

LABORATORY METHODS FOR THE EVALUATION OF POTENTIAL RELEASE OF MERCURY FROM COAL UTILIZATION BY-PRODUCTS

Topical Report

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LABORATORY METHODS FOR THE EVALUATION OF POTENTIAL RELEASE OF MERCURY FROM COAL UTILIZATION BY-PRODUCTS

EXECUTIVE SUMMARY

Under a 3-year effort funded by the U.S. Department of Energy (DOE) and industry entitled “Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization,” the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of coal utilization by-products (CUBs). The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. Results will be used to determine if mercury release from CUBs, both as currently produced and as produced with mercury and other emission controls in place, will potentially impact CUB management practices. In order to adequately address the potential for release of mercury from CUBs, sorbents, and combinations, release mechanisms that must be evaluated include 1) leaching, 2) elevated- and ambient-temperature vapor-phase releases, and 3) microbiologically mediated releases. The EERC initiated research on the potential release of mercury from CUBs in 1999 and found that methodologies for evaluating the release of mercury from CUBs using these mechanisms were not documented in the scientific literature, with the exception of leaching. As a result, method development work was initiated under the U.S. Environmental Protection Agency (EPA) Center for Air Toxic Elements and the Coal Ash Resources Research Consortium.

The EERC concluded Year 2 of this effort in April 2005, and this report details the results to date from Task 2: Analytical Methods Selection. As noted in several forums in recent years, the methods used to evaluate CUBs must be relevant to the material and the management of CUBs where possible. EERC researchers reviewed methods currently being used at the EERC and elsewhere to determine the best possible methods for this effort.

Laboratory methods were selected based on early work performed at the EERC but method development and modification continued. The methods being employed to evaluate the release of mercury from CUBs by direct leaching, exposure to ambient and elevated temperatures, and exposure to biota are described, and method limitations are discussed.

LABORATORY METHODS FOR THE EVALUATION OF POTENTIAL RELEASE OF MERCURY FROM COAL UTILIZATION BY-PRODUCTS

INTRODUCTION

The stability of mercury associated with coal utilization by-products (CUBs) has become a prominent question as the coal-fired utility industry develops and tests mercury emission controls that may consequently increase the mercury associated with CUBs. The reasons for evaluating the release of mercury from CUBs are 1) to determine if mercury captured on CUBs is stable or if it will be released, thus negating the purpose of the removal of the mercury from the emissions, and 2) to aid utilities in determining and understanding changes in CUBs associated with mercury control and associated CUB management.

Under a 3-year effort funded by the U.S. Department of Energy (DOE) and industry entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization," the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of CUBs. The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. Results will be used to determine if mercury released from CUBs, both as currently produced and as produced with mercury and other emission controls in place, will impact CUB management practices.

The EERC concluded Year 2 of this effort in April 2005, and this report details the results to date from Task 2: Analytical Methods Selection. As noted in several forums in recent years, the methods used to evaluate CUBs must be relevant to the material and the management of CUBs where possible. EERC researchers reviewed methods currently being used at the EERC and elsewhere to determine the best possible methods for this effort. A summary of research in this area was published in 2004 (1).

BACKGROUND

Recent projections from the Energy Information Administration indicate that U.S. demand for energy will increase from 97.3 quadrillion to 130.1 quadrillion Btu between 2001 and 2020, reflecting an annual growth rate of 1.5%. By 2025, total energy consumption is projected to reach 139.1 quadrillion Btu (2). Fossil fuel combustion, including the burning of coal, natural gas, or oil, provides about 85% of the present energy production in the United States. Of this amount, over 50% is provided by coal-fired utilities (2). As a result of energy production from coal, CUBs are generated, and CUBs, as produced in the United States, are primarily a result of emission control technologies installed to meet emission regulations.

Emission regulations first mandated reduction of particulate matter released to the atmosphere by utilities, which required utilities to install collection devices for generated fly ash. Later emission regulations significant to CUB production mandated limits on SO_x emissions. As

a result, utilities using high-sulfur coal could change coal sources, resulting in a different by-product character, or scrub the flue gas using sorbents to remove the SO_x gases. The result of flue gas desulfurization (FGD) was high volumes of spent FGD sorbent material. There is a wide range of FGD technologies, so FGD materials have broadly varied characteristics, but generally contain high concentrations of calcium and sulfur. Currently, utilities are responding to regulation placing limits on NO_x emissions, which also impacts the character of ash by-products, including potentially increasing the amount of unburned carbon in fly ash or adding ammonia to the fly ash. Issues related to air toxic emissions, including mercury, are currently under technical and regulatory scrutiny.

Figure 1 includes an excerpt from a U.S. Environmental Protection Agency (EPA) Fact Sheet titled “EPA Proposes Options for Significantly Reducing Mercury Emissions from Electric Utilities,” in which some of the concerns about mercury are summarized. On December 14, 2000, EPA announced that it would regulate mercury emissions from coal- and oil-fired electric utility steam-generating power plants (3); propose regulations by December 15, 2003; and finalize regulations by December 15, 2004. On December 15, 2003, EPA signed the Utility Mercury Reductions proposal, which seeks comments on two approaches for reducing mercury by up to nearly 70%. On March 15, 2005, the EPA issued the first federal rule to permanently cap and reduce mercury emissions from coal-fired power plants (a power plant is defined as an electrical generating facility that provides >25 MWe). The rule is a market-based cap-and-trade program (Section 111 of the Clean Air Act) and is similar to the program in place for SO₂. The rule is to be administered in two phases. The first phase places a cap of 38 tons per year of mercury beginning in 2010. The second phase sets a final cap of 15 tons by 2018. Coal-fired power plants currently emit about 48 tons per year; therefore, the reduction in mercury emissions will be 21% and 69%, respectively.

Mercury Emissions – Both Naturally Occurring and Man-made Sources

- Mercury is a toxic, persistent pollutant that accumulates in the food chain. Fossil fuel-fired utilities are the largest source of human-generated mercury emissions in the United States.
- Concentrations of mercury in the air are usually low and of little direct concern. However, atmospheric mercury falls to Earth through rain or snow and enters lakes, rivers, and estuaries. Once there, it can transform to its most toxic form, methylmercury, and accumulate in fish and animal tissues.
- Americans are exposed to mercury primarily by eating contaminated fish. Because the developing fetus is the most sensitive to the toxic effects of mercury, women of child-bearing age are regarded as the population of greatest concern. Children who are exposed to low concentrations of methylmercury prenatally are at increased risk of poor performance on neurobehavioral tasks, such as those measuring attention, fine motor function, language skills, visual-spatial abilities, and verbal memory.

EXCERPTED FROM EPA FACT SHEET:
**EPA Proposes Options for Significantly Reducing
Mercury Emissions from Electric Utilities**
December 15, 2003

Figure 1. Information from EPA on mercury emissions (4).

