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Evaluation of Equalization Basins as Initial Treatment for Flue Gas Desulfurization Waters

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EVALUATION OF EQUALIZATION BASINS AS
INITIAL TREATMENT FOR FLUE GAS
DESULFURIZATION WATERS

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ABSTRACT

Coal-fired power plants are introducing flue gas desulfurization (FGD) scrubbers to reduce sulfur dioxide and mercury emissions in order to meet air quality standards. FGD scrubber systems utilize a mixture of limestone, water, and organic acids to precipitate sulfur compounds. The resulting FGD water and associated particulates often contain constituents of concern including chlorides, inorganic elements (Hg, As, and Se), and sulfates that must be treated before discharge. Constructed wetland treatment systems, consisting of an equalization basin followed by wetland reactors, present a viable option to efficiently treat FGD waters. Equalization basins are designed to cool and homogenize FGD water and settle particulates. Specific research objectives focused on equalization basins are: 1) to characterize FGD particulates in terms of elemental and mineralogical composition; 2) to determine size and settling rates of FGD particulates; 3) to determine if Hg, As, and Se concentrations within FGD water stored in an equalization basin change with time; and 4) to determine if toxicity of FGD water within an equalization basin changes during a 24 hr hydraulic retention time.

The most common FGD particle type was characterized as gypsum. Other particle types identified included fly ash and iron oxides. FGD particulates settled in an equalization basin are interpreted to have originated during coal combustion and FGD processes. The majority of FGD particulates were determined to be silt size, and settling analysis shows that 95% of these particulates settled to the bottom of a typical 2.5 m deep equalization basin within approximately 4 hrs. FGD particulates contained concentrations of Hg, As, and Se, and as particulates settled, constituents were removed

from the water column. Analysis of FGD water samples indicate that aqueous

concentrations of Hg and Se decreased in the pilot-scale equalization basins by 20 µg/L

and 200 µg/L, respectively, during a 24 hr hydraulic retention time. Data from toxicity

tests indicate that equalization basins do not decrease toxicity of FGD water to aquatic

organisms. Equalization basins are necessary for initial treatment of FGD water by

settling particulates, which may contain Hg, As, and Se. Additional treatment for these

waters occurs in the wetland reactors.

DEDICATION

This thesis is dedicated to my parents for their endless support, encouragement, and understanding throughout this endeavor.

ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

Background and Significance

Coal combustion accounts for about half of the energy produced currently in the United States (EIA, 2005). In 2004, coal burned by electrical power plants reached 1,016 million short tons (EIA, 2005), which accounts for 92% of the total coal used in the United States. Coal varies in composition of both organic and inorganic compounds. Organic compounds in coal occur from the remains of plant material and include C, H, O, N, and S as major elements (Malvadkar et al., 2004). Over 120 inorganic compounds can be found within different types of coal (Schweinfurth, 2005). Some of the primary inorganic elements in coal include aluminum, silicon, calcium, magnesium, sodium, and sulfur with secondary elements including zinc, cadmium, manganese, arsenic, molybdenum, and iron (Malvadkar et al., 2004).

Coal used for electrical power is crushed, pulverized, and blown into a combustion chamber where it immediately ignites (Kalyoncu, 1999) (Figure 1.1). The specific composition of coal determines the way in which the coal burns. On the basis of several parameters, including fixed carbon, volatile matter, and moisture content, coal is ranked into four different classes: anthracite, bituminous, subbituminous, and lignite (Malvadkar et al., 2004). Quality of coals that are used in electrical power plants is determined by observing the environmental issues that surround the characteristics of burning the coal. These include sulfur dioxide emissions, hazardous air pollutants, carbon dioxide emissions, and ash properties (Schweinfurth, 2005).

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┌─────────────────────┐        ┌─────────────────────┐        ┌─────────────────────┐
│       COAL          │        │      BURNER         │        │     FLUE GAS        │
│ (containing organics │  ═▷    │   (coal is crushed  │  ═▷    │ (containing SO₂, NOₓ,│
│   and inorganics)   │        │    and ignited)     │        │   and particulates) │
└─────────────────────┘        └─────────────────────┘        └─────────────────────┘
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Figure 1.1: Schematic of coal-fired power plant processes.

COAL (containing organics and inorganics) ⟹ **BURNER** (coal is crushed and ignited) ⟹ **FLUE GAS** (containing SO_2, NO_X, and particulates)

SCRUBBER (flue gas desulfurization [FGD]) ⟸ **SLURRY** (limestone, water, and organic acids added)

DEWATERING OF PRODUCT

WATER (high concentrations of Cl, Hg, As, Se)   **GYPSUM** (used for the production of wallboard)

Figure 1.1: Schematic of coal-fired power plant processes.

As coal is burned, uncombusted material forms fly ash and some elements, such as mercury and selenium, volatilize and become part of flue gas (Schweinfurth, 2005). Flue gas contains high levels of sulfur dioxide (SO_2), nitrogen oxide (NO_x), particulates, and carbon dioxide (CO_2) (USEPA, 2005). Traditionally, flue gas has been emitted through smoke stacks. Amendments made to the Clean Air Act in 1977 included the reduction of power plant emissions for new coal-fired power plants. In 2003, the "Interstate Air Quality Rule" was incorporated by the United States Environmental Protection Agency (USEPA), which regulates sulfur dioxide and nitrous oxide emissions for existing and new power plants (Smith, 2004). For the first time in 2005, the USEPA added the "Clean Air Mercury Rule" to the pre-existing Clean Air Act to regulate mercury emissions from coal-fired powered plants (EPA, 2005). Power plants under the

jurisdiction of the USEPA must abide by these new emission reductions by the year 2010.

To comply with these laws, coal fired power plants are incorporating flue gas desulfurization (FGD) scrubbing processes to remove sulfur dioxide from flue gas. Several different scrubber options are available for coal-fired power plants. In the United States the most popular system is the calcium (limestone)-based wet scrubber (Kalyoncu, 1999). Wet limestone desulfurization systems can remove 95% of sulfur dioxide from flue gas (Termuehlen and Emsperger, 2003). Through this process, a mixture of limestone ($CaCO_3$), water, and organic acid are sprayed down onto the flue gas. Limestone reacts with sulfur dioxide to form calcium sulfite, which when further oxidized forms calcium sulfate ($CaSO_4$) (Mierzejewski, 1991). Organic acids, such as dibasic acid, are used to improve the sorption properties of the limestone (Karatepe, 2000). Reactions that remove sulfur dioxide from flue gas also have the ability to remove some of the harmful vapor pollutants including mercury and selenium. The degree to which these constituents are removed depends on their initial concentrations, the type of coal burned, and the type of scrubber. Although the FGD process removes constituents from the vapor form, it condenses byproducts that may enter the environment through new routes (Hatanpää et al., 1997), such as water discharge.

Sludge produced from the FGD process is dewatered using belt presses, vacuum filtration, or centrifugation. The resulting product is a solid material composed of gypsum used in the production of wallboard. By 1999, production of wallboard using synthetic gypsum from FGD sludge increased greatly from previous years to

approximately 4 million tons a year (Kalyoncu, 1999), and continues to increase with the construction of FGD scrubbers for existing and new coal-fired power plants.

In the dewatering process, the water and any suspended particulates not removed may not meet National Pollutant Discharge Elimination System (NPDES) permits for discharge. The degree of treatment required for FGD water continues to increase as discharge limits continue to decrease (Mierzejewski, 1991). Composition of this water varies among scrubber units and power plants because of differences in the original coal being burned and the limestone and water used during the flue gas scrubbing process. Constituents of concern within FGD water include, but are not limited to, inorganic elements (e.g. Hg, As, Se), chlorides, sulfates, and total suspended solids (TSS). Mercury, arsenic, and selenium are the major constituents of concern based on toxicity of the element, high concentrations of these elements measured in the water, and discharge permits.

Concentrations of major constituents of concern (Hg, As, and Se) may vary orders of magnitude depending on type of coal burned, scrubber unit and materials, and composition of any other water used within the system. Mercury, an inorganic element that occurs naturally in the environment at low concentrations, has increased in the atmosphere and surface waters due to coal-fired power plant emissions. Mercury occurs in several forms including elemental, mercurous [Hg(I)], mercuric [Hg(II)], and methylmercury (MADEP, 1996). The specific forms of mercury within flue gas and FGD water are still being studied. Although selenium occurs naturally in the environment and is a micronutrient for organisms, excessive amounts of selenium elicit

toxic effects (ATSDR, 2003). There are four major forms of selenium including elemental, selenate [Se(VI)], selenite [Se(IV)], and selenide [Se(-II)]. Arsenic is found naturally in the environment, and its concentration has increased due to anthropogenic processes (ATSDR, 2005). There are three main forms of arsenic including elemental, arsenite [As(III)], and arsenate [As(V)]. The fate of mercury, arsenic, and selenium are greatly influenced by pH, Eh (redox potential), and other chemical species present within the system.

Large volumes of water from FGD scrubbers are produced daily. In a single North Carolina power plant 0.5 – 1.75 million gallons per day of water are produced (Mooney et al., 2006). Because FGD water contains toxic constituents, there is a tremendous need to treat the water efficiently. The treatment options available must also be cost effective and economically feasible to efficiently remove constituents of concern.

Specifically designed constructed wetland treatment systems (CWTS) can provide effective treatment to several types of wastewater and are being utilized by industry to meet water quality discharge limits. Some of the more common uses for CWTS have been to treat municipal wastewater, acid mine drainage, pulp mill effluent, refinery effluent, agricultural wastes, urban runoff, and landfill leachate (Watson et al., 1989). CWTS are designed to target specific constituents, such as organic and inorganic elements and compounds, for maximum removal through transfers and transformations. Specific transfers and transformations include, but are not limited to, retention, sequestration, precipitation, biotransformation (microbial activity), and abiotic transformations (oxidation, hydrolysis, and photolysis) (Rodgers, 2004). Constructed

wetland treatment systems are largely self maintaining and a cost-effective method to treat constituents of concern in different FGD waters. From experiments with FGD water and pilot-scale constructed wetland treatment systems, targeted constituents have been effectively removed and specific discharge limits have been met.

CWTS generally contain an equalization basin followed by a series of reactors containing vegetation and hydrosoil selected to promote specific transfers or transformations of constituents of concern. At Clemson University microcosm constructed wetland treatment systems were configured to evaluate the removal of mercury, arsenic, and selenium from FGD waters. Treatment systems consisted of four separate 70-gallon wetland reactors (Rubbermaid® Utility Tanks) (Figure 1.2). Prior to entering the reactors, FGD water was retained in a 1,000-gal polypropylene equalization basin. This water was pumped from the equalization basin to the reactors using piston pumps (FMI®) calibrated to a specific flow rate to maintain a predetermined hydraulic retention time (HRT). The water was carried from one reactor to the next by gravity using PVC piping. The first and second reactors of each treatment system contained approximately 30 cm thickness of hydrosoil amended with organic matter to promote reducing conditions within the reactors. These reactors were planted with *Schoenoplectus californicus,* giant bulrush. The third wetland reactor featured a rock cascade constructed of medium-sized granite rocks to oxygenate the water as it entered the reactor. Both the third and fourth reactors contained approximately 30 cm of hydrosoil and were planted with *Typha agustifolia*, cattails, to aid in the oxidation of the hydrosoil.
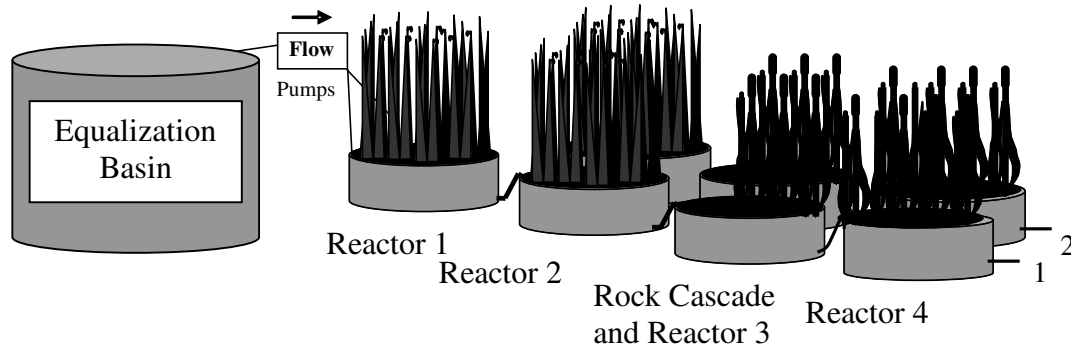
Figure 1.2: Schematic of two pilot-scale constructed wetland treatment systems. Reactors 1 and 2 are planted with *S. Californicus* and Reactors 3 and 4 are planted with *T. agustifolia*.

Full-scale equalization basins are constructed retention pools used to store water and as the primary step in many water treatment systems. Equalization basins have retained waters including sewage, ash sluice, surface mine, and surface runoff waters (Cherry et al., 1984; Greenburg, 1986; Somes et al., 2000). The selection for the design of equalization basins is based on many factors including the size of the power plant, local regulatory policy, site conditions, engineer's judgment and experience, and economics (WEF and ASCE, 1992).

Equalization basins of constructed wetland treatment systems have not been adequately studied. To date, there has been no treatment (transfers or transformations of constituents) for FGD water attributed to the equalization basin. Major purposes of equalization basins include cooling and homogenizing FGD water and settling particulates before this water enters the reactors of the system. FGD water entering an equalization basin is typically 40°C with up to 1,000 mg/L particulates (Mooney, 2006, written communication). The hydraulic retention time for FGD water in an equalization

basin is generally 24 hours. FGD water is cooled to avoid exposing the macrophytes

planted in the CWTS reactors to high temperatures. The settling of particulates in the

equalization basin increases the longevity of the CWTS by keeping unwanted particles

out of the wetland reactors.

Research Objectives and Methods

The specific objectives of this research include:

- Characterize FGD particulates (elements and minerals) from different burned coals that settled in an equalization basin.

- Measure particle size distribution of FGD particulate samples.

- Determine if FGD particles settle within an equalization basin and what the settling rates of these particles are within FGD water samples.

- Determine if Hg, As, and Se concentrations decrease over time within FGD water stored in an equalization basin.

- Determine if the toxicity of FGD water changes within an equalization basin during a hydraulic retention time of 24 hours.

The second chapter of this thesis focuses on characterizing FGD particulates

(elemental and mineralogical analysis and particle size) that settle in an equalization

basin. Four FGD particulate samples obtained from a pilot-scale scrubber were analyzed.

To determine the minerals and elements that comprise FGD particulates from different

burned coals, x-ray diffraction and scanning electron microscopy (SEM) equipped with

electron dispersive spectroscopy (EDS) were utilized. The pipette method (Folk, 1980)

was used to determine particle size distribution of FGD particulates.

The third chapter of this thesis focuses on the role of an equalization basin in treatment of FGD water. Size distribution of the FGD particulates was used along with settling velocity of particulates (Stokes' Law) to determine the time period for particulates to settle in a typical equalization basin with a certain depth. To determine the removal of targeted constituents (Hg, As, and Se) in equalization basins, two pilot-scale equalization basins were utilized. Chemical analyses of six FGD waters were determined for initial and final samples, which simulated inflow and outflow of an equalization basin. Particulates suspended in two of the FGD water samples were digested to determine the concentrations of Hg, As, and Se associated with the particulates. Toxicity of initial and final samples for two FGD waters was measured using a microcrustacean, *Ceriodaphnia dubia*.

Understanding the processes that occur in a constructed wetland treatment system is important for removal of specified constituents for different types of water. Each specific part of a CWTS plays an important role in the removal of constituents of concern and has been designed accordingly for performance. This research will provide further understanding of the role of the equalization basin as a component of a constructed wetland treatment system.

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CHAPTER II

CHARACTERIZATION OF FLUE GAS DESULFURIZATION
PARTICULATES IN EQUALIZATION BASINS

Abstract

Particulates that settle from flue gas desulfurization (FGD) water in an equalization basin of a constructed wetland treatment system were characterized physically and chemically. Powder x-ray diffraction and scanning electron microscopy with electron dispersive spectroscopy were used to identify mineralogy and elemental composition of the particulates. Settling analysis based on Stokes' Law was performed to determine particle size. The most common particle type was gypsum ($CaSO_4 \cdot 2H_2O$) comprising approximately 95% of the samples. A second particle type was interpreted as fly ash and comprises up to 5% of the samples. The fly ash particles contained carbon and metals including Al, Fe, Mg, and Ti. Minor particles containing Fe, Al, K, and Si were interpreted as oxides formed in the coal combustion chamber. FGD particulates contain a mixture of solids representing combustion and wet scrubbing processes at coal-fired power plants.

Introduction

New laws implemented by the United States Environmental Protection Agency (USEPA) require coal-fired power plants to reduce gaseous emissions of sulfur dioxide and mercury vapors (Schweinfurth, 2005). To comply with these laws, flue gas

desulfurization (FGD) scrubbers are being added to existing power plants. The most common system used in the United States is the calcium (limestone)-based wet scrubber (Kalyoncu, 1999), which can remove 95% of sulfur dioxide from flue gas (Termuehlen and Emsperger, 2003). In the FGD process, a slurry of water, limestone ($CaCO_3$), and organic acids mixes with the sulfur dioxide and forms calcium sulfite, which when further oxidized, forms calcium sulfate. This slurry is then dewatered, producing large amounts of water and gypsum, a byproduct used in production of wallboard (Kovacs and Molnar, 2003). In 2005, domestic coal-fired power plants in the United States produced 11.95 million metric tons of gypsum through the FGD process (American Coal Ash Association, 2006), with estimates showing that production will increase (Founie, 2004). Solid product not removed during the dewatering process remains suspended within FGD water.

Composition of the FGD water and associated particulates depends on composition of the burned coal, scrubbing materials such as limestone, and slurry water used in the FGD process (Mierzejewski, 1991). FGD water may require treatment prior to discharging to the environment in order to meet limits set by the USEPA for concentrations of inorganic and organic constituents. Mercury, arsenic, and selenium concentrations are of the greatest concern within FGD water.

Our investigation focuses on FGD particulates in equalization basins of constructed wetland treatment systems (CWTS). CWTS are being built at coal-fired power plants to treat FGD waters for discharge or reuse. CWTS are proving to be a viable option for this purpose. These systems target a wide range of constituents in many

types of wastewaters (Knight et al., 1999; Gillespie et al., 2000; Murray-Gulde et al., 2003a; 2003b) and can reduce concentrations of constituents that do not meet National Pollutant Discharge Elimination System (NPDES) limits. Pilot-scale treatment systems are used to monitor treatment and then predict performance of future full-scale CWTS. The basic design of CWTS used for treatment of FGD water includes an equalization basin followed by reactors containing vegetation and hydrosoil selected to promote specific transfers and transformations of constituents of concern.

An equalization basin is a constructed retention pool that allows water to cool and homogenize and particulates to settle. At thermo-electric power plants, FGD water enters the equalization basin at a temperature of approximately 40°C and may contain particulate concentrations of 1,000 mg/L (Mierzejewski, 1991; Doug Mooney, 2006, written communication). Equalization basins used for FGD water are usually designed to store water for one day and cool the water to 35°C (McCarthey et al., 2005). Equalization basin design parameters include daily water volume produced by the power plant, settling rate of particulates, and geographic location of the power plant.

Byproducts of coal combustion and flue gas desulfurization include fly ash, bottom ash, boiler slag, and FGD sludge. Many past studies (Khanra et al., 1998; Sulovsky, 2002; Gieré et al., 2003; and Pires and Qeurol, 2004) have focused on characterization of fly ash, which is uncombusted material produced after coal powders burn at temperatures between 1300 and 1500°C (Ma et al., 1999). However, very few studies (Laperche and Bigham, 2002; Kovacs and Molnar, 2003; and Bigham et al., 2005) have focused on FGD particulates and sludge.

The purpose of this investigation was to characterize particulates that settle within an equalization basin of a constructed wetland system used to treat FGD water. The objectives were: 1) to determine physical properties and elemental and mineralogical compositions of FGD particulate samples; and 2) to measure particle size distribution of the samples. Analytical results were compared with published descriptions of coal combustion byproducts from thermoelectric power plants. Origin of particulates was interpreted from characterizing minerals and elements present in the samples. Identifying types of particulates settling from FGD water in an equalization basin is necessary for determining optimal reuse and disposal procedures once the maximum capacity of the basin is reached. This analysis may be useful for the design of future equalization basins of CWTS.

Methods

Particles were collected from four FGD water samples (numbered 1 to 4), each of which was obtained from a pilot-scale wet scrubber located at a coal-fired power plant in North Carolina. Each water represented combustion of a different low-sulfur eastern bituminous coal. The FGD waters were transported to Clemson University for treatment in a pilot-scale CWTS. In addition, a fly ash sample collected from a coal-fired power plant in North Carolina was analyzed. The fly ash was the product of burning a low-sulfur bituminous coal.

Color, shape, crystal form, size, and surface texture of the FGD particulates were observed using a stereographic binocular microscope. Color provided a useful discriminator for separating particles. Black particles were separated into magnetic and

15

non-magnetic fractions using a hand magnet. Following methodology of Folk (1980),

particle size distribution was determined for FGD particulates collected from two of the

four waters (Table 2.1). Sample size was too small to determine particle size distribution

for the other two samples. Approximately 15-20 g of samples was needed to perform the

analysis. Sand size particles were separated using a 62 micron sieve, dried, and weighed.

