

# Toxicity of and metals in coal combustion ash leachate

Makesh Karuppiyah, Gian Gupta \*

*Department of Natural Sciences, University of Maryland Eastern Shore, Princess Anne, MD 21853, USA*

Received 10 November 1996; accepted 10 February 1997

---

## Abstract

Land disposal of coal combustion ash can have a potential impact on the ecosystem due to the leaching of metals with increasing acidity of precipitation. The objective of this research was to study the effect of pH on the concentration of metals leached from coal combustion ash and to measure the toxicity of the leachates. Bottom coal combustion ash was leached with hydrochloric acid (HCl) or acetic acid (CH<sub>3</sub>COOH) at pH 4, 5, 6 or 7. The toxicity of the aqueous leachates and concentrations of the metals (arsenic, cadmium, chromium, copper, iron, lead, nickel, silver and zinc) therein were measured using Microtox<sup>®</sup> (*Vibrio fischeri*—EC<sub>50</sub>%) and atomic absorption spectrophotometry, respectively. Toxicity and metal concentrations of the leachates were highest when ash was leached with HCl at pH 4. Toxicity and metal concentrations of ash leached with CH<sub>3</sub>COOH were significantly lower compared with ash leached with HCl. High correlation (*r*) was observed between the toxicity and the metal concentrations in both the acid leachates. © 1997 Elsevier Science B.V.

*Keywords:* Coal combustion ash; Leachate; Hydrochloric acid; Acetic acid; Metals; Microtox; Toxicity

---

## 1. Introduction

Bottom ash is one of the residues from coal combustion and accounts for 25% of all coal combustion residues produced in the USA [1,2]. Bottom ash is composed of both fine and coarse grained materials consisting of various trace elements in a silicate–oxide matrix. The physical and chemical characteristics of bottom ash depend on coal composition, combustion conditions, efficiency and type of emission control devices and disposal methods used [2].

---

\* Corresponding author. Tel.: +1 410 651 6030; fax: +1 410 651 7739.

Landfills and settling ponds are the two methods that are commonly used to dispose of bottom ash. Numerous toxic trace elements such as As, Cd, Cr, Cu, Pb, Ni and Zn occur in coal in wide concentration ranges [3]. Stockpiled bottom ash has potential impact on terrestrial and aquatic ecosystems and ground water; Shende et al. [4] reported that the stockpiled ash contributed toxicity to the adjoining rivers due to the presence of leachable metals in the ash.

Heavy metals are present in aqueous solutions of the ash, depending on the pH of the acidic precipitation [5,6]. Extraction of residues with sodium acetate buffer at pH < 5 or acetic acid at pH > 5, known as toxicity characterization leaching procedures (TCLP), are the main methods used by USEPA [7] to test coal combustion residues; TCLP has been used in many studies and in regulating hazardous materials. Coal combustion ash leached following TCLP showed that the range of metal concentrations was below the regulatory levels, indicating that the residues are non-hazardous wastes [8]. Extraction procedures such as TCLP have been misused in studies on incompatible site scenarios such as the determination of cyanide leaching from soil and to determine leaching of contaminants at sites that are not similar to the municipal landfill model [9].

The objective of this research was to study the toxicity and metal concentrations of bottom ash after leaching with a strong acid (HCl) and a weak acid (CH<sub>3</sub>COOH) at pH 4, 5, 6 and 7.

## 2. Material and methods

Bottom ash was collected from the Indian River Power Plant, Millsboro, DE, and sieved (< 125 μm). Acidic solutions in deionized water were prepared at pH 4, 5, 6 or 7 using 0.1 M HCl or CH<sub>3</sub>COOH. Bottom ash (10 g) was stirred with 150 ml of the acidic solution in Erlenmeyer flasks using a VWR orbital shaker (200 rpm, 24 h). The slurry was centrifuged at 1300 g in an IEC centrifuge (Needham Heights, MA, USA), and the supernatant was analyzed for toxicity and metal concentrations. Toxicity and metal concentrations of the controls (water + HCl or water + CH<sub>3</sub>COOH; pH 4, 5, 6 or 7) were also measured. The pH was determined using a Fisher Scientific (Pittsburgh, PA, USA) pH meter. Samples for metal determination were acidified with conc. HNO<sub>3</sub> [10].

