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Quantitative X-ray Powder Diffraction Methods for Clinker and Cement

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Abstract

Performance of concrete is influenced by the portland cement phase composition. Phase abundance determination has traditionally been accomplished using two different methods; optical microscopy, and a Bogue calculation based on a chemical analysis. However, optical microscopy is an arduous method for routine clinker evaluation. Phase compositions by Bogue calculation are often in error because of necessary assumptions of the true compositions of the cement phases. X-ray powder diffraction is a direct, bulk analytical method for phase analysis of fine-grained materials including clinker and cements. Each phase produces a unique diffraction pattern independently of the others with each pattern intensity being proportional to phase concentration. Difficulties in X-ray powder diffraction analysis include correction for sample absorption, selection of reference standards, and determination of individual pattern intensity. These problems are minimized by use of an internal standard, profile fitting, and careful reference standard selection. The availability of computers has revitalized interest in quantitative powder diffraction analysis by facilitating profile fitting for diffraction peak intensity measurement and whole pattern-fitting methods where the entire diffraction pattern, compared to discrete peaks, is used in the analysis.

Key Words: building technology, cement, clinker, phase abundance, X-ray powder diffraction, sample preparation

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1 INTRODUCTION

Portland cements are classified by ASTM into five types based, in part, on their phase composition. Type I cement is for general use while Types II through IV exhibit distinct performance properties that are exploited in producing a concrete that is better suited for the anticipated service conditions. Some examples of these modifications and their applications include the increased early age strength of a Type III cement due to an increase in alite content and fineness; the low heat evolution of Type IV cements due to lowered amounts of the most reactive phases, alite and aluminate, and a coarser grind; and the production of sulfate-resistant Type V cement by decreasing the amount of aluminate. High levels of periclase or free lime in any of the cement types creates durability problems associated with an increased risk of late expansion and cracking. The development of techniques for quantitative measurement of phase composition of cements will allow better understanding of compositional effects on performance and the prediction of concrete material properties.

While the importance of composition is recognized, the ability to accurately determine the composition of clinker and cement has proven to be a difficult task. Phase abundance evaluations of clinker are often performed by a point count technique using reflected light microscopy. The fine particle size of cements does not permit this type of analysis. An alternative method is estimation of potential phase composition using the Bogue calculation based on chemical analysis data. However, these results are often erroneous because the phase compositions assumed in the calculations can differ from those of industrial clinkers [1].

X-ray powder diffraction (XRD) analysis is the only technique for direct phase composition analysis of fine-grained materials cement. Each phase in a mixture produces its characteristic diffraction pattern independent of the others, and when these patterns are superposed, they form the powder diffraction pattern of the mixture (Fig. 1). This allows for explicit identification of the phases and polymorphs of each phase in the clinker or cement. Since the intensity of each phase's XRD pattern is proportional to its concentration, given proper calibration, quantitative phase abundance analysis is possible.

