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ADVANCED MINERALOGICAL CHARACTERIZATION AND
DISPOSED BYPRODUCT DIAGENESIS

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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 Descriptions

Task 1

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 2

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.

Task 3

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 Summary

Task 1

Progress to date:

Task 1 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 is now under the direction of Kurt Eylands of UND-EERC. Further subtle instrument problems following installation should be finally remedied by the end of calendar year 1998, to allow for completion of this task by the end of grant year three.

Characterization of an initially-chosen set of previously-analyzed CCB materials has been started, with completion awaiting final validation of the SEM facilities.

Future Work planned:

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 (part of the subject of Subtask 2 of Task 2) based on these reference samples. 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

Subtask 1

Progress to date:

The database is essentially completed.

Future Work planned:

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 to date:

This subtask is also nearly complete. Briefly, the effects of data collection parameters, peak overlap, choice of structure data including thermal parameters, internal standard, amorphous content, and microabsorption have all been addressed, including initial error analysis. Significant improvement over existing quantitative techniques has already been observed. A general outline of the analytical protocol has been developed. More detailed results and the protocol from this subtask are available in the enclosed manuscript in submission to *Advances in X-ray Analysis*.

Future Work planned:

Further error analysis and final determination of the effect of particle size and microabsorption on CCB materials will be performed.

Subtask 3

Progress to date:

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

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

Future Work planned:

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

Task 3

Progress to date:

Four sites have been sampled and a fifth is being negotiated. One site (Class F fly ash pond) has been thoroughly analyzed by XRD both qualitatively and quantitatively, using the Rietveld QXRD protocols developed in Task 2. Analysis of phase composition as a function of depth is underway (see also Figure 1). Our XRD work at this site is being done in collaboration with a larger consortium of investigators including the Kentucky Geological Survey, under the direction of the Bob Finkelman at the United States Geological Survey. Qualitative analysis of the second (dry-process flue gas desulfurization by-product stack) and third (circulating fluidized bed combustion ash used in embankment) sites is approximately 80% complete. Quantitation by Rietveld QXRD will be performed on selected samples from these three sites. Material from the fourth site (Class C fly ash pond) was recently retrieved (August, 1998). A set of samples from this site has been selected and qualitative and quantitative XRD studies are underway for this set also.

Future Work planned:

A fifth sampling is being negotiated. XRD analysis of the three in-house sample sets will be completed, including quantification. Selected samples from the retrieved materials will also be analysed *in situ* by SEM/EPMA. Spatial relationships observed among various phases will provide information on alteration and diagenesis.

Figure 1. Composition distribution vs depth for one of two boreholes from a Class F fly ash pond. Presence of ettringite unusual; not predicted.

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.

Submitted

- 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*, v41.

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.

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.

Students Receiving Support from Grant

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Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. Testing with Standard Mixtures

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ABSTRACT

Quantitative XRD (QXRD) analysis of coal combustion by-products (CCBs) and their hydration products is not straightforward. CCBs typically include large numbers of crystalline phases and substantial amorphous content. Many CCB phases have varying levels of crystalline order and solid solution. When prepared as XRD specimens, a number exhibit strong preferred orientation, and with quite variable linear absorption coefficients, have the potential for microabsorption problems in mixtures. The conventional internal standard QXRD methods have two problems when applied to CCBs: (1) finding representative standards for analyte phases, and (2) finding sufficiently intense, non-overlapped, analytical peaks. The Rietveld QXRD (RQXRD) method, however, appears to be capable of modeling each of the sample, specimen and instrumental problems. This study focuses on establishing a level of confidence in the ability of RQXRD to handle each of the sample and specimen problems characteristic of CCBs utilizing test mixtures having known amounts of crystalline and amorphous phases.

INTRODUCTION

Coal combustion by-products (CCBs) are the wide variety of solid residuals resulting from the burning of coal. These solid residuals include fly ash, bottom ash, products of the technologies for the reduction of SO₂ emissions (i.e, flue gas desulfurization (FGD) and fluidized bed combustion (FBC)), and disposed material that may be a mixture of all of the above. In order to understand the behavior of these materials, the mineralogy of these systems must be characterized. X-ray powder diffraction is a convenient method for this mineralogical characterization..

