

Quality Assurance Manual

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Holcim Technology Ltd, Cement Manufacturing/Materials Technology, Holderbank/Switzerland



Quality Assurance Manual

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Introduction

The general quality management framework for the cement plants in the Holcim Group is given in the ISO 9000 standard, the national standards for cements and cement testing, and the Holcim Product Quality Management model.

The present Quality Assurance Manual contains guidelines for best practices and technologies to carry out the quality assurance during cement manufacturing in a plant, including the following main aspects:

- Quality management
- Quality control department
- Process related quality control
- Sampling and sample preparation
- Quality control laboratories and equipment
- Automated quality control systems
- X-ray fluorescence
- Other analytical methods

The part of AFR quality control is already covered in a separate manual and is not included.

The basic objectives that are pursued by the quality assurance in cement manufacturing are the following:

- Comply with the cement standard specifications and market relevant requirements and to provide the customers with a product of high uniformity.
- Achieve the defined quality levels at high consistency throughout the whole manufacturing process
- Ensure a trouble free and efficient operation of the processing equipment (e.g. kilns and mills).
- Use the raw mix components and fuels in an optimum way
- Carry out the acceptance control of all incoming materials

The proper set-up of quality assurance is thus an important element in the context of the customer excellence and cost leadership and the manual shall finally help the Group companies to apply the best practice in this field.

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Part I: Quality Management

1. Introduction

An appropriate and for our industry applicable definition of quality management is given in the ISO 9000 standards:

“Quality management includes all the activities that organizations use to direct, control and coordinate quality. These activities include formulating a quality policy and setting quality objectives. They also include quality planning, quality control, quality assurance, and quality improvement”

Frameworks that guide Holcim companies to establish a quality management system are given from (at least) four sides; they are briefly outlined in the following chapters:

- ISO 9001 Standard for Quality Systems: World-wide acknowledged and certifiable system defining requirements and processes for quality management. Mandatory for Holcim group plants.
- National cement standards and cement testing standards: Providing limits or ranges of cement characteristics, to which most of produced cements have to comply, as well as providing standards for testing relevant cement properties. This may extend to procedures and requirements for product certification.
- Holcim PQM Model: Guidelines for addressing – and measuring – crucial system elements to assure customer satisfaction and levels and consistency of cement quality, including performance in concrete.
- Holcim Quality Assurance Manual (this document): Guidelines for best practices and technologies to carry out quality assurance in a plant.

2. ISO 9000 quality management systems

Frameworks for structured, generally recognized quality management systems have for a long time been provided in form of the ISO 9000 standards.

In context of introducing the Holcim brand in 2002, it was decided that all Holcim group companies shall implement and certify an ISO 9000 quality management system, in order to comply with the industry recognized standard to ensure the quality of products sold on the market. The pertinent standard is the ISO 9001, of which the actual version is the ISO 9001:2008.

As shown in Figure I- 1, the ISO model starts with the customer requirements and ends with the final evaluation of customer satisfaction, including all the intermediate processes to ensure that the delivered product has the right quality.

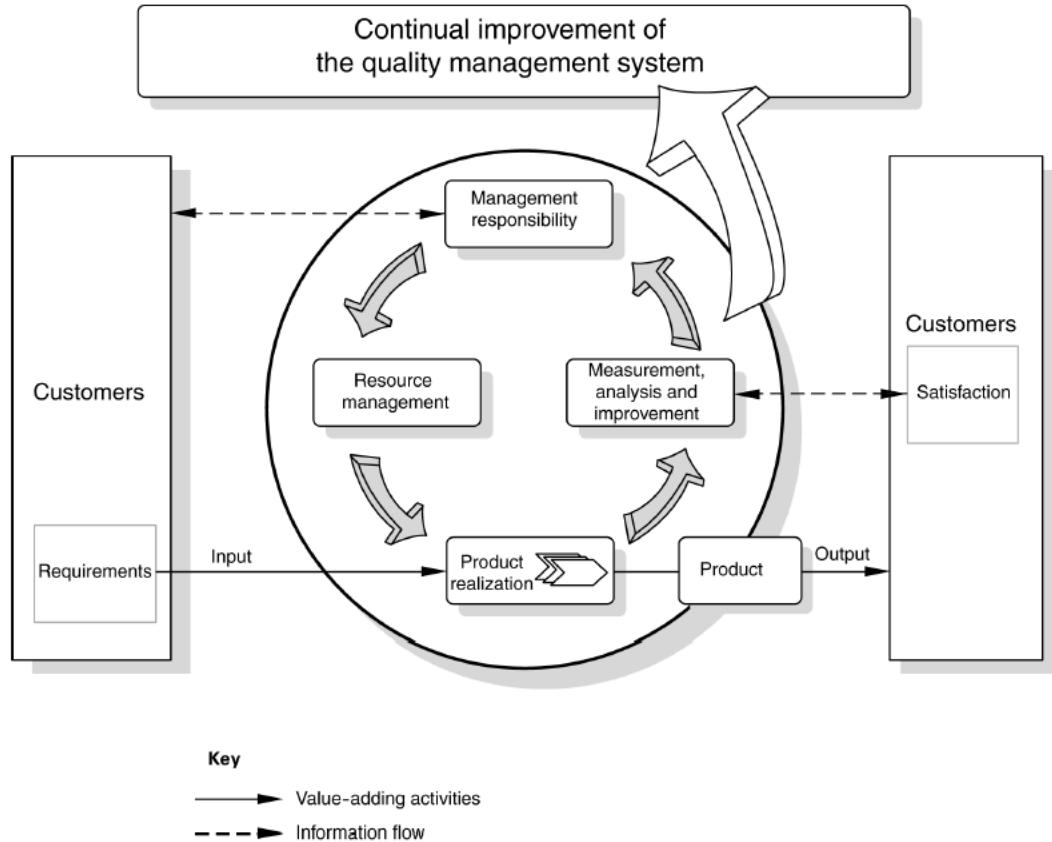


Figure I- 1: Model of process-based quality management systems (ISO 9001:2008(E))

The ISO 9001:2008 lays down what requirements the quality system must meet. The main elements it addresses are:

- Quality management system, including documentation requirements
- Management responsibility, including customer focus, planning, reviews
- Resource management, including human resources, infrastructure
- Product realization, including design (and development), production, control of measuring equipment
- Measurement, analysis and improvement, including control of nonconforming product, analysis of data, improvements

ISO 9001:2008 lays down what requirements the quality system must meet, but it does not dictate how they should be met in any particular organization. This leaves great scope and flexibility for implementation.

The quality management system according ISO 9000 involves the entire company, not only e.g. the Quality Control department. Furthermore, companies may have to comply with other management systems, notably for environmental aspects (ISO 14001) and OH&S (OHSAS 18001). Therefore, OpCos may choose to implement Integrated Management System covering the requirements of all mentioned sub-systems.

Document and data management, as well as management of all system related activities (e.g. customer complaint investigations, improvement activities) are mostly done on specific software platforms.

3. Product and testing standards

Cement manufacturers are generally not entirely free to design their products, with the exception of specialized products for particular applications. Most products are subject to meet national Cement Standards, providing limits or ranges for various product characteristics. Thus, the quality management has to ensure that at the same time applicable standards are strictly met, and that the degree of freedom left by the standards is exploited to produce cements at appropriate quality levels to meet market requirements and at low production costs and low environmental impact.

Cement standards define product characteristics through:

- Descriptive properties: Chemical and mineralogical composition, types and proportioning of constituents, etc.
- Performance properties: Compressive strength, setting time, soundness, etc.

Major cement standards are:

- ASTM C150; ASTM C595; ASTM C1157
- EN 197
- AS 3972

Many national standards are based on one or the other of these major standards.

As part of the cement standardization, testing standards exist for basically all cement characteristics specified in cement standards. Many of them are directly applied in routine testing of product quality; others can be replaced by alternative (usually faster) methods and mainly serve as reference methods.

Certain cement standards, notably the European cement standards, include standardized schemes for product certification. Such schemes may require the existence of certain elements of a quality management system (e.g. based on clauses of ISO 9000), as well as the statistical prove of meeting cement standard specifications, based on testing at the plant and on samples taken and tested by an external organization (EN 197-2).

Plant laboratories, as well as central laboratories of customer service laboratories, have in principle the possibility to certify selected testing methods according to the ISO 17025 standard (General requirements for the competence of testing and calibration laboratories).

4. Holcim PQM model

As pointed out, ISO 9000 quality management systems as well as cement standards are providing frameworks for managing product quality, but they leave scope and flexibility regarding **how** things are managed and **what** specific product types and quality levels need to be produced to meet market needs.

In a survey carried out in 2006 within the Holcim Group, it was observed that product quality issues are not always sufficiently addressed and that there is a need to strengthen the management elements related to product quality. In order to do so, the PQM Model was developed and described in the Holcim Product Quality Management Reference Manual. The application of this model became a Group Roadmap target in 2009.

