

Identification and Quantification of Cement Phases by X-Ray Diffraction

ARL X'TRA Powder Diffraction System

Key Words

- ARL X'TRA
- Cement
- X-Ray Diffraction
- XRD

Introduction

The microstructure of a material is one of the main link between the process and its final properties. Cements do not escape to this rule. However, the study of microstructure of this type of materials is a constant challenge for specialist mainly due to a complex and heterogeneous mineralogy. Cement or clinker consists in lot of different phases in order to achieve specific properties such as reactivity, setting time, colour, etc... However, quality of products is dependent on the phase mineralogy of cements.

It is well known that reactivity will depend of the C3S/C2S ratio, that C3A will influence the setting time and that C4AF will give a different colour to the cement. Therefore, an accurate and reproducible analysis has to be carried out. A combination of XRF and XRD seems to be an excellent solution for routine, on-line process and quality control of clinker phases in addition to free lime. A stand-alone XRD on the other hand allows more flexible and investigative phase analysis in a central laboratory.

The first step in this note will be to identify phases in the cement and then to quantify these phases.

Two main data will be treated: the first will concern NIST standard 8487 and 8488, and the second some unknown clinkers. An example of reproducibility for fast measurement is also reported.

Instrumentation

The Thermo Scientific ARL X'TRA diffractometer has been used first to have qualitative analysis of phases in samples and secondly to determine phase content by Rietveld algorithm.

Analysis conditions

All samples have been analyzed with a **basic configuration** (no special attachment) in para-focusing $\Theta:\Theta$ configuration with a Cu ceramic 2.2kW X-ray tube and equipped with a Peltier detector and normal optic.

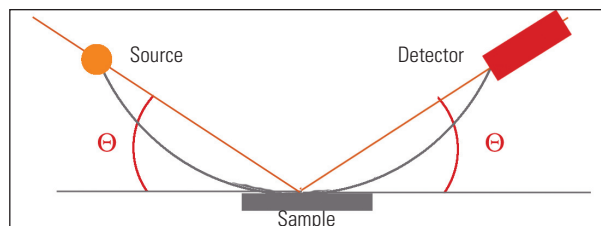
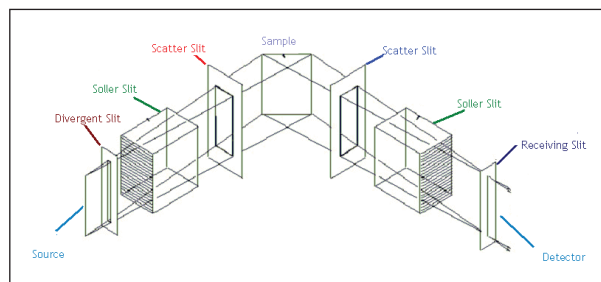


Figure 1: $\Theta:\Theta$ geometry - the sample is stationary in the horizontal position, the X-ray tube and the detector both move simultaneously over the angular range Θ

The sufficient energy resolution of this type of solid-state detectors (used more than 20 years ago) allows electronically discriminate $K\beta$ and sample fluorescence background (due to iron rich sample). This eliminates the need for beta filters and diffracted beam monochromators, which absorb at least half of the intensity of the X-ray beam. The enhanced intensity allows collecting data more rapidly.

The basic system is equipped with a set of fixed slits, which are manually adjustable from 0 to 4° for the divergent slit (DS) and 0 to 2 degrees for the receiving slit (RS). Scatter slits (SS) and removable soller slits (default 1.3°) are also used on both sides of the goniometer in order to reduce scattering and axial divergence of the incident and diffracted beam (see picture 2).



Picture 2: Optic configuration on basic ARL X'TRA diffractometer

The two standards have been provided in correct granulometry and can directly fill the top-loading cup whereas the two unknown cements have been ground in order to minimize the influence of particle size on measurements (preferred orientation or inhomogeneities).

