

# Leaching of CCBs: Observations from Over 25 Years of Research

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## ABSTRACT

Leaching of coal combustion by-products (CCBs) using various batch laboratory methods has been ongoing at the Energy & Environmental Research Center (EERC) for over 27 years. It became apparent early in EERC work that the methods being advocated and used were generating scientifically invalid and often misleading data. The EERC identified the inappropriate use of acetic acid in leaching solutions for CCBs understanding that CCBs would be unlikely to contact acetic acid under typical management conditions. Agreement by numerous research groups and government agencies that the use of acetic acid-based leaching solution is not appropriate for CCBs has led to many questions regarding what leaching methods are appropriate. Work at the EERC identified formation of specific secondary hydrated phases in alkaline CCBs, and it was determined that formation of these hydrated phases had a demonstrated influence on concentrations of certain trace elements in leachate. As a result of these observations, the EERC developed the SGLP (synthetic groundwater leaching procedure), including long-term leaching (LTL), to address discrepancies with existing methods. Data collected over the last 25 years are presented to demonstrate the need for the use of proper leaching solutions and LTL.

## INTRODUCTION

Even following the U.S. Environmental Protection Agency (EPA) determination to place coal combustion by-products (CCBs) under Resource Conservation and Recovery Act (RCRA) Subtitle D for solid wastes,<sup>1</sup> 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<sup>2</sup> 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.<sup>3</sup> The extensive method proposed by EPA brought the question of which leaching method to use for CCBs back to the fore front for the CCB industry. The EERC believes that the question is not as difficult to answer 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.<sup>4,5</sup> This result is consistent throughout 25+ years of laboratory investigations at the Energy & Environmental Research Center (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  $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26 \text{H}_2\text{O}]$ , can substitute other oxyanions for sulfate during formation.<sup>5-7</sup> 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. The EERC developed a leaching method to allow the use of synthetic groundwater and longer leaching times. These tests came to be known as the synthetic groundwater leaching procedure (SGLP) and LTL.<sup>8-11</sup> These tests have been used to evaluate numerous types of CCBs, and results indicated that the LTL provides significant added data only for reactive CCBs.<sup>8</sup> Short-term leaching is adequate for evaluating CCBs with pH <9 and low calcium concentrations, unless they are stabilized with calcium compounds or otherwise combined with calcium-based materials.

Even though it is generally agreed that the toxicity characteristic leaching procedure (TCLP) is not appropriate for use with CCBs, its use continues because it is still requested by some states or industry groups. It is often requested because it was designed by EPA and generally understood to be mandated for use in determining hazardousness of materials.<sup>12</sup> In fact, it was mandated for use in determining hazardousness for materials to be disposed of in a municipal landfill where acetic acid and acetate buffer are typically generated by 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 for selecting a leaching solution that has relevancy to the CCB management scenario rules 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,<sup>13</sup> 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 responsible for concrete strength development are also responsible 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 hours) 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.<sup>14,15</sup>

Understanding the information that can be ascertained from laboratory leaching is important. A laboratory leaching method can only be used to determine a few important 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 conditions with any high degree of accuracy. This, however, is not as limiting as it might seem for several reasons. First, the concentration of chemical constituents under natural leaching conditions will be a product of several factors that are not easily duplicated in laboratory leaching: rate of flow through the leached material and rate of flow around the mass of leached material, assuming that there is a flow of water through and around the individual site. In properly engineered disposal or utilization sites, this should not be the case. Assuming, however, that there is flow in and around the material, simple modeling using known flow rates can be used to determine likely field concentrations under natural groundwater flow conditions. Since flow in many natural settings is extremely slow ( $10^{-5}$ – $10^{-7}$  cm/sec), it is impractical to use laboratory column leaching tests to determine potential for environmental impact of reactive alkaline CCBs. Column leaching could be used and supported both legally and scientifically if the flow rate through the column were slow enough to allow for the formation of secondary hydrated phases, but since this takes months or longer, a flow rate that low through a 50–100-cm column is too slow to be practical. The problem with faster flow rates is that individual components required for secondary hydrated phase formation are washed away before reactions can occur. Ettringite formation requires the presence of alkalinity, soluble calcium, aluminum, and a source of suitable oxyanion such as sulfate. Since these must be leached from the ash, and since the leaching and dissolution rates are different for each of the elements, a relatively high water flow would be expected to wash away critical parameters necessary for ettringite formation.

