

BEFORE THE ILLINOIS POLLUTION CONTROL BOARD

NATURAL RESOURCES DEFENSE COUNCIL,)
PRAIRIE RIVERS NETWORK and SIERRA)
CLUB,)

Petitioners,)

vs.)

ILLINOIS ENVIRONMENTAL PROTECTION)
AGENCY and DYNEGY MIDWEST)
GENERATION, INC.,)

Respondents.)

PCB 2013-17
(APPEAL FROM IEPA
DECISION GRANTING
NPDES PERMIT)

NOTICE OF ELECTRONIC FILING

To: See Attached Service List

PLEASE TAKE NOTICE that on January 10, 2013, I electronically filed with the Clerk of the Pollution Control Board of the State of Illinois, c/o John T. Therriault, Assistant Clerk, James R. Thompson Center, 100 W. Randolph St., Ste. 11-500, Chicago, IL 60601, a SECOND SUPPLEMENT TO THE RECORD, a copy of which is attached hereto and herewith served upon you.

Respectfully submitted,

PEOPLE OF THE STATE OF ILLINOIS

LISA MADIGAN,
Attorney General of the
State of Illinois

MATTHEW J. DUNN, Chief
Environmental Enforcement/Asbestos
Litigation Division

BY: 
Rachel R. Medina
Assistant Attorney General
Environmental Bureau

500 South Second Street
Springfield, Illinois 62706
217/782-9031
Dated: January 10, 2013

CERTIFICATE OF SERVICE

I hereby certify that I did on January 10, 2013, cause to be served by First Class Mail, with postage thereon fully prepaid, by depositing in a United States Post Office Box in Springfield, Illinois, a true and correct copy of the following instruments entitled NOTICE OF ELECTRONIC FILING and SECOND SUPPLEMENT TO THE RECORD upon the persons listed on the Service List.



Rachel R. Medina
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This filing is submitted on recycled paper.

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GENERATION, INC.,)	
)	
Respondents.)	

SECOND SUPPLEMENT TO THE RECORD

Respondent, ILLINOIS ENVIRONMENTAL PROTECTION AGENCY ("Illinois EPA"), in accordance with the procedural rules of the Illinois Pollution Control Board ("Illinois PCB") as set forth in 35 Ill. Adm. Code 105.212 and 105.116, hereby supplements the Record with the following documents:

Permit File Documents

66. Letter dated November 9, 2010, from Michael T. Lowder, Unit Manager, Leaking Underground Storage Tank Section, Division of Remediation Management, Bureau of Land, Illinois EPA to Illinois Power Company, regarding Leaking UST Incident No. 932233. (This letter is the attachment to Document #27 of the Record referenced as "SKMBT_42110041314190.pdf.")
67. *Activated Carbon Injection: Effect on Simulated Fly Ash Sluice Water*, Technical Updated, March 2007, P. Chu, EPRI Project Manager, Electric Power Research Institute.

In addition, please note that Document #60 of the Record is also "Attachment A" to Document #56 of the Record.

Respectfully submitted,

LISA MADIGAN,
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7009 2820 0001 7494 6104

NOV 09 2010

Illinois Power Company
500 South 27TH Street
Decatur, Illinois 62525

Re: LPC #1250205003 -- Mason County
Havana/Illinois Power Co.
Rt. 78
Leaking UST Incident No. 932233
Leaking UST Technical File

Dear Owner/Operator:

The Illinois Environmental Protection Agency (Illinois EPA) has reviewed the file for the above-referenced incident. This review was conducted on November 4, 2010. Citations in this letter are from the Environmental Protection Act (Act), as amended by Public Act 92-0554 on June 24, 2002, and Public Act 96-0908 on June 8, 2010, and 35 Illinois Administrative Code (35 Ill. Adm. Code).

Based on the information currently in the Illinois EPA's possession, this incident is not subject to Title XVI of the Act or 35 Ill. Adm. Code 731. The incident was reported on August 19, 1993 due to a release from an underground oil transfer line which connected an aboveground tank to a dispensing pump. The release was not from an underground storage tank and therefore, the Illinois EPA Leaking Underground Storage Tank Section has no reporting requirements regarding this incident.

If you have any questions or require further assistance, please contact Mohammed Zillur Rahman at (217) 782-9848.

Sincerely,

Michael T. Lowder
Unit Manager
Leaking Underground Storage Tank Section
Division of Remediation Management
Bureau of Land

Cc: BOL File

RELEASABLE

NOV 10 2010

REVIEWER MD



**Activated Carbon Injection:
Effect on Simulated Fly Ash Sluice Water**

1013314

**Activated Carbon Injection:
Effect on Fly Ash Sluice Water**

Technical Update, March 2007

EPRI Project Manager

P. Chu

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CH2M HILL

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

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

Activated Carbon Injection: Effect on Simulated Fly Ash Sluice Water, EPRI, Palo Alto, CA: 2007, 1013314.

SUMMARY

The primary objective of this study was to investigate the effect of activated carbon injection (ACI) for mercury flue gas control on the composition of the fly ash sluice water and ash pond settleability. If the fly ash and spent carbon are wet sluiced to an ash pond, carbon particles that do not settle in an ash pond may be a compliance concern for total suspended solids (TSS), mercury as well as any other trace element that may be volatile in the flue gas and is adsorbed onto the carbon particle. A series of laboratory tests were conducted to simulate fly ash sluicing and then settling of solids in an ash pond. This investigation was a preliminary review of a small number of samples intended to identify potential issues and guide future research.

Preliminary conclusions were drawn regarding TSS, volatile metals, bromine, arsenic speciation, and selenium speciation on the three pairs of fly ash (with and without carbon) analyzed in this study. Laboratory fly ash sluicing experiments followed by settling studies were conducted to simulate fly ash sluicing followed by solids removals in a settling ash pond. The limited results indicated that most of the carbon appeared to settle and TSS did not significantly increase in the fly ash sluice water with carbon. Therefore, the performance of fly ash ponds to remove TSS and carbon does not appear to be significantly impacted. Concentrations of volatile metals (mercury, selenium, and boron) in the sluice water did not appear to be affected by the carbon addition. Bromide, the reduced form of bromine (a chemical treatment for some carbon), was elevated in the fly ash sluice water generated from the fly ash/carbon mixture for both carbons tested (one with bromine enhancement and the second without any halogen enhancement). Arsenic and selenium were predominantly arsenate (+5) and selenite (+4), which is consistent with past fly ash sluice water samples.

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ACRONYMS AND ABBREVIATIONS

ACI	activated carbon injection
CAIR	Clean Air Interstate Rule
CAMR	Clean Air Mercury Rule
CCR	coal combustion residues
cf/d	cubic feet per day
EPA	U.S. Environmental Protection Agency
ESP	Electrostatic Precipitators
FAP	fly ash pond
FGD	flue gas desulfurization
lb/MMacf	pounds per million actual cubic feet
mg/L	milligrams per liter
mgd	million gallons per day
ng/L	nanograms per liter
NO _x	nitrogen oxides
PAC	powdered activated carbon
PM	particulate matter
SCR	selective catalytic reduction
SO ₂	sulfur dioxide
TSS	total suspended solids
ug/L	micrograms per liter
WQA	Water Quality Association

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INTRODUCTION AND METHODOLOGY

The primary objective of this study was to investigate the effect of activated carbon injection (ACI) for flue gas mercury emission control on the composition of the fly ash sluice water and ash pond settling of the carbon byproduct. If the fly ash and spent carbon are wet sluiced to an ash pond, carbon particles that do not settle may be a compliance concern for total suspended solids (TSS), mercury as well as any other trace element that may be volatile in the flue gas and is adsorbed onto the carbon particle. A series of laboratory tests were conducted to simulate fly ash sluicing and then settling of solids in an ash pond.

