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: September 1, 1997

REPORTING PERIOD END DATE: February 28, 1998

PRINCIPLE AUTHOR(s): Gregory J. McCarthy, Dean G. Grier

DATE REPORT ISSUED: March, 1998

GRANT NO.: DE-FG22-96PC96207--04

INSTITUTION: Chemistry Department
North Dakota State University
Box 5516
Fargo, ND 58105-5516

Ph: (701) 231-7193
Fax: (701) 231-8831
gmccarth@prairie.nodak.edu
dgrier@plains.nodak.edu

Progress Report, March 31, 1998

DOE Contract DE-FG22-96PC96207

Goals and Tasks

The goals of the project are two-fold: 1) to upgrade semi-quantitative X-ray diffraction (QXRD) methods presently used in analyzing complex coal combustion by-product (CCB) systems, with the quantitative Rietveld method, and 2) to apply this method to a set of by-product materials that have been disposed or utilized for a long period (5 years or more) in contact with the natural environment, to further study the nature of CCB diagenesis.

The project is organized into three tasks to accomplish these two goals: 1) thorough characterization of a set of previously analyzed disposed by-product materials, 2) development of a set of CCB-specific protocols for Rietveld QXRD, and 3) characterization of an additional set of disposed CCB materials, including application of the protocols for Rietveld QXRD developed in Task 2.

Task 1

Task Description

Thorough characterization of a reference set of CCB materials is accomplished by chemical analysis of individual, identifiable mineral grains under scanning electron microscopy with electron probe microanalysis (SEM/EPMA). It serves as a known reference point for testing the Rietveld method for use with CCB systems (Task 2). Knowledge of crystalline phase composition is especially important for parameterization of solid solution stoichiometry dependence on Rietveld QXRD solutions, and for generating a generalized set of protocols to follow in the use of the Rietveld method with CCBs. Task I was to be completed during study year one, with SEM/EPMA training under the direction of Dave Brekke (at the University of North Dakota Energy & Environmental Research Center, UND-EERC). Setbacks due to severe flooding of the microscope facilities has delayed this task, which will be completed by the end of year two, and which is now under the direction of Kurt Eylands of UND-EERC.

Progress Toward Task 1

Characterization of the set of samples initially chosen and described in the previous reports has resumed, following full restoration of SEM/EPMA capabilities at UND-EERC. As mentioned previously, severe flooding of the facilities had destroyed these capabilities. Analysis is presently concentrated on ettringite-structure individual mineral grains from the dispersed mounts generated before the flooding. One sample has been thoroughly characterized in this regard, with 59 elemental point analysis having been taken. While these data were collected very recently, and have not been fully analyzed, one trend that emerged during the collection is that of chemical variation within ettringite-structure mineral grains along the length of the grains. The grains were found to all be prismatic, approximately 1.5 μm along the long axis, and approximately 1.0 μm along the short axis. Each had a high aluminum to silicon ratio towards the center of this

axis, with much more silicon (compared to aluminum) content toward the terminations. The terminations of the crystals were also noticeably wider than the centers. Additional prismatic crystals assumed by morphology and qualitative EPMA data to also be ettringite-structure phases were observed with much larger length to width ratios (nearly acicular in habit). These grains unfortunately were very narrow ($<0.5\ \mu\text{m}$). The elemental signal returned was too low for quantitation. Additionally, these grains had a tendency to decompose upon irradiation under the electron beam, presumably from the rapid expulsion of gases (primarily water) from the crystal structure.

Two of the originally chosen samples were also studied, and found to lack identifiable mineral grains with distinct crystal morphology, and thus were not extensively studied for quantitative elemental results. Distinct morphology is required to provide qualitative assessment of individual mineral grains. Without this assurance, it is possible to collect quantitative elemental data simultaneously from more than one mineral (in an aggregate, for example). This type is not useful for the purposes intended in this study.

Summary of Task 1

Progress:

Characterization of an initial set of previously analyzed CCB materials has resumed, including collection of a full set of high quality data for one of the seven initially chosen CCBs.

Future plans:

Characterization by SEM/EPMA of a reference set of CCBs will be completed by the end of year two. This characterization will be used in determining the errors associated with Rietveld analysis of CCB materials, and in setting guidelines for use of the Rietveld technique for CCBs based on these reference samples (part of the subject of Subtask 2 of Task 2). Once characterized, the reference set of CCBs will be stored frozen to eliminate, or at least minimize, alteration over time. Following analysis of the reference set, SEM/EPMA analysis will also be applied to representative specimens from each of the disposed materials recovered in Task 3.

