

# Rapid Determination of the Phase Assemblage in Hydraulic Binders with High Accuracy and Precision

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The rapid and precise determination of the actual phase assemblage using X-ray diffraction with Rietveld analysis allows a consistent production of hydraulic binders. The requirements and advantages for this method are presented.

Identification of the gypsum phases (dihydrate, hemihydrate, anhydrite) in cementitious binders is highly important as they influence hydraulic properties, such as setting times, workability and microstructure development. The quantities of dihydrate and hemihydrate added during production are not present in the cement after milling as high temperatures and mechanical effects lead to their dehydration, yielding hemihydrate and anhydrite in unknown ratios. X-ray diffraction allows the direct determination of the gypsum phases present, thus, they are being quantified rapidly by automated analysis in order to counteract immediately when unintended changes in phase assemblage have occurred.

Similarly, amorphous phases in blended cements are being determined by standardless X-ray analysis, allowing a rapid and accurate quantification of the blast-furnace slag content.

## 1 Introduction

Calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), calcium sulfate hemihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) and anhydrous calcium sulfate ( $\text{CaSO}_4$ ) are added during the cement manufacturing process as set retarders. However, the added amounts are often not present in the cement after milling as high temperatures and mechanical effects cause dehydration of these phases, leading to the formation of hemihydrate and anhydrite in unknown ratios. The gypsum phases are commonly quantified by thermal analysis when the properties of the cement have changed. However, this method is time consuming and does not allow a direct determination of anhydrite. Therefore, it is not a practical method for controlling the cement milling. X-ray powder diffraction allows the direct determination of the crystalline components present in a multi-phase mixture. According to Rietveld [1,2], the observed and calculated intensities in a powder diffraction pattern are matched by least-square fitting. The gypsum phases can be determined rapidly by means of automated analytics, which in turn allows the adjustment of phase assemblage if changes have occurred unintentionally.

X-ray analysis also allows a quick and accurate quantification of amorphous components, such as ground granulated blast-furnace slag in

blended cements, enabling an accurate monitoring of changes in production in order to maintain a high quality level.

## 2 Experimental

All studies were carried out on a Bruker D4 Endeavor diffractometer equipped with a one-dimensional VANTEC-1 line detector. X-ray powder patterns were recorded in a range  $10\text{-}65^\circ$   $2\theta$  using  $\text{CuK}\alpha$  radiation. The measuring time was 0.05 seconds per step with step size  $0.02^\circ$  yielding an overall measuring time of less than 5 minutes. Rietveld analyses were performed using the TOPAS software. For automated Rietveld analyses the TOPAS BBQ software has been used. The observed profile shape was calculated from first principles using the fundamental parameters approach combining instrumental contributions and emission functions. The specimen contributions were calculated by refining simultaneously scaling factor, lattice parameters and crystallite size for each phase present. The background was calculated using a Chebyshev polynomial function with five free parameters.  $2\theta$  was corrected by refining the zero point error. All parameters were constrained in a way to avoid the outcome of physically meaningless values. This is particularly important where pairs of parameters are strongly correlating. The observed and calculated data were fitted by means of non-linear squares routine until the minimum  $\chi^2$  was obtained.

Structures used for the cement phases alite, belite, aluminate, ferrite, lime, arcanite, periclase, calcite, quartz, gypsum, bassanite, anhydrite, dolomite and portlandite were obtained from the literature. Where several structures exist for a phase, the data set resulting in the best fit (expressed by  $R_{\text{Bragg}}$ ) was chosen for all further experiments. For the quantification of tricalcium aluminate ( $\text{C}_3\text{A}$ ) two structures for describing the cubic and orthorhombic polymorph, respectively, were used simultaneously.

All refined parameters were checked for mathematical and physical reasonability. The calculated powder patterns were also inspected visually using difference plots.

### 2.1 Sample preparation

The existence of optimal-sized crystals is an essential requirement for X-ray diffraction. Since the clinker phases after cement milling are usually still too coarse for X-ray diffraction, a further grinding step on laboratory scale is required. Attention has to be paid that the gypsum phases are not too much ground, as it would lead to the destruction of their crystallinity. Practical experience has shown that the grinding should be adjusted for each cement type. Further details about sample preparation have been reported in the literature [3].

