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Assessment of a synchrotron X-ray method for quantitative analysis of calcium hydroxide

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Abstract

Thermogravimetric analysis (TGA) and quantitative X-ray diffraction (QXRD) are widely used to determine the calcium hydroxide (CH) content in cementitious systems containing blends of Portland cement, fly ash, blast furnace slag, silica fume and other pozzolanic and hydraulic materials. These techniques, however, are destructive to cement samples and subject to various forms of error. While precise weight losses can be measured by TGA, extracting information from samples with multiple overlapping thermal events is difficult. And, however, while QXRD can offer easier *deconvolution*, the accuracy for components below about 5 wt.% is typically poor when a laboratory X-ray source is used. Furthermore, the destructive nature of both techniques prevents using them to study the in situ hydration of a single contiguous sample for kinetic analysis. In an attempt to overcome these problems, the present research evaluated the use of synchrotron X-rays for quantitative analysis of CH.

A synchrotron X-ray source was used to develop calibration data for quantification of the amount of CH in mixtures with fly ash. These data were compared to conventional laboratory XRD data for like samples. While both methods were found to offer good quantification, synchrotron XRD (SXRD) provided a broader range of detectability and higher accuracy than laboratory diffraction and removed the subjectivity as compared to TGA analysis. Further, the sealed glass capillaries used with the synchrotron source provided a nondestructive closed, in situ environment for tracking hydrating specimens from zero to any desired age.

Keywords: Synchrotron XRD; X-ray diffraction; Calcium hydroxide; Fly ash; Quantitative

1. Introduction

Kinetic data for the reaction between calcium hydroxide (CH) and various CH consuming supplemental cementitious materials such as fly ash, silica fume and blast furnace slag are somewhat limited, despite a number of studies that have investigated these reactions [1–6]. Quantitative analysis of the amount of CH in hydrated samples of cement, blended with various types of fly ash, slag and other natural pozzolans, has been accomplished using thermal analysis techniques, mainly thermogravimetric analysis (TGA) [5] or by using quantitative X-ray diffraction (QXRD) [6]. When applying TGA, a hydrated cement sample is heated through the decomposition point of CH, and the weight change due to the loss of water vapor upon decomposition is measured. Though TGA is extensively used for quantitative calculation of the amount of CH in hydrated cementitious samples, there are disadvantages with this technique. For example, the carbonation of CH in the presence of CO_2 is described by the following equation:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

This reaction occurs rapidly and is difficult to avoid when handling CH containing samples in air. Care is required to prevent reaction with ambient CO_2, therefore, samples need to be sealed in a CO_2-free environment. Typically, TGA methods require at least limited exposure to air because samples must be transported to and from the instrument for analysis. Consequently, the amount of $CaCO_3$ must also be determined during the TGA analysis and related to CH, a task that is even more difficult than quantification of the CH weight loss [5].

Native chemical species often confound quantification when TGA is used, especially when dealing with hydrated

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samples of cement or fly ash. The poorly crystalline calcium silicate hydrate (C-S-H), as well as AFm phases (phases having general formula $[Ca_2(Al, Fe)(OH)_6]\cdot X\cdot xH_2O$, where X is a unit of singly charged anion or half a unit of doubly charged anion), for example, tends to liberate their waters of hydration in steps over a broad temperature range with the majority being liberated by 500 °C. Tightly bound waters, however, may not be evolved until 1000 °C. The decompositions of CH and $CaCO_3$ begin around 400 and 550 °C, respectively. The hydration products in fly ash systems, including C-S-H, cause peak superposition with CH and $CaCO_3$ decompositions. Furthermore, the decomposition of CH does not always occur at exactly the same temperature in all samples, either because of transport effects or subtle differences in chemical environment. Using TEM, Groves [7] and Viehland et al. [8] have shown that a form of cryptocrystalline CH forms as an intimate mixture with C-S-H, which may also lead to observed variation in decomposition temperature and rate.

Determination of the weight lost due to the presence of CH is typically performed by constructing tangents to the leading and trailing portions of the TG curve, which straddle the CH decomposition region [9]. Constructing these tangents is strictly left to the *eye* of the experimentalist, a practice that introduces error. Therefore, monitoring the CH decomposition is somewhat subjective, even with the high sensitivity of modern TGA instruments.