CCBs have been typically been quantified using the reference intensity ratio (RIR) QXRD method. Bender, et al. have previously shown that the RIR method is semi-quantitative, at best, for these systems [1]. Reasons for the lack of accuracy in the RIR method for these systems include: (1) extensive overlap of peaks, (2) preferred orientation, (3) specimen effects, such as peak broadening due to crystallite size or strain, and (4) lack of pure, representative standard materials.

The Rietveld method [2] applied to QXRD appears to be better suited for characterizing these materials. RQXRD uses the entire pattern, reducing the effect of peak overlaps; it can model sample and specimen effects, including peak broadening due to crystallite size or strain and

preferred orientation; and it does not require phase pure and representative standards. RQXRD does require structure data and solid solution chemical compositions for the phases being examined. And, as discussed here, correction of RQXRD results for microabsorption requires knowledge of particle size.

CCBs typically contain between six and twelve crystalline phases plus X-ray amorphous phase [1,3,4]. The Rietveld method has been extensively tested for accuracy and precision in multi-phase analyses [5-13]. However, only a few of these studies [12,13] have examined systems of the scope as complex as typically encountered with CCBs. The objective of this study was to develop a protocol for analyzing CCB materials and determine the precision and accuracy of that protocol for complex mixtures of known materials (test mixtures). The test mixtures were chosen such that they include one or more of the following: extensive overlapping peaks, microabsorption, preferred orientation, and amorphous content. The test mixtures range from five to eight phases plus an internal standard, with and without an amorphous phase.

Other factors that affect the accuracy and precision of RQXRD have been examined, including modeling of the instrumental parameters, data collection strategies, microabsorption, and various other sample and specimen parameters.

EXPERIMENTAL

All data were collected using a Philips X'Pert Multi-purpose Diffractometer (MPD) employing a long line focus Cu X-ray tube, divergence and anti-scatter slits fixed at 1° , a receiving slit (0.2mm), diffracted and incident beam Soller slits (0.04 rad), a curved graphite diffracted beam monochromator, and a sealed proportional counter. Generator settings used were 45 kV and 30 mA.

The rutile (TiO₂) internal standard was micronized for 30 minutes prior to use to reduce the particle size to under 10 μm . Each sample was ground with the internal standard for 5 minutes with a mortar and pestle under 95% ethanol. The specimens were then prepared by side drifting the sample into an aluminum well mount.

The structure data were obtained from literature values collected at a CCB Analysis Web Site prepared by the senior author (RSW) (<http://QXRD.chem.ndsu.nodak.edu/ccbs/>) or the ICSD database [14]. These structures were carefully selected and reviewed as previously described [15].

The Rietveld code used was the publicly available DOE package, GSAS [16]. The instrumental parameters, including peak profiles (pseudo-Voigt), were determined using the NIST Alumina plate (SRM 1976). Parameters refined included the background, weight fractions, lattice parameters, specimen displacement, the Lorentzian Scherrer broadening component (LX) and a peak asymmetry term.

RESULTS AND DISCUSSION

Determination of Inherent Amorphous Content of Reference Materials

Each reference material chosen for the test mixtures was characterized prior to its use for phase purity, particle size and inherent amorphous content. All materials had only a single phase detectable by XRD. The materials used in this study with their associated inherent amorphous content are shown in Table 1. The inherent amorphous content was determined by difference in a 50:50 mixture with a rutile internal standard using RQXRD. The rutile, which had been fired at 1200°C for 2 hours, was assumed to be 100% crystalline. The weight fractions were then corrected for microabsorption using particle sizes obtained by SEM analysis.

Table 1. Phases used for test mixtures and their associated amorphous content.

