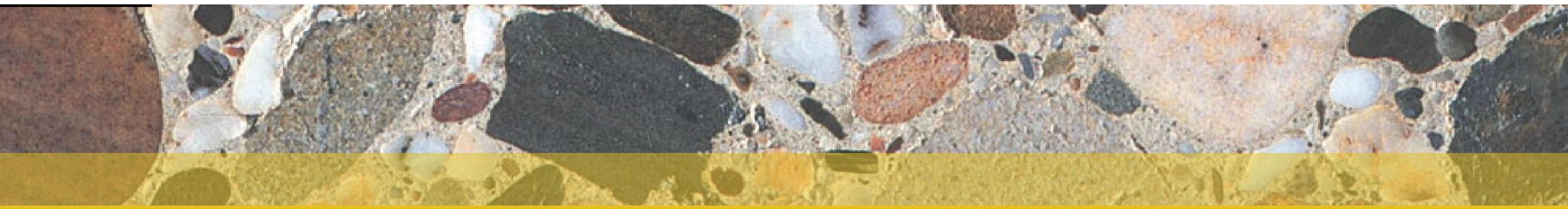
ecra

european cement research academy



1 / 2006

# NEWSLETTER

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- X-Ray Diffraction and Retvield Refinement –
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  May 4, 2006

- Secondary Abatement Techniques
  June 7-8, 2006

- Behaviour of Organic Compounds in the
  Clinker Burning Process
  June 13-14, 2006

# ecra begins its fourth year

## The European Cement Research Academy on the way to become a research platform

The European Cement Research Academy under the chairmanship of Daniel Gauthier may look back on the third successful year of its existence. The number of ecra members increased further. By the end of the year the Academy counted the total of 38 member companies and associations. Participation in the ecra seminars and workshops in 2005 was even better than in previous years.

Due to the positive experience ecra made with its close cooperation with cement producers during the preceding year, several seminars took place not in the ecra premises in Düsseldorf, but in the vicinity of cement plants in different European countries and in the plants themselves. Those seminars were highly appreciated because of their practical aspects. Furthermore they allowed the participants to get into closer contact to other experts and also to representatives of equipment suppliers. We appreciate the cooperation of Buzzi (Robilante plant/Italy), (**Fig. 1** and **2**) Lafarge (Kujawy plant/Poland), HeidelbergCement (plant in Lixhe – Visé/Belgium) and last but not least Betonson (pre-fab plant in Eindhoven/The Netherlands) regarding the seminars held in 2005.

### Research project on $^{14}C$ determination of $CO_2$ from biomass

For the first time ecra provides a research environment for a dedicated research project. The subject of this project is the determination of biomass in waste fuels by the $^{14}C$ method.

The project has to be seen in the framework of $CO_2$ emissions regulations. Under the European emissions trading scheme for example, $CO_2$ from biomass is considered as neutral. As a consequence the monitoring of those emissions is important for those cement plants which use secondary materials as fuels or as raw materials. Usually $CO_2$ from biomass is determined in solid recovered fuels by means of selective dissolution. However, there is a strong interference of the determined concentrations from different substances. Also systematic errors occur for dedicated fuels. As a conclusion: this method is not really adequate for the cement industry. Also, taking the samples and doing the analysis seems to be not very efficient economically.

It is known from Archaeometry that the determination of $^{14}C$ allows the determination of the age of organic material. Where living organisms in the atmosphere provide a stable ratio between $^{12}C$ and $^{14}C$, the $^{14}C$ concentration in dead organic material will decrease (half time roughly 5,000 years). As a consequence, the $^{14}C$ concentration in waste fuels or in stack gases will provide information about the biomass content being used in the kiln.

The objective of this methodology project will be the validation of methods for biomass determination including the $^{14}C$ method. This will also include the measurement of biomass $CO_2$ using the $^{14}C$ method.

The project team has already been formed. Participants will be the ECN (Energy Research Center Netherlands), ecra (European Cement Research Academy), HeidelbergCement, IAE (Institut für nachhaltige Abfallwirtschaft und Entsorgungstechnik, Montanuniversität Leoben), VDZ (Verein Deutscher Zementwerke), VÖZ ( Vereinigung der Österreichischen Zementindustrie).

