ELECTRIC POWER
RESEARCH INSTITUTE

Review of Water Treatment Technologies for Selenium Removal Implemented at Power Plants

1020813

Review of Water Treatment Technologies for Selenium Removal Implemented at Power Plants

1020813

Technical Update, March 2010

EPRI Project Manager

P. Chu

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

CH2M HILL, Inc.

This is an EPRI Technical Update report. A Technical Update report is intended as an informal report of continuing research, a meeting, or a topical study. It is not a final EPRI technical report.

NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

CITATIONS

This document was prepared by

CH2M HILL, Inc.
155 Grand Avenue Suite 1000
Oakland, CA 94612

Principal Investigators
T. Higgins
C. DiSante
D. Fink

This document describes research sponsored by the Electric Power Research Institute (EPRI).

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

Review of Water Treatment Technologies for Selenium Removal Implemented at Power Plants. EPRI, Palo Alto, CA: 2010. 1020813.

PRODUCT DESCRIPTION

This technical update provides a review of commercially available selenium removal technologies that have been implemented full-scale at power plants. In the report, case studies of treatment technologies for selenium removal at 10 power plants are presented. Included in the review is a description of the treatment processes, treatment configurations, typical removal levels for selenium, factors that affect selenium removal, robustness of the technology to treat other constituents in flue gas desulfurization (FGD) water, advantages and limitations of the technology, operations and safety issues, and capital and operating costs.

Results and Findings

The case studies evaluated include treatment to low part per billion (µg/L) levels of selenium. Because a variety of factors affect treatment, removal to low µg/L is not considered applicable to all power plants. Case studies of anaerobic/anoxic biological reduction of selenium were able to treat to lower levels than physical/chemical treatment systems applied full-scale at power plants. However, it should be noted that all but one of the plants using physical/chemical treatment processes were operating at pH levels for overall trace metals removal and were not optimized for selenium removal.

Challenges and Objectives

This report is intended for managers at coal-fired power plants who are interested in learning about treatment technologies for the removal of selenium from power plant water, including FGD water. Selenium treatment is a challenge because the fate of selenium in power plants is inconsistent (for example, ash, water, or FGD solids) and the form of selenium tends to vary significantly with FGD design, coal, and limestone. Regulators are increasingly requiring selenium treatment to the low µg/L levels, posing a challenge to most commercially available treatment technologies. Further, power plant FGD wastewaters can be challenging to treat—the matrix is complex, with many ions that can negatively affect treatment technologies.

Applications, Value, and Use

Selenium treatment is becoming more important as discharge limits are tightened. The perception that FGD water represents a concentrated stream of selenium in power plant wastewater discharge is heightening the potential for increased scrutiny from both regulators and power plant managers.

EPRI Perspective

This survey represents the results of 10 case studies of FGD wastewater treatment of selenium. Many of the results from these case studies were provided by the host utility. The Electric Power Research Institute (EPRI) made only limited efforts to confirm the quality of the results as well as their consistency from site to site. The results indicate that physical/chemical and biological wastewater treatment systems have the potential to achieve substantial selenium removal; however, there appeared to be significant variability among the 10 case studies.

Approach

Interviews were conducted with managers from various coal-fired power plants that currently employ treatment technologies for the removal of selenium from FGD water. The data presented

are based on historical EPRI reports, publicly available information from the EPA docket, and interviews conducted with coal-fired power plants on their FGD water treatment systems.

Information on selenium chemistry in power plant wastewater as well as emerging treatment technologies gained from other EPRI projects is also incorporated.

Keywords
Selenium
Selenite
Selenate
FGD
Fly ash pond

ACKNOWLEDGMENTS

EPRI would like to thank its member utilities that contributed their experiences in management of selenium in FGD water as documented within this Technical Update.

ACRONYMS AND ABBREVIATIONS

°C	degrees Celsius
°F	degrees Fahrenheit
µg/L	micrograms per liter
BOD	biochemical oxygen demand
CE-ICP-MS	capillary electrophoresis inductively coupled plasma mass spectrometry
CRC	collision/reaction cell
DBA	dibasic acid
DRC	dynamic reaction cell
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	electrostatic precipitator
FGD	flue gas desulphurization
GAC	granular activated carbon
GC-ICP-MS	gas chromatography inductively coupled plasma mass spectrometry
gpm	gallons per minute
HRT	hydraulic retention time
H_2SeO_3	selenious (or selenous) acid
HG-AAS	hydride generation atomic absorption spectrometry
IC-ICP-MS	ion chromatography inductively coupled plasma mass spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
LC-ES-MS	liquid chromatography electrospray ionization mass spectrometry
mg/L	milligrams per liter
mgd	million gallons per day
mm	millimeter
MS/MSD	matrix spike/matrix spike duplicate
MVR	mechanical vapor recompression
NO_x	nitrogen oxides

NPDES	National Pollutant Discharge Elimination System
ORP	oxidation reduction potential
SBR	sequencing batch reactor
SCR	selective catalytic reduction
Se	selenium
Se^0	elemental selenium
Se^{-2}	selenide
SeO_2	selenium dioxide
SeO_3^{-2}	selenite
SeO_4^{-2}	selenate
SO_2	sulfur dioxide
TDS	total dissolved solids
TSS	total suspended solids
VFW	vertical flow wetlands
WQBEL	water quality-based effluent limit
ZLD	zero liquid discharge

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1
INTRODUCTION

Purpose

Although selenium discharges to water has been identified as a problem since the 1980s, developing effective treatment technologies has been a challenge. This Technical Update presents an analysis of state-of-the-practice treatment technologies for selenium removal from process waste streams at power plants. This Technical Update has been created in part to address a request from the North American Metals Council- Selenium Work Group to assemble case studies of full-scale applications of technologies for removal of selenium from waste streams at power plants. The focus of this Technical Update is on demonstrated selenium removal technologies applied at full scale for flue gas desulphurization (FGD) water. This stream represents a major contribution of mass load of selenium in a power plant and is challenging to remove due to the complex matrix. A summary of EPRI-led pilot-scale selenium-removal technologies being tested for selenium removal in FGD water is also discussed.

Regulatory Background

Increasingly, selenium is identified by electric utilities as a significant regulatory challenge. Discharge concentrations are increasing and regulatory limits are becoming more stringent. The ambient selenium water quality criteria are generally consistent from state to state: 5 part per billion (µg/L) for chronic aquatic life use and 20 µg/L for acute aquatic life use. Water quality criteria are not end-of-pipe limits but are used to derive individual plant effluent limits, otherwise called water quality-based effluent limits (WQBELs) incorporated into National Pollutant Discharge Elimination System (NPDES) permits for power plants. If a discharger's effluent has a "reasonable potential" to cause or contribute to an exceedance of those standards, then a WQBEL is justified. The WQBEL is calculated based on the flow of the effluent, the concentration of the pollutant in the effluent, the flow of the receiving water, and the concentration of pollutant in the receiving water. As a result, plant effluent limits vary from state to state and between plants in each state, depending on discharge and receiving stream characteristics.

Furthermore, ambient numeric selenium criteria are subject to change. The U.S. Environmental Protection Agency (EPA) is currently evaluating use of a fish tissue-based chronic criterion, which could lead to lower water quality standards and WQBELs for selenium.

In September 2009, after conducting a detailed study of the industry, the EPA announced it is planning to revise the current effluent guidelines for the steam electric power generating industry. Over the course of their study, the EPA reviewed technologies that are commercially available to treat wastewater associated with power plants [1]. There are limited technologies currently available that treat selenium to low µg/L levels, and many of those technologies are still unproven beyond bench scale or pilot scale. Conventional water treatment technologies have not been demonstrated to consistently remove selenium to low µg/L levels from complex wastewater matrices.

Overview of Sources and Fate of Selenium in Power Plants

Selenium is a naturally occurring trace element in coal. As coal is combusted, selenium can partition into solid, liquid and vapor phases. Figure 1-1 illustrates the fate of selenium at coal-fired power plants.

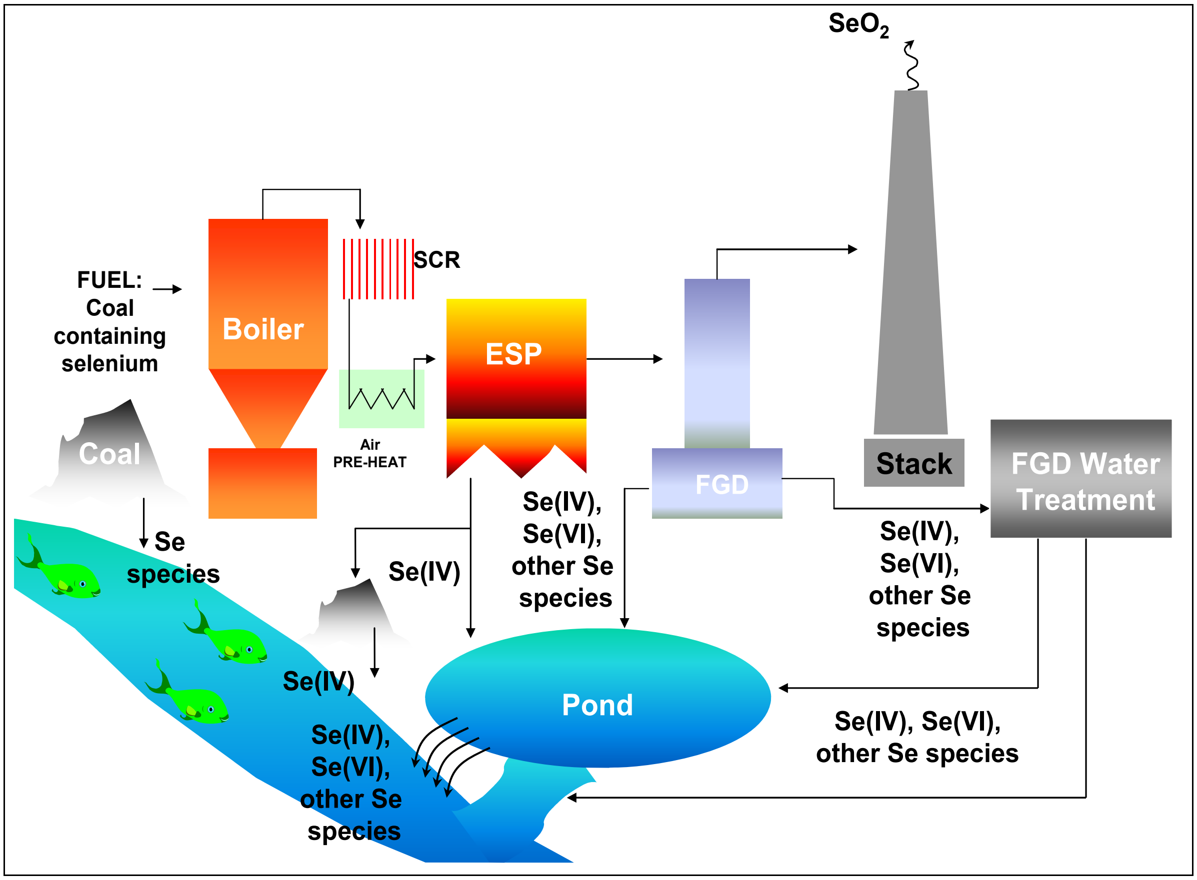

Figure 1-1
Fate of Predominant Selenium Species in Coal-Fired Power Plants

In solid form, selenium is found primarily in fly ash. In vapor form, selenium is likely present as a volatile metal in flue gas as selenium dioxide (SeO_2) and may be captured by the wet FGD system. Selenium may be present in the liquid phase in various water streams throughout a plant, including the following:

- ***Wet flue gas desulphurization***: Although scrubbers have been in place at some facilities for many years, a number of FGD systems have been installed in response to the proposed and now vacated Clean Air Interstate Rule and Clean Air Mercury Rule, as well as the Clean Air Visibility Rule, consent decrees, and state regulations to reduce sulfur dioxide (SO_2) in flue gas in the recent past. Most wet FGD scrubber systems periodically blow down or purge a portion of the absorber slurry to limit buildup of chlorides and suspended solids. For many of these new wet FGD systems, the blowdown represents a new liquid stream which requires some treatment for solids removal, and in some cases, removal of potentially toxic trace elements, e.g., selenium.

The FGD purge stream contains a slurry of water, dissolved solids and suspended solids (mainly calcium sulfate [gypsum] or calcium sulfite solids), fly ash, and inert constituents from limestone. The purge is separated into coarse (typically > 0.1 mm) and fine solid fractions (< 0.1 mm), usually using hydrocyclones, and the coarse fraction is dewatered by vacuum belt filters or settling ponds. A portion of the hydrocyclone overflow (fines) and the vacuum filter filtrate may be returned to the FGD. However, to control buildup of chlorides and fines in the FGD scrubber system, a portion of the hydrocyclone overflow and/or vacuum filter filtrate is separated for disposal. This stream is often referred to as chloride purge stream, FGD purge water, or FGD blowdown. Since this stream has not yet undergone treatment, the term “untreated FGD water” will be used in this Technical Update. Figure 1-2 shows an example of a limestone forced oxidation FGD scrubber system, which is one of many possible configurations.

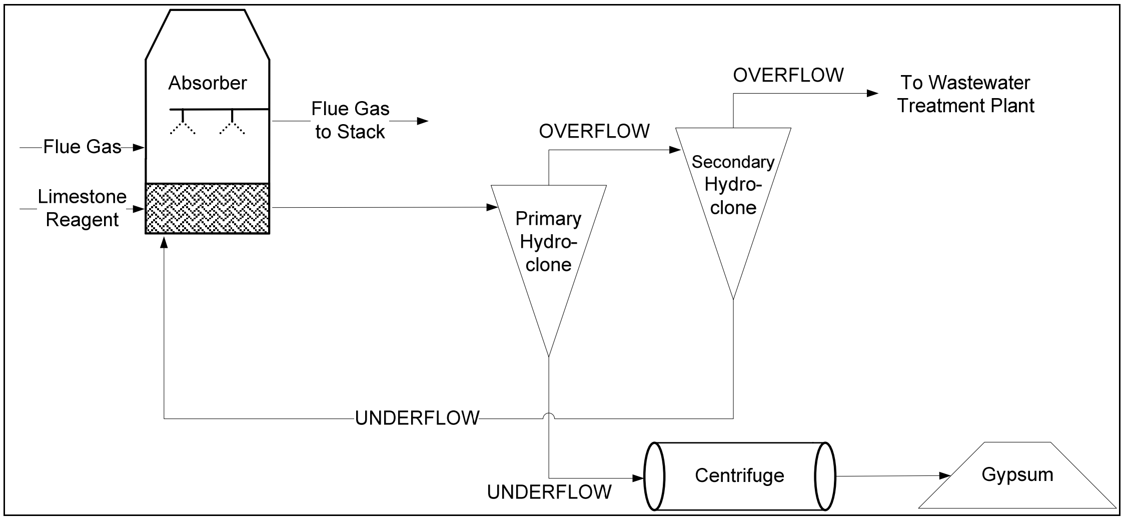

Figure 1-2
Limestone Forced Oxidation Flue Gas Desulphurization System Example Configuration

- ***Fly ash sluice water and ash pond water:*** Selenium in coal is volatilized during combustion to SeO_2 in the flue gas [2]. As the flue gas cools, a portion of the selenium condenses onto the fly ash. Wet fly ash handling operations involve sluicing fly ash with water to a pond for long-term disposal. The fly ash sluice water is sent to a pond to settle suspended solids and metals prior to discharge. A fly ash pond may receive other process liquid streams such as untreated or treated FGD water that may also contain selenium.
- ***Other streams:*** Other wastewater streams that contain selenium include fly ash leachate (at plants that handle fly ash dry and send to on-site landfills), FGD landfill leachate, coal pile runoff, economizer ash sluice water, and other low-volume water streams. These streams contribute a smaller mass load of selenium as compared to fly ash ponds or untreated FGD water at a typical coal-fired power plant.

The focus of this technical update will be on treatment of FGD water, as our search found no examples of successful, commercial treatment for selenium from fly ash sluice water and pond water applied at facilities. There are several facilities that have installed FGD water treatment systems and many of these systems consist of physical/chemical or biological treatment scenarios. Section 2 presents a summary of selenium characteristics, including selenium speciation in these various streams, and discusses the variability in selenium observed based on historical data collected at various plants.

Approach

Interviews were conducted with managers from various coal-fired power plants that currently employ treatment technologies for the removal of selenium from FGD water. In addition, publicly available information on selenium-removal technologies from various power plants was also used for this Technical Update. Data presented are based on historical EPRI reports, publicly available information from the federal docket, and plant manager interviews.

Study Limitations

As noted above, the data presented in this study come from a variety of sources, including previous EPRI reports, the federal docket, and power plant manager interviews. Because samples were collected by various sources, the quality of the data could not be verified. Sample methods, sample filtration, sample preservation, and analytical methods differed among the data reviewed. Matrix spike/matrix spike duplicate (MS/MSD) samples were not available for each data set used within this study.

The data presented within this study are not paired results, meaning that sample collection across the treatment system was not timed to reflect the amount of time it takes the FGD water to pass through the treatment system.

Some of the data sets for the case studies presented within this Technical Update were one-time sampling events, and therefore the data do not represent variation due to the many factors that influence selenium levels in FGD water on a daily basis.

The focus of this Technical Update is to summarize case studies of full-scale technologies implemented for selenium removal from wastewater at power plants. This is based on technologies currently implemented at facilities and therefore represents a snapshot in time of selenium removal technologies being used in the industry.

2

CHARACTERIZATION OF SELENIUM IN WATER AT POWER PLANTS

This section presents an overview of the various selenium species within fly ash ponds and untreated FGD water and the factors that affect total and dissolved selenium concentrations and selenium speciation in these streams. The speciation of selenium is important because the effectiveness of water treatment technologies varies depending on the species of selenium present in a power plant's water.

Overview of Selenium Chemistry

Selenium can be transformed into a variety of forms that differ in mobility and toxicity based on biological and chemical processes. Inorganic selenium typically occurs in the environment in one of four oxidation states: Se(IV), Se(VI), Se(-II), and Se(0). Se(IV) is usually found as the oxyanion selenite (SeO_3^{-2}) and Se(VI) is usually found as selenate (SeO_4^{-2}) in oxidized systems, while selenium typically occurs as elemental selenium (Se^0) and Se(-II) as selenide (Se^{-2}) in anaerobic zones. Reduced selenium species such as Se^0 and Se(-II) and strongly absorbed selenium species are insoluble. A simplified selenium-water system Pourbaix diagram showing major thermodynamically stable selenium species as a function of pH and redox potential is shown in Figure 2-1. The element sulfur lies just above selenium in the periodic chart. Correspondingly, the chemistry of selenium is similar to that of sulfur.

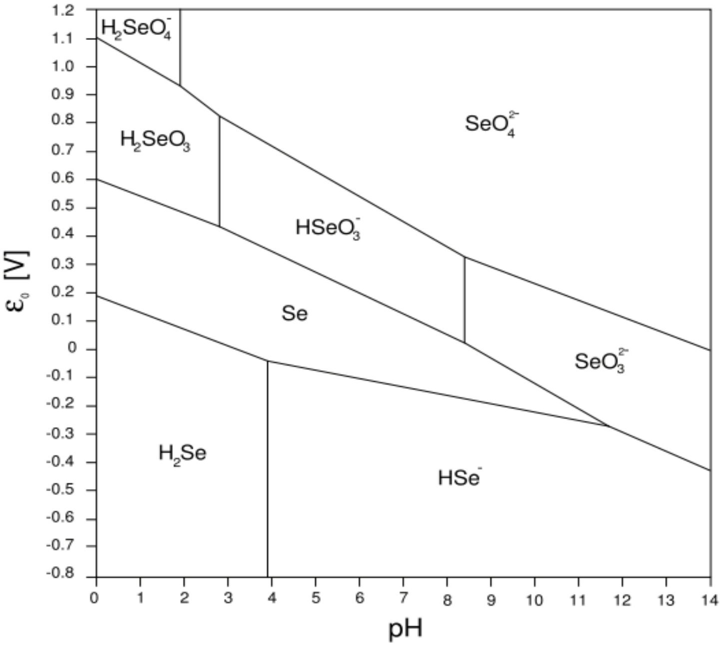

Figure 2-1
Pourbaix Diagram for Selenium

Analytical Methods for Determination of Selenium

The assessment of selenium in liquid streams at power plants depends heavily upon adequate analytical methods for reliably measuring concentrations of total and dissolved selenium as well as various selenium species. Chemical analysis of FGD water is often very difficult because of high solids, including high sulfates, chlorides, and calcium. These constituents can interfere with commonly used metals analytical methods such as EPA Methods 200.7 and 200.8. High total suspended solids (TSS) levels (greater than 1% solids) in FGD or ash pond influent may require biphasic separation and analysis of samples (the separation of sample into liquid and solid fractions, followed by analysis of each part, and summation of results to derive the total concentration in the sample).