All the samples were placed onto top loading cups using a rough glass slide in order to achieve flat surface. These cups have been mounted on a 12-position sample changer (cf. photo 1).

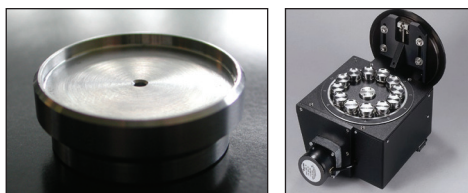


Photo 1: Top loading cup and 12 positions sample changer with spinner

Moreover, to increase speed analysis without losing too much resolution, the interchangeable soller slit on the detector side has been removed (see photo 2). Thanks to this optic flexibility, 5 min scan can be realized with a good signal to noise ratio (see figure 1).

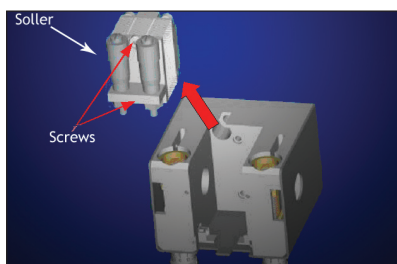


Photo 2: Slit bloc with interchangeable soller

Data collection and basic data treatment has been carried out with the WinXRD software running under Windows XP environment. SIROQUANT™, a Rietveld technique corresponding in a whole-pattern-fitting least-squares technique, has been used for quantification work.

Phase identification

Difficulty in cement identification results in large peak overlap but also in large polymorphs coexistence. Indeed, C3S exists in 3 different forms: Monoclinic, Triclinic and Rhomboedric. C2S can also exist in 3 different polymorphs: α , β and γ . However, C2S beta is the most used and expected due to its reactivity; it is the most common in cement. α shows a slower reactivity and γ does not react. C3A is also well known to have two possible polymorphs in cement like cubic or orthorhombic phases.

Moreover, more to the polymorph coexistence, some trace phases are present (lime, portlandite, periclase...) and some additives are added in cement to improve final properties. Gypsum is one of them and will control the milling dehydration process; this phase is often accompanied with bassanite, anhydrite and hemi-hydrate phases.

Phase identification takes place in three steps: background subtraction is the first one and it is always required in this kind of material, then a peak finder procedure has to be performed and finally a search/match can be processed quickly. For a more efficient search/match, a cement database can be created with the software.

Fast analysis - Hydration process of calcium aluminate cement

Measurement has been performed every 2 minutes during the hydration process. Figure 1 shows the evolution of phases from the initial cement powder to the final form. Each scan represents the cement paste (mixture of calcium aluminate cement with water) after each 2min during 30min.

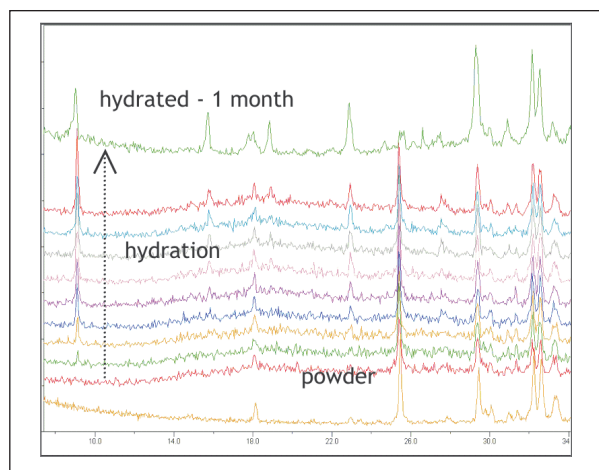


Figure 1: 2 min scan of calcium aluminate cement during hydration process.