Despite these advantages, XRD is not widely used in the cement industry. No standard analytical methods exist, and calibration and analysis can be a difficult, time-consuming process. The advent of automated powder diffractometers facilitates the slow, manual tasks of phase identification and quantitative analysis. However, significant difficulties common to all XRD analyses as well as those inherent to clinker and cement continue to exist. Powder diffraction patterns of clinker and cement are weak, complex, and exhibit numerous peak overlaps. The diffraction pattern of alite, the predominant phase, dominates those of other phases. These overlapping peaks create difficulties in quantitative analysis by presenting few easily resolvable, strong diffraction peaks. Other difficulties include variability of diffraction patterns due to compositional or polymorphic variation, and with the ferrites, peak broadening due to compositional zoning or imperfect crystallinity [1]. With careful sample treatment and analytical technique, many of these difficulties can be minimized.
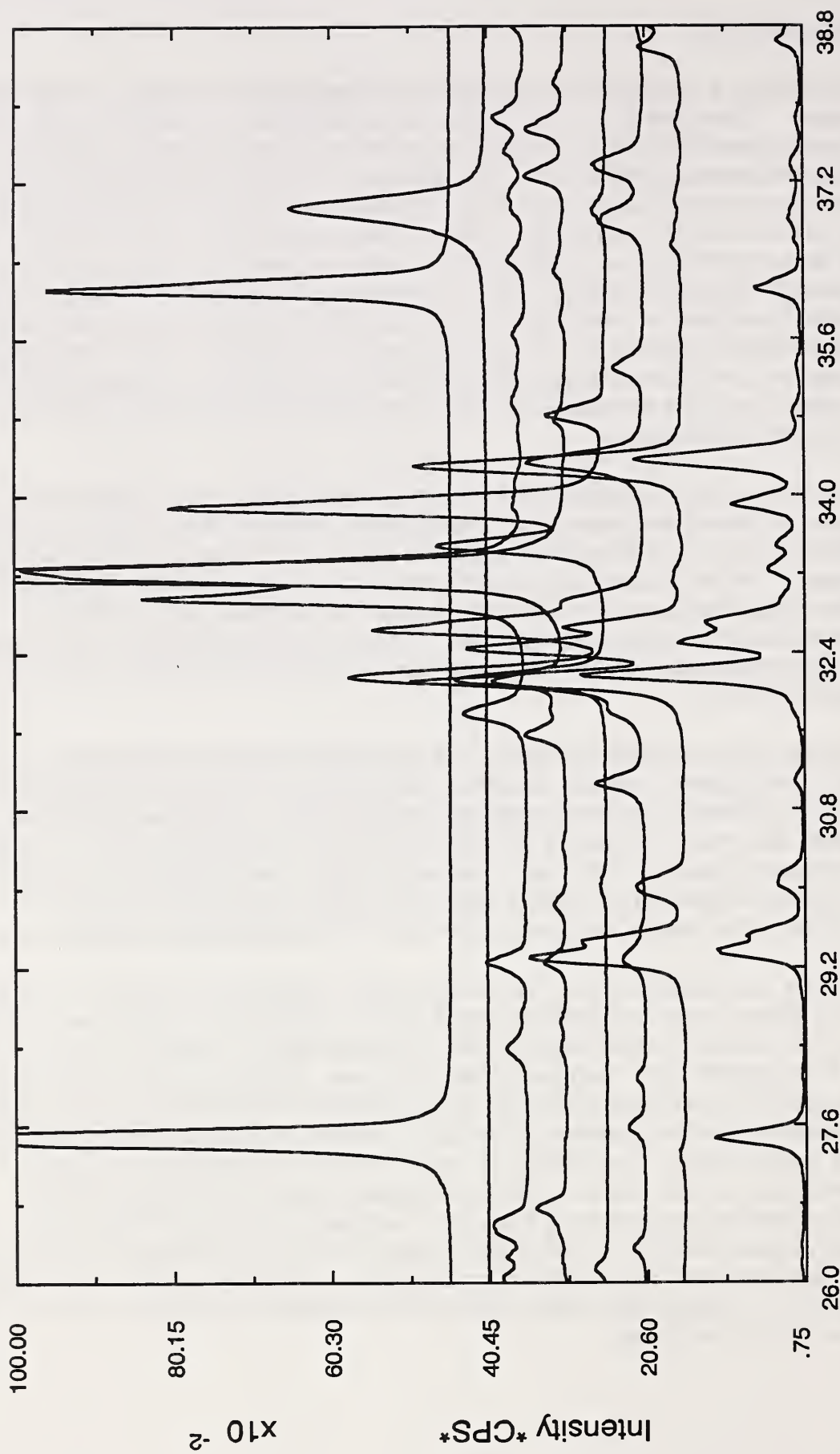
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Figure 1. A segment of an X-ray powder diffraction pattern (bottom) of a mixture of cement clinker phases, (A) alite, (B) belite, (C) ferrite, (D) cubic aluminate, (E) orthorhombic aluminate, (F) periclase, and (G) internal standard rutile illustrates the superposition of individual phase patterns and resultant peak overlapping.