Three pairs of fly ash were collected from two different power plants evaluating carbon injection for flue gas mercury control. Each pair consisted of one sample without carbon injection and one with carbon injection. The carbon, injected into the flue gas to remove mercury, is primarily removed with the fly ash in the ESP, and, therefore, the fly ash has a small amount of carbon mixed with it.

This technical memorandum presents:

- Background on Carbon Addition to the Air Stream
- Description of the Test Methodology
- Effect on Simulated Fly Ash Sluice Water and Ash Pond Effluent
 - TSS
 - Volatile Trace Elements
 - Bromide
 - Other Parameters
 - Arsenic and Selenium Speciation

Carbon Addition to Air Stream

Regulations to decrease flue gas mercury emissions from coal power plants drive the need for emission control options such as activated carbon injection (ACI). At facilities using wet fly ash handling, the activated carbon will be primarily captured in the electrostatic precipitator or other particulate control device. If the fly ash/carbon mixture is wet sluiced to the ash pond, this could potentially impact the wastewater effluent.

During ACI, powdered activated carbon (PAC) is injected into the flue gas prior to the PM control device (typically ESP or fabric filter). The mercury binds with the carbon and the carbon is then captured in the PM control device. The ability for the mercury to bind to the carbon depends on numerous factors, including surface area and pore size of the carbon, temperature, and concentration of the mercury in the flue gas. [1]

Carbon, along with the volatile metals sorbed to it, is captured in the particulate control device along with the fly ash and, at facilities using wet ash handling, is typically sluiced to a fly ash pond (Figure 1-1). The objective of this study is to further understand specific effects that carbon

addition may have on the wastewater stream. To simulate the sluicing, this study included laboratory sluicing of fly ash samples with and without carbon injection.

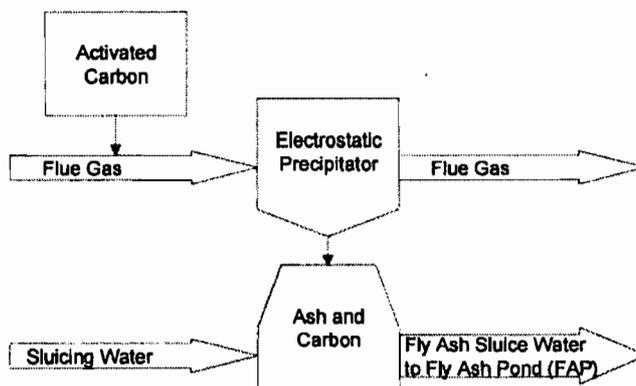


Figure 1-1
Schematic of Activated Carbon Injection for Mercury Control

Information about the samples, including coal type, ESP type, type of carbon injected, sample description, and date collected is shown in Table 1-1.

Sample Pairs A and B

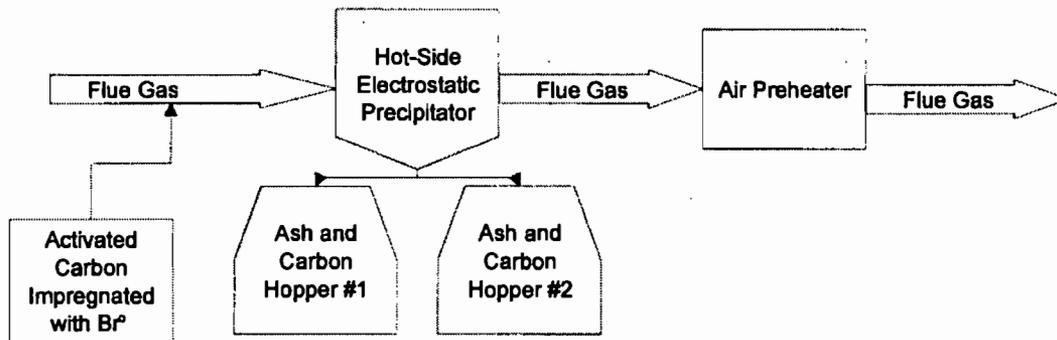
This tangentially-fired power plant burned several coal blends while evaluating carbon injection for Hg control. Pair A was obtained while burning a 75/25 blend of eastern bituminous coals. This power plant employed a hot-side ESP with parallel paths, with only one path being evaluated for carbon injection while a second path did not employ carbon injection (Figure 1-2). Sample Pair B was obtained while burning a 75/25 blend of eastern bituminous coal and Powder River Basin (PRB) coal, respectively. At this site, a bromine-enhanced carbon was tested for Hg control.

Sample Pair C

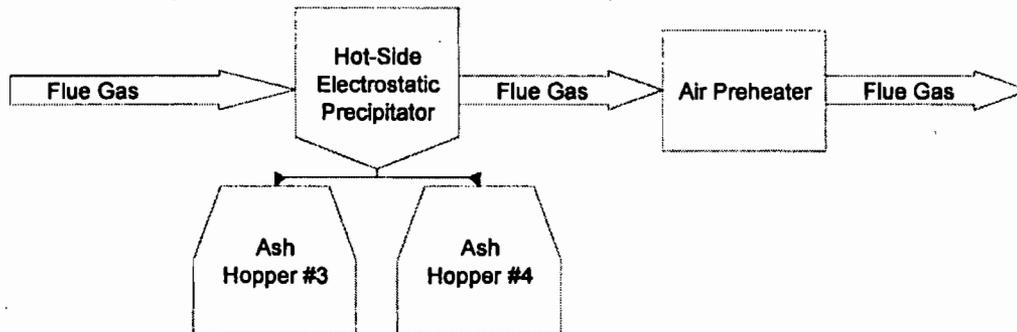
This tangentially-fired power plant burned a high-sulfur eastern bituminous coal, and is configured with two sequential ESPs with specific collection areas of approximately 82 and 230 ft²/1000 acfm, respectively. Sample C (without carbon) was obtained from the second ESP on July 21, 2006, before any carbon had been injected. Sample C (with carbon) was obtained from the same second ESP on August 1, 2006, with carbon injection. The first ESP was estimated to have captured approximately 80 percent of the fly ash, while the second ESP captured 98.3 percent of the incoming fly ash (Figure 1-3). No information was provided about changes in coal supply that may or may not have occurred between sample dates. A number of carbons were tested at this power plant. Sample C was obtained during long-term tests using a HOK carbon without any halogen enhancement.

