

The Effect of Ammonia on Mercury Partitioning in Fly Ash

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Technical Update, March 2008

EPRI Project Manager

K. Ladwig

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PRODUCT DESCRIPTION

Management options and environmental assessments for fly ash are driven primarily by their physical and chemical characteristics. This report describes the results of a laboratory study on the leaching of mercury from several paired fly ash samples from facilities employing powdered activated carbon (PAC) injection for mercury control. While previous EPRI research has shown that mercury leaching from ash with PAC is negligible, it has also been found that ammonia complexes can increase the mobility of some divalent cations. This study evaluated the roles of mercury-ammonia and mercury-chloride complexes and their impacts on mercury mobility.

Background

The U.S. Environmental Protection Agency issued two air emission control regulations in March 2005—the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR). CAIR permanently caps emissions of nitrous oxides (NO_x) and sulfur dioxide (SO_2) from large stationary sources, including coal-fired plants in the eastern United States. It is likely that more than 55% of the coal-fired power generating capacity will install ammonia-based technologies, either selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR), to control NO_x emissions. Ammonia is also commonly used as a flue gas conditioner to enhance fly ash capture by electrostatic precipitators. These controls will result in fly ashes that contain varying amounts of ammonia. CAMR, on the other hand, requires improved efficiencies in the capture of mercury from flue gas. Approaches to reduce mercury air emissions are currently being tested, including injection of PAC prior to primary particulate collection. Although previous EPRI studies have indicated that mercury release from carbon-injected fly ash is generally not a significant environmental concern, ammonia in the fly ash can form complexes with many cationic metals, including mercury, and may increase mercury mobility.

Objectives

- To investigate the leaching behavior of mercury from several types of fly ash under a variety of conditions.
- To determine the impacts of ammonia, chloride, and carbon content on the partitioning of mercury in fly ash.
- To develop a model to quantify mercury partitioning in fly ash that contains ammonia.

Approach

Investigators collected four paired fly ash samples from power plants testing the use of PAC for mercury control. Each pair consisted of one baseline sample and one sample taken while PAC was being injected. The investigators conducted laboratory batch tests on raw and washed ash samples to assess mercury leaching from the fly ash under varying conditions of pH, ammonia concentration, chloride concentration, and number of washing cycles. Mercury adsorption experiments were also conducted using raw and washed ashes in order to understand the fundamental mercury partitioning. Using the acidimetric-alkalimetric titration method, investigators determined the surface acidity of the fly ash. Finally, they developed an adsorption model to predict mercury partitioning as a function of ammonia concentration.

Results

Leaching of mercury from the fly ash samples in this study was a function of pH, ammonia concentration, chloride concentration, and carbon content. In general, mercury leaching from the raw fly ash samples was low, always below 200 ng/L. The maximum leaching usually occurred in the pH range between 8 and 10. Mercury leaching increased with increasing ammonia concentration, apparently due to the formation of less readily adsorbed mercury-ammonia complexes between pH 8 and 10. Conversely, increasing chloride concentration decreased mercury leaching, possibly due to the formation of more adsorbable $\text{Hg}(\text{OH})\text{Cl}$ complexes. Unburned carbon and PAC also reduced mercury leaching. The mercury leaching potential (available mercury) was approximately 20–30% of total mercury, based on the samples studied.

Ammonia also enhanced mercury leaching from washed ash, in a manner similar to that for the raw ash. However, higher mercury concentrations were leached from the washed ash than from the raw ash, possibly due to increased availability of the mercury after removal of the soluble surface salts. Batch adsorption tests with an added mercury concentration of 1 mg/L showed that nearly all of the added mercury was adsorbed by the ash. Even in the presence of high ammonia concentrations (1000 mg/L), more than 98% of the added mercury was adsorbed. An adsorption model was developed that simulates the trend of mercury partitioning in fly ash for a range of ammonia concentrations and pH conditions.

EPRI Perspective

As power companies develop compliance strategies in response to CAIR and CAMR, attention will shift to the fate of mercury and other constituents retained in the fly ash and flu gas desulfurization solids—with a new emphasis on their impacts on coal combustion product (CCP) disposal and use options. Information on the release and fate of such constituents allows utilities to make informed risk-based management decisions. EPRI has been a leader in CCP characterization for disposal and use. Previous related EPRI work includes *Characterization of Field Leachates at Coal Combustion Product Management Sites* (1012578, December 2006) and *Mercury in Coal Combustion Products* (1010061, December 2005).

Keywords

Coal Combustion Product (CCP)

Mercury

Fly Ash

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1

INTRODUCTION

This report describes a laboratory study on the effect of ammonia on the leaching of mercury from various fly ashes, including those from mercury control facilities using powdered activated carbon (PAC) injection methods. This study builds upon EPRI's previous research involving ammonia impact on the leaching of cationic elements, including copper, cadmium, lead, nickel, and chromium and is part of a larger research effort to assess the potential environmental impact of ammonia and trace element release at ash storage or disposal sites as a result of new air emission control regulations. Laboratory batch tests were conducted to assess the effect of ammonia on mercury leaching under varying conditions of pH, ammonia concentration, washing cycles, and chloride concentration for fly ashes from power plants with and without activated carbon injection for enhanced mercury removal. Mercury adsorption experiments were also conducted using raw and washed ashes in order to understand the fundamental mercury leaching and adsorption behavior.

Background

The U.S. Environmental Protection Agency (USEPA) issued two air emission control regulations in March 2005, the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR)¹ (USEPA, 2005a). CAIR permanently caps emissions of nitrous oxides (NO_x) and sulfur dioxide (SO₂) from large stationary sources including coal-fired plants in the eastern United States. It is expected that over 55% of the coal-fired power generating capacity will install ammonia-based technologies, either selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR), to control NO_x emission (Chu et al., 2001). Ammonia is also commonly used as a flue gas conditioner to enhance the fly ash capture by electrostatic precipitator (ESP). These implementations will result in fly ashes that contain ammonia. The ammonia-based NO_x controls can also increase the oxidation of elemental mercury and therefore enhance the mercury capture (Miller et al., 2006). CAMR requires enhanced capture of mercury from flue gas. Various approaches to reduce mercury air emission are currently being tested, including injection of PAC prior to primary particulate collection. This will increase the mercury concentration in fly ash.

Several studies indicated that mercury release from ammonia-free, traditional or carbon-injected fly ash is not a significant environmental concern (EPRI, 1999; 2001; 2002; Gustin and Ladwig, 2004; Kazonich and Kim, 2003; USEPA, 2005b; 2006; Xin et al., 2006). However, both theoretical and experimental studies indicated that ammonia can form complexes with many cationic metals including mercury (Stumm and Morgan, 1996; Wang et al., 2003a; 2003b; Teng et al., 2003a; 2003b; Wang et al., 2006). Therefore, the presence of ammonia could change the mercury leaching characteristics in the fly ash. It is important to understand the role of ammonia on mercury leaching in order to predict potential environmental impacts.

¹ The CAMR rule was vacated by the Circuit Court of Appeals for the District of Columbia on February 8, 2007, after completion of this report.

Objectives

The objectives of the proposed project were to investigate the leaching behavior of mercury from several types of fly ashes, to determine the impacts of ammonia, chloride, and carbon content on the partitioning of mercury in fly ash, and to establish a model to quantify mercury partitioning in fly ash.

Report Organization

The remainder of this report describes laboratory studies conducted to evaluate effects of ammonia and other factors on the leaching of mercury, and modeling to understand the role of ammonia in the adsorption-desorption process. Section 2 describes the material and laboratory methods used for this research. Section 3 describes the leaching results for raw ash samples under various conditions including pH, ammonia, and chloride. Section 4 describes leaching results for washed ash, and impact of washing on mercury leaching. Section 5 presents a mathematical model to quantify impact of pH and ammonia on mercury adsorption.

2

MATERIALS AND METHODS

Fly Ash Samples

Four sets of paired fly ash samples were used in this study, for a total of eight samples. For each of the paired samples, one sample was collected while injecting PAC. Other sample characteristics of the paired samples include:

- One pair from a unit burning bituminous coal, with a cold-side electrostatic precipitator (ESP)
- One pair from a unit burning bituminous coal, with a cold-side ESP and an SNCR
- One pair from a unit burning bituminous coal, with a hot-side ESP
- One pair from a unit burning blended bituminous-subbituminous coal, with a hot-side ESP

Table 3-1 shows the source and major characteristics of these ash samples.

Ash Characterization

Important characteristics of fly ash related to mercury leaching are loss-on-ignition (LOI), specific surface area (BET area), total mercury concentration, and total ammonia concentration. LOI was used as an indicator for unburned carbon, and was determined using a gravimetric method based on the weight loss at 550°C for samples dried at 105°C. The BET area was determined using a Quantachrome Autosorb-1-C high performance surface area and pore size analyzer. The total mercury concentration in fly ash was determined using EPA method 3052 procedure for total digestion of the ash. The total mercury concentration was then determined using the method specified below. The total soluble ammonia concentration in the fly ash leachate was determined using a Nitrogen-Ammonia Reagent Set, Test 'N Tube, Salicylate Method, 0.4-50 mg/L, with estimated detection limit of 0.4 mg/L (Hach Comp., USA). The ammonia concentration was then calculated on a dry ash basis.

Mercury Analysis

Mercury concentrations in liquids were determined using EPA Method 1631 procedures. A Tekran® Series 2600 Ultra-trace Mercury Analysis System (Tekran Inc., Toronto, Canada) was used to determine the mercury concentration in all liquid samples. Tekran Series 2600 is characterized by dual stage gold pre-concentration followed by Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS) as a detector. Samples and standards were pre-digested with 0.5% BrCl stock solution for 12 hours, to convert all forms of Hg in the sample to Hg²⁺. The BrCl stock solution was prepared with 11 g KBr + 15 g KBrO₃ + 200 mL H₂O + 800 mL hydrochloric acid solution. Both KBr and KBrO₃ were heated in a mercury free oven prior to BrCl preparation

in order to drive off any Hg present in them. After oxidation, the sample was reduced with $\text{NH}_2\text{OH}\cdot\text{HCl}$ to destroy the free halogens. $\text{NH}_2\text{OH}\cdot\text{HCl}$ was prepared by weighing out 75 g $\text{NH}_2\text{OH}\cdot\text{HCl}$ and dissolving it in 250 mL DI water, then purified using 3% SnCl_2 reducing solution and purging using ultra high purity argon for at least 2 hours. The sample was then reduced with SnCl_2 to convert Hg(II) to volatile Hg(0) . The Hg(0) was separated from solution by purging with mercury free argon onto a gold coated sand trap and then a gold trap. The trapped Hg was then thermally desorbed from the gold trap into the argon gas stream that carried the released Hg(0) into the cell of a CVAFS for detection. The linear working range of the system was 1-200 ng/L, and spiking recoveries were in the 85 – 110% range.