Phase	Amorphous Content (%)	Phase	Amorphous Content (%)
Corundum (Al_2O_3)	2	Silicon	0
Cr_2O_3	0	ZnO	3
Cristobalite (SiO_2)	3	Periclase (MgO)	0
Calcite (CaCO_3)	6	Hematite (Fe_2O_3)	0
Quartz (SiO_2)	0	Maghemite (Fe_2O_3)	8
Magnetite (Fe_3O_4)	26	Merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$)	23
C_3A ($\text{Ca}_3\text{Al}_2\text{O}_6$)	13		

The first phase analyzed for its inherent amorphous content was corundum (Al_2O_3 , NIST SRM 676 Alumina). This quantitative analysis SRM has been determined to have 1.6% amorphous content [17]. Our results gave an amorphous content of 2%, indicating the method can yield accurate amorphous contents. The remaining phases show amorphous content ranging from essentially zero to 26%. The high amorphous contents of some phases are remarkable, but reproducible.

Test Mixtures

The phases used for the test mixtures are shown in Table 1. The test mixtures range from five phases plus an internal standard to eight phases plus an internal standard. The weight percentages for each of the test mixtures were corrected for the inherent amorphous content of each phase. One test mixture, used to examine each parameter (except the determination of the internal standard) is shown in Table 2. This mixture was chosen because it exhibits microabsorption effects, preferred orientation and peak overlap.

Table 2. Test mixture used for many of the studies reported here. The weight percentages are corrected for the inherent amorphous content of each phase.

Phase	Weight %	Phase	Weight %
Hematite	26.8	Calcite	25.2
Quartz	13.4	Cr ₂ O ₃	11.0
Silicon	7.3	ZnO	7.1
Corundum	3.6	Cristobalite	3.5
Amorphous	2.0		

Determination of Scan Parameters

The data collection strategy was examined to determine the minimum counting time and maximum step size that could be utilized and still obtain accurate results. Two different sets of scan parameters were investigated: (1) 20-140°2 θ , 8 second count time and 0.025° step size (“long scan”), and (2) 20-80°2 θ , 2 second count time and 0.03° step size (“short scan”). The instrument time required for the long scan is 10 hours 46 minutes, while the short scan is 1 hour 6 minutes. Using the test mixture in Table 2, there was no significant change in the weighted relative error for the entire sample: 5.6% for the long scan, 5.5% for the short scan. Apparently the counting statistics were satisfactory in the short scan for the parameters refined in our study, so the following results were all obtained using the short scan conditions.

Microabsorption

CCB materials contain phases with linear absorption coefficients, μ , that range from 1176 cm⁻¹ (magnetite) to 80 cm⁻¹ (cristobalite). For this study, microabsorption was dealt with in a post-refinement spreadsheet calculation using the method outlined by Brindley [18] and applied to Rietveld analysis by Taylor [19]. For mixed powders, Brindley showed that the correction factor for phase A, τ_a , is given by:

$$\tau_a = \frac{1}{V_a} \int_0^{V_a} \exp[-(\mu_a - \mu^*)x] dv_a \quad (1)$$

where V_a is the volume of a particle of A, v_a is the volume of phase A that is correctly oriented for diffraction, x is the path length of the beam through particle A, μ_a and μ^* are the linear absorption coefficients of phase A and the sample, respectively. Brindley then solved this expression numerically and tabulated the results as a function of $(\mu_a - \mu^*)R$, where R is the particle size. Taylor then applied the microabsorption correction to Rietveld analysis using the relation:

$$Wt. \text{ Frac. } A = \frac{\frac{(SMV)_A}{\tau_A}}{\sum_{j=1}^N \frac{(SMV)_j}{\tau_j}} \quad (2)$$

where S is the scale factor for phase A, M is the unit cell mass, V is the unit cell volume and N is the number of phases present. It can be shown that this is equivalent to:

Using the weight fractions calculated in a Rietveld refinement, a spreadsheet corrects for the microabsorption effects. The required average particle sizes for the phases included in the test mixtures have been determined by SEM.

$$Wt. \text{ Frac. } A = \frac{\frac{(Wt. \text{ Frac. } A)}{\tau_A}}{\sum_{j=1}^N \frac{(Wt. \text{ Frac. } j)}{\tau_j}} \quad (3)$$

A typical example of the effect of the microabsorption correction and the particle sizes used for the microabsorption correction is shown in Table 3. In this example, the largest effect of microabsorption is seen in the amorphous phase, going from 270% relative error (and a negative value) to 54% relative error.