Task 2

Task Description

Task 2 is composed of 3 major subtasks: 1) create a database of relevant phases, 2) develop a structured set of protocols for Rietveld QXRD analysis of CCBs, and 3) create a Web page to make this information accessible to the research community. Subtasks one and three have been discussed extensively in the previous report. This report will provide only recent developments in these areas.

Progress Toward Task 2

Subtask 1.

The database is essentially complete, with two minor exceptions. First is the inclusion of some additional less common phases, such as sodalite. These will be added

as experimental diffraction data from these minor CCB phases are generated. Second, despite initial screening and selection of crystal structures in the database, some of these structures have been found which are inappropriate. As a result, the database is constantly being re-examined to determine the applicability of the phases present to Rietveld analysis of CCBs. An example of this is the structure of magnetite that was originally present in the database, which was replaced with an alternate structure. The reason for this substitution was the original structure did not "fit" the experimental pattern well, and an alternate structure was found that yielded a better fit in the Rietveld refinements. This alternate structure has now replaced the original structure in the database.

Subtask 2.

The second step towards completing Task 2 is the development of a structured set of protocols for Rietveld QXRD analysis of CCBs. The object is to give occasional users a "set of rules" for using the Rietveld method for quantitative analysis of CCB materials and an estimate of the errors that can be expected when following those "rules." A set of standards has been developed to determine this protocol for Rietveld QXRD analysis of complex phases. This set of standards contains National Institute of Standards and Technologies (NIST) Standard Reference Materials (SRMs) and stable laboratory chemicals (such as hematite, Fe_2O_3 , and calcite, CaCO_3).

A standard protocol has been developed and is in the testing stage at the moment. The protocol was developed over the course of this study, being modified as necessary as new data has become available. The protocol is designed to give acceptable errors for quantitative analysis at a minimal cost in both computational time (the Rietveld refinement) and instrumental time (the collection of data). The protocol is currently being tested on mixtures ranging from two to nine phases (the limit of GSAS, General Structure Analysis System, a Rietveld program by Allen C. Larson and Robert B. Von Dreele, LANSCE, ms-h805, Los Alamos National Laboratory, Los Alamos, NM 87545, developed under U.S. Government contract W-7405-ENG-36), including an internal standard plus an amorphous phase. As mentioned earlier, the phases are either NIST SRMs or stable laboratory chemicals. These were chosen for their accessibility, stability and, in the case of the SRMs, previous thorough characterization.

In determining the standard protocol, many factors that will influence the success and accuracy of the refinement had to be addressed, including:

- amorphous content of the standard materials
- effects of structure, including thermal parameters, on accuracy
- determination of instrumental parameters
- preferred orientation
- choice of data acquisition parameters
- microabsorption effects
- choice of internal standard
- effect of amorphous content on the error propagation in Rietveld analysis
- effect of severe overlap on Rietveld analysis procedures

Many of these problems have been fully addressed, while others are still being examined to more completely understand their effects on the accuracy of the Rietveld refinements. These are addressed in fuller detail in the following section.

Amorphous content of the standard materials. Previous Rietveld QXRD studies using NIST SRM and other crystalline phase materials have typically assumed that each phase was 100% crystalline. However, the commonly used NIST Respirable Quartz SRM is known to be $4.5 \pm 1\%$ amorphous. In order to get a true estimate of the uncertainties associated with the Rietveld method, this amorphous content must be accounted for. However, the amorphous content of many of the SRM materials used during this project has not yet been determined. We then undertook an innovative study, which is still underway, of determining the amorphous content of each of the phases used in the test mixtures, and correcting the weight percentages to account for that amorphous content. The amorphous content is determined by Rietveld analysis of a two-phase mixture, the phase under investigation and an internal standard, rutile (TiO_2 , assumed 100% crystalline). The two phases are mixed in a 50:50 ratio and examined using our protocol. The amorphous content is then extracted from the results of the Rietveld refinement.

Effects of structure, including thermal parameters, on accuracy. The effects of the structure were thought to be straightforward from the outset of the project. The structure was assumed either right or wrong, with no middle ground. It appears, however, that there are shades of gray in this area. The structures are *critical* to doing a Rietveld analysis correctly. The necessary structure data are the space group, lattice parameters, atomic positions, site occupancies, and thermal parameters. Typically the choice is easy to make for the space group and lattice parameters of a compound, however, the last three variables often show minor differences between existing solved structures. The largest variation is commonly seen in the thermal parameters, if they are even included in the structure information. An example of this is silicon, NIST SRM 640b. The structure of silicon is simple and has been well known for a number of years. Unfortunately, this means there is no thermal parameter information available for the structure. A study on the effects of the choice of thermal parameters was undertaken. A nine phase mixture was studied that included silicon. Literature values of thermal parameters for eight of the phases were used, while the default value given by either GSAS or a commercial Rietveld program was used for silicon. The results were astounding with calculated weight percentages of silicon varying by 1.2% (9.4% in one case, 8.2% in the other), simply by choice of thermal parameter. This prompted us to be extremely careful when selecting the structure for a phase.