Surface Acidity

A batch equilibrium titration method was employed to determine the surface acidity (site density and acidity constant) of washed ash samples. The procedure was similar to the leaching experiment for raw ashes, except that 0.01 M NaNO_3 solution (instead of DI water) was used as the leaching solution. The volume of acid or base used, and the corresponding final pH in each bottle, were recorded to plot the overall titration curve. The 0.01 M NaNO_3 solution was also titrated as a blank. The net titration curve was obtained by subtracting the acid/base consumption by the blank from the overall titration curve for the same pH condition. The net titration curve was then modeled using a non-linear regression program, Kaleidagraph (Synergy Software, Reading, PA), based on a titration equation to determine the surface acidity. The detailed calculation procedure was shown in Wang et al. (2004).

Batch Leaching

Batch methods were used to determine the impact of ammonia on mercury leaching or adsorption under different pH conditions for both raw ash and washed ash samples. Ten grams of dry ash were mixed with 100 mL of leaching solution (S/L = 1:10) in a series of 125 mL bottles. Stock HNO_3 or NaOH solution was added to these bottles to adjust pH. These bottles were then sealed and shaken for 24 hours. After shaking, all bottles were allowed to settle for at least 12 hours, and supernatants were collected for mercury analysis. The supernatant samples were not filtered due to the potential adsorption loss of mercury by the filter paper. The final pH values were determined using the remaining contents in the bottle, using an Orion pH electrode (model 9207BN) and an Orion pH meter (perpHecT LogR model 370).

Leachants with different ammonia concentrations were prepared by dissolving varying amounts of NH_4NO_3 in 1000 mL of deionized (DI) water. The solutions were mixed to obtain final ammonia concentrations of 0, 100, 1000, 5000, and 10,000 mg/L. These concentrations, which were 2 to 200 times higher than typical raw ash leaching concentrations, were added to induce a response in the leaching behavior rather than simulate expected field conditions. The pronounced ammonia effect data can provide mechanistic information for better understanding of the leaching process. For washed ash leaching or adsorption experiments, the leachants contained 0.01 M NaNO_3 as the support electrolyte. Similar adjustments were made to evaluate the effect of added chloride concentrations. For all adsorption (partitioning) experiments, the leachants also contained pre-selected amount of mercury addition.

Ash Washing

Washed samples are needed to determine surface acidity characteristics. Washed samples also may represent highly weathered ashes that have been exposed to large volumes of liquid under field conditions. Batch experiments were conducted using washed ash to simulate the impact of ammonia on mercury leaching from weathered ashes. Deionized (DI) water was used to wash the ash sample. A batch method with an S/L ratio of 1:5 was used for ash washing, and air was used to mix the ash-water mixture during the washing process. Each washing cycle lasted for approximately 24 hours. Depending on the purpose of the experiment, different washing cycles were applied to the fly ash. Ash samples were totally dried in an oven at 103 – 105°C (normally 24 hours) prior to experiments. The supernatants of each washing cycle were collected for Hg and TDS measurements.

3

MERCURY LEACHING FROM RAW FLY ASH SAMPLES

Ash Characterization

The total mercury concentration, LOI, specific surface area, pH, and ammonia concentration of each ash sample are given in Table 3-1. These are essential characteristics related to the total mercury leaching potential/availability and adsorption capability (adsorption capacity and adsorption strength).

The two ashes from Plant 33106, which employed an SNCR, were generated from burning different bituminous coals. Both samples contained much more mercury than other ashes in the study. The ashes from Plant 33104 contained approximately one-third the total mercury than those from Plant 33106. The ashes from Plant 33103 contained much less mercury than those from Plants 33104 and 33106.

The LOI values are similar for the paired samples from each plant, compared to the larger variation between plants. In two of the sample pairs, LOI was slightly higher for samples with activated carbon, and in two of the sample pairs the LOI was slightly higher for the samples without activated carbon. This reflects the variability in the unburned carbon content, since the total mass of injected PAC is relatively low compared to the unburned coal carbon. However, the injection of activated carbon significantly increased the specific surface area (BET area) of fly ash at all four plants, due to the high specific surface area of the activated carbon. Mercury concentrations were higher in all four of the samples with activated carbon, although for plants 3310 two-fold in the samples with activated carbon. Table 3-1 and Figure 3-1 also indicate that for the four ashes without injected activated carbon, the LOI is proportional to the specific surface, suggesting that the total surface in the fly ash is mostly contributed by unburned carbon.

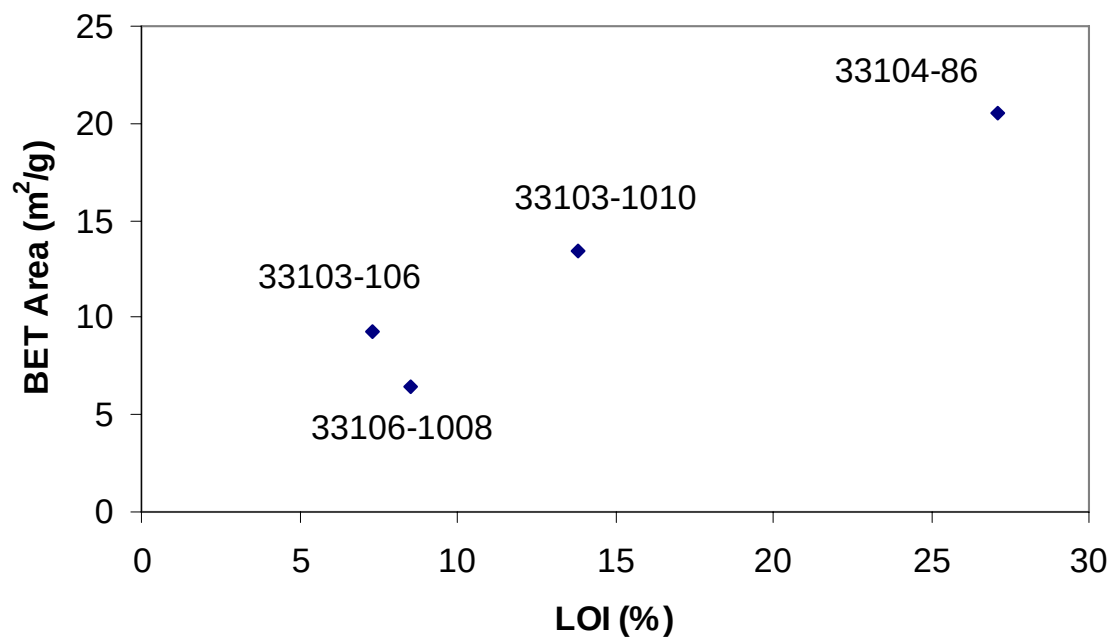


Figure 3-1
Relationship between LOI and BEI Area for Samples without Activated Carbon

Table 3-1
Major Physical and Chemical Characteristics of Fly Ash

Plant ID	Sample ID	Coal Type	ESP ²	Hg Control ³	NO _x Control ⁴	Total Hg (mg/kg)	LOI ⁵ (%)	BET Area (m ² /g)	NH ₃ ⁶ (mg/kg)	Natural pH ⁷
33106	1008	Bituminous	ESPc	None	SNCR	0.57	8.5	6.48	500	8.02
33106	99	Bituminous	ESPc	PAC	SNCR	0.60	6.8	16.67	13	4.69
33104	86	Bituminous	ESPc	None	None	0.17	27.1	20.53	ND	7.50
33104	85	Bituminous	ESPc	PAC	None	0.20	19.5	30.37	ND	8.17
33103	106	Bituminous	ESPh	None	None	0.013	7.3	9.28	ND	6.61
33103	107	Bituminous	ESPh	PAC	None	0.045	9.2	18.13	ND	6.92
33103	110	Bit/Sub (3:1) ¹	ESPh	None	None	0.023	13.8	13.46	ND	9.60
33103	111	Bit/Sub (3:1) ¹	ESPh	PAC	None	0.065	15.1	31.21	ND	8.87

Notes:

¹ Bit/Sub = Blend of bituminous coal and sub-bituminous coal;

² ESP = electrostatic precipitator; ESPc = cold side ESP; ESPh = hot side ESP;

³ PAC = powered activated carbon;

⁴ SNCR = selective non-catalytic reduction;

⁵ LOI = loss-on-ignition;

⁶ ND = below detection limit;

⁷ Natural pH = the pH value measured for the control sample, under S/L ratio = 1:10.

Background Leaching as a Function of pH

Figure 3-2 shows the leaching of mercury from raw ash as a function of pH, using DI water with added acid/base as a leachant. The purpose is to obtain the background information on the leaching characteristics of the tested fly ashes. A leaching peak in the pH range between 8 to 11 was observed for most samples, suggesting that mercury leaching is significantly related to the pH condition. All mercury concentrations were relatively low—less than 150 ng/L across the entire pH range, and less than 40 ng/L outside of the peak areas.

