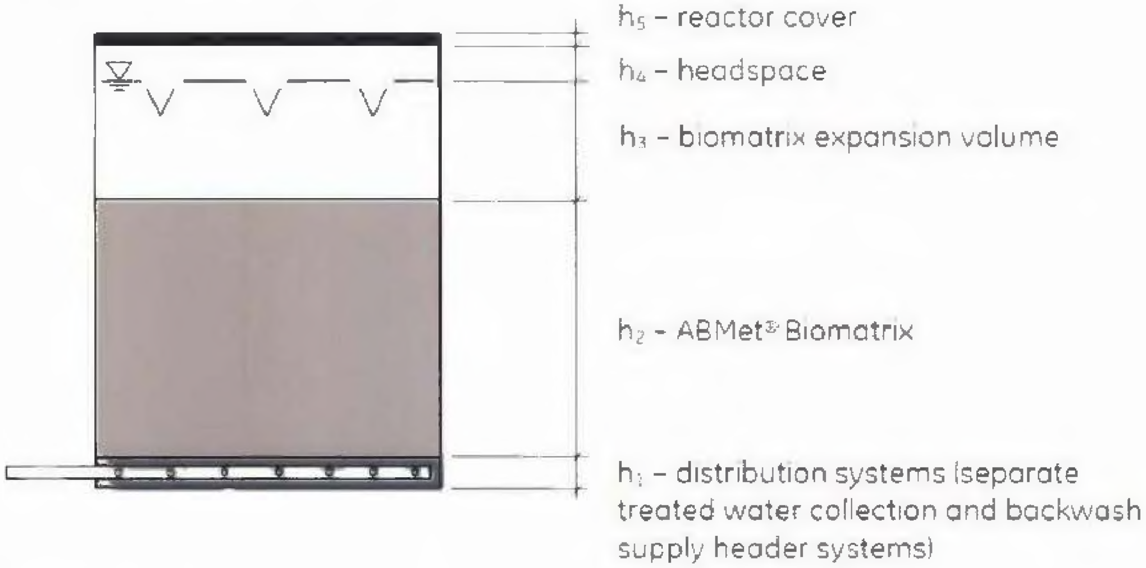

Figure 2-3
ABMet biofilter cross-section
Courtesy of GE Water & Process Technologies

The ABMet process uses certain heterotrophic facultative bacteria, which, in addition to reducing nitrate to nitrogen gas, reduce selenate and selenite to elemental selenium. Elemental selenium then exists as insoluble solids along with bacterial solids in the filter bed. An image of the ABMet selenium reducing bacteria and elemental selenium particles is presented in Figure 2-4.

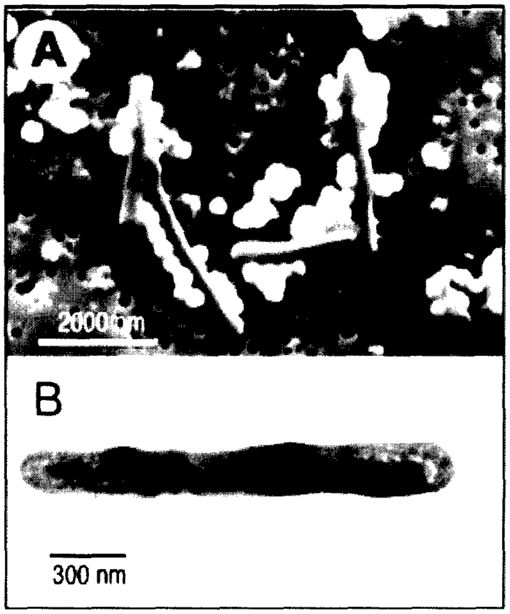

Figure 2-4
ABMet selenium reducing bacteria with selenium particles
Courtesy of GE Water & Process Technologies

The microbes are selected as a site-specific inoculum for the bioreactors. These bacteria are mesophilic bacteria requiring the wastewater temperature to be typically between 50 degrees Fahrenheit (°F) and 100°F (10 degrees Celsius [°C] and 38°C) and pH between 6 and 7 S.U. These microbes use oxygen (O_2) and the oxygen in the nitrate (NO_3^-), selenate (SeO_4^{2-}), and selenite (SeO_3^{2-}) oxyanions as an electron acceptor for their respiration and an organic carbon (electron donor) source to meet their food/energy requirements. Biochemical reactions for the reduction of nitrate/nitrite and selenate/selenite (excluding biomass production) are presented below.

$$NO_3^- + organic\ carbon \rightarrow NO_2^- + organic\ carbon \rightarrow N_2 + CO_2 + H_2O$$

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

The carbon source can be either organic compounds present in the wastewater, typically expressed as chemical oxygen demand (COD), or an organic compound from an external source (such as methanol, acetic acid, ethanol, molasses, or corn syrup). The ABMet system typically uses a molasses-based nutrient supplement (supplied by GE), which also is a source of phosphate for the bacteria, however acetic acid was used for this study as a carbon source for both nitrate and selenium reduction processes. Nutrient addition can also impact pH of the system, where too much nutrient may cause an increase in production of organic acids and CO_2 (both produced by bacteria) that lower the pH.

Biological reduction converts the selenate or selenite ions into elemental selenium, which exists as a particle and is enmeshed and attached to the biofilm within the reactor. The reactors are backwashed periodically to prevent excess biomass and solids buildup and resulting hydraulic head loss, and the waste stream is then treated by dewatering the solids and disposing of the sludge with concentrated selenium. The system is also routinely degassed (similar to backwash, but for a shorter time period) to remove accumulated gases (such as carbon dioxide and nitrogen) from the filter bed to reduce hydraulic head loss. The effluent water from the ABMet unit may be aerated in a polishing aeration tank to increase the DO and to aerobically treat any excess soluble degradable COD-contributing organics, if required.

Monitoring of pH and ORP is performed to control the chemical dosing and ensure selenate and selenite reduction. ORP is an indicator of biological activity in the ABMet system, where lower ORP correlates to anaerobic conditions created by biological activity in reducing oxygen, nitrate/nitrite, and selenium. Once nitrate and nitrite are fully utilized as electron acceptors, selenate, selenite, and sulfate will be used as the primary electron acceptor with remaining biodegradable COD by a different population of heterotrophic microbes. These sulfate-reducing microbe species are generally naturally occurring and their presence/biological activity results in the formation of hydrogen sulfide[2].The sulfate-reducing bacteria may overgrow and outcompete selenate and selenite reducing bacteria for electron donors at high sulfate concentrations. The electron donor (organic carbon) for the ABMet system must also be carefully monitored and controlled to avoid providing too much carbon source for the sulfur-reducing microorganisms. Allowable total sulfide concentrations in the ABMet effluent should be defined during pilot testing for specific applications to minimize competition from sulfate-reducing bacteria.

Solids generated from backwashing (which contain selenium) can generally be recycled upstream to the physical/chemical treatment system (if used) for removal or be treated separately. The resulting dewatered solids are typically tested using the toxicity characteristic leaching procedure (TCLP) to verify nonhazardous classification for disposal, but standards and requirements should be referenced for each site. Solids can generally be processed using solids dewatering equipment such as a plate-and-frame filter press with other solids.

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[2] Hydrogen sulfide is an odorous gas that is detectable at low concentrations (around 1 part per million [ppm]) and can be a human health issue at sufficient concentrations (the U.S. Department of Labor maintains exposure limits under the Occupational Safety and Health Administration standards).

3
PILOT DEMONSTRATION DESIGN

Pilot System Design

Effluent from P4's full-scale physical/chemical treatment system (that is, hydrated lime addition, primary solids removal, trace metals precipitation, and secondary solids removal) was collected and blended with service water (originating from Lake Michigan and untreated) at a 1:1 ratio in the 500-gallon pilot equalization tank. GE designed and operated the pilot system and determined that dilution of the full-scale physical/chemical effluent to minimize the potential impacts of scaling, high TDS concentration, and toxicity was required. For purposes of ELG compliance, however, this sort of dilution would require application of more stringent (i.e., lower) ELGs for constituents. Therefore, treatment without dilution would be preferable to the extent it is feasible. Blended wastewater from the equalization tank provided influent to the nitrification/denitrification pretreatment membrane biological reactor (MBR) system. Effluent from the pretreatment MBR system was collected in a feed tank for the two-stage ABMet system.

An overview of the P4 Pilot system is provided on Figure 3-1.

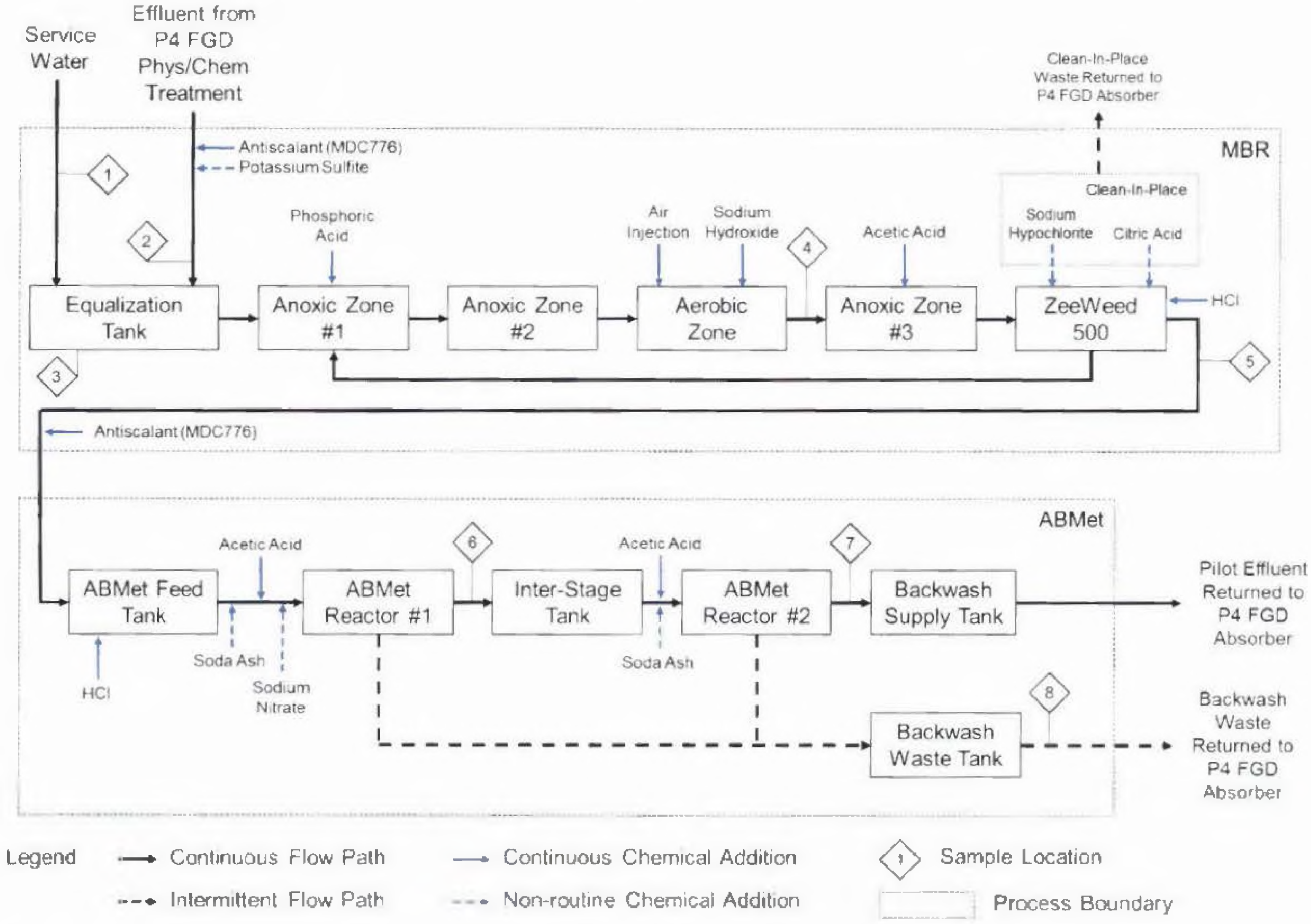

Figure 3-1
Pilot process block flow diagram

Equalization Tank

The 500-gallon equalization tank was provided for blending of P4's full-scale physical/chemical effluent and service water from Lake Michigan (untreated) at a 1:1 volume ratio. A combination of hand valves, flow meters, and flow control valves was used to balance the flows and achieve the targeted 1:1 volume ratio. The blended water from the equalization tank was pumped via submersible pump to anoxic zone #1 in the pretreatment MBR system.

While initial provisions were made to feed different types of chemicals, only antiscalant (MDC776) and potassium sulfite were added to the EQ Tank during testing.

- Antiscalant (MDC776) – To mitigate scaling of calcium, sulfate, phosphate, and other precipitating species. A dosage of 5 mg/L was maintained throughout the study.
- Potassium sulfite – For removal of potential oxidants for mitigating negative impacts to biological activity that may inhibit selenium reduction. Addition began on January 5, 2016, near the end of Condition 2 through Condition 3.

Pretreatment Membrane Biological Reactor

The pretreatment MBR pilot system was seeded with 2,500 gallons of municipal mixed liquor from the Kenosha Wastewater Treatment Plant located in Kenosha, WI. The seeding occurred on October 20, 2015 and the acclimation period, after seeding, lasted four weeks. The system consisted of four zones (anoxic #1, anoxic #2, aerobic, and anoxic #3) followed by the membrane tank, which are described in Table 3-1.

Table 3-1
Pilot MBR System Description

Item	Volume (gallons)	Chemical Addition	Description
Anoxic zone #1	100 [working volume]	Phosphoric acid – macronutrient for bacteria; began in Condition 2 due to switch in acetic acid source from a blended product (which contains phosphorus, but the concentration was deemed too high) to an 80% product (20% balance is water). Target phosphorus concentration was $\leq$3 mg/L in MBR permeate and $\leq$ 0.5 mg/L in the ABMet effluent.	• Received blended water from equalization tank and mixed liquor recirculation from the membrane tank • Mixing provided via mechanical mixer
Anoxic zone #2	100 [working volume]	None	• Received water from anoxic zone #1 • Mixing provided via mechanical mixer
Aerobic zone	1,000 [working volume]	• Ferric chloride – To reduce phosphorus that had been added by the acetic acid blended product, used only during 2-day period in Condition 3; originally intended for soluble arsenic precipitation if it had been needed (but soluble arsenic was not present at concentrations higher than the target value). The blended acetic acid product contained excess phosphorus which may have led to the precipitation of material that created issues with excess solids building in the ABMet biofilter during testing. Scaling and excess solids were ultimately controlled by adjusting the phosphorous content in the nutrient. • Sodium hydroxide – to increase pH	• Received water from anoxic zone #2 • Continuous aeration provided by a blower and fine bubble diffusers
Anoxic zone #3	1,000 [working volume]	• Acetic acid – carbon source for denitrification and partial selenate/ selenite reduction; blended type used during Condition 1; change to 80% acetic acid made in Condition 2. Switched made due to high concentration of phosphorus in blended product.	• Received water from aerobic zone • Mixing provided via mixing pump
ZeeWeed Membrane tank	270	• Sodium hypochlorite – membrane cleaning • Citric acid – membrane cleaning • Hydrochloric acid – to decrease pH (beginning in Condition 2)	Three ZeeWeed modules provided, but only one was placed in service

The blended water was pumped from the equalization tank to anoxic zone #1, which had an underflow to anoxic zone #2. The water then overflowed to the aerobic tank. The aerobic tank was fitted with 10 fine bubble diffusers to achieve the desired dissolved oxygen (DO) concentration of 2 to 4 mg/L. Also, pH monitoring, with a control set point of 6 - 7[3] S.U., was provided in the aerobic tank. Level controls within the aerobic tank controlled the flow to anoxic zone #3. A mixing pump and eductors were provided in anoxic zone #3 for mixing and allowed for the water to be pumped to the membrane tank.

The membrane tank consisted of three 370 ft^2 ZeeWeed 500 membranes, which is a scaled-down version of a full-scale membrane system. Only one membrane, located in the middle module, was in service for this pilot; the other two membranes/modules were plugged and not placed into service. This configuration allowed for normal operation of the air diffuser system that is located inside the membrane tank. Suction drives the treated water through the hollow fibers of the membrane using an outside-in configuration. Membranes were cleaned with constant air scouring along with periodic chemical cleans. For a full-scale system, all waste streams would be evaluated for treatment, potentially by recycle to the physical/chemical process upstream. Overflow from the membrane tank was recirculated to anoxic tank #1.

The main objectives of the pretreatment MBR were as follows:

- Nitrify influent TKN/ammonia nitrogen – oxidation of ammonia nitrogen to nitrate nitrogen
- Denitrify influent and produce nitrate nitrogen – reduce nitrate/nitrite nitrogen to nitrogen gas
- Produce an effluent with very low TSS suitable for treatment in the downstream ABMet system
- Remove insoluble selenium in influent and produced in the MBR anoxic tank

Permeate from the pretreatment MBR was collected in the ABMet system's feed tank. A picture of the MBR pilot equipment is shown in Figure 3-2.

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[3] The pilot MBR pH control set point of 6 - 7 S.U. was established by GE. CH2M suggested that a slightly higher control range of 6.8 - 7.5 S.U. would minimize impacts on nitrification. Actual operating range, as discussed in Section 4, was 6.8 - 7.2 S.U.

Figure 3-2
ZeeWeed 500 MBR pilot
Courtesy of GE Water & Process Technologies

ABMet

The ABMet pilot system consisted of two reactor stages (each with 1,270 L of GAC), feed and inter-stage tanks, a backwash system, and chemical feed systems, which are described in Table 3-2. The ABMet reactors were seeded with GE's bacteria on November 20, 2015, and placed into forward flow on November 23.