**Table 1-1
Sample Summary Information**

Sample	A	B	C
Coal Type	Blend of 75/25 Eastern Bituminous	Blend of 75% Eastern Bituminous & 25 % PRB	High Sulfur Eastern Bituminous
ESP Description	Hot Side-ESP	Hot-Side ESP	ESP in Series
Carbon Treatment	Bromine Enhanced	Bromine Enhanced	RWE Rheinbraun HOK carbon derived from German lignite No Chemical Treatment
Sample Description	(Without Carbon) : U6 Fly Ash, No ACI, Inlet Hoppers 9F3 & 9F4, 50/50 Composite Grab (With Carbon): U6 Fly Ash, A5B Absorbent, Inlet Hoppers 9F1 & 9F2, 50/50 Composite Grab	(Without Carbon) : U6 Fly Ash, No ACI, Inlet Hoppers 9F3 & 9F4, 50/50 Composite Grab (With Carbon): U6 Fly Ash, A5B Absorbent, Inlet Hoppers 9F1 & 9F2, 50/50 Composite Grab	(Without Carbon) ESP2 Hopper 1 Composite Ash (With Carbon) HOK Carbon Injection 10.6 lb/MMacf Composite Ash from ESP 2 Hopper 1 and 2
Date Collected	With and Without Carbon: 5/12/05	With and Without Carbon: 6/9/05	Without Carbon: 7/21/06 With Carbon: 8/1/06



Samples A and B (carbon): 50% Hopper #1 and 50% Hopper #2 Composite Sample.



Samples A and B (no carbon): 50% Hopper #3 and 50% Hopper #4 Composite Sample.

**Figure 1-2
Sample Pairs A & B Sampling Locations**

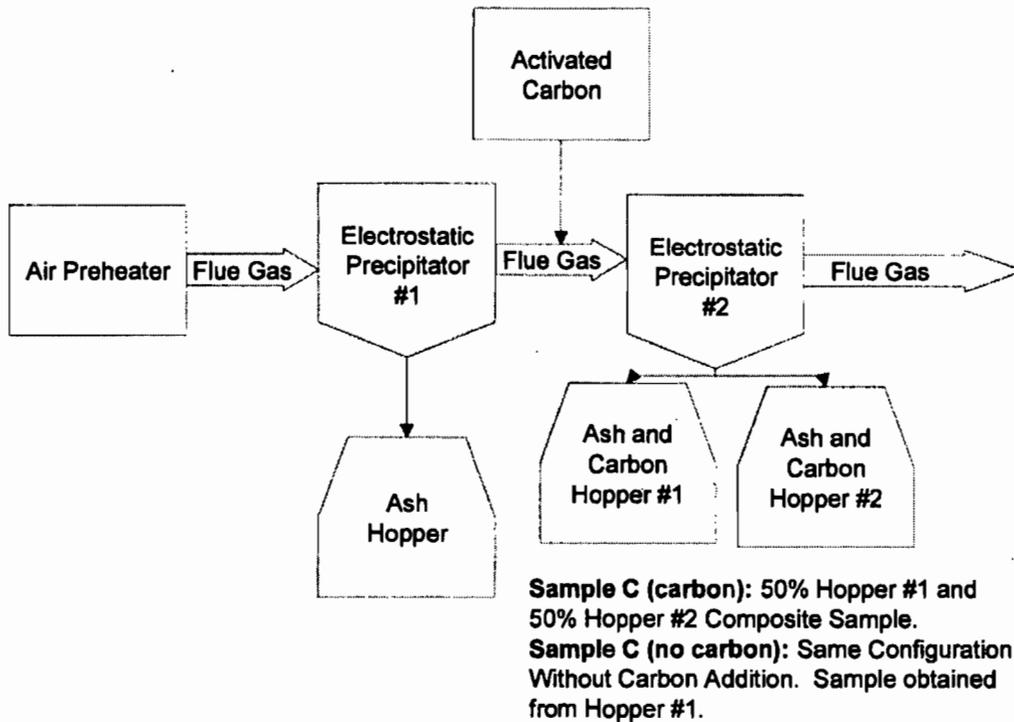


Figure 1-3
Sample Pair C Sampling Location

Description of Simulated Sluicing Methodology Used

The dry samples were mixed with water in a laboratory to simulate fly ash sludge water. The simulated sludge water was then allowed to settle to simulate settling that occurs in an ash pond; water samples were taken from the middle of the water column over time and analyzed.

Fly ash was collected at the stations from the air pollution control devices and shipped to the laboratory. Sludge water was collected from the river near the laboratory in Corvallis, Oregon. The ash and water (at a uniform concentration of 70 g/L to allow for cross-plant comparison) were mixed for 15 minutes with a re-circulating pump. In this type of process, carbon can be expected to comprise 1 to 10 percent of the sorbent-fly ash mixture based on sorbent injection concentrations in the range of 1.5 to 15 lb/MMacf [2] and therefore does not need to be subtracted from the quantity of fly ash collected. Figure 1-4 provides a photograph of the ash sluicing setup. Measurements of pH were taken on the plant intake water prior to mixing,

immediately after the 15-minute sluicing, and again after the 1-hour settling period. After 1 hour of settling, the supernatant was siphoned off for separation from the solid and analyzed.

Sample Pairs A and B (which include both samples with carbon and samples without carbon), from the same plant, were analyzed first. Lessons learned from their sluicing were incorporated into the sluicing of Sample Pair C (from a separate plant). Sample Pairs A and B were sluiced at room temperature. The procedure was repeated at low temperature (12.5 degrees C; 54.5 degrees F) to simulate cooler weather. Because the objective was to determine if carbon floated, the sluice water generated with ash and carbon were settled and analyzed at 1, 12, 36, and 72 hours. The simulated sluice water without carbon was not analyzed over time.

Sample Pair C (baseline and carbon) were both settled at the cooler temperature (12.5 degrees C; 54.5 degrees F) for consistency. Both the carbon and baseline (non-carbon) sluices were sampled and analyzed at 1, 12, 36, and 72 hours.



Figure 1-4
Fly Ash Sluicing Setup

To be useful to power plants to understand the effect of TSS in a given size pond, time of settling is combined with the distance settled to calculate settling velocity, which is then converted to "overflow rate." Overflow rate is the effluent flow rate (Q in cubic feet per day [cf/d] or million gallons per day [mgd]) divided by the surface area (A in square feet or acres) of the pond. Overflow rate represents the superficial liquid velocity at which particles are removed from the pond. Particles with this velocity or a higher settling velocity are removed completely in the pond. Slower particles are carried out of the pond and would add to the effluent TSS. This relationship is illustrated in Figure 1-5.

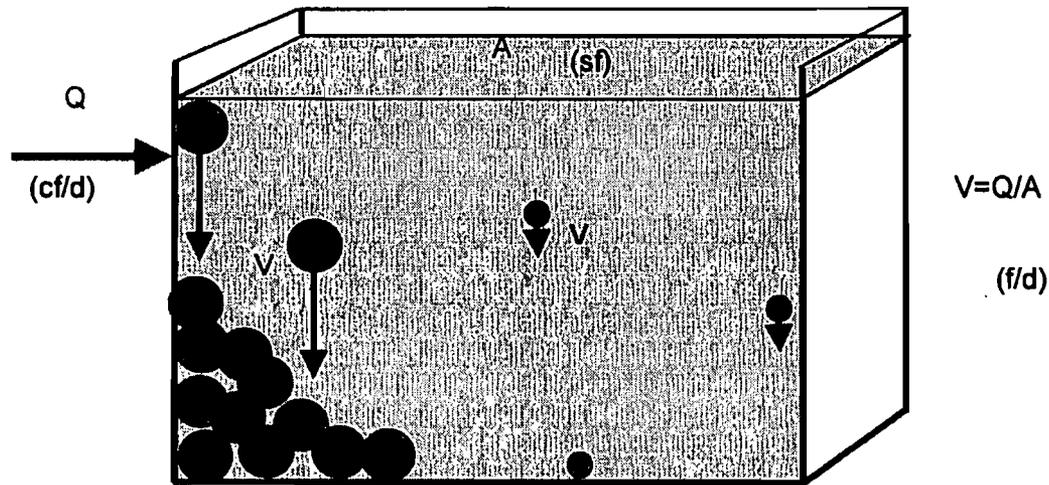


Figure 1-5
Settling of Inert Particles (Fly Ash and Carbon)

Table 1-2 shows the settling times for the samples and the associated overflow rates.