2   DIFFICULTIES IN X-RAY DIFFRACTION ANALYSIS

X-ray powder diffraction has long been used in the cement industry for identification of phases and their polymorphs. Some of the early studies [2, 3] by cement researchers recognized the potential of XRD in the quantitative phase abundance analysis of clinker and cement. These efforts emphasized the necessity for attention to areas that pose the greatest difficulties in clinker and cement analysis:

> 1) sample preparation;
> 2) selective dissolution techniques;
> 3) selection of reference standards;
> 4) quantitative analysis method; and
> 5) calculation of peak intensities.

2.1   Sample Preparation

The success of any quantitative XRD experiment depends on careful sample preparation, the goal of which is to present a homogeneous, representative powder sample for analysis. Klug and Alexander [4] identified the critical factors in sample preparation as particle or crystallite size, sample thickness, preferred orientation, strain, and surface planarity.

A particle size between 1 and 5 μm is recommended for quantitative XRD analysis fine size distribution as powders of this fineness have been shown to produce diffraction patterns of the greatest intensity while minimizing problems such as microabsorption, extinction, preferred orientation, and sample homogeneity, all of which can produce peak intensity errors [4]. Wet grinding for 18 minutes with 20 ml of 200-proof ethanol in a Micronizing Mill[1,2] reduces the particle size of a 4 gm sample of -200- mesh clinker ground to a powder of 99 percent finer than 7 μm but not more than 8 percent finer than 0.5 μm [5]. Other grinding mills have been shown to produce suitable particle size distributions provided the sample is wet-ground [6]. Overgrinding or dry grinding may strain the crystallites or produce an amorphous surface layer, indicated by a decrease in peak intensity and an increase in peak width [4].

2.2   Selective Dissolution Techniques

Concentrating specific phase fractions by extraction of other phases facilitates the identification and quantitative analysis of less abundant interstitial phases and the identification of phase polymorphs. The mass loss after an extraction also serves as an additional test of the accuracy of the XRD results. Extraction of the silicates is performed using a salicylic acid-methanol solution [1], while a potassium hydroxide/sucrose solution is used to extract the interstitial phases. By taking advantage of the different rates of dissolution of the silicates in salicylic acid-methanol extraction [7], these techniques are useful in producing belite-enriched residues. Details of these extraction procedures are given in Appendix A.

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[1]McCrone Micronizing mill, McCrone Research, Westmont, IL

[2]Mention of brand names is made to provide complete details of the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are the best available for the purpose.

2.3   Selection of Reference Standards

Reference standards for each phase can be purchased commercially or synthesized in the laboratory, but need to be representative of their respective phases with regard to composition, polymorphism, and crystallinity.   Calibrations using improper standards may result in significant error [8].   Gutteridge [9] reports that the British Cement Association (BCA) uses over thirty reference standards for calibrations, including ten for alite, six for belite, four for aluminates, and ten for the ferrites. For the BCA analysis, proper reference standards are selected by matching them with polymorphs identified in the unknowns. Selective dissolution techniques can be used to facilitate polymorph identifications. A reliability factor and the sum of the individual phase fractions can also be used to assess the fit of the references to the unknowns [9].

Alternative techniques employed for obtaining standards include the selective extraction of phases [10], use of multiple cements whose phase composition were determined by a Bogue calculation [11, 12], calculated diffraction patterns [13], and use of clinkers whose compositions were determined by microscopical point count [14, 5].