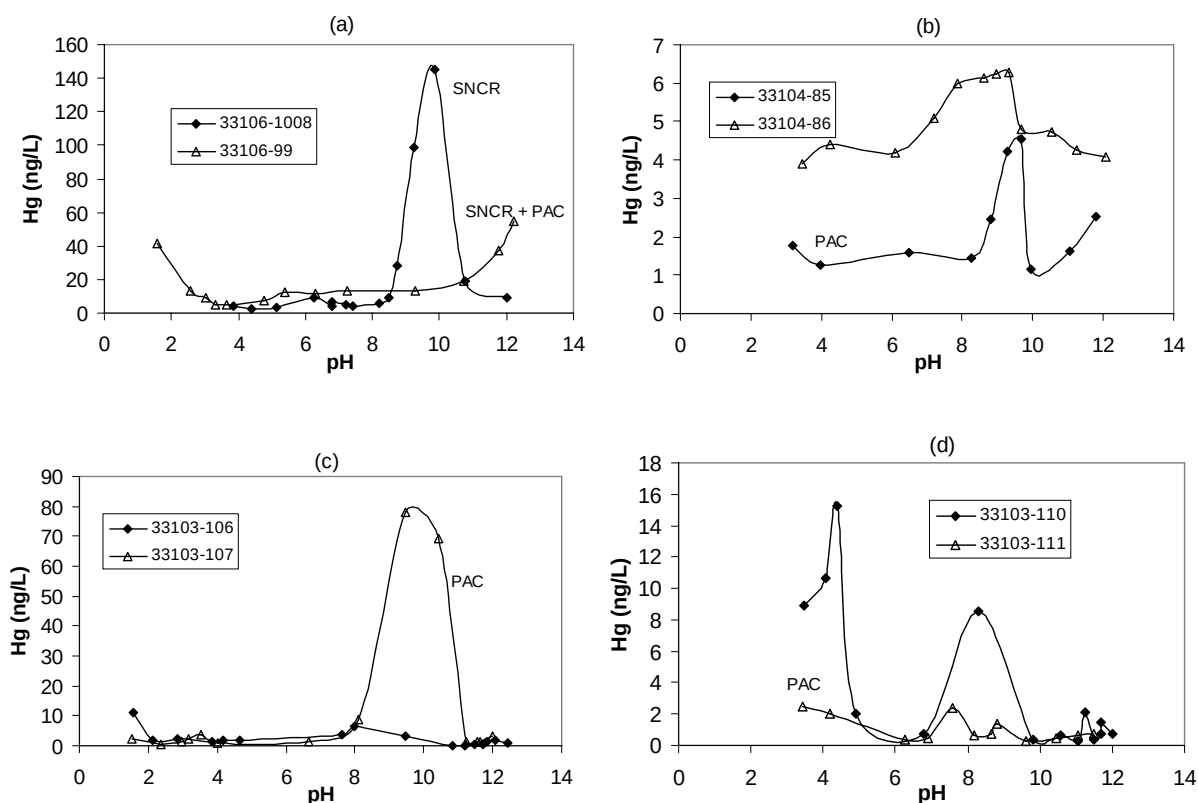


Figure 3-2

Mercury Leaching from Raw Ash as a Function of pH: (a) 33106-1008 and 33106-99; (b) 33104-85 and 33104-86; (c) 33103-106 and 33103-107; and (d) 33103-110 and 33103-111. Experimental Conditions: S/L = 1:10; Temperature = 20 – 25°C; Equilibration Time = 24 hours; Leachant = DI Water Plus Added Acid/Base

A few general observations with respect to the leaching characteristics follow:

- Samples 33106-1008 and 33106-99 have similar amounts of total mercury (Table 3-1). However, 33106-99 released significantly less mercury than 33106-1008 between pH 9 and 11. This may be caused by increased binding capacity of the activated carbon in sample 33106-99.
- Samples 33104-85 and 33104-86 also contained similar amounts of total mercury. The total mercury leaching from both samples was very low, less than 7 ng/L.
- For the 33106-106/107 sample pair, the sample with activated carbon had higher leached mercury concentrations between pH 8 and 11.
- For the 33103-110/111 sample pair, the sample with activated carbon had lower leached mercury concentrations across most of the pH range, however, all concentrations were very low.
- Leached concentrations were not directly related to total mercury concentrations in the ash samples. This is consistent with results published by others (Gustin and Ladwig, 2004; USEPA, 2006).

Impact of Ammonia on Mercury Leaching from Raw Ash

Figure 3-3 shows the leaching characteristics of mercury for six ash samples under different pH and added ammonia conditions, plotted as the soluble mercury concentration as a function of pH. The background leaching without ammonia addition was also plotted for comparison. For all samples, the leaching without ammonia addition was less than 100 ng/L with the exception of the peak concentration for sample 33106-1008, which was about 150 ng/L. However, when external ammonia was added, mercury leaching increased in the pH range between 7 and 11 with increasing ammonia addition. The presence of high concentrations of ammonia (>1000 mg/L) clearly enhanced mercury leaching. The effect was less clear at 100 mg/L ammonia. When pH was less than 7 or greater than 11, mercury leaching with and without ammonia addition was approximately the same.

- The addition of 1000 mg/L ammonia resulted in a maximum mercury leaching of 1250 ng/L for sample 33106-1008 (SNCR, no PAC). However, for sample 33106-99 (SNCR, PAC) which had the similar amount of total mercury in ash, the maximum mercury leaching was only 80 ng/L for the same ammonia addition. This may be due to increased mercury binding strength of the activated carbon in the fly ash.
- For samples 33104-86 (no PAC) and 33104-85 (PAC), the leaching patterns with ammonia addition are very similar. Sample 33104-86 leached slightly less mercury compared to 33104-85. The much greater unburned carbon in sample 33104-86 compared to 33104-85 may offset the impact of injected PAC in 33104-85, causing the two ashes to behave similarly.
- For sample pairs 33103-106/107 and 33103-110/111 (both hot-side ESPs, different coals), the samples with the activated carbon injection leached much more mercury when ammonia was added than their counterparts, possibly due to the greater availability of mercury in these carbon-injected fly ashes, or possibly due to the differences in adsorption caused by the hot-side ESPs at these facilities. The maximum release at about pH 9 for these samples is defined by a very narrow, sharp peak.

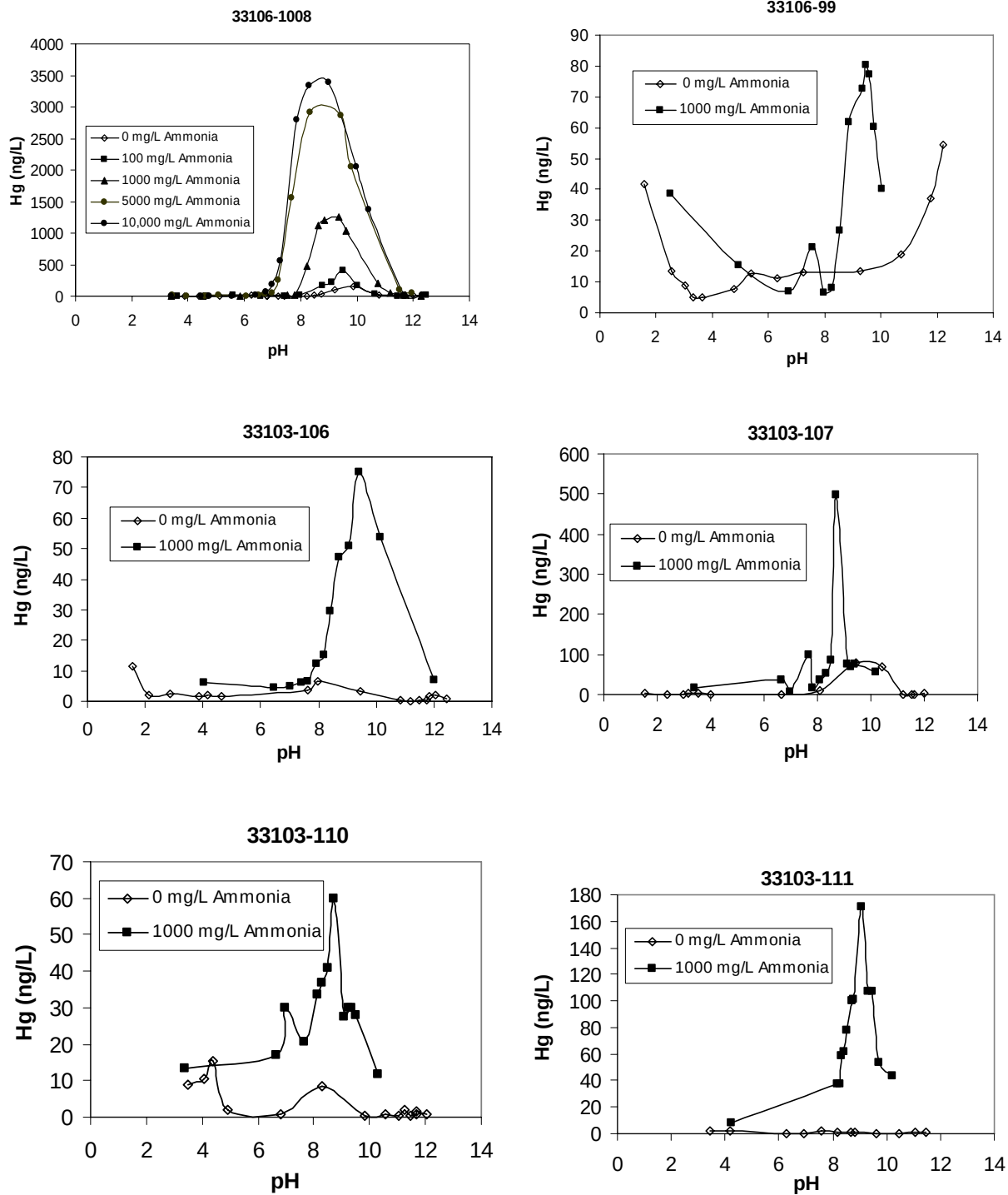


Figure 3-3
Impact of Added Ammonia on the Leaching Hg from Raw Fly Ashes. Experimental Conditions: S/L = 1:10; Temperature = 20–25°C; Equilibration Time = 24 hours; Leachants were Prepared using NH_4NO_3 . The Background Leaching Data using DI Water with Added Acid/Base were also Plotted

The characteristic peaks in mercury leaching at about pH 9 when ammonia is added can be explained by formation of less adsorbable ammonia-mercury complexes. The overall formation constants ($\log\beta$) for $\text{Hg}(\text{OH})^+$, $\text{Hg}(\text{OH})_2$, $\text{Hg}(\text{OH})_3^-$, $\text{Hg}(\text{NH}_3)^{2+}$, $\text{Hg}(\text{NH}_3)_2^{2+}$, $\text{Hg}(\text{NH}_3)_3^{2+}$, and $\text{Hg}(\text{NH}_3)_4^{2+}$ are, respectively, 10.6, 21.8, 20.9, 8.8, 17.4, 18.4, and 19.1 (Stumm and Morgan, 1996). Based on these constants, the mercury speciation as a function of pH with and without the presence of 1000 mg/L ammonia was calculated (Figure 3-4). If the solution does not have ammonia, the neutrally charged $\text{Hg}(\text{OH})_2$ dominates the system when pH is greater than 3. However, the mercury-ammonia complexes are the dominant species in the pH range between 2 and 10 with 1000 mg/L ammonia present in the system. Since the mercury release also increased with the increase of ammonia addition in the pH range corresponding to the formation of $\text{Hg}(\text{NH}_3)_3^{2+}$ and $\text{Hg}(\text{NH}_3)_4^{2+}$ species, these two mercury-ammonia complexes may be less adsorbable than other mercury-ammonia complexes, and therefore, responsible for the increased mercury leaching. As shown in Figure 3-4(b), when pH is greater than 10, the fraction of $\text{Hg}(\text{OH})_2$ increases. Since $\text{Hg}(\text{OH})_2$ has very high affinity for many adsorbents (MacNaughton and James, 1974; Kinniburgh and Jackson, 1978; Newton et al., 1976; Sarkar et al., 2000), the formation of $\text{Hg}(\text{OH})_2$ would reduce mercury leaching above pH 10, as indicated in Figure 3-3. When pH reaches 12, almost all mercury would be adsorbed by fly ash due to the domination of the $\text{Hg}(\text{OH})_2$ species in the system.

