QUANTIFICATION OF CLINKER AND CEMENT PHASES WITH THE HIGHEST SPEED AND ACCURACY

Introduction

The production of clinker and cement is a continuous process comprising the following steps:

- blending and grinding the raw materials
- feeding and firing of the raw materials in a kiln
- milling and blending of the clinker to form the final product for the market

Chemical control, usually performed by X-ray Fluorescence (XRF), forms the base of cement plant control by providing information for proportioning raw materials, adjusting kiln and burning conditions as well as cement mill feed proportioning. In addition, XRF is of the highest importance with respect to the environmentally relevant control of waste recovery raw materials, alternative fuels as well as filters, plants and sewage.

However, the performance of the product (and, therefore, of the plant) is governed by its mineralogy and not its elemental composition. With X-ray Diffraction (XRD) a full identification and quantification of the crystalline components of a sample can be obtained providing detailed mineralogical information about the clinker and cement products. As a result important parameters such as

grindability of raw materials and clinker, burnability of raw feed, cement strength development, and cement setting time can be controlled.

Latest developments of on-line XRD instruments, as well as dedicated software for quantitative phase analysis based on the Rietveld method (TOPAS), now allow fully automated on-line phase analysis for production control and quality management. As measurement and evaluation times can be brought down to minutes, a real-time control of the clinker and cement mineralogy is possible.

Experimental

In this study two NIST clinkers (standard materials RM 8486 and 8488) have been measured using a D5000matic process control diffractometer. Two different detector systems have been employed, a conventional scintillation counter (SC) as well as a position sensitive detector (PSD). Measurements times range from about 38 minutes per sample using the scintillation detector down to less than 4 minutes using the position sensitive detector. The system configurations are provided in Table 1a and b.

D5000matic process control diffractometer with scintillation counter	
Tube	2.2 kW Cu long fine focus
Tube power	40 kV, 40 mA
Incident beam optics	variable divergence slits fixed to 0.7° 4° Soller slit
Diffracted beam optics	variable anti-scatter slits fixed to 0.7° 4° Soller slit 0.2 mm detector slit
Measurement Range	10° - 55° 2θ
Step size	0.02° 2θ
Step time	1 s per step
Total measurement time	about 38 min.

Table 1a: Instrument specifications for D5000matic process control diffractometer with scintillation counter

D5000matic process control diffractometer with PSD	
Tube	2.2 kW Cu long fine focus
Tube power	40 kV, 40 mA
Incident beam optics	variable divergence slits fixed to 0.7° 4° Soller slit
Diffracted beam optics	no diffracted beam optics
Measurement Range	10° - 55° 2θ
Step size	0.016° 2θ
Measurement times	about 5 s, 25 s and 50 s per °2θ
Total measurement time	about 38 min, 19 min and 4 min

Table 1b: Instrument specifications for D5000matic process control diffractometer with position sensitive detector

The powder patterns of both detector configurations are shown in Figs. 1 and 2. As can be clearly seen in both Figs. with a position sensitive detector the identical data quality can be observed in about 1/10th of the time.

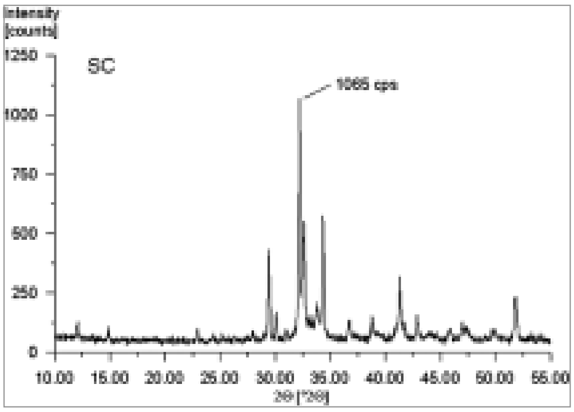

Fig. 1: Clinker pattern of RM 8486 taken with scintillation counter. Total measurement time is 38 minutes with 1 second per step.