QXRD is generally applied to dry, crushed cement samples. This quenches hydration and alters the microstructure, essentially *destroying* the sample, i.e. the sample can no longer be hydrated. Furthermore, although the accuracy of QXRD has been purported to be 1 wt.% [10], the limits of detectability are likely no better than 5 to 10 wt.% without extensive refinement of the technique. This limitation is generally due to low peak-to-background discrimination and, in cases where the sample contains some amorphous material, background interference. Peak-to-background discrimination can be greatly improved by increasing the scan time, and hence, the total photon (X-ray) count. In order to improve the counts by a factor of 10, however, scan times would increase from nominally 1 to 10 h for a typical 10° to 70° 2θ scan. While this may be acceptable for quenched (dried) samples, it is unacceptable for hydrating samples. In situ measurement must be rapid, particularly at early stages, as reaction rates are fast enough to cause significant compositional changes during the extended data collection time. Also, the amorphous background interference remains. These factors have limited the utility of conventional XRD for conducting in situ kinetic experiments at early ages particularly where the sample contains amorphous phases.

A number of other methods have been used to quantify CH in cement systems. These include various other thermal analytical methods such as differential thermal analysis (DTA) [11] and solvent-based chemical extraction methods [12]. Similar to TGA and QXRD, these other methods are subject to their own flaws. Yet, TGA and QXRD are considered to be the most reliable methods with TGA preferred in most cases [10]. All of these methods are destructive, and so, kinetic data obtained are pseudo-continuous, requiring several different samples to generate a rate curve. This can further complicate interpretation and analysis.

An alternative approach that resolves many of the stated problems including the continuity of sample analysis, exposure to air, peak-to-background discrimination, amorphous background interference, and to some extent, analysis time, is to use a capillary sample coupled with a synchrotron X-ray radiation source. A synchrotron X-ray beam is 10^6 times as intense (brilliant) and highly polarized compared to that of a sealed tube laboratory X-ray beam [13], thus enabling high-resolution, rapid data acquisition and improved sampling statistics.

A number of synchrotron-based techniques have been proposed and demonstrated for use with cement-based materials. Hall et al. [14] present a nondestructive tomographic energy-dispersive diffraction imaging technique. They employed high-energy, 20–125 keV, beams to penetrate specimens up to several centimeters in length and generate composition maps in bulk samples. Clark and Barnes [15] studied the kinetics of C_3S hydration using laboratory, synchrotron, and neutron diffraction. In their work, they used energy-dispersive powder diffraction (EDPD), which enabled them to simultaneously collect the entire diffraction spectrum in only 10 min. Their comparison indicated that the EDPD was nominally four times as precise as either the neutron or laboratory X-ray method for very early-age hydration. Kurtis et al. [16] used synchrotron soft X-ray transmission to observe the in situ formation of alkali silica gel. Images were collected for exposure times between 1 and 180 min. Winslow et al. [17] conducted small-angle scattering experiments using synchrotron X-rays to study the fractal nature of hydrated cement pastes. Scan times ranged between 10 and 15 min and samples surfaces were as-hydrated with surface saturations ranging between 0 and 100%.

The goal of this study was to determine if a synchrotron QXRD method provides a distinct advantage over conventional sealed tube laboratory QXRD. Control samples and calibrations were conducted using both methods to determine the viability for future kinetic studies.

2. Experimental

Two methods of XRD were investigated: Bragg–Brentano parafocusing geometry with a conventional sealed tube laboratory X-ray source and a transmission geometry with a synchrotron radiation source. In both methods, the samples were within sealed sample holders. This comparison embodies two superimposed comparisons between (1) flat plat reflection and capillary modes and (2) conventional laboratory and synchrotron modes. It should be pointed out, however, that no direct attempt was made to isolate the component effects. Rather, a comparison was made between a laboratory source using flat plate reflection and a synchrotron source with a capillary.

2.1. Conventional XRD

Rather than quenching and crushing, a sealed sample holder was developed to prevent sample exposure to air and provide an acceptable environment for hydration. The sample holder for this study was fabricated from 303 stainless steel with a polyvinyl chloride (PVC) film window. All edge surfaces were *polished* and rounded to eliminate tearing of the film. Stainless steel was chosen because it is inert at the temperatures (– 5 to 150 °F nominal) and in the presence of the strong alkali used in many cement hydration studies (pH between 13 and 14). In this way, XRD becomes a nondestructive method since the X-ray beam itself does not alter the chemical makeup of the sample. Furthermore, samples can be analyzed wet so hydration can take place before, during, and after analysis.

