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Fuel 84 (2005) 1378–1383
FUEL
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Leaching of CCBs: observations from over 25 years of research

David J. Hassett*, Debra F. Pflughoeft-Hassett, Loreal V. Heebink

Energy & Environmental Research Center, University of North Dakota, 15 North 23rd Street, Grand Forks, ND 58203, USA

Received 19 November 2003; received in revised form 13 October 2004; accepted 13 October 2004
Available online 15 December 2004

Abstract

Leaching of coal combustion by-products (CCBs) using various batch laboratory methods has been ongoing at the Energy & Environmental Research Center for over 25 years. Early on in the various investigations involving leaching it became obvious that the methods being advocated and used were generating scientifically invalid and often misleading data. This realization came about because:

1. The wrong leaching solutions were often being used. Methods such as the extraction procedure toxicity test and, later, the toxic characteristic leaching procedure used an acetic acid-containing solution that would be unlikely to contact CCBs under any conditions.
2. It was found that the formation of secondary hydrated phases such as ettringite could have a profound influence on concentrations of certain trace elements that exist as oxyanions in aqueous solution.

Because of these realizations, a method that included long-term leaching (LTL) was developed called the synthetic groundwater leaching procedure, which addressed many of the problems with existing methods.

Data collected over the last 25 years will be presented to demonstrate the need for the use of proper leaching solutions and LTL. Additionally, currently utilized and proposed methods will be discussed, including the new suite of leaching methods recently proposed by the US Environmental Protection Agency.

Keywords: Leaching; Synthetic groundwater leaching procedure (SGLP); Coal combustion by-products (CCBs)

1. Introduction

Even following the US Environmental Protection Agency (EPA) determination to place coal combustion by-products (CCBs) under Resource Conservation and Recovery Act (RCRA) Subtitle D for solid wastes [1], CCB generators are frequently asked to provide information on the environmental performance of CCBs that are being either disposed of or utilized. 'What leaching test should I use?' is the question that should be asked before proceeding to answer this request. In some instances, the leaching protocol to be used is mandated or recommended by the requesting party, but that should not preclude the generation of valid data, and this may require a dialogue with the requesting party. In order to have a focused and productive dialogue, an understanding of available procedures is useful.

An extensive effort to assemble information on available leaching procedures was performed by Sorini [2] for the American Coal Ash Association in 1997. More than 60 procedures were summarized, and many of these were not recommended specifically for CCBs. The listing does not answer the question of what leaching procedure to use. Recently, EPA proposed a leaching method for evaluating CCBs based on its interest in CCBs that may be affected by mercury emission controls [3]. The extensive method proposed by EPA brought the question of which leaching method to use for CCBs back to the forefront for the CCB industry.

The Energy & Environmental Research Center (EERC) believes that the question is not as difficult to answer

* Corresponding author. Tel.: +1 701 777 5192; fax: +1 701 777 5181.
E-mail address: dhassett@undeerc.org (D.J. Hassett).

0016-2361/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.fuel.2004.10.016

as might be suggested by the long list of available leaching methods or by the recently proposed EPA method. For a leaching test to be used to determine the potential for environmental impact of coal combustion ash and stand up to legal and scientific scrutiny, a series of criteria must be met:

1. The test must take into account any reactivity or unusual properties of the material being leached.
2. The test must as closely as possible utilize a leaching solution that mimics the leaching solution most likely to contact the material in a natural disposal setting.
3. If the ash is reactive with water, the test must take this into account by allowing the hydration reactions to occur during the course of the leaching test. This necessitates the use of long-term leaching (LTL).

It has been demonstrated that when water contacts alkaline ash, a primary hydration product is the mineral ettringite [4,5]. This result is consistent throughout 25+ years of laboratory investigations at the EERC. At times, this mineral may exhibit poor crystallinity, but it always forms. Ettringite, which is a calcium aluminate sulfate hydroxide hydrate with the nominal composition [$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$], can substitute other oxyanions for sulfate during formation [5–7]. Ettringite requires sources of calcium, aluminum, sulfate, excess water, and high pH (>11) in order to form. Variations in these requirements may play a role in the level of crystallinity of the ettringite formed. Oxyanions shown to participate in the ettringite formation include those of arsenic, boron, chromium, molybdenum, selenium, and vanadium. As a result of incorporating these elements into the ettringite structure, decreases in solution concentration of these elements can be observed. Since the time of the development of the synthetic groundwater leaching procedure (SGLP) and LTL, numerous types of CCBs have been subjected to leaching characterization, and results indicated that LTL provides significant added data only for reactive CCBs [8–11]. Short-term leaching is adequate for evaluating CCBs with pH<9 and low calcium concentrations.

A discussion of the toxicity characteristic leaching procedure (TCLP) is warranted as it is the leaching procedure most often requested. It is often requested because it was designed by EPA and is mandated for use in determining hazardousness of materials [12]. In fact, it was designed for use in determining hazardousness for materials to be disposed of in a municipal landfill where acetic acid and acetate ion are typically generated by bacterial action in municipal waste. Some CCBs are disposed of in municipal landfills, but the high volumes generated by utilities are generally not disposed of in municipal landfills. Ideally, utility-generated CCBs are utilized, but even those requiring disposal are generally placed in dedicated facilities. The criteria of selecting a leaching solution that has relevancy to the CCB management scenario rule out the acetic acid and acetate buffer used for TCLP for most CCBs. The EERC initiated the use of a synthetic groundwater solution for laboratory leaching based on the studies focused on mine placement of CCBs. The EERC also employed distilled deionized water, synthetic precipitation [13], and other synthetic solutions based on the specific management of the CCB of interest.

There are, of course, some experimental variables of leaching for which no answers have been discovered:

1. Determining the proper liquid-to-solid ratio.
2. Determining the maximum required equilibration time for LTL tests.

Virtually any reasonable liquid-to-solid ratio can be used. In the EERC lab, a 20:1 liquid-to-solid ratio is most commonly utilized because this ratio generally allows for the determination of actual concentrations of most trace elements and because it also allows comparison to TCLP leaching, for which a large base of data is available and with which many regulatory agencies are familiar. Research currently under way has indicated that the liquid-to-solid ratio may not be as important as once thought, especially for trace elements.

The maximum equilibration time for LTL could be an extremely long duration for some CCBs. It is well known that concrete can take up to years to reach its maximum strength. Some of the same hydration reactions are responsible for concrete strength development as for the reduced leaching of some CCB constituents. A leaching duration of years is impractical for most purposes. The EERC proposes that long-term experiments include a time series of up to 3 months and that the resulting data be interpreted relative to the short-term leaching (18 h) and at least two long-term data points. An evaluation of the resulting trend is part of the data interpretation. Field evaluation of high-calcium CCBs shows ettringite present in disposed masses for up to 10 years following placement [14,15].

Understanding the information that can be ascertained from laboratory leaching is important. A laboratory leaching method can only be used to determine a few specific elements of leaching, but these are extremely important and, if properly utilized, can provide information on which responsible CCB management decisions can be made, as listed below:

1. The mass of easily mobilized trace elements can be determined using a leaching test with a short equilibration time.
2. A comparison of bulk concentrations of elements with their leachate concentrations provides a means of estimating how various elements will be mobilized with respect to time.
3. The evolution of leachate concentrations can be determined with multiequilibration time LTL.

Laboratory leaching cannot provide an estimation of the concentration of elements in leachates under natural