It should be noted here that correcting for microabsorption is not straightforward. In these test mixtures, the particle sizes have been well characterized using SEM analysis. In other samples this will usually not be the case. If the particle size is only approximated, the accuracy of the results will be significantly changed, as shown in Table 4.

Choice of Internal Standard

Also examined was the choice of internal standard. Rutile was originally chosen because its linear absorption coefficient ($\mu=549 \text{ cm}^{-1}$) falls roughly in the center of the range of possible linear absorption coefficients in CCB materials. However, the rutile used in this study has a particle size of approximately 2 μm . This is about an order of magnitude larger than other internal standards available such as, ZnO (0.3 μm) [1] and corundum (0.5 μm) used for QXRD. Using a five phase mixture, all three internal standards were examined to determine the effect of particle size on these results. The results are summarized in Table 5. As indicated by the data, rutile was still the best choice for this mixture, giving a weighted relative error for the entire specimen of 5.3% after correcting for microabsorption.

Table 3. Results from RQXRD with and without using the microabsorption correction.
The reference weight percentages were corrected for inherent amorphous content.

Phase	Particle Size (μm)	Reference Wt. %	Uncorrected RQXRD	Relative Error	Corrected RQXRD	Relative Error
Hematite	0.3	26.8	28.3	6%	28.7	7%
Calcite	1.7	25.2	27.7	10%	25.3	0%
Quartz	1.0	13.4	13.9	3%	13.0	3%
Cr ₂ O ₃	0.4	11.0	10.3	6%	10.5	4%
Silicon	2.5	7.3	7.8	6%	6.7	9%
ZnO	0.3	7.1	7.3	3%	7.2	1%
Corundum	0.5	3.6	4.1	16%	4.0	12%
Cristobalite	1.2	3.4	4.0	14%	3.7	4%
“Amorphous”		2.0	-3.4	270%	0.9	54%
Weighted Relative Error*						
All Phases:				12.2%		5.3%
Crystalline Phases:				6.9%		4.3%

*Weighted average of the absolute values of relative errors for each phase.

Table 4. Results of RQXRD with microabsorption correction using 5, 1 and 0.1 μm particle sizes for the correction. Data corrected for inherent amorphous content.

Phase	Part. Size (μm)	Ref. Wt. %	5 μm RQXRD	Rel. Err.	1 μm RQXRD	Rel. Err.	0.1 μm RQXRD	Rel. Err.
Hematite	0.3	26.8	43.9	64%	30.9	15%	28.6	
Calcite	1.7	25.2	21.3	16%	26.4		27.6	10%
Quartz	1.0	13.4	9.7	27%	13.0		13.8	3%
Cr ₂ O ₃	0.4	11.0	13.6	24%	10.9		10.4	
Silicon	2.5	7.3	5.7	22%	7.3		7.7	
ZnO	0.3	7.1	6.0	16%	7.1		7.3	
Corundum	0.5	3.6	3.0	16%	3.9		4.1	15%
Cristobalite	1.2	3.5	2.8	20%	3.8		4.0	13%
Amorphous	-	2.0	-6.0	396%	-3.2	257%	-3.5	6275
Weighted Rel. Error				39.4%		11.5%		12.3%

Table 5. Rietveld refinement of a five phase mixture using rutile, ZnO and corundum as internal standards. Data corrected for amorphous content and microabsorption.

Phase	Reference Wt. %	Rutile RQXRD	Relative Error	ZnO RQXRD	Relative Error	Alumina QXRD	Relative Error
Hematite	30.1	31.9	6%	28.7	5%	28.2	6%
Quartz	29.9	29.7	1%	26.6	11%	26.0	13%
Calcite	23.4	21.8	7%	19.5	17%	20.0	15%
Periclase	10.0	11.4	14%	9.9	0%	10.2	3%
Silicon	5.0	5.0	1%	3.9	23%	3.8	24%
Weighted Rel. Error			5.3%	10.0%			11.0%

Amorphous Content

CCB materials contain a large amount of glassy amorphous material, typically accounting for between 50 and 90% of the mass of the sample. To examine the effects of a substantial amount of amorphous material on the accuracy of RQXRD, the eight-phase test mixture (Table 2) was diluted with 20%, 40%, 60% and 80% silica gel to simulate the amorphous material found in CCBs. The results for the 40% and 80% mixtures are summarized in Table 6.