Table 1-2
Settling Times with Overflow Rate

	Sample A (With Carbon) mgd/acre	Sample B (With Carbon) mgd/acre	Sample C (No Carbon) mgd/acre	Sample C (With Carbon) mgd/acre
1 hour	2.44	2.31	1.28	1.41
12 hours	0.18	0.16	0.11	0.13
36 hrs	0.04	0.05	0.03	0.04
72 hours	0.02	0.02	0.01	0.01

2

EFFECT ON SIMULATED FLY ASH SLUICE WATER AND ASH POND EFFLUENT

The samples were analyzed for TSS, mercury, selenium, boron, and bromide. Arsenic and selenium speciation was also conducted. Other parameters, that carbon should not affect, such as iron and magnesium, were also analyzed. The graphical results and interpretation of these analyses are described in this section. The complete data set is provided in the Appendix.

TSS

The limited data indicate that carbon injection into the flue gas does not significantly increase TSS concentrations in the simulated fly ash sluice water after a simulated settling that could be anticipated in an ash pond.

After 1 hour of settling (corresponding to an overflow rate of approximately 1.3 mgd/acre), much of the carbon is still suspended in the liquid (Figure 2-1). While at 1 hour of settling the sluice water is a dark brown shade, the TSS is actually similar to the TSS in the baseline sample. This is likely because while the TSS is darker in the fly ash sluice water with carbon, there are actually similar levels of suspended solids as in the baseline sluice water. Figure 2-2 shows that after 12 hours of settling (corresponding to an overflow rate of approximately 0.1 mgd/acre), the carbon has settled. At that overflow rate, the TSS was well below the typical 30 milligrams per liter (mg/L) TSS standard. Cenospheres and a small amount of carbon were observed to be floating on the top of the samples.

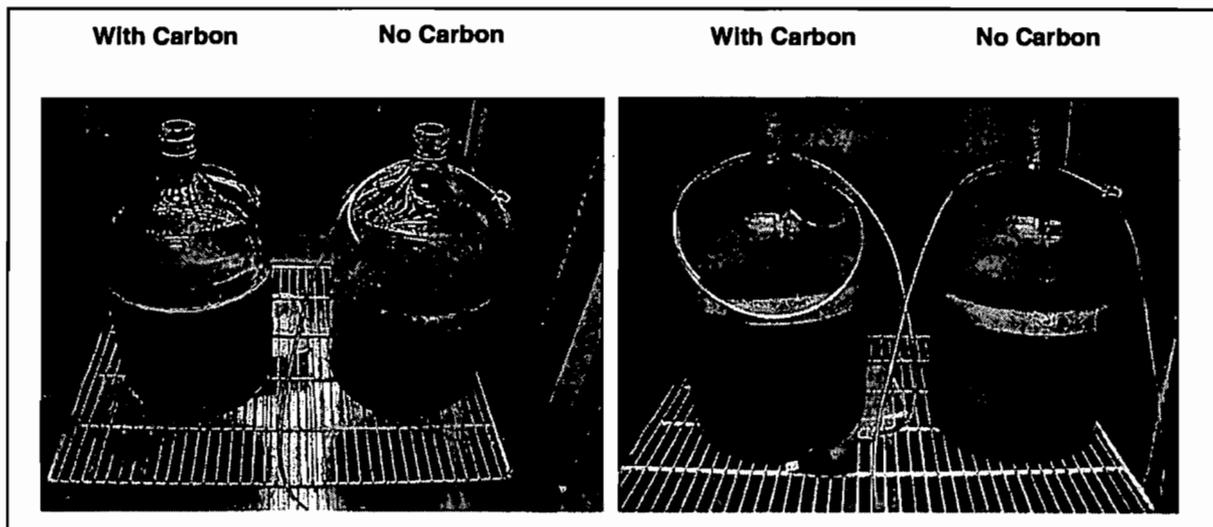


Figure 2-1
Sample Pair C After 1 Hour of Settling

Figure 2-2
Sample Pair C After 12 Hours of Settling

A TSS concentration of 30 mg/L is a typical effluent regulatory requirement and therefore was selected as a reference TSS for the sample data. At 1 hour of settling, corresponding to approximately 2.3 mgd/acre, the simulated sluice samples with carbon had lower concentrations of TSS than the samples without carbon (Figure 2-3). Sample Pairs A and B without carbon were not sampled over time; therefore, it is not possible to compare the expected overflow rates for 30 mg/L TSS between the carbon and non-carbon pairs. For Sample Pair C, based on a least square fit of the non-carbon and carbon data, a TSS value of 30 mg/L would be expected at overflow rates of approximately 0.29 mgd/acre and 0.36 mgd/acre, respectively, indicating that the sample with carbon settled more rapidly than the sample without carbon (Figure 2-3). A value of half of the method detection limit was graphed for sample concentrations below the method detection limit.

It appears from this very limited data that the carbon does not have a significant effect on the concentration of TSS in the fly ash sluice water; the slightly improved settling of solids could be due to differences in fly ash. Future research with more samples would be needed to confirm the results.

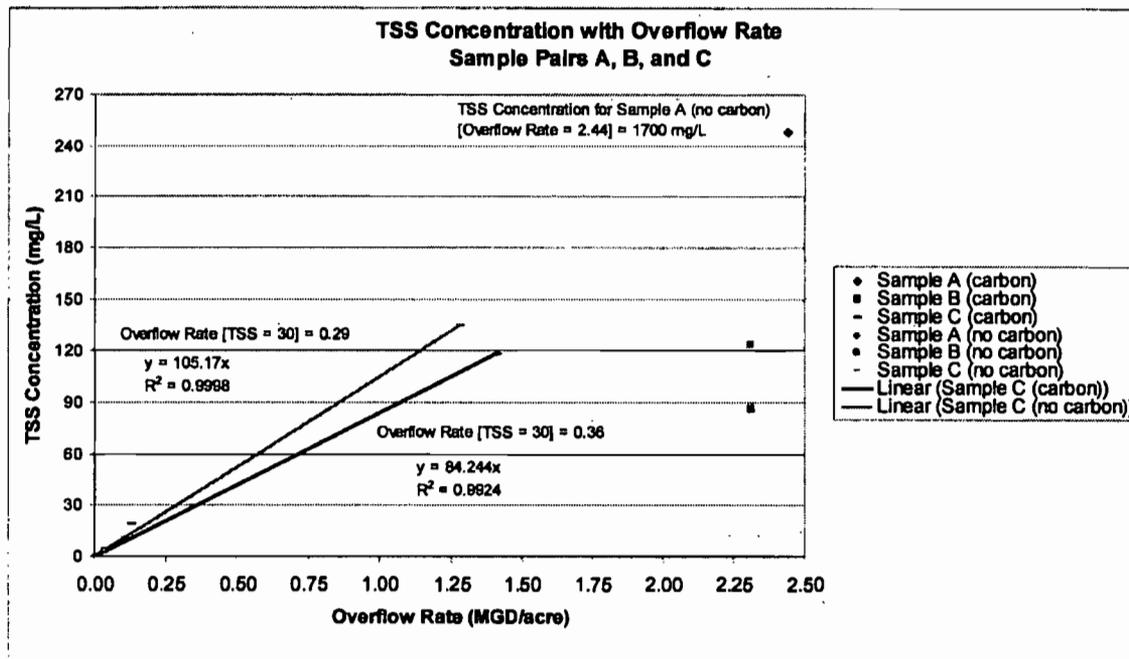


Figure 2-3
TSS as a Function of Overflow Rates (Sample Pairs A, B, and C)

