

# **Emerging Technologies and Approaches to Minimize Discharges Into Lake Michigan Phase 2, Module 3 Report**

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**Energy Systems Division**

**For copies of this report or questions regarding this work please contact:**

M. Cristina Negri  
Argonne National Laboratory  
Energy Systems Division  
(630) 252-9662  
negri@anl.gov

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# **Emerging Technologies and Approaches to Minimize Discharges Into Lake Michigan Phase 2, Module 3 Report**

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by  
M.C. Negri, P. Gillenwater, and M. Urgan Demirtas  
Energy Systems Division, Argonne National Laboratory

April 19, 2011

This report incorporates comments received from an external peer-review panel.  
The external peer review was held on October 29, 2010 at Purdue University  
in Hammond, IN.

## Executive Summary

Purdue University Calumet (Purdue) and Argonne National Laboratory (Argonne) have conducted an independent study to identify deployable technologies that could help the BP Whiting Refinery, and other petroleum refineries, meet future wastewater discharge limits. This study has been funded by BP. Each organization tested a subset of the target technologies and retains sole responsibility for its respective test design and implementation, quality assurance and control, test results obtained from each of the technologies, and corresponding conclusions and recommendations. This project was divided in two phases and modules. This report summarizes the work conducted by Argonne in Phase II Module 3 (Bench Scale Testing). Other Modules are discussed elsewhere (Emerging Technologies and Approaches to Minimize Discharges into Lake Michigan, Phase 2, Modules 1-3 Report, April 2011, prepared for BP Americas by the Argonne – Purdue Task Force).

The goal of this project was to identify and assess available and emerging wastewater treatment technologies for removing mercury and vanadium from the Whiting Refinery wastewater and to conduct bench-scale tests to provide comparable, transparent, and uniform results across the broad range of technologies tested. After the bench-scale testing phase, a previously developed decision matrix was refined and applied by Argonne to process and review test data to estimate and compare the preliminary performance, engineering configuration, preliminary cost, energy usage, and waste generation of technologies that were shown to be able to remove Hg and/or V to below the target limit at the bench scale. The data were used as the basis to identify the best candidates for further testing at the bench or pilot scale on a slip stream of effluent to lake (ETL) or clarifier effluent (CE) at the Whiting Refinery to determine whether future limits could be met and to generate other pertinent data for scale-up and sustainability evaluation. As a result of this technology assessment, Argonne identified several technologies that, at the bench-scale, could achieve the targeted performance for the removal of mercury and vanadium. A subset of those technologies were recommended for further testing either at the bench scale or at the pilot scale to determine whether future discharge limits could be met at the pilot-scale.

The objectives of this project module are to:

1. Test at the bench-scale a subset of the technologies previously identified in Module 1 for the removal of target heavy metals down to 1.3 ppt Hg and 280 ppb V;
2. Review and process bench-scale test results on the basis of the end-point performance measures matrix to determine preliminary comparative performance, cost-effectiveness, and potential engineering configuration of tested technologies;
3. Assess the technological feasibility and readiness of the identified technologies for implementation at the Whiting Refinery; and
4. Select technically and economically feasible mercury- and vanadium-removal technologies and vendors to be recommended for pilot-scale testing at the Whiting Refinery.

Key findings and achievements resulting from this project include:

- Data obtained from the treatability studies on batch samples of Whiting refinery CE or ETL showed that several technologies were able to achieve, at the bench-scale, mercury concentrations at or below the 1.3 ppt (or part per trillion [ppt], ng/L) target concentration, albeit with different efficiencies and engineering implications. This demonstrates that there is no fundamental physical or chemical barrier to achieving <1.3 ppt Hg in the tested refinery wastewater at the bench scale. Engineering issues will be addressed during the scale-up and optimization phases.
- During the Module 3 wastewater characterization work and bench-scale testing, which were conducted from December 2009 through August 2010, most of the mercury was found to be in particulate form. Very little mercury (< 1.0 ppt) was found to be in the dissolved form (i.e., present after 0.45  $\mu\text{m}$  filtration). During this testing period, researchers found that removal of particulate mercury by filtration was sufficient to meet the 1.3 ppt Hg target limit. However, historical BP data from the spring of 2009 (Module 2) show that mercury in the dissolved form was present at levels above 1.3 ppt approximately half the

time. Therefore, there is a need for wastewater treatment technologies for both particulate and dissolved mercury removal.

- The low mercury concentrations in the wastewater samples tested required the use of a Class-100 clean room environment; specialized equipment cleaning methods; the use of “clean hands-dirty hands” procedures to avoid cross-contamination; and a substantial reliance on method, reagent, and equipment blanks, as well as specialized analytical procedures with appropriate sensitivity (EPA method 1631E). These steps were critical to minimize and understand the experimental error and quality boundaries. The analytical labs contracted for this project needed to conduct extensive method refinement work to provide accurate and precise measurements of mercury at the target low concentrations in the wastewater studied.
- The selected technologies were tested under uniformed conditions at the bench-scale by using either effluent-to-lake (ETL) or clarifier effluent (CE) from the Whiting Refinery. These two streams were qualitatively the same over the study period. The data collected from the treatability experiments were processed and categorized on the basis of a comparative technology assessment protocol.
- In terms of mercury removal, the Module 3 test results showed that some technologies were effective (i.e., met the 1.3 ppt discharge limit) on *particulate* mercury, while others were effective on *dissolved* mercury. One emerging technology was found to be effective on both particulate and dissolved mercury. Three high-ranking mercury-removal technologies — namely, *ultrafiltration* (particulate mercury), *adsorption* (dissolved mercury), and an emerging *reactive filtration* technology (both particulate and dissolved mercury) — were recommended from the endpoint performance matrix evaluation for further testing (bench or pilot-scale testing on a slip stream of the CE or ETL at the Whiting Refinery).
- During the Module 3 testing period, vanadium was found exclusively in the dissolved form. The wide fluctuations in vanadium concentrations over the study period were primarily attributed to the periodic presence in the wastewater stream of vanadium from the Stretford purge.
- Argonne found several technologies to be effective in the removal of vanadium. Among the candidate technologies, iron precipitation offers a robust option to remove vanadium from the CE/ETL streams when the Stretford purge is on. Adoption is simplified by the fact that BP already has a permit to use ferric sulfate as a settling aid in the secondary clarifier at the existing Whiting Refinery Wastewater Treatment Plant. The research team concluded that no further study of vanadium removal was necessary.
- The project team developed a vendor selection protocol for the assessment of technology readiness and vendor qualifications for a future pilot demonstration at the Whiting Refinery. By using this selection protocol, among the subset of vendors available for the three high-ranking technologies, GE was selected for ultrafiltration (GE Zeeweed Technology — 0.04  $\mu\text{m}$  pore size and made up of polyvinylidene fluoride [PVDF]), while Mersorb LW (a sulfur-impregnated activated carbon) was selected for adsorption. The reactive filtration (Blue PRO) process was not subjected to the same vendor selection protocol, since it is supplied by only one vendor, Blue Water Technologies, Inc.
- Because of the large volume of water required for pilot testing, the project team agreed that pilot testing should be conducted at the Whiting Refinery on a slip stream of the CE or ETL.
- Upon further evaluation of testing protocols and objectives and following a recommendation from the external review panel, it was determined that while *ultrafiltration* is ready to be tested at the pilot scale, *adsorption* testing at the pilot scale would benefit from further bench scale studies, and will be dependent on the presence in the influent water of sufficient amounts of dissolved mercury to ensure a meaningful test.
- In the case of BluePro, the project team determined that piloting should be preceded by optimization at the bench scale of process reagents and processes in order to reduce the treatments to be tested at the pilot scale.
- The results of this work offer treatment alternatives for different forms of mercury. For example, some of the promising technologies are better suited for dissolved metal removal, while others can remove metals sorbed onto particulates. The tested technologies may be applicable to other types of wastewater that contain mercury.

- In support of the Great Lakes Initiative, the outcome of this research could provide valuable information to regulators and aid in the development of a rationale for identifying viable approaches to control mercury and other metals in industrial and municipal effluents.

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# 1. Introduction: Background and Report Organization

## a. Background

Purdue University Calumet (Purdue) and Argonne National Laboratory (Argonne) have conducted an independent study to identify deployable technologies that could help the BP Whiting Refinery, and other petroleum refineries, meet future wastewater discharge limits. This study has been funded by BP. In an effort to meet target discharge limits of 1.3 ppt<sup>1</sup> Hg (mercury) and 280 ppb V (vanadium) as a monthly average, Phase II examines technologies for the treatment of mercury and vanadium. This phase encompasses several modular elements that have been funded sequentially. Module 1<sup>2</sup> involved the search and identification of potentially applicable technologies. Module 2 (results discussed elsewhere) includes the sampling and analysis of a number of waste streams at the Whiting Refinery. In a companion task in this project, a separate report discusses a comparative analysis of Discharges into Lake Michigan conducted by Argonne<sup>3</sup>. Module 3, which is presented in this project report, covers the selection and bench-scale testing of the technologies selected in Module 1 to provide comparable, transparent, and uniform test results for a range of wastewater treatment technologies to remove mercury and vanadium from Whiting Refinery wastewater. To select best candidate technologies for pilot-scale testing at the Whiting Refinery, Module 3 also comprises data processing and review to determine each technology's comparative preliminary performance, engineering configuration, cost, energy usage, waste generation, and readiness to deployment. Each organization (Argonne and Purdue University Calumet) evaluated a subset of the target technologies and retains sole responsibility for its respective test design and implementation, quality assurance and control, test results obtained from each of the technologies, and corresponding conclusions and recommendations. This report summarizes the work conducted by Argonne.

## b. Objectives and the Scope of Work for Module 3

The aims of Argonne's work for the Module 3 project were to:

- Test at the bench-scale a subset of the technologies identified in Module 1 for the removal of the target heavy metals, using appropriately characterized wastewater batches, to meet the future discharge limits of 1.3 ppt Hg and 280 ppb V as a monthly average;
- Witness and/or direct test the technologies that could be tested only by using vendors' equipment at vendors' facilities;
- If possible, use bench-scale results to determine the preliminary performance, cost-effectiveness, and potential engineering configuration of the tested technologies; and
- Test a pilot-scale version of the selected technologies on a slip stream of the selected waste stream from the Whiting Refinery.

The scope of work for the Module 3 project includes five tasks:

1. Receipt and characterization of appropriate batches of Whiting Refinery wastewater over the study period;

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<sup>1</sup> Although the usage of ng/L, µg/L and mg/L is more accurate, this report will use ppt, ppb and ppm instead for simplicity.

<sup>2</sup> *Emerging technologies and approaches to minimize discharges into Lake Michigan, Module 1, Task 2 Deliverable: Assemble a general list of all technologies that are available for the removal of Mercury and Vanadium from refinery wastewater.* Purdue Calumet Water Institute and Argonne National Laboratory, March 30, 2010.

<sup>3</sup> *Comparative Analysis of Discharges into Lake Michigan. Phase I, Southern Lake Michigan.* Argonne National Laboratory, Environmental Science Division ANL/EVS/R-08/1, June 2008. *Comparative Analysis of Discharges into Lake Michigan. Phase II, The Entire Lake.* Argonne National Laboratory, Environmental Science Division. ANL/EVS/R-09/3, June 2010.

2. Preparation and review of bench-scale test plans;
3. Bench-scale testing of mercury and vanadium metal treatment technologies;
4. Analysis of data, selection of technologies for pilot-scale testing, and design of pilot testing; and
5. Support of further testing at the bench or pilot-scale.

Design and support of the pilot-scale testing will be discussed in a separate report.

### **c. Technology Selection for Bench-scale Testing**

The project task force included representatives of Argonne and Purdue University Calumet. The task force selected the heavy metal treatment technologies on which to conduct bench-scale tests. The technologies selected for bench-scale testing are shown in Table 1-1. The technology selection was based on the results from the screening of technologies for removal of vanadium and mercury conducted in Phase II, Module 1. This selection deliberately aimed at testing a broad range of technologies from the currently available wastewater treatment “toolbox,” so that a comprehensive assessment could be obtained. The rationale for this selection was derived from the literature-based removal efficiency and other screening criteria, as detailed in the Module 1 report. One conclusion from the Module 1 work was that most technologies, whether owned by specific vendors or available as general engineering practices, have scarcely been tested on refinery wastewater applications or for performance at the low concentrations required by Whiting and others that discharge to the Great Lakes. The task force members (Argonne and Purdue University Calumet) each were tasked independently to test a subset of technologies from the list in Table 1-1. Two technologies — namely, membrane filtration and co-precipitation by ferric-ferrous salts — were tested independently by both Argonne and Purdue University Calumet. The technologies that were tested by Argonne are shown in bold characters in Table 1-1. Those technologies shown in non-bold characters were tested by Purdue University Calumet and are reviewed in their report. Two technologies among those listed, GE ABMet and Siemens PetroMBR, were to be tested by Argonne at the vendors’ facilities using vendors’ equipment. However, these technologies eventually were not tested because of:

1. Withdrawal of the vendor (GE), and
2. Difficulties in signing the contract with the vendor (Siemens) and additional safety considerations using the candidate waste stream in the lab.

### **d. Report Organization**

**Chapter 2** summarizes the wastewater characterization work conducted during the course of this study. Metals concentration, speciation, and general characteristics (such as pH, TSS, redox conditions, oil and grease, and co-present ions) of the influent wastewater stream influence treatment effectiveness and performance. Through interaction with the wastewater environment, mercury and vanadium can transform into several forms. Mercury can be found as elemental mercury, ionic mercury, and organic mercury. Likewise, vanadium can be present in ionic, organic, complexed, and sorbed species in several oxidation states. Different forms of metals could determine the nature of the treatment process required for success. Therefore, proper characterization of influent and treated wastewater is essential to understand the performance of the technologies.

**Table 1-1. Technologies Tested at Bench-scale, Categorized by Metal of Interest and Testing Organization (in bold: technologies tested by Argonne and discussed in this report)**

Vanadium Technologies	Mercury Technologies	Vanadium and Mercury Technologies
<ul style="list-style-type: none"> <li>• <b>Adsorption with Dow-Adsorbis As 500</b></li> <li>• <b>Adsorption with Bayoxide E-IN-20</b></li> <li>• <b>Adsorption by Granular Ferric Hydroxide (GFH, Siemens)</b></li> <li>• <b>Ferric and ferrous chloride precipitation</b></li> <li>• Recovery system by Siemens (ion exchange based)</li> </ul>	<ul style="list-style-type: none"> <li>• <b>Sulfide precipitation</b></li> <li>• <b>Precipitation with Nalmet 1689</b></li> <li>• <b>Precipitation with GE MetClear</b></li> <li>• <b>Adsorption with activated carbon –Calgon F600 and OLC</b></li> <li>• <b>Adsorption with Mersorb LW</b></li> <li>• <b>Adsorption with Thiol-SAMMS</b></li> <li>• <b>Adsorption with Capttech</b></li> <li>• Precipitation (batch/continuous) by Siemens</li> <li>• Frontier Geosciences, Inc., FGS/MCX chelating agent</li> <li>• Siemens adsorption/filtration</li> <li>• Rohm and Haas ion exchange</li> <li>• DOW DOWEX XUS ion exchange</li> <li>• The Water Company, LLC (Capacitive Deionization/Se-Clear)</li> </ul>	<ul style="list-style-type: none"> <li>• DOW - DOWEX ion exchange</li> <li>• Mar Systems/Sorbster™</li> <li>• Sequestration of heavy metals using functionalized polymers</li> <li>• Microfiltration – Siemens Memtek system</li> <li>• <b>Membrane filtration systems (MF, UF, NF, and RO)</b></li> <li>• <b>Electrodeionization (EDI)</b></li> <li>• <i>GE ABmet (using vendors' equipment)</i></li> <li>• <i>Siemens PetroMBR (using vendors' equipment)</i></li> </ul>

**Chapter 3** describes the methods and results of the bench-scale tests of the selected technologies. The information gathered in Module 1 of this project shows that available performance data on metals treatment technologies are scarce, incomplete, difficult to compare across technologies, often based on opaque vendor claims, and generally obtained from waste streams that differ from refinery wastewater. Therefore, the first step in the identification of cost-effective technologies was to conduct a bench-scale set of tests using *uniform test conditions* and *a common refinery wastewater influent*, so that comparative data could be obtained. From the project start, Argonne devised a set of endpoint metrics that could be applied to uniformly evaluate each technology in comparison with the others to the highest extent possible. This chapter (with additional details provided in Appendices 1-4) also reviews the identification of potential sources of variability and error (i.e., sampling, analytical, experimental, and so forth) and the plans to address them in the testing methods for each treatment technology, as well as in the QA/QC plans.

Technologies were tested for the treatment of the end-of-pipe wastewater, namely effluent-to-lake (ETL) or clarifier effluent (CE). One particular challenge was the extremely low concentrations of mercury in the wastewaters of interest in this work. Future limits for refinery effluent mercury will be 1.3 ppt, and current end-of-pipe wastewater levels are usually in the ~1 to 10 ppt range. These low concentrations require special clean-hands procedures to avoid cross-contamination when conducting the sampling, testing and analyzing experimental samples, as well as specialized analytical procedures with appropriate sensitivity. The EPA method 1631E recommends that a Class 100 clean room be used for sample processing. Argonne has dedicated a certified Class 100 clean-room laboratory to conduct the mercury bench-scale tests. The low-level mercury analysis (total and speciation) of experimentally produced samples (treated wastewater) was conducted by third-party laboratories, as discussed in Chapter 2.

**Chapter 4** reviews data analysis and the selection of the best candidate technologies and vendors for pilot-scale testing, as well as pilot equipment design and specifications. Comparison of the testing results for the best candidate technologies is an important initial step in technology evaluation. As a part of the project, Argonne also developed a technology assessment protocol to process and review the experimental data (based on the end-point performance measures matrix developed at the onset of the project) and to select promising technologies for pilot testing at the Whiting Refinery.

## 2. Sampling and Analysis Overview, Wastewater Characterization, and Challenges in Analytical and Quality Control

### a. Sample Collection and Analysis

Argonne contracted two analytical laboratories to conduct analyses of the Whiting Refinery wastewater in support of the bench-scale tests. Of these two laboratories, Lab A in Indiana, was selected because it is local, is authorized to access the Whiting Wastewater Treatment Plant and collect samples, and is proficient both in collecting samples by using the “clean hands-dirty hands” procedure required by the EPA 1639 method and in conducting low-level mercury (Hg) analysis per the EPA 1631E method (1, 2). The second laboratory, Lab B was selected because it offers advanced analytical capabilities in mercury speciation and has been extensively involved in the development of the EPA 1631E method. It offers speciation analyses for mercury, vanadium (V), and other elements of interest to this project. Due to its distant location, Lab B did not do any sampling at the refinery. During the course of the work it also became clear that, although both laboratories offered certified quality-driven services and complied with all quality requirements mandated by regulators, Lab B offered an advantage in that it was able to further refine the EPA 1631E method so that the recovery rates were higher, thus providing better resolution of differences among samples at very low concentrations near the detection limit. This advantage was very useful in the R&D setting of this project.

During the test period, Lab A received weekly orders from Argonne to deliver the required amount of wastewater from the Whiting Refinery for the treatability studies. They collected the wastewater in 5 gal Teflon-lined pails (mercury-free, Teflon® PFA Film from Welch Fluorocarbon, Inc., of New Hampshire) by using the “clean hands-dirty hands” EPA 1639 procedure. The collection typically occurred on Monday mornings, and samples were delivered to Argonne the same day. The unopened pails were then stored in a cold room at 4 °C and used as necessary. Any remaining amount was discarded at the end of each week. The water sample storage time was determined after conducting “shelf-life” studies (see the following section and Appendix 1). For targeted work, Lab A also sent samples directly to Lab B, as instructed by Argonne.

### b. Characteristics of Whiting Refinery Wastewater

Treatability studies require a reasonable knowledge of the characteristics of the feed wastewater. Detailed characterization data regarding wastewater are necessary to determine the proper and effective experiment conditions, such as the required precipitant and adsorbent dosages, for each tested treatment technology. Three distinct sources of data regarding the composition of the wastewater were collected during the course of this study to determine variations in wastewater composition over the study period, as well as to make a comparison with BP’s historical data: (1) sampling events: each time a sample was collected from the refinery, an analysis was performed; (2) time 0 data: at the onset of each experiment, an untreated sample was also sent for analysis to document starting conditions; and (3) a shelf-life study was conducted to provide focused data on mercury and vanadium speciation over time.

Table 2-1 presents a summary of the influent wastewater characteristics during the sampling events from December 2009 to August 2010 at the Whiting Refinery. Initial treatability experiments were performed with effluent-to-lake (ETL) samples. Due to the reporting requirement to Indiana Department of Environmental Management (IDEM) when ETL is sampled, the sample collection point was moved to the clarifier outlet on February 15, 2010. The wastewater characteristics of these two streams were basically the same during the sampling events.

Cations, anions, and solids concentrations were measured, as these basic parameters were needed for the design of the treatability studies. The characteristics of ETL/CE varied, depending on loading and operating conditions upstream at the Whiting Refinery. For example, vanadium concentration in the wastewater depends on the

presence of absence of an intermittent process purge stream. Other parameters might just be normal variability associated with an industrial wastewater stream that has numerous upstream sources. The obtained data were also consistent with BP's historical data, except for dissolved mercury (Table 2-2). Although total suspended solids (TSS) concentrations were low in the ETL/CE samples, the total dissolved solids (TDS) concentrations ranged from 840 to 1,900 ppm. The impact of variable amounts of solids in the wastewater was considered during the sample collection and treatability experiments. These data showed that the consistent use of corrective techniques (i.e., mixing of water samples before subsampling, method blanks, and so forth) was necessary to obtain meaningful and representative test results.

**Table 2-1. Typical Concentration Ranges for Various Constituents of ETL/CE at the Whiting Refinery (averages of 4–29 sampling events, depending on the tested parameter)**

Parameter	Concentration	
	Range	Average
Metals		
As, ppb	7–17	11.3
Fe, ppb	78–2,000	386
Mn, ppb	8–190	78
Se, ppb	25–45	33
Pb, ppb	7.5–98	30
Zn, ppb	20–280	72
Cu, ppb	10–44	17
Ca, ppm	57	57
Silicon, ppm	3–5.5	4.1
Hardness as CaCO <sub>3</sub> , ppm	140–250	220
Alkalinity as CaCO <sub>3</sub> , ppm	160–170	165
Chloride, ppm	44–390	210
Fluoride, ppb	120–450	347
o-Phosphate as P, ppm	0.09–0.56	0.29
Sulfate, ppm	290–710	426
Sulfide, ppb	<50	<50
TDS, ppm	840–1,900	1,136
TSS, ppm	3.6–14	6.2
TOC, ppm	8.4	8.4

An understanding of the nature of vanadium and mercury in the ETL/CE samples is fundamental for the design and application of selected treatment technologies. Table 2-2 presents the variations in vanadium and mercury concentrations before and after filtration through 0.45 µm filters. As can be seen from Table 2-2, vanadium was mostly in a dissolved form in Whiting Refinery effluents, since there was no difference between total and dissolved vanadium concentrations. Moreover, based on a speciation study conducted by BP (3), it was indicated that vanadium in the ETL/CE samples was in the V<sup>+5</sup> form. The wide fluctuations in vanadium concentrations over the study period were primarily attributed to the Stretford purge. The Stretford process is a vanadium-carbonate organic-acid-based system for converting hydrogen sulfide to elemental sulfur. The measured vanadium concentrations were ~650 ppb when the purge was on, and they gradually decreased with time to 25–50 ppb when the purge was off.

Test results also revealed that most of the mercury in the ETL/CE was in a particulate form (Table 2-2). Dissolved mercury concentrations were <1.0 ppt after 0.45 µm filtration. These data confirm observations from a focused study on the shelf-life of samples (see the next section). More consistent data were also obtained during the treatability studies. Because of the heterogeneity of water samples caused by the presence of solids, an ETL/CE as-

is sample (time = 0) was collected and analyzed at the beginning of every experiment. Table 2-3 presents ETL/CE as-is and filtered ETL/CE data obtained during the treatability studies, which show trends similar to the sampling events data (Table 2-2). A total of 28 out of 29 samples met the 1.3 ppt discharge limit after 0.45  $\mu\text{m}$  filtration. Throughout the study, many water samples were filtered through 5  $\mu\text{m}$ , 1 $\mu\text{m}$ , and 0.45  $\mu\text{m}$  in-line-filters, because of the fouling characteristics of ETL/CE water when filtration was needed for the treatability studies, such as adsorption (dissolved mercury removal). Table 2-4 also shows the changes in mercury concentrations after using 5  $\mu\text{m}$  and 1  $\mu\text{m}$  filters in a series. The obtained data show trends similar to the data presented in Tables 2-2 and 2-3. The correlation between mercury concentration and particle size distribution is investigated in detail in the Filtration Experiments section of Chapter 3.

It seems that the filtration process essentially removed the particle-bound mercury. The mercury removal was primarily dependent on the amount of solids (particulates/colloidal) physically removed by a 0.45  $\mu\text{m}$  filter. These results also confirmed the necessity of particulate removal in achieving very low mercury concentrations (<1.0 ppt). This finding is consistent with literature data (4). The successful filtration test results have shown the need for testing membrane filtration technologies (micro/ultrafiltration). The obtained results could also be used as a baseline to predict the performance of membrane filters in achieving low levels of mercury in the treated water.

### **c. Challenges in Analytical and Quality Control**

#### **(i) Sample Variability and Shelf-life Studies**

Several different mechanisms may cause the composition of the wastewater to change with time. Microbial activity, sorption on a sample vessel, precipitation onto solids, and chemical oxidation/reduction are the main reasons that metal concentrations and speciation may change with time in a stored sample. Since the performance of treatment technologies may be dependent on the metals species/forms in the wastewater, and treatability testing requires a known and sufficiently constant composition of the wastewater tested, it is important to understand the changes that may occur with time as a function of storage conditions. Because the preservation additives required by standard methods may cause changes in the metal forms, additives may not be suitable for storing samples for the purpose of conducting treatability studies. From existing protocols, it has been determined that the most suitable storage method for treatability tests is refrigeration at 4 °C. However, it is unclear how long samples can be stored by simple refrigeration without unacceptable changes in sample quality.

For the purpose of conducting the technology treatability tests, a shelf-life study was conducted to determine the holding time or, "shelf-life," of ETL/CE samples with respect to the preservation of the original characteristics (i.e., total and speciated Hg, and total V) over time, for the purpose of conducting the technology treatability tests. Appendix 1 includes the details of the shelf-life study.

Data obtained from this study provided insight on the deterioration of the effluent composition as a function of time, thereby allowing us to determine how long batches of ETL could be stored by simple refrigeration prior to treatability testing (Appendix 1). Based upon the obtained data, it was decided to use water samples not more than one week from the collection date.

**Table 2-2. Variations in Vanadium and Mercury Concentrations during the Sampling Event at the Whiting Refinery**

Sampling Date	Sampling Event	Analysis	Results <sup>1</sup>	Method Detection Limits
12/7/09	ETL Sampling at Whiting	Hg <sub>tot</sub>	8.11 ppt	2.5 ppt Total Hg
		Hg <sub>dis</sub>	<1.0 ppt	1.0 ppt Dissolved Hg
		V <sub>tot</sub>	35 ppb	1 ppb
		V <sub>dis</sub>	42 ppb	1 ppb
2/1/10	ETL Sampling at Whiting	Hg <sub>tot</sub>	4.80; 4.12 ppt*	2.5 ppt Total Hg
		Hg <sub>dis</sub>	<1.0 ppt	1.0 ppt Dissolved Hg
		V <sub>tot</sub>	350 ppb	1 ppb
		V <sub>dis</sub>	340 ppb	1 ppb
2/8/10	ETL Sampling at Whiting	Hg <sub>tot</sub>	3.86; <2.5 ppt*	2.5 ppt Total Hg
		Hg <sub>dis</sub>	<2.5 ppt	2.5 ppt Dissolved Hg
		V <sub>tot</sub>	97 ppb	1 ppb
		V <sub>dis</sub>	92 ppb	1 ppb
2/15/10	ETL Sampling at Whiting	Hg <sub>tot</sub>	5.77; 5.38 ppt*	5 ppt Total Hg
		Hg <sub>dis</sub>	<2.5 ppt	2.5 ppt Dissolved Hg
		V <sub>tot</sub>	180 ppb	1 ppb
		V <sub>dis</sub>	170 ppb	1 ppb
2/22/10	ETL Sampling at Whiting	Hg <sub>tot</sub>	6.99; 10.8 ppt*	5 ppt Total Hg
		Hg <sub>dis</sub>	<5.0 ppt	5 ppt Dissolved Hg
		V <sub>tot</sub>	41 ppb	4 ppb
		V <sub>dis</sub>	33 ppb	1 ppb
3/1/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	5.14; 5.98; 5.77; 6.76 ppt* 2.27; 2.12 ppt	0.5 ppt Total Hg
3/8/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	4.28; 4.27 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	31 ppb	1 ppb
		V <sub>dis</sub>	28 ppb	1 ppb
3/15/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	1.36; 2.03; 2.17* ppt	0.5 ppt Total Hg
3/29/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	2.26; 1.87 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
4/5/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	1.39; 1.06 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
4/12/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	3.3; 3.48 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	12 ppb	1 ppb
		V <sub>dis</sub>	28 ppb	1 ppb

Table 2-2. (Cont.)

Sampling Date	Sampling Event	Analysis	Results <sup>1</sup>	Method Detection Limits
4/19/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	3.30; 3.31 ppt*	1 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	16 ppb	1 ppb
4/26/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	1.93; 1.97 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	<8 ppb	8 ppb
5/3/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	6.41; 5.13 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	200 ppb	1 ppb
5/10/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	3.57; 4.97 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	110 ppb	1 ppb
5/24/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	2.00; 1.69 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	510 ppb	1 ppb
6/7/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	3.30; 4.09 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	600 ppb	1 ppb
6/21/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	6.41; 5.13 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	490 ppb	1 ppb
6/28/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	2.83 ppt	0.5 ppt Total Hg
		Hg <sub>dis</sub>	0.98; <0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	650 ppb	1 ppb
7/19/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	2.49; 2.42 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	<0.5 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	180 ppb	1 ppb
8/23/10	Clarifier Effluent Sampling at Whiting	Hg <sub>tot</sub>	5.55; 6.09 ppt*	0.5 ppt Total Hg
		Hg <sub>dis</sub>	0.6; 0.55 ppt	0.5 ppt Dissolved Hg
		V <sub>tot</sub>	210 ppb	8 ppb

<sup>1</sup>The asterisk\* denotes duplicate samples.

**Table 2-3. Dissolved Mercury Concentrations in the ETL/CE after 0.45 µm Filtration (from treatability tests)**

CE as-is				CE after 0.45 micron filter		
Date	Sample ID	Hg (ppt)	MRL/MDL <sup>(1)</sup>	Sample Number	Hg (ppt)	MRL/MDL <sup>1</sup>
2/16/2010	CEAI-021610-001 <sup>2</sup>	2.88	0.5	CEAI-021610-003	<0.5	0.5
2/16/2010	ETPR-021710-13	2.62	0.5	ETPR-021710-14	<0.5	0.5
3/1/2010	CE-030110-001	5.14	0.5	CE-030110-002	<0.5	0.5
3/11/2010	CEFR-031110-001	4.0	0.08	CEFR-031110-004	0.52	0.08
3/11/2010	CEFR-031110-002	2.19	0.08	CEFR-031110-005	0.55	0.08
3/11/2010	CEFR-031010-003	4.57	0.08	CEFR-031110-006	0.74	0.08
3/11/2010	CEMB-031110-001	3.35	0.5	CEMB-031110-004	<0.5	0.5
3/11/2010	CEMB-031110-002	3.43	0.5	CEMB-031110-005	<0.5	0.5
3/11/2010	CEMB-031110-003	3.5	0.5	CEMB-031110-006	<0.5	0.5
3/26/2010	CEAIF-032610-005	6.95	1.01	CEAIF-032610-006	0.96	0.5
4/7/2010	CEAIF-040710-001	3.03	0.08	CEAIF-040710-002	2.65 <sup>3</sup>	0.08
4/13/2010	CEPR-041310-13	3.80	1.01	CEPR-041310-14	0.51	0.5
4/14/2010	CEAIF-041410-001	4.63	0.08	CEAIF-041410-002	0.57	0.08
4/14/2010	CEPR-041410-13	4.76	0.5	CEPR-041410-14	<0.5	0.5
4/15/2010	CEAIF-041510-001	4.55	0.08	CEAIF-041510-002	0.51	0.08
4/16/2010	CEPR-041610-13	4.99	0.5	CEPR-041610-14	<0.5	0.5
4/19/2010	CEAIF-041910-002	3.63	0.08	CEAIF-041910-003	0.6	0.08
4/21/2010	CEPR-042110-13	2.38	0.15	CEPR-042110-14	0.59	0.16
4/28/2010	CEAIF-042810-001	2.84	0.09	CEAIF-042810-002	0.84	0.16
5/13/2010	CEPR-051310-13	6.68	0.08	CEPR-051310-14	0.33	0.08
5/14/2010	CEPR-051410-13	5.71	0.08	CEPR-051410-14	0.54	0.08
6/21/2010	CEFILT-062110-01	4.29	0.08	CEFILT-062110-06	0.33	0.08
6/21/2010	CEFILT-062110-02	4.42	0.08	CEFILT-062110-07	0.36	0.08
6/21/2010	CEFILT-062110-03	4.46	0.08	CEFILT-062110-08	0.38	0.08
6/21/2010	CEFILT-062110-04	3.94	0.08	CEFILT-062110-09	0.35	0.08
6/21/2010	CEFILT-062110-05	4.29	0.08	CEFILT-062110-10	0.55	0.08
6/29/2010	CEAI-062910-001	5.11	0.16	CEAI-062910-003	0.68	0.08
7/21/2010	CEFILT-072110-01	4.67	0.08	CEFILT-072110-04	0.44	0.08
7/21/2010	CEFILT-072110-02	3.88	0.16	CEFILT-072110-05	0.40	0.08
7/21/2010	CEFILT-072110-03	3.73	0.08	CEFILT-072110-06	0.38	0.08

<sup>1</sup> Lab A reports MRL; Lab B reports MDL or MRL.

<sup>2</sup> Blue highlighted areas show Lab A test results.

<sup>3</sup> Yellow highlighted area shows Hg concentration >1.3 ppt.

**Table 2-4. Changes in the Mercury Concentrations after In-line Filtration**

Sample	Hg (ppt)	Average	Std. Dev.
CE as-is		4.75	0.32
CEAI-082310-003	4.41		
CEAI-082310-004	4.74		
CEAI-082310-005	4.54		
CEAI-082310-006	5.34		
CEAI-082310-007	4.70		
5 µm in-line filtration		1.05	0.6
CEAI-082410-021	0.73		
CEAI-082410-022	0.69		
CEAI-082410-023	1.75		
5 µm, then 1 µm in-line filtration		0.63	0.15
CEAI-082410-024	0.79		
CEAI-082410-025	0.61		
CEAI-082410-026	0.49		

Although the test results were not sufficiently robust to yield statistically significant differences, this study allowed us to determine that:

1. The majority of the mercury in the wastewater is in the non-dissolved form or particulate form.
2. The elemental mercury in the ETL is negligible.
3. The dissolved, ionic fraction in the ETL may be labile.
4. The spiking of ETL samples with Hg<sup>+2</sup> for testing purposes is reasonable, since ionic mercury is present in the ETL.
5. Samples collected sequentially may be substantially different from each other, even if collected in a short time frame, because of the heterogeneity of water samples due to the presence of solids.
6. The presence of headspace may significantly decrease the concentration of mercury in the wastewater.
7. Speciation at these low concentrations may not be precise enough for sample comparison.

**(ii) Challenges in Mercury Analysis by Method 1631E**

The EPA Method 1631 is a performance-based method, which means that labs have a certain level of discretion in adjusting their procedures to achieve the target performance. The method detection limits (MDLs) and quantifications are usually dependent on the level of interferences (1). The sample dilutions to increase recoveries and decrease matrix interferences resulted in an increase in the detection limits to 5 ppt in several cases (Table 2-2). With a detection limit this high, it was impossible to demonstrate the target mercury performance limit (<1.3 ppt). The test results reported in Table 2-2 were also important to demonstrate the challenges in implementing this method for the analysis of samples such as the Whiting Refinery wastewater. Although matrix spikes recoveries were within the EPA acceptance criteria (71–125%) and hence could be used for compliance reporting purposes, the initial test results obtained from Lab A were not useable as-is to evaluate the effectiveness of each treatment technology in achieving <1.3 ppt Hg levels for this study because of higher detection limits (in some cases, 5 ppt) and low spike recoveries (Appendix 1). It appears that concentrations lower than the 0.5 ppt detection limit still would have been below the 1.3 ppt regulatory limit, even with a recovery as low as 60%.

However, *detectable concentrations that were reported as 1.3 ppt or less, could in fact be above the regulatory limit if the analysis was performed at recovery percentages  $\geq 80\%$* . For example, several test results showed that residual Hg concentrations in the filtered wastewater were in the range of 0.5 to 1 ppt, which, depending on the analytical recovery, might be above 1.3 ppt when the percentage recoveries are  $\geq 70\%$  (Tables 2-2 and 2-3). In order to address this issue, Argonne worked with Lab A chemists to improve the method for the specific purposes of this study. Lab A increased the recovery percentages from their earlier reports and produced data of otherwise perfectly acceptable quality. However, Argonne preferred to use Lab B for the mercury analysis by Method 1631E<sup>4</sup>, since they appeared to provide enhanced accuracy and precision in low-level mercury analysis. To address the need to compare Argonne test results with the Purdue University Calumet test results analyzed by Lab A, Argonne also routinely collected three split samples from each wastewater batch and sent those samples to both Lab A and Lab B for a side-by-side comparison analysis. A total of 34 samples were collected from March 11, 2010, to August 30, 2010, for analysis by both Lab A and Lab B for comparison purposes. The comparison of Lab A and Lab B mercury test results for the same samples are given in Appendix 1. The results obtained from Lab B were usually higher because of the higher recoveries and low MDLs. Test results were also analyzed by a paired t-test at a 95% confidence interval, since the analyzed samples were from the same original batch. Statistical analysis confirmed that the test results obtained from the two labs were significantly different ( $P=0.0289$  at a 95% confidence interval).

## References

1. EPA Method 1631 (2002), "Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry," August 2002
2. EPA Method 1669 (1996), "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels," July.
3. Achar, R. (2009), BP, e-mail communication, Nov. 6.
4. Dean, J.D., and R.P. Mason (2009), "Estimation of Mercury Bioaccumulation Potential from Wastewater Treatment Plants in Receiving Waters: Phase I Final Report," Water Environment Federation, Report 05-WEM-10C.

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<sup>4</sup> Since these concerns were not present in the analysis of other analytes, such as vanadium, selenium, and arsenic, Lab A continued to be the lab of choice for these analyses.

### 3. Bench-scale Testing of Mercury and Vanadium Metal Treatment Technologies

#### Introduction and Summary

The selection of appropriate metal control technologies is limited by the lack of uniform and comparable data available for the concentrations required by the Great Lakes Initiative (see the Module I report and Chapter 1 of this report). In this project module, this research need was addressed through a systematic bench-scale treatability study of technologies to determine their performance in achieving target effluent limits when testing the Whiting Refinery effluent. To compare performance across a relatively broad set of technologies, an overall experimental plan was designed so that test conditions could be as uniform as possible, given the different mechanisms of action and engineering applications of the selected technologies. One relatively uniform test condition was the influent wastewater — all technologies were tested with batches of the same wastewater. While temporal variations of the wastewater feed were expected and found, sufficiently consistent general characteristics of the wastewater feed were present throughout the test period. Second, technologies that relied on the same mechanism of action and engineering application were tested by using a common test plan (e.g., all precipitants were tested under a similar test plan). In order to allow each technology the highest chance of success, Argonne developed test conditions to reflect recommendations from vendors, where applicable. To compare technologies across very different mechanisms of action (e.g., precipitation with adsorption), a comparison method was devised so that higher order performance metrics (e.g., the amount of metal removed per unit of treatment applied) could be obtained from the bench-scale tests alone or incremented with available literature data. This approach is discussed further in Chapter 4 and summarized in Figure 4-1.

This chapter reports the results of the bench-scale tests of the technologies (Table 1-1) that were conducted by Argonne. Adsorption, precipitation, membrane filtration, electrodeionization (EDI), and reactive filtration technologies were tested to determine their potential to achieve the future refinery discharge limits. The bench-scale treatability studies were designed and performed based on the information collected from the literature, vendor recommendations, and BP's historical data, as well as on the results of the wastewater characterization work during the study period (see Chapter 2).

As discussed in Chapter 2, understanding the nature of vanadium and mercury in the effluent-to-lake (ETL)/clarifier effluent (CE) samples is fundamental for the development of test procedures and their application to specific treatment technologies. Some of the selected technologies are better suited for dissolved metal removal from particulate-free wastewater, while others can remove metals sorbed onto particulates. Hence, for example, precipitation was tested on CE/ETL as-is samples, whereas other technologies, such as adsorption, were tested after pretreatment (filtration through a 0.45 µm filter) of wastewater samples.

One of the main problems that required thorough consideration was the extremely low concentrations of mercury (Hg) in the wastewater of interest in this work. These low concentrations required a clean-room environment; specialized equipment cleaning methods; the use of “clean hands-dirty hands” procedures (EPA method 1669) to avoid cross-contamination when conducting the testing and sample analysis; substantial reliance on method, reagent, and equipment blanks; and specialized analytical procedures with appropriate sensitivity (EPA method 1631E). These requirements were addressed by Argonne by implementing the following steps:

- Use of a dedicated, certified Class 100 clean-room laboratory to conduct the mercury bench-scale tests to minimize background contamination during the testing. This approach was critical to clearly identify background effects and attribute mercury losses and gains to the tested technologies or to other background-related causes.
- Thorough and consistent use of method, reagent, and equipment blanks. Due to the unique nature of the wastewater and the low mercury concentration (low ppt) in the CE/ETL samples, the challenges in measuring low and sub ppt levels in water (analytical restrictions), and the impurities present in the ACS-

grade chemicals, blanks were an especially critical component of the test protocols. During the treatability experiments, the comparison of blanks and data was important in order to understand the effectiveness of the tested technologies in achieving low mercury and vanadium levels in the treated wastewater (i.e., the amount of removal that was actually due to the technology).

Data obtained from the treatability studies showed that several deployable technologies were able to achieve, at the bench-scale, mercury concentrations below or at the 1.3 ppt target concentration, albeit with different efficiencies and engineering implications. This demonstrates that there is no fundamental physical or chemical barrier in achieving <1.3 ppt Hg in the tested refinery wastewater at the bench scale. Engineering issues that emerge will be addressed during the scale-up and optimization phases.

Most of the mercury in the ETL/CE was in a particulate form. The effectiveness of many technologies in achieving very low mercury concentrations (<1.0 ppt) in fact depended on the removal by filtration (as large as 0.45  $\mu\text{m}$  screen) of the physical particulates/colloidal fractions. Similar results were also obtained for some of the tested vanadium removal technologies, such as precipitation which relies on transforming dissolved vanadium into non-soluble form. Although vanadium was in the dissolved form in the CE/ETL samples, vanadium removal percentages increased significantly after filtration of the precipitated flocs. Dissolved mercury removal technologies that required prefiltration were tested by spiking the wastewater with 10 ppt of  $\text{Hg}^{+2}$ , since filtration removes most of the mercury (mercury <1.0 ppt) from the ETL/CE. This was done to simulate the presence of dissolved mercury. Spiking without filtration has proven difficult because of media heterogeneity and of the tendency of the mercury added with the spike to adhere to solids.

The process performance of each technology on a common refinery wastewater, using comparable methods and metrics and the same analytical methods, generated the most important data collected from the experiments, thereby enabling a uniform comparison. In addition to determining whether the targeted effluent limits for the CE/ETL could be met, other experimental data, such as waste generation, were also collected to facilitate comparison within the endpoint measures of the performance matrix. The findings from these bench-scale demonstration studies provide a clear picture of the performance of the tested technologies at the bench-scale. These data are an important contribution to the selection of the best candidate technologies for pilot-scale testing of Whiting Refinery wastewater. This chapter examines in detail the results of the bench-scale testing conducted at Argonne. Further evaluation of these results in the context of a broader technology performance assessment is provided in Chapter 4.

### **3a(i). Adsorption Isotherm Testing**

#### **1. Introduction and Objectives**

Several adsorbents were tested for their ability to remove the dissolved metals of interest: mercury (Hg), vanadium (V), arsenic (As), and selenium (Se). The testing of another adsorbent, Captech 10-250, is examined in Section 3a(ii) of this report, since the gel-like nature of the adsorbent required a different testing method.

The objective of this testing was to determine an adsorption isotherm for each adsorbent by using wastewater with known quantities of the dissolved metals of interest in the specific ETL/CE wastewater matrix. Varying amounts of adsorbent were added to fixed volumes of wastewater that had been filtered with a 0.45  $\mu\text{m}$  filter and spiked with mercury. For each adsorbent, the amount of mercury or vanadium adsorbed per weight of adsorbent was determined as a function of the mercury or vanadium concentration in the wastewater, thus enabling comparison of the data to both the Freundlich and Langmuir isotherm models.

## 2. Materials and Methods

### a. Adsorbent Media

The adsorbents tested for dissolved mercury removal included activated carbon (Calgon Filtrasorb 600 and Calgon OLC), Mersorb LW, and thiol-SAMMS. The activated carbon selection was based on Calgon Carbon Corp.'s recommendations (1, 2). Calgon's Filtrasorb 600, which is coal-based, has been used at Oak Ridge National Laboratory for mercury removal, and it has a fine pore structure for removing contaminants to low levels (1). Calgon's OLC also has a fine pore structure, but since it is coconut-shell based, it does not have the trace levels of mercury that are present in a coal-based activated carbon (2). Virgin (previously unused) activated carbons were used for testing. The Mersorb LW adsorbent is a sulfur-impregnated activated carbon produced by Nucon International, Inc., and sold by Selective Adsorption Associates, Inc. The thiol-SAMMS adsorbent, made by Steward Advanced Materials, Inc., consists of self-assembled mercaptan groups on mesoporous silica (3).

The adsorbents tested for dissolved vanadium removal included Adsorbsia As 500, Bayoxide E IN-20, and GFH. Adsorbsia As 500, a titanium oxide adsorbent produced by Dow Chemical Co., was tested instead of the Adsorbsia GTO previously recommended in the Phase II, Module 1, Task 2 report because it is an improved version that will replace Adsorbsia GTO. The composition is unchanged; however, the newer Adsorbsia As 500 is granular and less friable (4). Bayoxide E IN-20 is a granular ferric oxide adsorbent made by Lanxess Deutschland GmbH and sold by Severn Trent Services. Bayoxide E IN-20 is the same material as Bayoxide E33, except that it does not have the drinking water certification held by Bayoxide E33 (5). The GFH is a granular ferric hydroxide adsorbent produced by GEH-Wasserchemie and sold by Siemens.

The mercury removal adsorbents, with the exception of thiol-SAMMS, were individually ground to the 20 to 45  $\mu\text{m}$  size, as recommended by the EPA and vendors (6, 7). For each adsorbent, a dedicated mortar and pestle was used, followed by sieving with a vibratory sieve shaker. The ground adsorbents that passed through a 325 mesh (45  $\mu\text{m}$ ) screen, but retained by a 635 (20  $\mu\text{m}$ ) screen, were used for the isotherm testing. A 10 to 20  $\mu\text{m}$  size thiol-SAMMS, which is comparable to the ground adsorbents, was used as supplied by the vendor without grinding or sieving.

Only one of the vanadium removal adsorbents, Bayoxide E IN-20, was ground to the 20 to 45  $\mu\text{m}$  size by using the same procedure described above for the mercury removal adsorbents. Adsorbsia As 500 was used as received (16 x 60 mesh or 250–1,200  $\mu\text{m}$ ), per vendor recommendation (4, 8). Additionally, GFH, which is sold wet, was used as received (320–2,000  $\mu\text{m}$ ) to avoid difficulties with grinding and sieving wet material.

### b. Water Samples

The Whiting Refinery's ETL and CE were used for the testing. Samples were collected by using the "clean hands-dirty hands" procedures specified in EPA Method 1669 (9). Upon receipt, the wastewater was stored in a 4 °C cold room before use. The wastewater was tested in several different batches. Based on the results of the Shelf-life Study (Appendix 1), the wastewater was used for up to 5 days after collection from the refinery. This approach was taken to ensure that changes in mercury and vanadium speciation and composition would be negligible.

### c. Experimental Equipment

Prior to use, all experimental equipment was cleaned by using the method outlined in EPA Method 1631E and EPA Method 200.8 (10, 11). Specifically, the equipment was washed with laboratory soap (Sparkleen) and tap water, triple rinsed with MilliQ water (18 M $\Omega$ .cm resistivity), and then soaked overnight in a 5% HCl solution. The following morning, the equipment was triple rinsed in MilliQ water, brought into the clean room, and triple rinsed a second time in MilliQ water (18 M $\Omega$ .cm resistivity) before use.

Before the isotherm testing, the clarifier effluent was filtered with an in-line filtration system by using a peristaltic pump, as shown in Figure 3a(i)-1. Initially, a 0.45  $\mu\text{m}$  cross-flow hollow fiber filter made by Cantel Medical Corp. was used. Later, a series of three groundwater sampling filters (5  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 0.45  $\mu\text{m}$ ) was used. The 5  $\mu\text{m}$  and 1  $\mu\text{m}$  filters (Millipore GWSC5001 and GWSC10001) were made of high-density polyethylene (HDPE), while the 0.45  $\mu\text{m}$  filter (Whatman Polycap GW 6714-6004) consisted of a polyethersulfone (PES) membrane in

polypropylene housing. SEBS resin tubing was used, as specified in EPA Method 1669 (Trace Metal Sampling) (9). A new set of filters and tubing was used for each batch of wastewater.