A low-level analytical method that has been applied to FGD water for total and dissolved selenium determination is EPA Method 1638-- inductively coupled plasma mass spectrometry (ICP-MS). Method 1638 is not approved for NPDES permit compliance monitoring, although it has been allowed in some cases on a state-by-state basis. A modification of Method 200.8 that includes the clean procedures and performance specifications of Method 1638 is allowable [3]. For total selenium, the method of digestion may impact results. USEPA Methods 200.7 and 200.8 do not call for a closed vessel digestion. However, using a closed vessel can prevent volatilization loss of selenium during digestion [3]. A collision/reaction cell (CRC) or dynamic reaction cell (DRC) is often used to reduce FGD water matrix interferences using Methods 200.8 or 1638.

There are various methods available for selenium speciation analysis:

- Ion chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS)
- Hydride generation atomic absorption spectrometry (HG-AAS)
- Gas chromatography inductively coupled plasma mass spectrometry (GC-ICP-MS)
- Capillary electrophoresis inductively coupled plasma mass spectrometry (CE-ICP-MS)
- Liquid chromatography electrospray ionization mass spectrometry (LC-ES-MS)

Methods that rely on chemical conversion do not adequately characterize the composition of a complex matrix such as FGD wastewater. In the ‘90s, the most commonly used technique for measuring selenite and selenate determination was HG-AAS (Cutter method). In this approach, selenite is determined directly, while selenate is determined by subtraction after conversion to selenite. However, other selenium species may be present in FGD water such as selenocyanide, methylseleninic acid, selenosulfate, selenomethionine, and other unknown selenium compounds. These other selenium species can be quantified using IC-ICP-MS. This method uses a chromatographic column to separate the various species before directly measuring the quantity of each selenium-containing chemical by ICP-MS. The ICP-MS may be equipped with DRC to overcome interferences from other substances in the FGD water. IC-ICP-MS was employed by EPRI in developing its database on Se speciation of FGD waters.

Variation in Selenium Among and Within Power Plants

The main source of variation in selenium levels discharged to the environment is the total mass that partitions to the precipitators, and the conversion efficiency of vapor selenium to liquid selenium in the FGD absorber vessel. Selenium levels in coal used in coal-fired power plants vary widely and range from 0.5 to 10 parts per million (mg/L) with a median typically in the 1 to 3 mg/L range [4].

As described in Section 1, selenium is present in various liquid streams throughout a coal-fired power plant, including fly ash ponds, untreated FGD water, and various other miscellaneous streams such as fly ash leachate, coal pile runoff and bottom ash ponds. Figure 2-1 illustrates a range of dissolved selenium mass load by various streams for various coal-fired power plants. As shown in Figure 2-2, untreated FGD water can significantly increase a site's overall wastewater loading of solids and metals such as selenium.

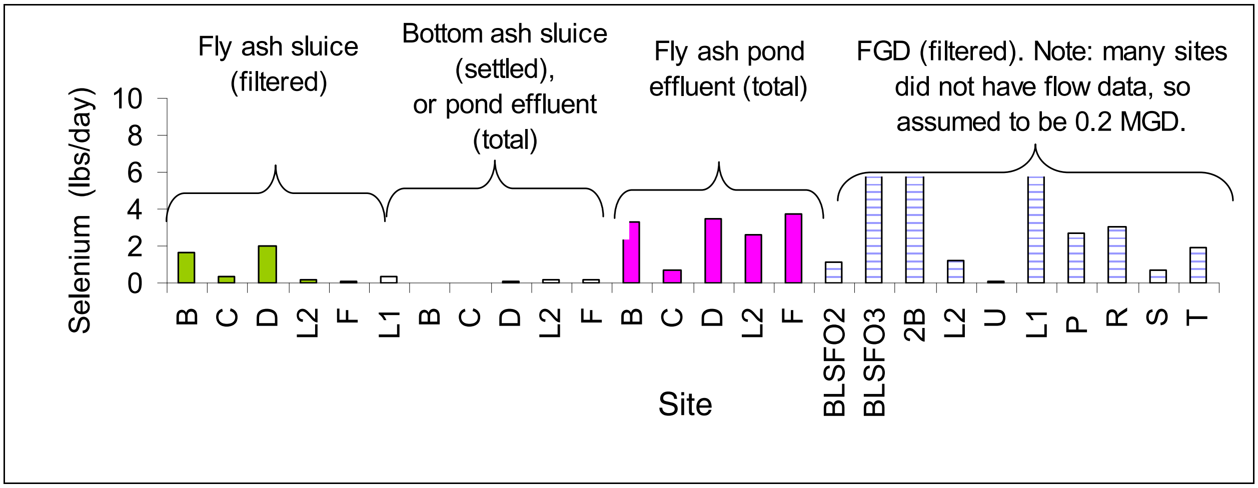

Figure 2-2
Dissolved Selenium Load in Untreated FGD Water Compared to Other Streams for Power Plants with FGD Systems Installed

Source: EPRI, Flue Gas Desulfurization (FGD) Water Blowdown Characterization and Management: 2007 Update*, 2008. [5]*

Untreated FGD water has a highly variable composition and is high in dissolved salts (e.g., total dissolved solids [TDS] typically in excess of 1%) and scale-forming ions (e.g., calcium and magnesium typically in excess of 500 mg/L, sulfate in excess of 3,000 mg/L). Selenium is volatile at the elevated temperatures of flue gasses, and therefore is not efficiently captured by particulate air pollution control devices (electrostatic precipitators or bag houses).

There are various factors that contribute to variation in selenium levels and speciation of selenium in untreated FGD water:

- ***Coal rank and elemental composition***: As described above, selenium levels in coal affect levels present in untreated FGD water.
- ***FGD absorber type and operating conditions:*** Selenium speciation is affected by the oxidation design and operating conditions of the scrubber. This is described further in the sub-section below on "Selenium Speciation in FGD Water."
- ***FGD reagent chemicals:*** Lime, limestone, and other FGD system reagents may contain trace levels of selenium, iron (which may precipitate selenium in the absorber), or various trace metals (e.g., manganese) which are believed to act as a catalyst for oxidation of selenite to

selenate. Selenate does not precipitate with or absorb onto iron hydroxide solids as selenite will [5, 6].

- ***FGD performance additives:*** Some facilities use organic acids such as dibasic acid (DBA) that may affect selenium speciation [5]. This is described further in the subsection below on "Selenium Speciation in FGD Water."
- ***FGD system purge cycle management:*** The chloride and sulfur content of the coal as well as the FGD equipment metallurgy determines the number of times that water can be cycled through an FGD system absorber. The more cycles, the lower the purge flow and concentrations of trace metals in the FGD liquid increase, but the overall mass loading remains constant.

Figure 2-3 shows the partitioning of selenium in untreated FGD water among various power plants, demonstrating that the selenium concentrations and partitioning between particulate and dissolved form varies widely [7]. Dissolved selenium is defined as that which passes through a 0.45 micron filter. Particulate selenium may be removed by solids separation processes. However, dissolved selenium may need to be removed by additional chemical or biological treatment, selection of which would depend on the species of the dissolved selenium.

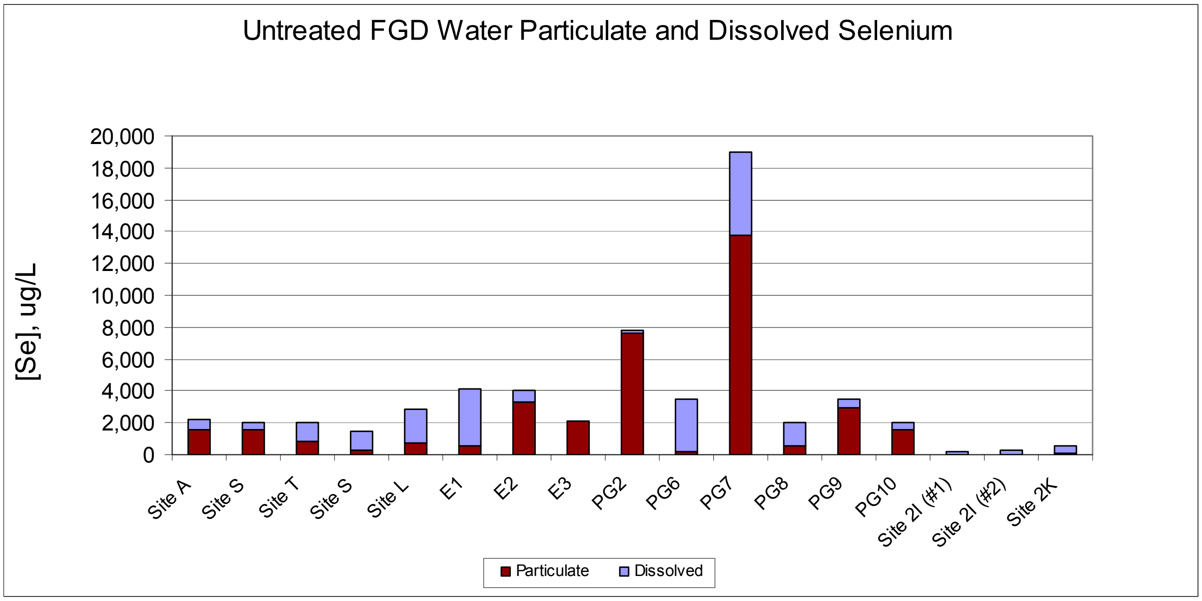

Figure 2-3
Dissolved and Particulate Selenium in Untreated FGD Water

Selenium Speciation in Power Plants

Selenium Species in Fly Ash Sluice Water

Selenium in the coal is volatilized as a gas during combustion, and emitted with the flue gas. Selenium dioxide, like sulfur dioxide, is an acidic oxide. As the flue gas cools, a portion of the selenium condenses and is removed with the fly ash. Since the flue gas contains little oxygen, the resulting selenium is in the selenite (reduced) form. Electrostatic precipitators, commonly used to remove fly ash, operate on a flue gas that is typically in excess of 300 °F. At this temperature, most of the selenium remains in the gas stream. If fly ash is sluiced, then the condensed selenium dissolves into the sluice water and is present as selenite.

Selenium dioxide has a much lower vapor pressure than SO_2 and consequently a much higher melting point (599 °F/315 °C). Above temperatures of 644-662 °F (340-350 °C), SeO_2 sublimes. This gas can be adsorbed onto fly ash as the gas cools and selenium dioxide condenses. Selenium dioxide is also soluble in water, forming selenious (or selenous) acid (H_2SeO_3). Reaction of this acid with base forms SeO_3^{-2}.

Selenium dioxide condenses on the surface of the fly ash particles as the ash and the SeO_2 come into contact at lower flue gas temperatures occurring further from the boiler. Selenium dioxide could also react with the alkaline components of fly ash, so higher alkalinity of coal/fly ash may enhance selenium removal. If these ashes are sluiced with water for transport and removal from the system, some of the selenium would likely partition into the water phase.

Selenite is a soluble species of selenium, but can be absorbed onto or co-precipitate with iron hydroxide if the pH of the water is maintained at pH less than 6.5, preferably between 5 and 6. The co-precipitated selenite can then be removed through settling. Because ash ponds generally receive water containing iron salts and tend to be acidic, the selenium in ash ponds may be removed using a combination of iron co-precipitation, sorption and settling. For ash ponds that receive an alkaline waste, or where there are other reasons for the pH to be alkaline, selenium removal is less effective, resulting in a higher selenium concentration in the effluent.

Selenium Speciation in FGD Water

The design of an FGD absorber affects the speciation of selenium present in untreated FGD water. There are three main types of wet FGD systems: natural, inhibited, and forced oxidation systems. Of the wet FGD systems currently in operation in the United States, approximately half are forced oxidation systems. In addition, the majority of planned FGD systems will also be forced oxidation systems [1]. While the predominant species of selenium in natural or inhibited oxidation systems appear to be selenite and selenosulfate, selenate is often formed in forced oxidation. Figure 2-4 shows a range of selenium species present for 8 sites that employ forced oxidation.

The range of oxidation to selenate in the forced oxidation samples was measured in a previous EPRI study to vary from very low percentages (<5%) of the total dissolved selenium to 100% [6]. Factors that may affect selenate conversion within an absorber may include operating conditions of the scrubber such as liquor residence time under forced oxidation conditions, concentrations of metallic catalysts or adsorbents in the scrubber slurry, scrubber operating pH, and oxidation reduction potential (ORP) of the FGD water [6].

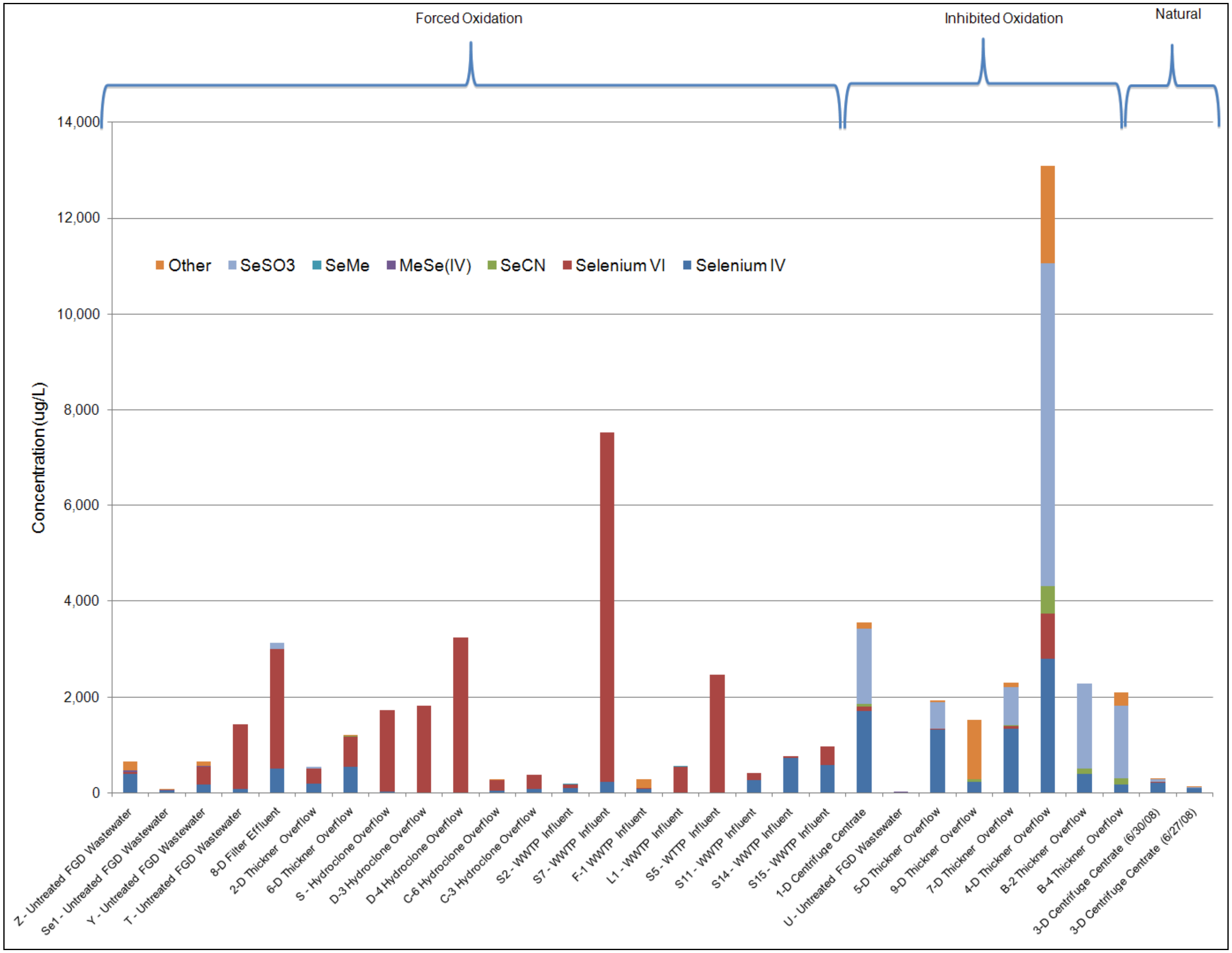

Figure 2-4
Effect of Forced Oxidation on Selenium Speciation in FGD System Liquid

Data from previous EPRI studies also support a general observation that the use of dibasic acid as a performance additive in wet FGD systems may promote the formation of other selenium species that have not been identified to date [5, 6].

Impact of Selenium Speciation on Treatment Technology Selection

The predominant form of selenium in fly ash sluice water or in wet FGD systems with natural or inhibited oxidation is selenite, which either forms particulate with metal (predominantly iron) oxides present in the wastewater and can then be removed through solids separation processes, or can be precipitated and removed using iron co-precipitation at slightly acidic pH. However, selenate which is formed in forced oxidation FGD systems is not removed by iron co-precipitation. As significant concentrations of selenate can be present in the purge water from limestone forced oxidation systems, alternatives to iron co-precipitation, such as anoxic biological treatment, are needed. Site-specific knowledge of the selenium species present and species variability as operating conditions of the FGD absorber change is needed to select the appropriate selenium treatment technology.

FGD Water Characteristics that Affect Selenium Removal

Table 2-1 shows the range of FGD water characteristics, including parameters that may affect removal of selenium and therefore treatment technology selection. The water is supersaturated with calcium sulfate and is hot, mildly acidic and corrosive.

Table 2-1
Typical Composition of FGD Water

Parameter	Typical Range
Flow	30 gpm to 2,300 gpm
Temperature	125ºF to 140 ºF
pH	4.5 to 9 (typically <7)
Total suspended solids	1.4% to 17%
Sulfate	1,500 to 35,000 mg/L
Chloride	1,000 to 28,000 mg/L
Calcium	750 to 4,000 mg/L
Magnesium	1,100 to 4,800 mg/L
Sodium	670 to 4,800 mg/L
Nitrate	10 to 1,000 mg/L
Total Kjeldahl nitrogen	2.5 to 58 mg/L as nitrogen

Note:
gpm = gallons per minute; mg/L = milligrams per liter
Source: Higgins et al., "Flue Gas Desulphurization Wastewater Treatment Primer," 2009 [8].

3

CASE STUDIES OF WATER TREATMENT TECHNOLOGIES FOR SELENIUM REMOVAL AT POWER PLANTS

Overview of Technologies Implemented at FGD Water Treatment Facilities

There are various technologies that have been implemented at FGD water treatment facilities in the United States that remove particulate and/or dissolved selenium. These technologies, which are discussed in detail within this section, fall into three main categories:

- Physical/Chemical Treatment Technologies–Various configurations are possible:
  - Solids settling (tank-based or settling pond; generally removes particulate selenium)
  - Lime addition and iron addition followed by clarification (removes particulate and dissolved selenium predominantly in the form of selenite at pH below 7)
  - Lime addition followed by clarification, then iron co-precipitation (removes particulate and dissolved selenium predominantly in the form of selenite at pH below 7)
- Biological Treatment:
  - Fixed film anaerobic/anoxic reactor-based biological treatment (generally removes various selenium species including selenate, as well as other trace metals)
  - Passive treatment: surface-flow wetlands (can remove various selenium species)
- Zero Liquid Discharge (ZLD) Technologies (eliminates FGD water discharge):
  - Evaporation
  - Complete recycle
  - Conditioning dry fly ash
  - Underground injection

Although there are other technologies available in various stages of development and evaluation that may remove selenium, the focus of this section is on commercially installed selenium removal technologies at U.S. coal power plants. The ten sites presented as case studies in this section were selected because they either employ FGD water treatment systems specifically designed for selenium removal, or employ processes that may remove selenium as part of their solids or metals removal processes.

Some facilities have installed tank-based treatment systems to remove solids and metals prior to discharging the FGD water, while others utilize settling ponds. The EPA estimates that more than 192 plants will be operating wet FGD scrubbers by 2020 and that 158 of these plants will have water discharges [1]. Of the 53 facilities in EPA's survey that currently discharge FGD wastewater [1], 4% utilize anoxic/anaerobic biological treatment and 2% utilize constructed wetlands for selenium removal (Figure 3-1). The other treatment technologies were designed for either solids or metals removal, with some facilities optimized for removal of selenium.

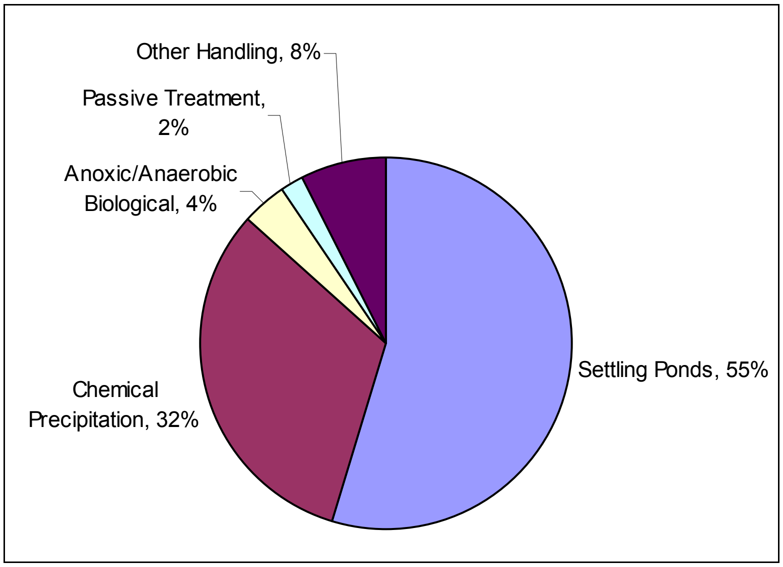

Figure 3-1
Types of FGD Water Treatment Technologies Implemented in the United States

Note: Data obtained from EPA survey of existing FGD water treatment facilities [1].