The finer fraction (<62 µm) was suspended in a 1,000 mL graduated cylinder filled with

distilled water. Following methodology of Folk (1980), a pipette was used to withdraw

samples from the graduated cylinder at specific time intervals. The samples were then

dried at 100ºC for 24 hours and weighed. The times and withdrawal depths for particles

were calculated using Equation 1:

$$T = \frac{Depth}{1500 * A * d^2} \qquad\qquad Equation\ 2.1$$

where T is time (min), $Depth$ is the sampling depth (cm), A is a constant based on

viscosity of water, gravity, and density of the particles, and d is the particle diameter

(mm). An A value for a particle density of 2.32 gm/cc (gypsum) was extrapolated using

known A values (Folk, 1980; Gee and Bauder, 1986) for particle densities 2.4, 2.65, 3.0,

and 3.35 gm/cc. The A value used in this experiment was 3.00, which was based on a

water temperature of 22ºC. Cumulative particle size distribution curves were constructed

from weights of the size fractions. Statistical parameters including graphic mean,

median, mode, inclusive graphic standard deviation and skewness, and graphic kurtosis

were calculated using values from the distribution curves.

An Hitachi 3400 Scanning Electron Microscope (SEM) was used to characterize features of particles and identify any particle types not recognized using a binocular microscope. Samples for SEM analysis were prepared by adhering dried particles to carbon tape-covered stubs (specimen mounts). Each particle type was mounted on a separate stub. Elemental composition of individual particles was determined with elemental dispersive spectroscopy (EDS) using an Oxford Inca 400 EDS with the Oxford Instrument software package INCA.

Mineral composition of particles was determined by powder x-ray diffraction (XRD) using a Scintag 2000 diffractometer and a Rigaku Miniflex diffractometer. Samples were powdered using a porcelain mortar and pestle. The XRD data were collected from 2-60° 2θ at a step scan rate of 0.04 deg/min using a CuKα x-ray source. In addition to samples listed in Table 2.1, sand size particles separated from FGD samples 1, 3, and 4, and silt and clay size particles separated from FGD samples 1 and 2 were analyzed by XRD. A mixture of sand size black and white particles was analyzed separately from the other particle samples. Splits of FGD samples 3 and 4 were exposed to dilute acetic acid for removal of carbonate minerals according to United States Geological Survey (USGS) methods (Poppe et al., 2001) and then analyzed by XRD. Diffraction peaks were identified using Scintag-DSMNT and Jade 5 software and by matching d-spacings to published values.

Table 2.1: Summary of procedures used to characterize solid material in FGD water samples. The methods include visual observation, particle size distribution (PSD), x-ray diffraction (XRD), and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS).

Sample	Procedures			
	Visual	PSD	XRD	SEM/EDS
FGD Sample 1	X		X	X
FGD Sample 2	X		X	X
FGD Sample 3	X	X	X	X
FGD Sample 4	X	X	X	X
White Particles[1]	X		X	X
Black Particles[2]	X		X	X
Orange Particles[3]	X			X
Other (rare) Particles				X
Fly Ash Particles	X	X	X	X

[1]from all FGD samples   [2]from FGD Samples 4   [3]from FGD Samples 1, 2, 3

Results

Bulk FGD Particulates

FGD samples 1 through 4 ranged in color from light brown to dark-grayish brown. Wet FGD samples were muddy in consistency due to a high content of silt and clay size material. After drying the particulate samples, it was observed that three main types of particles were present based on color: white, orange, and black (Figure 2.1).

Particle size distribution was unimodal in both samples analyzed (Tables 2.2; Figure 2.2), with each sample consisting predominantly of silt-size particles (2-62.5 µm). The graphic mean size of FGD sample 3 is 5.3 φ with an inclusive graphic standard deviation of 0.34 φ, indicating very well sorted medium silt (Table 2.3). FGD sample 4 particles have a graphic mean of 4.7 φ with an inclusive graphic standard deviation of

0.29 φ, which corresponds to very well sorted coarse silt. The inclusive graphic

skewness for both samples was determined to be near symmetrical, indicating that the

size distribution curve is approximately symmetrical about the mean. The graphic

kurtosis determined by the size distribution curve indicates that FGD sample 3 is very

leptokurtic and FGD sample 4 is leptokurtic. Therefore, particle sizes near the mean are

better sorted than particle sizes further from the mean. The statistical parameters indicate

that the FGD particulate samples have a narrow range in size.
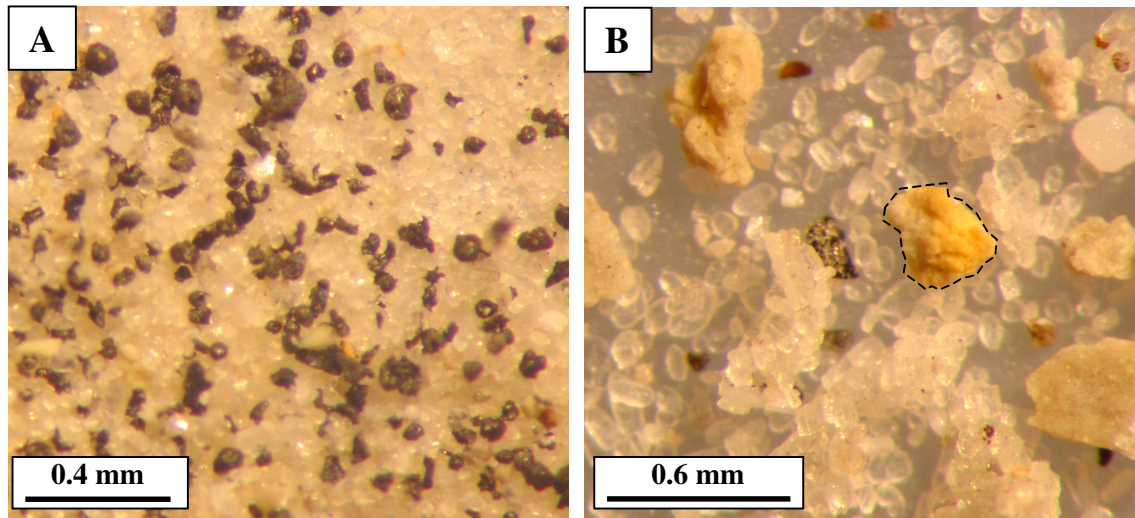
Figure 2.1: Photographs of FGD particulate samples. (A) Sand size white particles and
black particles from FGD sample 4. (B) White particles and an orange aggregate
(outlined) within the >62.5 µm (sand size) fraction of FGD sample 1.

Table 2.2: Particle size distribution for FGD samples 3 and 4, phi (φ) = -$\log_2$ (diameter in mm); grain size name based on Wentworth (1922). Cumulative values were interpolated from the grain size curves (Figure 2.2).

Diameter (mm)	Phi Scale (φ)	Wentworth Size Class	Cumulative % FGD sample 3	FGD sample 4
0.0625	4	v. fine sand	0.65	2.27
0.053	4.25	coarse silt	3.05	6.90
0.044	4.5	coarse silt	5.10	18.5
0.037	4.75	coarse silt	7.41	52.2
0.031	5	coarse silt	14.5	78.1
0.022	5.5	medium silt	87.1	96.6
0.016	6	medium silt	96.5	97.8
0.011	6.5	medium silt	98.0	99.1
0.0078	7	fine silt	98.5	99.3
0.0055	7.5	fine silt	99.0	99.5
0.0039	8	v. fine silt	99.0	99.8
0.0028	8.5	v. fine silt	99.1	99.8
0.002	9	clay	99.1	99.9
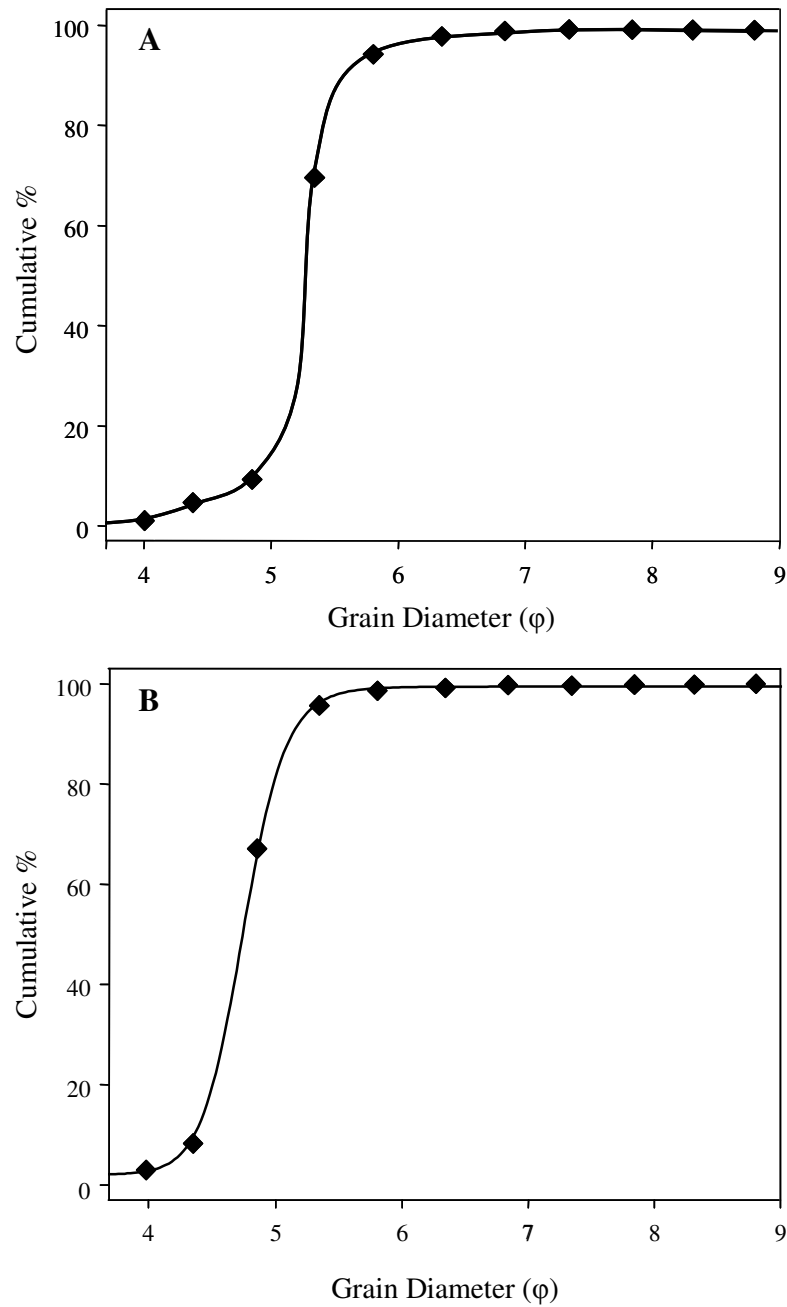
Figure 2.2: Cumulative size distribution curves. (A) FGD sample 3 (B) FGD sample 4

Table 2.3: Graphic formulas and statistical values (Folk, 1980) for FGD samples 3 and 4. All values (φ_{16}, φ_{50}, φ_{84}, etc.) in the equations are determined from the cumulative curves (Figure 2.2), where φ_x corresponds to the phi value at x cumulative percent. IG = Inclusive graphic, NS = Near symmetrical

		Value	
Name	Equation	FGD sample 3	FGD sample 4
Graphic Mean	$Mz = \dfrac{(\varphi_{16} + \varphi_{50} + \varphi_{84})}{3}$	5.3 φ medium silt	4.7 φ coarse silt
Median	$Md = \varphi_{50}$	5.3 φ	4.7 φ
Mode	$M_o = $ Most frequently-occurring particle diameter	5.2 φ	4.8 φ
IG Standard Deviation	$\sigma_1 = \dfrac{\varphi_{84} - \varphi_{16}}{4} + \dfrac{\varphi_{95} - \varphi_5}{6.6}$	0.34 φ v. well sorted	0.29 φ v. well sorted
IG Skewness	$Sk_1 = \dfrac{\varphi_{84} + \varphi_{16} - 2\varphi_{50}}{2(\varphi_{84} - \varphi_{16})} + \dfrac{\Phi_{95} + \varphi_5 - 2\varphi_{50}}{(\varphi_{95} - \varphi_5)}$	-0.09 NS	0.06 NS
Graphic Kurtosis	$K_G = \dfrac{(\varphi_{95} - \varphi_5)}{2.44(\varphi_{75} - \varphi_{25})}$	2.8 v. leptokurtic	1.2 leptokurtic

FGD Particle Types

Translucent White Particles

White particles were the most common (~95% based on visual observation) particle type represented in FGD samples 1 through 4. The size of these particles ranged from clay to sand. The sand-size particles were mostly vitreous and translucent. Many of the white particles were crystalline with a rhombohedral shape. The surfaces of the rhombehedral particles appeared smooth with rare divots (Figure 2.3A). Shape of non-rhombehedral white particles (Figure 2.3B) were rounded, and sphericity was high based on the classification of Powers (1953) cited by Folk (1980). Small rows of indentations were present across the surface of the non-rhombehedral white particles (Figure 2.3B).

SEM examination revealed that small spheres (<1 µm diameter) were attached to the white particles (Figure 2.3B).

Based on elemental analysis by EDS, individual white particles contained oxygen, carbon, calcium, and sulfur with trace amounts (~1%) of silicon and aluminum (Table 2.4). A dark, circular indentation was observed in one white particle. EDS analysis of the indentation detected fluorine (5%), aluminum (~1%), and silicon (~1%) in addition to carbon, oxygen, calcium, and sulfur.

Calcium sulfate hydrate (gypsum) was identified by XRD as the predominant mineral in FGD samples 1 through 4, the sand size particles collected from FGD samples 1, 3, and 4, and the silt and clay size particles separated from FGD samples 1 and 2 (Figure 2.4A). Samples treated with acetic acid for removal of carbonates did not show a difference in XRD pattern between pre-treatment and post-treatment, indicating that carbonate minerals are not present within FGD samples 3 and 4 or do not represent a large enough fraction to be identified using XRD.

The white particles in the FGD samples were identified as gypsum ($CaSO_4 \cdot 2H_2O$) based on crystal shape, EDS analysis, and XRD. The EDS data indicate that the molar ratio between sulfur and calcium is 1:1 and the molar ratio between calcium and oxygen is 1:6. The sulfur to calcium ratio is consistent with the empirical formula for calcium sulfate. However, the empirical formula for calcium sulfate requires only four moles of oxygen per mole of calcium instead of the observed six. The excess oxygen is accounted for by the presence of water in hydrated calcium sulfate (gypsum).
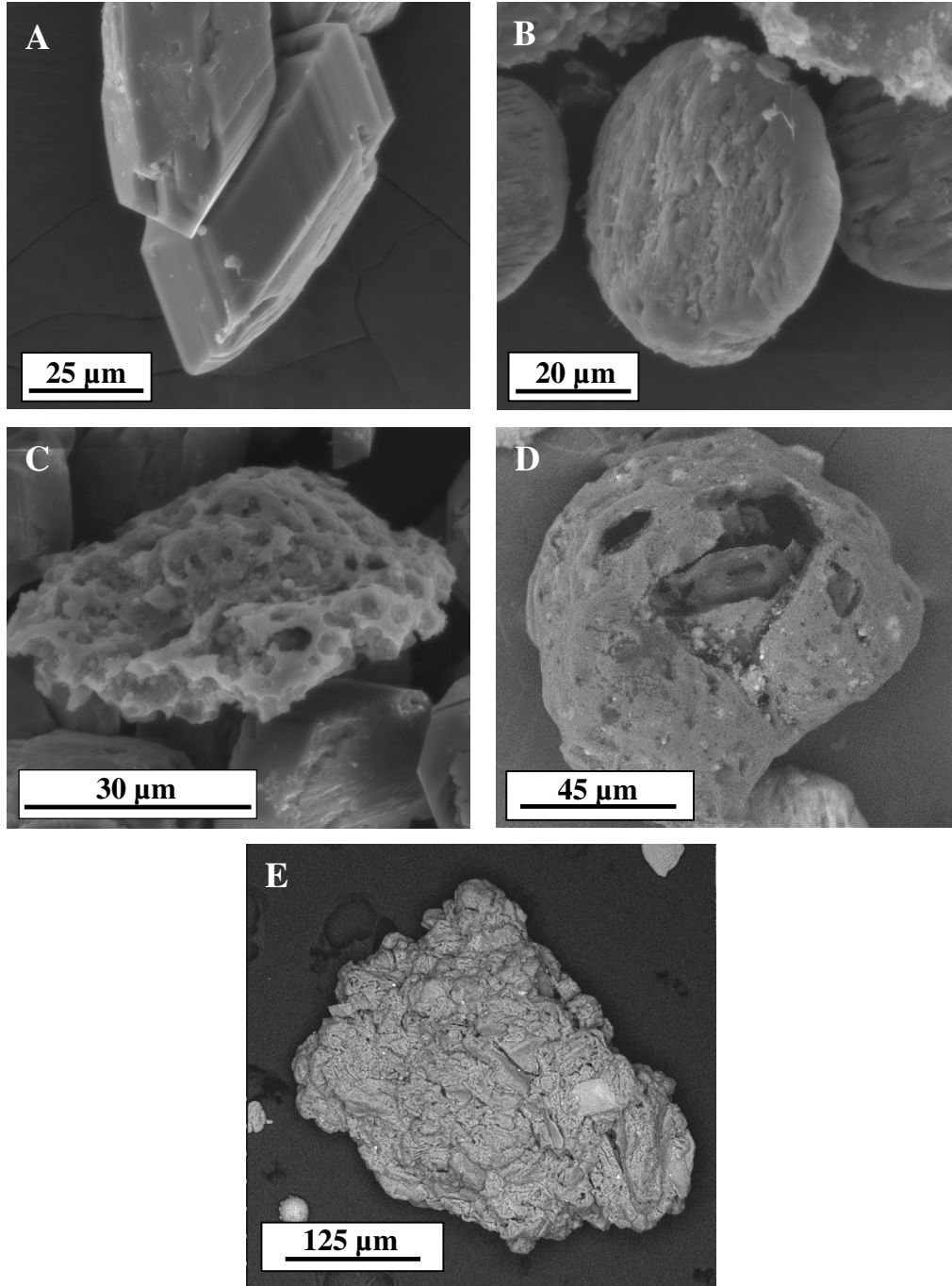
Figure 2.3: SEM photomicrographs of the three main FGD particle types. (A) White particle with well defined rhombehedral crystal form; small divots are present on the grain surface. (B) White particle with round shape and rough surface; small spheres are attached to upper portion of the particle. (C) Black particle with pitted surface. (D) Black particle with partially hollow interior. (E) Orange aggregate.

