

# EVALUATING COAL COMBUSTION BY-PRODUCTS (CCBs) FOR ENVIRONMENTAL PERFORMANCE

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## Abstract

Determining the environmental performance of CCBs is no small task and has long been investigated, scrutinized, and debated by groups interested in the environmentally safe management of CCBs. A regulatory perspective of this issue frequently requires some predetermined testing of CCBs based upon the designation of solid waste under RCRA (Resource Conservation and Recovery Act) Subtitle D. A variety of laboratory leaching methods have been developed and/or applied to CCBs. These include batch tests, column tests, and serial and sequential leaching tests, but few of these procedures are designed specifically for CCBs. Because the tests are not designed for use with CCBs, they do not account for several typical reactions in CCBs under hydration. It has long been known that laboratory leaching procedures cannot precisely simulate field conditions nor predict field leachate concentrations. However, with careful application of scientifically valid laboratory procedures, it is possible to improve laboratory-field correlations and modeling efforts focused on predicting field leachate concentrations.

The CCB industry needs to develop a selection of laboratory leaching procedures that more closely simulate field management scenarios. These procedures need to follow guidelines raised by the U.S. Environmental Protection Agency (EPA) in its recent reevaluation of waste characterization. It is anticipated that a limited number of procedures can be identified and selected to accomplish goals for various management options. Some of the technical/scientific variables that need to be addressed for different scenarios are:

- Long-term hydration reactions that can impact leachate concentrations of several constituents of interest.
- The means by which water contacts the CCB in order to simulate the reduced permeability frequently exhibited in CCB utilization applications.
- Impact of pH and other CCB properties on the leachate and resultant leaching.
- Prediction of, and changes in, leaching over time.

A discussion of these issues is intended to initiate an industrywide evaluation of the use of laboratory evaluations to predict environmental performance of CCBs in mine settings and in other management scenarios.

## EPA Leachate Methods

According to the U.S. Environmental Protection Agency (EPA), the following information relates to SW-846:

1. Any reliable analytical method may be used to generate the vast majority of environmental data for the Superfund and Resource Conservation and Recovery Act (RCRA) programs.
2. EPA regulations do not routinely restrict the choice of analytical methods to those published in SW-846.
3. The choice of methods other than SW-846 methods, or modifications of SW-846 methods, is encouraged to improve site-specific analytical performance.

This is good news to those who recognize the limitations of toxicity characteristic leaching procedure (TCLP) leaching when used to evaluate CCBs for potential for environmental impact.

The TCLP is often used in a generic manner for the prediction of leaching trends of wastes, although the intent of this test was for the prediction of leaching under co-disposal conditions in sanitary landfills. The application of acidic conditions to predict field leaching that can occur under a wide range of conditions may lead to false prediction of leaching trends. Additionally, conditions imposed on leaching systems by inappropriate leaching solutions may alter the distribution of redox species that would be found in the field and, in some cases with reactive wastes, 18 hours, as specified in the TCLP and other short-term leaching tests, may be an insufficient equilibration time. In order for a batch leaching test to be useful in determining potential for environmental impact, several

qualities must be embodied by the protocol:

1. The test must be relevant with respect to providing both scientifically and legally defensible data.
2. The test must be relatively easy to conduct.
3. When being used with CCBs, the test must take into account the unique properties of the material, especially the hydration reactions of alkaline CCBs.

## **Synthetic Groundwater Leaching Procedure (SGLP)**

A generic test of leachability, the synthetic groundwater leaching procedure (SGLP), with a long-term leaching (LTL) procedure, developed at the Energy and Environmental Research Center (EERC) at the University of North Dakota, has been used for nearly 20 years to predict leaching of coal combustion residues and other similar solid waste materials under field conditions (Hassett, D.J., 1987; 1997). Specific uses have included characterization of coal ash disposed of in monofills and prediction of mobility of selenium in mined areas. In many applications, this test has demonstrated trends significantly different from TCLP and other commonly used leaching protocols. In the case of coal ash, the trends indicated for leaching by the SGLP show very different trends than the TCLP. These differences can be explained by the fact that many commonly used leaching tests impose conditions different from those in a field environment on samples and, thus, bias data in a manner leading to inappropriate interpretation for environmental impact. Elements most often affected include arsenic, boron, chromium, vanadium, and selenium.