Of the ten case studies presented in this section (identified here as Sites PG1 through PG10), one physical/chemical treatment plant, two biological treatment plants, and one passive treatment system were specifically designed for selenium removal. The biological treatment plants and passive treatment system were built within the last two years. In addition, six of the case study sites have physical/chemical treatment plants that remove selenium as part of their solids and metals removal targets. The physical/chemical treatment cases are presented within this section because these facilities have either optimized their existing treatment to enhance selenium removal or are evaluating options for removal of selenium from their FGD water.

The case studies presented within this report employ the technologies presented below. Some sites make use of more than one technology, such as Site PG3, which has solids separation followed by biological treatment. Table 3-1 summarizes the plant design, coal type, FGD design and wastewater treatment configuration for each site. The case study wastewater treatment technologies include:

- Physical/chemical treatment:
  - Solids separation (Sites PG3, PG4, PG5)
  - Lime addition followed by clarification, then iron co-precipitation (Sites PG7, PG10)
  - Lime and iron co-precipitation in same reactor followed by clarification (Sites PG1, PG2, PG6, PG8, PG9)
- Anoxic/anaerobic reactor-based biological treatment (Sites PG2, PG3)
- Passive treatment: constructed wetland (Sites PG4, PG5)

Table 3-1
Case Study Power Plant Summary

Site	Coal Type	FGD Design	Wastewater Treatment
PG1	Eastern bituminous and petroleum coke	Limestone forced oxidation	Lime addition/ferrous chloride addition/clarification/ filtration
PG2	Eastern bituminous	Limestone forced oxidation	Lime addition/ferric chloride addition/clarification/ filtration/anaerobic biological treatment
PG3	Eastern bituminous	Limestone forced oxidation	Settling pond/anaerobic biological treatment
PG4	Eastern bituminous	Limestone forced oxidation	Clarification/equalization and 1:1 service water addition to reduce chlorides/constructed wetland
PG5	Eastern bituminous	Limestone forced oxidation	Clarification/ equalization with 3:1 service water addition to reduce chlorides/constructed wetland
PG6	Eastern bituminous	Limestone forced oxidation	Lime addition/ ferric chloride addition/clarification/ filtration
PG7	Sub-bituminous	Limestone forced oxidation	Lime addition/primary clarification/ ferric chloride addition/organosulfide addition/secondary clarification
PG8	Eastern bituminous	Limestone forced oxidation	Lime addition/ ferric chloride and sodium sulfide addition/ clarification/ aerobic biological treatment/ filtration
PG9	Eastern bituminous	Limestone forced oxidation	Two stages of lime addition/ferric chloride addition/ clarification; aerobic biological treatment/ filtration
PG10	Eastern bituminous	Limestone forced oxidation	Lime addition/ primary clarification/ ferric chloride addition/ secondary clarification

The treatment technologies in each case study were evaluated in the following areas to assess factors associated with implementation, effectiveness, and operability of each technology:

- Treatment effectiveness based on removal achieved from plants for which data are available
- Extent and significance of any confounding factors (e.g., sulfate, nitrate, other metals, etc.)
- Main advantages and disadvantages
- Space required for treatment system
- Capital and operating costs, if available

Utilities interested in implementing selenium removal technologies can use this section to assist in the evaluation of various commercially available technologies implemented at other power plants.

Physical/Chemical Treatment Technologies for Selenium Removal

Solids Separation

Solids separation processes within power plants consist of tank-based separation or settling ponds. Typically, tank-based separation processes consist of separation within a clarifier with addition of polymers for separation. These processes remove selenium in the particulate form and do not remove dissolved selenium.

As shown in Figure 3-1, some facilities have installed treatment systems to remove solids and metals prior to discharging the FGD water, while others send the untreated water to an on-site settling pond or ponds to settle out the solids. FGD settling ponds are designed to remove suspended solids to a concentration generally below 30 milligrams per liter (mg/L) and selenium is precipitated along with the suspended solids, similar to the function of a fly ash pond. Treatment within an FGD settling pond also may include pH adjustment, using either acid or caustic to raise or lower the pH of the effluent as needed. The effluent of an FGD settling pond may be mixed with other water streams, or untreated FGD water may be co-mingled with ash ponds.

Primary and secondary hydrocyclones also provide solids removal upstream of FGD wastewater treatment systems, and improve particulate selenium removal in FGD water prior to discharge to the plant. One facility noted that addition of a secondary hydrocyclone resulted in increased selenium removal [9].

Sites PG3, PG4, and PG5 use solids separation as a first step in their treatment processes. The effectiveness of selenium removal across solids separation is presented below for these three cases.

Solids Separation: Case Study Site PG3

Site PG3 burns eastern bituminous coal and operates a selective catalytic reduction (SCR), ESP, and wet limestone forced oxidation FGD system, and operates both primary and secondary hydrocyclones to dewater the gypsum produced in their scrubbers. The FGD water flows from the secondary hydrocyclones to a settling pond. Figure 3-2 contains a process flow diagram of the Site PG3 FGD water treatment system. The FGD water treatment system consists of the following processes:

- Physical treatment
  - Settling pond (lined, 16-acre)
- Biological treatment
  - Nutrient addition
  - First stage biological reaction
  - Nutrient addition
  - Second stage biological reaction
  - Flush pond

The purpose of the settling pond is to remove TSS and lower the temperature of the water to below 105 °F. The biological treatment process is discussed later in this section.

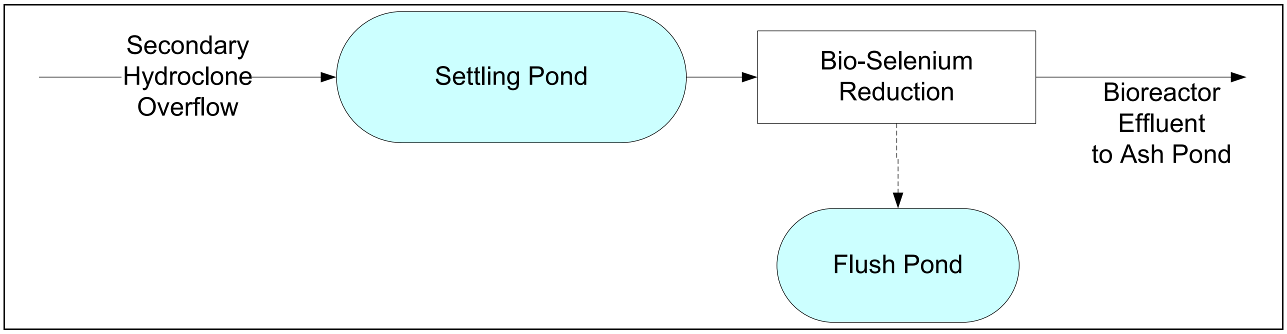

Figure 3-2
Site PG3 FGD Water Treatment Plant Process Flow Diagram

Solids separation across the settling pond resulted in an average 38% removal of total selenium across the pond. Figure 3-3 shows total selenium at the influent and effluent of the pond over time. Levels fluctuate over time, due to both varying levels of total selenium as well as varying levels of particulate versus dissolved selenium over time. It should be noted, however, that the total selenium levels after in-pond settling are still considerably higher than levels that would be permitted at a regulated outfall. Particulate and dissolved selenium data for effluent of the settling pond (Figure 3-4) show that selenium is almost 100% in the dissolved form, indicating that the pond effectively removes the particulate selenium. The data regarding particulate and dissolved effluent concentrations and the removal efficiency of 38% of total selenium indicates that the bulk of the selenium in the untreated FGD entering the settling pond is in the dissolved form that will not settle out in the pond. During an interview with staff at Site PG3, it was noted that selenate is generally the predominant species of selenium present in the dissolved form within FGD water at the plant.

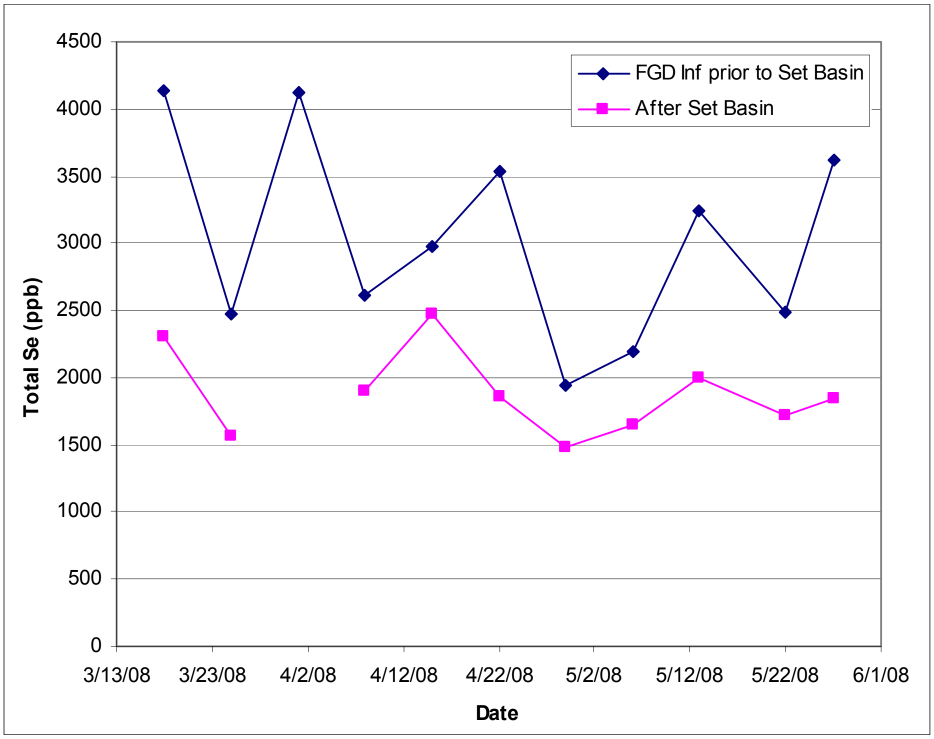

Figure 3-3
Site PG3 Total Selenium Before and After Solids Settling

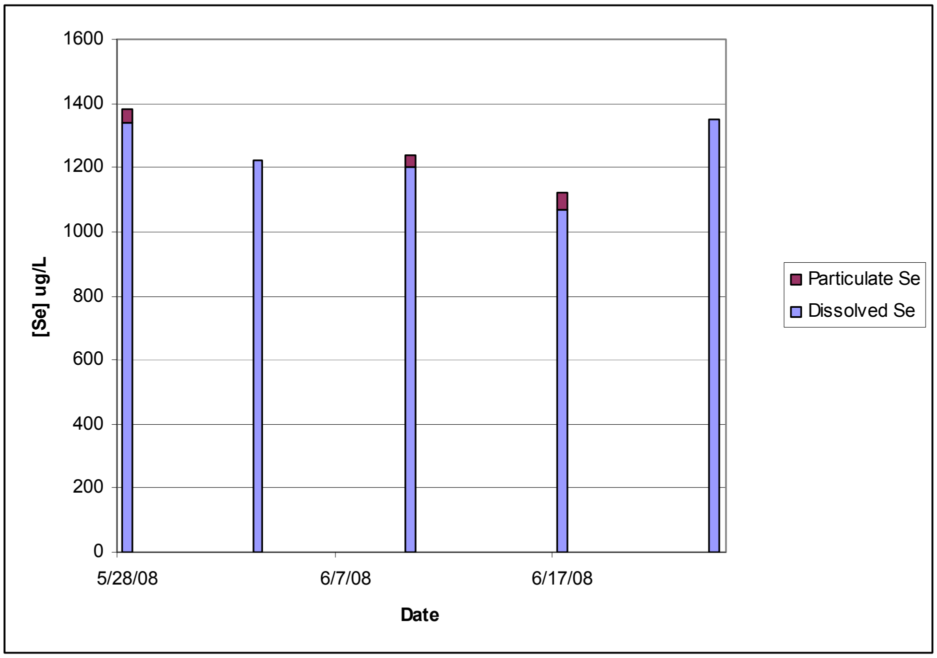

Figure 3-4
Site PG3 Particulate and Dissolved Selenium After Solids Separation

Solids Separation: Case Study Site PG4

Site PG4 burns eastern bituminous coal and operates a wet limestone forced oxidation FGD system. Primary and secondary hydrocyclones are used for solids separation. The chloride purge stream from the scrubber is blown down approximately four of every six hours. The overflow from the secondary hydrocyclones is sent to a holding tank and then sent to the FGD water treatment plant. Figure 3-5 shows a process flow diagram of the Site PG4 FGD water treatment system. The FGD water treatment system consists of the following processes:

- Physical treatment
  - Equalization
  - Polymer flocculation and clarification
- Constructed wetlands
  - Equalization/cooling
  - Wetlands
- Solids handling

The FGD water flows continuously from the equalization tank to the clarifier. A cationic polymer is used to promote floc formation and solids settling. The solids from the clarifier are sent to a sludge holding tank and then dewatered using a filter press. The constructed wetlands system is discussed in a later section.

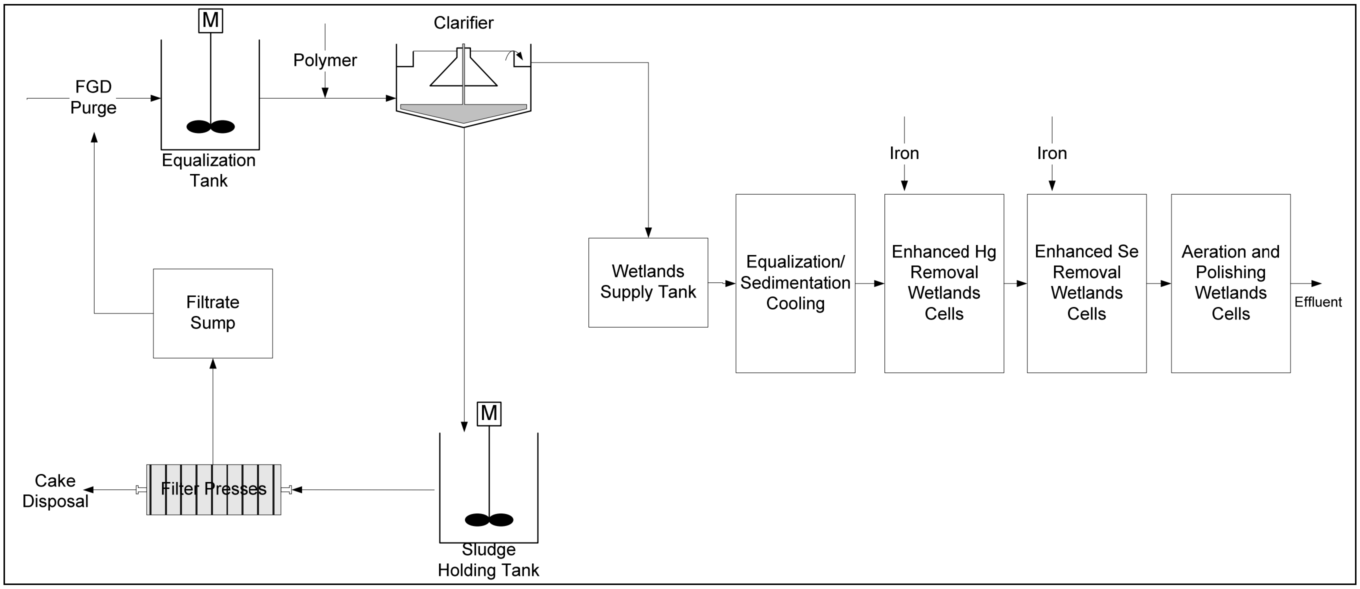

Figure 3-5
Site PG4 FGD Water Treatment Plant Process Flow Diagram

Total selenium before and after clarification for Site PG4 is shown in Figure 3-6. The data indicate that an average of 85% of the total selenium is removed in the clarifier. This suggests that selenium is largely in the particulate form at Site PG4, a contrast to Site PG3 where selenium was largely in the dissolved form. Selenium speciation and dissolved selenium data are not available from this plant.

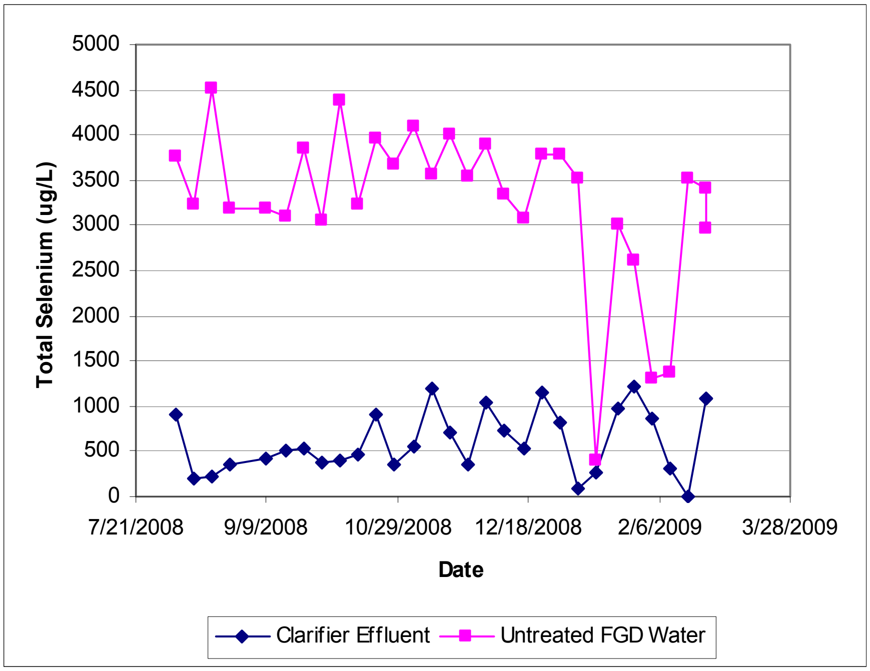

Figure 3-6
Site PG4 Total Selenium Before and After Solids Separation

Solids Separation: Case Study Site PG5

Site PG5 burns eastern bituminous coal and operates a wet limestone forced oxidation FGD system. Figure 3-7 shows a process flow diagram of the FGD water treatment system. The FGD water treatment system consists of the following processes:

- Physical treatment
  - Polymer flocculation and clarification
  - Equalization
- Constructed wetlands
- Solids handling

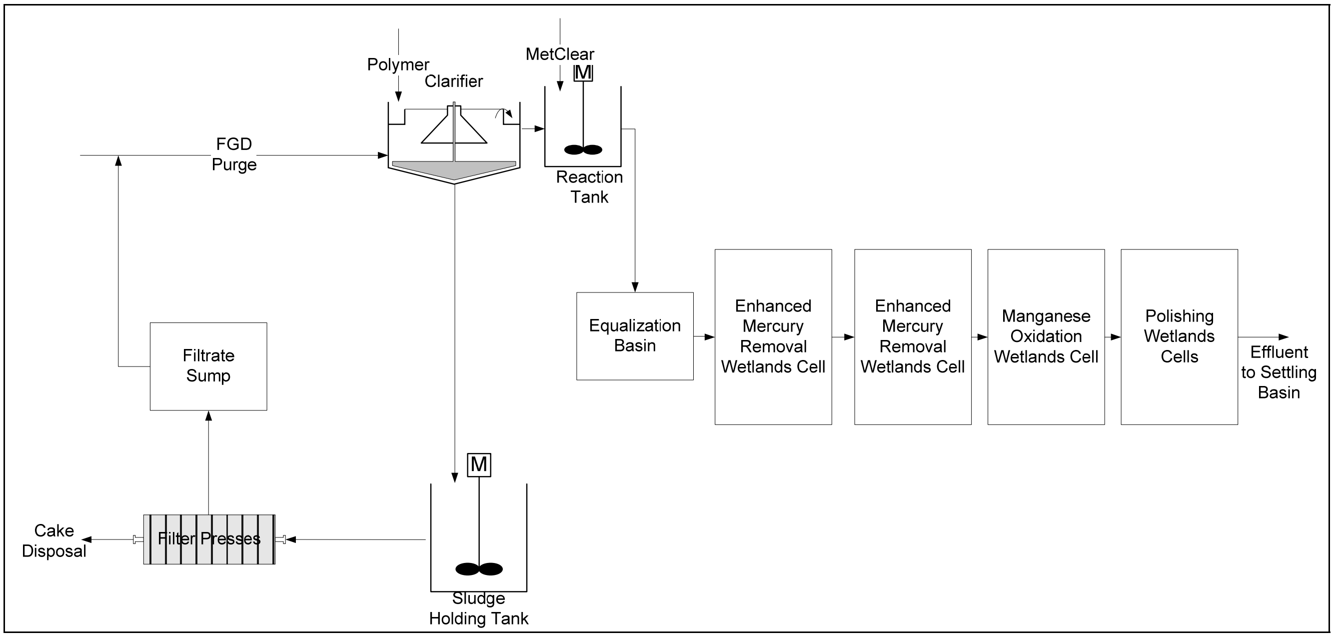

Figure 3-7
Site PG5 FGD Water Treatment Plant Process Flow Diagram

The FGD water flows into a clarifier where polymer is added to promote floc formation and settling, followed by a reaction tank where MetClear™ is used to promote metals removal in the equalization basin. The solids from the clarifier are sent to a sludge holding tank and then dewatered using a filter press.