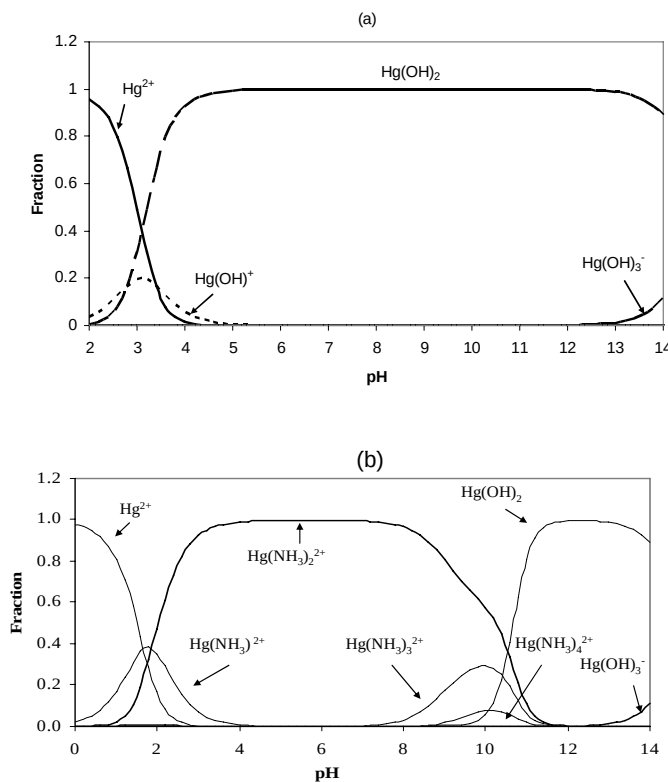


Figure 3-4
Mercury Speciation: (a) No Ammonia; (b) with 1000 mg/L Ammonia

Impact of Chloride on Mercury Leaching from Raw Ash

Figure 3-5 shows mercury leaching from sample 33106-1008 when ammonium chloride (NH_4Cl) solution was used as a leachant. The results are very similar to those when NH_4NO_3 was used as a leachant. However, the maximum mercury concentrations for the same ammonia addition when NH_4Cl solution was used as a leachant were approximately 30% less than those when NH_4NO_3 was used. This suggests that chloride reduces mercury leaching.

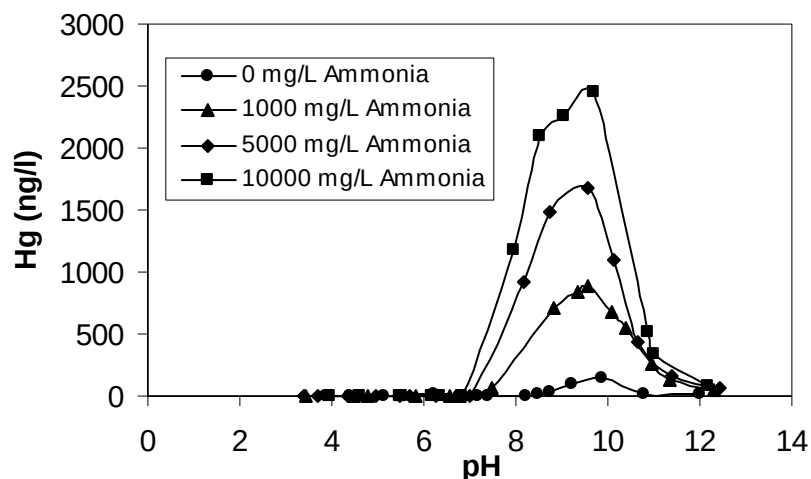


Figure 3-5
Impact of Ammonia and Chloride on Hg Leaching from Sample 33106-1008. Experimental Conditions: S/L = 1:10; Temperature = 20–25°C; Equilibration Time = 24 hours; Leachant = NH_4Cl Solution with Acid/Base Addition

To further test the chloride impact on mercury leaching, a solution prepared using NaCl was used as a leachant. In order to remove interferences from other ash components, fly ash 33106-1008 was washed using DI water, and then dried for this experiment (see next section for washing procedures). Figure 3-6 shows the soluble mercury concentration as a function of pH, under different chloride addition conditions up to 10,000 mg/L Cl . Results indicate that increasing chloride addition consistently decreased the leaching of mercury.

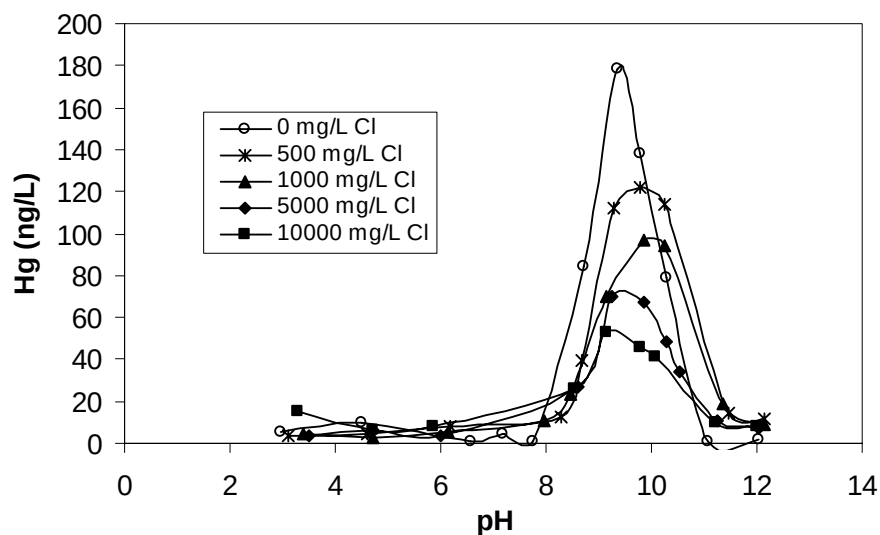


Figure 3-6
Impact of Chloride on Hg Leaching from Washed Ash Sample 33106-1008 (Washing Conditions: S/L = 1:5; 5 Washing Cycles; 24 Hours per Cycle), for Different Chloride Addition Conditions. Experimental Conditions: S/L = 1:10; Temperature = 20–25°C; Equilibration Time = 24 Hours; Leachant = NaCl Solution with Added Acid/Base

Figure 3-7 shows the mercury speciation diagram in 1000 mg/L chloride solution. $\text{Hg}(\text{OH})\text{Cl}$ species is formed in the pH range of 8 to 11, where mercury leaching was reduced. Therefore, the formation of $\text{Hg}(\text{OH})\text{Cl}$ may be responsible for the reduced mercury release.

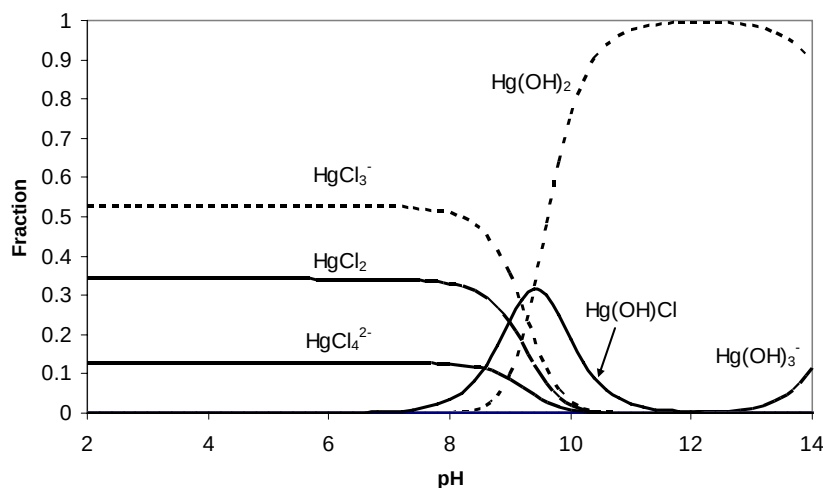


Figure 3-7
Mercury Speciation in 1000 mg/L Chloride Solution

Mercury Partitioning in Raw Ash

Mercury partitioning with raw ash was investigated using batch systems, by adding 1 mg/L (1,000,000 ng/L) mercury and 1000 mg/L ammonia to the batch system. The purpose of this experiment was to estimate the mercury desorption potential in the ash in the presence of ammonia. In this case, the added mercury was significantly greater than the background mercury concentration. Therefore, the partitioning ratio of the added mercury under 1000 mg/L ammonia concentration condition reflects the partitioning ratio of the available mercury in the fly ash under the same ammonia addition condition.

Figure 3-8 shows the soluble mercury concentration as a function of pH for raw ash samples 33106-1008, 33104-85, and 33104-86, when a solution containing 1000 mg/L of ammonia and 1 mg/L of mercury was used as a leachant. The leaching results with 1000 mg/L ammonia solution but no added mercury are also displayed. The soluble mercury concentration for the experiment without external mercury addition was negligible compared to that with 1 mg/L mercury addition. Therefore, the total leachable mercury concentration in the system with 1 mg/L Hg addition can be treated to be 1 mg/L. Only a very small fraction of added mercury remained in the solution even in the pH range favorable for leaching.

The adsorption ratio (adsorbed Hg/total Hg) of the spiked mercury as a function of pH for all three ashes was calculated (Figure 3-9). Most added mercury was adsorbed by the ash across the entire experimental pH range. When pH was in the range between 9 and 10, the adsorption ratio decreased slightly but was always greater than 90% for all three ashes. The maximum fraction of soluble mercury for ash 33106-1008, ash 33104-85, and ash 33104-86 were 8.8%, 2.9%, and 3.3%, respectively. The greater soluble mercury ratio for ash #1 compared to the other two samples could be a result of the lower LOI in this ash since the unburned carbon has stronger adsorption strengths than other ash components (Hwang et al., 2002).

