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Web: www.coalcgp-journal.org

ISSN# 1946-0198

Volume# 3 (2011)

Editor-in-chief: Dr. Jim Hower, University of Kentucky Center for Applied Energy Research

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Suggested Citation format for this article:

Roy, W.R., Berger, P.M., 2011, Geochemical Controls of Coal Fly Ash Leachate pH. *Coal Combustion and Gasification Products* 3, 63-66, doi: 10.4177/CCGP-D-11-00013.1

CCGP Coal Combustion and Gasification Products

ISSN 1946-0198

journal homepage: www.coalcgp-journal.org

Geochemical Controls of Coal Fly Ash Leachate pH

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ABSTRACT

When coal fly ash is initially mixed with water, the initial pH of resulting extract or leachate may be strongly acidic (pH 4) or alkaline (pH12). With time, however, this pH range tends to narrow because of geochemical buffering reactions. Because pH is the major variable that controls the leaching of many potential groundwater contaminants, understanding the long-term pH behavior of fly ash leachate is crucial to evaluating the environmental impacts of fly ash management. Using laboratory extract data, kinetic-geochemical models were created to gain a better understanding of the potential buffering that influences the long-term pH of ash leachate. The initially low pH of acidic fly ashes may be short-lived because the acidity is neutralized by the dissolution of calcium and magnesium oxides, is ultimately buffered by carbon dioxide yielding a pH of 7 to 8. Alkaline fly ash leachate ($pH > 10$) tends to absorb carbon dioxide, and the resulting pH of the liquid phase will decrease with time to a pH between 8 and 9. Kinetic modeling suggests that the chemical composition of short-term laboratory extracts of coal fly ash will not be representative of long-term leachate after equilibrating with the atmosphere.

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ARTICLE INFO

Article history: Received 24 June 2011; Received in revised form 1 August 2011; Accepted 9 August 2011

Keywords: buffer; kinetic modeling; carbon dioxide; acidity

1. Introduction

Solution pH is the master variable that controls the extent of leaching and mobility of potential groundwater contaminants that may be present in coal combustion products (CCPs) such as Al, Cd, Cr, or Zn. Therefore, understanding the chemical reactions that control pH and their associated time-frames that occur when CCPs come in contact with water is essential for environmental management. When CCPs are mixed with water, the initial pH of the mixture can range from about 4 to greater than 12. Spears and Lee (2004) generalized that about 70% of all fly ashes produce a neutral or alkaline leachate. Coal fly ash derived from U.S. bituminous coal can yield an alkaline or acidic reaction when initially mixed with water. Alkaline leachate from fly ash was the result of the hydrolysis of Ca and Mg oxides that form during the combustion of coal.

Spears and Lee (2004) generalized that acidic fly ash leachate can be attributed to the sorption of SO_2 or the condensation of sulfuric acid from the gas stream onto ash particle surfaces. Another possible source of acidity could stem from the hydrolysis of Al^{3+} derived from aluminum sulfates. Fishman et al. (1999) proposed that leachate acidity could also be derived from the hydrolysis of Al^{3+} derived from an aluminum-potassium sulfate phase. Also, acidic fly ash is more likely to occur when the ash is exposed for longer periods to exhaust gases.

The pH of ash-water systems can change with time. Talbot et al. (1978) reported that the pH values of alkaline fly ash samples derived from subbituminous coal in Montana initially ranged from pH 10.5 to 11.5 when mixed with distilled water. After about five days, the pH of the extracts decreased to about 8.7, and remained constant for about six months when the study ended.

The pH values of the extracts of two initially acidic fly ash samples generated by the combustion of bituminous coal in Illinois increased from 4.1 to about pH 7 after 21 to 36 days. Roy and Griffin (1984) attributed this change in pH as the result of neutralization of a finite amount of sulfuric acid. As the pH increased, the concentrations of Al, Cd, Cr, Cu, Fe, Ni, and Zn

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doi: 10.4177/CCGP-D-11-00013.1

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Table 1
Composition of the model rain water.