The PVC film used in this study was chosen because it is relatively transparent to X-rays. XRD scans of the sample holder and film with no sample and a holder with CH sample covered with the PVC film were collected. The film was found to display a small amorphous hump between 15° and 30° 2θ. A large peak at 43.35° 2θ due to the stainless steel (displaced from the focusing circle) was also present. The stainless steel peak was eliminated in the CH scan because the sample holder was covered by a thick layer of CH. Due to the fact that the amorphous PVC peak overlaps with the (001) CH reflection (at 18.089° 2θ for Cu K_α radiation), the (001) reflection was not considered in the quantitative analyses.

XRD scans were obtained using a Scintag PAD-V diffractometer with a vertical θ–2θ goniometer and a Peltier-cooled energy-dispersive detector. All samples were analyzed using Cu K_α radiation ($\lambda = 1.54056$ Å). Scans were obtained as continuous scans between 10° to 70° 2θ with a step size of 0.02° and rate of 1°/min. This 2θ range was chosen because it contains five rutile peaks (a calibration standard) along with four CH peaks, and various fly ash peaks all of which can be used for quantification. The scan rate was chosen to achieve a 1-h analysis time in view of the time-sensitive kinetic data for which the method was being developed.

2.2. Synchrotron XRD (SXRD) method

XRD was also performed using beamline X-14A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) [18,19] A six-circle Huber diffractometer with a Xe–CO_2 filled proportional counter was employed with a 1 × 4 mm incident beam cross section [19].

Samples were placed in 2 mm inner diameter borosilicate capillaries and rotated at 78 rpm to increase particle statistics and minimize preferred orientation. The data were collected in transmission using 14.996 keV radiation ($\lambda = 0.8268$ Å) with 2θ scan range between 8° and 28° (this is equivalent to 14.54° and 53.59° 2θ at 8 keV) with a step size of 0.01°. For the experiments reported here, the incident beam was accumulated to 60,000 counts per step in the ion chamber.

The 2-mm capillary, a relatively large capillary for synchrotron X-ray work, was required since wet pastes were used in this study. Capillaries were filled by injecting the paste through a syringe needle inserted into the capillary tube, and so, smaller caliber capillaries could not be used.

Large diameter capillaries, however, can be problematic in that they provide a long beam path (R) through the sample, thereby increasing X-ray absorption. This is further exacerbated if the materials being studied have high linear absorption coefficients [20] as does calcium. Calculations for the CH/ash system, however, indicated that the 2-mm capillaries would not cause excessive absorption. Experiments verified this result. A particular advantage of this method of analysis is that the sealed glass capillary can provide a completely closed environment. Using a glass capillary, however, does add to the amorphous background.

2.3. Materials

Fly ash designated 9703 was obtained from the American Coal Ash Association through the Building and Fire Research Laboratory at the National Institute of Standards and Technology (NIST). 9703 is a Type F ash, which principally contains SiO_2, Al_2O_3 and FeO. Detailed chemical and physical properties have been reported by Biernacki et al. [5].

Reagent grade CH was obtained from Mallinckrodt. To prevent the formation of calcium carbonate due to exposure to carbon dioxide in air, bottles of CH were placed in a glove box filled with nitrogen in sealed bags filled with nitrogen. Reagent grade sodium hydroxide was obtained from Fisher Chemical. XRD grade rutile (TiO_2) was obtained from the Building and Fire Research Laboratory at NIST. Rutile samples were thoroughly crushed using a mortar and pestle before use. All water used for reaction was distilled.

2.4. Preparation of XRD samples

The components of the mixtures, listed in Table 1, were placed in 50-ml beakers. The samples were aggressively mixed for 5 min or until visibly homogeneous. For conventional XRD work, the paste was placed in the stainless steel sample holder (crucible) and the top edge was smoothed with a flat glass plate. The sample holder was then covered with PVC film and the film was tightly twisted and sealed with tape along the bottom of the crucible. For synchrotron work, the pastes were placed by spatula into a 10-ml plastic syringe fitted with a 1.2-mm pipette needle. The pastes were injected into 2-mm borosilicate glass capillaries from Glas of Germany. Once the samples were filled, the top of the

Table 1
Samples used for calibration scans

Sample ID	Mass fraction			Water/ solid ratio
	CH	Fly ash	Rutile	
6.25/93.75	0.061	0.839	0.100	0.80
12.5/87.5	0.113	0.788	0.100	0.80
25/75	0.225	0.675	0.100	0.80
50/50	0.450	0.450	0.100	0.80
75/25	0.675	0.225	0.100	0.80

capillary was sealed by heating the capillary opening with a propane torch. The capillary was heated until no openings were visible using a × 5 magnifying glass. This process took only seconds to achieve and little heat was transferred into the sample so that the state of hydration of the sample would not be altered.