Total selenium in untreated FGD water before and after clarification is shown in Figure 3-8. Based on the data set provided from 2007 through June 2009, there is a 17% average removal of total selenium by clarification. This suggests that there is relatively little particulate selenium within the PG5 FGD water and most of the selenium is in the dissolved or fine particulate form.

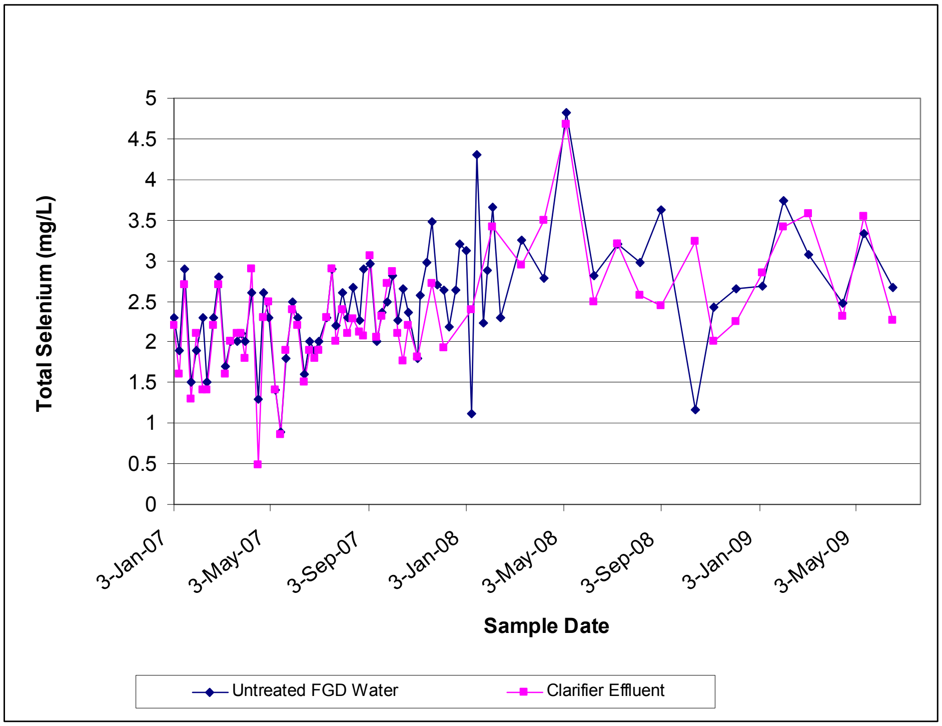

Figure 3-8
Site PG5 Total Selenium Before and After Solids Separation

Table 3-2 shows the median for speciation of untreated FGD water at Site PG5. The selenium present in the FGD water is almost 100% dissolved selenium as selenate. Selenate is not removed well using physical/chemical treatment methods, as evidenced by the little or no removal seen (Figure 3-8).

Table 3-2
Selenium Speciation for Untreated FGD Water at Site PG5

Form of Selenium	Concentration (µg/L)
Total Selenium	2,720
Dissolved Selenium	2,500
Selenate	2,460
Selenite	7

Chemical Treatment: Lime Addition and Iron Co-Precipitation in Same Reactor Followed by Clarification

Case Study Site PG1

Site PG1 burns a mixture of petroleum coke and eastern bituminous coal in each of its generating units and operates a wet limestone forced oxidation FGD system. The plant periodically adds DBA to the FGD system as necessary to achieve desired SO_2 removal efficiencies. Figure 3-9 includes a process flow diagram for the FGD water treatment plant. The FGD water treatment plant was designed for selenium removal and the processes employed are as follows:

- Equalization
- Lime addition/pH adjustment
- Chemical precipitation—ferrous chloride addition
- Clarification
- Multi-media filtration
- Solids handling

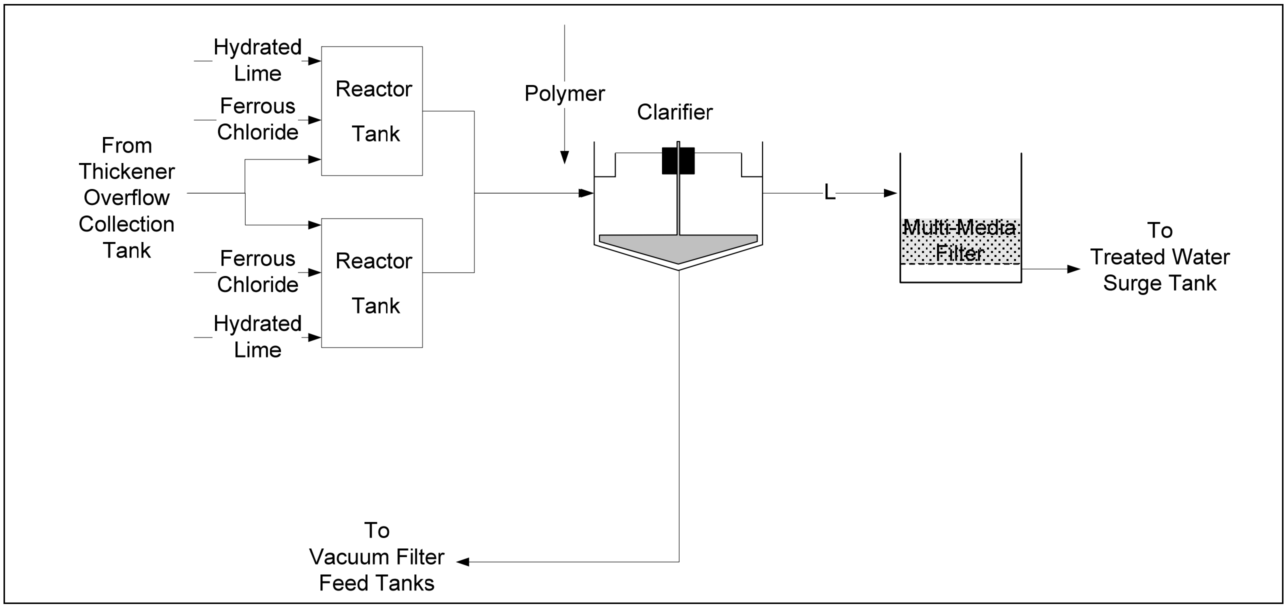

Figure 3-9
Site PG1 FGD Water Treatment Process Flow Diagram

The overflow from the thickeners is transferred to a collection tank where a percentage of the water is transferred to the FGD water treatment plant. The FGD water treatment plant operates at a flow rate of 300 gpm. The reactors operate in parallel as a batch process: one reactor is filled and operating, while the other finishes operation and drains. The pH is adjusted by lime addition to a pH of approximately 8.0. Once the pH is adjusted, the agitator speed is reduced in the reactor and ferrous chloride is added to enhance selenium removal. Site PG1 adds ferrous iron to enhance selenate treatment, as compared with most FGDs that add ferric iron. Polymer is added to the effluent of the reactors and the effluent from the reactors flows to a clarifier for solids settling. The clarifier residence time is approximately 3 days. The overflow from the clarifier flows to a multimedia filter containing gravel and sand. The sand filter effluent mixes with other process water streams in a surge tank prior to being discharged.

Table 3-3 demonstrates the removal efficiency across the treatment system for Site PG1. This is based on median concentrations from three sample events. Site PG1 was designed for selenium removal and adds ferrous chloride as the iron source. Site PG1 also processes the FGD water in batches instead of continuous treatment. Staff at site PG1 observed that 90% selenium removal is achieved with their batch treatment system with ferrous chloride as long as the chloride levels in the FGD water is below 15,000 mg/L. If the chloride level is above 18,000 mg/L, selenium removal drops to around 60%. The variation in removal may also be linked to the variation in predominant selenium species observed at Site PG1; both selenite and selenate have been observed as the predominant selenium species at times. PG1 plant staff believe that seleno-nitrogen and selenocyanate species are present as well.

Table 3-3
Site PG1 Selenium Removal

Treatment	Total Influent Selenium (µg/L)	Total Mid-point Selenium (µg/L)	Total Effluent Selenium (µg/L)	Removal Efficiency
Lime addition/pH adjustment/ chemical precipitation—ferrous chloride addition/ clarification/ multi-media filtration	337	NA	55	84%

Note:
NA = not available

Case Study Site PG2

Site PG2 employs physical/chemical FGD water treatment prior to anaerobic biological reduction treatment.

Site PG2 burns eastern bituminous coal and operates a wet limestone forced oxidation FGD system, SCR, and ESPs. The units blow down intermittently to maintain a chloride concentration in the scrubbers between 8,000 and 10,000 mg/L. The limestone slurry is made from limestone pulverized in onsite ball mills. Primary and secondary hydrocyclones are used for solids separation.

The flow rate of the FGD wastewater treatment plant is 600 gpm and is designed to receive intermittent flows. The FGD water treatment plant is laid out on approximately 5 acres, although 2.5 of those acres are dedicated for truck access and turnarounds to the facility. Figure 3-10 presents a process flow diagram for the system. The FGD water treatment system consists of the following processes:

- Physical/chemical treatment
  - Equalization
  - Lime addition
  - Organosulfide addition (the system is designed for organosulfide addition to Reaction Tank #2 for enhanced mercury removal; however, at present, organosulfide is not added as mercury removal can be achieved with solids removal and polishing by the bioreactor)
  - Ferric chloride addition
  - Polymer addition for improved flocculation
  - Clarification
  - Filtration
- Biological treatment
  - Cooling

  - Nutrient addition
  - First stage biological reaction
  - Nutrient addition
  - Second stage biological reaction
- Solids handling

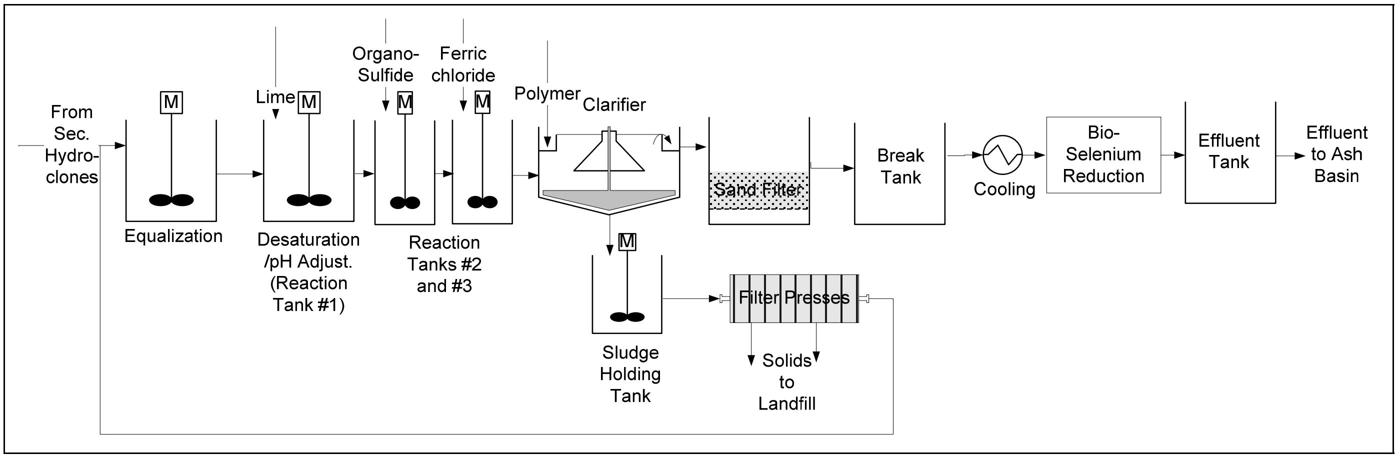

Figure 3-10
Site PG2 FGD Water Treatment Plant Process Flow Diagram

Note: Organosulfide can be added to Reaction Tank #2 as shown in the schematic to enhance mercury removal, although this is not done at present because mercury removal can be achieved with solids removal and polishing by the bioreactor.

The secondary hydrocyclone overflow enters the equalization tank and flows to Reaction Tank #1. Lime slurry is added to this tank to raise the pH of the water to between 8.5 and 9.2. As noted above, organosulfide was designed to be added to a second reaction tank (Reaction Tank #2) to enhance mercury removal, but is not currently added. Ferric chloride is added in Reaction Tank #3, which serves to generate ferric hydroxide which aids in the precipitation of a number of metals of interest. Polymer is added for floc formation and solids are settled in clarifiers. The overflow from the clarifiers flows to a bank of sand filters. Prior to reaching the filters, hydrochloric acid is added to neutralize the pH [1].

Sludge from the clarifier is transferred to a Sludge Holding Tank. When there is sufficient volume in the tank the sludge is processed through one of four filter presses. The solids concentration is the sludge typically ranges from 15 to 20%.

The treatment efficiency across the physical chemical treatment system is expressed in Figure 3-11. An average 97% of the total selenium is removed through the physical/chemical treatment process. Figure 3-12 shows the dissolved selenium before and after physical treatment, which shows that in addition some dissolved selenium likely present as selenite is removed in the physical/chemical treatment plant. Selenium speciation results indicate that there is generally slightly more selenate than selenite in the dissolved fraction of the untreated FGD water. The selenate present in the FGD water was not removed by physical/chemical treatment.

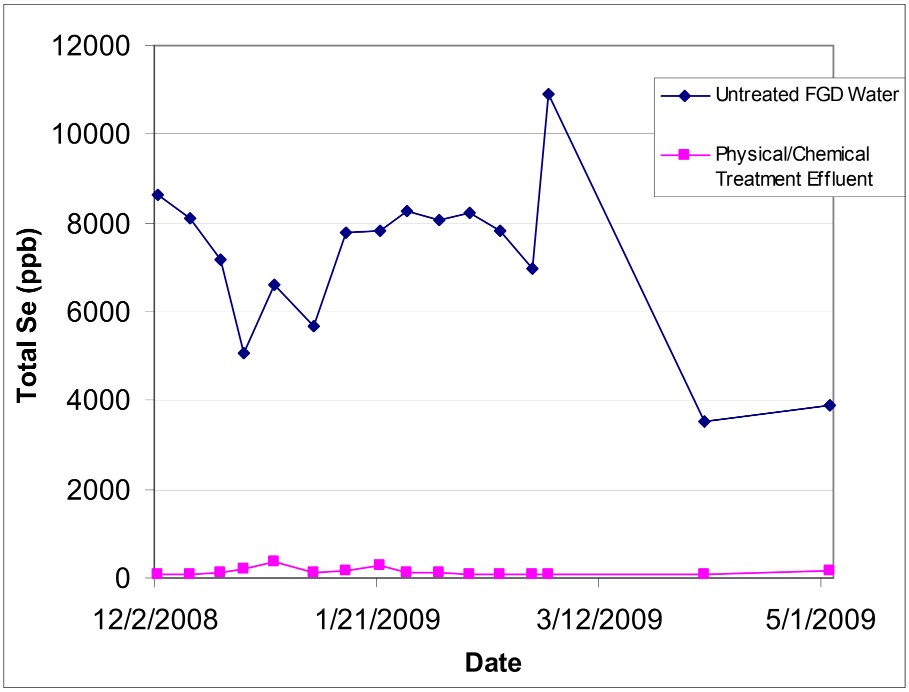

Figure 3-11
Site PG2 Total Selenium Removal by Physical/Chemical Treatment

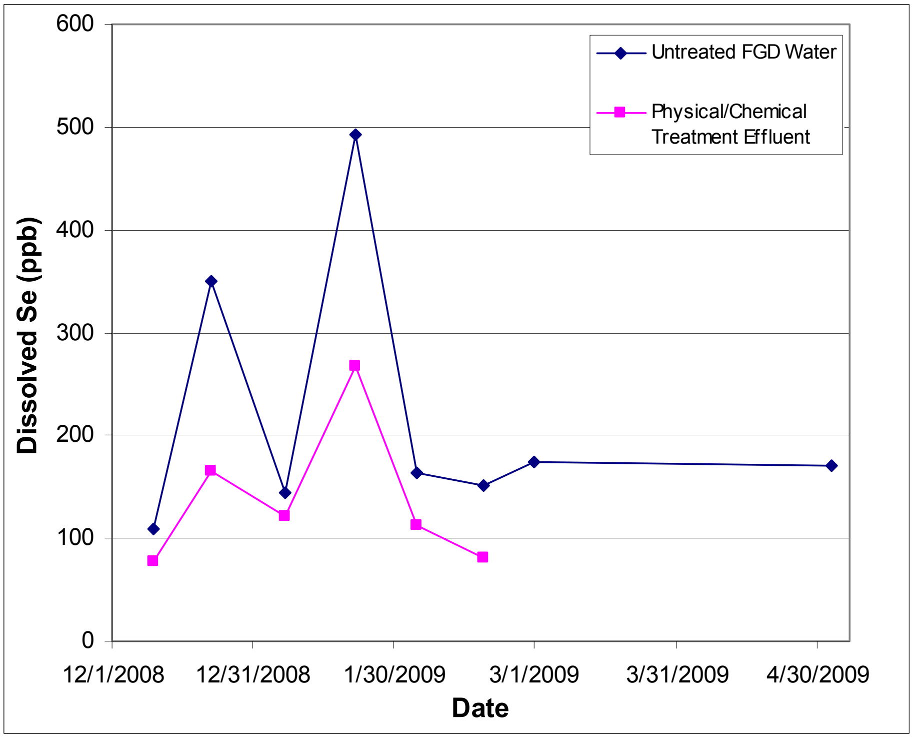

Figure 3-12
Site PG2 Dissolved Selenium Removal by Physical/Chemical Treatment

Case Study Site PG6

Site PG6 burns eastern bituminous coal. Secondary hydrocyclone overflow discharges to the FGD water treatment plant continuously at a flow rate of approximately 200 to 225 gpm. The residence time of the treatment plant is 24 to 32 hours. The chlorides concentration of the FGD influent is approximately 15,000 to 30,000 mg/L and contains approximately 1 to 3% solids. Figure 3-13 presents a process flow diagram of the Site PG6 FGD water treatment system. The FGD water treatment system contains the following operations:

- Equalization
- Lime and ferric chloride addition
- Polymer flocculation
- Clarification
- Final pH adjustment (hydrochloric acid addition)
- Filtration
- Solids handling

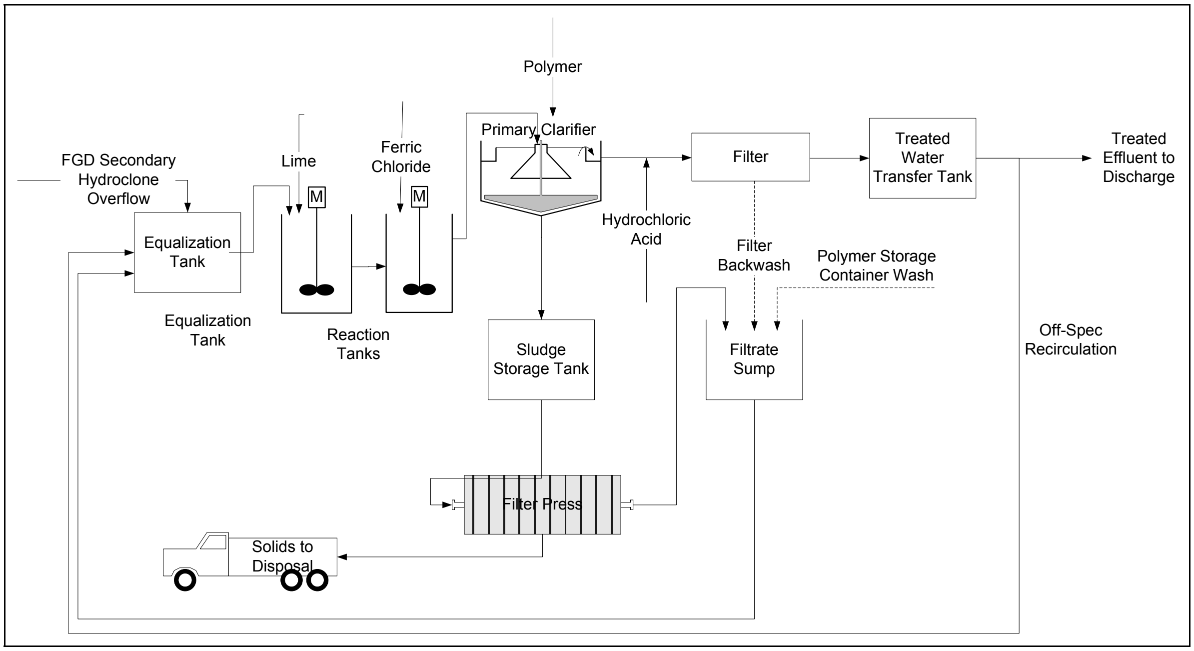

Figure 3-13
Site PG6 FGD Water Treatment Plant Process Flow Diagram

The FGD water influent has a pH of approximately 6.0. At Reaction Tank 1, the pH is raised to 9.0 using hydrated lime. From Reaction Tank 1, the FGD water flows to Reaction Tank 2, where ferric chloride (55 to 65 gallons per day) is added to co-precipitate metals. The overflow from Reaction Tank 2 is transferred to Reaction Tank 3, which provides an environment to build floc to enhance metals precipitation. From Reaction Tank 3, the wastewater is transferred to the clarifier. A flocculating polymer is added to the clarifier feed pump discharge.

