Travaux Pratiques de Matériaux de Construction

Section Matériaux

Etude de Matériaux Cimentaires par Diffraction des Rayons X sur Poudre

Study of Cementitious Materials by X-ray powder diffraction

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Rapport / Report

Soumis deux semaines après la TP, avec la date, le nom de groupe spécifié, le rapport doit être en anglais

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1. Introduction

X-ray powder diffraction is a technique widely used in material science to investigate crystalline materials in finely divided or powder form, it can also be applied to non-crystalline solids. The method is ideal for analyzing crystalline phases (e.g. minerals) because diffracted X-rays are direct probes of the repeating atomic units in solids.

Qualitative analysis is based on the fact that each crystalline structure has a certain distribution of repeat distances which result in a diffraction pattern that is muck like a fingerprint. The particular distribution and intensity of diffraction peaks is uniquely characteristic of each crystalline phase.

Quantitative analysis, i.e. determination of the amounts of more than one phase in a mixture, can be done because the diffraction intensities are directly related to crystal structure and the amounts of each phase. Quantitative analysis methods range from those using one or more reflections to those using the entire diffraction pattern. The latter can employ either measured standard patterns or patterns calculated based on the crystal structures of the component phases, known as the Rietveld method.

The Rietveld method uses all intensity data in a pattern and thereby allows to overcome some of the most encumbering problems of methods employing only one or a few of the most intense reflections. The method finds wide application in research and industry, including cement production, ceramics, mineral trading, mining and hydrocarbon exploration, metallurgy and waste management.

1.1. Aim

This practical course elaborates and illustrates the X-ray powder diffraction technique and its application to cementitious materials. The students are expected to acquire a basic understanding of:

- the principles of X-ray powder diffraction
- the design and operation of a standard laboratory X-ray powder diffractometer
- scope of materials and sample preparation
- qualitative analysis of a X-ray powder diffraction pattern using a dedicated software program
- quantitative analysis of the X-ray powder diffraction pattern of an unknown sample using the Rietveld method implemented in a dedicated software program

1.2. Basic principles

X-ray diffraction methods measure the interference pattern produced by the coherent scattering of an incoming monochromatic X-ray by a three-dimensional periodic grated material, here a crystal lattice. To obtain a characteristic interference or diffraction pattern of the crystal lattice, it is important that the wavelength of the incoming beam is of the same order of magnitude as the repeat distances of the crystal. Therefore monochromatic X-rays (wavelengths typically between 1-2 Å, depending on the X-ray source) are necessary to study the atomic structure of materials.

For a specific crystal lattice, constructive interference (peaks of scattered X-rays in the diffraction pattern) takes place only at angles (between the incoming and scattered radiation) defined by the specific repeat distances of the lattice. *Bragg's law* defines the relationship between the X-ray wavelength, a specific repeat distance of the lattice and the angle at which constructive interference (or a peak) can be found, for a first order diffraction peak (also called reflection):

$$\lambda = 2d\sin(\theta)$$

where λ is the X-ray wavelength, d the repeat distance between two reflection planes and ϑ the angle at which constructive interference occurs.

X-ray diffraction experiments can be conducted on single crystals but also on powders. Powder diffraction has the advantage that mixtures of phases can be investigated relatively easily and no relatively rare well-formed crystals are necessary. Instead in powder diffraction, the original material is ground very finely (5-15 µm grain size) and mounted on a sample holder. The powder mount consists ideally of crystalline particles in completely random orientation. If the orientation is truly random, then for each characteristic repeat distance (*d*) there are many particles that satisfy the Bragg's law.

1.3. The Bragg-Brentano X-ray powder diffractometer

Flat powder mounts are usually measured in reflection or Bragg-Brentano parafocusing geometry. In this geometry the incident beam from the line focus of the X-ray tube diverges until it is reflected by the sample. The diffracted beam converges from the sample and is focused at the point where the focusing circle and the goniometer circle intersect (Fig. 1). Here a receiving slit is positioned to filter out any unfocused radiation. A secondary monochromator can be used to ensure that only elastically scattered radiation (i.e radiation that has retained the same wavelength as the source) is allowed to enter the detector device. The latter measures considerably improve the angular resolution (peaks become narrower, less overlap of reflection peaks).