Table 3-2
Pilot ABMet System Description

Item	Volume (gallons)	Chemical Addition	Description
ABMet feed tank		• Hydrochloric acid – to decrease pH (beginning in Condition 2) • Soda ash – to increase alkalinity (Condition 2 only) • Antiscalant, MDC776 (Began at Condition 2)	Received pretreatment MBR permeate
ABMet stage 1	335	• Acetic acid – carbon source for denitrification and selenate/ selenite reduction; used blended version that contained nutrients (ammonium and phosphorus) starting in Condition 2 • Sodium nitrate – nitrate (electron acceptor) source to enhance denitrification, but added only mid-way through Condition 4	Received pretreatment MBR permeate from the ABMet feed tank
ABMet inter-stage tank		Soda ash – to increase alkalinity (Condition 2 only)	Received ABMet stage 1 effluent

Table 3-2 (continued)
Pilot ABMet System Description

Item	Volume (gallons)	Chemical Addition	Description
ABMet stage 2	335	Acetic acid – carbon source for denitrification and selenate/selenite reduction; used blended product (containing acetic acid, ammonium, and phosphorus) during Condition 1 and 80% acetic acid product (20% water) during Conditions 2, 3, and 4.	Received ABMet stage 1 effluent from the ABMet inter-stage tank
ABMet effluent tank		None	Received ABMet stage 2 effluent
Backwash supply tank	3,000	None	Received ABMet stage 2 effluent from the ABMet effluent tank to degas and backwash the ABMet filters
Backwash waste tank	800	None	Received backwash waste from ABMet stage 1 and ABMet stage 2

Permeate from the pretreatment MBR was collected in the ABMet feed tank from where it was pumped to the top of the ABMet stage 1 reactor. Effluent from the ABMet stage 1 was collected in an inter-stage tank from where it was pumped to the top of the ABMet stage 2 reactor. Effluent from the ABMet stage 2 was collected in an effluent tank and then pumped to the backwash supply tank that allowed the effluent to overflow from the system to the effluent where all waste was returned to the P4 FGD Absorber.

The GAC media in each ABMet stage reactor provided surface area for bacteria to grow and develop a biofilm. Nutrient addition, pH control, and alkalinity adjustment were provided for each ABMet stage to provide a suitable/optimized environment for selenium reduction.

The main objectives of the ABMet system operation were as follows:

- Denitrify any remaining influent nitrate nitrogen and reduce nitrate/nitrite nitrogen to nitrogen gas.
- Reduce soluble selenium species (selenate and selenite) to particulate, elemental selenium and remove it from the wastewater.

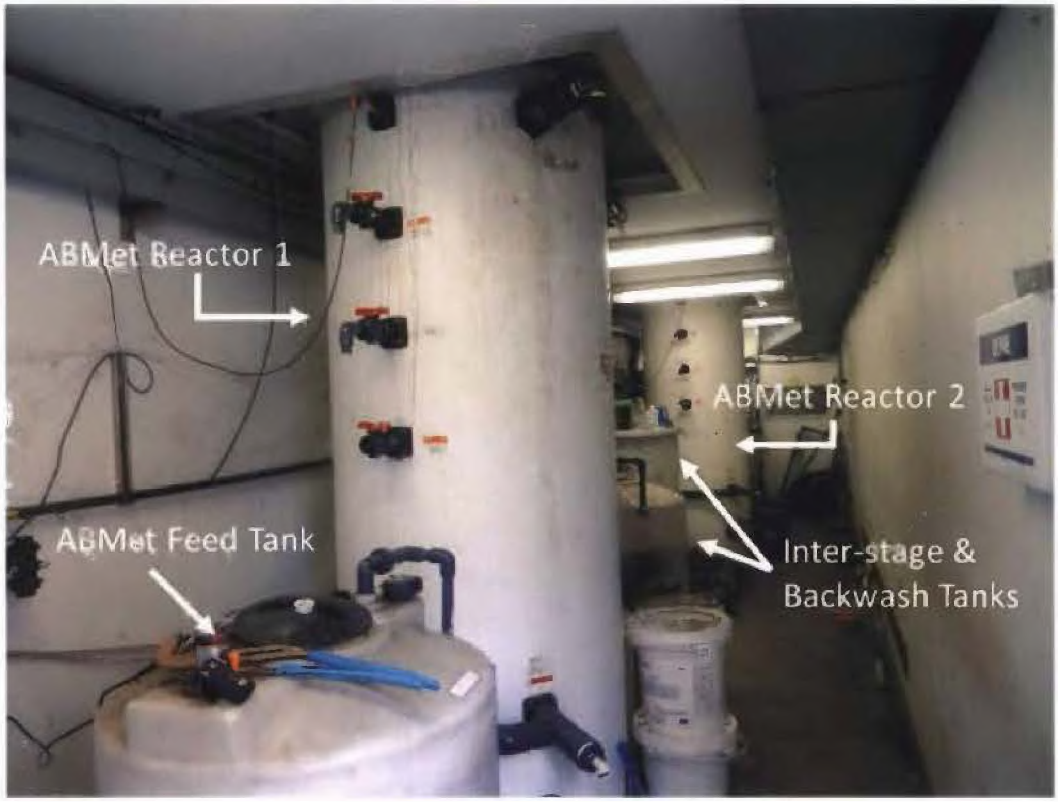

Figure 3-3
ABMet pilot equipment

Pilot Schedule and Conditions

Operating data for the MBR and ABMet systems have been divided into the following four conditions:

- Condition 1 – Startup and Acclimation (October 26, 2015 to December 16, 2015) – period where bacteria are growing and becoming established in the treatment system.
- Condition 2 – Initial Operation (December 17, 2015 to January 10, 2016) – operational period defined by GE's original test plan.
- Condition 3 – Increased Flow/Reduced HRT (January 11, 2016 to February 13, 2016) – operational period intended to more closely simulate full-scale HRT/EBCT conditions.
- Condition 4 – Process Adjustments (February 14, 2016 to March 3, 2016) – period where GE responded to decreased selenium removal performance of the ABMet.

Increasing the flow rate under Condition 3 was a conscious decision made by the project team in an effort to simulate full-scale conditions (i.e., to match HRT/EBCT for each process technology). Due to factors that resulted in poor selenium removal performance, of which increased flow rate is not believed to be a sole-contributor, additional process changes were made during Condition 4 in attempt to return the pilot systems back to original selenium removal performance (which had been meeting the effluent/treatment targets).

- The project team was able to extend the duration of the pilot demonstration past its original end date, but testing concluded when the P4 units entered an outage and were not able to supply FGD wastewater. For two weeks prior to pilot shutting down, the ABMet system was operated by feeding blended physical/chemical treatment effluent from the storage tanks with ABMet effluent; the MBR did not operate during this time.
- Details on the process conditions, adjustments, and performance changes are provided in the following sections.

Field and Laboratory Analytical Plans

Field and laboratory analyses were conducted to control system operation and optimize performance. Field analyses were conducted by GE throughout the demonstration on the MBR and ABMet pilot systems. A summary of field parameters and frequency of the analyses are provided in Table 3-3.

Table 3-3
Field Analyses

Parameter	Minimum Frequency (per week)
Chemical tank levels (inches)	3
pH (S.U.) by handheld meter	5
Dissolved oxygen (mg/L) by handheld meter	5
Conductivity (μS/cm) by handheld meter	5
ORP (mV) by inline meter	5
Nitrate/nitrate (mg of N/L) by HACH test kit	5
Temperature (°F)	5
Raw Water Totalizer (gallons)	5
Service Water Totalizer (gallons)	5
Anoxic zone #1 level (inches)	5
Anoxic zone #2 level (inches)	5
Anoxic zone #3 level (inches)	5

Laboratory analyses were conducted by We Energies' corporate lab, TestAmerica Laboratories, Inc., and Brooks Applied Labs for analytical chemistry evaluations. Parameters analyzed by each lab are summarized in Table 3-4, Table 3-5, and Table 3-6. Turnaround times for parameter results varied with each lab, but were generally one to two weeks with the exception of selenium by We Energies which was within three days. Samples were shipped to We Energies' lab and TestAmerica same-day and all samples requiring dissolved parameter analysis were filtered by the labs. Samples sent to Brooks Applied were on 24-hour delivery shipping. Samples analyzed by We Energies and TestAmerica were taken every Monday, Tuesday, and Thursday during Conditions 1 and 2 and only Tuesday and Thursday during Condition 3. The entire analytical plan, which identifies the sample locations and frequencies, is provided in Appendix A.

Table 3-4
We Energies Lab Analyses

Parameter	Analytical Method
Aluminum, total and filtered	EPA 200.7
Arsenic, total and filtered	EPA 200.8 DRC-O2
Boron, total and filtered	EPA 200.7
Cadmium, total and filtered	EPA 200.7 / EPA 200.8
Calcium, total and filtered	EPA 200.7
Cobalt, total and filtered	EPA 200.7
Copper, total and filtered	EPA 200.7 / EPA 200.8
Iron, total and filtered	EPA 200.7
Lead, total and filtered	EPA 200.7 / EPA 200.8
Magnesium, total and filtered	EPA 200.7
Manganese, total and filtered	EPA 200.7
Mercury low-level, total and filtered	EPA 1631E
Mercury low-level, 0.45 µm	EPA 1631E
Molybdenum, total and filtered	EPA 200.7
Molybdenum, filtered	EPA 200.7
Nickel, total and filtered	EPA 200.7
Selenium, total and filtered	EPA 200.8 DRC-NH3
Silver, total and filtered	EPA 200.7
Sodium, total and filtered	EPA 200.7
Thallium, total and filtered	EPA 200.8
Tin, total and filtered	EPA 200.7
Zinc, total and filtered	EPA 1638 DRC

Table 3-5
TestAmerica Lab Analyses

Parameter	Analytical Method
Alkalinity	SM2320B
Ammonia	SM4500
Bicarbonate	SM2320B
BOD	SM5210B
Carbonate	SM2320B
Chlorides, filtered	SM4500
COD	SM5220C
Conductivity, µS/cm	SM2510B
Fluoride, total	SM4500
Nitrate/Nitrate (N)	SM4500
Phosphorus, total	SM4500
Sulfate, filtered	SM4500
Sulfide	SM4500
TDS	SM2540C
TKN	SM4500
TOC	SM5310C
TSS	SM2540D

Table 3-6
Brooks Applied Lab Analyses

Parameter	Analytical Method
Arsenic, total and filtered	EPA 200.8/6060
Arsenic Speciation, filtered[1]	EPA 200.8/6060
Selenium, total and filtered	EPA 200.8/6060
Selenium Speciation, filtered[1]	EPA 200.8/6060

[1] Speciation analyses only conducted on pilot influent and effluent samples

4

RESULTS AND DISCUSSION

This section presents the results associated with the P4 pilot study. Raw data from the pilot study are presented in Appendix C.

During the pilot study, influent water quality/chemistry was considered typical for the site (no major upsets/excursions or abnormal conditions occurred in any process upstream of the pilot system). The P4 wastewater treatment system was offline for two weeks in mid-November 2015 (during the MBR and ABMet acclimation period in Condition 1) due to mechanical issues, but stored effluent water provided consistent flow and chemistry to the pilot. In mid-February 2016, the P4 system shut down again through the beginning of March, but stored water (with consistent chemistry) was provided to the pilot. The demonstration ended March 3, 2016. There were many performance changes in the pilot MBR and ABMet processes throughout the demonstration. These changes are documented and described to the best of the project team's capabilities.

Pilot Influent Water Quality

Table 4-1 presents a summary of the blended pilot influent water quality (50 percent full-scale physical/chemical treatment effluent and 50 percent service water from Lake Michigan [untreated] by volume). The blended pilot influent total selenium concentration averaged 1,175 μg/L with a range of 770 to 2,500 μg/L. The blended pilot influent dissolved selenium concentration averaged 1,093 μg/L. Comparisons between each data set revealed most of the blended influent selenium was in the soluble form. Nitrate/nitrite nitrogen averaged 98 milligrams of nitrogen per liter (mg-N/L), with a range of 65 to 160 mg-N/L. Ammonia averaged 52 mg/L with a range of 10 to 180 mg/L[4]. The ranges indicate variability in the full-scale physical/chemical effluent, which was observed over the course of the pilot study. The variability could be explained in part by the site's normal maintenance process of shutting down the physical/chemical system every week for manual cleaning of the components. During this time, the concentrations of components build in the absorbers and a new "batch" of water is delivered to the system every Monday morning.

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[4] The higher concentrations of ammonia may be attributed to selective catalytic reduction (SCR) layers approaching end of life at P4, causing higher ammonia injection rates to be used for meeting NO_x removal requirements which subsequently increases the ammonia concentration in the FGD wastewater. SCR catalyst life decays naturally over many years until replacement is needed. The replacement is generally scheduled with a steam generator/boiler outage.

Table 4-1
Blended Pilot Influent Water Quality

Parameter	Units	Pilot Influent – All Operating Conditions		
		Minimum	**Maximum**	**Average**
Total Selenium	µg/L	770	2,500	1,175
Dissolved Selenium	µg/L	710	1,900	1,093
NO_2/NO_3-N	mg/L	65	160	98
Total Mercury	ng/L	20	240	72
Dissolved Mercury	ng/L	6.9	29	13.5
Total Arsenic	µg/L	0.45	8.10	4.67
Dissolved Arsenic	µg/L	0.45	8.50	4.68
pH[1]	S.U.	6.6	7.7	
Total Calcium	mg/L	400	830	479
Dissolved Calcium	mg/L	400	840	471
Total Magnesium	mg/L	1,600	3,100	2,039
Dissolved Magnesium	mg/L	1,600	3,100	2,023
Ammonia	mg/L	10	180	52
Conductivity	µS/cm	11,000	22,000	13,378
COD	mg/L	360	1,600	596
BOD	mg/L	1.00	2.60	1.8
TOC	mg/L	5.1	77.0	28.1
Chloride	mg/L	2,300	3,200	2,690
Fluoride	mg/L	18.0	43.0	24.0
Sulfate	mg/L	6,200	11,000	7,805
Ortho-Phosphate	mg/L	<0.027	0.74	0.10
Total Phosphorus	mg/L	0.027	0.750	0.093
Total Kjeldahl Nitrogen (TKN)	mg/L	42	220	101
Sulfide	mg/L	<0.22	1.70	0.15
TSS	mg/L	4	31	12
TDS	mg/L	12,000	25,000	16,452
Total Alkalinity	mg/L	78	120	103
Bicarbonate Alkalinity	mg/L	78	120	103
Carbonate Alkalinity	mg/L	<3.9	<3.9	<3.9

Notes:
Blended Influent: 50 percent full-scale physical/chemical treatment effluent and 50 percent service water from Lake Michigan (untreated)
[1] Analysis performed onsite
BOD = biochemical oxygen demand
µS/cm = microSiemen per centimeter
S.U. = standard units
TDS = total dissolved solids
TOC = total organic carbon

Variability (the difference between minimum and maximum concentration values) was also observed in arsenic and mercury throughout the study. The data indicate pilot feed water contained arsenic mostly in the soluble form whereas mercury was mostly in the particulate form. The TDS ranged from 12,000 to 25,000 mg/L during the pilot study.

The following sections discuss the pilot study results, including operational parameters and effluent water quality for each operating condition.

Membrane Biological Reactor

Operating Parameters

MBR operational parameters are discussed in this section. As previously mentioned, the P4 full-scale physical/chemical treatment effluent was blended with service water from Lake Michigan at a 1:1 ratio in the pilot's equalization tank. This blended stream served as influent to the pilot system and was pumped to the MBR anoxic zone #1.

After the initial seeding with biomass from the local municipal wastewater treatment plant, the mixed liquor was recirculated through the MBR for two days with 300 gallons of blended pilot feed water. The system was placed in forward flow through the MBR after these two days and acclimation continued for four weeks. Table 4-2 compares the MBR operational parameters at the four test conditions. The flow rate to the MBR averaged approximately 1 GPM during Conditions 1 and 2 and 1.5 to 1.6 GPM in Conditions 3 and 4. This resulted in combined HRT in the bioreactor zones decreasing from approximately 35 hours during Conditions 1 and 2 to approximately 23 hours during Conditions 3 and 4. The increase in flow rate and subsequent reduction in HRT was part of the initial pilot test plan. Operating at the lower flow rate initially was intended to allow for adequate acclimation of the biomass and the plan was to increase the flow rate after acclimation in order to simulate full-scale conditions.

Table 4-2
MBR Operational Parameters

Condition Description	**Startup and Acclimation**	**Initial Operation**	**Increased Flow/ Reduced HRT**	**Process Adjustments**
Condition Number	**1**	**2**	**3**	**4**
Parameter/Dates	**10/26/15 to 12/16/15**	**12/17/15 to 1/10/16**	**1/11/16 to 2/13/16**	**2/14/16 to 3/3/16**
Influent Flow Rate				
Average	1.05 GPM	1.01 GPM	1.54 GPM	1.6 GPM
Range	1 to 2.6 GPM	1 to 1.25 GPM	1.25 to 1.6 GPM	1.6 GPM
MBR pH Control Set Point	6.8 to 7.2	6.8 to 7.2	6.8 to 7.2	6.8 to 7.2
MBR HRT Anoxic Zone #1	1.6 hours	1.7 hours	1.1 hours	1.0 hour
MBR HRT Anoxic Zone #2	1.6 hours	1.7 hours	1.1 hours	1.0 hour
MBR HRT Aerobic Zone	15.9 hours	16.5 hours	10.8 hours	10.4 hours
MBR HRT Anoxic Zone #3	15.9 hours	16.5 hours	10.8 hours	10.4 hours
ZeeWeed 500 Flux	10 GFD (first 3 weeks) 5.8 GFD	5.8 GFD	5.8 GFD	5.8 GFD
ZeeWeed 500 Backwash Flux	20 GFD	20 GFD	20 GFD	20 GFD
MBR Aeration Rate	12 SCFM	12 SCFM	12 SCFM	12 SCFM

Table 4-2 (continued)
MBR Operational Parameters

Condition Description	Startup and Acclimation	Initial Operation	Increased Flow/ Reduced HRT	Process Adjustments
Condition Number	**1**	**2**	**3**	**4**
Parameter/Dates	**10/26/15 to 12/16/15**	**12/17/15 to 1/10/16**	**1/11/16 to 2/13/16**	**2/14/16 to 3/3/16**
MBR MLSS				
Average	5,760 mg/L	3,950 mg/L	2,690 mg/L	4,183 mg/L
Range	3,400 to 6,500 mg/L	3,700 to 4,200 mg/L	1,000 to 6,500 mg/L	2,900 to 5,800 mg/L
RAS Flow Rate	6 to 8 GPM	6 to 8 GPM	6 to 8 GPM	6 to 8 GPM
Sludge Wasting Rate	none	none	80 GPD	none
MBR DO Anoxic Zone #1				
Average	0.93 mg/L	2.55 mg/L	3.37 mg/L	0.12 mg/L
Range	0.11 to 2.4 mg/L	1.74 to 3.90 mg/L	1.12 to 6.23 mg/L	0.02 to 0.49 mg/L
MBR DO Anoxic Zone #2				
Average	0.23 mg/L	0.29 mg/L	1.34 mg/L	0.02 mg/L
Range	0.01 to 2.06 mg/L	0 to 2.49 mg/L	0 to 5.53 mg/L	0 to 0.2 mg/L
MBR DO Aerobic Zone				
Average	3.20 mg/L	3.19 mg/L	4.02 mg/L	2.84 mg/L
Range	0.86 to 5.90 mg/L	1.7 to 4.93 mg/L	0.17 to 9.00 mg/L	0.43 to 5.22 mg/L
MBR DO Anoxic Zone #3				
Average	0.14 mg/L	0.02 mg/L	0.02 mg/L	0.01 mg/L
Range	0 to 0.56 mg/L	0 to 0.05 mg/L	0 to 0.13 mg/L	0 to 0.04 mg/L
MBR ORP Anoxic Zone #3				
Average	-387 mV	-423 mV	-331 mV	-354 mV
Range	-143 to -489 mV	-376 to -477 mV	-58 to -427 mV	-83 to -416 mV
Number of Membranes in Service	1	1	1	1
Chemical Doses				
Hydrochloric Acid (to ZeeWeed Tank)	950 mg/L	950 mg/L	400 mg/L	400 mg/L
Sodium Hydroxide (to Aerobic Zone)	350 mg/L	350 mg/L	350 mg/L	none
COD Added via Acetic Acid to Anoxic Zone #3				
Average Added	897 mg/L	618 mg/L	447 mg/L	643 mg/L
Range	563 to 1,464 mg/L	452 to 807 mg/L	227 to 565 mg/L	630 to 756 mg/L
Ferric Chloride (to Aerobic Zone)	60 mg/L (2 days only)	none	none	none
Phosphoric Acid (to Anoxic Zone #1)	none	5 mg/L	5 mg/L	5 mg/L
Potassium Sulfite (to Equalization Tank)	none	none	25 to 200 mg/L	none

Notes:

GFD = gallons per square feet per day

SCFM = standard cubic feet per minute

GPD = gallons per day

GPM = gallons per minute

mV = millivolt

RAS = return activated sludge (the flow from ZeeWeed tank to MBR Anoxic Zone #1)

On average, the DO was maintained above 2.8 mg/L (2-4 mg/L target) in the aerobic zone and was less than 0.1 mg/L (<0.5 mg/L target) in anoxic zone #3 during Conditions 2, 3, and 4. The ORP in anoxic zone #3 averaged less than -330 mV during all four conditions. These values were within GE's target range.

