International Research Journal of Environment Sciences ISSN 2319–1414
Vol. **1(5),** 76-80, December **(2012)** *Int. Res. J. Environment Sci.*

Trace Metal Leaching and Bioavailability of Coal-Generated Fly Ash

McNally D.[1], Crowley-Parmentier J.[1] and Whitman B.[2]
[1]Bryant University, Smithfield, Rhode Island, USA
[2]Wilkes University, Wilkes-Barre, Pennsylvania, USA

Available online at: www.isca.in
Received 12th November 2012, revised 20th November 2012, accepted 15th December 2012

Abstract

Coal-generated fly ash (FA) is being used for various applications, although there is evidence that indicates leaching or vegetative uptake of trace metals can potentially reach hazardous concentrations. In this study, FA was obtained from a coal-burning power plant in Pennsylvania and was tested for its leaching potential of selected trace metals (Al, As, Ba, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Se, Sr, V, and Zn). SEM observations show the FA has an abundance of large, porous, irregular-shaped grains that would absorb water, which would adversely affect the quality of a cement application. A comparison with another FA with typical glass spheres demonstrates the differences in FA structure and physical characteristics. An analysis of FA total metal content indicated a number of trace metals are over the cleanup standard limits for residential land over an aquifer. The FA leaching potential was determined by the Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitate Leaching Procedure (SPLP) tests. The results show that Se was over the TCLP limit, while As and V were over the U.S. drinking water Maximum Contaminate Level (MLC) for the SPLP test. However, these leachate tests have been criticized for not appropriately simulating the complex deposition and use conditions. Further research is required to develop applicable leaching test protocols for the various applications of FA.

Keywords: Coal-generated fly ash, leaching, hazardous

Introduction

The proper management of fly ash (FA) generated from coal-burning electrical power plants remains a controversial issue and has received increasing attention since the coal ash spill in 2008 at the Kingston Fossil Plant, a Tennessee Valley Authority electrical generating plant[1]. Although the coal burning industry claims FA does not pose a threat to the health of humans and the environment[2], numerous studies present sufficient evidence to justify FA concerns[3, 4].

In the U.S. alone, about 64 metric tons (71M short tons) of FA are produced annually from 460 coal burning power plants[5] and about 65% of FA is retained in on-site ash ponds or disposed of in landfills. The remaining 35% of FA is currently used in various applications, including landfill cover and backfilling mines[6], construction fill[7], soil stabilization[8], and agricultural supplements[9, 10]. As the volume of FA continues to accumulate and new options for reuse are developed, regulators need to decide whether this material is safe for reuse or needs to be taken to regulated waste management facilities.

In response to the FA controversy, the U.S. Environmental Protection Agency (EPA) has proposed to regulate FA by offering two possible options: i. treat FA as a "special waste" under subtitle C of RCRA when it is destined for disposal in landfills and surface impoundments, or ii. treat FA as nonhazardous waste under subtitle D of RCRA and set performance standards for waste management facilities that would be enforced by the states. The "special waste" classification is a category for wastes that require further study and assessment to determine the risk to human health and the environment. These "special wastes", typically generated in large volumes, are believed to present less risk than regulated hazardous waste[11]. But final determination requires further research.

The composition of FA has been well characterized and generally consists of trace metals, dioxins, and PAHs, which can cause cancer and neurological problems[12]. Trace metals in FA typically include As, Be, B, Ca, Cr, Co, Pb, Mn, Hg, Mo, Se, Sr, Tl, V and Zn. These trace metals, can enter the environment by surface runoff, rainwater leaching[13] or uptake by vegetation[10, 14]. The primary objective of this study was to provide knowledge on potential leaching and resulting bioavailability of selected trace metals which is critical to understanding potential risks of FA reuse or unmanaged disposal. Results will provide insight to a revised risk assessment approach[15] in the determination of proper FA management.

Material and Methods

All chemicals used were of high-purity and trace metal grade. Ultrapure water provided by a Millipore Direct Q5 (EMD Millipore Corp) was used for all analytical work. All glassware was made of borosilicate glass. Both glassware and polypropylene plastic vessels were acid washed prior to use in accordance with U.S. EPA washing SOP[16].

