BENEFITS OF X-RAY DIFFRACTION ANALYSIS IN CEMENT PROCESS AND QUALITY CONTROL

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Why X-ray Powder Diffraction?

- The quality of the product and therefore of the production process is mainly governed by its phase composition (mineralogy) and **NOT** by its elemental composition
- The classical methods like the Bogue analysis cannot describe the reality or are too slow for process control like optical microscopy
- XRD enables quality and process control of raw material, hotmeal, clinker and cement, based on the knowledge of the true phase composition, that is information not accessible by other analysis techniques

Benefits are manifold, and depend on the size of plant, type of products, quality of local raw materials, local energy costs, and local environmental regulations
Bogue analysis

- Bogue calculates a potential clinker phase composition based on assumptions, not describing the real phase formations. It can therefore only be a first estimation.
- It does not take into account solid solution effects and can never consider polymorphs.
- During clinker cooling no thermal equilibrium is reached, which is the prerequisite of such a normative phase calculation.
- Neither the absolute values of Bogue can be right, nor relative changes can be monitored correctly, in particular if secondary fuels and secondary raw materials are used.
The results of the Bogue calculation are often called potential phase compositions, because when the procedure was devised, it was generally considered that the principal source of error was failure to reach equilibrium during cooling. The results do indeed differ, probably often markedly, from the true phase compositions, notably in underestimating alite and overestimating belite (Section 4.4.6), and it is unlikely that equilibrium is maintained during cooling, but the direct source of error is that the compositions of the clinker phases differ considerably from those of the pure compounds. Bogue compositions are used in some specifications, and for proportioning by setting up and solving equations to calculate the relative amounts of raw materials needed to obtain given ‘potential’ contents of C₃S or other phases. They have often been misused for other purposes on the assumption that they are close to the actual phase compositions. Spohn et al. (S19) have indicated the dangers of such uncritical use.
Optical Microscopy

Optical microscopy is a perfect tool for studying the microstructure of the clinker, but shows severe limitations for quantitative analysis:

- Poor discrimination of interstitial phases (C3A / C4AF)
- Poor or no detection of polymorphs (C3S, C2S, C3A)
- Poor detection of minor phases
- Labour intensive, operator dependent
- Slow, not suited for process control
X-Ray Powder Diffraction (XRD) and Rietveld analysis

- Enables direct and accurate quantitative phase analysis
- Is a standardless method - no calibration involved
- Is independent of equipment and operator
- Can be fully automated and thus operated free of human interaction

Fully automated XRD with Rietveld analysis provides

- Quantitative phase compositions
- Detection and quantification of polymorphs (C3S, C2S, C3A)
- Lattice parameters / cell volumes
- Crystallite sizes
Cement Production Process
XRD Application Areas

1. Raw Materials / Raw Meal
2. Bypass / Hotmeal
3. Clinker
4. Cement
5. Offline Quality Control / Research and Development
XRD Application Areas

1. Raw Materials

Quality control of a wide range of raw materials

- Purity of limestone
  - Early warning in case of detrimental phases, e.g. Pyrite
- Purity of (natural) gypsum
  - Anhydrite, semihydrate, dihydrate, calcite, dolomite, quartz
- Purity of Blast Furnace Slag, Flyash
- Purity of Ca(OH)$_2$ for SO$_3$ absorption
  - High lime and calcite contents decrease absorption quality
- Purity of Iron sulfates for Cr(VI+) reduction
- XRD as a backup for XRF
  - phase composition $\rightarrow$ calculation of chemical composition
  - chemical composition $\rightarrow$ calculation of LSF, SR, AR
Minimization of energy losses and cloggings

- Degree of decarbonation
- Clinker dust determination
  - Measure of energy losses due to dust cycles and inappropriate kiln operation
- Formation of phases causing build-ups / clogging
  - Improved clogging prevention

Hotmeal phase analysis does not only allow to stabilize the preheater operation at high SO₃ and Chlorine levels, but also to reduce the bypass rate.
Process control based on the actual phase composition

- Check and control of kiln operation / quality control of clinker
  - Freelime analysis always included
  - Polymorphism C3S / C2S / C3A
  - Detection of minor phases (Alkalisulphates, Quartz, Pericalse, ...)
- Operation with secondary fuels / secondary raw materials
  - Spectacular failures of Bogue method!
- Setting time / strength development / degree of sulphatisation
- Clinker grindability
- Clinker color (amount and Al/Fe composition of C4AF)
- XRD as a backup for XRF
Clinker Polymorphism C3A and sulphatisation

- High amounts of Sodium and Potassium lead to the formation of orthorhombic instead of cubic C3A
- Both modification show differences in reactivity and hydration
  - The ratio $\text{C3A}_{\text{cubic}}/\text{C3A}_{\text{orthorhombic}}$ influences the water consumption of the cement
  - Higher water consumption by $\text{C3A}_{\text{orthorhombic}}$
- If Na and K are fixed in Alkali-Sulphates these elements are not available for the incorporation in C3A
- By changing the degree of sulphatisation the ratio of $\text{C3A}_{\text{cubic}}/\text{C3A}_{\text{orthorhombic}}$ can be controlled
Clinker Polymorphism C3A and sulphatisation