The overflow from the clarifiers flows to sand gravity filters. As the wastewater is pumped to the gravity filters, the plant adds hydrochloric acid to the wastewater to ensure the pH is between 6.0 and 9.0.

From the gravity filters, the wastewater is transferred to the treated water transfer tank and discharged from the plant. The plant commingles the effluent from the FGD water treatment system with the plant's once-through cooling water prior to discharge.

The underflow from the clarifiers is transferred to the sludge storage tank and from there is pumped through one of two filter presses.

Total selenium removal efficiency was characterized across the system based on a one-time sample event (Table 3-4). The data likely do not represent the average or the potential range of removal efficiency of selenium across the system. Of the 3,470 µg/L total selenium present within the influent sample, 3,280 µg/L was dissolved selenium. The total selenium concentration measured in the effluent of the treatment system was 2,500 µg/L, of which 2,460 µg/L was selenate.

Table 3-4
Site PG6 Selenium Removal

Treatment	Total Influent Selenium (µg/L)	Total Mid-point Selenium (µg/L)	Total Effluent Selenium (µg/L)	Removal Efficiency
Lime addition/ferric chloride addition/ clarification/ filtration	3,470	NA	2,500	28%

Note: NA – not available

Case Study Site PG8

Site PG8 burns eastern bituminous coal. Secondary hydrocyclone overflow enters the FGD water treatment plant on an intermittent basis with a chlorides concentration of approximately 20,000 mg/L. Site PG8 uses DBA at the scrubber for improved sulfur dioxide removal. Figure 3-14 presents a process flow diagram of the FGD water treatment system. The FGD water treatment system contains the following operations:

- Surge tank
- pH adjustment (lime addition)
- Ferric chloride/sodium sulfide addition
- Clarification
- Final pH adjustment (hydrochloric acid)
- Aerobic sequential batch reactor for organics removal
- Filtration
- Solids handling

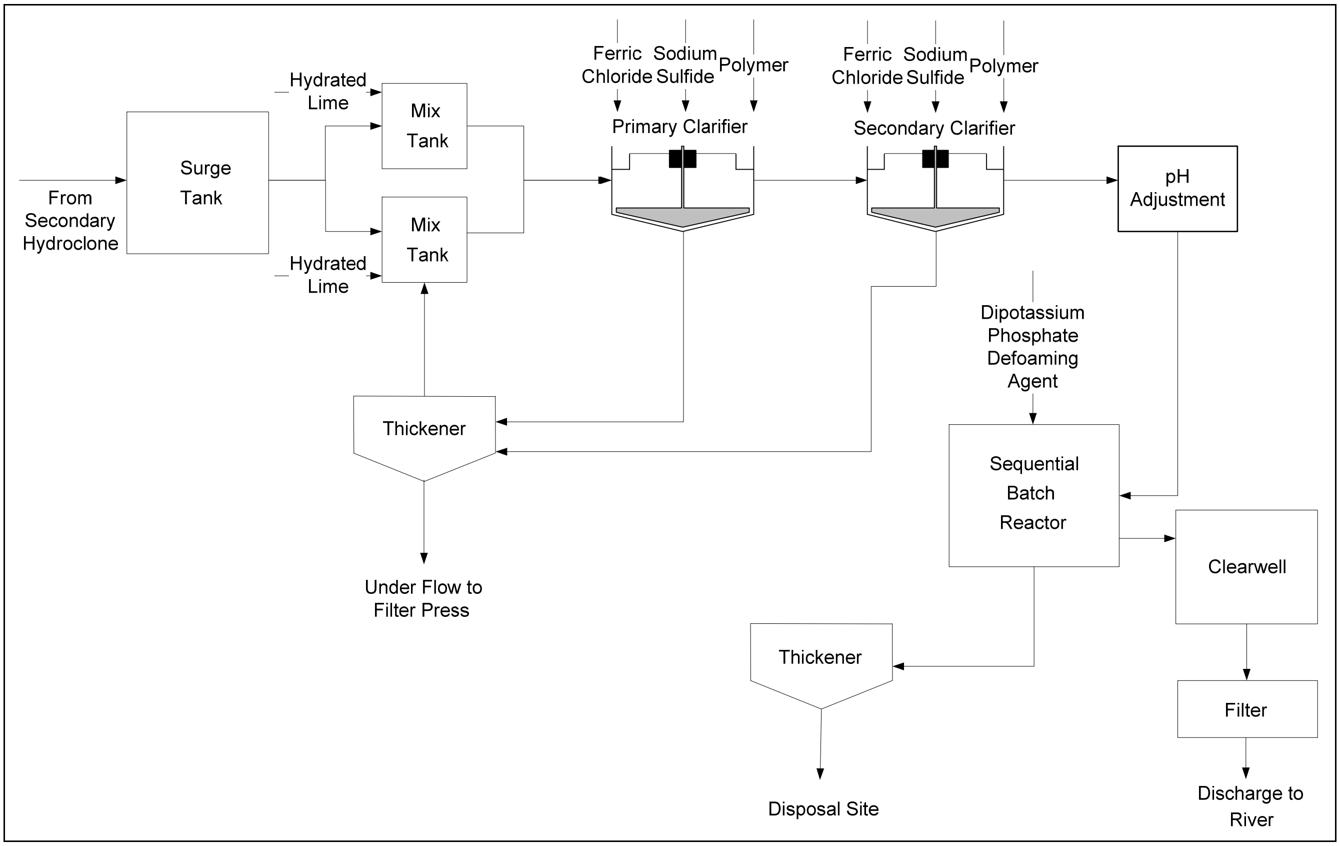

Figure 3-14
Site PG8 FGD Water Treatment Plant Process Flow Diagram

The flow rate from the surge tank is 150 to 175 gpm. From the surge tank the pH is raised to 8.6 using hydrated lime addition. From the pH adjustment tank, the FGD water flows to both primary and secondary clarifiers, where ferric chloride, sodium sulfide and polymer are added at each clarifier. The secondary clarifier overflow is routed to a pH adjustment tank where the pH is adjusted from 8.6 to 7.8. From the pH adjustment sump, the FGD water flows to two sequencing batch reactors (SBRs) for aerobic biological treatment to remove organics present in the water from DBA addition. Dipotassium phosphate is added as a nutrient for bacteria that break down DBA. The treated FGD water flows from the SBRs to a clearwell and through pressure filters before being discharged. The total residence time of the system is approximately 2.5 days [1].

The solids from the primary and secondary clarifiers are sent to a thickener followed by a filter press for dewatering of solids. Solids from the SBRs are dewatered using a thickener and sent to the ash disposal site.

Personnel at Site PG8 noted that there has been an improvement in selenium removal performance in 2008/2009 which correlates in part with a switch in coal supply. The plant uses approximately 15 to 20 sources of coal and selenium levels within the coal may affect the levels seen at the influent of the FGD water treatment plant. The plant staff noted that they have an average of 50% selenium removal efficiency. Table 3-5 includes results from a one-time sampling event and shows efficiency of removal of total and dissolved selenium. More than half the selenium was in the dissolved form and approximately 55% was removed by physical/chemical treatment. Selenium speciation data was not available for this sample event.

Table 3-5
Site PG8 Selenium Removal

Form of Selenium	Influent Selenium (µg/L)	Selenium After Physical/Chemical Treatment (µg/L)	Removal Efficiency
Total Selenium	2,025	785	65%
Dissolved Selenium	1,500	645	55%

Case Study Site PG9

Site PG9 burns eastern bituminous coal units and operates a limestone forced oxidation FGD system. The plant previously added DBA to enhance sulfur dioxide removal efficiency but switched to formic acid which resulted in improved selenium removal efficiency. The slurry is purged to maintain a chlorides concentration of approximately 15,000 to 20,000 mg/L.

Addition of secondary hydrocyclones reduced the solids content of FGD purge water and improved selenium removal. The FGD water treatment plant is operated on a continual basis but receives secondary hydrocyclone overflow intermittently, typically 12 to 18 hours per day. The hydraulic retention time (HRT) of the FGD wastewater treatment system is approximately 3.5 days. Figure 3-15 is a process flow diagram for the system. The processes employed in the FGD water treatment plant are as follows:

- Equalization
- Lime, ferric chloride, cationic polymer addition, and aeration
- Anionic polymer addition
- Clarification
- Lime, ferric chloride and cationic polymer addition and aeration
- Clarification
- Nutrient/phosphoric acid/substrate addition
- Cooling
- Aerobic biological treatment
- Sand filtration
- Solids handling

With the secondary hydrocyclones operating, the wastewater entering the FGD water treatment system contains less than one percent solids. After equalization, water enters the first stage chemical precipitation, where lime is added to adjust the pH to 8.1. Ferric chloride, air, and cationic polymer are added to enhance precipitation of metals. After first-stage clarification, the FGD water enters a second-stage chemical precipitation/clarification step, before nutrients and corn syrup are added in a pH adjustment tank. The pH of the FGD water entering the biological system is generally 7.5 to 8.0. The biological treatment system was designed to remove biochemical oxygen demand (BOD) from the FGD water by addition of formic acid at the scrubber. Afterwards, the FGD water is transferred to sand filters. Solids from the biological reactor and the clarifiers are dewatered in a thickener and vacuum filter. The filtrate from the solids dewatering is sent through the start of the treatment process and solids are landfilled [1].

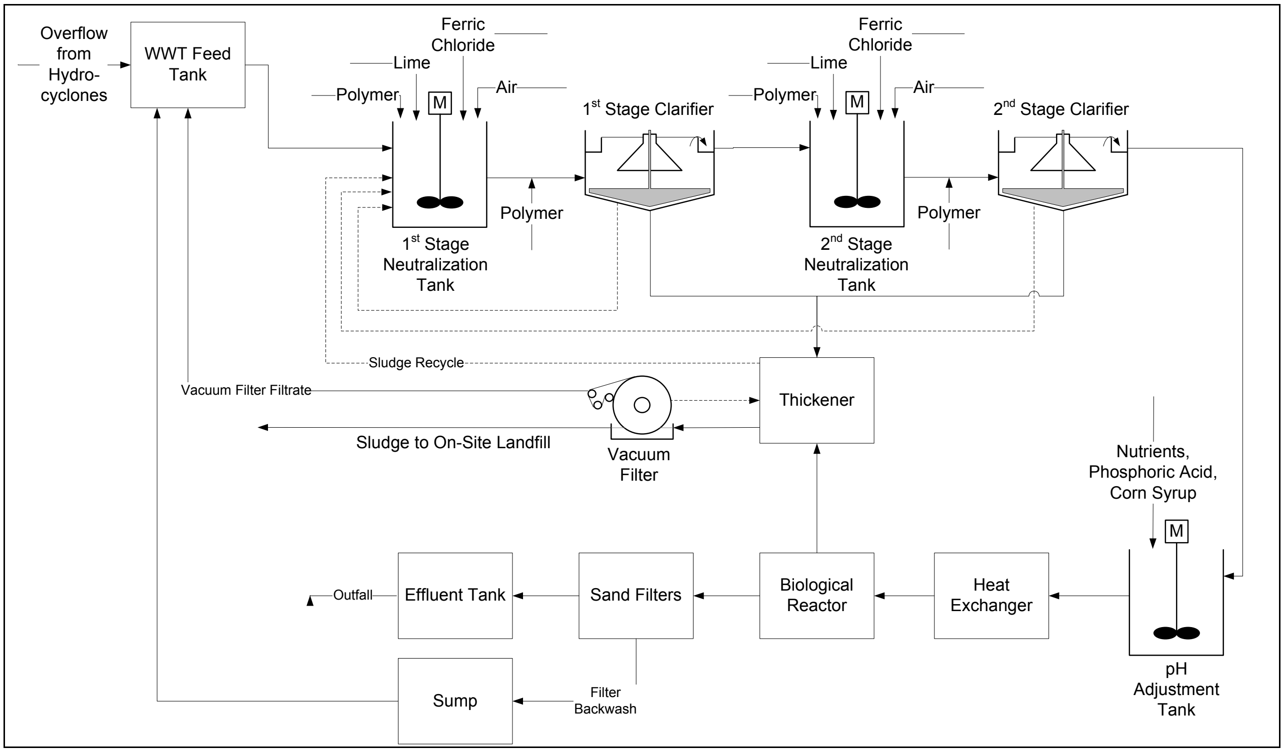

Figure 3-15
Site PG9 FGD Water Treatment Plant Process Flow Diagram

Table 3-6 includes results from a one-time sampling event at Site PG9 and shows efficiency of removal of total and dissolved selenium. Most of the selenium is in the particulate form and effectively removed through treatment.

Table 3-6
Site PG9 Selenium Removal

Form of Selenium	Influent Selenium (μg/L)	Selenium After Physical/Chemical Treatment (μg/L)	Removal Efficiency
Total Selenium	3,530	238	93%
Dissolved Selenium	584	241	58%

Chemical Treatment: Lime Addition Followed by Clarification then Iron Co-Precipitation

Case Study Site PG7

Site PG7 is a sub-bituminous coal-fired power plant with an SCR and a limestone forced oxidation FGD system. Figure 3-16 shows a process flow diagram of the FGD purge water treatment plant. The FGD water treatment plant consists of the following processes:

- Equalization tank
- Desaturation/pH adjustment (lime addition)
- Polymer addition
- Primary clarification
- pH adjustment (hydrochloric acid)
- Organosulfide addition
- Ferric chloride addition
- Polymer addition
- Secondary clarification
- Solids handling

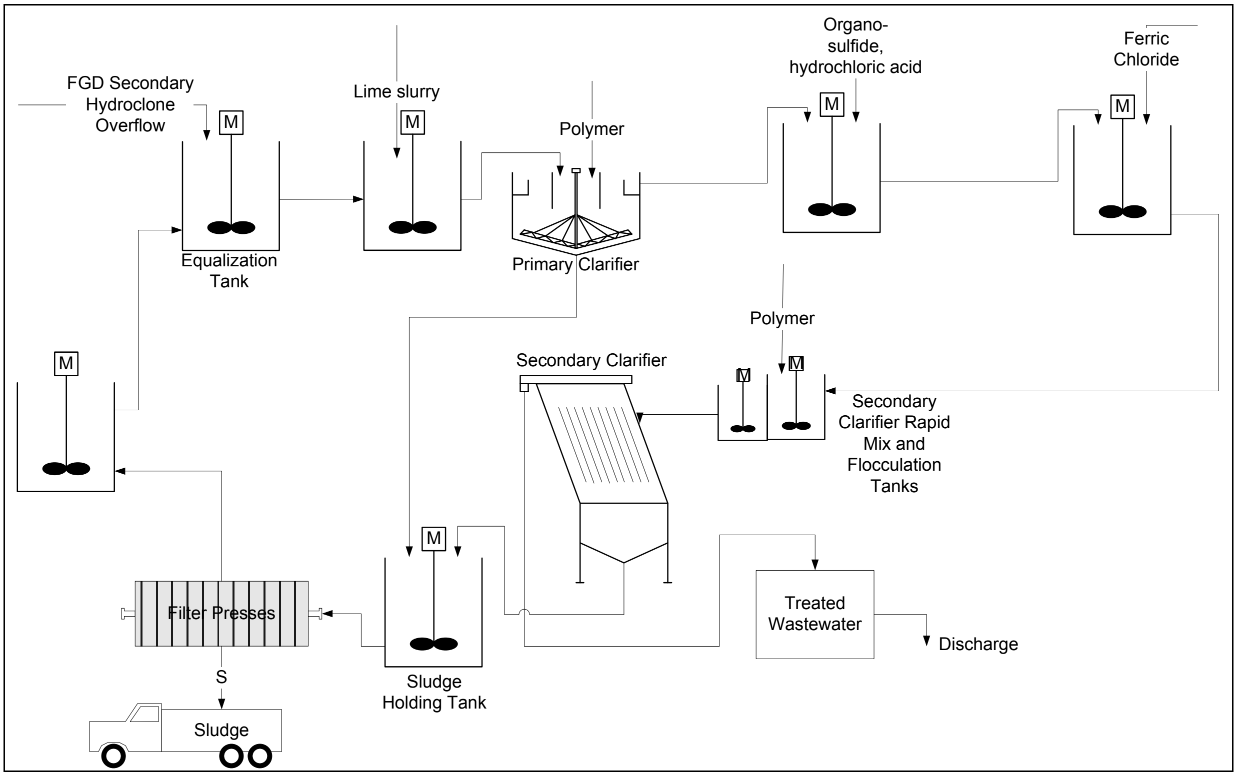

Figure 3-16
Site PG7 FGD Water Treatment Plant Process Flow Diagram

FGD blowdown is routed through primary hydrocyclones to separate gypsum solids from fines. Underflow is routed to a vacuum belt filter for gypsum dewatering. Overflow from the primary hydrocyclones passes to secondary hydrocyclones. Secondary hydrocyclone overflow is routed to the treatment plant equalization tank.

The plant was designed to treat 70 gpm of wastewater with a TSS concentration of less than 1.5%. It typically operates at about 35 gpm. After equalization, wastewater flows to Reaction Tank 1. Wastewater pH is adjusted from approximately 5.6 to 8.5 by adding hydrated lime to de-saturate the wastewater. Effluent from Reaction Tank 1 flows by gravity to a primary clarifier. Polymer is added to aid solids removal and sludge is recycled back to Reaction Tank 1.

The pH is lowered to approximately 7 and an organosulfide is added to Reaction Tank 2 to precipitate mercury. The effluent from Reaction Tank 2 flows by gravity to Reaction Tank 3, where ferric chloride is added for coagulation and for iron co-precipitation. Effluent from Reaction Tank 3 passes to a Flash Mix tank where polymer is added, and to a flocculation tank followed by a parallel plate clarifier. Sludge from this clarifier is recycled back to Reaction Tank 3 to aid floc formation and settling.

Solids from the primary and secondary clarifiers are sent to a sludge holding tank and dewatered using a filter press. The treatment system at Site PG7 is located in an approximately 80-foot by 80-foot building.

Results from a one-time sampling event at Site PG7 provide a limited characterization of efficiency of removal of total and dissolved selenium (Table 3-7).. Most of the selenium was in the particulate form and effectively removed through treatment. Some particulate selenium was solubilized, likely as selenite, during lime addition. This solubilized selenium along with a portion of the originally dissolved selenium was subsequently removed (after the pH was lowered) through iron co-precipitation and secondary clarification. The remaining selenium in the effluent was 100% dissolved. Selenium speciation data were not available for this sampling event, but is known to vary over time in the untreated FGD water at Site PG7 such that selenate is sometimes the predominant species, and selenite at other times.