### 2.1. Microtox toxicity test

Microtox<sup>®</sup> is a bacterial assay that uses luminescent bacteria developed by Beckman Instruments, Inc. [11]. Based on the reduction in bioluminescence of the marine bacterium *Vibrio fischeri* by the toxicants, the toxicity (EC<sub>50</sub>%) of bottom ash leachate was measured using the Microtox Toxicity Analyzer Model 2055. Microtox has been used in testing various industrial effluents to comply with environmental protection regulations and water quality surveys [12]. The pH of the test system may vary between 4 and 8 [13,14] without significant effect on the luminescence. The EC<sub>50</sub>% was calculated using the software (version 7.08) supplied by Beckman. A low EC<sub>50</sub>% value indicates high toxicity.

### 3. Heavy metals analyses

Metals were analyzed using a Perkin-Elmer (Norwalk, CT) atomic absorption spectrophotometer with graphite furnace and auto sampler. Detection limits for As, Cd, Cr, Cu, Fe, Ni, Pb, Ag and Zn were 0.2, 0.003, 0.1, 0.02, 0.02, 0.1, 0.05, 0.9 and  $0.001 \mu\text{g l}^{-1}$ , respectively.

### 4. Statistical analysis

Statistix [15] version 4.1 was used to analyze the data from the randomized complete block design (to minimize the experimental error due to coal combustion ash heterogeneity) experiments conducted in triplicate. Analysis of variance (ANOVA) and Pearson's correlation coefficients ( $r$ ) were computed between the toxicity and metal concentration of coal combustion ash.

### 5. Results and discussion

The pH of the ash leached with deionized water was 8.4 and the leachate was not toxic to *Vibrio fischeri*. Toxicity ( $\text{EC}_{50}\%$ ) of the leachate increased with increasing acidity (Table 1). The ash leachate with HCl was always more toxic than the leachate with  $\text{CH}_3\text{COOH}$ . The ash leachate with HCl at pH7 was as toxic as water + HCl at pH4; the leachate at pH6 (or 7) with  $\text{CH}_3\text{COOH}$  was almost non-toxic. Toxicity is a major disadvantage of using coal combustion ash in applications under acidic conditions [1].

The metal analyses revealed that As, Cd, Cr, Cu, Fe, Ni, Pb and Zn (but not Ag) were present in the leachates, both with HCl and  $\text{CH}_3\text{COOH}$ , at all pHs (Tables 2 and 3). The amounts of metals leached increased with decreasing pH; higher concentrations of metals were leached with HCl than with  $\text{CH}_3\text{COOH}$ . The toxicity and the metal concentrations had high correlation coefficients ( $r$ ) ranging from 0.98 to 0.79 with HCl and from 0.97 to 0.59 with  $\text{CH}_3\text{COOH}$ . A total of 25 potentially toxic elements have been reported in coal combustion ash [1].

Table 1  
Toxicity (Microtox<sup>®</sup>  $\text{EC}_{50}\%$ ) of coal combustion ash and water treated with HCl and  $\text{CH}_3\text{COOH}$

pH	Coal ash		Water (control)	
	HCl	$\text{CH}_3\text{COOH}$	HCl	$\text{CH}_3\text{COOH}$
4	$34.33 \pm 0.91^a$	$62.73 \pm 0.91$	$87.08 \pm 0.79$	$92.17 \pm 1.48$
5	$44.63 \pm 1.78$	$80.58 \pm 0.91$	$95.13 \pm 0.79$	$99.06 \pm 0.37$
6	$58.68 \pm 0.64$	$96.17 \pm 0.32$	NT <sup>b</sup>	NT
7	$89.08 \pm 0.53$	NT	NT	NT

<sup>a</sup>Standard deviations.

<sup>b</sup>Not toxic ( $\text{EC}_{50}\% > 100\%$ ).