## 2.2 Preferred orientation of gypsum phases

The intensities in a diffraction pattern are created by several factors, see Eq. (1).

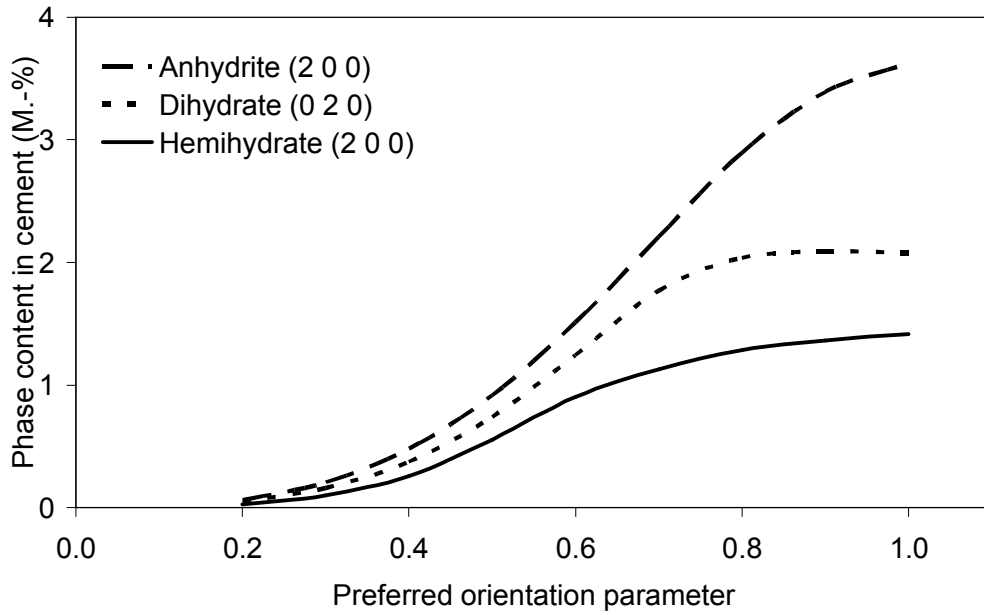
$$(Eq. 1) \quad I_{hkl} = S S M P F_{hkl} L(2q) F(2q) + b$$

where

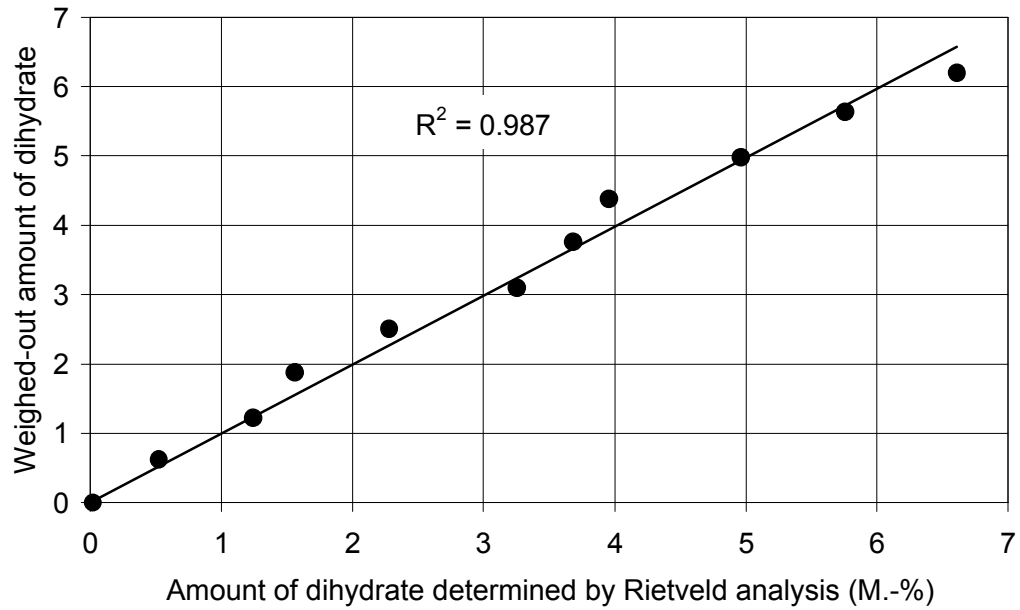
S	scale factor
M	multiplicity factor
P	preferred orientation
$F_{hkl}$	structure factor
L	Lorentz-polarisation factor
$\Phi$	peak profile function
b	background parameter