The objective of the PQM Model is to strengthen those elements of quality management that deal with achieving customer satisfaction and managing the cement and resulting concrete quality level and consistency. The following six so-called quality principles have been defined:

1. Measurement of customer satisfaction: Realization of customer surveys and monitoring of customer feedback through complaints and technical customer service reports.

2. Product benchmarking: Comparison of performance of own products against competitors' products.
3. Internal product specification: Formal agreement between Manufacturing and Marketing & Sales with regard to the product requirements.
4. Application-oriented product testing: Concrete testing to evaluate performance of the product in the final application.
5. Manufacturing quality targets and Key Performance Indicators (KPIs): Definition of adequate targets and KPIs for manufacturing to ensure compliance with internal product specifications.
6. Quality committee: Regular meetings between Manufacturing and Marketing & Sales to ensure alignment with regard to product quality.

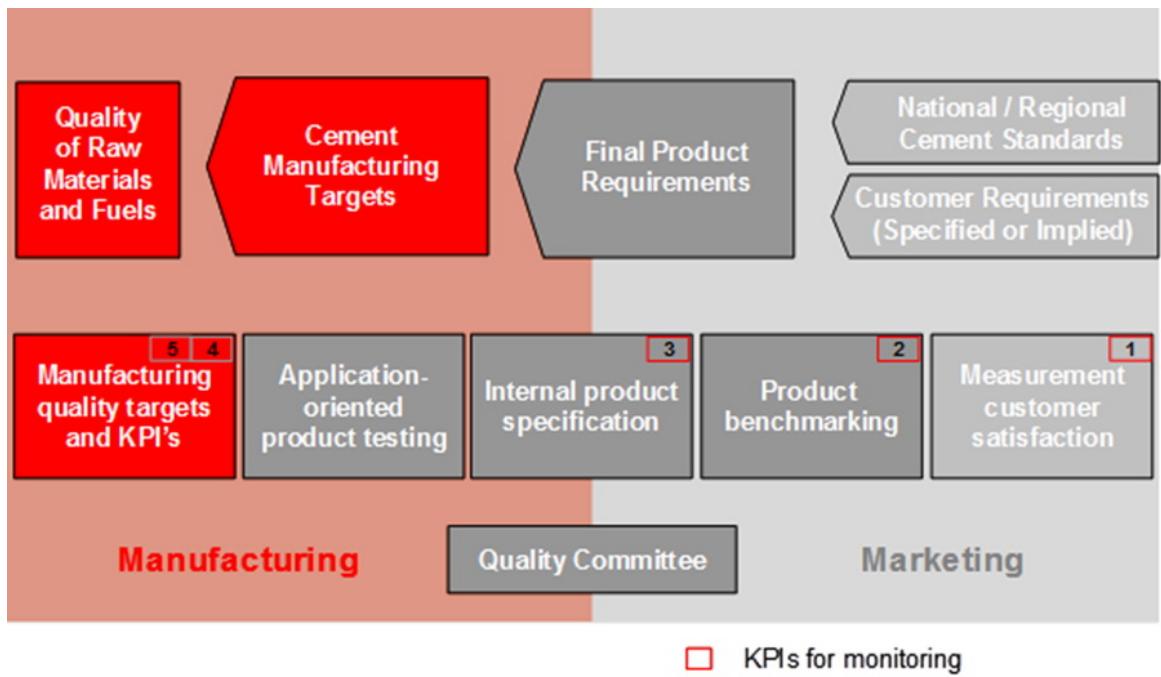


Figure I- 2: Holcim PQM model

For the monitoring of the PQM process, five quality KPIs have been selected related to measurement of customer satisfaction, product benchmarking, internal product specification and manufacturing quality targets. These five indicators are integrated into a Product Quality Index, which is used for the manufacturing performance analysis.

Index	Indicators used for index calculation	Target
Product Quality Index	1 Customer complaints related to product quality issues	Company or plant specific, ratio actual vs. target ≤ 1
	2 Product performance benchmarking	Company or plant specific $\geq 95\%$ of market reference
	3 Compliance to internal product specification	Group standard $\geq 95\%$
	4 Product uniformity (Coefficient of variation early strength)	Group standard $\leq 7\%$ (2d CoV) $\leq 5\%$ (3d CoV)
	5 Compliance to clinker specification	Group standard $\geq 90\%$

Figure I- 3: Five quality KPI's used in PQM

5. Quality assurance manual

In complementation to the PQM Model, which supports companies to deal with quality management aspects addressing quality level and consistency of cement and concrete made thereof, the present Quality Assurance Manual shall provide information on best practices and technologies applicable to organize and carry out quality assurance in cement plants.

It will address organizational aspects, tasks and objectives of quality control throughout the process from quarry to dispatch, and technologies, methods and equipment applicable for sampling and testing.

References:

Holcim Product Quality Management Reference Manual

Part II: Quality Control Department

1. Organization / Structure

1.1 Organization at plant and company level

The most recommended quality organization of a cement plant is shown in Figure II- 1. The quality manager as well as the managers for production, process and maintenance report all directly to the plant manager.

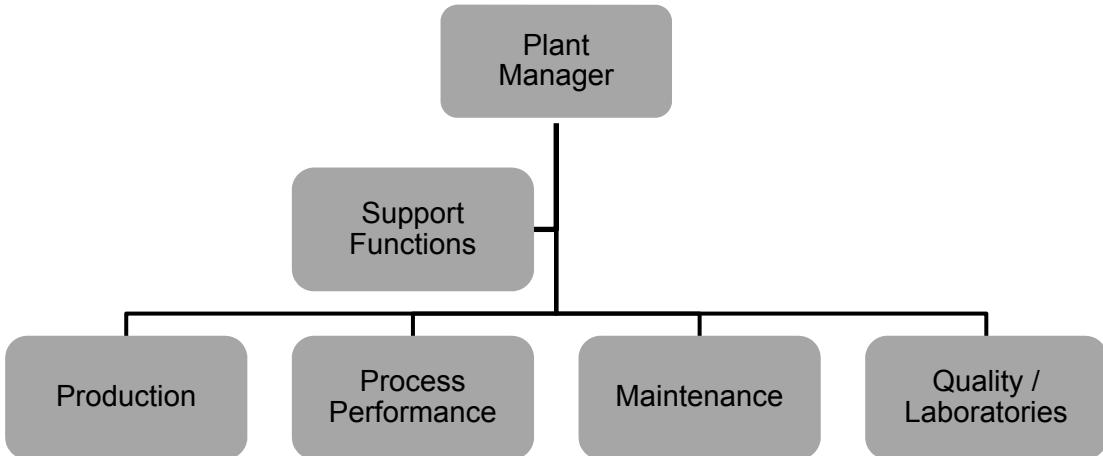


Figure II- 1: Quality organization at a cement plant

Other organization forms where the quality manager reports to the production manager present the risk that the independence of the quality function is not effective enough.

On a Group company level, the technical director, the plant managers and the company quality manager (or quality responsible in RMSO) are involved in the quality management. From the marketing side, the counterparts are typically the marketing & sales director, the regional marketing & sales responsibles and the technical customer service manager respectively (see also Figure II- 2).

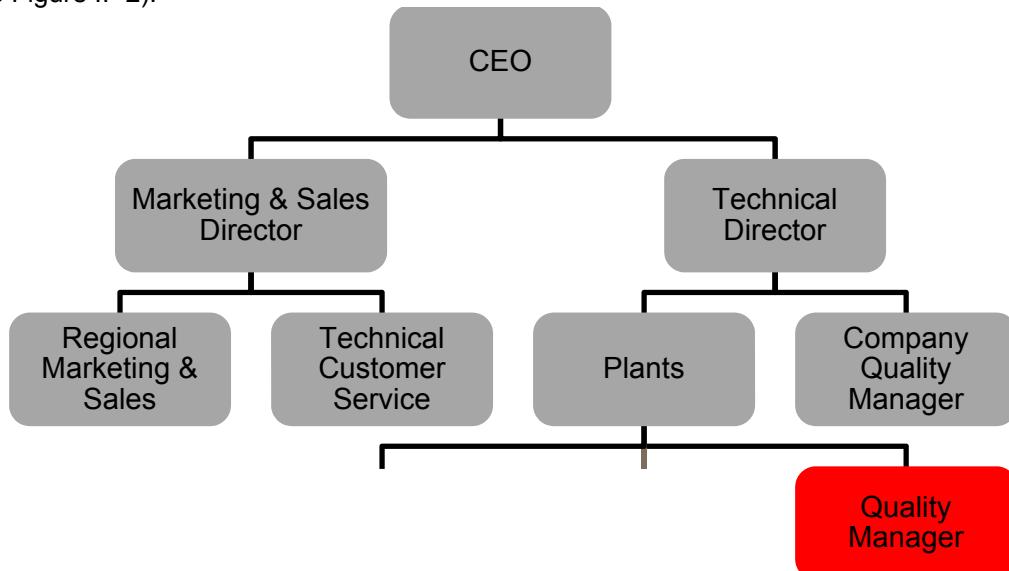


Figure II- 2: A typical Group company manufacturing and marketing & sales organization

The two examples mentioned above are recommended typical constellations. Individual plant organization structures may need to consider certain local requirements and circumstances, which may result in a different organization set up.