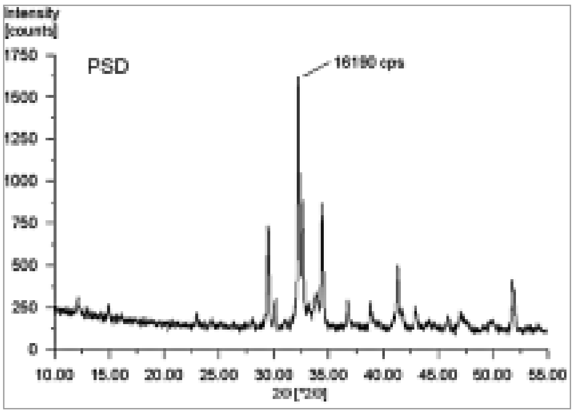

Fig. 2: Clinker pattern of RM 8486 taken with position sensitive detector. Total measurement time is less than 4 minutes with 0.1 seconds per step. Note the enormous increase in intensity when expressed in cps.

For phase quantification the new Rietveld software package TOPAS has been used. TOPAS allows full quantification of relevant clinker and cement phases without any user input. The number of phases is unlimited, typical calculation time is less than 30 seconds with a Pentium III PC system. The quantification results are compared in Tables 2a and b with microscopical results as given in the standards certificate by NIST.

	Time	C_3S	C_2S	C_3A	C_4AF	MgO
NIST[1)]		**58.47**	**23.18**	**1.15**	**13.68**	**3.21**
D5000matic SC	38 min	59.36	22.43	4.27	10.33	3.61
D5000matic PSD	38 min	60.12	20.83	4.02	11.29	3.73
D5000matic PSD	19 min	59.97	20.91	4.23	11.19	3.70
D5000matic PSD	3.8 min	59.59	21.45	3.89	11.54	3.53

[1)]Microscopic results used for certification

Tab. 2a: TOPAS Quantification results for NIST RM 8486

	Time	C_3S	C_2S	C_3A	C_4AF
NIST[1)]		**64.97**	**18.51**	**4.23**	**12.12**
D5000matic SC	38 min	66.91	18.01	3.19	11.89
D5000matic PSD	38 min	66.22	17.63	5.08	11.07
D5000matic PSD	19 min	65.62	18.42	4.51	11.44
D5000matic PSD	3.8 min	66.05	17.48	4.31	12.16

[1)]Microscopic results used for certification

Tab. 2b: TOPAS Quantification results for NIST RM 8488

The refinement results for both standards, RM 8486 and RM 8488, are shown in Tab. 2a and b, respectively. The accuracy of the results is significantly better than +/- 3% with respect to the NIST certificate. In contrast to this, the deficits of the Bogue calculations, which are also provided in the tables, are clearly seen. Differences of up to 10% for the main phase C_3S compared to the microscopy and XRD results demonstrate that Bogue calculations are not suited for reliable phase quantification.

A detailed look at RM 8486 shows another deficiency of microscopical point counting. Often identification and distinction of the interstitial phases C_3A and C_4AF are difficult. In this case it could be shown that the XRD results are more reliable and a reinvestigation of this standard material, which was done recently by NIST, confirmed this result. (Stutzman, P.E. and Leigh, S., "Compositional Analysis of NIST Reference Material Clinker 8486", Accuracy in Powder Diffraction III, Gaithersburg, 2001, in press)

The results obtained from the measurements with the different detector systems can be compared extremely well. In addition, this proves the high reproducibility to be obtained from measurement to measurement.

Conclusions

The unique capabilities of the D5000matic with PSD and the new TOPAS Rietveld software allows the full control of cement mill and clinker kiln operation. The mineralogical phase amounts in clinkers and cements can be quantified directly, real-time and on-line. As a result product quality, plant performance as well as quality management can be significantly improved.

Of particular interest is the fact, that the use of a PSD allows the determination of highly accurate results in a fraction of time compared to conventional instruments.

In combination with our XRF and automation instrumentation Bruker AXS provides the most advanced and reliable solutions for the cement industry.

BRUKER AXS GMBH

OESTLICHE RHEINBRUECKENSTR. 50
D-76187 KARLSRUHE
GERMANY

TEL. (+49) (721) 595-2888
FAX (+49) (721) 595-4587
http://www.bruker-axs.de
Email: info@bruker-axs.de

BRUKER AXS, INC.

5465 EAST CHERYL PARKWAY
MADISON, WI 53711-5373
USA

TEL. (+1) (800) 234-XRAY
TEL. (+1) (608) 276-3000
FAX (+1) (608) 276-3006
http://www.bruker-axs.com
Email: info@bruker-axs.com