**Figure 3a(i)-1. In-line Filtration System**



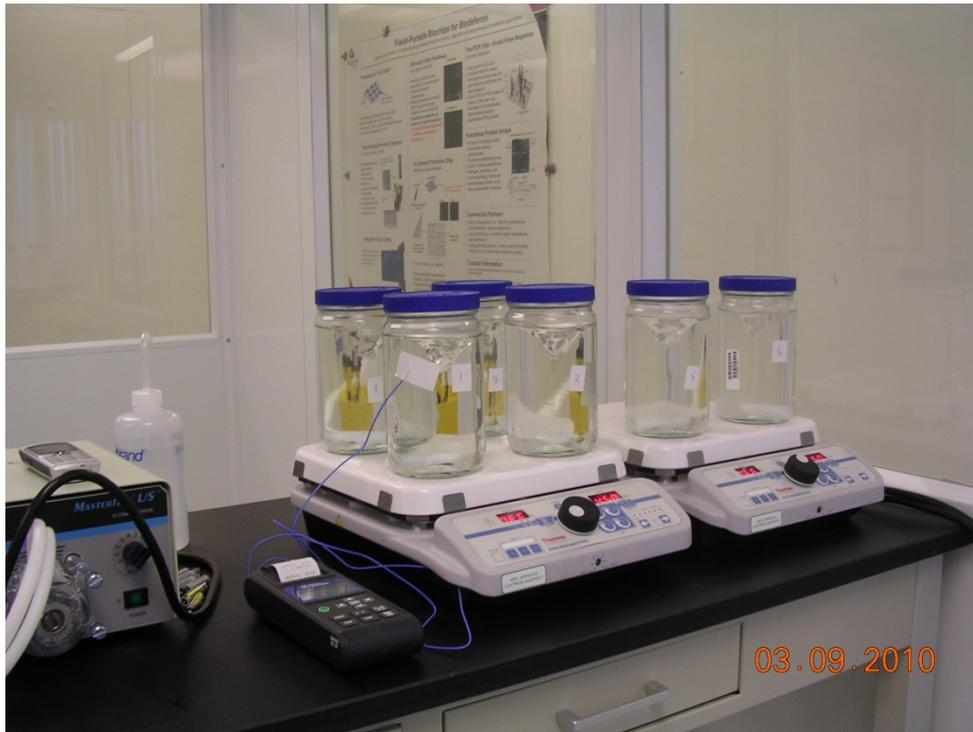
The isotherm testing was done with 1L I-CHEM 300 series borosilicate glass jars. A separate set of Teflon-coated magnetic stir bars was used for each adsorbent. The mixing was done using magnetic stir plates with individual controls for up to four jars, as shown in Figure 3a(i)-2. The CE was transferred from the in-line filtration system to the jars using a glass graduate cylinder. The filled jars were weighed on an electronic scale. The temperature was measured with a Type K thermocouple taped to the external surface of one of the glass jars. A Fisher Scientific digital thermometer (model 15-077-16) with a paper printout was used to record the temperature.

At the end of the isotherm mixing, the contents of each jar were vacuum filtered through a 0.45  $\mu\text{m}$  filter (Millipore, MF-Mixed Cellulose) to prevent fines from contaminating the treated sample. A glass filtration system consisting of a filter holder and an Erlenmeyer flask was used, as shown in Figure 3a(i)-3.

#### **d. Experimental Procedure**

The isotherm procedure was based on recommendations obtained from the vendors of the adsorbents to be tested (4, 5, 8, 12, 16). The GAC isotherm testing information provided in the EPA Drinking Water Treatability Database (6) was also included. Additionally, based on recommendations from both Siemens and Severn Trent Services, the published literature work of Paul Westerhoff of Arizona State University (17, 18) was consulted.

**Figure 3a(i)-2. Isotherm Mixing Equipment**



**Figure 3a(i)-3. Isotherm Filtration Equipment**



All the adsorbents were tested in Argonne’s Class 100 clean room (Bldg. 202, room B354) using the Clean Room Procedures detailed in Section 5c, Attachment 5, of the Project Binder. Using a peristaltic pump, BP’s ETL/CE was filtered through a series of 5, 1, and 0.45 µm in-line filters before a measured and weighed amount (750 mL) was added to each glass jar. The ETL/CE, which had been stored in a 4 °C cold room, was brought to room temperature in the closed jars by using the heaters on the magnetic stir plates. A spike was used in the samples because of inconsistencies in the concentration of soluble metals in the influent stream. For the mercury removal testing, the ETL/CE was spiked to a level of 10 ppt of Hg<sup>+2</sup> with using a 10 ppm mercury standard solution (Spex Certiprep, New Jersey). For the vanadium removal testing, spiking to a level of 250 ppb V<sup>+5</sup> with a 1,000 ppm vanadium standard solution (Spex Certiprep, New Jersey) was done, if necessary. In both cases, the spike solutions were prepared the day of testing to prevent deterioration over time. The spiking occurred immediately before a weighed amount of adsorbent was added to the jar and mixing was started. The adsorbent/effluent mixtures, with the exception of the GFH adsorbent/effluent mixture, were continuously stirred at 450 rpm for 24 hours, as recommended by the vendors, to achieve pseudo-equilibrium. The GFH adsorbent/effluent mixture was allowed to mix for a period of 7 days to compensate for the fact that the adsorbent was used as-is and was not ground. At the end of the isotherm, the treated effluent in each jar was vacuum filtered with a 0.45 µm filter and sampled for analysis.

An initial screening was done at ambient temperature using three different widely varying amounts of adsorbent added to three different aliquots of effluent, as shown in Table 3a(i)-1.

**Table 3a(i)-1. Adsorbent Screening Testing**

Conditions/Adsorbent	Contaminant Removed	Effluent (L)	Adsorbent Added For Initial Screening (g)	References
Activated carbon (Calgon F600)	Hg	0.75	0 (control), 0.002, 0.2, 2.0	19
Activated carbon (Calgon OLC)	Hg	0.75	0 (control), 0.002, 0.2, 2.0	
Mersorb LW	Hg	0.75	0 (control), 0.002, 0.2, 2.0	19, 20
Thiol-SAMMS	Hg	0.75	0 (control), A, B, C, D, E <sup>1</sup>	21, 22
Bayoxide E IN-20	V	0.75	0 (control), 0.02, 0.2, 2.0	17, 18, 23
GFH	V	0.75	0 (control), 0.018, 0.177, 1.770	17, 18, 23
Adsorbsia As 500	V	0.75	0 (control), 0.03, 0.3, 3.0	17, 18, 23

<sup>1</sup>The doses tested are proprietary information that cannot be disclosed in this report. Initial screening results were used to determine the adsorbent concentration range used for focused testing.

In addition to the testing with adsorbents, method blanks were performed using CE. Equipment blanks were done with MilliQ water (18 MΩ.cm). Adsorbent blanks, consisting of adsorbents in MilliQ water (18 MΩ.cm) undergoing the same experimental procedure, also were completed.

**e. Experimental Procedure: SAMMS Step-wise Testing**

In addition to the isotherm testing described above, thiol-SAMMS was also tested with a vendor-recommended method by using sequential sampling (21, 22). The testing was done with 10 to 20 µm thiol-SAMMS. No grinding or sieving was performed. Although vendor testing demonstrated that the Whiting Refinery ETL met the 1.3 ppt level after the first sampling, a three-step test was conducted at Argonne to ensure completeness, per vendor recommendation (22). Due to the proprietary nature of this information, details cannot be disclosed in this report.

**f. Analyses**

Prior to testing, the pH of the untreated ETL/CE was measured with an Oakton pH/CON 510 benchtop meter. Additionally, the ETL/CE was sampled and sent to a certified independent lab for analysis of the following parameters:

Total and dissolved mercury	EPA 1631e
Total and dissolved vanadium	EPA 200.8
Cations: As, Cu, Fe, Pb, Mn, Se, Si, Zn	EPA 6010/200.7
Anions: Cl <sup>-</sup> , PO4 <sup>3-</sup> , SO4 <sup>2-</sup>	EPA 300.0
Fluoride	EPA 340.1
Total hardness as CaCO <sub>3</sub>	EPA 130.2

Table 2-1 and Table 2-2 show the influent wastewater characteristics.

At the end of each test, the treated ETL/CE samples were placed into clean sample bottles provided by the independent lab. Sample preservation was done, as specified by the analytical methods at the independent analytical lab.

The ETL/CE that was treated with the mercury adsorbents (activated carbon [F600 and OLC], Mersorb LW, and thiol-SAMMS) was sampled and analyzed by a certified independent lab for total mercury (EPA Method 1631e), total arsenic, and total selenium (EPA Method 200.7). The ETL that was treated with the vanadium adsorbents (Adsorbis As 500, Bayoxide IN 20, and GFH) was sampled and analyzed by a certified independent lab for total vanadium, total arsenic, and total selenium (EPA Methods 200.7/200.8).

**3. Results and Discussion**

**a. Blanks**

Equipment blanks were conducted on the filtration equipment for the isotherm experiments using MilliQ (18 MΩ.cm) water. The results, presented in Table 3a(i)-2, showed no detectable addition of the metals of interest to the MilliQ water. Therefore, the filtration equipment should not be expected to contaminate the wastewater samples during testing.

**Table 3a(i)-2. Equipment Blanks**

	Hg (ppt)	As (ppb)	Se (ppb)	V (ppb)
Series of in-line filters 5, 1 (capsules), and 0.45 μm (hollow fiber)	<0.5	-	-	-
Series of in-line filters 5, 1, and 0.45 μm (all capsules)	<0.5	<1	<1	<1
Vacuum filtration apparatus 0.45 μm nitrocellulose filter paper	<0.5	<1	<1	<1

Additionally, adsorbent and reagent blanks were performed. For the adsorbent blanks, the amount of adsorbent used was selected from the middle of the focused testing range for that adsorbent. For each adsorbent, an isotherm was done with MilliQ water instead of CE/ETL. The entire isotherm process was included — 24 hours of mixing followed by vacuum filtration. The results, presented in Table 3a(i)-3, indicated that only thiol-SAMMS had any measureable mercury leaching out from the adsorbent. The amount of mercury found with thiol-SAMMS was still very low, only 0.15 ppt, and would not be considered a major mercury contaminant. In the case of arsenic, GFH, Bayoxide E IN-20, and thiol-SAMMS showed very low, but measureable, amounts of arsenic in the adsorbent blanks. For all adsorbents, neither selenium nor vanadium could be detected in the blanks.

**Table 3a(i)-3. Adsorbent and Reagent Blanks**

<b>Adsorbent</b>	<b>Adsorbent Wt. (g)</b>	<b>Hg (ppt)</b>	<b>As (ppb)</b>	<b>Se (ppb)</b>	<b>V (ppb)</b>
Calgon Filtrasorb 600	0.2	<0.08	<1	<1	<1
Calgon OLC	0.2	<0.08	<1	<1	<1
Mersorb LW	0.2	<0.08	<1	<1	<1
GFH	0.035	<0.08	1.1	<1	<1
Bayoxide E IN-20	0.08	<0.08	1.3	<1	<1
Adsorbisia As 500	0.035	<0.08	<1	<1	<1
Thiol-SAMMS	Dose C	0.15	1.7	<1	<1
MilliQ water (18 MΩ)	-	<0.08	<1	<1	<1

Method blanks were performed to determine the amount of mercury, arsenic, selenium, and vanadium that was lost while undergoing the isotherm testing process. The mercury method blanks were done with CE that had been in-line filtered with a 0.45 μm filter and then spiked to a level of 10 ppt of Hg<sup>+2</sup>. The isotherm process was broken down into steps. Samples were taken after 24 hours of mixing, and other samples experienced only the vacuum filtration process. Additionally, samples that had gone through the entire isotherm process were taken for comparison. Five replicates were done for each sampling event. The results, presented in Table 3a(i)-4, indicated that a significant amount of mercury is lost during the isotherm process. The individual steps of the process, mixing and vacuum filtration, showed about the same amount of mercury loss as samples that go through the entire process — 22–25% vs. 26% for the entire process, respectively. These percentages are with respect to the average of the filtered and spiked CE samples. Based on these findings, the mercury results presented in this report have been corrected for method blank losses. A sample calculation is shown in Appendix 4.

Similar method blank testing was performed to determine arsenic, selenium, and vanadium losses. For simplification, only the feed and the wastewater undergoing the entire isotherm process were sampled and analyzed. As was done with the mercury method blank testing, CE that had been in-line filtered with a 0.45 μm filter was used. Five replicates were done for each sampling event. Table 3a(i)-5 details the method losses for arsenic, selenium, and vanadium. In the case of arsenic, a 1.4% gain occurred between the feed and the wastewater that had undergone the isotherm process. Selenium showed a 6.0% loss, while vanadium showed a 1.6% loss. In contrast to the results for mercury, these gains/losses are relatively small. It should also be noted that the analytical method detection limit for As, Se and V analysis is 1 ppb. For this reason, the arsenic, selenium, and vanadium results presented in this report have not been corrected for method gains/losses.

**Table 3a(i)-4. Method Blanks: Mercury**

	Hg (ppt)	Average of Five Samples	Standard Deviation	% Standard Deviation	% Hg Loss with respect to Initial 10 ppt Spike	% Hg Loss with respect to Average of Filtered and Spiked CE
CE as-is	3.03					
CE in-line filtered, 0.45 micron	2.65					
CE, 0.45 micron filtered, 10 ppt spike		9.07	0.550	6.1%	9.3%	
CE, 0.45 micron filtered, 10 ppt spike, 24 hours mixing		7.11	0.205	2.9%	29%	22%
CE, 0.45 micron filtered, 10 ppt spike, vacuum filtered		6.77	0.211	3.1%	32%	25%
CE, 0.45 micron filtered, 10 ppt spike, 24 hours mixing, vacuum filtered		6.74	0.639	9.5%	33%	26%

**Table 3a(i)-5. Method Blanks: Arsenic, Selenium, and Vanadium**

	Contaminant	Contaminant Concentration (ppb)	Average (ppb)	Standard Deviation	% Standard Deviation	% Loss with respect to Filtered CE
CE as is	As	10				
CE in-line filtered, 0.45 micron	As		10.2	0.447	4.4%	-
CE after entire isotherm process	As		10.34	1.014	9.8%	-1.4%
CE as is	Se	26				
CE in-line filtered, 0.45 micron	Se		26.6	0.5480	2.1%	-

**Table 3a(i)-5. (Cont.)**

	<b>Contaminant</b>	<b>Contaminant Concentration (ppb)</b>	<b>Average (ppb)</b>	<b>Standard Deviation</b>	<b>% Standard Deviation</b>	<b>% Loss wrt Filtered CE</b>
CE after entire isotherm process	Se		25	0.7070	2.8%	6.0%
CE as is	V	490				
CE in-line filtered, 0.45 micron	V		494	11.402	2.3%	-
CE after entire isotherm process	V		486	5.477	1.1%	1.6%

**b. Mercury Adsorbents**

The results of the initial screening testing are shown in Table 3a(i)-6. In addition to mercury removal, data were also collected for arsenic and selenium removal. Vanadium removal was not included in the analysis, since these adsorbents are mercury-specific.

The screening testing was conducted at the beginning of the study, and the analytical work was done by Lab A. The spike recovery of 4.07 ppt from a 10 ppt spike of the filtered CE combined with the high detection limits (2.5 ppt) were among the reasons that the analytical method was investigated and the laboratory used was changed, as detailed in Chapter 2 and Appendix 1 of this report. However, analytical recovery problems aside, the testing showed that all of the adsorbents were capable of removing mercury down to low levels. Further, and more importantly, a range for the focused testing was determined. This screening testing also indicated that these mercury adsorbents essentially did not remove any arsenic or selenium.

The focused testing was conducted with Lab B as the analytical laboratory. Unlike the previous screening testing, these samples were heated during the digestion step of the analysis. The mercury removal results for the activated carbons are detailed in Table 3a(i)-7. The Thiol-SAMMS results are shown separately in Table 3a(i)-8 because of the differences in the adsorbent amounts used. In all cases, the mercury method loss was considered. The results are summarized in a Freundlich plot, shown in Figure 3a(i)-4. A Freundlich plot was used because it provides the best fit to the data, and it is commonly used for activated carbon adsorbents (6, 7). All of the mercury adsorbents at some tested dosages were able to provide effluent below the upcoming 1.3 ppt discharge limit. Based on the comparison shown in Figure 3a(i)-4, at the same concentration of mercury in solution, Mersorb LW and thiol-SAMMS were able to remove more mercury per unit weight of adsorbent than Calgon's Filtrasorb 600 and OLC.

**Table 3a(i)-6. Mercury Adsorbent Screening Testing\***

	<b>Adsorbent Dosage (g)</b>	<b>Mercury (ppt) (1)</b>		<b>Arsenic (ppb)</b>		<b>Selenium (ppb)</b>	
		<b>Initial Filtered CE/ETL with 10 ppt Hg Spike</b>	<b>Final CE/ETL</b>	<b>Initial Filtered CE/ETL</b>	<b>Final CE/ETL</b>	<b>Initial Filtered CE/ETL</b>	<b>Final CE/ETL</b>
Calgon F600 testing with ETL	blank	4.07	1.94	9.2	14	33	35
	0.002	4.07	1.36	9.2	14	33	34
	0.200	4.07	<0.5	9.2	14	33	33
	2.000	4.07	<0.5	9.2	27	33	31

Table 3a(i)-6. (Cont.)

	Adsorbent Dosage (g)	Mercury (ppt) (1)		Arsenic (ppb)		Selenium (ppb)	
		Initial Filtered CE/ETL with 10 ppt Hg Spike	Final CE/ETL	Initial Filtered CE/ETL	Final CE/ETL	Initial Filtered CE/ETL	Final CE/ETL
Calgon OLC testing with ETL	blank	4.07	1.94	9.2	14	3.3	3.5
	0.002	4.07	1.72	9.2	14	3.3	3.5
	0.200	4.07	<0.5	9.2	14	3.3	3.6
	2.000	4.07	<0.5	9.2	12	3.3	3.4
Mersorb LW testing with ETL	blank	(2)	0.844	<10 (3)	5.4	<3 (3)	3.4
	0.002	(2)	2.39	<10 (3)	5.7	<3 (3)	3.2
	0.200	(2)	<0.5	<10 (3)	4.4	<3 (3)	3
	2.000	(2)	<0.5	<10 (3)	5.7	<3 (3)	3.2
Thiol-SAMMS testing with CE	blank	<2.5 (4)	2.34				
	A	<2.5 (4)	<0.5				
	B	<2.5 (4)	<0.5				
	C	<2.5 (4)	<0.5				
	D	<2.5 (4)	<0.5				
	E	<2.5 (4)	<0.5				

\*(1) Lab A analyses.  
 (2) Dissolved Hg prior to 10 ppt spike = <2.5 ppt Hg.  
 (3) Initial sampling at the Whiting Refinery during ETL collection on 2/8/10.  
 (4) Dissolved Hg prior to 10 ppt spike = <0.5 ppt Hg.

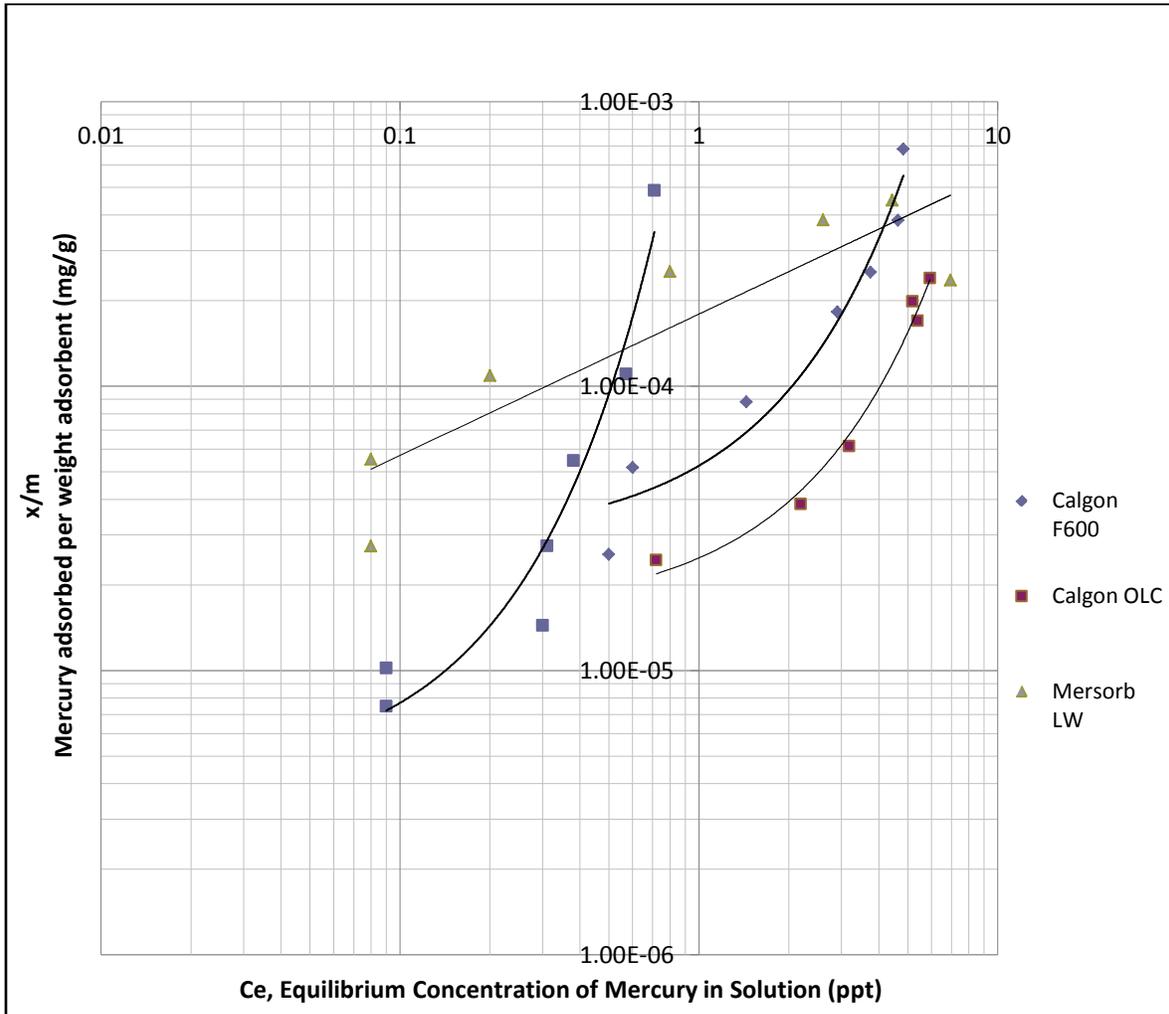
Table 3a(i)-7. Mercury Adsorbent Focused Testing: Activated Carbons

Adsorbent Dosage	Initial Hg (ppt)	Calgon F600		Calgon OLC		Mersorb LW	
		Final Hg (ppt)	% Removal after Method Blank Loss	Final Hg (ppt)	% Removal after Method Blank Loss	Final Hg (ppt)	% Removal after Method Blank Loss
0	10	6.81	7.0%	7.95	-10.2%	8.6	-16.2%
0.002		4.83	33.8%	6.75	6.7%	6.95	5.6%
0.005		4.63	36.5%	5.93	17.7%	4.43	39.6%
0.01		3.75	48.5%	5.18	28.3%	2.6	64.6%
0.02		2.91	60.2%	5.4	25.1%	0.8	89.1%
0.05		1.44	80.2%	3.18	56.0%	0.2	97.3%
0.1		0.6	91.8%	2.19	69.7%	<0.08	98.9%
0.2		<0.5	93.2%	0.72	90.0%	<0.08	98.9%

Table 3a(i)-8. Thiol-SAMMS Focused Testing

Amt. Thiol-SAMMS (g)	Initial Hg (ppt)	Final Hg (ppt)	Percent Hg Removed
Blank	10.84	8.45	-11.9%
A	10.84	0.71	90.6%
B	10.84	0.57	92.5%
C	10.84	0.38	95.0%
D	10.84	0.31	95.9%
E	10.84	0.3	96.0%
F	10.84	<0.09	98.8%
G	10.84	0.09	98.8%
CE as-is	2.84		
CE 0.45 $\mu\text{m}$ filtered	0.84		

Figure 3a(i)-4. Mercury Adsorbent Isotherm Summary: Freundlich



The Mersorb LW and Thiol-SAMMS focused testing was initially performed by using different batches of CE. It was then decided to test these adsorbents on the same batch of CE to enable a better performance comparison. The results for mercury removal are detailed in Table 3a(i)-9, and the results for arsenic, selenium, and vanadium removal are shown in Table 3a(i)-10. Both adsorbents again demonstrated their ability to remove mercury to a level below the upcoming 1.3 ppt discharge level. Figure 3a(i)-5 shows the Freundlich plot of the mercury removal results, which indicates that there is no clear-cut difference in the performance between the two adsorbents.

With regard to the other dissolved metals of interest, both adsorbents showed slight removals. When the minimum dosage of thiol-SAMMS required to meet the 1.3 ppt mercury standard was used, 19% of the arsenic, 36% of the selenium, and 7% of the vanadium were removed. When the minimum dosage of Mersorb LW required to meet the 1.3 ppt mercury standard was used, a slight gain (3%) in arsenic was found, while 13% of the selenium and 2% of the vanadium were removed. Therefore, it would seem that thiol-SAMMS removes more arsenic, selenium, and vanadium than Mersorb LW.

**Table 3a(i)-9. Mersorb LW and Thiol-SAMMS Comparison: Same Wastewater — Mercury Removal**

Mersorb LW			Thiol-SAMMS		
Adsorbent Dosage	Final Hg (ppt) <sup>1</sup>	% Removal after Method Loss	Adsorbent Dosage	Final Hg (ppt) <sup>1</sup>	% Removal after Method Loss
0	4.78	35.9%	0	5.25	29.3%
0.002	4.29	42.02%	A	3.69	50.5%
0.01	3.02	59.3%	B	0.96	87.1%
0.05	0.72	90.3%	C	0.19	97.4%
0.1	0.47	93.7%	D	0.39	94.8%
0.2	0.69	90.7%	E	<0.08	98.9%

<sup>1</sup>Initial wastewater spiked to 10 ppt Hg<sup>+2</sup>.

In addition to the batch isotherm testing, thiol-SAMMS was also tested with a step-wise sampling procedure recommended by the vendor. This procedure previously had been used at the vendor's lab with a sample of Whiting Refinery's ETL. In this testing, measured amounts of thiol-SAMMS were added to the stirred CE, which had been spiked to a level of 10 ppt of Hg<sup>+2</sup>. Samples were removed at timed intervals. Two sets of data were collected each time the step-wise testing was done, as shown in Table 3a(i)-11. In all cases, very low levels of mercury were achieved after the first time interval. The results obtained with the Lab A analysis were identical to those obtained during the vendor's testing, which utilized an in-house analysis (19). However, during the second testing event, which was analyzed by Lab B, the level of mercury increased after 30 minutes and then decreased after 60 minutes. These samples were very problematic for Lab B to analyze — they had to be digested four times to attain sufficient oxidation before the analysis could be done. Interestingly, neither Lab A nor the vendor reported any difficulty in analyzing their set of samples. From these results, it can be concluded that a mercury level of 0.65 ppt can be achieved within the first time interval.

Figure 3a(i)-5. Mersorb LW and SAMMS Comparison: Same Wastewater — Mercury Removal

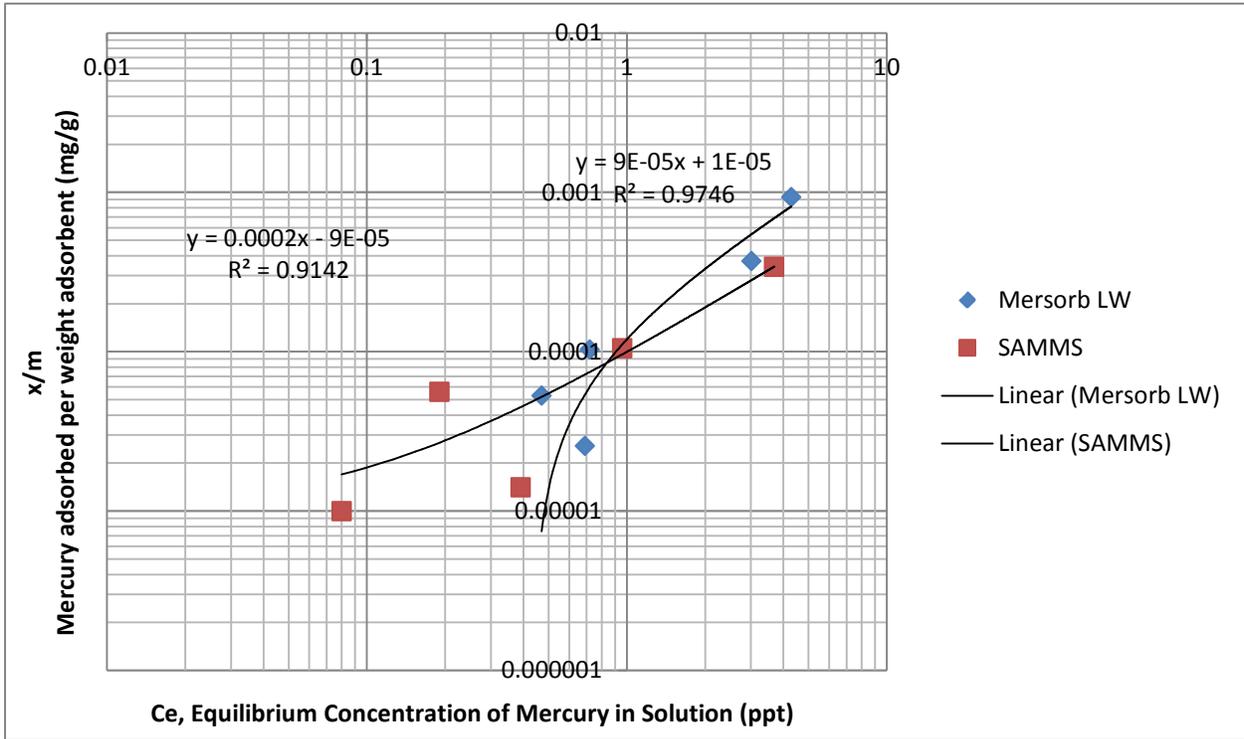


Table 3a(i)-10. SAMMS and Mersorb LW Comparison: Same Wastewater — Arsenic, Selenium, and Vanadium Removal

	Arsenic		Selenium		Vanadium	
	As (ppb)	% Removal	Se (ppb)	% Removal	V (ppb)	% Removal
CE as-is	9.4		21		830	
CE 0.45 $\mu$ m filtered	9.4	0.0%	22	-4.8%	800	3.6%
SAMMS blank	8.9	5.3%	20	9.1%	790	1.3%
SAMMS dose A	8.4	10.6%	17	22.7%	750	6.3%
SAMMS dose B	7.6	19.1%	14	36.4%	740	7.5%
SAMMS dose C	8.2	12.8%	12	45.5%	740	7.5%
SAMMS dose D	7.5	20.2%	7.9	64.1%	670	16.3%
SAMMS dose E	8.3	11.7%	8.2	62.7%	640	20.0%
Mersorb blank	10	-6.4%	22	0.0%	760	5.0%
Mersorb 0.002 g	7.9	16.0%	19	13.6%	730	8.8%
Mersorb 0.01 g	8.7	7.4%	20	9.1%	760	5.0%
Mersorb 0.05 g	9.7	-3.2%	19	13.6%	780	2.5%
Mersorb 0.10 g	8.4	10.6%	19	13.6%	730	8.8%
Mersorb 0.20 g	9.1	3.2%	19	13.6%	730	8.8%

**Table 3a(i)-11. SAMMS Step-wise Testing**

Test	Elapsed Time (min)	SAMMS (g)	2/18/10 Testing Hg: Lab A Analysis (ppt)	4/30/10 Testing Hg: Lab B Analysis (ppt)
1	Time 1	A	<0.5	0.65
1	Time 2	B	<0.5	7.58
1	Time 3	C	<0.5	<3.05
2	Time 1	A	<0.5	0.36
2	Time 2	B	<0.5	27.1
2	Time 3	C	<0.5	<3.05

**c. Vanadium Adsorbents**

A screening test was conducted with the three vanadium adsorbents tested: GFH, Bayoxide E IN-20, and Adsorbsia As 500. As shown in Table 3a(i)-12, all of the adsorbents removed increasing amounts of arsenic, selenium, and vanadium with increasing doses of adsorbents.

**Table 3a(i)-12. Vanadium Adsorbents Screening Testing Summary**

Adsorbent	Adsorbent Dose (g)	Initial As (ppb)	Final As (ppb)	Initial Se (ppb)	Final Se (ppb)	Initial V (ppb)	Final V (ppb)
GFH	0	<10	1	<30	36	92	87
	0.018		6.5		30		9.8
	0.177		4.8		17		<1
	1.770		3.3		14		<1
Bayoxide E IN-20	0	<10	5.4	<30	34	92	89
	0.02		2.8		1.7		12
	0.2		<1		1.6		<1
	2		<1		1.5		<1
Adsorbsia As 500	0	<10	8.3	<30	33	87	89
	0.03		4.3		27		<1
	0.3		4.1		16		<1
	3		2.4		15		<1

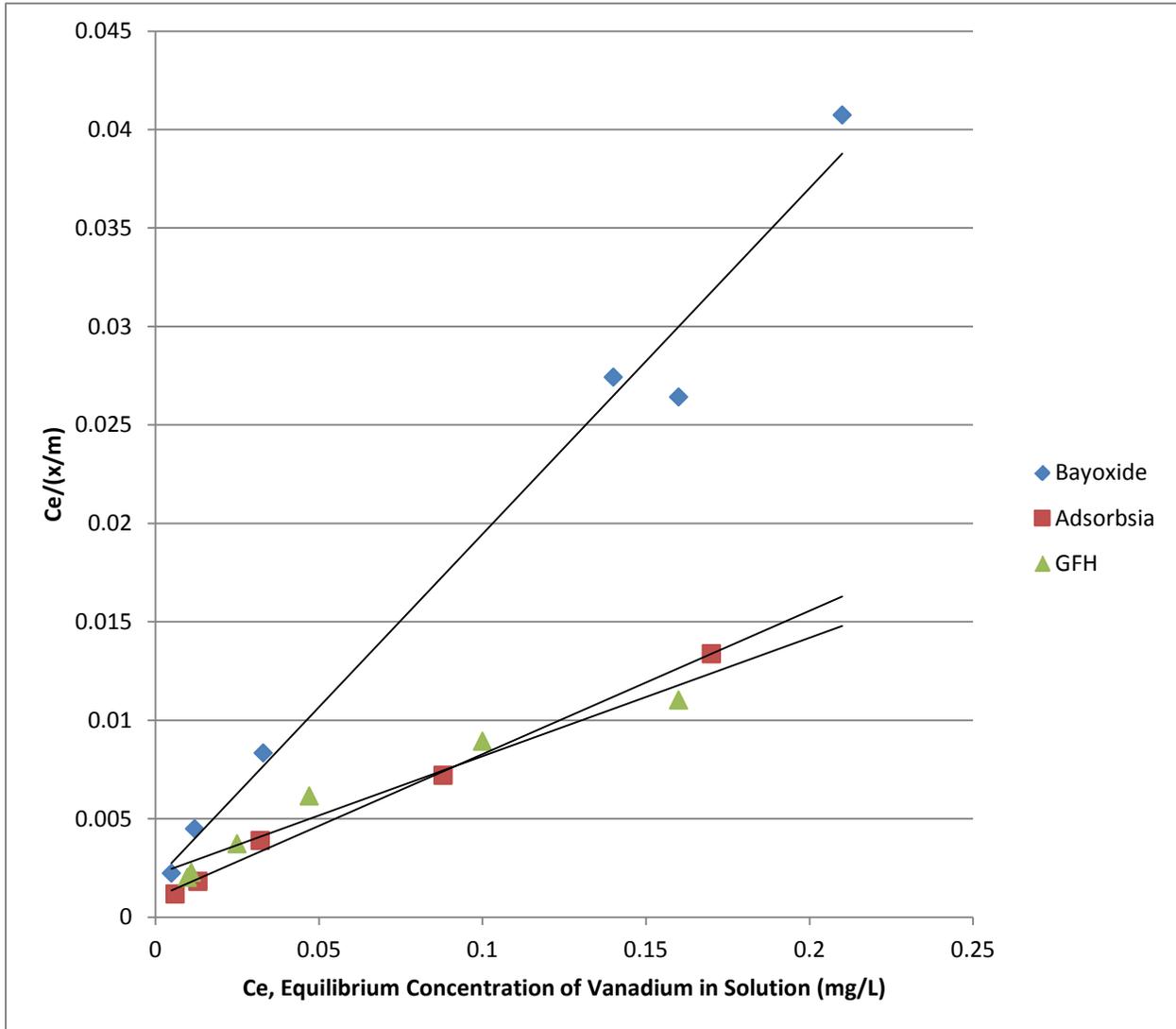
The screening test results were used to determine the adsorbent dosage range on which to focus additional testing. The results from the focused testing are shown in Table 3a(i)-13. For consistency, the focused testing used CE that had been spiked to a level of 250 ppb of V<sup>+5</sup>. All of the adsorbents were able to remove 95–97% of the vanadium, achieving levels ranging from 4.9 to 11 ppb. The GFH was able to remove the most arsenic (66%), while the other adsorbents could remove approximately half of the arsenic. Bayoxide E IN-20 and GFH were able to remove some selenium at higher doses (42% and 29%, respectively). In contrast to the results obtained during the screening testing, Adsorbsia As 500 did not remove an appreciable amount of selenium.

**Table 3a(i)-13. Vanadium Adsorbents Focused Testing**

	Vanadium			Arsenic			Selenium		
	Initial (ppm)	Final (ppb)	% Removal	Initial (ppb)	Final (ppb)	% Removal	Initial (ppb)	Final (ppb)	% Removal
Bayoxide (g)									
0	0.25	280	-12.0%	15	21	-40.0%	34	46	-35.3%
0.005		210	16.0%		16	-6.7%		36	-5.9%
0.01		160	36.0%		15	0.0%		35	-2.9%
0.015		140	44.0%		13	13.3%		35	-2.9%
0.04		33	86.8%		9.8	34.7%		3	11.8%
0.08		4.9	98.0%		7.1	52.7%		2	41.2%
Adsorbsia (g)									
0	0.25	240	4.0%	12	13	-8.3%	34	34	0.0%
0.005		170	32.0%		12	0.0%		34	0.0%
0.01		88	64.8%		11	8.3%		34	0.0%
0.02		32	87.2%		8.7	27.5%		34	0.0%
0.025		13	94.8%		6.9	42.5%		33	2.9%
0.035		6	97.6%		6	50.0%		32	5.9%
GFH (g)									
0	0.25	280	-12.0%	12	14	-16.7%	34	38	-11.8%
0.005		160	36.0%		11	8.3%		34	0.0%
0.01		100	60.0%		10	16.7%		33	2.9%
0.02		47	81.2%		7	41.7%		32	5.9%
0.025		25	90.0%		6.4	46.7%		29	14.7%
0.035		11	95.6%		4	66.7%		24	29.4%

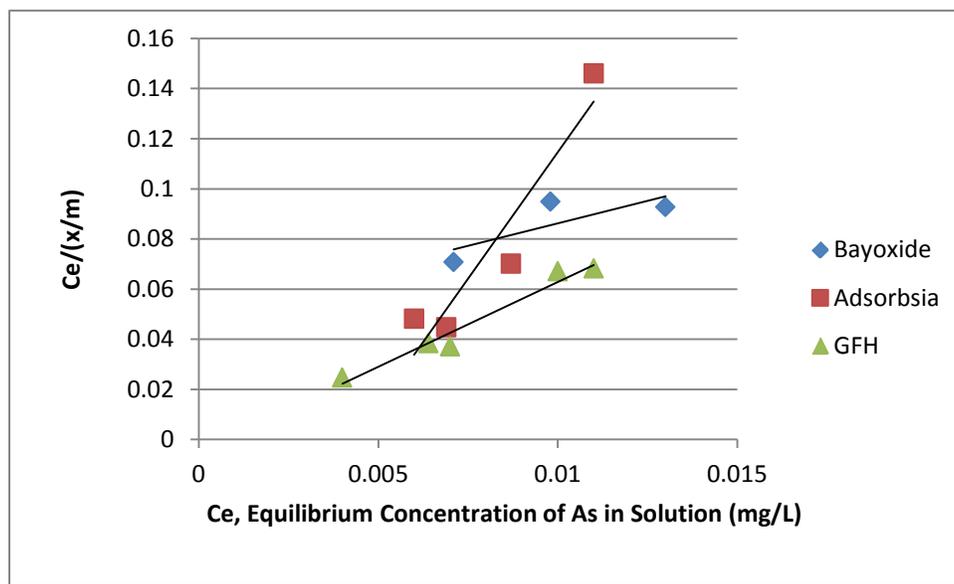
The focused testing vanadium results are summarized in Figure 3a(i)-6, which shows an isotherm plot using the Langmuir model. The Langmuir method was chosen because it provides a better fit to the data than a Freundlich plot, as independently confirmed by Naeem et al. (17). The GFH and Adsorbsia As 500 performed equally well in terms of vanadium removal per unit mass of adsorbent. Their performance was clearly better than that of Bayoxide E IN-20.

Figure 3a(i)-6. Vanadium Isotherm Testing Summary: Langmuir



A similar Langmuir plot for arsenic is presented in Figure 3a(i)-7. It shows that the GFH removed a higher amount of arsenic per unit weight of adsorbent than either Adsorbisia As 500 or Bayoxide E IN-20. The GFH was chosen for further column testing, since it had among the best vanadium removal of the adsorbents tested, as well as the best arsenic removal.

Figure 3a(i)-7. Arsenic Isotherm Summary: Langmuir



#### 4. Conclusions

- Method blanks determined that a significant amount of mercury (26%) was lost during the isotherm process. To compensate, mercury removal results have been corrected for these losses. In contrast, method blanks showed that very small amounts of arsenic, selenium, and vanadium were gained or lost (1.4% gain, 6.0% loss, and 1.6% loss, respectively). Removal results for arsenic, selenium, and vanadium were not corrected for these small gains or losses.
- All of the mercury adsorbents were capable of removing mercury below the 1.3 ppt level, but Mersorb LW and thiol-SAMMS were the most efficient adsorbents in terms of mercury removal per unit weight of adsorbent. When tested on the same wastewater, the performance of Mersorb LW and thiol-SAMMS was so similar that a distinction could not be made between the two based upon the Freundlich isotherm.
- The mercury adsorbents also removed a small amount of arsenic, selenium, and vanadium. When tested on the same wastewater, thiol-SAMMS removed more of these other metals of interest than Mersorb LW. Specifically, at the minimum dose required to achieve the 1.3 ppt mercury level, thiol-SAMMS removed 19% of the arsenic, 36% of the selenium, and 7% of the vanadium. A comparable dose of Mersorb LW with similar mercury results showed a 3% gain in arsenic and a 13% and 2% removal of selenium and vanadium, respectively.
- All of the vanadium adsorbents were capable of removing significant amounts of arsenic, selenium, and vanadium. The vanadium removal was higher than the arsenic removal (95–97% of the vanadium vs. 50–66% of the arsenic) for all the adsorbents.
- The GFH and Adsorbsia As 500 had similar vanadium removal efficiencies. The vanadium removal efficiency of Bayoxide E IN-20 was less than that of GFH and Adsorbsia As 500.
- The GFH was selected for bench-scale column testing because it had the best arsenic removal efficiency, as well as one of the highest vanadium removal efficiencies.

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### **3a(ii). Captech 10-250 Adsorbent Testing**

#### **1. Introduction and Objectives**

In this study, several solid adsorbents were tested to assess their ability to remove mercury, vanadium, arsenic, and selenium by using a batch isotherm method. The gel-like nature of Captech 10-250 prevented it from being tested with the procedure developed for the solid adsorbents. Instead, this adsorbent was tested in a flow-through column by using a procedure supplied by the vendor.

The objective of this testing was to determine the maximum amount of mercury that could be removed under varying flow conditions, such as flux and empty bed contact time. Testing until breakthrough was not done because of the length of time and the amount of wastewater required.

#### **2. Materials and Methods**

##### **a. Adsorbent Media**

Captech 10-250 adsorbent was developed by Captur Technologies Company and presented at the 2009 MRS Spring Meeting (1). It is a polymer that is chemically grafted and cross-linked to a coated silica substrate, thereby creating an open gel structure. The silica substrate is coated with a silane linker from Dow Corning or Evonik Degussa, so that the polymer can be chemically grafted onto the silica. The polymer, polyethyleneimine from BASF, can cross-link itself and form a mesh-like structure to trap and bind charged toxic metals (1).

Additionally, two different samples of Captech 10-200 (made with a different size of silica) were received but not used for performance testing. The difference between the two samples is the manufacturing process used for the silica. The Captech 10-200 is a newer version of Captech and, according to the manufacturer, it has been used for most field demonstrations. Although columns were loaded with both samples, each permitted similar flow rates of wastewater. Captech 10-250 was selected for performance testing to facilitate comparison with Captur Technology's bench-scale testing, since most of their testing involved the older Captech 10-250. All of the samples received were in slurry form. They were used without any grinding, contrary to what was done for some of the solid adsorbents.

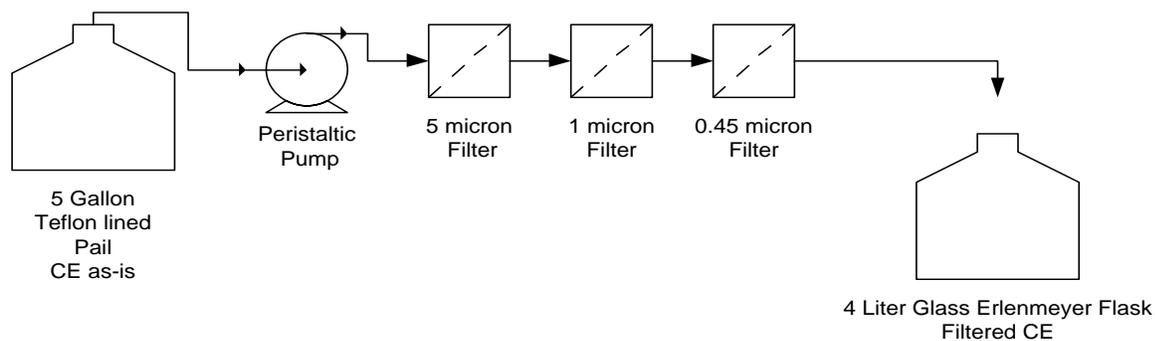
##### **b. Water Samples**

The Whiting Refinery's ETL and CE were used for the testing. Samples were collected by using the "clean hands-dirty hands" procedures specified in EPA Method 1669 (3). The ETL and CE were collected in 2-mil Teflon PFA liners inside of 5-gal HDPE pails. The Teflon liners were closed with cable ties so that no headspace was present. Upon receipt, the wastewater was stored in a 4 °C cold room before use. The wastewater was tested in several different batches. Based on the results of the Shelf-life Study (Appendix 1), the wastewater was used within 5 days after collection from the refinery. This approach was taken to ensure that changes in mercury and vanadium speciation and composition would be negligible.

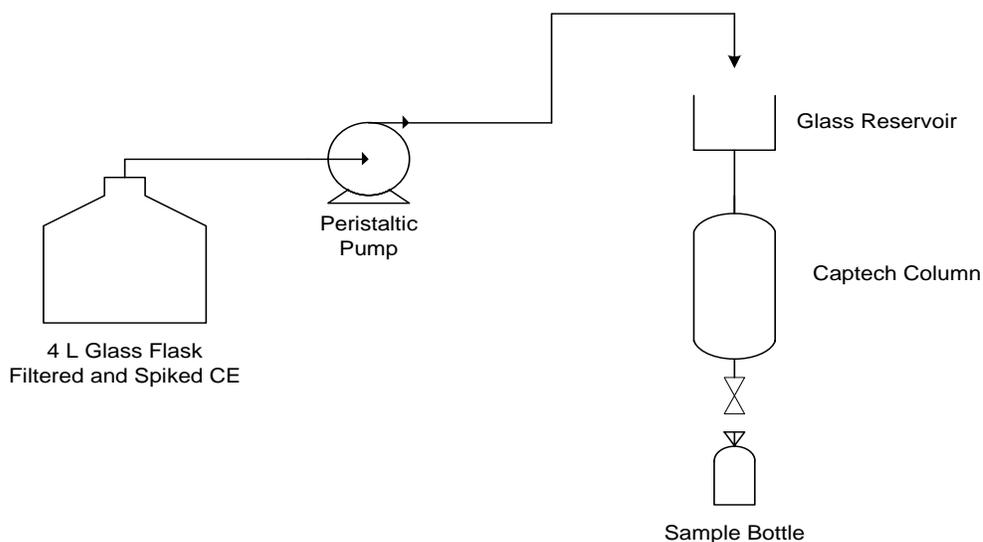
##### **c. Experimental Equipment**

Prior to use, all experimental equipment was cleaned by using the methods outlined in EPA Method 1631E and EPA Method 200.8 (4, 5). Specifically, the equipment was washed with laboratory soap (Sparkleen) and warm tap water, triple rinsed with MilliQ water (18 MΩ.cm resistivity), and then soaked overnight in a 5% HCl solution. The following morning, the equipment was triple rinsed in MilliQ water, brought into the clean room, and triple rinsed a second time in MilliQ water (18 MΩ.cm resistivity) before use.

Figure 3a(ii)-1. Captech Experimental System



Step 1: Feed Preparation

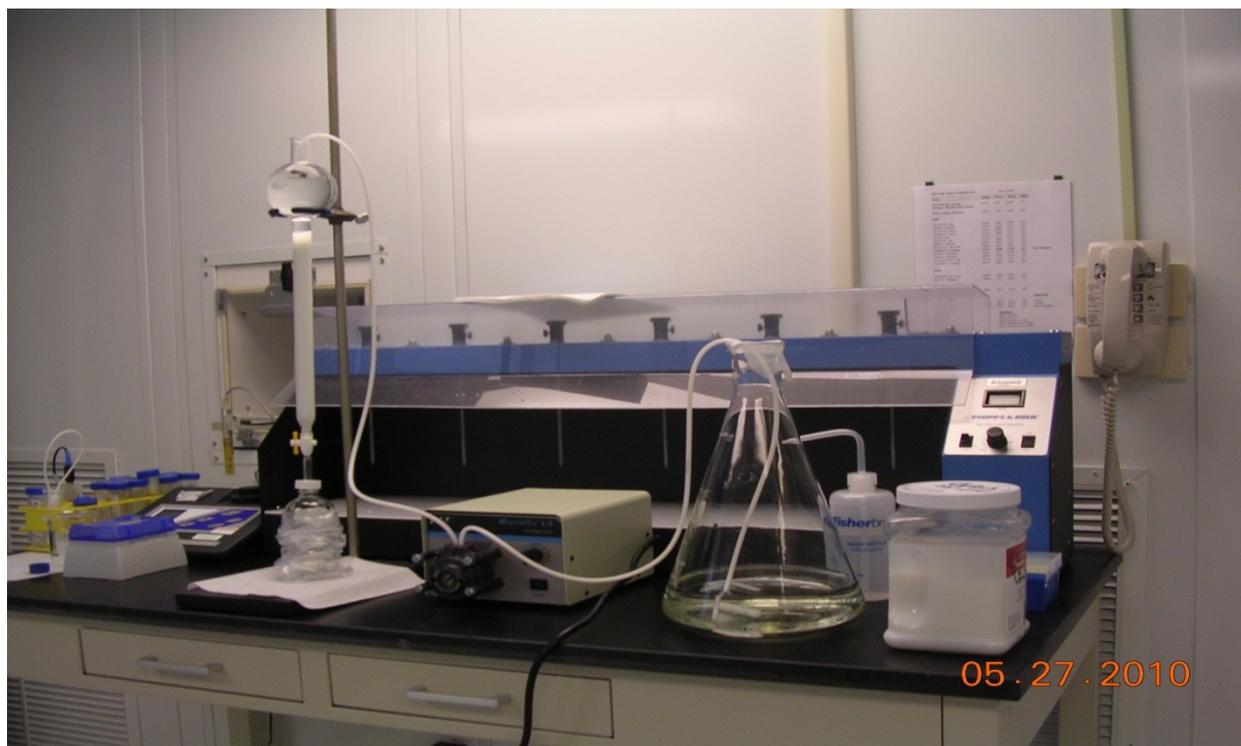


Step 2: Filtered and Spiked CE Feed to Column

An in-line filtration system consisting of a peristaltic pump and a series of three groundwater sampling filters (5  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 0.45  $\mu\text{m}$ ) was used to prepare the CE before testing. The 5  $\mu\text{m}$  and 1  $\mu\text{m}$  filters (Millipore GWSC5001 and GWSC10001) were made of HDPE, while the 0.45  $\mu\text{m}$  filter (Whatman Polycap GW 6714-6004) consisted of a PES membrane in polypropylene housing. SEBS resin tubing was used, as specified in EPA Method 1669 (Trace Metal Sampling) (3). A new set of filters and tubing was used for each batch of wastewater. The filtered CE was collected in a glass 4 liter flask.