One such modification relates to combine the functions of process, quality and environment: The increasing complexity and mutual influences of measures aiming at process optimization, emission control and quality optimization have initiated in some cases that an experienced process performance engineer bears the overall responsibility on process performance, quality, and environment, in order to ensure a holistic approach to these aspects. Risks are, among others, that it may be difficult to find suitable profiles for such a function, and, again, that the independence of the quality function is not effective enough.

Reference is made here to the development made in 2007 of a EMMS (European Manufacturing Management System) Handbook and the Plant Organization Handbook contained therein.

1.2 Functional organization of quality control (QC) department

Following diagram shows a typical functional organization of a QC department in a cement plant:

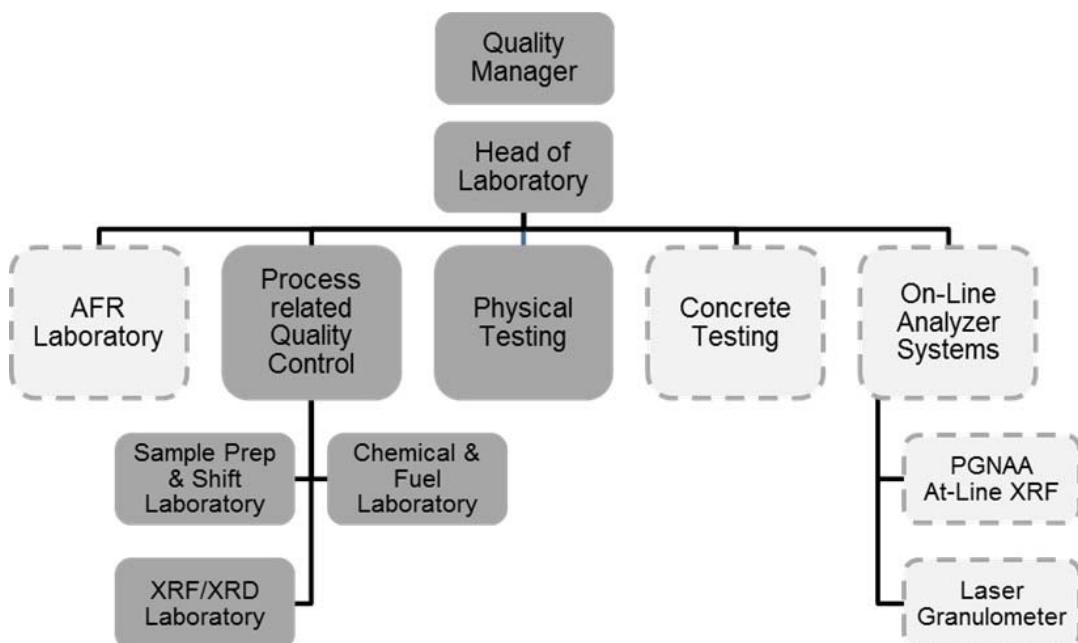


Figure II- 3: Typical functional organization of a QC department

The two main sections of the department are:

- Process related quality control: Testing of all materials from quarry to cement dispatch on chemical, mineralogical and fineness properties; testing of fuels
- Physical testing: Physical cement, paste and mortar testing

The laboratories or functions, indicated with a dotted line, are optional, depending on the individual plant organization, application of AFR and degree of automation:

- On-line systems: If on-line analyzing systems, such as PGNAA, at-line XRF systems or in-line LASER granulometers are installed in the plant, the monitoring, supervision and maintenance is usually a shared function between the Quality Control, Production and Automation departments.
- Concrete laboratory: If emphasis is given to frequent testing of produced cements on concrete as part of the routine quality control, a plant specific concrete laboratory is the best solution. In case of lower concrete testing frequencies, concrete testing can be done at a centralized concrete laboratory, or externally.

- AFR laboratory: A specialized AFR laboratory at plants using AFR is often required. This may be due to local legislation (in context of permitting), particularly when “hazardous” materials are used and strict control of incoming materials is mandatory. Specialized equipment may then be required.

Non-hazardous waste materials such as plastics, tires, woodchips/biomass etc. can often be analyzed with default equipment installed in the fuel laboratory, and a separate AFR laboratory is not required. For further details on AFR quality control please refer to the *AFR Quality Control Manual* by CM/MT.

2. Personnel

2.1 Job description / qualification

2.1.1 General

Job descriptions for the functions in a QC department are a requirement of an ISO 9000 system. In general, they have to address the following items:

- Hierarchical position (reporting to whom; supervising who)
- Tasks
- Education / skills
- Experience

2.1.2 Quality Manager

A Standard Job Description for a Quality manager was developed for the European region (European Manufacturing Management System) and is used as a template for plant specific job descriptions in companies of that region. The above mentioned items are stated as follows (summarized; details see Annex Part II-1):

Hierarchical Position	Reporting to plant manager
Tasks	<p>Operation quality control</p> <ul style="list-style-type: none"> – Plan, organize and manage quality control – Ensure calibration and maintenance of equipment <p>Quality assurance</p> <ul style="list-style-type: none"> – Analyze quality performance, identify deviations and causes, collaborate with production and process performance <p>Standards</p> <ul style="list-style-type: none"> – Ensure compliance with pertinent standards for quality management (ISO 9000) and for products and product certification <p>People management</p> <ul style="list-style-type: none"> – Ensure availability and performance, promote motivation and professional development (coaching, training) <p>Planning and cost control</p> <ul style="list-style-type: none"> – Plan resources; budgeting and cost control <p>OH&S and environment</p> <ul style="list-style-type: none"> – Guarantee and foster compliance with OH&S and environmental policies; ensure cleanliness – Innovation and continuous improvement – Evaluate impacts of changes in products and process on quality; consider and propose new methods and technologies to optimize costs and improve quality

Education / skills	Degree in chemistry, chemical engineering, material science Computer / language skills Leadership skills
Experience	3 years of experience in laboratories Knowledge in cement and cement application, ISO 9000, statistics

2.1.3 Typical positions in QC department

An outline of typical positions required in a cement laboratory is given below:

Head of laboratory	
Tasks	Process related quality control, automation systems, applied analytical methods (PGNAA, XRF, XRD, LASER-PSD etc).
Education	Chemical Engineer or Process Engineer, trained on modern analyzer systems and analytical methods (e.g. in training programs by equipment suppliers)
Experience	5 years plant experience

Laboratory chemist	
Tasks	Non-routine sample preparation and analytical work (drill hole samples, composite samples, combustibles etc), crosscheck verification of automated testing (e.g. free lime, fineness)
Education	Chemist, or trained laboratory technician
Experience	3 years laboratory experience

Physical testing technician	
Tasks	Physical testing of ground and dispatch cement according to local cement standard
Education	Material tester or trained laboratory technician
Experience	-

Shift personnel for 24h / 7d per week production control	
Tasks	Sampling & sample preparation, routine XRF & XRD analyses, PSD & Blaine, Sieve analyses, Moisture
Education	Trained laboratory technician
Experience	-

Concrete testing technician	
Tasks	Physical testing of concrete according to internal standards
Education	Material tester or trained laboratory technician
Experience	3 years laboratory experience

Laboratory chemist for AFR	
Tasks	AFR sampling, sample preparation and analyses, trained on standard and specialized chemical analyses methods
Education	Chemist, laboratory technician
Experience	3 years laboratory experience, focusing on analytical chemistry

The necessity for concrete tester and for AFR chemists, respectively, depends on the individual local circumstances.

Depending on the degree of automation and the technical standard of the applied equipment, further people such as mechanical and electrical educated personnel is required. These personnel do not necessarily belong to the quality control department but have to apply routine maintenance service and troubleshooting to quality control equipment such as automated centralized laboratories, laboratory equipment or on-line analyzers and sampling systems in the plant. This kind of maintenance has to be in accordance with the equipment supplier and is meant to achieve maximum system availability. It shall not substitute service, applied by specialists from the system and equipment suppliers, which typically is provided in the context of a service contract.

Annex Part II-2 contains a few examples of job descriptions from a plant, as illustration (courtesy Midlothian plant, Holcim US).

2.1.4 Number of personnel

The number of people for the quality control department has to be chosen in view of several aspects, such as:

- Degree of automation (sample transport, automated laboratory, local control systems)
- Complexity of plant/number of production lines
- Number of produced cement products
- 24h/7d control service
- Manpower costs

Typically, the number of personnel in the quality control department of a plant in medium to high labor cost areas ranges between 5 and 15 persons. It may go up above 30 in other areas.