Volatile Trace Elements

Carbon is injected into the flue gas predominantly to remove mercury. Other volatile trace elements may be adsorbed onto the carbon, removed from the flue gas stream, and eventually transferred via the carbon into the wastewater stream (fly ash sluice water). In this study, supernatant samples were analyzed after 1, 12, 36, and 72 hours of settling. The samples were analyzed for a variety of total metals, dissolved selenium and arsenic, bromide, and other

parameters. From the limited samples in this study, the carbon did not appear to have an effect on the mercury, selenium, or boron concentrations in the fly ash sluice water. The complete data set is included as Tables 1 and 2 in the Appendix of this report.

Mercury: Sample Pair C Fly Ash Sluice Water Sample (with and without carbon) at 1 hour of settling was analyzed at a clean laboratory using a method based on EPA Method 1631[3] with reportable limit of 0.5 nanograms per liter (ng/L). The fly ash sluice water with carbon had a mercury concentration of 3.3 ng/L. The fly ash sluice water without carbon had a concentration of 2.5 ng/L. It is not possible, from this limited data, to determine whether the difference between these low mercury concentrations is statistically significant, however, the low magnitude of the concentrations would suggest that mercury captured from the flue gas by the carbon is generally stable and does not leach out during the simulated sluicing process. Mercury concentrations in the fly ash samples were not determined, so a mass balance could not be conducted, however, this conclusion about leaching is consistent with previous EPRI, et.al research evaluating the stability of spent sorbent via leaching tests. A recent EPA study of leaching of mercury and other elements from coal combustion residues (CCR) with and without various carbon-based sorbents concluded that, "Mercury is strongly retained by the CCR and unlikely to be leached at levels of environmental concern." [6] Long-term fate of the mercury, such as mercury adsorbed to carbon that settled to the bottom of the pond, was not measured during this test. Mercury data were not obtained for Sample Pairs A and B, based on the agreement with the host utility. Additional research is recommended to further evaluate the observation made based on just one sample pair.

Selenium: The carbon addition appeared to have no significant effect on selenium concentration. Selenium concentration (dissolved and total) was non-detect (<30 ug/L) in Sample Pairs A and B. For Sample Pair C, the fly ash sluice water with carbon had similar selenium concentrations as the fly ash sluice water without carbon at different overflow rates (Figure 2-4). This held true for both dissolved and total selenium. The dissolved concentration of selenium is similar to the total concentration of selenium, indicating that selenium is predominantly dissolved. The concentration of selenium at different overflow rates was therefore steady (Figure 2-4).

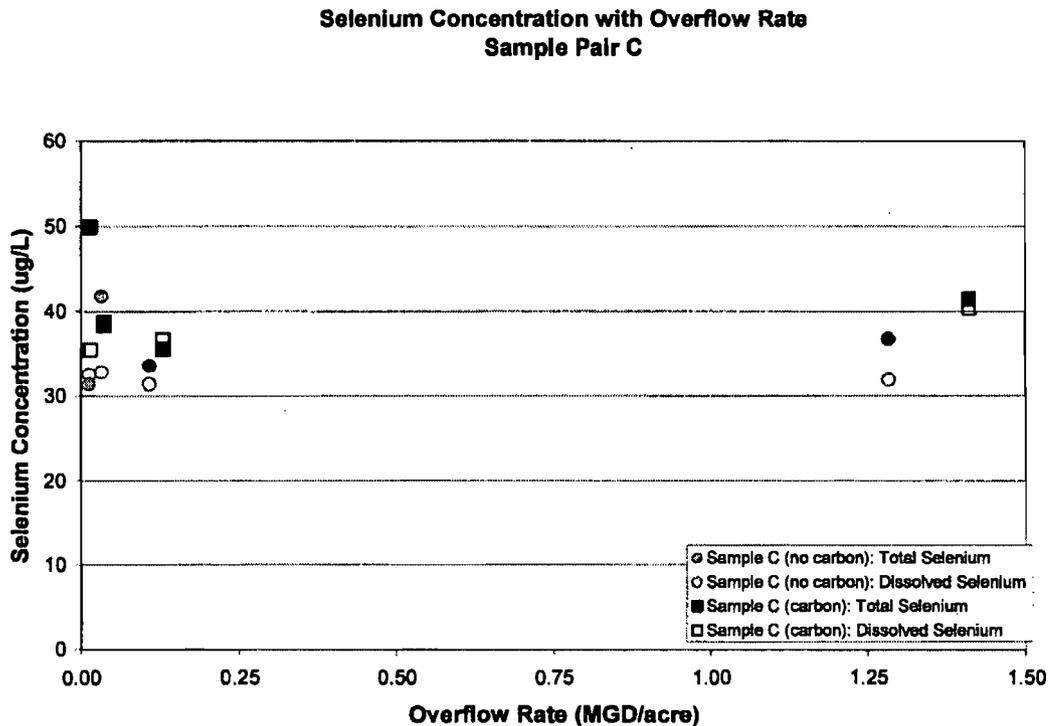


Figure 2-4
Selenium Concentration with Overflow Rate (Sample Pair C)

Boron: The carbon addition appeared to have no conclusive effect on boron concentration. Like selenium, boron is primarily dissolved in water and therefore its concentration does not vary significantly with time or overflow rate. The samples with carbon had higher levels of boron in Sample Pairs A and B, but lower boron concentrations in Sample Pair C (see Figure 2-5). Based on this limited data set, the differences in the boron concentrations appear to be due to potential differences in the fly ash within the pair.