3.0   QUANTITATIVE METHODS

3.1 The Internal Standard Method for Quantitative Analysis

While peak intensity is proportional to phase concentration, this relationship is usually not linear due to absorption of the x-ray beam by the mixture [4]. The mass absorption coefficient (μ/ρ), a measure of a phases X-ray 'stopping power', is equal to the sum of the μ/ρ of each element times the mass fraction of that element. A table of μ/ρ values can be found in Klug and Alexander, Appendix V. The μ/ρ of the mixture is dependent on the mass fraction of each phase (table 1).   The μ/ρ of the mixture is difficult to measure and the mass fraction of the phases are not known.   In the rare case where a mixture is composed of two polymorphs, where the $\mu/\rho_{MIXTURE} = \mu/\rho_{PHASE\ 1} = \mu/\rho_{PHASE\ 2}$, there is a linear relationship between mass fraction and peak intensity ratio of the phase in the mixture to the pure phase. However, the most common case is where the μ/ρ of the mixture is not known, and the μ/ρ of the phases are not equal. In a diffraction pattern with a weak absorber, such as periclase, and a strong absorber, such as rutile, the periclase peaks will appear weaker and those of rutile will appear stronger than expected if there were a linear relationship between peak intensity and concentration.

Klug and Alexander [4] derived the equations for quantitative phase abundance analysis by x-ray powder diffraction showing that the intensity of a diffraction peak i from phase α in a flat, packed powder mixture is given by:

$$I_{i\alpha} = \frac{K_{i\alpha}\, X_\alpha}{\rho_\alpha\, \left(\frac{\mu}{\rho}\right)_m}$$

(1)

where,

$I_{i\alpha}$	=	the intensity of diffraction peak i of phase α,
$K_{i\alpha}$	=	a constant dependent on the diffractometer, peak i of phase α, and the experimental conditions,
X_α	=	the mass fraction of phase α,
ρ_α	=	the density of phase α, and
$(\mu/\rho)_m$	=	the mass absorption coefficient of the mixture.

Also, Klug and Alexander demonstrated that in a multi-component mixture of phases with different μ/ρ values, and where the $(\mu/\rho)_m$ is unknown, an internal standard (I_s) added to the sample in a known proportion can be used to correct for absorption effects. By using the peak intensity ratio, $I_{i\alpha}/I_s$, the absorption factors are eliminated. Calibration curves are determined for each phase using mixtures of known phase proportions (x_α and x_s) and plotting the peak intensity ratio $I_{i\alpha}/I_s$ versus the mass fraction of the phase (Fig. 2).

Table 1. Clinker and Cement Phases, Compositions, and Mass Absorption Coefficients.

| Phase		μ/ρ (Cu Kα Radiation)
Alite	Ca_3SiO_5	92.3
Belite	Ca_2SiO_4	89.5
Aluminate (cubic)	$Ca_3Al_2O_6$	85.9
Aluminate (orthorhombic)	$NaCa_4Al_3O_9$	79.0
Ferrite (low Al)	$Ca_4Fe_4O_{10}$	177.7
Ferrite	$Ca_4FeAl_3O_{10}$	107.1
Periclase	MgO	27.8
Free Lime	CaO	119.1
Arcanite	K_2SO_4	84.8
Thenardite	Na_2SO_4	35.0
Gypsum	$CaSO_4 \cdot 2H_2O$	82.4
Bassanite	$2CaSO_4 \cdot H_2O$	70.1
Anhydrite	$CaSO_4$	74.1
Internal Standards		
Rutile	TiO_2	129.3
Corundum	Al_2O_3	31.4
Silicon	Si	60.6
Flourite	CaF_2	91.9
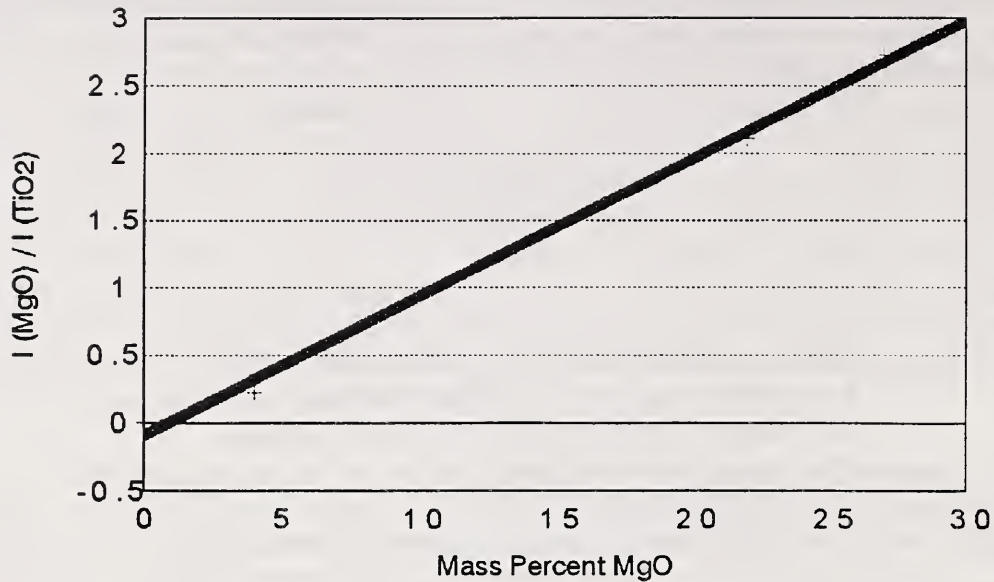
Figure 2. Calibration plot relating diffraction peak intensity ratio (I_{MgO}/I_s) vs mass fraction (X_{MgO}) periclase.