Originally, the structures were run through a commercial software package, which calculated a X-ray diffractogram from the structure data and the corresponding bond lengths and angles. The results of these calculations were then used to narrow the list of structures acceptable for use. The remaining structures were then examined to determine which was the "best" structure to date (R factor, the goodness of fit or factor of merit, being one of the most important categories in this decision). Due to the unexpected findings of the thermal parameter study mentioned above, each structure being used is now thoroughly examined during a Rietveld refinement. This is accomplished by closely comparing the calculated diffraction pattern to the experimental diffraction pattern. If

any discrepancies exist between the two patterns that cannot be accounted for by a known factor, such as preferred orientation, the structure is deemed inadequate for Rietveld analysis and a new structure is obtained and used in the analysis.

Determination of instrumental parameters. One of the most important recommendations that we are making is prior determination of instrumental parameters and peak profiles in order to lower the number of refinement parameters for Rietveld QXRD. This is done using a profile standard that has been certified by NIST, typically LaB₆ (SRM 660) or an alumina plate (Al₂O₃, SRM 1976). Our recommendation is to use the alumina plate, but the same procedure will hold true if the LaB₆ standard is used. The procedure for determining the instrumental parameters can be found on the Web site mentioned in Subtask 3. Once these instrument-dependent parameters are determined by Rietveld analysis, the majority are then fixed for the subsequent Rietveld analyses.

Preferred orientation. The effects of preferred orientation have been cursorily investigated over the course of this subtask. Preferred orientation is handled fairly well by the Rietveld method. GSAS offers two choices for correcting preferred orientation. One method uses the March model, the other uses spherical harmonics. Both methods work well for estimating the effect of preferred orientation. One should note, however, that the errors associated with a phase showing preferred orientation will typically be higher than other phases with comparable weight percentages, even after correction.

Choice of data acquisition parameters. As mentioned earlier, the goal of this subtask is to develop a protocol that minimizes both computational time *and* instrumental time. A study of the data acquisition parameters was also undertaken to minimize the instrumental time while maintaining an acceptable level of error. Three sets of data acquisition parameters were investigated:

- 20-100° 2 θ , 0.02° step size, 3 seconds count time per step: 3 hours 20 minutes
- 20-80° 2 θ , 0.02° step size, 3 seconds count time per step: 2 hours 30 minutes
- 20-80° 2 θ , 0.03° step size, 2 seconds count time per step: 1 hour 6 minutes

The results of this study indicate that the last set of acquisition parameters did not yield significantly greater errors.

Microabsorption effects. Microabsorption is also an important factor in QXRD. In CCB samples, this is especially important in mixtures containing iron-bearing phases. Microabsorption effects occur when a specimen contains phases that have linear absorption coefficients, μ , that differ greatly. An example of this is found with two common CCB phases, quartz (SiO₂) and hematite. Quartz has a linear absorption coefficient of 93 cm⁻¹ while that for hematite is 1153 cm⁻¹. This effect is also dependent on the particle size of the phases. A material with a large particle size will give a larger microabsorption effect than one with a small particle size (for a reference, 5 μ m is a large particle size, <1 μ m is typically small and will contribute little to the microabsorption effects). The internal standard of choice in our lab is rutile, which has a particle size of approximately 5 μ m after micronizing it for 30 minutes. Other possible internal

standards are alumina (SRM 676, 1-1.5 μm) and zincite (ZnO, SRM 674a, 0.5-1.0 μm). Thus rutile, our initial choice for internal standard, would be expected to show a large microabsorption effect. The effect of microabsorption on the results of a Rietveld refinement will be discussed in more detail in the next section. GSAS and the commercial code available to our lab at this time do not have a specific parameter to account for this type of microabsorption, so the calculations must be done post-refinement in a spreadsheet. However, there are commercial codes available that do take this into account in the Rietveld refinement. Our results thus far indicate that microabsorption *must* be accounted for in the quantitative analysis of any sample using the Rietveld method. If they are not, the results may be vastly different from their true values.