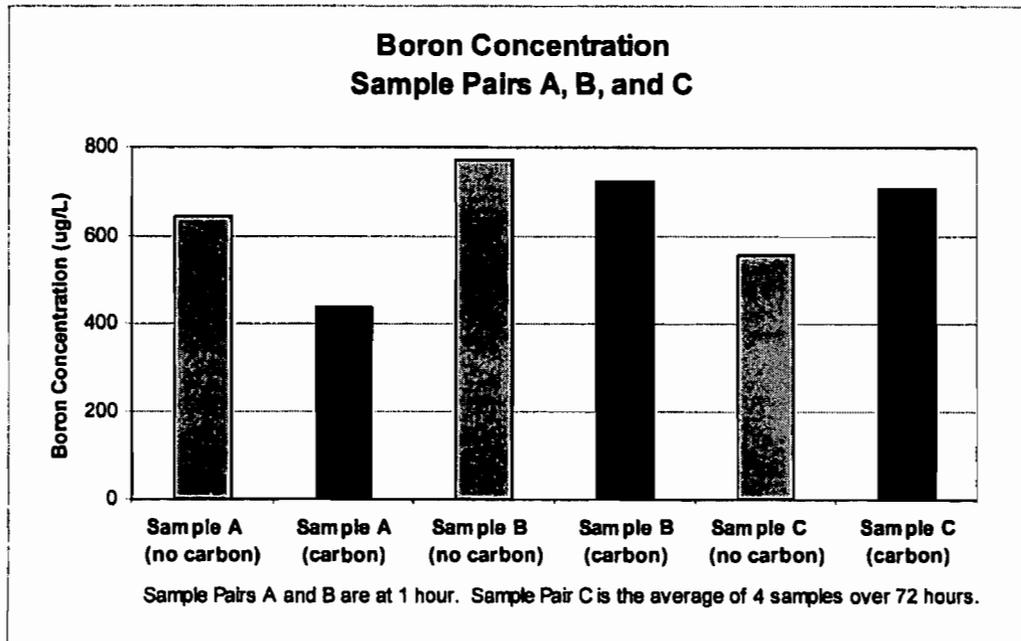


Figure 2-5
Boron Concentration (Sample Pairs A, B, and C)

Bromide

The carbon injected into the flue gas and collected with the fly ash from Sample Pairs A and B (samples with carbon) was reported by the facility to be bromine-treated activated carbon, while Sample C was activated carbon without halogen enhancement. Treating activated carbon with bromine may improve the mercury sorption performance of the carbon. In all three sample pairs, the bromide concentration in the sluice water was slightly higher (1 to 2 mg/L higher) from the ashes with the activated carbon. (Figure 2-6). Because Sample Pair C did not have halogen enhanced carbon, yet the bromide concentration increased in a similar manner as Sample Pairs A and B. It is possible that the increase in bromide concentration is due to something other than the halogen treatment of the carbon. A possible explanation is that the carbon adsorbed bromide from the flue gas, which is subsequently leached from the carbon. This is feasible because the 1 to 2 mg/L of bromide in the sluice water is a low enough that it could have originated from the bromide in the flue gas.

The concentration of bromide slightly increased with time in the simulated fly ash sluice water (Figure 2-7). For Figures 2-6 and 2-7, a value of half of the method detection limit was graphed for sample concentrations below the method detection limit.

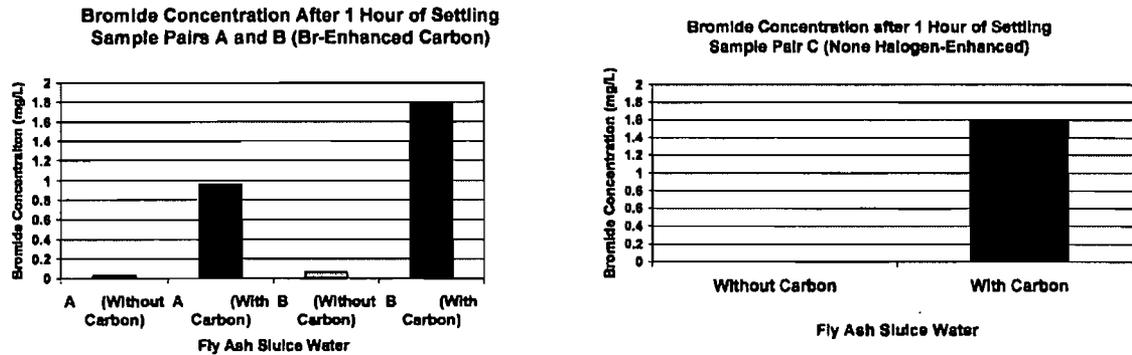


Figure 2-6
Concentration of Bromide in Simulated Fly Ash Sluice Water After Settling for 1 Hour

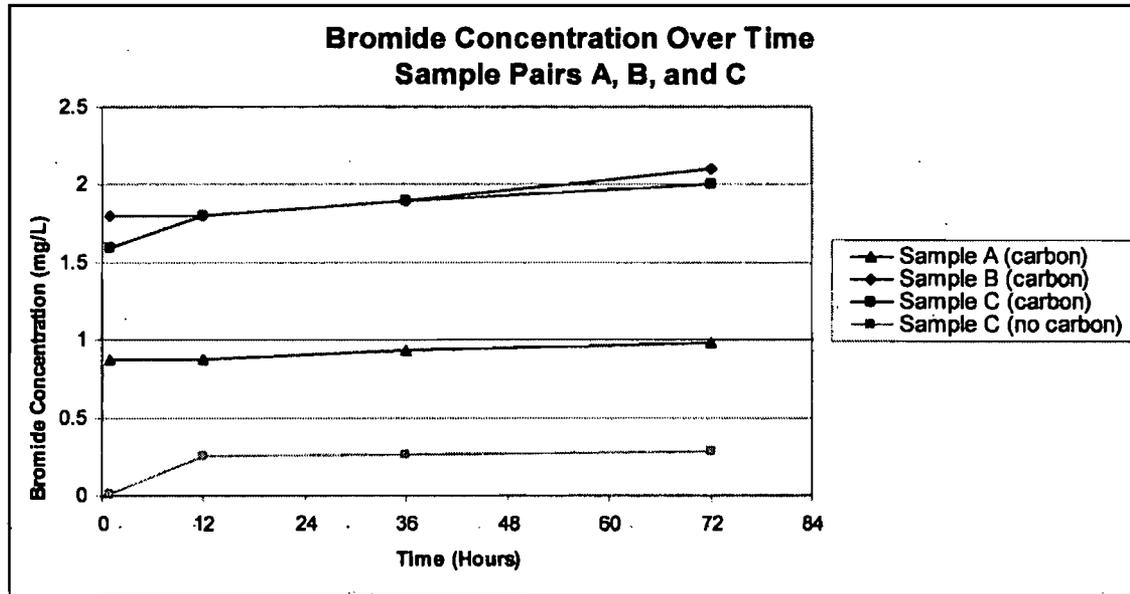


Figure 2-7
Concentration of Bromide in Simulated Fly Ash Sluice Water as a Function of Time

Other Parameters

The trace metal results for the other metals from Sample Pairs A and B would suggest a decrease in many of these metals. However, this was not observed in Pair C. The results are presented in the Appendix. Activated carbon is commonly used for removal of organic constituents from wastewater, among other uses. It is recognized as effective for use in drinking water applications for removal of organic arsenic and chromium complexes. However, it is not effective for use in removal of sodium, nitrates, fluoride, iron, lead, and other heavy metals. [4] Therefore, the

decreased levels of arsenic, iron, and aluminum in the carbon fly ash sluice water observed are most likely related to the variance in fly ash composition. Additional testing would be required to warrant assertions that other metals could be removed the carbon in the wastewater. One possible test would be to add "virgin" carbon (not exposed to flue gas) addition into the ash sluice water.

In this study, parameters such as sulfate, chloride, potassium, and magnesium were analyzed to determine how well the samples with and without carbon match as a pair. These parameters were not typically within 25 percent of each other (Tables 1 and 2 of the Appendix). Therefore, a portion of the difference in volatile metals and TSS could also be attributed to chemical differences in the fly ash samples within the pairs.