As noted in Table 3-1, the acetic acid product used to supply nutrients for the biological process was changed during the study. The blended acetic acid product was first used during Condition 1, and contains an organic carbon source (acetic acid), ammonium, and phosphorus (the latter two are nutrients). Due to the higher than anticipated phosphorus concentration (20 times higher) in the blended acetic acid, the carbon source was switched to an 80 percent solution of unblended acetic acid (the balance 20 percent is water) for Conditions 2, 3, and 4 to limit excess phosphorus in the final effluent. The excess phosphorous led to precipitation of excess solids which, if left untreated, could cause prolific scaling in the process equipment. To prevent scaling with the blended nutrient product, ferric chloride was added to the aerobic zone for two days until the nutrient product was changed. Afterward the acetic acid source was changed, ferric chloride dosing was stopped. Phosphoric acid was fed after the acetic acid product was changed to achieve less than 3 mg/L in the MBR permeate. The reduction in COD added by the nutrient from Conditions 1 to 2 to 3 (noted in Table 4-2) coincides with the project team's attempts to increase nitrate/nitrite concentration in the MBR permeate in attempt to improve ABMet selenium reduction. Additional discussion is provided in the ABMet section.

The ZeeWeed membrane flux was initially set to 10 GFD with an operating cycle time[5] of 10 minutes and resting mode duration of 30 seconds. During the first three weeks of operation in the acclimation period, the ZeeWeed TMP averaged less than 1 PSI. It was also during this time that the acetic acid feed point was inadvertently placed at the aerobic zone instead of the anoxic zone #3. Once the feed point was moved, an increase in TMP was observed and the membrane flux set point was reduced to 5.8 GFD. A second spike in TMP occurred gradually from December 12 through 24, 2015. Once the TMP reached 8 PSI, the system was placed in automatic standby and from December 24 through 28, the MBR and ABMet systems were offline due to the high MBR TMP. A recovery clean was completed on December 27 and 28; the recovery clean included soaking the membranes in a 1,000 mg/L solution of sodium hypochlorite, followed by soaking in a 2,000 mg/L solution of citric acid. The system was placed back into operation on December 28 and the maintenance cleaning schedule was adjusted for a citric acid cleaning every other day.

The MBR process accumulates solids that come from biomass production and naturally by precipitation of various chemical species in the wastewater. The MBR solids, referred to as mixed liquor suspended solids (MLSS), were purged from the system beginning in early January 2016 at 80 GPD. The MLSS purge rate was set to 20 gallons every 6 hours to avoid reducing flow to the ABMet. Discharge of MLSS ended in mid-February due to low MLSS concentrations and decreased selenium reduction performance (additional details are provided in the next section).

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[5] Cycle time refers to the changing of the membrane operating mode from filtration to resting. In filtration mode, a vacuum is maintained to pull water through the membrane and produce treated effluent. In resting mode, no vacuum is applied to the membranes and the air scour is maintained to help remove solids. [1]

Treated Water Characteristics

This section discusses the characteristics of the MBR pilot treated effluent (permeate). The MBR process was operated to remove ammonia, nitrates, and selenium while being monitored for potential impacts from chemical scaling and high TDS. Membrane performance and optimization of the HRT and SRT were monitored throughout the study.

Table 4-3 summarizes the treated effluent water quality based on samples collected during each operating condition. Figures 4-1, 4-2, 4-3, 4-4, and 4-5 present MBR influent and effluent COD and phosphorus; ammonia and total Kjeldahl nitrogen (TKN); nitrate/nitrite nitrogen; selenium; and mercury, respectively.

As seen in Table 4-3, the MBR effluent phosphorus concentration was higher during Condition 1; however, as Figure 4-1 shows, the influent phosphorus concentration was consistent for the pilot study. The increased MBR effluent phosphorus concentration during Condition 1 was due to the higher-than-planned-for phosphorus content of the nutrient balanced acetic acid blend being added. Once the acetic acid was switched to the 80 percent solution in the first week of December 2015 (near the beginning of Condition 2), the MBR effluent phosphorus concentration decreased.

Table 4-3
MBR Treated Effluent (Permeate) Water Quality[1]

Parameter	Units	Condition 1			Condition 2			Condition 3			Condition 4		
		Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.
Total Selenium	μg/L	120	350	200	110	260	173	170	590	337	170	460	231
Dissolved Selenium	μg/L	120	340	190	120	260	167	170	600	330	160	460	233
NO_2/NO_3-N	mg/L	0.19	160	35	0.12	0.24	0.15	0.13	21	4.0	0.09	0.18	0.13
Total Mercury	ng/L	1.44	3.94	2.46	1.60	3.68	2.58	1.01	5.67	2.67	1.93	1.94	1.94
Dissolved Mercury	ng/L	1.10	3.33	2.02	0.23	3.06	1.96	0.64	2.97	1.92	0.66	0.90	0.78
Total Arsenic	μg/L	3.7	5.1	4.7	4	5	4	--	--	--	--	--	--
Dissolved Arsenic	μg/L	3.6	5.0	4.5	4	5	4	--	--	--	--	--	--
Total Calcium	mg/L	440	520	476	420	530	456	440	490	454	460	470	465
Dissolved Calcium	mg/L	450	510	476	420	540	460	430	480	457	460	470	465
Total Magnesium	mg/L	1,900	2,500	2,107	1,700	2,100	1,840	--	--	--	--	--	--
Dissolved Magnesium	mg/L	2,000	2,500	2,138	1,700	2,100	1,840	--	--	--	--	--	--
Total Sodium	mg/L	--	--	--	420	420	420	410	500	476	500	500	500
Ammonia	mg/L	0.31	13.0	3.75	4	14	9	0.23	12.0	5.09	1.3	110	37
Conductivity	μS/cm	13,000	16,000	13,923	11,000	14,000	12,429	11,000	13,000	12,500	12,000	13,000	12,200
COD	mg/L	260	640	501	370	570	513	370	550	433	370	570	455

Table 4-3 (continued)
MBR Treated Effluent (Permeate) Water Quality[1]

Parameter	Units	Condition 1			Condition 2			Condition 3			Condition 4		
		Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.
BOD	mg/L	--	--	--	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
TOC	mg/L	--	--	--	14	14	14	6	69	37	2.5	3.8	3.0
Fluoride	mg/L	21	25	23	22	27	24	22	25	24	25	27	26
Sulfate	mg/L	--	--	--	6,700	6,900	6,800	6,000	9,100	7,100	6,300	7,900	6,917
Ortho-Phosphate	mg/L	13	36	19	1.2	1.2	1.2	--	--	--	--	--	--
Total Phosphorus	mg/L	2	25	14	1.2	6.5	3.9	0.86	4.30	2.64	0.03	3.00	2.06
TKN	mg/L	32	94	67	73	100	81	59	78	69	53	96	71
Sulfide	mg/L	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22
TSS	mg/L	--	--	--	4	4	4	2	6	4	3	6	5
TDS	mg/L	14,000	20,000	17,286	12,000	16,000	14,714	13,000	16,000	14,600	14,000	16,000	14,600
Total Alkalinity	mg/L	200	200	200	100	110	105	40	180	116	220	270	240
Bicarbonate Alkalinity	mg/L	200	200	200	100	110	105	40	180	116	220	270	240
Carbonate Alkalinity	mg/L	--	--	--	<3.9	<3.9	<3.9	<3.9	<3.9	<3.9	<3.9	<3.9	<3.9

Notes:

[1] Average soluble concentrations were higher than total for some results due to analytical imprecision.

µS/cm = microSiemen per centimeter
Avg. = average
Max = maximum
Min = minimum
-- = no data

Figure 4-1 also shows that the MBR influent and effluent COD concentrations were similar. Given this, and the readily biodegradable nature of acetic acid, the data suggest that the influent COD was non-biodegradable. Also, from Table 4-3, it is evident that all the COD added through acetic acid was consumed in the MBR since the MBR effluent BOD and TOC concentrations were very low (higher BOD and TOC would indicate potential for additional biological activity in the oxidation of organic matter and the amount of carbon in organic material, respectively). This also raises the question whether all the COD in the influent reported is contributed by analytical interference or some other oxygen-demanding constituents, as opposed to organic carbon. It could also suggest that the organic compounds present were not fully oxidized in TOC tests (thus TOC readings would be lower than actual concentrations). The theory on analytical interference is drawn from low TOC concentrations reported during period of higher COD concentration measurements.

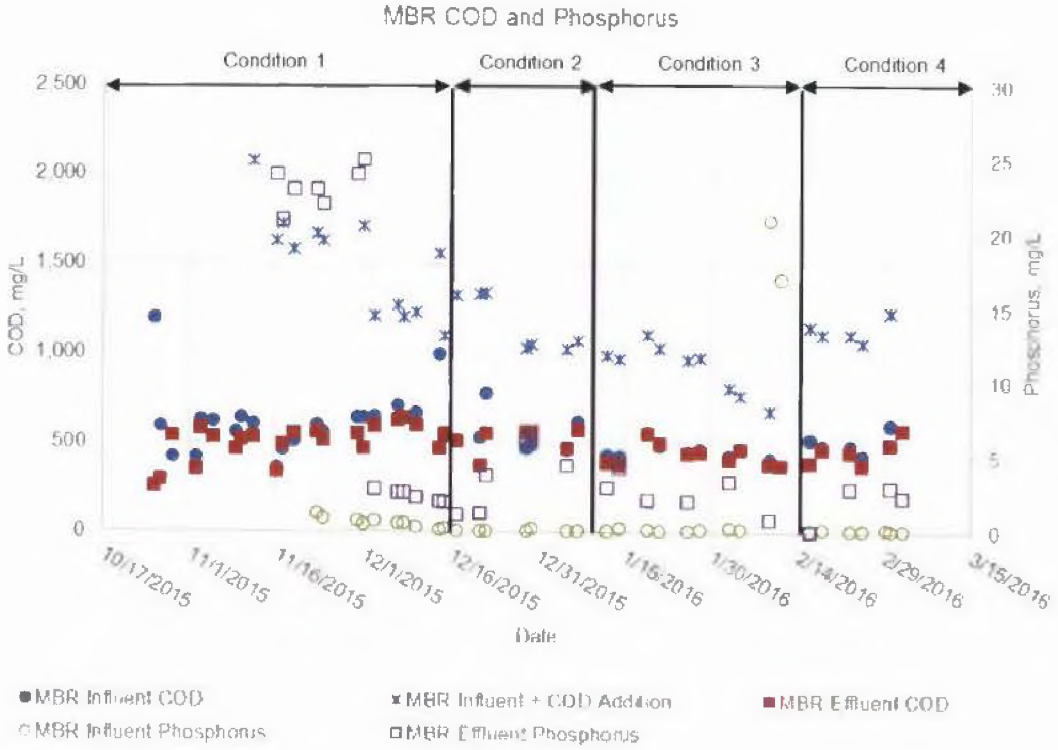

Figure 4-1
MBR influent and effluent COD and phosphorus

The data in Figure 4-2 show complete nitrification during October and November 2015. During this time, the influent ammonia concentration was high (ranging from 50 to 130 mg/L). Towards the end of Condition 1 and into Conditions 2 and 3, the influent ammonia concentration decreased to 10 to 20 mg/L, and nitrification appeared to stall (as seen by an increase in MBR effluent ammonia concentration).

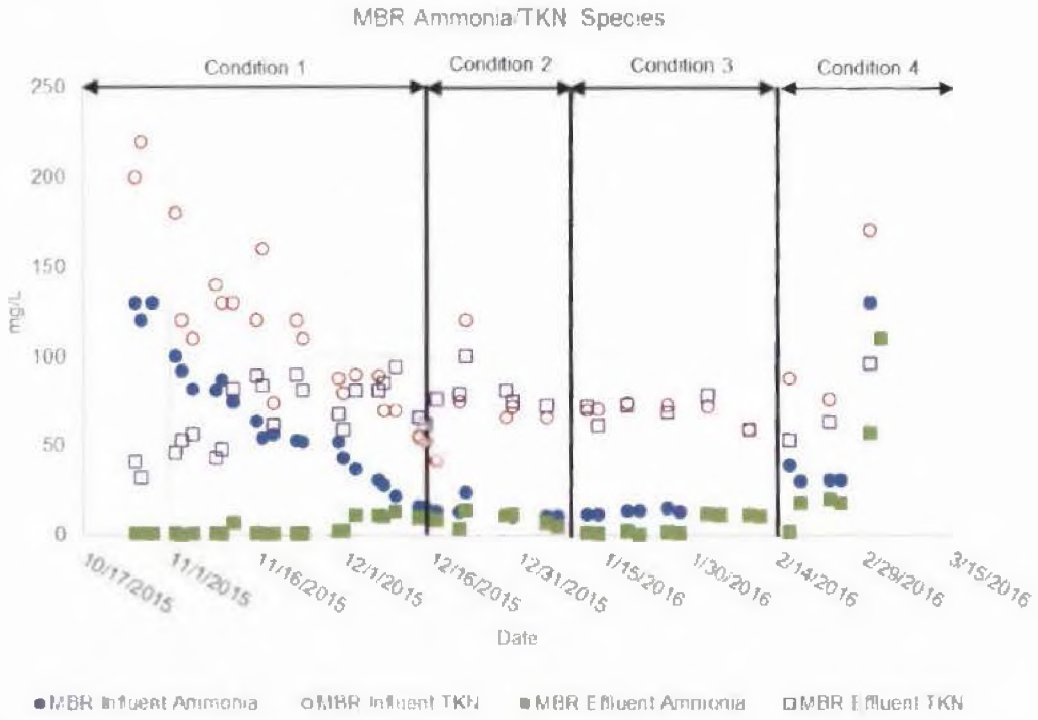

Figure 4-2
MBR influent and effluent ammonia and TKN

Also during this time, it was noticed that the pilot feed water alkalinity was lower than at the beginning of the demonstration and higher ammonia concentrations were coming from the P4 boiler units and creating higher pH values.

The generation of MLSS in the MBR varied throughout the pilot study. Wasting solids (MLSS) from the MBR was initiated during the middle of Condition 2 on December 28, 2015, at a rate of 80 GPD and was stopped in the middle of Condition 3 on January 30, 2016. This resulted in decreased MLSS concentrations during Conditions 2 and 3 from approximately 6,000 mg/L down to approximately 3,000 mg/L and an increase in MLSS concentration during Condition 4 to approximately 4,200 mg/L. These changes were not the cause of the loss of nitrification as the loss of complete nitrification occurred on November 30, 2015, one month prior to initiating the solids wasting. These changes do not appear to have impacted denitrification as full reduction of nitrate-nitrogen to nitrogen gas occurred throughout the pilot study. During Condition 4, the influent ammonia concentration started to increase with a corresponding increase in MBR effluent ammonia concentration, further indicating that nitrification had been lost. The reason(s) for losing the nitrification in the MBR could not be identified, but suspected to be caused by toxic or inhibitory compounds in the water.

In order to understand if toxicity/inhibitory compounds were contributing to the loss in nitrification, potassium sulfite was dosed to the Equalization Tank starting January 5, 2016, at a rate of 50 mg/L (to achieve 25 mg/L after dilution with service water). Higher dosages were added throughout Condition 3. The potassium sulfite was added to reduce potential oxidants that may have been contributing to the loss in nitrification performance. There were also concerns that the reduction in nitrification performance indicated the presence of inhibitory or toxic compounds that could have potentially also affected the ABMet bacteria and selenium reduction performance.

Nitrification performance did not noticeably improve when dosing potassium sulfite and dosing was discontinued on January 27. In an attempt to rule out the effectiveness of potassium sulfite versus the presence/impact of inhibitory compounds, 20 kg of powdered activated carbon (PAC) was added to MBR on February 6, 2016. The PAC should have absorbed inhibitory compounds present in the water; however, MBR nitrification performance did not improve with PAC addition.

Another observation from Figure 4-2 is that the blended influent contained recalcitrant TKN concentrations averaging 65 to 81 mg/L during all four conditions. TKN is comprised of ammonia and organic-nitrogen and the high concentrations in the MBR effluent suggest that a significant portion of the organic nitrogen fraction of the influent TKN was in a non-biodegradable form.