### Future development of ecra

After the successful start with seminars and workshops ecra is developing into a research platform as the example of the research project on $^{14}C$ determination of $CO_2$ from biomass shows. This was its intention from the start. Other interesting projects are discussed, for instance on: Reactivity of slag as influence on compressive strength on concrete and mortar, on $CO_2$ reduction and on Alkali-silica reaction.

### ecra projects in the years to come

This year's programme comprises seminars on X-Ray Diffraction and Rietveld Refinement - Applications in the Cement Industry, Secondary Abatement Techniques, Behaviour of Organic Compounds in the Clinker Burning Process, Alkali-Silica Reaction (ASR), Modern Clinker Cooler Technology and a workshop on Chromate Reduction. Further information can be found on the website of ecra. A seminar on Secondary Fuel Combustion in the Calciner is already scheduled for 2007. The next ecra conference is projected for spring of 2008.

The way ecra has functioned from the beginning has proven to be successful. However it is and it will remain open-minded about ideas and suggestions, from which ecra as well as its members will benefit as has been proved in the first years of ecra's existence.


**Fig. 1: ecra seminar on Burner Technology for Multi-Fuel Combustion in Cuneo/Italy**

**Fig. 2: Visit at Buzzi Robilante plant**

## Members of the European Cement Research Academy (April 2006)

1. Aalborg Portland A/S
2. BUZZI UNICEM S.p.A.
3. Cement Australia PTY LTD.
4. Cementeria Aldo Barbetti S.p.A.
5. Cementos Molins Industrial, S.A.
6. Cemex Deutschland AG
7. Cemex Trademarks Services, Ltd
8. CEMKUT
9. Cemsuisse
10. Ciments Luxembourgeois S.A.
11. CIMPOR – Cimentos de Portugal, SGPS, S.A.
12. CRH Ltd.
13. Dyckerhoff AG
14. Gujarat Ambuja Cements Ltd
15. HeidelbergCement Group
16. Hellenic Cement Industry Association
17. Holcim (Baden-Württemberg) GmbH
18. Holcim (Deutschland) AG
19. Holcim Group Support Ltd
20. Holcim (Schweiz) AG
21. Italcementi Group
22. jura cement
23. LAFARGE CTEC GmbH
24. Nesher Israel Cement Enterprises Ltd
25. Phoenix Zementwerke Krogbeumker GmbH & Co. KG
26. Portland Cement Association – PCA
27. Portlandzementwerk Wittekind
28. Povaská Cementáren, a.s.
29. SCHWENK Zement KG
30. SECIL-Cª Geral de Cal e Cimento, SA
31. Spenner Zement GmbH
32. Suwannee American Cement
33. Titan Cement Company S.A.
34. Turkish Cement Manufacturers´ Association
35. Uniland Cementera, S.A.
36. Verein Deutscher Zementwerke e.V.
37. Vereinigung der Österreichischen Zementindustrie
38. Wietersdorfer & Peggauer Zementwerke GmbH

# Progress of X-ray diffraction and Rietveld refinement

### Fast measuring devices and modern software solutions are increasingly applied in cement production control

During the past years, the use of X-ray diffraction in the cement industry has increased considerably. A precondition for the growing number of users in cement research and quality control has been the development of modern measuring devices as well as data evaluation programs which can deliver quantitative results with a minimum of operating expense.

The basic information to be analysed by means of X-ray diffraction is the crystalline phase composition of a material usually prepared as a powder sample. The X-ray diffraction method provides the possibility to examine all kinds of crystalline materials such as clinker phases and other cement constituents, raw meal and corrective materials' components, setting regulators and chromate reducing agents. By using the Rietveld method, the diffraction data can be evaluated quantitatively. Modern software solutions enable the implementation of the results to common laboratory automation systems.

As a prerequisite for quick and reliable results, an X-ray diffractometer needs to be at hand, being rugged and equipped with a modern detector, that permits fast measurements with sufficient counting statistics. Pressed powder samples to be analysed can be prepared by hand or automatically, e.g. by robot systems. Inside the diffractometer a monochromatic X-ray beam is directed onto the sample surface. The X-rays are scattered by the crystal lattices in certain diffraction angles which are characteristics of the crystal structures. A subsequent Rietveld refinement to evaluate the diffraction pattern requires the availability of suitable crystal structure proposals for all crystalline phases implied in the sample.