Table 2.4: Elemental composition of particle types analyzed by EDS. Mean percent (and range) are listed based on 6 white particles (18 points of elemental analysis), 7 orange particles (23 points of elemental analysis), and 8 black particles (5 non-magnetic, 3 magnetic; 17 points of elemental analysis). ND = Not Detected

	White Particles Mean (Range)	Orange Particles Mean (Range)	Non-magnetic Black Particles Mean (Range)	Magnetic Black Particles Mean (Range)
C	14 (3.7 - 30)	20 (9.5 - 45)	70 (54 - 82)	27 (4.0 – 70)
O	48 (31 - 57)	42 (19 – 54)	17 (12 - 24)	37 (19 - 54)
Al	0.10 (0 - 0.72)	3.7 (0.35 – 12)	1.7 (0 - 3.5)	3.8 (0.85 - 7.7)
Si	0.16 (0 - 0.98)	17 (0.63 – 30)	4.0 (0.91 - 8.3)	13 (1.3 – 22)
S	15 (0.91 - 22)	0.40 (0 - 1.2)	2.3 (0.81 - 4.6)	4.2 (0.40 - 15)
Ca	19 (4.1- 28)	1.8 (0 - 3.2)	3.6 (0.94 - 8.0)	4.2 (0.58 - 10)
Fe	ND	13 (0.86 – 53)	0.52 (0 - 2.6)	6.5 (0.86 - 33)
K	ND	0.78 (0 - 10)	0.51 (0 - 2.8)	3.4 (0 - 8.6)
Mg	ND	0.41 (0 - 0.86)	ND	0.78 (0 – 2.2)
Ti	ND	0.75 (0 - 1.4)	ND	0.22 (0 - 1.2)
Mo	ND	0.10 (0 - 1.3)	ND	ND
F	ND	ND	0.24 (0 – 2.2)	ND
Na	ND	ND	ND	0.20 (0 – 1.2)
Cl	ND	ND	ND	0.23 (0 – 1.4)
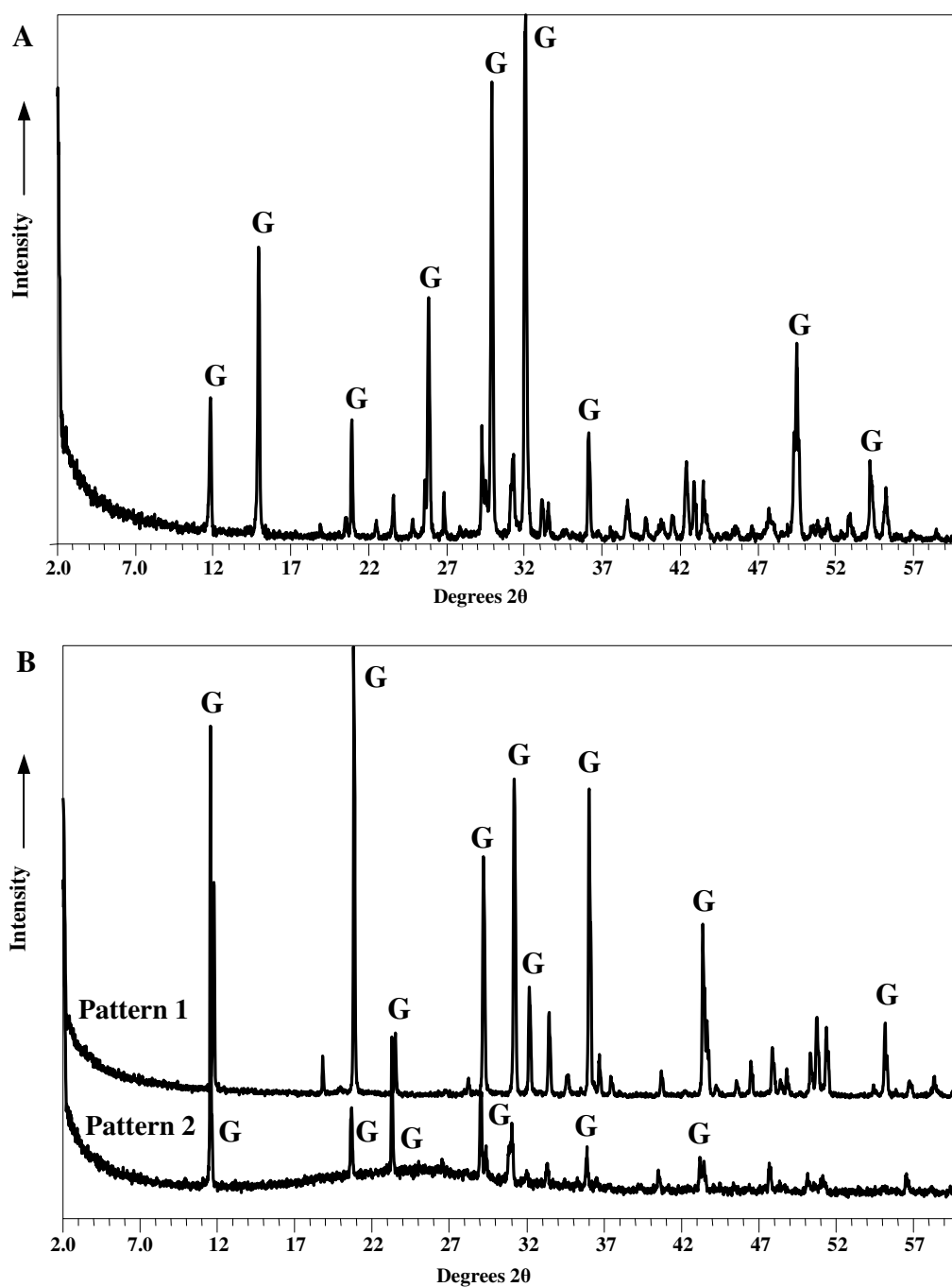
Figure 2.4: Powder XRD patterns. (A) FGD sample 1: gypsum is the predominant mineral present. (B) FGD sample 4: Pattern 1, which is for the bulk sample, indicates gypsum; Pattern 2, which is from analysis of a mixture of white and black particles. The presence of amorphous material is indicated by the broad hump between 17º and 32º 2θ. G = Gypsum

Black Particles

Black particles, which were metallic in luster, comprised up to approximately 5% of the FGD samples. Black particles ranged from clay to sand in size. The shape of the black particles was highly variable and ranged from angular to subrounded; sphericity ranged from low to high. Surfaces of the black particles were pitted and porous (Figure 2.3C). The surface of several particles was broken, exposing a hollow interior that contained small spheres (Figure 2.3D). These spheres, less than 2 µm in diameter, were similar in size and shape to the small spheres attached to the white particles.

Approximately 5% of the black particles were magnetic. Based on EDS analysis both magnetic and non-magnetic black particles contained carbon, oxygen, silicon, calcium, aluminum, sulfur, iron, and potassium (Table 2.4). In addition, fluorine was present in the non-magnetic particles, while the magnetic particles contained trace amounts of magnesium, chlorine, sodium, and titanium. As expected, iron content in the magnetic particles was greater than that in the non-magnetic particles. The XRD pattern for a mixture of white particles and black particles, including both magnetic and non-magnetic, was similar to that for the particle sample containing only white particles. The pattern indicated mineralogy of gypsum. Based on the presence of a broad hump in the XRD pattern, the black particles are interpreted to be amorphous material.

Orange Particles and Aggregates

Orange silt-size particles and sand-size aggregates represented a trace amount (~1%) of the FGD particulate samples. Sand-size orange aggregates were composed of the smaller silt-size orange particles. The luster of the orange particles ranged from

greasy to resinous, and all orange particles were opaque. Most of the particles were angular and low in sphericity with an uneven surface texture (Figure 2.3E). Orange particles contained carbon, oxygen, iron, and silicon, with trace amounts of aluminum, sulfur, calcium, magnesium, titanium, potassium, and molybdenum (Table 2.4).

Other (Rare) Particles

In addition to the three major particle types described, three additional particle types that occur rarely in the FGD samples were observed using SEM: 1) subangular aggregates; 2) a sphere (25 µm diameter) with raised surface features; and 3) a flat, angular particle with a slightly uneven surface (Figure 2.5). Based on EDS analysis the subangular aggregates consisted of predominantly calcium (18-41%), carbon (12-19%), and oxygen (36-56%). Sulfur content (2%) was too low for the particles to be gypsum. The EDS data indicated a molar ratio of Ca to C equal to 1:1 and a ratio of C to O of 1:3. These ratios are consistent with the empirical formula for calcium carbonate ($CaCO_3$). The sphere contained mostly oxygen (33-37%), carbon (24-27%), iron (13-22%), silicon (10-12%), aluminum (6-7%), and magnesium (3-4%). The raised features on the sphere contained mostly calcium, sulfur, and oxygen, which could indicate the presence of calcium sulfate crystals on the particle surface. The flat, angular particle with a slightly uneven surface consisted of predominantly zinc (26-42%), oxygen (25-28%), and carbon (28-40%), with trace amounts of chlorine and iron.
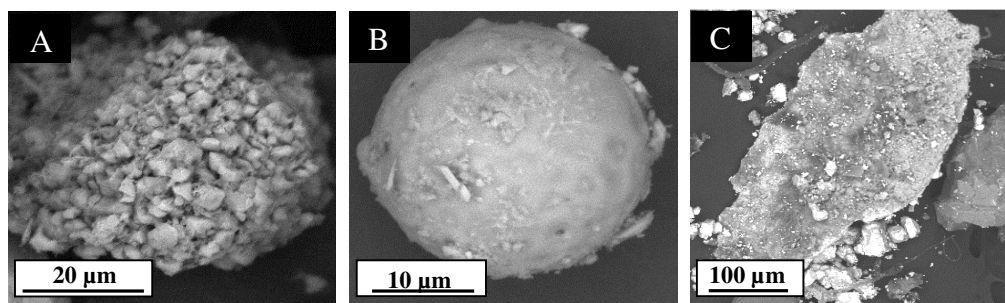
Figure 2.5: SEM photomicrographs of other (rare) particles. (A) Subangular aggregate; (B) Sphere; (C) Flat, angular zinc-rich particle

Fly Ash Particles

Based on visual observation, bulk fly ash particles studied were fine-grained (less than 80 µm). Separating the particles by size revealed that sand-size particles were black, and clay and silt-size particles were dark gray. SEM analysis identified two major particle types present within the fly ash: smooth, spherical particles and pitted, non-spherical particles (Figure 2.6A). The smooth, spherical particles, which were 10 to 50 µm in diameter, were the most common particle type (~90%). Smaller spheres (~1-5 µm) were attached to many of these particles. The pitted, non-spherical particles were sand size, angular in shape and low to high in sphericity.

Based on EDS analysis, smooth, spherical particles within the fly ash contained oxygen (25-53%), iron (1.5-47%), silicon (7-24%), and aluminum (4-22%). Pitted, non-spherical particles contained carbon (76-85%) and oxygen (12-19%), with trace amounts of silicon and aluminum. Based on XRD analysis (Figure 2.6B), the fly ash particles consisted of synthetic mullite (aluminum silicon oxide). A broad hump was present in the XRD patterns, indicating the presence of amorphous material.

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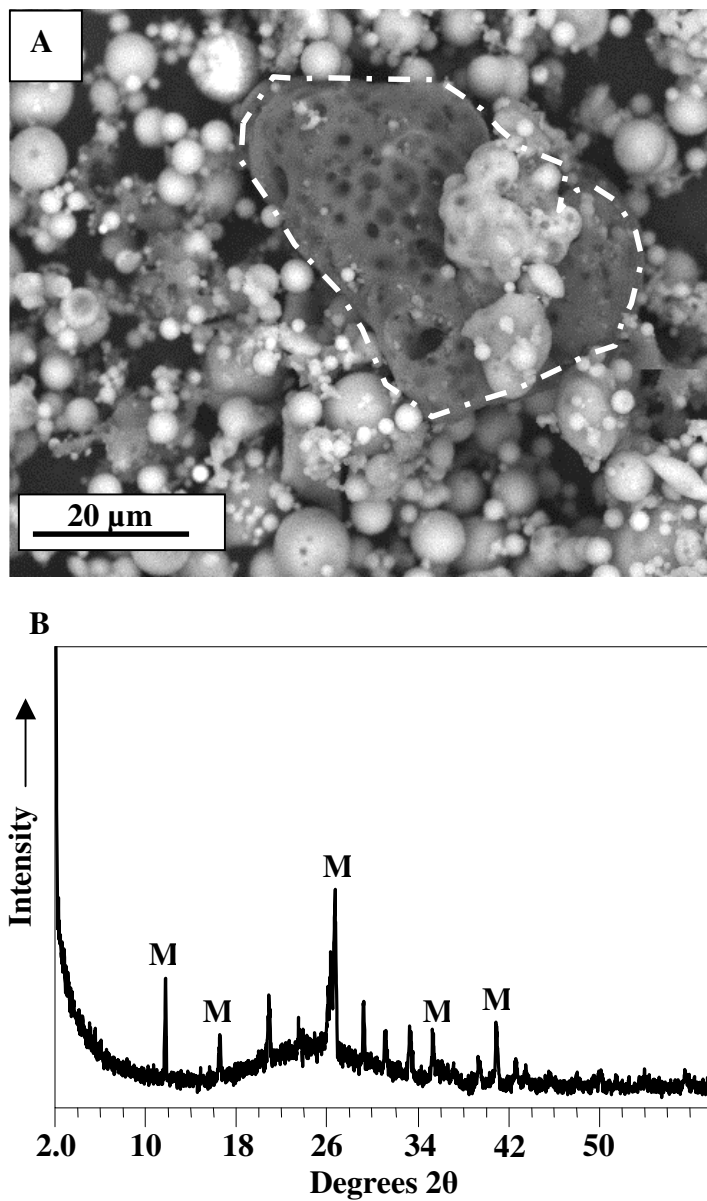
Figure 2.6: Fly ash sample. (A) SEM photomicrograph showing abundant smooth, spherical particles and a pitted, non-spherical particle (outlined). (B) XRD pattern indicating mineralogy of mullite within the silt and clay fraction. M = Mullite

Discussion

Results indicated that the dewatering step in the FGD process did not completely

separate the solid product from the water, and that approximately 95% of particles

remaining in the water was gypsum ($CaSO_4 \cdot 2H_2O$). Abundance of gypsum in FGD

particles is expected due to reactions that occur during the scrubber process. The amount

of gypsum in FGD water may vary depending on the scrubbing process, efficiency of the

dewatering process, and amount of particulates removed by clarifiers before FGD water

enters the equalization basin. The predominance of silt-size particles in the samples

analyzed is consistent with observations of Kovacs and Molnar (2003). Their study

determined that the average grain size of dewatered FGD gypsum byproduct from a wet-

scrubber was 0.043 mm (4.6 φ), which is slightly larger than mean size (4.7 φ and 5.2 φ)

of FGD samples analyzed in this investigation. The narrow range in size of the FGD

particulates may indicate that most of the particles represent the same process of

formation.

Kost et al. (2005) and Bigham et al. (2005) characterized mineralogy of FGD

products from different dry FGD processes and concluded that many of these products

contain portlandite ($Ca(OH)_2$), hannebacite ($CaSO_3 \cdot 0.5H_2O$) (from duct injection and

spray dryers), lime (CaO), anhydrite ($CaSO_4$), and calcite ($CaCO_3$) (from lime injection

and fluidized bed processes). The differences in wet and dry scrubbing techniques are

responsible for differences in mineralogy: dry processes produce calcinated products and

wet processes produce hydrated calcium sulfate (gypsum). Dry scrubber processes use a

lime slurry that creates a dry product lacking the moisture content necessary to form

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gypsum. Kovacs and Molnar (2003) examined FGD material collected from a wet scrubber and found that calcite was absent indicating complete conversion to gypsum.

The non-magnetic black FGD particles are interpreted as fly ash because of their similarity to the non-spherical fly ash particles based on the following properties: color, shape, surface texture, and chemical composition (Table 2.5). Shape of both particle types is angular with low sphericity, and both have a pitted surface. The most abundant elements in both particle types are carbon and oxygen, with trace amounts of aluminum and silicon present. Because of these similarities, the non-magnetic black FGD particles are interpreted as fly ash. Külaotos et al. (2003) interpreted particles similar to the non-magnetic black particles as unburned carbon within coal fly ash.

Based on elemental composition and shape, the magnetic black FGD particles are similar to magnetic particles within fly ash identified by Hower et al. (1999) and Kukier (2003). Magnetic fractions of fly ash analyzed in previous studies contain magnetite (Fe_3O_4) and hematite (Fe_2O_3), with smaller fractions of quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$) (Hower et al., 1999; Kukier et al., 2003). The major elements represented in these fly ash minerals are the same as those identified in the magnetic black FGD particles: iron, silicon, oxygen, and aluminum. Kukier et al. (2003) observed that some magnetic fly ash particles were "vesiculate and spongy", which is analogous to the magnetic black FGD particles described in the current study. We interpret the magnetic black FGD particles to be magnetic fly ash particles that originated from the coal combustion chamber, where coal is burned and fly ash is generated (Gieré, 2003).

Spherical particles in the fly ash sample and FGD particulate samples (Figure 2.7), including the small spheres attached to FGD particles, are identified as cenospheres based on similarities in size, shape, surface texture, and elemental composition to cenospheres described in previous studies (Gieré et al., 2003; Vassilev et al., 2004; Goodarzi, 2006). Cenospheres are defined as hollow, ceramic microspheres produced within thermo-electric power plant combustion chambers; size of cenospheres is typically 20-250 µm (Vassilev et al., 2004). Cenospheres found in the FGD particulates of our study are interpreted to have been transported by flue gas to the scrubber system. Composition of the cenospheres identified in our investigation is similar to that of cenospheres analyzed in previous studies (Vassilev et al., 2004; Goodarzi, 2006), with high concentrations of oxygen, iron, aluminum, silicon, calcium, and magnesium. The mineral composition of cenospheres includes aluminosilicates, mullite, quartz, calcite, Fe oxides and Ca silicates (Hulett and Weinberger, 1980; Gieré et al., 2003; Vassilev et al., 2004).

Table 2.5: Characteristics of particle types identified in FGD particulate samples. Fly ash included for comparison. Major elements (>10%) and minor elements (<10%) are listed from most abundant to least abundant. sa = subangular, sr = subrounded, FGDS = Flue gas desulfurization scrubber, OC = Uncombusted material from original coal, CCB = Coal combustion byproduct produced within the coal combustion process

Particle Type	Size	Roundness/ Sphericity	Surface Texture	Major Elements	Minor Elements	Identification	Interpreted Origin
White	clay-sand	rounded/high*	smooth divots, indentations	O, C, Ca, S	Si, Al	Gypsum	FGDS
Black							
non-magnetic	clay-sand	sa-sr/low-high	pitted, porous	C, O	Si, Ca, S, Al, Fe, K, F	Unburned carbon	OC
Magnetic	clay-sand	sa-sr/low-high	pitted, porous	C, O, Fe, Si	Ca, S, Al, K, Mg, Cl, Ti, Na	Magnetic fly ash	CCB
Orange	silt-sand	angular/low	uneven	O, C, Si, Fe	Al, Ca, K, Ti, Mg, S, Mo	Iron oxide**	CCB
Other							
aggregate (rare)	silt-sand	sa/high	---	O, Ca, C	Mg, S, Si, Al	Limestone**	FGDS
sphere (rare)	silt	rounded/high	raised features	O, C, Fe	Si, Ca, Al, S, Mg,	Cenospheres**	CCB
flat, Zn rich (rare)	sand	angular/low	uneven	C, Zn, O	Cl, Fe	Fly ash**	OC
Fly Ash							
smooth, spherical	clay-silt	rounded/high	smooth	O, Si, C, Al	Fe, K	Mullite	CCB
pitted, non-spherical	sand	angular/low-high	pitted	C, O	Si, Al	Mullite	OC

* Many particles were rhombehedral in shape.

** Interpreted from similar size, shape, and elemental composition of coal combustion and FGD byproducts identified in previous studies (Khanra et. al, 1998; Ma et al., 1999; Sulovsky et. al, 2002; Gieré et al, 2003; Kovacs and Molnar, 2003; Vassilev et al., 2004, Bigham et al., 2005; Vassilev et al., 2005; Goodarzi, 2006).
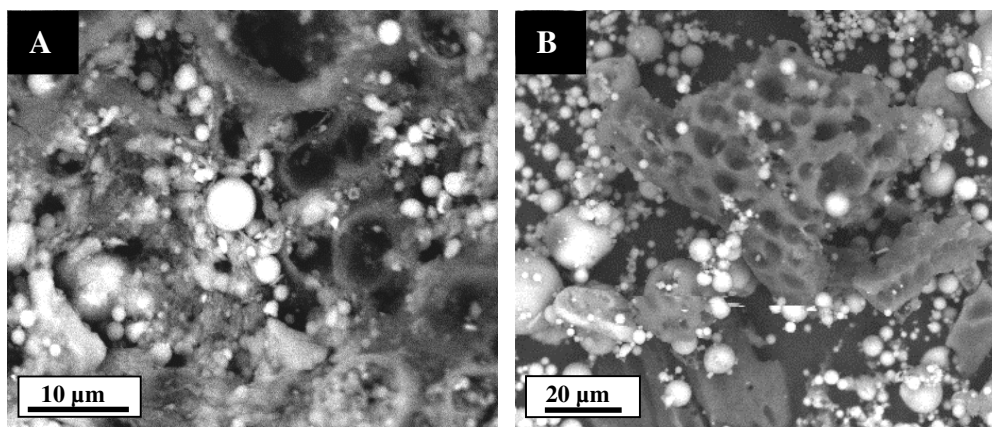
Figure 2.7: SEM photomicrographs comparing FGD particles with fly ash. (A) Black FGD particle with spheres attached. (B) Fly ash sample containing both pitted, non-spherical particles and smooth, spherical particles. Spheres in both samples are interpreted as cenospheres formed during coal combustion.

Large iron content (up to 53%) of the orange particles suggests that their color is caused by the presence of oxidized iron. Iron oxides (hematite), iron spinel (magnetite), and pyrite (oxidized to limonite/goethite) (Table 2.6) have been identified in previous studies of fly ash (Khanra et al., 1998; Sulovsky et al., 2002; Vassilev et al., 2005). Khanra et al. (1998) suggested that the iron-bearing minerals are derived from coal burned within the combustion chambers of coal-fired power plants. We interpret orange particles of the FGD particulate samples to have formed within the power plant combustion chamber and transported by flue gas to the scrubber.

Table 2.6: Typical byproducts from coal combustion and scrubber processes identified in previous studies (Ma et al., 1999; Gieré et al, 2003; Kovacs and Molnar, 2003; Vassilev et al., 2004, Bigham et al., 2005; Vassilev et al., 2005). Materials identified in samples of our study include limestone, gypsum, and mullite. FA = Fly ash, FGD = Flue gas desulfurization

Byproduct	Composition	Origin
Gypsum	$CaSO_4\ H_2O$	FGD / wet scrubber
Calcite/limestone	$CaCO_3$	FGD / lime injection, wet scrubber
Mullite	$Al_6Si_2O_{13}$	FA / combustion chamber
Portlandite	$Ca(OH)_2$	FGD / duct injection, spray dryer process
Hannebachite	$CaSO_3 \cdot 0.5H_2O$	FGD / duct injection, spray dryer process
Periclase	MgO	FGD and FA / fluidized bed process
Lime	CaO	FGD / lime injection
Hematite (iron oxide)	Fe_2O_3	FA / original coal, combustion chamber
Magnetite (iron spinel)	Fe_3O_4	FA / original coal, combustion chamber
Quartz	SiO_2	FA / original coal, combustion chamber
Pyrite	FeS_2	FA / original coal, combustion chamber
Aluminum oxide	Al_2O_3	FA / combustion chamber

Based on EDS analysis, the rare subangular aggregate was determined to be $CaCO_3$. Because $CaCO_3$ is used as the initial material for the FGD reactions, we interpret the origin of this particle to be from limestone that did not react with elements or compounds in flue gas during the scrubbing process. The rare, flat, zinc rich particle is interpreted to be unburned coal or a coal combustion byproduct produced in the coal combustion chamber. Zinc is commonly found as a trace element within coal fly ash (Khanra et al., 1998; Pires and Querol, 2004; Vassilev et al., 2004) and as a secondary inorganic element within coal (Malvadkar et al., 2004).