Arsenic and Selenium Speciation

The results of this study agreed with past fly ash sluice water data [5] in that selenium is predominantly selenite (+4) and arsenic is predominantly arsenate (+5) (Figure 2-8). Sample A (with carbon) was analyzed over time for arsenic and selenium speciation. Over time, the speciation remained predominantly selenite and arsenate (Figure 2-9). Arsenic and selenium were analyzed with ion chromatography – inductively coupled plasma – mass spectrometry (IC-ICP-MS). For Figures 2-8 and 2-9, a value of half of the method detection limit was graphed for sample concentrations below the method detection limit. This is important to note especially for selenate. The method detection limit of selenate was 1.4 ug/L and therefore graphed at 0.7 ug/L. Therefore this value may be lower than the graphic representation.

Selenite and selenate were the only species identified in the chromatograph for all of the samples. All the samples had an unidentified arsenic species with a concentration of less than 1 ug/L. This is a minimal amount compared to the concentration of arsenate (+5) ranging from 23.9 ug/L to 265 ug/L in the samples.

Selenite (+4) is more toxic than Se (+6) but is more easily removed through iron coprecipitation. Arsenate (+5) is more easily removed than arsenite (+3) by coprecipitation with ferric hydroxide. The complete arsenic and selenium speciation data for Sample Pairs A and B are included in the Appendix of this report in Table 3.

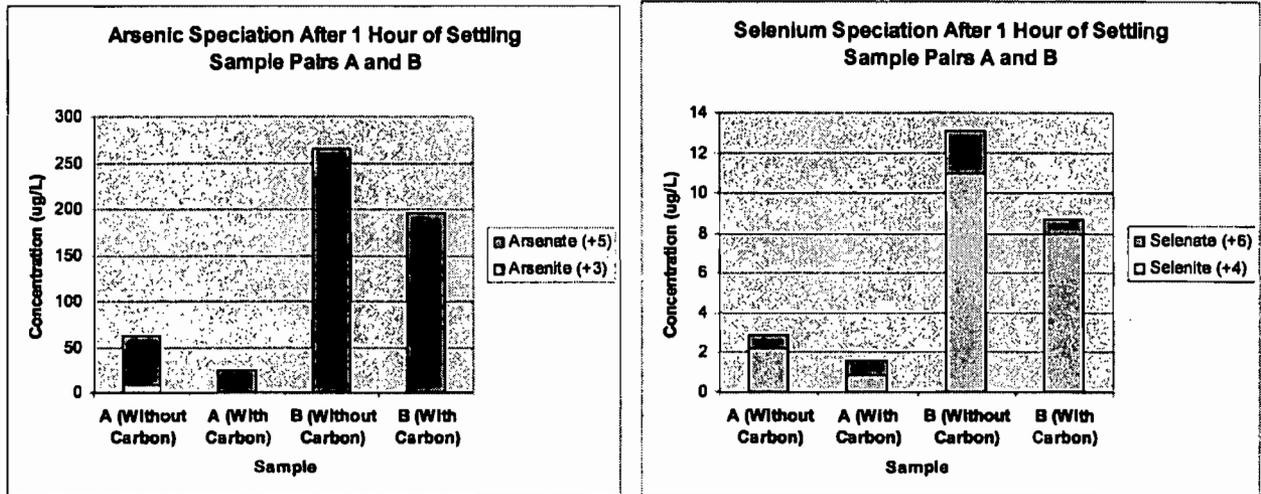


Figure 2-8
Arsenic and Selenium Speciation in Simulated Fly Ash Sluice Water (Sample Pairs A and B)

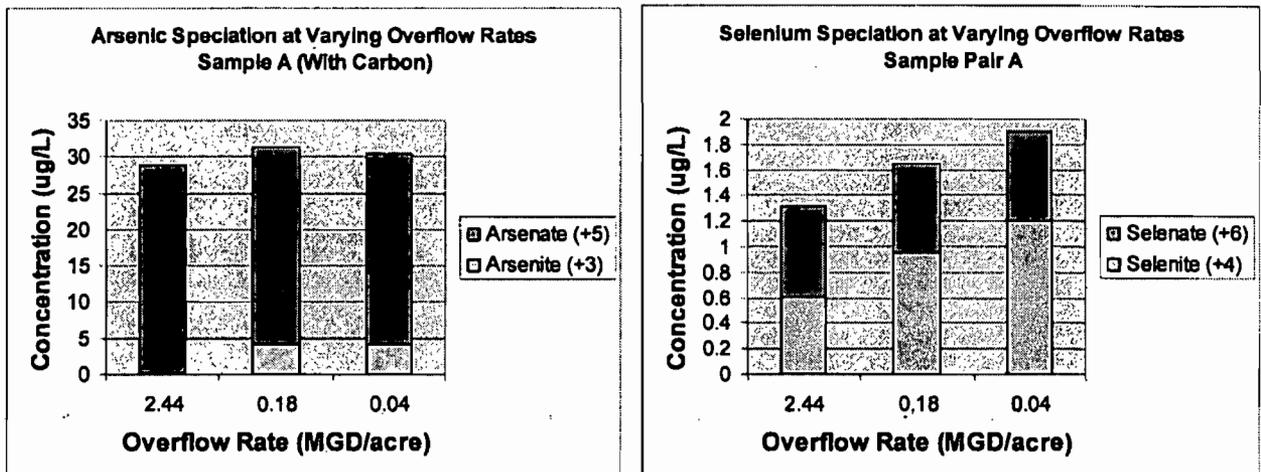


Figure 2-9
Arsenic and Selenium Speciation in Simulated Fly Ash Sluice Water Sample A (With Carbon) at Various Overflow Rates

3

RECOMMENDED FUTURE RESEARCH

Fly ash by nature is variable; therefore, it is important to obtain numerous samples to confirm that results are reproducible. This study included only three pairs of fly ash with and without carbon. While valuable preliminary conclusions were made from this research, the results should be confirmed with additional sample pairs. The recommended future research is described as follows.

- Of significant interest is whether the TSS and specifically the carbon particles are removed in the ash pond. Since the carbon particles may contain Hg, carbon particles that do not settle may be a compliance concern. Mercury is the main parameter targeted for removal from the flue gas via the carbon injection, and data from only one sample pair of mercury were available in this study. Thus additional data with mercury would be beneficial.
- The release of volatile metals from carbon is not likely to occur in aerobic water. In fact, carbon is used in water treatment to remove parameters from the water. However, under anaerobic conditions, mercury may be released from ash. Mercury has been shown to convert to soluble methyl mercury under anaerobic conditions in the bottom of streams containing organic sediments and mercury. When this conversion occurs, it causes a higher concentration of mercury than would be expected from inorganic mercury solubility. Fly ash ponds typically have very little organic material. However, the possibility exists that the decay of an algae bloom, due to ammonia levels, settled on the bottom of the pond could create an anaerobic condition – a layered combination of algae and fly ash with carbon. A lab simulation could potentially involve alternate layers of harvested algae and ash and sparged with nitrogen to create an anaerobic environment. Samples of the gas could be taken for methane analysis to ensure an anaerobic environment exists and mercury concentration to measure any releases of volatile mercury. Samples of the water could be analyzed to understand if soluble forms of mercury are released.
- Additional research on the effect of carbon addition on the bromide in wastewater is recommended. The available data suggests that Br is removed from flue gas, some of which may be leached into the fly ash water.
- Another focus should be on the consistency of the pairs. Parameters that carbon should not affect, such as sulfate, chloride, potassium, and magnesium, should be compared after initial sluicing to determine if the carbon and non-carbon samples match as a pair.