The Rietveld refinement itself works as a software routine, which starts with a simulation of a diffractogram calculated from the crystal structures chosen. By an automatic variation of predefined parameters the contribution of each phase is fitted to the measured pattern, until a best possible agreement between the calculated and the measured pattern is achieved (**Fig. 1**). The quantitative phase composition is obtained as one of the refinement results.

A number of issues can be addressed by quantitative X-ray diffraction, mainly by supporting and controlling the clinker burning and cement production process.

In basic clinker characterisation, the distinctive advantage of phase determination by Rietveld refinement consists of the direct analysis of the crystalline phases in the sample examined. In contrast, Bogue analysis, for example, is an indirect method: By use of the chemical composition the phase contents are calculated, assuming conditions of chemical equilibria without any impurities within the specific clinker phases. This assumption causes systematic errors. On the other hand, microscopical investigations including point counting techniques give a direct visual survey of the clinker phase assembly. The major difficulty with microscopy is, besides its rather large preparational expense and the technical limits of computational image analysis, that interstitial mass phases cannot be identified properly, if they are very small in size. Depending on the clinker burning and cooling condition, this can lead to systematic counting errors.

Exceeding its practical advantages in routine analyses, X-ray diffraction gives evidence to further information of the samples' properties examined. For example, local reducing conditions during the clinker burning process can be addressed, when associated clinker phase modifications such as gamma-$C_2S$ are identified. After dissolution of the silicate phases, the examination of the residue allows an estimation of the clinker reactivity by identifying and quantifying different $C_3A$ modifications.

In Portland cements, however, the corresponding sulphate agents can be characterised with an accuracy similar to that of thermoanalytical methods.

Moreover, the Rietveld method in principle is not restricted to identifying and determining clinker phases and sulphate agents in the cement, respectively. It lends itself to solving numerous questions in which phase composition and crystalline constituents, respectively, are involved. These, for example, include raw material input control, the quantification of the limestone content as a main or a minor additional constituent, the determination of the insoluble residue of Portland cements by means of the quartz content, and the investigation of kiln dust or kiln coatings.

Although blastfurnace slag is amorphous to X-rays, Rietveld refinement even allows determination of the composition of Portland-slag and blastfurnace cements with a precision that is at least equal to that of the microscopic and chemical methods previously applied.

As long as all phases are crystalline and their crystal structures are known, the quantitative diffraction pattern evaluation can be performed completely by using the Rietveld method. On the other hand, substances that are amorphous to X-rays, such as blastfurnace slag glass, can be detected in a diffractogram by an increase in the background intensity (**Fig. 2**). This means that it is not possible to determine the blastfurnace slag content directly just from the diffraction peaks. However, there are various possible ways of determining systematically the percentage of blastfurnace slag with the aid of X-ray diffraction.

One approach is to determine the increase of the background intensity caused by the slag. As the increase of the background intensity appears in the shape of a "hump", it is possible to determine the areal intensity by implementing an additional wide peak into the Rietveld refinement method. Its calculated area can be calibrated as a measure for the slag content.

A direct study of the absolute intensity of a region of the amorphous hump that is not overlaid by diffraction peaks can also be useful. The diffraction intensity at this point can be calibrated as a measure of the blastfurnace slag content. Favourable angular positions are, for example, the positions at approximately 28.5 and approximately 30.5° (2 theta). The methods for determining the blastfurnace slag content, that are based exclusively on an increase in the background, can, however, only be applied if the portion of glass in the slag is constant.

An alternative approach to determine the percentage of X-ray amorphous substances is to add a crystalline internal standard (a "spike") to the sample. The Rietveld refinement calculates the total of all the crystalline phases considered to be 100 wt.-%. As the amorphous fraction is not taken into account in the calculated 100 %, the Rietveld refinement calculates a higher content of the spike than was actually added. With a known weight of added spike, the fraction of material not included in the refinement can be determined by simple proportional calculation. However, practical experience with this approach indicates that even with the use of an internal standard the results must be submitted to an additional calibration step to counteract possible matrix effects caused by the spike material.