It is evident that besides the phase content described by the scale factor also the preferred orientation of the crystals contributes significantly to the peak intensity. This in turn means that if a preferred orientation exists for one or more phases it has to be considered in the Rietveld analysis in order to obtain an accurate quantitative result. For this purpose the application of the March-Dollase function [4] has proven to be adequate. The correlation between the phase content determined and the preferred orientation parameter of the gypsum phases (dihydrate, hemihydrate, anhydrite) is illustrated in Fig. (1). With the knowledge of the appropriate preferred orientation parameters, a very good correlation between the measured and the actual gypsum phases present can be obtained, as shown in Figs. (2.1) and (2.2).

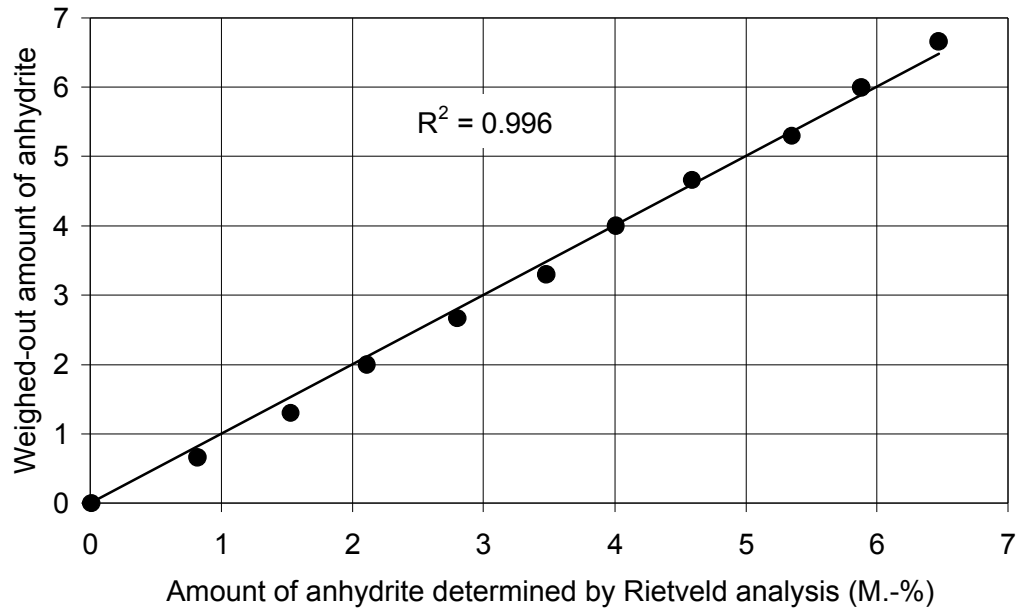
Hereafter, the term 'anhydrite' is applied for the anhydrite II polymorph with the crystallographic space group  $A_{\text{mma}}$ . Soluble anhydrite III, also called  $\gamma\text{-CaSO}_4$ , exhibits another crystal structure (space group  $C_{222}$ ) and, hence, a different X-ray powder diffraction pattern [5].