During the testing, a peristaltic pump was used to transfer and meter the filtered and spiked CE to the Captech column, as shown in Figures 3a(ii)-1 and 3a(ii)-2. A combination reservoir and column glass apparatus, equipped with a Teflon stopcock at the bottom, was used. The column internal diameter was 2.0 cm, and the length was 25 cm. The reservoir's volume was 250 mL. Glass wool was used instead of a frit to hold the Captech material in place. A sample bottle cap, which had been drilled to the same size as the glass tubing extending from the bottom of the column, was used on top of the sample bottles during sample collection to minimize the loss of volatiles.

**Figure 3a(ii)-2. Captech Experiment Apparatus**



#### **d. Experimental Procedure**

The Captech 10-250 adsorbent was tested in Argonne's Class 100 clean room (Bldg. 202, room B354) using the Clean Room Procedures detailed in Section 5c, Attachment 5, of the Project Binder. The procedure used was based on recommendations from Captur Technology (6, 7, 8).

The initial sample sent by Captur Technologies was Captech 10-200. The initial column loadings with that sample produced very low flow rates through the columns — significantly lower than those predicted by the vendor. After a consultation, the vendor sent a new sample of Captech 10-200, as well as a sample of Captech 10-250. The columns were loaded with both samples, but they each delivered similarly low flow rates. The decision was made to conduct the performance testing with Captech 10-250 to facilitate comparison with Captur Technologies' bench-scale data, which had been obtained with Captech 10-250.

##### *Column Preparation*

Glass wool was inserted in the bottom of the column and tapped with a piece of Teflon tubing, so that it formed a uniform 2 mm thick layer across the column base. The 500 mL of MilliQ (18 M $\Omega$ .cm) water, which had been heated to 40 °C, was poured through the glass wool to remove any water-soluble impurities. An equipment blank was done by pouring an additional 0.5 L of unheated MilliQ (18 M $\Omega$ .cm) water through the glass wool and sampling it after 0.25 L had passed through the column. A small amount of this MilliQ water was left in the column to ensure that the glass wool did not dry out.

Method blanks were then done with 0.45  $\mu$ m filtered CE that had been spiked to a level of 10 ppt of Hg<sup>+2</sup>. The filtered CE was brought to room temperature before it was spiked with a freshly prepared 10 ppm mercury standard solution. The spiked feed was allowed to mix for 45 minutes in a covered 4 liter glass flask before use. A peristaltic pump was used to feed the CE from the 4 liter glass flask to the reservoir/column apparatus.

After the method blanks were completed, the column was loaded with the Captech 10-250 adsorbent. To do this, approximately 80 grams of slurry were weighed and then immediately poured into the column. The Captech 10-250 slurry was thixotropic — the material quickly returned to a gel-like state when it was not mixed. The slurry was poured all at once to avoid creating an interface or channels at the glass column walls. The water in the slurry was drained through the glass wool, collected, and weighed before disposal as waste. An additional 1 L of MilliQ water was then added to the reservoir and allowed to drain through the column. After the slurry was poured into the column, a header of either MilliQ water or CE was kept above the column at all times so that the slurry would not dry out.

#### *Column Testing with CuSO<sub>4</sub>*

The initial poured column was tested with a 100 ppm Cu as CuSO<sub>4</sub> solution to check the column loading technique. When the CuSO<sub>4</sub> solution was fed to the column, a blue copper interface was formed, thereby providing a visual way to check the column loading method. The copper sulfate solution was prepared with cupric sulfate pentahydrate crystals (Fisher Scientific, ACS certified) by using MilliQ (18 MΩ.cm) water. A peristaltic pump was used to transfer the solution to the reservoir at the top of the column. The copper sulfate solution was added to the reservoir in such a way that the column bed was not disturbed. As shown in Figure 3a(ii)-3, a sharp line of demarcation was visible at the beginning of the column, which indicated that the column had been properly loaded.

**Figure 3a(ii)-3. Testing Column Loading Technique with CuSO<sub>4</sub> Solution**



#### *Column Testing with CE*

After the column loading technique had been practiced and tested with the copper sulfate solution, the column was cleaned and new glass wool was installed. The column was then reloaded with fresh Captech 10-250 slurry by using the procedure described above.

The CE that had been filtered through a 0.45 μm filter and spiked to a level of 10 ppt Hg<sup>+2</sup> was used for the testing. Although the original plan was to test the column's performance at several different flow rates, the column permitted only a very low flow rate of approximately 5.4 mL/min.

### e. Analyses

Prior to testing, the pH of the untreated ETL/CE was measured with an Oakton pH/CON 510 benchtop meter. Additionally, the ETL/CE was sampled and sent to a certified independent lab for analysis of the following parameters:

Total and dissolved mercury	EPA 1631e
Total and dissolved vanadium	EPA 200.8
Cations: As, Cu, Fe, Pb, Mn, Se, Si, Zn	EPA 6010/200.7
Anions: Cl <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup>	EPA 300.0
Fluoride	EPA 340.1
Total hardness as CaCO <sub>3</sub>	EPA 130.2

The ETL/CE that had been treated with Captech 10-250 was sampled and analyzed for total mercury (EPA Method 1631e) by Lab B, a certified independent lab.

## 3. Results and Discussion

### a. Blanks

Results from the blanks that were taken prior to testing the performance of Captech 10-250 are summarized in Table 3a(ii)-1. Neither the equipment nor the adsorbent contributed significant amounts of mercury. The amount of mercury lost by the method (filtered and spiked Hg CE passing through the column without adsorbent) was approximately 3% — not a significant loss.

**Table 3a(ii)-1. Summary of Captech Blanks**

	Hg (ppt)
Equipment blank	0.16
Adsorbent blank	0.39
Method blank	
Feed (avg. of 5)	5.77
Standard dev.	0.60
Effluent (avg. of 5)	5.6
Standard dev.	1.11
Percent loss	2.95%

### b. Captech Performance

The column used for testing contained approximately 89 grams of Captech 10-250 and was 27.0 cm (11.0 in.) tall. It was tested at a flow rate of 5.4 mL/min, which corresponds to a flux of 0.47 gpm/ft<sup>2</sup> and an empty bed contact time (EBCT) of 14.7 minutes. This flow rate is significantly lower than the reported rate of 100–400 mL/min for a 25 cm-long column with a 2 cm diameter (1).

During the testing, brown contaminants appeared to be removed from the filtered and spiked CE, as shown in Figure 3a(ii)-4. This is consistent with reports that Captech 10-250 is nonspecific for mercury; it can also remove Fe, Mg, Pb, Cu, Se, V, Cd, Al, and Zn. The order of binding from strongest to weakest is Cu~Hg>Fe>Pb>Au>Ag. Copper and mercury are expected to displace the other ions listed (1).

**Figure 3a(ii)-4. Captech Testing with CE**



During the performance testing, three effluent samples were taken, as summarized in Table 3a(ii)-2. The effluent samples indicated that 32% of the mercury entering the Captech column was removed. Even if the second sample was discarded due to possible contamination issues, only 52% of the mercury was removed. Although some of the mercury was removed, none of the effluent samples from the Captech 10-250 column were below the upcoming 1.3 ppt target limit concentration. Although Captech 10-250 has shown better results (1 ppt) for groundwater in tests conducted by others (1), it is possible that other components of the CE interfered with and prevented some of the mercury removal in this test.

**Table 3a(ii)-2. Captech 10-250 Performance**

Feed Hg (ppt)	Effluent (ppt)	All Effluents		Effluents 1 and 3	
		Average	Percent Removal	Average	Percent Removal
9.92	4.49	6.76	31.9	4.80	51.6
	10.70				
	5.10				

#### 4. Conclusions

- The low flow rate (5.4 mL/min) obtained through the Capttech 10-250 column was significantly lower than vendor claims and suggests that larger installations would require a pressurized system in order to get practical flow rates through the column.
- Although effluent from the Capttech 10-250 adsorbent showed 32–52% mercury removal, it wasn't less than the target 1.3 ppt limit. This suggests that other components of the CE possibly interfered with and prevented some of the mercury removal.

#### 5. References

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### 3a(iii). Adsorption Column Testing

#### 1. Introduction and Objectives

Batch isotherm testing, previously described in Section 3a(i), was used to determine which vanadium adsorbent would be tested in a bench-scale column. Although the isotherm testing showed that both Adsorbisia As 500 and GFH removed vanadium equally well, GFH was selected for column testing because it also showed the best arsenic removal capability. Originally, the plan was to conduct column testing of the best performing mercury adsorbent. However, the decision was made to use the resources to do a comparison of thiol-SAMMS and Mersorb LW on the same wastewater. The previous testing was conducted on different batches of wastewater.

The objective of this testing was to determine the maximum amount of vanadium, arsenic, and selenium that could be removed under varying flow conditions, such as flux and empty bed contact time. Testing for each condition was of short duration to enable the testing of multiple conditions. Testing until breakthrough was not done due to the length of time and amount of required wastewater.

#### 2. Materials and Methods

##### a. Adsorbent Media

The adsorbent tested was GFH. It is a granular ferric hydroxide adsorbent produced by GEH-Wasserchemie and sold by Siemens. The material was ground with a dedicated mortar and pestle. Next, it was sieved with a vibratory sieve shaker. The GFH, which is sold wet, was ground wet and sieved to a 100 x 140 mesh size (105–149  $\mu\text{m}$ ).

##### b. Water Samples

The Whiting Refinery's ETL and CE were used for the testing. Samples were collected by using the "clean hands-dirty hands" procedures specified in EPA Method 1669 (1). Upon receipt, the wastewater was stored in a 4 °C cold room before use. The wastewater was tested in several different batches. Based on the results of the Shelf-life Study (Chapter 2 and Appendix 1), the wastewater was used for up to 5 days after collection from the refinery. This approach was taken so that changes in vanadium speciation and composition would be negligible.

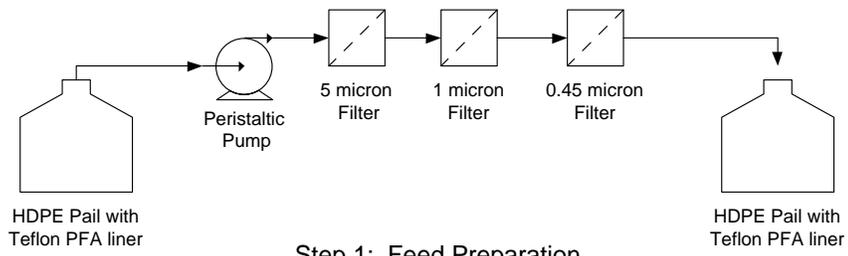
##### c. Experimental Equipment

Prior to use, all experimental equipment was cleaned by using the methods outlined in EPA Method 1631E and EPA Method 200.8 (2, 3). Specifically, the equipment was washed with laboratory soap (Sparkleen) and tap water, and then triple rinsed with MilliQ water (18 M $\Omega$ .cm resistivity). A 5% HCl solution was recirculated through the system for 75 minutes and then drained. An additional 1.2 liters of MilliQ water was pumped through the system. Finally, 2 liters of fresh MilliQ water were recirculated through the system for 30 minutes.

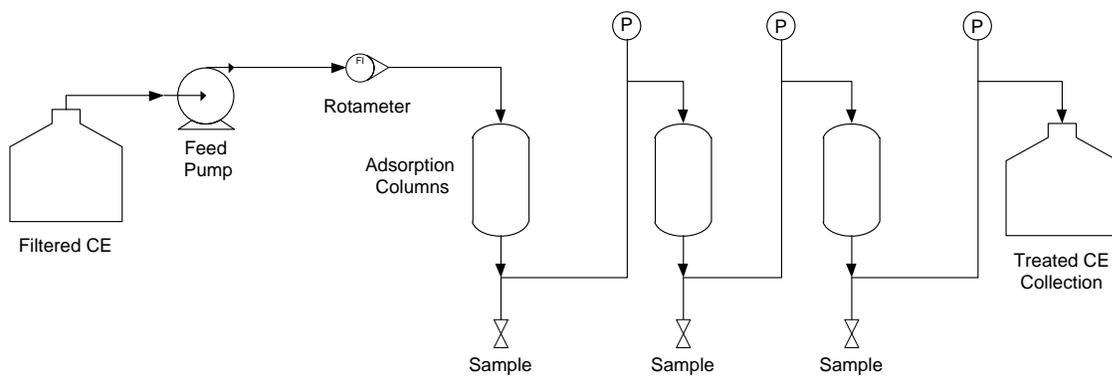
Before the column testing, the CE was filtered with an in-line filtration system consisting of a peristaltic pump and a series of three groundwater sampling filters (5  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 0.45  $\mu\text{m}$ ). The 5  $\mu\text{m}$  and 1  $\mu\text{m}$  filters (Millipore GWSC5001 and GWSC10001) were made of HDPE, while the 0.45  $\mu\text{m}$  filter (Whatman Polycap GW 6714-6004) consisted of a PES membrane in polypropylene housing. SEBS resin tubing was used, as specified in EPA Method 1669 (Trace Metal Sampling) (1). A new set of filters and tubing was used for each batch of wastewater. The filtered CE was collected in a Teflon PFA pail liner placed inside a 5-gal HDPE bucket.

The equipment set-up is shown in Figures 3a(iii)-1 and 3a(iii)-2. A peristaltic pump with SEBS resin tubing was used to feed the CE to the system. The flow rate was measured with a glass rotameter and controlled with a Teflon needle valve. The CE was fed through a series of three 1.1 cm diameter borosilicate glass columns. Glass wool was used before and after each GFH bed to keep it in place. The short length of the testing eliminated the need to cover these columns with aluminum foil to prevent algae growth. A sampling point was located at the inlet and outlet of each column. The wetted parts were Teflon or glass, with the exception of the in-line filters, which were made of HDPE or polypropylene. Teflon pressure gauge isolators were used to prevent CE contact with metal.

**Figure 3a(iii)-1. GFH Column Testing Flow Diagram**

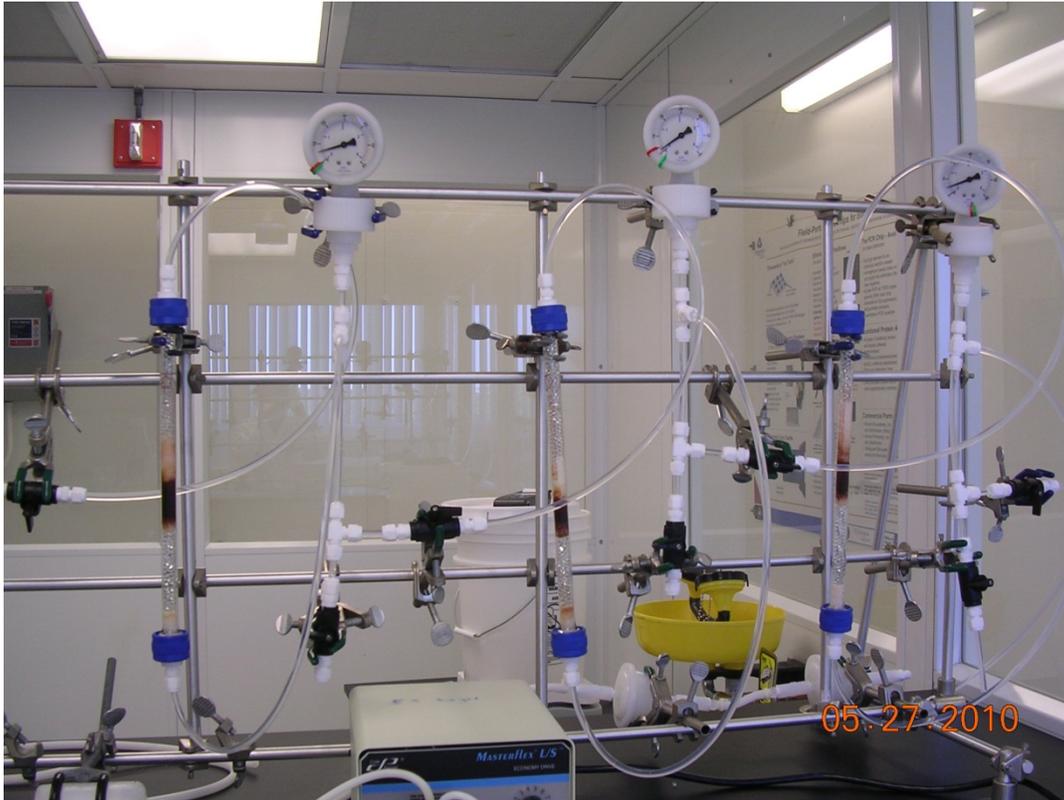


Step 1: Feed Preparation



Step 2: Column Testing

Figure 3a(iii)-2. GFH Column Testing Apparatus



Samples that were collected after each column were individually vacuum filtered through a 0.45  $\mu\text{m}$  nitrocellulose acetate filter. A glass filtration system consisting of a filter holder and an Erlenmeyer flask was used.

#### d. Column Scaling Approach

The original basis for the GFH column scaling approach was the ASTM method D 6586-03 for rapid small-scale column tests (RSSCTs) using activated carbon (4). This method, developed by John Crittenden et al., is based on mathematical modeling (5). It provides a method for scaling particle size, empty bed contact time, and hydraulic loading between large and small columns. The information obtained from bench-scale work through this method can be used to predict the performance of pilot- or full-scale carbon columns.

The RSSCT bench-scale testing uses dimensionless mathematical modeling to scale down a full-scale adsorber based on the similitude between solute transport mechanisms. In adsorption columns, the mass transfer mechanisms responsible for spreading of the mass transfer zone are (1) axial mixing resulting from dispersion, (2) external mass transfer resistance or film transfer, and (3) internal mass transfer resistances of pore and surface diffusion (5). In most cases, if the hydraulic loading is sufficiently high, then the effect of dispersion is negligible, thereby leaving the film transfer and the internal pore and surface diffusion as the main adsorption controlling mechanisms. Two different RSSCT models have been developed — one for constant diffusivity and the other for proportional diffusivity. The ASTM method for testing activated carbon uses the constant diffusivity model, which assumes that the intraparticle diffusivities are independent of particle size, and that film transfer is the mechanism that controls adsorption. In contrast, the proportional diffusivity model assumes that the intraparticle diffusion is the controlling mechanism, and that it is proportional to particle size (5).

The ASTM RSSCT method has also been used with other adsorption media besides activated carbon. Paul Westerhoff, of Arizona State University, has used it with some modifications with the vanadium-removing

adsorbents, Bayoxide E-33 (the drinking water version of Bayoxide E IN-20) and GFH (6, 7, 8). His first modification has been to scale by using the assumption of proportional diffusivity rather than constant diffusivity. He has decreased the particle size to be even smaller than that called for in the ASTM RSSCT method — 100 x 140 mesh instead of 60 x 80 mesh. He also scales by using half of the full-scale EBCT. Additionally, he reduces the RSSCT flux to reduce the column pressure drop. He does this while maintaining the product of the Reynolds number and the Schmidt number within the mechanical dispersion range of 200 – 200,000 so that the dominant transport mechanism is not changed. These changes have been implemented to reduce the amount of time and wastewater needed to achieve breakthrough. With this approach, Dr. Westerhoff has demonstrated experimentally that the breakthrough results from small-scale lab columns are comparable to the pilot-scale breakthrough results. Based on the recommendation of Siemens, the GFH column testing followed the methodology of Dr. Westerhoff (i.e., using the proportional diffusivity assumption, the 100 x 140 mesh particle size, scaling from half of the full-scale EBCT and reducing the RSSCT flux within the constraint of not changing the dominant transport mechanism) (9).

**e. Experimental Procedure**

The column testing was conducted in Argonne’s Class 100 clean room (Bldg. 202, room B354) by using the Clean Room Procedures detailed in Section 5c, Attachment 5, of the Project Binder.

Prior to testing with GFH, an equipment blank was performed with MilliQ water (18 MΩ.cm). An adsorbent blank was done during the isotherm testing, so it was not repeated here. Method blanks were performed with CE that had been filtered through a 0.45 µm filter. The method for these blanks included the entire process: pumping CE through the column apparatus, collecting CE samples, and vacuum filtering through a 0.45 µm filter.

The test was planned to run at a full-scale equivalent flux of 5 gpm/ft<sup>2</sup> which is at the low end of the 5 to 7 gpm/ft<sup>2</sup> range recommended by the vendor (9). Three different columns were used sequentially, so that three different empty bed contact times could be studied at the same time. A weighed amount of GFH was loaded into each column, and the height of each column was measured with a ruler to determine the GFH volume. The amount of GFH used in each column was set so that full-scale equivalent empty bed contact times of 3, 5, and 8 minutes could be evaluated. This range of empty bed contact times brackets the vendor recommendation of 5 minutes (9).

Actual column testing also used CE that had been passed through a 0.45 µm filter. Prior to sample collection, 29 bed volumes of CE were pumped through the system. Flow rates were measured with a graduate cylinder and a stopwatch. Two samples were collected from each column’s effluent sequentially, starting with Column 1. The collected samples were individually vacuum filtered through a 0.45 µm filter before being placed in the sample bottles provided by the independent lab.

**f. Analyses**

Prior to testing, the pH of the untreated CE was measured with an Oakton pH/CON 510 benchtop meter. Additionally, the CE was sampled and sent to a certified independent lab for analysis of the following parameters:

Total and dissolved vanadium	EPA 200.8
Cations: As, Cu, Fe, Pb, Mn, Se, Si, Zn	EPA 6010/200.7
Anions: Cl <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup>	EPA 300.0
Fluoride	EPA 340.1
Total hardness as CaCO <sub>3</sub>	EPA 130.2

The CE that had been treated with the GFH columns was sampled and analyzed by a certified independent lab for total vanadium, total arsenic, and total selenium (EPA Methods 200.7/200.8).

**3. Results and Discussion**

**a. Blanks**

Equipment blanks were conducted on the in-line feed filtration equipment, the glass column apparatus, and the vacuum filtration apparatus by using MilliQ (18M $\Omega$ .cm) water. The results, detailed in Table 3a(iii)-1, showed no measurable addition of the metals of interest to the MilliQ water. Therefore, the experimental equipment should not be expected to contaminate the wastewater samples during testing. For completeness, Table 3a(iii)-1 also includes data for the GFH adsorbent blank that was done during isotherm testing. The adsorbent did not add any selenium or vanadium to the MilliQ water. Although a small amount of arsenic (1.1 ppb) appeared to leach from the GFH, the amount is negligible, considering that the detection limit for the method is 1 ppb.

**Table 3a(iii)-1. Equipment and Adsorbent Blanks**

	<b>As (ppb)</b>	<b>Se (ppb)</b>	<b>V (ppb)</b>
Series of in-line filters 5, 1, and 0.45 $\mu$ m (all capsules)	<1	<1	<1
Column apparatus	<1	<1	<1
Vacuum filtration apparatus 0.45 $\mu$ m nitrocellulose filter paper	<1	<1	<1
GFH adsorbent (isotherm testing)	1.1	<1	<1

Method blanks were performed to determine the amount of arsenic, selenium, and vanadium lost while undergoing the column testing process. The method consisted of pumping CE through the column apparatus, collecting samples, and vacuum filtering through a 0.45  $\mu$ m filter. Five replicates were done for both the feed sample and the method sample. The results are summarized in Table 3a(iii)-2. Applying the method to CE resulted in a 7.7% loss of arsenic, a 4.9% loss of selenium, and a 1.9% loss of vanadium. Since these losses are relatively small, the arsenic, selenium, and vanadium results presented in this section have not been corrected for method losses.

**Table 3a(iii)-2. Column Testing Method Blanks: Arsenic, Selenium, and Vanadium**

	<b>Arsenic (ppb)</b>	<b>Selenium (ppb)</b>	<b>Vanadium (ppb)</b>
Feed (avg. of 5)	13	32.8	530
Standard dev.	1	1.8	12.2
Effluent (avg. of 5)	12	31.2	520
Standard dev.	0.7	0.8	10
Percent loss	7.7%	4.9%	1.9%

**b. Column Testing**

During the shake-down testing of the column system, the pressure drop across the GFH loaded columns was higher than anticipated — approximately 26 psig. In order to stay below the pressure rating of the glass, Teflon, and SEBS resin tubing system, it was necessary to reduce the CE flow rate. The actual operating conditions are shown in Table 3a(iii)-3. The lower flow rate resulted in a lower flux and increased empty bed contact times, as noted in Table 3a(iii)-3.

**Table 3a(iii)-3. Actual GFH Column Testing Conditions**

	Column 1	Column 2	Column 3
Flow rate (cc/min)			
Planned	16	16	16
Achievable	11.4	7.6	7.9
Bed height (cm)	3.30	2.34	3.29
Dry weight GFH (g)	1.716	0.971	1.591
Full-scale Flux (gpm/ft <sup>2</sup> )			
Planned	5	5	5
Achievable	3.56	2.37	2.47
Full-scale EBCT Equivalent (min)			
Planned	3	5	8
Achievable	4.1	10.6	16.2

The fact that lower fluxes were used for the testing brings up the question of whether the dominant transport mechanism has been changed. As stated previously, the proportional diffusivity model, which has been used for this work, assumes that intraparticle diffusion is the controlling mechanism (5). Within the context of the proportional diffusivity assumption, Westerhoff has proposed a method to determine the minimum Reynolds number for the RSSCT to ensure that the effects of dispersion are minimal. Specifically, if the product of the Reynolds number and the Schmidt number is within the mechanical dispersion region of 200–200,000, then dispersion is a minor transport mechanism (6). For this work, the Reynolds number was 24, while the Schmidt number was 1,000. The product of the Reynolds number and the Schmidt number (24,000) is within the mechanical dispersion region of 200–200,000 reported by Westerhoff. Therefore, despite the lower flow rates used, intraparticle diffusion should still be the controlling mechanism, and the assumption of proportional diffusivity is still valid.

The results for the GFH column testing are shown in Table 3a(iii)-4. The CE that was used for this testing contained relatively high levels of vanadium, 540 ppb, suggesting that the Stretford system had been recently purged. Despite this challenge of high vanadium concentration, 99.8% of the vanadium was removed in the first column of the GFH. The vanadium in the first column’s effluent was at the detection limit (<1 ppb), so the effect of additional columns could not be assessed. The GFH also effectively removed the majority of the arsenic (84–89%) and the selenium (72–74%). The selenium removal essentially did not change as it passed through the three columns, suggesting that the selenium was removed in the first column and that additional columns did not remove any selenium. One possible explanation for the only partial Se removal in the first column followed by no additional removal from either of the other two columns, is that Se might exist in multiple forms. The ~70% reduction may

represent the form that is removed by GFH, while the rest is not treatable with this method. Although it appears that arsenic removal decreases slightly as it passes through the three columns, the limited sampling (two samples per column) makes it difficult to draw a firm conclusion.

**Table 3a(iii)-4. GFH Column Testing Results**

	Column 1			Column 2		Column 3	
	Feed (ppb)	Effluent (ppb)	Average % Removal	Effluent (ppb)	Average % Removal	Effluent (ppb)	Average % Removal
Vanadium	540	<1	99.8	1.5	99.8	<1	99.8
		<1		<1		<1	
Arsenic	13	1.5	90.4	1.2	88.9	2.3	83.8
		1.0		1.7		1.9	
Selenium	32	8.4	73.4	8.3	74.1	9.4	72.0
		8.6		8.3		8.5	

#### 4. Conclusions

- Method blanks showed that very small amounts of arsenic, selenium, and vanadium were lost during the column testing (7.7%, 4.9%, and 1.9% loss, respectively). The removal results for arsenic, selenium, and vanadium were not corrected for these small losses.
- The GFH column system operating at the full-scale equivalent of a 3.56 gpm/ft<sup>2</sup> flux and a 4.1 minute empty bed contact time was able to remove the majority of the arsenic, selenium, and vanadium (90.4, 73.4, and 99.8%, respectively).
- Arsenic, selenium, and vanadium removal primarily occurred in the first GFH column. Little to no removal was observed in the second and third columns.

#### 5. References

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## 3b. Precipitation Experiments

### 1. Introduction and Objectives

Various precipitants were tested in this treatability study to evaluate the efficiency of heavy metal removal from the ETL/CE. The precipitants used in this study were:

1. Mercury: MetClear 2405 (GE), Nalmet 1689 (Nalco), Na<sub>2</sub>S (Sigma-Aldrich), and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Sigma-Aldrich); and
2. Vanadium: FeCl<sub>3</sub> (Sigma-Aldrich), FeCl<sub>2</sub> (Sigma-Aldrich), Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Sigma-Aldrich), and the Unipure process (FeCl<sub>2</sub> plus addition of air) (1, 2).

The objectives of this treatability study were to determine the best precipitant dose and pH on the basis of the operating range of a precipitating agent and the solubility characteristics of the mercury and vanadium at ambient temperature. The treatability evaluation included the following steps:

1. Determine the best precipitant dose and pH,
2. Identify the precipitate (sludge) characteristics,
3. Estimate the sludge production from chemical precipitation, and
4. Evaluate the fate of the precipitate in the treated water and produced chemical sludge (not done please see page 3-37).

### 2. Materials and Methods

#### a. Testing Equipment and Materials

The treatability test was performed in a jar-test apparatus with six Teflon-coated paddles (Phipps and Bird, Virginia, Model PB700). To prevent mercury loss and contamination from the containers, the experiments were performed in closed 2 L wide-mouth glass jars with Teflon caps (I-CHEM 300 series, which meets or exceeds U.S. EPA specifications and guidance for contaminant-free sample containers). The Teflon caps were tailored to allow the stirrer operation and to seal the jars to minimize loss and contamination.

The precipitation tests for vanadium removal were also done in the same closed jars to prevent contamination from outside sources. Prior to testing, the jars were cleaned by using the method outlined in EPA Method 1669 (3).

The stock solutions of Na<sub>2</sub>S, FeCl<sub>3</sub>, FeCl<sub>2</sub>, and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> were prepared in MilliQ water (18 MΩ·cm resistivity at 25 °C). The stock solutions of MetClear and Nalmet were prepared according to the vendors' instructions.

The high-purity laboratory grade-zero air (Airgas North Central, Inc., Illinois) was sparged to the jars to rapidly oxidize ferrous ion to ferric ion to test the effectiveness of the Unipure process in achieving low concentrations of vanadium in the treated water. A gas flow meter (316 SS rotameter, King Instrument Company, California) was used to measure the flow rate of air supplied to the reaction mixture (5 L/min) (1). The dissolved oxygen concentration in the water was also monitored with a DO meter.

#### b. Wastewater Samples

The treatability test was conducted on water samples taken from the Whiting Refinery ETL stream and CE. The ETL/CE were tested in several different batches, with each batch equal to the amount that would be used in a 1-week time period. This assumes that changes in mercury and vanadium speciation and composition within each batch over a 1-week time period were negligible (see Chapter 2). Lab A collected the wastewater samples at the source and delivered them to Argonne using the "clean hands-dirty hands" procedures (4).

### c. Experimental Procedure

The experimental protocol involved the determination of the best precipitant dose and pH level, as well as an evaluation of the sludge characteristics. A series of jar tests that followed the ASTM D2035-80 method (5) was conducted to identify the optimum precipitant to mercury or vanadium ratio, as well as the optimum pH. The precipitant dose and pH level at which all mercury and/or vanadium occurred in the lowest concentrations were chosen as the optimum reaction conditions.

The precipitation experiments were performed in three steps:

1. *Precipitation/flocculation/coagulation*: After dosing and pH adjustment, the samples were mixed for 20 minutes at 250 rpm, followed by slow mixing for 10 minutes at 30 rpm.
2. *Settling*: At the end of the combined 30 minutes of mixing, the stirrers were turned off to allow the precipitates to settle for about 30 minutes. The precipitate characteristics (e.g., particle size, settling characteristics, etc.) were also observed during the experiments. After the precipitates settled out, the supernatants were sampled and then analyzed for residual mercury and vanadium concentrations and turbidity.
3. After sample collection, the supernatant was filtered through a 0.45  $\mu\text{m}$  filter (Whatman Polycap 75 GW) and analyzed for mercury, vanadium, turbidity, and so forth. Figure 3b-1 shows photos of each step involved in the precipitation experiments.

The experimental protocol also called for testing to evaluate the effectiveness of precipitants in permanently binding mercury and vanadium (6). The plan was to investigate the stability of precipitate in the supernatant and sludge samples. However, the amount of sludge production was much lower than that required for toxicity characteristic leaching procedure (TCLP) testing (100 g) (EPA 1311) (7). As such, it was not possible to analyze the precipitate because (a) the required solid sample size (1 g or more) for analysis by certified laboratories was much higher than that of the samples obtained during the experiments (8, 9), and (b) the detection limits of the EPA Methods were much higher than that of the mercury and vanadium concentrations in the sludge samples (4, 8, 9).

The precipitants used for mercury and vanadium were evaluated in Argonne's Class 100 clean room (Bldg. 202, room B354). The work was done at a constant room temperature (68 °F). There were two blanks during each precipitation test. An equipment blank (method blank) was prepared by using 1 L of ETL/CE without any precipitant. The reagent blank was prepared by adding the second highest amount of precipitant given in Table 3b-1 into the 1 L of MilliQ water (18 M $\Omega$ .cm) and adjusting the pH (if required). One method blank and one reagent blank were run, and these underwent the same procedure with the samples at the same time. It should be noted that the jar testing equipment could accommodate six jars per run.

#### *Initial Screening*

The initial screening experiments included testing of different doses of precipitating agent and various pH levels to evaluate effective precipitation at ambient temperature. Table 3b-1 details the test conditions for the different precipitants to be used for mercury and vanadium removal. The experiments were performed by testing each precipitant at three different doses for each specified pH. The pH adjustments were done by using 0.1 N NaOH or 0.1 N HCl (Sigma-Aldrich). The test conditions were selected based on literature data and vendors' instructions, as well as by considering the characteristics of the ETL/CE and the regulatory limits.

#### *Focused Testing*

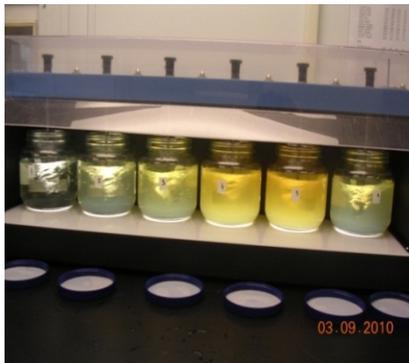
The second run of experiments involved the selection of dosages and pH among the initial screening test results that provided the best mercury and vanadium removal or that were within the targeted effluent limits (mercury <1.3 ppt and vanadium < 280 ppb).

**Table 3b-1. Treatability of Mercury and Vanadium by Different Precipitants at Different Doses and pH Ranges**

Precipitants	Effluent (L)	Conditions for Initial Screenings		References
		Precipitant Dose* ppm	pH	
Mercury				
Met Clear 2405 (GE)	1	10, 30, 50	As-is	10, 11
Nalmet 8702 (Nalco)	1	5, 15, 30	As-is	12, 13
Na <sub>2</sub> S (Sigma-Aldrich)	1	1, 5, 10 as S	As-is	14
Vanadium				
FeCl <sub>3</sub> (Sigma-Aldrich)	1	10, 50, 100 as Fe	5.0	15
FeCl <sub>2</sub> (Sigma-Aldrich)	1	10, 50, 100 as Fe	8.0	15
/ Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (Sigma-Aldrich)	1	10, 50, 100 as Fe	8.0	16
Unipure process (FeCl <sub>2</sub> plus addition of air)	1	10, 50, 100 as Fe	8.2	1, 2

\*Values are subject to change, depending on the tested ETL/CE characteristics.

**Figure 3b-1. Steps Followed during the Precipitation Experiments**



Mixing at 250 rpm



Sampling



Settling



Vacuum

#### d. Analyses

Prior to testing, the pH, temperature, conductivity, turbidity (EPA 180. 1), and total dissolved solids (TDS) (EPA 160.1) of the untreated ETL/CE were measured at Argonne. Additionally, the ETL/CE was sampled and sent to a certified independent lab for analysis of the following parameters:

Total and dissolved mercury	EPA 1631e
Total and dissolved vanadium	EPA 200.8
Cations: As, Cu, Fe, Pb, Mn, Se, Si, Zn	EPA 6010/200.7
Anions: Cl <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup>	EPA 300.0
Sulfide	EPA 276.2
Total hardness as CaCO <sub>3</sub>	EPA 130.2
Alkalinity	EPA 310.2

Each sample sent to the certified lab had a unique sample number. The samples were placed into clean sample bottles provided by the certified independent lab (Lab A and/or Lab B). The sample preservation was done as specified by the analytical methods. A trip blank was included, as required in section B4.2 of the BP Quality Assurance Plan, Phase 2, Module 3. The dissolved concentrations of mercury and vanadium in the treated ETL/CE samples were determined by filtering through a 0.45 µm filter (Whatman Polycap 75GW), as specified by the analytical methods.

#### e. Data Analysis

The optimum conditions for each precipitant were determined as a function of the precipitant concentration and pH. The data were plotted in the percentage of mercury and vanadium removal versus precipitant dose and pH. The precipitant dose and pH level at which all mercury and vanadium have the lowest concentrations were selected as the optimum dose and pH.

Test results of the method blank and reagent samples were compared with that of the treated CE/ETL samples to provide information on vanadium and mercury loss/gain during the experiments.

### 3. Results and Discussion

Various precipitants were tested in this treatability study to evaluate the efficiency of heavy metal removal from the ETL/CE. During the experiments, varying dosages of precipitants were added to ETL/CE samples. The samples were identically treated using a standard jar tester. The precipitates settled rapidly and left a clear supernatant (Figure 3b-1). The particles in the wastewater were also agglomerated into precipitates to form large floc sizes that settled to the bottom of the jars. Since good floc formation was observed in the jars for all tested precipitants, except the Unipure process, there was no need to add coagulants and coagulant aids. Finally, filtration (0.45 µm pore size) completed the metal removal process.

The tests were repeated on a total of seven different sampling events (batches) of wastewater from the Whiting Refinery.

#### V Precipitation

Initial screening experiments were performed with ETL samples based on the specified experimental conditions given in Table 3b-1. The ETL samples with no precipitant also went through the same treatment to determine any vanadium loss/contamination during the experiments. A reagent blank prepared with 50 ppm Fe in MilliQ water was used to identify any impurity in the tested precipitants (Table 3b-2). The effectiveness of the precipitants used for the vanadium precipitation experiments is shown in Table 3b-2. Since CE/ETL samples are of slightly basic character (pH = 7.6–8.0), heavy metal hydroxides can be effectively precipitated. Because all precipitants display similar effects, it is clear that the adjustment of pH with the use of 0.1 N NaOH did not increase the removal percentage of vanadium. Higher iron concentrations (>50 ppm) resulted in a decrease in the pH values by 0.5–1.0 unit, depending on the applied dosage. However, changes in pH values were not critical in vanadium removal.

It appears that the combined treatment of precipitation and filtration provided the best results for vanadium removal (Figure 3b-2). After filtration, there was no difference in the percentage of vanadium removal between the tested iron salts. A 10 ppm iron dose with filtration was found to be sufficient to remove 100% of the vanadium from the tested ETL that contained 90 ppb V.

It was also recognized that the ETL/CE samples treated with ferrous chloride contained sufficient quantities of iron to generate adequate amounts of ferric hydroxide upon mixing at a high rate, which increased air introduction, without the addition of the ferric ions from an outside source (1). In the Unipure process, air introduction into the jars oxidizes the ferrous ion ( $\text{Fe}^{+2}$ ) to ferric ion ( $\text{Fe}^{+3}$ ) and precipitates ferric ion, which entraps heavy metals into its matrix (1, 2). However, air introduction into the jars through spargers located by the side walls caused a dispersion of the flocs and resulted in a sludge with poor settling characteristics. This might explain why the 10 ppm iron dose used for the Unipure process was not sufficient to remove 90 ppb V (with no filtration).

**Table 3b-2. Removal of Vanadium by Different Precipitants at Different Doses and pH Ranges**

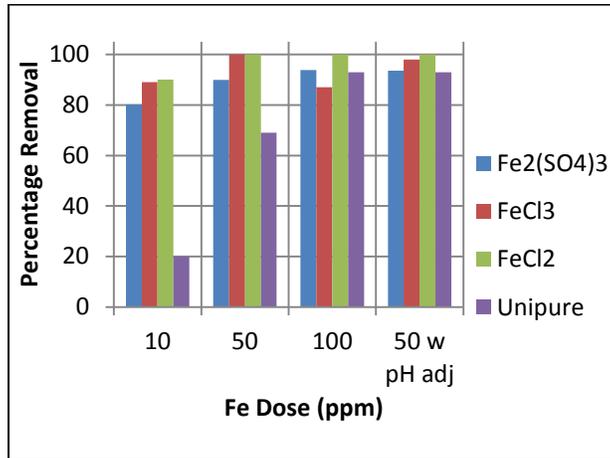
Jar	Experimental Conditions	V (ppb)	$\text{Fe}_2(\text{SO}_4)_3$	$\text{FeCl}_3$	$\text{FeCl}_2$	Unipure
1	Only ETL	Total	90	87	86	89
		Dissolved	79	79	85	88
2	MilliQ water+ 50 Fe ppm	Total	<1.0	<1.0	<1.0	<1.0
		Dissolved	<1.0	1.1	<1.0	<1.0
3	ETL+ 10 ppm Fe	Total	18	9.9	8.5	71
		Dissolved	<1.0	<1.0	<1.0	<1.0
4	ETL+ 50 ppm Fe	Total	9.2	<1.0	<1.0	28
		Dissolved	<1.0	<1.0	<1.0	<1.0
5	ETL+ 100 ppm Fe	Total	5.6	11	<1.0	6.5
		Dissolved	<1.0	<1.0	<1.0	<1.0
6	ETL+ 50 ppm Fe + pH adjustment	Total	5.8	1.4	<1.0	6.1
		Dissolved	<1.0	<1.0	<1.0	<1.0

Focused testing was performed with two different vanadium concentrations. Experiments were performed with  $\text{Fe}_2(\text{SO}_4)_3$ , since the Whiting Refinery already has a permit for the use of this chemical, and there was no difference in the percentage of vanadium removal between the iron salts, as discussed before. The effectiveness of  $\text{Fe}_2(\text{SO}_4)_3$  for vanadium removal was tested with 10, 20, 40, and 50 ppm of iron dosages to remove 250 ppb of total vanadium, and 20, 50, and 75 ppm of iron dosages to remove 500 ppb of total vanadium concentration. The CE samples were spiked with a standard  $\text{V}^{+5}$  solution ( $\text{NH}_4\text{VO}_3$  in 2%  $\text{HNO}_3$ , Spex Certi Prep, New Jersey) to maintain constant 250 ppb and 500 ppb of vanadium concentrations throughout the experiments.

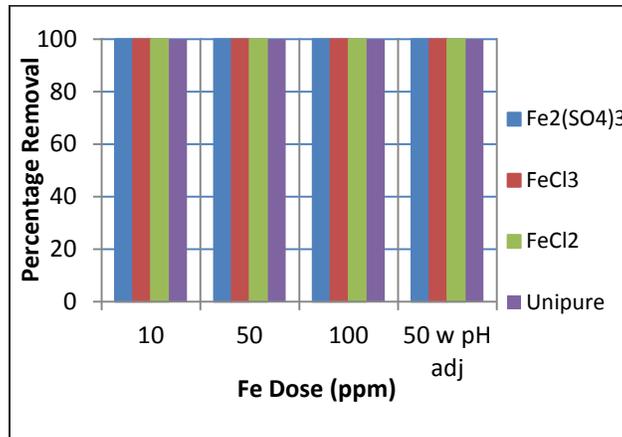
The experimental data present a consistent record of the effectiveness of ferric sulfate in removing 250–500 ppb of vanadium (Figure 3b-3). This graph also illustrates that a 10–20 ppm of iron dosage successfully removed 91–99% of vanadium from the tested CE that contained 250–500 ppb. The iron concentration of 10–20 ppm also satisfied the target vanadium effluent limits. Figure 3b-4 depicts metal removal efficiencies versus iron dosage in the CE samples. The 10–20 ppm of iron dosage also removed 60–73 % of the arsenic and 50–55% of the selenium. As shown in Figure 3b-4, vanadium removal was ~100% after filtration at all tested iron doses. The 10–50 ppm of iron dosage *did not* appear to create any additional problems with regard to the Whiting Refinery discharge limits (the facility has a 1 ppm iron NPDES discharge limit), since the measured iron concentrations in the supernatant were 300–720 ppb before filtration and 20–56 ppb after filtration (Figure 3b-4). Increasing or decreasing the pH of the reaction mixture did not change the percentage of vanadium removal.

Although significant fluctuations were observed in the characteristics of the CE during the treatability study, the variations in the CE composition had no significant impact on the vanadium removal efficiency of the iron salts. Co-precipitation with ferric sulfate at a 10–20 ppm of iron dosage consistently provided effluent that was below the target concentrations. This might be due to the capability of ferric salts to remove heavy metals regardless of their form (i.e., soluble, complexed, chelated, colloidal, emulsified, and particulate) because of the involvement of several different removal mechanisms, including adsorption, co-precipitation, encapsulation, complexation, ion exchange, and so forth (17).

**Figure 3b-2. Percentage of Vanadium Removal before (a) and after (b) Filtration**

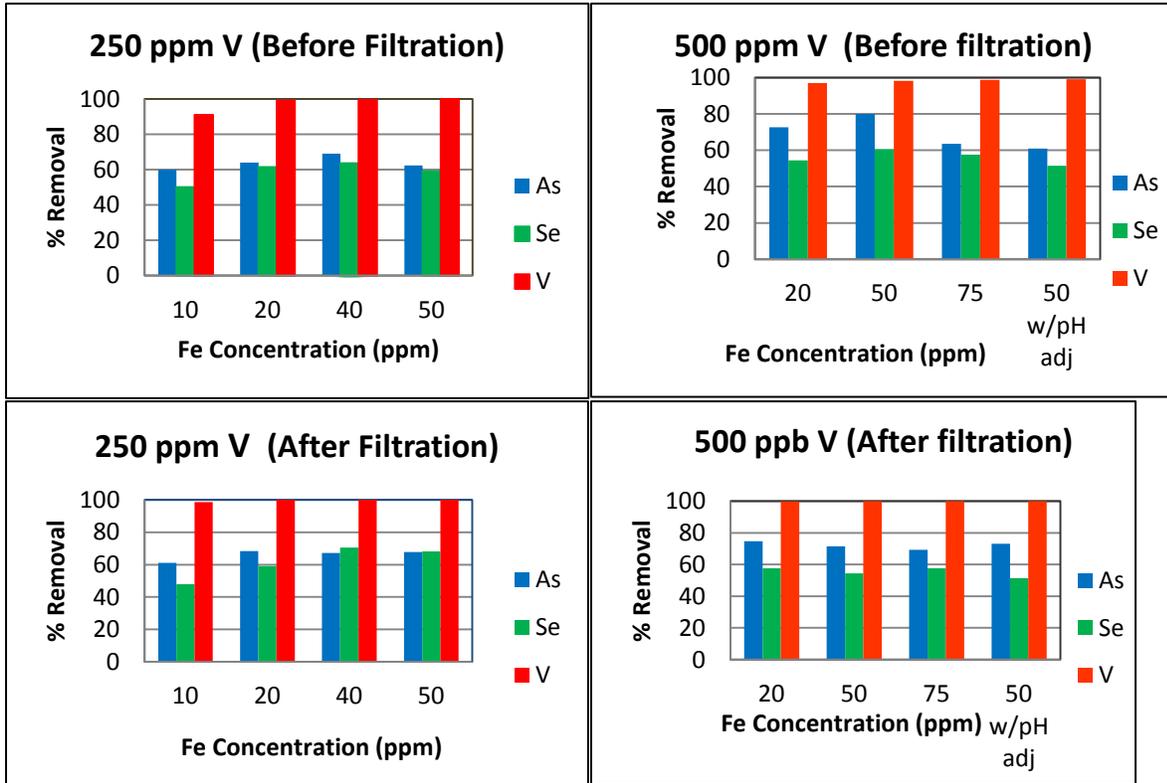


(a)

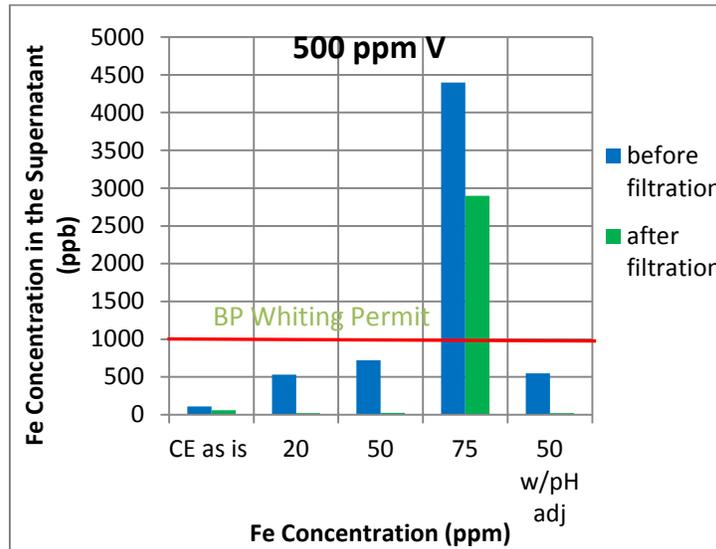
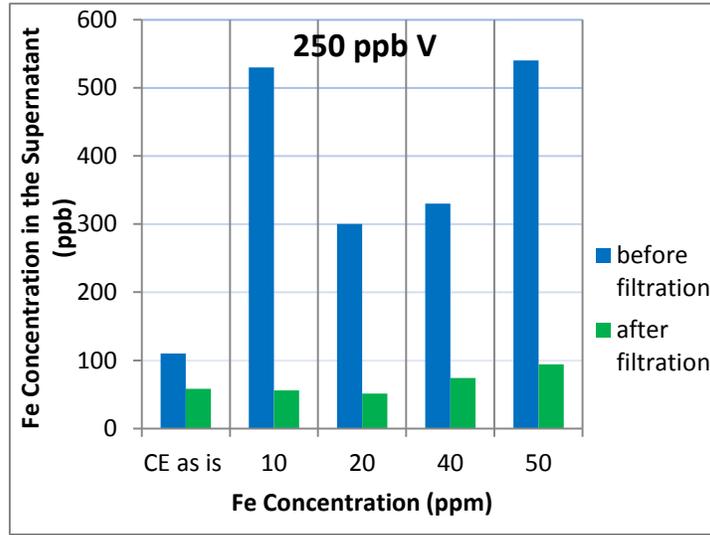


(b)

Figure 3b-3. Effectiveness of  $\text{Fe}_2(\text{SO}_4)_3$  in Vanadium, Arsenic, and Selenium Removal



**Figure 3b-4. Iron Concentration in the Supernatant**



**Mercury Removal**

*Screening Experiments*

Initial screening experiments were performed with two commercially available products: MetClear and Nalmet. These products are marketed for heavy metal removal — especially mercury — from wastewater. However, the initial experiments provided inconclusive results for the following reasons:

1. The higher method detection limits (5 ppt) of Lab A did not allow for any comparison of time 0, method blanks, and treated samples.
2. The obtained test results were inconsistent. For example, mercury removal with the second highest precipitant concentration was lower than that of the lower precipitant concentration.