Constituent	Concentration
pH	5.5
Eh	0.57 Volts
Temperature	25° C
Al^{3+}	0.01 mg/L
Ca^{2+}	0.1 mg/L
Cl^{-}	1.0 mg/L
Fe^{2+}	0.04 mg/L
K^{+}	0.001 mg/L
$HCO_3{}^{-}$	swapped with CO_2
HS^{-}	0.001 mg/L
Na^{+}	0.6 mg/L
Mg^{2+}	0.1 mg/L
SiO_2	0.3 mg/L
$SO_4{}^{2-}$	0.3 mg/L

decreased. For example, after one hour of extraction, the concentrations of Cd and Zn were 3.88 and 36.2 mg/L respectively. After about 36 days, the concentration of both metals was < 1 mg/L. The concentration of Al decreased from 158 to 0.13 mg/L after 21 days.

Schramke (1992) demonstrated that the introduction of CO_2 gas into alkaline fly ash leachate can reduce pH. When CO_2 is absorbed, calcite ($CaCO_3$) can precipitate, resulting in acidity:

$$Ca^{2+} + CO_{2(gas)} + H_2O \rightarrow CaCO_{3(s)}\downarrow + 2H^{+} \qquad (1)$$

Similarly, Loop et al. (2003) mixed fluidized bed combustion ash with deionized water in a laboratory study, and observed a pH of 11, followed by decrease to pH values of 8 to 9 resulting from the absorption of CO_2. The authors speculated that the pH of an ash pond would eventually decrease with time. Calcite had precipitated, and accumulated at the edges of the pond.

These studies suggest that although the initial pH of fly ash leachate may be relatively acidic or strongly basic, there may be geochemical buffers that subsequently narrow this wide pH range to about pH 7 to 9. The objective of this study was to apply a kinetic-geochemical model to ash-water systems to gain a better understanding of geochemical buffers that influence the long-term pH of ash leachate.

2. Materials and Methods

2.1. Kinetic Software and Conceptual Approach

To accomplish the goals of this study, we used the kinetic software REACT® which is a part of the software Geochemist's Workbench (Bethke, 1996), Release 7.0.5 with the thermodynamic database thermo.com.v8.r6+. For this investigation, two fly ash samples were chosen. The alkaline fly ash sample "159" that was investigated by Schramke (1992) was selected for this study to initially help validate the application of the model. Then the leaching of an acidic fly ash sample (I7) described in Suloway et al. (1983), Roy and Griffin (1984), and Roy et al. (1984) was modeled. These specific ash samples were selected because they appeared to be reasonably representative of an alkaline and acidic fly ash. These samples were also selected because of the availability of time-dependent leaching data, and detailed mineralogical and chemical characterization. In each case, 1 kg of a model rain sample (Table 1) was mixed in each model ash in proportions that matched the published studies. The model rain was designed to contain trace quantities of each solute that are required for REACT® to operate. As a first approximation, reaction rate constants were obtained from Palandri and Kharaka (2004). Surface area was estimated as 3/rρ where r is the radius of a particle, and ρ is the density of the solid phase. In many cases, however, surface areas were treated as variables, and revised to better match the experimental results.

Table 2
Ash Model 159.

Known reactants	Mass (g)	Rate constant normalized to surface area (mole/g-cm)
Ferrite-Mg ($MgFe_2O_4$)	2.0	9.63×10^{-11}
Hematite (Fe_2O_3)	1.5	2.86×10^{-14}
Sillimanite(1) (Al_2SiO_5)	0.5	3.33×10^{-17}
Quartz (SiO_2)	4.5	5.75×10^{-15}
SiO_2 (amorphous)	41.5	1.32×10^{-12}
Postulated reactants		
Anhydrite $CaSO_4$	0.45	Added as a simple reactant
Lime	0.01	9.00×10^{-10}
Periclase (MgO)	10 Cutoff = 0.02	Added as a simple reactant
CO_2 (gas)	2.25 mMole Cutoff = 0.55	Added as a simple reactant

[1] Mullite is a common aluminosilicate in fly ash and was detected in this sample. However, mullite is not present in the database used by REACT®. Therefore sillimanite, a high-temperature Al_2SiO_5 phase, was used as a surrogate for mullite.

2.2. Fly Ash Samples

As discussed by Schramke (1992), ash 159 was a fly ash sample derived from the combustion of subbituminous coal from an undisclosed location. The author placed 50 g of ash into a 1-L Teflon reaction vessel containing 1 L of deionized water. The slurry was then mixed continuously for about 600 days at 25°C. Based on the mineralogical data provided, a model of ash 159 was constructed (Table 2).

