Effects of Large-Scale CCB Applications on Groundwater

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Coal combustion byproducts (CCBs) in surface and deep coal mines have the potential to affect the environment slowly but permanently. For neutralizing acid mine drainage (AMD), CCBs have distinct advantages, including their availability, alkalinity, and pozzolonic activity. As such, CCBs have been used to fill mine voids and strip pits, encapsulate acidic materials in backfills, cap reclaimed surface mines, and neutralize acidic impoundments.

Nearly all CCB uses at mine sites have a single purpose, to eliminate or reduce acidic drainage from the site. All CCBs contain elements, some of them of environmental significance, which may leach into groundwater. The potential for leaching depends on the chemical composition of the

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CCB, the chemistry of the water in contact with the CCB, and because CCBs dissolve to neutralize acidity, the amount of contact time.

However, there have been few studies conducted to show the effects of CCBs on groundwater chemistry. It may take decades to exhaust the alkalinity of CCBs and to observe any adverse effects of CCBs on the environment. Therefore, it is essential that we have accurate, cost-effective methods to characterize metal leaching potential of CCBs, particularly when they are to be placed in AMD.

**The Mine Water Leaching Procedure (MWLP)**

There have been several methods proposed to determine the metal leaching potential of CCBs. These have used one or more complexing agents, and/or various concentrations of sulfuric, hydrochloric or nitric acids. While valuable, these approaches ignore any potential effects, positive or negative, of other components of AMD that may affect metals leaching from CCBs.

The mine water leaching procedure (MWLP) was developed specifically to account for the effects of AMD on metal leaching. It aims to quantify the time-dependent concentrations of metals leached from a specific ash when in contact with a specific AMD. The MWLP procedure continues until all alkalinity has been exhausted from the CCB.

The objectives of this research were to identify cases where CCBs had been placed in mine environments and summarize their effects on subsequent water quality, and to use the MWLP to characterize metal release from specific CCB-AMD combinations.

**AMD/CCB Exhaustion Study**

The MWLP was used with the modification that less CCB was added (Simmons et al., 2001). Other CCB leaching characterization procedures have used 0.5M acetic acid (Flemming et al., 1996), water (Dreesen et al., 1977; Querol, et al., 2001), simulated AMD (Bhumbla et al., 1996; Morgan et al., 1997), citric acid, hydrochloric acid, ammonium hydroxide or various concentrations of nitric acid (Dreesen et al., 1977). The MWLP is the only procedure that matches CCB with the specific mine water it is expected to be in contact with in the environment.

A known amount of each CCB and 2 L of either AMD or distilled, deionized water (DDIW) was added to labeled, acid-washed containers. All CCBs were used as received. Containers were sealed and then agitated for 18 hours at 30 rpm on a rotating platform.

Samples were collected after every 18-hour agitation cycle. Container contents were filtered through 0.7µ, acid-rinsed TCLP filter paper using a stainless steel pressure filtration unit at or below 40 psi. Solids were rinsed back into corresponding containers with additional AMD, and the agitation cycle repeated until alkalinity was exhausted from the CCB. CCB alkalinity exhaustion was indicated when filtrate pH was equal (or nearly equal) to initial AMD pH.

Two filtrate samples were collected in 250-mL bottles. One was acidified for inorganic constituents (Sb, As, B, Ba, Be, Cd, Cr, Pb, Hg, Se, Ag, Cu, Ni, Ti, V, Zn, Mo, Fe, Mn, Al, Ca, Mg, and sulfate). An unacidified sample was analyzed for pH, alkalinity, and acidity. Inorganic constituents were determined in initial AMD and after selected agitation cycles using U.S. Environmental Protection Agency (EPA)-approved methods in EPA-certified commercial laboratories.

AMD treatments were replicated twice. A DDIW control was included for all treatments at least once. Solid CCB samples were digested at 95° C on a block digester in concentrated HNO₃ and the inorganic constituents determined as described above.

MWLPs 2 and 5 had the same AMD source and were used to test the effect of ash source on inorganic constituent concentrations by analysis of variance (ANOVA) using MWLP cycle and ash source as categorical variables. MWLPs 1 and 3 had the same ash source, as did MWLPs 4a and 4b and so were used to test the effect of AMD source on inorganic constituent concentrations by ANOVA using MWLP cycle and AMD source as categorical variables.

Because the number of MWLP cycles was variable, only the first and last cycles were included in this analysis. AMD source was a categorical variable and means in the two cycles were separated using Scheffe’s Test.
Case Studies/Literature Review

Available case studies on field applications of CCBs were summarized for CCB use—noting whether there was a CCB analysis, pre- and post-CCB use water quality, monitoring time, elements of concern not measured, and whether the application was considered a success. Reports from conference proceedings and peer-reviewed literature were included.