Choice of internal standard. Due to the large effect of microabsorption on the results of QXRD using the Rietveld method, and especially considering that our internal standard of choice has an average particle size that places it in the region of having a considerable microabsorption effect, different choices of internal standards were examined. As mentioned previously, the typical internal standards used in this lab are rutile, alumina, and zincite. In addition to the varying particle sizes, these phases also have a range of linear absorption coefficients. Rutile has a linear absorption coefficient of 594 cm^{-1} , alumina is 124 cm^{-1} and zincite is 288 cm^{-1} . Rutile was originally chosen for its small number of overlapping peaks and a linear absorption coefficient that falls between the iron-bearing phases and the other phases typically found in CCB materials. However, its larger particle size causes it to have substantial microabsorption effects. Alumina and zincite, while having linear absorption coefficients farther from that of the iron-bearing phases, have smaller particle sizes, thus minimizing the preferred orientation effects. A mixture of five phases was studied, plus the internal standard. The five phases were quartz (SiO_2), hematite ($\alpha\text{-Fe}_2\text{O}_3$), calcite (CaCO_3), periclase (MgO), and silicon (Si). The results of the study indicate that microabsorption effects *are* present in these samples. This can be noted by the decrease in the average relative error for the uncorrected versus the corrected dropping from 10.6% to 5.9%, a decrease of almost **one half**. The effect of particle size can also be noticed in the fact that the specimen with the zincite internal standard (smallest particle size) showed a decrease in the average relative error of only 2.3% while the specimen with the rutile internal standard (largest particle size) showed a decrease of 8.1%. The rutile internal standard yielded the largest errors when uncorrected for microabsorption effects, but the smallest errors when microabsorption corrections were taken into account. Thus, rutile is still the recommended internal standard, *providing* that the user does take into account microabsorption effects.

Effect of amorphous content on error propagation in Rietveld analysis. An investigation on the effect of error propagation due to amorphous content is currently under way. Samples have been made that contain only the amorphous content resident in the materials used to make the mixtures. These samples will be extensively studied in this form. An amount of amorphous material (silica gel) will then be added, typically between 35% and 90% of the resulting mixture. This new sample will then be

investigated to examine how the errors are affected by the addition of the amorphous material.

Effect of severe overlap on Rietveld analysis procedures. The final factor affecting the Rietveld analysis to be studied is the effect of severe peak overlap on QXRD analysis. Two separate systems are being investigated to evaluate this effect. The first is a mixture of quartz, magnetite (Fe_3O_4), hematite, and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). In this system, maghemite shows no significant peaks in the diffraction pattern that do not have overlap with one of the other phases present. This system is an extreme case and if the Rietveld method can yield accurate results, then the degree of overlap encountered in typical CCB analysis will not be a concern. The second system contains tricalcium aluminum oxide (C_3A , $\text{Ca}_3\text{Al}_2\text{O}_6$) and merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$). The problem of C_3A /merwinite overlap has been under investigation in CCB systems for some time, thus making it an ideal system to study for this work.

Summary of reference materials testing. Initial results from various two and four phase mixtures containing NIST SRM materials are quite promising, yielding results with an average absolute error (|weight percent of material added - calculated weight percent|) of 0.9% with a range of 0.1% to 2.0%. The relative error (absolute error/weight percent of material added) for the same samples had an average of 3.0% with a range of 0.6% to 7.0%. As mentioned above, these results were quite promising, with the highest relative errors corresponding to the phases represented by the lowest weight percentages in the samples (for example the phase having a 7.0% relative error had an absolute error of only 0.4%). The results for a system containing five phases plus a rutile internal standard are summarized in Table 1. The results were obtained using the protocol as it stands at the time of this report, including corrections for microabsorption. The internal standard, rutile, was added such that it was 10% of the final mixture. The particle sizes used for the microabsorption correction were 5 μm for rutile, 1 μm for periclase, 0.5 μm for quartz, hematite and silicon, and 0.25 μm for calcite. The results from these mixtures is quite promising, with all errors being under 10%. Assuming these errors will carry over to the CCB materials, this would be a significant improvement over the methods currently being used.

Table 1. Refined weight percentages, including microabsorption correction for a five phase mixture of reference materials, with rutile as the internal standard.

Phase	Reference crystalline ^a weight percents	Rietveld QXRD Weight Percents ^b	Relative Error ($\pm\%$)
Quartz	28.6	29.2	2.0
Hematite	30.1	31.5	4.5
Calcite	23.4	22.1	5.9
Periclase	9.7	10.5	8.3
Silicon	5.0	5.3	4.8

^a as measured into the mixture, corrected for amorphous content of each phase

^b normalized to the weight percent of the rutile internal standard, corrected to the weight percent of the phase in the sample without the internal standard, and corrected for microabsorption effects

Subtask 2 is proving to be the most time consuming of Task 2. Refinement protocols are being developed and most are in the final stages of testing. Many factors necessary for obtaining accurate results have been studied and must be accounted for when doing a Rietveld refinement. These protocols and short discussions of the factors dealt with during this study will be presented on the Web site when fully developed and understood.