As discussed in Roy et al. (1984), I7 was a fly ash sample derived from the combustion of Illinois Basin coal. The authors placed 3,400 g of ash into a 19-L Pyrex reaction vessel containing 17 L of deionized water. The slurry was periodically stirred using a laboratory mixter for 106 days at room temperature (about 22° C). The reaction vessel was open to the atmosphere during mixing. Based on the chemical and mineralogical characterization data given in Suloway et al. (1983), an ash model was constructed to

Table 3
Ash Model I7.

Known reactants	Mass (g)	Rate constant normalized to surface area (mole/g-cm)
Anhydrite ($CaSO_4$)	1.7	3.23×10^{-4}
Hematite (Fe_2O_3)	18.5	2.86×10^{-14}
Lime (CaO)	0.2	9.00×10^{-10}
Magnetite (Fe_3O_4)	18.5	9.63×10^{-11}
Quartz (SiO_2)	10.0	5.75×10^{-15}
SiO_2 (amorphous)	76.8	1.32×10^{-12}
Postulated reactants		
Periclase (MgO)	0.38	1.50×10^{-9}
Pyrite (FeS_2)	0.47	3.02×10^{-9}
H_2SO_4	0.9 cutoff = 0.04	Added as a simple reactant
$Al_2(SO_4)_3$	30 cutoff = 0.02	Added as a simple reactant
Thenardite (Na_2SO_4)	30 cutoff = 4.0	Added as a simple reactant

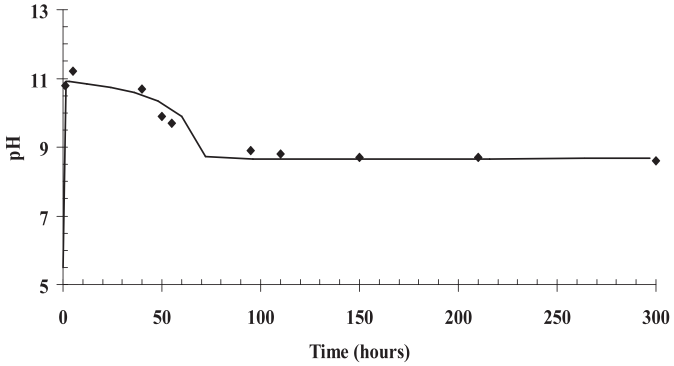

Fig. 1. Change in leachate pH for ash 159. The experimental data (diamonds) are compared with the pH-time relationship calculated by REACT® (solid line).

mimic I7 (Table 3) to yield an acidic reaction after its initial contact with water, then a neutral reaction later in time. For each model fly ash, the mineralogical composition was approximated by known reactants (those detected by x-ray diffraction), and postulated reactants which were inferred either by elemental data or by the chemical composition of the experimental leachate. In some cases, the postulated reactants were proposed to account for the chemical composition of the experimental leachate.

3. Results and Discussion

3.1. Ash Model 159

The results of adding the model rain water to ash 159 indicated that the pH of the model rain increased to 10.5 after about 3 hours of contact with the ash (Fig. 1). Most of the lime (CaO) had reacted by this time, yielding

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \qquad (2)$$

In the model results, the pH would decrease with time, matching the overall experimental trend. To accomplish this, CO_2 gas was added to the leachate as a simple reactant to mimic the diffusion of atmospheric CO_2 into solution, which generated an increase in HCO_3^- and acidity, viz.,

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \qquad (3)$$

The model was also able to reproduce the concentrations of Ca in solution after the initial part of the extraction interval (Fig. 2). The model was, however, unable to reproduce the experimental data during the initial contact with water. It is possible that some portion of the Ca in solution was derived from an unstable solid phase not included in Table 2. The relatively slow decrease in Ca in solution resulted from the precipitation of calcite (Fig. 3) as

