

Advances in quantitative XRD analysis for clinker, cements, and cementitious additions

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The Rietveld method allows a precise quantitative phase analysis of building materials. Thanks to the development of stable-functioning software and the use of high-performance detectors, a quantitative phase analysis by X-ray, including sample preparation, and measurement and evaluation, can be performed in fewer than ten minutes. This has made it possible to integrate the method into existing laboratory automation systems for process and quality control to provide a means of online monitoring. Due to the completely automated operating principle of the Rietveld software, no additional staff is required and the results are user-independent. The Rietveld method is now being employed in industrial laboratories and also in various cement plants owned by the Lafarge Group as the standard method of quantitative analysis of Portland Cement clinkers and Portland Cements (CEM I, CEM II A-L). © 2004 International Centre for Diffraction Data. [DOI: 10.1154/1.1649328]

INTRODUCTION

A reliable, precise, and very reproducible method to quantify the relative phase abundances in the Portland Cement clinker and Portland Cements is to use X-ray diffraction (XRD) in combination with the Rietveld method. This analysis is a powerful method for the determination of quantitative phase amounts in multiple phase mixtures. In order to apply the method there are two critical requirements: a stable and fast running software system and a precise working control file for each product that will be quantified. During the past few years several authors described the possibility for a quantitative Rietveld analysis of High Alumina Cements, Portland Cements and clinkers, gypsum raw materials, slags, fly ashes, and hydrated cement phases, as well as applications in industrial laboratories and technical centres (Aldrige, 1982; Füllmann *et al.*, 1999; Füllmann *et al.*, 2001; Gutteridge, 1984; Manias *et al.*, 2000; Möller, 1995; Pottie *et al.*, 2002; Struble, 1991; Taylor and Aldrige, 1993; Walenta *et al.*, 2001; Westphal *et al.*, 2002). Using modern software packages it is possible to analyse very complex mixtures of phases in the laboratory and to implement the method into existing automated quality and process control procedures. With suitable hardware a complete quantitative phase analysis of cements and clinkers can be performed in fewer than ten minutes. This time includes measurement and evaluation.

LIMITATIONS OF CONVENTIONAL QUANTITATIVE X-RAY ANALYSIS OF CEMENTS

Bogue calculation

Clinker and cement production is mainly controlled by X-ray fluorescence analysis (XRF), where phase abundance is calculated from the chemical composition using the Bogue

method. Unfortunately the absolute amounts of phase content cannot be determined. It can be, however, used for an estimation of the phase composition. The Bogue calculation does not account for the incorporation of foreign ions within the structures of the main phases, or for the occurrence of different solid solutions. Such an incorporation of ions can also occur as well in Alite, Belite, and the aluminate phase. The composition of the ferrite phase can be described by the solid solution series between C_2F and C_6A_2F (cement chemistry notation: C=CaO, A= Al_2O_3 , F= Fe_2O_3 , S= SiO_2). These factors can lead to high errors (even more than 10 wt.-% for Alite) in the quantitative phase analysis.

Conventional method by determination peak height and peak area

The classical method of determining the amount of a phase in a mixture is the comparison of peak height and peak area. The method is used for the analysis of the free lime content in Portland Cement clinker and gives acceptable results in most cases. Nevertheless this method enables not the quantitative analysis of the main clinker phases Alite and Belite. The peaks of both phases overlap nearly completely. Therefore precise results by conventional quantitative XRD analysis cannot be obtained. Preferred orientation effects that can occur in powder samples also limit the method. The sulphate phases in Portland Cement, especially gypsum, is influenced by this effect. A correct quantitative analysis by determining peak heights or peak areas is completely impossible in that case.