While focusing on the SGLP with LTL as a test that meets the criteria for a scientifically valid and legally defensible method, the EERC does not intend to minimize the usefulness of other leaching methods in scientific study. Rather, any leaching test that meets the three conditions stated above and that can stand up to legal and scientific scrutiny should be considered a useful test. However, a more exhaustive leaching procedure is not the measure of an appropriate method nor is a method designed to totally remove all CCB components more likely to provide improved data.

## EXPERIMENTAL

The SGLP batch leaching procedure is a relatively simple test that follows many of the conditions of the TCLP procedure.<sup>12</sup> The test utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, 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 ash, or distilled deionized water. For the long-term component of this procedure, multiple bottles are set up and analyzed at different time intervals. A

typical SGLP and LTL test might consist of 18-hour, 30-day, and 60-day equilibration times. Although 60 days is often not long enough to have achieved 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.

## RESULTS AND DISCUSSION

Over the last nearly 28 years, researchers at the EERC have leached a large number of varying CCBs, initially using the more common standard tests. EP-TOX<sup>16</sup> leaching was done during the first year or two. It was apparent from the beginning that this method had several weaknesses including the method of shaking and the incremental addition of the required acid. As a result, EERC researchers initiated an effort to identify a more appropriate methodology with a focus on high-calcium alkaline CCBs. Simultaneously, research on ash hydration reactions was being performed in parallel efforts. The two studies intersected suddenly with the realization that ettringite was the primary hydration phase that was always seen during the reaction of alkaline ash with water. It was observed that upon continued equilibration several trace elements that existed as oxyanions in aqueous solution began to decrease in concentration. These trace elements, which included arsenic, boron, chromium, molybdenum, selenium, and vanadium, all exhibited what the EERC refers to as anomalous leaching behavior. These elements increased in concentration initially but then decreased in the 30-day and 60-day equilibration periods. This behavior was not completely predictable but was shown to be closely related to the formation of the mineral ettringite.

The first example of anomalous leaching that was observed in our laboratory was seen about 25 years ago in a first-time LTL experiment. We noticed a decrease in boron concentration in a reanalysis of a large-scale leaching experiment done after about 21 days. Seeing this initial decrease in the concentration of boron and several other elements, we decided to continue the experiment and did so for over 550 days. It was eventually determined that the loss in boron concentration could be correlated specifically to an increase in the concentration of the mineral ettringite. The results of this LTL procedure for boron are shown in Figure 1.