2.5. Calibration method

Quantification of samples obtained from XRD is performed by measuring the intensity of the peaks acquired in the scan. In samples containing a mixture of materials, the intensity of a peak is proportional to the mass fraction and the atomic number of the elements responsible for that reflection. The derivation of the equations relating intensity and mass are described by Nuffield [21].

The basic equation describing the intensity of a peak from a given material, ‘a’, in a mixture of n materials is given by:

$$I_a = K_a \frac{W_a/\rho_a}{\sum_1^n W_n \mu_n^*} \tag{2}$$

where I_a = intensity of peak associated with component ‘a’, K_a = a constant dependent on the nature of the component ‘a’ and the instrumental arrangements, W_a = weight fraction of component ‘a’, ρ_a = density of component ‘a’, W_n = weight fraction of component ‘n’, and μ_n = mass absorption coefficient associated with component ‘n’, If Eq. (2) is applied to two components in a heterogeneous mixture of materials, then the ratio of the intensities of the two components is given by:

$$\frac{I_a}{I_b} = K \frac{W_a}{W_b} \tag{3}$$

where I_b = intensity of peak associated with component ‘b’, K = constant representing $(K_a/K_b)(\rho_b/\rho_a)$ and W_b = weight fraction of component ‘b’. This equation shows that the intensity ratio of two peaks from different materials in a heterogeneous sample is proportional to the weight ratio of the two components. This equation is valid for any mixture containing the two materials.

If a standard of known weight fraction is added to a sample and K is known, the weight fraction of the second material can be determined. As mentioned before, a constant amount of rutile (10 wt.%) was placed in all calibration samples. Eq. (3) is thus further simplified by using a constant amount of rutile in each sample. The resulting equation is:

$$W_{CH} = C \frac{I_{CH}}{I_{rutile}} \tag{4}$$

where W_{CH} = weight fraction of CH, $C = W_{rutile}/K$ = constant, I_{CH} = intensity of CH peaks and I_{rutile} = intensity of rutile peaks.

The breadth of the peak is a function of instrumental parameters and the size of the crystallites in the powder, but is constant for each sample. Smaller crystallites produce broader peaks, but as mentioned earlier, decrease the risk of preferred orientation. To determine the peak area (intensity), a pseudo-Voigt profile shape was used that allows overlapping peaks to be resolved.

3. Discussion

3.1. Control experiments

3.1.1. Preferred orientation in Lab XRD samples

Preferred orientation can lead to false analysis due to inaccurate peak intensities which causes erroneous QXRD results. Preferred orientation can be present at the wet sample surface in contact with the sealing film, particularly after using a glass slide to level the surface of the slurry. To determine if preferred orientation was present, a dry CH sample sealed with film, a dry crushed CH sample sealed with film, and a wet CH sample with a water-to-solid weight ratio of 0.8 were analyzed under the same conditions. The most effective method for altering preferred orientation is to crush a sample to change the particle size distribution, thereby improving crystallite morphology (increasing the sphericity) and randomness of crystallites and, as an additional benefit, increasing sampling statistics [13]. No changes in intensity were observed. Therefore, preferred orientation effects were considered negligible when wet samples were sealed. Only peaks that are not on top of the amorphous film hump were considered since overlap makes interpretation difficult.

The results of these analyses show that this method provides the characteristics needed to monitor and obtain continuous CH kinetics data for samples during hydration. As the edges of the polymer film are difficult to seal, this method, however, may not be reliable for long-term analysis (>24 h).

3.1.2. Effect of water on capillary samples

The effect of analyzing wet samples was determined by scanning a dry sample of fly ash and a wet sample of fly ash with a water-to-solids ratio of 0.8. Fly ash was chosen for this analysis instead of CH because the particle size distribution of ash varies greatly and includes particles as large as 100