3.2 The Reference Intensity Ratio Technique

The Reference Intensity Ratio (RIR) technique [8] is a adaptation of the internal standard method where the slope K of the calibration plot is given by:

$$\frac{I_{i\alpha}}{I_{js}} \frac{I_{js}^{rel}}{I_{i\alpha}^{rel}} \frac{X_s}{X_\alpha} = K = RIR_{\alpha,s} \tag{2}$$

where:

I^{rel}_{js} =   the relative peak intensity of diffraction peak j of internal standard s

$I^{rel}_{i\alpha}$ =   the relative peak intensity of diffraction peak i of phase α.

The RIR is defined as the ratio of the strongest diffraction peak intensities of phase α to internal standard s [8]. While the International Center for Diffraction Data/Joint Committee for Powder Diffraction Standards (ICDD/JCPDS) database contains relative intensity data and RIR values with corundum (α-alumina) as an internal standard ($I_\alpha/I_{Corundum}$), these values are best measured using the same diffractometer used for the analyses. In practice any pure phase may be used as the internal standard; those commonly used for clinker and cement include rutile, corundum, and silicon. Better estimates of RIRs are obtained using experimentally determined relative intensities for pure phases, and multiple calibration mixtures with different phase proportions [8].

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Measurement of RIRs requires:
  1) collection of diffraction patterns of pure phases for measurement of relative
     intensity values;
  2) collection of diffraction data on binary or multi-phase mixtures of known
     composition with a known amount of internal standard intermixed; and
  3) calculation of areas of selected diffraction peaks and RIR values using eq. (2).

Analysis of unknown mixtures involves:
  1) the addition and homogenization of a known amount of internal standard;
  2) collection of three replicate diffraction patterns, repacking the sample
     for each scan;
  3) measurement of background-subtracted peak intensities; and
  4) calculation of mass fraction of each phase using eq. (3).

$$ X_\alpha = \frac{I_{i\alpha}}{I_{js}} \frac{I_{js}^{rel}}{I_{i\alpha}^{rel}} \frac{X_s}{RIR_{\alpha,s}} \tag{3} $$

This mass fraction is based on a mixture <u>including</u> the internal standard. The
concentration of each phase fraction in the original sample is given by eq. (4):

$$ X_\alpha = \frac{X_\alpha}{(1-X_s)} \tag{4} $$

Two variations of the RIR technique include use of an internal standard that is not present
in the sample (the most common method) or use of one of the unknown phases as the
internal standard and assuming a total accounting for all phases for normalizing the results.
The normalization approach may produce errors not easily detectable if all the components
have not been identified or the assumed total is in error.