For illustration, Table II- 1 gives the median number of laboratory personnel as reported in the ATR 2011 for the different geographical areas (grinding plants excluded):

Region	FTE Quality Control and Laboratory median	Number of plants
Europe	9	29
North America	7	11
Africa & Middle East	9	5
Latin America	12	19
Asia, Oceania	29	50

Table II- 1: FTE's in Quality Control Department (source: ATR 2011)

2.1.5 Training

Training is provided at internal Holcim seminars and courses as well as externally. Recommended internal Holcim courses for personnel involved in quality control are:

- Cement Manufacturing Course
- Quality Manager Course
- AFR workshops on Quality Control
- Microscopy workshop
- QSO Seminar
- Cement Application Course

External seminars or training provided by external specialists are offered as well, e.g. by the system suppliers, focusing on the operation and handling of specific control equipment (e.g. PGNAA and XRF workshop).

In case complex automated control systems are installed, such as automated laboratories and/or on-line analyzers (PGNAA, at-line XRF, at-line Laser Granulometer, etc.), it is recommended to have a sufficient number of quality control and maintenance personnel trained by the supplier.

This may comprise training at the supplier's facilities or at different plant sites, where similar equipment is operated.

The Quality Manager and/or Head of Laboratory shall provide training to the laboratory personnel in terms of:

- Entire cement production process
- Significance of sampling and analyzing accuracy
- Repeat training on existing analyzing equipment & methods
- Introduction of advanced and new analyzing equipment & methods
- New/modified production equipment
- OH & S

Training material (Workforce Training) for this purpose has been developed by HGRS. Check Holcim Portal and local, HGRS Human Resources or training departments.

Part III: Process Related Quality Control

1. Principles

The general quality control concept in a cement plant is based on the following principles:

Adequacy	Emphasis has to be put on areas associated with high risks and high impacts on costs for process and quality of product
Anticipation	Prevention rather than cure. Concentrate efforts at earliest possible stage, to enable corrections before process or product is affected. This is particularly important for production lines with high capacity.
Rationalization	Liberation of personnel from simple routine work, by application of fast, reliable and possibly automated sampling and testing equipment.
Integration	Ensure compatibility of quality control concept with process control; link quality and process control (on-line quality control) as far as possible.

The quality control concept has to take into account the following aspects:

- Number, types and heterogeneity of raw materials (incl. mineral components) and fuels
- Number, types and quality requirements of final products
- Complexity of plant design (e.g. number of kiln lines and finish mills)
- Investment costs
- Operation costs (e.g. labor costs)

Furthermore, decisions have to be made – based on cost considerations and evaluation of technical solutions available - on:

- Degree of automation
- Centralized or de-centralized control systems

Quality control practices have certainly gone through some important developments over the past 20 to 30 years. In a very simplified way, ongoing trends can be summarized as follows:

- Start of control as early in the process as possible
 - Start at the raw material deposit and quarry, not only at the raw mill
- Acquisition of more information
 - Measurement of minor and trace elements, not only of main elements
 - Monitoring of clinker mineral phases, not only of free lime
 - Determination of particle size distribution, not only of Blaine
- Control at higher frequency
 - Control hourly to real-time, not only once per shift
- Less personnel
 - Performance of process-related quality without personnel over nights and weekends, not with 3 persons per shift
- Product testing closer application
 - Testing of concrete strength and rheology, not only of mortar strength

2. Basic elements for quality control

2.1 Quality Control Plan

The QC plan defines the scope of routine quality control in each important step along the cement production process. It is tailored to the needs of the individual plant and a requirement for ISO 9000 certification. The following aspects need to be covered by the quality control plan:

- **What material** should be examined
- **Where** does the sampling and testing take place
- **How often** has the material to be tested within a certain time period
- **Which information** is required
- **How accurate** must the testing result be
- **What** is the appropriate testing method
- **When** must the information be available, to enable effective control
- **Who** is in charge of the testing
- **To whom and how** is the result reported

A quality control plan typically has entries for

- Raw materials (from own quarry or purchased from third party)
- Premix (in case of pre-blending systems)
- Raw meal
- Kiln feed (for each kiln line)
- Clinker (for each kiln line)
- Fuels
- Hot meal
- Filter dust, bypass dust
- Mineral components (gypsum, slag, fly ash, etc.) and chemical additives
- Cement out of mill (per product and mill)
- Cement out of dispatch silo (per product)

Plant Area	Material	Sampling location	Sampler type	Sample type	Sampling Frequency	Sample transport	Analyses	Responsible
Quarry	Drill hole Chips	Drill rig	Auto sampler	composite	1 sample per drill hole	manual	Moisture Chemistry (XRF)	Quarry
Preblending	Crushed limestone	After crusher	none (PGNAA)	Continuous	Continuous	none	Elemental analysis	Quarry / lab
Raw mill	Raw meal	After mill cyclones	Automated screw sampler	composite	1/h	pneumatic	Chemistry (XRF)	
					every 2h		Moisture	
					every 2h		R200, R90	
Homo silo	Kiln feed	Exit homo silo	Automated screw sampler	1h composite	every 4h	manual	Chemistry (XRF)	Shift lab
Preheater	Hot meal	Exit bottom cyclone	(Safe) manual sampler	spot	every 8h	manual	Chemistry (XRF)	Shift lab
Cooler	Clinker	Top of clinker silo	Automated spoon sampler	spot	1/h	manual	free lime Chemistry (XRF)	Shift lab
Coal mill	fine coal	Transport to main burner	Automated screw sampler	composite	every 2h	manual	fineness	Shift lab
Unloading	MIC / correctives	Conveyor to storage	Hammer sampler	Weekly composite	On unloading	manual	calorific value ash content	Shift lab
Cement mill	Cement	Exit mill	Automated screw sampler	composite	every 2h	manual	Chemistry (XRF) moisture	Sift lab
Cement dispatch	Cement	Exit silo	Manual screw sampler	spot	daily	manual	Chemistry (XRF) Fineness	Physical lab
							physical testing	

Table III- 1: Example of a tabular quality control plan

2.2 Product specifications

For each intermediate and final product the desired quality targets and the acceptable tolerances have to be defined.

Starting point are the market-relevant final product specifications, as agreed and mutually signed by the Marketing & Sales and the Manufacturing departments, along with the applicable cement standard specifications (see Part I and the Holcim Product Quality Management Manual). Such

specifications will primarily involve performance parameters for cement mortar and for concrete (along with chemical parameters). Many of them require long time delays for measurement (e.g. compressive strength of mortar and concrete) and can therefore not be used as parameters for short-term, process related quality control. An example is shown in Table III- 2 below:

Cement name	Mortar						Concrete	
	R1 [MPa]	R2 [MPa]	R28 [MPa]	SO ₃ [%]	Init. set [min]	Final set [min]	R1 [MPa]	R28 [MPa]
CPC 40	> 11	> 11	45 - 60	< 3.5	> 45	< 600	> 9	> 26.5

Table III- 2: Example for market-relevant product specifications (cement); upper and/or lower limits are specified

The selection and definition of the detailed and readily measureable quality targets for the final products, all intermediate products, as well as raw materials and fuels has to be done by Manufacturing at plant level. This has to be done in view of:

- Achieving the market-relevant specifications and Cement Standard specifications (based on established relationships/correlations between readily controllable parameters such as component proportioning, fineness, chemical composition with performance parameters such as compressive strength, setting time, soundness, etc.)
- Achieving trouble-free and efficient operation of equipment
- Optimal use of raw components and fuels
- Acceptance control of incoming materials

Table III- 3 below shows an example and indicates possible quality targets and tolerances for clinker. More details on control parameters for intermediate products are given in chapter 2.3.

Parameter	Unit	Target	min	max	Uniformity criterion
Lime saturation		96	93.5	98.5	s
Free lime	%	1.2	0.7	2.2	
Silica ratio		2.5	2.4	2.6	s
Alumina ratio		1.8	1.7	1.9	s
C3S (Bogue)	%	57	54	60	
C3A (Bogue)	%	9.5	8.5	10.5	
SO ₃	%	1	0.9	1.1	
Sodium equivalent	%	0.8	0.7	0.9	
Alkali/sulfur ratio		0.7	0.6	0.8	
Plant specific parameter definition					
P ₂ O ₅	%	0.30	0.20	0.40	
F	%	0.25	0.20	0.30	
MgO	%	3.0	2.50	3.50	

Table III- 3: Quality targets for clinker (example only)

2.3 Quality control loop

The materials must be controlled along the process to verify whether the intermediate product specifications (e.g. clinker) and the final product specifications are met. The classical quality control loop in a cement plant is shown in Figure III- 1.