Table 1 summarizes the identified phases, and figure 2 is an expanded view of figure 1 to highlight the most important peak intensity variation. The peaks of ettringite, mayenite and anhydrite can be seen to undergo distinct intensity change

PHASES	POWDER	HYDRATION	HYDRATED
C3S	Y	Y	Y
C2S	Y	Y	Y
$C_{12}A_7$	Y	Y	Y
Anhydrite	Y	Y	-
C3A	Y	Y	Y
CaO, MgO	Y	-	-
Ettringite	-	Y	Y
Portlandite	-	Y	Y

Table 1: Phase identification of calcium aluminate cement during hydration process

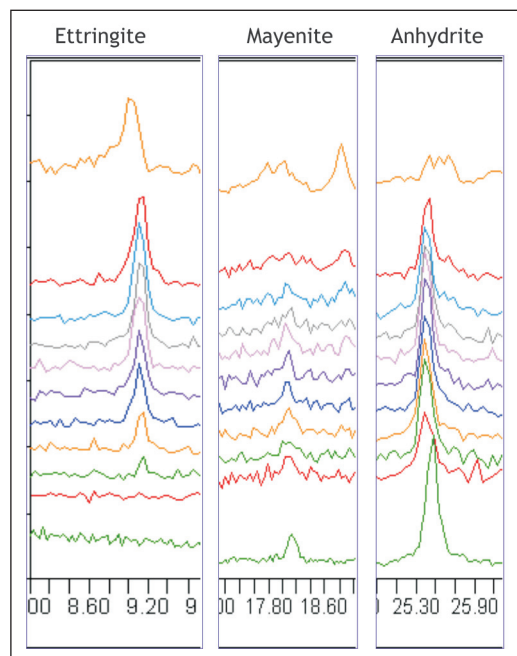


Figure 2: Peak intensity variation during hydration

Nist Standard 8488 and 8487

Both show same type of scan except in terms of intensity (See figure 3 for detailed measurement condition).

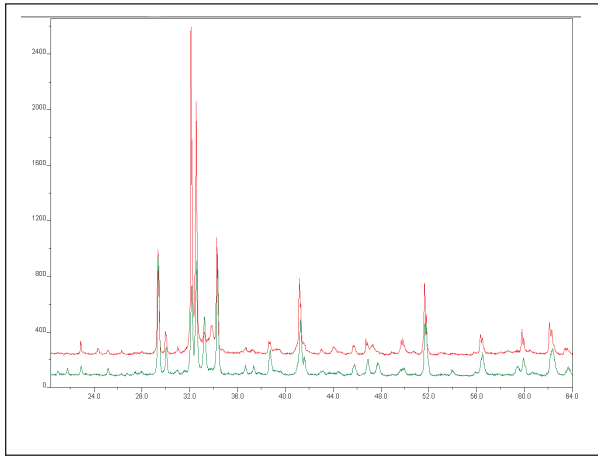


Figure 3: Comparison between NIST 8488 (red curve) and NIST 8487 (green curve) measured with the basic ARL X'TRA diffractometer

Scan conditions are noted below:

STEP SIZE (°)	INCIDENT SLIT CONFIGURATION SOLLER 1.3°	DIFFRACTED SLIT CONFIGURATION SOLLER 1.3°	
	DIVERGENCE	ACCEPTANCE	RS*
0.02	1.2°	0.7°	0.2 mm

*: Receiving slit - corresponding resolution = 0.04°

Phase identification has been performed with NIST 8487, which consists in more phases (figure 4).

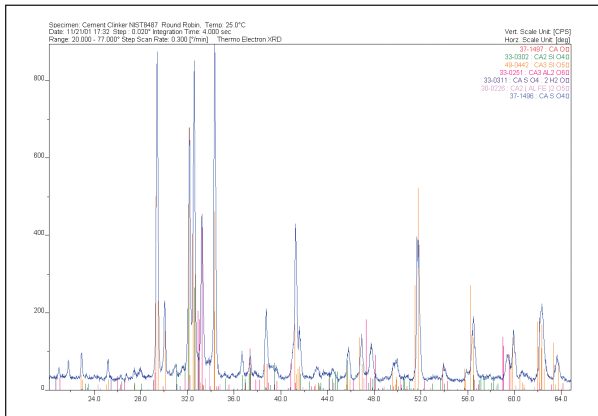


Figure 4: Phase identification of sample 8487 measured with the basic ARL X'TRA diffractometer

Unknown clinkers

An interesting point would be the integration of phase quantification by Rietveld in process control in cement plant; therefore, fast XRD measurement would be required in a first step, and then automated-Rietveld software would be helpful to treat the data.