THE RIETVELD METHOD

Working principles

The Rietveld method was developed by Hugo M. Rietveld in 1969 (Rietveld, 1969) to refine neutron diffraction data. Later the method was adapted to X-ray diffraction data by Malmros and Thomas (1977) and by Young *et al.*

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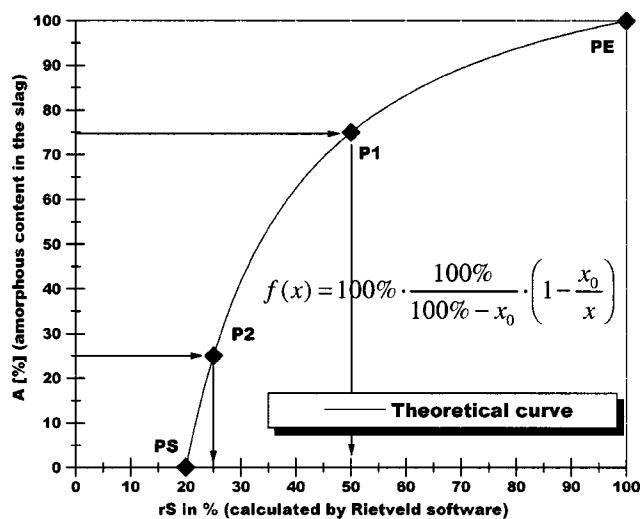


Figure 1. Determination of amorphous material by crystalline standard.

(1977). The principal of the method is, that the intensities calculated from a model of the crystalline structure are fitted to the observed X-ray powder pattern by a least squares refinement. This is done by varying the parameters of the crystal structures and of the peak profiles to minimise the difference between observed and calculated powder patterns. Because the whole powder pattern is taken into consideration, problems of peak overlap are minimised and accurate quantitative analyses can be obtained. To assess the success of the refinement, the so-called R-value quantifies the fit between the measured and observed patterns in %. However, in addition to this numerical value it is always useful to consider the graphical representation of the calculated and measured pattern and the difference plot. In that way, problems such as incorrect crystal structures or inhomogeneous phases can be easily recognised. To verify the precision and accuracy of the method it is therefore necessary to compare the results with alternative analysis methods. Detailed information of the theory and mathematics of the Rietveld method are given by Young (1993).

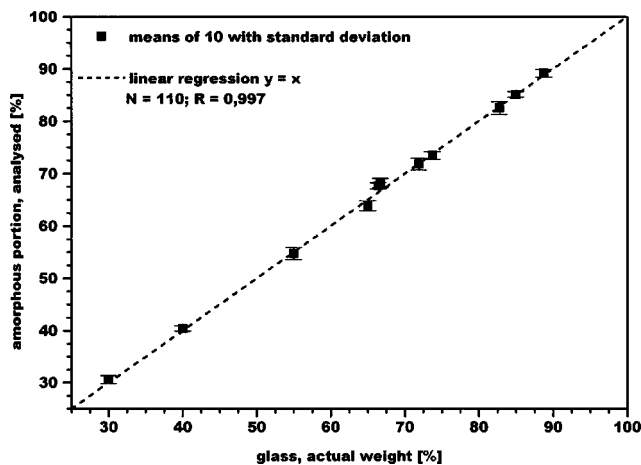


Figure 2. The correlation between the actual weight and Rietveld analysed amount of an amorphous portion in fly ash model mixtures (Westphal *et al.*).

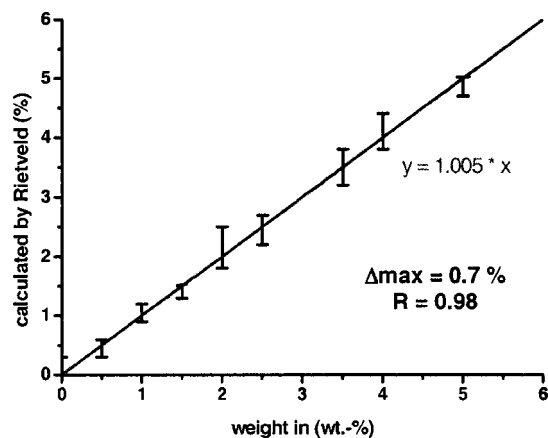


Figure 3. Quantification of model mixtures: gypsum content.