Subtask 3.

As reported previously, the CCB Analysis Web Site is accessible at the URL <http://qxrd.chem.ndsu.nodak.edu/ccbs/>. The web site has been modified slightly to allow for simplified navigation among the various sections. A section that outlines any updates to the web site has been added to the web site. This section will allow repeat visitors to determine what has changed since their last visit without having to search through the entire site. In the near future, the web site will include our recommendations for test mixtures for "testing" the Rietveld method in a user's laboratory. Also to be included are our recommendations for refinement procedures for determining weight percents of crystalline phases and the amorphous content of CCB materials, as well as the errors expected when using each procedure.

Summary of Task 2

Subtask 1

Progress:

The database is essentially completed.

Future plans:

Structures must constantly be examined for their use in Rietveld analysis. Any structures that are found to be inadequate for Rietveld analysis will be replaced as necessary.

Subtask 2

Progress:

A suite of test mixtures is currently under investigation. The effects of overlap, thermal parameters, internal standard, and amorphous content are being thoroughly examined. Preliminary results on two, four, and six phase mixtures indicate that the Rietveld method shows promise for yielding errors that are significantly reduced compared to methods previously used for CCB materials. Many sources of error are being investigated, ranging from the choice of structure to microabsorption effects. These sources of error must be minimized to obtain accurate results.

Future plans:

Complete the analyses mentioned above. Using the experience obtained from these analyses, determine specific methodologies for obtaining desired results; i.e. weight percent of quartz, full quantitative analysis, and amorphous content. Determine the errors associated with each methodology. Include the determined methodologies on the CCB Analysis Web Site and their associated errors. Obtain powder patterns for previously

studied CCB samples with known composition and apply the previously determined methodologies to them.

Subtask 3

Progress:

A Web site is available and can be accessed to at any time. The address of the Web site is:

<http://qxrd.chem.ndsu.nodak.edu/ccbs/>

Future plans:

Site maintenance, including adding/updating links to the Web site, as necessary.

Task 3

Task Description

Task 3 involves study of an additional set of disposed CCBs, including SEM/EPMA and detailed qualitative XRD analysis, as well as Rietveld QXRD application, based on knowledge and protocols gained in Task 2.

Progress Toward Task 3

Three of the five disposed materials targeted for retrieval are in-house, and mineralogical analysis by XRPD is underway, following extensive delays in installation of the instrument being used. These materials are from 1) landfill of a Midwest utility burning Wyoming and Montana coals, and using dry process flue gas desulfurization. This material ranges in age from as much as five years old to recently deposited; 2) core material recovered from a road base embankment in Illinois. This material was produced by circulating fluidized bed combustion (CFBC), and has been emplaced for up to three years. Detailed histories of ash analysis and emplacement exist for each of these two sites, allowing for potential correlation with original bulk chemistry. Additional material will be retrieved from this embankment during the spring of 1998; 3) a Class F fly ash from the ash disposal pit of an electric power-generating utility in Kentucky. Pore water solutions were simultaneously collected from the Kentucky landfill by Cindy Rice, a representative of the U.S.G.S., for equilibrium aqueous geochemical studies. Extensive characterization of the ash produced at the Kentucky plant is being undertaken by a team of collaborators based at the U.S.G.S. Denver Center. Dr. Robert Finkelman of the U.S.G.S is coordinating this multi-institutional collaboration. In addition to the recovered ash from the disposal pit, this collaboration has also provided our laboratory with a set of magnetic separations from more recently produced ash. The separations are being used in developing the Rietveld protocols of Task 2, and have been particularly useful in considerations of extreme peak overlap (see Subtask 2).

A verbal agreement for sampling of cementitious North Dakota fly ash buried up to 18 years has been obtained. Much of this ash has been studied extensively (as collected, prior to burial) in our laboratories. Drilling will be performed during July or August of 1998 depending on specific drilling schedules available at that time.

An additional site is being negotiated for collection of disposed FBC by-products.

Summary of Task 3

Progress:

Three sites have been sampled. Characterization by XRD is underway on these three materials.

Future plans:

Sampling of a fourth material is set for the late summer of 1998, and a fifth sampling is being negotiated. Following completion of the Rietveld protocol for CCBs, this technique will be applied for quantitative analysis of selected samples from each of these materials.