In summary, X-ray diffraction together with Rietveld analysis is a versatile method to investigate raw materials as well as virtually all kinds of products in cement manufacture. The measurement itself and the quantitative results can be implemented in automatic process analysis systems. A number of analytical solutions are being developed with the aim to support factory production control as well as third party inspection issues. Particularly effects of a rising use of secondary fuels, raw materials and cementitious components can be controlled providing a tool to keep stable process conditions and product properties.

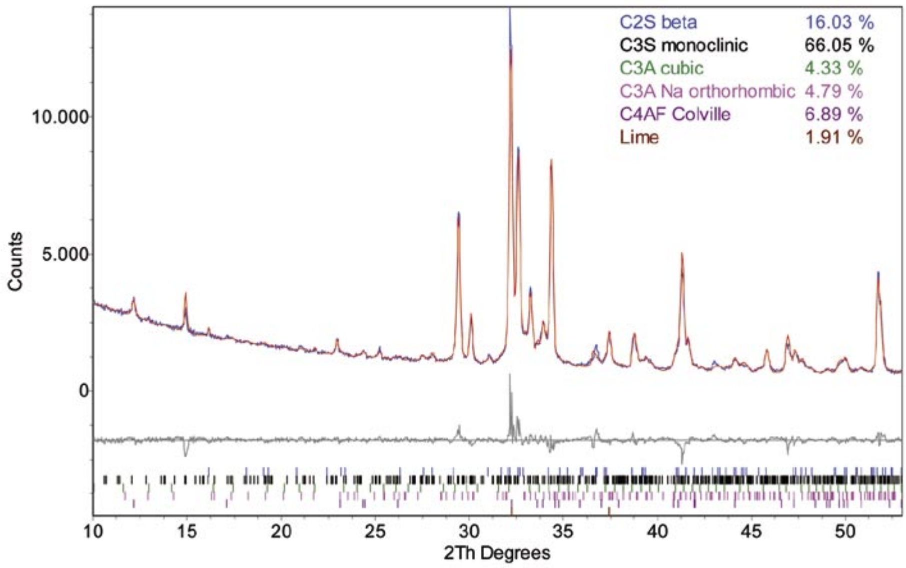


**Fig. 1: Rietveld refinement result of a clinker diffractogram, showing the measured (blue) and the calculated (red) pattern, the difference plot (grey) of both curves and the calculated phase composition**

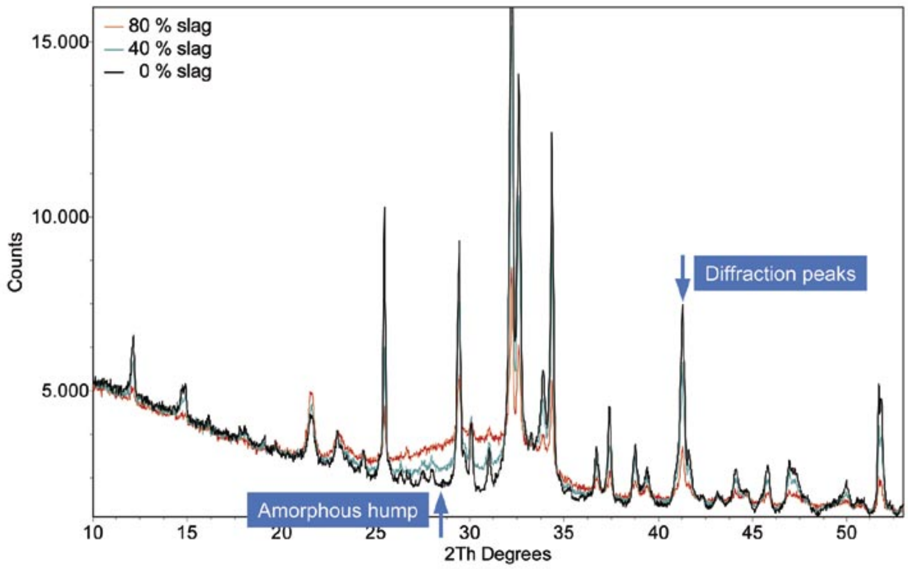


**Fig. 2: Contribution of the amorphous components to the background in X-ray diffractograms of cements containing blastfurnace slag**

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