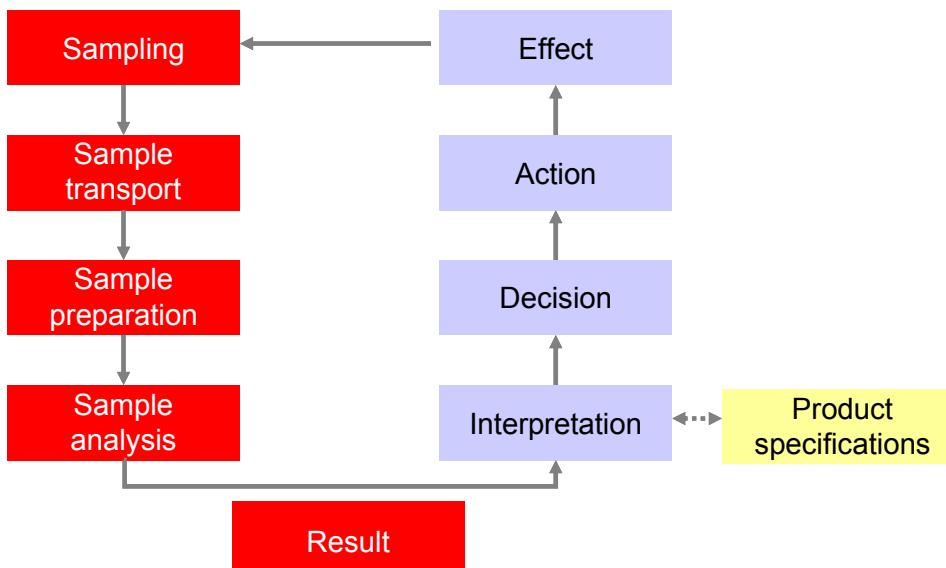


Figure III- 1: Quality control loop in a cement plant

3. Control concepts and automation

3.1 Centralized quality control concept

The centralized quality control concept is the classical and still most widely applied concept. With centralized quality control all analyses are carried out at the central laboratory. This requires that all samples from the different sampling points are transported to the laboratory and that the laboratory has the appropriate capacity to analyze the samples within reasonable time.

Advantages of a centralized QC concept are:

- Very flexible, can cope with complex plant designs (e.g. several kiln lines, several mills)
- High analytical accuracy
- Testing activities easy to supervise
- High degree of automation is possible

Potential disadvantages – especially at low degree of automation - are:

- Low testing frequency due to transport delay and constraints on personnel resources
- Reduced scope of testing during nights or weekends

3.2 De-centralized quality control concept

In a decentralized quality control setup, major quality control functions are carried out by control systems installed locally, i.e. close to the production equipment. Distances between production/sampling and the analytical equipment are short. Decentralized systems typically include a sampling unit, a sample preparation unit and an analytical unit. Few systems– e.g. PGNAA – measure directly the full material stream, and thus do not require sampling.

Decentralized systems have mainly been developed for

- **Stockpile control:** Monitoring/control of chemical composition of crushed, coarse raw materials on conveyor belt by PGNAA technology
- **Raw mix control:**
 - Raw mix at mill inlet: Chemical control on conveyor belt by PGNAA technology
 - Raw meal at mill outlet: Chemical control by means of automatically sampling, sample preparation and XRF-based analysis. This takes place in a small container or enclosed area close to the raw mill. Low powered energy dispersive XRF spectrometers are typically employed.

- **Clinker control:** Automated free lime control, including sampling, crushing and grinding. Chemical (SO_3 , XRF) and mineralogical (XRD) analyses are in principle also possible.
- **Cement control:** Solutions exist for fineness determination by laser granulometry, for chemical parameters (such as SO_3) or for mineralogical phases (XRD).

The systems operate in a fully automated way. Some of them are presented in Part VI.

Advantages of decentralized systems are:

- Short distance between sampling point and analytical equipment, allowing for high analysis frequency and therefore fast process interaction. Provides best support for integrated quality and process optimization for a single production unit (raw mill, kiln, cement mill)
- Inherent advantages of automated systems (e.g. repeatability, see below)
- Reduces work load for central laboratory (both for a manually operated or an automated central laboratory)

Disadvantages are:

- Isolated solution for one particular application; can be difficult to integrate in the overall QC concept of a plant
- Systems have to be multiplied in case of more than one process equipment (e.g. several cement mills), thus increasing costs. Sharing of one system between two or more process units is in some cases possible, but always involves compromises
- More difficult supervision and maintenance
- Often employs low power equipment, thus lower analytical accuracy

De-centralized units are considered suitable for focused, local upgrade of QC systems in an existing plant.

3.3 Automation in quality control

Main objective of automation is increased product quality and reduced operation costs through improved uniformity. Furthermore, working safety – particularly for sampling – can be improved. Benefits of automation are:

- High testing frequency, enabling fast interaction with process control
- High standard of sample preparation and analysis (good repeatability)
- Around the clock system availability
- Low routine workload for laboratory staff, enabling reduction of shift laboratory personnel. Automation is possible to the extent that routine, process-related quality control functions can be carried out without human intervention, enabling personnel-free operation during night shifts and week-ends
- Lower operational costs, due to trouble-free, energy-efficient operation of process equipment

Critical aspects of automation are

- CAPEX required
- With increasing complexity of the systems (mechanically and software-wise), intensity and skills for support and maintenance increase to ensure high availability. Highly skilled and trained personnel have to be allocated for this purpose.
- Requirement for backup system in case the automated system fails

Automation is primarily applied in areas where high testing frequency is required, such as for raw meal, clinker and cement control. Automation can be applied for individual steps of a quality control loop (Figure III- 1), or for sequences of steps, up to the extent of full automation for all routine quality control tasks (e.g. automated central laboratory systems).

- **Sampling:** Several types of automated and programmable samplers exist (see Part IV). Manually operated sampling devices (i.e. no motor) are nowadays only used for materials tested at low frequency (e.g. kiln dust) or for specific sampling campaigns. It has to be noted that automatic sampling can eliminate safety hazards involved with manual sampling, e.g. manual sampling from conveyor belts or pan conveyors.
- **Sample transport:** Most common are pneumatic tube systems where powdery or granular samples are filled into a capsule and then transported through a tube system to the laboratory. For specific applications (e.g. transport over short distances only) alternative systems are available such as direct (air-born) pneumatic conveying of powder through a tube, or systems based on cable/disk transport (see Part IV).
- **Sample preparation:** Automated sampling preparation systems exist for size reduction and splitting of coarse materials. They are typically combined with the corresponding sampling equipment (e.g. clinker sampling, sampling from drill rigs). Furthermore, different solutions for automated preparation of pressed tablets or fused beads for XRF/XRD analysis are available. For description of some equipment see Parts V and VI.
- **Analysis:** Analytic equipment can by itself dispose of a high degree of automation (automated sequences of operation). In addition to that, analytical instruments can in most cases be connected to sample preparation units by small conveyor belts or with robots. Job scheduling and execution can be fully automated as well as the communication with LIMS and PLC systems.

Depending on the degree of automation, sometimes the terms “manual”, “semi-automated” and “automated” are used, although without exact definitions for each term.

3.4 Holcim Standard Concept

This chapter elaborates on the Holcim recommended quality control concept for a new plant or major expansion project. The main objectives of the concept and the associated quality control equipment are as follows:

- Achievement of required quality level of final products at high consistency, to ensure competitiveness on the market
- Achievement of required quality level and high consistency of all intermediate products, to ensure optimal operation and high efficiency of production equipment
- Minimization of risks to (temporarily) produce final or intermediate products deviating from specifications, to minimize loss of customer satisfaction, loss of production rate and increased operation costs
- Ensure safety of all quality control related operations

New large projects are usually associated with all or parts of the following characteristics:

- High production rates (e.g. > 4000 t/d clinker)
- Use of state-of-the-art production equipment (vertical roller mills, pre-calcer kilns, etc)
- Sometimes two or more raw or cement mills
- High degree of process automation
- Use of (or provision for) different fuel types, including alternative fuels
- Complex raw material situation
- Production of various cements with maximized clinker substitution, using different mineral components

Considering the above objectives and conditions, the recommended concept is one with:

- Local, de-centralized PGNAA control of stockpile composition and of raw mix composition fed to raw mill
- Central, automated laboratory connected to automated sampling stations with pneumatic tube transport for all main final and intermediate materials

In more detail, the elements of the concept are:

Raw material extraction, raw material preparation, raw meal preparation:

- Drill hole analyses and QuarryMaster application
- PGNAA control/monitoring of material fed to (integrated) stockpiles
Circular stockpile preferred in case material heterogeneity allows for it.
- Mechanical sampling device for delivered raw materials and fuels (to be evaluated case by case).
- PGNAA control of raw mix fed to the raw mill
(not feasible in case that the raw mix on the conveyor belt is not complete, as for example if fly ash is fed to the raw mill separator)

Raw meal preparation, clinker manufacturing, cement grinding, cement dispatch

- Sampling and transport as per following table:

Material	Sampling	Transport
Raw meal	automatic	Pneumatic tube
Kiln feed	automatic	Pneumatic tube
Hot meal	Automatic or manual (safe design!)	Pneumatic tube or manual
Clinker	automatic	Pneumatic tube
Coal/petcoke	automatic	Manual
AFR	Case by case	manual
Cement ex mill	automatic	Pneumatic tube
Cement dispatch	automatic	Manual
Filter dust	manual	Manual
Bypass dust	manual	Manual

- Central laboratory with following functions

Function	Standard	Minimum
Pneumatic tube reception	automatic	manual
Compositing	automatic	manual
Pressed tablet preparation	automatic	automatic
XRF	automatic	manual
XRD free lime	automatic	manual
XRD Rietveld	optional	--
Laser granulometer	automatic	--
Others (Blaine, color)	optional	--

Comments:

- The emphasis that has to be laid on product quality and operation efficiency justifies the high degree of automation
- The required operation, support and maintenance of such a system does not require skills that go beyond what is also required to operate and maintain modern process equipment

4. Quality control along the process

In the following every main point for quality control shown in Figure III- 2 is discussed.

