TITLE: RESIDUES FROM COAL CONVERSION AND UTILIZATION:
ADVANCED MINERALOGICAL CHARACTERIZATION AND
DISPOSED BYPRODUCT DIAGENESIS

TYPE OF REPORT: Semiannual Technical Progress Report

REPORTING PERIOD START DATE: March 1, 1999

REPORTING PERIOD END DATE: August 31, 1999

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DATE REPORT ISSUED: January, 2000

GRANT NO.: DE-FG22-96PC96207--06

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Progress Report, January 11, 2000

DOE Contract DE-FG22-96PC96207

Goals and Objectives

The goal of the project is to learn more about the phenomenon of coal conversion byproduct (CCB) diagenesis, first described by our group and co-workers at UND EERC seven years ago. CCB diagenesis is a change in the mineralogy that occurs after some CCBs are disposed in a landfill or utilized for a civil engineering application. Regulatory environmental tests and civil engineering tests are typically performed on as-generated CCBs, or on CCBs hydrated and cured for relatively short periods such as 7 or 28 days. One would like to know whether the results of these short-term tests will be valid years later. A change in mineralogy means a gain, loss or chemical redistribution of major, minor and trace elements, and alteration of physical properties.

To attain this goal, two objectives were defined:

1. to develop improved methodology for quantitating mineralogy of these complex crystalline phase assemblages, and
2. to investigate the phenomenon of CCB diagenesis further by studying materials recovered from disposal landfills or civil engineering works.

The schedule listed in our 1995 proposal translates into the following dates when it was hoped that various tasks would be accomplished.

Objective 1. Hydrated CCBs are chemically and mineralogically complex, which makes quantitative mineralogy determination by conventional X-ray diffraction unusable or unreliable. The whole-pattern Rietveld quantitative X-ray diffraction (RQXRD) method, however, can overcome many of the problems and seems well suited to improve reliability. Two tasks were defined in the proposal:

Task 1. Completion by October 1997. *Prepare a reference set of CCBs for use in developing Rietveld QXRD. The reference materials will come primarily from in-house samples of advanced coal technology byproducts. The work will include SEM/EMPA characterization at UND EERC.*

Task 2. Completion by October 1997. *Develop protocols for Rietveld QXRD analysis of CCBs. Make CCB structure data and protocols available on a Website. Determine levels of sensitivity, precision, and accuracy.*

Objective 2. Five types of CCBs disposed in landfills were studied between 1989 and 1994. Diagenesis was observed in three of the five materials. To obtain a more generic understanding of CCB diagenesis, additional materials and different environmental settings need to be studied.

Task 3. Completion by end of project. *Apply RQXRD protocols developed in Task 2 to core samples of utilized or disposed CCBs from at least five additional sites. Use results to gain a better understanding of CCB diagenesis.*

Progress Status

Task 1.

SEM EPMA work at the EERC was just getting underway, and several days of work were scheduled during mid-April 1997 when the Grand Forks flood occurred. The instruments were lost, and their replacements were not available to the project until mid-1998. Samples that were to be used for the reference set of CCBs were stored on the EERC ground floor, and were also lost. Due to these losses, we will focus our efforts with the EERC SEM/EPMA subcontract for characterization of new samples collected during 1997 and 1998. Approximately half of the subcontract balance remains for this project, which will be performed in the Spring of 2000.

Task 2.

The website was established, and structure data have been available since the fall of 1997. We have developed RQXRD protocols that can deal with mixtures of a dozen or more CCB crystalline phases, and have tested them with standard mixtures. Developing protocols for using DOE's GSAS Rietveld code with these complex multiphase mixtures proved to be even more challenging than originally thought, and some aspects of the research are still in progress. RQXRD protocols have been developed, and analytical sensitivity, precision and accuracy have been determined using standard mixtures of NIST Standard Reference Materials (SRMs) and other CCB phases. They have been tested on a group of NIST SRM Fly Ashes, with surprising similarity to previous results by another method. This work was presented at two international conferences and published in three refereed journal articles. Relative error determined from the standard mixtures is currently in the 15% range (e.g., for a phase found to be 50 wt% of a CCB, the reported error would be $\pm 7.5\%$). Incremental improvements are anticipated prior to the completion of the project, especially when more is learned (from the SEM/EPMA work) about the chemical compositions of ettringite group phases and particle sizes. The protocols are in use now for characterization of CCB core samples. These improvements can be easily applied later by repeating the refinement of each computer archived sample data set with the improved input information.

Task 3.

CCB core materials have been recovered from four sites:

1. Landfill of FGD material from a Midwest utility burning subbituminous coal – up to 5 years old;
2. Landfill of a Class F fly ash from a utility in Kentucky burning bituminous coal [cooperative work with a consortium of entities headed by the USGS] – up to 20 years old;
3. Landfill of Class C fly ash and FGD material from a North Dakota utility burning lignite – up to 20 years old;
4. Road embankment in Indiana constructed with a mixture of CFBC and stoker ash materials – up to 5 years old.

Quantitative mineralogical analysis of retrieved CCB material from three of the four sites is now complete, and analysis of the (most complex) materials from the fourth site (Midwest FGD) is underway. A computer program has been written that filters the final results of most interest from the lengthy GSAS output files. This program has been used to tabulate the data from each borehole into spreadsheet format for detailed examination, which will be completed during the Spring of 2000. Since the previous report, results from this task have been presented at two regional and three international conferences, including a poster presentation which received an award.