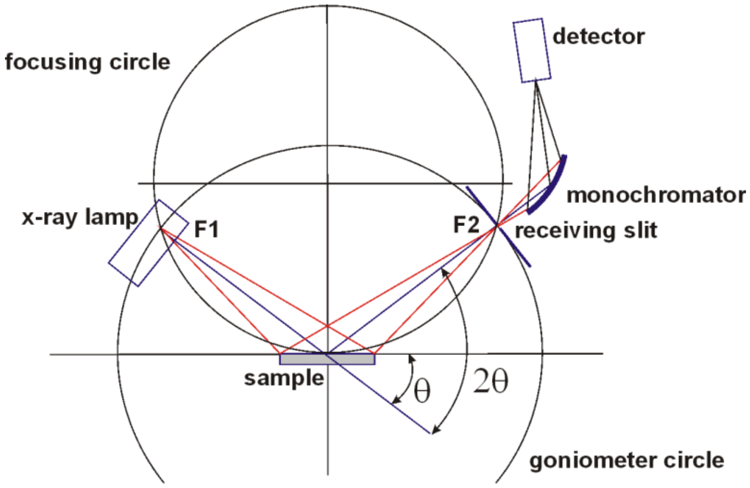

Fig. 1. Bragg-Brentano geometry of a θ-θ diffractometer.

Recent developments in detector technology have enabled the measurement of a range of diffraction angles at the same time using parallel counting chains or position sensitive CCD detectors. This has allowed to drastically shorten data collection times, typically for routine measurements 15 min are sufficient.

Various Bragg-Brentano configurations exist. In the θ-θ system both the X-ray source and the detector system rotate simultaneously along the goniometer circle, the sample stage in the center of the goniometer circle is fixed. Thus if the angle between the surface normal and the incident beam has changed by θ, in fact the angle between the incident and the diffracted beam has changed by 2θ.

In a typical X-ray powder diffraction pattern (see Fig. 2) the positions (given as 2θ angles) of the peaks are determined by the symmetry and size of the unit cell (and the wavelength of the incident radiation). The relative intensities of the peaks are determined by the crystal structure (the nature of the atoms and their locations) of the investigated material. The peak shape or profile allows investigation of the microtextural parameters such as size of coherently diffracting domains or crystallites and micro-strain caused by defects in these crystallites. Typically a grain of a material contains many crystallites.

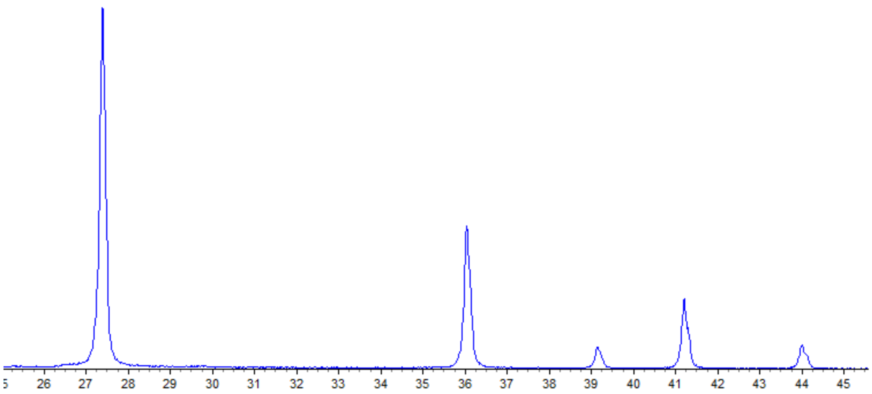

Fig. 2. Excerpt of the X-ray powder diffraction pattern of rutile (TiO_2). The x-axis is the reflection angle (2θ).