The reduction of emissions at coal-fired power plants has historically impacted the quantity and character of resulting CUBs. The removal or reduction of mercury emissions at coal-fired power plants has high potential to do the same because several proposed mercury emission control technologies involve the use of solid sorbents that will likely be introduced in the flue gas and collected with the fly ash. Other candidate emission control technologies focus on increasing the mercury sorbed on FGD materials. These mercury emission control technologies will impact the mercury content of CUBs. The question that this project was designed to answer is, “Will the changes in CUBs associated with mercury emission controls change the management options for those CUBs as they relate to the potential release of mercury?”

Since the large volumes of CUBs produced annually in the United States are managed either by disposal or utilization, the design of various tasks in this project focused on simulating potential behavior of CUBs in environments where they are typically managed. Examples of utilization scenarios include:

- The use of fly ash in concrete, soil stabilization, or fills that could be exposed to natural waters or to microbial action.
- The use of FGD gypsum in wallboard, where it may be exposed to high temperatures in production or to natural water under disposal.
- The use of fly ash in cement clinker production, where it would be exposed to extremely high temperatures.
- The use of FGD gypsum or fly ash as an agricultural soil amendment or mine fill, where it would be exposed to natural water and, potentially, microbial action.

In order to adequately address the potential for release of mercury from CUBs, sorbents, and combinations, release mechanisms that must be evaluated include leaching, elevated- and ambient-temperature vapor-phase releases, and microbiologically mediated releases. The EERC initiated research on the potential release of mercury from CUBs in 1999 and found that methods for evaluating the release of mercury from CUBs using these mechanisms were not documented in the scientific literature, with the exception of leaching. As a result, the EERC initiated a program under EPA’s Center for Air Toxic Metals[®] and the Coal Ash Resources Research Consortium[®] to develop laboratory methods that would provide information on the potential for CUBs to release mercury and other air toxic elements under conditions associated with the proposed release mechanisms of direct leaching, direct ambient- and elevated-temperature vapor-phase release, and microbiologically mediated leaching and vapor-phase release.

OBJECTIVES

The goal of the methods selection task was to select or develop appropriate laboratory methods to evaluate the potential for release of mercury from CUBs under conditions that are relevant to management options applied to CUBs. Supporting objectives were as follows:

- Select and apply one or more leaching procedures appropriate for environmental characterization of CUBs.
- Select, develop, and apply a method to evaluate the release of mercury through offgassing from CUBs at elevated temperatures.
- Select, develop, and apply a method to evaluate the release of mercury through offgassing from CUBs exposed to ambient temperature air.
- Select, develop, and apply a method to evaluate the release of mercury through leaching and offgassing from CUBs exposed to biota commonly found in natural settings.
- Select and apply laboratory analytical methods required to determine mercury in solutions, collected on analytical traps, and in solid materials.

METHODOLOGIES – ANALYTICAL AND CHARACTERIZATION METHODS

Chemical and Physical Characterization

Chemical characterization of samples included total mercury and total bulk chemical composition on major, minor, and trace constituents. Physical characterization included carbon forms, pH, moisture, and loss-on-ignition (LOI) measurements. Eh measurements were taken on samples used for microbiological experiments. Methodologies used for these characterizations are further described below.

Total Mercury

The total mercury content of solid samples was determined using a direct mercury analyzer or digestion followed by cold-vapor atomic absorption spectrometry (CVAAS).

Total Air Toxic Elements

The total concentration of the other air toxic elements of arsenic, cadmium, chromium, lead, nickel, and selenium was determined using standard methods. Acid digestion was used on the CUB followed by detection using inductively coupled atomic emission spectroscopy (ICP–AES) or ICP mass spectroscopy (ICP–MS).

Total Bulk Chemical Composition

The major bulk composition, reported as percent oxides, was determined using x-ray fluorescence spectrometry. American Society for Testing and Materials (ASTM) D4326-04 Standard Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence was used (5).

LOI and Moisture

Standard characterization techniques were used to measure LOI and moisture content. ASTM C311-04 Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete was used (6).

pH

The pH of samples was determined using distilled water and/or 1 M KCl. The method employing 1 M KCl is required for many types of solid samples that exhibit a double electric layer that impacts the determination of pH. For this task, a slurry of 25 mL of 1 M KCl solution was mixed with 10 g of CUB, and the resulting pH was measured and recorded. As previously noted, the pH was also determined in slurry of distilled, deionized water. Where both methods were employed in this effort, it was noted that the pH values were similar. A comparison of these data for a relatively broad range of CUB types led researchers to conclude that it is not necessary to use 1 M KCl in determining the pH of CUB; therefore, remaining samples were evaluated using distilled, deionized water slurries. It is likely that the high concentration of total dissolved solids generated in the pH determination eliminated the double electric-layer effect that requires the use of KCl solution in the determination of pH in other types of solid samples.

Carbon Forms

Dominant carbon forms were identified in a select group of project samples. The samples on which carbon forms were determined were prepared by mounting them in epoxy resin. The sample was dispersed in the bottom of a 1-inch-diameter rubber cup mold. The epoxy was stained using Sudan black, which results in a high contrast between the particles of interest and the mounting medium. The surfaces to be analyzed were polished with incrementally smaller grits with ¼ µm being the final polishing grit used. The samples were then examined using a reflected-light microscope.

Eh

Eh was determined using a platinum electrode with a standard reference electrode.

Method Used to Measure Mercury on Gold-Coated Quartz Traps

Gold-coated quartz mercury collection traps were desorbed for analysis by heating to approximately 500°C, and the mass of mercury released was determined using double-gold amalgamation with atomic fluorescence (AF) detection. A Brooks Rand Model III cold-vapor atomic fluorescence spectrophotometer (CVAFS) was utilized for mercury concentration determination.

Method Used to Measure Mercury on Carbotraps

Supelco Carbotrap™ collection traps were analyzed for total mercury by heating them to approximately 300°C, passing the released organomercury through a tube held at about 800°C, and collecting the mercury on a gold-coated quartz trap, which was analyzed as described above.

METHODS FOR THE EVALUATION OF THE RELEASE POTENTIAL OF MERCURY AND OTHER AIR TOXIC ELEMENTS FROM CUB

Direct Leaching

Leaching is the most likely mechanism of transport of constituents from disposed or utilized CUBs contacted by water. Leaching is typically performed on CUBs to characterize them for management purposes. The leaching tests performed on the samples in this project were the toxicity characteristic leaching procedure (TCLP [EPA Method 1311 (7)]), the synthetic groundwater leaching procedure (SGLP), and long-term leaching (LTL) with 30- and 60-day equilibration periods.

TCLP is a leaching procedure designed for the evaluation of leaching of wastes when codisposed in a sanitary landfill. Leaching with TCLP utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, an 18-hour equilibration time, and one of two extraction fluids. The extraction fluid used is dictated by the pH of the material being leached. Extraction Fluid 1, used when the pH is below 5, is prepared by adding glacial acetic acid and sodium hydroxide to reagent water, and has a fluid pH of 4.93 ± 0.05 . Extraction Fluid 2, used when the pH of the material is above 5, is prepared by adding glacial acetic acid to reagent water, resulting in a fluid pH of 2.88 ± 0.05 .