3.3   Measurement of Diffraction Intensities

Accurate measurement of X-ray intensity is necessary for quantitative analysis and requires
longer counting times than those typically used for qualitative analysis. X-ray generation is
a random process, so the net error in counting is an inverse function of the total counts
measured at each step, or for each peak area.   The random error is proportional to $N^{-1/2}$
where N is the total counts after the background has been subtracted [15]. The diffraction
pattern intensities are determined for each phase in order to relate intensity to phase
concentration in a mixture. Two approaches of diffraction intensity measurement have
been successfully used in quantitative XRD studies, peak areas and peak heights.   Peak
area measurement can be performed by profile fitting (Fig. 2) or by planimetry.   Profile
fitting estimates the background, separates overlapping peaks, fits a profile to each peak,
and computes both the peak location and background-subtracted peak areas. The
advantages of profile fitting are speed in analysis, consistency, and the ability to run
interactively or in a batch mode. Difficulties in profile fitting can be encountered in
attempting to resolve peak groups that are severely overlapped.   Peak height
measurement is generally restricted to mixtures that exhibit similar peak shape
characteristics or, as will be discussed later, as individual scan step intensities for whole
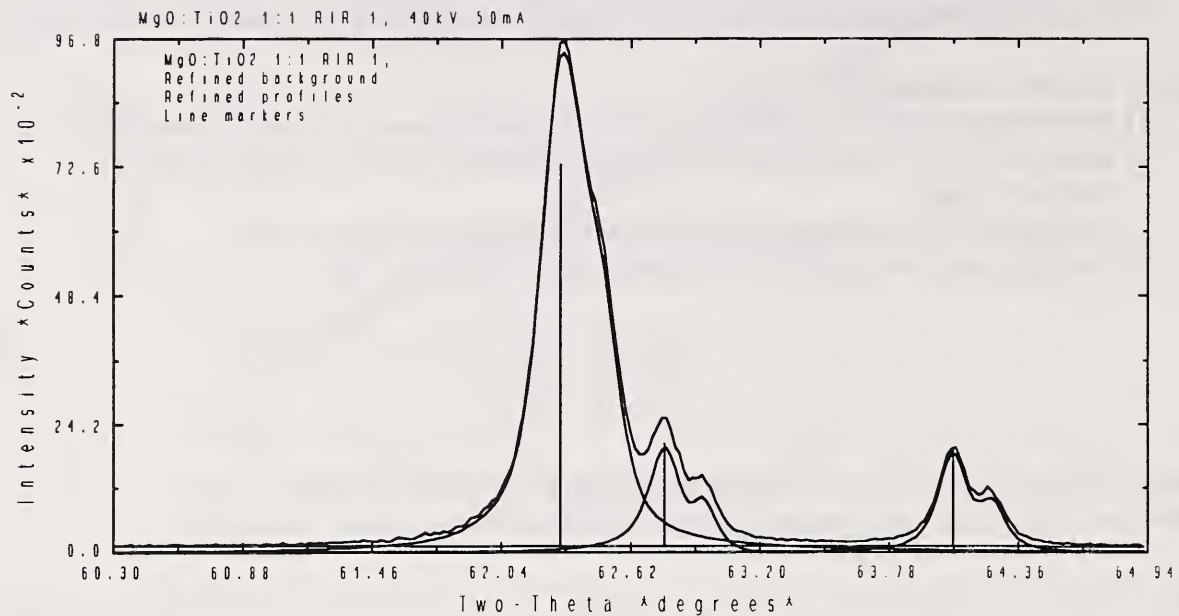pattern-fitting routines.

Figure 3. Profile fitting is used to estimate a background level, fit a profile to the peaks, and calculate the background-subtracted integrated peak area.