### **Long-Term Leaching**

Long-term leaching using the LTL procedure, which is an extended-time SGLP, is used for waste materials after disposal that may undergo hydration reactions upon contact with water. The implication for the usefulness of these tests is magnified by the increase in reactive wastes that will be produced using advanced combustion systems to comply with the Clean Air Act. These materials, which are almost always reactive, behave much differently under field conditions than would be predicted using the TCLP or other short-term leaching procedures. At the present time, the SGLP test, along with long-term leaching, has been used in a number of States, including Minnesota, North Dakota, and Indiana, for determination of environmental impacts of coal conversion solids. The test has been written up in draft form for consideration by the American Society for Testing and Materials (ASTM) as a standard for leaching of coal ash.

Since many CCBs are reactive materials that become chemically altered upon contact with water, leaching tests must be based on an experimental protocol that takes this into account. Appropriate leaching must include long-term contact between water and ash to allow chemical and mineralogical changes to take place. The inappropriate or premature removal of leachate constituents must be absolutely avoided. Sequential batch and column leaching often remove potentially reactive constituents from ash-water systems and, although appropriate for other uses, will provide misleading information when applied to CCBs. Static, long-term batch leaching most appropriately mimics natural conditions of ash disposal with water infiltration since fly ash typically becomes relatively impermeable upon contact with water. The use of a batch leaching test where ash-water equilibrate for up to 30 or 60 days allows for the formation of important secondary hydrated phases such as ettringite and promotes equilibrium conditions with respect to environmentally important major, minor, and trace elements. Because of the importance of hydration reactions, interpretation of the potential for environmental impact should be based upon the longest-term leaching test results.

### **Liquid-to-Solid Ratio**

The SGLP is appropriate for the screening of ash for potential environmental impact. The liquid-to-solid ratio, at 20:1, is the same as specified in the EPA TCLP and has a scientific basis for determining hazardousness. As with the TCLP, end-over-end agitation is used; however, the leaching solution in the SGLP is dependent on local conditions at the disposal location and also determined by the solution most likely to contact the waste material. Solutions that have been used include: synthetic acid precipitation, distilled deionized water, and groundwater either from the site or prepared in the laboratory based on groundwater analyses from the disposal site. Although not perfect, this type of batch leaching test is, for the present time, what is being used and is considered by many to be adequate, perhaps even conservative. Arguments have been made for alternative tests. Although arguments can be made for the use of these alternative tests, they are usually made in the absence of an understanding of the

fundamental nature and chemistry of CCBs. For this reason, arguments that may appear reasonable may, in the broader context of ash hydration mechanisms and ash chemistry, be fundamentally flawed and provide misleading information if used to predict the environmental impacts of CCBs.

The proposed test is intended to provide a true indication of leachability of ash constituents based on a current state-of-the-art understanding of ash chemistry, mineralogy, and hydration reactions. Certain chemical reactions can occur when ash and water are mixed, which are referred to as hydration reactions. Although the common understanding of hydration is usually limited to incorporation of water, the term is used in this document in a broader sense to refer to all reactions, including incorporation of water, that ash undergoes when contacted by water, either as groundwater or rain infiltration. Although the simple introduction of water does not ensure that leachate will be generated, it can be assumed that in the case of reactive ash, there will be chemical reactions (ash-ash interactions) forming, what are generally referred to as, secondary hydrated phases.

### **Ettringite Formation**

The most notable of these hydrated phases is ettringite. Ettringite is a mineral with 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. Ettringite formation can result in the chemical incorporation of trace elements that exist as oxyanions in aqueous solution. These include, but are not limited to arsenic, boron, chromium, molybdenum, selenium, and vanadium. In the incorporation of these trace elements into ettringite, the trace element is substituted for the sulfate in the nominal structure. Thus, true chemical fixation is the most important removal mechanism, although sorption of arsenic species has been reported in the literature.

The general conditions that allow for ettringite formation are the presence of soluble aluminum, calcium, and sulfate and a source of alkalinity. A pH environment of between about 11 and 12.5 is most favorable, although ettringite has been known to form in pH environments below these limits. Since calcium, aluminum, and sulfate are involved in ettringite formation, it is not uncommon to see reductions in the solution concentrations of these constituents as ettringite forms. Further, ettringite consists of more than 38 percent water. Thus, ettringite formation is often accompanied by an apparent drying of the material in which it is forming. Ettringite formation can occur over several hours or can take months, depending on the availability of the essential constituents required for synthesis. The solubility of calcium, aluminum, and sulfate is highly variable between ash types. The rates of solubility can vary between the three constituents. This means that the rate of formation of ettringite is difficult to predict from a simple chemical analysis of the ash and will generally be related to the rate of availability of one limiting constituent.

In areas with high-sulfate groundwater, cases have been documented where infiltration of natural waters through CCBs has resulted in an improvement of water quality.