Nitrate/Nitrite

One of the main goals of the pretreatment MBR was to remove (denitrify) the nitrate/nitrite-nitrogen present in the influent and produced via nitrification in the aerobic zone. The average effluent nitrate/nitrite-nitrogen concentration during Condition 1 was 35 mg/L, indicating incomplete denitrification. This was due to the acetic acid dosing point inadvertently being installed in the aerobic zone of the MBR, which resulted in poor denitrification caused by anoxic zone #3 being carbon limited. After three weeks of poor denitrification, this situation was discovered and the acetic acid dosing point was relocated to the planned location (i.e., anoxic zone #3) on November 11, 2015.

As can be seen in Figure 4-3, once the acetic acid dosing point was relocated, complete denitrification occurred. Complete denitrification continued in the MBR throughout the remainder of the pilot study (other than a 2-week period towards the end of Condition 3, when the acetic acid dose was reduced intentionally to allow nitrate-nitrogen to pass through the pretreatment MBR to the ABMet system). Although nitrification was lost during Conditions 3 through 4, nitrate-nitrogen removal (denitrification) was never a problem in the MBR. For some unknown reason, more sensitive nitrifying bacteria were inhibited but the heterotrophic denitrifying bacteria were not inhibited.

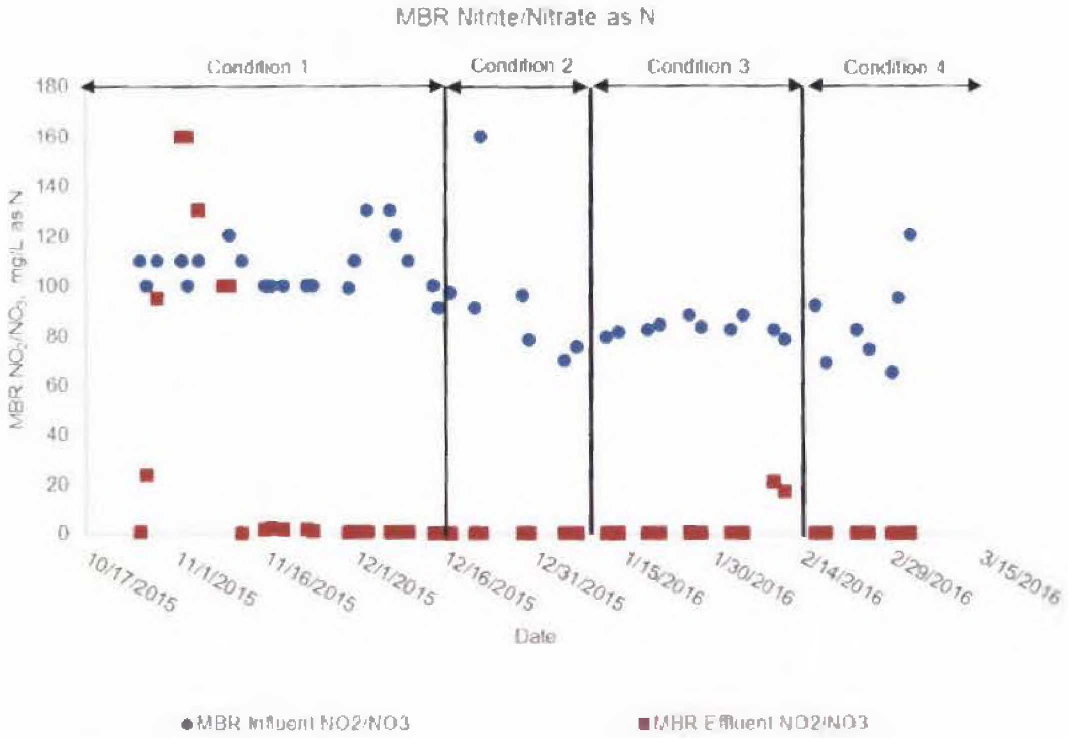

Figure 4-3
MBR influent and effluent nitrate/nitrite as nitrogen

Selenium

As seen in Figure 4-4, significant selenium reduction occurred in the pretreatment MBR. The overall average influent total selenium concentration was 1,175 µg/L, and the overall average effluent total selenium concentration was 250 µg/L. On average throughout all conditions, approximately 75 percent reduction in selenium concentration was observed. This is attributed to maintaining a very low ORP (approximately -350 mV) in the anoxic zone #3 with high acetic acid dosage. This ORP is comparable to that maintained in the ABMet reactors. Another observation from Figure 4-4 is that almost all of the influent selenium was soluble, which indicates that removal across the pretreatment MBR was by biological reduction to elemental selenium (which exists in particulate form) followed by filtration via the ultrafiltration membrane.

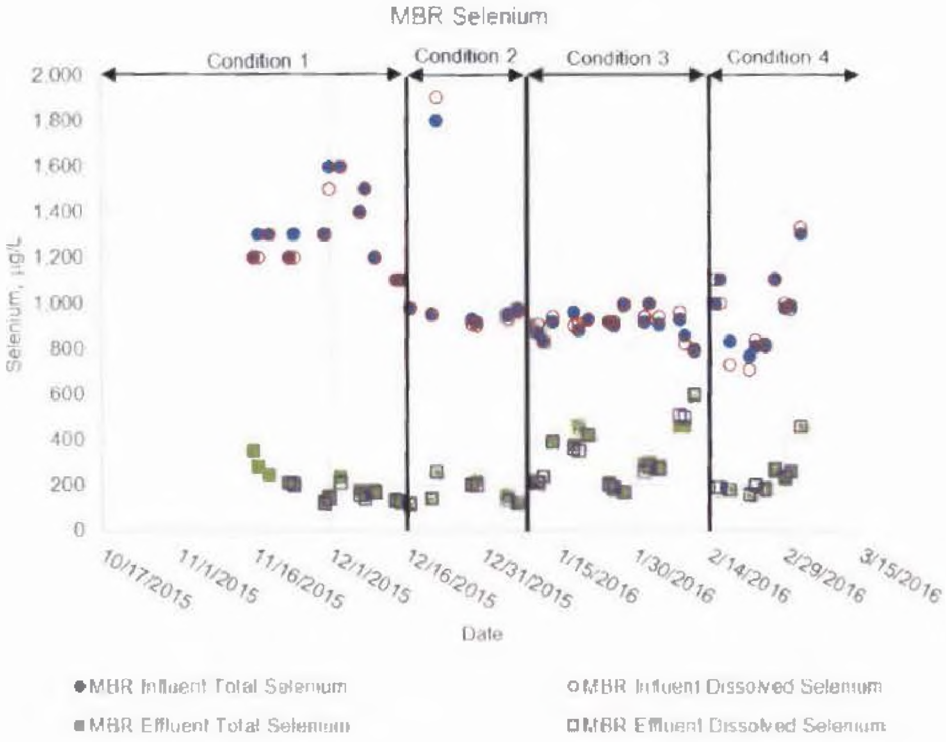

Figure 4-4
MBR influent and effluent selenium

On January 11, 2016, the MBR flow rate was increased from 1 GPM to 1.6 GPM. Prior to making this change, the MBR effluent was sampled and the selenium result was higher than previous results (220 µg/L vs. 120 µg/L from January 7). Acetic acid (nutrient) feed was increased proportionally with the feed rate and no changes in ORP were observed; there were no immediate indications as to why the effluent selenium concentrations began to increase.

Higher selenium concentration results continued until midway through Condition 3, when they decreased but again increased until the start of Condition 4. The increase in effluent selenium at the beginning of Condition 3 is not likely to be caused solely by the increased flow rate since the change occurred after the initial sample was taken that provided the indication. Selenium concentration results from the ABMet 1 and 2 reactor effluents were also higher that day (with no changes observed in either ORP or pH); again, emphasizing the increased flow rate was not the sole contributor.

Mercury

As seen in Figure 4-5, significant mercury reduction also occurred in the pretreatment MBR. The average influent total mercury concentration to the pretreatment MBR was approximately 72 ng/L, and the average effluent was 3 ng/L. The pretreatment MBR stage achieved approximately 96 percent reduction of mercury throughout the pilot study. This is likely due to mercury entering the MBR in mostly particulate form (see Table 4-1), the particulate mercury being removed by the ultrafiltration membrane, and potentially due to some of the soluble mercury precipitating to a particulate with sulfide generated under low ORP in the anoxic zone #3.

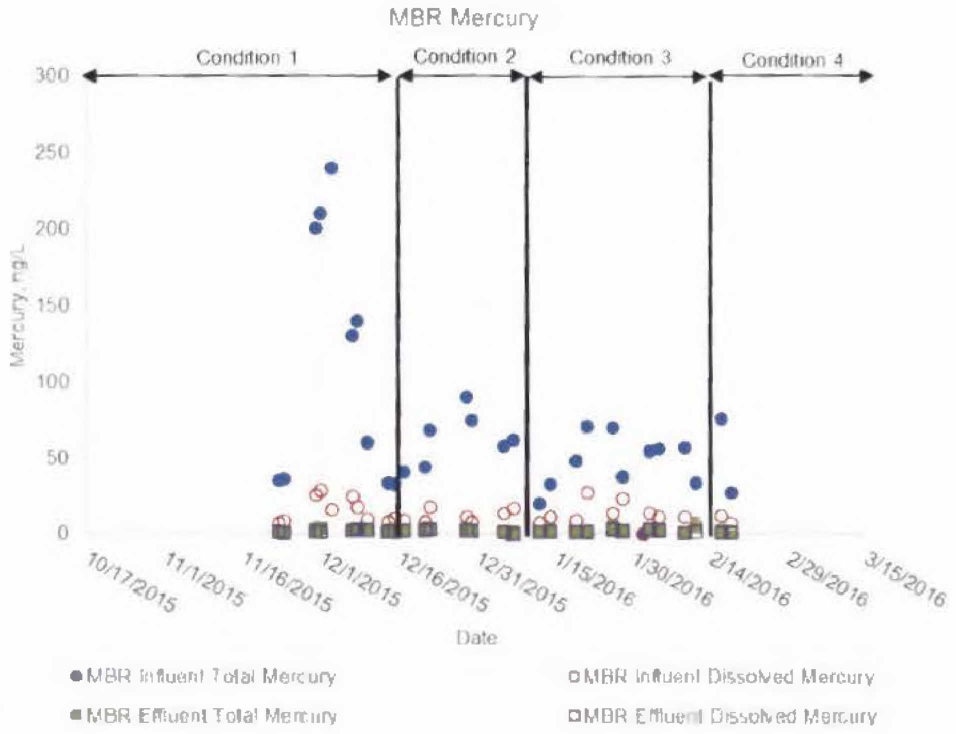

Figure 4-5
MBR influent and effluent mercury

Arsenic

Several weeks' worth of arsenic data were collected, which indicated no removal of arsenic in the pretreatment MBR. Average influent and effluent concentrations were both approximately 4.6 µg/L. This is indicative of the arsenic entering the MBR in mostly dissolved form, and not precipitating to a particulate form in the MBR (see Table 4-1).

ABMet

Operating Parameters

ABMet operational parameters are discussed in this section. The MBR effluent (permeate) was collected in the ABMet feed tank. From the feed tank, the water was pumped to the ABMet Stage 1. Table 4-4 compares the ABMet operational parameters at the four test conditions.

Table 4-4
ABMet Operational Parameters

Condition Description	**Startup and Acclimation**	**Initial Operation**	**Increased Flow/ Reduced HRT**	**Process Adjustments**
Condition Number	**1**	**2**	**3**	**4**
Parameter/Dates	**10/26/15 to 12/16/15**	**12/17/15 to 1/10/16**	**1/11/16 to 2/13/16**	**2/14/16 to 3/3/16**
ABMet Stage 1 Flow Average	0.5 GPM	0.6 GPM	0.9 GPM	0.9 GPM
ABMet Stage 1 EBCT	11.2 hours	9.4 hours	6.2 hours	6.2 hours
ABMet Stage 2 Flow Average	0.5 GPM	0.6 GPM	0.9 GPM	0.9 GPM
ABMet Stage 2 EBCT	11.2 hours	9.4 hours	6.2 hours	6.2 hours
ABMet Influent ORP				
Average	183 mV	91 mV	94 mV	368 mV
Range	110 to 263 mV	52 to 151 mV	34 to 224 mV	261 to 454 mV
ABMet Effluent ORP[1]				
Average	-125 mV	-184 mV	-365 mV	-350 mV
Range	-500 to 106 mV	-364 to 295 mV	-419 to -310 mV	-412 to -318 mV
Backwash Flow Rate	80 GPM	80 GPM	80 GPM	80 GPM
Degas Flow Rates	100 GPM	100 GPM	100 GPM	100 GPM
Feed Tank HRT	4 hours	4 hours	4 hours	4 hours
Chemical Doses				
Antiscalant, MDC776 (MBR Permeate to ABMet Feed Tank)	none	5 mg/L	5 mg/L	5 mg/L

[1] ORP data varied significantly, including positive values, potentially due to analytical error with the inline probes.
EBCT = empty bed contact time, calculated as total boundary volume occupied by the GAC media divided by the flow rate passing through the vessel

The average flow rate to the ABMet system during Condition 1 was 0.5 GPM, which corresponds to a total empty bed contact time (EBCT) of approximately 22.4 hours (11.2 hours for each stage). During Condition 2, the average flow rate increased to 0.6 GPM (due to mechanical issues, not intentionally increased), which corresponds to a total EBCT of approximately 18.8 hours. During Conditions 3 and 4, an intentional increase in flow rate to 0.9 GPM occurred. This corresponds to an average total EBCT of 12.4 hours. The project originally intended to increase flow rates to achieve EBCT closer to GE's target design of approximately 4 hours per reactor (8 hours total).

The average ORP in the ABMet effluent during each condition ranged from -125 to -365 mV, with the lowest average values of -365 and -350 mV occurring during Conditions 3 and 4, respectively. These correspond to increased acetic acid dosing during Conditions 3 and 4 and were within GE's target range of -250 to -400mV. The average ORP values during Conditions 1 and 2 may be artificially elevated due to several reported positive values that may have resulted from analytical error and/or issues with the inline measurement probes. A plot of inline ORP data from the MBR permeate (ABMet feed), ABMet stage 1 effluent, and ABMet stage 2 effluent are presented in Figure 4-6. Spikes in ORP from the ABMet locations are primarily associated with backwash and degas events. The ABMet system was taken offline from December 24 through 28 due to high TMP in the MBR system which required a cleaning. Both stages returned to <0 mV approximately one day after startup.

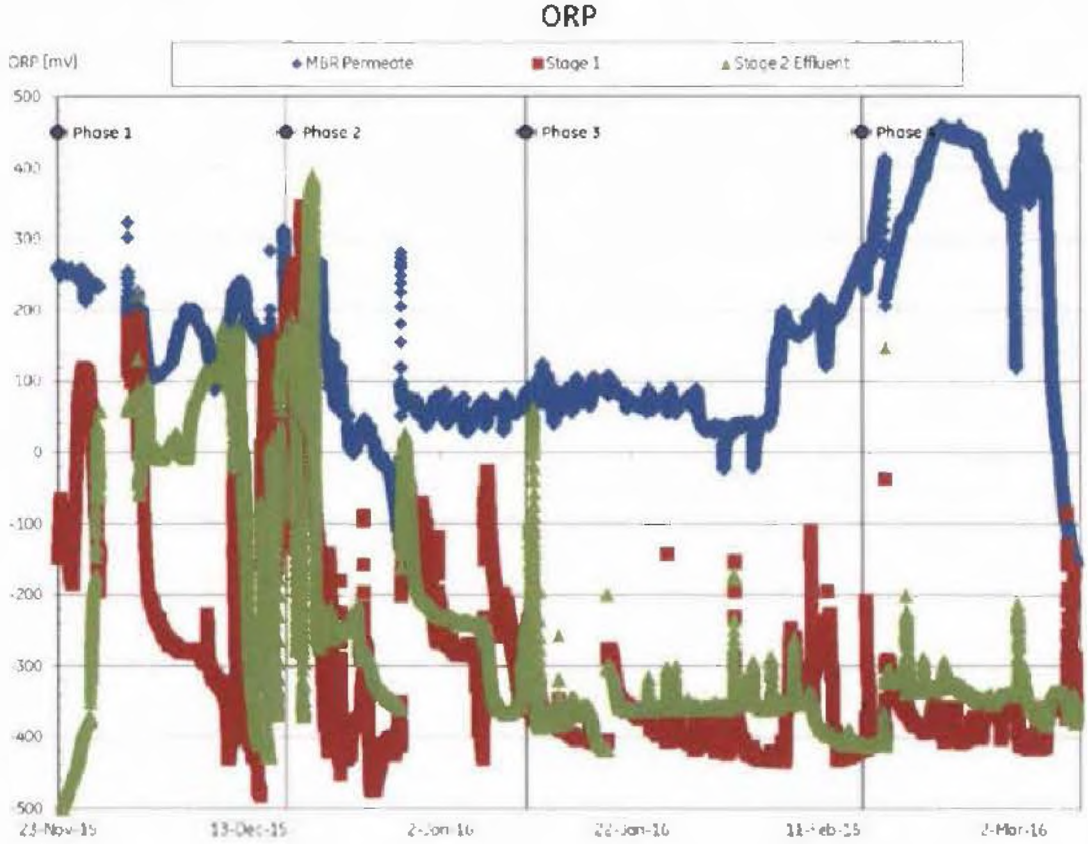

Figure 4-6
ABMet inline ORP trends
Courtesy of GE Water & Process Technologies

Four different nutrients were trialed for the ABMet pilot system. The initial nutrient was a blend of acetic acid, ammonium, and phosphorus (the same blend used initially for the MBR pilot). Due to formation of excess solids on the top of each ABMet reactor, a second nutrient containing 80% acetic acid (20% water) replaced the blended product. Three inches of carbon-containing excess solids were removed from each reactor. The third was a diluted blend of the first blended product, made up of 50% pure acetic acid and 50% blended product. During the final phase of operation, molasses was added to the nutrient mix of pure acetic acid and blended product. A summary of the nutrient dosages and resulting COD concentration ranges are provided in Table 4-5.