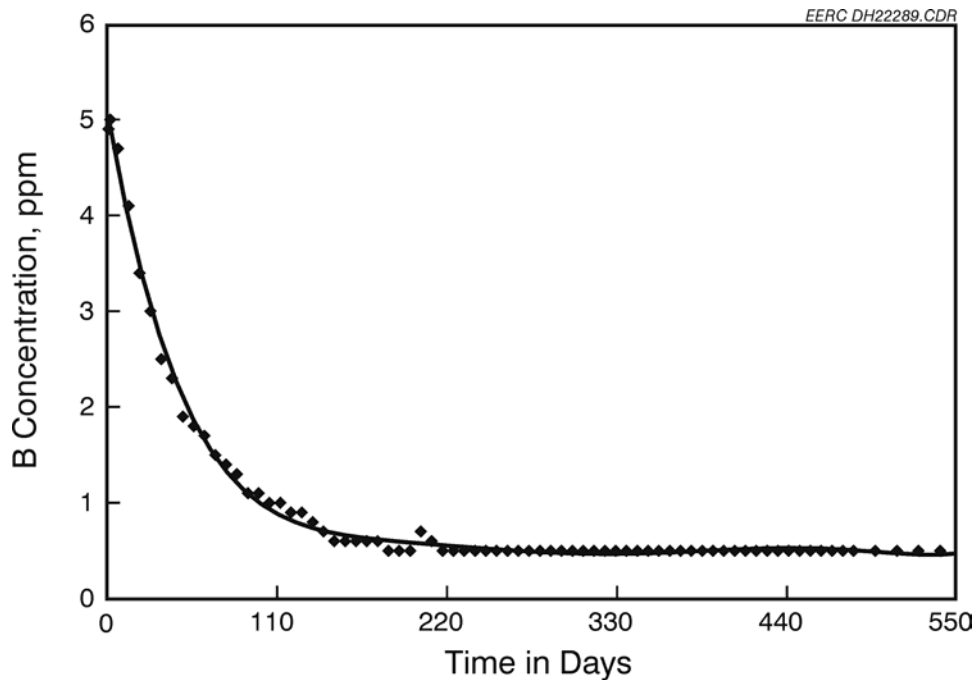


Figure 1. Long-term leaching results for boron.

Boron was one of several elements that showed a decrease in concentration over time. Other elements that also exhibited decreasing trends in concentration were arsenic, chromium, selenium and sulfate, calcium, and aluminum. Following these experiments, EERC researchers discovered the presence of ettringite in the leached solids through the use of x-ray diffraction, and the formation of ettringite was hypothesized to play a role in reducing the leachate concentrations of these elements.

Following leaching experiments were generally conducted using LTL after this trend of decreasing concentration was observed. Further examples of anomalous leaching are shown in Figures 2–3. Additional features are indicated in these figures: “max” and “RCRA”. Max represents the maximum concentration that could be achieved with complete dissolution of the CCB or element of interest, and RCRA is the appropriate RCRA standard. These values are included for ease of interpretation.

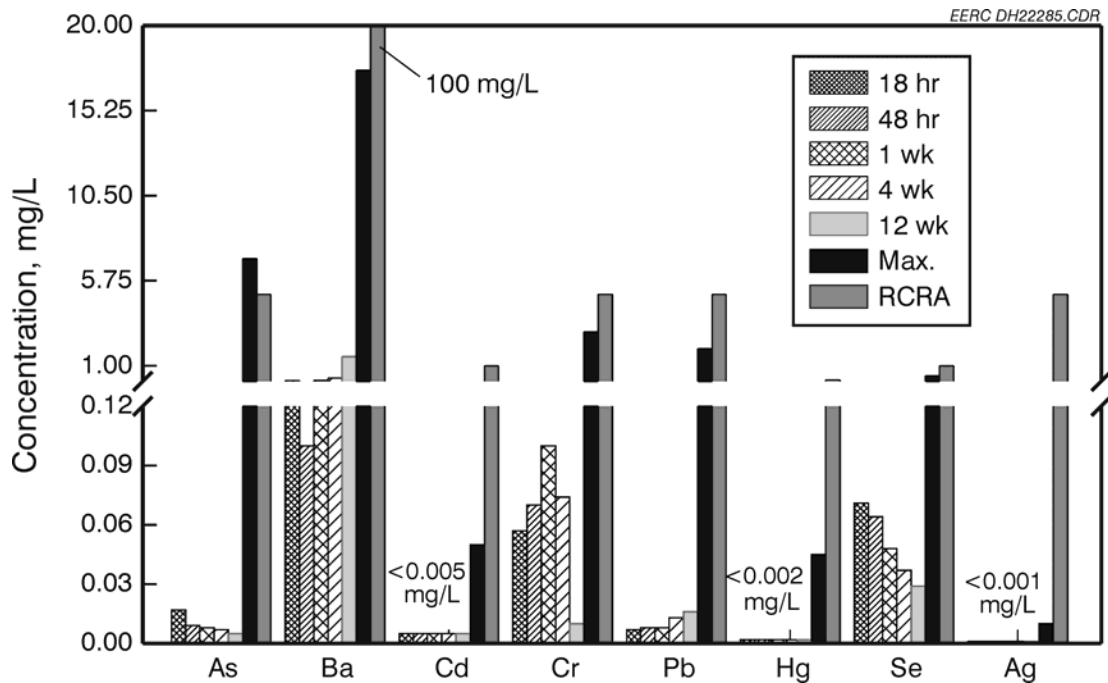


Figure 2. Anomalous and normal leaching of alkaline fly ash.

