X-RAY DIFFRACTION STUDY OF HYDRATION PROCESSES IN THE PORTLAND CEMENT

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Abstract: This paper presents a study performed on the Portland cement (CEM I 52,5) presented as powder and slurry to highlight the hydration occurring in the cement at various time intervals (1, 3, 7, 14 and 28 days), making use of the X-ray diffraction method. The diffraction spectra have identified the hydration products: portlandite, ettringite and tobermorite, as well as the mineralogical compounds still unhydrated as the hydration processes occur in time and at 28 days are still unfinished. The mechanical present a rising evolution also due to the hydration processes that continue to take place as time goes on.

Keywords: Portland cement, X-ray diffraction

INTRODUCTION

When water is present, the silicates and aluminates (mineralogical compounds) undergo hydration processes (i.e. water molecules are added) and hydrolysis processes. Following these process, new hydrated compounds are produced (calcium hydroaluminates and hydroferrites, calcium hydroxide), in the form of a jelly or in a crystalline form [1, 2].

Alite (C₃S) is a mineralogical compound to be found in cement, in the largest proportion (50%); this is presented as colourless equi-sized grains. This is a calcium silicate that has the highest hydrolysis speed and reacts very easily with water. C₃S hydration characterises to a large extent the behaviour of cement, it does not occur at a constant speed and not even the modifications of the speed are not constant. C₃S hydrates and sets very quickly the cement slurry and gives cement its high initial (at 1 – 3 days) and final mechanical strengths.

Belite (C₂S) is a mineralogical compound known to take three even four polymorphous forms, which easily reacts with water and transforms into hydrated dicalcium silicate. The latter hydrates and slowly sets the cement slurry and contributes to the strengths of cement at 7 days. After 28 days

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days, the mineralogical compound hardens and presents a mechanical strength that is very close to that of calcium hydrosilicates originating C₃S. The hydration and hydrolysis reactions of the two mineralogical compounds field hydrosilicates with an initial jelly structure similar to that of the natural mineral tobermorite; hence, they are also called tobermoritic calcium hydrosilicates. The calcium hydrosilicates form the majority of the hydration products, have a jelly structure, with a solid phase made of a lattice of microcrystals at first the size of angstroms with eyes filled with a saturated solution of components; later on these crystals grow, consolidate (age) and in this way contribute to higher strengths [3].

Celite (C₃A) is a mineralogical compound present as crystals in clinkers, when slowly cooled down or as vitreous mass, when the clinker is cooled down fast. In this latter case, it fills in the voids in the alite and belite. Pure celite has a very violent reaction with water that leads to the instantaneous setting of the slurry; it is for this reason that when grinding the cement clinker, gypsum (CaSO₄2H₂O) is added. The amount of gypsum added to the cement clinker must be carefully controlled as too large amount leads to expansion and then to the damage of the set slurry. The optimal gypsum quantity to be added is found by following the hydration heat released. Gypsum also reacts with brownmillerite (C₄AF), with which it forms calcium hydrosulphate-ferrite and hydrosulphatealuminate whose presence can accelerate the hydration of calcium silicates. The two calcium hydroaluminates act as fondants; they diminish the burning temperature of the clinker. When cement is treated with water, the mineralogical components are transformed in hydration compounds (hydroderivatives) tobermorite, portlandite and ettringite. The hydroderivatives have colloidal structures, concentrated as jells in time, and giving the cement slurry more and more consistency. Later on, the jellies, that is the hydroderivatives of the mineralogical components begin losing hydration water and crystallise. Consequently, the cement slurry transforms into a rigid body with very high strengths [1, 4, 5, 6].

MATERIAL AND METHOD
1. Experimental Program
1.1. Preparation of the Portland Cement Slurry

The cement slurry was prepared by making tests according to SR EN 196-3/A1:2009, the final formula being: 300g Portland cement and 96ml water. From the paste of normal consistency, cakes were made and were kept at a relative humidity of 55% and a temperature of 20°C, for 28 days. Samples were taken from these cakes, at one, three, seven, 14 and 28 days and were investigated by X-ray diffraction.
**X-Ray Research Methods.** A crystalline material can be formed of only one crystalline phase or from a mixture of more crystalline phases. A crystalline phase is defined by a certain system (triclinic, monoclinic, rhombic, tetragonal, trigonal, hexagonal, cubic), by a certain elementary cell (simple, with centred bases, with a centred volume, with centred faces) and by the parameters of the elementary cell. In crystallography, the planes and families of atomic planes (Fig.1.) are noted with the help of Miller’s indices (h k l), fielded by the intersection of the atomic planes with axes x, y, z, [7, 8]. In Fig.2., we illustrate some atomic planes for a cubic crystalline structure.