2. Sample preparation and measurement

In order to obtain accurate and precise results, systematic sample preparation-related problems should be minimized. X-ray powder diffraction is based on two basic assumptions, namely 1) that the sample consists of an infinite number of crystallites in 2) a random orientation. Thus, the 'ideal' powder consists of material with a grain size of 5-15 µm (for low X-ray absorption materials). The powder should be mounted with randomly oriented grains with a flat and smooth sample surface forming a specimen large enough to avoid beam overflow.

In order to have a representative subsample, grinding, homogenization and splitting have to be carried out without loss of material, contamination, phase separation, phase transformation, or destruction/modification of crystal structures. Grinding is best done using a mechanical device and a grinding liquid (ethanol, isopropanol or acetone) to obtain the required particle size and avoid damage to the crystal structures. To increase the amount of particles satisfying the diffraction criterion a sample spinner can be used.

The sample mount should be large enough to avoid beam overflow at small diffraction angles, and thick enough (several hundred µm) to satisfy the requirement of infinite thickness. Ideally the sample surface should be flat, with no roughness or curvature, and not tilted in any direction. Any roughness or curvature has the potential to produce systematic deviations in the positions and widths of observed reflections related to the sample-height displacement and flat-specimen errors.

One of the most serious problems in quantitative analysis is the elimination of preferred orientation of sample particles. Procedures that minimize preferred orientation include side- or back-loading of powders. One of the most important conditions to obtain an orientation-free sample mount is the use of material of a sufficiently fine particle size. Coarser grains are much more easily oriented.

3. Analysis of the X-ray patterns

3.1. Qualitative analysis: phase identification

Qualitative phase analysis is carried out on the basis of the positions (*d* spacings) and relative intensities of the peaks in an XRD pattern in comparison with patterns of known compounds (a so-called 'search/match' procedure). These databases can be collections of patterns of pure phases or most commonly the Powder Diffraction Files (PDF) maintained by the International Centre for Diffraction Data (ICDD).

Automatic search/match procedures using a complete peak list are possible with the X'Pert HighScore Plus program. However, the results should be considered as a list of suggestions. Ultimately, it is up to the analyst to determine the correct solution(s) that are reasonable. Any additional information about the sample can be quite helpful in obtaining an accurate qualitative analysis, such as chemical information, hints from microscopic investigation, information about the system (is the occurrence of the suggested phase reliable for this system?) or information from persons more experienced with such materials.

Controlled phase enrichment by selective dissolution, density or magnetic separation before the XRD measurement can be of great help in concentration and thus identification of trace phases. It can be particularly useful to link phase identification with subsequent quantitative Rietveld analysis as this can highlight the existence of previously unidentified phases in regions showing a bad fit between calculated and measured patterns.

3.2. Quantitative analysis: the Rietveld method

Quantitative analysis provides information about the composition of multiphase mixtures e.g. for raw-material analysis. The base of most methods of quantitative analysis used today is the relationship between the intensity of the reflection of phase α (S_α) in a mixture (mixture *m*) and its concentration in the mixture (W_α):

$$S_\alpha = K_e \frac{W_\alpha}{(\rho V^2)_\alpha \mu_m}$$

where K_e is a constant depending on the diffractometer and the component α, ρ_α and V_α is the density and cell volume of component α, and μ_m is the mass absorption coefficient of the mixture.

There are two families of quantification methods. The first one relates to extracted intensities of distinct (single) lines in the XRD pattern. Different approaches include the addition/dilution method, the use of standards or the direct Reference Intensity Ratio (RIR) method. The second group of methods (Rietveld method) relate, in full-pattern fitting, to the whole-pattern phase intensities with or without refinement of structural parameters of the phases present.

In the Rietveld method the X-ray powder diffraction pattern is calculated from crystal structure data. The calculated pattern is compared and fitted to the experimental pattern using a refinement (i.e. by varying) a selected set parameters. Refinement is conducted by minimizing the sum of the weighted squared differences between observed and calculated intensities at every step in the digital powder pattern. The Rietveld method requires knowledge of the approximate crystal structures of all phases of interest (not necessarily all phases present) in a mixture. The input crystal structure data are the space group symmetry, the atomic positions and site occupancies, and the lattice parameters. In a typical refinement, individual scale factors (related to the weight percents of each phase) and profile, background and lattice parameters are varied. To constrain the shifts of the varied structural parameters, typically hard limits (constraints) need to be imposed on profile and lattice parameters.