(Fig. 1) Determined phase content in dependence on the preferred orientation parameter



(Fig. 2.1) Comparison of weight-out amounts of dihydrate mixed with clinker meal and quantitative results obtained by Rietveld analysis



(Fig. 2.2) Comparison of weight-out amounts of anhydrite mixed with clinker meal and quantitative results obtained by Rietveld analysis

### 2.3 Quantification of gypsum phases

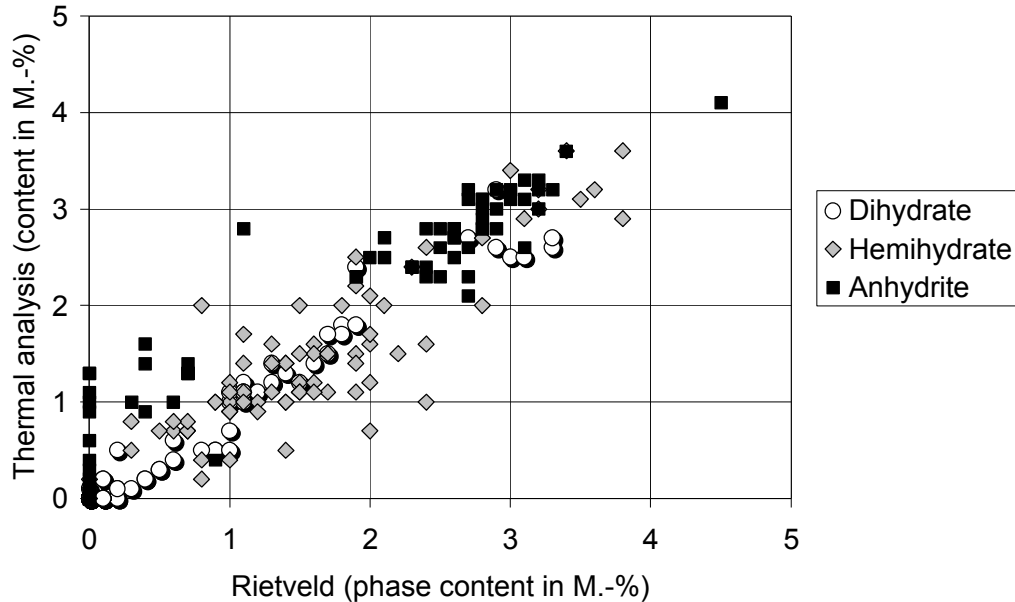
The accurate quantification of gypsum and hemihydrate contents in hydraulic binder materials is possible using thermal analysis, consisting of combined thermogravimetry (TG) and differential scanning calorimetry (DSC). However, despite the high precision of this method, the major drawback is that anhydrite cannot be determined directly but only be calculated in the following manner:

- 1) Determination of  $\text{SO}_3$  in cement by XRF or titration
- 2) Subtraction of  $\text{SO}_3$  in clinker determined by XRF or titration
- 3) Subtraction of  $\text{SO}_3$  present as gypsum determined by TG/DSC
- 4) Subtraction of  $\text{SO}_3$  present in hemihydrate determined by TG/DSC
- 5) The remaining  $\text{SO}_3$  content should be present as anhydrite.

Because of the uncertainty propagation it is questionable if with four measurements altogether an accurate determination of the anhydrite content is possible, which is also reflected in the poor correlation with the Rietveld analysis results, see Fig. (3).

The anhydrite content determined in the manner described above yields values exceeding 1 % although this phase is not being detected by Rietveld analysis as the main peak (2 0 0) is not present in the X-ray powder pattern. Problems with overlaps cannot occur for OPC and, hence, the results for anhydrite obtained from Rietveld are more precise and accurate than those calculated. The dihydrate determination shows a good correlation between thermal analysis and the Rietveld method, which

is also due to the fact that the peaks of the gypsum phase are well-pronounced in the X-ray pattern. Therefore, the quantification of gypsum phases by means of diffraction-based techniques is a very useful method for on-line monitoring the cement production [6].