Points in red color indicate areas where high frequent sampling and quality control is desired as the information is directly used for process control. The blue colored points indicate areas with typically medium to low testing frequencies.

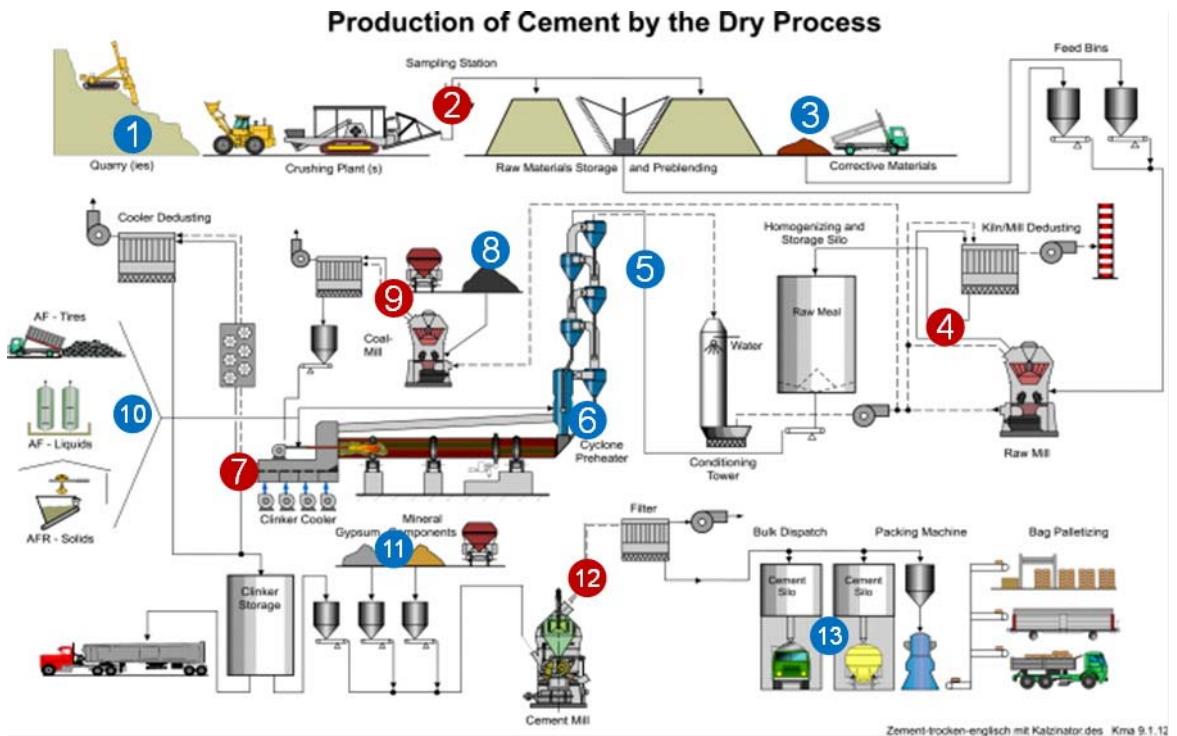


Figure III- 2: Major points for Quality Control

4.1 Quarry (1)

In Holcim operations, especially in the limestone quarries, the quality control is mostly performed by means of blast hole sampling and the analysis of drill cuttings. To a lesser extent, and depending on the material and mining type, also channel sampling of the face and pile sampling of muck-piles or temporary stockpiles can be performed.

Reference is made to the Raw Materials Management Manual, available from HGRS CM/MT.

Objectives

- Ensure correct composition of (integrated) pre-blending beds. Sampling in the quarry provides the only opportunity to control minor elements (such as MgO, SO₃, Alkalies, P₂O₅ and Cl) or minerals (such as quartz) during the manufacturing process.
- Quarry planning (data is used as input for software such as Quarry Master); Optimal utilization of materials and equipment

Sampling and sample transport

Sampling practice in quarries is discussed in Part IV: Sampling and size reduction. The samples typically are transported manually to the central laboratory.

Preferred sampler: Recommended are automated samplers at drill rig, though the practice and experience is still scarce. Manual sampling is still the most applied method (see Part IV).

Parameters and control frequency

Parameter	Frequency
Chemical composition	On each drilling/blasting. Pattern for sampling (e.g. composite sample of 4 blast holes) to be established case by case.

Analytical Methods

XRF is the standard method for chemical analyses. In cases, where the quarry is far from the plant, it can be beneficial to install a small XRF unit and required sample preparation at the quarry office.

4.2 Raw material after crusher (before stockpile) (2)

The need for quality control of main raw components after crusher depends on the raw material handling concept:

- Separate storage/pre-blending of individual raw components:
This may not require a chemical control, unless the heterogeneity of the material calls for it.
- Blending of two or more components on an integrated pre-blending bed which can account for typically 80 to 95 % of the final raw mix (in extreme cases 100 %):
The dosing of the components can either be done by corresponding scheduling of truck loads dumped into to a single feed hopper, or by two (or more) feed hoppers with controllable rate of the apron feeder to the crusher. This set-up makes an intense chemical control mandatory.

The accepted standard method for analyzing raw components after crushing is the PGNAA technology (see Part VI), which provides quasi-continuous chemical data of the material on the conveyor belt.

Objectives

- Control composition of (integrated) pre-blending beds to ensure the desired quality at maximum uniformity (main application)
- Sorting of crushed material to different storage locations (relatively rare application)
- In case of two (or more) feed hoppers: Adjustment of apron feeders for correct pre-mix composition
- Get information on raw material composition for quarry planning software (e.g. Quarry Master)
- Monitor moisture content if critical for equipment operation (material sticking in transfer chutes, storage and feed systems)
- Occasional determination of granulometry (to determine state of condition of the crusher) or moisture content

Sampling and sample transport (see also Part IV)

- PGNAA technology is strictly recommended for routine chemical control of crushed material, actually not requiring any sampling and sample transport.
- It is equally strictly recommended not to apply any manual sampling on running conveyor belts.
- The formerly applied technology for accurate control of crushed materials – still applied in some plants – is the application of a “sampling tower”, i.e. a rather complex mechanical installation to take a large primary sample (e.g. 10-15 % from a flow rate of 500 – 1000 t/h), and to comminute, dry and split the sample stepwise to typically 1 kg/h final sample.
- In case a physical sample is required e.g. for occasional determination of granulometry or moisture the recommended method is to collect a sample of one or more increments from the stopped conveyor belt (typically 1 meter sections).

- The installation of simple mechanical sampling devices on a conveyor belt transporting materials requiring a routine control (as above) is not recommended. It can be an appropriate option for non-routine sampling e.g. of supplied minor raw materials or fuels (see chapter 4.3).

Parameters and control frequency

Parameter	Frequency
Chemical composition	PGNAA: real-time (Sampling tower: hourly composite)
Moisture	Real time, integrated to PGNAA unit (He-3 detectors or based on microwave technology)

Analytical methods

- Chemical composition:
 - PGNAA provides accurate analyses of the main elements Si, Al, Fe and Ca, and generally reasonably reliable analyses of MgO, SO₃ and K₂O if present at levels above 0.5 %. Monitoring of Na₂O and Cl is difficult due to the low concentration levels. Same applies to P₂O₅.
 - If accurate control of such minor elements is needed, it is advisable that the information is complemented with blast drill chip analyses by XRF. XRF would also be used in case the sample is taken with a sampling tower.
- For routine monitoring of moisture content, continuously operating analyzer systems can be integrated into PGNAA systems or separately installed (micro-wave based analyzers mounted across conveyor belt).

4.3 Delivered corrective materials and fuels (3), (8)

Corrective materials are added to the raw mix after crusher or at the raw mill in order to fine tune the chemical composition of the raw mill feed material to ensure correct raw meal composition and uniformity. Usually these materials are of fairly high purity and uniformity and are utilized in small amounts only (i.e. < 5%). Hence a high frequent chemical analysis of the correctives is normally not requested and the focus of control is mainly verification of contract specifications on delivery.

Similarly, a control of incoming traditional fuels – coal or petcoke – should be done for verifying contract specifications.