The method blanks were prepared by using CE as-is samples with no precipitant to identify mercury loss/removal during the precipitation experiments. Method blanks were carried through the complete precipitation procedure. Since the precipitation experiment protocol involved more than one step, method blanks at each step were taken and analyzed as follows: (a) time = 0 sample, (b) after 30 minutes of settling, and (c) after filtration. MilliQ water also was sent through the same process to determine any mercury contamination during the experiments.

The lab test results from Lab B showed that mercury loss/removal in the method blank samples was 41% after settling and 94% after filtration. A second set of experiments was designed and conducted to identify the causes of these losses, especially mercury loss after settling. Samples were taken according to the protocol described above, as well as after 30 minutes of mixing to determine any loss before settling. This second set of method blank experiments was performed with five replicates to obtain statistically validated data, such as the t-test. In this second set, experiments were conducted in closed jars to eliminate or minimize mercury loss during the experiments (open jars were used for mixing during the first set of method blank experiments). Table 3b-3 summarizes the mercury loss/removal in the method blank samples. Test results for CE as-is (time = 0) and CE after mixing were not statistically different (per the t-test). However, 35% of the mercury was removed after settling. The mercury removal was 75% after filtration, since most of the mercury was in particulate/colloidal form. The test results obtained from these experiments are important. Without any addition of precipitant, the mercury removal was 75% at the end of the precipitation experiments. Method blanks must be involved in each precipitation experiment, since the mercury loss/removal is wastewater-specific and dependent on the particulate mercury concentration in the CE/ETL samples.

**Table 3b-3. Mercury Loss/Removal at Method Blank Samples**

Sample	Avg. Hg (ppt)	St. Dev.	% St. Dev.	% Hg Loss/Removal Based on Average Test Results	
CE as-is (time = 0)	2.75	0.45	16%	Not applicable	Test results are not statistically different
CE after mixing	2.64	0.44	16%	4%	
CE after settling	1.72	0.08	5%	37% 35%	with respect to time = 0 After mixing
CE after filtration	0.66	0.06	9%	75% 62%	with respect to time = 0 After settling

The second set of screening experiments was performed with four precipitants, as shown in Figure 3b-5. Nalmet and MetClear were retested to determine their effectiveness in removing mercury from the CE samples. Sulfide precipitation is one of the most frequently applied treatment methods for removal of mercury from industrial wastewaters. To achieve complete mercury removal, the molar ratio of added sulfide-to-mercury ranged from  $1 \times 10^6$  to  $10 \times 10^6$  during the precipitation experiments, which was higher than that of the suggested 100 micromoles of sulfide per liter ( $3.3 \times 10^6$  sulfide-to-mercury ratio) (14).

Mercury precipitation experiments also were performed with  $\text{Fe}_2(\text{SO}_4)_3$ , since the Whiting Refinery has a permit for the use of this chemical in a secondary clarifier, and higher vanadium removal was obtained with the use of ferric salts. Because a high precipitant (ligand)-to-metal dosage is typically required (18) to achieve low levels of heavy metals in the wastewater, higher dosages of tested precipitants also were used to precipitate low ppt Hg levels in the CE. No pH adjustments were done, since the reaction mixture pH for MetClear and Nalmet were within the vendors' suggested optimum pH range.

The addition of precipitants at the tested concentration ranges without subsequent filtration did not improve the mercury removal (Table 3b-4). The obtained test results were the same as those for the method blanks that went

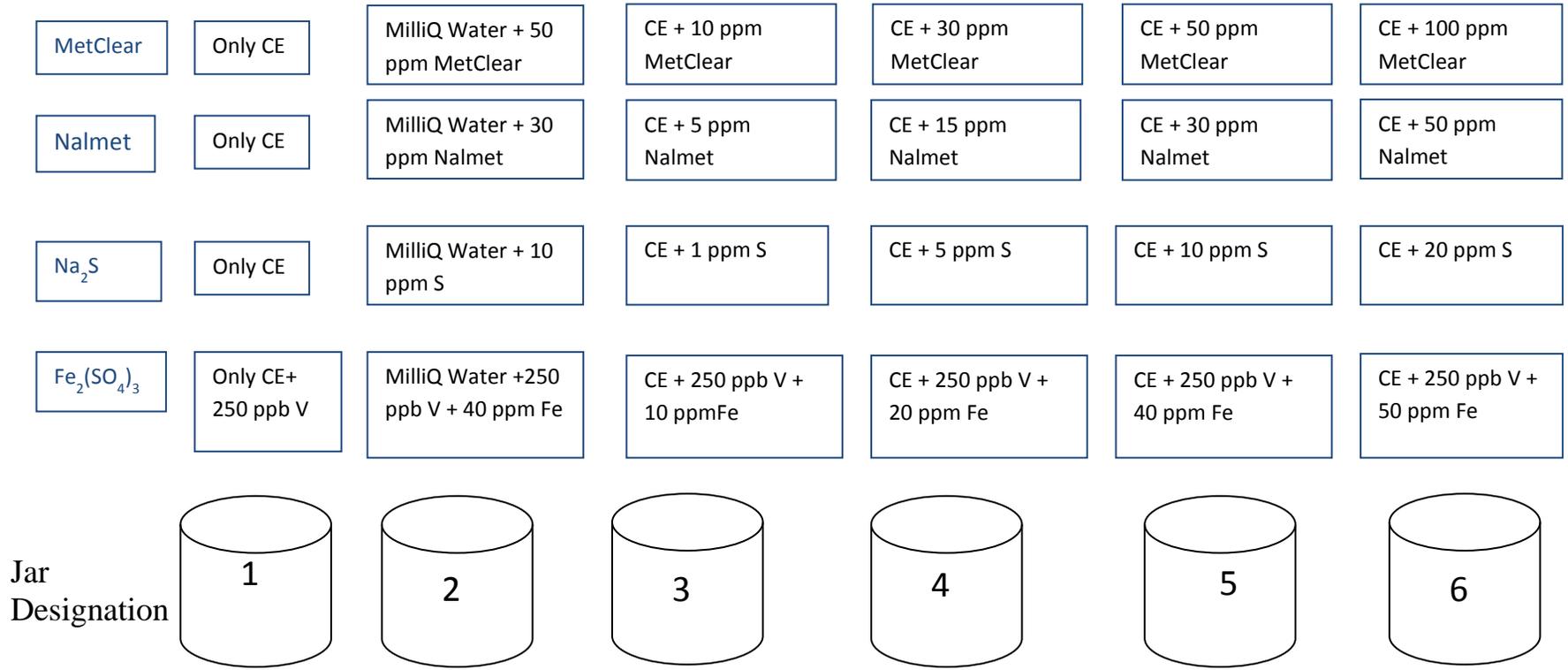
through the same treatment. The residual mercury concentrations did not meet the target effluent concentrations (1.3 ppt). In addition, even higher concentrations of these products failed to meet targeted mercury effluent limits. Furthermore, the purity of these products mostly interfered with the effectiveness of the precipitants to remove metal. All of the tested precipitants, except Nalmet, contained mercury (0.5–16.4 ppt). Among the four tested precipitants, Na<sub>2</sub>S and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> had the highest mercury concentrations — 2.5 and 16.4 ppt Hg, respectively. It is difficult to draw any conclusions about the performance of these precipitants, because the impurities in the ACS-grade chemicals masked the effectiveness for mercury removal.

However, when filtration (0.45 μm pore size) was employed, mercury removal was significantly improved in all of the tested precipitants (Table 3b-4). Both MetClear and Nalmet removed ~100% of mercury after filtration.

**Table 3b-4. Screening Test Results for Mercury Precipitation**

Jar	Hg Concentration (ppt)				
		MetClear	Nalmet	Na S <sub>2</sub>	Fe (SO) <sub>4 3</sub>
1	Total	1.65	1.87	2.07	1.17
	Dissolved	<0.5	<0.5	<0.5	0.39
2	Total	0.51	<0.5	2.75	16.4
	Dissolved	<0.5	<0.5	1.41	13.8
3	Total	1.95	2.43	3.56	3.91
	Dissolved	<0.5	<0.5	<0.5	3.77
4	Total	2.42	1.92	3.62	5.8
	Dissolved	<0.5	<0.5	<0.5	4.77
5	Total	2.74	2.31	4.95	5.9
	Dissolved	<0.5	<0.5	0.67	4.32
6	Total	2.33	2.38	3.0	6.34
	Dissolved	0.77	0.61	1.27	4.72
Time = 0	Total	3.8	4.76	4.99	2.98
Time = 0	Dissolved	0.51	<0.5	<0.5	0.59

**Figure 3b-5. Treatability of Mercury by Different Precipitants at Different Doses (closed jar)**



*Focused testing*

The focused testing was performed with MetClear and Nalmet 1689 at a 50 ppm dose in triplicate samples. The obtained test results confirmed the initial screening data, which indicated that target mercury concentrations of 1.3 ppt could not be achieved by these precipitants without filtration (Table 3b-5). The reported vendor data were showing only data at ppb levels, not ppt levels (10–13). Precipitation followed by filtration was successful in achieving target concentrations of mercury. GE also reported similar test results (19), thereby confirming that a combined treatment of MetClear and microfiltration/ultrafiltration was necessary to achieve extremely low mercury effluent concentrations ( $\leq 1.1$  ppt) in refinery wastewater.

The effectiveness of commercially available precipitants also was tested for arsenic, selenium, and vanadium removal. (However, since the focus was mercury, the dose was not specifically adjusted to remove these contaminants; see Tables 3b-5 and 3b-6.) Both Nalmet and Metclear were able to remove 38% and 50% of selenium before filtration, respectively. Neither of the tested precipitants had the capability to remove arsenic. Nalmet was not efficient for vanadium removal (%7 after filtration), whereas MetClear removed 36% of vanadium after filtration at the tested dosages.

**Table 3b-5. Focused Test Results for Mercury and Other Heavy Metals Precipitation**

Experimental Conditions	Jar	Sample	MetClear				Nalmet			
			As (ppb)	Se (ppb)	V (ppb)	Hg (ppt)	As (ppb)	Se (ppb)	V (ppb)	Hg (ppt)
Only CE	1	Total	9.4	35	110	3.23	9.5	32	110	1.94
		Dissolved	9.9	35	110	0.42	9.4	22	100	0.38
MilliQ water + 50 ppm of precipitant	2	Total	<1	<1	6.3	<0.08	<1	<1	<1	0.12
		Dissolved	<1	<1	3.9	<0.08	<1	<1	<1	<0.08
CE+ 50 ppm of precipitant	3	Total	9.1	16	98	3.87	11	21	110	2.88
		Dissolved	8.8	17	76	0.17	10	17	100	0.23
CE+ 50 ppm of precipitant	4	Total	8.8	18	110	3.18	10	20	100	2.73
		Dissolved	8.3	17	79	0.10	9.6	17	98	0.18
CE + 50 ppm of precipitant	5	Total	11	18	110	2.84	9.9	19	100	2.85
		Dissolved	10	14	56	0.13	9.9	19	110	0.20
CE	Time=0	Total	11	34	115	6.98	10	33	110	5.71
	Time=0	Dissolved	10	34	110	0.33	10	32	110	0.52

**Table 3b-6. Effectiveness of Commercial Reagents in Removing Heavy Metals**

Precipitant	Percentage Removal			
	As	Se	V	Hg*
MetClear				
Before filtration	-2 ± 13	50 ± 3	4 ± 6	53 ± 8
After filtration	4 ± 9	54 ± 5	36 ± 11	98 ± 1
Nalmet				
Before filtration	-8 ± 6	38 ± 3	6 ± 5	51 ± 1
After filtration	-4 ± 2	45 ± 4	7 ± 6	96 ± 0

\*1) Percentage removal was calculated with respect to time CE t=0

2) Method loss: before filtration: 54–66%; after filtration: 94%.

#### 4. Conclusions

- A 10–20 ppm iron dose successfully removed 91–99% of vanadium from the tested CE that contained 250–500 ppb V. The vanadium removal was ~100% after filtration. The residual iron concentrations in the treated wastewater also satisfied the Whiting Refinery iron discharge limits (1 ppm).
- A 10–20 ppm iron dose also removed 60–73 % of arsenic and 50–55% of selenium.
- Treatment with iron salts offers a robust option to remove vanadium from the CE/ETL streams when the Stretford unit is on. Although disposal would be necessary for the relatively large quantities of sludge generated, this method could be implemented at the existing Whiting Refinery Plant because BP has a permit to use ferric sulfate as a settling aid in secondary clarifier. Iron co-precipitation for vanadium removal was not considered for piloting, since BP could test the effectiveness of iron co-precipitation on a split stream for a side-by-side comparison with the full-scale plant performance, if needed.
- Commercially available mercury precipitants did not perform any better than method blanks. Method losses were 54–66% before filtration and 94% after filtration. The precipitants did not remove additional mercury from the CE samples.
- Both Nalmet and Metclear were unable to remove arsenic. Although Nalmet was not effective for removing vanadium (7% after filtration), MetClear removed 36% of vanadium after filtration. Both Nalmet and Metclear had the capability to remove 38% and 50% of selenium (before filtration), respectively.
- The effectiveness of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and sulfide precipitation for mercury removal was not clear because of the higher mercury concentration in the ACS reagents. Commercial-grade reagents employed in full-scale operations also would need to be analyzed for mercury.

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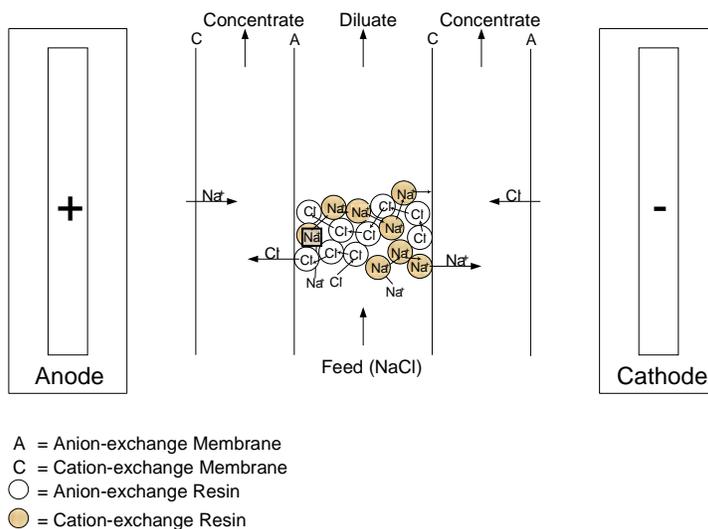
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### 3c. Electrodeionization Testing

#### 1. Introduction and Objectives

Electrodeionization (EDI) is a hybrid of the electrodialysis (ED) and ion-exchange processes. It is similar to ED in that ionic components of a solution are separated through the use of semipermeable ion-selective membranes situated between two electrodes. For both ED and EDI, an electrical potential is applied between the electrodes, causing the cations to move toward the cathode and the anions to move toward the anode. The anion- and cation-permeable membranes are spaced in an alternating pattern, forming cells of concentrated and dilute salts. The main difference is that the dilute compartments of an EDI reactor are filled with ion-exchange resin either in a loose form or in a wafer form, as shown in Figure 3c-1 for an example feed (NaCl). This testing used ion-exchange resins in a wafer form that was developed at Argonne. The ion-exchange resin is used in EDI to facilitate ion transfer in low ionic strength solutions. It is continuously regenerated electrochemically by hydrogen and hydroxide ions produced by water electrolysis splitting on ion-exchange membranes as well as ion-exchange resin beads (1).

Figure 3c-1. EDI Reactor Schematic



In this testing, the ion-exchange resins used in the wafers were chosen to improve selectivity for mercury and vanadium. The objective of this testing was to determine the maximum mercury and vanadium removal from ETL/CE that could be obtained by EDI at typical operating conditions.

#### 2. Materials and Methods

##### a. Reagents

The preliminary screening runs used a surrogate feed that was made of sodium sulfate (anhydrous, low nitrogen), sodium chloride (ACS reagent grade), and a vanadium standard in MilliQ water (18 MΩ.cm resistivity). The vanadium standard added to the surrogate feed was in the V<sup>+5</sup> form (NH<sub>4</sub>VO<sub>3</sub> in 2% HNO<sub>3</sub>, Spex Certi Prep, New Jersey). The electrode rinse solution was made of sodium sulfate (anhydrous, low nitrogen) in MilliQ water, and the initial concentrate solution was made of hydrochloric acid (trace metal grade) in MilliQ water.

During the actual testing on CE, the wastewater was spiked with a standard  $\text{Hg}^{+2}$  solution (10 ppm  $\text{Hg}^{+2}$  in 5%  $\text{HNO}_3$ , Spex Certi Prep, New Jersey) to ensure a 10 ppt mercury concentration. For the last run, the wastewater was also spiked with a standard  $\text{V}^{+5}$  solution ( $\text{NH}_4\text{VO}_3$  in 2%  $\text{HNO}_3$ , Spex Certi Prep, New Jersey) to ensure a 250 ppb vanadium concentration. The electrode rinse solution was made of sodium sulfate (anhydrous, low nitrogen) in MilliQ water, and the concentrate solution was made of either sodium chloride (ACS reagent grade) or hydrochloric acid (trace metal grade) in MilliQ water.

#### **b. Water Samples**

The Whiting Refinery's CE was used for the testing. Samples were collected by using the "clean hands-dirty hands" procedures specified in EPA Method 1669 (2). Upon receipt, the wastewater was stored in a 4 °C cold room before use. Two different batches of wastewater were tested. Based on the results of the Shelf-life Study (see Chapter 2 and Appendix 1), the wastewater was used for up to 5 days after collection from the refinery. This approach was taken to ensure that changes in mercury and vanadium speciation and composition would be negligible.

#### **c. Experimental Equipment**

Prior to use, all equipment was cleaned by using the methods outlined in EPA Method 1631E and EPA Method 200.8 (3, 4). Specifically, the equipment was washed with laboratory soap (Sparkleen) and tap water, and then triple rinsed with MilliQ water (18 MΩ.cm resistivity). The glass tanks for the electrode rinse and concentrate were soaked in a 5% HCl (trace metal grade) acid bath overnight. The following morning, the equipment was triple rinsed in MilliQ water, brought into the clean room, and triple rinsed a second time in MilliQ water (18 MΩ.cm resistivity) before use. The EDI system, excluding the reactor, was filled with a 5% HCl solution, which was recirculated through the system for 80 minutes. The system was drained, and MilliQ water was recirculated through the system for 1 hour.

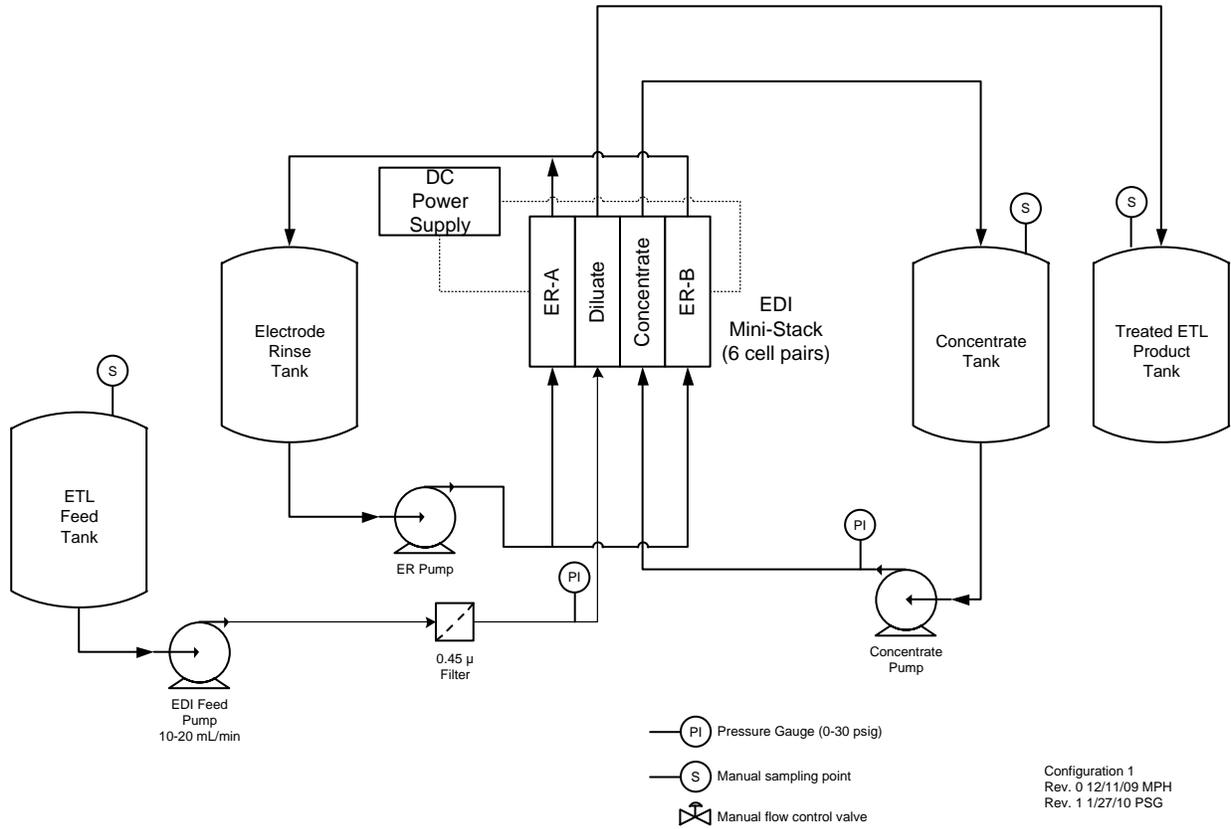
Before the testing, the CE was filtered with a series of in-line filters (5 micron, 1 micron, and 0.45 micron). Immediately prior to use, the filtered CE was spiked to a 10 ppt level with  $\text{Hg}^{+2}$  and mixed in a Teflon PFA liner placed inside a 5-gal HDPE pail with a magnetic stir plate. During this mixing, the flexible Teflon liner served to minimize the headspace above the wastewater.

An RW-EDI mini-stack with three cell pairs was assembled for the evaluation. The wafers were made of ion-exchange resins that were selected for vanadium removal. The manifold portion of the mini-stack was made of fluoropolymer (FEP or PTFE) material. Other major wastewater wetted parts included ED membranes, concentrate spacers, wafers made of ion-exchange resins, a binder, and a porosigen. To a much lesser extent, within the mini-stack the wastewater also contacted platinum-coated  $\text{TiO}_2$  electrodes, high-density polyethylene flow diffusers, and wafer gaskets made of ultra-high molecular weight polyethylene and closed cell foam.

The membranes, concentrate spacers, and wafer components used in the test stack were selected from commercial offerings that are available off the shelf. The wafers and gaskets that formed the diluate compartments inside the stack were fabricated at Argonne by using previously established methods.

The rest of the RW-EDI system is shown in Figures 3c-2 to 3c-4.

Figure 3c-2. EDI Test System for Removal of Vanadium and Mercury from Refinery Wastewaters



**Figure 3c-3. EDI Stack in the Clean Room**



**Figure 3c-4. EDI System: Power Supply and Pumps**



The RW-EDI stack used a DC power supply. Wastewater was pumped continuously from a feed tank through a 0.45 micron filter before entering the diluate chambers in the stack. Treated wastewater was collected in a separate treated water tank. Ions from the wastewater were transported across the ED membranes into the concentrate solution, which was continuously recirculated from a small storage tank (0.25–1 L) with a pump. An electrode rinse solution was held in a separate small storage tank and recirculated through separate chambers within the RW-EDI stack. The electrode rinse solution functioned as a conductive medium to allow electron flow from the stack electrodes to the rest of the stack. The components of the RW-EDI system that were wetted by the wastewater included tubing, fittings, and storage vessels. These components were made of fluoropolymer (FEP or PTFE) or borosilicate glass, as much as possible, to minimize trace metal loss from the wastewater and to prevent wastewater contamination.

#### **d. Experimental Procedure**

##### *Screening Testing*

The initial screening testing was conducted in an Argonne wet chemistry laboratory. It focused on the effect of wafer composition and CE flow rate on  $V^{+5}$  removal. The wafer compositions, feed flow rates, and other process conditions used for testing were selected on the basis of past experience with similar feeds.

Prior to each screening test, the mini-stack's resin wafers were preconditioned with a standard  $V^{+5}$  solution in order to saturate the wafers. During the testing, the surrogate CE feed was filtered through a 0.45  $\mu\text{m}$  in-line filter to remove particulates that may interfere with stack operation.

Three different types of resin wafer compositions were tested: a cation-excess resin wafer (1.3:1.0 cation: anion), an anion-excess resin wafer (1.0:1.3 cation:anion), and an equal-capacity (equal amounts of cation and anion) resin wafer (1.0:1.05 cation:anion). A 6-hour run was made with each wafer composition by using surrogate CE feed containing 350 ppb of  $V^{+5}$ , 300 ppm of  $\text{SO}_4^{2-}$  as sodium sulfate, and 500 ppm of  $\text{Cl}^-$  as sodium chloride. The surrogate feed was fed once through the EDI stack at a flow rate of 10 mL/min. The electrode rinse consisted of 25 g/L of  $\text{Na}_2\text{SO}_4$  and was recirculated at 20 mL/min through each compartment (cathode and anode). The concentrate solution was made of 1 g/L of hydrochloric acid, and it also was recirculated at a flow rate of 20 mL/min. The voltage supplied to the stack was 26 V DC. Based on these short screening tests, the best performing wafer composition was selected for the remainder of the testing.

The effect of the surrogate feed flow rate also was evaluated with two screening tests. The best performing wafer composition was used for the EDI stack. The run conditions for each test were the same as for the wafer screening tests, with the exception of the surrogate feed flow rate, which was varied. The two feed flow rates studied were 4.7 and 2.9 mL/min. The EDI stack operated for 48 hours at each feed flow rate. Performance information from these tests was used to determine the best feed flow rate to use for the rest of the testing.

##### *Clean Room Blanks*

After the initial screening, the EDI system was cleaned by using the methods outlined in EPA Method 1631E and EPA Method 200.8 (3, 4) and moved into Argonne's Class 100 clean room, where the testing on actual CE was conducted. Prior to testing the EDI process with the CE, equipment and method blanks were run. For the equipment blank, MilliQ water (18  $\text{M}\Omega\cdot\text{cm}$  resistivity) was run through the empty system with no power applied to the EDI stack. Samples were taken to determine whether the equipment was contributing mercury or other metals of interest. The method blank used surrogate feed that was prepared with the same components and concentrations as that for the screening testing. This surrogate feed, which was made with 350 ppb of  $V^{+5}$ , was then spiked to a level of 10 ppt of  $\text{Hg}^{+2}$  with freshly prepared spike solution. The surrogate feed was run through the system with no power applied to the EDI stack. The feed and diluate outlet (stack effluent) were sampled to determine the gain or loss of mercury, vanadium, arsenic, and selenium.

##### *Performance Testing with Actual Clarifier Effluent*

The performance testing, conducted in Argonne's Class 100 clean room, used CE from the Whiting Refinery and focused on the removal of both  $V^{+5}$  and  $\text{Hg}^{+2}$ . Arsenic and selenium removal efficiencies were also evaluated. The

EDI stack used the optimal wafer composition, as determined from the screening testing. The CE feed flow rate to the stack was the rate that provided the best performance during the screening testing.

Two different runs were made with CE that had been in-line filtered with a 0.45 µm filter and then spiked to a level of 10 ppt of Hg<sup>+2</sup>. For the second run, additional spiking with V<sup>+5</sup> was performed with freshly prepared spike solution, so that the total level of V<sup>+5</sup> in the CE feed was at 250 ppb. The level of 250 ppb of vanadium was chosen to ensure consistency with that done with the adsorption isotherms. Unlike the screening runs, the wafers were not saturated with vanadium before the start of the performance tests. Instead, the performance tests were conducted for a longer time period so that steady-state conditions were obtained, thereby eliminating the need for wafer saturation prior to testing.

For both runs, the CE feed was fed once through the EDI stack at a flow rate of 4.7 mL/min. The electrode rinse, which consisted of 25 g/L Na<sub>2</sub>SO<sub>4</sub>, was recirculated at 20 mL/min through each compartment (cathode and anode). For the first run with CE, the concentrate solution was made of 5 g/L sodium chloride. The second run used a concentrate solution that consisted of 1 g/L hydrochloric acid. In both runs, the concentrate solution was recirculated at a flow rate of 20 mL/min. The voltage supplied to the stack was 26-V DC for both runs. The first run lasted for 43 continuous hours, and the second run lasted for 41.5 continuous hours.

#### e. Analyses

##### *Initial Screening*

For each screening test, samples were taken of the surrogate CE feed, the EDI stack effluent, and the concentrate solution at 1 hour intervals. The pH and conductivity of these samples were measured at Argonne. These samples were then sent to a certified independent lab for analysis of total vanadium by using EPA Method 200.8. A mercury analysis was not conducted on the initial screening samples.

##### *Performance Testing*

Prior to the performance testing with CE from the Whiting Refinery, the pH of the untreated CE was measured at Argonne. Additionally, the CE used was sampled and sent to a certified independent lab for analysis of the following parameters:

Total and dissolved mercury	EPA 1631e
Total and dissolved vanadium	EPA 200.8
Cations: As, Cu, Fe, Pb, Mn, Se, Si, Zn	EPA 6010/200.7
Anions: Cl <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup>	EPA 300.0
Fluoride	EPA 340.1
Total hardness as CaCO <sub>3</sub>	EPA 130.2

For each performance test, including the equipment and method blank tests, samples were taken of the CE feed, the effluent treated by the EDI stack, and the concentrate solution at regular intervals. The pH and conductivity of these samples were measured at Argonne. The wastewater samples that required mercury analysis were sent to Lab B. The acidic concentrate tank samples that required mercury analysis were sent to Lab A Laboratory. All samples that required arsenic, selenium, and vanadium analysis also were sent to Lab A Laboratory. The total mercury analysis at both labs was conducted by using EPA Method 1631e. The total vanadium, arsenic, and selenium analysis was performed as specified by EPA Method 200.7/200.8.

### 3. Results and Discussion

#### a. Screening Testing

The screening testing focused on identifying the wafer composition and feed flow rate that would provide the best vanadium removal from a surrogate feed solution. From this testing, it was determined that an equal capacity wafer with a cation-to-anion ratio of 1.0 to 1.05 provided the best vanadium removal performance. This testing also established that a 5 mL/min feed flow rate was the optimum in terms of vanadium removal and process flux (gal/m<sup>2</sup>/hr).

#### b. Clean Room Blanks

The results of the EDI system equipment blanks are presented in Table 3c-1. For the most part, mercury, arsenic, and selenium could not be detected in the feed, diluate effluent, or concentrate. Although a significant amount of vanadium (32 ppb) could initially be seen in the diluate effluent, over time it was reduced to a level below the analytical method's detection limit of 1 ppb. Most likely this vanadium was leaching from the wafers inside the EDI stack, which previously had been saturated with vanadium before each screening study.

**Table 3c-1. EDI System Equipment Blanks**

Sample No.	Elapsed Time (hr.)	Hg (ppt)	As (ppb)	Se (ppb)	V (ppb)
Feed					
Initial	-	<0.08	<1	2.8	<1
Diluate (effluent)					
1	0	0.46	<1	<1	32
2	0.75	<0.08	1	1	6.3
3	1.25	<0.08	<1	1	<1
Concentrate					
Initial	-	<0.08	<1	1	<1
1	0	0.19	<1	1	<1
2	0.75	<0.08	1.8	1.8	<1
3	1.25	<0.08	<1	<1	<1

In order to determine the amount of loss during the method, a set of blanks were done with surrogate CE feed that had been spiked to a level of 350 ppb V<sup>+5</sup> and 10 ppt Hg<sup>+2</sup>. The results, summarized in Table 3c-2, showed a significant loss for both mercury and vanadium (90% and 27.5%, respectively). Although further study is needed for confirmation, it is possible that the dissolved mercury and vanadium may be attaching to the ion-exchange resins in the wafers inside the EDI stack.

#### a. Performance Testing

Two different tests were conducted in Argonne's Class 100 clean room with CE that had been filtered with a 0.45 µm filter and spiked with 10 ppt Hg<sup>+2</sup>. The first test (BP-EDI-8) used a concentrate solution made with 5 g/L sodium chloride. Previously during the screening testing, a 1 g/L HCl solution had been used for the concentrate. The results of this first test, summarized in Table 3c-3, showed that the diluate effluent was unable to meet the upcoming mercury target limit of 1.3 ppt. A conclusion about vanadium removal could not be made because of the low vanadium concentration in the feed. During the first few sampling events, it appeared that vanadium was leaching from the wafer from the previous vanadium saturation that occurred before the screening tests. The arsenic and selenium removal results from this test are shown in Table 3c-4. The process was able to remove a significant amount of arsenic. Selenium, however, appeared to be added to the CE from the system, which was not seen during the equipment blank testing.

**Table 3c-2. EDI Method Blank Summary**

<b>Sample No.</b>	<b>Elapsed Time (min.)</b>	<b>Hg (ppt)</b>	<b>V (ppb)</b>
Feed			
Initial	0	8.51	400
1	24	7.85	400
2	48	7.38	410
3	72	7.48	390
4	96	7.67	390
5	120	7.86	390
Avg.		7.79	397
Std. dev.		0.40	8
Diluate effluent			
Initial	0		
1	24	0.44	270
2	48	0.76	280
3	72	0.79	280
4	96	0.93	300
5	120	0.98	310
Avg.		0.78	288
Std. dev.		0.21	15
Concentrate			
Initial	0	0.14	<1
1	24	0.10	1.6
2	48	0.28	<1
3	72	0.15	<1
4	96	0.22	7.7
5	120	0.16	9.3
Avg.		0.18	4
Std. dev.		0.06	4
Method loss Feed vs. diluate Effluent		90.0%	27.5%

**Table 3c-3. CE Performance Testing (BP-EDI-8): Mercury and Vanadium Removal**

Elapsed Time (hr)	Mercury			Vanadium		
	Feed (ppt)	Diluate Effluent (ppt)	% Removal without Method Blank Applied	Feed (ppb)	Diluate Effluent (ppb)	% Removal without Method Blank Applied
2.5	8.52	2.44	71.4%	7.2	25	-247.2%
4.5	32.1	1.57	95.1%	5.8	14	-141.4%
20	6.88	2.87	58.3%	8.4	3.9	53.6%
23.5	7.64	2.65	65.3%	7.4	<1	86.5%
26	7.1	2.43	65.8%	5.6	5.1	8.9%
43	7.64	4.55	40.4%	(1)*	3.6	-

\*(1) denotes not sampled for analysis due to a lack of feed.

**Table 3c-4. CE Performance Testing (BP-EDI-8): Arsenic and Selenium Removal**

Elapsed Time (hr)	Arsenic			Selenium		
	Feed (ppb)	Diluate Effluent (ppb)	% Removal without Method Blank Applied	Feed (ppb)	Diluate Effluent (ppb)	% Removal without Method Blank Applied
2.5	3.2	<1	68.8%	7.2	7.6	-5.6%
4.5	2.9	<1	65.5%	5.8	7.2	-24.1%
20	3.8	1.5	60.5%	8.4	11	-31.0%
23.5	0.002.9	1.1	62.1%	7.4	10	-35.1%
26	2.4	1.2	50.0%	5.6	11	-96.4%
43	(1)	15	-	(1)*	13	-

\*(1) denotes not sampled for analysis due to a lack of feed.

For the second test (BP-EDI-9), the concentrate solution was switched back to the 1 g/L HCl solution that previously had been used in the screening testing. Additionally, the CE feed was spiked with V<sup>+5</sup>, so that the total vanadium was 250 ppb. As shown in Table 3c-5, changing the concentrate solution composition did not improve the mercury removal performance of the EDI stack — the upcoming target limit still was not met. This run also produced an order of magnitude higher vanadium concentration in the diluate effluent as compared with the first run with CE (BP-EDI-8). The diluate effluent averaged 180 ppb in the second run vs. 6 ppb in the first run. As shown in Table 3c-6, during this run the EDI process also partially removed the dissolved arsenic and selenium that were present in the CE, for an average removal of 30 and 39%, respectively.

**Table 3c-5. CE Performance Testing (BP-EDI-9): Mercury and Vanadium Removal**

Elapsed Time (hr)	Mercury			Vanadium		
	Feed (ppt)	Diluate Effluent (ppt)	% Removal without Method Blank Applied	Feed (ppb)	Diluate Effluent (ppb)	% Removal without Method Blank Applied
1.5	6.21	(1)	-	260	98	62.3%
18.5	5.71	2.85	50.1%	240	170	29.2%
21.5	5.87	2.73	53.5%	250	160	36.0%
24.5	6.12	2.71	55.7%	240	190	20.8%
41.5	6.15	3.1	49.6%	250	190	24.0%

(1) Sample bottle was broken in transit.

**Table 3c-6. CE Performance Testing (BP-EDI-9): Selenium and Arsenic Removal**

Elapsed Time (hr)	Arsenic			Selenium		
	Feed (ppb)	Diluate Effluent (ppb)	% Removal without Method Blank Applied	Feed (ppb)	Diluate Effluent (ppb)	% Removal without Method Blank Applied
1.5	10	5.1	49.0%	35	17	51.4%
18.5	9.3	7	24.7%	33	20	39.4%
21.5	11	5.7	48.2%	32	20	37.5%
24.5	9.5	8.8	7.4%	32	21	34.4%
41.5	11	8.7	20.9%	31	21	32.3%

In both runs, the effect of the wafer's ion-exchange resins is not clear. Both runs give indications of dissolved metals adhering to the wafer and then later possibly leaching from the wafer. Further study is needed to obtain a clear picture of the interaction of the dissolved metal ions with the ion-exchange resins in the wafer.

#### 4. Conclusions

- Effluent from the EDI system was in the 2–3 ppt range for mercury, and it did not meet the upcoming 1.3 ppt mercury target limit.
- The vanadium removal from the EDI system appeared to be dependent on the composition of the concentrate solution. The first performance run, which used 5 g/L NaCl as the concentrate solution, produced an order of magnitude lower vanadium concentration as compared with the second performance run, which used 1 g/L HCl as the concentrate solution — 6 ppb vs. 180 ppb.
- Arsenic and selenium removal also appeared to be affected by the concentrate solution composition. The arsenic levels in the first run were at roughly half of the levels seen in the second run's effluent (averaging 3.5 vs. 7.1 ppb). Likewise, the selenium levels showed a similar trend (averaging 10 ppb in the first run vs. 20 ppb in the second run). This suggests that the EDI system that used 5 g/L NaCl as the concentrate solution was more effective in removing arsenic and selenium.
- Further study is needed to determine the interaction of the dissolved metal ions with the ion-exchange resins in the wafer, so that the removal due to the process can be distinguished from the removal/gain from the wafer.

## 5. References

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4. EPA Method 200.8, Revision 5.4 (1994), "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma — Mass Spectrometry," [http://www.epa.gov/waterscience/methods/method/files/200\\_8.pdf](http://www.epa.gov/waterscience/methods/method/files/200_8.pdf), accessed 1/12/11.

### 3d. Filtration Experiments

#### 1. Introduction and Objectives

The treatability study involved the bench-scale testing of membrane filtration technologies to achieve stringent mercury and vanadium concentrations in the CE samples. A series of tests was conducted to assess the effectiveness of (a) microfiltration (MF) (GE Osmonics), (b) ultrafiltration (UF) (Koch), and (c) nanofiltration (NF) (GE Osmonics) and reverse osmosis (RO) (GE Osmonics) membranes in achieving the target mercury and vanadium concentrations in the treated wastewater.

The objective of this treatability study was to investigate the potential of filtration to treat the Whiting Refinery's CE stream and to determine its ability to meet the targeted effluent limits (mercury <1.3 ppt and vanadium < 280 ppb). The bench-scale treatability tests were designed to address the following goals:

1. To determine the capability of different membrane filtration technologies to achieve the targeted mercury and vanadium concentrations (mercury <1.3 ppt and vanadium <280 ppb) in the CE in as-is conditions;
2. To simulate the flow dynamics within the full-scale membrane unit, by using a bench-scale membrane cell unit, such as evaluate the filter and flow characteristics of membranes operating under different pressures; and
3. To investigate systematically the flux and rejection properties as a function of pressure of the tested membranes.

#### 2. Materials and Methods

##### a. Testing Equipment and Materials

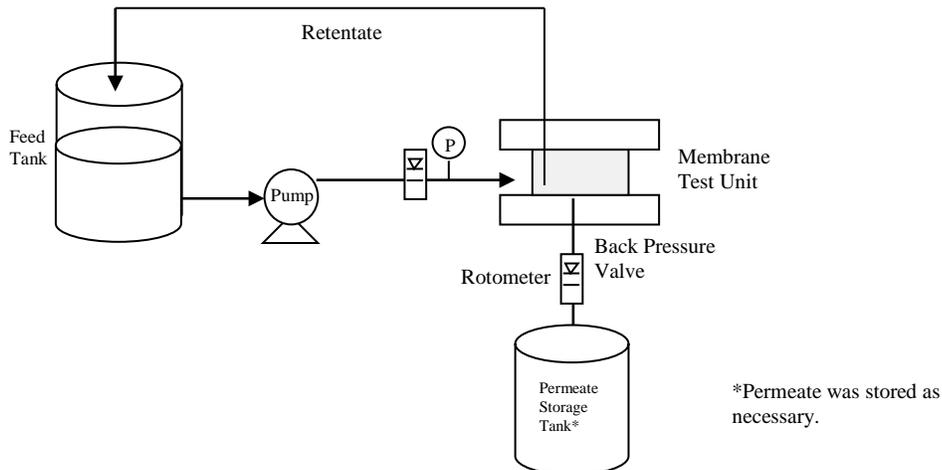
The filtration test was performed in a membrane cell (CF 042, Sterlitech), which is a lab-scale cross-flow filtration unit designed to provide fast and accurate performance data with a minimal amount of water, expense, and time (Figure 3d-1) (1, 2). The CF 042 can be used in a variety of membrane filtration applications and with a variety of membranes. The cell unit simulates the flow dynamics within the full-scale membrane unit, which can be laminar or turbulent, depending upon the CE viscosity and velocity (2). The cell body is made of delrin acetal. The top and bottom plates are made of stainless steel to accommodate pressures up to 1,000 psig. The module was connected to the pump and the measuring devices to accommodate flow and pressure differences (Figures 3d-1 and 3d-2). A high-pressure stainless-steel braided hose, rated at 2,500 psi, was used for the pump in the feed line. All other fittings were also rated for high pressure (greater than 1,000 psi). A rupture disc (pressure relief) for pressure release, rated at 935 psi, was also used to maintain safe operation of the membrane unit.

Table 3d-1 shows the properties of the flat sheet membranes used in the filtration experiments. The MF has the largest pore size (0.3  $\mu\text{m}$ ) among the tested varieties of membrane filters. Both MF and UF are typically used for the removal of suspended solids and microorganisms, as well as for turbidity and color reduction in water and wastewater treatment applications. They are also used as a pretreatment for NF/RO processes and require low operating pressure. The equipment and flat sheet membranes were cleaned before and after testing, according to the vendor's instructions (1).

**Figure 3d-1. CF042 Membrane Cell Unit (1, 2) and Photos of the Experimental Set-up**



**Figure 3d-2. Flow Diagram of the Bench-scale Membrane Test Unit**



**b. Wastewater Samples**

The treatability test was conducted on water samples taken from the Whiting Refinery’s CE. The CE samples were tested in several different batches, with each batch equal to the amount that would be used less than 1 week time period. (This assumes that changes in mercury and vanadium speciation and composition within each batch over a 1 week time period were negligible; see Chapter 2.) Lab A was subcontracted for the collection of wastewater samples at the source and for the delivery to Argonne using “clean hands-dirty hands” procedures (3). The initial screening experiments were performed with 5-gal of wastewater, and focused testing was performed with 9-gal of wastewater.

**c. Experimental Procedure**

The CE was pumped from the feed tank into the membrane module by means of a volumetric pump (Figures 3d-1 and 3d-2). Next, pressurized CE was exposed to the membrane. The permeate stream was collected into an acid-clean glass container (3) to determine the permeate ( $J_v$ ) flow rate, as well as to analyze its characteristics, including mercury and vanadium concentrations, turbidity, conductivity, and so forth.

Membrane selection and operating conditions are important issues to optimize the process technically and economically. The membrane type and operating conditions were selected based upon literature review and manufacturers’ suggestions (1, 3, 5–10).

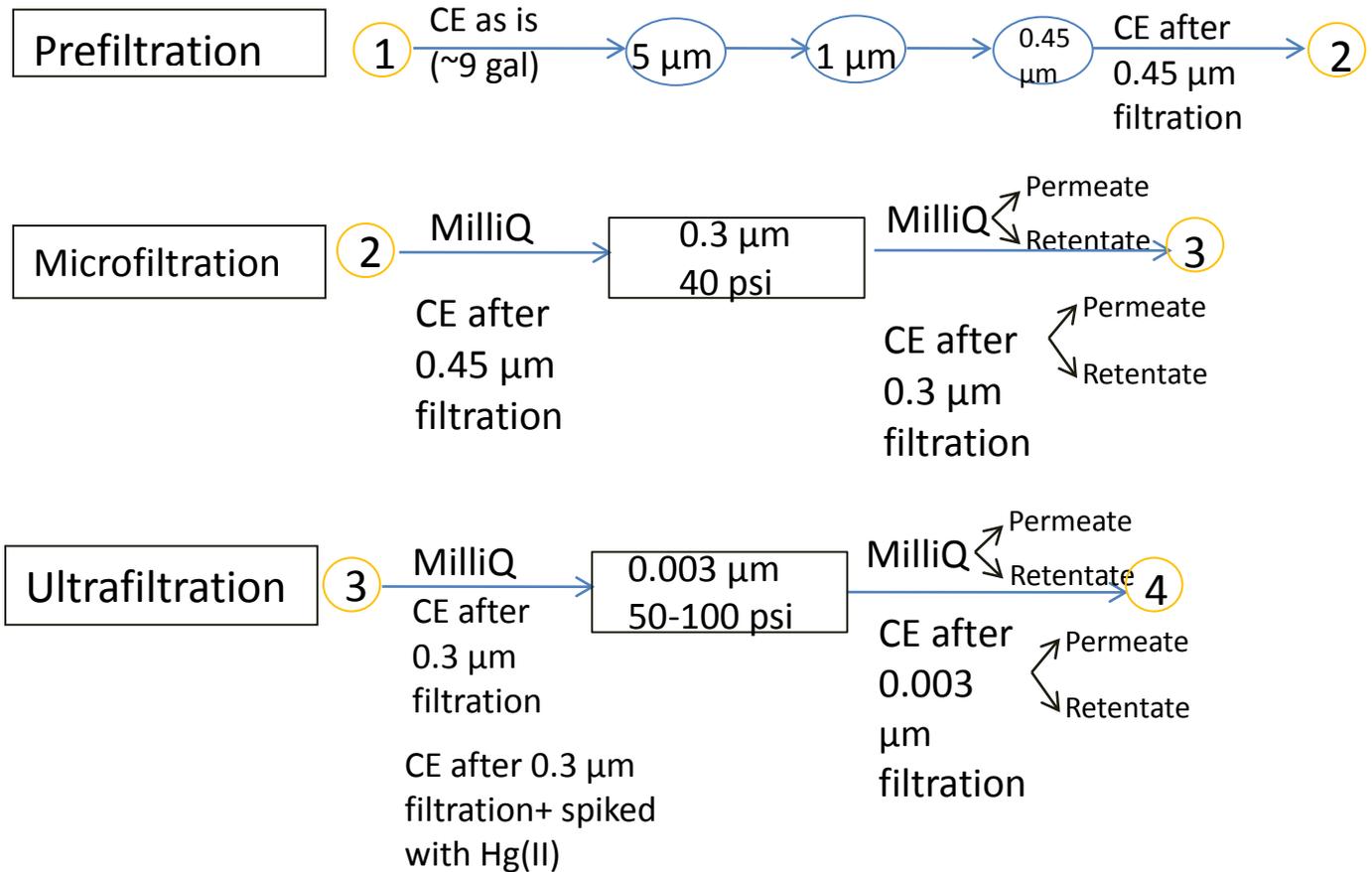
The initial screening experiments were performed with the CE “as-is;” that is, no prefiltration was done. The focused tests were performed with CE that had been filtered through 5  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 0.45  $\mu\text{m}$  with in-line-filters (Millipore GWSC5001 and GWSC10001, and Whatman Polycap GW 6714-6004). The filtration was done to enable the membrane filtration unit to run stably and successfully, since in many membrane applications one membrane process is typically followed by another for the purpose of producing high-purity water and decreasing operational problems (4). The experimental layout for the focused testing is shown in Figure 3d-3.