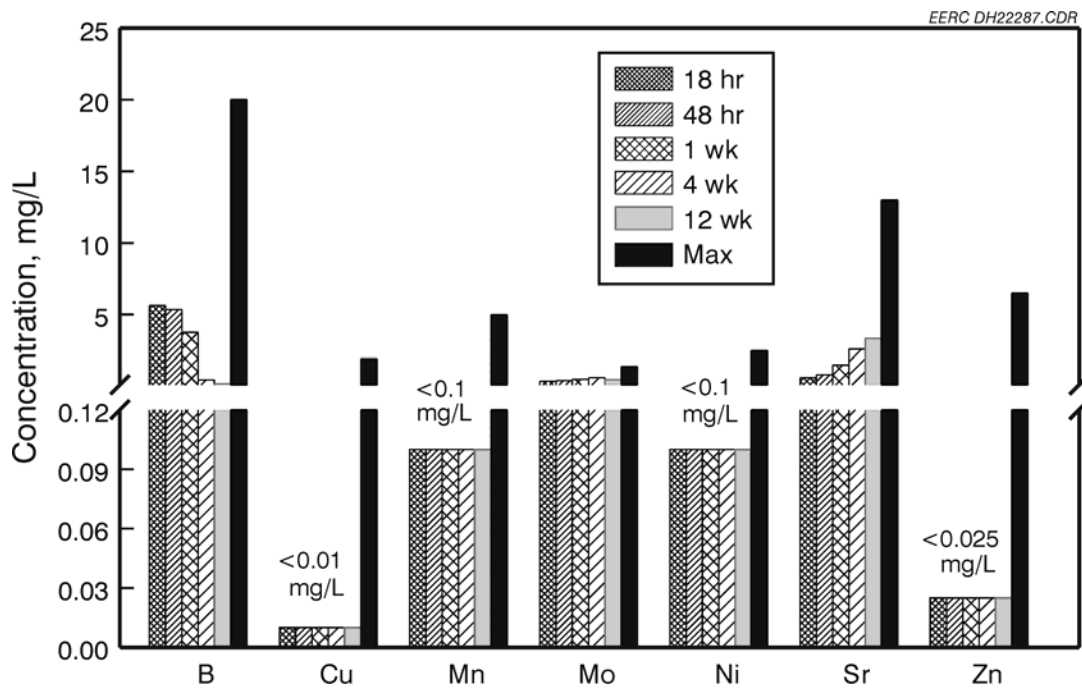


Figure 3. Anomalous and normal leaching.

It can be seen in Figure 2 that lead is really the only detectable RCRA element that exhibits a leaching profile one would normally expect, with increasing concentrations over time. Arsenic and selenium show trends of decreasing concentrations with respect to time while chromium appears to be decreasing at 12 weeks of equilibration time. It is

known that a selectivity series exists among the oxyanionic trace elements that can form substituted ettringites. This may be, in part, the explanation for the trend seen for chromium in Figure 2. Several factors complicate the explanation and interpretation of leaching results associated with ettringite formation. First, the building blocks of ettringite, which are calcium, aluminum, sulfate or other suitable oxyanion, and alkalinity, available differentially as CCBs slowly dissolve and leach their various constituents. Second, not all oxyanionic constituents can form completely substituted ettringites. Arsenic is an example of an oxyanion that is too large to fit into the spaces available for oxyanions in the ettringite crystal. Arsenic can form terminal bonds and is also one of the trace elements that can sorb onto already-formed ettringite.

Leaching results for a duct injection sample are shown in Figure 3. The sample is a bituminous ash into which alkaline calcium-based material has been injected. The bituminous ash alone does not have the required composition to form ettringite, but the added alkalinity and calcium provide the missing components needed for ettringite formation. Anomalous leaching can be seen for boron in this example.