$$Ca^{2+} + HCO_3^- \leftrightarrow CaCO_3\downarrow + H^+ \qquad (4)$$

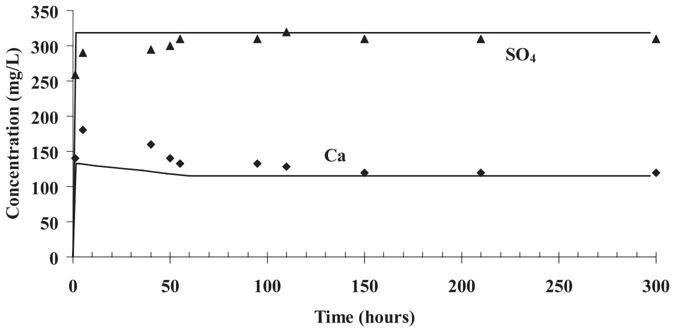

Fig. 2. Concentration of Ca and sulfate in ash 159 leachate as a function of time. The experimental data are compared with the calculated results.

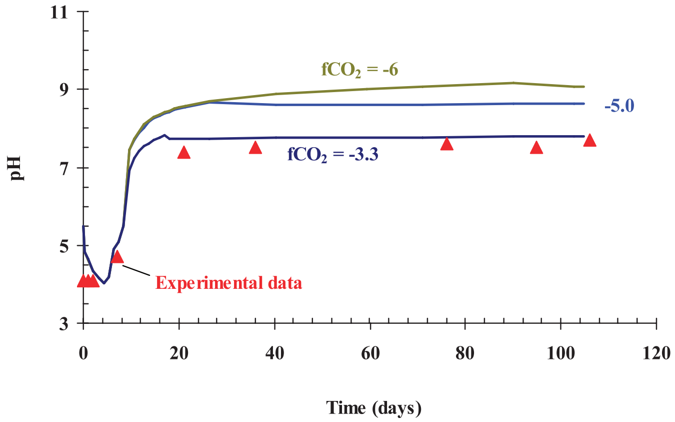

Fig. 3. Leachate pH as a function of time for ash I7. The experimental data are compared with the calculated results at different log fugacities of carbon dioxide.

The model also matched the experimental sulfate concentrations (Fig. 2). The anhydrite that was postulated to be present in the ash sample dissolved completely within a few hours. After the anhydrite was exhausted, the amount of sulfate in solution remained constant because the solubility of gypsum was not exceeded.

3.2. Ash Model I7

The results of our simulations were generally consistent with the experimental pH data (Fig. 3). The initial decrease in pH was simulated by dissolving both pyrite and sulfuric acid as postulated reactants. About 8.5% of the sulfur in the sample occurred as a sulfide.

The subsequent dissolution of lime and periclase (MgO) (Fig. 4) then increased leachate pH. The dissolution of both minerals was not complete at the end of the extraction interval. If not for the absorption of CO_2, their dissolution could have increased pH to

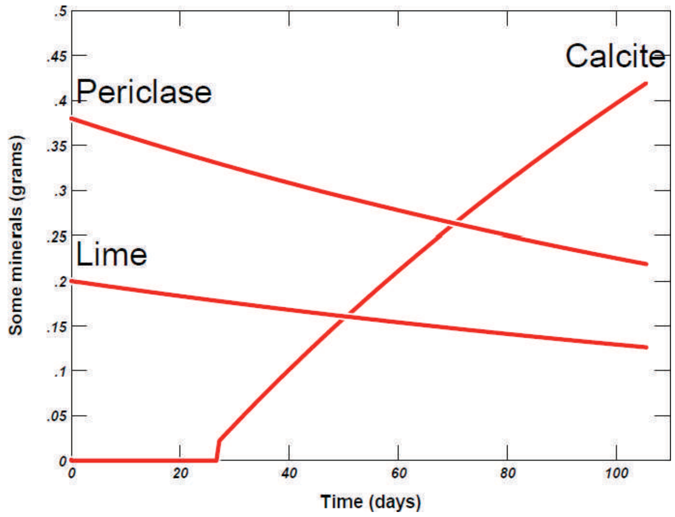

Fig. 4. Dissolution of periclase (MgO) and lime (CaO) and the precipitation of calcite as a function of time in the model of ash I7.