The maximum mercury concentrations in leachates for raw ashes 33106-1008, 33104-85, and 33104-86 under the same condition as above (with 1000 mg/L ammonia addition) but without Hg addition were 1258, 158, and 115 ng/L, respectively (see Figure 3-3). Assuming the available mercury (or the total leaching potential) in the raw ash has the same adsorption ratio, the total available mercury in the above ashes at S/L = 1:10 are estimated to be 14295, 5448, and 3485 ng/L, respectively. This can be converted to concentrations in the solid phase of 0.143, 0.054, and 0.035 mg/kg. Therefore, the percentages of available mercury for these three ashes were 25%, 27%, and 21%, respectively. This suggests that approximately 20% - 30% of total mercury is available for leaching on the fly ash surface under ideal leaching conditions (1000 mg/L added ammonia, pH = 9).

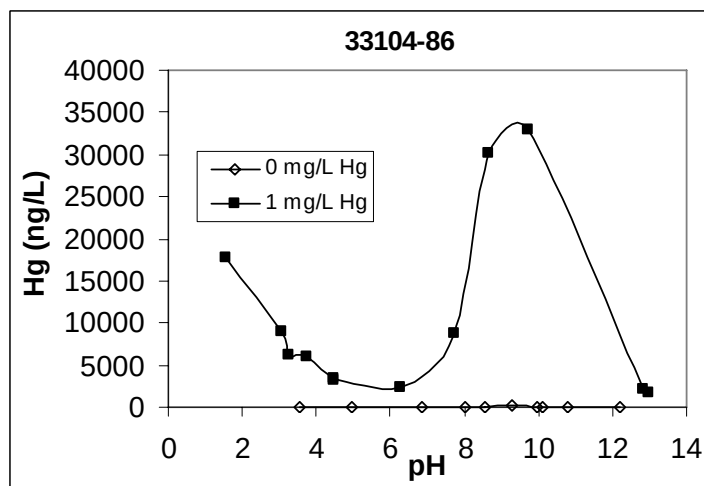
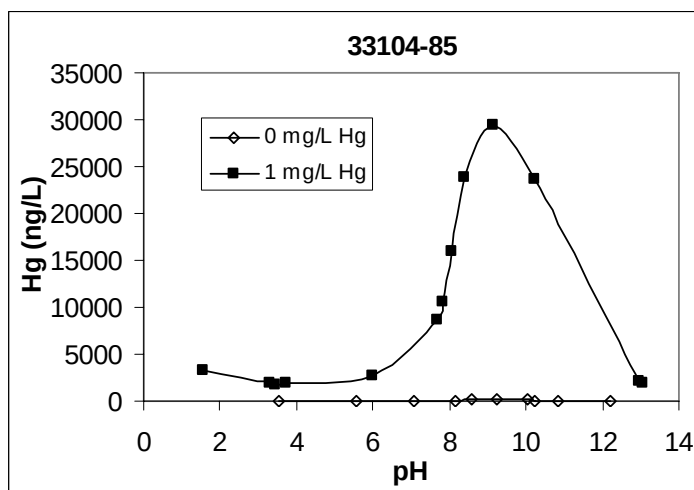
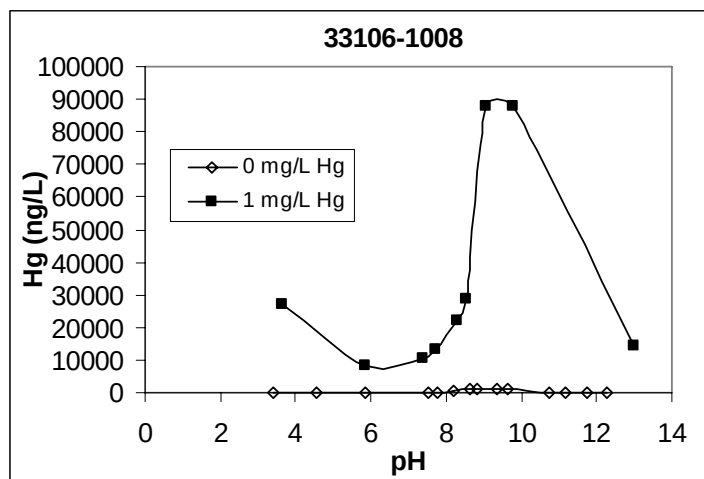


Figure 3-8
Impact of 1000 mg/L Ammonia on Mercury Partitioning. Experimental Conditions: S/L = 1:10;
Temperature = 20–25°C; Equilibration Time = 24 Hours; Leachant = NH_4NO_3 Solution with Added
Acid/Base

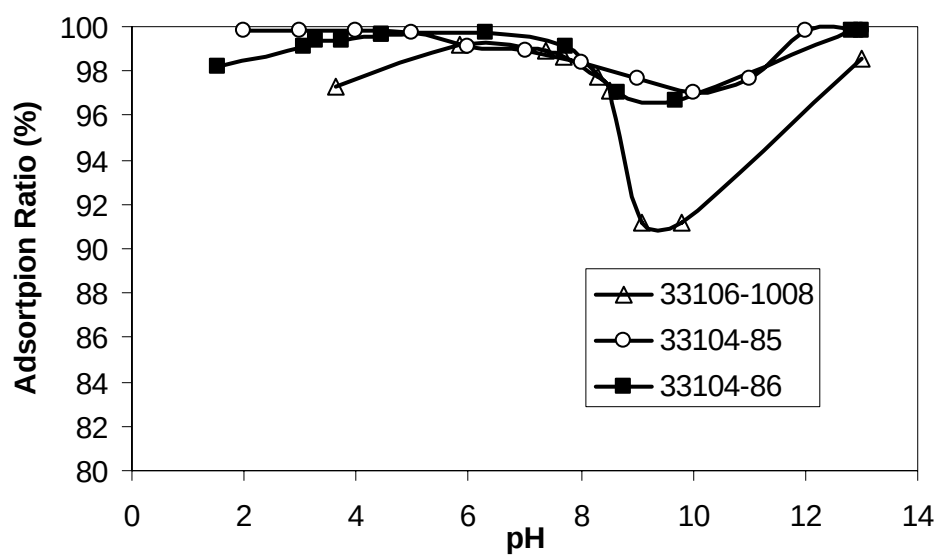


Figure 3-9
Mercury Adsorption Ratio as a Function of pH in the Presence of 1000 mg/L Ammonia

4

MERCURY LEACHING FROM WASHED FLY ASH SAMPLES

Impact of Ammonia on Mercury Leaching from Washed Ash

Figure 4-1 shows Hg leaching from washed ash 33106-1008 under different ammonia concentration conditions. The washing removes readily soluble constituents from the ash surface. For this experiment, no external mercury was added.

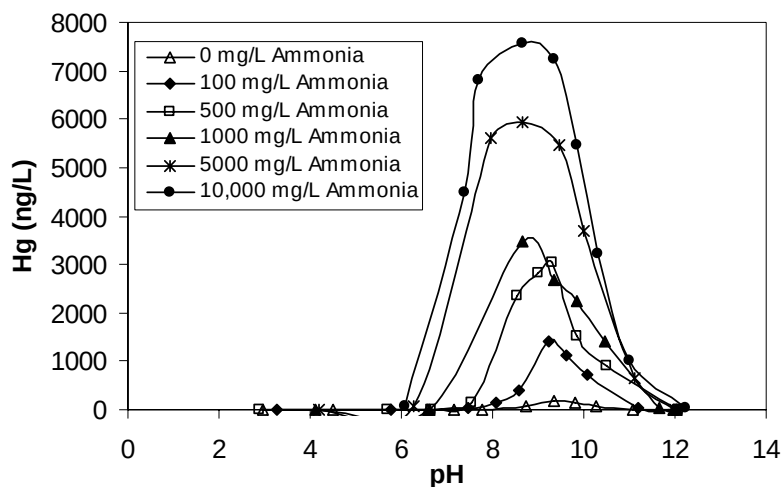


Figure 4-1
Mercury Release from Washed Ash 33106-1008 (5 Washing Cycles) Under Different Ammonia Conditions. Experimental Conditions: S/L = 1:10; Temperature = 20–25°C; Equilibration Time = 24 Hours; Leachants were Prepared using NH_4NO_3 with Added Acid/Base

Figure 4-1 shows that the leaching patterns were similar to those for the raw ash sample shown in Figure 3-3, again showing that ammonia enhanced mercury leaching in the alkaline pH range. Compared with Figure 3-3 data for the same ash, about two to three times more mercury was leached from the washed ash than from the raw ash for the same ammonia addition condition. The data suggest that the removal of some soluble ash components during the washing process increased the amount of mercury available for complexation with ammonia, or decreased the adsorption strengths of mercury species.

Impacts of ash washing on mercury leaching were further investigated using ash 33104-85 (fly ash with activated carbon) to verify the results with 33106-1008. Raw ash (without washing) and DI water-washed ash samples with washing cycles of 1, 5, and 10 were used. All experiments were conducted under the 1000 mg/L ammonia addition condition. Figure 4-2 indicates that the release of mercury increased with increase in the number of washing cycles, up to 5 cycles. After 5 washing cycles, further washing did not increase the mercury leaching. The concentrations of mercury and total dissolved solids (TDS) in decants for different washing cycles were also determined (Table 4-1). Mercury concentrations in all decants were extremely low, less than 10 ng/L. These low concentrations reflected the strong adsorption of mercury by the fly ash surface under ammonia-free conditions. The total loss of mercury during the washing process was less than 0.3 ng/g. However, the TDS results indicate that some soluble ash components were removed during the washing process, especially in the first two washing cycles. The dissolution of some ash components may have exposed more mercury on the ash surface available for leaching. This suggests that highly weathered ash may leach more mercury if exposed to high ammonia concentrations.