Table 3-7
Site PG7 Selenium Removal

Form of Selenium	Influent Selenium (µg/L)	Selenium After Primary Clarification (µg/L)	Effluent Selenium (µg/L)	Removal Efficiency
Total Selenium	19,000	8,500	3,000	84%
Dissolved Selenium	5,200	8,600	3,000	42%

Case Study Site PG10

Site PG10 burns eastern bituminous coal. Primary hydrocyclone overflow is discharged to the FGD purge water treatment plant continuously at a flow rate of approximately 500 gpm. The chlorides concentration of the FGD water treatment plant influent is approximately 5,500 to 8,000 mg/L and contains 5.7% solids [1]. Figure 3-17 presents a process flow diagram of the FGD water treatment system. The FGD water treatment system contains the following operations:

- Lime desaturation
- Primary clarification
- Equalization
- Ferric chloride addition
- Polymer addition
- Secondary clarification
- Solids handling

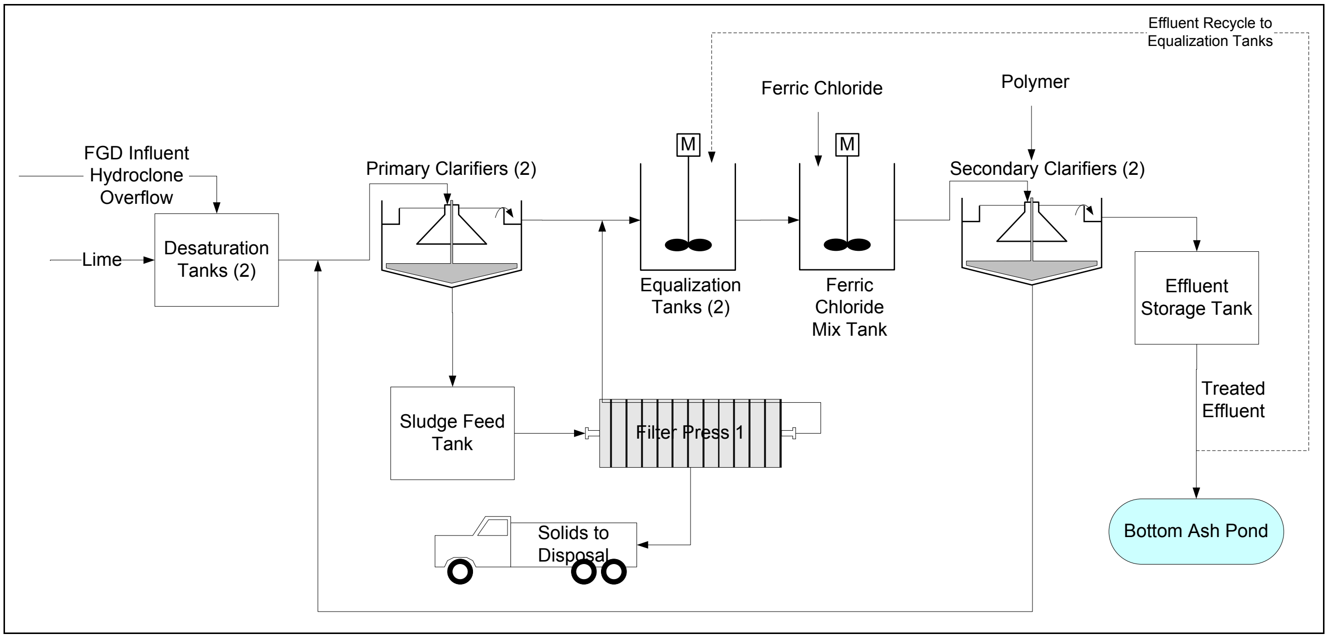

Figure 3-17
Site PG10 FGD Water Treatment Plant Process Flow Diagram

The FGD water influent has a pH of approximately 6.5 to 7.0. At the desaturation tank, the pH is raised to a value between 8.2 and 8.7 using hydrated lime addition. From the desaturation tank, the FGD water flows to the primary clarifier. The overflow of the primary clarifier contains approximately 0.1% solids. The overflow from the primary clarifier flows to a ferric chloride mix tank where ferric chloride is added to enhance solids removal. The effluent from the ferric chloride mix tank flows to a secondary clarifier where polymer is added to promote floc formation and settling. The effluent of the secondary clarifier flows to an effluent tank prior to discharge to the bottom ash pond.

Results from a one-time sampling event at Site PG10 provide a limited characterization of removal efficiency for total and dissolved selenium (Table 3-8). Most of the selenium is in the particulate form and is effectively removed through treatment. Dissolved selenium is not effectively removed through this facility’s physical/chemical treatment process. This is to be expected, as the iron addition is carried out at elevated pH, which is not likely to result in selenite removal by iron co-precipitation. The remaining selenium in the effluent was almost 100% dissolved. Selenium speciation data were not available for this sampling event.

Table 3-8
Site PG10 Selenium Removal

Form of Selenium	Influent Selenium (µg/L)	Selenium After Primary Clarification (µg/L)	Effluent Selenium (µg/L)	Removal Efficiency
Total Selenium	1,990	234	431	78%
Dissolved Selenium	443	472	407	8%

Effect of pH on Physical/Chemical Treatment

Each of the case study sites operates at a pH above the optimal pH range of 4 to 6 for selenium removal with iron co-precipitation. Among these, site PG7 has been optimized for mercury removal and operates at a pH below 7 which is better for selenite removal than the higher pH maintained at other sites. However, Site PG7 wastewater also has a large selenate fraction, and total selenium removal through iron co-precipitation is therefore reduced.

Site PG8 performed a study using their FGD water to determine the optimal pH for selenium removal and found that selenium removal was most effective at pH 5 to 5.5. Another lesson learned from the pilot study conducted at Site PG8 was that optimization of selenium removal occurred when solids were removed prior to final pH adjustment. Selenium was approximately 250 µg/L in the effluent during this study. It has been observed at Site PG1's FGD water treatment plant that target pH may vary over the year, which is likely to affect selenium removal efficiency.

Operations and Safety Issues for Physical/Chemical Treatment

Operational issues that are typically observed within a physical/chemical treatment plant include issues with plugging of media used in filtration and scaling of equipment and piping. FGD water tends to be supersaturated with calcium sulfate which can cause scaling. Even after desaturation, FGD water has a tendency to scale and cause plugging of lines or scale formation on equipment, and plugging of media used for filtration. The sand filter at Site PG7 scaled up during its first year of operation and was removed from service. Scale buildup in the underground discharge piping has restricted flow and requires periodic mechanical cleanout. Site PG7 burns sub-bituminous coal and utilizes a relatively high magnesium (~2%) limestone, which results in a much higher sulfate concentration in the purge water and exacerbates their scaling problems.

Solids dewatering can be an issue for Site PG1 at times and the sludge from the ferrous chloride precipitation process is sometimes mixed with fly ash to stabilize the sludge prior to disposal in a landfill.

Safety issues at physical/chemical treatment plants arise from the operations of mechanical equipment and handling of corrosive chemicals such as hydrochloric acid and ferric chloride.

Capital and Operations and Maintenance Costs for Physical/Chemical Treatment

The capital costs of the treatment systems presented in the case studies above ranged from $15-$30 million dollars, with operations and maintenance costs of approximately $450,000 to $2 million per year. The greatest portion of the operations costs are attributed to chemical usage and disposal of dewatered solids. For example, one facility reported chemical usage costs of $140,000 per year and sludge (non-hazardous) disposal of $100,000 per year out of their $450,000 total annual costs. Additional operations costs include labor for operations of the FGD water treatment system, utilities, and maintenance labor and materials. Labor needed to run the FGD water treatment systems are typically 1 to 2 full-time equivalents.

Biological Treatment Technologies for Selenium Removal

Treatment Description

Anaerobic/anoxic biological treatment processes have been developed for targeted removal of selenium. The fixed-film GE ABMet® system is the only tank-based biological system currently installed at full scale for selenium removal from FGD purge water. A total of four GE ABMet® systems have currently been installed (two in 2008 and two in 2009) and another system is to be installed in 2010 [10].

The GE ABMet® treatment process (Figure 3-18) biologically reduces dissolved selenite and selenate to elemental selenium, which is a solid.

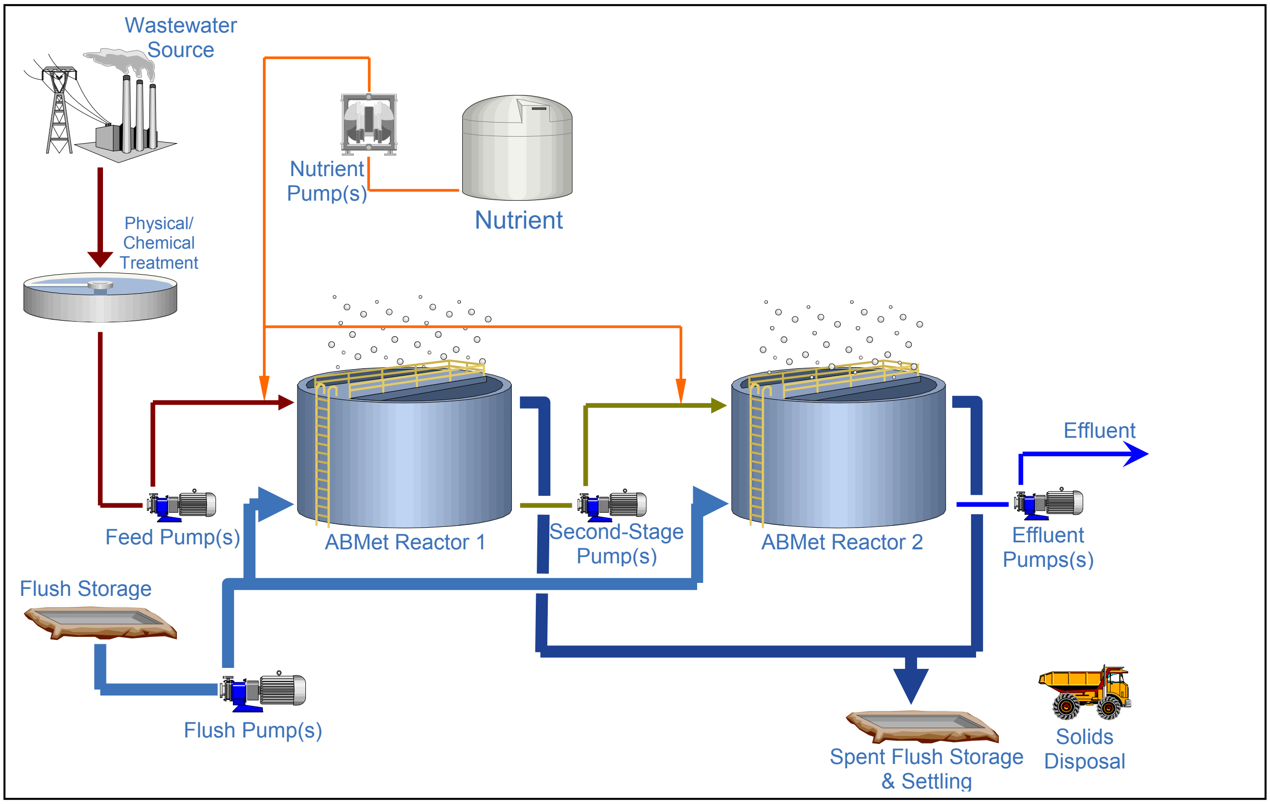

Figure 3-18
Layout of GE ABMet System

Source: Modified from GE Water's schematic as cited in Higgins et al. [8].

In this process, an organic nutrient is added to promote growth of anaerobic bacteria on a granular activated carbon media, with selenite and selenate being reduced to elemental selenium. The microbes are developed as a site-specific seed-culture for the bioreactors. As substrate is consumed by bacteria the substrate is oxidized, and selenate and selenite act as electron acceptors converting the selenium to elemental selenium which sorb to the bacteria and biofilm created within the activated carbon media [11]. These bacteria require the wastewater temperature to be typically between 45 and 105 °F. Therefore, cooling of the FGD water is required prior to biological treatment [12].

A molasses-based nutrient/substrate source is added to the FGD water as it enters the biological treatment system. The bacteria present within the system require an organic source of carbon for energy as well as nitrogen and phosphorus for growth and synthesis.

In the absence of selenite, selenate, nitrate, and nitrite electron acceptors, sulfate will be used as an electron acceptor by a different population of microbes resulting in the formation of hydrogen sulfide, which can inhibit selenate and selenite reduction.

Nitrates and nitrites are ubiquitous from nitrogen oxides (NO_x; specifically NO_2) dissolution into the scrubber water from the flue gas. Due to the slow growth of selenium-reducing organisms, nitrates need to be reduced before selenium is reduced. The size of the treatment system and the need for organic nutrients is driven by nitrate concentration in the wastewater.

Nutrient addition occurs in two stages. The second stage of nutrient addition is generally a fraction of the first stage dosage [12]. The first and second stage bioreactor cells operate in series and utilize a down-flow design. Each bioreactor contains granular activated carbon on top of a layered gravel bed. Selenium reduction performance by biological treatment has been reported to treat to target levels as low as 5 micrograms per liter (µg/L) of total recoverable selenium. Monitoring of pH and ORP is performed to control the stoichiometry and ensure selenate reduction [12].

Carbon dioxide and nitrogen gases accumulate within the bioreactor cells over time from biological reduction. The trapped gases reduce the flow path and increase head losses through the system. Therefore, the bioreactor cells are periodically backwashed for degassing. Additional backwashes are performed on a less frequent basis to remove precipitated solids and excess biomass [12]. The backwash water may be pumped to the head of the plant for re-processing through the bioreactors once the solids are removed.

Case Study Summary

Treatment Configuration, Removal Effectiveness, Reliability and Robustness

Sites PG2 and PG3 both have biological treatment processes as part of their FGD water treatment system. Both sites PG2 and PG3 have pre-treatment for FGD water to be cooled to below 95 to 105 °F and to remove suspended solids, as discussed in the previous section on physical/chemical treatment.

A process flow diagram for the FGD water treatment system at Site PG2 is shown in Figure 3-10. The flow rate of the FGD wastewater treatment plant is 600 gpm. Site PG2 employs physical/chemical pre-treatment in the form of equalization, lime addition/desaturation, ferric chloride addition, clarification, and filtration prior to biological treatment. The FGD water is cooled with a heat exchanger that uses service water discharged as once-through cooling water which is mixed with the effluent of the FGD water treatment system. The GE ABMet® treatment system consists of two-stage bioreactors in series. The biological treatment system at Site PG2 consists of sixteen bioreactor cells configured in a two-stage arrangement of eight cells each. Each stage is further broken down into two trains. The system is equipped with recycle pumps, allowing for multiple configurations of the system, including the transfer of effluent back to the front end of the system for seeding or plant outages [12].

A proprietary molasses-based nutrient is added prior to the water entering the first stage bioreactor cells. The cells use a down-flow design. The influent is distributed across the top of a granulated activated carbon (GAC) bed through a system of sixteen sparger nozzles. The effluent from the first stage bioreactor cells flows into a large holding compartment prior to flowing into the second stage of equipment. The second stage is similar to the first stage, and includes nutrient addition and an additional eight bioreactor cells [12].

The backwash system is used to precipitate solids and excess biomass from media. In addition to backwashing, a degas sequence is employed periodically to release gases that build in the bioreactor. The trapped gases reduce flow through the cells. The backwash water is pumped back to the equalization tank for solids removals and re-processing.

A process flow diagram for Site PG3 is shown in Figure 3-2. Site PG3 contains an FGD settling pond which reduces suspended solids and cools the FGD water prior to biological treatment.

The footprints of these two systems vary significantly. The Site PG2 treatment system (including the physical/chemical treatment system) has a footprint of 2.5 acres and the entire treatment area is a total of 5 acres, which includes truck turnaround and access. Site PG3 contains a 16-acre FGD settling pond and the entire treatment area is approximately 25 to 30 acres.

The flow (average 600 gpm) is split in parallel at Site PG2 for a total of 16 bioreactors (8 two-stage modules in parallel). Site PG3 consists of a total of four parallel trains that contain two bioreactors in series each and treats an FGD water flow rate of 1,400 gpm. A molasses-based nutrient is added as part of the biological treatment system. The bioreactors are designed for 4-hour retention time.

The bioreactor needs to be flushed periodically to remove solids from the system. The source of water for backwashing is the FGD settling pond. Backflush wastewater is transferred to the flush pond, which is located directly next to the settling pond.

Figure 3-19 shows total selenium over time at Site PG2 before and after biological treatment. The physical/chemical treatment plant removed an average of 98% of the total selenium in the FGD water, which reduced total selenium levels to the low 100s μg/L. The biological treatment plant resulted in consistent removal over a six-month period to below detection levels (<10 μg/L), resulting in greater than 99% overall removal for the overall system on a consistent basis. The biological treatment system was also able to treat other parameters to low levels such as mercury (average 8.3 ng/L), arsenic, copper, and nickel. The biological treatment system also treated nitrate to below detection (<32 mg/L) but did not on average effectively remove ammonia or organic nitrogen.

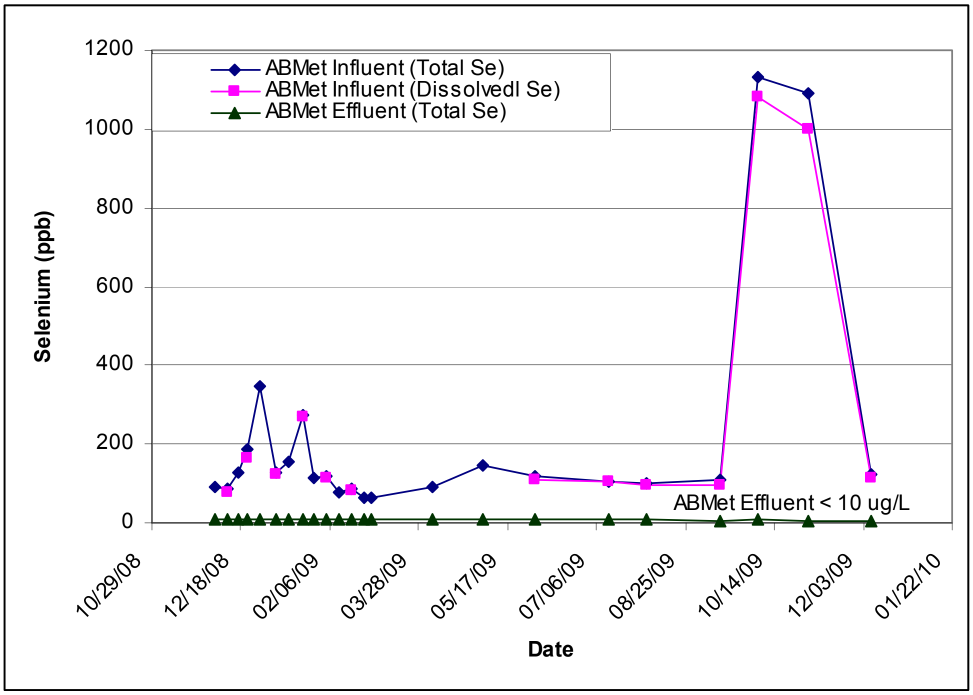

Figure 3-19
Site PG2 Total Selenium Removal by Biological Treatment

Figures 3-20 and 3-21 illustrate selenate and selenite removal through treatment, respectively.

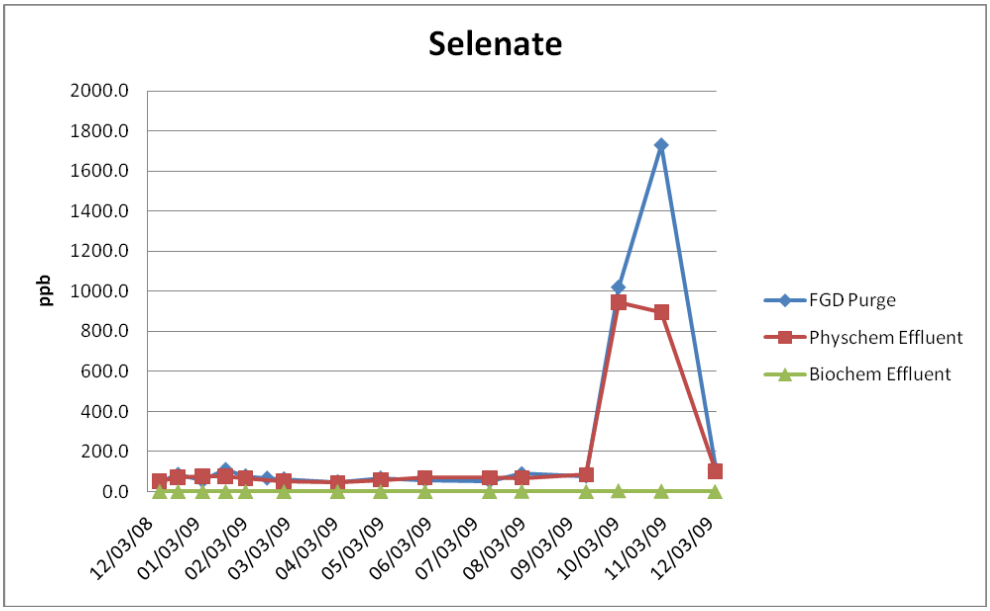

Figure 3-20
Site PG2 Selenate Removal by Biological Treatment

Source: adapted from EPRI, unpublished [12].