Determination of amorphous materials

Amorphous phases cannot be detected directly by X-ray diffraction analysis, because they do not produce additional visible reflexes in the X-ray diffraction diagram, but only increase the background. However, by using a defined quantity of crystalline standard material it is possible to determine the ratio of crystalline material in the sample to the crystalline standard and thus calculate the content of amorphous material in the sample. The backward calculation principle is illustrated in Figure 1.

This example shows the theoretical determination of amorphous content by means of 20% by weight of crystalline standard material. A calculated value of crystalline standard of 20% means that the sample contains no amorphous phase and a value of 100% indicates that the sample is completely amorphous. The calculation of the amorphous content can be done using the formula shown in Figure 1, where x_0 is the true amount of added standard and x the calculated one.

Experimental

High performance X-ray equipment (Bragg–Brentano working principle) with efficient X-ray detectors enables short time data acquisition in the range of about 5 minutes. Modern Rietveld programs permit a stable-functioning quantitative analysis of cement and clinker in less than two min-

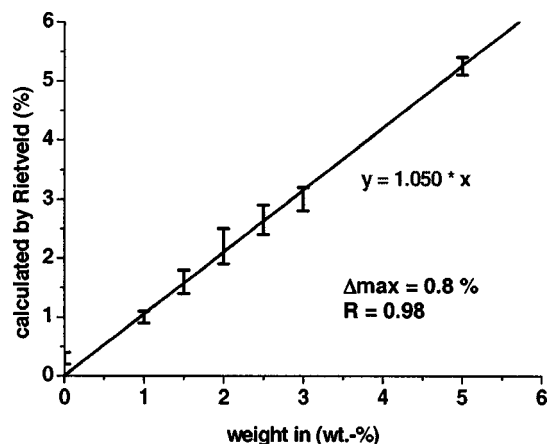


Figure 4. Hemihydrate content.

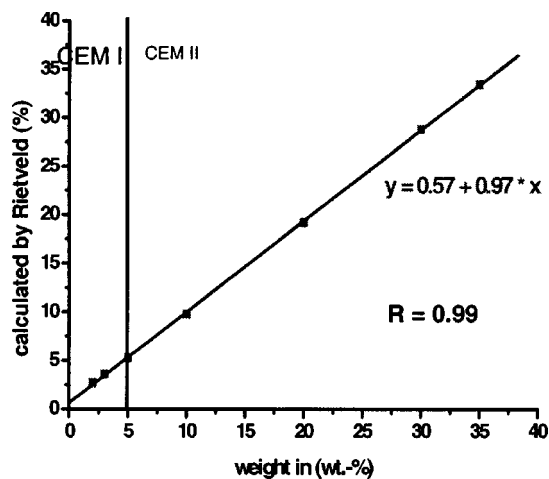


Figure 5. Quantification of model mixtures: Calcite content.

utes. The precision and accuracy of the calculation is directly linked to the quality of the generated diffractogram and to the so-called control file. This file contains all the information regarding the crystalline structures of the phases contained in the material to be analysed, as well as the crystallographic parameters that needs to be refined. The quantitative analysis can only take account of phases that are contained in the control file. Precise knowledge of the phase content of the respective material is therefore the prerequisite for application of the Rietveld method. The use of different raw materials and alternative fuels, as well as the occurrence of different burning conditions during the Portland Cement clinker manufacturing process, can result in various modifications of the main and secondary phases. This demands the use of different and suitable adapted structure models. The reliability and accuracy of the control file and thus of the quantification must always be established by quantifying model mixtures with known contents and by comparing with the results of other quantification techniques. A further criterion for the analysis precision is the sample preparation. In order to obtain a reproducible result, the sample material should be ground to a specific particle size for analysis by X-ray. However, if the grinding period is too long, the crystalline structures can be destroyed. An X-ray can then no longer identify particularly the gypsum contained in Portland

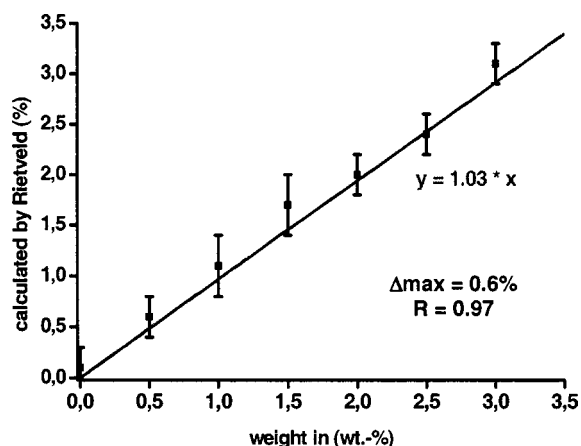


Figure 6. Portlandite content.