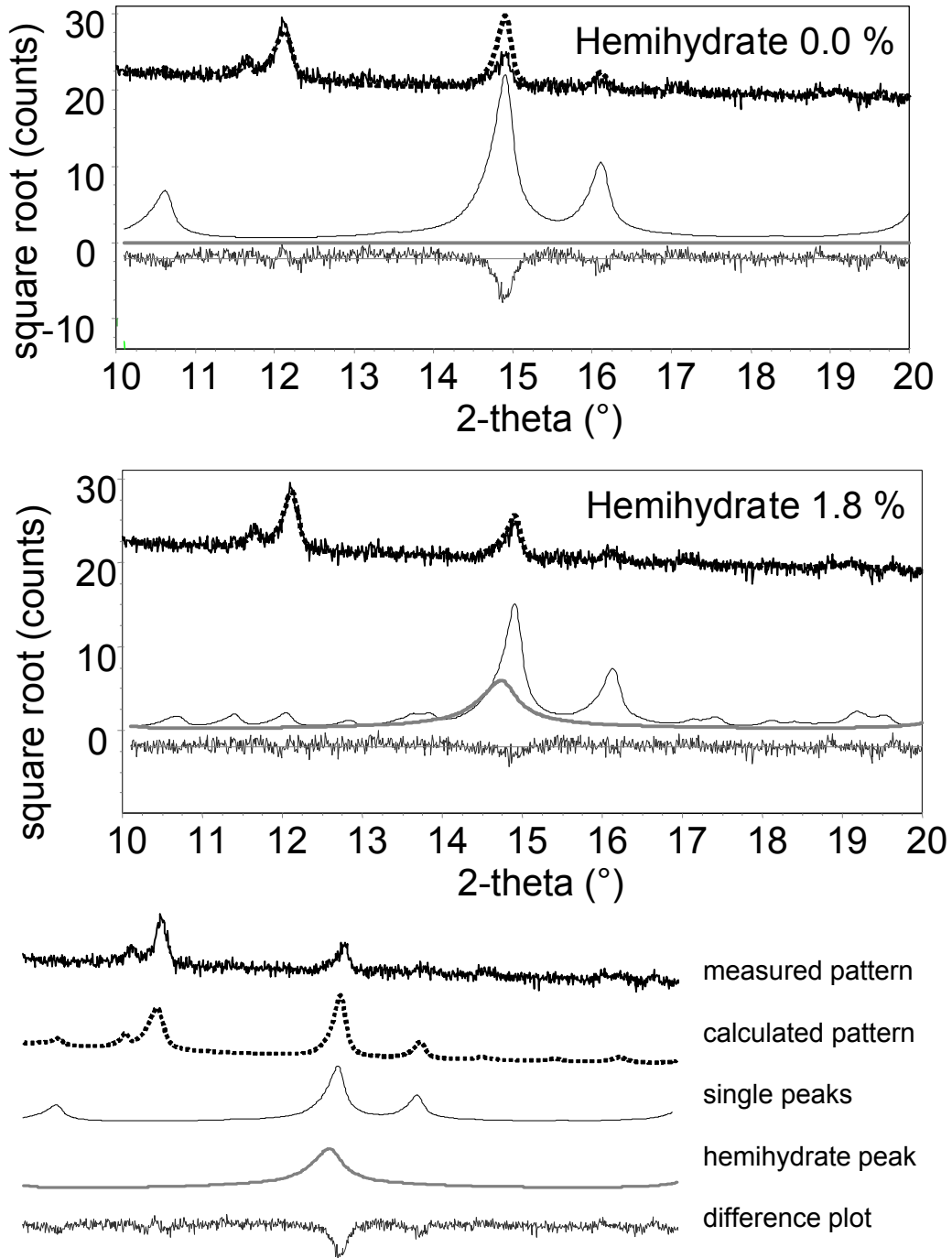


(Fig. 3) Comparison of amounts of gypsum phases determined by thermal analysis and Rietveld analysis

