

The Effect of Ammonia on the Leaching of Cu(II) and Cd(II) from Fly Ash

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ABSTRACT

This paper presents a theoretical model for the adsorption/desorption of cationic metals and metal-ammonia complexes on fly ash surfaces. The effect of ammonia on the adsorption of Cu(II) and Cd(II) by a fly ash derived from eastern bituminous coal was investigated using a batch experimental method. Results indicated that high ammonia concentration (> 5000 mg/L) can significantly decrease the adsorption of these metals onto the fly ash in the alkaline pH range. There is little or no effect on adsorption at lower ammonia concentrations. Based on theoretical analyses, a mathematical model was developed to quantify the ammonia effect on metal adsorption. The adsorption constants of free metal, metal-hydroxide species, and metal-ammonia complexes for the fly ash were determined by fitting the model to the experimental data. Metal speciation calculation indicated that the formation of less adsorbable metal-ammonia complexes resulted in the decrease of metal adsorption in alkaline pH range. Therefore, the presence of ammonia could increase the leaching of Cu(II) and Cd(II) from fly ash at concentrations of 5,000 mg/L or higher, but has no significant effect on leaching at lower ammonia concentrations.

INTRODUCTION

Coal fly ash is a combustion by-product from coal-fired power plants. According to American Coal Ash Association (ACAA), U.S. electric utilities generated 122 million tons of coal combustion products (CCPs) in 2003, and 58% of the CCPs were fly ash.¹ Depending on the source of coal, the fly ash may contain various levels of trace elements such as antimony, arsenic, barium, boron, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, silver, and zinc.²⁻⁴ These trace elements have the potential to contaminate soil, surface water, and ground water if they are released into the environment.

Previous studies indicated that pH is one of the most significant factors affecting metal leaching from fly ash. Results showed that the leachability of cationic metal ions such as cadmium, chromium, zinc, lead, mercury, and silver increases with decreasing pH.^{2; 3; 5-11} However, metal leaching under natural conditions from ammonia-free fly ash is generally not a significant environmental concern.³

Recent EPA regulations on controlling regional transport of ground level ozone require 22 eastern states in US to adopt NO_x emission controls on large stationary sources. To meet these regulations, ammonia-based NO_x control technologies, such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) processes, have become

increasingly common in coal-fired power plants. Their use will continue to grow significantly over the next ten years. Over 55% of the coal-fired power generating capacity is expected to install either SCRs or SNCRs.¹² Excess ammonia that escapes in the flue gas, referred to as ammonia slip, can be adsorbed onto the fly ash. The concentration of ammonia can be as high as 2,500 - 2,700 ppm in fly ash under high slip conditions,¹³⁻¹⁶ although much lower concentrations are expected in practice. Column leaching experiments showed that ammonia concentration in the leachate from ammoniated fly ash can reach a concentration (in ppm) of 7 times higher than that found in the fly ash.¹⁴ In addition to SCR and SNCR, ammonia is sometimes used as an ash conditioner to control ash resistivity for better particulate control in electrostatic precipitators (ESPs).

Ammonia can form strong water-soluble complexes with many heavy metals.¹⁷ It has been used as a chelating agent to extract metals such as Cu(II), Ni(II), Co(II), and Zn(II) in industry.¹⁸ Our preliminary investigations indicated that the presence of high concentrations of ammonia in fly ash (> 5000 ppm) can increase the release of the heavy metals such as Cu(II), Ni(II), Cd(II), and Hg(II).¹⁹⁻²² However, the details of ammonia-enhanced metal leaching processes was not fully understood.

The objectives of this research are to provide more detailed information to understand the ammonia-enhanced metal leaching process in the fly ash, and to develop a mathematical model to quantify the metal adsorption by fly ash in the presence of ammonia.

CHEMICAL REACTIONS

In a system containing fly ash, cationic metal ions, and ammonia, the following reactions could occur concurrently:

(a) Ash surface site dissociation:

Assuming that there is only one type of surface site responsible for metal binding, the dissociation reaction of the surface site can be written as:



where $\underline{\text{SOH}}$ and $\underline{\text{SO}}^-$ are respectively protonated and free surface sites, and K_{H} is the acidity constant (M).

(b) Metal hydroxide formation:

Free metal ions can react with hydroxide ions in water to form metal hydroxides:



where M^{2+} and $\text{M}(\text{OH})_n^{2-n}$ are respectively free metal ion and metal hydroxide, $\beta_{(\text{OH})_n}$ is the overall formation constant for the metal hydroxide, and n is the number of hydroxide ions associated with each metal ion, $n = 1, 2, \dots$

(c) Metal adsorption:

Free metal ion and metal hydroxides can be adsorbed by free surface sites. The adsorption reactions can be expressed as:



where $\underline{\text{SO}}\text{-M}^+$, $\underline{\text{SO}}\text{-M}(\text{OH})$, and $\underline{\text{SO}}\text{-M}(\text{OH})_2^-$ are surface complexes of free metal and metal hydroxides, and K_S , $K_{S(\text{OH})1}$, and $K_{S(\text{OH})2}$ are stability constants of these surface complexes (i.e., adsorption constants).

(d) Ammonia speciation:

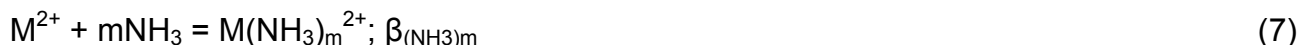
The pH condition affects the speciation of ammonia. The reaction can be expressed as:



where K_{NH_3} is the acidity constant of ammonium (NH_4^+), and $\text{p}K_{\text{NH}_3} = 9.25$.²³

(e) Metal complexation with ammonia:

Free metal ion can react with free ammonia (NH_3) to form metal-ammonia complexes:



where $\text{M}(\text{NH}_3)_m^{2+}$ is a metal-ammonia complex, $\beta_{(\text{NH}_3)m}$ is the stability constant of the metal-ammonia complex, and m is the number of ammonia molecules associated with each metal ion, $m = 1, 2, \dots$

(f) Adsorption of metal-ammonia complexes:

The metal-ammonia complexes could also be adsorbed by free surface sites. The adsorption reaction can be written as:



where $\underline{\text{SO}}\text{-M}(\text{NH}_3)_m^+$ is the surface complex of metal-ammonia complexes, and $K_{S(\text{NH}_3)m}$ is the adsorption constant of the metal-ammonia complex.