The abundance of carbon associated with FGD particulates determined by EDS has not been documented by previous research studies. Possible cause may include the effect from the carbon tape, a film coating across the particle, or added to the particle during the coal combustion and FGD processes. Effect of the carbon tape is unlikely to account for the abundance of carbon. Particulates used in this investigation were approximately 10-30 microns thick and penetration of the EDS is no more than 1 µm. Evaluation of the points of identification on each particulate showed no correlation between actual location of the point and carbon content (i.e. closer or further from the edge of the particle). Particulates were removed from the FGD water that contained a non-purgeable organic carbon (NPOC) content of 13 to 48 mg/L. This carbon may have coated the particulates. The formation of the particulates in FGD water includes both coal combustion and flue gas desulfurization. Carbon is a major component in coal, exists in the flue gas as carbon dioxide, and is a component of the lime slurry. These processes may incorporate the carbon into the particulates. Further investigation is needed to determine the actual source of the carbon determined by EDS in this investigation.

Disposal or reuse of the large quantity of solid byproducts of the FGD scrubbing process is an important economic and environmental issue. As environmental air quality regulations become more stringent, thermo-electric power plants will increasingly incorporate FGD systems, and the volume of FGD water and associated particulates will increase. Additional storage and new options for reuse are needed. Coal combustion and FGD byproducts are being used for cement and construction materials, wallboard,

agriculture, and mining (Punshon et al., 1999; Kalyoncu, 2001; Iyer and Scott, 2001, Laperche and Bigham, 2005; and Yazıcı, 2007). Major factors impacting reuse are purity of FGD byproducts, state regulations for reuse, toxicity of particulates, and ease of transporting FGD sludge. Our evaluation indicates that particulates settled from FGD water are similar to coal combustion and FGD byproducts in terms of physical properties (size, shape, and texture) and chemical properties (mineral and element content). Therefore, reuse of FGD particulates that settle in equalization basins of CWTS may be feasible. However, additional analyses of the FGD particles are needed including a toxic characteristic leaching procedure (TCLP) and toxicity tests using aquatic organisms.

Conclusions

Three major types of particles were identified in particulate samples from FGD water. The most abundant particle type is gypsum, which forms during wet scrubbing of flue gas produced by coal combustion and transported in FGD water to the equalization basin. Particle size distribution analysis determined that the majority of FGD particulates are silt size. Other major types are interpreted as fly ash and iron oxide particles, both produced within the combustion chamber. Multiple particle types present within FGD particulates originated from both coal combustion and flue gas desulfurization.

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CHAPTER III

THE ROLE OF AN EQUALIZATION BASIN IN
A CONSTRUCTED WETLAND TREATMENT SYSTEM

Abstract

Laboratory analyses were performed to investigate the role of equalization basins in the treatment of flue gas desulfurization (FGD) water by constructed wetland treatment systems (CWTS). Pilot-scale equalization basins were used to evaluate the removal of constituents of concern (Hg, As, and Se) and toxicity of FGD water. Hg, As, and Se concentrations were measured in FGD water and in particles suspended within the water. Settling analysis using Stokes' Law was performed to determine size distribution and settling rates of FGD particles. Analysis of FGD water samples indicated that aqueous concentrations of Hg, As, and Se and toxicity remained constant or changed very slightly in the pilot-scale equalization basins during a 24 hr hydraulic retention time. FGD particles were predominantly silt size, and approximately 99% of particles suspended in FGD water settled to the bottom of a 2.5 m deep equalization basin within the first 4 hrs of the 24 hr hydraulic retention time. As the particles settled the Hg, As, and Se in these particles were removed from the water column. Approximately 90% of the total As concentration (water and particles) was removed by particle settling in the equalization basin. This investigation supports the use of equalization basins for treatment of FGD waters in CWTS, specifically to settle particles.

Introduction

The purpose of this investigation was to examine the role of equalization basins as a component of constructed wetland treatment systems (CWTS) designed to treat flue gas desulfurization (FGD) water. Equalization basins are constructed retention pools used to store water and are the primary step in many water treatment systems. Equalization basins have retained waters including sewage, ash sluice, surface mine, and surface runoff waters (Cherry et al., 1984; Greenburg, 1986; Somes et al., 2000).

Specifically designed CWTS are used in industry to effectively treat several types of waters including municipal wastewater, acid mine drainage, pulp mill effluent, refinery effluent, agricultural waste, urban runoff, and landfill leachate (Watson et al., 1989). CWTS are designed to promote specific reactions for the transfer or transformation of inorganic and organic constituents to non-bioavailable forms (Knight et al., 1999; Gillespie et al., 2000; Murray-Gulde et al., 2003a; 2003b). The most important design components are hydrosoil, macrophytes (plants), and hydroperiod (hydraulic retention time).

Flue gas desulfurization, the process of removing sulfur dioxide and other harmful vapors from flue gas of coal combustion chambers, is an innovative technology used by coal-fired power plants to meet U.S. Environmental Protection Agency (USEPA) standards for air emissions. In the United States, 85% of operating FGD systems are wet-limestone based scrubbers (USEPA, 2003). Wet-limestone scrubbers use a slurry of water, limestone, and organic acids to react with sulfur dioxide to form calcium sulfite

($CaSO_3$) (Equation 1), which when further oxidized forms calcium sulfate ($CaSO_4$)

(Equation 2) (Mierzejewski, 1991; Laperche and Bigham, 2002).

$$SO_2 + CaCO_3 + H_2O \rightarrow CaSO_3 \cdot 0.5H_2O + CO_2 + 0.5H_2O \qquad \textit{Equation 3.1}$$

$$CaSO_3 \cdot 0.5H_2O + 0.5O_2 + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad \textit{Equation 3.2}$$
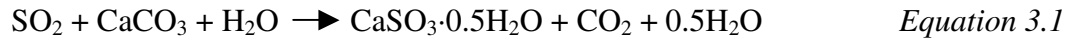
The slurry is dewatered by belt presses, vacuum filtration, or centrifugation. The

resulting solid product is composed primarily of gypsum ($CaSO_4 \cdot 2H_2O$).

Water produced by dewatering the slurry is typically high in chlorides, sulfates,

total suspended solids, and other constituents released from coal combustion and

scrubbing processes. Mercury (Hg), arsenic (As), and selenium (Se) are the major

inorganic constituents of concern within FGD water due to their toxicity to aquatic

organisms and concentrations that exceed EPA discharge limits. Other inorganic

elements that may be of concern in FGD water include copper, zinc, lead, boron, nickel,

cobalt, iron, and magnesium (Arrington, 2005).

Design of equalization basins is based on factors such as power plant size, local

regulatory policy, site conditions, engineer's judgment and experience, and economics

(WEF and ASCE, 1992). Parameters for an equalization basin designed to store FGD

water also include the amount of water produced and holding period for the water. In a

single North Carolina coal-fired power plant, the scrubber generates up to 1.75 million

gallons of FGD water per day (Mooney et al., 2006). The hydraulic retention time (HRT)

for FGD water in an equalization basin is generally 24 hrs.

Equalization basins for CWTS provide storage for particles to settle and for cooling and homogenizing of FGD water prior to entering CWTS reactors. The temperature of FGD water entering an equalization basin is approximately 40°C (Mierzejewski, 1991; Doug Mooney, 2006 written communication). This water is cooled to approximately 35°C to avoid exposing macrophytes in the CWTS reactors to high temperatures. Particle concentrations (total suspended solids) in FGD water in an equalization basin of a CWTS can vary depending on the dewatering and clarifier techniques, but may average approximately 1,000 mg/L (Doug Mooney, 2006 written communication). Settling of particles in the equalization basin increases longevity of the CWTS by reducing the volume of solid material entering the wetland reactors.

Methods of removing constituents of concern in FGD water may include both chemical and physical processes, including particle settling within equalization basins. However, these processes in equalization basins have not been adequately studied. To date, there has been no documented treatment (transfers or transformations) of constituents in FGD water attributed to equalization basins.

The purpose of the current research was to investigate physical processes of treatment that may occur within equalization basins of CWTS used to treat FGD water. Specific objectives of the research were (1) to determine settling rates for FGD particles within an equalization basin; (2) to determine if removal of Hg, As, and Se occurs within an equalization basin by measuring change in concentrations over time; and (3) to determine if toxicity of FGD water changes within an equalization basin during a 24 hr HRT.

Methods

Samples Analyzed

Six FGD waters were obtained from three coal-fired power plants located in the South Eastern United States: four from a pilot-scale wet scrubber and two from full-scale wet scrubbers (Table 3.1). Each of the pilot-scale scrubber waters represented combustion of a different coal. All waters were delivered to Clemson University by tanker truck. FGD particles used in this study were collected from two of the pilot-scale waters (Table 3.1) from the bottom valve opening of the tanker truck after the contents had settled for approximately two days.

All FGD waters were diluted with municipal water to achieve a chloride concentration of approximately 4,000 mg/L. In a full-scale equalization basin of a CWTS, water must be diluted to this chloride concentration to eliminate negative effects to macrophytes of the wetland system (McCarthey et. al, 2005). Therefore, in order to provide results representative of full-scale equalization basins, data presented in this paper are for diluted FGD waters. In addition, general water chemistry was measured on FGD water samples prior to dilution.

Table 3.1: Analyses performed for waters and particles. PSD = Particle size distribution, D = Density, V= Viscosity

	Analyses				
ID (Source)	PSD	Water D and V	Aqueous Chem.	Particle Chem.	Toxicity
FGD Waters					
PS-1 (Pilot-scale scrubber)			X		
PS-2 (Pilot-scale scrubber)			X		
PS-3 (Pilot-scale scrubber)			X		
PS-4 (Pilot-scale scrubber)			X		
FS-A (Full-scale scrubber)		X	X		X
FS-B (Full-scale scrubber)		X	X		X
FGD Particle Samples					
BP-3 (from Water PS-3)	X				
BP-4 (from Water PS-4)	X				
PFS-A (added to Water FS-A)*				X	
PFS-B (added to Water FS-B)*				X	

* Particles from BP-4 were added to waters FS-A and FS-B to simulate particle concentrations in FGD waters of equalization basins of CWTS.

Particle Size and Settling Rates

The pipette method (Folk, 1980) was used to determine particle size distribution of FGD particle samples (Table 3.1). Sand-size particles were separated from samples BP-3 and BP-4 using a 62.5 µm sieve, then dried and weighed. Remaining silt and clay-size particles were suspended in de-ionized water in a 1,000 mL graduated cylinder, and 20 mL samples were withdrawn at specific times. Using methodology of Folk (1980), grain size diameter was calculated for each 20 mL sample withdrawn using a particle density for gypsum (2.32 g/cm³), which is the most common (approximately 95%)

mineral in FGD particles based on results of this investigation. Cumulative particle size

distribution curves were constructed from weights of the size fractions.

To determine settling rates of particles within actual FGD water, Stokes' Law was

applied (Gee and Bauder, 1986). The settling velocities corresponding to selected

particle diameters were calculated using Equation 3:

$$v = \frac{g(\rho_s - \rho_l)X^2}{18\eta}$$
<div align="right">*Equation 3.3*</div>

where v is the settling velocity of particles (cm/s), g is the acceleration due to gravity

(cm/s²), ρ_s is the particle density (g/cm³), ρ_l is the fluid density (g/cm³), X is the particle

diameter (cm), and η is fluid viscosity (g/cm-sec).

A particle density of 2.32 g/cm³ (gypsum) was used in Equation 3. The viscosity

of waters FS-A and FS-B was measured using a Cannon-Fenske Opaque Viscometer

according to ASTM methods D445 and D446 (2001) for glass capillary kinematic

viscometers. Fluid density was measured by weighing 1 mL of FGD water using a

calibrated pipette. All measurements were performed at 22ºC water temperature

(ambient room temperature), which eliminates effects of heating or cooling of water

during experiments. Settling velocities were calculated for particle diameters at 0.5 φ

intervals between 5 and 9 φ and 0.25 φ intervals between 4 and 5 φ. The value of φ is

calculated by Equation 4 (Krumbein, 1936),

$$\varphi = -\log_2(d)$$
<div align="right">*Equation 3.4*</div>

where d is the grain size diameter (mm). The calculated settling velocities were used to determine the time required for each particle size to reach the bottom of an equalization basin with a depth of 2.5 m, a typical depth of equalization basins.

Water Chemistry
Pilot-Scale Scrubber Waters

Pilot-scale scrubber waters (Table 3.1) were analyzed to determine if storage of FGD water in an equalization basin influences Hg, As, and Se concentrations over a 24 hr hydraulic retention time (HRT). The HRT was selected based on the holding period of water in full-scale equalization basins of CWTS. Each FGD water (PS-1 to PS-4) was diluted to achieve a chloride concentration of approximately 4,000 mg/L in a 3,780 L polypropylene pilot-scale equalization basin and then circulated using a submersible pump. Samples ("initial samples") were collected in 1 L HDPE bottles immediately after contents of the equalization basin were thoroughly mixed and the submersible pump was turned off (Figure 3.1). Two water samples ("final samples") were collected 24 hrs later at the equalization basin outflow prior to entering the wetland reactors of two separate treatment series. Values from analysis of the two final samples were averaged for each water. Conductivity, pH, alkalinity, hardness, dissolved oxygen, chloride , and sulfate concentrations were measured for each water (Table 3.2). Initial and final samples from each of the four pilot-scale waters were analyzed for Hg, As, and Se by ICP-MS (Perkin Elmer, Sciex Elan 9000).
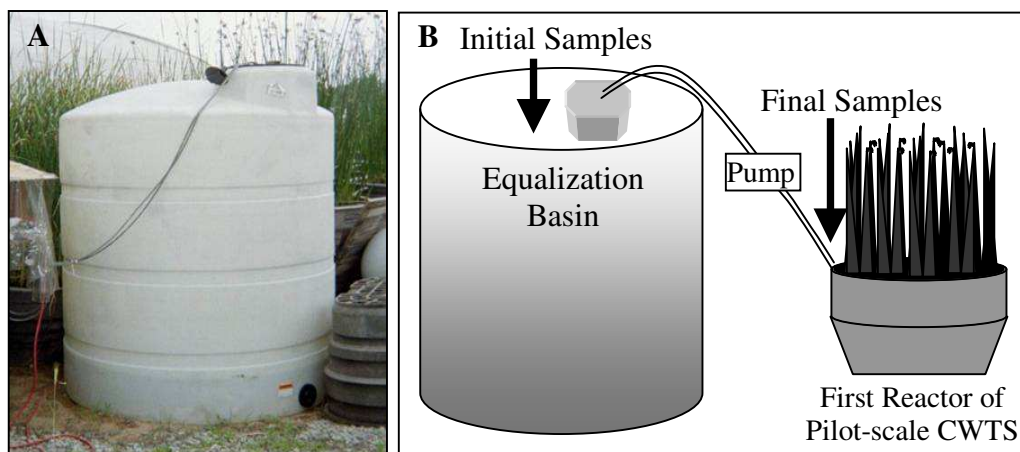
Figure 3.1: A) Pilot-scale 3,780 L equalization basin. B) Schematic showing sampling locations for initial and final samples of waters PS-1 through PS-4.

Table 3.2: Methods for general water chemistry and inorganic analysis.

Parameter	Method	Detection Limit
pH	Direct Instrumentation: Orion Model 420A	0.01
Conductivity	Direct Instrumentation: YSI 30	0.1 mS
Alkalinity	Standard Methods: 2320 B (APHA, 1998)	2 mg/L as $CaCO_3$
Hardness	Standard Methods: 2340 C (APHA, 1998)	2 mg/L as $CaCO_3$
DO[1]	Direct Instrumentation: YSI Model 52	0.1 mg/L
Chloride	HACH Colorimetric Method 8207	25 mg/L
Sulfate	Standard Methods: 4500 E (APHA, 1998)	1.0 mg/L
Se[2], As[2]	Inductively Coupled Plasma with Mass Spectrometry (ICP-MS): USEPA 200.8	1.0 µg/L
Hg[2]	(ICP-MS): USEPA 200.8	0.1 µg/L
Hg[3], As[3], Se[3]	Atomic Fluorescence Spectroscopy (AFS) (Aurora Instruments, AI 3200)	1.0 µg/L

[1] Dissolved Oxygen
[2] Used for pilot-scale scrubber waters
[3] Used for full-scale scrubber water and digested particle samples

Water and Particle Chemistry
Full-Scale Scrubber Waters

Full-scale scrubber water (FS-A and FS-B) was diluted to approximately 4,000 mg/L chlorides in a static, 73 L rectangular storage bin used as a pilot-scale equalization basin. A representative split of particle sample BP-4 was added within the 73 L bin to waters FS-A and FS-B to create water with a particle concentration (1,000 mg/L) typical of full-scale equalization basins used with CWTS. To fully suspend particles in the water column, the FGD water and particles were mixed for approximately one minute. Water samples ("initial samples") were collected immediately after mixing to simulate water entering an equalization basin. Water samples ("final samples") were collected after 24 hrs to simulate water leaving an equalization basin after a 24 hr HRT.

General water chemistry analyses were performed on initial and final samples of the full scale scrubber waters (Table 3.2). A 200 mL aliquot of initial and final samples from waters FS-A and FS-B was filtered through a 0.45 µm filter to separate the particles. The water was preserved using nitric acid (trace metal grade) for measurement of Hg, As, and Se concentrations. Following methods outlined by Hatanpää et al. (1997), particles (samples PFS-A and PFS-B) collected on the filter paper were dried, weighed, and digested. Although both initial and final samples were filtered, the final samples contained too few particles for analysis, and therefore only particles collected from the initial samples were digested. FGD particles were digested for As and Se analysis in closed Teflon PFA vessels in a microwave oven (Mars5 System, CEM model) using 10 mL nitric acid (HNO_3, Certified ACS Plus). FGD particles were digested for Hg analysis using 10 mL nitric acid and 5 mL sulfuric acid (H_2SO_4, Certified ACS Plus) under a

reflux condenser. The full-scale scrubber waters and digested particle samples were

analyzed for Hg, As, and Se by atomic fluorescence spectroscopy (AFS) (Aurora

Instruments, AI 3200).

To determine the cumulative removal of Hg, As, and Se associated with particles

settling from the water column, it was assumed that the constituents were distributed

evenly among all particle sizes. Therefore, the removal rate of constituents is

proportional to the mass of particles settled. Removal rates for Hg, As, and Se associated

with particles during settling were estimated using a two point slope estimation

performed on the data for constituent concentration over time:

$$R = \frac{C_{n+1} - C_n}{t_{n+1} - t_n}$$
<div align="right">*Equation 3.5*</div>

where R is the removal rate of constituents [(µg/L)/hr], C is the concentration of the

constituent (µg/L), t is time (hrs), and n is the data point.

<div align="center">Toxicity Experiments</div>

Toxicity of initial samples was compared to that of final samples for waters FS-A

and FS-B using a standard 7-day static/renewal toxicity test following USEPA methods

(Lewis et al., 1994). The test organism, *Ceriodaphnia dubia* (a water flea), is commonly

used for toxicity testing in the United States (Lewis et al., 1994). Toxicity endpoints for

the *C. dubia* experiments were mortality and reproduction. To remove the effect of

chloride on toxicity, chloride concentrations were reduced to below the no observable

effect concentration (NOEC). A series of dilutions for FS-A and FS-B, initial and final,

were prepared with moderately hard water (70 mg/L as $CaCO_3$). Chloride concentrations

after dilution for each water sample were 500, 300, 150, 75, and 50 mg/L Cl^-. All

dilution treatments were compared to a control of moderately hard water. To determine

differences in survival data between initial and final sampling, a Chi-Square Analysis

using critical values from Fishers Exact Test ($\alpha = 0.05$) was performed. *C. dubia*

reproductive data were evaluated in comparison to control organisms using a one-way

analysis of variance test (ANOVA; $\alpha = 0.05$) and mean separation using a least

significant difference test (LSD). General water chemistry analyses, including pH,

conductivity, hardness, alkalinity, and dissolved oxygen were conducted on days 1, 3, 5,

and 7 of the toxicity experiments. These data were used to determine if mortality was

affected by changes in general water chemistry.

Results

Size and Settling Rates of FGD Particles

FGD particles analyzed consist predominantly of silt-size material (between 4 and

9 φ) (Figure 3.2, Table 3.3). The graphic mean size of sample BP-3 is 5.3 φ with an

inclusive graphic standard deviation of 0.34 φ, indicating very well sorted medium silt.

Graphic mean size of sample BP-4 is 4.7 φ with an inclusive graphic standard deviation

of 0.29 φ, indicating very well sorted coarse silt. The size distribution of both particle

samples is unimodal and nearly symmetrical.

Values of dynamic viscosity measured for waters FS-A and FS-B are 0.0099

g/cm-sec and 0.0103 g/cm-sec, respectively. The measured fluid densities of FS-A and

FS-B are 1.010 g/cm³ and 1.013 g/cm³, respectively. The settling rate of particles

calculated by Stokes' Law in water FS-A is slightly greater than that for water FS-B

(Table 3.3) because of minor differences in viscosity and density between the two waters.

Using the calculated settling rates and the measured particle size distributions,

greater than 98% of particles settle to the bottom of a 2.5 m deep equalization basin of a

CWTS within a 24 hr HRT (Table 3.3). This indicates that the typical HRT within an

equalization basin is adequate to remove nearly all of the suspended particles. For

sample BP-4, 78% of the particles settle within the first hour (Figure 3.3, Table 3.3).