The SGLP batch-leaching procedure is a relatively simple test that follows many of the conditions of TCLP. The test utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, an 18-hour equilibration time, and usually employs a leaching solution consisting of water from the site, water that has been prepared in the lab similar to water likely to contact the CUB, or distilled deionized water. When distilled water is used as the leaching solution for SGLP, the method is equivalent to the ASTM D3987 Standard Test Method for Shake Extraction of Solid Waste with Water (8). Distilled deionized water was used in this effort. For the long-term component of this procedure, multiple bottles are set up and analyzed at different time intervals. A typical SGLP–LTL test might consist of 18-hour, 30-day, and 60-day equilibration times. Although 60 days is often not adequate to achieve complete equilibrium, it is generally long enough to determine the concentration evolution of individual parameters. The most important factor when performing LTL is to have at least three equilibration times to determine a true trend. A draft of the SGLP–LTL method prepared for consideration by ASTM is in Appendix A.

For all leaching procedures, the solids were filtered from the leaching solution through a 0.45- μm filter, the pH of the resulting leachate was measured, and the leachate was preserved with HCl for mercury determination and with HNO₃ for determination of other trace elements.

Mercury leachate concentrations were determined using CVAAS and CVAFS as noted in the analytical methods section. Other trace elements were determined using inductively coupled argon-plasma spectrometry, ICP-MS, or graphite furnace atomic absorption spectroscopy.

The SGLP method was used preferentially for the project samples, and where TCLP was applied, SGLP was also applied. TCLP was included because some regulatory groups continue to use TCLP results to determine whether a “waste” is hazardous. The SGLP short-term leaching procedure was applied to all samples, but for samples with a pH >10, the LTL option was also used. CUBs exhibiting a high pH have the potential to undergo hydration reactions that can change the leaching profile with time. The EERC documented the impact of ettringite formation on leachate concentrations of several elements that are frequently present in CUBs such as selenium and boron (9–12). The elements that are most likely to be incorporated into the ettringite structure and exhibit a change in leaching profile with time are those that are present as oxyanions at high pH. Examples of leaching profiles of high pH CUBs for some trace constituents commonly found in CUBs are shown in Figures 2 and 3.

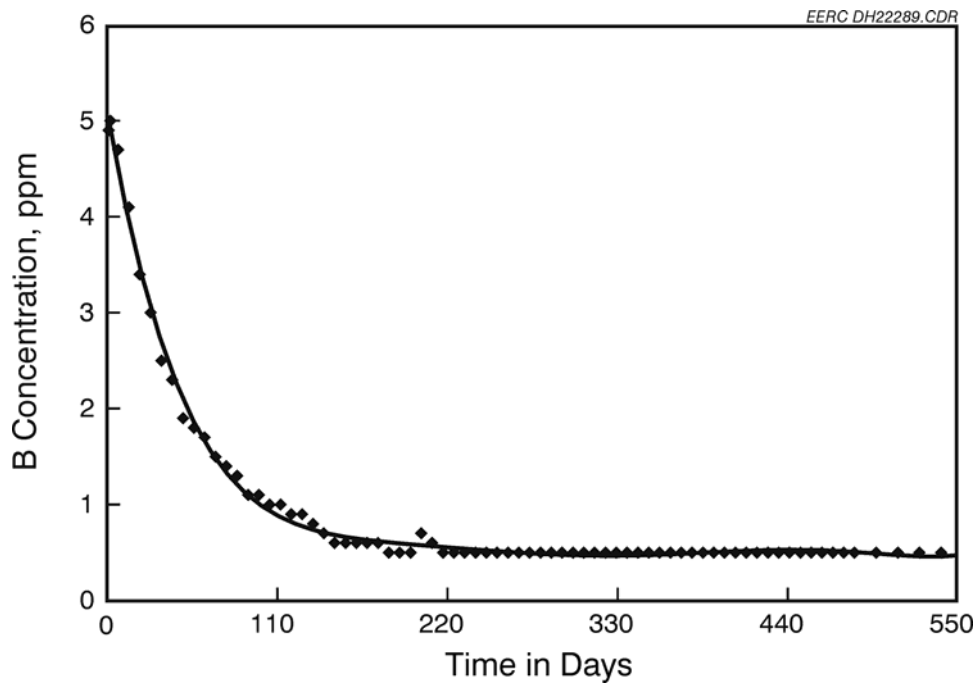


Figure 2. Long-term leaching results for boron.

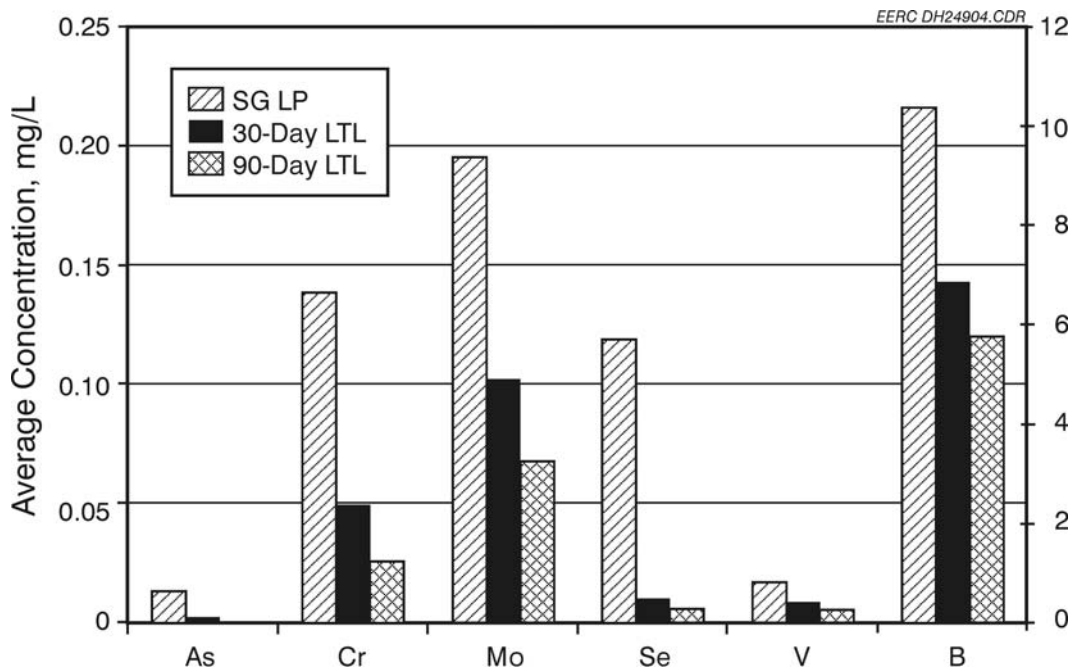


Figure 3. Indirect evidence of ettringite formation using SGLP and LTL (note: boron is on a secondary axis).