In this paragraph, an example for two unknown clinkers was reported.

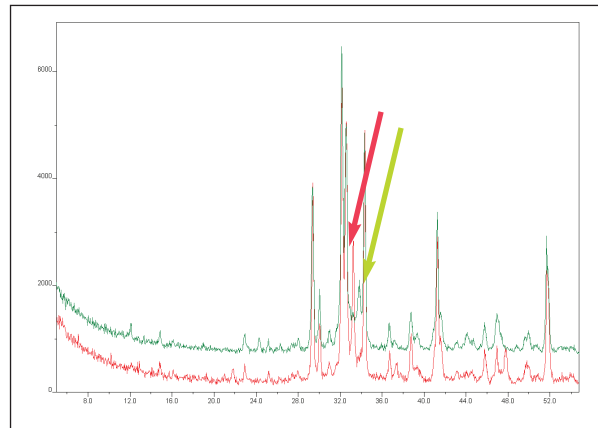


Figure 5: Comparison between Clinker#1 (red curve) and Clinker#6 (green curve) measured with the basic ARL X'TRA diffractometer

Scan conditions are noted below:

#	MODE °/MIN	INCIDENT SLIT CONFIGURATION SOLLER 1.3°	DIFFRACTED SLIT CONFIGURATION NO SOLLER		
		DIVERGENCE	WIDTH	ACCEPTANCE	RS*
#1	10	1.2°	3mm	1.2°	0.3 mm
#6	10	1.2°	3mm	1.2°	0.3 mm

*: Receiving slit – corresponding resolution = 0.066°

These two clinkers show some small difference in XRD pattern; indeed, clinker#1 has a C3A peak more intense (red arrow) whereas clinker#6 has a more intense C4AF peak (green arrow).

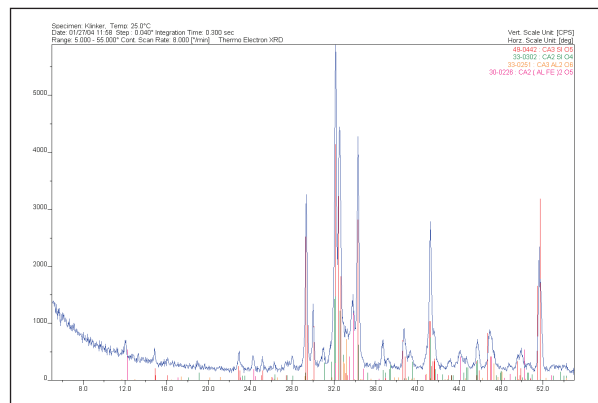


Figure 6: Phase identification of clinker#6 measured with the basic ARL X'TRA diffractometer

Phase quantification

Unfortunately, an easy and standard quantification is made hard and hazardous because of large overlap between all major phases (C3S, C2S, C3A and C4AF). By the way, the use of Rietveld algorithm for quantification can be a solution. It is a semi-quantitative analysis; therefore like all semi-quantitative analysis all phases have to be identified and correctly chosen.

The most successful C3S structures in Siroquant are the Mumme structure (monoclinic) and the Belov one (triclinic); the rhombohedral structure is never the major one. Moreover, C3S has also tendency to be preferred oriented. C3A is also present in two polymorphic structures: cubic and orthorhombic). C2S β is always preferred and is the most relevant phase. C4AF has only one crystallographic structure therefore no structural choice has to be done. Except these main phases, some trace phases - such as free lime or periclase - and/or additives - such as calcite, gypsum, anhydrite, hemi-hydrate or bassanite - can be found and their concentrations will depend on the final use.