Table 4-5
ABMet Nutrient Dosages

Condition Description	**Startup and Acclimation**	**Initial Operation**	**Increased Flow/ Reduced HRT**	**Process Adjustments**
Condition Number	**1**	**2**	**3**	**4**
Parameter/Dates	**10/26/15 to 12/16/15**	**12/17/15 to 1/10/16**	**1/11/16 to 2/13/16**	**2/14/16 to 3/3/16**
Nutrient	Blended acetic acid product containing acetic acid, ammonium, and phosphorus		50/50 mix of pure acetic acid (80%) and blended product	Molasses and 50/50 mix of pure acetic acid and blended product
Acetic Acid (COD) - ABMet Stage 1				
Average	28 mg/L	100 mg/L	76 mg/L	112 mg/L
Range	28 mg/L	87 to 175 mg/L	69 to 90 mg/L	90 to 134 mg/L
Acetic Acid (COD) - ABMet Stage 2				
Average	none	28 mg/L	37 mg/L	36 mg/L
Range	none	28 mg/L	28 to 70 mg/L	34 to 40 mg/L

The ABMet reactor head loss trends in Figure 4-7 provide indications of backwash and degas frequencies throughout the demonstration. Head loss is the water level above the media where a higher head loss is associated with an increased hydraulic resistance through the carbon media (and is indication of increased water level). For ABMet systems, increased head loss can indicate a need to backwash and/or degas the filters due to increased biomass and other solids or gases, respectively. Starting the week of January 11, 2016, degassing frequency was based on a schedule of once every Tuesday and Thursday (after water samples were taken). The length of each degassing event was originally set to 30 seconds, but was changed in mid-February to 90 seconds. According to GE, 90 seconds is more representative of full-scale systems.

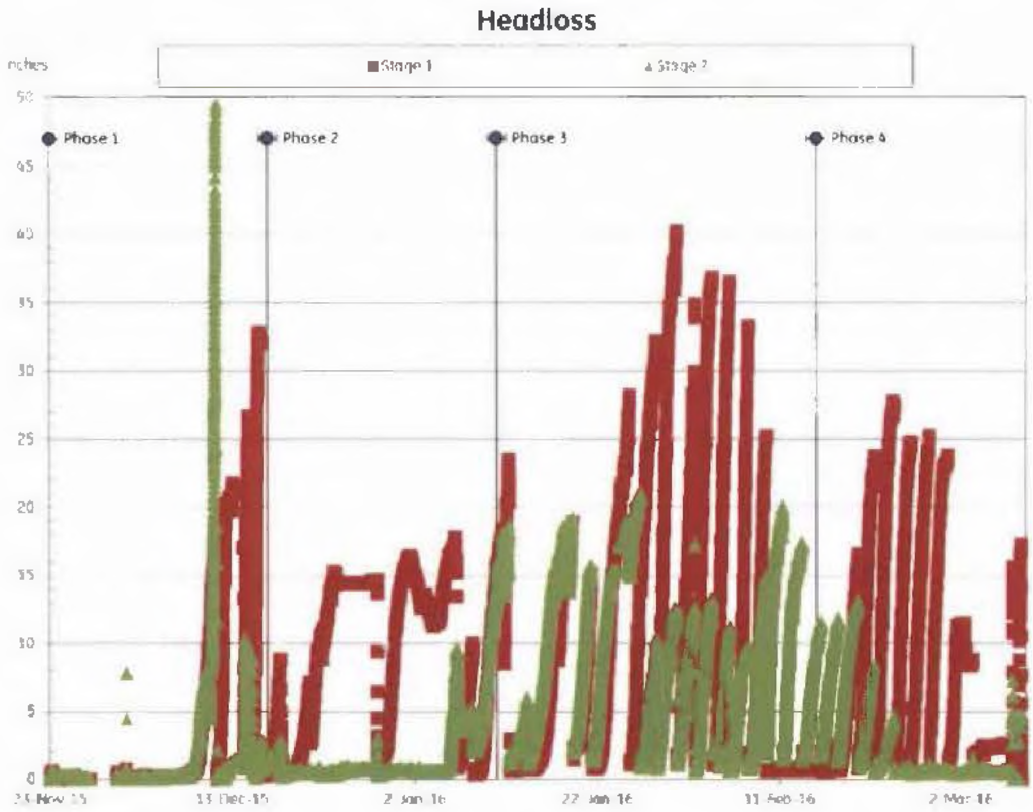

Figure 4-7
ABMet headloss trends
Courtesy of GE Water & Process Technologies

One backwash was completed for each ABMet stage during the demonstration. Stage 1 backwash occurred on January 25 and stage 2 occurred on January 26. Analytical results from samples taken at the Backwash Waste Tank after two backwash events are provided in Table 4-6. Note the selenium values are reported in mg/L as opposed to µg/L.

Table 4-6
ABMet Backwash Analysis

Sample Location and Date	Total selenium (mg/L)	Dissolved selenium (mg/L)	NO_2/NO_3 (mg-N/L)	Total Suspended Solids (mg/L)
ABMet Stage 1 1/25/2016	78	57	0.060	8.0[1]
ABMet Stage 2 1/26/2016	53	51	<0.045	7.5[1]

[1] According to GE, solids in backwash were lower than expected, which may be due to sampling error.

Treated Water Characteristics

This section discusses the characteristics of the ABMet pilot effluent. Table 4-7 summarizes the effluent water quality based on samples collected during each operating condition. Figures 4-8, 4-9, 4-10, 4-11, 4-12, and 4-13 present ABMet influent and effluent COD and phosphorus; ammonia and TKN; nitrate/nitrite nitrogen; selenium; mercury; and arsenic, respectively.

Table 4-7
ABMet Stage 2 Effluent Water Quality[1]

Parameter	Units	Condition 1			Condition 2			Condition 3			Condition 4		
		Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.
Total Selenium	μg/L	7	110	36	3	6	5	15	62	36	14	39	21
Dissolved Selenium	μg/L	5	76	27	3	7	5	15	56	37	11	26	17
Se(IV)[2]	μg/L	--	--	--	--	--	--	0.29	51.8	13	0.8	4.6	3.8
Se(VI)[2]	μg/L	--	--	--	--	--	--	<0.25	11.5	5.7	<0.25	<0.25	<0.25
MeSe[2]	μg/L	--	--	--	--	--	--	<0.25	1.3	0.9	<0.25	<0.25	<0.25
SeCN[2]	μg/L	--	--	--	--	--	--	0.52	69.7[3]	18	2.1	10.8	7.2
NO_2/NO_3-N	mg/L	<0.045	0.14	0.06	<0.045	0.13	0.081	<0.045	0.060	0.036	<0.045	0.081	0.046
Total Mercury	ng/L	0.50	4.57	1.45	0.41	2.25	1.21	0.37	1.20	0.84	0.53	1.16	0.85
Dissolved Mercury	ng/L	<0.31	3.16	0.73	0.23	0.59	0.42	0.45	1.20	0.76	0.68	0.90	0.79
Total Arsenic	μg/L	1.1	4.0	2.0	<0.36	1.8	0.9	<0.36	0.76	0.54	0.82	0.82	0.82
Dissolved Arsenic	μg/L	1.2	3.6	2.0	<0.36	2.0	0.9	0.38	0.76	0.61	0.82	0.82	0.82
Total Calcium	mg/L	430	580	477	410	500	451	430	480	452	460	500	480
Dissolved Calcium	mg/L	420	590	477	400	520	460	440	470	455	460	500	480
Total Magnesium	mg/L	1,900	2,400	2,150	1,600	1,900	1,743	1,800	2,100	1,950	1,900	2,100	2,000
Dissolved Magnesium	mg/L	1,900	2,400	2,140	1,600	2,000	1,786	1,800	2,100	1,950	1,900	2,100	2,000
Ammonia	mg/L	11	86	49	5	6	5	0.3	22	6.4	0.47	98	31

Table 4-7 (continued)
ABMet Stage 2 Effluent Water Quality[1]

Parameter	Units	Condition 1			Condition 2			Condition 3			Condition 4		
		Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.
Conductivity	µS/cm	14,000	16,000	14,500	11,000	14,000	12,250	11,000	13,000	12,500	12,000	14,000	12,400
COD	mg/L	290	1,600	674	150	540	383	260	370	335	340	600	427
BOD	mg/L	--	--	--	54	54	54	4.6	46	22.3	26	74	49
TOC	mg/L	--	--	--	19	19	19	2.0	12	8.3	0.73	0.93	0.86
Chloride	mg/L	--	--	--	2,700	2,700	2,700	2,600	3,300	2,940	2,700	2,900	2,800
Fluoride	mg/L	16	24	21	23	24	24	23	25	24	26	28	26
Sulfate	mg/L	--	--	--	6,500	7,000	6,750	6,300	8,300	6,860	5,600	8,200	6,817
Total Phosphorus	mg/L	0.59	3.5	2.2	2	2	2	1.3	5.4	4.1	0.75	7.90	5.36
TKN	mg/L	53	150	72	48	83	62	45	69	56	45	72	58
Sulfide	mg/L	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	30	18	25	58	36
TSS	mg/L	12	44	28	11	18	13	4.0	8.0	6.1	3.0	21	8.3
TDS	mg/L	15,000	18,000	16,750	4,900	19,000	12,725	13,000	16,000	14,800	14,000	17,000	15,200
Total Alkalinity	mg/L	--	--	--	79	160	120	130	200	167	190	420	300
Bicarbonate Alkalinity	mg/L	--	--	--	79	160	120	130	200	167	190	420	300
Carbonate Alkalinity	mg/L	--	--	--	<3.9	<3.9	<3.0	<3.9	<3.9	<3.9	<3.9	<3.9	<3.9

[1] Average soluble concentrations were higher than total for some results, due to analytical imprecision

[2] Analyzed at Brooks Applied Labs: Se(IV) – selenite; Se(VI) – selenate; MeSe – selenomethionine; SeCN – selenocyanate

[3] SeCN concentration max value during Condition 3 appears to be biased high when compared to total and dissolved selenium maximum concentrations

Figure 4-8 shows that there was little removal of influent COD by the ABMet as the ABMet influent and effluent COD concentrations were similar; this trend was also observed in the pretreatment MBR system. The data again suggest that the influent COD was contributed by analytical interference or some other oxygen-demanding constituent, as opposed to organic carbon. The average ABMet influent and effluent COD concentrations for all conditions together were approximately 482 and 465 mg/L, respectively, during the pilot test.

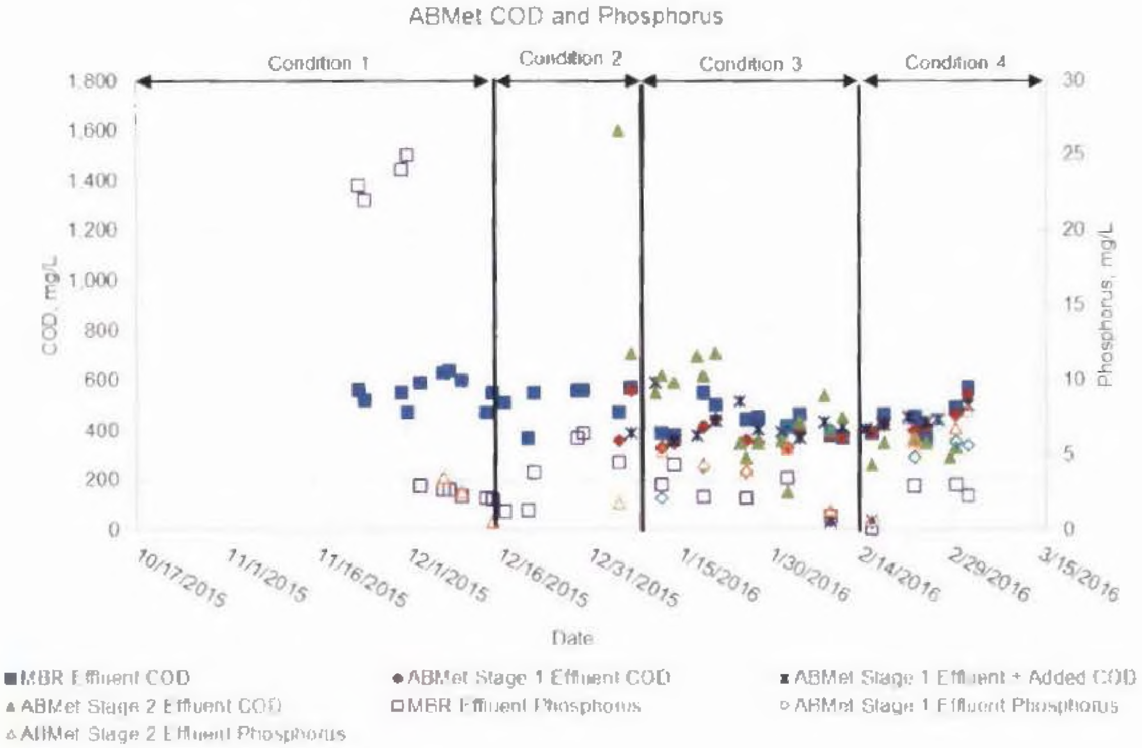

Figure 4-8
ABMet influent and effluent COD and phosphorus

A slight increase in phosphorus concentration in the ABMet can be seen at times in Figure 4-8 (presented on the secondary y-axis). This was due to the fact that the nutrient blended acetic acid (containing phosphorus) was used as a carbon source for the ABMet throughout the pilot study. Optimization of effluent phosphorus concentration was not an objective of this study. The phosphorus concentration could be reduced by separating the carbon source from the phosphorus source.

Nitrate/Nitrite

As seen in Figure 4-9, TKN and ammonia were not significantly impacted in the ABMet. The presence of nitrate/nitrite nitrogen in the ABMet influent only occurred during Condition 1 (when the acetic acid was being added to the wrong zone in the pretreatment MBR) and for a few weeks during Condition 3 (when nitrate/nitrite nitrogen was intentionally being maintained in the MBR effluent to provide the ABMet with electron donors) (Figure 4-10).

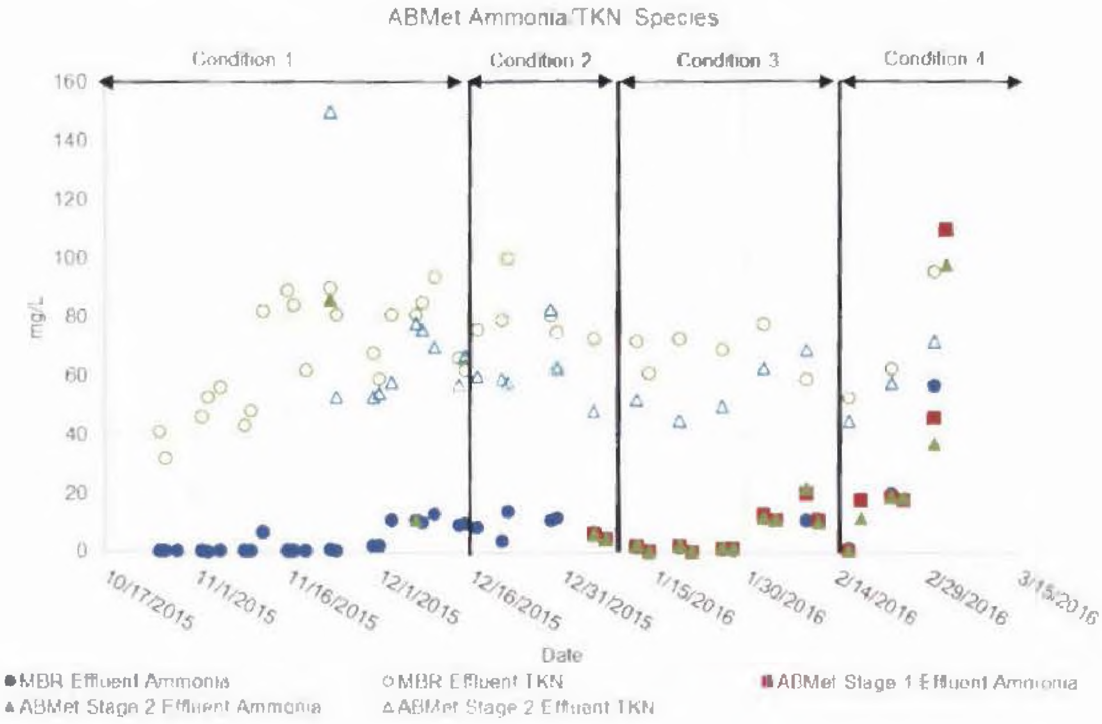

Figure 4-9
ABMet influent and effluent ammonia and TKN

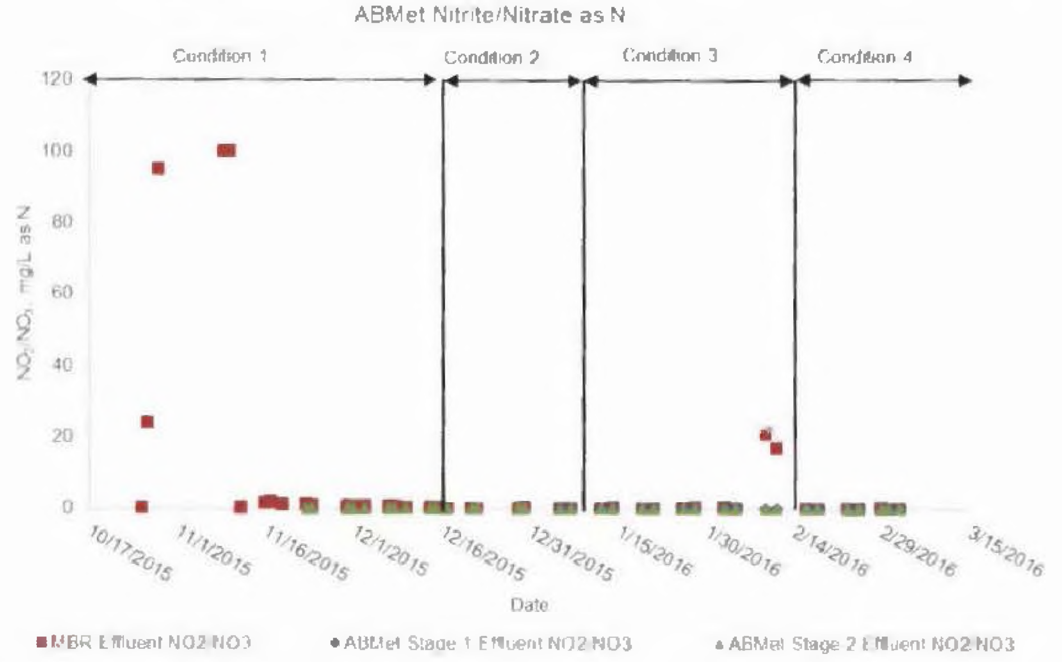

Figure 4-10
ABMet influent and effluent nitrate/nitrite as nitrogen

Selenium

Selenium removal in the ABMet varied throughout the pilot study, as seen in Figure 4-11.