Table 2  
Concentrations of metals ( $\mu\text{g l}^{-1}$ ) in coal combustion ash leachate (HCl)

pH	Metal							
	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
4	12.3 $\pm$ 2 <sup>a</sup>	26.3 $\pm$ 2.0	13.7 $\pm$ 3.0	277.3 $\pm$ 10	518.7 $\pm$ 46	29.0 $\pm$ 1	30.0 $\pm$ 2.0	381.0 $\pm$ 10
5	10.3 $\pm$ 1	23.0 $\pm$ 2.0	7.3 $\pm$ 1.0	113.3 $\pm$ 15	423.7 $\pm$ 50	23.7 $\pm$ 2	25.3 $\pm$ 2.0	284.3 $\pm$ 18
6	10.0 $\pm$ 1	16.7 $\pm$ 5.0	4.0 $\pm$ 0.3	88.0 $\pm$ 4	223.7 $\pm$ 31	15.7 $\pm$ 1	22.3 $\pm$ 1.0	234.7 $\pm$ 21
7	6.3 $\pm$ 1	2.0 $\pm$ 0.1	2.0 $\pm$ 0.1	55.0 $\pm$ 3	22.7 $\pm$ 1	7.7 $\pm$ 1	1.2 $\pm$ 0.1	196.0 $\pm$ 4

<sup>a</sup>Standard deviation.

Table 3  
Concentrations of metals ( $\mu\text{g l}^{-1}$ ) in coal combustion ash leachate ( $\text{CH}_3\text{COOH}$ )

pH	Metal							
	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
4	8.7 $\pm$ 1.0 <sup>a</sup>	2 $\pm$ 0.1	3 $\pm$ 0.1	74.3 $\pm$ 8	82.3 $\pm$ 15	13.0 $\pm$ 1.0	3.0 $\pm$ 0.1	214.0 $\pm$ 2
5	7.3 $\pm$ 0.5	2 $\pm$ 0.1	3 $\pm$ 0.1	61.3 $\pm$ 1	27.3 $\pm$ 3	9.7 $\pm$ 1.0	2.0 $\pm$ 0.1	202.7 $\pm$ 2
6	6.0 $\pm$ 0.5	2 $\pm$ 0.1	2 $\pm$ 0.1	39.7 $\pm$ 2	21.0 $\pm$ 2	7.0 $\pm$ 0.5	1.6 $\pm$ 0.5	184.0 $\pm$ 3
7	1.0 $\pm$ 0.1	1 $\pm$ 0.1	1 $\pm$ 0.1	34.7 $\pm$ 1	15.3 $\pm$ 1	4.0 $\pm$ 0.2	0.1 $\pm$ 0.05	129.3 $\pm$ 15

<sup>a</sup>Standard deviation.

The removal and adsorption of metals from coal combustion ash residues is dependent on the pH of the solution; acidic and basic pHs favor the removal and adsorption of metals, respectively [16]. The leaching of metals has been explained on the basis of an aqua-complex formation with the oxides in the ash; Viraraghavan and Rao [17] found that a negative charge develops on the surface of the oxides of ash in an alkaline medium, favoring the adsorption of metals, whereas in acidic medium the release of metals is enhanced.

In the ash leachate with HCl at pH 4 Cd, Cu and Zn concentrations were higher than the EPA fresh water acute criteria; only Cu and Zn were higher when  $\text{CH}_3\text{COOH}$  was used (Table 4). Bilski and Alva [18] found that low soil pH aided the increase in leachability of metals; metal availability in soils was altered by change in pH due to

Table 4  
Fresh water acute criteria ( $\mu\text{g l}^{-1}$ ) and concentrations of metals ( $\mu\text{g l}^{-1}$ ) in coal combustion ash leachate (HCl and  $\text{CH}_3\text{COOH}$ ) at pH 4

Metal	EPA fresh water acute criteria [21]	HCl	$\text{CH}_3\text{COOH}$
As	3600	12.3	8.7
Cd	3.9	26.3	2
Cr	16	13.7	3
Cu	18	277.3	74.3
Fe	NV <sup>a</sup>	518.7	82.3
Pb	83	30	3
Ni	1400	29	13
Zn	120	381	214

<sup>a</sup>No value.

addition of coal combustion ash, whereas increased pH generally reduced the availability of Cd, Cu, Ni, Pb, Zn and other metals [19]. Murarka et al. [8] also found highest concentrations of Cu and Zn on leaching the ash with water. Since acid precipitation contains a higher concentration of predominantly reactive HCl than of CH<sub>3</sub>COOH [20], using HCl for ash leaching better simulates natural conditions.

