DOE/MC/28060-96/C0558

Chemistry, Mineralogy, and Artificial Weathering of PFBC By-Products

Authors:

R.K. Fowler  
U.I. Soto  
J.M. Bigham

Contractor:

Dravo Lime Company  
Research Center  
3600 Neville Road  
Pittsburgh, PA  15225

Contract Number:

DE-FC21-91MC28060

Conference Title:

12th Annual Pittsburgh Coal Conference

Conference Location:

Pittsburgh, Pennsylvania

Conference Dates:

September 12-15, 1995

Conference Sponsor:

University of Pittsburgh and American Coal Foundation

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.
DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.
CHEMISTRY, MINERALOGY AND ARTIFICIAL WEATHERING OF PFBC BY-PRODUCTS

R.K. FOWLER, U.I. SOTO, AND J.M. BIGHAM
School of Natural Resources
2021 Coffey Road
The Ohio State University
Columbus, OH 43210, U.S.A.

ABSTRACT

Chemical and mineralogical analyses were performed on spent bed residues and cyclone ashes acquired from the TIDD pressurized fluidized bed combustion (PFBC) demonstration plant operated by American Electric Power in Brilliant, OH. The cyclone ashes were composed of fly ash, dolomite, anhydrite, periclase, and calcite in decreasing order of abundance. By comparison, bed residues contained less dolomite and fly ash but more anhydrite, calcite and periclase. All samples were highly alkaline with paste pH values ranging from 9.9 to 12.3. The major element chemistry of the by-products was dominated by Ca, Mg, S, Fe, Al and Si. All materials met the criteria for ceiling concentrations of Cd, Cr, Cu, Pb, Mo, Ni, Se and Zn as defined for land application of sewage sludges. Arsenic exceeded the ceiling level in one of six samples.

An artificial weathering study was conducted to evaluate the impact of PFBC by-products on water quality in mined land reclamation. The study was performed using two mine spoils (pH 3.8 and 5.6) mixed with cyclone ash at rates of 0, 10, 20 and 40 wt % by-product. The composition of leachates from the mixtures was mostly a function of rate of by-product application and equilibration time. In general, the addition of PFBC by-product increased pH, conductivity, and the concentrations of dissolved Ca, K, Mg, Mo, Na, S, and Sr whereas the concentrations of Al, Fe, and Mn decreased. Six metals (Ag, As, Ba, Cd, Cr, and Pb) regulated by the Resource Conservation Recovery Act were below concentration levels defined for drinking water standards. No significant alteration of native spoil minerals was observed over the course of the study; however, hydration/precipitation reactions resulted in the rapid formation of gypsum. No evidence of ettringite crystallization was available after 132 days of periodic leaching.

INTRODUCTION

The 1990 amendments to the Clean Air Act and the U.S. DOE Clean Coal Technology program have stimulated much interest in coal combustion techniques that are both commercially viable and environmentally acceptable. In PFBC systems, a calcium based sorbent (usually limestone or dolomite) and crushed coal are introduced into a boiler bed where they are "fluidized" or suspended by jets of air. The resulting by-product streams include a heavy, granular bed ash material and a fine, cyclone ash that is suspended in the flue gases. Both materials contain reaction products and unspent sorbent as well as conventional fly ash. The specific composition of the by-product may vary depending upon the coal and sorbent properties and the plant operating conditions. Large quantities of dry FBC wastes may be produced in the near future [1], and it is important that beneficial uses be developed to reduce landfill demands. Recent studies have demonstrated clear potential for the use of such by-products in agriculture and horticulture [2]. In this investigation, characterization analyses and laboratory weathering experiments were designed to evaluate the potential impact of dry PFBC materials on water quality in mined land reclamation.
MATERIALS

Six samples of dry PFBC by-products, including three cyclone and three bed ash materials, were collected during 1991-1992 from a commercial demonstration facility operated by American Electric Power near Brilliant, OH. Following chemical and mineralogical characterization, one cyclone ash (PFBC-03) was chosen for an artificial weathering study involving mixtures of the ash with two different mine spoils from eastern OH. One spoil (Fleming) possessed a clay texture and a natural pH of 3.0. The other (R & F) was a silty clay loam with a native pH of 5.2. Both spoils were composed mostly of quartz, kaolinite, mica, and feldspars.