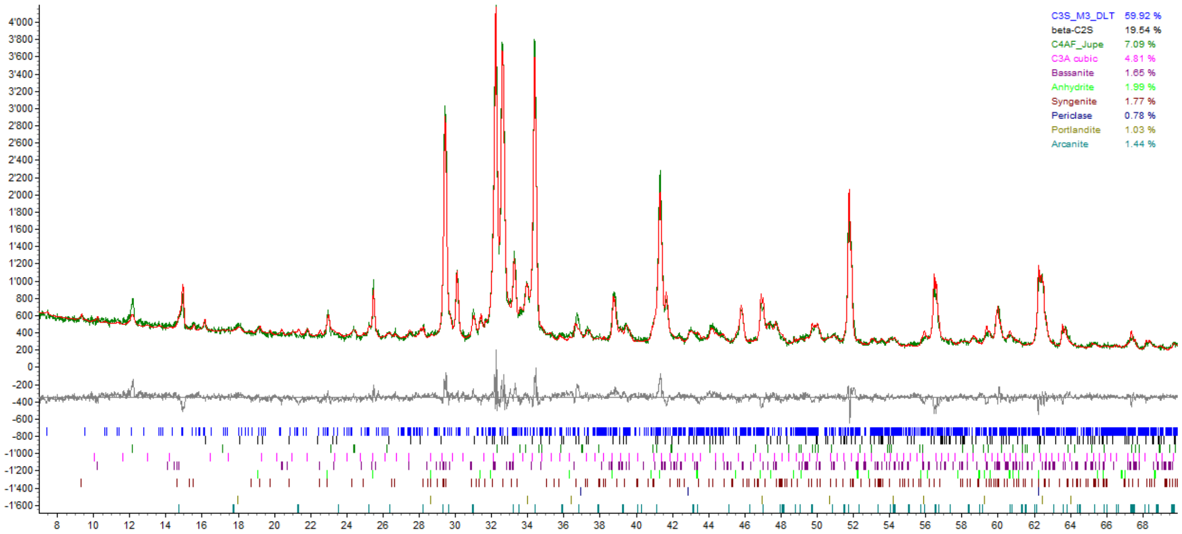

Fig. 3. Rietveld refinement dialog (Topas academic software) showing the refinement results for a grey Portland cement. The measured pattern (green), the calculated pattern (red), the difference curve (grey) and the individual phase tick marks (reflection peak positions) are displayed.

4. Demonstration

The entire sequence of sample preparation, data collection, qualitative and quantitative analysis will be demonstrated for a grey Portland cement.

5. Assignment

You will be given three blind samples (A, B and C) of materials commonly encountered in construction practice:

- White Portland cement
- Hydrated Portland cement
- Iron blast furnace slag

You should:

(1). Identify all crystalline phases present in the samples

(2). Determine which sample corresponds to which material by using X-ray powder diffraction (and your background knowledge on construction materials).

(3). Quantify the phase content for the unhydrated Portland cement using the Rietveld method.

Prepare the samples for the measurements and – with the help of the instructor – launch your X-ray powder diffraction measurements.

6. Additional questions to be filled out:

6.1. Sample preparation

(1). What kind of samples can be measured using X-ray powder diffraction and how should they be prepared?

(2). What properties should the ideal powder mount have?

6.2. Qualitative analysis

(3). Describe the different steps of the phase identification procedure using the X'Pert HighScore Plus software.

(4). Suggest different ways/methods to confirm the presence of minor phases.

6.3. Quantitative analysis

(5). What parameters are refined during the Rietveld quantitative phase analysis? Give for each type of parameter the effect on the calculated powder pattern.

(6). Give additional methods/techniques that enable to independently check the quantification results.

6.4. Interpretation

(7).The four main clinker phases react with water (and sulphate) to form hydration products.

a. Write down the stoichiometric reactions.
b. Which hydration products are difficult to quantify with X-ray powder diffraction?
c. What additional technique can be used to quantify the amount of portlandite?