## 6. Conclusions

The following conclusions can be made from this study:

1. The toxicity and metal concentrations of the ash increased with decreasing pH of the leaching solution, both with HCl and with CH<sub>3</sub>COOH.
2. The toxicity and metal concentrations on leaching with HCl were higher than on leaching with CH<sub>3</sub>COOH.
3. The toxicity and metal concentrations of the leachates showed high correlation, indicating that metals present in the ash contribute significantly to the toxicity of the leachate.
4. Copper and Zn were leached using both the acids at pH 4 at a concentration higher than the EPA fresh water acute criteria. Use of HCl also resulted in the release of Cd from the ash at a concentration higher than these criteria.

## References

- [1] Keefer, R.F. and Sajwan, K.S., Trace Elements in Coal and Coal Combustion Residues, CRC Press, Boca Raton, FL, 1993.
- [2] C.L. Carlson, D.C. Adriano, Environmental impacts of coal combustion residues, *J. Environ. Qual.* 22 (1993) 227–247.
- [3] X. Querol, R. Juan, A.L. Soler, J.L.F. Turiel, C.R. Ruiz, Mobility of trace elements from coal and combustion wastes, *Fuel* 75 (1996) 821–838.
- [4] A. Shende, A.S. Juwarkar, S.S. Dura, Use of fly ash in reducing heavy metal toxicity to plants, *Resource Conserv. and Recycling* 12 (1994) 221–228.
- [5] United States Environmental Protection Agency, Wastes from the Combustion of Coal Electric Utility Power Plants, Report 530-SW-88-002, Washington, DC, 1988.
- [6] S. Sharma, M.H. Fulekar, C.P. Jayalakshmi, Fly ash dynamics in soil–water systems, *Crit. Rev. Environ. Control* 19 (1989) 251–275.
- [7] United States Environmental Protection Agency, Hazardous Waste Management System: Identification and Listing of Hazardous Waste: Toxicity Characteristics Revisions: Final Rule, Fed. Regist. 55, Washington, DC, 29 March 1990.
- [8] Murarka, I.P., Mattigod, S.V. and Keefer, R.F., in: Keefer, R.F. and Sajwan, K.S. (Eds.), Trace Elements in Coal and Coal Combustion Residues, CRC Press, Boca Raton, FL, 1993, pp. 11–24.
- [9] D.C. Susan, M. Sharma, A.D. Wait, The misuse of TCLP methods, *Environ. Lab.* 8 (1996) 22–25.
- [10] American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 17th edn, Washington, DC, 1989.
- [11] Bulich, A.A., in: Liu, D. and Dutka, B.J. (Eds.), Toxicity Screening Procedures using Bacterial Systems, Marcel Dekker, New York, NY, 1984, pp. 55–64.
- [12] K.L.E. Kaiser, V.S. Palabrica, *Photobacterium phosphoreum* toxicity data index, *Water Poll. Res. J. Canada* 26 (1991) 361–431.
- [13] Beckman Instruments, Microtox System Operating Manual, Microbics Corp., Carlsbad, CA, 1986.

- [14] J.M. Ribo, K.L.E. Kaiser, *Photobacterium phosphoreum* toxicity bioassay, I. Test procedures and applications, *Tox. Assess.* 5 (1987) 135–152.
- [15] Statistix, User's Manual: Version 4.1, Analytical Software, Tallahassee, FL, 1994.
- [16] C.H. Weng, C.P. Huang, Treatment of metal industrial wastewater by fly ash and cement fixation, *J. Environ. Eng.* 120 (1994) 1470–1487.
- [17] T. Viraraghavan, G.A.K. Rao, Adsorption of cadmium and chromium from wastewater by fly ash, *J. Environ. Sci. Health A26* (1991) 721–753.
- [18] J.J. Bilski, A.K. Alva, Transport of heavy metals and cations in a fly ash amended soil, *Bull. Environ. Contam. Toxicol.* 55 (1995) 502–509.
- [19] E.D. Vance, Land application of wood-fired and combustion boiler ashes: An overview, *J. Environ. Qual.* 25 (1996) 937–944.
- [20] Harrison, R.M., *Pollution: Causes, Effects and Control*, 2nd edn, Royal Society of Chemistry, UK, 1990, pp. 157–179.
- [21] United States Environmental Protection Agency, *Combined Sewer Overflows—Guidance for Long-term Control Plan*, Report EPA 832-B-95-002, Washington, DC, 1995.