Fly Ash (FA) Characterization: FA from an anthracite coal-burning electrical power plant in Pennsylvania and collected by electrostatic precipitators was used in this study. The pH was verified using EPA Method 9045D[17] for soil and waste. A visual perspective was provided by a JSM – 6010LA InTouchScope SEM (JOEL Ltd).

Trace metal concentrations for Al, As, Ba, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, NI, Se, Sr, V, and Zn in the FA were determined using a HNO_3 acid digestion SOP method for trace elements in soil[18]. Modifications included using aluminum heater blocks (custom made) placed on hot plates set at 120-130°C. After the digestion process, all samples were filtered (0.20 µm) for ICP/MS analysis.

Trace Metal Leaching Analysis: Modified TCLP (Toxicity Characteristic Leaching Procedure) EPA Method 1311(1992)[19] and SPLP (Synthetic Precipitation Leaching Procedure) EPA Method 1312[20] were conducted to determine the leaching potential of the FA when disposed in landfills or *in situ*, respectively. The methods were modified by adding 25 g of FA dried for 48 hours at 60°C to 250 ml of extraction fluid (1:20 ratio) in narrow-mouth 500ml bottles with Teflon-lined screw caps. Extraction fluid no. 1 was required for the TCLP test. The extraction fluid for the SPLP test consisted of a 3:2 ratio of H_2SO_4 and HNO_3 diluted with de-ionized water to a pH of 4.2 (east of the Mississippi River). The pH was measured using a Fisher Scientific Accumet Excel XL 60 multi-meter. Both the TCLP and SPLP sample bottles and blanks filled with only the extraction fluids were placed in a Rugged Rotator (Glas-Co, LLC). All samples and blanks were filtered (0.20 µm) before ICP/MS analysis.

ICP/MS Analysis: All filtered samples were diluted 1:25 to obtain a TDS below 2000 µg per L and a pH less than 5% before analysis on an ICP/MS 7700 series (Agilent Technologies, Inc). Internal standards Sc, Y, and Tb were introduced at 100ppb during the sample injection process and were monitored for matrix interferences.

Results and Discussion

Fly Ash (FA) Characterization: Major constituents of the FA consisted of approximately 50% silicon oxide, 25% aluminum oxide, 10% iron oxide, and 8% carbon (LOI) as determined by a previous analysis[21]. The pH of the FA was also reported to be 6.9. In our study, pH was measured at 6.72 ± 0.31 (α=0.05). Because the pH was not above 7, the US EPA would not allow the power plant to dispose of their FA by backfilling mines.

Figure-1 is a SEM photomicrograph of the FA used in this study (a) and is compared to a typical FA used in a U.S. Department of Transportation study (b) for its pozzolanic properties for highway construction.

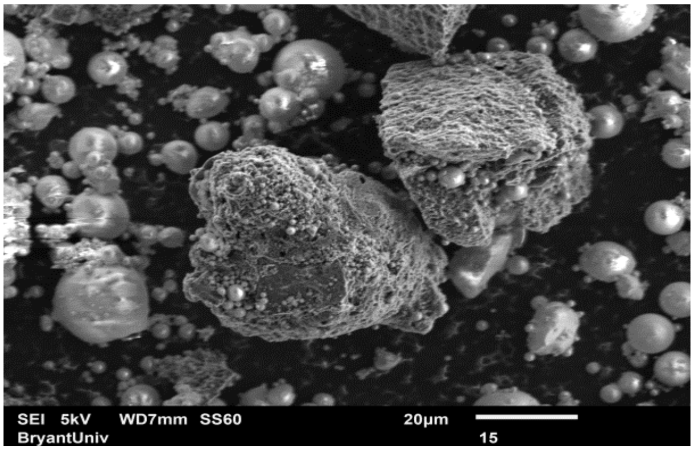

Figure-1a
SEM photomicrograph of this study's fly ash (950x)