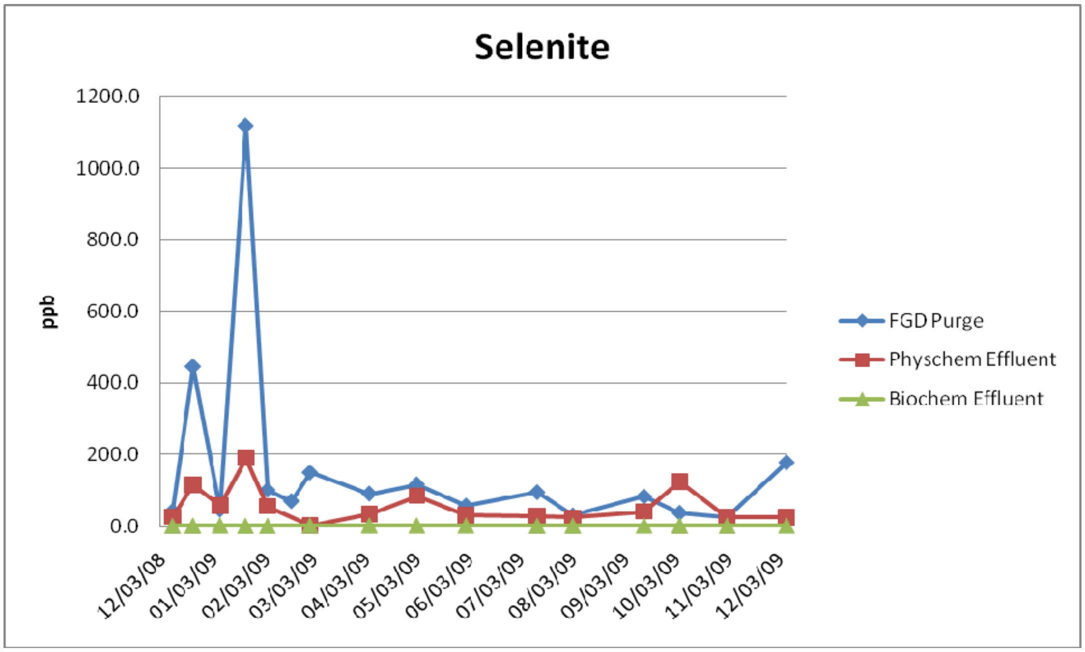

Figure 3-21
Site PG2 Dissolved Selenite Removal by Biological Treatment

Source: adapted from EPRI, unpublished [12].

Figure 3-22 shows median values of particulate and selenium removal across each of the biological treatment cells at Site PG3. The data collected were taken over a five-week period in 2008 so do not represent the fluctuations in the influent that are observed long-term. The data indicate that approximately one-third of the total selenium removed from the FGD water takes place within the settling pond. The effluent of the biological treatment system results show levels less than 50 µg/L. Selenium speciation data collected indicates that the effluent of the settling pond contains almost 100% dissolved selenium at levels greater than 1,000 µg/L, which is removed to low concentrations in the biological treatment system.

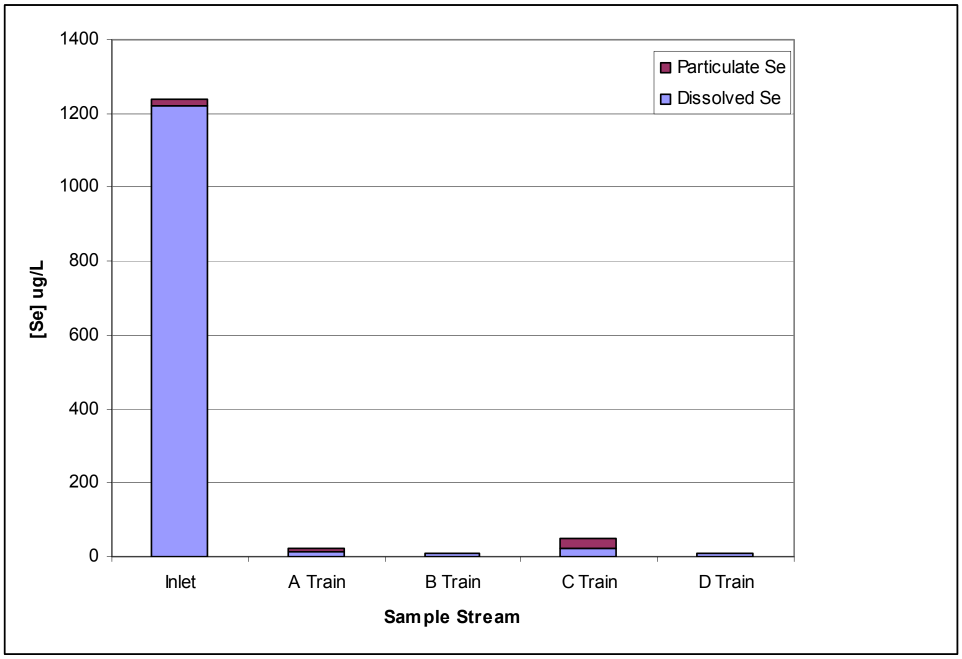

Figure 3-22
Site PG3 Particulate and Dissolved Selenium Through Biological Treatment

Biological Treatment: Operations and Safety Issues

The staff at Sites PG2 and PG3 have stated that operational issues during routine operations have not been observed to date regarding the bioreactors. Site PG2 reported backwashing of the bioreactor cell twice per month. Site PG2 pumps the backwash water after backwashing to the equalization tank at the head of the biological treatment plant (see Figure 3-10) above for the process flow diagram). The solids from backwashing are minimal in volume and are disposed of along with the solids from the filter press operations at the physical/chemical treatment plant. At Site PG3, the forward flush pond is used to store backwash water. Hydrogen sulfide may be produced within the bioreactors so hydrogen sulfide monitoring is conducted as a safety precaution at both sites.

Biological Treatment: Capital and Operations and Maintenance Costs

The capital cost for the FGD water treatment plant including the settling pond at Site PG3 is approximately $33 million, of which approximately $22 million is for the biological treatment system. Operations costs are unknown as the systems have not been in operation long enough to determine what the long-term operations costs are for the system. Costs to re-seed the system with microbes if needed at Site PG3 were estimated to be approximately $200,000 (2006 $USD). However, this re-seeding was not required. The cost of biological treatment systems varies greatly from site to site and a site-specific estimate is recommended.

Passive Treatment: Constructed Wetlands

Treatment Description

A constructed wetland is an engineered system that has been designed and constructed to use natural processes that involve wetland vegetation, soils, and associated microbial activity for removal of constituents from water. There are two basic types of constructed wetlands: surface-flow and subsurface-flow wetlands (Figure 3-23). Surface flow systems typically have water flowing at shallow depths over the soil surface and through plants, while subsurface flow wetlands maintain the water below the soil surface.

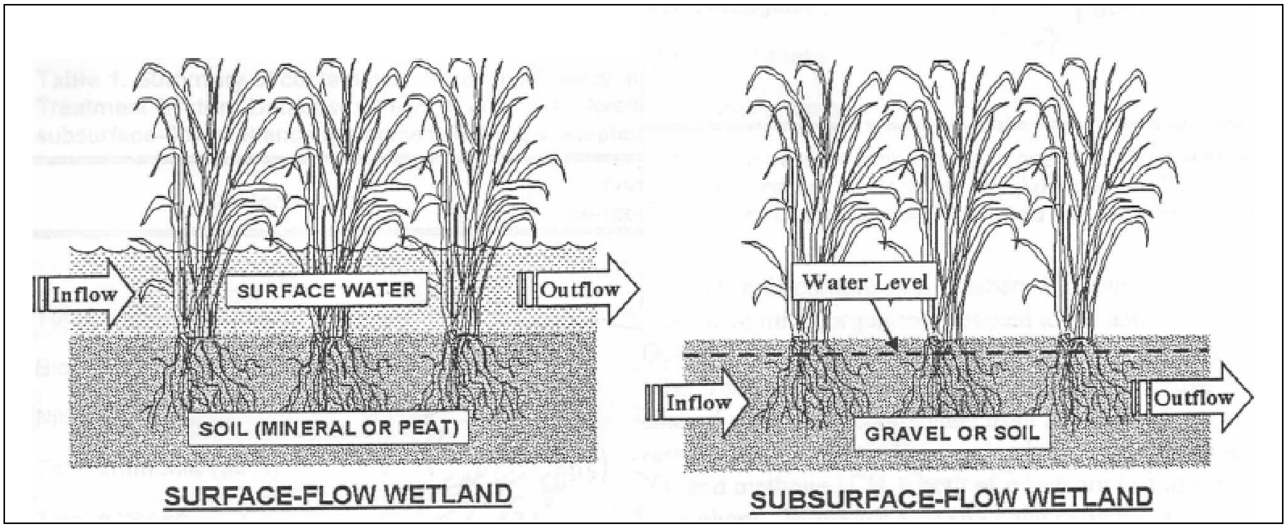

Figure 3-23
View of Surface Flow Wetland and Subsurface Flow Wetland

Source: EPA, A Citizen's Guide to Phytoremediation, 2001 [13]

Selenium is removed within a wetland through various processes. Selenium may be taken up into the plant tissues where it is bioaccumulated, biotransformed to less toxic or immobile states, and/or volatilized to the atmosphere. Wetlands plants provide a fixed carbon supply for bacteria in sediments.

Passive treatment systems can include oxidation/precipitation basins, surface flow wetlands, subsurface or vertical flow wetlands (VFWs), manganese-oxidizing beds, and various forms of phytoremediation [14]. The components can be grouped into aerobic or anaerobic categories, with certain components used to target a particular parameter. Anaerobic/anoxic reducing conditions are preferred within a constructed wetland to achieve significant selenium removal.

Case Study Summary

Treatment Configuration, Removal Effectiveness, Reliability and Robustness.

Sites PG4 and PG5 use constructed wetlands for removal of metals. Site PG4 constructed wetlands are designed for selenium and mercury removal and Site PG5 constructed wetlands are designed for mercury removal. Organic matter additions are not currently made at either of the wetlands.

Pre-treatment is required for the wetlands to reduce suspended solids. Both Sites PG4 and PG5 operate clarifiers for solids separation as a treatment step prior to the FGD water entering the constructed wetlands (see Figures 3-5 and 3-7). Service water is also added to reduce levels of chlorides, boron, and high temperature. At Site PG4 service water is added at a 1:1 ratio and at Site PG5 water is added at a 3:1 ratio with the FGD water prior to entering the wetlands to reduce chlorides to acceptable levels (below 4,000 mg/L). The FGD water is also cooled with the service water to keep temperatures below 95 ºF and to keep boron levels below 50 mg/L.

The overall footprint of the treatment system at Site PG4 is approximately 12 to 15 acres. At Site PG5, the footprint of the passive treatment system is 6.5 acres. Relatively large footprints are required for surface-flow wetlands.

Both Sites PG4 and PG5 are designed as surface-flow wetlands. Site PG4 consists of nine surface-flow treatment cells arranged in three parallel banks of three cells each. Each train consists of two cells of bulrush, a third aeration cell containing cascading rocks, and a fourth cell containing cattails. Total selenium removal across the wetland averaged 10%. ORP readings taken across the system indicated that reducing conditions, which are conducive to selenium removal, are present within some of the cells, but that there are also areas with oxidizing conditions which do not promote selenium removal. Reduction of oxidized forms of selenite and selenate to elemental form cannot occur without anoxic conditions. Varying oxidizing and reducing conditions may result in alternating periods of selenium sequestration and remobilization at Site PG4 [14].

Selenium removal has been variable at the constructed wetlands at Sites PG4 (Figure 3-24) and PG5 (Figure 3-25). The wetland is designed as a free surface wetland and contains two trains, each of which consists of two cells of bulrush, a third manganese oxidation cell, and a fourth cell containing cattails. There is no addition of substrate currently at the wetland to target selenium removal. Average total selenium removal achieved through the constructed wetland for the time period shown below is approximately 10% at Site PG5. Average total selenium removal at Site PG4 is generally 20%.

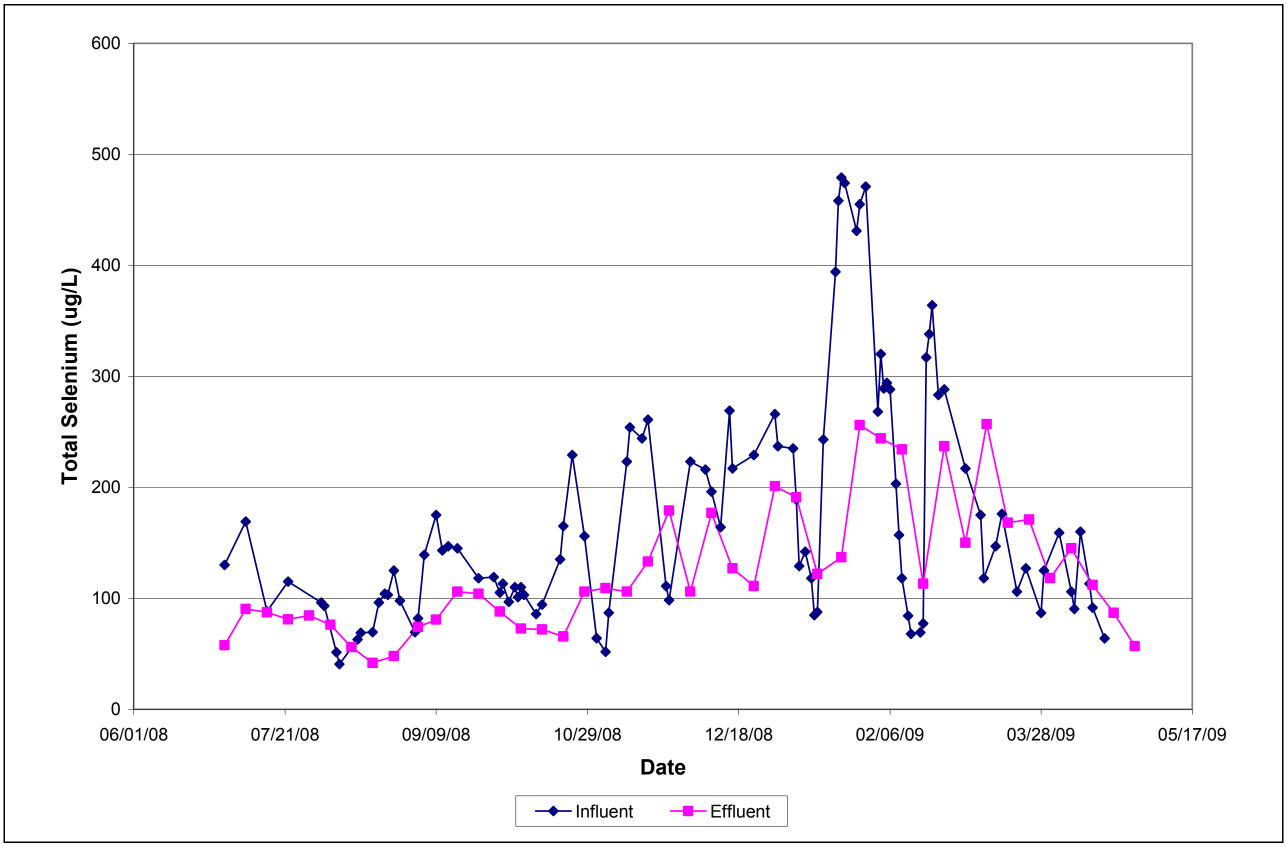

Figure 3-24
Site PG4 Total Selenium Removal through Constructed Wetland

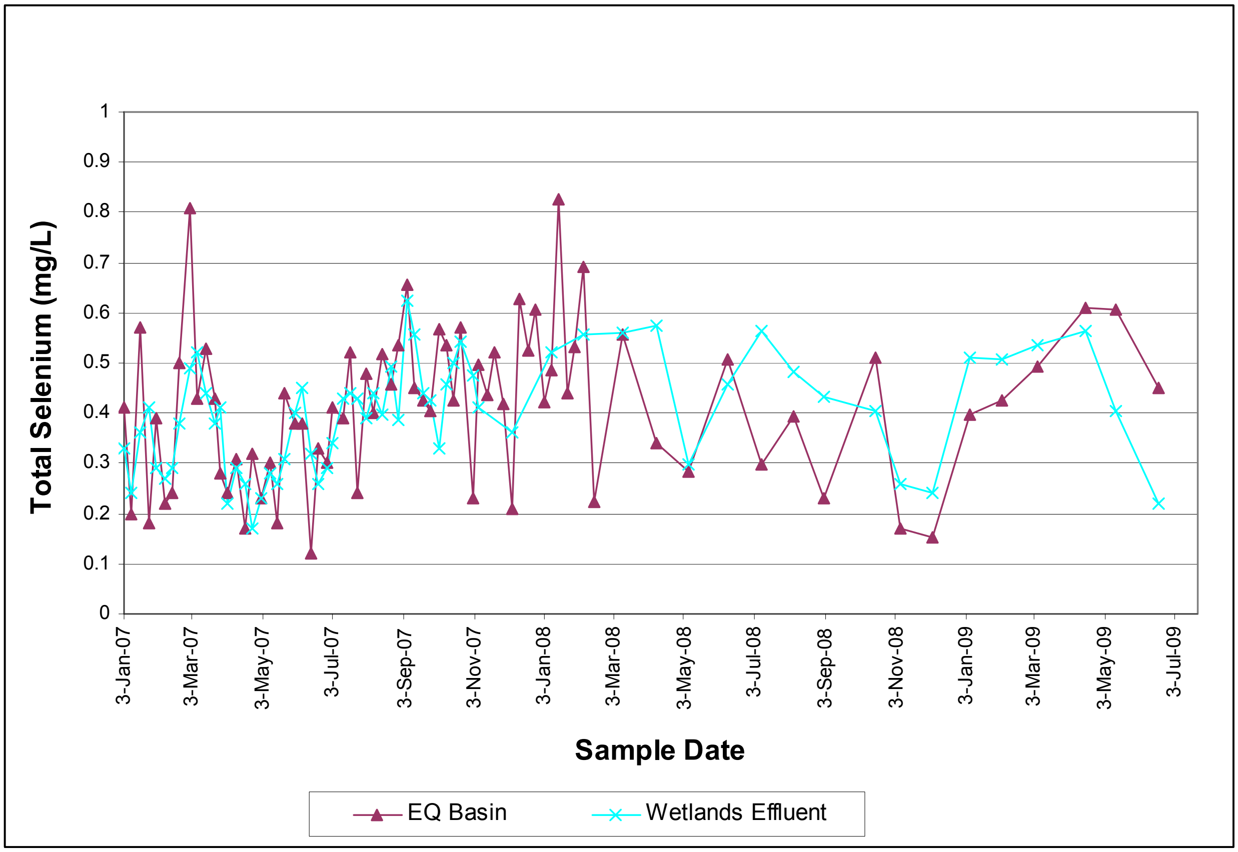

Figure 3-25
Site PG5 Total Selenium Removal through Constructed Wetland

A study was conducted at Site PG4 that tested organic addition for one of the treatment trains of the constructed wetland. The test consisted of yeast and sugar addition at varying amounts over the course of a seven-month period. The train treated with the sugar/yeast addition achieved up to 40% selenium removal while 19% removal of selenium was observed for the wetland train that did not have additions.

Site PG4 has been piloting a vertical flow wetland at their site as part of a long-term pilot study. The vertical flow wetland pilot study has shown removal of selenium to low µg/L levels with removals of 85% across the wetland pilot test cell for total and dissolved selenium as part of a long-term pilot test [14]. This is discussed further in Section 4.

Operations and Safety Issues

Operational difficulties at Site PG4 have been observed at startup due to the presence of boron in the FGD water. Effects of boron on wetlands plants have been observed where the tips of the plants have turned brown. Service water is now added to maintain boron to ≤50 mg/L. At Site PG4, the wetlands plants have taken a long time to grow to cover the entire treatment cell, which may affect selenium removal. Maintenance costs of the wetlands treatment system is low with no maintenance required to date for either of the systems constructed in 2007/2008, other than routine inspections.

Capital and Operating Costs

Capital costs of the Site PG5 constructed wetland are approximately $13 million. Operating costs of the constructed wetlands are low, with costs mainly due to chemical usage for polymers used during pre-treatment and disposal of solids.

Zero Liquid Discharge Technologies

In 2008, EPRI compiled an inventory of ZLD water management systems currently operating at U.S. power generating stations [15]. The study was not limited to coal-fired facilities but included a large number of gas-fired combined cycle facilities (57% of the facilities documented were gas-fired). Also, the study was not limited to systems treating FGD wastewater. Many of the ZLD systems listed were used for cooling tower blowdown and other waste streams. The report also documented some planned installations that may or may not be completed. The study included the following main ZLD technologies:

- Brine concentrators
- Conventional and specialized reverse osmosis systems
- Evaporation ponds
- Staged cooling towers
- Dry cooling towers

Additional ZLD operations included feeding plant wastewater to the plant's FGD operations, discharging to the sewer, land applications, or deep well injection. No significant correlations were found between power plant fuel type (gas or coal) and the ZLD technologies in use.

Some plants completely recycle their FGD water without creating a purge stream that needs to be treated. Plants that do not produce gypsum for re-sale may be able to operate their FGD systems such that the moisture retained with the landfilled solids entrains sufficient chlorides that a separate purge stream is not required [1]. The ability to purge the untreated FGD water with the gypsum is dependent on the chloride to sulfur ratio of the coal. Most plants do not have the ability to purge the chlorides stream with the unwashed gypsum, particularly if the sulfur levels in the coal are relatively low and the chlorides are high.

Evaporation ponds are typically constructed in a warm dry climate such as that of the southwestern part of the United States where the evaporation rate of ponded FGD wastewater is greater than the rate of combined wastewater and precipitation inputs [1].

An underground injection well has been constructed at one facility to discharge FGD wastewater. However, there have been operational difficulties associated with this system, so this is not yet a demonstrated technology.

Fly ash conditioning is performed for dry fly ash handling systems to prevent fly ash from blowing away when it's trucked. EPA's study indicated that only one facility uses FGD wastewater to condition ash, and one other facility uses this in combination with an evaporator [1].