MATERIALS AND METHODS

Fly Ash Sample Preparation

The fly ash used in this experiment was generated from a full-scale power generating unit burning medium sulfur eastern bituminous coal. The ash was collected from an electrostatic precipitator that uses ammonia as a flue gas conditioner to enhance precipitator performance. This resulted in an ash with an ammonia concentration of approximately 150 ppm (by weight). The ash has the BET surface area of 2.6 m²/g, carbon content (by CHN analyzer) of 3.6%, and loss on ignition (LOI) of 4.3%.²⁴

It is expected that adsorption plays the major role on metals fate and transport in fly ash. To better understand the adsorption process, a clean surface is needed for adsorption experiments. To obtain a clean ash surface, the raw fly ash was washed according the

following procedure: (a) mix the ash with distilled and deionized water (DD water) at solids/liquid (S/L) ratio of 1:5; (b) agitate the sample using air or a mechanical mixer for 10 hours; (c) allow the mixture settle for approximately 1 hour after the mixing is stopped; (d) decant the supernatant; (e) repeat the above procedure for another 4 times; (f) dry the sample completely at a temperature of 103 – 105 °C; (g) sieve the dried ash sample using a #200 sieve (75 µm opening); and (h) mix and store the sieved sample in an air-tight container for later use. After the above preparation process, it is expected that most readily soluble components in raw fly ash are removed and relatively clean ash surfaces are obtained.

Batch Metal Adsorption Experiments

A batch method was used to generate metal adsorption data under different pH and ammonia conditions. All experiments were conducted in single-metal systems. The experiments were carried out according to the following procedure:

(a) A 10 g fly ash sample was added to each of the 125-mL bottles, except the blank. There were 6 groups of bottles corresponding to 6 different initial ammonia concentrations to be tested. Each group had 14 sample bottles for 14 pH conditions plus one blank. (b) One hundred mL prepared water solution containing 0.01 M of NaNO₃, a pre-selected concentration of heavy metal ion, and a pre-selected concentration of ammonia (use NH₄NO₃) were added to all bottles, including the blank. The same water solution was distributed to all bottles in the same group. (c) The pH was adjusted for all bottles in each group to a desired distribution in the pH range of 2 to 12 using trace-metal grade 1 M nitric acid (HNO₃) or sodium hydroxide (NaOH) solutions. No acid or base was added to the blank sample. (d) All bottles were tightly sealed and placed in a mechanical shaker for 24 hours at 130 revolutions per minute (rpm), and then allowed to settle for at least 30 minutes. (e) Twenty mL of the supernatant were filtered using a 0.45 µm syringe filter, and acidified. (f) Dissolved metal concentrations were measured on the acidified sample and final pH was measured on the mixture remaining in bottles.

Chemical Analyses

An atomic absorption spectrometer (AAAnalyst 800, Perkin-Elmer Corp., Norwalk, Connecticut) was used to determine heavy metal concentrations in the solutions. The pH was measured using an Orion model 720A pH meter with Orion Ross model 81-02 pH electrode. An Orion model 95-12 ammonia electrode with ionic strength agent (ISA) was used to measure the ammonia concentration.

RESULTS AND DISCUSSION

Ammonia Impact on Cu(II) Adsorption

Figure 1 shows the ratio of Cu(II) adsorption as a function of pH under 5 different total ammonia concentration conditions. The figure shows that a) Cu(II) adsorption is not affected by ammonia when the pH is lower than 6; b) Cu(II) adsorption is not affected by ammonia in the entire pH range when ammonia concentration is less than 1000 mg/L; c) Cu(II) adsorption decreases significantly with the increase of ammonia concentration in the alkaline pH range when ammonia concentration is greater than 5000 mg/L; and d) at high ammonia concentrations, Cu(II) adsorption decreases with the increase of pH starting from neutral pH, reaches the lowest value at pH of 9.5, and then increases with further increase in pH.

Figure 2 is an ammonia speciation profile. It shows that the relative concentration of free ammonia increases significantly with the increase of pH in the alkaline pH region. Once the pH is greater than 9.25, free ammonia is the dominant species. Since free ammonia can form complexes with Cu(II), it can be hypothesized that the decrease of Cu(II) adsorption with the increase of pH under alkaline pH conditions is caused by the formation of less adsorbable Cu(II)-ammonia complexes. The ammonia impact on Cu(II) adsorption may also be affected by many other reactions in the system including the surface site speciation, metal hydroxide formation, and the adsorption of metal-hydroxides by fly ash.

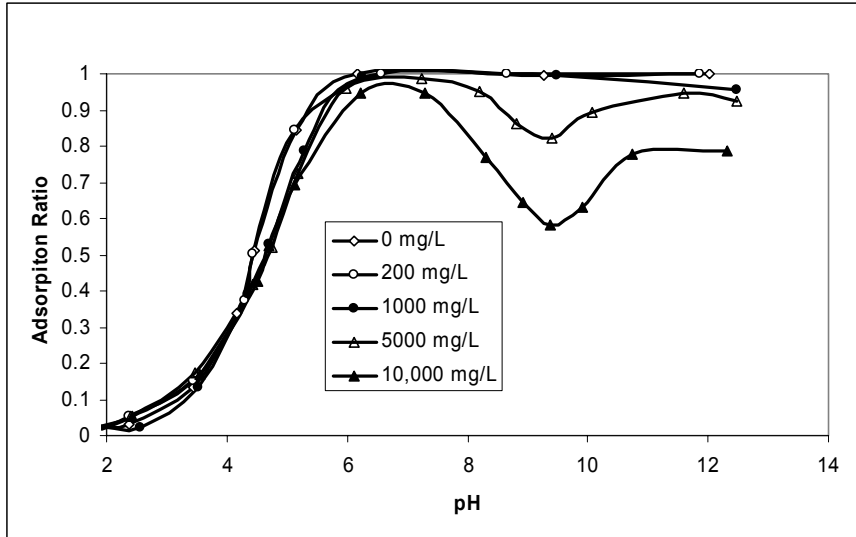


Figure 1. Cu(II) partitioning under 5 different ammonia concentrations. Experimental conditions: metal concentrations = 5 mg/L; ion strength = 0.01M (NaNO₃); temperature = 20 – 25 °C; and equilibration time = 24 hours.