### 2.3 Determination of hemihydrate

The poorer correlation between hemihydrate contents determined by means of thermogravimetry and Rietveld analysis, respectively, shown in Fig. (3), has been described in earlier works where it was attributed to hemihydrate originating from dehydrating gypsum [7]. However, in our studies this amount was taken into account still showing the discrepancy which is actually caused by an overlap of the (2 0 0) main peak with the alite reflex at  $d \sim 5.95$ , corresponding to  $14.9^\circ 2\theta$  using  $\text{CuK}\alpha$  radiation. For the quantification of most cements this is not a problem as the diffraction peaks are accurately described by the existing structural models for the phases present and thus can be deconvoluted by the Rietveld method. However, in some cases foreign ion incorporation into the alite phase, particularly magnesium, cause structural changes in the crystal lattice, which in turn leads to a shift in peak positions and intensities, due to different X-ray scattering. The altered structures are not being matched by the structural model previously used which cause misfits in the Rietveld analysis leading to erroneous hemihydrate contents, as shown in Fig. (4). This problem can be avoided by checking the structure models regularly and adjusting them if required, particularly when different clinker types are being used in the production process. In this context, it is pointed out that

$\alpha$ - and  $\beta$ -hemihydrate can not be distinguished in powder patterns obtained with the measuring conditions commonly applied [8].

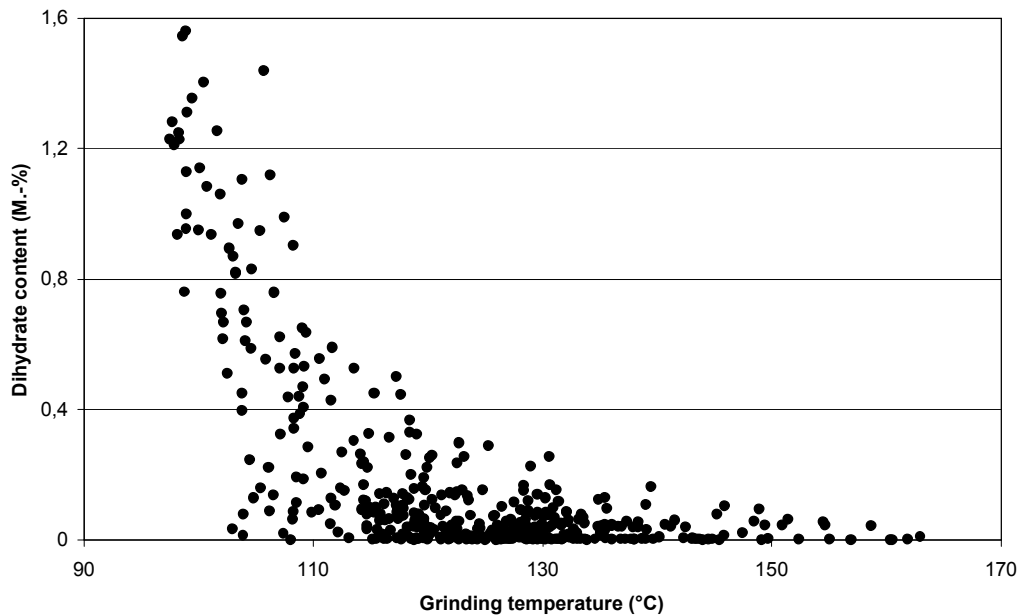


(Fig. 4) Application of an unsuitable alite structure [9] leading to a misfit of the peak  $\sim 14.9^\circ 2\theta$  ( $\text{CuK}\alpha$  radiation); the use of an appropriate structure [10] is demonstrated below

## 2.4 Technical application

Maintaining an even product quality is a major concern in cement production. Important properties of fresh and hardened mortars and concretes, such as workability, setting and strength development, depend strongly on the cement composition. In particular, alterations in gypsum contents may heavily affect those properties, causing problems on the construction sites and leading to customer complaints.

In this particular case, dihydrate and anhydrite at a fixed ratio were used in the cement milling process. Rietveld analysis revealed that the cement contained dihydrate in varying amounts after milling and sometimes even no dihydrate was present, see Fig. (5). Depending on the temperature of the mill dihydrate dehydrated partly or sometimes even completely to hemihydrate and anhydrite.