4

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A
APPENDIX

Figure A-1
All Data for Sample Pairs A and B

Parameter	Sample ID	Sample A (carbon)		Sample A (no carbon)		Sample B (carbon)		Sample B (no carbon)		Sample B (carbon)	Sample B (carbon)	
		1	2	1	2	1	2	1	2			
Settling Time	hour	2.44	2.44	0.19	0.04	0.02	0.02	2.31	2.31	0.16	0.05	0.02
Overflow Rate	MG/Direct Reporting Units											
Aluminum	µg/L	58300	7920	4060	859	342	8440	5880	6760	2010	1000	545
Arsenic (dissolved)	µg/L	71.5	27.4	28.3	27.2	28	288	226	199	257	260	264
Arsenic (total)	µg/L	117	43.7	38.4	31.7	36.2	292	248	259	259	274	289
Boron	µg/L	643	439	451	432	429	771	720	713	681	668	680
Bromide	mg/L	0.028	0.96	0.88	0.93	0.98	0.094	1.8	1.8	1.8	1.9	2.1
Calcium	µg/L	17400	13900	15000	14900	15200	52300	51100	51100	50000	50700	51200
Iron	µg/L	18800	2480	1330	278	106	3010	1870	2330	633	251	112
Magnesium	µg/L	8900	4570	6810	4240	4370	6760	6220	6300	5880	5630	5770
Manganese	µg/L	127	49.6	50.3	44	43.5	17.1	16.5	16.2	<10	<10	<10
Potassium	µg/L	25600	19200	22000	14700	14000	15800	19200	19200	18200	18300	17700
Selenium (dissolved)	µg/L	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Selenium (total)	µg/L	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Sodium	µg/L	8520	8730	9310	8850	9150	17500	19100	18800	18400	18400	18500
Acidity as CaCO3	mg/L	<10	10	<10	<10	<10	<10	<10	<10	<10	<10	10
Alkalinity, Total as CaCO3	mg/L	14	8	10	11	11	42	34	34	36	36	37
Alkalinity, Carbonate as CaCO3	mg/L	<5	<5	<5	<5	<5	16	<5	8	8	20	<5
Chloride	mg/L	2.2	2.8	2.7	2.6	2.6	2.5	3	3.1	3.1	3.4	3.2
Conductivity	µmhos/cm	208	227	243	245	252	404	432	428	435	368	366
Hardness as CaCO3	mg/L	52	52	52	52	52	156	156	156	148	144	152
pH	pH Units	7	6.5	7	6.9	7.1	8.1	6.8	8	8	6.7	6.7
Sulfate	mg/L	71	84.4	85.1	86.2	82.4	155	187	185	185	189	189
Total Dissolved Solids	mg/L	150	172	183	225	179	296	339	346	338	321	333
Total Suspended Solids	mg/L	1700	248	921	100	<5	124	88.4	141	18	3.2	<2

Notes:
Light blue highlight indicates 3 day activated carbon settling tests (3 days at cooler temperature).
Gray highlight indicates normal settling (1 hour at room temperature).

Figure A-2
All Data for Sample Pair C

Sample ID	Raw Wastewater	Sample C (no carbon)	Sample C (carbon)	Sample C (no carbon)	Sample C (carbon)	Sample C (no carbon)	Sample C (carbon)	Sample C (no carbon)	Sample C (carbon)	Sample C (no carbon)	Sample C (carbon)
Settling Time	0	1	1	12	12	36	36	72	72	72	72
Overflow Rate	0	1.28	1.41	0.11	0.13	0.03	0.04	0.01	0.01	0.01	0.01
Parameter	Reporting Units										
Aluminum	µg/L	15800	6370	8510	1730	8310	1370	7880	1280		
Arsenic (dissolved)	µg/L	254	182	258	167	265	152	260	145		
Arsenic (total)	µg/L	354	225	283	178	288	171	281	164		
Boron	µg/L	589	739	517	645	595	738	521	689		
Bromide	mg/L	<0.02	1.6	0.25	1.8	0.26	1.9	0.28	2		
Calcium	µg/L	76400	100000	77100	98100	78600	97500	77400	96300		
Iron	µg/L	342	1810	1810	320	1680	107	1580	<100		
Magnesium	µg/L	2130	13200	5240	12500	5250	12800	5180	13100		
Manganese	µg/L	21.7	219	212	199	211	203	205	204		
Mercury	µg/L	<0.1	0.0025*	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
Potassium	µg/L	20300	18500	18800	19700	18800	19100	18800	18600		
Selenium (dissolved)	µg/L	31.9	40.4	31.4	36.7	32.8	38.4	32.5	35.5		
Selenium (total)	µg/L	36.8	41.4	33.6	35.8	41.8	38.7	31.4	49.9		
Sodium	µg/L	12200	17500	12800	16400	12700	17100	12000	17000		
Acidity as CaCO3	mg/L	53	11	51	11	52	11	52	10		
Ammonia, as N	mg/L	1.9	2.2	1.9	2.4	2.1	2.4	2	2.3		
Alkalinity, Bicarbonate as CaCO3	mg/L	<5	8	<5	6	<5	5	<5	6		
Alkalinity, Total as CaCO3	mg/L	<5	8	<5	6	<5	5	<5	6		
Alkalinity, Carbonate as CaCO3	mg/L	<5	<5	<5	<5	<5	<5	<5	<5		
Chloride	mg/L	3	5.5	3.4	6.3	3.5	6.5	3.6	6.6		
Conductivity	µmhos/cm	66.1	683	617	707	557	641	603	684		
pH	pH Units	7.2	5.8	4.5	5.8	4.7	6.1	4.6	6		
Sulfate	mg/L		288	288	340	294	324	303	337		
Total Inorganic Carbon	mg/L	6.2	2.6	0.63	2.2	0.58	1.9	0.51	1.6		
Total Organic Carbon	mg/L	1.8	<0.5	5.6	<0.5	5.5	<0.5	5.9	<0.5		
Total Dissolved Solids	mg/L	46	552	467	531	450	552	433	523		
Total Suspended Solids	mg/L	9.2	118	10.8	19.2	2	4.4	<2	<2		

* = Analyzed at a Clean Laboratory

Figure A-3
As-Se Speciation of Sample Pairs A and B

Parameter	Sample ID		Sample A (no carbon)	Sample A (carbon)	Sample B (no carbon)	Sample B (carbon)				
	hour	hour								
Settling Time	1	1	1	1	1	12	36	1	1	1
Overflow Rate	1	1	2.44	2.44	0.18	0.04				2.31
Parameter Reporting Units										
Arsenite (+3)	8.35	<0.22	<0.22	<0.22	4.24	4.27		<0.22	<0.22	<0.22
Arsenate (+5)	53.8	23.9	28.7	28.7	27.1	28.2		265	196	196
Selenite (+4)	2.17	0.87	0.81	0.81	0.85	1.22		11.0	8.01	8.01
Selenate (+6)	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4		2.1	<1.4	<1.4

Notes:

Light blue highlight indicates 3 day activated carbon settling tests (3 days at cooler temperature).

Gray highlight indicates normal settling (1 hour at room temperature).

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