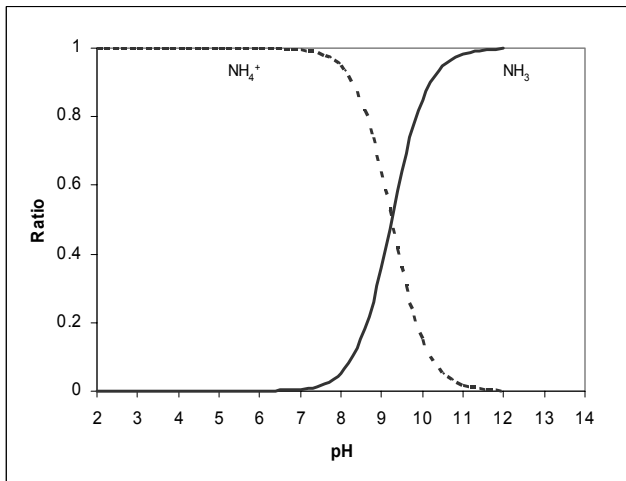


Figure 2. Ammonia speciation profile.

Surface Site Speciation

The surface site density and acidity constant of the fly ash used in this investigation were determined previously.²² Results indicated that this fly ash surface contains 3 types of acid sites. Their densities are 2.1×10^{-4} , 1.8×10^{-5} , and 5.3×10^{-5} mol/g-fly ash, with acidity constants

(pK_H) of 2.7, 7.8, and 11.0, respectively. Previous study also indicated that the acid site with pK_H of 2.7 does not participate in the metal adsorption reaction.²⁵

Most cationic heavy metal ions are in neutral or negatively charged hydroxide forms if the pH is greater than 10. Since the adsorption of zero-charged metal hydroxide is not related to surface electric characteristics, and there will be no adsorption of negatively charged metal hydroxides by negatively-charged free surface sites, the surface site with a pK_H of 11 may not play a significant role on the metal adsorption reactions.

Therefore, we can assume that only the acid site with a pK_H of 7.8 is responsible for metal adsorption. Figure 3 shows the site speciation under different pH conditions in an ash sample with S/L ratio of 1:10. Since the total metal binding site density for this ash is 1.8×10^{-5} mol/g, and the total solids concentration is 100 g/L for the S/L = 1:10 ash sample, the total metal binding site concentration (S_T) in the system is 1.8×10^{-3} M.

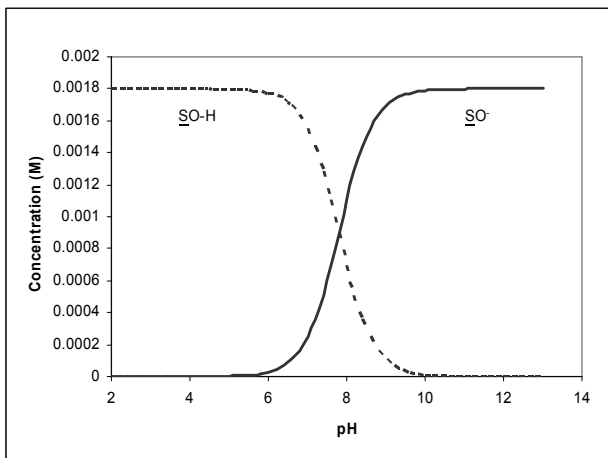


Figure 3. Surface site speciation profile for ash concentration of 100 g/L (S/L = 1:10).

Metal Hydroxide Formation

Metal hydroxide species can be formed at alkaline pH. For Cu(II), the overall formation constants ($\log\beta_{(OH)}$) for $Cu(OH)^+$, $Cu(OH)_2$, and $Cu(OH)_4^{2-}$ are, respectively, 6.3, 11.8, and 16.4.¹⁷ Based on this information, Cu(II) speciation was calculated. Figure 4 shows the calculated Cu(II) speciation in pure water. It shows that when pH approaches 10, the concentration of positively charged species, Cu^{2+} and $Cu(OH)^+$, are negligible.

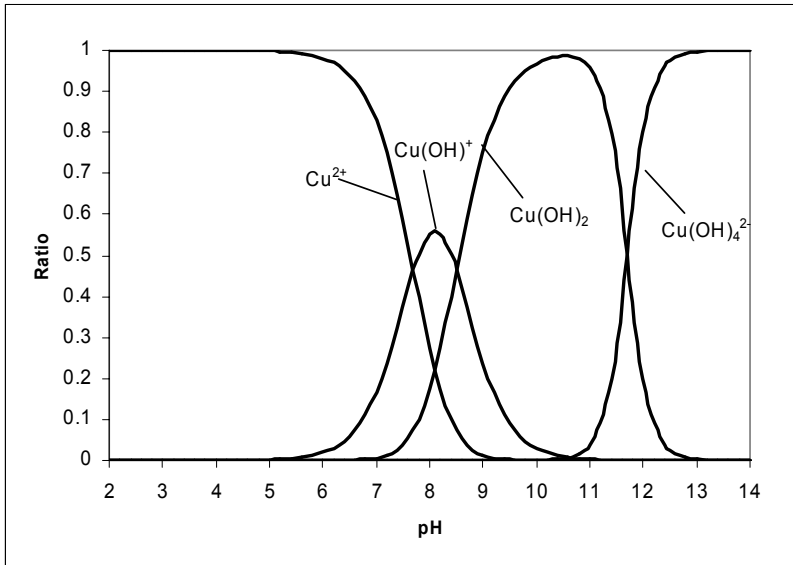


Figure 4. Cu(II) speciation in water solution.