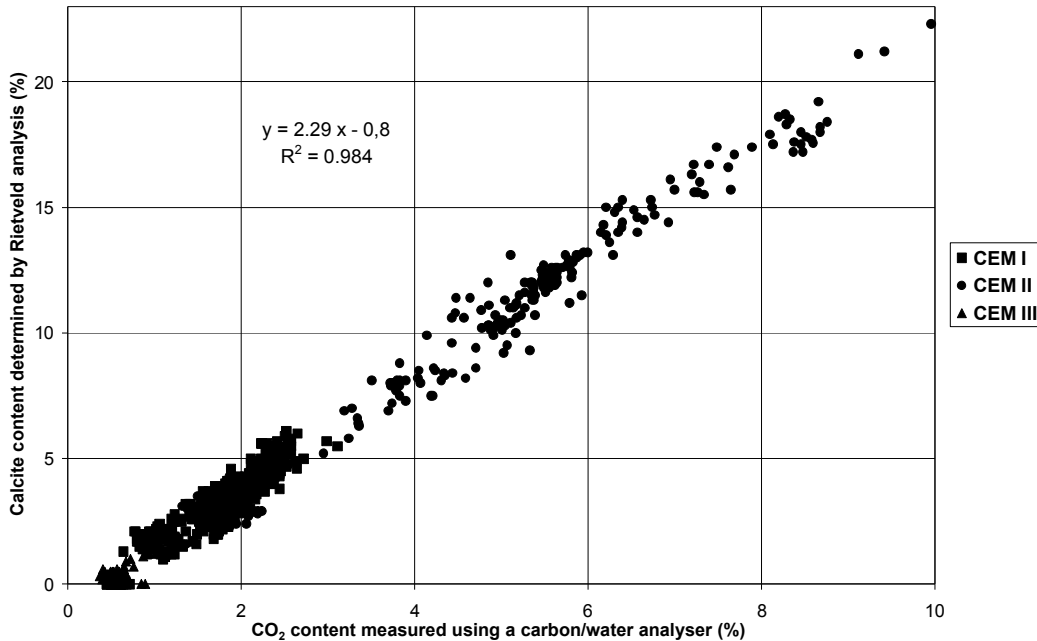
(Fig. 5) Dehydration of dihydrate during cement grinding depending on the mill temperature

## 3 Quantification of limestone

The determination of limestone in cement can be performed in a similar manner as the quantification of gypsum phases. Calcite is the main phase in limestone and shows a preferred orientation in the (1 0 4) reflection. By applying the appropriate orientation parameter a good correlation between the amount of calcite and the carbon dioxide content is obtained, shown in Fig. (6). This confirms other studies reporting a deviation of less than 0.5 weight percent between the actual calcite content and the analysed value [3]. The slightly higher deviation between the amount of calcite and CO<sub>2</sub> content is caused by the fact that not all the carbon dioxide is bound in



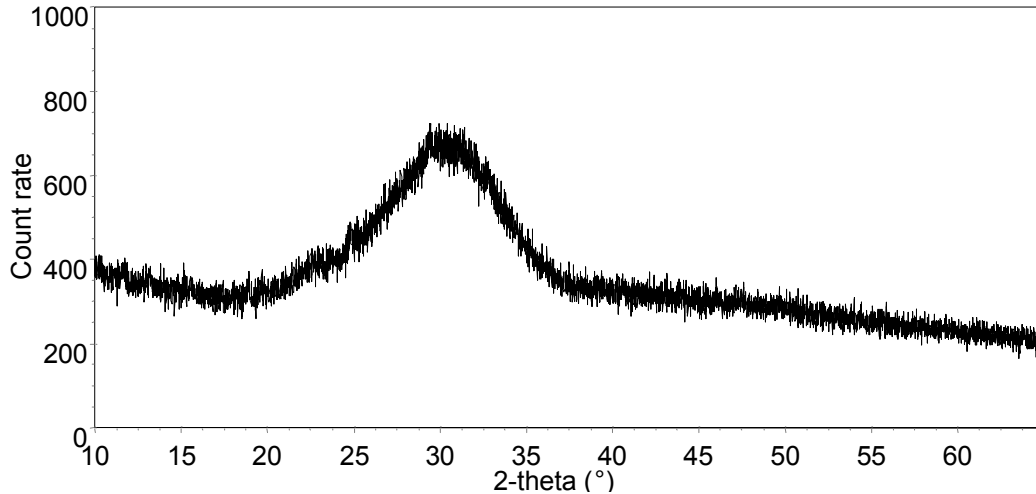
calcite by also by other phases such as dolomite. Thus, the Rietveld results can be considered as more accurate for calcite quantification than the values re-calculated from CO<sub>2</sub> analysis. It can be applied for all cement types and allows an even product quality in the manufacture of Portland limestone cements.