Because the particle size is slightly finer in sample BP-3, more time is required for

settling, with approximately 73% of the articles removed from suspension during the

second hour of settling.
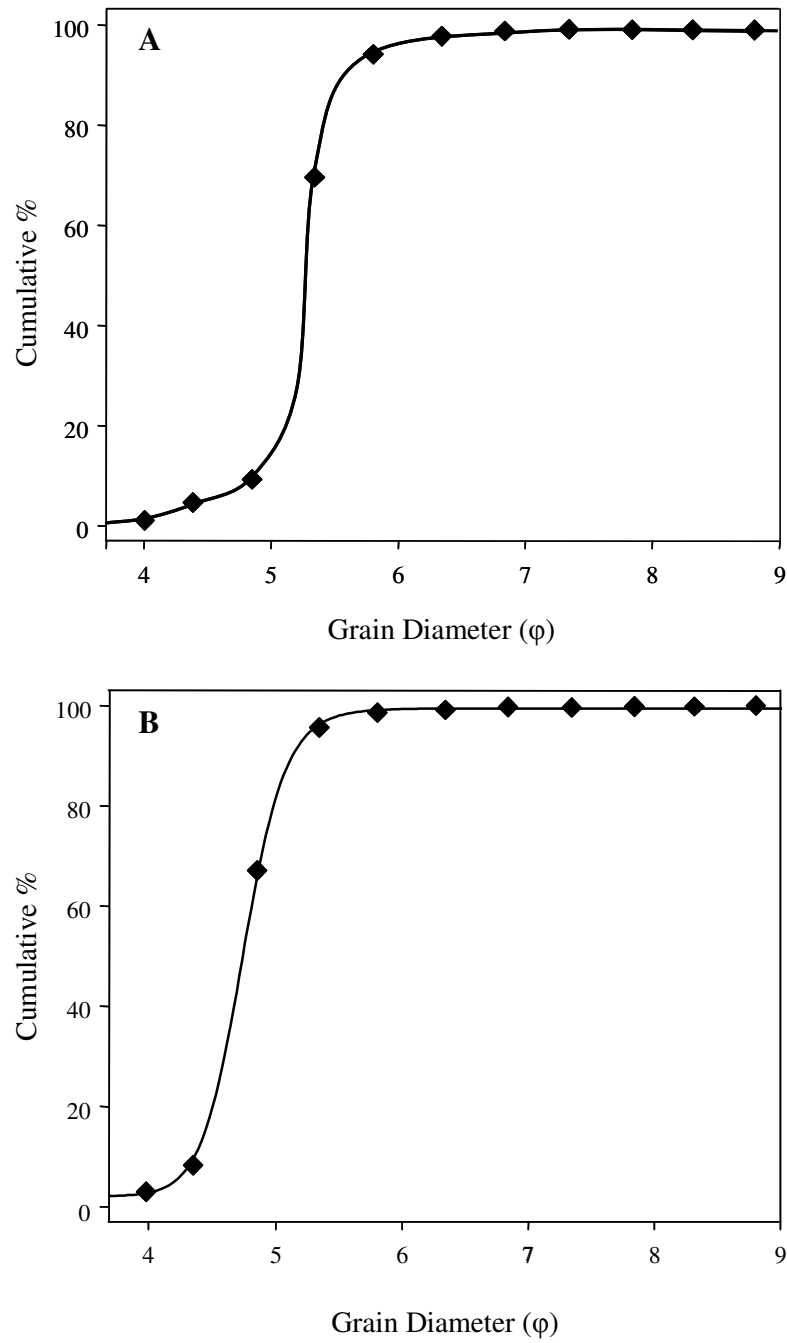
Figure 3.2: Cumulative size distribution curves for FGD particle samples.
A) Sample BP-3. B) Sample BP-4.

Table 3.3: Size distribution measured in FGD particle samples BP-3 and BP-4; settling rates (cm/s) and settling times (hrs) calculated using Stokes' Law; and measured viscosity and density of waters FS-A and FS-B. Times calculated for settling to the bottom of a 2.5 m deep equalization basin.

Grain Diameter (mm)	(φ)	Wentworth (1922) Size Class	Size Distribution (Cumulative %)		Settling Rate (cm/s)		Settling Time (hrs)	
			BP-3	BP-4	FS-A	FS-B	FS-A	FS-B
0.0625	4	v. fine sand	0.65	2.27	0.28	0.27	0.25	0.26
0.053	4.25	coarse silt	3.05	6.90	0.20	0.19	0.34	0.36
0.044	4.5	coarse silt	5.10	18.5	0.14	0.13	0.50	0.52
0.037	4.75	coarse silt	7.41	52.2	0.099	0.095	0.70	0.73
0.031	5	coarse silt	14.5	78.1	0.070	0.067	1.00	1.04
0.022	5.5	medium silt	87.1	96.6	0.035	0.034	1.98	2.07
0.016	6	medium silt	96.5	97.8	0.019	0.018	3.75	3.90
0.011	6.5	medium silt	98.0	99.1	0.0088	0.0084	7.93	8.26
0.0078	7	fine silt	98.5	99.3	0.0044	0.0042	15.8	16.4
0.0055	7.5	fine silt	99.0	99.5	0.0022	0.0021	31.7	33.0
0.0039	8	v. fine silt	99.0	99.8	0.0011	0.0010	63.1	65.7
0.0028	8.5	v. fine silt	99.1	99.8	0.00057	0.00054	122	127
0.0020	9	clay	99.1	99.9	0.00029	0.00028	240	250
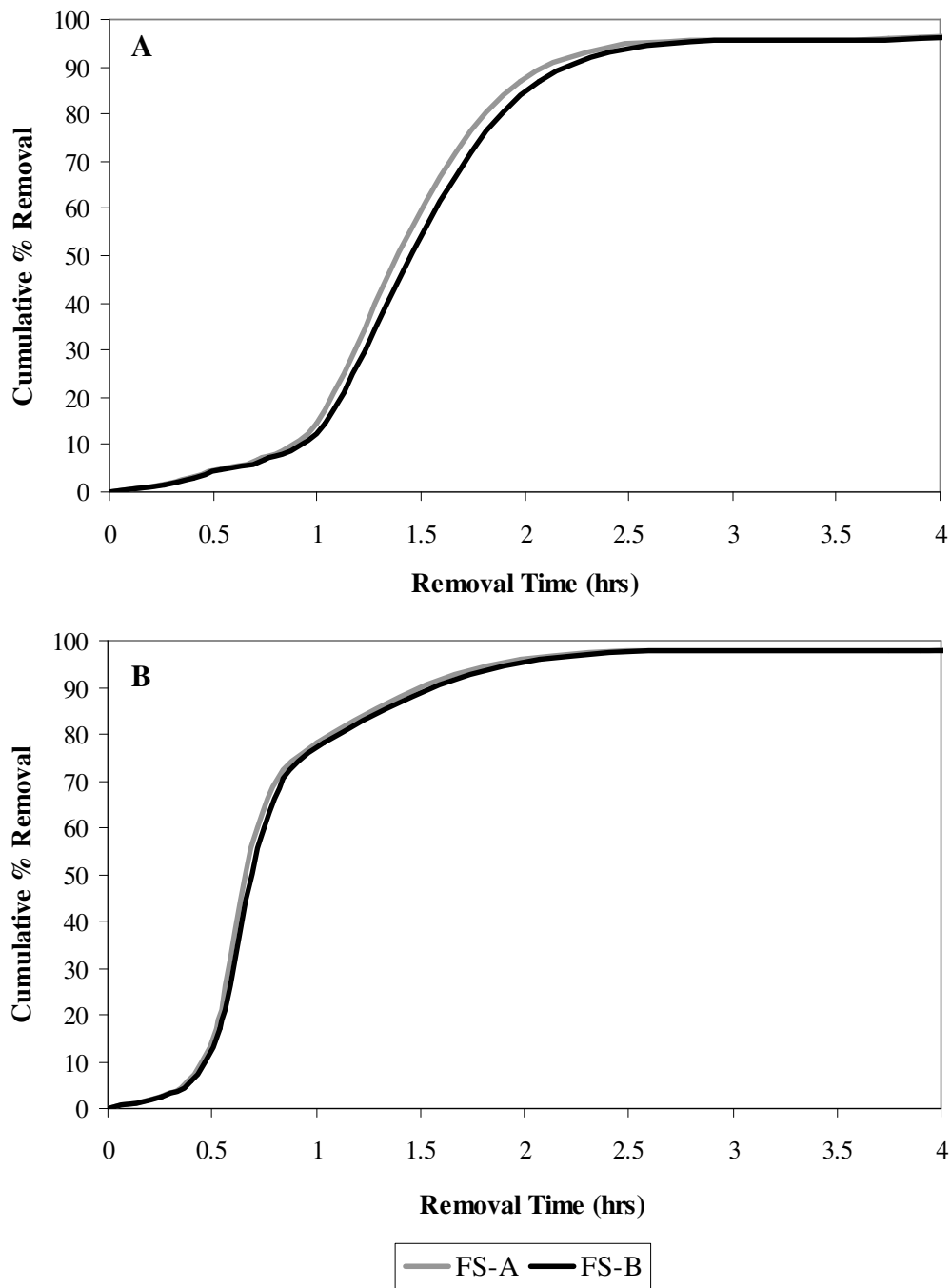
Figure 3.3: Cumulative percent removal of FGD particles in an equalization basin with a depth of 2.5 m. Based on settling rates calculated from particle size distribution measured for particle samples BP-3 and BP-4 and viscosity and density measured for waters FS-A and FS-B (Figure 3.2 and Table 3.4) A) Sample BP-3. B) Sample BP-4.

Water Chemistry
Pilot-Scale Scrubber Waters

General water chemistry values for the pilot-scale scrubber waters prior to dilution are listed in Table 3.4. Following dilution to achieve targeted chloride concentrations representative of equalization basins of CWTS, general water chemistry values for initial samples of the pilot-scale scrubber waters (PS-1 to PS-4) were: 8.66 to 9.09 mg/L dissolved oxygen, 6.79 to 7.11 (su) pH, 24 to 46 mg/L (as $CaCO_3$) alkalinity, 4,200 to 9,800 mg/L (as $CaCO_3$) hardness, 10.1 to 12.0 mS conductivity, and 1,250 to 1,610 mg/L sulfate. The general water chemistry of final samples is similar to that of initial samples (Table 3.5).

Mercury concentrations in initial samples of pilot-scale scrubber waters (PS-1 to PS-4) in the equalization basin ranged from 0.4 to 43 µg/L (Table 3.5). Decrease in mercury concentration from initial to final samples was observed for two of the four waters (PS-1 and PS-2). The highest initial mercury concentration (43 µg/L in PS-2) decreased to a final concentration of 22 µg/L, resulting in 49% removal of mercury. Initial concentration for PS-1 was 0.9 µg/L Hg, and the final concentration decreased by 0.3 µg/L, resulting in 33% removal. The only removal of arsenic from the pilot-scale scrubber water within the equalization basin was 1 µg/L (2.8%) in PS-4. Selenium concentrations in initial samples of pilot-scale scrubber water ranged from 610 µg/L to 2,980 µg/L. Decrease in Se concentration from initial to final samples was observed for three of the four waters. The highest initial selenium concentration (2,980 µg/L in PS-2) decreased to a final concentration of 2,750 µg/L, resulting in 7.7% removal. Initial selenium concentrations for PS-1 and PS-4 were 610 µg/L and 650 µg/L, respectively.

Percent removal of Se was 1.2% (7 µg/L decrease) for PS-1 and 3.4% (22 µg/L decrease) for PS-4.

<div align="center">Water Chemistry and Particle Analysis
Full-Scale Scrubber Waters</div>

General water chemistry values for the full-scale scrubber waters prior to dilution are listed in Table 3.4. Following dilution, general water chemistry values for initial samples of the full-scale scrubber waters (FS-A and FS-B) were: 7.96 mg/L dissolved oxygen, 6.83 to 7.69 (su) pH, 2,800 to 4,000 mg/L (as $CaCO_3$) hardness, 11.0 to 13.2 mS conductivity, and 890 to 980 mg/L sulfate. Alkalinity values differed between the initial samples: 18 mg/L ($CaCO_3$) for FS-A and 220 mg/L for FS-B. General water chemistry of final samples did not differ from that of initial samples (Table 3.5).

Arsenic concentrations in the aqueous phase of initial samples of the full-scale scrubber waters were 2.68 µg/L in FS-A and 2.02 µg/L in FS-B (Table 3.5). Initial selenium concentrations in the aqueous phase were 1350 µg/L in FS-A and 1440 µg/L in FS-B. Aqueous mercury concentration in the initial sample for FS-A was 12.9 µg/L, while the aqueous mercury concentration in FS-B was below the detection limit (less than 1.0 µg/L). A decrease of approximately 1 µg/L of Hg was observed in FS-A. Selenium removal was 10% in FS-A with approximately 2% removal from FS-B. There was no removal of As from either water.

Table 3.4: General water chemistry for the six FGD waters used in this investigation prior to dilution and parameter ranges for full-scale scrubber FGD waters characterized by Mierzejewski (1991) and Arrington (2005). ND = Not determined

| Parameter | Units | FGD Waters | | | | | | | |
		PS-1	PS-2	PS-3	PS-4	FS-A	FS-B	Arrington	Mierzejewski
pH	Su	7.1	ND	7.3	7.4	6.6	7.5	6 - 7	4 - 7
Alkalinity	mg/L[1]	84	ND	56	46	26	840	152 - 600	ND
Hardness	mg/L[1]	3200	5000	8000	7200	10500	14000	10400 – 24800	ND
Conductivity	mS	13.3	12.8	14.3	13.1	19.7	42	20.3 – 36.3	ND
Chloride	mg/L	5375	5250	5750	5350	14200	21000	1640 – 15900	10000 – 40000

[1] mg/L as $CaCO_3$

Table 3.5: General water chemistry and concentrations of Hg, As, and Se for pilot-scale scrubber waters (PS-1 to PS-4) and full-scale scrubber waters (FS-A and FS-B) following dilution. DO = Dissolved oxygen, BDL = Below detection limit (1 µg/L)

| Parameters and Constituents | Units | Waters and Samples | | | | | | | | | | | |
| | | PS-1 | | PS-2 | | PS-3 | | PS-4 | | FS-A | | FS-B | |
		Initial	Final[1]	Initial	Final[1]	Initial	Final[1]	Initial	Final[1]	Initial	Final	Initial	Final
DO	mg/L	8.66	7.87	9.09	8.84	9.00	8.94	8.66	8.26	7.96	9.40	7.96	6.90
pH	su	7.00	7.00	6.79	6.77	7.10	7.00	7.11	7.09	6.83	6.86	7.69	7.65
Alkalinity	mg/L[1]	46	45	26	24	32	33	24	25	18	20	220	210
Hardness	mg/L[1]	4200	3800	9800	6000	6400	7800	6400	6100	2800	3100	4000	3800
Conductivity	mS	10.1	10.0	10.9	10.9	12.0	12.2	11.7	11.6	11.0	11.2	13.2	13.3
Chloride	mg/L	3150	3375	3550	3490	4230	4330	4050	4200	4280	4200	5000	5025
Sulfate	mg/L	1610	1490	1520	1390	1360	1350	1250	1260	980	1030	890	910
Mercury	µg/L	0.9	0.6	43	22	36	44	0.4	0.4	12.9	12.0	BDL	BDL
Arsenic	µg/L	4.7	5.7	101	124	47	50	35	34	2.68	3.67	2.02	2.08
Selenium	µg/L	610	603	2980	2750	2100	2220	650	628	1350	1220	1440	1400

[1] Final values are averaged from two water samples, one for each outflow (see Methods)
[2] mg/L as $CaCO_3$

Mercury content of particle samples PFS-A and PFS-B was 0.91 and 1.2 µg/g, respectively. Arsenic content in PFS-A and PFS-B was 19 and 21 µg/g. Selenium content differed between particle samples PFS-A and PFS-B at 45 µg/g and 19 µg/g, respectively. Because each liter of water in the equalization basin contained 1 g of particles, the amount of mercury in waters FS-A and FS-B waters due to particle content was 0.91 and 1.2 µg/L, respectively. Arsenic content due to particles was 19 µg/L in FS-A and 21 µg/L in FS-B. Selenium content due to particles in FS-A and FS-B was 45 µg/L and 19 µg/L, respectively. Over time, Hg, As, and Se associated with particles in the water are removed by settling of FGD particles to the bottom of the equalization basin (Figure 3.4).

The calculated removal rates (Table 3.6) indicate the time at which maximum removal of constituents occurs by particle settling in an equalization basin. These rates show that maximum removal of Hg, As, and Se associated with particles occurs approximately 0.6 hrs after the start of the HRT for both waters FS-A and FS-B. After approximately 2.4 hours, the removal rates are two orders of magnitude less than the maximum, which indicates that by this time further removal of constituents is negligible.
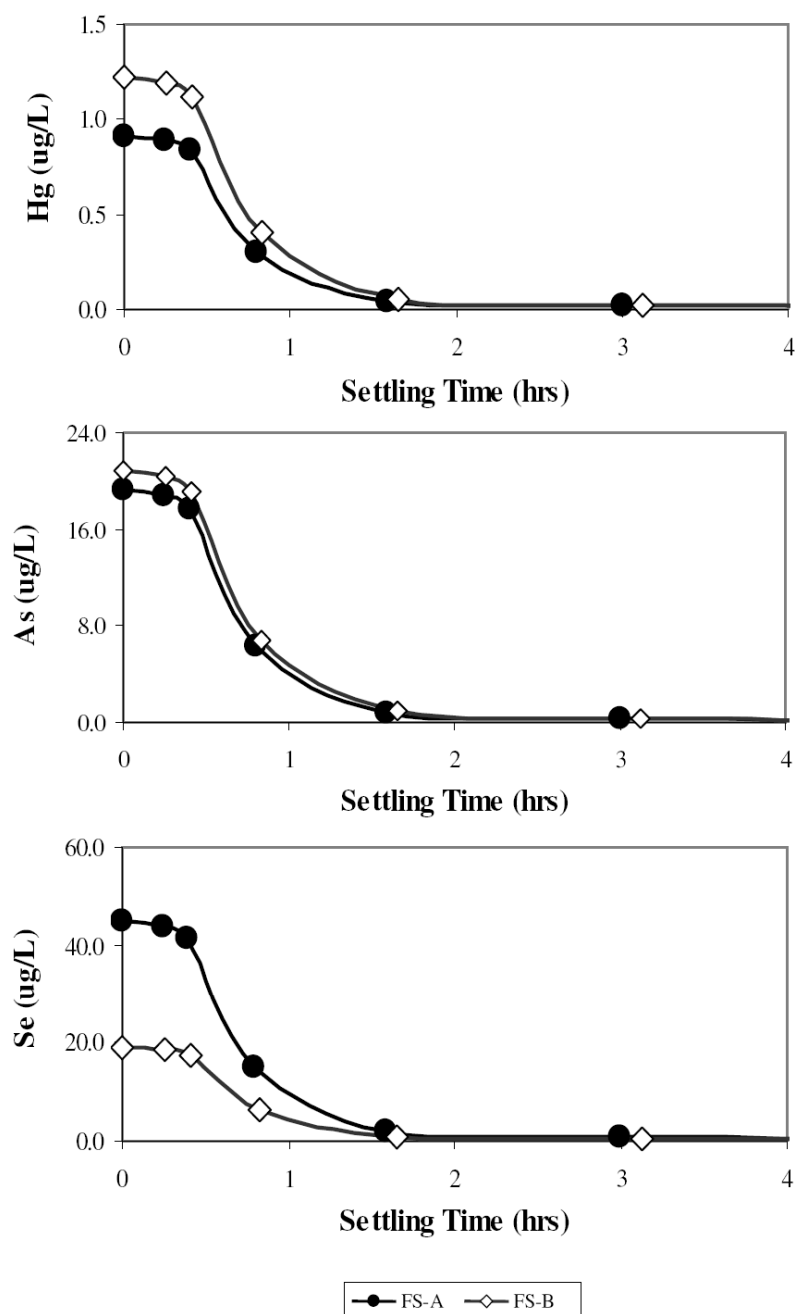
Figure 3.4: Mass of Hg, As, and Se (µg) removed per liter of water by particle settling, assuming a particle concentration of 1,000 mg/L. Change in concentration with settling time is based on particle settling rates, content of Hg, As, and Se in particles, and a 2.5 m depth of basin. Points on each graph represent known settling times for φ values used to construct the cumulative size distribution curves (Figure 3.2). Time = 0 represents water entering the equalization basin.

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Table 3.6: Removal rates of Hg, As, and Se by particle settling in FS-A and FS-B for an equalization basin depth of 2.5 m based on a two-point slope estimation (Equation 5) of the known points used to construct the concentration curves (Figure 3.4).

Time (hrs)	FS-A Removal Rates [(μg/L)/hr]		
	Hg	As	Se
0.32	0.36	7.7	18
0.60	1.3	28	66
1.2	0.33	7.0	16
2.3	0.017	0.35	0.82
4.7	0.0025	0.054	0.13
9.5	0.00076	0.016	0.037

Time (hrs)	FS-B Removal Rates [(μg/L)/hr]		
	Hg	As	Se
0.33	0.47	8.0	7.3
0.62	1.7	29	27
1.2	0.43	7.3	6.6
2.4	0.021	0.36	0.33
4.9	0.0033	0.056	0.051
9.9	0.0010	0.017	0.015

Toxicity

Survival of *C. dubia* was affected by exposure to water FS-A at chloride dilutions of 300 and 500 mg/L Cl⁻ (Figure 3.5A). At 500 mg/L Cl⁻, exposure to initial samples resulted in 50% survival, and exposure to final samples resulted in 70% survival. Exposures at 300 mg/L Cl⁻ resulted in 70% survival for initial samples, and *C. dubia* was not affected (100% survival) by final samples. Initial and final samples for the dilutions of 150, 75, and 50 mg/L Cl⁻ did not affect survival of *C. dubia*. Reproduction of *C. dubia* was impaired at the 300 and 500 mg/L Cl⁻ dilutions of initial and final samples compared to the control (Figure 3.5B). Reproduction of *C. dubia* was not affected by initial or final

samples for chloride concentrations of 50 and 75 mg/L. Treatment of water by the

equalization basin was suggested only by survival for the 300 mg/L Cl⁻ dilution;

however, treatment was not seen in terms of reproduction for this dilution.