**Table 3d-1. Characteristics of Membrane Filters Used in the Treatability of Mercury and Vanadium**

Filtration Type/ Manufacturer	Membrane Specifications			Operating Conditions	References
	Polymer	Pore size	Designation	Pressure (psi)	
Microfiltration GE Osmonics	PVDF	0.3 $\mu\text{m}$	JX	1, 10, 30	1, 7,8
Ultrafiltration Koch	Polysulfone	0.003 $\mu\text{m}$	HFK-131	15, 30, 75	1, 3, 7
Nanofiltration GE Osmonics	Thin film	0 MWCO	DK	20, 70, 150	1, 5-10
RO GE Osmonics	Polyamide	0 MWCO	AD	50, 200, 800	1, 7, 10

Table 3d-1 also shows the operating conditions to be used for mercury and vanadium removal. The focus of this testing was to evaluate the permeate quality when treating CE with different membrane types. The feed and permeate flow rates were measured during the experiments to calculate the system recovery, which is defined as the ratio of permeate flow to feed flow. The permeate rate measurements were also used to calculate the flux of each tested membrane type under varying operating pressures (Table 3d-1). Once the system reached each of the required operating pressures, the permeate sample was collected after a 30 minute filtration run. This time was reported to be sufficient to reach constant permeate flux and rejection at pressure-driven membranes (5, 6). The permeate was collected for analysis and weighed for flux measurements. Then, the pressure was set to the next higher value, and the procedure was repeated as needed. All four membrane units were operated at a constant feed flow rate of 2.5 L/min in order to obtain the permeate required for analysis of treated wastewater in a short period of time.

Figure 3d-3. Experimental Layout for Focused Testing



The initial experiments were conducted with MilliQ water (18 MΩ.cm resistivity) to minimize or eliminate mercury contamination, as well as to determine clean membrane flux at the specified pressure range, as noted in Table 3d-1. The membrane filters used for mercury and vanadium removal were evaluated in Argonne’s Class 100 clean room (Bldg. 202, room B354) by using the Clean Room Procedures detailed in the Project Binder in Section 5a of Attachment 3.

**d. Analyses**

Prior to testing, the pH, temperature, conductivity (EPA 120. 1), turbidity (EPA 180. 1), TSS (EPA 160. 2), and TDS (EPA 160.1) of the *untreated CE* were measured at Argonne. Additionally, the CE, permeate, and retentate samples were collected and analyzed for mercury, vanadium, arsenic, and selenium to determine the removal percentage of each tested membrane process. Samples were sent to a certified independent lab for analysis of the following parameters:

Total and dissolved mercury	EPA 1631e
Total and dissolved vanadium	EPA 200.8
Cations: As, Cu, Fe, Pb, Mn, Se, Si, Zn	EPA 6010/200.7
Anions: Cl <sup>-</sup> , PO4 <sup>3-</sup> , SO4 <sup>2-</sup>	EPA 300.0
Total hardness as CaCO <sub>3</sub>	EPA 130.2
Alkalinity	EPA 310.2
Particle size distribution (light obscuration and dynamic light scattering)	SM 2560B

Each sample sent to the certified independent lab had a unique sample number. The samples were collected into clean sample bottles provided by the certified lab. A trip blank was included, as required in section B4.2 of the BP Quality Assurance Plan, Phase 2, Module 3. The sample preservation was done as specified by the analytical methods. The dissolved concentrations of mercury and vanadium in the *untreated CE* samples were determined by filtering through a 0.45 µm filter, as specified by the analytical methods.

### 3. Results and Discussion

The best operating condition for each type of membrane was determined as a function of the operating pressure. The performance of each membrane technology was also compared in terms of its ability to meet targeted effluent limits in the treated CE. Experiments were performed with relatively high volumes of water (5–9 gal) to maintain a constant mercury concentration within the system and to identify any mercury loss or contamination during the experiments. This procedure was used because of the unique nature of mercury and the low mercury concentration (low ppt) in the CE, as well as the challenges encountered when measuring low ppt levels in water and sludge samples (analytical restrictions). In addition, the membrane unit was operated in batch mode. Only samples were taken out from the system for analysis. The retentate stream was also analyzed for mercury, vanadium, arsenic, and selenium to identify any contamination (gain) or loss during operation of the membrane unit (method blank). The permeate and retentate samples from initial experiments performed with MilliQ water were also analyzed to determine any loss/contamination in the membrane unit (equipment blank).

The work for this treatability study was separated into two phases. Phase I consisted of initial screening experiments to determine which membrane filtration process(es) would be suitable for BP’s wastewater characteristics and also would allow us to meet stringent mercury levels in the treated wastewater. The objective of this testing was to evaluate the permeate quality when treating the CE with different membrane types. Important preliminary performance parameters, such as permeate flux, system recovery, and membrane fouling rates, were identified for each tested membrane type under varying operating pressures, as described in Table 3d-2. Since the experiments were performed with CE as-is with no pretreatment, the tested operating pressure values were much higher than the planned operating pressures because of the fouling characteristics of the CE (Table 3d-2). Initial experiments were performed with MilliQ water (18 MΩ.cm resistivity) to determine the clean membrane flux at the pressure range specified in Table 3d-2. The CE water flux for each tested membrane was considerably lower than that of the MilliQ water flux (Table 3d-3). The comparison of both flux data is important to understand the fouling characteristics of the CE. It has been established that the manufacturer’s reported flux values also were higher than that of the data obtained from the MilliQ run, except for the RO filters. In addition, it should be noted that no information on the tested water characteristics was included in the manufacturer’s reported data.

**Table 3d-2. Operating Conditions for Screening and Focused Experiments**

Filtration Type/ Manufacturer	Operating Conditions Pressure (psi)		
	Planned	Tested	
		Screening	Focused
Microfiltration GE Osmonics	1, 10, 30	14.7, 40, 60	40
Ultrafiltration Koch	15, 30, 75	14.7, 50, 75	50, 100
Nanofiltration GE Osmonics	20, 70, 150	300, 500, 700	
RO GE Osmonics	50, 200, 800	300, 500, 700	

**Table 3d-3. Typical Product Recovery and Flux Values for Different Membrane Applications**

Membrane	Water	Pressure (psi)	Reported Flux* (L/m <sup>2</sup> -h)	Initial Flux (L/m <sup>2</sup> -h)	% Reduction in Initial flux	% Recovery Rate <sub>initial</sub>	Reported % Product Recovery [(7)]
Microfiltration	MilliQ CE	40 40	221 @ 30 psi	38 11	70%	35	94-98
Ultrafiltration	MilliQ CE	50 50	781 @50 psi	34 9	73%	30	70-80
RO	MilliQ CE CE CE	300 300 500 700	25 @ 800 psi	39 6 196 12	85%	56 20 45 87	70-85
Nanofiltration	MilliQ CE CE CE	300 300 500 700	37 @100 psi	29 13 31 14	55%	49 31 41 51	80-85

\* Manufacturers' reported flux

Operating conditions and water quality data for the tested membrane technologies are summarized in Tables 3d-4 to 3d-7. The performance of four types of membranes, MF, UF, NF, and RO, were compared to assess their ability to meet the more stringent heavy-metal limits — especially for mercury. Achieving the <1.3 ppt Hg target in the treated water was one of the most significant requirements in the membrane filtration experiments. The MF and UF processes were very successful in achieving the required discharge criteria for mercury (Tables 3d-4 and 3d-5). It should be noted that the percentage of removal for MF was calculated based on the assumption that the initial mercury concentration was 5.95 ppt. This assumption was necessary because of a large discrepancy in the test results of two CE t = 0 samples (16.3 and 2.71 ppt). The discrepancy might have occurred because of variations in the characteristics of the collected samples. However, the test results for two retentate samples were 5.94 ppt and 5.96 ppt. The retentate samples were basically the same as the t = 0 samples, since no contamination and losses were detected during the operation of the membranes, as shown in Tables 3d-4 to 3d-7.

Both NF and RO also were able to meet the target mercury concentration when operated at lower pressure values (300 psi) (Tables 3d-6 and 3d-7). The initial screening data also indicated that the RO and NF membrane processes were necessary to remove dissolved heavy metals. In addition, it should be noted that the vanadium concentrations shown in Table 3d-6 are 10 times lower than those reported in Tables 3d-4, 3d-5, and 3d-7, even though the same wastewater was used for the NF experiments.

Operating pressures had a significant effect on NF and RO flux and fouling rates, as well as on permeate quality. The NF and RO flux and fouling rates increased significantly with an increase in pressure. No pressure drop occurred during the operation of the membranes that would suggest membrane breakage; the pressure was very stable throughout the experiments. Also, no water leakage was observed from the system — the volume of water at the beginning of the experiments was the same as the sum of the volumes of collected samples and retentates. Based on these observations, it was concluded that low permeate quality is not dependent on membrane operation or failure, but presumably is related to the fouling characteristics of the CE water that was tested. From the particle size analysis of the “CE as-is” samples provided in Table 3d-11, it can be seen that the mean particle size is 1.1  $\mu\text{m}$  and that 95% of the particles are  $<1.7 \mu\text{m}$ . Therefore, it can be concluded that the CE that had  $\sim 1,000$  ppm of dissolved solids (see Chapter 2) and an average of 15 ppm of TOC (BP’s historical data) contained high concentrations of colloidal particles that covered a wide size range — from a few nanometers to a few micrometers. Winfield (1979) reported that dissolved colloidal materials ( $<5 \mu\text{m}$ ) in secondary effluent wastewater contributed significantly to RO membrane fouling (12). Severe fouling was observed when the small colloids (75 nm) were present along with natural organic matter and salts in the surface water (13). In this treatability study, the RO and NF membranes were fed CE potentially containing a high concentration of colloidal particles, which most likely contributed to the observed fouling.

Furthermore, there is also the possibility that operation of membranes at high pressures might impact the particle morphology. It has been reported that excessive pressure can lead to aggregate break-up, which may result in reduced rejection (13). In another study, Sioutopoulos et al. (2010) reported that the presence of a complicated shear field during the RO operation is most likely to affect the size distribution of the iron oxide particles, as well as their deposition and detachment pattern on the membrane surface (14). In our case, the particle-associated mercury may have become detached from the particles and then dissolved and released as such into the permeate. It should be noted that dissolved mercury (MW = 200 g/mole) is small enough to pass through the RO and NF membranes. This might explain the high mercury concentrations in the six samples collected after operation of the RO and NF membrane filters.

In our tests, the NF and RO flux and fouling rates of the membranes increased significantly with an increase in pressure. This finding also has been reported by Zhu and Elimelech (1997) (15). High operating pressure leads to high convective flow on the membrane surface and high permeate flux rates. This might be the cause of rapid solids accumulation and concentration polarization on the membrane surface, which in turn hinders the membrane permeability (15). The accumulation of solids or the adsorption of particulates on the membrane surface might change the membrane surface characteristics, presumably due to following mechanisms (16–19):

- a) Poly-dispersity in particle size distribution causes an increase in cake layer resistance.
- b) Concentration polarization produces a hindered back diffusion. The convective flow brings the solute toward the membrane surface, while Brownian diffusion and shear-induced diffusion transport the solute back to the bulk fluid. However, the formation of a cake layer restricts the back diffusion of smaller solutes. Therefore, the concentration of the solute increases at the membrane surface (concentration polarization).
- c) The adsorption of particulates on the membrane surface results in narrower membrane pores.
- d) The decrease in mass transport by the imposed hindrance of the fouling partitions causes a higher diffusion of solutes across the membrane, and hence a significant increase in permeate concentration. This has been seen even with high-molecular-weight (MW) solute plastic additives (16).

- e) Depending on the type of membrane and wastewater characteristics, variations in rejection are the result of concentration polarization, or a combination of concentration polarization and electrostatic effects.
- f) Changes in the membrane characteristics, such as hydrophobicity, can also change the partitioning and rejection of hydrophobic/hydrophilic compounds.

Based on the information obtained from literature, the low permeate quality and significant decline in flux rates obtained from our RO and NF testing can be explained as follows:

1. Operation of the membranes at high pressures (300–700 psi) resulted in high convective flow and rapid accumulation of a cake layer on the membrane surface.
2. Operation of the membranes at high pressures created a shear field on the membrane surface, which most likely impacted the particle size distribution of the CE water and the detachment/attachment pattern of particles on the membrane surface. High pressure also probably resulted in aggregate break-up in the wastewater. In that case, particle-associated mercury may have been detached from the particles and become dissolved. The accumulation of dissolved mercury on the membrane surface, as well as the subsequent release into the permeate, produced higher mercury concentrations than expected.
3. Operation of the RO and NF membranes at high pressures for the treatment of CE “as-is,” which presumably contained a high concentration of colloids, resulted in severe fouling of the membranes. The cake layer formation, which was due to the adsorption of particles and the resultant concentration polarization, caused a sharp decline in the amount of permeate, and hence low flux rates were seen at the end of 1–3 hours of operation.

A similar impact of fouling on permeate quality also has occurred with organics, such as plastic additives with molecular weight ranges of 78–266 g/mole, endocrine disruptors such as hormones, pharmaceutical compounds, and humic acids (~100 kDa) (16, 17, 19). Additionally, other organics, such as sodium alginate-polysaccharide (>100 kDa), disinfection by-products, and inorganic colloidal materials (silica colloids, iron oxide), have similarly caused fouling and impacted permeate quality (14, 15, 18). Since fouling has a significant impact on the permeate quality, pretreatment of water for the removal of potential foulants is crucial to ensure consistent high-quality water production from the operation of RO and NF membranes (16, 17). The rapid fouling of all the membranes, especially the high-pressure membranes (NF and RO), suggests that the CE should have been prefiltered to maintain stable and constant operation, as well as to obtain higher flux rates at the membrane units.

**Table 3d-4. Inlet and Effluent Characteristics and Performance Summary for Microfiltration**

Sample Description	As	Se	V	Hg	% Removal			
	ppb			ppt	As	Se	V	Hg <sup>1</sup>
CE as-is, t = 0	9.4	35	210	16.3				
CE as-is, t = 0	9.5	34	190	2.71				
MilliQ retentate	<1	<1	<1	0.15				
MilliQ permeate	1.1	<1	<1	0.15				
CE permeate at 14.7 psi	7.6	31	160	2.07	20%	10%	20%	65%
CE retentate at 14.7 psi	9.2	33	200	5.96	3%	4%	0%	0%
CE permeate at 40 psi	8.4	31	160	0.34	11%	10%	20%	94%
CE retentate at 40 psi	10	34	200	5.94	-6%	1%	0%	0%
CE permeate at 60 psi	8.3	31	170	0.55	12%	10%	15%	91%
CE retentate at 60 psi	9.1	32	190	5.69	4%	7%	5%	5%

<sup>1</sup> The % removal for mercury was calculated based on the retentate concentrations.

**Table 3d-5. Inlet and Effluent Characteristics and Performance Summary for Ultrafiltration**

Sample Description	As	Se	V	Hg	% Removal			
	ppb			ppt	As	Se	V	Hg
CE as-is, t = 0	8.9	34	190	5.47				
CE as-is, t = 0	9.8	33	200	5.58				
MilliQ permeate at 50 psi	<1	<1	4.6	0.22				
MilliQ permeate at 50 psi	<1	<1	4.3	0.13				
MilliQ retentate at 50 psi	<1	<1	<1	0.19				
CE permeate at 50 psi	7.7	29	150	1.04	18%	13%	23%	81%
CE retentate at 50 psi	9.4	34	200	5.12	-1%	-1%	-3%	7%
CE permeate at 75 psi	5.4	17	84	0.26	42%	49%	57%	95%
CE retentate at 75 psi	11	35	200	4.53	-18%	-4%	-3%	18%

**Table 3d-6. Inlet and Effluent Characteristics and Performance Summary for Nanofiltration**

Sample Description	As	Se	V	Hg	% Removal			
	ppb			ppt	As	Se	V	Hg
CE as-is, t = 0	14	33	19	3.39				
CE as-is, t = 0	13	30	16	3.46				
MilliQ permeate at 300 psi	<1	<1	1.6	0.19				
MilliQ permeate at 300 psi	<1	<1	3.6	0.22				
MilliQ retentate at 300 psi	<1	<1	<1	0.19				
MilliQ retentate at 300 psi	<1	<1	3.9	0.2				
CE permeate at 300 psi	13	28	19	1.26	4%	11%		63%
CE retentate at 300 psi	12	30	17	3.46	11%	5%		-1%
CE permeate at 500 psi	12	29	20	1.77	11%	8%		48%
CE retentate at 500 psi	14	31	17	3.12	-4%	2%		9%
CE permeate at 700 psi	13	30	21	1.91	4%	5%		44%
CE retentate at 700 psi	12	29	20	3.16	11%	8%		8%

**Table 3d-7. Inlet and Effluent Characteristics and Performance Summary for Reverse Osmosis**

Sample Description	As	Se	V	Hg	% Removal			
	ppb			ppt	As	Se	V	Hg
CE as-is, t = 0	11.0	38	210	6.34				
CE as-is, t = 0	9.8	34	200	5.2				
MilliQ permeate at 300 psi	1.4	<1	<1	<0.08				
MilliQ permeate at 300 psi	<1	<1	<1	0.62				
MilliQ retentate at 300 psi	<1	<1	<1	1.05				
MilliQ retentate at 300 psi	<1	<1	<1	0.21				
CE permeate at 300 psi	9.1	32	170	1.15	13%	11%	17%	80%
CE retentate at 300 psi	8.9	33	200	5.34	14%	8%	2%	7%
CE permeate at 500 psi	9.0	34	190	1.91	13%	6%	7%	67%
CE retentate at 500 psi	8.4	31	190	4.48	19%	14%	7%	22%
CE permeate at 700 psi	8.9	32	190	2.11	14%	11%	7%	63%
CE retentate at 700 psi	9.5	34	200	4.17	9%	6%	2%	28%

From the initial screening experiments, the following conclusions can be made:

- The permeate quality was dependent upon operating pressure, membrane type, and wastewater characteristics.
- Both MF and UF produced effluent concentrations below 1.3 ppt Hg at pressures ≥40 psi. The sharp decrease in permeate flux after 1–3 hours of operation was due to a rapid build-up of a fouling layer on the membrane surface.
- The RO and NF membranes operating at 300 psi also provided effluent mercury concentrations of <1.3 ppt. The increase in the operating pressure resulted in an increase in the permeate mercury concentration, presumably because of the fouling characteristics of the CE. Fouling can create a high concentration of mercury on the RO and NF membrane surfaces, which leads to higher mercury permeation and therefore a poorer rejection of divalent mercury, as well as arsenic, selenium, and vanadium.

- The sharp decrease in permeate flux after 1–3 hours of operation was due to a rapid build-up of a fouling layer on the membrane surface.

Phase 2 experiments (focused tests) were conducted based upon the test results obtained from the initial screening experiments and wastewater characterization studies (see Chapter 2). Since the higher solids concentration was the primary cause for the membrane fouling during the operation, focused tests were performed by operating the membrane filters sequentially to maintain stable permeate flow and low operating pressure, as shown in Figure 3d-3. Experiments were performed with approximately 9 gal of CE, which were filtered through 5  $\mu\text{m}$ , then 1  $\mu\text{m}$  and 0.45  $\mu\text{m}$ , in-line capsule filters to reduce the fouling of the membranes. The characteristics of the initial CE and the CE filtered through in-line filters are summarized in Table 3d-8. The permeate from the 0.45  $\mu\text{m}$  filter was used to feed the MF unit.

The MF unit was operated under 40 psi pressure. The permeate from the MF unit was collected and used to feed the UF unit. The UF filtration experiments were performed with two different operating pressures: 50 psi and 100 psi. Tables 3d-8 to 3d-10 show the influent and effluent characteristics, as well the performance summary for the MF and UF membranes. The percentage of mercury and vanadium removal, as well as the particle removal abilities of the membranes, provided the basis for the membrane performance comparison. The obtained test results confirmed the test results from the screening experiments. Both membranes demonstrated excellent mercury removal (<0.5 ppt).

The permeate from 0.3  $\mu\text{m}$  MF was also spiked with 20 ppt Hg (soluble/ionic Hg in 5%  $\text{HNO}_3$ , Spex Certi Prep, New Jersey) to investigate the removal of soluble Hg with UF as well. The overall percentage of Hg removal was 69%. This result might be due to the complexation of soluble mercury ions with colloidal particles existing in the wastewater. To bring mercury concentrations to 1.3 ppt in the presence of soluble mercury, either carbon adsorption or RO and NF membranes should be used to remove the dissolved mercury. The nature of the mercury in wastewater is important in membrane selection. Therefore, it is crucial to identify the mercury forms in the raw wastewater.

It was observed that flux rates increased significantly after prefiltration of the CE (Microfiltration<sub>time=0</sub>: 232 l/m<sup>2</sup>-h and Ultrafiltration<sub>time=0</sub>: 187 l/m<sup>2</sup>-h). Differences in the fouling rates of the MF and UF, with and without prefiltration, can be shown in the differences in time = 0 fluxes (Table 3d-3), as well as in the decrease in flux rates (Figure 3d-4). When the CE was prefiltered, the MF and UF operated well with fewer energy requirements, since higher flux rates shortened the operation time. Using MF as a pretreatment would enhance UF performance by increasing the removal of particulates, which in turn would produce a significant increase in the flux rates (Table 3d-3 and Figure 3d-4). The UF flux slightly decreased over the period that was studied. However, the flux reduction was higher with MF. The permeate flux decline was 66% with MF and 32% with UF at the end of the experiments. The steady decrease in the flux rates of MF could be attributed to the membrane unit, with the 42 cm<sup>2</sup> filter area having reached its performance limit by filtering 9 gal of prefiltered CE, or to foulants that remained in the prefiltered CE. These results also suggest the possibility of potentially different fouling mechanisms, since the chemistry of the membrane materials were not the same.

**Table 3d-8. Inlet and Effluent Characteristics and Performance Summary for Prefiltration (averages of five replicates)**

Sample Description		As	Se	V	Hg	% Cumulative Removal			
		ppb			ppt	As	Se	V	Hg
CE as-is, t = 0	Avg.	9.6	25.40	486	4.28				
	St. dev.	0.8	0.89	8.94	0.20				
After 0.45 µm	Avg.	9.8	25.20	476	0.39	-2%	1%	2%	91%
	St. dev.	1.2	1.10	8.94	0.09	13 %	4%	2%	2%

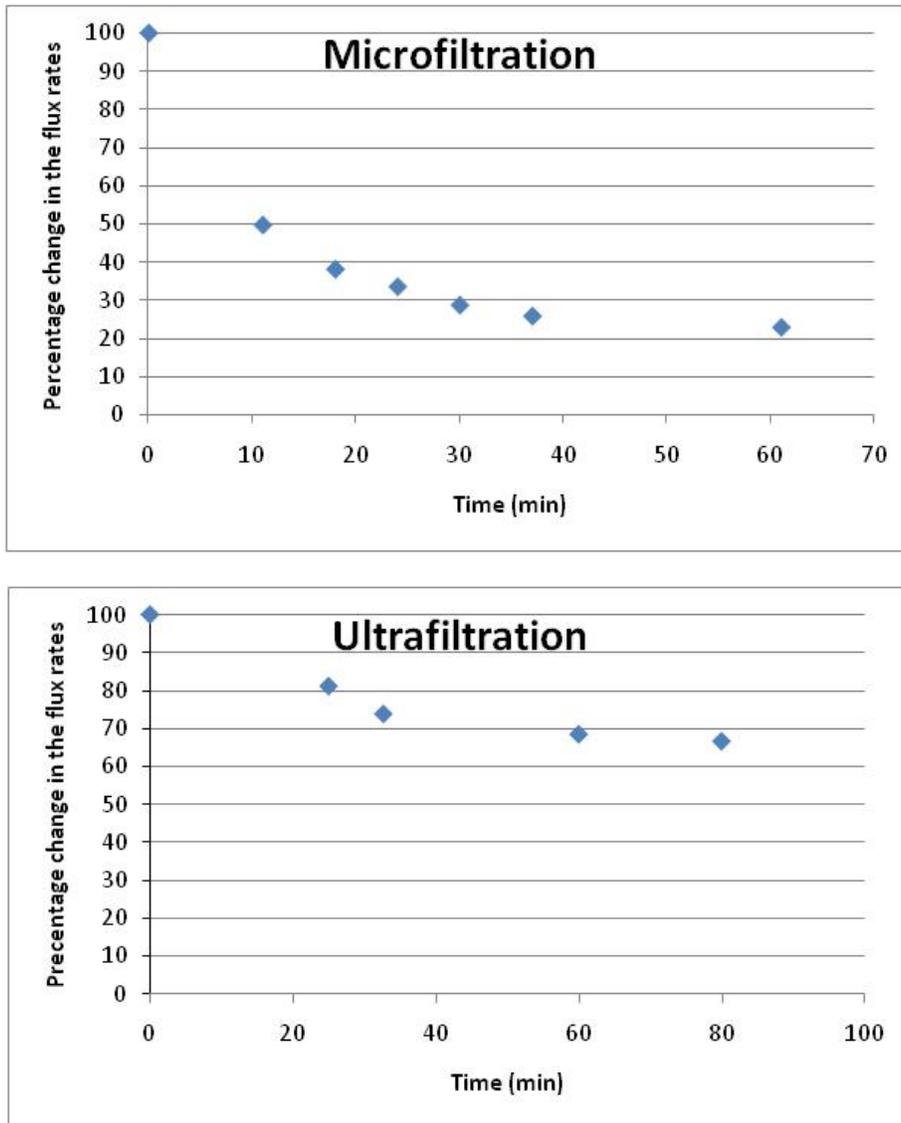
**Table 3d-9. Inlet and Effluent Characteristics and Performance Summary for Microfiltration (averages of five replicates)**

Sample Description		As	Se	V	Hg	% Cumulative Removal			
		ppb			ppt	As	Se	V	Hg
MilliQ retentate	Avg.	<1	<1	1.67	0.10				
	St. dev.			1.07	0.01				
MilliQ permeate	Avg.	<1	<1	<1	0.10				
	St. dev.								
CE retentate at 40 psi	Avg.	9.2	24.6	476	0.30				
	St. dev.	0.3	0.5	13.4	0.12				
CE permeate at 40 psi	Avg.	9.9	25.8	478	0.15	-3%	-2%	2%	96%
	St. dev.	1.2	1.9	8.4	0.03	13%	8%	2%	1%

**Table 3d-10. Inlet and Effluent Characteristics and Performance Summary for Ultrafiltration (averages of three replicates)**

Sample Description		As	Se	V	Hg	% Cumulative Removal			
		ppb				ppt	As	Se	V
MilliQ permeate at 50 psi	Avg.	<1	<1	<1	<0.08				
	St. dev.								
MilliQ retentate at 50 psi	Avg.	<1	<1	<1	<0.08				
	St. dev.								
CE permeate at 50 psi	Avg.	9	23	463	0.18	5%	8%	5%	96%
	St. dev.	0	1	6		2%	5%	1%	
CE retentate at 50 psi	Avg.	8.8	23.3	480	0.23				
	St. dev.	0.2	0.6	10	0.11				
CE permeate at 100 psi	Avg.	7.0	21.3	460	0.14	27%	16%	5%	97%
	St. dev.	0.5	0.6	0	0.03	5%	2%	0%	1%
CE permeate at 100 psi with spike	Avg.	7.2	22.3	473	7.25	25%	12%	3%	69%
	St. dev.				1.21	2%	2%	4%	3%
CE retentate at 100 psi with spike	Avg.	8	22	477	20.83				
	St. dev.	0	0	5.77	1.88				
Spiked and filtered CE through 0.3 μm	Avg.				23.57				
	St. dev.				1.21				

Figure 3d-4. Changes in the Permeate Flux Rates with the Operating Time



### Particle Size Distribution

The correlation between mercury concentration and particle size distribution was also investigated in this study to obtain a better understanding of mercury removal mechanisms by membrane filtration technologies. A particle size distribution analysis was conducted by using the Accusizer 770 with an MDL of 0.5  $\mu\text{m}$ , which works on the principle of light obscuration (Particle Technology Labs, Downers Grove, Illinois). The test results were presented both as number and volume distributions based on the average of three measurements. As shown in Table 3d-11, the mean particle size decreased with filtration. The mean particle size of CE as-is samples was  $1.1 \pm 0.0 \mu\text{m}$ , decreasing to  $0.74 \pm 0.2 \mu\text{m}$  after UF. Table 3d-11 also shows that 90% of the particles contained in the CE as-is samples were below 1.2  $\mu\text{m}$ , while 90% of the particles were less than 0.85  $\mu\text{m}$  after UF. Less than 10% of the particles in all of the tested samples were below 0.54  $\mu\text{m}$ . This indicates that the membranes with a  $\leq 0.45 \mu\text{m}$  cut-off pore size can reject more than 90% of the particles contained in the samples. The further reduction in the particle size distribution was noticed after MF and UF, as shown in Figure 3d-5. The size and frequency of the particles decreased relatively after the MF and UF processes.

Consistently low mercury levels (<1.3 ppt) after 0.45 µm filtration indicate that mercury is mostly in particulate/colloidal form, and particles greater than 0.45 µm should be removed to achieve low levels of mercury (<1.3 ppt) in the treated water, as concluded in Chapter 2. Table 3d-12 provides a comparison of particle analysis test results obtained from last year’s sampling events versus BP’s study in November 2007 through December 2007. The obtained test results from these two studies were very similar. BP’s particle size analysis data (November through December 2007) support our findings, since more than 90% of the particles in the CE were larger than 0.54 µm, based on particle count analysis.

The same samples also were analyzed with the photon correlation spectroscopy/dynamic light scattering technique (Malvern Zetasizer Nano, with MDL of 0.4 nm) to determine the size distribution of the submicron particles. Figure 3d-6 shows that the CE as-is samples had a wide particle size distribution range, but after filtration this range became narrower. The mean particle diameter also decreased with filtration, as shown in Table 3d-13. The mean particle size of the CE as-is samples was 570 nm. It decreased to 170 nm after MF. The mean particle size for the samples filtered through 0.003 µm membranes could not be determined, since the samples included only a couple of very large particles. Because of their size, they have skewed the average diameter calculations.

**Table 3d-11. Particle Size Analysis by Accusizer (by number and volume)<sup>1</sup>**

Sample	Arithmetic Mean	Mode	Median	Number-Based Percentiles Less than Indicated Size (µm)			
				10%	50%	90%	95%
CE as-is	1.1±0.0	0.60±0	0.67±0	0.54±0	0.67±0	1.2±0.1	1.7±0.2
CE after 0.3 um	1.01±0.1	0.54±0	0.65±0.0	0.53±0	0.65±0.0	1.2±0.1	1.86±0.3
CE after 0.003 µm	0.74±0.2	0.56±0.0	0.62±0.04	0.54±0	0.62±0.0	0.85±0.3	1.05±0.6

Sample	Arithmetic Mean	Mode	Median	Volume-Based Percentiles Less than Indicated Size (µm)			
				10%	50%	90%	95%
CE as-is	35.1±0.3	33.9±16.1	29.5±2.2	13.1±0	29.5±2.2	66.2±5.0	80.1±9.1
CE after 0.3 um	39.0±4.0	43.0±2.3	38.7±3.5	19.8±5.8	38.7±3.5	57.5±6.3	63.6±6.5
CE after 0.003 µm	38.9±1.5	42.3±1.3	38.5±0	20.9±1.3	38.5±0	58.3±3.7	62.2±4.1

<sup>1</sup> Experiments were performed with triplicate samples.

**Table 3d-12. Comparison of Particle Size Distribution Data**

Argonne									
CE as-is	90 % of particles are greater than:	0.54 $\mu\text{m}$	number-based	50 % of particles are greater than:	0.67 $\mu\text{m}$	number-based	10 % of particles are greater than:	1.20 $\mu\text{m}$	number-based
		13.1 $\mu\text{m}$	volume-based		29.5 $\mu\text{m}$	volume-based		66.2 $\mu\text{m}$	volume-based
BP November–December 2007									
CE as-is	90 % of particles are greater than:	0.54 $\mu\text{m}$	number-based	50 % of particles are greater than:	0.68 $\mu\text{m}$	number-based	10 % of particles are greater than:	1.21 $\mu\text{m}$	number-based
		12.5 $\mu\text{m}$	volume-based		28.6 $\mu\text{m}$	volume-based		78.4 $\mu\text{m}$	volume-based

**Figure 3d-5. Cumulative Percentage Frequency Particle Size Distributions between Membranes Filtration Processes**

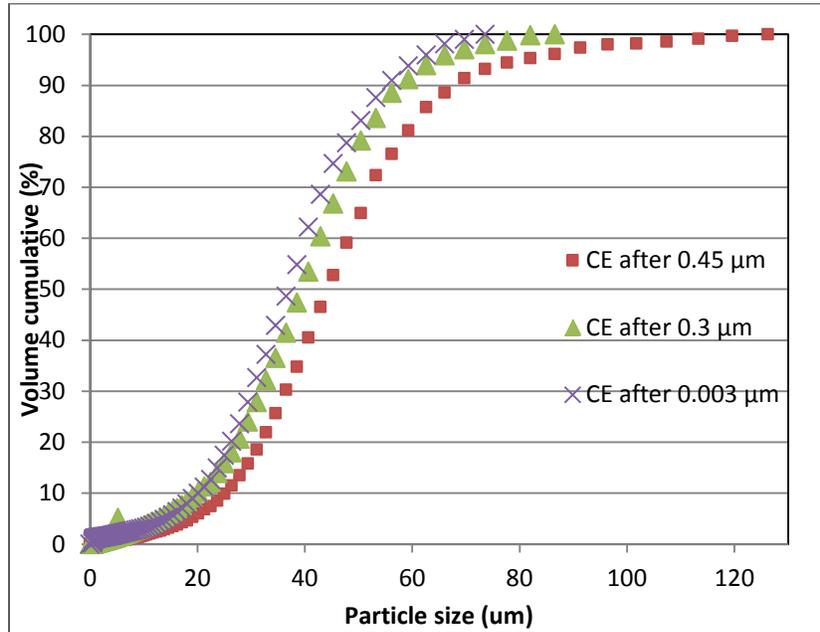


Figure 3d-6. Particle Size Distribution of CE Samples Analyzed with Malvern Zetasizer Nano

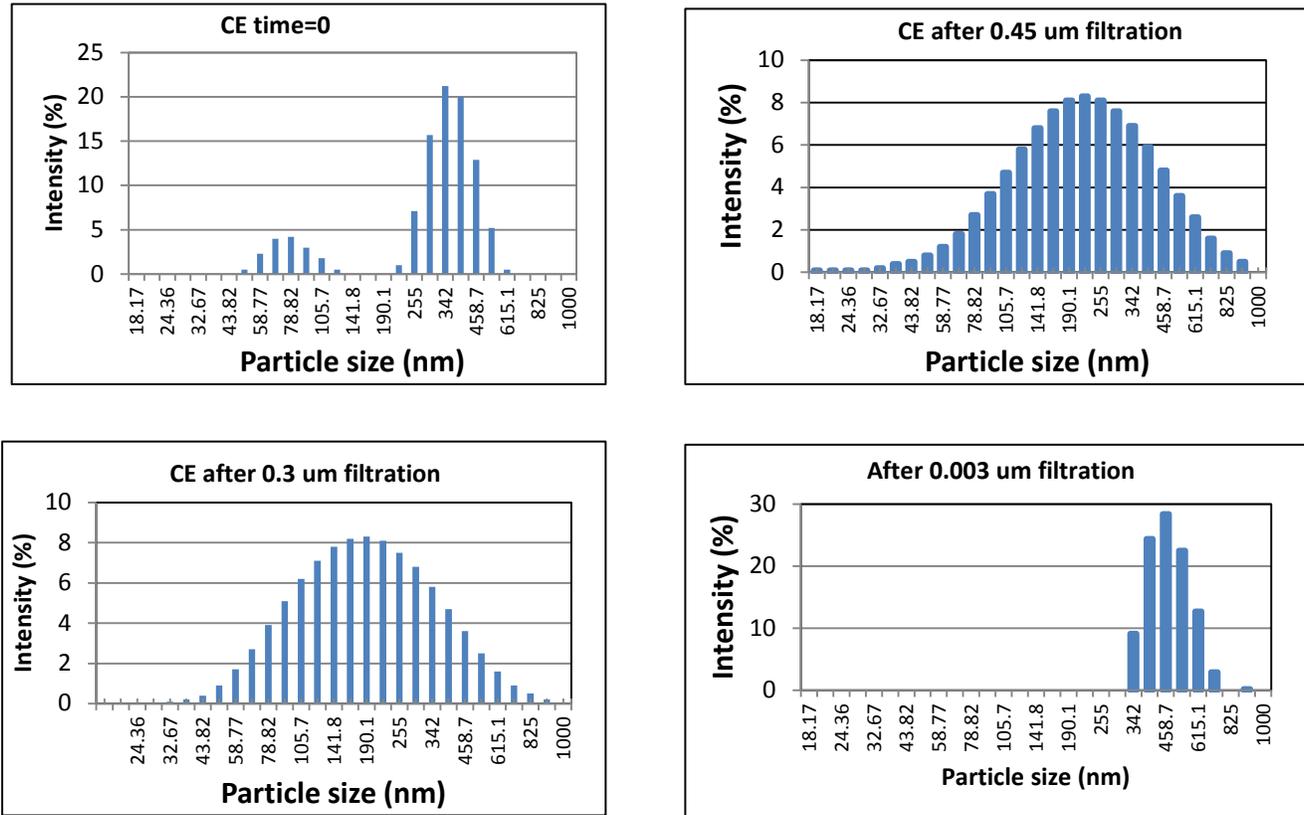


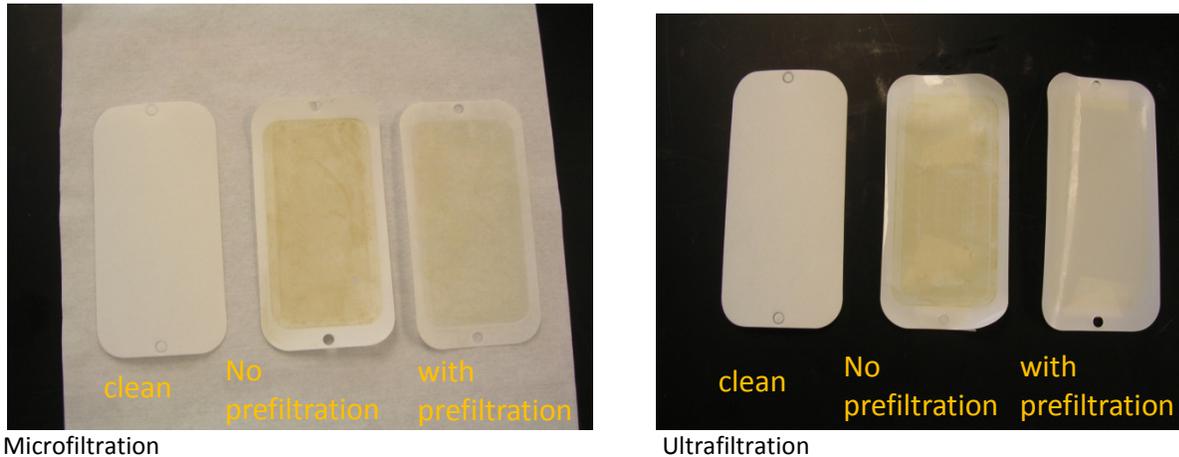
Table 3d-13. Average Particle Diameter Size for Particles Less than 1 µm by Zetasizer

Sample	Average Diameter (nm)
CE as-is	570
CE after 0.45 µm	185
CE after 0.3 µm	170
CE after 0.003 µm	Not applicable

### Membrane Fouling

Figure 3d-7 shows the clear advantage for flux rates of using a sequential filtration over no pretreatment. Prefiltration prior to MF and the subsequent use of permeate from MF into UF resulted in considerably higher flux rates and lower fouling at these membranes while it did not change the metal removal performance of UF. As depicted in the photos, the color of the deposition layer on the membrane surfaces was lighter in the prefiltered tests than in the tests with no prefiltration.

**Figure 3d-7. Fouling of Membrane Filters**



Conclusions from the focused tests are as follows:

- Sequential operation of membrane filtration units resulted in high permeate flow rates and stable low operating pressures during the operation of the membrane units.
- Both MF and UF confirmed the capability to achieve  $<1.3$  ppt Hg concentration under  $\geq 40$  psi operating pressure. Also, 91% of the mercury was removed after  $0.45 \mu\text{m}$  filtration, and 96% of the mercury was removed after  $0.3 \mu\text{m}$  filtration.
- Arsenic, selenium, and vanadium removal was negligible after MF, while the percentage of removal of arsenic and selenium increased to 27% and 16%, respectively, after UF at 100 psi.

#### 4. Conclusions

- This study provided an evaluation of four different membrane technologies to achieve  $<1.3$  ppt Hg levels in the treated CE. The membrane processes were operated at three different pressures to demonstrate the potential of each membrane technology for treating the Whiting Refinery wastewater.
- The initial screening and focused test results indicated that MF and UF were highly effective in removing mercury, which was present mostly in particulate form. The water quality goal of  $<1.3$  ppt Hg was met and exceeded throughout the experiments.
- The RO and NF membranes with no pretreatment were unable to remove mercury completely from the CE. This result might be due to concentration polarization because of solids deposition on the membrane surface.
- Despite no pretreatment, the RO and NF membrane testing demonstrated only very limited ability to remove arsenic, selenium, and vanadium, which were mostly in the dissolved form in the CE.
- The fouling characteristics of the CE required prefiltration to operate the system at higher fluxes with greater recovery percentages. Sequential filtration was very effective in reducing solid accumulation on the membrane surfaces.
- Pilot-scale studies are needed to determine the flux and rejection properties of the tested membranes systematically and to confirm mercury removal performance. Backwash volume and concentrate disposal should also be considered and determined during these studies.

## 5. References

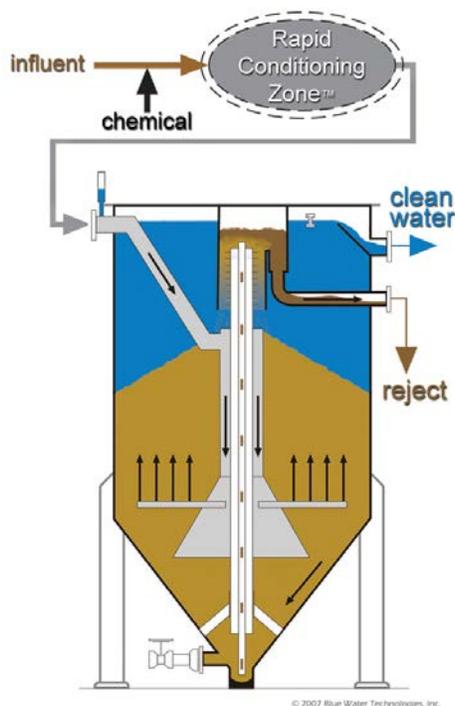
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### 3e. Blue PRO Testing

#### 1. Introduction and Objectives

The Blue PRO process, provided by Blue Water Technologies, Inc., is a reactive filtration process that combines precipitation, sand filtration, and adsorption. The process uses ferric sulfate and a polymer as the precipitants, which are added to the wastewater before it is fed to a moving bed sand filter, as shown in Figure 3e-1. Within the moving bed sand filter, silica sand coated with ferric sulfate provides the sand filtration. The ferric sulfate coating on the sand enables additional contaminant removal through adsorption.

Figure 3e-1. Blue PRO Process



In order to test this process at the bench-scale, the process was simplified to a series of two columns of ferric sulfate coated sand, as recommended by the vendor (1). The chemical precipitants, ferric sulfate and a polymer, were added to the wastewater before they were fed to the columns. Although this testing is not an exact duplicate of the process, according to the vendor it can be used to indicate the required reagents and dosage for a specific type of wastewater. The objective of this testing was to determine the maximum amount of mercury, vanadium, arsenic, and selenium that could be removed with the process by using varying chemical precipitant dosages.

## 2. Materials and Methods

### a. Reagents

The ferric sulfate solutions were prepared with ACS-grade iron (III) sulfate hydrate (97%) provided by Sigma-Aldrich. The polymer was provided by the vendor, who obtained it from the manufacturer. The ferric-sulfate coated silica sand was provided by the vendor. The 10 ppm mercury standard that was used for spiking the filtered CE was manufactured by Spex Certiprep, New Jersey.

### b. Water Samples

The Whiting Refinery's CE was used for the testing. Samples were collected by using the "clean hands-dirty hands" procedures specified in EPA Method 1669 (2). Upon receipt, the wastewater was stored in a 4 °C cold room before use. Two different batches of wastewater were tested. Based on the results of the Shelf-life Study (Appendix I), the wastewater was used for up to five days after collection from the refinery. This approach was taken to ensure that changes in mercury and vanadium speciation and composition would be negligible.

### c. Experimental Equipment

Prior to use, all equipment was cleaned by using the methods outlined in EPA Method 1631E and EPA Method 200.8 (3, 4). Specifically, the equipment was washed with laboratory soap (Sparkleen) and tap water and then triple rinsed with MilliQ water (18 MΩ.cm resistivity). The system was filled with a 5% HCl solution. After 4 hours, the acid was drained from the system, and four system volumes of MilliQ water were pumped through the system.

The CE was used either as-is or prefiltered with a series of in-line filters (5 micron, 1 micron, and 0.45 micron). Immediately prior to use, the prefiltered CE was spiked to a 10 ppt level with Hg<sup>+2</sup> by using a freshly prepared spike solution. It was then mixed in a Teflon PFA liner placed inside a 5-gal HDPE pail with a magnetic stir plate. During this mixing, the collapsible Teflon liner was used to minimize the headspace above the wastewater.

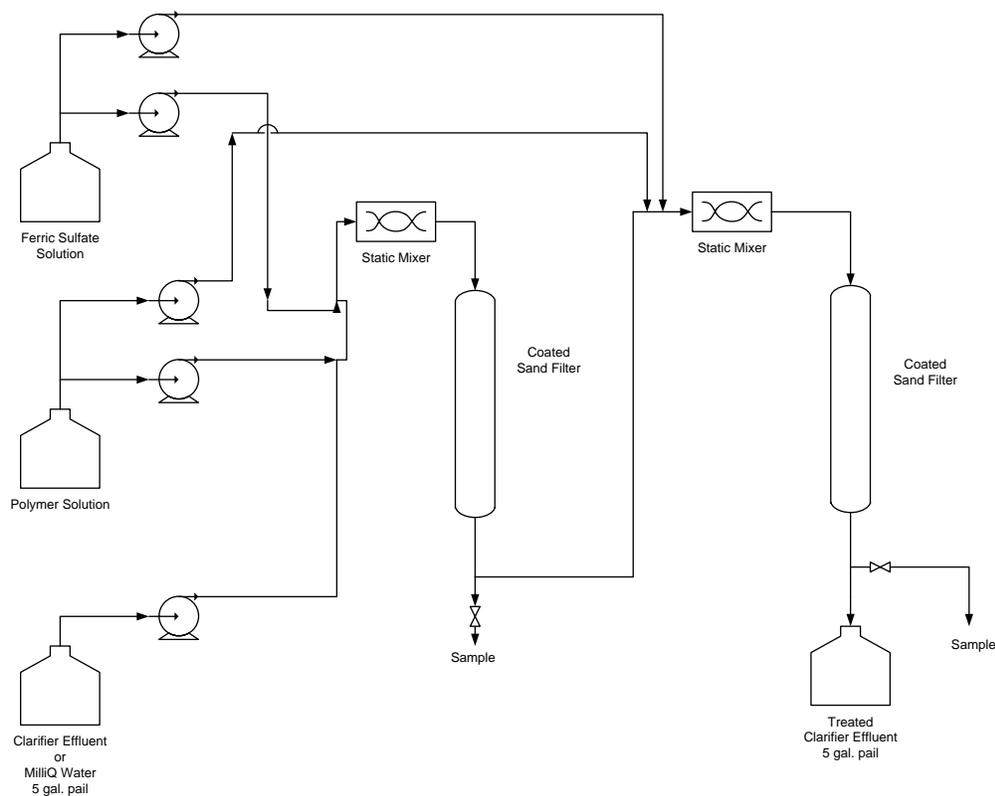
The equipment set up is shown in Figures 3e-2 and 3e-3. The CE feed was pumped directly from the Teflon liners inside the HDPE sampling pails with a peristaltic pump. A ferric sulfate solution in a glass flask was added to the CE stream with a peristaltic pump. Downstream of the ferric sulfate addition, a polymer solution in a glass flask was added separately with a peristaltic pump. The SEBS resin tubing and Teflon PFA fittings were used throughout the set-up, as specified in EPA Method 1669 — Trace Metal Sampling (2). The ferric sulfate, polymer, and CE were premixed with an in-line Teflon static mixer before being fed downflow to a series of two columns. The glass columns were filled with sand that had been coated with ferric sulfate by Blue Water Technologies. A sampling point was located at the outlet of each column. Additional ferric sulfate and polymer solution was added to the effluent of the first column and mixed with an in-line Teflon static mixer before it was sent to the second column.

Before being used, the peristaltic pumps that feed the CE, ferric sulfate, and polymer solutions were calibrated by measuring the flow rate as a function of the pump setting. During calibration, each flow rate was measured with a graduate cylinder and stopwatch three times, for three minutes each time. An average flow rate for each pump setting was determined and used.

**Figure 3e-2. Blue PRO Testing Set-up in the Clean Room**



Figure 3e-3. Blue PRO Equipment Set-up



Blue PRO Bench-Scale  
System  
6/17/10 PSG

#### d. Experimental Procedure

##### *Initial Blanks*

Prior to testing the Blue PRO process, three different blanks were run: equipment, method, and adsorbent. For the equipment blank, MilliQ water (18 M $\Omega$ .cm resistivity) was run through the empty columns and system. It then was sampled to determine whether the equipment was contributing mercury or other metals of interest. Two different method blanks were run. The first method blank was performed to determine dissolved mercury loss. It was run by using CE that had been in-line filtered with a 0.45  $\mu$ m filter and then spiked to a level of 10 ppt of Hg<sup>+2</sup> with a 10 ppm of mercury standard solution (Spex Certiprep, New Jersey). The second method blank was done to identify particulate mercury loss. It was run with untreated CE. For both method blanks, the system was completely filled with the CE being tested. The CE was sampled before and after the system to determine the gain or loss of mercury, vanadium, arsenic, and selenium. The adsorbent (coated sand) blank used MilliQ water (18 M $\Omega$ .cm resistivity) that had passed through columns loaded with the coated sand to determine whether the coated sand was adding mercury or other metals of interest to the system.

##### *Column Loading*

Before the adsorbent blank and the screening testing, the columns were loaded with the coated sand, which was moist when received from the vendor. The coated sand was weighed and added to the columns as-is. According to the vendor's recommendations (1), the column was loaded by tapping down the sand during the loading process and loading to the vendor-specified height. The height of the coated sand in the column was measured with a standard ruler. Within the column, glass wool was used below the sand bed to keep the sand in place.

##### *Screening Testing*

The screening testing procedure was based on the vendor’s recommendations (1, 5, 6). At the start of each test, MilliQ water (18 MΩ.cm resistivity) was fed to the columns for 10 minutes in order to remove fines or ferric precipitate that was not coating the sand. During this time, the flow rate was checked with a graduate cylinder and stopwatch. After this initial flush, MilliQ water continued to be fed to the columns at the same flow rate while the addition of the precipitants (ferric sulfate and/or polymer) began. The flow rates of the precipitants were checked with a graduate cylinder and a stopwatch. After all the flow rates of the MilliQ and precipitant solutions were checked, the feed was switched from MilliQ water to CE while the addition of precipitants to the column influent continued. During testing, the addition of air to the column was avoided.