Conclusions

Although most researchers considered their use of CCBs in mine environments a success, only one long-term study could be found, and in no study was water quality followed to CCB alkalinity exhaustion. Also, some elements known to be of concern during the initial phases of CCB dissolution (B, Mo, Se, As) and others identified in this study (Sb, Cr, Pb, T, Be, Cd) were not measured in some studies.

In laboratory tests (MWLP procedure) CCBs in contact with distilled, deionized water (DDIW) water was alkaline, at least pH 7.1, but more typically above pH 9 and sometimes as high as pH 11.7. Elements of concern in the DI water control samples include Sb, Cr, Pb, Tl, Be and Cd, all of which exceeded drinking water standards in at least one MWLP.

Other elements present in the DDIW water treatment at relatively high concentrations include As and B. The highest observed As concentration was 0.022, which exceeds the 2006 As standard of 0.010 mg L\(^{-1}\). The highest observed B concentration was 2.71 mg L\(^{-1}\). Boron is frequently observed at elevated concentrations in CCB leachates, but the metals Cd, Pb and Cr are not typically thought of as problems in high pH waters. However, in all cases, Cd, Pb and Cr concentrations were below their hydroxide solubility product minima, indicating that pH dependent precipitation as metal hydroxides was not controlling solution phase concentrations.

When CCBs were in contact with AMD, at alkalinity exhaustion some elements decreased in concentration and some increased in concentration, compared to the initial AMD water quality. Trace elements that decreased in concentration but still exceeded drinking water standards included Ni, Be and Cu. Those elements of concern that increased in concentration, indicating that the ash was a net source for these elements, included Mn, Cr, Pb, Ni and Cd. Nickel concentrations in solution at alkalinity exhaustion exceeded drinking water standards in all seven MWLPs; Cr and Pb exceeded drinking water standards in 3 MWLPs.

There were statistically significant effects from AMD source on MWLP results when the same CCBs were used, but the results were not consistent for each element. CCBs could be a source or a sink for B, Pb and Zn, depending on the specific CCB-AMD combination.

During the course of the MWLP procedure, Mn, Ni, Zn, Pb, Cu, Be, Cr and Cu concentrations increased in at least one CCB-AMD combination. A separate laboratory experiment indicated that CCBs could be a source of Zn, Cu and Ni at alkalinity exhaustion in solutions with low initial iron concentrations, but could remain a sink for these elements in solutions with high initial iron concentrations.

These results indicate that, as expected, at alkalinity exhaustion CCBs can release metals to solution. This suggests that careful planning and monitoring are necessary to prevent alkalinity exhaustion. When leachates were very alkaline (in contact with DDIW), elements such as B, Mn, Zn and Pb were present in leachates, sometimes in excess of drinking water standards. Further study of the geochemical controls on metal availability when CCBs are in contact with circumneutral water, including groundwater, is needed. It is suggested that CCBs not be placed in close proximity to primary drinking water supplies, especially where CCBs are not likely to contact AMD.
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Because metals release depends on the specific CCB-AMD combination, this work suggests that CCBs should be tested for their potentials to release metals under the specific conditions where they are to be placed.

References


For more information about this project, including the complete project report, please visit the CBRC Web site at http://wwwri.nrcce.wvu.edu/cbrc, or contact Louis McDonald at lmcdona4@wvu.edu.
Calendar of Events

March 2–3, 2005
Western Coal Power Project Development
Embassy Suites Downtown Denver, Denver, Colorado
Sponsored by Infocast

Contact Hiedy Vitug
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Fax (818) 888-4440
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www.infocastinc.com/coal.html

April 11–15
World of Coal Ash
Lexington Center’s Heritage Hall
Lexington, Kentucky

Contact Gretchen Tremoulet
(859) 257-0355
gtremoulet@caer.uky.edu
or Michael MacDonald
(720) 870-7897
info@acaa-usa.org

May 18–20, 2005
Spring Coal Conference
Scottsdale Plaza Resort, Scottsdale, AZ
Sponsored by the American Coal Council (ACC)

Contact: Janet Gellici, Executive Director, ACC, Pheonix, AZ
(602) 485-4737, Fax (602) 485-4847
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www.americancoalcouncil.org

May 18–20, 2005
Coal-Gen 2005, Revival of the Fittest,
San Antonio, Texas
Presented by PennWell

Contact: Registration Department
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