Vapor-Phase Transport

Long-Term Ambient Temperature Release

In order to develop a method to evaluate the potential for release of mercury from CUBs at ambient temperatures, several preliminary decisions were made based on the practicality of performing this type of evaluation in the laboratory, as follows:

- In order to measure mercury releases from CUBs, most of which have very low concentrations of mercury, samples with relatively high concentrations of mercury would be evaluated first.
- In order to evaluate multiple samples with available equipment and instrumentation, released mercury would be collected on analytical gold-coated quartz traps.
- Because very low release of mercury was anticipated, it was decided to expose a column of CUB to low-mercury air rather than expose only the surface of a CUB to the ambient temperature low-mercury air.

Using these preliminary premises, 250-mL wide-mouth glass test containers were designed with bonded Teflon liner caps. Two holes were drilled in the caps to accommodate a silicone tube for gas inlet and a Teflon outlet bulkhead fitting. The gas inlet tube extended nearly to the bottom of the container while the outlet tube extended only slightly into the container.

Using these test containers, approximately 150-g aliquots of CUB provided a column of material through which the low-mercury air could be transported. Breathing-quality air from a cylinder was passed through several sets of gold-coated quartz traps for mercury removal and admitted to each of the bottles through a gas distribution manifold that routed the gas through 0.25-mm-ID gas chromatography (GC) capillary tubing to each of the individual bottles. The pressure drop across the GC capillary tubing allowed for the regulation of air flow through each bottle by simply adjusting the length of tubing to each bottle. The length of tubing was a nominal 65 cm. This length of tubing, when pressurized to between 1 and 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm³/min. Because of the variability of particle sizes between different ash samples, the sample with the initial highest gas flow was left with a 65-cm length of GC tubing, and other samples had their tubing lengths shortened until all samples had approximately the same flow rate. The air exiting the GC tubing was given a final scrubbing to remove mercury vapor using a gold-coated quartz trap just prior to entering the bottle containing the CUB. After entering the bottles, the air passed through the ash and exited to a central mercury collection tube containing two separate gold-coated quartz traps. The second outlet or top trap was used to prevent mercury contamination from atmospheric mercury. This setup is illustrated in Figure 4.

The gold-coated quartz trap nearest the exit bulkhead fitting was analyzed multiple times with the most typical sampling scheme being one 7-day period followed by two consecutive 90-day periods. The gold-coated quartz analytical traps were evaluated according to the method described in the analytical method section. In order to determine the total mercury released over the duration of the experiment, the mercury results from all experimental time segments needs to be combined, and the container blank needs to be subtracted. The container blank was determined on the empty bottles used to hold the samples.

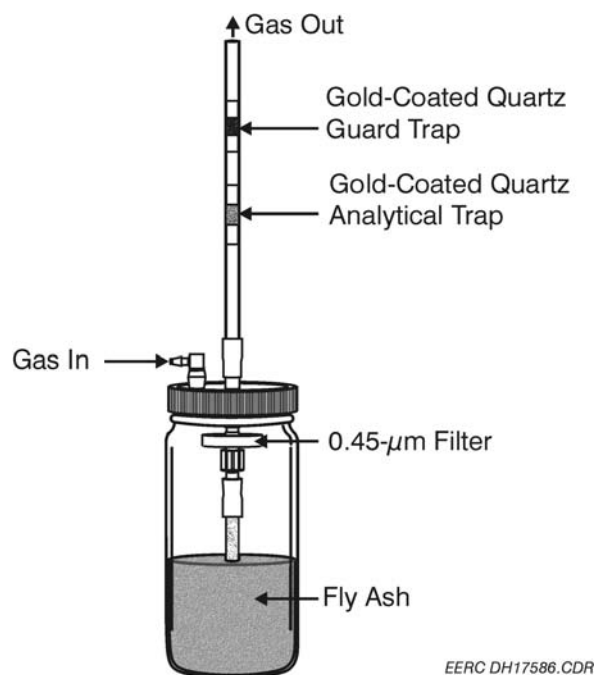


Figure 4. Mercury vapor release collection apparatus.

Examples of replicate data from a variety of CUB samples are shown in Figure 5.

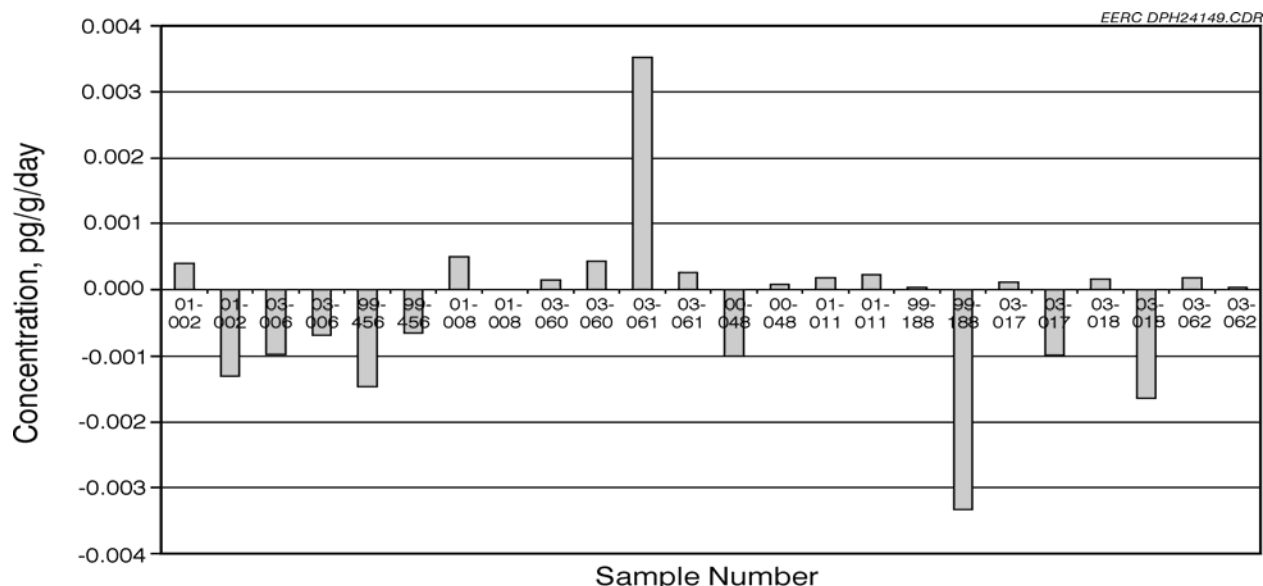


Figure 5. Average total long-term ambient-temperature mercury release or sorption as related to blank values, pg/g/day. Positive values indicate release and negative values indicate sorption of mercury.