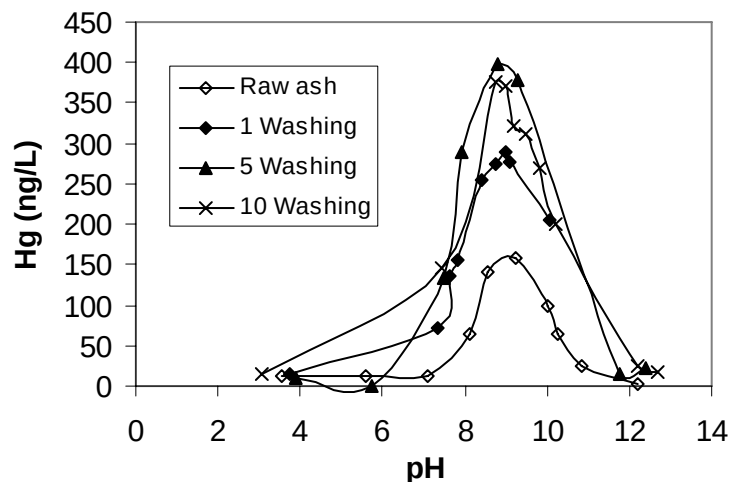


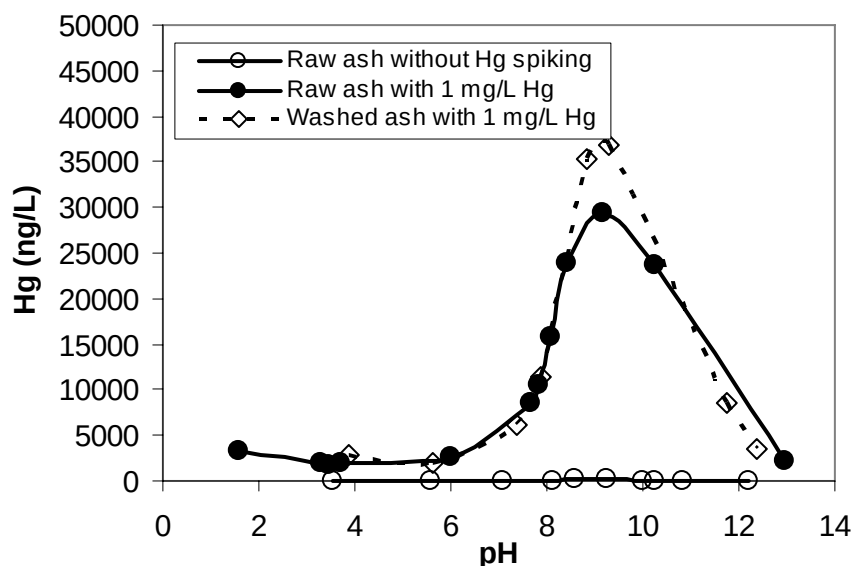
Figure 4-2
Impact of Washing Cycles on Mercury Release from 33104-85. Experimental Conditions: Ammonia Concentration = 1000 mg/L; Temperature = 20–25°C; S/L = 1:10; Equilibration Time = 24 Hours

Table 4-1**Concentration of Mercury and TDS in DI-Water Washing Decants for 33104-85**

Washing Cycle	1	2	3	4	5
Hg (ng/L)	2.0	6.2	1.6	6.8	9.5
TDS (mg/L)	1710	380	150	90	100

To determine the impact of washing on mercury adsorption strength, a volume of stock mercury solution was spiked into the system. As previously described, in this case, the spiked mercury can be treated as the total available mercury in the system. By monitoring the adsorption behavior of the spiked mercury, one can estimate the relative mercury adsorption strength on fly ash.

Figure 4-3 shows the soluble mercury concentration as a function of pH for raw and washed ash 33104-85, when a solution containing 1000 mg/L of ammonia and 1 mg/L of added mercury was used as a leachant. The leaching results with 1000 mg/L ammonia solution but no mercury are also displayed. The soluble mercury concentration for the experiment without external mercury addition was negligible compared to that with 1 mg/L mercury addition. Therefore, the total leachable mercury concentration in the system with 1 mg/L Hg addition can be treated to be 1 mg/L. Only a very small fraction of added mercury remained in the solution even in the pH range favorable for leaching.

**Figure 4-3**

Soluble Mercury Concentration as a Function of pH in the Presence of 1000 mg/L Ammonia for Raw and Washed Ash 33104-85, with and without Mercury Spiking. Experimental Conditions: Temperature = 20 – 25°C; S/L = 1:10; Equilibration Time = 24 Hours

As shown in Figure 4-3, in the pH range between 8 and 10, the solution Hg concentration for the washed ash with 1 mg/L Hg addition was slightly greater than that for the raw ash. Under pH less than 8 and above 10 conditions, soluble concentration curves for both ashes overlap. Since both systems have the same available mercury concentration (i.e. 1 mg/L), the increase of soluble mercury concentration for washed ash was a result of the reduced adsorption strength.

Leaching results in Figure 4-2 demonstrate that washing with 5 cycles increased the leachate mercury concentration by 150% for this ash at the maximum (pH=9, no external mercury addition), while those in Figure 4-3 indicate that washing with five cycles increased the leachate mercury concentration by only 25% at the maximum (pH = 9; 1 mg/L Hg added). Therefore, the enhanced mercury leaching from washed ash shown in Figure 4-2 was only partially contributed by the reduction of the adsorption strength after washing. The total available mercury in washed ash must also have increased compared to the raw ash.

The leaching curves using 1000 mg/L ammonia solution for systems with and without mercury addition follow the same pattern (see Figure 4-2 for raw ash leaching details). These results further suggest that adsorption-desorption was the primary mechanism governing the mercury release from the raw fly ash.

Mercury Adsorption on Ash in the Presence of Ammonia

Figure 4-4 shows the adsorption results for washed ashes 33106-1008 and 33104-85 under different ammonia conditions. In addition to the ammonia, the leachants also contained 1 mg/L of Hg and 0.01 M NaNO₃. Since the total mercury concentrations in these two ashes (based on the total digestion method) were 0.57 and 0.20 mg/kg, respectively, the added 1 mg/L mercury at S/L = 1:10 (equivalent to 10 mg/kg ash) was significantly greater than the total available Hg in the original ash. Therefore, the total available can be approximated as 1 mg/L.

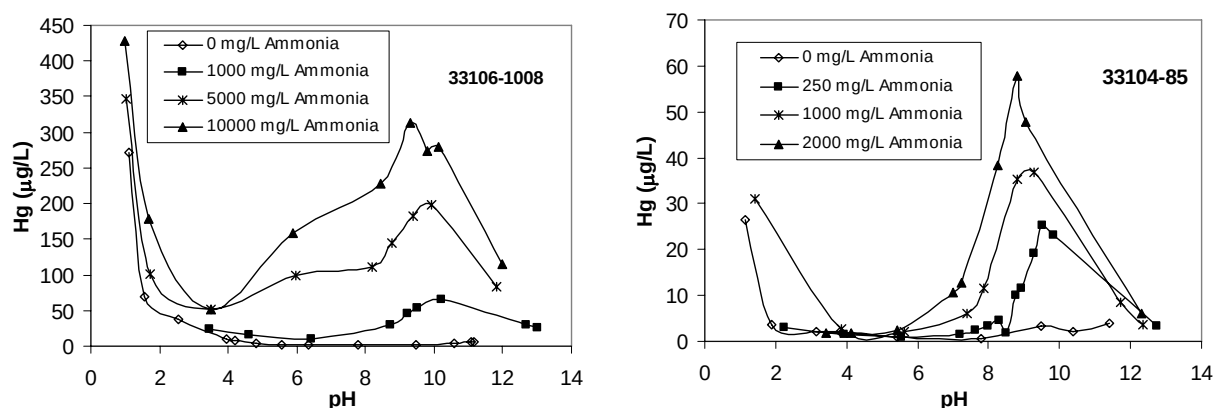


Figure 4-4
Impact of Ammonia on Mercury Adsorption for Washed Ash 33106-1008 and 33104-85.
Experimental Conditions: S/L = 1:10; Temperature = 20 – 25°C; S/L = 1:10; Equilibration Time = 24 Hours; Hg Addition = 1 mg/L

The ammonia addition enhanced the solubility of mercury. These results agree with those for the raw ash and washed ash when no external mercury was added. The soluble mercury concentrations for 33104-85 were significantly less than those for 33106-1008 under same conditions.

The mercury adsorption ratio was calculated for these two ashes, based on the soluble mercury concentration and the total mercury concentration in the system (Figure 4-5).

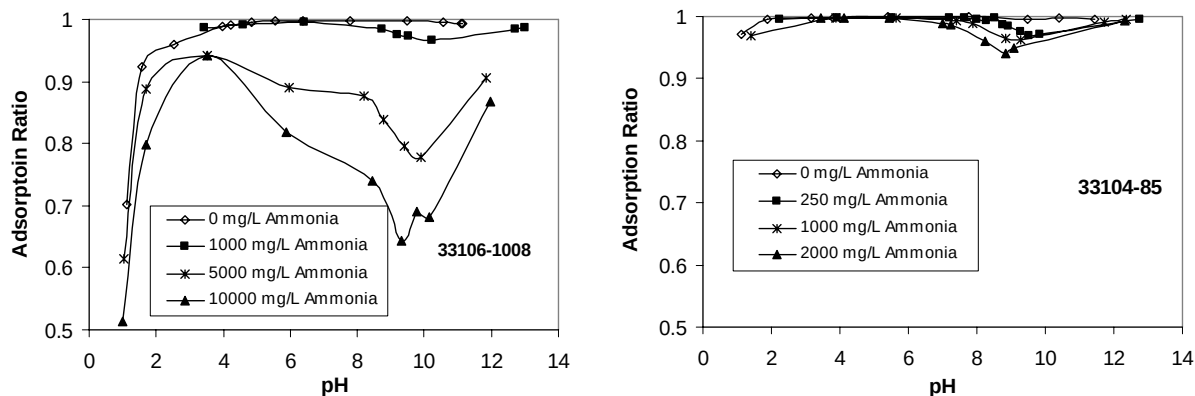


Figure 4-5
Mercury Adsorption Ratio as a Function of pH Under Different Ammonia Conditions for Washed Ash 33106-1008 and 33104-85. Experimental Conditions: S/L = 1:10; Temperature = 20 – 25°C; S/L = 1:10; Equilibration Time = 24 Hours; Hg Addition = 1 mg/L

5

MERCURY ADSORPTION MODELING

Theory

Surface Acidity of the Fly Ash

Fly ash was considered as a combination of several weak monoprotic acids. The deprotonation reaction of the monoprotic acid can be written as:



where $\underline{\text{SOH}}$ represents the protonated form of the surface sites and SO^- represents the free form of the surface sites; K_{H} represents the acidity constant for that particular site.

If we define S_{T} as the total acid site concentration:

$$S_{\text{T}} = \{\underline{\text{SOH}}\} + \{\underline{\text{SO}}^-\} \quad \text{Eq. 5-2}$$

The concentration of the deprotonated surface site is expressed as:

$$\{\underline{\text{SO}}^-\} = \frac{S_{\text{T}} K_{\text{H}}}{[\text{H}^+] + K_{\text{H}}} \quad \text{Eq. 5-3}$$

The relationship between acid/base consumption and the solution pH for an ash containing “ n ” types of sites is expressed as (Wang et al., 2004):

$$\Delta V_{\text{SS}} = \sum_{i=1-n} \frac{V_0 S_{\text{Ti}} K_{\text{Hi}}}{C} \left\{ \frac{1}{[\text{H}^+] + K_{\text{Hi}}} - \frac{1}{[\text{H}^+]_0 + K_{\text{Hi}}} \right\} \quad \text{Eq. 5-4}$$

where ΔV_{ss} is the net volume of stock base (or acid) solution consumed by the fly ash in mL; C is the concentration of the base/acid added; V_0 is the total volume of the ash solution; $[H^+]_0$ is the hydrogen ion concentration of the control unit without acids or base addition.