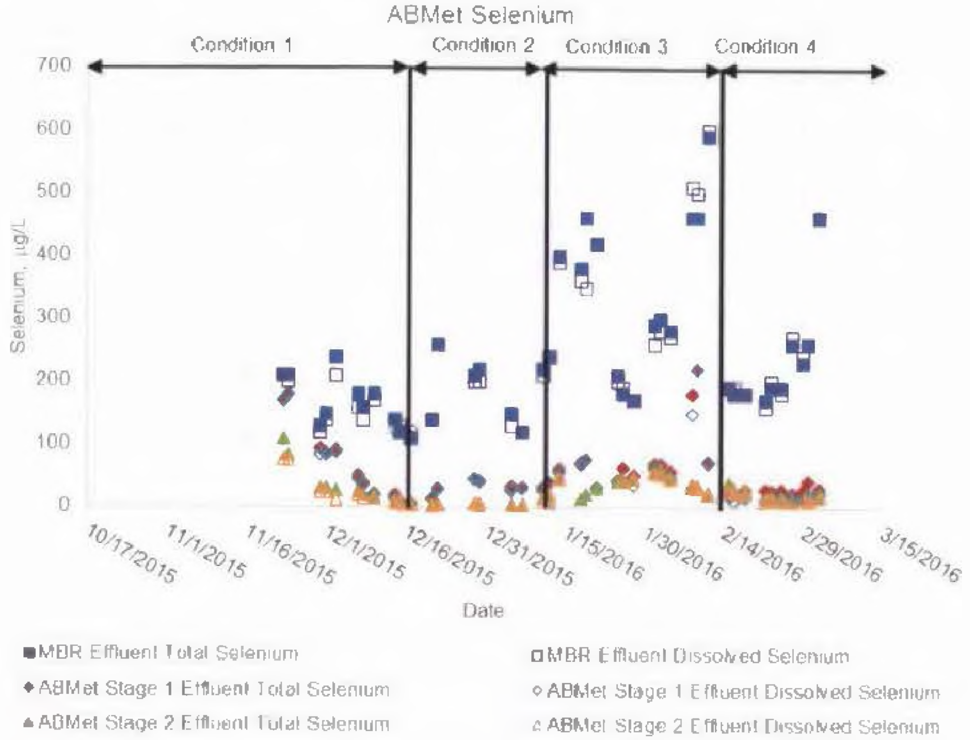

Figure 4-11
ABMet influent and effluent selenium

During Condition 1, improved performance is observed as the system is acclimating and the bacteria are being established. The best performance occurred during Condition 2, when the influent average total selenium concentration to Stage 1 was 173 µg/L and the effluent average total selenium concentration from Stage 2 was 5 µg/L. This is the only condition where the target effluent total selenium goal of 6 µg/L (half of the ELG limit due to 1:1 dilution) was achieved.

Selenium reduction during Condition 3 declined as the average ABMet effluent total selenium concentration increased from 6 to 36 µg/L. From Table 4-7, it can be seen that the predominant selenium species in the ABMet effluent during Condition 3 were selenite and selenocyanate. Unfortunately, selenium speciation data were not available in the MBR effluent. As described in the section on the MBR operating performance, the initial increase in effluent selenium from the ABMet coincided with flow rate increases (HRT and EBCT decreases) in the MBR and ABMet systems. However, the samples with the resulting higher selenium concentrations were taken prior to changing the flow rates that same day. On January 7, total selenium in the final ABMet effluent was 5.0 µg/L while on January 11, the same day flow rates were increased, total selenium was 15 µg/L. Given the strong performance of both systems leading up to this time, there were no indications that increasing the flow rate would have dramatic impacts on performance. Had the selenium result from January 11 been available, the project team may have decided to forgo increasing flow rates until the underlying issue(s) could be addressed.

Complicating the matter even further, results for total selenium from the ABMet effluent (stage two reactor effluent) from January 18, 19, and 21 failed We Energies' lab QA/QC checks. In these samples, the matrix spike recovery values were on the low end of the acceptable range, indicating the presence of analytical interferences. All matrix spike recoveries up to this point had been within the method control limits and the lab did not change anything in the sample preparation or analysis protocol. These were the first sets of results that failed matrix spike QC and We Energies' lab staff performed various tests in attempt to provide accurate analyses. On January 18, the We Energies lab staff who collected the samples noted a strong sulfide odor that had not been present in prior samples. The same odor was present in this sample for the duration of the test. This issue resulted in total selenium values being reported much lower than values later determined to be actual. Total selenium concentration results from these dates were originally reported as 13 µg/L, 11 µg/L, and 8.2 µg/L vs. 15 µg/L, 22 µg/L, and 31 µg/L reported after oxidizing the samples in the sample bottles using hydrogen peroxide. At the time, these lower values falsely indicated the ABMet had recovered from the unconfirmed upset and was tracking back to total selenium concentration of 6 µg/L or less. The project team decided not to alter the current pilot conditions until the accuracy of analytical results improved. By the time the analytical interferences had been overcome, the pilot system had been outside of the performance targets for three weeks. Comparisons of reported vs. verified selenium concentrations are provided in Table 4-8 and additional information on We Energies' evaluations is presented in Appendix B.

Table 4-8
Comparison of ABMet Effluent Selenium Concentrations During Period of Matrix Spike Recovery Failures

Sample Date	Total selenium initially reported (µg/L)	Dissolved selenium initially reported (µg/L)	Total selenium reported after improving matrix spike recovery (µg/L)	Dissolved selenium reported after improving matrix spike recovery (µg/L)
1/18/2016	13	12	15	Not measured
1/19/2016	11	10	22	
1/21/2016	8.2	7.7	31	

The sulfide odor that became present in samples taken after January 18 correspond to higher sulfide concentrations in the ABMet effluent (see Figure 4-12). The presence of sulfide is expected as bacteria naturally reduce sulfate to hydrogen sulfide gas. The decline in selenium reduction performance suggests that sulfate-reducing bacteria were present and may have become too predominant in the 2nd stage reactor.

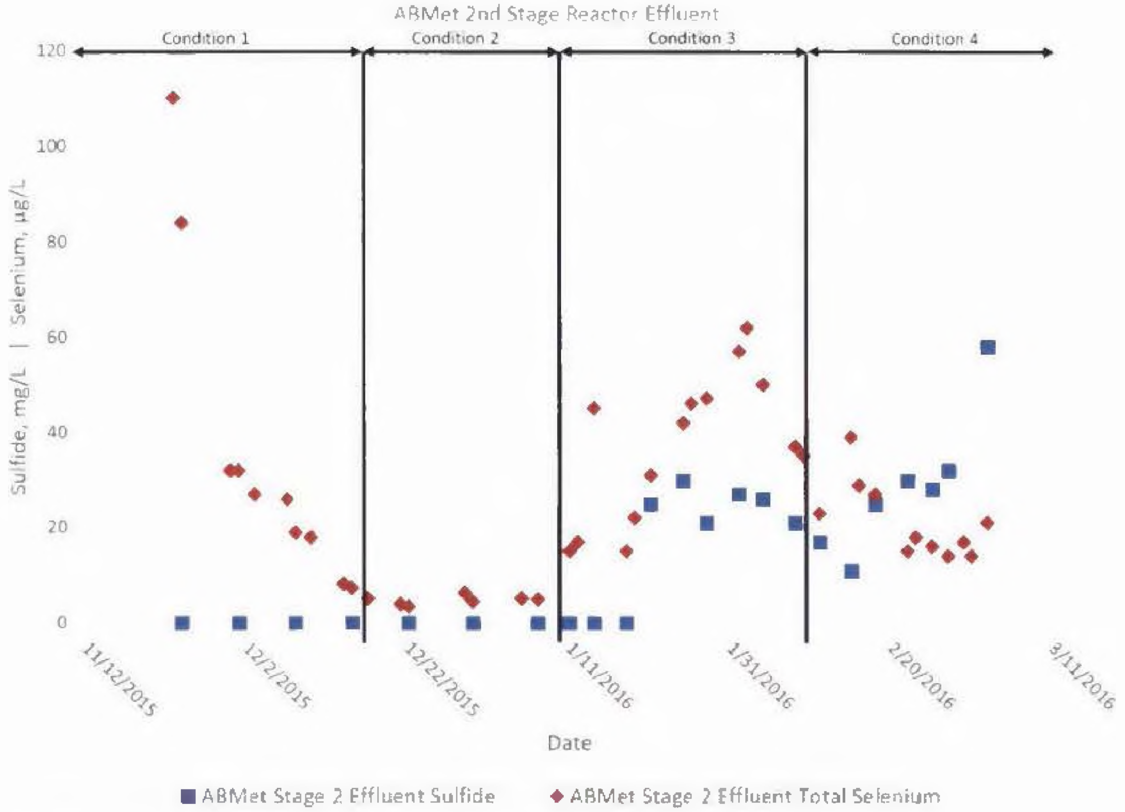

Figure 4-12
ABMet effluent sulfide and selenium

During Condition 3, several activities were done in attempt to improve performance in the ABMet. Reducing the ABMet flow rate was not implemented because the flow rate change was not believed to be a major contributing factor to the loss of selenium reduction performance.

The following actions were taken to improve ABMet performance.

- Potassium sulfite had been added to the Equalization Tank in an attempt to target oxidants potentially impacting the MBR nitrifying bacteria. Reducing oxidants was expected to also improve ABMet bacteria performance.
- 20 kilograms of PAC were added to the MBR in an attempt to adsorb any potential inhibitor compounds. Again, this was already part of the MBR plan in case the potassium sulfite addition not improved nitrification in the MBR.
- Nitrate was allowed to pass through the MBR to the ABMet, by reducing the acetic acid feed to the MBR, to provide more electron acceptors.

While performance did improve slightly in Condition 4 (where the average ABMet effluent total selenium decreased from 36 µg/L to 21 µg/L), the performance observed during Condition 2 and achievement of the effluent total selenium goal of 6 µg/L were not attained during Condition 4. Given the number of variables that may have impacted performance in the ABMet that occurred relatively close together, it is difficult to definitively say why performance decreased, as it may have been any one of, or a combination of, the variables and the trial concluded before complete recovery of performance occurred. Total and dissolved selenium concentration values from the ABMet stage 1 and stage 2 reactors are provided in Figure 4-13.

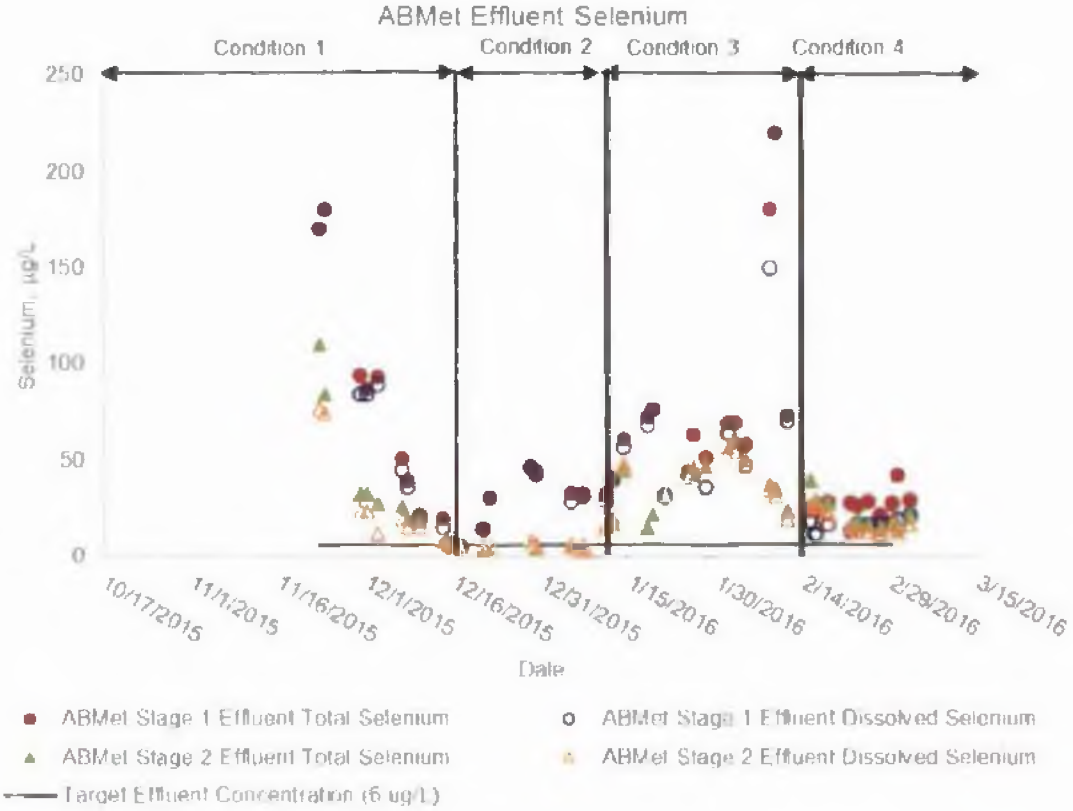

Figure 4-13
ABMet effluent selenium

As noted in discussion of Figure 4-1 (graph of MBR influent and effluent COD and phosphorus), influent and effluent COD concentrations were similar, suggesting that the influent COD was non-biodegradable. Jar tests with Fenton reagent were conducted on site to preliminarily investigate the feasibility of Advanced Oxidation Processes (AOPs) to partially oxidize these non-biodegradable organics in wastewater [2]. However, the jar tests were inconclusive due to high levels of inorganic scavengers, such as nitrate, sulfate, and chloride, and the limited time available. Simple onsite analytical tests were performed for COD, NO_3-N, NH_4-N, and pH on samples that had AOP (Fenton process) reactions as well as control samples. The results of this testing did not show any clear trends, and were likely not very accurate as they were performed using field test methods and were not performed in a controlled lab environment.

Mercury

Further reduction of mercury was observed in the ABMet data and can be seen in Figure 4-14. Mercury was reduced from an average of 2.5 ng/L in the MBR effluent to 1.1 ng/L in the ABMet effluent. These averages are consistent with performance over the entire length of the demonstration. The influent to the pilot system was compliant with the effluent mercury goal of 178 ng/L (half of the monthly ELG limit due to 1:1 dilution).

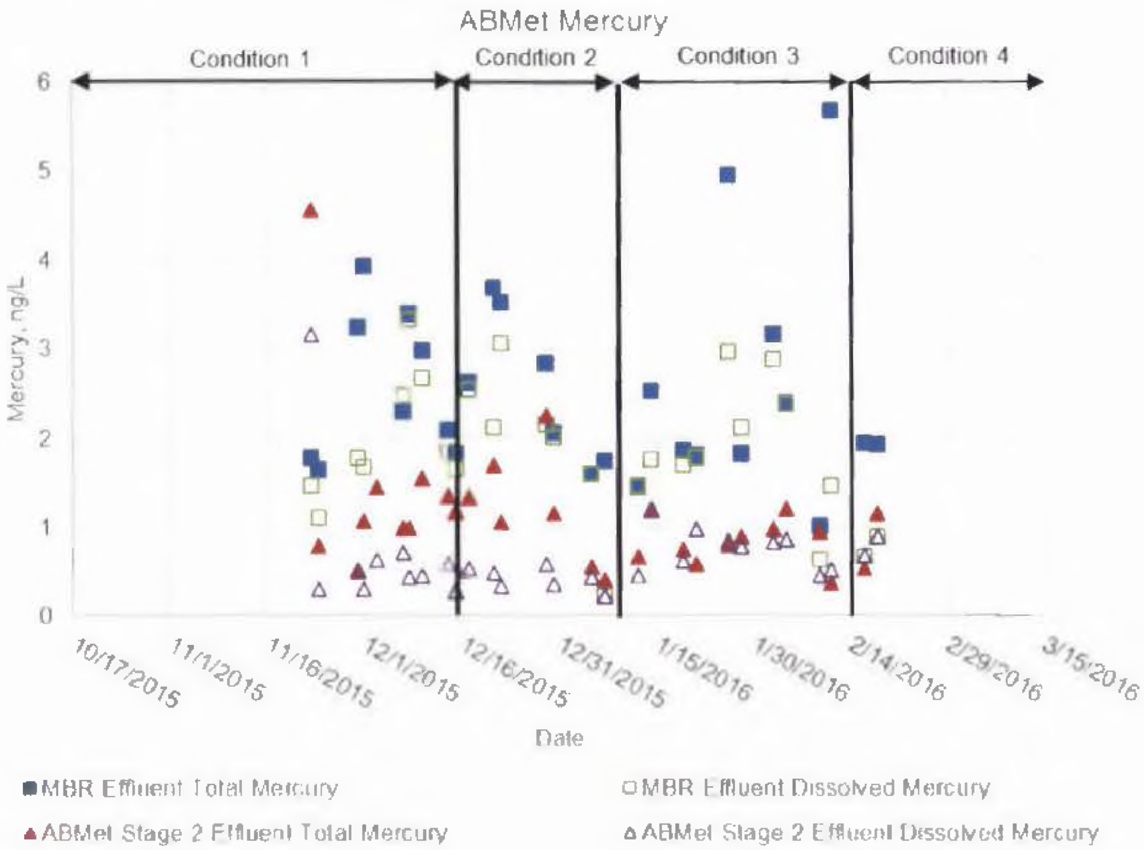

Figure 4-14
ABMet influent and effluent mercury

Arsenic

As described above, arsenic was not removed in the MBR; however, as seen in Figure 4-15, removal of arsenic in the ABMet did occur. The average ABMet influent arsenic concentration was 4.6 µg/L, and the average effluent over the entire demonstration was 1.4 µg/L, which is an average reduction of approximately 70 percent. During Conditions 3 and 4, the average total arsenic in the effluent was 0.67 µg/L (despite the loss of performance in selenium reduction during this time). This is significant given the effluent arsenic goal of 4 µg/L due to the dilution with service water.