Cu(II) Speciation in the Presence of Ammonia

If a system contains heavy metal and ammonia, the free metal ion can react with free ammonia to form metal-ammonia complexes. For Cu(II), the overall formation constants ($\log\beta_{(\text{NH}_3)}$) for $\text{Cu}(\text{NH}_3)^{2+}$, $\text{Cu}(\text{NH}_3)_2^{2+}$, $\text{Cu}(\text{NH}_3)_3^{2+}$, and $\text{Cu}(\text{NH}_3)_4^{2+}$ are, respectively, 4.0, 7.5, 10.3, and 11.8.¹⁷ Based on these formation constants and the assumption that the metal concentration is much lower than the total ammonia concentration (so that the formation of metal-ammonia complexes does not significantly reduce the free ammonia concentration), the metal speciation as a function of pH was calculated. Figure 5 shows the Cu(II) speciation profile in a system with a total ammonia concentration (N_T) of 0.6 M (10,000 mg/L). It shows that in the pH range from 6 to 12, most copper in solution is in the form of Cu(II)-ammonia complexes. It also shows that when pH is greater than 12, the negatively charged $\text{Cu}(\text{OH})_4^{2-}$ is the dominant specie.

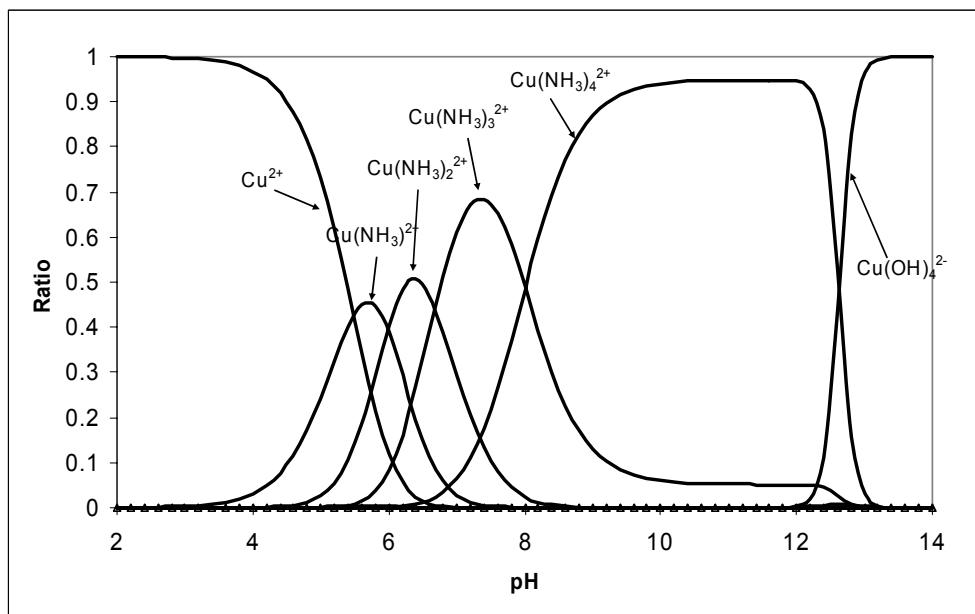


Figure 5. Calculated Cu(II) speciation in water solution containing 0.6 M (10,000 mg/L) of total ammonia.

Based on the Cu(II) speciation profile shown in Figure 5, it can be concluded that the decrease of Cu(II) adsorption in the pH range between 7 and 12 in Figure 1 is caused by the formation of less adsorbable Cu(II)-ammonia complexes. It can also be concluded that the decrease of Cu(II) adsorption with the increase of pH when pH is greater than 12 is caused by the formation of negatively charged Cu(OH)_4^{2-} , which is considered non-adsorbable by negatively charged free surface sites.

Model Describing Ammonia Impact on Metal Adsorption

If a system contains heavy metal ions, ammonia, and solids, the following metal species could be adsorbed by the solid surface: free metal ion (M^{2+}), metal hydroxide species (M(OH)^+ and M(OH)_2), and various metal-ammonia complexes (they are positively charged). Their adsorption constants determine the overall metal adsorption equilibrium.

To simplify the modeling process, we assume that the total metal concentration is relatively low compared to the total surface site concentration and the total ammonia concentration. Thus, the adsorptions of free metal ion, metal hydroxides, and metal-ammonia complexes are in the linear range of the Langmuir adsorption isotherm, and the complexation between free metal ion and ammonia is also in the linear range of the complexation reactions. Therefore, the concentrations of the adsorbed metal species are proportional to their respective concentrations in the solution, and the concentrations of the soluble metal-ammonia complexes are also proportional to the free metal ion concentration in the solution. Since all metal-ammonia complexes have the same charge, we further assume that the adsorption constants for all metal-ammonia complexes are the same ($K_{\text{S(NH}_3\text{)}}$). Such assumptions allow us to further simplify the modeling process by using the theoretical model to directly fit the experimental data.