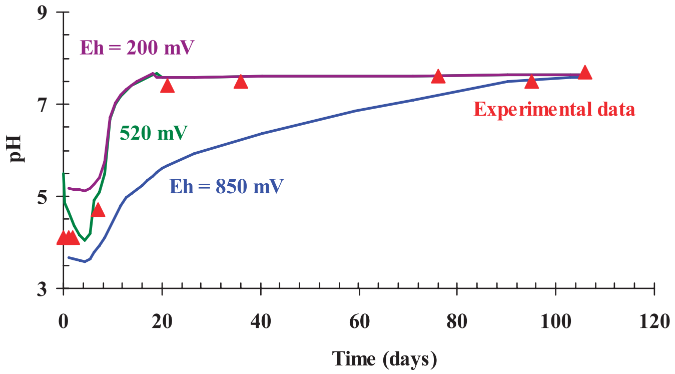

Fig. 5. Leachate pH as a function of time for ash I7. The experimental data are compared with the calculated results at different oxidation-reduction potentials (Eh).

alkaline values. However, the pH of the leachate was maintained at near-neutrality by the absorption of CO_2 and precipitation of calcite via eqs. 3 and 4. Model I7 was treated as an open system, and the experimental data best matched the model results when the fugacity of CO_2 was set as $\log fCO_2 = -3.3$. When the fugacity of CO_2 was decreased, the pH of leachate became more basic (Fig. 3).

Because pyrite was used as a reactant in the ash model, the oxidation-reduction potential (Eh) will influence the stability of pyrite, and the subsequent production of acidity. The experimental data best matched the model when Eh was set at 520 mV (Fig. 5). For example, when Eh was 850 mV, the pH of the leachate was more acidic because of the greater instability of pyrite under relatively oxidizing conditions. When Eh was 200 mV, a greater amount of pyrite was stable because of the relatively reduced state of the ash-leachate system, and therefore the initial and transient "dip" in pH was not well duplicated.

At the end of the 106-day simulation, REACT® calculated the pH of the liquid phase as 7.6, which agreed with the measured value of 7.5. At the end of the simulation, the solution was in equilibrium with calcite and pyrite, and near equilibrium with gypsum.

Lastly, the hypothesis of Fishman was tested by using $Al_2(SO_4)_3$ as a source of acidity instead of pyrite and H_2SO_4. The results (Fig. 6) suggested that the hydrolysis of Al^{3+} could have resulted in the initial acidity. In actual systems, a combination of Al and Fe sulfate sources may contribute to acidic CCP leachate.

4. Conclusions

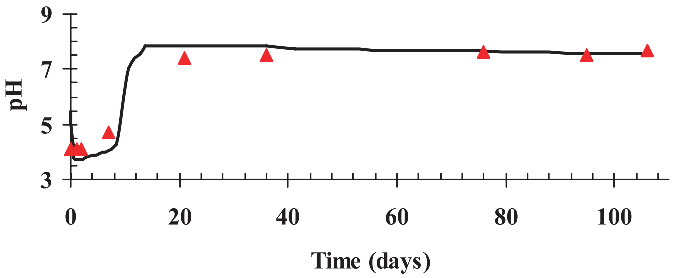

Fig. 6. Leachate pH as a function of time for ash I7. The experimental data are compared with the calculated results.

Although the initial reaction of coal ash with water may yield a relatively acidic or strongly alkaline solution, geochemical buffering can narrow this pH range with time. Laboratory studies and the results of the geochemical kinetic modeling presented in the current study demonstrate that carbon dioxide can buffer the pH of CCP leachate. The pH of acidic fly ash may be short-lived because the acidity is neutralized with time by the dissolution of CaO and MgO, and the reaction path is ultimately buffered by the absorption of carbon dioxide yielding a pH of 7 to 8. Moreover, it appears that when alkaline CCP leachate is open to atmospheric carbon dioxide, the pH of the liquid phase will decrease with time to a pH between 8 and 9 because of carbonate buffering and the consequent precipitation of calcite. The chemical composition of short-term, laboratory extracts of fly ash samples may not be representative of leachate from ash under long-term environmental conditions. The rate of change in pH, however, was accelerated in the laboratory studies because the slurries were well mixed. Under field conditions, the impacts of passive carbonate buffering would likely require longer periods of time. It appears that kinetic software such as REACT® can be used to estimate the pH of CCP leachate for time frames that are not practical under laboratory conditions. Additional research is needed, particularly using field-scale data.

Acknowledgements

Publication authorized by the Director of the Illinois State Geological Survey. We thank Ken Ladwig of the Electric Power Research Institute for many stimulating conversations for this study.

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