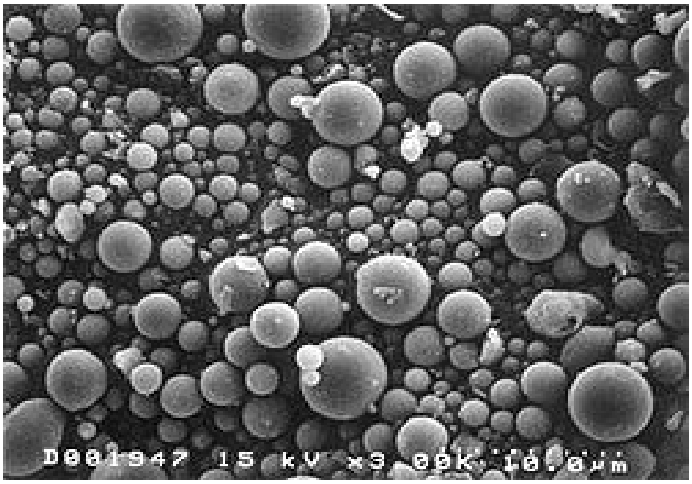

Figure-1b
SEM photomicrograph of U.S. DOT fly ash (2,000x)

It appears that the FA used in this study has a large grain size when compared to the DOT FA (consider the magnification differences between the two photomicrographs). The high LOI (carbon content) and large grain size for this FA do not meet U.S. ATSM C618 standards for cement replacement in concrete construction. Additionally, it appears that approximately 50% of the FA particles in this study are irregularly shaped. Typically, FA particles cool rapidly while suspended in exhaust gases and solidify without time to crystallize. The solidified particles end up becoming spherical beads made up of quenched glass. The FA in this study has a large fraction that didn't melt entirely and remained in crystalline form. These particles are described in another study as being spongy carbonaceous or mineral formless particles[22]. A high percentage of these particles would also prevent this FA from being a cement replacement. Adsorbed water would likely be retained longer causing prolonged curing, which would affect the concrete's quality. But this same characteristic might be beneficial for a soil additive application. This is a good example of the complexity and differences of FA and how their understanding is important for targeted uses.

Trace Metal Leaching from Disposed Fly Ash (FA): The Toxicity Characteristic Leaching Procedure (TCLP) is used to determine if a material is suitable for municipal landfill disposal or should be considered a hazardous waste (HW). The procedure is designed to simulate the leaching potential of the material when it is deposited in an unlined landfill containing municipal solid waste. The extraction solution is acetic acid, which is thought to be created when rainwater infiltrates the landfill. The regulatory limits for leached toxic chemicals are based on preventing groundwater contamination that would pose a risk to human and environmental health.

For comparison purposes, the Synthetic Precipitation Leaching Procedure (SPLP) was performed and analyzed for the same selected metals. The SPLP can be used to simulate the leaching potential of FA spread on the ground surface as fill, to stabilize soil, or as a supplement in agriculture. The extraction solution contains dilute nitric and sulfuric acid to simulate acid rain. The regulatory limits are based on the drinking water standard Maximum Contamination Limits (MCLs) applied to surface and groundwater. The results for the TCLP, SPLP, and total selected metal concentrations for this study and a previous analysis[21] on the FA from the same power plant in 1999 are shown in table-1.

Total trace metal contamination limits for soil are set by each state as cleanup standards. Since the FA in this study originated from the state of Pennsylvania, their Medium-Specific Concentrations (MSCs) would apply[23]. Of the selected metals in this study, only As (12 ppm) would be over the cleanup standard for land designated for nonresidential use. However, for land designated for residential use over a used aquifer, As (1 ppm), Cr (10 ppm), Co (1 ppm), Cu (100 ppm), Pb (0.5 ppm), Mn (30 ppm), Ni (20 ppm), Se (5 ppm) and V (26 ppm) would be over the cleanup standards. Additionally, the FA total metal concentrations for this and the previous analysis[21] are relatively similar even though the source of coal (and composition) is most likely different given the duration between tests. When compared to a particular top soil (The Scotts Company, LLC), the FA contained greater concentrations of As, Se, and V[24]. Therefore, the focus of this study was primarily on these trace metals.