The extent of such control needs to be evaluated case by case, and depends on contract conditions and characteristics of the specific materials.

Objectives:

Verify quality of received correctives and fuels, e.g. in view of contact specifications.

Sampling and sample transport:

- Sampling of correctives and fuels upon delivery is preferably done from conveyed material, as this allows for more representative samples than sampling from stationary material.
- Mechanical, automated sampling devices should be used, such as hammer samplers. Manual sampling should strictly be avoided. Arising sample quantity, particularly when taking several increments, can be appreciable (>> 20 kg) and may require sample splitting at site.
- An alternative to the above is sampling from the stockpile after delivery, which can be done with manually operated tools; increased sampling errors, however, have to be accepted.
- In case information on the quality of correctives is required during operation, manual sampling from the feeders at the raw mill can be an option, though safety aspects need to be strictly considered.
- The samples (quantity 1 to 20 kg) are manually transported to the laboratory.

Parameters and control frequency

Correctives	
Parameter	Frequency
Chemical composition	Low frequent / On delivery, e.g. per batch or weekly/monthly composite
Coal / Petcoke	
Moisture	Low frequent / On delivery, e.g. per batch or weekly/monthly composite
Calorific value, ash (or other contract parameters)	Low frequent / On delivery, e.g. per batch or weekly/monthly composite

4.4 Raw meal (4)

To achieve the desired raw meal composition, the raw materials are proportioned in front of the raw mill according to the targeted raw mix design. The raw mix design takes into account the desired clinker composition (C_3S , C_3A , alkalis, SO_3 , etc), but also characteristics related to the burnability (fineness, clinker liquid phase). Usually, this is expressed in terms of the controllable chemical parameters lime saturation (LS), silica ratio (SR) and alumina ratio (AR) and the fineness parameters R90 μm (residue on 90 μm sieve).

Since the chemical composition of the applied raw materials is subject to more or less high variation, the proportions (feeder set-points) of the raw materials need to be adjusted accordingly. The proportioning is based on the chemical analyses of the raw mill feed and the produced raw meal. Feeder set-point adjustments can be done manually or by a dedicated control software (see Part VI: Automated quality control systems).

The raw mill is the last possibility to adjust the chemical and physical properties of the meal before it is fed to the kiln. Thus the quality control of raw meal production has to receive highest attention.

Two principal QC setups are possible for raw mills:

- Control of raw mix before raw mill, pre-mill control **(a)**
- Control of raw meal after raw mill, post-mill control **(b)**

(a) Controlling the raw mill feed before the raw mill is only possible with a PGNAA analyzer (see chapter 6) due to problematic sampling of coarse bulk material. This option offers a very fast raw mix control due to chemical analysis in real-time and the short distance between feed bins and PGNAA-Analyzer. Feeder set-point adjustments typically occur in 5-20 minutes intervals. It is thus especially suitable for ball mills with long residence time of the material. For most new plants this is the recommended setup. Upgrading of existing plants with PGNAA control can be very beneficial in many cases, but may not be possible or becomes too costly when

- Some raw mix components bypass the grinding system
- Space for PGNAA is lacking
- Low belt load (< 50 kg/m) is encountered
- Multiple raw mill lines exist

It has to be pointed out that PGNAA control does not render post-mill control unnecessary. For initial calibration of the PGNAA, for regular independent cross-check (drift correction) as well as for fineness control, an automated sampling unit after the mill is still indispensable.

(b) The control of the raw meal after the mill has been the only solution before PGNAA technology was available. The raw meal is sampled by means of screw samplers and then is either transported to the central laboratory and analyzed, or is analyzed on-site (decentralized systems). Depending on the raw mill system the time delay between sampling and the next feeder set-point adjustment can be 0.5 - 2 hours.

The chemical control parameters (LS, SR and AR) for the raw mix or the raw meal have to be strictly and repeatedly aligned with the resulting clinker composition, in order to achieve the **clinker target values**. The difference between the clinker composition and the raw meal composition is affected by

- Fuel ash incorporation
- Kiln dust recirculation to the raw mill (kiln dust composition can strongly deviate from the average raw meal composition)
- Kiln dust or bypass dust extraction
- Analytical differences (different XRF programs applied for raw meal and clinker)

These impacts need not be stable over time, thus the difference between clinker and raw meal composition needs to be continuously monitored and adaptation to the raw meal targets be applied when necessary.

Objectives:

- Blending of raw mix components to target composition
- Achieve target fineness
- Achieve high uniformity for both chemical composition and fineness

Sampling and sample transport

- Raw mix control by PGNAA does not require sampling and sample transport
- Raw meal has to be sampled at a suitable location between raw mill and homogenizing silo. It is generally preferred that the dust from the precipitator is returned to the main raw meal flow at a sufficient distance up-stream the sampler location, to provide a representative, well-blended sample of what is fed to the silo. In some cases, however, it has proven to be advantageous for control stability to sample ahead of the dust return.
Screw samplers, installed at a transfer chute (e.g. to bucket elevator or air-lift) are preferred over air-slide samplers. In both cases, the samplers should operate automatically and continuously (or in repeated intervals), and ideally be equipped with a mixer.
- Depending on the degree of automation the raw meal sample is transported either manually or via pneumatic tube system to the laboratory.

Parameters and control frequency

Parameter	Frequency
Chemical composition (LS, SR, AR, etc.)	Every 0.5 – 1 h (composite sample) for post-mill control
	Every 4 - 12 h (hourly composite) with simultaneous PGNAA control
Fineness: Typically R90 μ m and R200 μ m	Every 2-4h
Moisture	According to requirement

Analytical Methods

- XRF is the standard method for chemical analysis of raw meal. In most cases, pressed tablet preparation is adequate for routine control and is almost exclusively applied in automated systems. Fused beads can be applied with manual operation (it provides highly accurate and stable analyses, free of mineralogical effects), and should be used as reference method (see Part VII: XRF).
- Dry sieving is the standard method for fineness determination, manually or preferable with an air-jet sieve; in automated laboratory systems, laser granulometry can be applied.

4.5 Kiln feed (5)

General:

The raw meal is transported to one or more silo or silo systems which basically serve two purposes:

- Blending (continuous flow silos) or homogenization (batch silos) of the meal
- Storage (Capacity typically 0.5 to 3 days kiln operation)

Depending on the type of silo, its state of condition and mode of operation, the blending efficiency may vary and hence can impact the final kiln feed uniformity and, correspondingly, the burning process in the kiln.

The kiln feed uniformity is of very high importance to the burning process and the resulting clinker quality. Therefore Holcim introduced kiln feed uniformity guidelines (see chapter 5).

Monitoring of kiln feed composition has in most cases primarily informative character. In few cases, where two or more kiln feed silos are available which can be simultaneously extracted, the practice is applied to build-up the silos to somewhat different composition ("high" and "low" in LS) and to make use of this difference for fast adaptations to changing fuel situations resulting in markedly different ash intakes.

Objectives:

- To provide information for kiln operators on the quality and uniformity of actual material fed to the kiln (only in exceptional cases possibility for control actions, see above)
- Verification of target composition and fineness
- Evaluation of uniformity and blending performance of homogenization systems
- Retrospective analysis of kiln operation (e.g. impacts of dust cycles)

Sampling and sample transport

- Recommended are automated, programmable screw samplers installed in a chute after kiln feed silo (e.g. at inlet to bucket elevator or air lift) to make a composite sample over one hour; alternatives are air-slide samplers; in either case ideally equipped with a mixer. Manual spot sampling is also practiced and can be acceptable for situations with low complexity (low production capacity; generally uniform and stable material flow)
- Depending on the degree of automation the sample is transported either manually or via pneumatic tube system to the laboratory.

Parameters and control frequency

Parameter	Frequency
Chemical composition (LS, SR, AR, etc)	Every 2-4 h Recommended is a composite sample over 1 to 2 hours. In case of 4 hourly control, it is recommended that the sampler is idle for 3 hours and compositing over the 4 th hour)
Fineness: Typically R90 μ m and R200 μ m	Every 2-4 h

4.6 Hot meal (6)

Volatile elements, such as alkalis, sulfur and chlorides tend to re-circulate in the rotary kiln/pre-heater system, forming salts of low melting temperature in the hot meal. This enhances stickiness and causes build-up formation in the lower pre-heater/inlet chamber area of the kiln system; falling of such build-ups can cause cyclone blockages and in kiln stops. Design of the process (by-pass), constructional measures (cyclone and pipe dimensioning, refractory selection), but also intense cleaning activities are applied to reduce the effects of volatile element circulation.

Hot meal analysis provides information about the tendency of build-up formation. It can be directly used for adjustment of kiln burning conditions, pre-calciner operation, fuel mix, and bypass rate. Besides the classical analytical parameters (volatile elements) also information from mineralogical phase analysis (XRD) has recently proven to be useful for process control and optimization (Example SG; [Lit 1]).