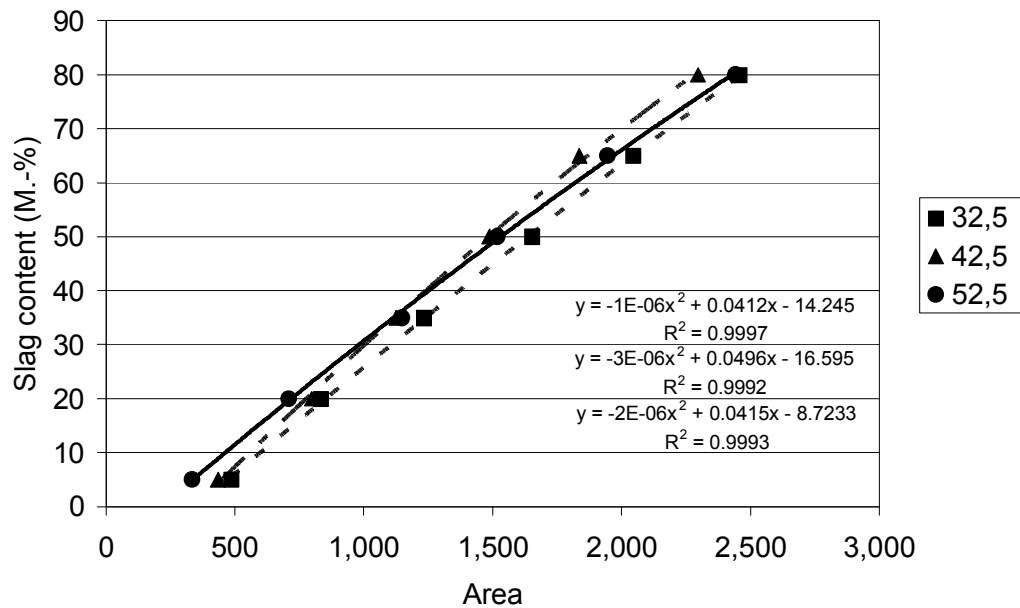
(Fig. 6) Correlation between the amount of calcite and carbon dioxide content in different cement types

#### 4 Quantification of blast furnace slag in CEM II and CEM III type cements

The presence of X-ray amorphous components in a phase mix causes an elevated background in the X-ray powder pattern. This rise does not occur evenly over the whole  $2\theta$  angular range, see Fig. (7). Instead, it appears as a strongly widened reflection which can be described mathematically using one or several functions, such as the Voigt function, combining the Lorentzian and the Gaussian function [11]. The peak area under this reflection is proportional to the amount of amorphous phases. Thus, the knowledge of this correlation allows the direct determination of the X-ray amorphous phase content. A calibration curve should be made regularly as the analytical conditions may change (e.g. decrease in beam intensity). The quantification of blast furnace slag has already been implemented in routine analytics where the origin of the slag has shown no relevance. Occasionally, the fineness can be important in which case a separate calibration is required for varying grading as shown in Fig. (8).



(Fig. 7) X-ray powder pattern of an amorphous ground granulated blast furnace slag



(Fig. 8) Effect of the grinding fineness on the background at different BFS contents

## 5 Summary and conclusion

The phase assemblage of hydraulic binders can be determined with high accuracy and precision by means of X-ray powder diffraction and subsequent Rietveld analysis. The results obtained allow a conclusion of operational processes [12,13]. X-ray amorphous blast furnace slag can be quantified in CEM II and CEM III type cements besides the crystalline components using a standardless method. Rietveld analysis succeeded as a valuable tool for monitoring production processes and quality control since all requirements for the fully automated operation have been fulfilled.

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