Therefore, in a system containing fly ash, ammonia, and heavy metals, the following metal species are present:

(a) free metal ion: M^{2+} ;

(b) metal hydroxides: $M(OH)^+$; $M(OH)_2$; $M(OH)_3^-$; $M(OH)_4^{2-}$;

(c) metal-ammonia complexes: $M(NH_3)^{2+}$; $M(NH_3)_2^{2+}$; $M(NH_3)_3^{2+}$; $M(NH_3)_4^{2+}$; $M(NH_3)_5^{2+}$;

(d) adsorbed free metal and metal hydroxides: $\underline{SO}-M^+$; $\underline{SO}-M(OH)$; $\underline{SO}-M(OH)_2^-$;

(e) adsorbed metal-ammonia complexes: $\sum \underline{SO}-M(NH_3)_m^+$ (including $\underline{SO}-M(NH_3)^+$; $\underline{SO}-M(NH_3)_2^+$; $\underline{SO}-M(NH_3)_3^+$; $\underline{SO}-M(NH_3)_4^+$; $\underline{SO}-M(NH_3)_5^+$ );

The concentration of metal-hydroxide species, metal-ammonia complexes, and all adsorbed metal species can be expressed as a function of free metal ion concentration:

$$\begin{aligned}
 [M(OH)^+] &= \beta_{(OH)1} [OH^-] [M^{2+}]; \\
 [M(OH)_2] &= \beta_{(OH)2} [OH^-]^2 [M^{2+}]; \\
 [M(OH)_3^-] &= \beta_{(OH)3} [OH^-]^3 [M^{2+}]; \\
 [M(OH)_4^{2-}] &= \beta_{(OH)4} [OH^-]^4 [M^{2+}]; \\
 &\dots \\
 [M(NH_3)^{2+}] &= \beta_{(NH3)1} [NH_3] [M^{2+}]; \\
 [M(NH_3)_2^{2+}] &= \beta_{(NH3)2} [NH_3]^2 [M^{2+}]; \\
 [M(NH_3)_3^{2+}] &= \beta_{(NH3)3} [NH_3]^3 [M^{2+}]; \\
 [M(NH_3)_4^{2+}] &= \beta_{(NH3)4} [NH_3]^4 [M^{2+}]; \\
 [M(NH_3)_5^{2+}] &= \beta_{(NH3)5} [NH_3]^5 [M^{2+}]; \\
 &\dots \\
 \{\underline{SO}-M^+\} &= K_S \{\underline{SO}^-\} [M^{2+}]; \\
 \{\underline{SO}-M(OH)\} &= K_{S(OH)1} \{\underline{SO}^-\} [M(OH)^+] = K_{S(OH)1} \beta_{(OH)1} \{\underline{SO}^-\} [OH^-] [M^{2+}]; \\
 \{\underline{SO}-M(OH)_2^-\} &= K_{S(OH)2} \{\underline{SO}^-\} [M(OH)_2] = K_{S(OH)2} \beta_{(OH)2} \{\underline{SO}^-\} [OH^-]^2 [M^{2+}]; \\
 \sum \{\underline{SO}-M(NH_3)_m^+\} &= K_{S(NH3)} \{\underline{SO}^-\} \sum [M(NH_3)_m^{2+}] = K_{S(NH3)} \{\underline{SO}^-\} (\beta_{(NH3)1} [NH_3] + \beta_{(NH3)2} [NH_3]^2 + \\
 &\beta_{(NH3)3} [NH_3]^3 + \beta_{(NH3)4} [NH_3]^4 + \beta_{(NH3)5} [NH_3]^5 + \dots) [M^{2+}].
 \end{aligned} \tag{9}$$

where

$$\{\underline{SO}^-\} \text{ is the concentration of the free surface site (M), } \{\underline{SO}^-\} = \frac{K_H \underline{S}_T}{[H^+] + K_H};$$

\underline{S}_T is the concentration of total metal binding site (M), which is a product of solids concentration (g/L) and the metal binding site density (mol/g-solids);

$$[NH_3] \text{ is the free ammonia concentration (M), } [NH_3] = \frac{K_{NH3} N_T}{[H^+] + K_{NH3}};$$

N_T is the total ammonia concentration (sum of free ammonia and ammonium) in the system (M).

Therefore, the ratio of free metal ion concentration to the total metal concentration in the system, $\frac{[M^{2+}]}{M_T}$, can be expressed as:

$$\begin{aligned}
 \frac{[M^{2+}]}{M_T} &= (1 + \beta_{(OH)1} [OH^-] + \beta_{(OH)2} [OH^-]^2 + \beta_{(OH)3} [OH^-]^3 + \beta_{(OH)4} [OH^-]^4 + \dots + \beta_{(NH3)1} [NH_3] + \\
 &\beta_{(NH3)2} [NH_3]^2 + \beta_{(NH3)3} [NH_3]^3 + \beta_{(NH3)4} [NH_3]^4 + \beta_{(NH3)5} [NH_3]^5 + \dots + K_S \{\underline{SO}^-\} + K_{S(OH)1} \beta_{(OH)1} \\
 &\{\underline{SO}^-\} [OH^-] + K_{S(OH)2} \beta_{(OH)2} \{\underline{SO}^-\} [OH^-]^2 + K_{S(NH3)} \{\underline{SO}^-\} (\beta_{(NH3)1} [NH_3] + \beta_{(NH3)2} [NH_3]^2 + \beta_{(NH3)3} \\
 &[NH_3]^3 + \beta_{(NH3)4} [NH_3]^4 + \beta_{(NH3)5} [NH_3]^5 + \dots))^{-1} \tag{10}
 \end{aligned}$$

Based on Equation group (9), the ratio of other metal species to the total metal in the system can be expressed as a function of $\frac{[M^{2+}]}{M_T}$.

The total adsorbed metal concentration can be expressed as:

$$M_{\text{ads}} = \{\underline{\text{SO}}\text{-M}^+\} + \{\underline{\text{SO}}\text{-M(OH)}\} + \{\underline{\text{SO}}\text{-M(OH)}_2^-\} + \sum\{\underline{\text{SO}}\text{-M(NH}_3)_m^+\} \quad (11)$$