Degree of sulphatisation

$C_3A$ in wt.%

$C_3A$ cubic

$C_3A$ orthorhombic
Clinker
XRD versus Bogue Method

Deuna plant case study, 2003;
Dyckerhoff (Buzzi Unicem) - Polysius - Bruker AXS
Deuna plant case study, 2003; Dyckerhoff (Buzzi Unicem) - Polysius - Bruker AXS

- There is no linear relation between the Alite abundance and the LSF, as indicated by Bogue
- Depending on the individual plant scenario, there is a maximum Alite level, which cannot be exceeded by increasing the LSF
- Generally the clinker phase composition is more complex and more variable as indicated by Bogue

A too high LSF results in waste of energy and raw materials!
4. Cement

Control of cement mill operation

- Check and control of mill operation
  - Dehydration of gypsum
  - Cold start of the mill can be controlled
- Quality control of the finished cement
  - Fillers and additions such as Limestone, Blast Furnace Slag and Flyash can be analyzed directly
    - Meet requirements of norms (CEM)
- Quality management (archive XRD data as a fingerprint)
Benefits in Quality and Process Control

Cement

- Control of the cement mill operation
- Dehydration of Gypsum
- Cold start of the mill can be controlled
- Control of the CO2 setpoints (Limestone filler)
- Control of Blast-Furnance Slag addition
- Check of competition
- Quality management (keep measurement data as a fingerprint)

Importance of sample preparation!!!!!
Miscellaneous offline applications

- Characterization of competition products
- Analysis of materials forming build-ups and cloggings
- Customer complaints
- Cement hydration studies
- Research and development, ambient and non-ambient studies
- Characterization of any raw material deliveries - at the gate
Phase Analysis in the Production Process
Benefits and Payback

- XRD versus Bogue method
- Polymorphism C3A and Sulphatisation
- Polymorphism Alite (C3S) and Strength Development
- Hotmeal phase analysis and clogging/blockage prevention
- Seamless integrated analysis of amorphous phases
Instrumentation

- Bruker offers XRD instrumentation for analysing the entire process mineralogy starting with the preheater processes, to the clinker burning and the cement milling
The D2 PHASER
The Most Powerful Desktop X-ray Diffractometer

- World's fastest desktop X-ray diffractometer
- Compact all-in-one instrument
- Plug'n Analyze
- Mobile for on-location operation
- Little power consumption max. 650 W
- Zero water consumption: Internal cooling circuit
- No consumables
The D8 ADVANCE
The most versatile X-ray diffractometer

- Automatic Alignment
- 9 position FLIP-STICK and 90 position AUTO-CHANGER
- TWIN-TWIN optics
- Unlimited flexibility and upgrade-ability thanks to DAVINCI.DESIGN
- Free choice between all D8 ADVANCE optics and detectors
The D4 ENDEAVOR
High Sample Throughput

- Choice of detectors:
  - Scintillation counter
  - LYNXEYE detector (covering 4°)
  - VANTEC-1 detector
- Various sample magazines (66, 72, 120 samples)
- Offline or fully automated operation
- Connections via robot or conveyor belt
- Automation interface fully supporting priority levels
- Manual and automated operation simultaneously!
The LYNXEYE Detector

- Active area: 14.4x16 mm
- Fluorescence suppression eliminating the need for secondary monochromators
- More than 150 times faster / more intensity than a scintillation counter
- The ideal detector for all applications in the cement industry

D2 PHASER / D4 ENDEAVOR / D8 ADVANCE with LYNXEYE
The world's fastest X-ray diffractometers
D4 ENDEAVOR & LYNXEYE & TOPAS
Repeatability of analysis (values in wt.%)
TOPAS defines a new generation of Rietveld software

- Fundamental Parameters Approach (FPA)
- Numerically stable and extremely fast
- Typical calculation time is a few seconds per sample
- Easy to use and fully automatic analysis without user input
- Large convergence radius
- No need to stop calculation before convergence is reached
- No need for a parameter turn-on sequence
- Seamless integrated analysis of amorphous phases
The Bruker Cement solution

Instrumentation
- D2 PHASER
- D4 ENDEAVOR
- D8 ADVANCE
- LXNXEYE Detector

Software
- TOPAS Rietveld
- PolySnap Cluster analysis

Application Support
- Covering the complete process mineralogy
- Including Alite polymorphs
- Seamless integrated analysis of amorphous phase amounts by PONKCS
X-Ray Fluorescence (XRF) Product Solutions

- **S4 PIONEER**
- **S8 TIGER****
- **S8 DRAGON/LION**
- **ARTAX**
- **S2 PICOFOX**
- **S2 RANGER**
- **S1 TURBO**
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workshop

office area
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Service Car - We go where you are!

Remote diagnost support!

We offer the best systems on the market and the fatest support avaible, you can count on us!