Several different screening tests were conducted to determine the effect of varying the amounts of ferric sulfate and polymer fed to the influent of each column, as recommended by the vendor (6). The CE flow rate was held constant throughout all testing. To evaluate how effectively the process removed dissolved mercury, an additional test was done with CE that had been prefiltered with a 0.45 µm filter and then spiked to 10 ppt Hg<sup>+2</sup>. The screening test conditions are shown in Table 3e-1.

**Table 3e-1. Blue PRO Screening Test Conditions<sup>1</sup>**

Test Number	Clarifier Effluent Feed	Influent to First Column		Influent to Second Column	
		Ferric Sulfate Concentration (ppm as Fe)	Polymer Concentration (ppm)	Ferric Sulfate Concentration (ppm as Fe)	Polymer Concentration (ppm)
1	As-is	High	0	Medium	0
2	As-is	Medium	0	Low	0
3	As-is	Medium	As specified	Low	As specified
4	Filtered through 0.45 µm and spiked to 10 ppt Hg <sup>+2</sup>	Medium	As specified	Low	As specified
5	As-is	0	As specified	0	As specified

<sup>1</sup>Actual dosages are proprietary and therefore cannot be disclosed.

For each test, eight bed volumes of CE were fed through the columns before the feed and effluents were sampled. Three feed samples and three effluent samples were taken for each test condition. After each test, the columns were flushed with MilliQ water for 20 minutes prior to starting the next test.

**e. Analyses**

The equipment, method, and adsorbent blanks were analyzed for total mercury (EPA 1631e), total vanadium (EPA 200.8), and total arsenic and selenium cations (EPA 200.7). Prior to screening testing, the pH of the untreated CE was measured at Argonne. Additionally, the CE used was sampled and sent to Lab B , a certified independent lab, for analysis of the following parameters:

Total and dissolved mercury	EPA 1631e
Total and dissolved vanadium	EPA 200.8
Cations: As, Se, Fe	EPA 6010/200.7
Anions: Cl <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup>	EPA 300.0
Total hardness as CaCO <sub>3</sub>	EPA 130.2

During the screening testing, samples were taken of the feed as well as the effluent from each column. These samples were analyzed for total mercury (EPA 1631e) and total arsenic, iron, selenium, and vanadium (EPA 200.7/EPA 200.8).

**3. Results and Discussion**

### a. Blanks

The results of the equipment and reagent blanks are presented in Table 3e-2. Most of the metals of concern could not be detected in either the in-line filtration system or the Blue PRO bench-scale apparatus. A small amount of selenium (1.1 ppb) was seen in the Blue PRO bench-scale apparatus blank, but only slightly more than the 1 ppb detection limit of the analytical method. In contrast, the 300 ppm of iron as ferric-sulfate reagent blank showed a significant amount of mercury (165 ppt), as did the ferric sulfate (1.73 ppt). The polymer reagent blank showed only 0.1 ppt of mercury. The other metals of interest — arsenic, selenium, vanadium, and iron — either were at levels below the detection limit or were present at very low and insignificant levels in the reagents tested.

**Table 3e-2. Equipment and Reagent Blank Summary**

	<b>Hg (ppt)</b>	<b>As (ppb)</b>	<b>Se (ppb)</b>	<b>V (ppb)</b>	<b>Fe (ppm)</b>
In-line filtration blank	<0.5	<1	<1	<1	-
Blue PRO equipment blank	0.09	<1	1.1	<1	<0.10
Coated sand blank	1.73	<1	2	2.4	0.31
Ferric sulfate blank	165	<1	1	2.6	-
Polymer blank	0.1	<1	<100	<1	<0.001

In order to determine the losses during the method, two different blanks were done — one with the CE as-is, and the other with CE that had been in-line filtered with a 0.45  $\mu\text{m}$  filter and then spiked to a level of 10 ppt  $\text{Hg}^{+2}$ . Both method blanks are summarized in Table 3e-3. The CE as-is method blank showed a slight gain of mercury (1.1%), as well as some fairly significant losses of arsenic, selenium, and vanadium (32.5%, 16.6%, and 5.8%, respectively). The standard deviations associated with the arsenic and selenium samplings, however, were relatively high compared with the actual values. For example, arsenic in the CE as-is feed was 13 ppb, while the standard deviation was 5 ppb. These results, in combination with analytical values that are very close to the 1 ppb method detection limit, suggest that the method losses may not be as large as they appear. In contrast, the filtered and spiked CE showed very small gains or losses of the metals of concern. The gains and losses of arsenic, selenium, and vanadium determined from these method blanks were applied to the results presented below.

### b. Process Testing

Five different tests were conducted with the bench-scale Blue PRO system, with each test varying the amount of ferric sulfate and polymer added to the columns. It is important to keep in mind that these tests used a static version of the Blue PRO process. As such, the tests essentially provided an indication of how the chemistry of the process works with the components of the CE. The tests were conducted with two different batches of wastewater. Tests 1, 2, and 5 were conducted with the first batch, and Tests 3 and 4 were conducted with the second batch. For each batch of wastewater, the feed pails were used in the order in which they were sampled.

**Table 3e-3. Blue PRO Method Blank Summary**

	Hg (ppt)	As (ppb)	Se (ppb)	V (ppb)
CE as-is method blank				
Feed (avg. of 5)	4.75	13	33	242
Standard deviation	0.36	5	10	4
Effluent (avg. of 5)	4.80	9	27	228
Standard deviation	0.26	0.3	0.4	8
Method percent loss/gain	1.1%	-32.5%	-16.6%	-5.8%
CE filtered and spiked method blank <sup>1</sup>				
Feed (avg. of 5)	8.27	8.5	27.4	228
Standard deviation	0.81	0.0	1	4
Effluent (avg. of 5)	8.09	9	27	236
Standard deviation	0.48	0.4	0.0000	5.5
Method percent loss/gain	-2.2%	5.65%	-1.46%	3.51%

<sup>1</sup> CE was 0.45 μm filtered and spiked to 10 ppt with Hg<sup>+2</sup>.

The mercury results presented in Table 3e-4 show that the future 1.3 ppt target limit was met in all three tests that used polymer. The bench-scale Blue PRO columns were effective in removing up to 98.7% of the mercury attached to particulates, as shown in Tests 3 and 5. The results of Test 4, which used CE that had been 0.45 μm filtered and spiked with 10 ppt of dissolved Hg<sup>+2</sup>, indicate that 92.2% of the dissolved mercury also was removed by this process. The fifth test was able to meet the target limit with polymer alone, thereby suggesting that the addition of ferric sulfate may not be needed if all of the mercury is attached to particulates. Taken together the first and fifth tests also indicate that increasing the size of particulates (for example through polymer addition) followed by sand filtration could be very effective at particulate mercury removal. The effect of polymer only on dissolved mercury removal was not tested.

The effectiveness of the Blue PRO process in removing other contaminants of concern also was tested. For all conditions tested, the process was found to be highly effective for vanadium removal, ranging from 88–99% removal, as shown in Table 3e-5. Despite the challenge of a high vanadium concentration (650–680 ppb) in the second batch of wastewater feed, 88–99% of the vanadium was removed. The addition of ferric sulfate alone or polymer alone produced essentially the same amount of vanadium removal (99%), which suggests that the vanadium removal (the majority of which is in the dissolved form) is achieved through adsorption onto the sand coated with ferric sulfate. Although no ferric sulfate was added in the case of test number 5, the sand was pre-coated with ferric sulfate.

**Table 3e-4. Blue PRO Testing Results: Mercury**

Test	Feed	Column 1 Effluent		Column 2 Effluent	
	Avg. Hg (ppt)	Avg. Hg (ppt)	% Hg Removal	Avg. Hg (ppt)	% Cumulative Hg Removal
1: CE as-is Ferric sulfate, high and medium No polymer	4.82 – total <0.5 diss.	3.17	34.2%	5.34	-10.8%
2: CE as-is Ferric sulfate, medium and low No polymer	4.67 – total <0.5 diss.	2.15	54.0%	2.61	44.1%
3: CE as-is Ferric sulfate, medium and low Polymer as specified	7.88 – total <0.5 diss.	0.92	88.3%	0.79	90.0%
4: CE filtered and spiked Ferric sulfate, medium and low Polymer as specified	9.46 – diss.	1.81	80.9%	0.74	92.2%
5: CE as-is No ferric sulfate Polymer as specified	26.47 – total <0.5 diss.	0.52	98.0%	0.35	98.7%

**Table 3e-5. Blue PRO Testing Results: Vanadium**

Test	Feed	Column 1 Effluent		Column 2 Effluent	
	Avg. V (ppb)	Avg. V (ppb)	% V Removal (1)	Avg. V (ppb)	% Cumulative V Removal <sup>1</sup>
1: CE as-is Ferric sulfate, high and medium No polymer	230	6.9	96.8	<1	99.5
2: CE as-is Ferric sulfate, medium and low No polymer	230	30	86.2	1.8	99.2
3: CE as-is Ferric sulfate, medium and low Polymer as specified	680	131	79.5	78	87.8
4: CE filtered and Hg spiked Ferric sulfate, medium and low Polymer as specified	650	140	79.2	7.1	98.9
5: CE as-is No ferric sulfate Polymer as specified	240	73	67.7	2.1	99.1

<sup>1</sup>Method loss applied.

The process also removed the majority of the arsenic (69–93%) for all conditions tested, as shown in Table 3e-6. In contrast to the mercury removal, the results presented in Table 3e-6 indicate that the addition of ferric sulfate to the CE improves arsenic removal. The lowest arsenic removal (69%) occurred in Test 5, which added only polymer to the CE fed to the columns. As mentioned before, the sand was pre-coated with ferric sulfate.

**Table 3e-6. Blue PRO Testing Results: Arsenic**

Test	Feed	Column 1 Effluent		Column 2 Effluent	
	Avg. As (ppb)	Avg. As (ppb)	% As Removal (1)	Avg. As (ppb)	% Cumulative As Removal <sup>1</sup>
1: CE as-is Ferric sulfate, high and medium No polymer	9	1.7	72.0%	1.2	80.2%
2: CE as-is Ferric sulfate, medium and low No polymer	8.6	2.5	56.9%	1	82.8%
3: CE as-is Ferric sulfate, medium and low Polymer as specified	16	4.1	62.0%	2.9	73.1%
4: CE filtered and Hg spiked Ferric sulfate, medium and low Polymer as specified	11	2.5	78.5%	1.2	93.0%
5: CE as-is No ferric sulfate Polymer as specified	9.1	4.5	26.7%	1.9	69.1%

<sup>1</sup>Method loss applied.

A significant portion of the selenium also was removed from the CE by this process. As shown in Table 3e-7, removal efficiencies ranged from 52–93%. Test 5, which added only polymer to the CE, provided the best selenium removal, at 93%. However, the other tests that also used polymer (Tests 3 and 4, with 52% and 73% removal, respectively) did not show a significant improvement in selenium removal efficiency over the tests that added only ferric sulfate to the CE feed (Tests 1 and 2, 72% and 67% removal). Further testing is needed to determine an optimal selenium removal process configuration.

In addition to examining the removal of the contaminants of concern, process effluent samples also were tested for iron to determine whether the 1 ppm discharge limit was met. As shown in Table 3e-8, effluent from the second column was consistently <0.10 ppm for all conditions tested, which is well below the Whiting Refinery iron discharge limit of 1 ppm.

**Table 3e-7. Blue PRO Testing Results: Selenium**

Test	Feed	Column 1 Effluent		Column 2 Effluent	
	Avg. Se (ppb)	Avg. Se (ppb)	% Se Removal (1)	Avg. Se (ppb)	% Cumulative Se Removal <sup>1</sup>
1: CE as-is Ferric sulfate, high and medium No polymer	28	1.1	95.3%	6.5	72.2%
2: CE as-is Ferric sulfate, medium and low No polymer	28	14	40.0%	7.8	66.6%
3: CE as-is Ferric sulfate, medium and low Polymer as specified	50	25	40.0%	19.7	52.8%
4: CE filtered and Hg spiked Ferric sulfate, medium and low Polymer as specified	39	25	34.9%	10.3	73.2%
5: CE as-is No ferric sulfate Polymer as specified	29	26	-7.5%	1.7	93.0%

<sup>1</sup>Method loss applied.

**Table 3e-8. Iron Concentration in the Column Effluent**

Test	Feed	Column 1 Effluent	Column 2 Effluent
	Avg. Fe (ppm)	Avg. Fe (ppm)	Avg. Fe (ppm)
1: CE as-is Ferric sulfate, high and medium No polymer	0.12	0.17	<0.10
2: CE as-is Ferric sulfate, medium and low No polymer	0.14	0.413	<0.10
3: CE as-is Ferric sulfate, medium and low Polymer as specified	0.14	<0.10	<0.10
4: CE filtered and spiked Ferric sulfate, medium and low Polymer as specified	<0.10	0.15	<0.10
5: CE as-is No ferric sulfate Polymer as specified	0.64	<0.10	<0.10

#### 4. Conclusions

- Effluent from the bench-scale static version of the Blue PRO process consistently was below the 1.3 ppt mercury limit when polymer was added to the CE feed. The addition of ferric sulfate alone did not meet the mercury standard.
- Bench-scale testing removed 98.7% of the particulate Hg and 92.2% of the dissolved Hg when feed concentrations were 5-27 ppt particulate Hg or 9.5 ppt dissolved Hg.
- Blue PRO column testing removed 88–99% of the V. The lowest effluent concentrations (<1 – 2.1 ppb V) were obtained when the feed was 230 ppb V. Higher effluent concentrations (7.1 – 78 ppb V) were seen when the feed was 650 – 680 ppb V.
- The Blue PRO columns also removed the majority of the arsenic (69–93%) from feed containing 8.6 – 16 ppb As for all conditions tested, which yielded arsenic effluent concentrations that ranged from 1–2.9 ppb.
- For arsenic removal, the results suggested that removal is improved with the addition of ferric sulfate to the CE feed.
- Selenium removal efficiencies with the Blue PRO columns from feed containing 28 – 50 ppb Se ranged from 52–93%. The lowest effluent concentration (1.7 ppb Se) was obtained when the feed was 29 ppb Se while the highest effluent concentration (19.7 ppb Se) was seen when the feed was 50 ppb Se.
- Iron concentrations in the final column effluent were consistently <0.10 ppm for all conditions tested. This result is well below the 1.0 ppm discharge standard for iron for the Whiting Refinery.
- Optimization of process reagents and processes will need to be further tested at the bench or pilot scale.

#### 5. References

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## 4. Data Analysis, Selection of Technologies for Pilot-scale Testing, and Pilot Equipment Design/Specification

### Summary

This chapter provides an assessment of the mercury (Hg) and vanadium (V) removal technologies tested at the bench-scale. As a part of the project (Task 4), a technology assessment protocol was developed to process and review the experimental data based on the endpoint performance measures matrix, as well as to select promising technologies for pilot testing at the Whiting Refinery. Among the candidate technologies, iron precipitation offers a robust option to remove vanadium from the clarifier effluent (CE)/effluent-to-lake (ETL) streams when the Stretford unit is on. Adoption of this technology is simplified by the fact that BP already has a permit to use ferric sulfate at the Whiting Refinery Wastewater Treatment Plant (WWTP). No pilot experiments were recommended for vanadium removal. Three high-ranking mercury removal technologies — namely, ultrafiltration, adsorption, and an emerging reactive filtration technology (the Blue PRO process) — were prioritized from the endpoint performance matrix evaluations for further bench-scale evaluation and piloting at the Whiting Refinery. For the technologies that had multiple vendors, a suitable selection protocol was also developed to assess the technology readiness of the selected technologies and the vendor qualifications. Among the subset of vendors listed, GE (Zeeweed Technology — 0.04  $\mu\text{m}$  pore size and constructed of polyvinylidene fluoride [PVDF]) and Mersorb LW (a sulfur-impregnated activated carbon) for ultrafiltration and adsorption, respectively were selected as recommendations for pilot demonstrations at the Whiting Refinery. The reactive filtration (Blue PRO) process was not subjected to the same selection protocol because it is supplied by only one vendor, Blue Water Technologies, Inc. Due to the large volumes of water required for pilot testing, the project team recommended that pilot testing needs to be conducted at the Whiting Refinery by using clarifier effluent (CE) or effluent-to-lake (ETL). This chapter also summarizes the utility requirements for each technology relative to the specific site operational requirements at the Whiting Refinery.

### Technology Assessment Protocols

This section addresses major considerations for the selection of treatment processes for piloting at the Whiting Refinery. In order to evaluate the tested bench-scale technologies, the data reduction, processing, and review were conducted under Task 4 of this project. The objectives of the technology evaluations were:

- a. To select promising bench-scale technologies for pilot testing;
- b. To identify performance factors that can influence scale-up;
- c. To determine factors that can influence cost, which is important for the applicability of technology at full-scale; and
- d. To evaluate the readiness for full-scale application of the selected technologies.

A decision matrix was developed as the basis for the comparative assessment of each technology's test data, as well as for the selection of technologies and vendors for piloting. The decision matrix was subdivided into a two-phase evaluation, as follows:

### **Tier 1: Endpoint Measures of the Performance Matrix (Figure 4-1)**

#### **Step 1**

- Can the technology meet the target concentration limits?

#### **Step 2**

- If so, further evaluate promising technologies for other performance criteria, as specified in the performance matrix.
- Select the high-ranking technologies for further evaluation.

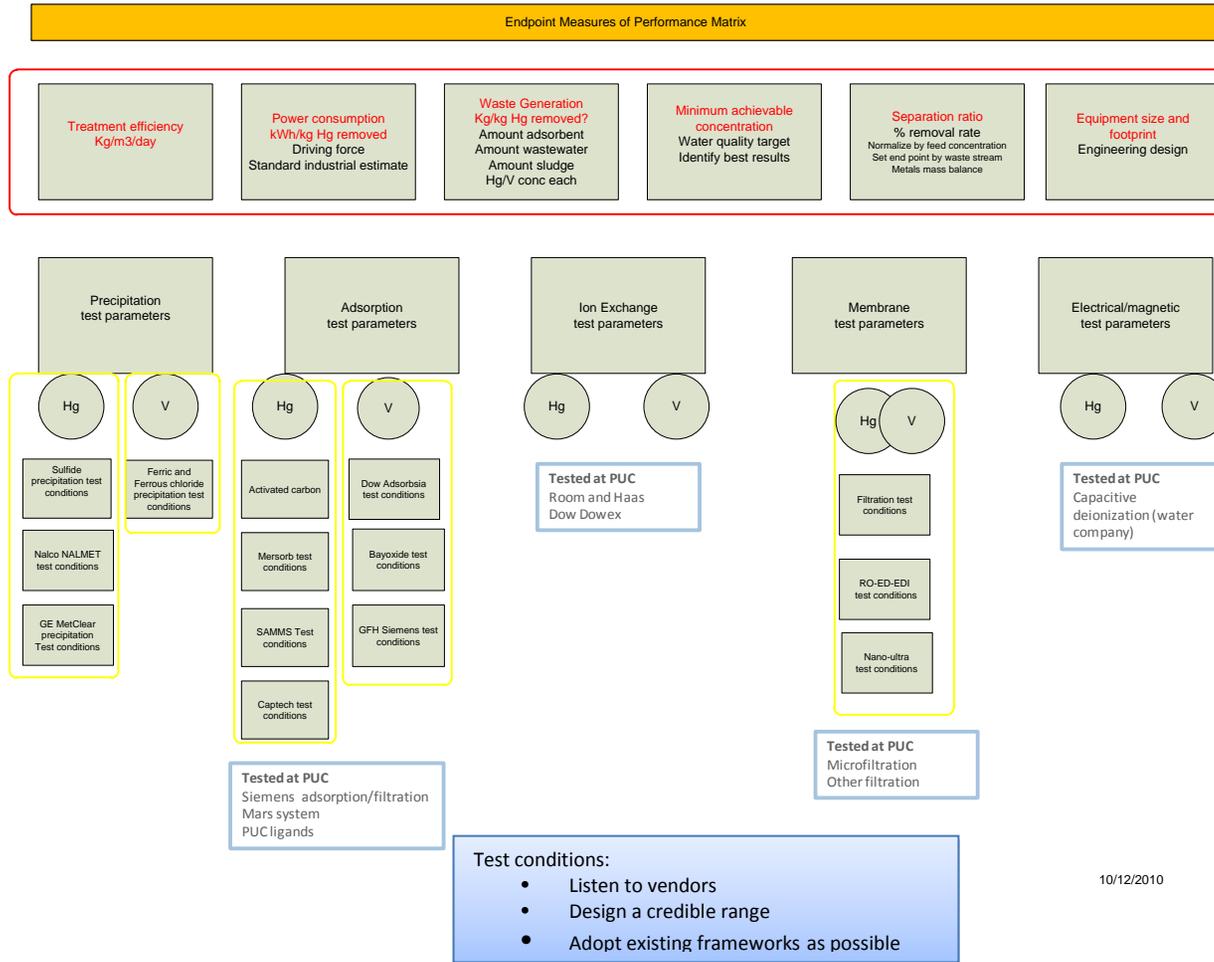
### **Tier 2: Technology Readiness and Vendor Selection for Pilot/Full-scale Applications**

#### **Step 3**

- Identify the full-scale readiness of the selected technologies.
- Determine trade-offs and select the finalist vendor(s).

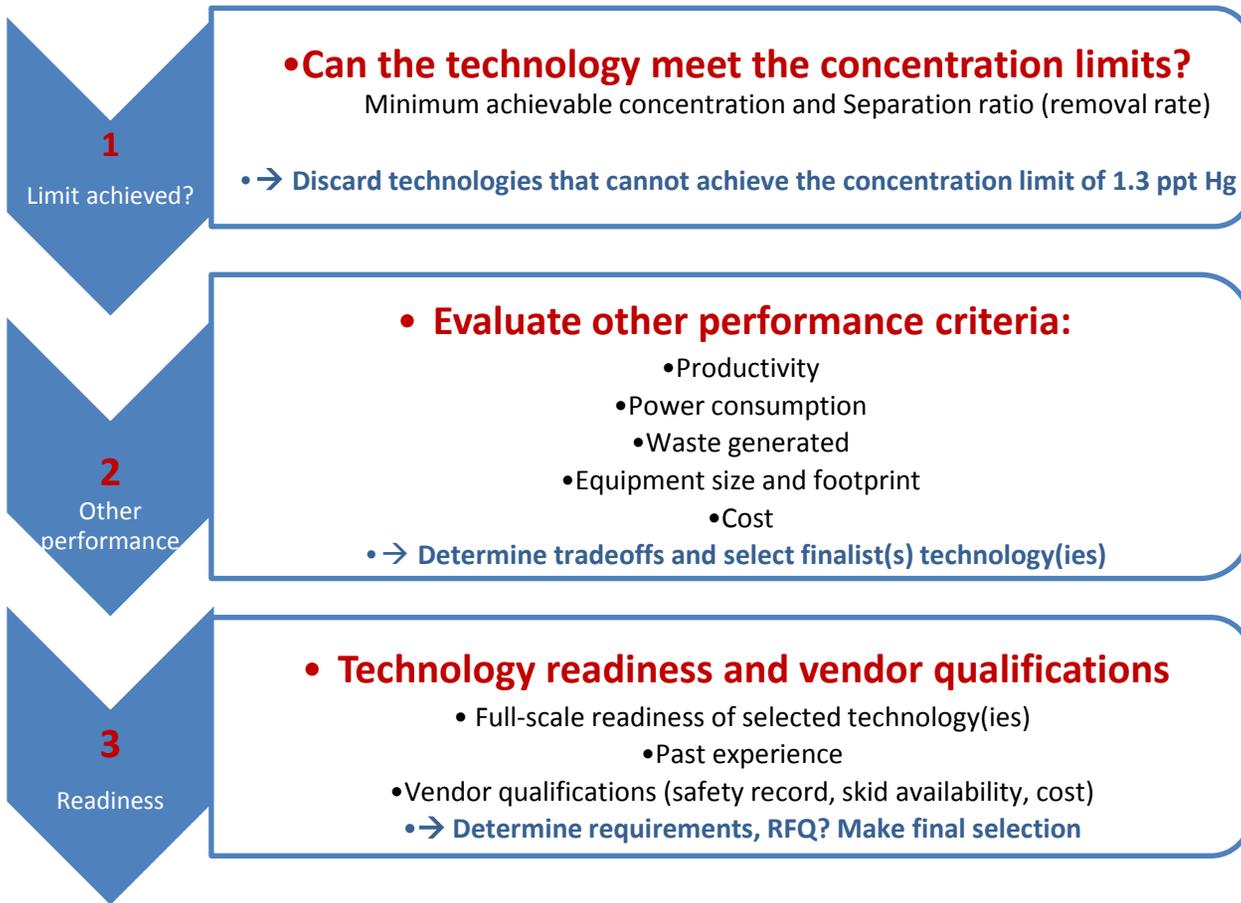
Figure 4-2 summarizes the step-wise evaluation protocol that was followed to determine the most promising technologies to achieve target vanadium and mercury concentrations in the treated wastewater.

**Figure 4-1. Endpoint Measures of the Performance Matrix\* (groups of technologies tested with a common test plan are circled in yellow)**



\*Not all info available for all tested technologies

Figure 4-2. Steps in the Technology Assessment Protocol



### **9step 1: Determine the Ability to Meet Target Mercury and Vanadium Effluent Concentrations in the Treated Wastewater**

The preliminary evaluation of the treatment alternatives involved selecting the technologies that were shown to be capable of meeting the target mercury and vanadium limits in the treated wastewater. In the selection of the best candidate treatment technologies, first consideration was given to the minimum achievable concentration and separation ratio (removal percentage) (Table 4-1). Because of the wide variety of characteristics in the Whiting Refinery wastewater, the wastewater characteristics were also reported along with the achievable limits and separation ratio. Table 4-1 also highlights the technologies that met the target effluent limits (280 ppb V and <1.3 ppt Hg). Non-highlighted technologies that could not meet the expected discharge limits were excluded from further consideration for pilot-scale testing.

Table 4-1 also summarizes the performance of available technologies for dissolved mercury removal. Although the Whiting Refinery wastewater did not contain dissolved mercury (<1 ppt dissolved mercury) during the sampling events from December 2009 to August 2010, historical data from BP indicate the potential for dissolved mercury to be present. Therefore, the decision was made to test and evaluate technologies with the capability to remove dissolved mercury.

**Table 4-1. Evaluation of Mercury and Vanadium Removal Technologies (ability to meet target mercury and vanadium effluent limits )<sup>1</sup>**

Technology	Use	Tested Chemicals/ Materials	Tested Conditions	Separation Ratio (% removal rate)	Minimum Achievable Concentration	Notes
Precipitation	Hg	Sodium sulfide Nalmet 1689 <sup>a</sup> GE Met Clear <sup>a</sup> Ferric sulfate	1-20 ppm as S 5-50 ppm 10-100 ppm 10-50 ppm as Fe	% 56.5; same as with the method blank % 56.5; same as with the method blank % 56.5; same as with the method blank Cannot be determined*	Not applicable <sup>b</sup> 6.98→3.3→0.13 ppt <sup>a</sup> 5.71→2.8→0.2 ppt <sup>a</sup> Not applicable*	<sup>a</sup> MetClear and Nalmet removed 98% and 91% of Hg after filtration, respectively. <sup>b</sup> All the tested reagents, except Nalmet, contain high levels of Hg (0.5-16.4 ppt).
	V	Ferric chloride Ferrous chloride Ferric sulfate  Unipure	10-100 ppm as Fe 10-100 ppm as Fe 10-100 ppm as Fe  10-100 ppm as Fe	10-20 ppm can remove 91-99% of V at tested CE containing 250-500 ppb V. This ratio increases to 100% after filtration.  Flocs did not settle because of air bubbles.	<30 ppb and <10 ppb V with filtration	The 10-20 ppm of Fe dose <i>does not</i> appear to create any discharge limits problem (1 ppm Fe as effluent; <530 ppb Fe unfiltered).
Filtration	Hg	Microfiltration <sup>c, d</sup> Ultrafiltration <sup>c, d</sup> Nanofiltration <sup>c</sup> RO*	14.7-60 psi 14.7-100 psi 300-700 psi 300-700 psi	65-96%, depending on pressure 81-97%, depending on pressure 44-63%, depending on pressure 63-83%, depending on pressure	0.15-0.6 ppt@ ≥40 psi 0.14 <sup>d</sup> -1.05 <sup>c</sup> ppt@ ≥50 psi 1.3 ppt@ 300 psi 1.2 ppt@ 300 psi	<sup>c</sup> CE as-is <sup>d</sup> After prefiltration
	V	Microfiltration <sup>c</sup> Ultrafiltration <sup>c</sup> Nanofiltration <sup>c</sup> Reverse osmosis <sup>c</sup>	14.7-60 psi 14.7-100 psi 300-700 psi 300-700 psi	2 -20% 8-57%, depending on pressure No removal 7-17 %, depending on pressure	If the initial V is >300 ppb, the obtained removal percentages do not meet the 280 ppb target V concentration.	<sup>c</sup> CE as-is

**Table 4-1. (Cont.)**

<b>Technology Type</b>	<b>Technology</b>	<b>Use</b>	<b>Separation Ratio (% Removal Rate)</b>	<b>Minimum Achievable Concentration</b>	<b>Notes</b>
Adsorbent	Calgon F600 –	Dissolved Hg	95.0% Hg	<0.5 ppt Hg	Initial Hg 10 ppt
	Calgon OLC –	Dissolved Hg	92.8% Hg	0.72 ppt Hg	Initial Hg 10 ppt
	Mersorb LW	Dissolved Hg	99.2% Hg	<0.08 ppt Hg	Initial Hg 10 ppt
	Thiol-SAMMS	Dissolved Hg	98.8% Hg	<0.09 ppt Hg	Initial Hg 10.84 ppt
	Captech	Dissolved Hg	51.6% Hg	4.80 ppt Hg	Initial Hg 9.92 ppt
	<i>Mars System</i>	<i>Dissolved Hg</i>	<i>60.6% Hg</i>	<i>10.4 ppt Hg Retest</i>	<i>Initial Hg 26.4 ppt</i>
	Filtration/ precipitation/ adsorption	Blue PRO	Hg, V (particulate and dissolved)	98.7% Hg particulate 92.2% Hg dissolved 99.6% V	0.35 ppt Hg particulate 0.74 ppt Hg dissolved <1 ppb V
Electrical	EDI	Dissolved Hg and V	79.2 % Hg 85.5 % V	1.57 ppt Hg <10 ppb V	Initial Hg 7.5 ppt
	<i>Capacitive Deionization</i>	<i>Dissolved Hg and V</i>	<i>81.6% Hg</i>	<i>0.74 ppt Hg</i>	<i>Initial Hg 4.02 ppt</i>
Ion exchange	<i>Keylex</i>	<i>Dissolved Hg</i>	<i>90.8 % Hg</i>	<i>0.71 ppt Hg</i>	<i>Batch test Initial Hg 7.62 ppt</i>
	<i>Keylex</i>	<i>Dissolved Hg</i>	<i>83.7% Hg</i>	<i>1.74 ppt Hg</i>	<i>Column test 5.8 minute contact time Initial Hg 10.5 ppt</i>

**Table 4-1. (Cont.)**

<b>Technology Type</b>	<b>Technology</b>	<b>Use</b>	<b>Separation Ratio (% Removal Rate)</b>	<b>Minimum Achievable Concentration</b>	<b>Notes</b>
Adsorbent	Bayoxide E-IN-20	V	98.0%	4.9 ppb	Spiked up to 250 ppb V, if needed
	GFH	V	95.6%	11 ppb	Spiked up to 250 ppb, if needed
	Adsorbsia	V	97.6%	6 ppb	Spiked up to 250 ppb, if needed

<sup>1</sup> Includes technologies tested by Purdue University Calumet (in italics).

## Step 2: Evaluate Other Endpoint Measures of the Performance Matrix and Select Finalist Technologies

### Evaluation of Other Endpoint Measures of the Performance Matrix

Technologies with the capability to achieve the target mercury and vanadium concentrations were further evaluated and compared for other endpoint performance measures, as illustrated in Figure 4-1. Treatment productivity, power consumption, waste generation, equipment size and footprint, and cost were also analyzed.

CapdetWorks software (version 2.5, 2007) was used to estimate the parameters in the endpoint measures of the performance matrix, such as power consumption, chemical usage, waste generation, and so forth, to the extent that these parameters can be measured or derived during the bench-scale evaluation of technologies. This software also provided reasonable cost estimates (for this preliminary stage of analysis), which were used in the comparative assessment of treatment technologies.

CapdetWorks, developed by Hydromantis, is based upon designs by the U.S. Environmental Protection Agency (EPA) and U.S. Army Corps of Engineers. It is an easy-to-use, planning-level tool that can assist in the rapid design and cost determination of each tested wastewater treatment process. CapdetWorks also allows users to determine estimates of plant sizes and the capital costing of each treatment process, which are necessary in the comparison of tested technologies for scaling-up purposes (1). CapdetWorks is a proven software that has been used for many years by the EPA (2–4) and dozens of industries, municipalities, and consultants throughout the world (1). It is the industry standard.

To determine estimates for the endpoint performance matrix and the cost for each tested treatment process, the following criteria were used:

- A process layout involving the required unit operations for each treatment technology was generated.
- Required input variables, such as wastewater flow rate, wastewater influent quality, and desired effluent quality or other performance coefficients specific to each treatment technology, were defined by considering the target effluent limits, literature data, bench-scale data and vendor recommendations. For example, adsorption inputs included the adsorbent capacity (wt. Hg/wt. adsorbent) as determined from bench-scale testing, adsorbent price as well as flux and empty bed contact times recommended by vendors. In some cases, default values developed by Hydromantis, based on the various design and vendor data historically used in wastewater treatment plants, were chosen because we did not know details about the design and operation of the Whiting Refinery WWTP.
- Next, the software calculated the required sizes of the unit operations and used cost-curve models from the software's database to estimate the capital, labor, chemical, and energy costs that would be incurred.
- Although the outputs from CapdetWorks included capital and construction costs and equipment size and footprint (see Appendix 2), these estimates were not included in Table 4-2, since these calculations are site-specific (e.g., land and labor) and equipment/vendor-specific. It should also be noted that the cost estimates in Table 4-2 do not represent the cost to implement the entire process of an alternative. The cost estimates are for comparison purposes only among the tested technologies.
- The model uses several standard indices, including the *Engineering News-Record* (ENR) *Construction Cost Index*, the *Marshall & Swift Index*, and the *Pipe Index*. July 2010 cost indices were used to update the costs from September 2007 to current dollars (5, 6).

Table 4-2 presents the benchmark analysis with the resulting endpoint measures of performance for the candidate treatment technologies, as well as a comparison of the various cost estimates that were evaluated to assess the cost effectiveness of each treatment option. The estimates included only four categories of cost calculations: power/electricity, chemical purchase, waste disposal, and other operations and maintenance (O&M) costs. For comparison, the treatment productivity was calculated as kilograms of removed contaminants per unit of applied treatment (such as the amount of adsorbent or ferric sulfate) per day. The estimate for each treatment technology

was calculated on a 14.1 MGD flow basis (ETL average flow rate). Although the average flow of ETL was used during the calculations, the real systems should be designed to treat the maximum flow of ETL (40 MGD). The disposal of residuals generated from each process must be carefully considered because several options exist. A detailed study is beyond the scope of this treatability study and should be performed by BP, since they are cognizant of their operating permits, their facility footprint, and their corporate policy regarding hazardous waste management. The piloting work will provide additional information regarding the quantity and composition of the generated waste streams, which will facilitate decision making regarding waste disposal. The piloting work should also include the development of strategies to manage the residuals generated by the recommended processes.

In general terms, it can be stated that precipitation generates sludge, which probably would need to be thickened, filter pressed, and then stabilized before disposal. Ion exchange resins can be regenerated and reused. However, doing so creates a mercury-laden acidic or basic waste stream that must be disposed of, most likely as a hazardous waste. Membrane filtration has an associated retentate (or concentrate) stream (as high as 5–10% of influent for ultrafiltration) that must be either recycled within the system or further concentrated and disposed of. Additionally, membrane filtration creates backwash and chemical cleaning waste streams that require disposal. The amount of these streams is dependent on the fouling characteristics of the wastewater and can be determined through piloting. The Blue PRO reactive filtration process also produces a residual stream (up to about 7% of the influent stream) (7) that can be either recycled to the beginning of the wastewater treatment plant or concentrated, dewatered, and stabilized prior to disposal.

Most adsorption processes generate a backwash stream that requires disposal. In the case of Mersorb LW, the vendor claims that backwash is not needed (8). This claim would have to be confirmed at the pilot-scale. Disposal of the spent adsorbents requires additional study. For thiol-SAMMS, the mercury adsorbed can be stripped off with acid, and the adsorbent reused for mercury adsorption. However, this process generates a mercury-laden acid stream that would require disposal. For all the applications tested to date, used thiol-SAMMS have passed the toxicity characteristic leaching procedure (TCLP) test. However, the vendor recommends that spent thiol-SAMMS be disposed of as hazardous waste in case an acidic leaching condition is encountered during final disposal (9). Both Mersorb LW and activated carbon can be retorted to remove the mercury from the adsorbent. In the case of Mersorb LW, it cannot be reused once its capacity has been spent because high-temperature retorting changes the Mersorb, thereby preventing further use as a mercury adsorbent. Retorting Mersorb does have the benefit of enabling its disposal as a nonhazardous waste (10). Although activated carbon could theoretically be retorted and then reused, doing so increases the pore size, which may have an adverse effect on mercury adsorption (11) — this would need to be tested. At this time, limited facilities exist for retorting either Mersorb or activated carbon, since current demand is limited. Another possibility may be an on-site retort furnace at the Whiting Refinery. The vanadium adsorbents (GFH, Bayoxide E IN-20, and Adsorbisia As 500) cannot be processed and reused once their capacity has been spent. Each vendor claims that their product passes the TCLP test and therefore can be disposed of as a nonhazardous waste (12-14). However, such claims would need to be verified through testing.

The costs and amounts of chemicals (e.g., reagents, adsorbents, and resin) are also given in Table 4-2, along with the waste production rates (kilogram of waste per kilogram of removed contaminant) and disposal costs. Higher costs are associated with the replacement of adsorbents and the disposal of generated sludge due to chemical addition. For simplicity, it is assumed that the adsorbents cannot be reprocessed and reused once their capacity is spent, although further study may determine a way to do so, given the economic incentive. The energy used to power pumps, mixers, and other equipment components was also calculated as kilowatt-hour per kilogram of removed contaminant for each treatment alternative.

The waste generation, energy, and cost data obtained from the filtration experiments were not truly representative because of scalability issues from bench-scale to pilot/full-scale. Therefore, they are not provided in Table 4-2. These parameters are also highly vendor-specific. However, some of the indicative full-scale data given in Table 4-3 were derived from literature (15, 16).

## Technology Selection for the Pilot Study

The endpoint performance measures matrix developed in this project provides a framework for the selection of one or more technologies from a number of alternatives that are technically feasible for achieving target mercury and vanadium concentrations. The cost assessments at the planning level also assisted with the further evaluation of treatment alternatives. The findings from these technology and cost assessment studies could be extremely useful in the selection of wastewater treatment systems for achieving very low effluent mercury and vanadium levels. Several successful technologies with lower waste generation, power requirements, and/or cost estimates were recommended for pilot-testing alternatives at the Whiting Refinery.

Among the candidate technologies, iron precipitation offers a robust option to remove vanadium from the CE/ETL streams when the Stretford unit is on. Adaptation of the Whiting Refinery WWTP to accommodate this technology is simplified, since BP already has a permit for the use of ferric sulfate as a settling aid in the secondary clarifier. Moreover, the vanadium concentration in the ETL/CE exceeded the future discharge limits only 5 times out of 21 sampling events at the Whiting Refinery (see Chapter 2), and these events were clearly attributed to the Stretford purge — a smaller flow effluent that could be treated separately. Because of these considerations, vanadium removal technologies were not included in the final selection for pilot-scale testing. Therefore, candidate technologies specifically for vanadium removal were excluded from further evaluations, thus allowing the team to focus on the prioritization of technologies for pilot-scale testing of mercury removal.

In terms of mercury removal, the Module 3 testing results found that some technologies were effective on particulate mercury, while others were effective on dissolved mercury. One emerging technology was found to be effective on both particulate and dissolved mercury. During the Module 3 treatability testing, it was found that particulate mercury removal was sufficient to enable the wastewater to meet the proposed 1.3 ppt Hg target limit most of the time. However, historical data from the spring of 2009 show that mercury in the dissolved form was present approximately half the time at levels above 1.3 ppt. Hence, there might be a need to consider testing technologies that can treat both particulate and dissolved mercury removal, alone or in combination.

Three high-ranking potential mercury removal technologies from the endpoint performance matrix evaluations were chosen for piloting at the Whiting Refinery: microfiltration/ultrafiltration (for particulate mercury); adsorption (for dissolved mercury); and an emerging technology (for both particulate and dissolved mercury), the Blue PRO reactive filtration process, which may be effective on both particulate and dissolved mercury. Although Blue PRO is still in the development stage (1.25 MGD), it was considered for further evaluation because of the promising test results. The potential application points of promising technologies at the Whiting Refinery WWTP are shown in Figure 4-3.

### Step 3: Evaluate Technology Readiness and Vendor Qualifications

The selected highly ranked technologies were further evaluated for technology readiness in full-scale applications by engaging with several vendors that offer the technology (for wastewater or water treatment applications). A questionnaire was prepared to obtain answers to the same set of questions from each vendor. Each vendor was requested to disclose only non-proprietary or non-confidential information, as follows:

- Type of technology and its description (e.g., hollow fiber, flat sheet, crossflow, etc.).
- Use of the technology. Where has the technology been used (e.g., types of wastewater, maximum flow rates, number of installations)?
- References for the project team to contact regarding project delivery and process performance.
- Safety records of the vendor — critical to determine whether vendor personnel would be allowed on-site at the Whiting Refinery.
- Schedule and availability of the pilot-scale equipment.

- Operation of the pilot-scale equipment. Can the pilot-skid be operated for 24 hours/7 days (to determine the required manpower needed for pilot testing)? Depending on where the skid will be located, especially can they help with coverage over weekends?
- Location of the laboratory. Does the vendor have a lab to analyze the samples to monitor process performance, or do they prefer samples to be collected and analyzed by a third party lab?
- Footprint of the pilot-skid — critical to determine the test location at the Whiting Refinery.
- Cost of the pilot-skid.
- Pretreatment requirement for the technology.

Vendor technologies were examined in detail to assess the level of development (through previous case history) and readiness to treat up to 40 MGD of wastewater (the maximum flow rate). The results indicated that several vendor technologies had potential for pilot-scale testing at the Whiting Refinery (Tables 4-4 to 4-6). The following sections describe how vendors were selected for pilot testing at the Whiting Refinery.

Figure 4-3. Application Points of Promising Technologies at the Whiting Refinery WWTP

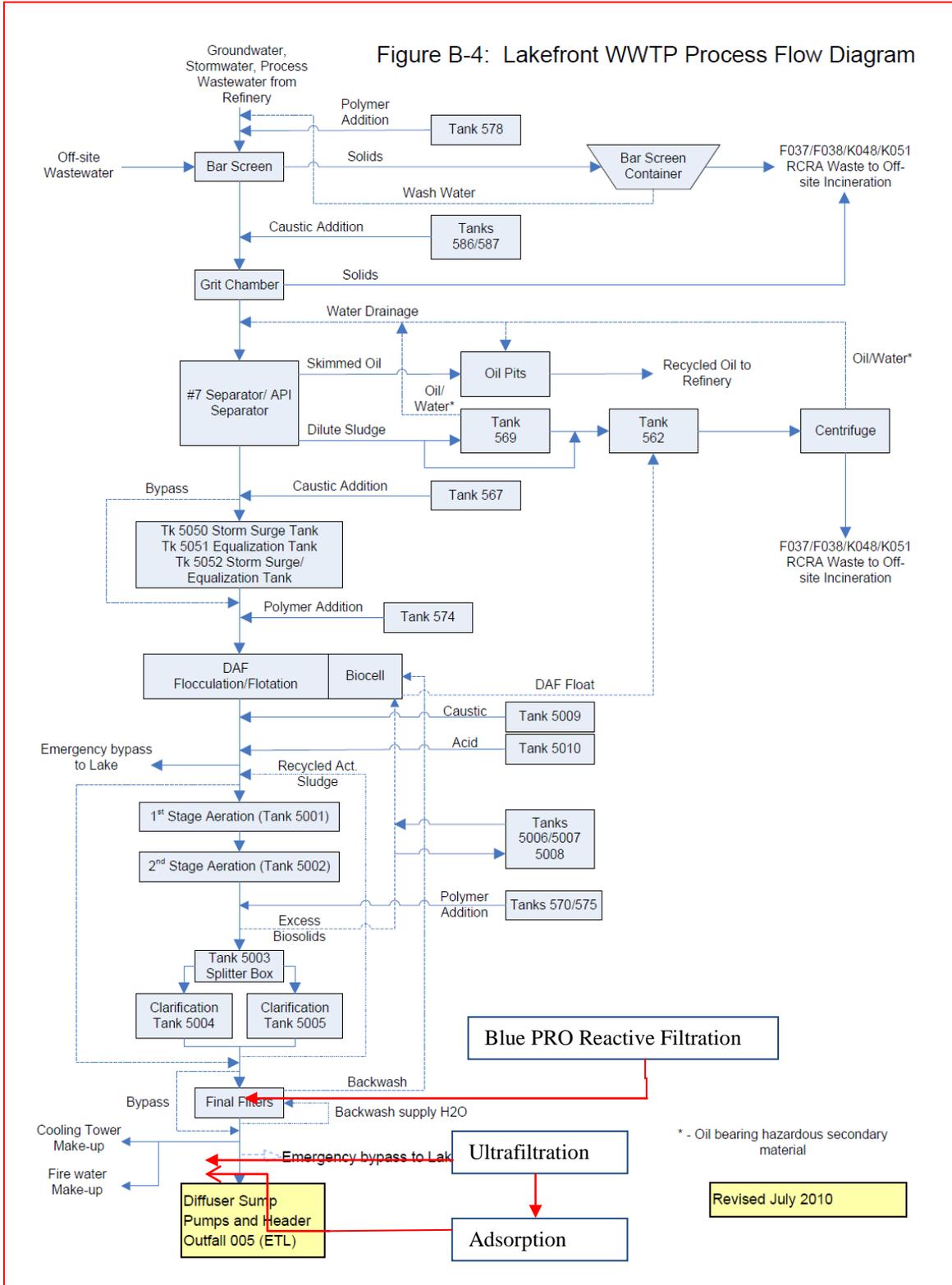


Table 4-2. Evaluation of Candidate Treatment Technologies for Scale-up<sup>1</sup>

Technology	Use	Separation Ratio (% removal)	Minimum Achievable Concentration	Treatment Productivity	Cost <sup>2</sup>	Power Consumption (kWh/kg removed)	Waste Generation (kg waste/kg removed)
Precipitation	V	99%	250 ppb → 3 ppb	$1.24 \times 10^{-2}$ kg V removed/kg Fe; 2,330 lb iron required/day	Chemical: \$900,000/yr; Power: \$16,100/yr; Operation: \$340,000/yr	34 kWh/kg V removed	197 kg dry solids/kg V removed
SAMMS Adsorbent	Hg	98.8%	<0.09 ppt	$3.1 \times 10^{-7}$ kg Hg removed/kg adsorbent; 3,281 lb SAMMS required/day	Adsorbent: \$59.9 Million/yr; Power: \$192,100/yr; Operation: \$92,700/yr	$11.41 \times 10^6$ kWh/kg Hg removed	$3.23 \times 10^6$ kg spent adsorbent/kg Hg removed
Mersorb LW Adsorbent	Hg	99.2%	<0.08 ppt	$1.9 \times 10^{-7}$ kg Hg removed/kg adsorbent; 5,353 lb Mersorb required/day	Adsorbent: \$10.9 Million/yr; Power: \$192,100/yr; Operation: \$92,700/yr	$11.41 \times 10^6$ kWh/kg Hg removed	$5.26 \times 10^6$ kg spent adsorbent/kg Hg removed
Calgon F600 Adsorbent	Hg	95.0%	<0.5 ppt	$8.5 \times 10^{-8}$ kg Hg removed/kg adsorbent; 11,965 lb F600 required/day	Adsorbent: \$24.4 Million/yr; Power: \$192,100/yr; Operation: \$92,700/yr	$11.41 \times 10^6$ kWh/kg Hg removed	$11.76 \times 10^6$ kg spent adsorbent/kg Hg removed

Table 4-2. (Cont.)

Technology	Use	Separation Ratio (% removal)	Minimum Achievable Concentration	Treatment Productivity	Cost <sup>2</sup>	Power Consumption (kWh/kg removed)	Waste Generation (kg waste/kg removed)
Calgon OLC Adsorbent	Hg	92.8%	0.72 ppt	$3.0 \times 10^{-8}$ kg Hg removed/kg adsorbent; 33,900 lb OLC required/day	Adsorbent: \$69 Million/yr; Power: \$192,100/yr; Operation: \$92,700/yr	$11.41 \times 10^6$ kWh/kg Hg removed	$33.3 \times 10^6$ kg spent adsorbent/kg Hg removed
Bayoxide E-IN-20	V	98.0%	4.9 ppb	$5.56 \times 10^{-3}$ kg V/kg adsorbent; 5,043 lb Bayoxide required/day	Adsorbent: \$10.7 Million/yr; Power: \$192,000/yr; Operation: \$92,700/yr	414 kWh/kg V removed	180 kg spent adsorbent/kg V removed
GFH	V	95.6%	11 ppb	$1.47 \times 10^{-2}$ kg V/kg adsorbent; 1,908 lb GFH required/day	Adsorbent: \$2.11 Million/yr; Power: \$192,100/yr; Operation: \$92,700/yr	414 kWh/kg V removed	68 kg spent adsorbent/kg V removed

Table 4-2. (Cont.)