ΔV_{ss} needs to be corrected in order to account for the acid/base consumed by the water, by subtracting the acid or based consumed by water pH decrease/increase from the overall titration curve:

$$\Delta V_{ss} = \Delta V_{\text{overall}} - \Delta V_{\text{water}} \quad \text{Eq. 5-5}$$

Mercury Speciation in Water in the Presence of Ammonia

Reactions related to formation of mercury hydroxides in water are expressed as:



where $\beta_{(\text{OH})1}$, $\beta_{(\text{OH})2}$, and $\beta_{(\text{OH})3}$ are the overall formation constants for $\text{Hg}(\text{OH})^+$, $\text{Hg}(\text{OH})_2$, and $\text{Hg}(\text{OH})_3^-$, respectively. The values of $\log \beta$ for $\text{Hg}(\text{OH})^+$, $\text{Hg}(\text{OH})_2$, and $\text{Hg}(\text{OH})_3^-$ are, respectively, 10.6, 21.8, and 20.9 (Stumm and Morgan, 1996).

The concentrations of mercury hydroxide species are expressed as:

$$[\text{Hg}(\text{OH})^+] = \beta_{(\text{OH})1} [\text{OH}^-] [\text{Hg}^{2+}] \quad \text{Eq. 5-9}$$

$$[\text{Hg}(\text{OH})_2] = \beta_{(\text{OH})2} [\text{OH}^-]^2 [\text{Hg}^{2+}] \quad \text{Eq. 5-10}$$

$$[\text{Hg}(\text{OH})_3^-] = \beta_{(\text{OH})3} [\text{OH}^-]^3 [\text{Hg}^{2+}] \quad \text{Eq. 5-11}$$

The total dissolved mercury and mercury hydroxide species:

$$\begin{aligned} \text{Hg}_{\text{disl}} &= [\text{Hg}^{2+}] + [\text{Hg}(\text{OH})^+] + [\text{Hg}(\text{OH})_2] + [\text{Hg}(\text{OH})_3^-] \\ &= [\text{Hg}^{2+}] \{1 + \sum \beta_{(\text{OH})m} [\text{OH}]^m\} \end{aligned} \quad \text{Eq. 5-12}$$

The ammonia in the system has two species. The deprotonation equation is written as:



where K_{NH_3} is the acidity constant of NH_4^+ , and $\text{p}K_{\text{NH}_3} = 9.25$ (Stumm and Morgan, 1996).

The concentration of free ammonia can be expressed as:

$$[\text{NH}_3] = \frac{K_{\text{NH}_3} N_T}{[\text{H}^+] + [K_{\text{NH}_3}]} \quad \text{Eq. 5-14}$$

where N_T is the total ammonia concentration (ammonium and ammonia).

If ammonia is present in the system, the following reactions would also take place:



where $\beta_{(\text{NH}_3)1}$, $\beta_{(\text{NH}_3)2}$, $\beta_{(\text{NH}_3)3}$, and $\beta_{(\text{NH}_3)4}$ are overall formation constants of $\text{Hg}(\text{NH}_3)^{2+}$, $\text{Hg}(\text{NH}_3)_2^{2+}$, $\text{Hg}(\text{NH}_3)_3^{2+}$, and $\text{Hg}(\text{NH}_3)_4^{2+}$, respectively. The values of $\log\beta$ are 8.8, 17.4, 18.4, and 19.1, respectively (Stumm and Morgan, 1996).

The concentrations of mercury-ammonia complexes are expressed as:

$$[\text{Hg}(\text{NH}_3)^{2+}] = \beta_{(\text{NH}_3)1} [\text{NH}_3] [\text{Hg}^{2+}] \quad \text{Eq. 5-19}$$

$$[\text{Hg}(\text{NH}_3)_2^{2+}] = \beta_{(\text{NH}_3)2} [\text{NH}_3]^2 [\text{Hg}^{2+}] \quad \text{Eq. 5-20}$$

$$[\text{Hg}(\text{NH}_3)_3^{2+}] = \beta_{(\text{NH}_3)3} [\text{NH}_3]^3 [\text{Hg}^{2+}] \quad \text{Eq. 5-21}$$

$$[\text{Hg}(\text{NH}_3)_4^{2+}] = \beta_{(\text{NH}_3)4} [\text{NH}_3]^4 [\text{Hg}^{2+}] \quad \text{Eq. 5-22}$$

The sum of the dissolved Hg-ammonia species can be represented as:

$$\begin{aligned} \text{Hg}_{\text{dis}2} &= [\text{Hg}(\text{NH}_3)^{2+}] + [\text{Hg}(\text{NH}_3)_2^{2+}] + [\text{Hg}(\text{NH}_3)_3^{2+}] + [\text{Hg}(\text{NH}_3)_4^{2+}] \\ &= [\text{Hg}^{2+}] \{ \beta_{(\text{NH}_3)1} [\text{NH}_3] + \beta_{(\text{NH}_3)2} [\text{NH}_3]^2 + \beta_{(\text{NH}_3)3} [\text{NH}_3]^3 + \beta_{(\text{NH}_3)4} [\text{NH}_3]^4 \} \\ &= [\text{Hg}^{2+}] \sum \beta_{(\text{NH}_3)n} [\text{NH}_3]^n \end{aligned} \quad \text{Eq. 5-23}$$

Mercury Adsorption Reaction

It is assumed that the positively charge mercury species, Hg^{2+} and $\text{Hg}(\text{OH})^+$, are adsorbed by free surface site, SO^- . Due to the strong adsorption of $\text{Hg}(\text{OH})_2$ at very low pH condition where free surface sites, SO^- are unavailable, it was assumed that all surface sites, protonated and unprotonated, are responsible for adsorbing the neutrally charged mercury species. It was also assumed that the negatively charged mercury species, $\text{Hg}(\text{OH})_3^-$, is not adsorbable. The mercury adsorption reactions can be written as:



$$\underline{S}_T + \text{Hg}(\text{OH})_2 = \underline{S}\text{-Hg}(\text{OH})_2; K_{\text{S}(\text{OH})2} \quad \text{Eq. 5-26}$$

where K_S , $K_{\text{S}(\text{OH})1}$, and $K_{\text{S}(\text{OH})2}$ are respectively adsorption constants of Hg^{2+} , $\text{Hg}(\text{OH})^+$, and $\text{Hg}(\text{OH})_2$.

Adsorbed mercury and mercury-hydroxide species are expressed as:

$$\{\underline{S}\text{O-Hg}^+\} = K_S \{\underline{S}\text{O}^-\} [\text{Hg}^{2+}] \quad \text{Eq. 5-27}$$

$$\{\underline{S}\text{O-Hg}(\text{OH})\} = K_{\text{S}(\text{OH})1} \{\underline{S}\text{O}^-\} [\text{Hg}(\text{OH})^+] = K_{\text{S}(\text{OH})1} \beta_{(\text{OH})1} \{\underline{S}\text{O}^-\} [\text{OH}^-] [\text{Hg}^{2+}] \quad \text{Eq. 5-28}$$

$$\{\underline{S}\text{-Hg}(\text{OH})_2\} = K_{\text{S}(\text{OH})2} \{\underline{S}_T\} [\text{Hg}(\text{OH})_2] = K_{\text{S}(\text{OH})2} \beta_{(\text{OH})2} \{\underline{S}_T\} [\text{OH}^-]^2 [\text{Hg}^{2+}] \quad \text{Eq. 5-29}$$

The total adsorbed mercury and mercury-hydroxide species:

$$\begin{aligned} \text{Hg}_{\text{ads1}} &= \{\underline{S}\text{O-Hg}^+\} + \{\underline{S}\text{O-Hg}(\text{OH})\} + \{\underline{S}\text{-Hg}(\text{OH})_2\} \\ &= [\text{Hg}^{2+}] \{ K_S \{\underline{S}\text{O}^-\} + K_{\text{S}(\text{OH})1} \beta_{(\text{OH})1} \{\underline{S}\text{O}^-\} [\text{OH}^-] + K_{\text{S}(\text{OH})2} \beta_{(\text{OH})2} \{\underline{S}_T\} [\text{OH}^-]^2 \} \\ &= [\text{Hg}^{2+}] D_{\text{ads1}} \end{aligned} \quad \text{Eq. 5-30}$$

$$\text{where } D_{\text{ads1}} = K_S \{\underline{S}\text{O}^-\} + K_{\text{S}(\text{OH})1} \beta_{(\text{OH})1} \{\underline{S}\text{O}^-\} [\text{OH}^-] + K_{\text{S}(\text{OH})2} \beta_{(\text{OH})2} \{\underline{S}_T\} [\text{OH}^-]^2$$

In the system containing ammonia, the mercury-ammonia species are also adsorbable. Due to the strong adsorption of mercury ammonia species at very low pH where free surface sites are unavailable, it was assumed that all surface sites, protonated and unprotonated, are responsible for the adsorption of mercury-ammonia complexes. The adsorption reactions can be expressed as:

$$\underline{S}_T + \text{Hg}(\text{NH}_3)^{2+} = \underline{S}\text{-Hg}(\text{NH}_3)^{2+}; K_{\text{S}(\text{NH3})1} \quad \text{Eq. 5-31}$$

$$\underline{S}_T + \text{Hg}(\text{NH}_3)_2^{2+} = \underline{S}\text{-Hg}(\text{NH}_3)_2^{2+}; K_{\text{S}(\text{NH3})2} \quad \text{Eq. 5-32}$$

$$\underline{S}_T + \text{Hg}(\text{NH}_3)_3^{2+} = \underline{S}\text{-Hg}(\text{NH}_3)_3^{2+}; K_{\text{S}(\text{NH3})3} \quad \text{Eq. 5-33}$$

$$\underline{S}_T + \text{Hg}(\text{NH}_3)_4^{2+} = \text{S-Hg}(\text{NH}_3)_4^{2+}; K_{\text{S}(\text{NH}_3)_4} \quad \text{Eq. 5-34}$$

where $K_{\text{S}(\text{NH}_3)_1}$, $K_{\text{S}(\text{NH}_3)_2}$, $K_{\text{S}(\text{NH}_3)_3}$, and $K_{\text{S}(\text{NH}_3)_4}$ are adsorption constants of $\text{Hg}(\text{NH}_3)^{2+}$, $\text{Hg}(\text{NH}_3)_2^{2+}$, $\text{Hg}(\text{NH}_3)_3^{2+}$, and $\text{Hg}(\text{NH}_3)_4^{2+}$, respectively.