As illustrated in Figure 1, clinker and cement diffraction patterns have few resolvable diffraction peaks. The peaks that can be resolved are very weak and therefore are difficult to measure accurately. Copeland and Bragg [2] developed a method whereby overlapped peaks could be used if a resolvable diffraction peak of an internal standard was measured. This method involves measurement of at least n intensity regions for n phases and solving a set of simultaneous linear equations. This method was later augmented by including chemical data from X-ray florescence analysis. The combined diffraction/chemical analysis was found to produce greater accuracy [16]. Taylor [13] used a similar approach but calculated the areas of 49 regions encompassing individual peaks or peak groups and, in addition, used calculated diffraction patterns as reference standards.

Alternatives to discrete peak intensity measurement are methods in which the entire diffraction pattern, or selected portions, is used on a point-by-point basis. This whole pattern approach eliminates the need to resolve individual diffraction peaks and is not as sensitive to the effects of preferred orientation and extinction [17]. Two distinct whole pattern methods are being developed for QXRD. The whole pattern fitting method (WPF) uses standard diffraction patterns of phases selected as being representative of the unknowns. The Rietveld method [17] calculates diffraction patterns from crystal structure data, refining the structure data as it seeks the diffraction patterns that best fit those of the unknown mixture.

3.4 The WPF Method

The extension of the Copeland-Bragg method to measurement of diffraction patterns on a point-by-point basis has been implemented in a number of studies and is commonly referred to as the whole pattern fitting method [9, 11, 12, 14, 18 - 20]. This method treats the intensity of each data point from a diffraction pattern of a mixture as the sum of the background intensity and a linear combination of intensities from each phase in the mixture, and seeks to find the weighted sum of reference patterns that best matches the unknown pattern. This is performed point-by-point across the entire pattern by setting up a series of linear equations with m unknown phase intensities. A least-squares method is employed to find the 'best-fit' combination of reference diffraction patterns to that of the unknown mixture. When the unknown has been intermixed with a known amount of internal standard the weighting factors for each reference pattern are converted into mass fractions using the RIR technique. In cases where pure phases are not available synthesized diffraction patterns have been substituted [19]. This method still relies on the assumption that the reference standards are similar in composition and structure to those of the unknowns. Gutteridge's [9] procedure employs a set of polymorphs for each phase for use as reference standards and attempts to match references to the polymorphs identified in the unknowns. In an attempt to better match the reference standards to the unknowns, some studies [5, 10 - 12, 14] have used commercial cements and clinker as reference standards.

3.5 The Rietveld Method

The Rietveld method [8, 17] has been adapted to processing XRD data from a procedure developed for neutron diffraction. Like the whole pattern fitting routine, the Rietveld method uses the entire diffraction pattern to find the best-fit set of reference patterns to the diffraction pattern of the unknown. However, the Rietveld method uses calculated diffraction patterns as references, which requires knowledge of the approximate crystal structure of each phase. The diffraction pattern is calculated by refining structural parameters, background, and profile parameters using a least-squares procedure. The result is a set of pattern intensity weighting factors that can be used with the RIR method for quantitative analysis and, in addition, the Rietveld method provides information on refined crystal structure, refined unit cell parameters, and approximate chemical compositions for each phase. The Rietveld method has been applied in numerous geological applications and in the examination of alite polymorphs in a portland cement [21].

4 SUMMARY

Performance characteristics of portland cements can be related to their compositions. The ability to measure compositions will facilitate the relating of cement and concrete performance to the phase compositions of the materials. X-ray powder diffraction has long been used as a qualitative tool as well as for quantitative analysis of phase abundance of cements. The basis for quantitative phase abundance analysis by X-ray powder diffraction was established decades ago but the method has not been widely used due to difficulties in calibration and analysis. The advent of the computer and improvement in sample preparation methods has aided in the analysis. Difficulties in calibration and analysis, and

those inherent to clinker and cements, can be minimized by careful sample preparation and analysis. The trend in diffraction methods toward whole pattern fitting routines has produced encouraging results. The advantages of these methods is in their use of the entire diffraction pattern and, for the Rietveld method, the ability to calculate a reference diffraction pattern that matches the pattern of the unknown. Application of these methods in the cement manufacturing industry may eventually result in the X-ray powder diffractometry, a direct analytical method, replacing the indirect combined methods of X-ray florescence chemical analysis and Bogue calculation for estimating the phase abundances of cement and clinker.