One facility in the United States currently employs evaporator/crystallizer technology, with the plant going online in 2009. The first step involved in evaporation/crystallization is pre-treatment of the FGD wastewater using physical/chemical treatment including clarification, chemical treatment such as with iron and/or sodium sulfide or other organosulfide, and softening to reduce suspended solids, calcium, magnesium, and heavy metals.

The second step involves the use of a falling film evaporator or brine concentrator. Evaporators operate by transferring latent heat from condensing steam across a tube surface to evaporate the FGD wastewater. The influent wastewater is preheated using a heat exchanger that is typically made of titanium plates. Fluoride is typically a problem with ZLD systems employing titanium heat exchangers, due to corrosion of the titanium when in contact with hydrofluoric acid.

Brine concentrators are specific types of falling film evaporators used to treat wastewaters saturated or supersaturated with calcium sulfate or silica [1]. The brine concentrator or falling film evaporator employs calcium sulfate seed crystal in the circulating brine in the evaporator. This process produces a concentrated wastewater stream and salts. The brine concentrator can typically concentrate the FGD scrubber purge five to ten times, which reduces the inlet FGD scrubber purge water volume by 80 or 90%. An example of brine concentrating evaporator configuration is shown in Figure 3-26.

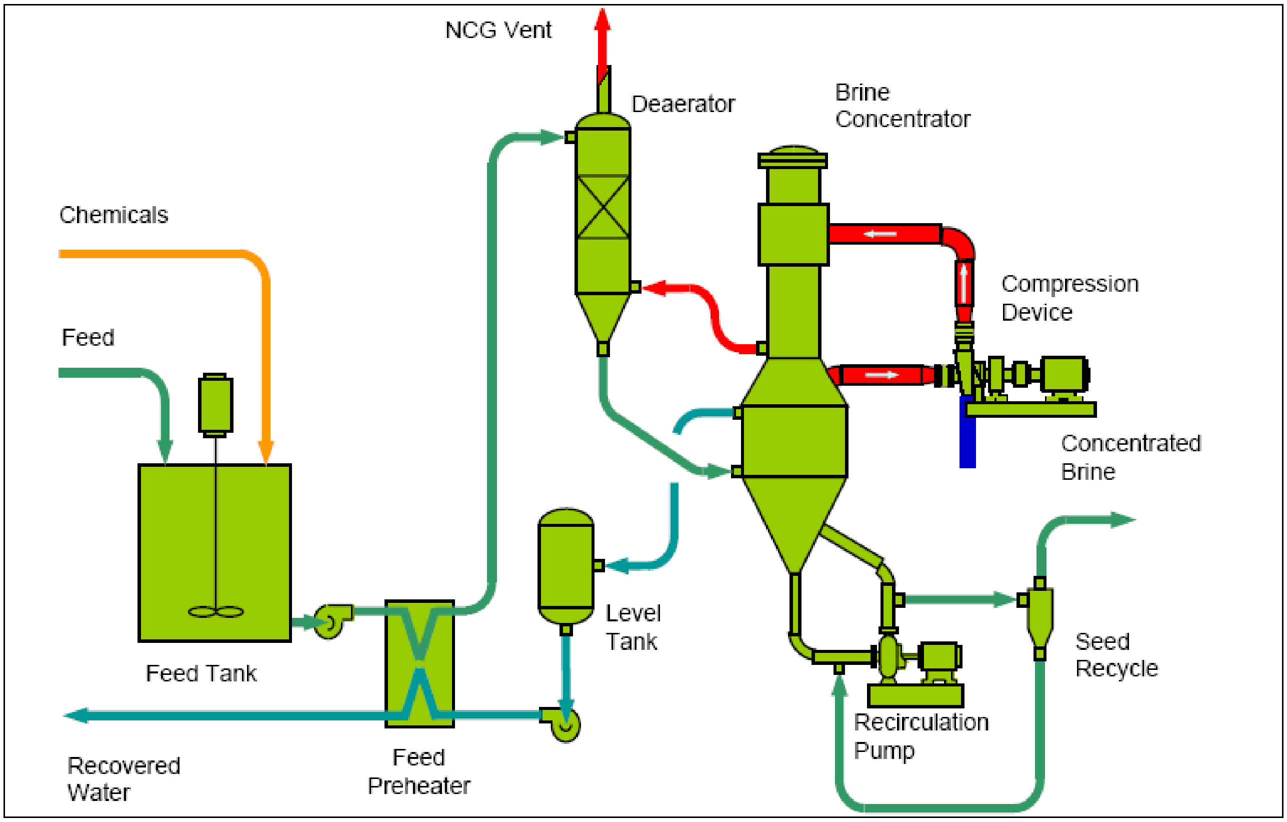

Figure 3-26
Brine Concentrating Vapor Compression Evaporator

Source: Shaw, “A New Low Temperature ZLD Process,” 2009 [16]

Three options are typically considered to be available for eliminating the brine concentrate: (1) final evaporation in a brine crystallizer; (2) evaporation in a spray dryer; or (3) using the brine to condition dry fly ash or other solids and disposal of the mixture in a landfill.

Crystallizer systems (Figure 3-27) use mechanical vapor recompression (MVR) technology to recycle the steam vapor, which is clean enough to reuse in the plant. The solid cake produced by the crystallizer is generally 25% solids and is disposed of in a landfill.

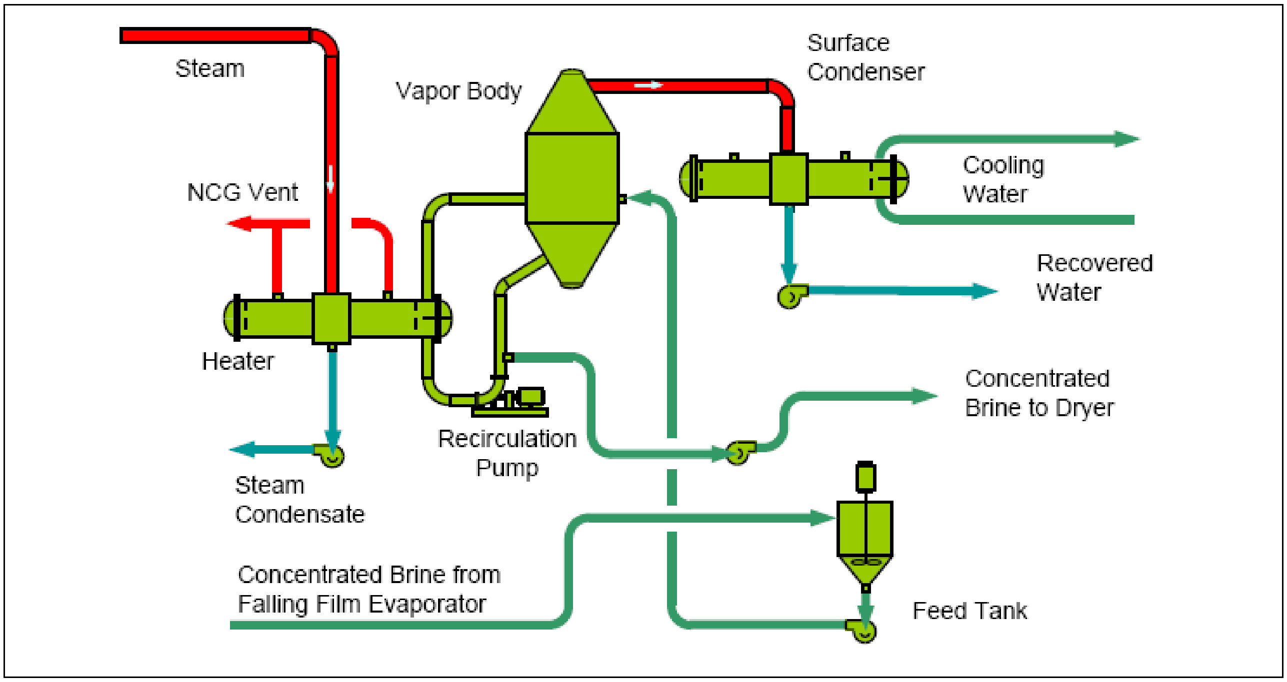

Figure 3-27
Evaporator/Crystallizer

Source: Shaw, "A New Low Temperature ZLD Process," 2009 [16]

4

EMERGING WATER TREATMENT TECHNOLOGIES FOR SELENIUM REMOVAL

This section presents a description of the technologies that have been evaluated by EPRI for selenium removal from FGD water at pilot scale. These technologies were selected based on a literature review of available technologies that showed promise for selenium removal including successful bench-scale testing and/or similar pilot-testing of the technologies. An evaluation of these technologies is provided in separate EPRI reports [14, 17].

Vertical Flow Wetlands (Subsurface Flow Wetlands)

VFWs are a promising technology for removal of selenium from FGD water. The process employs an organic compost to promote anoxic conditions for biological reduction of selenate and selenite to elemental selenium, which is subsequently removed by solids separation in the media. VFWs generate strongly reducing conditions with organic-rich substrates for reduction of selenate and selenite to elemental selenium, sulfide minerals such as ferroselite ($FeSe_2$) and possibly organo-selenium compounds.

A VFW test cell was constructed at Site PG4 to receive a portion of the discharge from the equalization basins and subsequently monitored into 2009 to evaluate three organic substrate configurations. The equalization basins contain FGD water that has been treated for solids separation through equalization, primary clarification with polymer addition, and dilution with wash water to reduce chloride and boron levels prior to entering wetlands [14].

The vertical flow wetland pilot test cell was composed of organic substrate consisting of spent mushroom compost placed over a gravel bed. The pilot-scale test measured the performance of three organic substrate configurations. The influent total selenium concentration ranged between 47.8 μg/L to 182 μg/L during this timeframe. The influent to the pilot study was mainly comprised of selenite to selenate ratios of 2:1 or greater. Figure 4-1 shows the influent and effluent selenium removal over three configurations tested.

Strongly reducing conditions favoring selenium and mercury removal, as indicated by ORP measurements, are developed within the first foot of the VFW substrate. It should be noted that influent water contained relatively low concentrations of selenium, as much of the selenium was removed in the solids removal step, upstream of the pilot. Also, though most selenium in the pilot influent was present as the more easily treated selenite, the smaller selenate fraction was also effectively captured in the pilot VFW. Site PG4 recently decided to install a full-scale VFW which is expected to be operational by 2012.

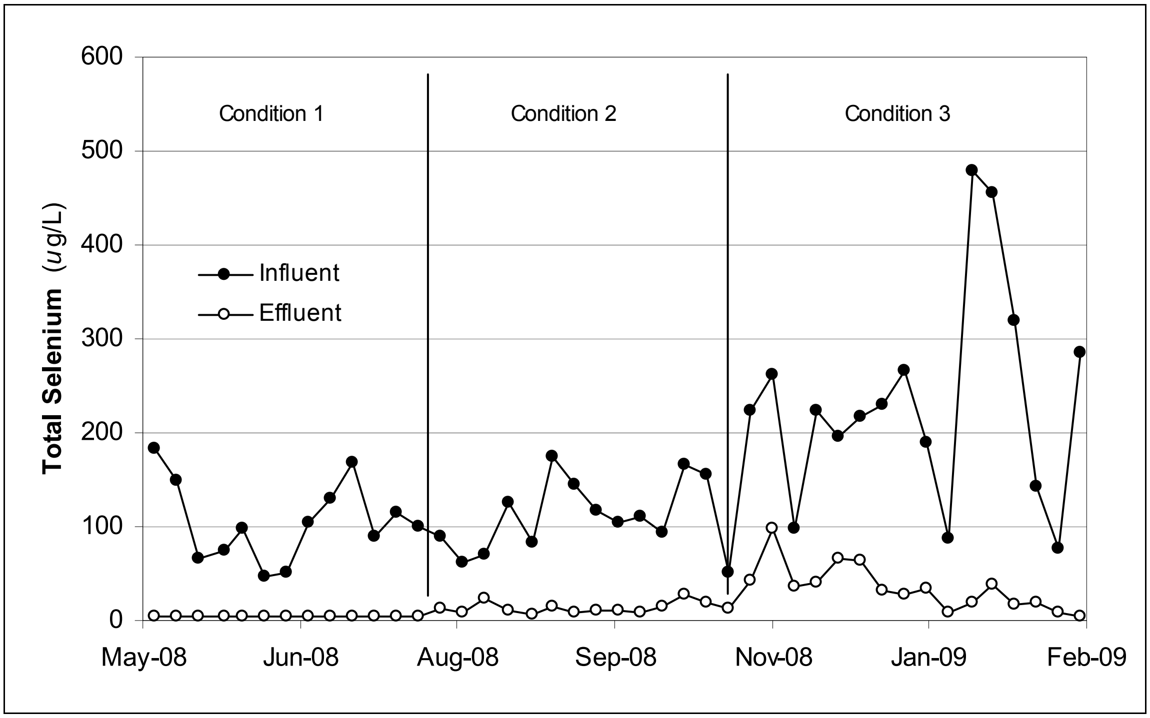

Figure 4-1
Vertical Flow Wetland Pilot Test Results for Total Selenium

Source: EPRI, Vertical Flow Wetland Pilot Study, to be published [14]

Iron Cementation

The iron cementation technology uses oxidation of elemental iron to chemically reduce selenium (selenite and selenate) to elemental selenium or iron selenide which is then removed by solids separation processes. The resulting ferrous iron from the reaction is precipitated as a hydroxide by raising the pH. Nitrate, present in FGD wastewater, is a significant interference with the process, as nitrate consumes treatment chemicals by being oxidized to ammonia [17].

Batch laboratory testing of this technology indicated that selenate and selenite could be reduced to less than 50 µg/L [16]. Based on these results, this technology was selected for pilot-scale evaluation by EPRI. The purpose of this pilot-scale study was to evaluate the iron cementation technology under continuous flow conditions at a coal-fired power plant. The pilot study was conducted at a facility that burns sub-bituminous coal.

The pilot study was conducted using a continuous sidestream of primary clarifier effluent from the FGD water treatment plant as the influent to the pilot study and was operated at a flow rate of approximately 0.2 gpm. The pilot test was conducted over a nine-week period testing 8 different conditions. The influent dissolved selenium concentration ranged from 5,060 to 7,060 µg/L [17].

The results of the studies showed that selenium is reduced by iron cementation; however, it is more effective at lower pH and is enhanced by increasing the HRT, which also improves dissolution of the metallic iron. Maximum removal occurred at a reaction time of 150 minutes and pH of 4.5, which resulted in an effluent selenium concentration of 159 µg/L [17]. Additionally, the reduction of selenite appeared to occur relatively quickly, while reduction of selenate occurs more slowly. Data from the remaining tests indicated that selenium removal decreased as HRT decreased and pH increased. The decrease in selenium removal corresponded with a decrease in the iron concentration in the cementation reactor.

Selenium speciation data revealed that selenite, methylseleninic acid, and the unknown selenium species were easily removed from the primary clarifier effluent. Selenate removal was 95% at low (4.5) pH but was more persistent during tests at higher pH levels [17].

5

CONCLUSIONS

Selenium is present in power plant water streams associated with fly ash handling and flue gas desulphurization systems. The selenium in water associated with fly ash handling and inhibited or natural oxidation FGD systems tends to be in the chemically reduced form (selenite). Selenium in water associated with forced oxidation FGD systems can have a significant portion present in the oxidized selenate form. When first absorbed in the FGD absorber, selenium is predominantly in the reduced selenite form, which is then oxidized to selenate. The proportion of selenate to total selenium varies widely, and the mechanism or factors affecting the rate of selenite oxidation in an FGD environment is not known.

There are fully demonstrated technologies for removal of selenite from either fly ash handling or FGD systems. They involve the tendency of selenite to be adsorbed onto iron oxyhydride solids at a pH below 6.5. The oxyhydride can either be provided as a solid or can be generated in the wastewater by adding a ferric salt to the wastewater at an acidic pH. The resulting iron hydroxide precipitate adsorbs the selenite. Selenate is not removed by iron salt addition and cannot be optimized for selenate removal due to the chemistry associated with the removal mechanism.

There are a number of technologies being evaluated for selenate removal from FGD water. Of these, the biological treatment process developed by GE under the ABMet® name is the only commercially available technology that has been implemented at power plants that has achieved selenate and selenite removal to low µg/L levels (less than 50 µg/L). However, ABMet® systems have been implemented at a limited number of plants so applicability to a wide range of FGD water constituents (e.g. chlorides) is unknown. [10].

The ABMet® plants are installed as a polishing step, following physical and chemical treatment or settling pond treatment to remove suspended solids and other contaminants prior to polishing for selenium removal. Nitrates can be present in significant concentration in FGD water. Biological treatment of nitrate is required as part of any biological treatment for selenium removal, and can have a significant impact of equipment sizing and treatment chemical demand.

Other technologies such as subsurface or vertical flow wetlands have been tested in pilot scale, but have not been demonstrated at full scale. These wetlands depend on biological reduction of nitrates and selenium species. Surface flow wetlands can result in some removal of selenium by plants, but are primarily aerobic processes, and not very effective at selenium removal for FGD water.

The development of low cost, reliable technologies to remove total selenium from FGD waste streams is a priority for the utility industry, as environmental standards/criteria applicable to the NPDES program are expected to become more stringent. In addition, U.S. EPA's upcoming regulatory determination on the hazards of coal combustion byproducts, and the revision of the steam electric source category effluent guidelines, could put more pressure on the utility sector to develop proven removal technologies in a relatively short period of time.

6
REFERENCES

1. U.S. Environmental Protection Agency. 2009. *Steam Electric Power Generating Point Source Category: Final Detailed Study Report.* EPA-821-R-09-008. Washington, D.C. October.
2. Electric Power Research Institute. 2007. *Arsenic and Selenium Speciation in Fly Ash and Wastewater.* Palo Alto, CA: Product ID: 1005567.
3. Electric Power Research Institute. 2009. *Guidelines for FGD Sampling and Analyses: Trace Metals.* Palo Alto, CA. Product ID: 1018223. January.
4. Electric Power Research Institute. 2005. *PISCES Database Version 2005a.* Palo Alto, CA.
5. Electric Power Research Institute. 2008. *Flue Gas Desulfurization (FGD) Water Blowdown Characterization and Management: 2007 Update*. Product ID: 1014073.
6. Electric Power Research Institute. 2009. *Impact of Wet Flue Gas Desulfurization (FGD) Design and Operating Conditions on Selenium Speciation*. Product ID: 1017952.
7. Electric Power Research Institute. 2009. *Flue Gas Desulfurization (FGD) Water Characterization: 2008 Update*. Product ID: 1014073. March.
8. Higgins, T.E., T.A. Sandy and S.W. Givens. "Flue Gas Desulphurization Wastewater Treatment Primer." *Power Magazine*. Volume 153, No.3, p. 34-43 (March 2009).
9. Eastern Research Group. 2007. Engineering Site Visit Report for EME Homer City Generation L.P.'s Homer City Power Plant. DCN 04718. August 9.
10. S. Blankinship. "'Bugs' Used to Treat FGD Wastewater." *Power Engineering* (September 2009).
11. Pickett, T., et al. "Using Biology To Treat Selenium." *Power Engineering (November 2008).*
12. Electric Power Research Institute. To be published. *Evaluation of the GE ABMet System at Duke Energy's Belews Creek Stream Station.* Palo Alto, CA. Product ID: 66517.
13. U.S. Environmental Protection Agency. 2001. *A Citizen's Guide to Phytoremediation*. Publication. 542-F-01-002.
14. Electric Power Research Institute. To be published. *Vertical Flow Wetland Pilot Study.* Palo Alto, CA. Product ID: 1016811.
15. Electric Power Research Institute. 2008. *Summary of ZLD Water Management Installations at U.S. Power Plants.* Product ID: 1015592.
16. Shaw, W. "A New Low Temperature ZLD Process." International Water Conference, Orlando, FL (October 2009).
17. Electric Power Research Institute. 2009. *Selenium Removal by Iron Cementation From a Coal-Fired Power Plant Flue Gas Desulfurization Wastewater in a Continuous Flow System – a Pilot Study.* Palo Alto, CA. Product ID: 1017956. March.

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case-by-case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

The Electric Power Research Institute Inc., (EPRI, www.epri.com) conducts research and development relating to the generation, delivery and use of electricity for the benefit of the public. An independent, nonprofit organization, EPRI brings together its scientists and engineers as well as experts from academia and industry to help address challenges in electricity, including reliability, efficiency, health, safety and the environment. EPRI also provides technology, policy and economic analyses to drive long-range research and development planning, and supports research in emerging technologies. EPRI's members represent more than 90 percent of the electricity generated and delivered in the United States, and international participation extends to 40 countries. EPRI's principal offices and laboratories are located in Palo Alto, Calif.; Charlotte, N.C.; Knoxville, Tenn.; and Lenox, Mass.

Together…Shaping the Future of Electricity

© 2010 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute, EPRI, and TOGETHER…SHAPING THE FUTURE OF ELECTRICITY are registered service marks of the Electric Power Research Institute, Inc.

1020813

Electric Power Research Institute
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com