Technology	Use	Separation ratio (% removal)	Minimum Achievable Concentration	Treatment Productivity	Cost <sup>2</sup>	Power Consumption (kWh/kg removed)	Waste Generation (kg waste/kg removed)
Adsorbsia	V	97.6%	6 ppb	$1.32 \times 10^{-2}$ kg V/kg adsorbent; 2,124 lb Adsorbsia required/day	Adsorbent: \$4.51 Million/yr; Power: \$192,100/yr; Operation: \$92,700/yr	414 kWh/kg V removed	76 kg spent adsorbent/kg V removed
Blue PRO Precipitation/ Filtration/ Adsorption	Hg, V	98.7% Hg particulate 92.2% Hg dissolved 99.6% V	0.35 ppt Hg, particulate; 0.74 ppt Hg, dissolved; <1 ppb V	No make-up sand needed	Chemicals: \$1.23 Million/yr; Power: \$105,774/yr; Operation: \$265,000/yr; Landfilling: \$240,000/yr	6.28 $\times 10^6$ kWh/kg Hg removed	86 kg dry solids/kg V removed
<i>Keylex Ion Exchange</i>	<i>Hg</i>			<i>2.68 × 10<sup>-10</sup> kg Hg removed/kg adsorbent; 4.6 × 10<sup>+6</sup> lb Keylex required/day</i>	<i>Resin: \$43.6 Billion/yr; Power: \$192,100/yr; Operation: \$92,700/yr</i>	<i>11.41 × 10<sup>6</sup> kWh/kg Hg removed</i>	<i>Resin cannot be regenerated</i>
<i>Water Company</i>	<i>Hg, V</i>				<i>Very high — cannot be applied to full-scale</i>		
Micro/ Ultrafiltration	Hg	>95 %	<0.18 ppt	Vendor and technology specific (see Table 4-3)			*After prefiltration

<sup>1</sup> Includes technologies tested by Purdue University Calumet (in italics).

<sup>2</sup> (a) Design basis: 14-MGD EFL in cost calculations; (b) adsorbent and ion-exchange resin calculations were made based on the *no regeneration* assumption.

**Table 4-3. Indicative Cost and Energy Consumption Data for Membrane Filtration Technologies (5, 6)**

Technology	Operational Cost	Energy Consumption	Membrane Price
Micro/ultrafiltration	\$0.2–0.25/m <sup>3</sup> (\$757-946/MGD)	0.1kWh/m <sup>3</sup> (378.5 kWh/MGD)	\$10/m <sup>2</sup> (\$0.93/ft <sup>2</sup> )
Nanofiltration	\$0.33–0.46/m <sup>3</sup> (\$1,259-1,741/MGD)	≤ 0.5kWh/m <sup>3</sup> (≤ 1,893 kWh/MGD)	\$10/m <sup>2</sup> (\$0.93/ft <sup>2</sup> )
RO	<\$0.53/m <sup>3</sup> (<\$2,006/MGD)	~0.5kWh/m <sup>3</sup> (1,893 kWh/MGD)	\$10/m <sup>2</sup> (\$0.93/ft <sup>2</sup> )

**Vendor Selection for Membrane Filtration**

Ten vendors were contacted as potential providers of pilot-scale equipment. Among them, only four vendors responded to our inquiries (Table 4-4). Kruger was not selected for further consideration, since they do not have the available skid and personnel to treat refinery wastewater. Table 4-5 shows the details of the membrane units and services offered by the remaining three vendors. Koch Membranes was also excluded from the vendor list, because of the lack of experience to treat very large flows of wastewater, such as the 40 MGD potentially for the Whiting Refinery. As such, Siemens and GE remained as the finalists for the filtration pilots. Meetings were organized at the Whiting refinery to select the preferred filtration vendor. Organizing these meetings at the refinery helped to provide an opportunity for a) the vendors to make a presentation to PUC/ANL/BP about their technology details (including details about their pilot-scale units) as well as application case studies, b) the vendors to tour potential pilot-scale locations at the refinery to better tailor their offers.

Subsequently, the project team reviewed the vendors’ presentations and meeting notes. Both vendors have basically the same membrane technology, which utilizes the same PVDF hollow fiber membrane (0.04 micron pore size), an outside-in flow path, an outside air scour/drain down backwash, and a vacuum system to draw flow through the membrane. Siemens also has pressurized systems with the same basic membrane components. The operation mode (pressurized versus vacuum) and accessories are the main differences between the two vendors. The maximum trans-membrane pressure (TMP) for a submerged (vacuum) system is 12 psi, while the maximum TMP for a pressurized system is 22 psi, so that the system is claimed to be operated at a higher flux (requiring less membrane area). The relationship between the flux to the applied TMP has yet to be determined. In addition, higher flux rates result in a higher convection flow on the membrane surface. If the wastewater has higher fouling characteristics, it can significantly increase the fouling rate of the membranes (17). In that case, higher flux rates might not be desirable, depending on the Whiting Refinery wastewater characteristics.

The maximum operating temperature is 104 °F (40 °C) for both vendors’ technologies. Both vendors indicated that operating membranes at 104 °F for 10 consecutive days might impact the membrane integrity. This issue could occur because the glue used to seal the components of the membrane might melt at this temperature and result in leaks in the system. Table 4-6 highlights the pros and cons for both vendors’ offers and technologies.

**Table 4-4. Capabilities of the Filtration Vendors for the Pilot-scale Study at the Whiting Refinery<sup>1</sup>**

Vendor	Technology Description	Installations	Skid Availability	Skid Cost	Operation Assistance	Analytical
Siemens	Memcor CP, low-pressure hollow fiber, PVDF, 0.04 μm	Up to 130 mgd <sup>2</sup> , including petroleum refinery	Available immediately	\$10,000 per month	Start-up and troubleshooting assistance available	Client's responsibility
GE	Zeeweed 500, low-pressure hollow fiber, PVDF, 0.04 μm	50 systems worldwide, 2–100 mgd <sup>2</sup> , including petroleum refinery	Available immediately	\$26,500 initially, then \$6,500 per month	Start-up and troubleshooting assistance available	Client's responsibility
Koch Membranes	1) 1×16 pressurized inside-out for tubular membranes only; 2) Universal, pressurized inside-out for tubular and hollow fiber; 3) Puron™ tertiary, outside-in hollow fiber	Up to 10 MGD, no experience at large plants	Available immediately	\$10,000 per month	Start-up and troubleshooting assistance available	Client's responsibility
Kruger-Veolia	Norit-X, hollow fiber, PES, 0.01 μm	70 mgd (water reclamation)			Kruger- Veolia	Norit-X, hollow fiber , PES, 0.01 μm

<sup>1</sup> All vendors are able to provide references and safety records.

<sup>2</sup> Very high flow rates are for potable water treatment and not wastewater service.

**Table 4-5. Comparison of the Vendors' Pilot-scale Membrane Units and Services**

<b>Vendor</b>	<b>Trial Unit Description</b>	<b>Pilot-scale Capacity</b>	<b>Scalability Factor to Full-scale Installations</b>	<b>Membrane Installation and Start-up</b>
SIEMENS	Memcor pilot equipped with trial unit and compressor	35–50 gpm (one to three modules)	~100% (The same module is used in the full-scale applications.)	The unit can be operational within 3–5 working days after delivery.
GE	ZeeWeed* 500D	10–50 gpm (three modules)	~100% (The same module is used in the full-scale applications.)	The unit can be operational within 5–7 working days after delivery. ( <i>Local support is a couple of miles from Whiting.</i> )
KOCH Membranes	<ul style="list-style-type: none"> <li>•1×16 pressurized inside-out for tubular membranes only</li> <li>•Universal, pressurized inside-out for tubular and hollow fiber</li> <li>• Puron™ tertiary, outside-in hollow fiber</li> </ul> (*Depending on the wastewater characteristics, KOCH prefers to run two pilot-scale units.)	1–5 gpm (*depending on the type of membrane)	~100 % (in terms of flux)	The customer is responsible for positioning and installing the equipment. KMS process engineering requires at least 4 days on-site for start-up and operator training.

**Table 4-6. Vendor Comparison for Pilot-scale Filtration**

<b>Criteria</b>	<b>Siemens</b>	<b>GE</b>
Vendor representation	Sr. Account Manager and Technical Sales Manager	Global Pilot Team Leader and Business Development Leader
Membrane technology	Vacuum (submerged) OR Pressurized (separate units)	Vacuum (submerged)
Full-scale experience	Mostly municipal wastewater.	Refinery and petrochemical wastewater treatment, as well as municipal wastewater.
Pilot-scale experience on heavy metals removal, especially mercury from refinery wastewater	Not specifically presented.	Yes; both MBR and tertiary treatment.
Troubleshooting assistance	Sent from Massachusetts.	Readily available — field engineers are within a few-mile radius of the Whiting Refinery.
Handling backwash waste	Plans to send it back to headworks (which is not desirable). However, after the meeting, Siemens suggested a treatability study to determine options.	Zero discharge team at GE to advice of disposal options.
Weekly progress updates	Not mentioned.	Weekly 30-minute teleconference meetings with BP, Purdue, and Argonne.
Cost of pilot study; costs are essentially the same	\$10,000 per month includes 3 days of start-up. Transportation costs will be paid by the customer. Additional technical help carries extra charges: \$1,000 per day, plus travel costs.	\$52,500 for 17 weeks of study includes 5 days of start-up and transportation costs. This cost also includes weekly meeting and technical help.
Limitations in application of vendor technology	Temperature (104 °F/40 °C) 5 < pH < 9.5 The magnitude of FOG (>15 ppm) and/or the duration that the membranes must operate with high FOG might be a concern.	Temperature (104 °F/40 °C) 5 < pH < 9.5 No limitation on FOG, since the same technology has been used in MBR.
% recovery	95–97% per municipal wastewater data.	90–95% per refinery wastewater data. However, GE would provide assistance to optimize the recovery rates.
Confidentiality and ownership of test results	More restrictive.	Less restrictive.

The project team requested Siemens to address the following issues before making a decision:

1. What are the advantages of using the pressurized unit over the vacuum unit? Are there any savings in footprint, flux rate, recovery rate, etc.?

Response from Siemens: *“The difference between a Siemens 40 MGD pressurized system (called CP) and submerged system (called CS) is in the economics of the full-scale design, not the water source to be treated. Both systems utilize the same PVDF hollow fiber membrane (0.04 micron pore size), outside in flow path, and outside air scour/drain down backwash. The maximum TMP for a CS system is 12 psi while the maximum TMP for a CP system is 22 psi so Siemens is able to build full-scale CP systems that operate at a higher flux (provide less membrane area) due to the wider TMP operating envelope. The quality of the membrane filtered water is identical between CS and CP systems.”*

Siemens also indicated that *“a CP system will be more economical to construct on the shoreline of BP's Whiting Refinery due to its lack of vertical construction element, i.e. a CP system can sit on a slab located at grade level while being pressurized from a single pumping station which pressurizes the system from water supplied at the current discharge level. A CS system has a vertical element which would require pumping the water twice, once to lift it up from the outfall level to fill the membrane cells and then a second pumping system would pull a vacuum to pull the water through the membranes for discharge to the Lake.”* For these reasons, Siemens has recommended piloting a pressurized system.

2. Are the pressurized and vacuum units two different systems or the same system? Can the pressurized pilot-scale unit operate both on pressurized and vacuum mode?

Response from Siemens: *“They are completely separate designs with different pilot units. After piloting a pressurized unit for a few months, Siemens could swap one pilot for the other to compare its performance with a submerged unit. The price is the same and the utility set-up requirements are nearly identical.”*

The project team decided to select GE for pilot-scale testing at the Whiting Refinery for the following reasons:

- The technologies of both companies are basically the same, but GE has more experience with heavy metals removal from industrial wastewater. GE has done 12 pilot studies in the last 18 months on the treatment of refinery wastewater. Two of the studies were specifically for mercury removal.
- GE has local technical personnel within a radius of a few miles of the Whiting Refinery. Their assistance will be free of charge during the troubleshooting.
- Conditions for data sharing in GE's pre-proposal were less restrictive than those of Siemens.

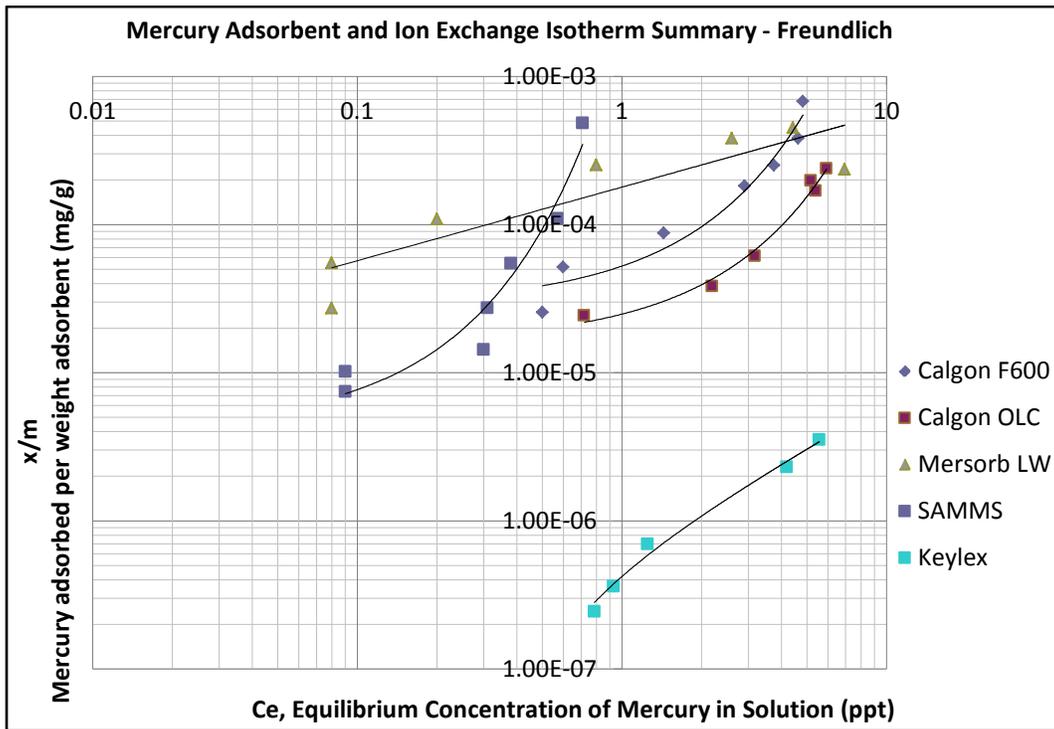
GE later informed the project team that they also have vacuum membrane units, which have been used mostly for the reclamation of water for drinking water purposes. Since GE did not know the wastewater characteristics, they offered the submerged units, which have been used for the treatment of industrial wastewater treatment. GE also indicated that submerged membranes can handle fouling better than that of pressurized systems, since the same membrane technology has been used in MBR applications.

## Vendor Selection for Dissolved Mercury Removal

In order to select the vendor for dissolved mercury removal, data obtained from both adsorption treatability experiments and from the best performing ion-exchange product were compared. Ion-exchange technologies (specifically Keylex) were tested by Purdue University Calumet (PUC). Figure 4-4 shows the Freundlich isotherms of the tested adsorbents and the ion-exchange resin Keylex (Purdue Calumet data) plotted together. To select the most suitable product that could address dissolved mercury across the technologies tested by Argonne and Purdue University Calumet, the best performers from the two teams were compared and plotted on the same graph. As shown in Figure 4-4, the required ion-exchange resin dose was about 1,000 times more than that of the adsorbent doses to obtain the same equilibrium concentration of mercury. It should also be noted that the adsorbents were very finely ground, whereas the resin was used as-is. Therefore, the adsorbents had considerably more surface area than that of the resin. However, the required cost, including the purchase of resin and power, for the operation of the ion-exchange process was 2–4.4 times higher than that of the adsorption process, as shown in Table 4-2. Half the cost was for the purchase of resin, which, according to the vendor, cannot be regenerated. *Since Mersorb ranked in first place in terms of meeting the target effluent criteria, applicability, and cost effectiveness (Tables 4-2 and 4-7), it was selected as the best candidate for piloting at the Whiting Refinery to remove dissolved mercury, even though it had not yet passed a column capacity test. Recommendations for further bench scale testing by the external review panel will be incorporated in future pilot-scale testing plans.*

Additionally, the emerging Blue PRO reactive filtration process was also selected as a promising candidate for both particulate and dissolved mercury removal, even though it has not yet been implemented at a 40 MGD scale. The Blue PRO process combines several different processes, including precipitation, sand filtration, and adsorption, which may be able to control both particulate and dissolved mercury. The data obtained from the bench-scale testing showed that Blue PRO was effective in removing up to 98.7% of the particulate mercury (CE as-is) and 92.2% of the dissolved mercury (CE filtered through a 0.45  $\mu\text{m}$  filter and spiked with  $\text{Hg}^{+2}$ ). Blue PRO was also effective in the removal of vanadium (88–99%) and arsenic (69–93%). The promising bench-scale results, as well as the advantage of employing one technology to treat both particulate and dissolved mercury, led to the selection of Blue PRO for piloting. Pilot test planning will determine if and what additional tests at the bench scale will be required to optimize process reagents and conditions in preparation for a full pilot-scale test.

Figure 4-4. Comparison of Freundlich Isotherms of Adsorbents and Ion Exchange Resin



**Table 4-7. Adsorption Vendors for the Pilot-scale Study at the Whiting Refinery<sup>1</sup>**

<b>Technology/ Vendor</b>	<b>Technology Description</b>	<b>Installations</b>	<b>Skid Availability</b>	<b>Cost</b>	<b>Footprint</b>	<b>Operation Assistance</b>	<b>Analytical</b>
Mersorb LW, Selective Adsorption Associates, Inc.	6-gpm skid, two columns	Standard designs for 10, 100, and 300 gpm; full-scale: scrubber water, desalter water, chlor-alkali groundwater and spent alkali	Design complete; about 1 month to build	\$25 K; purchase, not rental	6' x 9' x 10.5' high	Start-up assistance available	Client's responsibility
Thiol-SAMMS, Steward Advanced Materials, Inc.	8-gpm skid, CSTR/membrane configuration, 20-µm particles	Full-scale – none; pilot studies (1 or 8 gpm) on ash pond wastewater, steel wastewater, and chemical industry equipment wash water	Available immediately		8' x 8'	Start-up and troubleshooting assistance available	Client's responsibility
Thiol-SAMMS, Steward Advanced Materials, Inc.	Packed bed configuration, 600-µm particles	Full-scale – none					
Blue PRO, Blue Water Technologies, Inc.	25-gpm precipitation/ moving bed sand filter	Municipal wastewater research installation (1.3 mgd); pilot studies (25 gpm) on two municipal wastewaters and one industrial processor wastewater	Available immediately	\$7,500 per week; 2-week minimum	10' x 60' or 20' x 50'	Start-up, troubleshooting, and operation assistance available	Client's responsibility
Keylex, SolmetX, Inc.	2-gpm skid, one column		Available in 3–4 weeks	\$3K purchase	1' x 1' x 6' tall		Client's responsibility

<sup>1</sup> All vendors are able to provide references and safety records.

## Details of the Selected Technologies for Pilot Testing at the Whiting Refinery

This section provides pilot-scale demonstration details for the three selected technologies: ultrafiltration (GE Zeeweed Technology — 0.04  $\mu\text{m}$  pore size and made up of PVDF); adsorption using Mersorb LW, a sulfur-impregnated activated carbon; and the Blue PRO reactive filtration process. Because of the large amount of water required for pilot testing, the project team recommended that the pilot testing be conducted at the Whiting Refinery by using clarifier effluent (CE) or effluent to lake (ETL). A synopsis of each technology's technical details and utility requirements for hook-up at the Whiting Refinery is given in the following sections.

### GE-ZeeWeed® 500D Ultrafiltration

A ZeeWeed 500 pilot is a scaled-down version of a full-scale membrane ultrafiltration process. The pilot-skid will be rented from Zenon Environmental Corporation of GE Water & Process Technologies. The skid contains three ZeeWeed® 500 membrane modules used in full-scale applications. Figure 4-5 shows a picture of the pilot-skid, which consists of the following main components:

- Three (3) ZeeWeed®500D modules (340  $\text{ft}^2$  of active membrane area/module);
- One (1) 240-U.S. gal (900 L) stainless-steel process tank;
- One (1) 25-U.S gal (100 L) polypropylene backpulse tank;
- One (1) self-priming centrifugal permeate pump;
- One (1) regenerative blower;
- One (1) turbidimeter (feed and permeate);
- One (1) particle counter (feed and permeate);
- One (1) NaOCl chemical dosing pump; and
- All necessary piping, valves, and instrumentation.

The utility requirements for the GE pilot-skid are summarized as follows:

- *Power requirements:* 240 V, 1 phase, 60 amp (100 amp with heater) service for the pilot is required. In addition, the pilot has the ability to supply power to one additional air compressor (GE has a limited number of these compressors, if needed) and one additional pump that could be used as a transfer pump or feed pump if site conditions allow. It might be good to have a couple of extra 120 V, 30 A or 240 V, 20 A circuits for transfer pumps, plus three or four regular 110 V, 15 A circuits for miscellaneous use, such as for additional flocculation or any other treatment process.
- *Air requirements:* Oil-free compressed air at 2–3 scfm @ 120 psi is needed. GE has a limited number of pilot compressors available, but prefers to have this supplied by the customer where possible.
- *Feed water requirements:* 10–50 gpm at 20–50 psi is required. *Water requirements:* A normal potable water hose bib (like a home garden hose) must be supplied by the customer. This will not be needed by the ZW500 pilot on a regular basis, but ~400 gal will be required during commissioning for various purposes. It also will be needed throughout the pilot-study to mix chemicals (~10 gal/week or less). Further, another ~500 gal will be required for each recovery clean, which will occur about once per month.

Figure 4-5. GE-ZeeWeed\* 500D Pilot-scale Membrane Skid



- *Sewer requirements:* When in normal operation, the permeate flow will match the feed flow, so this will be ~15–35 gpm, depending on the feed water quality. The flow and frequency of non-permeate wastes, such as cleaning wastes and backwash wastes, can vary widely and depend on the mode of operation used by the pilot, which is highly dependent on the feed water quality. For "worst-case" conditions, ~20 gal of backwash waste will exit the pilot every 10 minutes at a flow rate of 50 gpm for ~20 seconds, and 250 gal of backwash waste will exit the pilot every 3 hours at a flow rate of 50 gpm for 5 minutes. Lastly, chemical cleaning typically will occur once per day and include the addition of citric acid, phosphoric acid, or NaOCl. The pHs could be 2–10, depending on the chemicals. They will be drained at about 50 gpm for 5 minutes, with a total volume of about 250 gal. Since all drains (permeate and backwash waste and spent cleaning solutions) function via gravity, the drainage location must be at a lower elevation than the pilot (the bottom of the pilot tank is about 12 in. from the ground).
- *Weatherproofing requirements:* The pilot must be placed indoors to prevent exposure to rain. The pilot and the associated feed and drain pipes must be in an area that prevents the water from freezing. The pilot does not have any built-in heating or heat tracing of any lines. All heat tracing of feed and drain lines must be done at the site by the customer. Also, the pilot must be located in a place where the temperature does not exceed 40 °C (104 °F).
- *Footprint (battery limits dimensions):* 20 ft (L) x 20 ft (W) x 15 ft (H) is required. To ensure the safety of the staff, the shelter should allow for >3 ft of space around the pilot on all sides to permit free access.
- *Electrical equipment classification:* The electrical enclosures are NEMA4, and the pilot is CSA and UL stamped. It is not suitable for any locations where explosion-proof type of equipment is required.
- *Chemical types and usage:* Typically, 100 ppm NaOCl maintenance cleaning of the membrane is performed once per day (250 gal of 100 ppm solution results). GE prefers the customer to supply a 12% NaOCl solution, if possible. Then, about once per month, a 500- or 1,000 ppm NaOCl cleaning will occur. In addition, an acid cleaning using citric acid or phosphoric will take place. If the water is very scaling, this

may require an acid cleaning to a pH of 2 once per day or once per week. If the water is not very scaling, it will include only one acid cleaning per month.

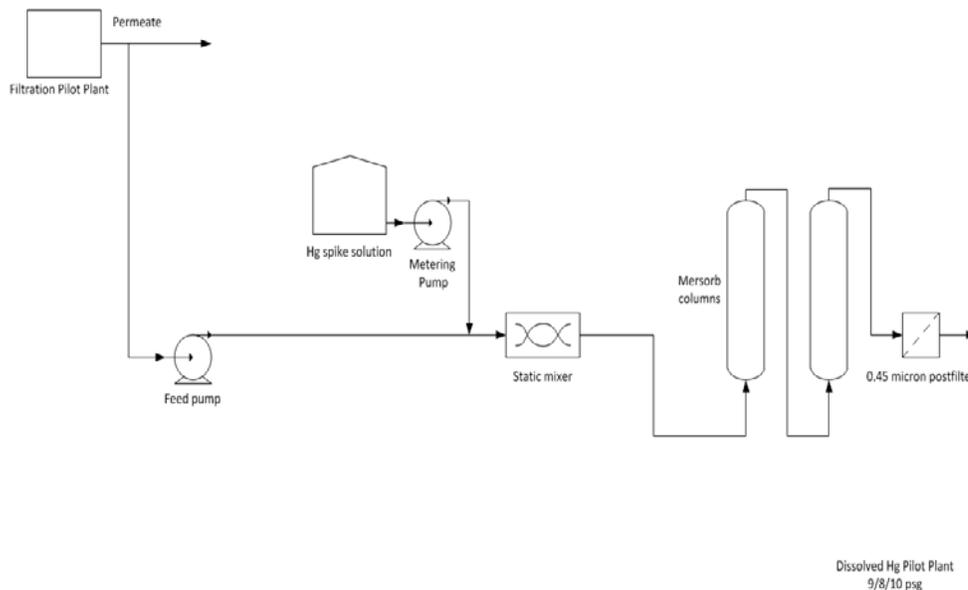
- *Other requirements:* A forklift is required to take the pilot off the delivery truck and reload it at the end of the study. If a loading dock is not available, the vendor should be made aware of the situation, so that a flatbed truck is used to deliver and retrieve the pilot. The doorway must be large enough to fit the pilot without tipping it sideways. A feed pump is required. Also, if a flocc tank or other pretreatment tank is used, there likely will be a need for a pump to transfer from the source to the flocc tank and then from the flocc tank to the pilot. An electrician should be available to connect the power. A telephone line is required to enable the pilot to send data and allow GE to remotely connect to the pilot. An alternative could be a GE-supplied cell modem, if reception is possible.

#### Mersorb LW (Sulfur-Impregnated Carbon) Adsorption

For the Mersorb LW testing, a 6 gpm dual column skid is available for purchase from Selective Adsorption Associates, Inc. A rental option is not available. Selective Adsorption Associates holds the world-wide license for Mersorb LW, which is made by Nucon International. Figure 4-6 shows the schematic of the Mersorb pilot plant.

The Mersorb LW adsorbent is designed to remove dissolved mercury, which, based on previous experience, may or may not be present in the Whiting Refinery ETL during the testing period. If sampling and analysis demonstrate that dissolved mercury is not present, a joint decision will be made by BP, Argonne, and Purdue University Calumet to either abandon the Mersorb LW testing or to do Hg<sup>+2</sup> spiking of batches of filtered wastewater to be fed to the Mersorb LW skid.

**Figure 4-6. Dissolved Mercury Pilot Plant Schematic: Mersorb**



Details about the Mersorb LW pilot plant are summarized as follows:

- Two adsorption vessels are available (36 in. wide x 6 ft high); bodies are constructed of FRP with a PP liner.
- Backwashing is not needed (runs upflow).
- Prefiltration is needed (1–2 μm).
- Post-filtration (0.45 μm) and spare are included.

- The feed pump is not included; 2–6 gpm must be provided.
- Piping and valves are FRP or PP, with 2 in. flanged inlet and outlet connections.
- The system is rated for 75 psig; the pressure relief valve is included.
- The skid is 6 ft x 9 ft x 10.5 ft high.
- The initial filling of adsorber vessels is included: NUSORB GC-60 bed support media (3 mm) and MERSORB LW adsorbent (1.5 mm pellets).
- Each adsorber vessel contains 3.9 ft of loaded adsorbent.
- At 6-gpm operation, flux is 0.84 gpm/ft<sup>2</sup>, and total EBCT (both adsorbers) is 64.8 minutes. Per the vendor, longer contact times (perhaps 90 minutes) may be needed to achieve 1.3 ppt.

The utility requirements for the Mersorb pilot plant are summarized as follows:

- *Power requirements:* The water pump, electric motor, and electric supply are provided by others.
- *Air requirements:* None needed; all valves are manual, and no other moving parts require instrument or pneumatic drivers.
- *Water requirements:* The initial fill requires clean water — potable water would work; no backwash is needed.
- *Sewer requirements:* A 2–6 gpm continuous discharge is required.
- *Weatherproofing requirements:* An indoor location is necessary; cannot heat trace because of plastic construction.
- *Footprint:* 6 ft x 9 ft x 10.5' high.
- *Chemicals used:* None.

### **Reactive Filtration (Blue PRO Process)**

A 25 gpm dual-pass Blue PRO reactive filtration system is available for rental from Blue Water Technologies, Inc. for the testing. Another option made available by Blue PRO is the purchase of a Blue PRO pilot skid in order to have more flexibility as to the duration of the pilot study. The pilot equipment available for rental includes two Centra-flo™ CF-7 moving-bed continuous backwash sand filters mounted on frames, with the internals modified for the Blue PRO process (Figures 4-7 and 4-8). An additional cargo container includes influent water pumps, an air compressor, a chemical containment area, chemical pumps, and ancillary equipment. Figure 4-9 shows the details of the process. The wastewater inlet flow is 25 gpm, and the reject flow is 6 gpm. The reject flow can be either recycled to the clarifier or sent to solids handling. The skid, either rented or purchased, will be manned by Blue Water Technology personnel for 8 hours per day during the initial start-up. Blue Water Technology personnel will visit the pilot periodically throughout the course of the testing to assess the operation and performance.

The utility requirements for Blue PRO pilot plant are summarized as follows:

- *Power requirements:* A 240 V, 50 amp, single-phase power source is required. (A 208 single-phase or 480 three-phase could also be used.) Blue Water will provide a pigtail connection to the client-supplied male (and female) plug.
- *Air requirements:* None.
- *Water requirements:* Potable or utility water is not needed.
- *Chemical requirements:* The site must provide approximately two 55 gal drums of ferric sulfate and two 55 gal drums of polymer.
- *Wastewater access:* Access to wastewater is required within 50 ft. of the pilot plant (1 in., 1.5 in., or 2 in. pipes can be used).

Figure 4-7. Blue Pro Pilot Plant Schematic

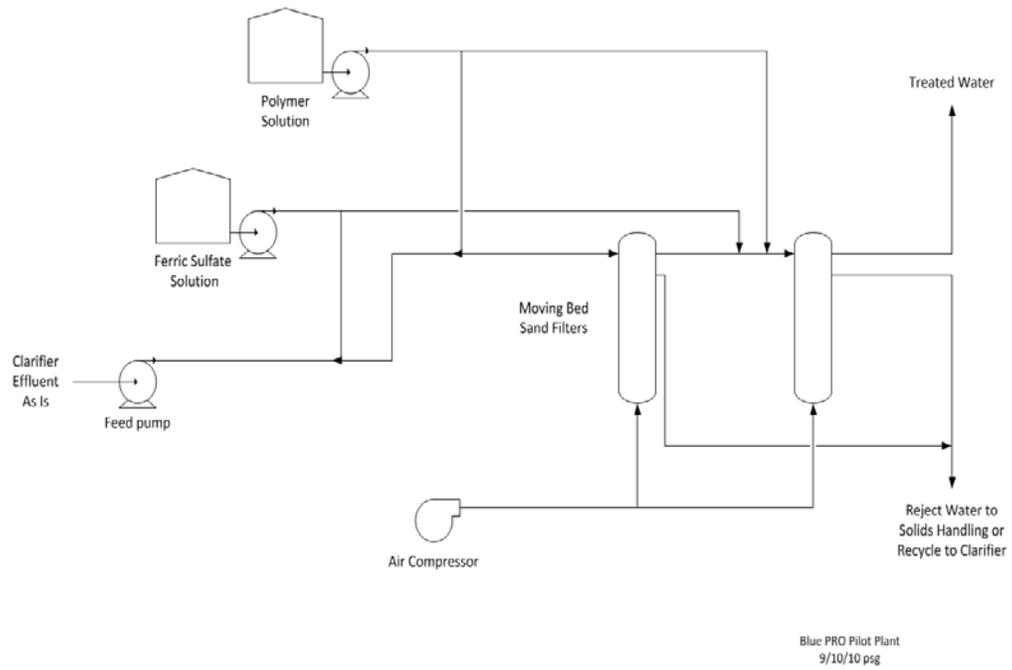
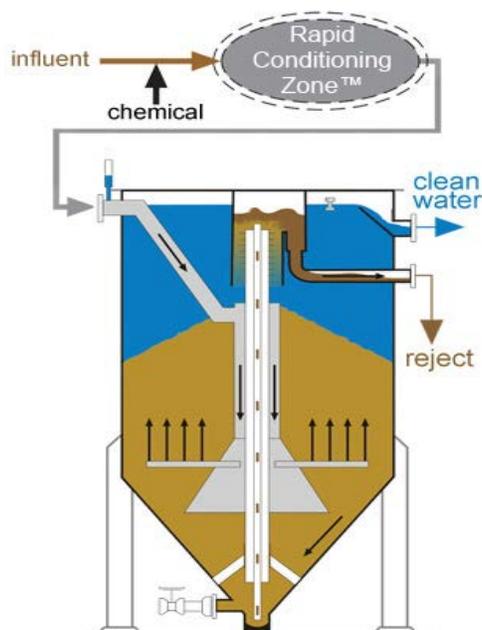


Figure 4-8. Blue PRO Pilot System



Figure 4-9. Blue PRO Process



- *Receiving points:* Receiving points are required for the clean effluent (25 gpm) and for the waste reject (6 gpm) lines. These must be gravity flow and within 50 ft of the pilot plant.
- *Footprint:* 10 ft x 60 ft is required for the trailer and filters; 10 ft x 30 ft is required if the cargo container is unloaded from the trailer. Filters will be on a 5 ft x 10 ft area and weigh 16,000 lb.
- *Lifting:* Capability to lift four 3,000 lb sacks of sand, either by forklift with an extendable boom or with a small crane, is necessary.
- *Outdoor use:* Can be used outdoors if the temperature is above -18 °C (0 °F).

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## 5. Summary and Conclusions

The Great Lakes Initiative established new water quality-based discharge criteria for mercury (Hg), thereby increasing the need for many municipal and industrial wastewater treatment plants (WWTPs) in the region to lower the mercury in their effluents. Information on deployable technologies to satisfy these requirements in industrial and municipal dischargers in the Great Lakes region is scarce. Therefore, BP funded Purdue University Calumet and Argonne to identify deployable technologies to meet future wastewater discharge limits at its Whiting Refinery in Indiana. These discharge limits also include controls on discharges of vanadium (V), for which the removal from wastewater has scarcely been studied.

In this project module, Argonne focused on the assessment of available and emerging wastewater treatment technologies previously identified in Module 1 to remove mercury and vanadium from Whiting Refinery wastewater. Treatability studies were conducted at the bench-scale to provide comparable, transparent, and uniform results across the broad range of technologies tested. The team designed and performed these bench-scale treatability studies on the basis of information collected from the literature, available standardized test protocols, vendor recommendations, BP's historical data, and the results of the wastewater characterization work during the study period. To compare performance across a relatively broad set of technologies, the Argonne team designed an overall experimental plan, so that test conditions could be as uniform as possible given the different mechanisms of action and engineering applications of the selected technologies. Importantly, the bench-scale experiments were conducted in a certified Class 100 clean-room laboratory to minimize background interferences during the testing, in light of the low concentrations of mercury (1–10 ppt) in the refinery samples and the even lower post-treatment targets.

Among the metal removal processes, adsorption, precipitation, membrane filtration, electrodeionization, and reactive filtration technologies were tested to determine their potential to achieve the future refinery discharge limits. Technologies were tested using the Whiting Refinery's end-of-pipe wastewater: effluent-to-Lake (ETL) and/or clarifier effluent (CE). The characteristics of these two streams were basically indistinguishable during the study period.

The project team developed a set of endpoint metrics at the onset of the project that could be applied to uniformly evaluate each technology in comparison to the others to the greatest extent possible. The data collected from the treatability experiments were processed and categorized on the basis of this technology assessment protocol. The technology assessment was accomplished in three steps. First consideration was given to the minimum achievable concentration (with the target of <1.3 ppt Hg and <280 ppb V).

1. The first step of the evaluation involved selecting the technologies, among those tested, that showed the capability to meet the target mercury and vanadium limits in the treated wastewater.
2. The second step of the evaluation was a more comprehensive analysis of the treatment alternatives. The technologies that met the target effluent limits were further evaluated for other performance criteria, including their power consumption, waste generation rate, footprint, and chemical requirements, among others.
3. Third, the finalist technologies were assessed for vendor readiness to support a pilot-scale test and their suitability for full-scale installation at the Whiting Refinery.

The decision matrix developed was not only the basis for the comparative assessment of each technology's test data, but also for the selection of technologies and vendors for a future pilot-testing phase at the Whiting Refinery.

The major findings in this module can be summarized as follows:

Effluent concentrations below the target metal concentrations:

- **Data obtained from the treatability studies showed that several readily deployable or emerging wastewater treatment technologies were able to achieve, at the bench-scale, mercury concentrations below or at the 1.3 ppt target concentration, albeit with different efficiencies and engineering implications. This demonstrates that there is no fundamental physical or chemical barrier in achieving <1.3 ppt Hg in the tested refinery wastewater. Engineering issues that emerge have to be addressed during the scale-up and optimization phases.**
- Most of the mercury in the ETL/CE was classified as a particulate or non-dissolved form. The removal of particulate mercury from the wastewater via simple filtration at 0.45  $\mu\text{m}$  was sufficient to meet the proposed 1.3 ppt of mercury effluent limit, since very little mercury was found to be in the dissolved form (supernatant) during the bench-scale study.
- The effectiveness of many technologies in achieving very low mercury concentrations (<1.0 ppt) in fact depended on the removal by filtration (as large as 0.45  $\mu\text{m}$  screen) of the physical particulates/colloidal fractions. This was particularly true for some of the tested vanadium removal technologies, such as precipitation.
- Most of the “established” and emerging mercury adsorbents tested, including Calgon F600 and OLC, Mersorb LW, and thiol-SAMMS, were capable of removing dissolved mercury below the 1.3 ppt level, but Mersorb LW and thiol-SAMMS were the most efficient adsorbents in terms of mercury removal per unit weight of adsorbent. Microfiltration and ultrafiltration membrane processes were highly effective in removing mercury, which was mostly present in particulate form. Additionally, an emerging technology — the Blue PRO reactive filtration process — was also effective in both particulate (98.7%) and dissolved mercury removal (92.2%).
- Commercially available mercury precipitants did not perform any better than method blanks. Method losses (i.e., the removal of mercury by the method itself) were 54–66% (before filtration) and 94% (after filtration). The precipitants did not remove additional mercury from the CE samples. The effectiveness of some of the precipitants in mercury removal was not clear because of mercury impurities in the ACS reagents. Technical-grade reagents employed in full-scale operations will most likely contribute some mercury to the process, thereby adding to the process’s mercury removal burden.
- Several technologies were found to be effective for the removal of vanadium. By using precipitation, a 10–20 ppm iron dose as ferric sulfate successfully removed 91–99% of vanadium from the tested CE containing 250–500 ppb of vanadium. All of the adsorbents tested — Adsorbisia As 500, Bayoxide E IN-20 and GFH — had the capability to remove 95–97% of vanadium from CE containing 250 ppb V. Among the candidate technologies, iron precipitation offers a robust option for removing vanadium from the CE/ETL streams when the Stretford purge is on. Adoption of this technology is simplified by the fact that BP already has a permit for the use of ferric sulfate as a settling aid in the secondary clarifier at the Whiting Refinery WWTP. The research team concluded that no further action was necessary on vanadium removal.
- Although arsenic and selenium removals from the wastewater were not among the objectives of Module 3, the effectiveness of the tested technologies for arsenic and selenium removal was also investigated because it may be an issue at other refineries. Among the tested adsorbents, thiol-SAMMS removed 19% of the arsenic and 36% of the selenium, while all of the vanadium adsorbents were capable of removing 50–66% of the arsenic. Both the Nalmet and Metclear precipitants had the capability to remove 38% and 50% of selenium. A 10–20 ppm iron dose as a precipitant also removed 60–73% of the arsenic and 50–55% of the selenium.

Challenges and limitations during the bench-scale technology demonstration and evaluation:

- The low mercury concentrations in the influent wastewater required the use of a clean room environment; specialized equipment cleaning methods; the use of “clean hands-dirty hands” procedures

to avoid cross-contamination during the testing and sample analysis; and a substantial reliance on method, reagent and equipment blanks, as well as specialized analytical procedures with appropriate sensitivity (EPA method 1631E). These steps were critical to minimize and understand experimental error and quality boundaries. Approved and certified analytical methods required modification within the constraints of the method to ensure not only compliance with the discharge limits, but a defensible comparison of data at near-detection limit concentrations. During the Module 3 testing, the method blanks used ETL/CE samples, which had undergone the entire process in order to understand the fate of mercury and vanadium within the system before the addition of any reagent or the application of any treatment protocol. The data obtained from treatability studies presented in this report have been corrected for method blank losses, if these were found to be substantial. Equipment and reagent blanks were also prepared to identify possible sources of target metal contamination during the experiments. The comparison of blanks and experimental data was essential to understand the amount of removal that could be attributed to the tested technologies themselves.

- Challenges in mercury analysis by EPA Method 1631: Initially, the team was not able to confidently compare different treatment technologies closely because of higher detection limits and low spike recoveries. In several cases, sample dilutions to increase the recoveries and decrease the matrix interferences resulted in an increase in the detection limits to as high as 5 ppt. With this high detection limit, it was impossible to demonstrate achievement of the target mercury performance limit (<1.3 ppt). Most recoveries from matrix spike/matrix spike duplicates were within the recoveries needed to fulfill the requirements of Method 1631E (a large bracket of 71–125%). However, recoveries in the lower end were not sufficient to ensure that all detectable concentrations reported below 1.3 ppt would, in fact, be truly so. Extensive work had to be conducted by the contracted analytical laboratories to provide accurate and precise measurements of mercury at the target low concentrations in the wastewater studied. An increase in the accuracy of the analytical results was necessary not only to strengthen experimental data but also, ultimately, to increase the understanding of the performance of the technologies tested at Argonne.
- The technology assessment protocol developed in this project provided a good framework to use for the selection of technologies from a number of alternatives that are technically capable of meeting the discharge limits. The cost assessment performed for each tested technology was at the planning level, but it provided reasonable cost estimates (for this preliminary stage of analysis) that were used in the comparative assessment of treatment technologies.

#### Pilot-scale considerations and planning:

- During the Module 3 testing from December 2009 through August 2010, most of the mercury in the Whiting Refinery wastewater was found to be in particulate form. The elemental mercury in ETL samples was negligible, and the dissolved, ionic fraction in the ETL may be labile. A need to find options for dissolved mercury removal is however clear when the historical BP data from the spring of 2009 are considered.
- **On the basis of the benchmark analysis with the resulting endpoint measures of performance for candidate treatment technologies, the Argonne team recommends three high-ranking mercury removal technologies for pilot testing at the Whiting Refinery: *ultrafiltration* (particulate mercury), *adsorption* (dissolved mercury), and an emerging *reactive filtration* technology (both particulate and dissolved mercury).**
- **Additional tests at the bench scale to optimize the selected technologies will be determined when planning for the pilot-scale trials.**
- As shown in the available literature, these technologies have been implemented at existing WWTPs for different uses, and some have been implemented at the scale of Whiting Refinery [flow rate of 40 MGD of wastewater]. The proven effectiveness of ultrafiltration in the removal of other particulate contaminants at existing full-scale applications suggests an increased likelihood of success in achieving target mercury concentrations at the Whiting Refinery, following optimization and scalability studies. For the removal of dissolved mercury, although carbon adsorption has been used to treat 40 MGD of drinking water,

Mersorb LW has not been tested at that scale. The Mersorb LW manufacturer, Nucon Inc., may need to substantially increase production to meet the needs of the Whiting Refinery. The last technology proposed for pilot tests, the Blue PRO reactive filtration process, was selected because of its potential ability to remove both particulate and dissolved mercury, even though it has never been demonstrated at flow rates higher than 1.3 MGD for mercury removal. More bench scale work will be needed to appropriately prepare to scale up to pilot scale.

- Among the subset of vendors available for the three high-ranking technologies, GE was selected by using the developed selection protocol for ultrafiltration (GE Zeeweed Technology — 0.04  $\mu\text{m}$  pore size and constructed of PVDF), while Mersorb LW (a sulfur-impregnated activated carbon) was selected for adsorption. The reactive filtration (Blue PRO) process was not subjected to the same vendor selection protocol because only one vendor supplies it: Blue Water Technologies, Inc.
- Module 3 testing shows that vanadium was in the dissolved form in the Whiting Refinery wastewater and that its concentration varied widely over the study period, depending on the periodic blown down from the Stretford unit at the Whiting Refinery. Since BP already knows of a preferred approach for vanadium removal (shutdown of the Stretford unit), a pilot-scale test for vanadium removal was not considered a priority.
- Due to the large volumes of water needed for pilot testing, the project team agreed that the pilot testing of the mercury removal technologies should be conducted at the Whiting Refinery by using ETL.

Other observations and conclusions:

- The results of this work offer treatment alternatives for different forms of mercury. For example, some of the promising technologies are better suited for dissolved metal removal, while others can remove metals sorbed onto particulates. The tested technologies may be applicable to other types of wastewater that contain mercury.
- The outcome of this research could provide valuable information to regulators and aid in the development of a rationale for identifying viable approaches to control mercury and other metals in industrial and municipal effluents in support of the Great Lakes Initiative.

## 6. ACKNOWLEDGEMENTS

PROJECT MANAGER: M. CRISTINA NEGRI

PRINCIPAL ENGINEER (ADSORPTION, REACTIVE FILTRATION): PATRICIA GILLENWATER

PRINCIPAL ENGINEER (PRECIPITATION, MEMBRANE FILTRATION): MELTEM URGUN DEMIRTAS

PRINCIPAL ENGINEER (EDI): YUPO LIN

ASSISTANT ENGINEERS: MICHAEL HENRY, MICHAEL FURLAN, AND PAUL BENDA

ADVISORY TEAM: YUPO LIN, RICHARD DOCTOR, SETH SNYDER, AND JORGE ALVARADO

QA/QC ENGINEER: LINDA PIERCE

THIS REPORT WAS WRITTEN BY PATRICIA GILLENWATER AND MELTEM URGUN DEMIRTAS WITH CONTRIBUTIONS FROM M. CRISTINA NEGRI.

For copies of this report or questions regarding this work please contact:

M. Cristina Negri  
Argonne National Laboratory  
Energy Systems Division  
(630)252-9662  
[negri@anl.gov](mailto:negri@anl.gov)

## **APPENDIX 1**

### **Analytical Data**

#### **A. Studies on the Shelf-life of Mercury and Vanadium in ETL Samples for the Treatability Studies**

##### **Objectives**

The objective of this study was to determine the holding times, or shelf-life, of samples of effluent-to-lake (ETL), with respect to the preservation of the original characteristics (total and speciated mercury [Hg] and total vanadium [V]) over time, for the purpose of conducting the technology treatability tests. Several different mechanisms could cause the composition of the wastewater to change with time. Microbial activity, sorption on the sample vessel, precipitation onto solids, and chemical oxidation/reduction are the main reasons that metal concentrations and speciation may change with time in a stored sample. The performance of treatment technologies may be dependent on the metal species/forms in the wastewater, and treatability testing requires a known and sufficiently constant composition of the wastewater tested. Therefore, it is important to understand the changes that could occur with time as a function of storage conditions. This study was conducted at the very onset of the project.

##### **Background**

Procedures for wastewater analysis require the use of preservation chemicals or conditions to ensure the quality of the sample over time. Preservation methods and chemicals are typically selected based on the analyte(s) and analytical methods of choice. Because the preservation additives required by standard methods could cause changes in the metal forms, additives may not be suitable to store samples for the purpose of conducting treatability studies. The most suitable storage method for the treatability tests was determined to be refrigeration at 4 °C. However, it was unclear how long samples could be stored by simple refrigeration without unacceptable changes in sample quality.

##### **Methods**

A simple study was conducted to evaluate the effect of refrigerated storage on selected mercury species, as well as total mercury and vanadium concentrations as a function of time. For mercury, the effect of the presence of headspace (HS) (and the related potential for mercury losses by volatilization) on total mercury concentrations over time was also investigated to determine the best way to handle the water samples that remained after opening the pails. In this study, aliquots of the same discharge were collected in a series in identical containers by Lab A and sent directly to Lab B for analysis.

The containers were filled to capacity (no headspace), except for a subset that was filled at 50% capacity (with headspace). Containers suitable for trace metals analysis were provided by Lab B. Periodically, a subset of samples was analyzed for total metals (mercury and vanadium), their dissolved fractions, and representative mercury forms to determine their recovery in the stored sample as a function of time. The first subset of analyses included a comprehensive mercury speciation [Hg total, Hg(II), and Hg(0)] on both the unfiltered and filtered (dissolved) fractions of the wastewater. Subsequent analyses focused on the unfiltered Hg total and the filtered (dissolved) Hg total, Hg(II), and Hg(0). A similar sequence was conducted on unfiltered samples spiked to a ~10 ppt Hg by Lab B upon sample receipt [Hg(II) compound was used for spiking]. The analyses and sample spiking also were performed by Lab B.

This test offered insight into the probable forms of metals present in the wastewater. In addition, the test allowed us to determine the frequency and delivery schedule of the ETL batches for the technology treatability tests.

### **Sample Collection, Shipment, and Storage**

Lab A personnel collected samples in suitable containers (provided by Lab B) from ETL outfall by using the “clean hands-dirty hands” method (EPA Method 1669), immediately placed them under ice, and shipped them to Lab B via same-day delivery service. The samples were collected in individual 500 mL and/or 250 mL sample bottles. Lab B stored each sample refrigerated until the scheduled analysis.

### **Test Plan**

Upon receipt, Lab B spiked 21 (twenty one) 250 mL bottles with Hg(II) at 10 ppt concentration. Each time an analysis was conducted, both an unspiked and a spiked bottle were analyzed. The Hg(II) spikes allowed us to understand the recovery of a known amount of Hg(II) over time.

Lab B analyzed individual samples, according to the schedule given in Table A1-1, to simulate storage conditions for the treatability experiments. Samples for the dissolved metals analysis were not filtered immediately after collection, but rather were filtered at the moment of analysis to simulate storage conditions. All bottles were filled entirely so that no headspace was present, except for the “headspace” treatment bottles. Each individual sample bottle was used for the determination of one analyte only (e.g., one bottle for total mercury, one for dissolved total mercury, and so forth).

Trip blanks (reagent water) and field blanks (reagent water collected in the vicinity of the sample collection point) were also analyzed for total mercury and vanadium on the first analysis time (24 hours). The analysis at 24 hours from receipt was conducted with a fast turnaround time to provide appropriate guidance to the technology testing.