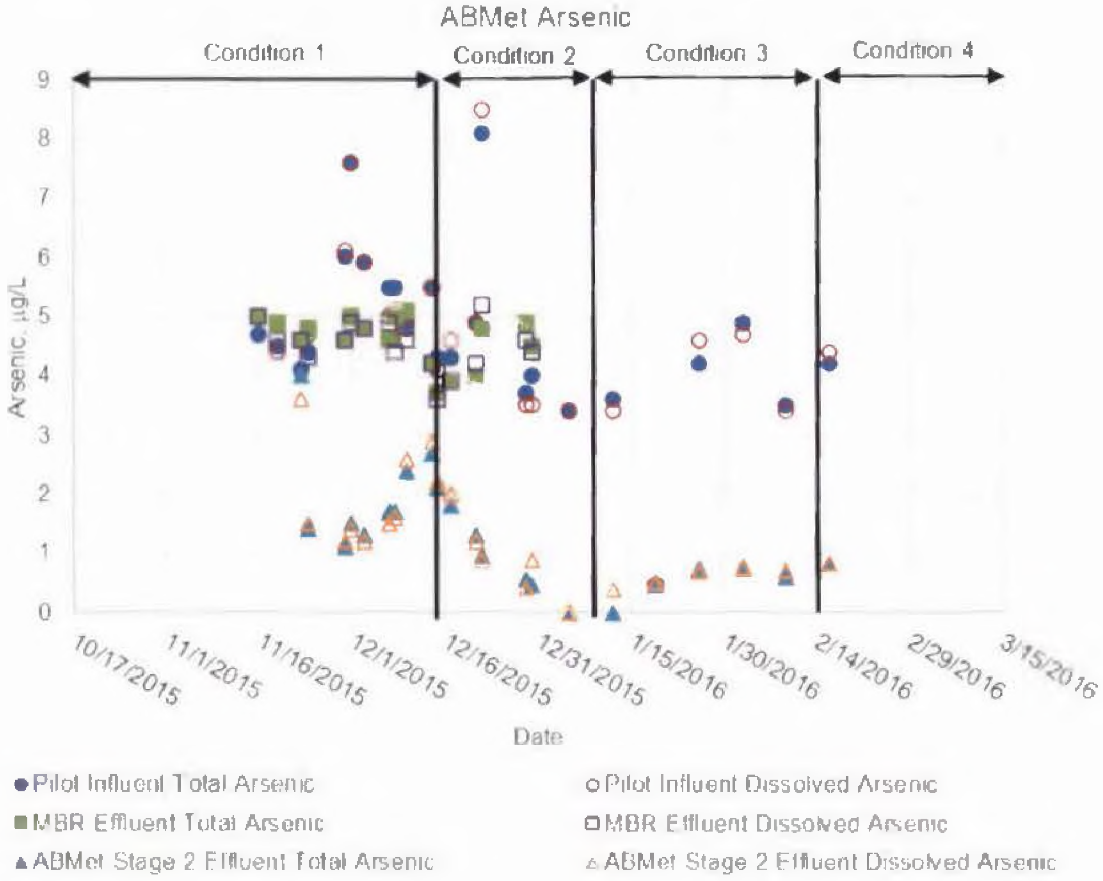

Figure 4-15
ABMet influent and effluent arsenic

5

SUMMARY AND CONCLUSIONS

Pilot Summary

A pilot demonstration of the GE MBR and ABMet processes ran from October 26, 2015 to March 3, 2016 (19 weeks). Results from the demonstration are described under four conditions that summarize performance changes observed. These conditions are summarized below.

- Condition 1 – Startup and Acclimation (October 26, 2015 to December 16, 2015) – period where bacteria are growing and becoming established in the treatment system.
- Condition 2 – Initial Operation (December 17, 2015 to January 10, 2016) – operational period defined by GE's original test plan.
- Condition 3 – Increased Flow/Reduced HRT (January 11, 2016 to February 13, 2016) – operational period intended to more closely simulate full-scale HRT/EBCT conditions.
- Condition 4 – Process Adjustments (February 14, 2016 to March 3, 2016) – period where GE responded to decreased selenium removal performance of the ABMet.

Other than one complete system shutdown from December 24 through December 28 to perform a recovery cleaning on the MBR membranes, the system ran consistently through the duration of the demonstration.

The full-scale FGD wastewater treatment process at P4 has an average operating flow rate of 40 GPM and is typically operated five days per week to allow for equipment cleanings (scale removal from the secondary clarifier plates) on the weekends. The two P4 boilers burn Powder River Basin coal which allows their FGD systems to reach high cycles of concentration and therefore generates wastewater with high TDS and significant scaling potential. The FGD wastewater treatment process consists of a chemical precipitation system that includes hydrated lime addition; primary clarification; organosulfide, ferric chloride, and flocculation polymer addition; and secondary clarification. Two effluent discharge tanks after the secondary clarifier hold approximately 10,000 gallons each. The pilot system in this demonstration received water from the discharge tanks which was blended with plant service water (untreated water from Lake Michigan) in a small equalization tank prior to the MBR process.

GE Water & Process Technologies supplied and operated the ZeeWeed 500D MBR and ABMet pilot systems. We Energies maintained operation of the physical/chemical treatment system. After initial evaluations of the FGD wastewater, GE determined that blending with service water (50/50 by volume) was required to minimize the impacts of scaling and TDS on the pilot systems and bacteria performance. Removing scale-forming compounds (calcium, magnesium, and sulfate) with chemical softening would have required an impractical amount of chemicals (approximately 1,300 lbs./day) and produced high quantities of sludge (approximately 2,000 lbs./day).

The MBR process consisted of pre-anoxic, aerobic, and post-anoxic zones (to target denitrification [in the anoxic zones] and nitrification [in the aerobic zone]) and the ZeeWeed 500 membrane unit to filter biomass and other solids prior to the ABMet pilot. Permeate from the MBR was treated by two ABMet reactors in series.

The MBR pilot was operated at 1 GPM (combined HRT of 35 hours) during Conditions 1 and 2 and at 1.6 GPM during Conditions 3 and 4 (combined HRT of 23 hours). The increase in flow rate was intentionally made by the project team to simulate full-scale conditions. Due to ABMet performance issues, the full-scale conditions for MBR HRT were not implemented. The MBR pilot ran consistently with only one shut down early in the demonstration for a membrane recovery cleaning. Following this cleaning, citric acid maintenance cleans were conducted every other day.

Acetic acid products were used to supply nutrients (in the form of COD, ammonium, and phosphorus) to the MBR pilot. During Condition 1, a blended acetic acid product containing ammonium and phosphorus was used but resulted in excess solids scale formation. To mitigate this issue in Conditions 2 through 4, an 80% acetic acid (20% water) product was used in conjunction with a separate phosphoric acid product.

The ABMet pilot was operated at 0.5 GPM (combined EBCT of 22.4 hours) during Condition 1, 0.6 GPM (combined EBCT of 18.8 hours) during Condition 2, and 0.9 GPM (combined EBCT of 12.4 hours) during Conditions 3 and 4. The increase in flow rate during Condition 2 was not intentional, but the increase in Conditions 3 and 4 were made by the project team in order to more closely simulate GE's commercial EBCT target of 4 to 4.5 hours per reactor (8 to 9 hours total). Due to ABMet performance issues, the full-scale conditions for ABMet EBCT were not implemented. Each stage of the ABMet pilot underwent only one backwash during the demonstration. Starting in Condition 3, degassing was conducted twice per week.

As with the MBR process, acetic acid products were used to supply COD and nutrients to the ABMet reactors. For Conditions 1 and 2, the blended acetic acid product was used. A 50/50 mix of blended product and pure (80%) acetic acid product was used in Condition 3. Molasses was added to this mix in Condition 4.

A summary of pilot influent, MBR effluent, and ABMet effluent water qualities for Conditions 2, 3, and 4 is provided in Table 5-1. The pilot evaluation failed to demonstrate that the ABMet system (with the feed water diluted by 50% and supplemented with the MBR ZeeWeed system) can meet the ELG limits on this water source. Limited information are available to explain the exact issue(s) related to the loss of selenium reduction performance and several variables were identified during the demonstration which may have impacted selenium removal performance.

Table 5-1
Summary of pilot results

Parameter	Units	Pilot Influent			MBR Effluent			ABMet Effluent			Pilot Objectives	
		Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	ELG monthly avg. limit	Target based on 100% dilution
Condition 2												
Total Selenium	μg/L	920	1800	1071	110	260	173	3	6	5	12	6
Dissolved Selenium	μg/L	900	1900	1071	120	260	167	3	7	5	-	-
NO_2/NO_3-N	mg/L	70	160	95	0.12	0.24	0.15	<0.045	0.13	0.081	4.4	2.2
Total Mercury	ng/L	41	90	63	1.60	3.68	2.58	0.41	2.25	1.21	356	178
Dissolved Mercury	ng/L	8.1	18	12.2	0.23	3.06	1.96	0.23	0.59	0.42	-	-
Total Arsenic	μg/L	3.4	8.1	4.7	4	5	4	<0.36	1.8	0.9	8	4
Dissolved Arsenic	μg/L	3.4	8.1	4.7	4	5	4	<0.36	2.0	0.9	-	-
Condition 3												
Total Selenium	μg/L	790	1000	910	170	590	337	15	62	36	12	6
Dissolved Selenium	μg/L	800	1000	915	170	600	330	15	56	37	-	-
NO_2/NO_3-N	mg/L	78	88	83	0.13	21	4.0	<0.045	0.060	0.036	4.4	2.2
Total Mercury	ng/L	20	71	48	1.01	5.67	2.67	0.37	1.20	0.84	356	178
Dissolved Mercury	ng/L	7	27	13	0.64	2.97	1.92	0.45	1.20	0.76	-	-
Total Arsenic	μg/L	0.45	4.9	3.3	no data	no data	no data	<0.36	0.76	0.54	8	4
Dissolved Arsenic	μg/L	0.45	4.7	3.3	no data	no data	no data	0.38	0.76	0.61	-	-
Condition 4												
Total Selenium	μg/L	770	1100	932	170	460	231	14	39	21	12	6
Dissolved Selenium	μg/L	710	1100	919	160	460	233	11	26	17	-	-
NO_2/NO_3-N	mg/L	65	95	80	0.09	0.18	0.13	<0.045	0.081	0.046	4.4	2.2
Total Mercury	ng/L	27	76	52	1.93	1.94	1.94	0.53	1.16	0.85	356	178
Dissolved Mercury	ng/L	7.4	12	9.7	0.66	0.90	0.78	0.68	0.90	0.79	-	-
Total Arsenic	μg/L	no data	no data	no data	no data	no data	no data	0.82	0.82	0.82	8	4
Dissolved Arsenic	μg/L	no data	no data	no data	no data	no data	no data	0.82	0.82	0.82	-	-

MBR Conclusions

- The increased MBR effluent phosphorus concentration during Condition 1 was due to the higher-than-planned-for phosphorus content of the nutrient balanced acetic acid blend being added.
- Influent and effluent BOD and TOC concentrations were low, indicating that all of the acetic acid added was degraded and this suggests that the influent and effluent COD concentrations of approximately 600 mg/L may be caused by analytical interference or some other oxygen-demanding constituents as opposed to organic carbon.
- Complete denitrification (reduction of nitrate nitrogen to nitrogen gas) was achievable in the pretreatment MBR.
- Although nitrification was lost during Conditions 3 and 4, nitrate-nitrogen removal (denitrification) was never a problem in the MBR. For some unknown reason, more sensitive nitrifying bacteria were inhibited while the heterotrophic denitrifying bacteria were not inhibited.
- Selenium, present mainly in dissolved form, was significantly reduced by the pretreatment MBR (approximately 75 percent on average for the entire demonstration).
- Mercury, present mainly in particulate/insoluble form, was significantly reduced by the pretreatment MBR (approximately 96 percent on average for the entire demonstration).
- Arsenic, present mainly in dissolved form, was not removed in the pretreatment MBR.

ABMet Conclusions

- To EPRI's knowledge, this is the first pilot to attempt to treat FGD wastewater from a power plant burning 100% subbituminous coal.
- The pilot test did not consistently demonstrate that the MBR/ABMet combination of technologies adequately treats selenium to meet the 2015 ELGs limits.
- The flow rate to the ABMet was increased on January 11, 2016 from an average of 0.6 GPM to an average of 0.9 GPM. This resulted in the combined EBCT in the ABMet decreasing from 18.8 to 12.4 hours. GE's target of approximately 8 hours for full-scale applications was a goal for the pilot demonstration but was never achieved.
- The flow rate was also increased to the MBR on January 11, 2016 from 1 to 1.5 GPM, which decreased the anoxic HRT from 20 to 13 hours. After this flow rate change (during Condition 3), the average MBR effluent total selenium increased by a factor of 2, doubling the selenium load on the downstream ABMet. However, analytical results taken prior to the flow rate increase were already showing an increase in ABMet effluent selenium. This information was not yet available to the project team when the decision was made to increase flow rates.

- Another variable that may have impacted performance is the complete denitrification that was achieved in the pretreatment MBR. The low nitrate-N available to the ABMet may have resulted in the desired heterotrophic bacteria capable of reducing nitrate/nitrite and selenate/selenite being displaced by sulfate-reducing bacteria in the absence of nitrate-nitrogen as electron acceptor (ABMet average effluent sulfide increased from non-detect to 18 mg/L from Condition 2 to Condition 3 and increased sulfide odors were observed by onsite personnel). The high cycles of concentration associated with the P4 absorbers results in sulfate concentrations approximately five to seven times higher than FGD wastewater from units that burn eastern bituminous coals [3].
- The presence of sulfate-reducing bacteria, indicated by the high concentration of hydrogen sulfide (H_2S) in the second reactor effluent, may also have influenced the loss of selenium reduction. The high COD available to the ABMet from dosing acetic acid may have resulted in the desired bacteria, capable of reducing selenate/selenite, being outcompeted by sulfate-reducing bacteria in the presence of the highly reducing conditions.
- Different nutrient product combinations were used in the demonstration (blended acetic acid containing ammonium and phosphorus, 80% acetic acid (20% water), an even mixture of the previous two products, an even mixture of the first two products and also molasses). Nutrient dosages were maintained based on COD concentrations, pH, and ORP and were within specifications throughout the demonstration. During Condition 4, GE began adding molasses in an attempt to mitigate excessive sulfate-reducing bacteria growth, but by the end of the demonstration (which ended due to a lack of FGD wastewater/pilot feed water supply) the target for selenium reduction had not been re-achieved. Acetic acid products may not provide benefits over molasses for selenium reduction (which is used at GE's commercial ABMet systems treating FGD wastewater for selenium), but there is insufficient information at this time to confirm this possibility.
- Significant arsenic reduction (approximately 70 percent on average for the entire demonstration) occurred in the ABMet. The effluent goal of 4 µg/L was achieved. This is notable, as other EPRI research has shown that for those few plants that have significant dissolved arsenic in their FGD wastewater, little removal is achieved by the physical/chemical treatment system [4].

Recommendations for Additional Research

As previously identified, many variables may have contributed to the loss of performance in the MBR nitrification process and the ABMet selenium reduction process. The following recommendations for additional research are made based on the results of this pilot demonstration.

- Future studies should aim to identify compounds present in FGD wastewater that may be inhibitory or toxic to bacteria used for nitrification, denitrification, and metals reduction. EPRI suspects that oxidants naturally present in FGD wastewater are one potential source of inhibitory effects, but their identity and control have not been fully defined [5]. Further studies to remove non-biodegradable organics in FGD wastewater are recommended. This demonstration tested the use of potassium sulfite, powder activated carbon, and advanced oxidation processes (Fenton reactions), but results are inconclusive.
- The impacts of TDS on bacteria performance should be studied in a controlled environment. Testing should evaluate how increasing FGD wastewater TDS concentration could inhibit reduction of metals or slow down biochemical reactions. Variability in FGD wastewater chemistry is a consistent challenge and potential upsets to treatment technologies are a risk for regulatory compliance. For this demonstration, dilution of P4's chemical precipitation treatment effluent reduced the TDS from an average of 32,300 mg/L to 18,600 mg/L. The dilution was also required to mitigate the high scaling potential of this wastewater. Dilution may not be an option for every site.
- The potential impacts of chemical scale formation in biological treatment FGD wastewater applications should be considered in future demonstrations. For this demonstration, dilution was used as a means to mitigate scale formation in the pilot systems, but dilution may not be an option for every site. General guidance for chemical softening are provided in the Wet Flue Gas Desulfurization Wastewater Physical/Chemical Treatment Guidelines [6].
- The pilot MBR process demonstrated strong performance in reducing nitrate/nitrite prior to the ABMet, but with the potential for competing sulfate-reducing bacteria to negatively influence selenium reduction, it is suggested that nitrate/nitrite reduction as a pretreatment step be more closely evaluated. At this time, there is no clear guidance or rule of thumb for denitrification prior to selenium reduction for a specific range of influent nitrate/nitrite. Future studies that evaluate denitrification as a pretreatment step could consider bypassing a portion of the feed stream directly to the selenium reduction step because controlling denitrification to a target effluent concentration (such as 5 to 10 mg-N/L) may not be feasible or practical. Future studies should also evaluate if sulfate concentrations are also related to the loss of selenium reduction performance due to the influence of sulfate-reducing bacteria.
- Three different nutrients were fed throughout the study. The use of the acetic acid products was a departure from GE's current commercial systems treating FGD wastewater and use molasses. The balance of COD, nitrogen, and phosphorus is important for maintaining bacteria performance in reducing metals. Future studies should focus on the control and application of nutrient products related to nitrification, denitrification, and selenium reduction performance for FGD wastewater.

- The analytical interferences observed in the ABMet pilot effluent (stage two reactor effluent) should be further studied to determine ways to improve accuracy for total selenium analysis. It is hypothesized that the highly reducing conditions of the water resulted in selenium remaining in a reduced valence state (insoluble) and reporting higher than actually present. There have been instances from other tests (see Appendix B) where insoluble selenium was adsorbed to sample bottles and led to total selenium results reporting lower than actually present and confirmed by dissolved species analyses.
- FGD wastewater is impacted by upstream air emission control equipment, boiler operation, fuel selection, and many other factors. Changes in chemistry and flow rates are common for many sites and the wide range of conditions could impact performance of wastewater treatment systems. Coordination with FGD and upstream operations should be considered for any FGD wastewater treatment application, including biological treatment. However, there are limits to what can be achieved by coordination with upstream systems. The final treatment system should be robust enough to handle system variability in a balanced and coordinated approach. Additionally, physical/chemical treatment systems upstream of biological treatment can have an impact on the reliability of selenium reduction and are an integral part of the treatment process.
- Limited data are publicly available on the operation and performance of biological treatment systems for FGD wastewater. The 2015 U.S. EPA Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category may result in many new commercial systems over the next two to seven years. Continued research is needed to ensure power plant operators have the information they need to design, operate, and maintain treatment systems.