Presentations and Publications to date

In print

- McCarthy, G.J., Butler, R.D., Grier, D.G., Adamek, S.D., Parks, J.A., and Foster, H.J., "Long-Term Stability of Disposed Coal Combustion Byproducts," *Fuel*, 76, 697-703 (1997).
- McCarthy, G.J., Grier, D.G., Winburn, R.S., "Coal Combustion Byproduct Diagenesis," in *Proc. Second Intern. Ash Utilization Symp.*, (Publ. by the Center for Applied Energy Research, Univ. of Kentucky, Lexington) 8 pp., October, 1997.
- Winburn, R.S., Lerach, S.L., Jarabek, B.R., Wisdom, M.A., Grier, D.G., and McCarthy, G.J. Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. Testing with Standard Mixtures. In *Advances in X-ray Analysis*, v42.
- Winburn, R.S., Lerach, S.L., McCarthy, G.J., Grier, D.G., and Cathcart, J.D. Quantification of Ferrite Spinel and Hematite in Fly Ash Magnetically Enriched Fractions. Accepted in *Advances in X-Ray Analysis*, v43.
- Winburn, R.S., Grier, D.G., McCarthy, G.J., and Peterson, R.B. Rietveld Quantitative X-Ray Diffraction Analysis of NIST Fly Ash Standard Reference Materials. Submitted to *Powder Diffraction*.

Oral presentations

- Winburn, R.S., Grier, D.G. and McCarthy, G.J., "Quantitative XRD Analysis of Coal Combustion By-products by the Rietveld Method," 1997 Denver Conference on Applications of X-Ray Analysis, Steamboat Springs, CO, August, 1997.
- McCarthy, G.J., Butler, R.D., Grier, D.G., Adamek, S.D., Parks, J.A., and Foster, H.J., "Long-Term Stability of Disposed Coal Combustion Byproducts," 1997 International Ash Utilization Symposium, Lexington, KY, October, 1997.
- McCarthy, G.J., Grier, D.G., Jarabek, B.R. and McCarthy, G.J. "Diagenesis of High-Sodium Lignite Combustion By-Products and Carbonation of Stored Samples Containing Ettringite," Fall Meeting of the Materials Research Society, Boston, MA, November 1997.
- Winburn, R.S., Lerach, S.L., Jarabek, B.R., Wisdom, M.A., Grier, D.G., and McCarthy, G.J. Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. Testing with Standard Mixtures. 1998 Denver Conference on Applications of X-Ray Analysis, Colorado Springs, CO, August, 1998.
- Winburn, R.S., Lerach, S.L., McCarthy, G.J., and Cathcart, J.D. Quantification of Ferrite Spinel and Hematite in Fly Ash Magnetically Enriched Fractions. 1999 Denver Conference on Applications of X-Ray Analysis, Steamboat Springs, CO, August, 1999.
- Grier, D.G., Wisdom, M.A., Lerach, S.L., Peterson, R.B., Walsh, J.J., Winburn, R.S., and McCarthy, G.J. Toward Improved Quantitative Analysis of Coal Combustion By-Products Through Rietveld QXRD. 1999 Denver Conference on Applications of X-Ray Analysis, Steamboat Springs, CO, August, 1999.
- Grier, D.G., Wisdom, M.A., Lerach, S.L., Peterson, R.B., Walsh, J.J., Winburn, R.S., and McCarthy, G.J. Coal Conversion Byproduct Diagenesis II. International Ash Utilization Symposium, Lexington, KY, October, 1999.
- Winburn, R.S., Grier, D.G., and McCarthy, G.J. Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. Materials Research Society Fall 1999 Meeting, Symposium GG. November, 1999.

Poster presentations

- Vilhauer, R.L., Jarabek, B.R., Grier, D.G., Winburn, R.S., and McCarthy, G.J. "A Study of Coal Combustion By-Products from Two Landfills Using Quantitative Rietveld Analysis," 215th Meeting, Am. Chem Soc., Dallas TX, March 1998.

Lerach, S.L., Wisdom, M., Grier, D.G., Winburn, R., and McCarthy, G.J. Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. REU Conference. Grand Forks, ND. July 31, 1998.

*Lerach, S.L., Wisdom, M., Grier, D.G., Winburn, R., and McCarthy, G.J. Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. Denver X-ray Conference. Colorado Springs, CO. August 3-7, 1998.

Lerach, S.L., Wisdom, M., McCarthy, G.J., Grier, D.G., Winburn, R., and Walsh, J.J. Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. American Chemical Society National Meeting. Anaheim, CA. March 20-25, 1999.

Lerach, S.L., Winburn, R.S., McCarthy, G.J., and Cathcart, J.D. Quantification of Fly Ash Magnetically Enriched Fractions. Denver Conference on Applications of X-Ray Analysis. Steamboat Springs, CO. August, 1999.

*Peterson, R.B., Wisdom, M.A., Lerach, S.L., Winburn, R.S., Grier, D.G., and McCarthy, G.J. Rietveld Quantitative X-Ray Diffraction Analysis of Landfilled North Dakota Class C Fly Ash. Denver Conference on Applications of X-Ray Analysis. Steamboat Springs, CO. August, 1999.

*Posters presented by undergraduate researchers at professional full poster sessions, which received awards.

Students Receiving Support from Grant

Dean G. Grier, candidate for M.S. in Soil Science, Research Assistant and Co-Principal Investigator.

Ryan S. Winburn, candidate for Ph.D. in Chemistry.

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