Cement. In order to ensure that a precise Rietveld analysis is obtained, it is therefore necessary not only to adapt the control file of the Rietveld software to the respective diffractometer and the measuring conditions, but also to optimise the sample preparation.

APPLICATIONS TO BUILDING MATERIALS

Quantitative analysis of raw materials

Blast furnace slag and fly ash are used as alternative raw materials for cement and concrete production. In order to guarantee a constant product quality constant it is necessary to control the quality of these raw materials. Westphal *et al.* (2002) already described the possibility and the precision of a quantitative analysis of these materials. The main chemical compounds of slag are CaO (33%–47%), SiO₂ (33%–39%), Al₂O₃ (5%–13%), and MgO (6%–11%). The mineralogical phase composition was determined as melilite (as an akermanite–gehlenite solid solution), merwinite, quartz, and the amorphous phase. Model mixtures were created for the validation of the quantification. Therefore merwinite and melilite were synthesised as pure phases. Simulating the glass phase a completely amorphous slag sample was used. Each of the mixtures was prepared and measured 10 times. Measurement uncertainties were estimated by statistical evaluation of model mixture quantification. These uncertainties are approximately ±1% for each, glass, melilite, and merwinite. Fly ashes build up a more complicated system compared to blast furnace slag. Fly ashes are mainly composed by anhydrite, hematite, magnetite, mullite, and quartz. The occurrence of gypsum in fly ash is a hint of wet treatment or storage. Thereafter, Belite, aluminate, calcite, lime, melilite, merwinite, and periclase were integrated to the model system. For the validation of fly ash phase quantification by Rietveld analysis again model mixtures were produced. Each mixture was prepared and measured ten times.

The results were statistically evaluated. Especially the correlation of the actual weight and analysed amount of an amorphous portion is remarkably good, as shown in Figure 2. The quantification uncertainty for the quantification of crystalline phases is about ±1%; for an amorphous portion, about ±2%.

Quantification of Portland Cement clinker

The Rietveld method is being increasingly employed in industrial applications for the quantitative phase analysis of Portland Cement Clinker and Portland Cement. During the last years many papers were published describing the precision of the quantitative Rietveld analysis of the clinker in the laboratory and in the industrial approach. The precision of analysis was mainly proven by quantifying NIST standards or model mixtures of synthetic phases. To check the accuracy of the Rietveld analysis of the clinker, the results were compared with those obtained by optical microscopy and a Bogue calculation. It can be summarized that the Rietveld method is a tool, which is more accurate for a quantitative analysis of the clinker than the Bogue calculation and can be compared with the phase quantification obtained by optical microscopy (point counting). In the case of Alite and Belite, the correlation between optical microscopy and the Rietveld

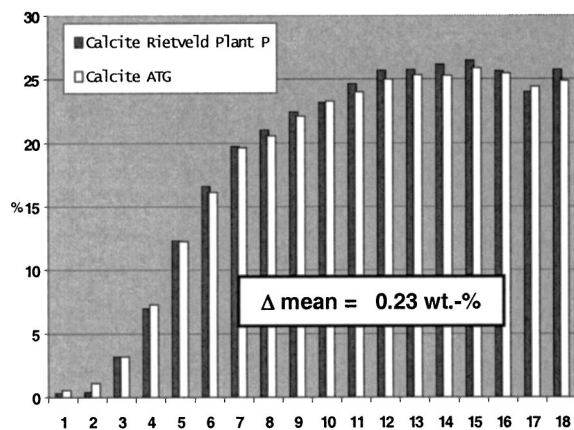


Figure 7. A comparison of the Rietveld analysis of calcite with TGA.