Vapor-Phase Transport

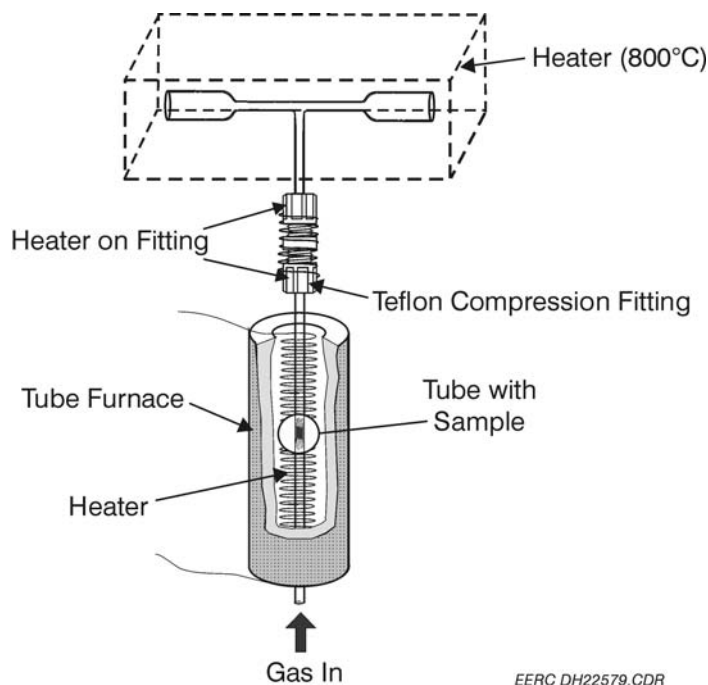
Thermal Desorption at Elevated Temperature

Since mercury and mercury compounds are highly volatile, mercury was expected to be released from CUBs when they were exposed to elevated temperatures. Even mercury that is sorbed on fly ash, FGD material, or sorbents developed to remove mercury in flue gas is expected to have high potential to be released if exposed to high enough temperatures. Instrumental and equipment constraints existed for the physical testing of elevated temperature release of mercury from CUBs. These constraints included the following:

- Furnaces available for the experimental apparatus could only achieve maximum temperatures of 750°C.
- Fittings and connecting tubing needed to be heated in order to minimize the loss of mercury in the system.
- Gas flow to remove the mercury from the heated sample cell to the analytical cell needed to be constant.
- Temperature ramping needed to be controlled and consistent between sample runs.

The apparatus was constructed as shown in Figure 6. The CUB sample was weighed into a quartz tube with quartz wool used to keep the sample in place in the tube. Nominal sample size was approximately 1 g. The sample tube was placed into a small tube furnace capable of achieving a maximum of 750°C. A programmed temperature controller ramped the furnace from ambient to maximum temperature at 25°C per minute. In preliminary experiments, the maximum temperature achievable was 700°C, but an improved furnace was incorporated into the apparatus to increase the maximum to 750°C. A nitrogen gas flow of 5 cm³/min was introduced into the tube furnace. As the mercury and mercury compounds desorbed from the CUB in the sample tube, the nitrogen flow carried them through the system to the electrically heated quartz analytical cell. The quartz analytical cell was operated at 800°C, allowing the detection of mercury compounds by thermally decomposing compounds to form elemental mercury, which can be detected by atomic absorption (AA). The analytical cell at the top of the diagram was placed in the center-focused beam path of an AA spectrophotometer (AAS). A mercury hollow cathode lamp was used as the light source, and the AAS detector was set to the 253.7 nm line for mercury. A Hewlett Packard 3395 integrator was used for data collection.

Examples of thermal desorption curves generated with this method are shown in Figures 7 and 8.



EERC DH22579.CDR

Figure 6. Mercury thermal desorption apparatus.

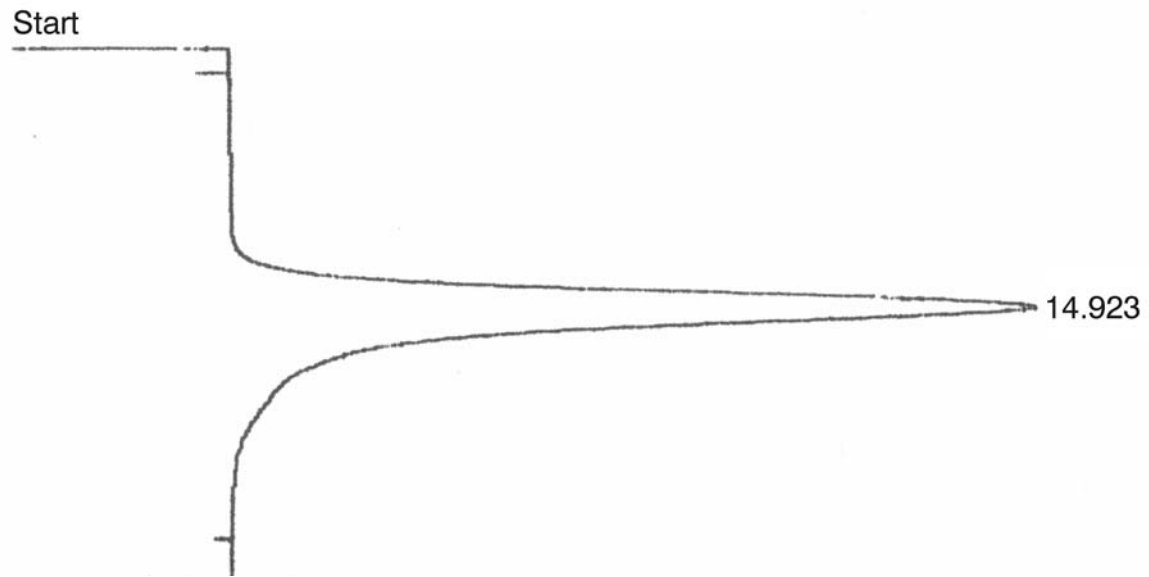


Figure 7. Typical thermal desorption curve for fly ash.

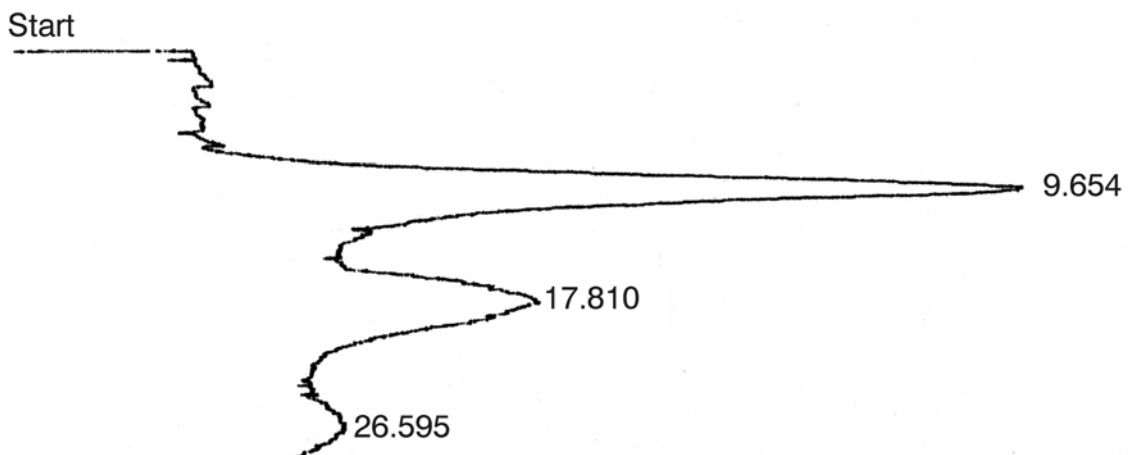


Figure 8. Example of thermal desorption curve for an FGD material.