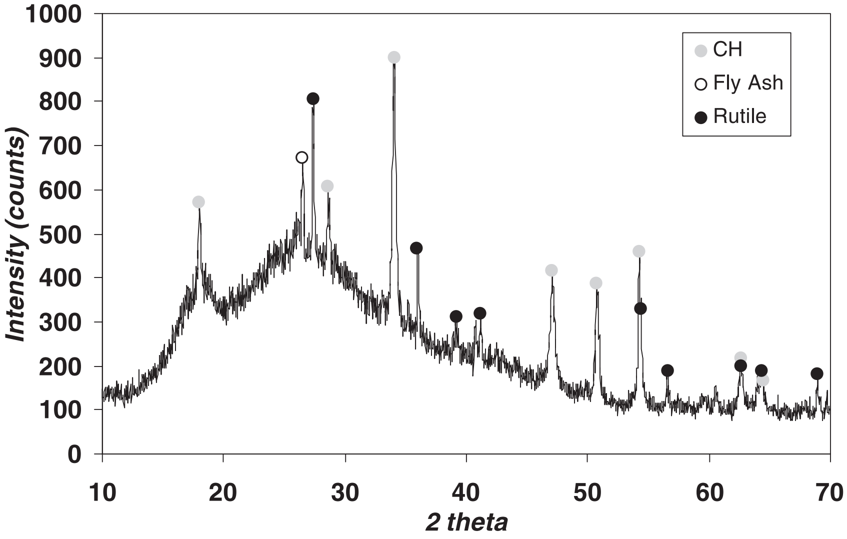

Fig. 1. XRD scan of 25/75 (CH/ash) sample with 10 wt.% rutile standard.

μm. Large and agglomerated particles are greatly affected by this method so the greatest possible variance due to sample preparation would be associated with the distribution of ash particles during injection into the capillary. No appreciable difference between wet and dry samples was found. Samples prepared in glass capillaries were also noted to retain 100% of their original moisture over long periods of time.

3.2. Comparison of XRD and SXRD

As expected, preliminary scans showed that the SXRD method has much better peak-to-background discrimination than laboratory XRD [14]. In order to compare the two methods, all samples of CH/ash were mixed with a 10 wt.% rutile (TiO_2) standard. Results for a representative sample containing 22.5% CH, 68.5% fly ash and 10% rutile (see Figs. 1 and 2) show large differences in amorphous humps. In conventional XRD, the origin of this hump is the glassy phase in the fly ash and the PVC sealing film. The SXRD scan shows very high peak-to-background discrimination with only a small baseline amorphous effect from 10° to 18° 2θ, despite the added amorphous content of the glass capillary. The strong singlet peaks in the SXRD scan are six times stronger than those in the conventional sealed tube XRD scan which include the Cu $K_{\alpha1}$, $K_{\alpha2}$ doublet phenomena. Combined with the lower background, the SXRD offers considerable improvement in peak-to-background discrimination and peak resolution. These results illustrate the advantage of SXRD for partly amorphous or semicrystalline containing samples such as those found in blended cement systems containing fly ash, blast furnace slag and related materials.

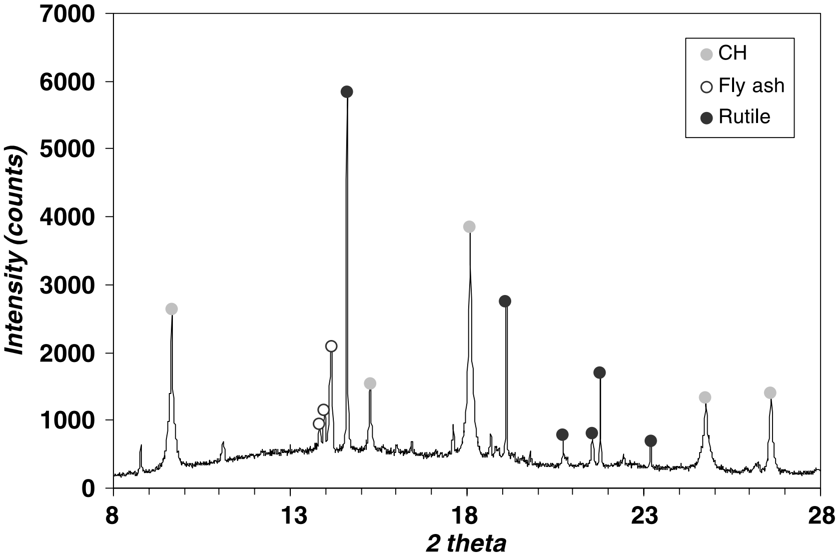

Fig. 2. SXRD scan of 25/75 (CH/ash) sample with 10 wt.% rutile standard. Amorphous hump begins to merge with background at 2θ>20°, but still appears at 28°.

3.3. Calibration scans

To calibrate both of the analysis methods, samples containing different CH/rutile/fly ash ratios were formed. To simulate the environment of hydrating fly ash/CH, samples used for calibration were analyzed wet with the same water-to-solids ratio typically used during hydration (see Table 1). The calibration scans were found to be similar to the preliminary scans. There was considerable amorphous background for all of the XRD scans and the intensity of the strong peak, I_o, had a maximum value of about 1700 counts, whereas the I_o peak of the SXRD scans was above 8000 counts.