Therefore, the ratio of metal adsorption, R, can be expressed as a function of $\frac{[M^{2+}]}{M_T}$:

$$\begin{aligned} R = \frac{M_{\text{ads}}}{M_T} &= \frac{\{\underline{\text{SO}}\text{-M}^+\}}{M_T} + \frac{\{\underline{\text{SO}}\text{-M(OH)}\}}{M_T} + \frac{\{\underline{\text{SO}}\text{-M(OH)}_2^-\}}{M_T} + \frac{\sum\{\underline{\text{SO}}\text{-M(NH}_3)_m^+\}}{M_T} \\ &= (K_S \{\underline{\text{SO}}\} + K_{S(\text{OH})1} \beta_{(\text{OH})1} \{\underline{\text{SO}}\} [\text{OH}] + K_{S(\text{OH})2} \beta_{(\text{OH})2} \{\underline{\text{SO}}\} [\text{OH}]^2 + K_{S(\text{NH}_3)} \{\underline{\text{SO}}\} (\beta_{(\text{NH}_3)1} [\text{NH}_3] \\ &+ \beta_{(\text{NH}_3)2} [\text{NH}_3]^2 + \beta_{(\text{NH}_3)3} [\text{NH}_3]^3 + \beta_{(\text{NH}_3)4} [\text{NH}_3]^4 + \beta_{(\text{NH}_3)5} [\text{NH}_3]^5 + \dots)) \frac{[M^{2+}]}{M_T} \quad (12) \end{aligned}$$

Equation (12) in conjunction with Equations for $\frac{[M^{2+}]}{M_T}$, $\{\underline{\text{SO}}\}$, and $[\text{NH}_3]$ express the relationship between metal uptake ratio as functions of pH, total ammonia concentration, and total surface site concentration. It also shows that the ratio of metal adsorption is not related to the initial metal concentration if the total metal concentration is relatively low.

Metal Adsorption Modeling

Equation (12) was used to fit the experimental data in Figure 1. Multiple variable non-linear regression programs such as SigmaPlot® were used for curve fitting. Since the formation constants for Cu(II) hydroxides ($\beta_{(\text{OH})n}$) and Cu(II)-ammonia complexes ($\beta_{(\text{NH}_3)m}$) can be found from references, the only unknown constants in Equation (12) are K_S , $K_{S(\text{OH})1}$, $K_{S(\text{OH})2}$, and $K_{S(\text{NH}_3)}$. Curve fitting results indicate that the above adsorption constants (logK) are 6.0, 7.7, 9.6, and 2.9, with respective standard errors of 0.04, 0.40, 0.14, and 0.10. Figure 6 shows the curve fitting results (solid curves) in reference to the experimental data (points). As shown in Figure 6, the calculated results agree with the experimental data very well. The correlation coefficient (R^2) for this curve fitting is 0.974. The curve fitting results suggest that it is appropriate to assume that all metal-ammonia complexes have the same adsorption constants.

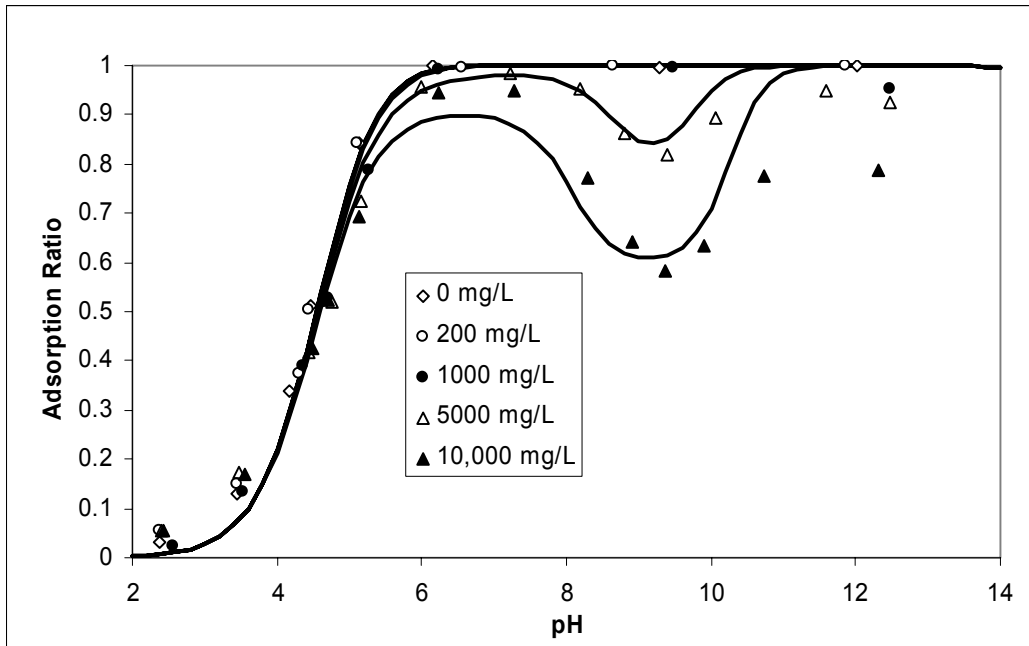


Figure 6. Curve fitting results for Cu(II) adsorption in a system containing 100 g/L of fly ash and five different ammonia concentrations.

According to our previous study,²⁵ the adsorption constant ($\log K_S$) of Cu^{2+} for this fly ash determined in a system without ammonia is 6.1. The value from the current study in a much more complex system agrees with the previous result.

Figure 6 indicates that the calculated Cu(II) adsorption ratio under extremely high pH conditions ($\text{pH} > 11$) is greater than the experimental data. This could be caused by two possible reasons: (a) the actual formation constants for non-adsorbable negatively-charged Cu(II)-hydroxide species are greater than those cited from the reference; (b) the adsorption constants for Cu(II)-ammonia complexes decreases with the increase of the number of ammonia (m) associated with each Cu(II) in the complex. However, because the model can correctly predict the results in the pH range between 2 and 11, the assumption that all metal-ammonia complexes have the same adsorption constants is still appropriate in practice and simplifies the calculation.

Cu(II) Speciation in a System Containing Fly Ash and Ammonia

Figure 7 shows the calculated Cu(II) speciation results in a system containing 100 g/L of fly ash ($S/L = 1:10$) and 0.6 M (10,000 mg/L) of ammonia. Results show that when pH is less than 8, the major soluble species is free Cu(II) ion. If pH is greater than 8, Cu(II)-ammonia complexes are the major soluble species. The concentrations of soluble Cu(II) hydroxide species are not significant in the entire experimental pH range, primarily due to their high adsorption capability.

