Characterization of Mercury in Coal Utilization By-Products

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INTRODUCTION

It is expected that increased controls on mercury (Hg) emissions will shift the environmental burden from the flue gas to the solid coal utilization by-products (CUB), such as fly ash and flue-gas desulfurization residues. If Hg can be leached from fly ash, it will have an impact on utilization, particularly for those uses that may allow for transport of the mercury into surface or ground water. Determining the effectiveness of mercury removal and the stability of mercury on coal utilization by-products (CUB) is critically dependent on the characterization methods. The precision of the concentration value for Hg in both solid and liquid samples is a function of the accuracy and sensitivity of the analytical methods used.

Composition

On a proximate basis, CUB can be described as consisting of moisture (H_2O), mineral matter (MM) and carbon (C). The moisture content of a particular CUB depends on the combustion and handling systems that produced it. The moisture content can be determined as the loss of weight when the sample is heated to 105 ˚C.[1-2] Fly ash from dry handling systems usually has a low moisture content (<2%), and the moisture content may not be determined, since it will have relatively little affect on the concentration of other elements. The mineral matter is the major constituent of CUB, and its concentration can be determined by a combustion weight loss method[3] or by difference if the moisture and carbon content are known. The amount of C in CUB has usually been determined by loss on ignition methods.[4-5] The carbon in CUB can be organic (450 ˚C), combustible (750 ˚C) or carbonate (900 ˚C). The temperature at which the LOI was determined should be known in order to evaluate the results. A thermogravimetric method[6] has been proposed to more accurately characterize the types and amount of C in CUB.

Determining the concentration major and trace elements requires the dissolution of the sample and analysis of the resulting solution. Commonly used dissolution methods for solid samples that are insoluble in common solvents are fusion[7] with an inorganic flux at high temperature or by microwave assisted acid dissolution.[8-9] There are drawbacks to both types of methods. Fusion is done in an open vessel, and volatile elements can be lost. Acid digestion techniques do not dissolve unburned carbon, and elements adsorbed on the C may not be transferred to the solution being analyzed. The aqueous solutions produced by these methods are usually analyzed by and inductively coupled plasma – spectrophotometric technique ICP-_ES) or by cold vapor atomic absorption (CVAA). Mercury concentration in the solid can be determined by direct desorption from the solid.[10]

The mineralogical composition of CUB is also a determining factor in the stability of most elements. Minerals that are crystalline can be identified by X-ray diffraction. Scanning electron microscopy (SEM) and spectroscopy can be used to determine elemental associations for elements present in concentrations greater than 2%. And the use of EPA Methods 3051 and 3052 can be used to determine the silicate/non-silicate distribution of elements.

Hg Release

The potential release of an element, such as Hg, from CUB is usually characterized by a leaching test.[11] There are more than 100 leaching methods to remove soluble components from a solid matrix. Many are intended to mimic natural conditions or to obtain information about the nature of the extractable material within a particular solid. The methods vary in the mass and particle size of the sample, the type and volume of leachant solution(s), the leachant delivery method, and time. Leaching behavior of all types of materials is related to several critical factors, including specific element solubility and availability or release potential. Solubility is also a function of pH, time and leachant volume. Leaching methods can be categorized by whether the leaching fluid is a single addition (static extraction tests) or is renewed (dynamic tests). Methods can also be classified as batch leaching in which the sample is placed in a given volume of leachant solution, as column or flow through systems. In determining the release potential for Hg, its volatility and the oxidation/reduction conditions of the test must also be considered.

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[1] ASTM D3173-03. Standard Test Method for Moisture in the Analysis Sample of Coal and Coke. ASTM Book of Standards 05.06, www.ASTM.org.

[2] ASTM D3302. Test Method for Total Moisture in Coal. ASTM Book of Standards 05.06, www.ASTM.org.

[3] ASTM D3174-14. Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal. ASTM Book of Standards 05.06, www.ASTM.org.

[4] ASTM D6316-04. Standard Test Method for Determination of Total, Combustible, and Carbonate Carbon in Solid Residues from Coal and Coke. ASTM Book of Standards 05.06, www.ASTM.org.

[5] ASTM WK9165. New proposed Standard Test Method for Loss on Ignition of Solid Combustion Residues. Committee D05.29, 9-29-2005.

[6] Fan, M. and Brown, R.C. 2001. Comparison of the Loss-on-Ignition and Thermogravimetric Analysis Techniques in Measuring Unburned Carbon in Fly Ash. Energy and Fuels, v15, 1414-1417.

[7] EPA. Sample Dissolution. Multi-Agency Radiological Laboratory Analytical Protocols Manual (Final). Chapter 13 www.epa.gov/radiation/docs/marlap/402-b-04-001b-13-final.pdf.

[8] EPA SW-846. Method 3051. Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils. 14 p.

[9] EPA SW-846. Method 3052. Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices. 20p.

[10] Milestone Direct Mercury Analyzer. www.milestonesci.com/mercury.php

[11] Kim, Ann G. 2003. Leaching Methods Applied To CUB: Standard, Regulatory And Other. PROC. 15th International Symposium on Management and Use of Coal Combustion Products, January 27-30, 2003; St. Petersburg, FL, pp. 29-1 to 29-12.