3.4. Quantification of calibration curves

Calibration was performed by measuring the integrated intensity of each of the characteristic peaks associated with CH and rutile. Calibration curves were obtained by plotting the intensity ratio of the CH peaks and the rutile peaks vs. the weight fraction of CH in the system. The sum of the strong reflections from the 100, 101, 102 and 110 planes for CH and from the 110, 101 and 111 planes for the rutile was used for analysis. The XRD calibration is shown in Fig. 3 while the results for SXRD calibration is shown in Fig. 4. Multiple data sets were collected, in some cases in quadruplet, so as to improve statistical confidence. The calibration data were fitted to a straight line. The resulting least-squares fits are reported along with the errors for the fit parameters in parentheses. The results show higher linearity with SXRD (R^2=.996) than XRD (R^2=.927). The 95% confidence interval is also much smaller using SXRD. The results for both analyses show an intercept associated with the linear curve fit. While the intercept should be zero using this method, both calibrations show a non-zero intercept, however the error associated with the intercept using XRD is six times larger than that for the SXRD method. It is also noteworthy to mention that since no significant preferred orientation effects were observed when flat plat reflection was used, the improvement in quantification is due to the brilliance and parallelity of the synchrotron radiation. Finally, it should be pointed out that improved calibration statistics are likely possible for both techniques if whole pattern fitting methodologies are used [22]. Though, these more advanced techniques would not alter the underlying differences between the laboratory and synchrotron sources.

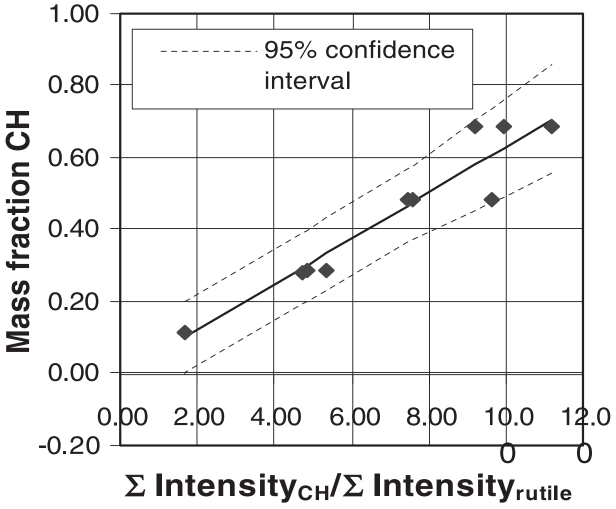

Fig. 3. Calibration curve and regression of data obtained using XRD. Values in parentheses are the 95% confidence interval.

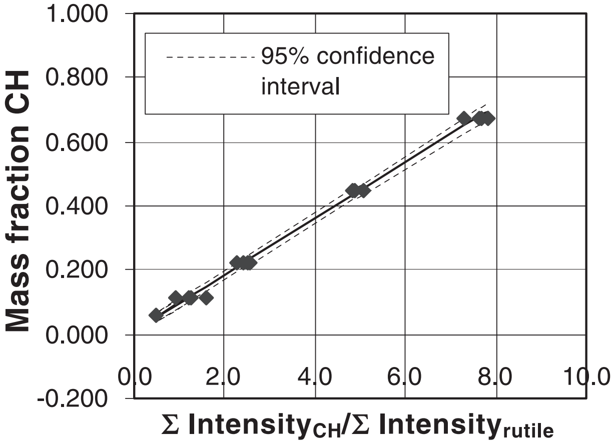

Fig. 4. Calibration curve and regression of data obtained using SXRD. Values in parentheses are the 95% confidence interval.

4. Summary

Both the laboratory XRD and SXRD methods were evaluated for a continuous rate study on the system fly ash/CH. The samples sealed in film for use with the laboratory XRD method may not be hermetic and may begin to dry due to evaporation over time, though this should be controllable by sealing the film better. Evaporation did not occur in the SXRD samples. The results of the calibration analysis comparison showed that the SXRD method provided a much higher level of certainty in QXRD of CH as well as a broader range of detectability with good confidence for samples containing as little as 5 wt.% of CH. These results suggests that capillary SXRD appears to be a suitable methodology for conducting continuous, real-time XRD-based kinetic studies of Portland cement-based materials.

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