![Fig.1. Miller’s indices (h k l) for plane cubic atomic structure](image1)

![Fig.2. X-rays diffraction for a structure with cubic volume centered](image2)

X-rays are electromagnetic waves, similar to light, but with a much shorter wave length ($\lambda=0.2$-200 Å). Diffraction is a physical phenomenon that consists in electromagnetic waves avoiding of obstacles when obstacles have a size that compares to the wavelength. This phenomenon can be used to analyse materials as the atomic planes in a material (i.e. obstacles) are at comparable distances to the X-ray wavelength. When a monochromatic pen of X rays falls on a crystal, the spherical waves emitted by the crystal periodically displayed atoms will interfere with one another. A destructive interference will be present in all the space, except for some directions, called diffraction directions.

In a periodic display of atoms (crystalline state), the various parallel planes are situated at a distance”d”. The constructive interference of the waves occurs, that is diffraction peaks are reached for a given wavelength ”$\lambda$,” only if Bragg’s law is observed [8]:

$$2d \sin \theta = n\lambda$$

where: n – is a whole number;
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\[ d \] – is the distance between the atomic planes;  
\[ \theta \] - is Bragg’s diffraction angle.

X-rays diffraction is produced as a reflection at well defined angles. Each crystalline phase has its own diffraction image. The diffraction image contains a small number of peaks, showing that not all the families of crystallographic planes give peaks, that all the crystalline phases with the same elementary cell will exhibit the same succession of Miller for the crystalline families giving peaks. For the X-ray diffraction analysis we used diffraction devices (diffractometers), in general in a Bragg–Brentano arrangement (the specimen is rotated by the diffraction angle „\( \theta \)‟ while the detector is turned by the angle „2\( \theta \)”, Fig.3.). In Fig.4., the X-ray diffractometer is shown.

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**Fig.3. The basic layout of an X-ray diffractometer**  
**Fig.4. X-ray diffractometer (Bruker)**

The diffractogram is formed of a succession of diffraction peaks, i.e. maximum values, which have the diffracted X radiation intensity, measured in pulses/second on the ordinate, and on the abscissa, angle „2\( \theta \)”, where „\( \theta \)‟ is the Bragg angle, measured in degrees. The diffraction image depends on the material structure.

Diffraction methods enables the performance of the following studies: the determination of the crystalline structures, the qualitative and quantitative analysis of the phases, the study of the transformations of the phases, the study of the crystallographic texture; the size of the crystallites, the internal stresses in the sample, etc.

**Identification of crystalline phases.** The identification of the crystalline phases (or their indexing) can be performed with X-ray diffraction in the case the respective phase covers minimum 3-4% of the weight. The identification can also be performed by calculating Bragg’s
relationship (1) or automatically with Match, XpertScore software, making use of the PDF (Powder Diffraction File) database, which has identification sheets for about 200,000 crystalline phases belonging to metals, alloys, oxides, salts, etc. All the phases in the sample are identified one after another, beginning with the phase in the largest amount. For instance, the identification of the NaCl crystalline phase follows the steps:

- first, the sample diffraction spectrum is identified by means of the X-ray diffract meter;
- the output data: the interplane distances „d” are calculated with the help of Bragg’s law (relationship 1), and the Miller indices of the diffraction lines (planes);
- with the data found as above (interplane distances „d”, relative intensity „I” and Miller indices), the corresponding sheet is searched in the PDF database, finding the full description of the crystalline phase from the crystallographic viewpoint.

2. Interpretation of Results

The x-ray diffraction analyses were made with a DRON 3 diffractometer, in the angular range of 2θ = 10 – 70 degrees, with a λ radiation =1.54182 Å, a25kV voltage and 25mA intensity, using a Bragg – Brentano arrangement. The diffraction samples were presented as powders (produced by milling) and as cakes.

2.1. Phase Quantitative Analysis of the Portland Cement Powder

For the direct identification of the phases, we used the Match diffraction software and we passed through the stages below:

- the diffraction spectrum is raised with the diffract meter;
- the search range is limited in the PDF database to combinations of chemical elements that are present in the sample (Ca, Si, S, O, Al, Fe, about 500 combinations of the elements);
- the phases in the test sample are identified with the help of the PDF sheets by matching sheets with the diffraction lines from Fig.5.;
- results are analysed and checked for the proper nomination of phases.