6
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A

SAMPLING AND LABORATORY ANALYTICAL PLAN

Table A-1
Analytical Plan – Frequency of Samples

Parameter	Laboratory	Method	Service Water (S1)	Phys/Chem Effluent (S2)	Inf/EQ Tank Effluent (S3)	MBR Mix Liquor (S4)	MBR Effluent (S5)	ABMet 1st Stage Effluent (S6)	ABMet 2nd Stage Effluent (S7)	ABMet Backwash (S8)
Condition 1										
Ammonia	TestAmerica	SM4500	2/month	2/month	3/week		3/week			
Arsenic, total	We Energies	EPA 200.8 DRC-O2	2/month	2/month	1/week		1/week		1/week	
Arsenic, filtered	We Energies	EPA 200.8 DRC-O2	2/month	2/month	1/week		1/week		1/week	
Calcium, total	We Energies	EPA 200.7	2/month	2/month	3/week		3/week	3/week	1/week	
Calcium, filtered	We Energies	EPA 200.7	2/month	2/month	3/week		3/week	3/week	1/week	
Conductivity, µS/cm	TestAmerica	SM2510B	2/month	2/month	3/week		3/week	3/week	1/week	
COD	TestAmerica	SM5220C	2/month	2/month	3/week		3/week		3/week	
Fluoride, total	TestAmerica	SM4500	2/month	2/month	3/week		3/week	3/week	1/week	
Magnesium, total	We Energies	EPA 200.7	2/month	2/month	3/week		3/week	3/week	3/week	
Magnesium, filtered	We Energies	EPA 200.7	2/month	2/month	3/week		3/week	3/week	3/week	
Nitrate/Nitrate (N)	TestAmerica	SM4500	2/month	2/month	3/week		3/week		3/week	
Phosphorus, total	TestAmerica	SM4500	2/month	2/month	3/week		3/week			
Selenium, total	We Energies	EPA 200.7* / 200.8 DRC-NH3	2/month	2/month	3/week		1/week	1/week	1/week	

Table A-1 (continued)
Analytical Plan – Frequency of Samples

Parameter	Laboratory	Method	Service Water (S1)	Phys/Chem Effluent (S2)	Inf/EQ Tank Effluent (S3)	MBR Mix Liquor (S4)	MBR Effluent (S5)	ABMet 1^{st} Stage Effluent (S6)	ABMet 2^{nd} Stage Effluent (S7)	ABMet Backwash (S8)
Condition 1 (continued)										
Selenium, filtered	We Energies	EPA 200.7* / 200.8 DRC-NH3	2/month	2/month	3/week		1/week	1/week	1/week	
Sulfite	We Energies	On-site; analyze immediately		2/month	3/week		3/week		1/week	
Sulfide	TestAmerica	SM4500		2/month	3/week		3/week	3/week	1/week	
TDS	TestAmerica	SM2540C	2/month	2/month	3/week		3/week	3/week	1/week	
TKN	TestAmerica	SM4500		2/month	3/week		3/week		3/week	
TSS	TestAmerica	SM2540D		2/month	3/week	3/week			1/week	
Conditions 2, 3 and 4										
Alkalinity	TestAmerica	SM2320B	1/month	1/month	2/week		2/week	2/week	2/week	
Aluminum, total	We Energies	EPA 200.7		1/month	1/week				1/week	
Aluminum, filtered	We Energies	EPA 200.7		1/month	1/week				1/week	
Ammonia	TestAmerica	SM4500	1/month	1/month	2/week		2/week	2/week	2/week	
Arsenic, total	We Energies	EPA 200.8 DRC-O2	1/month	1/month	1/week				1/week	
Arsenic, filtered	We Energies	EPA 200.8 DRC-O2	1/month	1/month	1/week				1/week	
Bicarbonate	TestAmerica	SM2320B		1/month	2/week		2/week	2/week	2/week	
BOD	TestAmerica	SM5210B	1/month	1/month	1/week		1/week	1/week	1/week	
Boron, total	We Energies	EPA 200.7		1/month	1/week				1/week	

Table A-1 (continued)
Analytical Plan – Frequency of Samples

Parameter	Laboratory	Method	Service Water (S1)	Phys/Chem Effluent (S2)	Inf/EQ Tank Effluent (S3)	MBR Mix Liquor (S4)	MBR Effluent (S5)	ABMet 1st Stage Effluent (S6)	ABMet 2nd Stage Effluent (S7)	ABMet Backwash (S8)
Conditions 2, 3 and 4 (continued)										
Boron, filtered	We Energies	EPA 200.7		1/month	1/week				1/week	
Cadmium, total	We Energies	EPA 200.7 / EPA 200.8		1/month	1/week				1/week	
Cadmium, filtered	We Energies	EPA 200.7 / EPA 200.8		1/month	1/week				1/week	
Calcium, total	We Energies	EPA 200.7	1/month	1/month	2/week		2/week	2/week	2/week	
Calcium, filtered	We Energies	EPA 200.7	1/month	1/month	2/week		2/week	2/week	2/week	
Carbonate	TestAmerica	SM2320B		1/month	1/week		1/week	1/week	1/week	
Chlorides, filtered	TestAmerica	SM4500	1/month	1/month	1/week				1/week	
Cobalt	We Energies	EPA 200.7		1/month	1/week				1/week	
COD	TestAmerica	SM5220C	1/month	1/month	2/week		2/week	2/week	2/week	
Conductivity, µS/cm	TestAmerica	SM2510B	1/month	1/month	2/week		2/week	2/week	2/week	
Copper, total	We Energies	EPA 200.7 / EPA 200.8		1/month	1/week				1/week	
Copper, filtered	We Energies	EPA 200.7 / EPA 200.8		1/month	1/week				1/week	
Fluoride, total	TestAmerica	SM4500	1/month	1/month	2/week		2/week	2/week	2/week	
Iron, total	We Energies	EPA 200.7		1/month	1/week				1/week	

Table A-1 (continued)
Analytical Plan – Frequency of Samples

Parameter	**Laboratory**	**Method**	**Service Water (S1)**	**Phys/Chem Effluent (S2)**	**Inf/EQ Tank Effluent (S3)**	**MBR Mix Liquor (S4)**	**MBR Effluent (S5)**	**ABMet 1st Stage Effluent (S6)**	**ABMet 2nd Stage Effluent (S7)**	**ABMet Backwash (S8)**
Conditions 2, 3 and 4 (continued)										
Iron, filtered	We Energies	EPA 200.7		1/month	1/week				1/week	
Lead, total	We Energies	EPA 200.7 / EPA 200.8		1/month	1/week				1/week	
Lead, filtered	We Energies	EPA 200.7 / EPA 200.8		1/month	1/week				1/week	
Magnesium, total	We Energies	EPA 200.7	1/month	1/month	2/week				2/week	
Magnesium, filtered	We Energies	EPA 200.7	1/month	1/month	2/week				2/week	
Manganese, total	We Energies	EPA 200.7		1/month	1/week				1/week	
Manganese, filtered	We Energies	EPA 200.7		1/month	1/week				1/week	
Mercury low-level, total	We Energies	EPA 1631E	1/month	1/month	2/week		2/week		2/week	
Mercury low-level, 0.45 μm	We Energies	EPA 1631E	1/month	1/month	2/week		2/week		2/week	
Molybdenum, total	We Energies	EPA 200.7		1/month	1/week				1/week	
Molybdenum, filtered	We Energies	EPA 200.7		1/month	1/week				1/week	
Nickel, total	We Energies	EPA 200.7		1/month	1/week				1/week	
Nickel, filtered	We Energies	EPA 200.7		1/month	1/week				1/week	

Table A-1 (continued)
Analytical Plan – Frequency of Samples

Parameter	Laboratory	Method	Service Water (S1)	Phys/Chem Effluent (S2)	Inf/EQ Tank Effluent (S3)	MBR Mix Liquor (S4)	MBR Effluent (S5)	ABMet 1st Stage Effluent (S6)	ABMet 2nd Stage Effluent (S7)	ABMet Backwash (S8)
Conditions 2, 3 and 4 (continued)										
Nitrate/Nitrate (N)	TestAmerica	SM4500	1/month	1/month	2/week		2/week	2/week	2/week	Each Occurrence
Phosphorus, total	TestAmerica	SM4500	1/month	1/month	1/week		1/week	1/week	1/week	
Selenium, total	We Energies	EPA 200.8 DRC-NH3	1/month	1/month	2/week		2/week	2/week	2/week	Each Occurrence
Selenium, filtered	We Energies	EPA 200.8 DRC-NH3	1/month	1/month	2/week		2/week	2/week	2/week	Each Occurrence
Silver	We Energies	EPA 200.7		1/month	1/week				1/week	
Sodium, total	We Energies	EPA 200.7		1/month	1/week		1/week		1/week	
Sodium, filtered	We Energies	EPA 200.7		1/month	1/week				1/week	
Sulfate, filtered	TestAmerica	SM4500	1/month	1/month	2/week		2/week	2/week	2/week	
Sulfite	We Energies	Onsite; analyze immediately		1/month	1/week				1/week	
Sulfide	TestAmerica	SM4500		1/month	2/week		2/week	2/week	2/week	
TDS	TestAmerica	SM2540C	1/month	1/month	2/week		2/week	2/week	2/week	
Thallium	We Energies	EPA 200.8		1/month	1/week				1/week	
Tin	We Energies	EPA 200.7		1/month	1/week				1/week	
TKN	TestAmerica	SM4500		1/month	1/week		1/week		1/week	
TOC	TestAmerica	SM5310C	1/month	1/month	1/week		1/week	1/week	1/week	

Table A-1 (continued)
Analytical Plan – Frequency of Samples

Parameter	Laboratory	Method	Service Water (S1)	Phys/Chem Effluent (S2)	Inf/EQ Tank Effluent (S3)	MBR Mix Liquor (S4)	MBR Effluent (S5)	ABMet 1st Stage Effluent (S6)	ABMet 2nd Stage Effluent (S7)	ABMet Backwash (S8)
Conditions 2, 3 and 4 (continued)										
TSS	TestAmerica	SM2540D		1/month	2/week	2/week	2/week	2/week	2/week	Each Occurrence
Zinc, total	We Energies	EPA 1638 DRC		1/month	1/week				1/week	
Zinc, filtered	We Energies	EPA 1638 DRC		1/month	1/week				1/week	
Arsenic, total	Brooks Rand	EPA 200.8/6060			1/month				1/month	
Arsenic, filtered	Brooks Rand	EPA 200.8/6060			1/month				1/month	
Arsenic Speciation, filtered	Brooks Rand	EPA 200.8/6060			1/month				1/month	
Mercury low-level, total	Brooks Rand	EPA 1631E DRC			1/month		1/month		1/month	
Mercury low-level, 0.45 µm	Brooks Rand	EPA 1631E DRC			1/month		1/month		1/month	
Mercury low-level, 0.1 µm	Brooks Rand	EPA 1631E DRC			1/month		1/month		1/month	

Table A-1 (continued)
Analytical Plan – Frequency of Samples

Parameter	Laboratory	Method	Service Water (S1)	Phys/Chem Effluent (S2)	Inf/EQ Tank Effluent (S3)	MBR Mix Liquor (S4)	MBR Effluent (S5)	ABMet 1st Stage Effluent (S6)	ABMet 2nd Stage Effluent (S7)	ABMet Backwash (S8)
Conditions 2, 3 and 4 (continued)										
Selenium, total	Brooks Rand	EPA 200.8/6060			1/month		1/month	1/month	1/month	
Selenium, filtered	Brooks Rand	EPA 200.8/6060			1/month		1/month	1/month	1/month	
Selenium Speciation, filtered	Brooks Rand	EPA 200.8/6060			3/month				1/week	

Notes:
Inf/EQ = influent equalization
Phys/Chem = physical/chemical

B

ANALTYICAL QA/QC DISCUSSION

Results for total selenium from the ABMet effluent (stage two reactor effluent) from January 18, 19, and 21 failed We Energies' lab QA/QC checks. In these samples, the matrix spike recovery values were on the low end of the acceptable range. Low matrix spike recovery could indicate selenium is adhering to the container walls or precipitating out of solution. All matrix spike recoveries up to this point had been within the method control limits and the lab did not change anything in the sample preparation or analysis protocol. These were the first sets of results that failed matrix spike QC and We Energies' lab staff performed various tests in attempt to provide accurate analyses. On January 18, the We Energies lab staff who collected the samples noted a strong sulfide odor that had not been present in prior samples. The same odor was present in this sample for the duration of the test.

Samples collected at the site for dissolved and total arsenic and selenium at We Energies' lab were not preserved in the field. The lab filtered a portion of the non-preserved sample for dissolved metals analysis and then acidified the filtered sample with nitric acid to achieve pH less than 2 s.u. The acidified samples were well shaken prior to pouring off the aliquot for totals metals digestion[6]. It was hypothesized that the low ORP in the ABMet stage two reactor effluent contributed to selenium remaining in a reduced valence state (insoluble). To test this hypothesis, the lab added 30% hydrogen peroxide and re-analyzed the samples. Select data comparing various sample preparation methods are presented in Table B-1. Analyses following peroxide addition resulted in matrix spike recovery improvements and total selenium concentrations reported higher than initial analyses. It is noted that EPA Method 200.7 does not include the addition of peroxide or other oxidants to improve accuracy.

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[6] To accomplish the quick turnaround time requests, the lab kept digestion time to two to three hours in the hotblock.

Table B-1
ABMet Second Stage Reactor Effluent Selenium Analysis Using Hydroxide Preparation Method

Date	Tot. Se (µg/L)	Dis. Se (µg/L)	Dilution	MS/MSD mean % recovery	Spike Level (µg/L)	Analysis Comments
1/18/2016	13	12	10	16	40	EPA 200.2 digestion: 1mL HNO^3 + 0.25 mL HCl
	15	15	10	14	40	re-analysis for confirmation
	27	no data	10	116	5	10x dilution direct from sample bottle + 5 µg/L bench spike
	15	no data	10	N/A	N/A	Re-digested with 3mL/50mL 30% H_2O_2
1/19/2016	11	10	10	6	40	EPA 200.2 digestion: 1mL HNO_3 + 0.25 mL HCl
	-	-	10	104	N/A	5 µg/L post-digest (bench) spike
	9.4	no data	50	N/A	N/A	1:5 serial dilution of 10x digestate
	10	no data	10	7	N/A	alternate digestion - capped
	26	no data	10	105	5	10x dilution direct from sample bottle + 5 µg/L bench spike
1/21/2016	8.2	7.7	10	11	40	EPA 200.2 digestion: 1mL HNO_3 + 0.25 mL HCl
	19	no data	10	32	40	digested at 10x dilution
	26	no data	25	32	40	digested at 25x dilution
	31	no data	10	120	80	Re-digested with 3mL/50mL 30% H_2O_2
1/25/2016	42	-	10	106	40	Modified EPA 200.2 digestion: 2mL 30% H_2O_2 + 1mL HNO_3 + 0.25 mL HCl
	11	9.0	10	19	40	non-H_2O_2 treated

MS = matrix spike
MSD = matrix spike duplicate

Samples taken during Condition 3 of the demonstration were sent to Brooks Applied Labs in Bothell, WA for speciation analysis. The lab used EPA 200.8 and a closed-vessel, polytetrafluoroethylene (e.g., Teflon™) bomb oven digestion. Sample analysis was performed by triple quadrupole mass spectrometry (ICP-QQQ-MS) to report total and dissolved selenium. Speciation analyses were conducted for selenite (Se(IV)), selenate (Se(VI)), selenomethionine (MeSe (IV)), selenocyanate (SeCN), and selenosulfate ($SeSO_3$). These data are presented in

Table B-2. With a high level of analytical accuracy, the speciated selenium products should add up to the dissolved selenium value for each sample. While minor variation may be expected, the January 28 sample had significant variance – total reported as 17 µg/L, dissolved reported as 9.28 µg/L, the sum of reported dissolved species is 135 µg/L. The current theory for this condition is that selenium adsorbs to the sample bottle, causing the analysis for total selenium to report lower than dissolved. The lab attempted to digest the sample in the sample bottle using 10% nitric acid, but the results were the same. The selenium may have already adsorbed to the bottle and the effect was irreversible.

EPRI has begun additional studies to evaluate methods to improve analytical results from FGD wastewater biological treatment effluent. These studies are considering sample container use, preparation techniques, and analytical methods.

Table B-2
ABMet Effluent Selenium Speciation Results

	Brooks Applied Lab									We Energies Lab	
Date	**Tot. Se**	**Dis. Se**	**Dis. Se(IV)**	**Dis. Se(VI)**	**Dis. MeSe (IV)**	**Dis. SeCN**	**Dis. $SeSO_3$**	**Dis. Unknown Se**	**Sum of Dis. Species**	**Tot. Se**	**Dis. Se**
1/12/16	16.6	**16.3**	1.79 B	1.56 B	0.250 U	7.27	1.10 B	0.00 U	11.7	17	20
1/14/16	32.6	**35.9**	4.41	11.5	0.385 B	no data	2.21 B	0.465	19	45	47
1/19/16	25.5	**25.5**	7.61	4.77	0.250 U	7.46	2.53	3.1	25.5	22	no data
1/21/16	30.2	**15.9**	5.89	0.250 U	0.250 U	14.7	2.53 U	4.60	25.2	31	no data
1/26/16	30.4	**27.6**	10.8	0.965	0.497 B	11.9	2.50 U	1.52	25.7	46	42
1/28/16	17.0	**9.28**	51.8	0.965 U	1.32	69.7	3.82	8.71	135.4	47	46
2/2/16	23.3	**12.5**	8.16	0.965 U	0.588 B	20.1	2.50 U	1.12	30	62	54
2/4/16	22.6	**9.69**	5.94	0.965 U	0.638 B	17.2	2.50 U	1.11	24.9	50	46
2/9/16	12.6	**13.0**	9.47	0.250 U	0.398	11.4	2.50 U	1.02	22.3	35	31
2/11/16	8.48 B	**6.28 U**	1.18 B	0.250 U	0.154 B	5.24	0.275 B	1.63	8.5	23	19
2/16/16	14.2	**9.26 B**	4.55	0.250 U	0.250 U	10.8	2.73	1.69	19.8	29	25
2/18/16	18.0	**4.88 B**	3.01	0.250 U	0.250 U	8.01	2.53 U	1.46	12.5	27	22
2/23/16	8.80	**5.23**	2.06 B	0.250 U	0.250 U	2.10 B	2.04 B	0.551	6.8	18	13
2/25/16	10.3	**3.79 B**	0.828 B	0.250 U	0.250 U	2.65	0.222 U	0.814	4.3	16	13

Note: all data reported as µg/L
U = not detected
B = analyte is found in the associated blank, as well as in the sample

C

RAW DATA

Raw data from the pilot study are provided in the attachment.

Export Control Restrictions

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