APPENDIX A   EXPERIMENTAL PROCEDURES IN X-RAY POWDER DIFFRACTION

1)   Particle Size Reduction by Grinding

Pure phase standards were crushed to pass as 100-mesh sieve, and powdered in a Micronizing mill for 18 minutes using 200-proof ethanol as a grinding fluid. The alcohol is removed from the suspension by vacuum filtering through a 0.45 filter in a Buchner funnel, and dried in a vacuum oven. The powder cake is disaggregated, placed in a glass vial, and stored in a vacuum desiccator. Reference mixtures are measured on a five-place balance, carefully homogenized using a mortar and pestle, and are stored in glass vials in a vacuum desiccator.

2)   Heat Treating Cement to Convert All Calcium Sulfates to Anhydrite

The sulfate addition to cement can occur as gypsum, hemihydrate or anhydrite, or a combination of these phases. Diffraction peaks of gypsum interfere with those aluminate peaks commonly used in quantitative analysis. Heat treating the cement at 500 °C for one hour will convert these forms of calcium sulfate to anhydrite.

3)   Data Collection Conditions

X-ray powder diffraction patterns are collected with a Philips[3] automated diffractometer using copper K-α radiation at 40kV and 50mA, and diffracted beam monochromater. Three replicate powder samples were carefully back-loaded in a standard cavity mount, and scanned over a range from 20° to 65° 2Θ, 0.02° step, and a 10-second count time.

4)   Resolvable Diffraction Peaks Used for Quantitative Analysis [5]

Phase	Peak 2-θ
ferrite	12.2
aluminate-orthorhombic	21.0
aluminate-cubic	21.1
aluminate-cubic	21.8
ferrite	24.4
alite	30.0
belite	31.0
periclase	42.9
alite	56.1

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[3]Philips Electronic Instruments, Mahwah, NJ.

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Appendix B SELECTIVE DISSOLUTION PROCEDURES

Chemical extraction procedures can be used to selectively concentrate phase fractions of a clinker or cement and are useful in the determination of phase polymorphs, isolation of phases for use as reference standards, and estimation of the mass fraction of the different phase groups. Given the fine texture and intergrowth of the phases, these extractions are most effective when performed using powders ground to a particle size optimum for XRD analysis. The following procedures were excerpted from Taylor [1].

1) Salcyclic Acid-Methanol Extraction (SAM)

The SAM extraction dissolves free lime, alite, and belite leaving a residue of the interstitial phases aluminate, ferrite, and minor phases periclase and alkali sulfates. As alite is the most readily dissolved of the silicates, this method has been used to obtain residues either pure or enriched in belite:

1) SAM solution; 20 g salcyclic acid to 300 ml methanol for removal of both alite and belite; 10-15 g salcyclic acid to 300 ml methanol for removal of alite (salcyclic acid about 5 times the mass of alite in the sample as given by the Bogue calculation),

2) stir 5 g. of cement (-10 μm) in a flask with the SAM solution for 2 h.,

3) allow the suspension to settle for about 20 minutes and filter using 0.45 μm filter in a Buchner funnel,

4) wash residue with methanol, dry in oven at 90° C, store in a vacuum desiccator.

2) Potassium Hydroxide-Sucrose Extraction (KOSH)

The KOSH extraction dissolves aluminate and ferrite leaving a residue of silicates and minor phases. This extraction followed by a SAM extraction for alite was used by Gutteridge [7] to produce a residue almost pure in belite.

1) 30 g of KOH and 30 g of sucrose dissolved in 300 ml of water,

2) 9 g of powdered cement is stirred in a 95° C KOSH solution for 1 minute,

3) filter the solution, wash the residue using 50 ml of water followed by 100 ml of methanol, dry the residue at 60° C, and store in a vacuum desiccator.

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