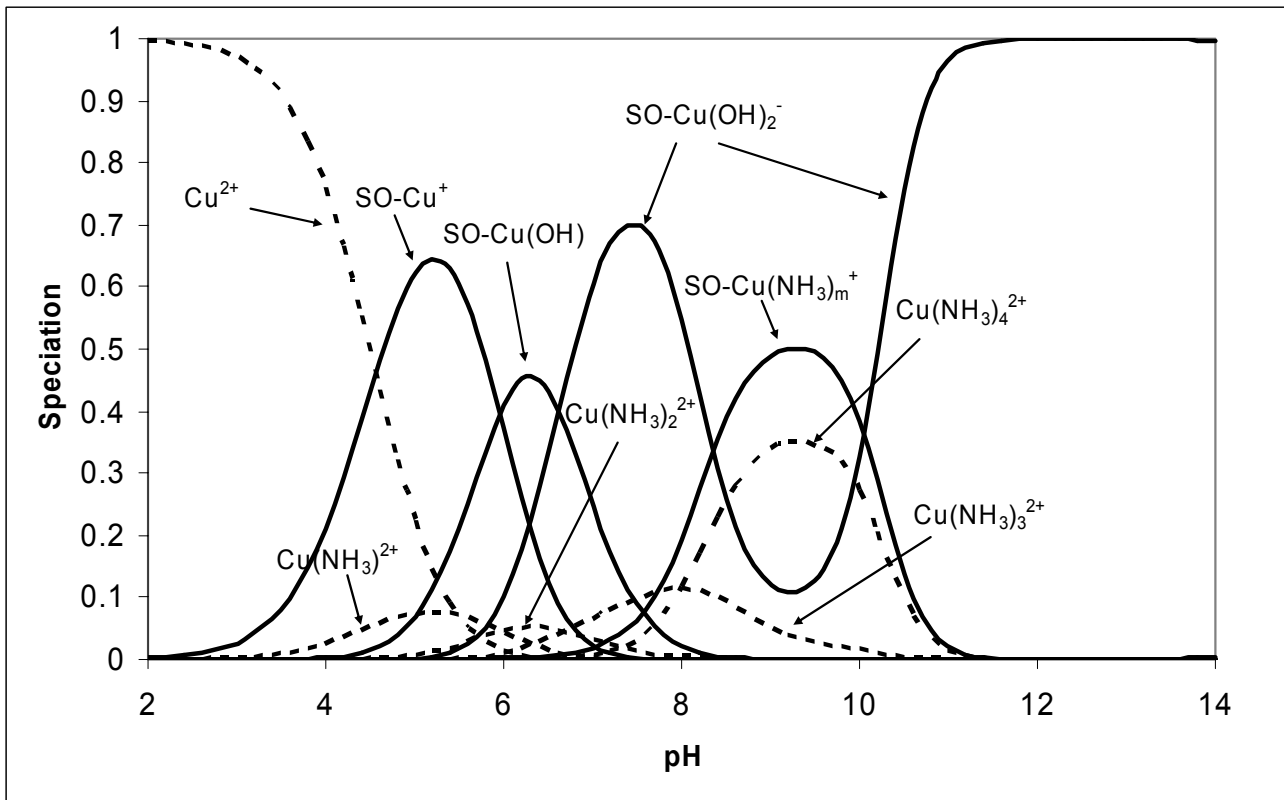


Figure 7. Cu(II) speciation in a system containing 100 g/L of fly ash and 0.6 M (10,000 mg/L) of total ammonia.

Cd(II) Adsorption in the Presence of Ammonia

For model validation purposes, Cd(II) adsorption under the impact of ammonia was also investigated based on the same procedure used for Cu(II). It was found that the overall formation constants ($\log\beta_{(\text{OH})}$) for $\text{Cd}(\text{OH})^+$ and $\text{Cd}(\text{OH})_2$ are, respectively, 3.9 and 7.6, and the overall formation constants ($\log\beta_{(\text{NH}_3)}$) for $\text{Cd}(\text{NH}_3)^{2+}$, $\text{Cd}(\text{NH}_3)_2^{2+}$, $\text{Cd}(\text{NH}_3)_3^{2+}$, and $\text{Cd}(\text{NH}_3)_4^{2+}$ are, respectively, 2.6, 4.6, 5.9, and 6.7.¹⁷ These constants were directly applied to the model. Based on the experimental Cd(II) adsorption results under different ammonia and pH conditions, adsorption constants for Cd^{2+} , $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2$, and Cd(II)-ammonia complexes were determined through non-linear regression. Results showed that the adsorption constants ($\log K$) for Cd^{2+} , $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2$, and Cd(II)-ammonia complexes are 4.3, 6.9, 8.8, and 2.6, respectively. The correlation coefficient (R^2) for this curve fitting is 0.961. Figure 8 shows the curve fitting calculations (solid curves) vs. the experimental data (points). It shows that the model results reasonably reflect the trend in experimental data. The $\log K_s$ value for Cd^{2+} determined in this study is comparable to the previous value of 4.8 determined without ammonia effect.²⁵

Figure 9 shows the Cd(II) speciation in the system containing 0.6 M (10,000 mg/L) of total ammonia and 100 g/L of fly ash. Results indicate that when pH is acidic ($\text{pH} < 7$), the major soluble specie in the system is Cd^{2+} . However, when pH is greater than 7, the Cd(II)-ammonia complexes are the major soluble species. Again, the soluble metal-hydroxide species are not significant in the entire experimental pH range.