![Fig.5. X-rays pattern of Portland cement powder](image)
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The diffractogram in Fig.6. gives the presence of the following phases:
- \( \text{Ca}_3\text{SiO}_5 \) – alite, in majority in the sample (monoclinically crystallised, sheet PDF00-042-0551);
- \( \text{Ca}_2\text{SiO}_4 \) – belite (monoclinically crystallised, sheet PDF00-033-0302);
- \( \text{Ca}_3\text{Al}_2\text{O}_6 \) – celite (cubic crystallised, sheet PDF00-038-1429);
- \( \text{Ca}_2(\text{Al},\text{Fe}^3+)\text{O}_5 \) – brownmillerite (orthorhombic crystallised, sheet PDF00-030-0226).

**Fig.6. Identifying phases of Portland cement powder**

2.2. Phase Quantitative Analysis of the Portland Cement Slurry

X-ray diffraction analysis was performed on the specimens of hydrated cement at 1, 3, 7, 14 and 28 days. The diffraction spectra of the hydrated specimens are given comparatively in Fig.7. The following phases were identified:
- \( \text{CS} - \text{Ca}_3\text{SiO}_5 \) – alite, in majority in the sample (monoclinically crystallised, sheet PDF00-042-0551);
- \( \text{CSH} - \text{Ca}_{1.5}\text{Si}_{3.5}\text{xH}_2\text{O} \) – hydrated calcium silicate (tobermorite), (sheet PDF-33-0306);
- \( \text{E} - \text{Ca}_6\text{Al}(\text{SO}_4)_3(\text{OH})_12\cdot26\text{H}_2\text{O} \) – ettringite (sheet PDF-04-0733);
- \( \text{CH} - \text{Ca}($\text{OH}$)$_2$ \) – portlandite (sheet PDF-41-1451).

The diffraction spectra show that alite represents the majority in the sample, a part of it is hydrated and the hydrated calcium silicate is produced. It is noticed that ettringite and portlandite are present in all the hydration stages. The changes occurring in the mineralogical components during the hydration processes were also noticed, where hydrosilicates and
hydroaluminates were present (tobermorite, portlandite and ettringite), Fig. 7. After three days, the highest peaks of the diffractogram correspond to alite and tobermorite jells. After seven days, the spectrum is similar to the spectrum at three days. As time passes, the process of hydration shows a diminution of values between the tobermorite and portlandite phases, between 3 and 7 days, as well as between 7 and 28 days.

![Fig. 7. X-rays pattern of Portland cement (cs-alite; csh-hydrated calcium silicate (tobermorite); p-portlandite; e-ettringite; b-belite; c-cellite; bw-browmillerit)](image)

This development is explained by the fact that during the first three days of hydration, tobermites originating from the alite are predominant; alite is present in a bigger quantity than belite, which is the source of portlandite, which is formed much slower. In time, a larger amount of portlandite is generated so that after 7 days the difference between tobermite and portlandite is reduced. At 28 days, the difference between the two compounds increases as tobermite increases very much.

### 2.3. Results of Mechanical Tests for Standard Mortar Samples

For the experimental tests, a standard mortar was used; the mortar had the following composition: Portland cement CEM I 52.5: 900 g; water: 450 ml; sand: (0.08 – 0.16)mm – 300 g; (0.16 – 0.50)mm – 600 g; (0.50 – 1.00)mm – 900 g; (1.00 – 2.00)mm – 900 g. The mechanical strengths, bending tensile strength and compressive strength were determined on six prism-shaped specimens of 40x40x160 mm, according to SR EN 196. The tests were carried out at 3, 7 and 28 days after hardening and are given in Fig. 8. One can notice the increase in time of the strengths, and this can be explained by the never ending hydration processes.
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Fig. 8. The mechanical strengths of standard mortar specimens

CONCLUSIONS
Cement hydration will never be complete. The method of X-ray diffraction allowed the highlighting of the mineral components from the initial powder stage and further slurry stage of the cement. In the time intervals under investigation the method used demonstrated the presence of hydration products (tobermorite, portlandite and ettringite) as well as the presence of other mineral compounds that will hydrate as time goes on. The continuous increase of the mechanical strengths of the cement can be explained by the hydration processes that never have an end.

REFERENCES