Microbiologically Mediated Leaching and Vapor-Phase Transport

The EERC review of published data on the release of mercury from CUBs (1) reported that the only published method demonstrated for use in evaluating the release of mercury from CUBs on exposure to natural biota was developed by the EERC. The EERC method has been under development since approximately 1999 and has undergone numerous modifications to achieve the goal of evaluating the mercury release potential by leaching and offgassing when CUBs are under microbiologically mediated conditions. The first experiments performed using early versions of the apparatus focused on mercury releases by offgassing.

The first apparatus assembled to conduct microbiologically mediated vapor-phase mercury release used a 250-mL Erlenmeyer flask fitted with an impinger inlet/outlet tube with the inlet center shortened to 6 cm below the standard taper. Cylinder gas was passed through several sets of gold-coated quartz traps for mercury removal and admitted to each of the flasks through a gas distribution manifold that routed the gas through 0.25-mm GC capillary tubing to each of the individual flasks. A GC capillary length of approximately 60 cm, when pressurized to between 1 and 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm³/min. The gas passed mercury vapor from the head space of the flasks to a mercury vapor collection system at the outlet of the flasks, consisting of two traps. The nearest trap contained Supelco Carbotrap™, which collected organomercury compounds, followed by a gold-coated quartz trap, which collected elemental mercury.

The flasks were placed on a 16-flask wrist-action shaker. The experimental matrix consisted of eight flasks under anaerobic conditions (using argon) and eight flasks under aerobic conditions (using breathing-quality air). In each set of eight flasks, two contained only buffer, three contained the CUB with buffer (starved), and three contained the CUB with buffer and glucose (fed). An 80-g aliquot of CUB was placed in the flasks, and 100 mL of a phosphate buffer (with or without glucose as appropriate) was added to create a neutral pH. The CUB-containing flasks also had 100 µL of mixed bacterial culture added. The source of bacteria was a mixed bacterial inoculum from a brackish wetland. This setup is illustrated in Figure 9.

This apparatus underwent several iterations as difficulties were identified and solved. The wrist-action shaker was abandoned because it was unable to provide adequate suspended sample. Instead of the wrist-action shaker, a 9-place stir plate was introduced. This was operated for about 20 minutes every 3 hours to maintain sample agitation over the 30-day period of the experiment. Additionally, the sample size was reduced to 20 g, and the buffer was increased to 150 mL to provide adequate sample volume for additional trace element analyses. The buffer composition was also altered. It was found that phosphate and nitrate interfered with a derivitization step in the determination of organomercury compounds in the solid-phase microextraction (SPME) determination using GC separation followed by detection of the mercury compounds by atomic fluorescence. This technique is described later. The original buffer utilized nominal concentrations of phosphate and nitrate salts. The improved buffer used only 100 ppm of phosphate and substituted potassium glutamate as the nitrogen source. This simple change appeared to remove the interferences. Additionally, later experiments did not involve the use of starved control samples. In current experiments, all samples are fed with glucose. This setup is illustrated in Figure 10.



Figure 9. Microbiologically mediated mercury vapor-phase collection apparatus utilizing a wrist action shaker to facilitate mixing.



Figure 10. Microbiologically mediated mercury vapor-phase collection apparatus utilizing a stir plate to facilitate mixing.

Analyses of mercury and air toxic element releases were performed after a 30-day period. The gold-coated quartz traps and Carbotraps™ were analyzed as described in the analytical methods selection. Total mercury concentrations of the leachate were determined using CVAFS. Total air toxic element concentrations were determined using ICP–AES or ICP–MS.

Bacterial counts were performed upon completion of the experiment. A 1-mL aliquot of solution was taken from each flask. The aqueous supernate was serially diluted in 0.1% sodium pyrophosphate buffer (pH 7) and then used to inoculate a series of tubes containing 1% PTYG (peptone, tryptone, yeast extract, glucose) broth. The tubes were incubated at 30°C and growth, as turbidity, was monitored over a 3-week period.

SPME was used in the determination of organomercury species in the liquid portions of the samples. SPME is a sample collection technique in our case utilizing a fiber coated with polydimethylsiloxane. Samples containing organomercury compounds are first derivatized to increase the volatility of organomercury halides such as methylmercuric chloride. The derivitization reagents used were sodium tetraethyl borate, sodium tetrapropyl borate, and sodium tetraphenyl borate. Sodium tetraethyl borate was most commonly used. In the derivitization procedure, derivatizing agent, acetate buffer, an internal standard (usually propyl mercuric chloride), and sample were mixed in a septum-capped vial. In a relatively fast reaction, the halide is replaced with the appropriate alkyl or aryl group, depending on which derivatizing agent is chosen. A SPME fiber was inserted through the septum cap, and the sample was stirred using a Teflon-coated stir bar for 20 minutes. After this equilibration time, the SPME fiber was introduced into the heated inlet zone of a GC. Sample separation can be accomplished using a 0.53-mm capillary column 15 or 30 meters in length. The exit end of the column was connected to a heated (800°C) quartz tube, and makeup helium gas was added to increase the total flow to 25–30 mL per minute. The gas was then routed to an AF detector for determination of the separated mercury compounds. An example of a SPME chromatogram generated with this method is shown in Figure 11.

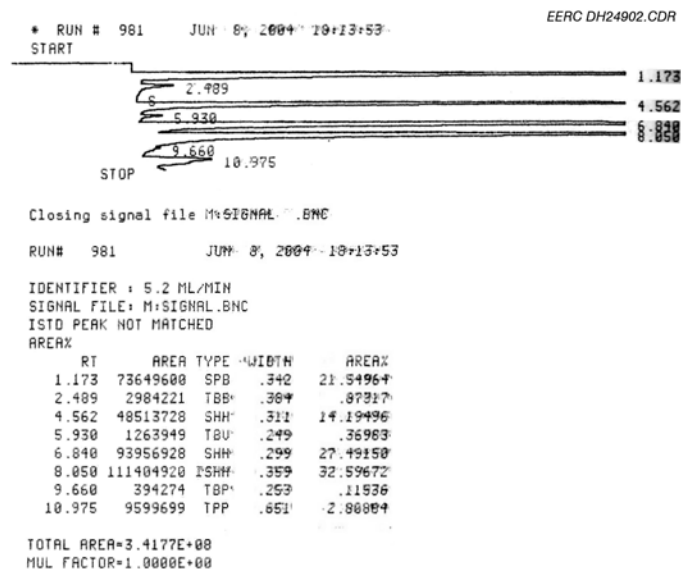


Figure 11. Example of a SPME chromatogram.

SUMMARY

Analytical methods were selected based on project needs and the sample types requiring analysis. Standard analytical methods were selected and used as frequently as possible. Replicate analyses were performed on a regular basis as part of the laboratory quality assurance/quality control program.

The leaching method selected, the SGLP-LTL, was selected based on EERC experience and familiarity with a large number of leaching procedures used to characterize CUBs and the appropriate application of those tests. The SGLP-LTL meets the criteria that EERC researchers have identified for leaching procedures to provide scientifically valid information. These criteria are as follows:

- Reactivity or other properties of the material being leached that may influence the leaching profile.
- The setting where the material is to be placed and the water that will most likely contact that material in that setting.
- The leaching time required to allow adequate time for hydration reactions to occur in reactive materials, such as high calcium coal fly ash.