Survival of *C. dubia* was affected by exposure to water FS-B at 150, 300, and 500

mg/L Cl⁻ dilutions. Both initial and final samples resulted in toxicity for all three

dilutions. Exposures at 500 mg/L Cl⁻ resulted in 100% mortality in initial and final

samples (Figure 3.5C). At 300 mg/L Cl⁻, exposure to initial samples resulted in 20%

survival, and exposure to final samples resulted in 10% survival. Exposures at 150 mg/L

Cl⁻ resulted in 60% survival in both initial and final samples. Reproduction of *C. dubia*

was impaired for both initial and final samples at all chloride dilutions to the extent that

no reproduction occurred. The pilot-scale equalization basin did not affect toxicity of
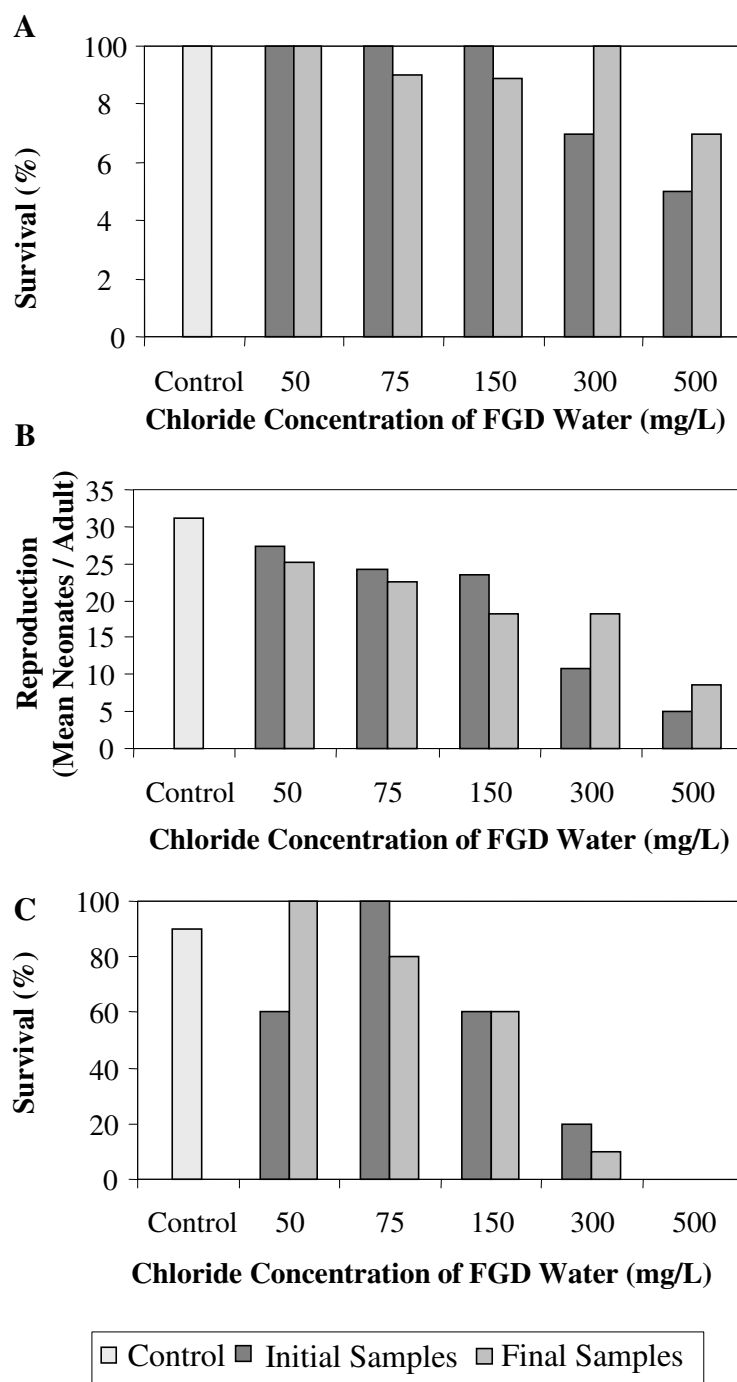
water FS-B to *C. dubia* during the 24 hr HRT.

Figure 3.5: Response of *C. dubia* to full-scale scrubber waters. A) Survival after exposure to water FS-A. B) Reproduction after exposure to water FS-A. C) Survival after exposure to water FS-B. Reproduction did not occur for organisms exposed to FS-B.

<center>Discussion</center>

Two mechanisms of potential treatment within equalization basins of constructed wetland systems were investigated for FGD waters: treatment by decrease in aqueous concentrations of constituents of concern (Hg, As, and Se) and treatment by particle settling. To determine treatment of FGD waters, concentrations of initial and final samples of each water were analyzed and toxicity experiments were used.

Treatment of aqueous phase constituents of concern in FGD waters of an equalization basin ranged from no removal to approximately 50% removal. The maximum removal of constituents of concern in the aqueous phase was observed for water PS-2. During a 24 HRT, Hg concentration in water PS-2 decreased from 43 µg/L to 22 µg/L and Se concentration from 2980 µg/L to 2750 µg/L. For the other FGD scrubber waters, removal in the equalization basin was 3 µg/L or less Hg and 130 µg/L or less Se. Removal of As from the aqueous phase within the pilot-scale equalization basins did not occur. The results of toxicity tests using *C. dubia* suggest that no decrease in toxicity of FGD water occurs within the equalization basin. Biogeochemical pathways for the transfer or transformation of Hg, As, and Se include reduction and binding of constituents (Fagerstrom and Jernelov, 1972; Masscheleyn and Patrick, 1993). Biogeochemical pathways remove constituents from the water and aid in the formation of stable minerals and insoluble elements that are non-bioavailable to aquatic life. Equalization basins do not contain reducing hydrosoils that promote these specific pathways, and therefore removal of dissolved constituents from FGD water in equalization basins is minimal.

Experiments adding FGD particles to full-scale scrubber waters (FS-A and FS-B) showed no increased removal of Hg, As and Se in aqueous concentrations when compared with aqueous concentrations of the pilot-scale scrubber waters (PS-1 to PS-4). This indicates that FGD particles are not removing the constituents of concern from the aqueous phase while settling. No removal may be attributed to the low cation exchange capacity of gypsum, which is the major component of the FGD particles. It is not expected that the gypsum particles are precipitating, and therefore aqueous concentrations of Hg, As, and Se are not incorporated into the particles during settling.

Based on data from this investigation, treatment of FGD water occurs by removal of Hg, As, and Se through particle settling in equalization basins of CWTS. Results of particle settling analysis indicate that approximately 99% of particles settle to the bottom of a 2.5 m deep equalization basin within 24 hrs. In a 10 x 10 m area of an equalization basin, the annual accumulation of Hg, As, and Se in the settled particles ranges from 82-110 g Hg, 1,700-1,900 g As, and 1,700-4,060 g Se (Table 3.7). A full-sized equalization basin (25 x 108 m) will remove 2.2-2.9 kg Hg, 45-50 kg As, and 45-110 kg Se per year based on calculations using data from the current investigation.

Table 3.7: Mass of Hg, As, and Se (g) removed from FGD waters calculated by using settling data from particle samples PFS-A and PFS-B in a section of an equalization basin and a full-size equalization basin. Calculations are based on an initial particle concentration of 1,000 mg/L and basin depth of 2.5 m. COC = constituent of concern, EQB = equalization basin

| | | Area | | | |
| | | 10 x 10 m² Area of EQB Settled Mass (g) | | 25 x 108 m² Full-size EQB Settled Mass (g) | |
COC	Time	PFS-A	PFS-B	PFS-A	PFS-B
Hg	24 hrs.	0.23	0.30	6.0	7.9
	100 days	23	30	600	790
	1 year	82	110	2200	2900
As	24 hrs.	4.7	5.2	120	140
	100 days	470	520	12000	14000
	1 year	1700	1900	45000	50000
Se	24 hrs.	11	4.7	300	120
	100 days	1100	470	30000	12000
	1 year	4060	1700	110000	45000

The settling of particles in the equalization basin helps meet National Pollutant Discharge Elimination System (NPDES) permits for settleable solid content of FGD waters (total suspended solids). The total maximum daily load (TMDL) set by NPDES permits for total suspended solids (TSS) in water is between 20-100 mg/L (USEPA, 2004). In our investigation, the TSS concentration in the pilot-scale equalization basin was 1,000 mg/L and decreased to approximately 10 mg/L after a 24 hr HRT. Settling of particles in an equalization basin increases longevity of CWTS by reducing the volume of particles deposited in the wetland reactors.

Although 99% of the particles settled during a 24 hr HRT, the total initial mass (mass in aqueous phase plus mass in particles) of Se removed by settling is only 3.2 %

for FS-A and 1.3% for FS-B. The low percent removal is attributed to nearly all (96 to 99%) of the total initial mass being in the aqueous phase (Table 3.8). Arsenic is more prominent in the particles (88 to 90% of total), and removal of As occurred only by particle settling with 87% and 90% of the total mass removed in waters FS-A and FS-B, respectively. The aqueous phase of FS-A contains 93% of the total initial mass of Hg, and total removal was 13%. Hg concentration in FS-B was detected in the particles only, and removal of approximately 99% of the total Hg content occurred by particle settling.

There have been very few studies identifying trace element content within FGD byproduct solids (Laperche and Bigham, 2002; Kost et al., 2005; Karies et al., 2006). Karies et al. (2006) evaluated the Hg content in material derived from wet-scrubber FGD systems and concluded that gypsum contained 0.14-1.46 µg/g Hg, which is consistent with the Hg content measured (0.91-1.2 µg/g) in the equalization basin particulates of our investigation. The As and Se content within the equalization basin particles of our investigation are in agreement with the published values of Kost et al. (2005). Kost et al. (2005) examined byproducts of multiple dry-scrubber processes and concluded that As content in particles was 5.2-386 µg/g and Se content was 2.3-23 µg/g.

General water chemistry values for the FGD waters in our investigation are representative of typical FGD waters described by Mierzejewski (1991) and Arrington (2005) (Table 3.4). General water chemistry did not differ between pilot-scale and full-scale scrubber waters, with the exception of alkalinity. Measured alkalinity for FS-B was an order of magnitude higher than the pilot-scale waters and FS-A. This alkalinity difference may be accounted for by the addition of an organic acid, such as dibasic acid

(DBA), to the limestone slurry during the scrubbing process. DBA is commonly used as a buffering agent to slow the decrease in pH in a wet limestone-based scrubber, improving the scrubbing process (additional SO_2 removal) (Frandsen et al., 2000; Srivastava, 2000).

The composition of FGD waters including Hg, As, and Se content varies depending on site-specific conditions and the coal burned (Arrington, 2005). Hg, As, and Se concentrations differed among the FGD waters in this investigation, with Hg concentration ranging over three orders of magnitude. Constituents of concern (Hg, As, and Se) for FGD waters analyzed by Arrington (2005) ranged from <0.2 to 58 µg/L Hg, 6 to 410 µg/L As, and 150 to 17,200 µg/L Se. Mierzejewski (1991) documented FGD waters as containing 50-800 µg/L Hg, 50-3,000 µg/L As, and 200-1,000 µg/L Se. Because FGD waters in our investigation were diluted, the concentrations of Hg, As, and Se were lower than the concentrations described in the previous studies. However, the range of concentrations for the published FGD water and our equalization basin waters both varied by several orders of magnitude. The composition of FGD water in an equalization basin should depend on the composition of the service water (dilution waters) and water produced by the FGD scrubber. The chloride concentration of FGD water, prior to dilution, determines the volume of service water needed to meet the required chloride concentration of 4,000 mg/L for a CWTS.

Table 3.8: Percent removal for Hg, As, and Se in FGD water and particles and percent total initial mass (TIM = aqueous and particles) removed by change in aqueous concentration and particle settling. BDL= Below detection limit, ND= Not determined, NR= No removal

	Aqueous			Particles				% of TIM removed by change in aq. concentration	% of TIM removed by particle settling
	Mass Initial (µg/L)	Mass Removed (µg/L)	% Removed	Mass Initial (µg/L)	Mass Removed (µg/L)	% Removed	Total Initial Mass (TIM) (µg/L)		
Hg									
FS-A	12.9	0.9	6.98	0.91	0.9	99	13.8	6.5	6.5
FS-B	BDL	BDL	ND	1.21	1.2	99	~1.21	0	99
As									
FS-A	2.68	NR	0	19	18.8	99	21.68	0	86.7
FS-B	2.02	NR	0	21	20.8	99	23.02	0	90.4
Se									
FS-A	1350	130	9.6	45	44.5	99	1395	9.3	3.2
FS-B	1440	40	2.8	19	18.8	99	1459	2.7	1.3

Determining settling rates for FGD particles contributes to the performance evaluation of existing or future equalization basin designs. Facilities that incorporate equalization basins as primary wastewater treatment utilize rectangular basins with a depth of 2.1 to 5 m (USEPA, 1975; Steel and McGhee, 1979; and Metcalf and Eddy, Inc., 1991). Recommended HRTs for these basins are between 1 and 4 hrs (Sunstrom and Klei, 1979; Steel and McGhee, 1979; Metcalf and Eddy, Inc., 1991). The HRTs required to remove targeted percent of particles for different depth equalization basins (Table 3.9) indicate that the recommended HRT (1 to 4 hrs) would allow for 85 to 95% of particles to reach the bottom of a basin with a depth between 2 and 5 m. Designing equalization basins to treat FGD water typically includes a 24 hr HRT for the cooling of water. This HRT is sufficient time to settle 95 to 99% of FGD particles in equalization basins with depths between 2 and 5 m.

Daily accumulation of solids within a full-size equalization basin has been estimated at 1,790 kg per day (Doug Mooney, 2006 written communication). This estimation is based on the average daily production of water (2.6 million liters), particle concentration (1,000 mg/L), and percent removal of particles (70%). From our investigation, approximately 99% of particles are removed in a 24 hr HRT, indicating that an additional 770 kg per day would settle, and maximum storage capacity will be reached at 18 months, instead of the estimated 24 months (Doug Mooney, 2006 written communication).

Table 3.9: HRT in an equalization basin required to achieve target percent removal (50%, 75%, 85%, 95%, and 99%) of particles (and associated Hg, As, and Se) from FGD waters. HRT calculated from particle size distribution measured for samples BP-3 and BP-4 and the measured density and viscosity of water FS-B.

| Water Depth (m) of Equalization Basin | HRT (hrs) Required to Achieve Targeted Removal of Particles | | | | | | | | | |
| | Sample BP-3 | | | | | Sample BP-4 | | | | |
	50%	75%	85%	95%	99%	50%	75%	85%	95%	99%
2.0	1.1	1.5	1.8	2.8	25	0.56	0.77	0.96	1.3	6.6
2.5	1.4	1.8	2.3	3.5	32	0.69	0.96	1.2	1.7	8.3
3.0	1.6	2.2	2.8	4.3	38	0.83	1.1	1.4	2.0	9.9
3.5	1.9	2.6	3.2	5.0	45	0.97	1.3	1.7	2.3	11.6
4.0	2.2	2.9	3.7	5.7	51	1.1	1.5	1.9	2.7	13.2
4.5	2.4	3.3	4.1	6.4	58	1.3	1.7	2.2	3.0	14.9
5.0	2.7	3.7	4.6	7.1	64	1.4	1.9	2.4	3.3	16.5

Conclusion

Equalization basins of CWTS effectively remove particles suspended in FGD water through settling. FGD particle samples in this investigation contained mostly silt-size material. For a 2.5 m deep equalization basin with a 24 hr HRT, 98 to 99% of particles and Hg, As, and Se contained in the particles settle out of the water column. Over the course of one year, several kilograms of each constituent of concern (2-2.9 kg Hg, 45-50 kg As, and 45-110 kg Se) would be removed from settling in a 2.5 m deep full-scale equalization basin. Neither aqueous concentrations of Hg, As, and Se nor toxicity of FGD water decreased significantly during a 24 hr HRT within the equalization basins. However, the percent removal due to settling for total (water and particles) Hg, As, and Se is 6.5-99% Hg, 87-90% As, and 1.3-3.2 % Se. Results of our investigation demonstrate that equalization basins of CWTS are most useful for settling particles from FGD waters prior to treatment in wetland reactors.

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CHAPTER IV

SUMMARY AND CONCLUSIONS

Introduction

Coal combustion continues to be a prominent energy source for the United States. Electric power plants are among the leading contributors of sulfur dioxide, nitrogen oxide, and carbon dioxide emissions (USEPA, 2005). As concerns for air quality increase, more stringent emission limits are placed on coal-fired power plants. To meet air quality standards, power plants are implementing flue gas desulfurization scrubber systems, which reduce sulfur dioxide and mercury emissions. Flue gas desulfurization (FGD) processes prevent gaseous pollutants from entering the atmosphere, but produce large quantities of water containing inorganic constituents (Hg, As, Se) and particulate matter. Direct discharge of this water to receiving systems may not be feasible due to limits set by the Clean Water Act and National Pollutant Discharge Elimination System (NPDES) permits.

To comply with water quality discharge limits, constructed wetland treatment systems (CWTS) present a viable option. These systems have been designed to treat a wide range of constituents (Gillespie et al., 2000; Murray-Gulde et al., 2003; Arrington, 2005), and generally contain an equalization basin followed by reactors containing specific plants and hydrosoil. Equalization basins of CWTS have been utilized to cool and homogenize water and settle particulates while storing FGD water. This research concentrated on processes occurring within an equalization basin of a CWTS. Overall,

this research provided insight to the types of particles that settle in an equalization basin of a CWTS used to treat FGD water, the time needed for particulates to settle in an equalization basin with a typical depth, and the treatment, in terms of constituent removal and toxicity, provided by an equalization basin before water enters the wetland reactors.

Characterization of flue gas desulfurization particulates in equalization basins

The second chapter of this research focused on characterizing FGD particulates that settle within an equalization basin of a CWTS (Table 2.5). The objectives were: 1) to determine elemental and mineralogical compositions of FGD particulate samples; and 2) to measure particle size distribution of the samples. FGD particulates contain several particle types. The most common particle type was gypsum, which is a byproduct of the FGD process. These particles were interpreted to have formed during reactions within the wet-limestone based scrubber. Black non-magnetic particles contained mainly carbon and oxygen, and were interpreted as unburned material from coal transported by flue gas produced during combustion. Black magnetic particles were similar to magnetic fly ash in terms of size, shape, and elemental composition, and were interpreted to have formed within the coal combustion chamber. Orange aggregates were interpreted to be iron oxides transported by flue gas to the scrubber system. Additional rare particles were identified within FGD particulate samples. These included subangular aggregates interpreted to be limestone that did not react with flue gas in the wet-scrubber; a sphere interpreted as a cenosphere, which is a common component in fly ash; and a flat particle containing zinc, which is a trace element in coal. Size distributions showed that FGD

particulate samples consisted of predominantly silt-size particles, and mean particle size ranged from medium to coarse silt. Abundance of particulates in FGD water indicates that the dewatering process is not effectively removing all solids, especially silt and clay size material.

The role of an equalization basin in a constructed wetland treatment system

The third chapter of this investigation evaluated the physical treatment of water by an equalization basin and included three main objectives: 1) to determine the settling rates of FGD particles within an equalization basin; 2) to determine if removal of Hg, As, and Se occurs within an equalization basin by measuring change in concentrations over time; and 3) to determine if toxicity of FGD water changes within an equalization basin during a 24 hr hydraulic retention time (HRT). The process of settling was the most effective mechanism for treatment within the equalization basin. For a 2.5 m deep equalization basin 98 to 99% of FGD particles settle within a 24 hr HRT. For FGD particle samples studied, 95% removal occurred within the first four hours of settling. Particulates in FGD water were determined to contain constituents of concern (Hg, As, and Se). As these particles settled, the associated Hg, As, and Se are removed from the water column. Aqueous concentrations of constituents of concern in FGD water did not significantly decrease from initial samples to final samples in the pilot-scale equalization basin experiments. Low removal of dissolved constituents within the equalization basin is expected, because an equalization basin, unlike the subsequent wetland, is not designed to provide conditions under which transfers and transformations of constituents will

occur. Based on toxicity experiments, pilot-scale equalization basins did not decrease

toxicity of FGD water during a 24 hr HRT. Treatment by the wetland reactors reduces

constituents of concern from FGD water to concentrations that meet NPDES permits and

discharge limits (Huddleston, et al., 2005; Eggert et al., 2005).

Conclusions

Results from this investigation indicate that equalization basins provide initial

treatment of FGD waters by settling particulates. Settling of particulates in an

equalization basin increases the longevity of CWTS by controlling the concentration of

unwanted particles deposited in the wetland reactors. By characterizing size, elemental

composition, and settling rates of these particulates, insight is gained to the type and

volume of material expected to settle in an equalization basin. Results from this pilot-

scale process study may be used in future designs of equalization basins and possible

reuse options for the settled material.

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APPENDICES

Appendix A

Standard Operating Procedures for Characterizing FGD Particulates

The procedures used to characterize FGD particulates are listed below and found on the pages that follow.