The concentration of adsorbed mercury-ammonia complexes can be expressed as:

$$\{\underline{\text{S-Hg}}(\text{NH}_3)^{2+}\} = K_{\text{S}(\text{NH}_3)_1} \{\underline{\text{S}}_T\} [\text{Hg}(\text{NH}_3)^{2+}] = K_{\text{S}(\text{NH}_3)_1} \beta_{(\text{NH}_3)_1} \{\underline{\text{S}}_T\} [\text{NH}_3] [\text{Hg}^{2+}] \quad \text{Eq. 5-35}$$

Similarly,

$$\{\underline{\text{S-Hg}}(\text{NH}_3)_2^{2+}\} = K_{\text{S}(\text{NH}_3)_2} \beta_{(\text{NH}_3)_2} \{\text{S}_T\} [\text{NH}_3]^2 [\text{Hg}^{2+}] \quad \text{Eq. 5-36}$$

$$\{\underline{\text{S-Hg}}(\text{NH}_3)_3^{2+}\} = K_{\text{S}(\text{NH}_3)_3} \beta_{(\text{NH}_3)_3} \{\text{S}_T\} [\text{NH}_3]^3 [\text{Hg}^{2+}] \quad \text{Eq. 5-37}$$

$$\{\underline{\text{S-Hg}}(\text{NH}_3)_4^{2+}\} = K_{\text{S}(\text{NH}_3)_4} \beta_{(\text{NH}_3)_4} \{\text{S}_T\} [\text{NH}_3]^4 [\text{Hg}^{2+}] \quad \text{Eq. 5-38}$$

The total adsorbed mercury-ammonia species:

$$\begin{aligned} \text{Hg}_{\text{ads2}} &= \{\underline{\text{S-Hg}}(\text{NH}_3)^{2+}\} + \{\underline{\text{S-Hg}}(\text{NH}_3)_2^{2+}\} + \{\underline{\text{S-Hg}}(\text{NH}_3)_3^{2+}\} + \{\underline{\text{S-Hg}}(\text{NH}_3)_4^{2+}\} \\ &= [\text{Hg}^{2+}] \{\text{ST}\} \sum K_{\text{S}(\text{NH}_3)_n} \beta_{(\text{NH}_3)_n} [\text{NH}_3]^n \\ &= [\text{Hg}^{2+}] D_{\text{ads2}} \end{aligned} \quad \text{Eq. 5-39}$$

$$\text{where } D_{\text{ads2}} = \{\underline{\text{S}}_T\} \sum K_{\text{S}(\text{NH}_3)_n} \beta_{(\text{NH}_3)_n} [\text{NH}_3]^n$$

Mercury Adsorption Model

The total concentration of all mercury species in the system can be expressed as:

$$\begin{aligned}
 \text{Hg}_T &= \text{Hg}_{\text{dis1}} + \text{Hg}_{\text{dis2}} + \text{Hg}_{\text{ads1}} + \text{Hg}_{\text{ads2}} \\
 &= [\text{Hg}^{2+}] \times \{1 + \sum \beta_{(\text{OH})m} [\text{OH}]^m + \sum \beta_{(\text{NH}_3)n} [\text{NH}_3]^n + D_{\text{ads1}} + D_{\text{ads2}}\} \\
 &= [\text{Hg}^{2+}] D_T
 \end{aligned}
 \tag{Eq. 5-40}$$

where $D_T = 1 + \sum \beta_{(\text{OH})m} [\text{OH}]^m + \sum \beta_{(\text{NH}_3)n} [\text{NH}_3]^n + D_{\text{ads1}} + D_{\text{ads2}}$

The Hg adsorption ratio is expressed as:

$$R = \frac{\text{Hg}_{\text{ads1}} + \text{Hg}_{\text{ads2}}}{\text{Hg}_T} = \frac{D_{\text{ads1}} + D_{\text{ads2}}}{D_T}
 \tag{Eq. 5-41}$$

Equation 5-41 was used for curve fitting to determine the adsorption constants for Hg^{2+} , $\text{Hg}(\text{OH})^+$, and $\text{Hg}(\text{OH})_2$.

Ash Surface Acidity

Figure 5-1 shows the net titration results (points) for two washed ash samples, 33106-1008 and 33104-85. Equation 5-4 was used to fit the experimental data. It was found that the 3-site assumption best fit the experimental results, namely, α , β , and γ . Therefore, the fly ash was assumed to have 3 types of surface sites. Table 5-1 shows the surface site density and acidity constant for the two ashes.

Table 5-1
Surface Site Density and Acidity Constants for Washed Ashes 33106-1008 and 33104-85

Ash ID	Parameters	α		γ
33106-1008	Site Density (10^{-5} mol/g)	39 $\pm$ 1	2.0 $\pm$ 2.1	22 $\pm$ 52
	Acidity Constant (pK_a)	3.2 $\pm$ 0.1	8.9 $\pm$ 2.0	12.2 $\pm$ 1.5
33104-85	Site Density (10^{-5} mol/g)	212 $\pm$ 326	3.2 $\pm$ 1.1	35 $\pm$ 51
	Acidity Constant (pK_a)	2.5 $\pm$ 0.8	7.6 $\pm$ 0.3	12.2 $\pm$ 0.9

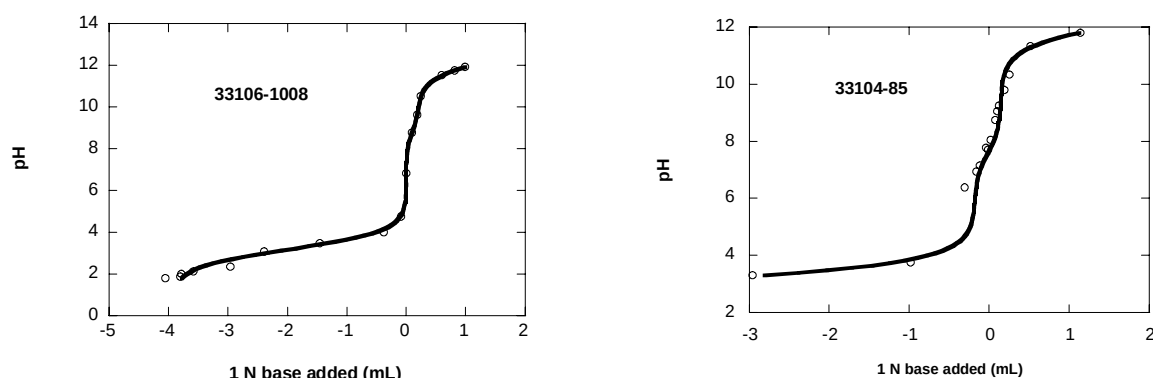


Figure 5-1
Titration and Curve Fitting Results for Washed Ashes: (a) 33106-1008 and (b) 33104-85

Mercury Adsorption Modeling

The adsorption data for ash 33106-1008, with 1 mg/L external mercury addition under different ammonia concentration conditions, were used to test the model (Equation 5-39). SigmaPlot was used to conduct the curve fitting, based on the adsorption ratio as functions of pH and ammonia concentration. Based on the modeling, it was found that the adsorption of the following species are very weak and therefore can be ignored: Hg^{2+} , $\text{Hg}(\text{OH})^+$, $\text{Hg}(\text{NH}_3)^{2+}$, and $\text{Hg}(\text{NH}_3)_3^{2+}$. The adsorption constants ($\log K^s$) of other three species, $\text{Hg}(\text{OH})_2$, $\text{Hg}(\text{NH}_3)_2^{2+}$, and $\text{Hg}(\text{NH}_3)_4^{2+}$ are 6.96, 3.36, and 2.95, respectively. Figure 4-7 shows the modeling results. Although the model calculation does not perfectly match the experimental data, it reflects the trend of the mercury partitioning under different ammonia conditions reasonably well.

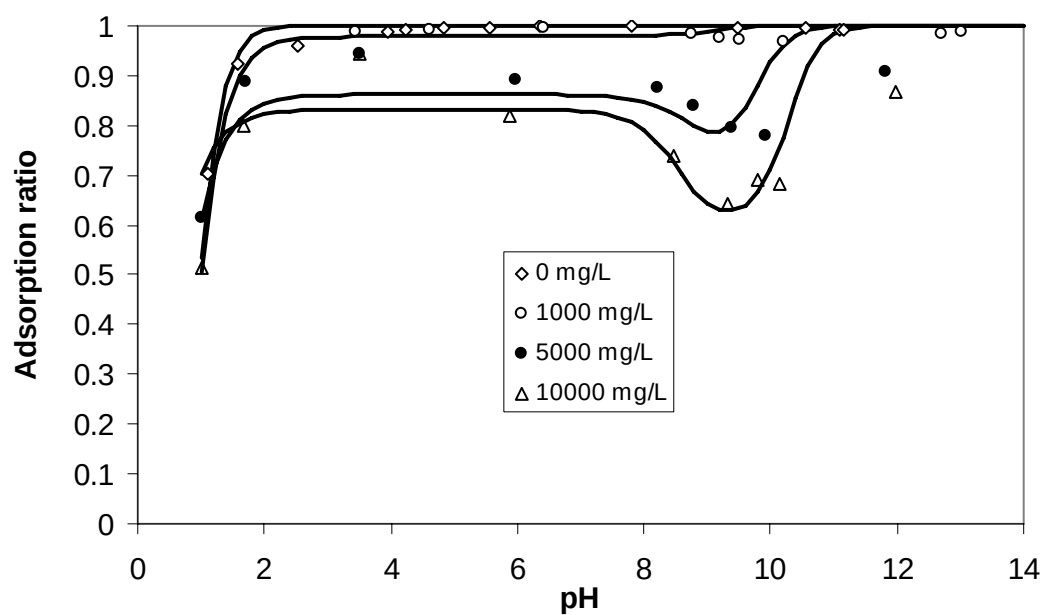


Figure 5-2
Mercury Adsorption Ratio in a System Containing 100 g/L Washed Ash 33106-1008 and 1 mg/L Mercury and 0 to 10,000 mg/L Ammonia: Experimental Data (points) vs. Modeling Results (solid lines)

6

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