The elevated-temperature vapor-phase release method underwent minor modifications early in the project but has been shown to provide reproducible data. The remaining technical challenge with the method as employed for this project is the limitations associated with the maximum achievable temperature to be applied to the CUB under investigation; and this cannot be addressed under this project.

The ambient-temperature vapor-phase release method developed for this work also presents technical challenges, but they are related to the quantitation limitations for mercury. The extremely low levels of mercury released at ambient temperatures are frequently near the levels of detection for the analytical system being used. The physical nature of the CUB samples also results in variable data and the need to modify the method. As an example, using the apparatus to evaluate the potential for release of mercury from a wet FGD material required modification of the apparatus to shorten the gas inlet tube to above the level of the sample because gas could not be forced through the material when the inlet was near the bottom of the sample container.

The method developed to evaluate the microbiologically mediated release of mercury underwent a relatively high degree of modification method over the first 2 years of the project. The final apparatus description and method now meets the project goals to produce reliable and relatively reproducible vapor and leachate samples. An evaluation of the particle-size reduction associated with the use of magnetic stir bars in the reaction vessels will be performed, and results of that evaluation will be included in future project reports.

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APPENDIX A

**DRAFT ASTM STANDARD METHOD FOR
SYNTHETIC GROUNDWATER LEACHING
PROCEDURE**

**DRAFT ASTM STANDARD METHOD FOR
SYNTHETIC GROUNDWATER LEACHING PROCEDURE**

1. Scope

- 1.1 This method determines the leachability of constituents in wastes, products, or materials using a leaching solution designed to simulate leachate anticipated in field conditions. The method allows for prediction of changes in leachability brought about as a result of the formation of secondary hydrated phases and new minerals through interaction of the waste and water over extended periods of time.
- 1.2 This method consists of the agitation of waste and a synthetic groundwater solution over an extended period of time (greater than 60 days) with sampling at regular intervals.
- 1.3 This method allows a comparison of maximum leachate concentration with actual concentrations of leachate at time intervals of from 18 hours to 2 months or greater. The method allows for determination of mass of analyte mobilized based on a leachate concentration and percent of total element leached and provides information to estimate leachate concentration trends with respect to time.
- 1.4 This method may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

- 2.1 American Society for Testing and Materials (ASTM) Standards:
D1129 Definitions of Terms Relating to Water
D1193 Specification for Reagent Water
D3987 Shake Extraction of Solid Waste with Water
D2216 Method for Laboratory Determination of Moisture Content of Soils
- 2.2 Toxicity Characteristic Leaching Procedure (TCLP) EPA Method 1311

3. Definitions

- 3.1 For definitions of terms in this test method, see Definitions D1129.
- 3.2 Ettringite: Ettringite is a mineral having the nominal composition $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$. Ettringite is also the family name for a series of related compounds as is the case for many mineral families. Ettringite has characteristic structural features that are fairly unique. The structure comprises of calcium aluminate columns $\{\text{Ca}_6\text{Al}_2(\text{OH})_{12}24\text{H}_2\text{O}\}^{6+}$ with the channels between these columns containing the other components, which include an oxyanion such as sulfate with hydroxide and water $\{(\text{SO}_4)_{2-4}(\text{OH})_{0-4}(\text{H}_2\text{O})_{0-6}\}^{6-}$. Ettringite is unique in that several elements that exist as oxyanions can substitute for the sulfate in the structure. These elements include but are not limited to arsenic, boron, chromium, molybdenum, selenium, and vanadium. Ettringite is known to form in the hydration of low-rank coal conversion solid residues

(CCSRs) and in CCSRs from advanced coal combustion processes such as fluidized-bed combustion (FBC) and limestone injection modified burner (LIMB).

- 3.3 Synthetic Groundwater: Synthetic groundwater as used in this application refers to a solution prepared in the laboratory containing the major geochemical parameters that would be found in water likely to contact the disposed CCSR. In the case of rainwater contact, this solution would be Type IV water, while with groundwater, a typical solution might contain calcium, magnesium, sodium, sulfate, and bicarbonate. Groundwater collected at the site of disposal could also be used, although if that were the case, corrections would have to be made for concentrations of trace elements already present in the water. It has been found with most CCSRs that it is the CCSR that regulates the equilibrium concentrations of major constituents in a synthetic groundwater leaching procedure; thus the inclusion of major geochemical constituents of actual groundwater may be unnecessary in many cases.

4. Significance and Use

- 4.1 This test is intended as a means for determining the mass of analyte readily mobilized by leaching with groundwater and also provides a means of determining the trend of leachate concentration change, if applicable. This test is intended for use with CCSRs and other materials formed under conditions of high temperature. The long-term nature of the test allows the determination of changes in concentrations of leached constituents as materials react with water to form secondary hydrated phases and other materials not present in the original material.
- 4.2 This test method is not intended to provide an accurate means of determining actual leachate concentrations under field conditions. The test does provide information about leaching under field conditions, however, and is useful in predicting the mobility of leachable constituents of CCSRs. The information provided from this test is an estimation of the mass of analyte that can be solubilized and trend of concentration change with respect to time. It should be noted that not all analytes will increase in concentration to an equilibrium level. Numerous elements, especially those trace elements that exist as oxyanions in aqueous solution, can exhibit a decrease in solution concentration after an initial and normally rapid increase in concentration. Additionally, major constituents can change solution concentration in a manner that would not be predicted on the basis of solubility calculations based on common mineral types, especially in CCSRs that form ettringite.
- 4.3 Since CCSRs are produced under conditions of high temperature, reactions with water during leaching can be expected. If these reactions produce ettringite, the concentrations of analytes present in solution as oxyanions can be expected to decrease with respect to time as ettringite forms. Other mineral formation can be expected to control leachate concentrations of additional analytes in ways not expected from simple solubility calculations based on the composition of ash before leaching. Additionally, the formation of secondary hydrated phases can be expected to affect the concentrations of major components.

5. Apparatus

- 5.1 For a complete description of the apparatus, see ASTM Standard Test Method for Shake Extraction of Solid Waste with Water. Any apparatus that can provide conditions of end-over-end agitation at 30 plus or minus 2 rpm as specified in the protocol for the TCLP can be used in this procedure.