The SPLP and TCLP tests indicated that a small fraction of the total concentration of FA would leach under the simulated conditions of each test. Interestingly, the greater leaching concentrations for the selected metals generally occurred with the TCLP test. In particular, about 15% of Se leached from the total FA in the TCLP test. However, both As and V had higher leaching concentrations under the conditions of the SPLP test (almost 2% and 0.5%, respectively). The U.S. EPA established

Table-1

Selected trace metal TCLP, SPLP and total metal concentrations for FA and total metal concentrations for the top soil. For comparison, previous metal analyses[33] on FA (shaded) were conducted in 1999 (Kirby Memorial Health Center, Wilkes-Barre, PA). Non-Detect (ND) for the previous analysis was below 0.05 mg/L. ND for the current analysis approximated 0.00001 mg/L. A dash indicates the metal was not tested. ($\alpha = 0.05$, n =2)

	Previous Analysis total metals (mg/kg)	Current Analysis total metals (mg/kg)	Previous Analysis leaching (mg/L)		Current Analysis Leaching (mg/L)	
			SPLP	TCLP	SPLP	TCLP
Al	13630.0	14451.8 ± 479.2	ND	3.10	0.501	165.2 ± 28.8
As	51.5	32.5 ± 1.4	0.33	0.42	0.705	0.56 ± 0.01
Ba	143.0	128.8 ± 9.7	ND	1.70	0.85	46.47 ± 0.55
Ca	< 1.0	0.31 ± 0.15	ND	ND	ND	0.102 ± 0.006
Cr	40.0	37.2 ± 2.0	ND	ND	0.083	1.35 ± 0.18
Co	5.0	6.43 ± 0.21	ND	-	< 0.001	0.34 ± 0.04
Cu	33.0	38.3 ± 1.6	ND	ND	0.014	0.66 ± 0.09
Fe	10675.0	8847.3 ± 530.4	0.06	ND	ND	6.26 ± 1.49
Pb	21.0	31.78 ± 0.75	ND	0.23	0.09	0.48 ± 0.35
Mg	850.0	663.2 ± 15.0	0.95	0.21	10.108	57.83 ± 2.32
Mn	81.0	91.0 ± 11.4	ND	ND	< 0.001	11.44 ± 0.73
Ni	17.0	21.2 ± 1.5	ND	ND	0.003	0.92 ± 0.03
Se	4.40	9.9 ± 1.3	0.14	0.10	ND	1.51 ± 0.12
Sr	68.0	35.41 ± 0.84	ND	-	0.745	5.80 ± 0.37
V	47.00	69.8 ± 8.2	0.10	-	1.598	0.32 ± 0.005
Zn	29.0	23.8 ± 5.6	ND	ND	ND	2.32 ± 0.09

Drinking Water Standards (DWS) are commonly used for the SPLP test. The DWS Maximum Contaminant Level (MCL) for As is 0.01mg/L and for Se is 0.05 mg/L[25]. The U.S. EPA has yet to assign a MCL for V, but the California Office of Environmental Health Hazard Assessment recommends 0.015 mg/L[26]. The SPLP results show that As is well above the MCL limit and V is well above the California limit.

Nevertheless, only the TCLP test is recognized by the U.S. EPA for hazardous waste determinations and it has different contamination limits than the SPLP test[27]. According to the TCLP test, only Se is over the limit of 1.0 mg/L. These results would indicate the FA used in this study should be classified as a hazardous waste. But it must be noted that these results should be treated as preliminary data and further testing should be conducted by a certified lab that specializes in TCLP testing, which is considered a "method defined parameter" test that must be performed as written[28]. Additionally, TCLP testing has been criticized as being inadequate for evaluating the leaching impacts of more realistic, complex conditions. In fact a 2006 report by the U.S. National Research Council found that the TCLP test is not suited for coal ash, and recommend the U.S. EPA select an appropriate alternative test for the hazardous waste determination of FA[29].