The final example of leaching data (Figure 4) shows that acidic leaching with TCLP solutions is not always a worst-case scenario. Molybdenum leaches at over twice that of either of the two TCLP solutions. In the case of this presentation of data, the trend from left to right with SGLP, TCLP #1, and TCLP #2 leaching is from the use of a neutral distilled deionized water leaching (SGLP), to increasing strengths of acetic acid in TCLP #1 and TCLP #2.

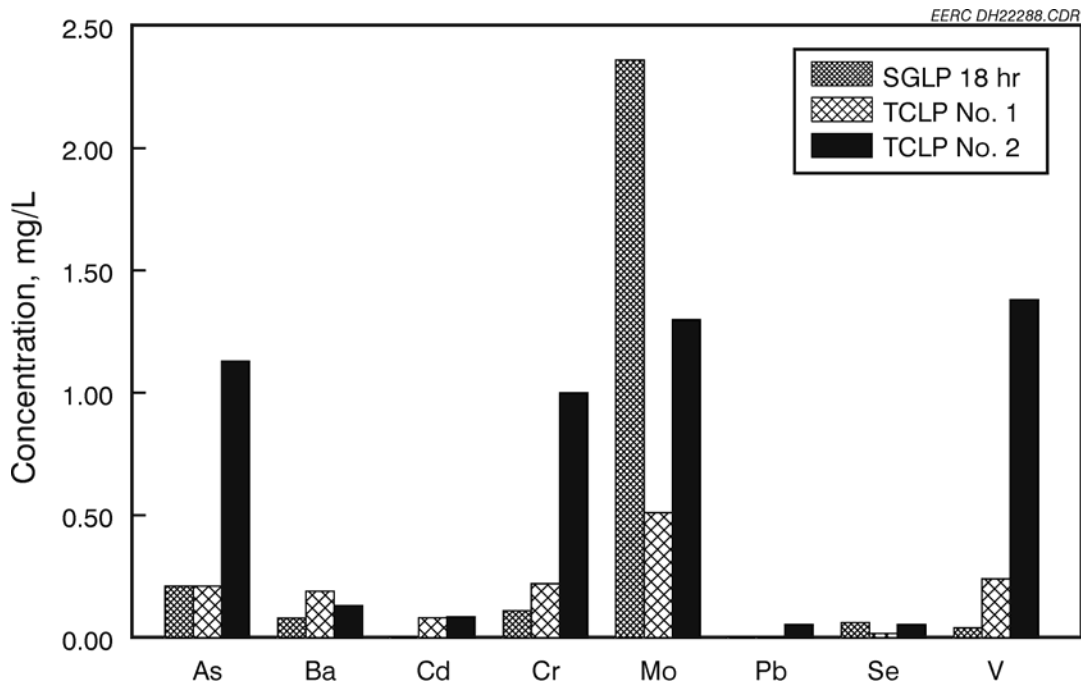


Figure 4. TCLP vs. SGLP leaching of a bituminous fly ash.



## CONCLUSIONS

The debate over which method, or methods, is appropriate for characterizing environmental performance of CCBs has not ended, but a useful dialogue has finally been initiated. Rather than drawing traditional conclusions, we would like to set out the questions that need to be answered in this dialogue, which must include government, industry, and scientists:

- 1) What is the objective of a CCB leaching method? If it is to predict elemental concentrations of potentially affected waters based on releases from CCBs, we do not believe this is an achievable objective. We submit that the objective should be to obtain leachate data that can be readily replicated in reasonable times and procedures, using a leaching solution relevant to a wide range of situations. The data should then be compared with a predetermined standard. Numerous examples of predetermined standards can be found in state regulation of CCB utilization. Experience can aid in developing this standard, which will be protective of surface and groundwater.
- 2) How should candidate methods be evaluated?
- 3) How is a consistent methodology and interpretation instituted?
- 4) How can research be used in developing appropriate methods, and where is research needed?

The EERC looks forward to continuing participation in the dialogue on environmental characterization of CCBs. The issue of accepting the environmental appropriateness of CCBs for utilization options needs to be resolved by all stakeholders in order to work jointly toward increased CCB utilization.

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