6. Reagents

- 6.1 Purity of Reagents – Reagent-grade chemicals can be used, provided they do not contain appreciable amounts of elements to be determined in the extraction test. Reagents must be of sufficient purity so they do not interfere with the accuracy of the test or introduce bias in the results of analyses of leachates.
- 6.2 Purity of Water – Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water at 18° to 27°C (Specification D1193). The method by which the Type IV water is prepared (distillation, ion exchange, reverse osmosis, etc.) should remain constant throughout the test.
- 6.3 Synthetic Groundwater – Synthetic groundwater is a leaching solution containing the major geochemical parameters important to groundwater likely to contact disposed CCSRs. As previously stated, in the case of CCSRs disposed above the water table and where the likely water to contact the disposed materials is rainwater, Type IV water can be used as the leaching solution. Where the water likely to contact disposed material is highly mineralized, either a sample of the water itself or a synthetic mixture prepared in the lab will be used. A typical North Dakota synthetic groundwater can be prepared by dissolving 0.50 grams of sodium sulfate and 1.00 grams of sodium bicarbonate in one liter of Type IV water. The analysis of this solution is as follows:

Na	436 mg/L
SO ₄	338 mg/L
HCO ₃	726 mg/L
pH	8.3–8.7

This sodium sulfate bicarbonate buffered water is typical for central and western North Dakota. Used for leaching low-rank coal ash, calcium was omitted since the ash itself ultimately determined the final calcium concentration.

Other formulas for synthetic groundwater can be prepared as needed for site-specific conditions. Care is required when preparing formulations containing calcium and magnesium that carbonates not be allowed to precipitate. This can be overcome by adding the reagents in the proper order, being certain that all carbonate is buffered to bicarbonate before adding the calcium and magnesium. Since sulfuric acid is used for sulfate and acid buffering, having excess sulfuric acid acidity will ensure this. A Lotus spreadsheet is available for the calculations necessary to select reagents for synthetic groundwater formulations, but with the limited components, the calculations can also be easily carried out manually.

7. Sampling

8. Sample Preparation

8.1 For sample preparation, see D3987 Standard Test Method for Shake Extraction of Solid Waste with Water.

9. Procedure

The laboratory protocol is similar to the U.S. Environmental Protection Agency (EPA) TCLP and ASTM D3987 Standard Test Method for Shake Extraction of Solid Waste with Water. The primary difference is in the selection and preparation of the extraction fluid and the extension of test equilibration time over the prescribed 18-hour period. The long-term leaching aspect of this test is especially important since CSSRs can form secondary hydrated phases upon contact with water that can have a profound impact on leachate concentration of trace elements, especially elements that tend to exist as oxyanions in solution. The formation of secondary hydrated phases is known to take time, depending on the source of reactants in the leaching system. Time for complete formation of secondary hydrated phases can be from days to months. The test is not intended to carry the leaching to complete equilibrium but rather to extend the leaching time long enough for prediction of leachate concentration trends. For specifics related to the test, see D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, or EPA Method 1311 TCLP, Federal Register, Vol 55, No. 126, June 29, 1990.

9.1 Record the physical description of the sample to be tested including particle size as known.

9.2 Solids Content – Determine the solids content of the sample as described in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Sections 9.2.1 through 9.2.4.

9.3 Shake Procedure – Prepare the apparatus and begin the test as described in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Sections 9.4 through 9.7, except that multiple shake test containers are prepared for each sample, the number depending on the duration of long-term leaching. Leaching solution shall be prepared as described in the following section. Long-term leaching intervals for this procedure are 18 hours, 1 week, 1 month, and 2 months. Longer times can be used if desired, although trends are usually identified within the 60-day duration of this long-term leaching procedure. An alternative to the use of 2 liters of leaching solution involves the use of 225-mL polysulfone bottles. To each bottle, 10 grams (dry weight) of ash is added along with 200 mL of leaching solution. Multiple bottles prepared in this

manner provide at least 150 mL of leachate and allow for the simultaneous extraction of a large number of samples with minimal space and equipment. It has been found that the standard equipment used for TCLP leaching will generally hold four of the polysulfone containers in the same position usually reserved for one 2-liter container.

- 9.4 Preparation of Leaching Solution: Leaching solution shall be prepared as recommended by an evaluation of field conditions. Where material disposed in a monofill is above the water table, the leaching solution shall be Type IV water (D1193 Specification for Reagent Water). Where the disposed material will likely be contacted by groundwater, either a sample of groundwater from the site or a synthetic groundwater shall be used for leaching. The synthetic groundwater if prepared in the lab shall contain all of the primary mineralization parameters as determined from an analysis of groundwater from the site or from an evaluation of data from analysis reports of water representative of the area of disposal.
- 9.5 Long-Term Leaching Sampling – Long-term samples are taken from containers prepared for the shake test in an identical manner to the specimen for the 18-hour sampling period. These containers are sampled at the end of 1 week, 1 month, and 2 months. Longer sampling intervals can be added as required. A convenient method for doing this procedure is to prepare the samples at time intervals so that all of the samples are finished at the same time. For example, one sample is prepared, a second is prepared 1 month later, a third sample 1 month later, and a final sample 18 hours before the other samples are due to be terminated. This saves considerable lab time and expedites the entire procedure.
- 9.6 Sampling of Leachate – Leachate is sampled for analysis as specified in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Section 9.8.
- 9.7 Analysis
 - 9.7.1 Selection of Analytes to Be Included in the Report. Analytes include all elements present in the ash in high enough concentrations to be problematic in disposal. These can be determined through screening procedures such as proton-induced x-ray emission (PIXE), instrumental neutron activation analysis (INAA), or plasma emission such as inductively coupled argon plasma (ICAP) spectroscopy or ICAP–mass spectrometry. Analytes for ash screening generally include the eight Resource Conservation and Recovery Act (RCRA) elements for regulatory purposes.
 - 9.7.2 Determination of Total Concentration of Select Analytes. Analytes selected on the basis of screening (9.6.1) are determined on a bulk sample prepared by digestion of sample in a microwave heated-sealed Teflon bomb. Analyses can be performed according to methods for trace analyses in SW846.
 - 9.7.3 Determination of Analyte Concentrations in Leachates. Concentrations of analytes in leachates shall be determined using methods as described in SW846 or by approved analytical techniques using EPA or other approved techniques.

All data shall be validated using good laboratory practice and approved quality assurance/quality control (QA/QC) procedures.

10. Calculation

- 10.1 Calculate the solids content as specified in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Section 10.1.
- 10.2 Calculation of maximum analyte concentration is determined by dividing the total mass of analyte in a sample by the volume of liquid used for leaching. $C = M/V$ where
 - C = Concentration of analyte
 - M = Mass of sample leached
 - V = Volume of leaching solution used

For this procedure the M:V ratio should be 1:20 as specified in the leaching protocol.

11. Report

- 11.1 The report shall include the following:
 - 11.1.1 Source of CCSR, date of sampling, and preservation method used for leachates.
 - 11.1.2 Description of CCSR including coal source, combustion technique, and method of sample collection (electrostatic precipitator, baghouse, etc.)
 - 11.1.3 Solids content (see Method D2216)
 - 11.1.4 A table of maximum analyte concentrations as determined by the method described in Section 10.2. (bulk chemical analysis)
 - 11.1.5 A table of analyte concentrations as determined from analysis of 18-hour, 1-week, 1-month, 2-month, and any additional extended time intervals selected.

12. Precision and Bias

- 12.1 No information is presently available on the precision and accuracy or bias of this standard practice. It is recommended that standard QA/QC procedures such as analysis of duplicate samples and spiking of analyte be used for verification.
- 12.2 The precision of this test will vary depending on the material being leached.