Nist Standard 8488 and 8487

The result of the quantification resulting from the least-square fitting of the XRD full patterns by the Rietveld algorithm can be seen in figure 7 for the sample 8488 and are summarized in tables 2a and 2b for 8488 and 8487, respectively.

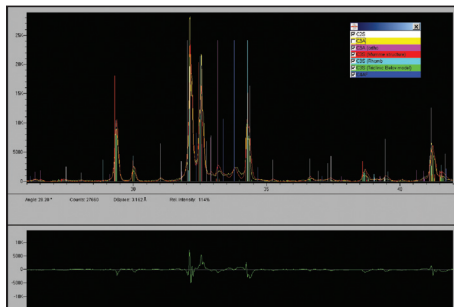


Figure 7: Fitting of full pattern of 8488: Yellow curve is the XRD pattern, red curve is the theoretical XRD profile; second box is the fit result corresponding to full-matrix least-squares refinement of the following Rietveld parameters: phase scales, line asymmetry, phase preferred orientation, phase line widths (U,V,W), instrument zero, the line shape parameter for each phase, and the phase unit cell dimensions

NIST 8488

PHASES	SIROQUANT		NIST CERTIFICATE	
C2S	18.4	0.73	18.51	0.58
C3S	64.9	0.9	64.97	0.56
C3A	5.1	0.52	4.34	1.35
C4AF	11.6	0.57	12.12	1.5
Lime	0	0	0	0
Periclase	0.1	0.52	0.05	0.09

Table 2a: Phase content in sample 8488 from Rietveld calculation

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NIST 8487

PHASES	SIROQUANT		NIST CERTIFICATE	
C2S	9.0	0.42	7.75	1.23
C3S	74.6	0.9	73.39	1.57
C3A	13.6	0.26	12.09	0.88
C4AF	1.7	0.21	3.27	0.7
Lime	1.0	0.15	2.45	0.48
Periclase	0.1	0.18	0.09	0.09

Table 2b: Phase content in sample 8487 from Rietveld calculation

Reproducibility

An important point is to be sure that x analyses of similar samples will give you same result. In this test, 10 measurements were performed on the same samples in order to see the reproducibility for free lime analysis. Analyses were carried out in 5 min!!

Free lime analysis

Concentration of free lime in this sample was about 2 % wt (figure 8). In general, free lime quantification is realized with a standard method by using a calibration curve. Therefore, peak area method is often chosen for more accurate result of free lime content.

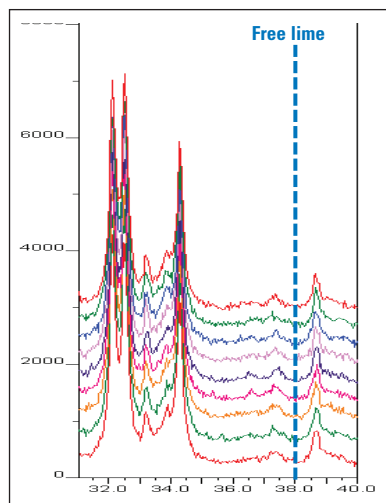


Figure 8: Analysis of sample for the determination of free lime content reproducibility

Calculation of peak area for this peak gives 0.7 % standard deviation.

Conclusion

The ARL X'TRA is ideally suited for flexible and high quality diffraction work in a central cement laboratory. Equipped with Peltier cooled Si(Li) detector, ARL X'TRA provides high sensitive XRD pattern on raw materials, clinkers, cement and additives such as slags, fly ash etc. In addition to the quantitative analysis using Rietveld programs, % of crystallinity and other structural properties can be studied.

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