Conclusion

The U.S. EPA and Congress continue to postpone the decision on whether to designate FA as a hazardous waste and regulate its management and disposal. The focus for further research is on the potential hazards of FA uses, such as a backfill for mines, construction fill, and a soil supplement in agriculture. In fact, the possible EPA designation of FA as a "special waste" indicates the need for more research in this area.

In this study, FA does have noticeably higher concentrations of As, Se, and V, which are considered toxic at certain concentrations. The leaching tests indicated that these three trace metals are also mobile, which could lead to contamination of groundwater and the likelihood of becoming bioavailable[30]. The SPLP test seems to be a good indicator of potential vegetative uptake.

Although the investigative process to determine the hazards of FA can be standardized, the results cannot be applied to all FA and its uses. Each FA is different due to the various types of coals, origins, coal burning methods, and ash management practices. Additionally, each use poses a different risk of contamination and exposure. Therefore, the determination of FA as a hazardous material or waste should be conducted on a case-by-case basis using a holistic approach for the planned FA use. This would include developing applicable protocols to determine the potential of FA to leach trace metals under a variety of conditions simulating the many uses of FA.

Acknowledgements

This work was funded by a NSF RI EPSCOR grant. Special thanks to Qin Leng for her SEM guidance and to the following research assistants: Josh Jones, Regan Marin, Jamie Pierce, Zoe White, and Amanda Smith.

References

1. Dewan S., Coal ash spill revives issue of its hazards, *New York Times*, December 24 **(2008)**
2. American Coal Ash Association, Analysis of new federal government data shows coal ash comparable to residential soils, Retrieved on July30, 2012 from the ACAA web site: http://www.acaa-usa.org/associations/8003/files/ Coal_Ash_Material_ Safety_Study_News_2012-06-06.pdf **(2012)**
3. Saewitz M. and McCabe R, Chesapeake takes steps toward superfund designation for site, Retrieved on August 20, 2012 from PilotOnline.com web site: http:// hamptonroads.com/2008/07/chesapeake-takes-steps-toward-superfund-designation-site, July 19 **(2008)**
4. McCabe R., above ground, a golf course. Just beneath it, potential health risks, Retrieved on August 20, 2012 from PilotOnline.com web site: http://hamptonroads.com /2008/03/above-ground-golf-course-just-beneath-it-potential -health-risks, March 30 **(2008)**
5. Johnson J., The foul side of "clean coal", *Chemical and Engineering News*, **87**, 44-47 **(2009)**
6. Coal combustion product, *Production and Use Survey Report*, Retrieved July 26, 2012 from the ACAA web site: http://acaa.affiniscape.com/associations/8003/files/2010_CCP_Survey_FINAL_102011.pdf **(2010)**
7. Pandian N., Fly ash characterization with reference to geotechnical applications, *Journal of Indian Institute of Science*, **84(6)**, 189-216 **(2004)**
8. Horiuchi S., Kawaguchi M. and Yasuhara K., Effective use of fly ash slurry as fill material, *Journal of Hazardous Materials*, **76(2-3)**, 301-337 **(2000)**
9. Jala S. and Goyal D., Fly ash as a soil ameliorant for improving crop production – a review, *Bioresource Technology*, **97(9)**, 1136-1147 **(2006)**
10. Arivazhagan K., Ravichandran M., Dube S., Mathur V., Khandakar R., Yagnanarayana K., Pasha M., Sinha A., Sarangi B., Tripathi V., Gupta S., Singh R., Ali M., Thakur A. and Narayan R, Effect of coal fly ash on agricultural crops: showcase project on use of fly ash in agricultural in and around thermal power station areas of National Thermal Power Corporation Ltd., India, World of Coal Ash (WOCA) conference, Denver, Co, USA, May 9-12, **(2011)**

11. Special Wastes. Retrieved June 13, 2012 from the US EPA Wastes – Non-Hazardous Waste – Industria Waste Web site: http://www.epa.gov/osw/nonhaz/industrial/special/index.htm **(2012)**