TITLE: METHOD FOR DETERMINING PARTICLE SIZE DISTRIBUTION FOR FGD PARTICULATES

Meg Iannacone, Dr. James W. Castle

1.0   OBJECTIVE

The measurement of particle size distribution is important for the characterization of sediment samples, and specifically for the characterization of FGD particulates settled in an equalization basin. The distribution can be broken down into sand, silt, and clay fractions, as well as different grain size diameters within the sand and silt fractions. The pipette method, which is based on Stokes' Law, is used for silt and clay analysis. The overall objective of this analysis is to determine the size distribution of FGD particulates for characterization as well as for further studies to determine settling rates of particles in FGD water in an equalization basin of a constructed wetland treatment system. By understanding the particle size distribution, the time for a targeted amount of particle removal within a basin with a certain depth can be determined.

2.0   HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0   PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0   REQUIRED AND RECOMMENDED MATERIALS

4.1   Supplies

Pre-weighed 50 mL glass beakers
250 mL glass beaker
1,000 mL graduated cylinder
Thermometer
Stop watch
62 µm mesh sieve
20 mL pipette
Metal stir rod

4.2   Equipment

Drying oven
Analytical balance
Dessicator

5.0   PROCEDURE

5.1   Separating Sand from Silt/ Clay (Wet Sieving)

Place FGD particulate sample into a clean 250 mL glass beaker and homogenize by
stirring with a small amount of de-ionized water for several minutes. Weigh and
record wet weight of samples using 15 to 20 grams of mostly mud samples (FGD
samples are generally muddy in consistency). Wet sieve sample through a 62 µm sieve
into a large evaporation dish. Use as little de-ionized water as possible for the
procedure. Transfer the contents in the evaporative dish, which are the silt and clay
particles, to a 1,000 mL graduated cylinder. Be careful to not spill contents or exceed
more the 1,000 mL mark on the graduated cylinder. Collect the material caught in the
sieve in a small pre-weighed 50 mL beaker and dry particles; these are the sand size
particles.

5.2   Analyzing the silt and clay

5.2.1   Determining sample withdrawal times for pipette analysis
Withdrawal times for pipette analysis are based upon Stokes' Law and can be
written as (Folk, 1980):

$$T = Depth / (1500*A*d^2) \qquad \qquad \textit{Equation 1}$$

Where:
   T = time in minutes
   Depth = sampling depth in cm
   A = a constant based on viscosity, gravity, and density of the particles
   d = particle diameter in mm

Generally, the sampling times are based on a density for quartz grains (see Folk,
1980), however, specifically for FGD particles; the density of gypsum may be more
accurate. Determine the times of sampling for ½ phi intervals and create a table for
reference. Phi is calculated by the $-\log_2$ (grain size diameter in mm). "A" values
can be extrapolated by using other "A" values at different densities and
temperatures. For these values see Gee and Bauder (1986) and Folk (1980). At
22ºC, the "A" value for gypsum particles is 3.00. The sampling depths can be the

same as Folk (1980) (See Table 1). Label each pre-weighed 50 mL beaker for each withdrawal time with a phi value.

Table 1. Example of sampling times, depths, and grain size for particle size distribution. Time has been calculated based on the density of quartz (Folk, 1980).

Grain Size (mm)	Grain Size (phi)	Sampling depth (cm)	Time (s)
0.0625	4	20	20
0.044	4.5	20	113
0.031	5	10	114
0.022	5.5	10	226
0.016	6	10	427
0.011	6.5	10	963
0.0078	7	10	1796
0.0055	7.5	10	3613
0.0039	8	10	7185
0.0028	8.5	5	6970
0.002	9	5	13661

5.2.2   Pipette Analysis

Obtain the graduated cylinder with silt and clay particles and add de-ionized water until the 1,000 mL mark is reached on the cylinder. Record the temperature of the graduated cylinder. This can be done by allowing a beaker of water to reach the room temperature of the water in the cylinder. Stir the water column vigorously with the metal stirring rod from bottom to top. Stir until material is evenly distributed throughout the column; there should be no particles settled to the base of the cylinder. Remove the rod, and begin the timer. When the first time is reached to sample, insert the pipette to a depth of 20 cm and withdraw exactly 20 mL of sample. Continue removing 20 mL samples at the designated times. Be sure to rinse the pipette between sampling. This can be done by pulling de-ionized water into the pipette, and expelling into the beaker of that same sampling time. This ensures that none of the sample is lost. Once all samples are taken, place glass beakers in a an oven at 100ºC for 24 hours. Remove beakers, and place in the dessicator to cool. Reweigh the beakers, and record the weight.

5.3   Calculations

Silt and clay weight
Subtract the weight of the cleaned initial beaker from the weight of the beaker plus the
sample. This gives the weight of the silt and clay in the beaker. This value is 1/50 of
the total amount in the graduated cylinder as long as the particles were uniformly
distributed. Therefore multiply each fraction by 50. Each value represents the amount
of mud still in suspension at the time removed, or the weight of particles finer than the
phi value corresponding to the sample time.

The total sample weight = total mud (g) + total sand (g)

Cumulative percent coarser is determined by the following:
100(Sand + Fines – later pipette sample multiplied by 50)/ (Sand + Fines)

5.4 Graphing

There are several ways to graph the data collected from the size analysis. The
cumulative curve, arithmetic ordinate is the most common method. This can be
graphed by plotting the cumulative percent of the grain size diameters in phi.
(Cumulative %/ phi). Draw a curve through all resulting points. The advantage of this
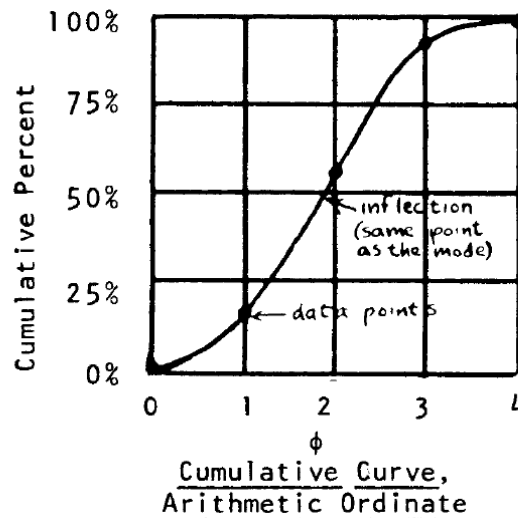graph is that all statistical parameters can be read directly from the graph.

Figure 1. Example of a cumulative curve from (copied from Folk, 1980).

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5.5 Statistical Analysis

Several statistical measurements can be determined from size data collected. Specifically, average grain size can be determined three ways: mode, median, and graphic mean. Additional measurements can be made for uniformity such as sorting, skewness, and kurtosis. These can be measured by finding specific cumulative percentages and corresponding phi values from the cumulative curves. Refer to Table 2 for formulas and statistical measurements.

Table 2. Graphic formulas and statistical measurements (Folk, 1980). All φ values in the equations ($\varphi16$, $\varphi50$, $\varphi84$, etc.) are determined from the cumulative curve plot, where each value indicates the percentage coarser than the corresponding diameter.

Name	Equation	Measures
Graphic Mean	$Mz = \dfrac{(\varphi_{16} + \varphi_{50} + \varphi_{84})}{3}$	Grain size
Median	$Md = \varphi_{50}$	Grain Size
Mode	$M_o =$ Most frequently-occurring	Grain Size
Inclusive Graphic Stnd. Deviation	$\sigma_1 = \dfrac{\varphi_{84} - \varphi_{16}}{4} + \dfrac{\varphi_{95} - \varphi_5}{6.6}$	Sorting
Inclusive Graphic Skewness	$Sk_1 = \dfrac{\varphi_{84} + \varphi_{16} - 2\varphi_{50}}{2(\varphi_{84} - \varphi_{16})} + \dfrac{\varphi_{95} + \varphi_5 - 2\varphi_{50}}{(\varphi_{95} - \varphi_5)}$	Symmetry
Graphic Kurtosis	$K_G = \dfrac{(\varphi_{95} - \varphi_5)}{2.44(\varphi_{75} - \varphi_{25})}$	Peakedness

6.0   QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

All procedures are subject to review by the Quality Assurance Unit.

7.0   SELECTED REFERENCES

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TITLE: METHOD FOR USING X-RAY DIFFRACTION TO DETERMINE ELEMENTS AND MINERALS IN FGD PARTICULATES

Meg Iannacone, Dr. James W. Castle, Dr. Brannon Andersen

1.0   OBJECTIVE

This is a method to identify minerals that comprise FGD particulates by using x-ray diffraction procedures. X-ray diffraction is a method used to identify unknown specimens by determining the crystal structure and comparing it to a standard powder diffraction pattern (Suryanarayana and Norton, 1998). FGD materials may contain several crystalline materials that have not been clearly identified. These methods are intended for use with the Rigaku Miniflex diffractometer and the Scintag 2000 diffractometer.

2.0   HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0   PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0   REQUIRED AND RECOMMENDED MATERIALS

4.1   Reagents
1 M Hydrochloric acid, HCl
Glacial acetic acid
Dispersant: sodium hexametaphosphate
Acetone

4.2   Supplies
Fine powders < 45 microns (FGD particulates)
Glass microscope slides / Specimen holders
Tweezers
Glass beakers
Glass stirring rod
Distilled water

Wide mouth glass jars
Centrifuge tubes / caps / rack
Spatula
Thermometer
Plastic syringe
Timer
Mortar and pestle

4.3   Equipment
X-ray source, diffractometer, sample holder

5.0   PROCEDURE

5.1   Collecting and Separating Samples
Several fractions of FGD particulates may be analyzed; examples are: bulk sample, bulk sample with selected particles removed, bulk sample after treatment with dilute HCl and acetic acid, bulk sample of specific grain sizes, and single grain. Color of FGD particles may also provide an acceptable separation technique. It is important to try to separate the different mineral species as much as possible before analysis.

5.1.1   Removing carbonates
 To determine if the FGD particulates contain carbonates a small amount of hydrochloric acid (1 M HCl) may be used to see if the sample effervesces. If carbonates are present, they should be removed from the sample for analysis of non-carbonate minerals. Acetic acid may also be used to remove carbonates as to not affect any clay materials (although clay may not be likely in FGD particulates). Add samples to beaker and add acetic acid (50-75 mL) or HCl solution. Stir and allow to stand overnight. Repeat until the suspension no longer effervesces. Remove leftover acid to prepare sample in section **5.2**.

5.1.2   Decantation for separation of clays and silts
 Label wide mouth jars with 0 and 5 cm depths. Suspension of clay and silt particles should be added to the jars along with distilled water to the 0 cm water depth line. Add a small amount of dispersant (no more than 0.5% of suspension by weight). Seal and shake jar until homogenized. Start the timer and check the temperature. After the appropriate time (see Table 1) and the silt has settled use the syringe to withdraw a substantial amount of clay and store in centrifuge tube until **Section 5.2**.

Table 1. Withdrawal time and temperature table for the separation of silt and clay (<2 micrometers) fractions by decantation (Poppe et al., 2001). All depths are assumed to be 5 cm; temperatures are in degrees C.

TEMPERATURE	TIME
20	1h1m30s
24	0h55m30s
32	0h47m0s

5.2 Preparation of Samples for Diffractometer

Powder each sample with a mortar and pestle to create a random orientation crystal sample. The material should be less than 50 microns in size and should pass through a US 325 mesh sieve. Take fine powders and add to sample holder. Amount of sample will depend on the diffractometer used. With the Rigaku Miniflex diffractometer, the sample must be firmly pressed into the sample holder and assure that the sample is smooth across the surface. This can be done with a glass slide. The Scintag 2000 diffractometer can use less sample and the sample does not need to be packed within the holder, but the surface should be smooth.

5.3 Using the Diffractometer

Depending on the diffractometer, procedures may vary, and should be monitored by a professional until persons are trained on the equipment.

5.4 Interpreting Diffraction Patterns

Each sample will have a corresponding pattern with diffraction spacings and peak intensities. Identification of the peaks can be determined by, 1) direct comparison of diffraction patterns from the samples and known minerals and measuring and 2) obtaining the actual diffraction spacings and comparing them to known spacings for minerals (Whittig and Allardice, 1986). The diffractometers equipped with computer software provide both patterns and diffraction spacings for minerals, and may provide valuable assistance for identifying the diffraction patterns.

6.0   QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

All procedures are subject to review by the Quality Assurance Unit.

7.0　SELECTED REFERENCES

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　　　A., ed., Methods of Soil Analysis, Part I-Physical and Mineralogical
　　　Methods (second edition): Madison, Wisconsin, American Society of
　　　Agronomy, Inc., p. 383- 411.

TITLE: METHOD TO PREPARE FGD PARTICULATE SAMPLES FOR USE WITH SCANNING ELECTRON MICRSOSCOPY (SEM) AND ELECTRON DISPERSIVE SPECTROSCOPY (EDS)

Meg Iannacone, Dr. James W. Castle

1.0   OBJECTIVE

Using scanning electron microscopy (SEM) allows the user to evaluate, observe, and characterize materials, such as particulates, on a nanometer to micrometer scale. Energy dispersive spectroscopy (EDS) is performed with SEM analysis to characterize the elemental composition of particles studied. This specific protocol will aid in the preparation of FGD particles for use with the Hitachi 3400 SEM equipped with EDS.

2.0   HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0   PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0   REQUIRED AND RECOMMENDED MATERIALS

4.1   Supplies
FGD particulates
Specimen holders
Tweezers
Double sided tape (Carbon)
Studs (for sample mount)

4.2   Equipment
Scanning electron microscope
Energy dispersive spectrometer

5.0 PROCEDURE

5.1 Preparing Samples

5.1.1 Separating types of samples
Use a dissecting microscope under a magnification of 50X to determine particles of interest. To successfully separate types of particles, use tweezers to remove larger particles. Particles types can be separated by wet sieving the sample through a specific sized sieve (Separating sand from silt and clay can be completed by using a 62 µm sieve.

5.1.2 Preparing stubs for the SEM
Prepare one stud per sample by applying double sided adhesive to each stud (either cut to size or have precut circles). Put your sample (particles) spread out on a piece of filter paper. Carefully, adhere particles to stub, without letting fingers touch the tape of the stub. Remove extra particles by gently blowing off excess. You do not want sample to clump or coat the adhesive with too many layers. Particles will move within the SEM chamber if not securely fastened to the stub adhesive. Continue creating and labeling samples. Particles may need to be coated with gold (or other coating) before being viewed with the SEM, this can be done using sputter coating equipment. If elemental characterization is needed, a stub with a standard (such as copper or cobalt) will need to be mounted separately. Fasten all stubs to specimen holder and map the position of each stub in a lab notebook for reference.

5.2 Using the Scanning Electron Microscope

Specific procedures for using the equipment will depend on the equipment. Those using the equipment should be properly trained and monitored by personnel in charge of the SEM and the lab. If the SEM 3400 is used for analysis, follow this procedure.

To begin press the air button to allow air into the main chamber. Once the chamber is ready, open the door to the chamber and carefully (using gloves to keep the chamber from becoming contaminated) place your samples on the sample holder into the designated place for the sample. Close the chamber and hit "evac" and wait until chamber is ready. Change the height of the stage to appropriately meet the needs of the prepared stub samples (generally between 5 and 10 cm). Follow further instructions on the computer before scanning samples. Specifically for uncoated samples the SEM should be in "variable pressure mode", set to 40 kv, set the probe current to 40, and begin observations.

5.3 Using the EDS

This will also depend on the equipment and the computer program used to evaluate the data. If the computer software INCA is used, refer to instruction manual. Depending

on what evaluation is to be made, Point and ID or Mapping may be used. Remember to properly calibrate the EDS using the standard stub (Cu or Co) in analysis mode. Try to achieve a "dead time" of 32 to 35% by adjusting the probe current.

6.0   QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

All procedures are subject to review by the Quality Assurance Unit.

Appendix B

Standard Operating Procedures to Determine Treatment
Within an Equalization Basin

The procedures used to analyze determine treatment in the equalization basin of a constructed wetland treatment system are listed below and found on the pages that follow.

TITLE: METHOD TO DETERMINE VISCOSITY AND DENSITY OF FGD WATER FOR USE WITH STOKES' LAW

Meg Iannacone, Dr. James W. Castle

1.0 OBJECTIVE

This is a method to determine kinematic viscosity and density of flue gas desulfurization (FGD) water by measuring the time for a volume of liquid to flow through a glass capillary viscometer and weighing a specific volume of water. The viscosity and density of FGD water is influenced by both temperature and total dissolved solids within the water. Total dissolved solids include, but are not limited to, chloride concentration (including magnesium, calcium, and sodium chlorides) and sulfate content. The best way to determine viscosity and density of different FGD waters is to measure the parameters directly. The viscosity and density of FGD water are important to determine settling velocity of particulates using Stokes' Law.

2.0 HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0 PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0 REQUIRED AND RECOMMENDED MATERIALS

4.1 Samples
FGD water (without particulates)

4.2 Supplies
Milli-Q water

4.3 Equipment
Cannon-Fenske Routine Viscometer
Heating plate (for water bath)
Thermometer
Viscometer holder
Stopwatch

Balance
1 mL pipette

5.0   PROCEDURE FOR MEASURING VISCOSITY

Select a clean, dry calibrated viscometer which will give a flow-time greater than 200 seconds. Charge viscometer (Figure 1) by inverting the viscometer and applying suction to the largest tube (Tube L) with the smaller tube (Tube N) immersed in the liquid sample. Draw the sample to timing mark F (located below the bottom bulb within viscometer). Mount viscometer in a constant temperature bath with the largest tube held vertical (±1°). Begin timing when sample reaches the E meniscus. Continue timing as water moves through the C bulb and stop when the sample reaches the F meniscus. Repeat three times, and record all times. Clean the viscometer thoroughly by rinsing several times between each water sample. Because liquids are very fluid, washing with specific solvents is not needed, and rinsing with Milli-Q water should be sufficient.
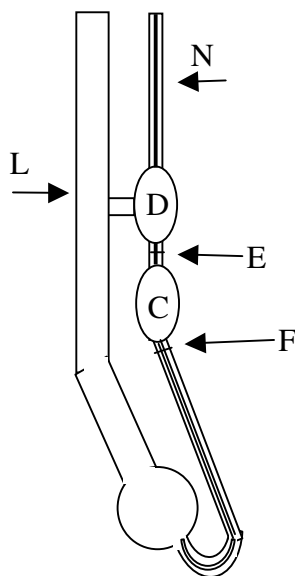

Figure 1. Cannon-Fenske Routine Viscometer for Transparent liquids. Follow procedure according to labels L, N, D, C, E and F.

5.1 Calculations

Calculate the kinematic viscosity (v in mm²/s) from the measured flow time (t in seconds) and the viscometer constant (C mm²/s/s) using the following equation:

$$V = C * t \qquad (1)$$

Then determine the dynamic viscosity using the equation:

$$\acute{\eta} = v*\rho*10^{-3} \qquad (2)$$

where:
  $\acute{\eta}$ = dynamic viscosity (mPa·s)
  ρ = density in kg/m^3
  v = kinematic viscosity (mm²/s)

The results should be reported to four significant figures along with the test temperature.

6.0 PROCEDURE FOR MEASURING DENSITY

Calibrate the 1 mL pipette by weighing 1 mL of de-ionized water until 1.0000 g is repeatedly measured by a balance. Adjust pipette as necessary. Use pipette to measure 1 mL of FGD water, and weigh this amount. Repeat several times to get an average reading of measurements to four significant figures. If different volumes of water are used calculate density by mass/volume.

7.0   REFERENCES

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TITLE: METHOD FOR MEASURING GENERAL WATER QUALITY PARAMETERS: pH, DISSOLVED OXYGEN, CONDUCTIVITY, TEMPERATURE, ALKALINITY, AND HARDNESS

Standard protocol for use at the Aquatic Ecotoxicology Laboratory at Clemson University

Brenda M. Johnson, Laura E. Ober, John H. Rodgers, Jr.

1.0   OBJECTIVE

The purpose of this protocol is to measure various general water quality parameters. Parameters such as pH, dissolved oxygen (DO), conductivity, temperature, alkalinity, and hardness are fundamental water quality parameters and are necessary for all water chemistry related studies.

2.0   HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0   PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0   REQUIRED AND RECOMMENDED MATERIALS

4.1   Reagents

Reagent:	Test:
Milli-Q water	all tests
pH buffers (4, 7, & 10)	pH, alkalinity
0.02 N standard sulfuric acid solution (H_2SO_4)	alkalinity
Eriochrome Black T indicator	hardness
Standard EDTA titrant (0.01M, 0.02N)	hardness
Buffer solution (Reference Standard Methods2340C)	hardness

4.2   Supplies

Supply:	Test:
Graduated cylinder	alkalinity, hardness

100-mL beakers	all tests
Magnetic stir bar	alkalinity, hardness
50-mL buret and stand	alkalinity, hardness

4.3   Equipment
Orion-model 420A pH Meter
YSI 500 Dissolved Oxygen Meter
YSI 30 Salinity, Conductivity, and Temperature Meter
Magnetic stir plate

5.0   PROCEDURE

5.1   pH
1. Calibrate the Orion Model 420A pH Meter using standard pH buffers 4, 7, and 10.
2. Rinse probe with milli-Q water to remove any prior contaminant.
3. Remove the small blue rubber stopper from the probe.
4. Submerge the tip of the probe in the sample and gently stir the sample with the probe or use a magnetic stir-bar.
5. When the pH meter beeps, record reading.
6. Rinse probe with milli-Q water and return to holder.