results is very good. However, the correlation for aluminate and ferrite is less good. This difference results from the fact that with optical microscopy these two phases, also called the interstitial phase, cannot be well separated. Very often optical microscopy can only give the results for the sum of these phases. An advantage of the Rietveld method compared to optical microscopy is that a distinction between the interstitial phases, ferrite and aluminate, is possible with a good accuracy. For checking reproducibility and repeatability of the method, different selected samples were prepared and analysed. The variation within the content of the main phases was in all cases lower than one weight-%.

Quantification of Portland Cement and blended cement

In addition to the clinker phases (Alite, Belite, ferrite, aluminate, lime, and periclase), the different Portland Cements contain sulphate phases, especially gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and anhydrite (CaSO_4), as well as calcite (CaCO_3), Portlandite $\text{Ca}(\text{OH})_2$, and quartz (SiO_2). Therefore a control file for Portland Cements (type CEM I) considers these 12 phases. All sulphate phases show a preferred orientation that can cause an overestimation of their quantitative content. However, the Rietveld software corrects this effect.

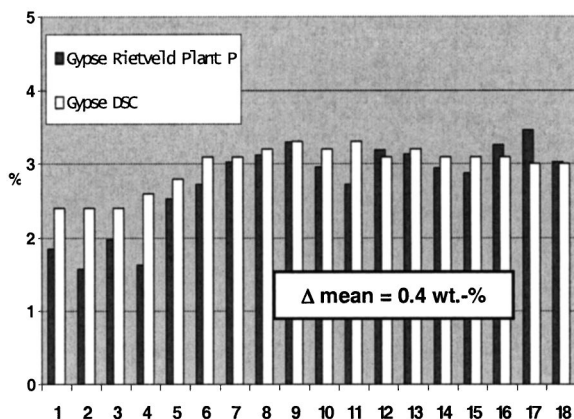


Figure 8. A comparison of the Rietveld analysis of gypsum with DSC analysis.

TABLE I. The maximum error to be expected from a quantitative Rietveld analysis of Portland Cement.

Alite:	65 wt.-% \pm 2.0 wt.-%	Gypsum:	2 wt.-% \pm 0.4 wt.-%
Belite:	15 wt.-% \pm 1.5 wt.-%	Hemihydrate:	1 wt.-% \pm 0.3 wt.-%
Ferrite:	6 wt.-% \pm 0.6 wt.-%	Anhydrite:	1 wt.-% \pm 0.3 wt.-%
Aluminate:	5 wt.-% \pm 0.6 wt.-%	Calcite:	1 wt.-% \pm 0.3 wt.-%
Lime:	1 wt.-% \pm 0.3 wt.-%	Portlandite:	1 wt.-% \pm 0.3 wt.-%
Periclase:	1 wt.-% \pm 0.3 wt.-%	Quartz:	1 wt.-% \pm 0.3 wt.-%

Figures 3–6 show quantifications of different model mixtures, demonstrating that the method also very precisely determines the secondary phases. For this purpose, defined quantities of the respective phase were interground into an industrially produced Portland Cement clinker. Calcite was added in quantities of up to 35% by weight, in order to ensure the precision of quantification in the case of cements with high calcite contents (CEM II A-L). All the mixtures were prepared and X-rayed several times.

The high precision of the quantitative analysis of gypsum and calcite was confirmed by a comparison to other quantification techniques such as DSC (differential scanning calorimeter) and TGA (thermo-gravimetric analysis). Therefore 18 technical produced cements from a Lafarge plant were investigated. Here, too, a close correspondence with the Rietveld results was established. The comparisons are shown in Figure 7 and Figure 8.

Depending on these results, the absolute error related to the phase content of the Portland Cement clinker and Portland Cement can be estimated, as shown in Table I.