12. RTI, Research Triangle Park, Human and ecological risk assessment of coal combustion wastes, prepared for the U.S. EPA, August 6 **(2007)**

13. Yufeng Z., Zhenghua W., Xianorong W., Lemei D. and Yijun C., Mobility of the rare earth elements with acid rainwater leaching in the soil column, *Bulletin of Environmental Contamination and Toxicology*, **67(3)**, 399-407 **(2001)**

14. Tripathi R., Vajpayee P., Singh N., Rai U., Kumar A., Ali M., Kumar B. and Yunus M., Efficacy of various amendments for amelioration of fly-ash toxicity: growth performance and metal composition of *Cassia siamea* Lamk, *Chemosphere*, **54(11)**, 1581-1588 **(2004)**

15. U.S. EPA, EPA promoted the use of coal ash products with incomplete risk information, *Evaluation Report No. 11-P-0173* from the Office of the Inspector General, March 23, **(2011)**

16. Talbot J. and Weiss A., Laboratory methods for ICP-MS analysis of trace metals in precipitation, EPA Hazardous Materials Lab, Hazardous Waste Research and Information Center, March **(1994)**

17. U.S. EPA Method 9045 D. Soil and waste pH. Retrieved on June 20, 2012 from the US EPA Web site: http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/9045d.pdf, November **(2004)**

18. University of Wisconsin – Madison, Analysis of Major, Minor and Trace Elements in Soil and Sediment Samples with ICP-OES and ICP-MS. Retrieved on June 20, 2012 from SOP Soil & Plant Analysis Laboratory web site: http://uwlab.soils.wisc.edu/files/procedures/soil_icp.pdf, October **(2005)**

19. EPA Method 1311 Toxicity Characteristic Leaching Procedure. Retrieved on June10, 2012 from the EPA web site: http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf, **(1992)**

20. EPA Method 1312 Synthetic Precipitation Leaching Procedure. Retrieved on June10, 2012 from the EPA web site: http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1312.pdf, **(1992)**

21. Kirby Memorial Health Center Analysis Report, Wilkes-Barre, PA August 13, **(1998)**

22. Del Monte M. and Sabbioni C., Morphology and mineralogy of fly ash from a coal-fueled power plant, *Meteorology and Atmospheric Physics*, **35(1-2)**, 93-104 **(1984)**

23. Statewide health standards, Retrieved on June 20, 2012 from the Pennsylvania Department of Environmental Protection Environmental Cleanup & Brownfields web site: http://www.dgs.state.pa.us/portal/server.pt/ community/ land_recycling_ program/10307/statewide_health_standards/552039, **(2012)**

24. McNally D., Crowley-Parmentier J. and Whitman B., Growth and Uptake of Trace Metals by *Lolium Perenne* (perennial ryegrass) on Coal-Generated Fly Ash, *International Research Journal of Biology*, (accepted) **(2012)**

25. U.S. EPA Region IX, Drinking water standards and health advisories table, San Francisco, CA. **(2009)**

26. Howd R., *Memorandum. Office of Environmental Health Hazard Assessment*. CA. **(2000)**

27. The EPA TCLP: Toxicity Characteristic Leaching Procedure and Characteristic Wastes (D-codes). Retrieved on August 21, 2012 from Environment, Health and Safety Online web site: http://ehso.com/cssepa/TCLP.htm. **(2011)**

28. Schaeffer E., EPA relies on inadequate test to assess dangerous leaching. Retrieved on August 21, 2012 PSR web site: http://www.psr.org/environment-and-health/environmental-health-policy-institute/responses/epa-relies-on-inadequate-test.html, **(2012)**

29. Committee on mine placement of coal combustion wastes, National Research Council (NRC), Managing coal combustion residues in mines. The National Academies Press, Washington D.C. **(2006)**

30. Abii T., Levels of Heavy Metals (Cr, Pb, Cd) Available for Plants within Abandoned Mechanic Workshops in Umuahia Metropolis, *Research Journal of Chemical Sciences*, **2(2)**, 79-82 **(2012)**