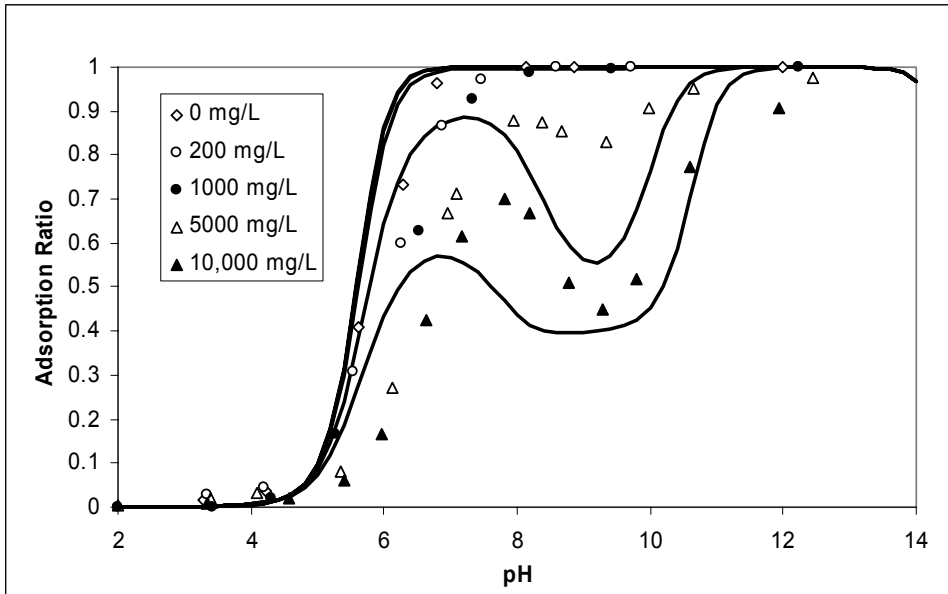


Figure 8. Curve fitting results for Cd(II) adsorption in a system containing 100 g/L of fly ash and five different ammonia concentrations.

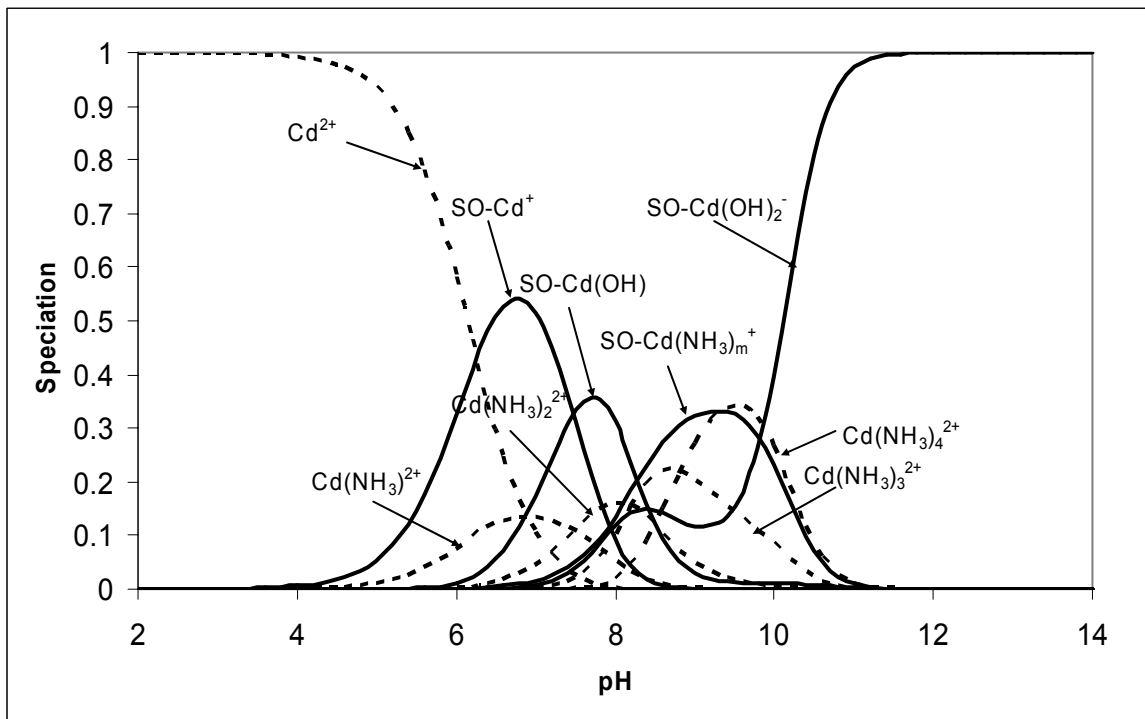


Figure 9. Calculated Cd(II) speciation results for a system containing 100 g/L of fly ash and 0.6 M (10,000 mg/L) of total ammonia.

Implications of the Metal Adsorption Model in the Complex System

This metal adsorption model considers the reactions among heavy metal, fly ash, and ammonia, as well as the pH effect on these reactions. It also includes the adsorption of metal hydroxides and metal-ammonia complexes. Therefore, it is a theoretical model rather than an empirical model. In the study, pH-independent adsorption constants of free metal ion, metal hydroxide species, and metal-ammonia complexes can be determined by fitting the model to

experimental data. Results from this study clearly show that the metal-ammonia complexes have lower adsorption constants than free metal ion and metal hydroxides. Therefore, the formation of metal complexes reduces the metal adsorption under high ammonia conditions. This same approach can be used to quantify the metal partitioning in systems that contain other metal ions and metal complexation ligands.

CONCLUSIONS

Experimental results indicated that high concentrations of ammonia can reduce the adsorption of Cu(II) and Cd(II) in the alkaline pH range. The mathematical model developed in this study based on chemical reactions among heavy metal, fly ash, ammonia, hydroxide ions, metal-hydroxides, and metal-ammonia complexes provided a quantitative description of the metal adsorption behavior by fly ash with the presence of ammonia. By fitting the model to metal adsorption data, the adsorption constants of free metals, metal-hydroxide species, and metal-ammonia complexes for the fly ash were determined. Results indicated that the formation of less adsorbable metal-ammonia complexes results in the decrease of metal adsorption by fly ash (i.e. increase the metal leaching) at high ammonia concentrations (greater than 5000 mg/L). There is little or no effect on Cu(II) and Ni(II) adsorption (or leaching) at lower ammonia concentrations.

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