**Table A1-1. Analytical Schedule (spike added by Lab B upon receipt, and filtration conducted by Lab B at the time of analysis)**

<b>Time</b>	<b>Samples to Analyze Hg</b>	<b>Samples to Analyze V</b>
24 hours after collection	1 (4 x 500 mL) ETL (total Hg <sub>tot</sub> ; dissolved Hg <sub>tot</sub> , Hg <sub>0</sub> , and Hg <sub>II</sub> ) 1 (4 x 500 mL) ETL + Hg(II) spike (total Hg <sub>tot</sub> ; dissolved Hg <sub>tot</sub> , Hg <sub>0</sub> , and Hg <sub>II</sub> ) 1 x 500 mL ETL HS¶* (Hg <sub>tot</sub> )	2 x 250 mL ETL (total and dissolved V <sub>tot</sub> )
3 days after collection	1 (4 x 500 mL) ETL (total and dissolved Hg <sub>tot</sub> ; dissolved Hg <sub>0</sub> and Hg <sub>II</sub> ) 1 (4 x 500 mL) ETL + Hg(II) spike (total and dissolved Hg <sub>tot</sub> ; dissolved Hg <sub>0</sub> and Hg <sub>II</sub> ) 1 x 500 mL ETL HS¶ (Hg <sub>tot</sub> )	2 x 250 mL ETL (total and dissolved V <sub>tot</sub> )
1 week after collection	1 (4 x 500 mL) ETL (total and dissolved Hg <sub>tot</sub> ; dissolved Hg <sub>0</sub> and Hg <sub>II</sub> ) 1 (4 x 500 mL) ETL + Hg(II) spike (total and dissolved Hg <sub>tot</sub> ; dissolved Hg <sub>0</sub> and Hg <sub>II</sub> ) 1 x 500 mL ETL HS¶ (Hg <sub>tot</sub> )	2 x 250 mL ETL (total and dissolved V <sub>tot</sub> )
2 weeks after collection	1 (4 x 500 mL) ETL (total and dissolved Hg <sub>tot</sub> ; dissolved Hg <sub>0</sub> and Hg <sub>II</sub> ) 1 (4 x 500 mL) ETL + Hg(II) spike (total and dissolved Hg <sub>tot</sub> ; dissolved Hg <sub>0</sub> and Hg <sub>II</sub> ) 1 x 500 mL ETL HS¶ (Hg <sub>tot</sub> )	2 x 250 mL ETL (total and dissolved V <sub>tot</sub> )
4 weeks after collection	1 (4 x 500 mL) ETL (total and dissolved Hg <sub>tot</sub> ; dissolved Hg <sub>0</sub> and Hg <sub>II</sub> ) 1 (4 x 500 mL) ETL + Hg(II) spike (total and dissolved Hg <sub>tot</sub> ; dissolved Hg <sub>0</sub> and Hg <sub>II</sub> ) 1 x 500 mL ETL HS¶ (Hg <sub>tot</sub> )	2 x 250 mL ETL (total and dissolved V <sub>tot</sub> )
Trip and field blanks	1 x 500 mL RW* trip blank (Hg <sub>tot</sub> ) 1 x 500 mL RW field blank (Hg <sub>tot</sub> )	1 x 500 mL RW trip blank (V <sub>tot</sub> ) 1 x 500 mL RW field blank (V <sub>tot</sub> )
Total sample #	40 x 500 mL samples ETL 5 x 500 mL ETL HS¶ 2 x 500 mL RW	10 x 250 mL ETL 2 x 500 mL RW

\*RW = Reagent-grade water; ¶HS = headspace present.

**Results and Discussion**

Data obtained from this study provided insight on the degradation of the effluent composition as a function of time. In addition, it enabled us to determine the length of time that batches of ETL could be stored by simple refrigeration prior to treatability testing (Table A1-2). Based upon the obtained data, the decision was made to use collected water samples within one week from the collection date.

**Table A1-2. Shelf-life Study (January 19, 2010, ETL sampling event at the Whiting Refinery)**

Holding Time (day)	Mercury, Unspiked Samples (ppt)					Mercury, Spiked Samples (ppt)		
	Total	Dissolved Total	Dissolved Hg(II)	Dissolved Hg(0)	Total with HS	Total	Dissolved	Dissolved Hg(II)
24 hours	38.6	1.93	5.49	<0.08	25.2	48.5	11.3	5.38
3 days	41.2	1.39	<0.74	<0.15	17.3	52.1	8.33	5.13
7 days	37.9	2.49	<0.15	<0.15	45.9	41.8	7.09	2.62

Sample	Method Mercury Recovery
24-hour ETL total	99.00%
24-hour ETL dissolved	93.70%

Sample	Hg (ppt)
Field blank Hg	<0.08
Trip blank Hg	0.22 (J)

The test results for vanadium are not given because they were inconclusive. However, the Lab A analytical results (Table 2-2) indicate that vanadium was very stable in the collected water samples. Differences in the test results might be due to the different methods used for vanadium analysis. Lab B uses Method 1638, which requires a higher dilution ratio, whereas Lab A uses Method 200.7, which requires a lower dilution ratio. The test results obtained from Lab A were more meaningful than those from Lab B.

**B. Challenges in Mercury Analysis by Method 1631**

Table A1-3 summarizes the test results obtained from Lab A. As can be seen from the table, the higher detection limits (in some cases 5 ppt) and low spike recoveries did not allow for a confident and comprehensive comparison of the different treatment technologies.

**Table A1-3. QC Data Analysis of the Lab A Test Results**

**Notes for Table A1-3:**

The method detection limits and spike recoveries that are outside the accepted limits are printed in red.

1. The different analysis data for the same samples are highlighted in blue.
2. The Argonne work orders for the mixed-up samples used in the QC analysis are highlighted in yellow.

Work Order Number	Sampling Event	Sample ID	Analyte	Method Detection Limits	Comments
ME1002033	ETL sampling at Whiting Refinery	ME1002033-05AMS, 05AMSD and 06AMS, 06AMSD	Hg	2.5 ppt total Hg 1.0 ppt dissolved Hg	Reported Hg matrix spike concentrations should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 67.6–76.3% in MS/MSD samples measured with the 1.0 ppt dissolved Hg method detection limit.
			V, Se, As, and other cations		Reported second QC data were not in this order and were from ME1002007 (samples: ME1002007-07AMS and -07AMSD).
ME0912292	ETL sampling at Whiting Refinery	ME0912292-02AMS, 02AMSD	Hg	2.5 ppt total Hg 0.5 ppt dissolved Hg	Reported Hg matrix spike concentrations should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 73.5–75.7% in MS/MSD samples measured with the 0.5 ppt dissolved Hg method detection limit, and 67.6–102% in MS/MSD samples measured with the 2.5 ppt total Hg method detection limit. Only one datum was reported for total and dissolved Hg concentrations in the ETL. No duplicate analysis was performed on the second ETL sample.
			V		Reported second QC data were not in this order and were from ME0912279 (samples: ME0912279-05FMS and -05FMDS).

ME1002272	ETL sampling at Whiting Refinery	ME1002272-03AMS, 04AMS,05AMS,06AMS, 03AMSD, 04AMSD, 05AMSD, 06AMSD	Hg	2.5 ppt total Hg 2.5 ppt dissolved Hg	Reported Hg matrix spike concentrations should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 84.1–98.2% in MS/MSD samples measured with the 2.5 ppt Hg method detection limit. Total Hg concentrations for two of the same ETL samples were 3.86 ppt and ND.
			V, Se, As, and other cations		Reported QC data were not in this order and were from ME1002216 (samples: ME1002216-01AMS, 01AMSD, and ME1002412-01AMS).
			Chloride, fluoride, and sulfate		Reported QC data were not in this order and were from ME1002247, ME1002269, and ME1002079 (samples: ME1002247-01AMS and -01AMSD; ME1002269-02CMS and 02DCMS; and ME1002079-03AMS and 03AMSD).
ME1002239	Adsorption experiments		Hg	0.5 ppt total Hg (filtered samples)	Reported QC data were not in this order and were from ME1002272 and ME1002506 (samples: ME1002272-03AMS, 03AMS, 04AMS, 04AMSD, ME1002506-05AMS, 06AMS, 05AMSD, and 06AMSD). Reported Hg matrix spike concentrations for these samples should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 60.4–67.6% for four of eight MS/MSD samples measured with the 2.5 ppt dissolved Hg method detection limit. The obtained recoveries for the other four MS/MSD samples were 86.3–91.8%.
ME1002191	Method, reagent, clean-room blanks, and filtered ETL sample	ME1002191-12AMS, 12AMSD	Hg	2.5 ppt total Hg	Reported Hg matrix spike concentrations should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 64.7–71.4% in MS/MSD samples measured with the 2.5 ppt total Hg method detection limit.
				0.5 ppt total Hg (filtered samples)	Reported QC data were not in this order and were from ME1002187 (sample: ME1002187-03AMS). Matrix spike recoveries were in the range of 72.3–74% in MS/MSD samples measured with the 0.5 ppt Hg method detection limit.

ME1002414	Adsorption (V, Hg, As, Se) precipitation (V) experiments		Hg	0.5 ppt total Hg (filtered samples)	Recoveries were in the range of 77.3–87.5% in MS/MSD samples measured with the 0.5 ppt total Hg method detection limit.
			V		Reported second QC data were not in this order and were from ME1002393 (samples: ME1002393-02AMS and 02AMSD).
ME1002506	Clarifier effluent sampling at Whiting Refinery	ME1002506-03AMS, 04AMS, 03AMSD, 04AMSD, 05AMS, 05AMSD, 06AMS, 06AMSD	Hg	5.0 ppt total Hg 2.5 ppt dissolved Hg	Reported Hg matrix spike concentrations should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 60.4–67.6% in MS/MSD samples (four samples) measured with the 2.5 ppt of dissolved Hg method detection limit, and 83.2–94.4% in MS/MSD samples (four samples) measured with the 5.0 ppt of total Hg method detection limit.
			V, Se, As, and other cations		Reported QC data were not in this order and were from ME1002412 (samples: ME1002412-01AMS and ME1002412-01AMS).
			Alkalinity		Reported QC data were not in this order and were from ME1002446 (sample: ME1002446-01ADUP).
ME1002512	Precipitation (V) experiments		V	No Hg analysis	Reported second QC data were not in this order and were from ME1002748 (samples: ME1002748-01AMS and -01AMSD).
ME1002636	Adsorption (V, Hg, As, Se) precipitation (Hg) experiments	ME1002236-05AMS, 05AMSD	Hg	2.5 ppt total Hg 0.5 ppt dissolved Hg	Reported Hg matrix spike concentrations should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 90.4–91% in MS/MSD samples measured with the 0.5 ppt dissolved Hg method detection limit, and 93.3–110% in MS/MSD samples measured with the 2.5 ppt total Hg method detection limit Total Hg concentrations for three samples taken from the same bucket were 3.02, 2.88, and <0.5 ppt.

ME1002684	Adsorption (V, Hg, As, Se) precipitation (Hg) experiments	ME1002684-10AMS, 21AMS, 10AMSD, 21AMSD	Hg	2.5 ppt total Hg	Reported Hg matrix spike concentrations should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 78.7–90.1% in MS/MSD samples measured with the 2.5 ppt total Hg method detection limit.
				0.5 ppt dissolved Hg	Reported second QC data were not in this order and were from ME1002686 (samples: ME1002686-05AMS and -05AMSD). Matrix spike recoveries were in the range of 69.9–77.4% in MS/MSD samples measured with the 0.5 ppt dissolved Hg method detection limit.
			V, Se, and As		Reported second QC data were not in this order and were from ME1002689 (samples: ME1002689-07AMS and -07AMSD).
ME1002686	Adsorption experiments		Hg	0.5 ppt total Hg (filtered samples)	Reported QC data were not in this order and were from ME1002630 and ME1002632 (samples: ME1002632-01AMS and -01AMSD; ME1002630-01AMS and -01AMSD). Reported Hg matrix spike concentrations for these samples should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 77.7–101% in MS/MSD samples measured with the 5.0 ppt Hg method detection limit.
ME1002748	Clarifier effluent sampling at Whiting Refinery	ME1002748-03AMS, 04AMS, 05AMS, 06AMS,03AMSD, 04AMSD, 05AMSD, 06AMSD	Hg	5.0 ppt total Hg 5.0 ppt dissolved Hg	Reported Hg matrix spike concentrations should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 77–101% in MS/MSD samples measured with the 5.0 ppt Hg method detection limit. Total Hg concentrations for two identical CE samples were measured with 5.0 ppt method detection limits as 6.99 and 10.8 ppt.
			Sulfate		Reported QC data were not in this order and were from ME1002767 (samples: ME1002767-02DMS and -02DMSD).
			Fluoride		Reported QC data were not in this order and were from ME1002767 (samples: ME1002767-02MS and -02MSD).

			Chloride		Reported QC data were not in this order and were from ME1002897 (samples: ME1002897-05AMS and -05AMSD).
			Alkalinity		Reported QC data were not in this order and were from ME1002863 and ME1002897 (samples: ME1002863-01ADUP and ME1002897-05ADUP).
ME1002882	Adsorption experiments		Hg	0.5 ppt total Hg (filtered samples)	Reported QC data were not in this order and were from ME1002922 (samples: ME1002922-07AMS and -07AMSD). Matrix spike recoveries were in the range of 104–108% in MS/MSD samples measured with the 0.5 ppt Hg method detection limit.
ME1002922	Adsorption experiments		V, Se, and As		Reported QC data were not in this order and were from ME1002897 (samples: ME1002897-05GMS and -05GMSD).
			Hg	0.5 ppt total Hg (filtered samples)	Matrix spike recoveries were in the range of 104–108% in MS/MSD samples measured with the 0.5 ppt Hg method detection limit
ME1003030	Method development on CE	ME1003031-01AMS, 01AMSD; ME 1003030-01AMS, 01AMSD	Hg	5.0 ppt total Hg (method development) 0.5 ppt dissolved Hg	Reported Hg matrix spike concentrations should have been multiplied by the dilution factor in the reported data. Matrix spike recoveries were in the range of 64.2–66.6% in MS/MSD samples measured with the 0.5 ppt dissolved Hg method detection limit, and 93.7–100% in MS/MSD samples measured with the 5.0 ppt total Hg method detection limit.

In order to address the challenges in mercury analysis by Method 1631, Argonne worked with Lab A chemists to improve the method for the specific purposes of this study, as described below.

1. **Accuracy** (or the closeness of agreement between the value that is accepted either as a conventional true value or an accepted reference value [MS, MSD] and the value found)).

The concerns about the accuracy of the test results were as follows:

- Most recoveries from Lab A of matrix spike/matrix spike duplicates were within the recoveries needed to fulfill the requirements of Method 1631E (a large bracket of 71–125%). However, several were below the recovery limits required by Method 1631E (Tables 2-2 and A1-3). In the case of wastewater, it was hypothesized that organic compounds may not fully break down under standard digestion procedures, thus leading to incomplete recoveries of mercury.
- Low recoveries of spiked MilliQ water and method blanks also were found. These low recoveries were particularly problematic, since they practically prevented the determination of losses from the method blanks vs. those from the treatment technologies tested.
- Sample dilutions to increase the recoveries and decrease the matrix interferences resulted in an increase in the detection limits to 5 ppt in several cases. With these high detection limits, it was impossible to demonstrate the target mercury performance limit (<1.3 ppt).
  - Based on the different % recoveries, the actual concentrations most probably differed from the reported values, as shown in Table A1-4. From this table, it appears that the concentrations lower than the 0.5 ppt detection limit would still have been below the 1.3 ppt regulatory limit, even with a 60% recovery. However, the detectable concentrations reported below 1.3 ppt could in fact have been above the regulatory limit. Several test results showed residual mercury concentrations in treated wastewater in the 0.8 to 2 ppt range (Tables 2-2 and 2-3).
- There was a need to closely compare data obtained from each treatability experiment. The recoveries in the lower end of the acceptable spectrum did not allow for a confident and comprehensive comparison of the different treatment technologies. An increase in the accuracy of the analytical results was necessary, not only to strengthen the experimental data, but also to ultimately increase our understanding of the performance of the technologies tested at Argonne.

**Table A1-4. Impact of % Recoveries on Reported Mercury Values**

<b>Actual vs. Reported Test Results at Different % Recoveries</b>			
<b>Reported ppt</b>	<b>Actual as high as:</b>		
	at 60% recovery	at 80% recovery	at 100% recovery
0.5	0.83	0.63	0.50
0.8	1.33	1.00	0.80
1	1.67	1.25	1.00
1.3	2.17	1.63	1.30
2	3.33	2.50	2.00
5	8.33	6.25	5.00
10	16.67	12.50	10.00
15	25.00	18.75	15.00

The following steps were taken to resolve concerns about the accuracy of the test results:

- Lab A, Argonne, and Purdue University Calumet participated in a meeting at the Lab A facility in Indiana, on March 12, 2010. As a result of that visit, Lab A worked to minimize dilutions and improve the recovery and detection limits of mercury from the ETL/clarifier effluent (CE) matrix by testing several approaches to achieve a more thorough sample digestion (e.g., use of heating and additional BrCl).
- Lab B also experienced low recoveries at the beginning of the shelf-life study (refer to the following section). At that time, they quickly and proactively responded by adding heating to their digestion procedure. It was our understanding that Lab A consulted with Lab B on this matter upon our request.
- Argonne prepared duplicate sets of CE samples, each in triplicate, and sent them to both Lab A and Lab B in an effort to understand and compare their accuracy. Table A1-5 details the test results obtained from Lab A and Lab B. Both labs used the improved (heated) digestion method for this test.<sup>5</sup> However, Argonne did not receive detailed information on their specific procedures.
- The data in Table A1-5 show that Lab B reported consistently higher concentrations than Lab A. Both Lab B and Lab A delivered recoveries within the limits mandated by Method 1631E. The average recoveries in these samples were 82.4% and 101.2%, for Lab A and Lab B, respectively.

**Table A1-5. Comparison of Lab A and Lab B Test Results (ppt)**

Lab	Data Summary	CE As-is	CE after Filtration	Filtered CE + 10 ppt Spike	Filtered CE + 5 ppt Spike	MilliQ + 5 ppt Spike	Trip Blank
Lab B		4.0	0.52	9.35	4.76	4.67	ND
		2.19	0.55	9.26	4.67		
		4.57	0.74	9.35	4.57		
	Average	3.59	0.60	9.32	4.67		
	std. dev.	1.24	0.12	0.05	0.10		
	deviation %	34.6	19.8	0.6	2.0		
Lab A		3.35	ND (RL 0.5)	7.26	3.06	3.9	ND
		3.43	ND (RL 0.5)	6.13	3.57		
		3.50	ND (RL 0.5)	6.32	3.88		
	Average	3.43		6.57	3.50		
	std. dev.	0.08		0.61	0.41		
	deviation %	2.2		9.2	11.8		
Duplicate was 4.19 ppt.							
Duplicate was 9.73 ppt.							
MS/MSD on this sample was 98.4–104%							
MS/MSD on this sample was 74.2–79%.							
MS/MSD on this sample was 87.8–88.8%.							

<sup>5</sup> Both Lab A and Lab B heat samples to 50 °C for 6 hours. Lab A uses a relatively low dose of 5 mL BrCl for a 500 mL sample (or 1 mL BrCl for a 100 mL sample). The method allows going up to 5 mL BrCl for a 100 mL sample. The amount of BrCl added by Lab B is not known.

2. **Precision** (or the closeness of agreement among a series of measurements obtained from multiple samplings of the same homogeneous sample under the prescribed conditions).

No data were available to verify Lab A's precision in this trial (no duplicates were provided in the QA/QC report). Two samples were duplicated by Lab B (4.0 vs. 4.19 ppt and 9.26 vs. 9.73 ppt, as shown in Table A1-5).

3. **Sample homogeneity** (or the closeness of agreement among the concentrations obtained by analyzing different subsamples of the same sample). Table A1-5 also shows the standard deviation and deviation % of each three-replication treatment.

- From Table A1-5, it can be concluded that CE as-is was the most variable in mercury concentration in the Lab B analysis. However, Lab A provided more variable values in the spiked samples. It should be noted that the CE as-is samples may inherently be more variable because of the presence of solids. Therefore, the recommendation was made to both labs to carefully shake the samples before subsampling.
- Lab B also appeared to provide more resolution around the detection limit, whereas a comparison using Lab A results was not possible (all data were below the detection limit).
- Upon t-test statistical analysis, even with the low number of replications (3), the "filtered CE + 10 ppt spike" treatment resulted in statistically significant differences ( $P = 0.0142$  at 95 % confidence interval) between the two labs.

Lab A improved the recovery percentages from their earlier reports and produced data of acceptable quality. However, because Lab B appeared to provide enhanced accuracy and precision in low-level mercury analysis, Argonne strongly preferred to use Lab B for the mercury analysis by Method 1631E.<sup>6</sup> To address the need to compare the Argonne test results with the results obtained by Purdue University Calumet by using Lab A, Argonne routinely collected three split samples from each wastewater batch and sent one set of the same samples to both Lab B and Lab A for a side-by-side comparison analysis. A total of 34 samples were collected from March 11 to August 30, 2010, to be analyzed by both Lab A and Lab B for comparison purposes. Table A1-6 shows the comparison of Lab A and Lab B mercury test results for the same samples. The results obtained from Lab B were usually higher because of the higher recoveries and low method detection limits. The test results also were analyzed by a paired t-test at 95% confidence interval, since the analyzed samples were from the same original batch. The statistical analysis indicated that the test results obtained from both labs were significantly different (Figure A1-1).

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<sup>6</sup> As these concerns were not present in the analysis of other analytes, such as V, Se, and As, Lab A continued to be the choice lab for these analyses.

**Table A1-6. Comparison of Lab A and Lab B Mercury Test Results for the Same Samples**

<b>Date</b>	<b>Sample Details</b>	<b>Lab A</b>	<b>Lab B</b>
3/11/2010	CE as-is	3.35	4.00
3/11/2010	CE as-is	3.43	2.19
3/11/2010	CE as-is	3.50	4.57
3/11/2010	CE filtered through 0.45 µm	0.49	0.52
3/11/2010	CE filtered through 0.45 µm	0.49	0.55
3/11/2010	CE filtered through 0.45 µm	0.49	0.74
3/11/2010	CE filtered spiked with 10 ppt	7.26	9.35
3/11/2010	CE filtered spiked with 10 ppt	6.13	9.26
3/11/2010	CE filtered spiked with 10 ppt	6.32	9.35
3/11/2010	CE filtered spiked with 5 ppt	3.06	4.76
3/11/2010	CE filtered spiked with 5 ppt	3.57	4.67
3/11/2010	CE filtered spiked with 5 ppt	3.88	4.57
3/11/2010	MilliQ with 5 ppt spike	3.90	4.67
3/26/2010	CE as-is	4.83	6.95
3/26/2010	CE as is filtered with 10 ppt spike	5.43	9.49
4/8/2010	CE as-is	2.64	2.68
4/8/2010	CE as-is	3.08	2.09
4/8/2010	CE as-is	3.01	3.16
4/28/2010	CE as-is	1.39	2.84
5/7/2010	CE as-is	2.52	3.39
5/7/2010	CE as-is	2.83	3.46
5/7/2010	CE retentate at 300 psi	2.58	3.46
5/14/2010	CE as-is filtered through 0.45 µm	0.49	0.54
5/14/2010	MilliQ+50 ppm	0.49	0.13
5/14/2010	CE after settling (method blank)	0.49	1.98
6/8/2010	AFU t = 0	12.10	6.04
6/8/2010	AFU t = 0	7.84	7.37
6/8/2010	AFU t = 0	9.39	5.86
6/21/2010	CE as-is	3.47	4.29
6/21/2010	CE as-is	4.70	4.42
6/21/2010	CE as-is	3.22	3.94
8/30/2010	CE as-is	3.95	7.55
8/30/2010	CE as-is	3.44	8.42
8/30/2010	CE as-is	3.23	7.67

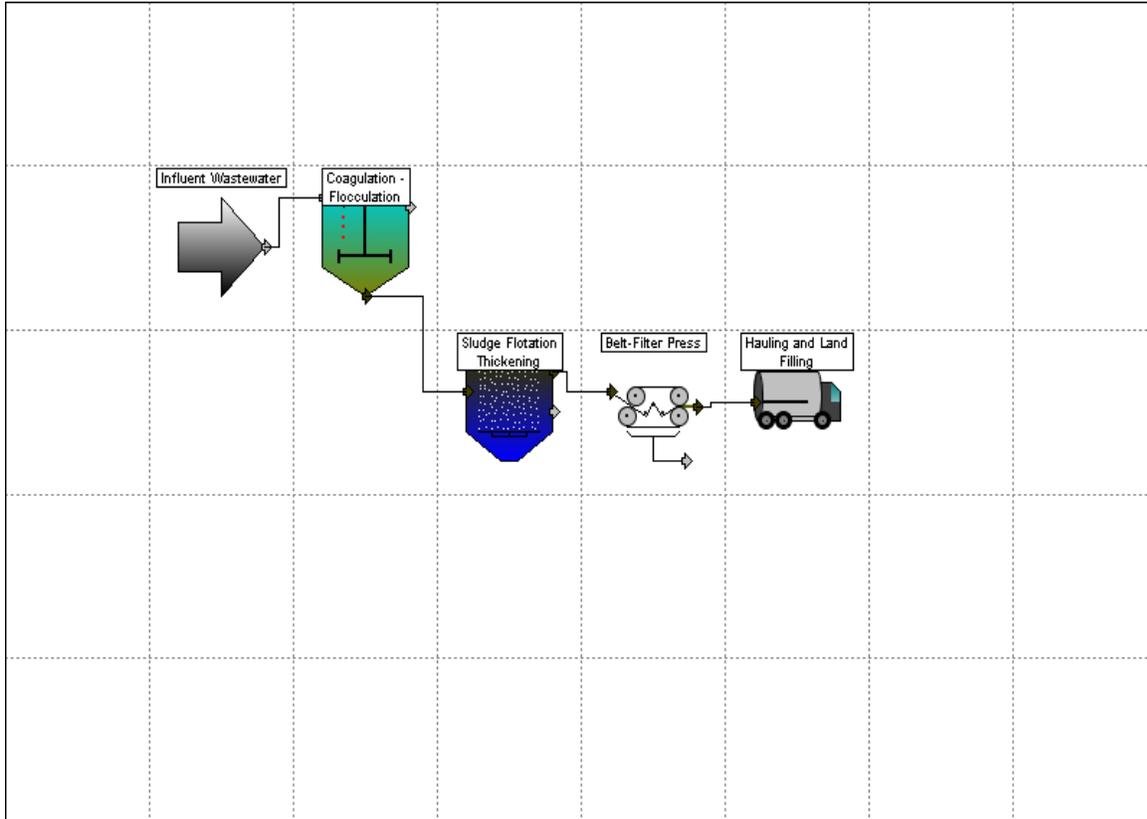
Figure A1-1. t-test for the Lab A and Lab B Reported Values

<b>P value and statistical significance:</b>		
The two-tailed P value equals 0.0289		
By conventional criteria, this difference is considered to be statistically significant.		
<b>Confidence interval:</b>		
The mean of Group One minus Group Two equals -0.8218		
95% confidence interval of this difference: From -1.5538 to -0.0898		
<b>Intermediate values used in calculations:</b>		
t = 2.2840		
df = 33		
standard error of difference = 0.360		
<b>Review your data:</b>		
<b>Group</b>	<b>Group One</b>	<b>Group Two</b>
Mean	3.7350	4.5568
SD	2.6092	2.7936
SEM	0.4475	0.4791
N	34	34

## APPENDIX 2 CADPETWORKS OUTPUTS

### A. Design and Cost Estimates for Vanadium Precipitation

#### Process Layout



<b>Summary</b>			
<b>Equipment Database</b>			
September 2007 (USA avg.)			
<b>Layout Summary</b>			
<b>Present Worth</b>	<b>Project</b>	<b>Operation (/yr)</b>	<b>Maintenance (/yr)</b>
<b>\$59,000,000</b>	<b>\$28,100,000</b>	<b>\$350,000</b>	<b>\$33,900</b>
<b>Process Summary</b>			
<b>Process</b>	<b>Construction</b>	<b>Operation (/yr)</b>	<b>Maintenance (/yr)</b>
<b>Coagulation – Flocculation</b>	<b>\$3,380,000</b>	<b>\$106,000</b>	<b>\$29,000</b>
<b>Sludge Flotation Thickening</b>	<b>\$426,000</b>	<b>\$46,200</b>	<b>\$4,350</b>
<b>Belt-Filter Press</b>	<b>\$700,000</b>	<b>\$3,440</b>	<b>\$632</b>
<b>Hauling and Land Filling</b>	<b>\$28,300</b>	<b>\$0</b>	<b>\$0</b>
<b>Iron Feed System</b>	<b>\$298,000</b>	<b>\$52,400</b>	<b>\$0</b>
<b>Other Costs</b>	<b>\$23,300,000</b>	<b>\$142,000</b>	<b>\$0</b>
<b>Summary of Costs for Layout</b>			
<b>Description</b>	<b>Value</b>	<b>Units</b>	
Other costs			
Quantities			
Required land	24	acre	
Administration labor hours	2,750	hr/yr	
Laboratory labor hours	3,650	hr/yr	
Costs			
<b>DIRECT COSTS</b>			
Mobilization	\$1,010,000	\$	
Site preparation	\$1,290,000	\$	
Site electrical	\$2,960,000	\$	
Yard piping	\$1,930,000	\$	
Instrumentation and control	\$1,570,000	\$	
Lab and administration buildings	\$2,300,000	\$	
Unit process construction costs	\$4,840,000	\$	
Profit	\$2,390,000	\$	
Total construction costs	\$18,300,000	\$	
<b>INDIRECT COSTS</b>			
Miscellaneous cost	\$915,000	\$	
Legal cost	\$366,000	\$	
Engineering design fee	\$2,740,000	\$	
Inspection cost	\$366,000	\$	
Contingency	\$1,830,000	\$	

Technical	\$366,000	\$	
Total indirect costs	\$6,590,000	\$	
MISCELLANEOUS COSTS			
Cost of land	\$480,000	\$	
Interest during construction	\$2,760,000	\$	
LABOR COSTS			
Administration labor cost	\$68,800	\$/yr	
Laboratory labor cost	\$73,100	\$/yr	
Unit process operation labor cost	\$208,000	\$/yr	
Unit process maintenance labor cost	\$33,900	\$/yr	
Total labor costs	\$384,000	\$/yr	
PROJECT SUMMARY			
Present worth	\$59,000,000	\$	
Total project cost	\$28,100,000	\$	
Total operation labor cost	\$350,000	\$/yr	
Total maintenance labor cost	\$33,900	\$/yr	
Total material cost	\$1,460,000	\$/yr	
Total chemical cost	\$915,000	\$/yr	
Total energy cost	\$32,400	\$/yr	
Total amortization cost	\$411,000	\$/yr	
<b>Summary of the Chemical Feed System for Iron</b>			
<b>Description</b>	<b>Value</b>	<b>Units</b>	
Iron Salt Solution Feed System			
Quantities			
Ferric chloride dosage rate	6,770	lb/d	
Iron salt dosage rate as equivalent iron	2,330	lb/d	
Liquid chemical solution fed	1,920	gpd (U.S.)	
Operation labor required	2,100	person-hr/yr	
Costs			
Construction and equipment cost	\$298,000	\$	
Operational labor cost	\$52,400	\$/yr	
Material and supply cost	\$5,960	\$/yr	
Amortization cost	\$25,000	\$/yr	
<b>Influent Wastewater</b>			
<b>Coagulation – Flocculation</b>			
<b>Design Output Data</b>			
<b>Description</b>	<b>Value</b>	<b>Units</b>	

Coagulation – Flocculation			
Design Information			
Ferric chloride dosage	58	mg/L	
Coagulant required	6,770	lb/d	
Quantities			
Operational labor required	4,230	person-hr/yr	
Maintenance labor required	1,580	person-hr/yr	
Electrical energy required	119,000	kWh/yr	
Volume of earthwork required	371,000	cu. ft	
Slab thickness	12.1	in.	
Volume of slab concrete required	32,400	cu. ft	
Wall thickness	15.5	in.	
Volume of wall concrete required	28,800	cu. ft	
Sidewater depth	17	ft	
Power required	4.45	HP	
Number of upflow clarifiers per battery	4		
Number of trains (batteries)	1		
Wastewater to be handled by one unit	3.5	MGD (U.S.)	
Design overflow rate dependent on coagulant type	500	gal (U.S.)/(sq. ft·d)	
Surface area of each individual unit	7,000	sq. ft	
Diameter of unit	94.4	ft	
Costs			
Construction and equipment cost	\$3,380,000	\$	
Operational labor cost	\$106,000	\$/yr	
Maintenance labor cost	\$29,000	\$/yr	
Material and supply cost	\$33,800	\$/yr	
Chemical cost	\$890,000	\$/yr	
Energy cost	\$11,900	\$/yr	
Amortization cost	\$322,000	\$/yr	
<b>Sludge Flotation Thickening</b>			
<b>Design Output Data</b>			
<b>Description</b>	<b>Value</b>	<b>Units</b>	
Sludge Flotation Thickening			
Design Information			
Air-to-solids ratio	0.02		
Air pressure	60	psig	
Solids loading rate	10	lb/(sq. ft·d)	
Recycle flow	0.336	MGD (U.S.)	
Surface area required	542	sq. ft	
Volume of pressure tank	62.5	cu. ft	
Volume of flotation tank	6,710	cu. ft	

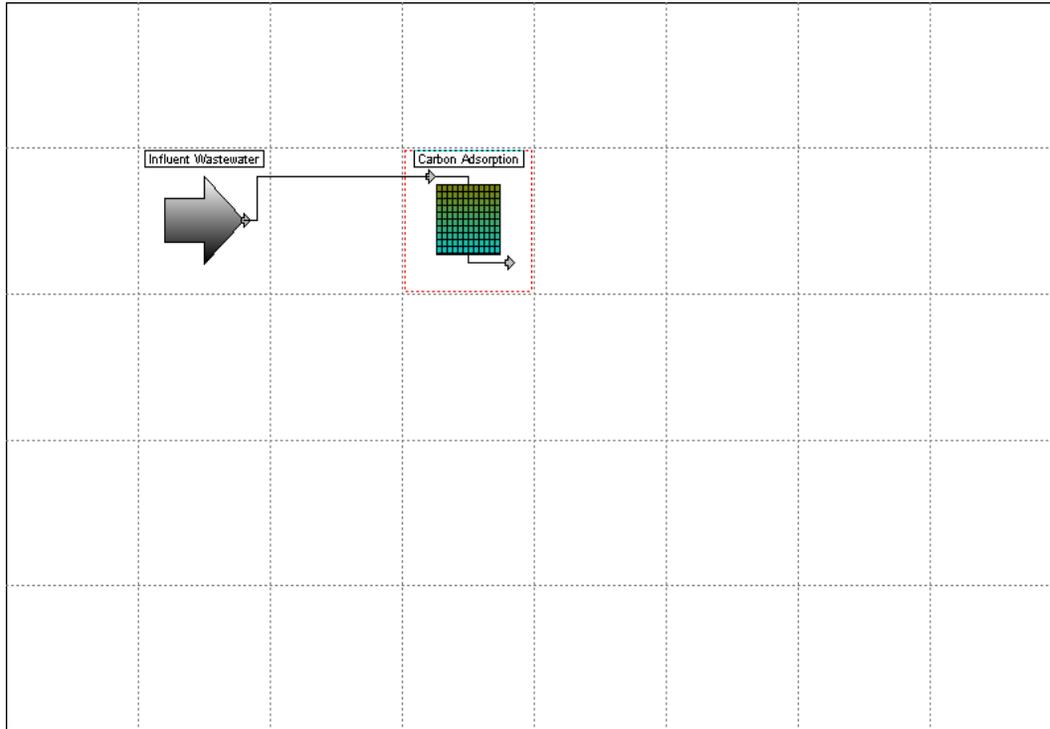
Pressure tank detention time	2	min	
Flotation tank detention time	3	hr	
Polymer required	2.71	lb/d	
Quantities			
Number of units	1		
Surface area per flotation unit	570	sq. ft	
Diameter per flotation unit	26.9	ft	
Amount of sludge generated	2.71	ton(long)/d	
Area of flotation building	924	sq. ft	
Volume of earthwork required	7,650	cu. ft	
Slab thickness	9.9	in.	
Volume of slab concrete required	652	cu. ft	
Wall thickness	11	in.	
Volume of wall concrete required	798	cu. ft	
Sidewater depth	8	ft	
Operation labor required	824	person-hr/yr	
Maintenance labor required	237	person-hr/yr	
Electrical energy required	161,000	kWh/yr	
Costs			
Construction and equipment cost	\$418,000	\$	
Operational labor cost	\$20,600	\$/yr	
Maintenance labor cost	\$4,350	\$/yr	
Material and supply cost	\$4,180	\$/yr	
Energy cost	\$16,100	\$/yr	
Polymer Feed System			
Quantities			
Polymer dosage	2.71	lb/d	
Liquid chemical solution fed	130	gpd (U.S.)	
O&M labor required	659	person-hr/yr	
Dry material handling and mixing labor required	366	person-hr/yr	
Total operation labor required	1,030	person-hr/yr	
Costs			
Construction and equipment cost	\$7,860	\$	
Operational labor cost	\$25,600	\$/yr	
Material and supply cost	\$157	\$/yr	
Chemical cost	\$1,290	\$/yr	
<b>Belt-Filter Press</b>			
<b>Design Output Data</b>			
<b>Description</b>	<b>Value</b>	<b>Units</b>	
Belt-Filter Press			
Design Information			

Belt filter width	1	m	
Number of units	1		
Hydraulic loading per unit per meter of belt width	70	gpm (U.S.)	
Hydraulic loading required per meter of belt width	36.1	gpm (U.S.)	
Final solids content	30	%	
Solids capture fraction	0.997		
Quantities			
Operation labor required	138	person-hr/yr	
Maintenance labor required	34.4	person-hr/yr	
Power	43,000	kWh/yr	
Polymer required	18,100	lb/yr	
Dry solids produced	4,950	lb/d	
Belt filter(s)	\$243,000	\$	
Building	\$228,000	\$	
Installation	\$60,800	\$	
Polymer system	\$72,900	\$	
Feed pumps	\$26,700	\$	
Conveyor system	\$68,000	\$	
Costs			
Construction and equipment cost	\$700,000	\$	
Operational labor cost	\$3,440	\$/yr	
Maintenance labor cost	\$632	\$/yr	
Chemical cost	\$23,500	\$/yr	
Energy cost	\$4,300	\$/yr	
Amortization cost	\$64,100	\$/yr	
<b>Hauling and Land Filling</b>			
<b>Design Output Data</b>			
<b>Description</b>	<b>Value</b>	<b>Units</b>	
Sludge Hauling and Land Filling			
Design Information			
Volume of sludge hauled		cu. yd/d	
Truck capacity		cu. yd	
Round trip time to disposal site	0	hr	
Truck loading time	0	hr	
Operational hours per day	0	hr	
Number of trucks required	1		
Distance to disposal site	0	mi	
Quantities			
Total sludge volume hauled		cu. yd/d	
Maximum anticipated landfill downtime		d	

Anticipated sludge storage height		ft	
Sludge storage shed area		sq. ft	
Width of sludge storage shed slab		ft	
Length of sludge storage shed slab		ft	
Volume of earthwork required		cu. ft	
Volume of slab concrete required		cu. ft	
Surface area of canopy roof		sq. ft	
Round trip haul distance		mi	
Round trips per day per truck			
Distance traveled per year per truck		mi	
Sludge hauled (dry solids)	2.25	ton/d	
Operation labor required	0	person-hr/yr	
Land-filling cost	\$479,388	\$/yr	
Costs			
Construction and equipment cost		\$	
Material and supply cost	\$479,388	\$/yr	

## B. Design and Cost Estimates for Adsorption

### Process Layout



<b>Adsorbent Summary</b>								
<b>Adsorbent</b>	<b>Present Worth</b>	<b>Project</b>	<b>Operation (/yr)</b>	<b>Maintenance (/yr)</b>	<b>Material (/yr)</b>	<b>Chemical (/yr)</b>	<b>Energy (/yr)</b>	<b>Amortization (/yr)</b>
SAMMS	\$225,000,000	\$235,000,000	\$270,000	\$10,000	\$165,000	\$0	\$310,000	\$10,500,000
Mersorb	\$51,200,000	\$45,300,000	\$282,000	\$10,000	\$48,800	\$0	\$395,000	\$1,330,000
F600	\$54,800,000	\$45,900,000	\$313,000	\$10,000	\$57,900	\$0	\$607,000	\$1,360,000
OLC	\$64,700,000	\$46,900,000	\$385,000	\$10,000	\$74,900	\$0	\$1,250,000	\$1,430,000
Bayoxide	\$54,700,000	\$49,200,000	\$280,000	\$10,000	\$50,800	\$0	\$384,000	\$1,520,000
Adsorbsia	\$52,600,000	\$48,800,000	\$261,000	\$10,000	\$43,300	\$0	\$281,000	\$1,490,000
GFH	\$40,400,000	\$35,700,000	\$260,000	\$10,000	\$34,200	\$0	\$273,000	\$853,000

## APPENDIX 3 Quality Assurance and Quality Control

### 1. Clean Room Certification

Argonne's clean room was tested on January 15, 2010, by HEF Technical Services before the experimental work began. The results of this testing indicated that the clean room met the specified requirements, and it was certified as a Class 100 clean room. A summary of the test results is available in Attachment 1. A second test was conducted on March 1, 2010, to verify that Argonne's clean-room operating procedures were sufficient to maintain the room at a Class 100 level during the experimental phase of the project. The room was again certified as a Class 100 clean room. The report for this testing can be reviewed in Attachment 2.

#### Attachment 1: Initial Clean Room Certification



Clean room  
certification-HEF.pdf

#### Attachment 2: Second Clean Room Certification



Clean Room Testing  
Report 3-1-10.pdf

### 2. Room Blanks

A series of room blanks was collected to determine whether any metals of concern were present in the air in Argonne's clean room. The results for the room blanks are summarized in Table A3-1. The room blanks were done by placing a wide-mouth, 1L beaker of MilliQ water next to or near the location of the experimental work. The main focus of the testing was to establish whether any of the mercury (Hg) present in the vapor was transferring to the liquid phase used in our experiments. Therefore, the testing for mercury occurred on a frequent basis. During the multiple test periods, the mercury level was consistently shown to be lower than the detection limits. An additional test for arsenic (As), selenium (Se), and vanadium (V) was conducted to ensure completeness. This test indicated that levels were below the detection limits for these three metals.

**Table A3-1. Summary of the Room Blanks**

Date	Sample ID	Time (hr)	Hg (ppt)	As (ppb)	Se (ppb)	V (ppb)
2/4/2010	Clean room blank	2	<0.5			
3/18/2010	CEAI-031810-009	4		<1	<1	<1
4/16/2010	CEAIF-041610-010	4	<0.5			
4/23/2010	CEAIF-042110-009	4	<0.08			

### 3. Acid Bath Monitoring

The acids baths that cleaned the glass and Teflon equipment used in the experiments were periodically sampled to track the levels of mercury, arsenic, selenium, and vanadium. An equal amount of sample was taken from each of the six acid baths during each sampling event. The frequency of the sampling was dependent on use — sampling did not occur during lulls in the experimental work. Table A3-2 presents a summary of the acid bath samplings and specifies when the baths were replaced. In some cases, an individual bath was replaced as a precaution because of a visual observation of a high level of particulate matter. In other cases, the baths were replaced because the mercury concentration exceeded 50 ppt.

**Table A3-2. Summary of the Acid Bath Samplings**

Date	Sample ID	Hg (ppt)	As (ppb)	Se (ppb)	V (ppb)
2/4/2010	Unused acid bath	<0.5			<1
2/4/2010	Used acid bath	0.889			<1
2/12/2010	AB-021210-001,002	2.04	<1	5	<1
2/19/2010	Acid bath replacement: one bath				
2/25/2010	CEAI-022510-004,005	3.82	<1	2.1	<1
3/24/2010	Acid bath replacement: all baths				
4/16/2010	CEAIF-041610-009 CEAI-041610-001	38.5	<1	1.9	<1
4/23/2010	AB-042310-01,02	77.0	<1	4.0	<1
4/30/2010	AB-043010-001,002	32.4	<1	2.1	<1
5/12/2010	Acid bath replacement: one bath				
5/17/2010	Acid bath replacement: one bath				
6/1/2010	AB-060110-001,002	94.8	<1	<1	<1
6/7/2010	Acid bath replacement: remaining baths				
6/28/2010	AB-062810-001,002	74.7	2.5	1	<1
7/6/2010	CEAI-070610-004,005	388	1.6	<1	<1

Over time, it became apparent that a main contributor to the mercury levels in the acid baths was the labware used to make the 10 ppb Hg<sup>+2</sup> spike solution, which was freshly made on the day that it was used. After identifying this correlation, a separate and smaller acid bath was used for the mercury-spike glassware to prevent contamination of the larger acid baths.

### 4. Trip Blanks for Analytical Samples

Initially, the trip blanks were sent with each sample shipment, as summarized in Table A3-3. The analysis performed on the trip blank was dependent on the type of samples that were being shipped. For example, the trip blank for the mercury samples was analyzed only for mercury. All 14 of the trip blanks that were analyzed for mercury indicated that the mercury level was below the detection limits. Given that the trip blanks consistently showed little-to-no detection of the metals of interest, the use of trip blanks was discontinued about half-way through the experimental phase as a cost savings measure.

**Table A3-3. Summary of the Trip Blanks for Analytical Samples**

Date	Sample ID	Lab	Hg (ppt)	As (ppb)	Se (ppb)	V (ppb)
2/4/2010	Trip blank	Lab A	<0.5	<1	<1	<1
2/5/2010	ETAI-020510-017,018	Lab A	<0.5	<1	3.2	2.4
2/10/2010	ETTB-021010-001,002	Lab A	<0.5	<1	<1	<1
2/12/2010	TB-021210-001,002	Lab A	<0.5	<1	1.3	<1
2/17/2010	TB-021710-01	Lab A	<0.5			
2/25/2010	CEAI-022510-001, 006	Lab A	<0.5	<1	3.6	<1
2/26/2010	TB-022610-001, 002	Lab A	<0.5	<1		<1
3/1/2010	CE-030110-005	Lab A	<0.5			
3/4/2010	MilliQ water system	Lab A		<1	<1	<1
3/11/2010	CEFR-031110-014	Lab B	<0.5			
3/11/2010	CEMB-031110-014	Lab A	<0.5			
3/18/2010	CEAI-031810-009	Lab A		<1	<1	<1
4/7/2010	CEAIF-040710-023	Lab B	<0.5			
4/8/2010	CEPR-040810-22	Lab B	<0.5			
4/16/2010	CEPR-041610-15	Lab B	<0.5			
4/21/2010	CEAIF-042110-010	Lab B	<0.08			

**5. Instrument Calibration: pH Meter, Turbidity Meter, and Balances**

Throughout the experimental work, the various instruments were calibrated according to the methods outlined in the vendor’s instruction manual. Each day and before use, the pH/mV/conductivity probe was calibrated with pH standard solutions (pH 4.0 and 7.0), as was the dissolved oxygen probe. The turbidimeter was calibrated weekly with three turbidity standards (<0.1, 20, 100 NTU).

The balances used in this testing were checked, calibrated, and maintained by an outside ISO-certified vendor, Mettler Toledo. After the balances were moved into the clean room, and shortly before the experimental work began, they were checked and calibrated by Mettler Toledo in place in the clean room.

## APPENDIX 4 Method Loss Application to Data

In order to determine the contaminant removal that could be attributed to a specific technology, method blanks were conducted to determine the contaminant loss due to the actual process. For example, for the adsorption isotherm method blanks, 0.45 µm filtered CE that was spiked with 10 ppt Hg<sup>+2</sup> was mixed for 24 hours and then vacuum filtered. The only difference from the actual isotherm process was that no adsorbent was used. Any Hg losses would be due to the mixing, pouring during the vacuum filtration or adherence to the glass or mixer.

A sample calculation that shows the application of the method loss to adsorption isotherm data is shown below. The data shown is from the SAMMS and Mersorb comparison testing (6/29 – 7/1/10).

1. To determine the initial Hg in an isotherm jar:

Amount of dissolved Hg in the CE

Initial CE after 0.45 µm filtration was 0.68 ppt (CEAI-062910-003).  
 $(0.750 \text{ L})(6.8 \times 10^{-7} \text{ mg/L}) = 5.1 \times 10^{-7} \text{ mg Hg}$

Amount of Hg added from spike solution

Using 750 µL of 10 ppb Hg<sup>+2</sup> standard

$$m_1V_1 = m_2V_2$$

$$(750 \times 10^{-6} \text{ L})(0.01 \text{ mg/L}) = x \cdot (0.75 \text{ L})$$

$$X = 0.00001 \text{ mg/L or 10 ppt}$$

$$\text{So amount of Hg added with spike is } (750 \times 10^{-6} \text{ L})(0.01 \text{ mg/L}) = 7.5 \times 10^{-6} \text{ mg Hg}$$

Method Loss

The adsorption isotherm method blanks (n=5) showed an average Hg loss of 33% with respect to the initial 10 ppt Hg spike.

$$\text{Applying to the spike, } 7.5 \times 10^{-6} \text{ mg Hg} \cdot 33\% = 2.475 \times 10^{-6} \text{ mg Hg method loss}$$

$$\begin{aligned} \text{Total Initial Hg} &= \text{Dissolved Hg} + \text{Spike Hg} - \text{Method Loss} \\ &= 5.1 \times 10^{-7} \text{ mg Hg} + 7.5 \times 10^{-6} \text{ mg Hg} - 2.475 \times 10^{-6} \text{ mg Hg} \\ &= 5.54 \times 10^{-6} \text{ mg Hg initially present in isotherm jar.} \end{aligned}$$

2. To determine Hg loss due to an adsorbent:

For example, using 0.2 dose of Mersorb from the 6/29 – 7/1/10 testing.

After isotherm, treated CE was 0.69 ppt (CEAI-070110-006).

$$\begin{aligned} \text{Final Hg} &= ((\text{CE wt. in g}) \cdot (\text{Hg in ng/L})) / ((1 \times 10^6 \text{ ng/mg}) \cdot (1 \text{ g/mL}) \cdot (1000 \text{ mL/L})) \\ &= ((742.5 \text{ g}) \cdot (0.69 \text{ ppt})) / ((1 \times 10^6) \cdot (1000)) \end{aligned}$$

$$\text{Final Hg} = 5.123 \times 10^{-7} \text{ mg Hg}$$

$$\% \text{ Hg removal} = 1 - (5.123 \times 10^{-7} \text{ mg Hg}) / (5.54 \times 10^{-6} \text{ mg Hg}) = 90.75\%$$



**Energy Systems Division**

Argonne National Laboratory  
9700 South Cass Avenue, Bldg. 362  
Argonne, IL 60439-4815

[www.anl.gov](http://www.anl.gov)



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