Cements of types CEM II and CEM III contain materials such as fly ash and blast furnace slag up to a content of 35%, respectively, 80% by weight. Apart from the main crystalline phases merwinite and mullite, these materials also contain amorphous constituents. These phases therefore also have to be taken into account when quantifying those cement types. To test the accuracy of quantitative analysis of the amorphous phase, different model mixtures consisting of Portland Cement, blast furnace slag, and fly ash were analysed. The results are shown in Table II. The added blast furnace slags and fly ashes had different amorphous contents. A comparison of the expected amorphous contents with the calculated contents showed a close correspondence. By repeating the preparation and measurements, a high reproducibility of the results was also proved.

TABLE II. A quantitative analysis of the amorphous content of model mixtures.

Mixture	Composition	Expected amorphous content	Calculated amorphous content
1	5% fly ash 95% CEM I	4.9%	7.4%
2	10% fly ash 90% CEM I	9.9%	8.4%
3	15% fly ash 85% CEM I	14.8%	14.5%
4	25% fly ash 75% CEM I	24.7%	26.8%
5	40% slag (1) 60% CEM I	26.7%	27.3%
6	70% slag (1) 30% CEM I	46.6%	42.8%
7	40% slag (2) 60% CEM I	38.0%	36.0%
8	50% slag (2) 50% CEM I	47.5%	49.5%
9	70% slag (2) 30% CEM I	66.6%	66.8%

Aspects for quantitative analysis of hydration reactions of cements

The early hydration reaction mechanisms of Portland Cements have been widely studied and reviewed during the last years. The qualitative progress of the hydration is therefore well known. Although Portland Cements produced by different competitors can be characterized considering their hydration behaviour. Quantitative investigations of the early ages of Portland Cement hydration are poorly cleared. The hydration reactions of mixed systems containing Portland Cements and calcium aluminate cements are not even qualitatively known very well. Using modern X-ray equipment, it is possible to characterize these early hydration reactions qualitatively. The application of the Rietveld method enables us also to calculate a very precise quantitative analysis of the hydration products. With short measurement times this quantifications can be done nearly online so as to follow the progress of hydration “*in-situ*.” Some advantages of online measurements are shown as follows: hydration needs not to be stopped for analysis; no grinding and sample preparation effects; the same sample preparation can be investigated; several times; the initial first reactions can be followed; and allows us to calculate reactions kinetics.

Because of the small volume of the usual sample holders the sample could dry and therefore the hydration probably stop after a few hours. To avoid this effect a special climatic chamber will be used for the measurements. This climatic chamber enables a relative humidity of 95% at a temperature of 50 °C. At lower relative humidity, even higher temperatures (more than 100°) can be reached. To avoid carbonation effects all measurements should be done in a CO₂ free nitrogen atmosphere. By quantifying the phase composition of the dry material and the early hydration products, it is possible to find correlations between the phase composition of cements, the hydration behaviour, and the physical properties. Beneath this also the influence of temperature and additives on the hydration reactions can be determined. The Rietveld method enables us to perform quantitative phase analyses as well as to determine solid solutions and the incorporation of foreign ions in phases. This means that storing these hardened cement samples in defined atmosphere also statements about the kinetics, for example, of carbonation effects or sulphate attack can be made.

CONCLUSIONS

The Rietveld analysis is a method allowing the precise and reproducible quantification of the Portland Cement clin-

ker and Portland Cement (CEM I). It very effectively determines the sulphate phases gypsum, hemihydrate, and anhydrite, as well as calcite and Portlandite. The results are comparable with those of TGA analysis, DSC analysis, and microscopic analysis. It also provides a precise quantitative analysis of blast furnace slag and fly ashes, particularly with regard to the amorphous content. The successful quantification of alternative raw materials and model mixtures provides a solid basis for the quantitative analysis of Portland Composite Cements and Blast Furnace Cements (CEM II and CEM III). However, the prerequisite for the applicability of the Rietveld method is an optimised control file that is suited both to the material to be analysed and to the respective X-ray diffractometer. In order to ensure a correct analysis, an individual adaptation to the respective place of application and sample material is therefore essential in every case.

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