Table 6. RQXRD analysis of standard mixture containing 40% and 80% amorphous material. Data corrected for inherent amorphous content and microabsorption.

Phase	40% Amorphous			80% Amorphous		
	Reference Wt. %	RQXRD	Relative Error	Reference Wt. %	RQXRD	Relative Error
Hematite	16.1	17.5	9%	5.4	5.5	2%
Calcite	15.1	14.5	4%	5.0	4.7	7%
Quartz	8.0	7.7	4%	2.7	2.4	10%
Cr ₂ O ₃	6.6	6.8	2%	2.2	2.2	2%
Silicon	4.4	4.1	6%	1.5	1.3	9%
ZnO	4.3	4.4	2%	1.4	1.3	10%
Corundum	2.2	2.2	2%	0.7	0.7	2%
Cristobalite	2.1	2.4	13%	0.7	0.8	16%
Amorphous	41.2	40.4	2%	80.4	81.1	1%
Weighted Relative Error			4.0%	1.9%		

Severe Peak Overlap

One of the advantages of the Rietveld method is the reduced effect of peak overlap on the results due to the use of the full profile. CCB materials often show phases that have strong peak overlaps, which makes them difficult to quantify using the RIR method. Two systems known to have severe peak overlaps were examined using RQXRD.

The first system was comprised of merwinite and C_3A , which occur together in high-calcium fly ash [20,21]. This pair of phases is a problem for the RIR QXRD method because of their many peak overlaps, including their 100% peaks, which both fall at $33.3^\circ 2\theta$. The Rietveld method handled this case well, giving relative errors of $\pm 15\%$ for mixtures ranging from 20:80 to 80:20.

The second system consisted of maghemite, quartz, magnetite and hematite, which occurs in the magnetic fraction of fly ash. This system is difficult because maghemite, which has a spinel-related structure similar to that of magnetite, has no independent reflections in the presence of the other three phases. Samples were prepared containing approximately 5% maghemite in the presence of the other three phases in varying amounts. It was not possible to quantify maghemite in these mixtures. In some cases, especially those with high magnetite content, the Rietveld refinement would not even converge.

CONCLUSIONS

A protocol for RQXRD of CCB materials has been developed and tested. The protocol assumes the instrumental peak functions have been predetermined, in this case using a pseudo-Voigt function, and these values are used as the initial values for the peak profiles. The protocol is as follows:

1. Refine background parameters (shifted-Chebyshev polynomial), including 6-18 coefficients, depending on amount of amorphous material.
2. Add phase and element fractions (weight percents)
3. Add lattice parameters
4. Add specimen displacement, constrained to be the same for all phases
5. Add a peak broadening term (in GSAS, LX)
6. Add a peak asymmetry term

The protocol yields results that are accurate to within $\pm 15\%$ of the actual amount and typically within $\pm 10\%$. The protocol is relatively fast, yielding results typically within approximately 1.5 hours from the beginning of data collection. The reduction in the time required for data collection is a major factor in the low turnaround time for the results of the refinements.

Several factors influencing the accuracy of RQXRD have been examined. It has been found that the presence of large amounts of an amorphous phase did not significantly alter the accuracy of the results. Microabsorption does contribute to the error associated with the method, but care needs to be taken when correcting for its affects. As was shown, the choice of particle size is of

utmost importance. Incorrect values of particle size will yield results that are less accurate than uncorrected results. Three internal standards were examined, and rutile yielded the most accurate results.

While the RQXRD method can model most instrumental, sample and specimen effects, severe peak overlap caused the method to fail with one combination of phases.

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