METHODS

By-Product Characterization Studies

A variety of chemical and mineralogical techniques were used to characterize the PFBC by-products. These methods are described elsewhere [3,4].

Laboratory Weathering Study

The two spoils selected for this study were blended with PFBC material (PFBC-03) to yield mixtures containing 0, 10, 20, and 40 wt. % by-product. Samples were placed into 60 mL polypropylene extraction tubes containing 2 g of polypropylene wool as a filter pulp [5]. All samples were periodically extracted with 50 mL deionized H2O over a 4-month period. The samples were stored at 25 °C and were left open to the atmosphere. The concentrations of elemental constituents released to solution were measured after each sampling event (1, 7, 14, 26, 62, and 132 days). Solid residues from the 40 wt. % rate were quick-frozen, freeze-dried, and analyzed by x-ray diffraction to determine the final mineralogical composition.

Elemental analysis of solutions for Al, Ag, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, S, Si, Sr, and Zn were conducted using inductively coupled plasma emission spectrometry with a Leeman PS2000 instrument. Anion (Cl-, SO3²⁻, and SO₄²⁻) analyses were performed on a Dionex 2000i ion chromatograph. Solution pH values were determined using a glass electrode.

X-ray diffraction (XRD) patterns were obtained from randomly oriented powder mounts using Cu Kα radiation and a Philips PW 1316/90 wide-range goniometer. Diffraction patterns were recorded from 15 to 60°2Θ with a step interval of 0.05°2Θ and a counting time of 4 sec per step.

RESULTS

By-product Characterization

Mineralogical analyses of the PFBC by-products showed that the cyclone ashes consisted primarily of fly ash, dolomite [CaMg(CO₃)₂], anhydrite (CaSO₄), periclase (MgO), and calcite (CaCO₃) (Table 1). By comparison, PFBC bed ashes contained less fly ash and dolomite but more calcite, anhydrite and periclase.
TABLE 1. Semiquantitative mineralogy of PFBC by-products†

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fly Ash</th>
<th>Calcite</th>
<th>Lime</th>
<th>Portlandite</th>
<th>Anhydrite</th>
<th>Dolomite</th>
<th>Periclase</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclone Ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFBC-01</td>
<td>33</td>
<td>9</td>
<td></td>
<td>20</td>
<td>31</td>
<td>11</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>PFBC-03</td>
<td>32</td>
<td>11</td>
<td></td>
<td>22</td>
<td>23</td>
<td>13</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>PFBC-06</td>
<td>40</td>
<td>13</td>
<td></td>
<td>22</td>
<td>17</td>
<td>18</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Bed Ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFBC-02</td>
<td>10</td>
<td>29</td>
<td>4</td>
<td>36</td>
<td></td>
<td>26</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>PFBC-04</td>
<td>10</td>
<td>27</td>
<td>3</td>
<td>1</td>
<td>36</td>
<td>27</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>PFBC-06</td>
<td>11</td>
<td>17</td>
<td>6</td>
<td>47</td>
<td></td>
<td>26</td>
<td>107</td>
<td></td>
</tr>
</tbody>
</table>

† Estimated by a combination of thermal, chemical and gasometric techniques [3].

The chemical composition of the PFBC samples was dominated by Ca, Mg, S, Fe, Al, and Si (Table 2). All samples were highly alkaline with paste pH values ranging from 9.9 to 12.3. The higher pH of the bed ashes can be attributed to the presence of reactive CaO and Ca(OH)₂ (Table 1). All by-products met the ceiling concentrations for Cd, Cr, Cu, Pb, Mo, Ni, Se, and Zn (data not shown) as defined for land application of sewage sludge. Arsenic exceeded the ceiling level in only one sample (PFBC-01). Although the geochemical forms of metals in sewage sludge are probably dissimilar to those in the PFBC by-products, the sludge guidelines provide a useful comparison.