### **Estimation of Leachate Mobility**

The SGLP provides data that can be used for the estimation of mass of analyte that can be mobilized in short-term and long-term field leaching scenarios. Additionally, this test can predict analyte concentration evolution, meaning in higher concentrations approaching an equilibrium concentration or decreasing concentrations leading to equilibrium concentrations that will be lower than predicted by a short-term batch leaching test. Column leaching tests are generally not applicable to the leaching of potentially reactive wastes described above. In column tests, flow through the waste can deplete readily mobilized constituents, several of which, including aluminum, calcium, and sulfate, are necessary for ettringite formation. In addition to potentially minimizing the formation of secondary hydrated phases, column tests are often run at artificially high flow rates. A measurable flow is necessary for a laboratory test in order to generate sufficient leachate for analysis. In many ash monofills, the compacted ash can have a lower hydraulic conductivity than surrounding sediments.

## **Summary**

The information presented above has described a leaching method suitable for use with alkaline CCBs or other reactive alkaline finely divided materials. The method described will generate legally and scientifically defensible data for the evaluation of CCBs for potential environmental impacts. While there are few researchers who rely on TCLP leaching to determine potential environmental impacts of CCBs, some regulatory agencies still routinely mandate this test. Because of the importance of the potential implications related to the disposal of up to

100 million tons of material each year, the significance of generating scientifically and legally defensible data cannot be overemphasized.

## References

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David J. Hassett is a Senior Research Advisor at the Energy and Environmental Research Center (EERC) of the University of North Dakota. He also serves as the Fuels Analyst for the State of North Dakota. He has authored or coauthored more than 200 publications and holds a patent entitled “Enhanced Ettringite Formation for the Treatment of Hazardous Liquid Wastes, U.S. Patent 5,547,588.” He is presently involved in several research projects. His principal areas of interest and expertise include the application of analytical chemistry to address environmental issues associated with trace element occurrence, transport, and fate; coal combustion by-product management; groundwater quality; and air quality. The most recent research focus has been on trace element transformations during coal conversion processes and interaction between groundwater and coal conversion solids as related to the leachability of trace elements. Additional areas of expertise include hydration reactions of coal conversion solid residues as well as organic synthesis, radiochemistry, x-ray spectrometry, analytical chemistry, and vegetable oil diesel fuels. In 1985, he presented his research on vegetable oil diesel fuels as a member of a People to People Biomass Utilization Delegation to the People’s Republic of China and, in 1998, was an invited keynote speaker at the 15th Conference on Clay Mineralogy and Petrology held in Brno in the Czech Republic. He has laboratory experience with infrared spectroscopy, gas chromatography, neutron activation analysis, atomic spectroscopy (atomic absorption and inductively coupled argon plasma), thin-layer chromatography, ultraviolet and fluorescence analysis, x-ray fluorescence spectroscopy, nuclear magnetic resonance spectroscopy, ion chromatography, laser spectroscopy, and capillary electrophoresis. He holds a B.S. in Chemistry and Mathematics from Winona State University in Minnesota.

Debra F. Pflughoeft-Hassett is a Research Manager in Residuals Research at the Energy and Environmental Research Center (EERC) of the University of North Dakota. Her principal areas of interest and expertise include utilization and characterization of coal combustion by-products (CCBs), waste management, and environmental impacts of CCB use and disposal. She has worked on the development of databases containing characterization information on CCBs and on the development of chemical characterization protocols. She has expertise in applying analytical chemistry, mineralogical and geological data, and engineering testing to demonstrations and field projects utilizing CCBs. She has participated extensively as an investigator on research investigations of CCB characterization, groundwater contamination, sediment attenuation, leaching characterization, and chemical fixation of trace elements. She participates as a principal researcher and project manager on several investigations of the characterization, utilization, and disposal of CCBs and currently manages the research effort of the Coal Ash Resources Research Consortium (CARRC) and other CCB research at the EERC. She is the director of the Western Region of the Combustion By-Products Recycling Consortium and is a member of several professional organizations, including: the North Dakota Academy of Science; represents the EERC in the American Coal Ash Association; and the American Society for Testing and Materials Committee on Environmental Assessment. She serves on the steering committee for the U.S. Department of the Interior Office of Surface Mining Coal Combustion By-Product Information Network and participates in the U.S. Environmental Protection Agency’s Mine Fill Research and Analysis/Modeling (MRAM) Project. In addition, she has coauthored more than 60 publications. She received her B.S. in Chemistry from the University of North Dakota in 1982.