5.2   Dissolved Oxygen (DO)/Temperature
1. Calibrate the YSI 500 Dissolved Oxygen Meter.
2. Rinse probe with milli-Q water to remove any prior contaminant.
3. Completely submerge the tip of the probe in the sample and turn on the mixer.
   ***Note: If sample contains live organisms, do not use the mixer. Instead, gently stir the sample with the probe.
4. When the DO meter beeps, record DO in mg/L (a "*" should also appear by the mg/L and the % symbol). Also record the Temperature to a tenth of a degree (i.e. 20.1°C).
5. Rinse probe with milli-Q water and return to holder.

5.3   Conductivity
1. Turn on the YSI 30 Salinity, Conductivity, and Temperature Meter.
2. Rinse probe with milli-Q water to remove any prior contaminant.
3. Submerge the probe in the sample and gently stir the sample with the probe.
4. When the conductivity reading has stabilized the conductivity. Conductivity will record in μS/cm (mS/cm) and temperature in degrees Celsius.
5. Rinse probe with milli-Q water and return to holder.
6. When finished turn off the meter.

5.4   Alkalinity
1. Using a graduated cylinder, measure 50mL of sample water and pour it into a

100mL beaker with a magnetic stir-bar.
2. Place sample beaker on magnetic stir-plate. Turn on stir-plate to begin mixing sample.
3. Calibrate pH meter. Place probe in the appropriate stand, with the tip completely submerged in the sample water. (Make sure the stir-bar does not hit the pH probe).
4. Record the initial level of titrant (0.02 N H_2SO_4) in the buret (fill buret as necessary).
5. Slowly drip titrant into the sample, allowing time for the pH meter to stabilize.
6. Titrate to pH 4.5.
7. Record the volume (mL) of titrant used to reach the pH endpoint (pH=4.5).
8. Calculate: Total Alkalinity (mg/L as $CaCO_3$) = vol. titrant (mL) x 20
9. Turn off stir-plate and discard sample.

5.5   Hardness
1. Using a graduated cylinder, measure 50mL of sample water and pour it into a 100mL beaker with a magnetic stir-bar.
   (Dilutions can be made to conserve EDTA titrant, be sure to calculate dilutions into the final equation.)
2. Add 2-5 mL of buffer solution (to give the sample a pH of 10.0-10.1).
3. Add 2-4 drops of Eriochrome Black T Indicator. Sample should turn gold (deep yellow).
4. Place sample beaker on magnetic stir-plate. Turn on plate to mix sample.
5. Record the level of titrant (EDTA) in the buret (fill buret as necessary).
6. Slowly drip titrant into the sample, allowing time for the color change to stabilize.
7. Titrate until the gold turns to a bright yellow (very similar to pH buffer 7).
8. Record the volume of titrant (mL) used to reach the color change.
9. Calculate: Hardness (mg/L $CaCO_3$) = volume titrant(mL) x 20
10. Turn off stir-plate and discard sample.

6.0   QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

All procedures are subject to review by the Quality Assurance Unit.

TITLE: METHOD FOR MEASURING CHLORIDE CONCENTRATION

Standard Protocol for use at the Aquatic Ecotoxicology Laboratory at Clemson University

Sarah E. Sundberg, Derek Eggert, J. Chris Arrington, John H. Rodgers, Jr.

1.0   OBJECTIVE

This is a titration method for determining the concentration of total chlorides in wastewater samples. A HACH Chloride Test Kit is used in this method. After the addition of a chloride indicator, silver nitrate is used to titrate the sample. Chloride concentration is measured at a color change from yellow to rusty brown.

2.0   HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0   PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0   REQUIRED AND RECOMMENDED MATERIALS

4.1   Reagents
Water, 18 M Ω cm
Chloride 2 Indicator PP
Silver nitrate solution, 1.128 N

4.2   Supplies
250 mL Erlenmeyer flasks
1 inch magnetic stir bars
100 mL graduated cylinder
HACH Chloride Test Kit Model CDS-DT, 10-10,000 mg/L range

4.3   Equipment
Magnetic stir plate

5.0   PROCEDURE

To a 250 mL Erlenmeyer flask, add 98 mL water and 2 mL sample. Place a stir bar in the flask and set on a stir plate. While stirring, add one packet of Chloride 2 Indicator PP (note the yellow color of the sample). Once the powder is dissolved completely, begin to titrate with the silver nitrate solution. Titration is complete when the sample turns a rusty-brown color. Record the digital reading from the titrator, and multiply this number by 25 to determine the concentration of chlorides in mg/L.

6.0   QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

All procedures are subject to review by the Quality Assurance Unit.

TITLE: METHOD FOR MEASURING SULFATE CONCENTRATION

Standard Protocol for use at the Aquatic Ecotoxicology Laboratory at Clemson University

Sarah E. Sundberg, Derek Eggert, J. Chris Arrington, John H. Rodgers, Jr.

1.0 OBJECTIVE

This is a turbidimetric method for determining the concentration of sulfate in wastewater samples. In this method, the sulfate ion (SO_4^{2-}) is precipitated in an acetic acid medium with barium chloride ($BaCl_2$) to form barium sulfate ($BaSO_4$) crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer and the SO_4^{2-} concentration is determined by comparison of the reading with a standard curve. The minimum detectable concentration using this method is approximately 1 mg/L.

2.0 HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0 PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0 REQUIRED AND RECOMMENDED MATERIALS

4.1 Reagents
Water, 18 M Ω cm
Magnesium chloride, $MgCl_2 \cdot 6H_2O$
Sodium acetate, $CH_3CHOONa \cdot 3H_2O$
Potassium nitrate, KNO_3
Acetic acid, CH_3COOH (99%)
Barium chloride, $BaCl_2$
Sodium sulfate, Na_2SO_4

4.2 Supplies
Stop watch
Measuring spoon

250 mL Erlenmeyer flask
100 mL graduated cylinder
1-inch magnetic stir bar
Cuvette

4.3   Equipment
Magnetic stir plate
Spectrophotometer, for use at 420 nm, providing a light path of 2.5 to 10 cm

5.0   PROCEDURE

5.1   Buffer solution preparation
Dissolve 30 g magnesium chloride, 5 g sodium acetate, 1 g potassium nitrate, and 20 mL acetic acid in 500 mL water and make up to 1,000 mL with water.

5.2   Preparation of calibration curve
Prepare a 100 mg/L standard sulfate solution by dissolving 0.1479 g anhydrous Na_2SO_4 in distilled water and dilute to 1,000 mL. Based on expected sulfate concentration is samples, prepare four standards, 0 ppm, 20 ppm, 40 ppm, and 80 ppm. Carry these standards through the entire procedure. Measure the turbidity of the standards on the spectrophotometer. Plot the turbidity readings and concentrations to determine the equation of the calibration curve.

5.3   Formation of barium sulfate turbidity
To a 250 mL Erlenmeyer flask, add 95 mL water and 5 mL sample. Place a stir bar in the flask and set on a stir plate. While stirring, add 20 mL buffer solution and a spoonful of barium chloride crystals. Begin timing immediately. Stir for 60 seconds at a constant speed. After stirring period has ended, pour the solution into a cuvette and measure turbidity after allowing the sample to set for 5 minutes. Use the calibration equation of $y = mx + b$ to determine the sulfate concentration by substituting the spectrophotometer reading for y and solving for x, then multiplying by 20.

6.0   QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

All procedures are subject to review by the Quality Assurance Unit.

TITLE: METHOD FOR DETERMINING REMOVAL OF HG, AS, AND SE IN FGD WATER OF AN EQUALIZATION BASIN

Meg Iannacone, Dr. James W. Castle, Dr. John H. Rodgers, Jr.

1.0   OBJECTIVE

This is a method to determine if an equalization basin of a constructed wetland treatment system decreases constituents of concern (Hg, As, and Se) from FGD wastewater during a 24 hour hydraulic retention time of water using a small-scale equalization basin. FGD wastewater entering the equalization basin contains concentrations of Hg, As, and Se as well as particulates. Storage of FGD water and settling of particulates have been the major functions of the equalization basin. No treatment (transfers and transformations of constituents) has been attributed to the equalization basin previously.

2.0   HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0   PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0   REQUIRED AND RECOMMENDED MATERIALS
4.1 Samples
FGD Wastewater
FGD particulates

4.2   Supplies
73 L plastic rectangular bin
50 mL centrifuge tubes
1,000 mL Nalgene bottle
Vacuum filtration apparatus
45um filter papers
Milli-Q water
Municipal water

5.0 PROCEDURE

5.1 Experimental Design

The basin is a no flow system, and the major parameter used for the experiment is settling of particulates over time. The dimensions of the equalization basin are 50 cm by 38 cm with a depth of 38 cm (Figure 1). Fill 73 liter basin with FGD wastewater (50 liters) diluted to 4000mg/L chlorides. Add 1,000mg/L (50g) FGD particulates to FGD wastewater and stir together.
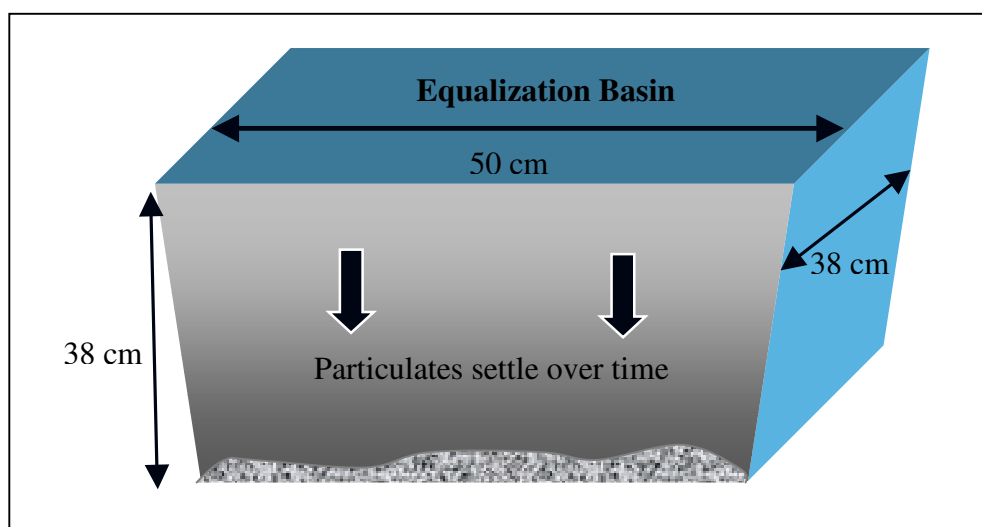

Figure 1. General design and dimensions of small-scale equalization basin.

5.2 Sampling

Take four samples (50 mL sample with centrifuge tube for As and Se, and a glass container for Hg) (2 reps) at a depth of 20 cm evenly spaced throughout the basin immediately after stirring. Allow settling of particulates for 24 hours. Resample water at same four locations (2 each) at a depth of 5 cm. Depth of sampling has been chosen based on Stokes' Law for settling of particulates (62 microns at initial, 2 microns at 24 hours using a specific gravity for quartz, 2.65). Time between sampling has been decided by hydraulic retention times (HRT) set for a full scale equalization basin. After each sampling time (initial and final) collect 1 liter sample of water for toxicity experiment (see SOP), 1 liter for particle digestions, and 1 liter sample for general water chemistry (pH, alkalinity, hardness, TDS, TSS, chloride concentration, sulfate concentration, COD, dissolved oxygen, temperature, and conductivity).

Table 1. Distribution of samples collected for experiment.

	Initial	Final	Total
Time	t=0	t=24hrs	
50 mL Samples for filtration	4	4	8
1 liter for each digestion	4	4	8
1 liter for toxicity test	1	1	4
1 liter water chemistry	1	1	2

5.3 Prep for Samples

All water should be brought immediately back to the lab and refrigerated or preserved until further analysis. The water samples needed for Se and As inorganic analysis should be acidified with 1.25 mL of trace metal nitric acid, and the samples needed for Hg analysis should be preserved with 0.25 mL of BrCl. The water preserved for Hg analysis should be placed in glass vials. This is done to keep the Hg from entering the plastic membrane. All water samples should be vacuum filtrated through a 0.45 µm filter paper to remove particles.

5.4 Analysis

Water samples can be analyzed for Hg and As by Atomic Fluorescence Spectroscopy (AFS) (Aurora Instruments, AI 3200) to determine concentrations in the ppb range. Se concentrations can be determined by Inductively Coupled Plasma-Atomic Emissions Spectrometry (ICP-AES) (Spectro Analytical Instruments, Spectro Flame-EOP) if concentrations are within the range of detection.

6.0 QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

All procedures are subject to review by the Quality Assurance Unit.

TITLE: METHOD FOR DIGESTING AND MEASURING HG, AS, AND SE CONCENTRATIONS IN FGD PARTICLES

Meg Iannacone, Dr. James W. Castle, Dr. David Bruce

1.0   OBJECTIVE

This is a method to determine if Hg, As, and Se are associated with FGD particulates settling in an equalization basin. Currently there has been no treatment attributed to the equalization basin. Through the process of settling, FGD particles may be providing treatment to the FGD water by not only removing total suspended solids but also by removing elements associated with these particulates.

2.0   HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0   PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0   REQUIRED AND RECOMMENDED MATERIALS
4.1   Samples
FGD particulates from filtered FGD water samples

4.2   Chemicals
HNO_3 65%
H_2SO_4 65%

4.3   Supplies
Vacuum filtration apparatus
0.45 um filter papers
Milli-Q water
Teflon PFA vessels

4.4   Equipment
Balance
Microwave Digester
Atomic Flame Spectrometer

Inductively Coupled Plasma-Atomic Emissions Spectrometer

5.0 PROCEDURE

5.1 Preparing Samples
To obtain FGD particulates from the water, filter 200 mL of FGD water through a 0.45 µm filter (preferably an ashless filter) using a vacuum filtration apparatus. Weigh the filter paper prior to filtration and after filtering to obtain the weight of the particulates only. Repeat this procedure 3 times for each water sample.

5.2 Digesting Particulates
Digesting particles should be completed according to Table 1. If most of the FGD particulates are gypsum, refer to the gypsum section only.

Table 1. Sample size and method for digestion for both coal fly ash and gypsum. Two methods (1 and 2)may be used for the digestion of gypsum to determine concentrations of As and Se (Hatanpää et al. 1997).

Sample Type	Element	Size (g)	Digestion acids (mL)
coal fly ash	As, Se	0.2	HNO_3 (10) + HF (1) + H_3BO_3 (10)
coal fly ash	Hg	0.5	HNO_3 (5) + H_2SO_4 (2.5)
gypsum	As, Se	0.5	1) HNO_3 (10)
gypsum	As, Se	0.25	2) HNO_3 (10) + HCl (5) + HF (0.5), H_3BO_3 (5)
gypsum	Hg	2	HNO_3 (10) + H_2SO_4 (5)

5.2.1 Digesting particulates for Hg analysis
Complete under a reflux condenser. Add to a weighed round bottom boiling flask the filter paper with particulates, 10 mL HNO_3 (Certified ACS Plus), and 5 mL H_2SO_4 (Certified ACS Plus), reweigh. Attach boiling flask to reflux condenser (remember to add grease around the base of the glass to prevent the two pieces of glass from sticking too tightly during heat expansion). Bottom of flask should be in a small container of mineral oil for heating and a thermometer should be placed in the mineral oil to record temperature. Turn on water to reflux condenser and slowly heat contents of flask. Heat until 100ºC is reached and held for 15 minutes. Allow contents to cool, leaving the water running through the reflux condenser. Reweigh round bottom flask. Repeat procedure three times for each water sample.

5.2.2 Digesting particulates for As and Se Analysis

To digest particulates for As and Se add particulates to Teflon PFA vessels (one sample per vessel). Add 10 mL HNO_3 (Certified ACS Plus), and weigh vessels. Close caps tightly. Add samples to the microwave digester and record where samples are within the microwave sample holder. Remember to balance the samples within the digester (similar to a centrifugation holder). Follow directions on microwave digester for using the instrument. The microwave digester should be initiated at 100% power for 3 minutes (600 W), 65% power for 15 minutes, and 40% power for 20 minutes. All samples should be prepared in triplicate.

5.3   Analyzing Digested Particulates for Hg, As, and Se

Digested particle samples can be analyzed for Hg and As by Atomic Fluorescence Spectroscopy (AFS) (Aurora Instruments, AI 3200) to determine concentrations in the ppb range. Se concentrations can be determined by Inductively Coupled Plasma-Atomic Emissions Spectrometry (ICP-AES) (Spectro Analytical Instruments, Spectro Flame-EOP) if concentrations are within the range of detection.

6.0   QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

All procedures are subject to review by the Quality Assurance Unit.

7.0   REFERENCES

Hatanpää, E., Kajander, K., Laitinen, T., Piepponen, S., and Revitzer, H., 1997, A study of trace element behavior in two modern coal-fired power plants, I. Development and optimization of trace element analysis using reference materials: Fuel Processing Technology 51: p. 205-217.

TITLE: METHOD TO COMPARE TOXICITY FOR PRE- AND POST-TREATMENT FGD WATER IN AN EQUALIZATION BASIN

Meg Iannacone, Dr. John H. Rodgers, Jr., Dr. James W. Castle

1.0   OBJECTIVE

This is a method to compare toxicity of FGD water at initial sampling (simulating inflow to an equalization basin) to that of FGD water at final sampling (simulating water leaving the equalization basin based on a 24 hour retention time). Full-scale equalization basins have been designed to hold water within a basin for 24 hours before entering the wetland cells of a CWTS, and therefore the time between sampling is 24 hours. The experiment includes collecting samples when particulates are suspended in a water column and after particles have settled. The toxicity is monitored throughout the pilot-scale constructed wetland treatment system from equalization basin to wetland cells using *C. dubia*. This study uses *C. dubia* to evaluate the toxicity of pre and post treatment of the equalization basin, which has not been previously studied.

2.0   HEALTH AND SAFETY

Proper lab attire, including scrubs, lab coat, gloves and safety glasses must be worn at all times.

3.0   PERSONNEL/TRAINING/RESPONSIBILITIES

Any graduate research assistant familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure.

4.0   REQUIRED AND RECOMMENDED MATERIALS
4.1   Samples
FGD water (diluted to ~4000 mg/L chlorides)
FGD particulates (at ~1,000 mg/L in water)

4.2   Supplies
73 liter rectangular Rubbermaid® container
Sampling containers (1 L Nalgene® bottles)
Glass vials and trays for toxicity experiment
Algae and YCT (yeast)
Moderately hard water (70 mg/L $CaCO_3$)

4.3   Organisms
Approximately 200 *Ceriodaphnia dubia* (less than 24 hour old neos)

5.0   PROCEDURE

5.1   Preparing small scale equalization basin and sampling
Fill 73 liter Rubbermaid® container with FGD water diluted to ~4000 mg/L chlorides. Add 1,000 mg of FGD particulates to each liter of FGD water and stir together. To make use of the actual size of the container, add 50 liters of FGD diluted water and 50 grams of FGD particulates. Take 1 liter Nalgene® bottle sample immediately after stirring at a depth of 10 cm for use in toxicity test. Allow settling of particulates for 24 hours. Resample water at a depth of 10 cm for toxicity experiment.

5.2   Range Finding Test
A preliminary test is needed to determine the appropriate range of survival for *Ceriodaphnia dubia* in FGD water. The acceptable range for chlorides for the test organism is less than 640 mg/L based on a 7 day-static renewal test for C. *dubia* previously studied. The Hg, As, and Se (or other) will show additional toxicity and dilutions of the water may be needed. Use 10 *C. dubia* per dilution in FGD waters diluted to find a specific range of survival, Table 1.   All dilutions should be prepared with moderately hard water.

Table 1. Examples of dilutions to start experiment and a continuation of dilutions if needed to observe toxicity differences. All dilutions should be prepared with moderately hard water.

Chloride conc. mg/L	% dilution	Examples of Dilutions			
800	20	6.25	5	2.5	1.25
500	12.5	0.5	0.1	0.05	0.01

5.3   Toxicity Experiment
Conduct a standard U.S. EPA 7-d static/renewal toxicity experiment with *Ceriodaphnia dubia*, a water flea, to determine the toxicity of the water in an equalization basin (Lewis et al., 1994). Add each test dilution for initial and final water samples to separate sets of 10 *Cerio* vials. Prepare a control using only moderately hard water and add to 10 vials. Add 100 µg each of algae and YCT to each

vial. Use ten organisms for each sample of water, one per glass vial. Collect data regarding mortality and reproduction for each day of the test by counting adults and neos. Transfer organisms each day into new vials with treatment water, algae, and YCT. *C. dubia* will be exposed to 16 hours light and 8 hours darkness in an incubator kept at 25° C.

5.4 General Water Chemistry Analysis
Conduct general water chemistry analysis on each test water on days 1, 3, 5, and 7. The water chemistry should include temperature, pH, dissolved oxygen, alkalinity, hardness, and conductivity. These data were used to determine if mortality was affected by changes in general water chemistry.

5.5 Statistical Analysis
Compare data using statistical analysis using the SAS program, if applicable. To determine differences in survival data between initial and final sampling use a Chi-Square Analysis using critical values from Fishers Exact Test ($\alpha = 0.05$). Evaluate reproduction data in comparison to control organisms using a one-way analysis of variance test (ANOVA; $\alpha=0.05$) and mean separation using a least significant difference test (LSD).

6.0 QUALITY CONTROL CHECKS AND ACCEPTANCE CRITERIA

All procedures are subject to review by the Quality Assurance Unit.

7.0 REFERENCES

Lewis, P.A., Klemm, D.J., Lazorchak, J.M., Norberg-King, T.J., Peltier, W.H., and Heber, M.A., 1994, Short-term methods for estimating the chronic toxicity of effluent and receiving waters to freshwater organisms, 3rd edition: US Environmental Protection Agency, EPA/600/4-91/002.