TABLE 2 Chemistry of PFBC by-products

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Al</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclone Ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFBC-01</td>
<td>9.9</td>
<td>3.8</td>
<td>17.9</td>
<td>5.8</td>
<td>10.8</td>
<td>4.7</td>
<td>7.7</td>
</tr>
<tr>
<td>PFBC-03</td>
<td>10.5</td>
<td>3.3</td>
<td>16.7</td>
<td>5.0</td>
<td>9.8</td>
<td>4.7</td>
<td>6.7</td>
</tr>
<tr>
<td>PFBC-06</td>
<td>10.1</td>
<td>5.8</td>
<td>15.3</td>
<td>5.1</td>
<td>9.4</td>
<td>5.1</td>
<td>35.0</td>
</tr>
<tr>
<td>Bed Ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFBC-02</td>
<td>11.2</td>
<td>1.0</td>
<td>25.5</td>
<td>1.6</td>
<td>15.9</td>
<td>9.5</td>
<td>2.0</td>
</tr>
<tr>
<td>PFBC-04</td>
<td>12.2</td>
<td>2.8</td>
<td>24.1</td>
<td>2.0</td>
<td>16.2</td>
<td>8.2</td>
<td>2.1</td>
</tr>
<tr>
<td>PFBC-07</td>
<td>12.3</td>
<td>1.1</td>
<td>24.7</td>
<td>1.8</td>
<td>16.0</td>
<td>11.7</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Laboratory Weathering Study

Leachate composition was mostly a function of rate of PFBC application and equilibration time. All application rates increased the leachate pH significantly, and a pH of 7.8 or greater was maintained after 132 days (Fig. 1). The addition of PFBC by-product also increased the concentrations of dissolved Ca, K, Mg, Mo, Na, S, and Sr in the leachates (data not shown). In contrast, the concentrations of Al, Fe, and Mn decreased. Six metals (Ag, As, Ba, Cd, Cr, and Pb) regulated by the Resource Conservation Recovery Act were below concentration levels defined for drinking water standards (Hg and Se were not measured).

![Fig. 1. Effect of PFBC by-product on leachate pH after 132 days of incubation.](image)

Leachates from the PFBC amended spoils were dominated by Ca, S, and Mg. The concentrations of dissolved Ca and S were independent of spoil type; however, Mg concentrations were higher with the Fleming spoil (Fig. 2). This result may reflect the lower initial pH of the Fleming mixtures and the rapid dissolution of periclase in the by-product.

Mineralogy

The most significant mineralogical alteration observed in the PFBC-spoil mixtures involved the rapid formation of gypsum (CaSO\(_4\).2H\(_2\)O) through precipitation and/or hydration reactions. No further conversion of the gypsum to ettringite [Ca\(_6\)Al\(_2\)(SO\(_4\)).3(OH)\(_{12}\).26H\(_2\)O] or ettringite-like compounds was detected after 132 days.
Fig. 8 Effect of PFBC by-product additions on leachate Mg from mine spoils.
This conversion appears to require the presence of water and soluble Al at pHs between 11 and 12.5 [6]. Such conditions suggest that the "low" pHs of the PFBC-spoil mixtures probably inhibited ettringite formation.

CONCLUSIONS

The chemistry and mineralogy of the PFBC by-products examined in this study suggest they could be useful for a variety of agronomic, engineering, and reclamation applications without serious environmental concerns. However, specific applications should always be evaluated prior to utilization.

ACKNOWLEDGMENTS

This research was conducted as part of the "Land Application Uses for Dry CCT By-Products" project which is a cooperative research project of the Ohio Agricultural Research and Development Center, The Ohio State University, The U.S. Geological Survey and the Dravo Lime Company. Funding support for this project was obtained from the Ohio Coal Development Office (Columbus, OH), the U.S. Department of Energy Morgantown Energy Technology Center (Morgantown, WV), Dravo Lime Company (Pittsburgh, PA), Electric Power Research Institute (Palo Alto, CA), Ohio Edison Company (Akron, OH), American Electric Power Company (Columbus, OH), and The Ohio State University (Columbus and Wooster, OH).

REFERENCES