Objectives

- Provide information on tendency of build-up formation (kiln control)
- Evaluation of calcination degree for pre-calciner control
- Determination of unburned combustibles (in context of special investigations)

Sampling and sample transport

- Hot meal sampling is a potential safety hazard. Hot meal samplers have to be designed to avoid operators being exposed to hot meal blown out in case of an overpressure situation, as well as to allow a safe handling the collected, still hot sample..
Safe samplers, both for manual and automatic sample collection, the latter usually equipped with water or air cooling, are available. For details on samplers and good practices see Part IV: Sampling and size reduction.
- Depending on the degree of automation the sample is transported either manually or via pneumatic tube system to the laboratory

Parameters and control frequency

Parameter	Frequency
Chemical composition (mainly SO ₃ , alkalis, Cl)	Every 4-8 h or as required (per preheater string)
LOI	Every 4-8 h or as required (per preheater string)
Organic carbon	As required

Analytical methods

- XRF analysis is the recommended method. For preparation of adequate calibration samples, refer to Part VII of this manual.
- Alternatively (or complementary), flame photometry or AAS can be used to measure alkalis, S-analyzer for SO₃ determination and potentiometric methods for Cl determination.

4.7 Clinker (7)

Clinker is the most important intermediate product in the cement production process. All quality and process control activities from quarry to the kiln aim at producing a clinker of desired quality and uniformity – at lowest costs.

Clinker control serves different purposes:

- *Support of kiln operation:*
The main information concerns the degree of burning of the clinker (completion of the chemical reaction to form alite), which governs the regulation of the heat input, i.e. of the fuel feed rates (or ratio of feed rates of raw meal and fuels). This information is usually provided by the free lime content (CaO_f) of clinker (alternative and complementary parameters see below). The required frequency of free lime analyses and the acceptable time delay between clinker passing the burning zone and availability of the test results is somewhat controversial and depends on the general kiln control strategy, which can also make use of additional, usually "real-time" parameters reflecting the burning regime (kiln amps, burning zone temperature, NO_x and others).
The actual Holcim concept, in line with the Holcim Kiln Master, considers an hourly free lime value, from a clinker taken after the cooler, as optimal. It is further recommended practice to provide at about the same frequency (1 hourly or 2 hourly) a complete chemical analysis of the

clinker. Only the combination of free lime value and LS value provides the complete information with regard to the degree of burning. Furthermore, chemical parameters such as SO₃- , alkali-, P₂O₅- or Cl- contents – which are relevant for clinker quality - can provide valuable indications regarding redox conditions, chemical impacts of the fuel mix, or instable build-up/coating formation, which are particularly important when using AFR. Last but not least, even more details on the clinker characteristics relevant to the burning process (and quality) can today be obtained in parallel to XRF analyses from complete mineralogical analyses using XRD (Rietveld).

Alternative concepts in terms of frequency of sampling and testing range from determining free lime values at intervals of 10 to 20 minutes on clinker samples taken at the discharge of the rotary kiln into the cooler (shortest time delay), to determining the free lime content in intervals of 4 hours or less on clinker samples taken anywhere between cooler outlet and clinker storage.

Other parameters used for determining the degree of burning are:

- Liter weight (weight of 1 liter of clinker of particle size fraction 5 to 8 mm (or similar) corresponding to the density of the clinker):

This method has been extensively used in the past, as it is simple and can be done on-site in intervals of 1 hour by production personnel. However, the relation to the burning degree is doubtful, in many cases non-existent. Correlations with free lime are generally poor (which, as such is no surprise, as the liter weight is not only depending on the burning regime but – among others – strongly on the silica ratio or clinker liquid phase content, resp.).

A certain advantage of the liter weight method is the practice of sieving out a size fraction of the clinker. This size fraction may well be considered to be representative to reflect the burning zone conditions, as it is more or less free of disturbances such as fallen coating or build-up pieces.

It is recommended to abandon the practice of liter weight control and to replace it with the above mentioned Holcim concept (hourly free lime, hourly to 2 hourly complete chemical analysis).

- Predicted free lime content:

This method, offered by the company Powitec, is based on a retrospective correlation between a set of real-time process parameters, in particular including the **burning zone temperature** (pyro camera), with the free lime content of clinker, which is then used as a model to predict the free lime content from actually measured process parameters.

Applications in several Holcim plants are partially successful, partially not providing value.

- *Control/verification of clinker quality:*

Clinker parameters influenced by the burning regime and fuels used – free lime, SO₃, alkalis, Cl – have an important impact on the clinker quality. 1 % free lime corresponds to about 4 % less C₃S being formed, which evidently impacts the strength potential. Excessive free lime (e.g. < 3.0 %) can cause unsoundness of cement (volume expansion). The absolute and relative contents of SO₃ and alkalis directly and significantly impact early strength development; furthermore, they influence the relationship between cubic and orthorhombic C₃A and hence the setting behavior. P₂O₅ or Cl introduced with fuels can impact strength development and strength potential (see also Holcim Product Optimization Manual).

Process-related clinker control as recommended by the Holcim concept is therefore also crucial for assuring the final clinker quality; again, importance increases with increasing use and diversity of AFR. It can be extended by preparation of a daily standard laboratory cement on which physical testing is performed, providing a very direct indication on the impact of clinker characteristics on cement performance. Furthermore, several group companies have adopted the practice to test standardized laboratory concrete made from industrially ground

pure OPC (e.g. CEM I 52.5) and to use the ratio of Blaine to 1 d concrete strength as an indicator for clinker reactivity (so called RIC, reactivity index of clinker).

- *Optimization of raw meal preparation and clinker burning:*

Routine, high-frequency clinker control (as outlined above), in combination with complementary, less frequent testing provides valuable information on the achieved overall clinker uniformity as well as on influences arising from raw meal grinding (fineness impact) and from the raw components (mineralogical impacts in particular of quartz). Such information is used for general optimization of the clinker production process.

Additional testing applied for this can include regular or occasional clinker microscopy, regular or occasional mineralogical analyses (XRD, Rietveld), grindability investigations, and burnability investigations.

Objective

- Provide information to kiln operators on actually produced clinker (process control)
- Decision for separate storage off-spec clinker, or for separate storage of different qualities
- Evaluate clinker uniformity (PQM indicator)
- Provide information on clinker quality regarding clinker grindability, expected strength potential, potential expansion problems, etc.

Sampling and sample transport

- Similar to the sampling of coarse raw material mix after crusher, manual sampling of clinker from a running pan conveyor is not recommended.
- Different locations and systems for clinker sampling exist. Typically, clinker is sampled from a closed chute after the cooler or at a chute along the clinker transport. It is strongly recommended that mechanical sampling systems are used, either operated manually or automatic. More details on locations and clinker sampler design are given in Part IV.
- It is recommended that the sampling systems rejects coarse clinker granules (e.g. > 25 mm), e.g. by means of a corresponding grate. This avoids unrepresentative impacts of lumps from coatings or build-ups that are not adequately burnt.
- While manual sampling will provide spot samples, automatic samplers can provide spot or composite samples. Composite samples over more than 2 hours are not considered useful for process control.
- Depending on the degree of automation, the sample is locally crushed, mixed, split and dispatched by means of a pneumatic tube system or transported manually to the central laboratory.

Parameters and control frequency

Parameter	Frequency
Chemical composition (LS, SR, AR, but also SO ₃ , K ₂ O, Na ₂ O, P ₂ O ₅ , Cl, etc)	Hourly or 2-hourly (spot or composite sample)
Free lime	Hourly (spot or composite sample)
Mineralogical phases (alite, belite, etc)	Hourly (e.g. in combination with free lime) or as required
Microscopic assessment	Optional (recommended). As required
Physical testing of laboratory cement	Optional (recommended case by case); on daily composite clinker, daily or once per week

Free lime targets (achieved average values) are recommended to be in a range between 0.8 to 1.6 %, whereby the lower end should primarily apply for clinker with moderate to low lime saturation (< 95), and the higher end to clinkers with high lime saturation (> 97).

Analytical methods

- Chemical composition: by XRF
- Free lime:
 - Wet chemical methods as per cement testing standards (or related methods)
 - XRD, with specific free lime “channel”, or as part of Rietveld refinement
 - Conductometric method (conductivity of a suspension in hot glycol), as applied in some automation systems or benchtop analyzers
- Mineralogical composition: By XRD, applying Rietveld refinement
- Microscopical assessment: See Holcim Clinker Microscopy Manual

4.8 Fuels (8), (9), (10)

Fuel quality has an important impact on the thermal process (heat supply, flame properties, build-ups and ring formation) as well as on the clinker quality (ash and SO₃ incorporation).

Preparation of coal and petcoke typically involves grinding and blending in dedicated coal mills. The quality of coal and petcoke is determined at two stages.

- On delivery, mainly to verify contract specifications (see chapter 4.3)
- After preparation, or feed to the process, to determine the properties relevant to the burning process (discussed in this chapter)

The quality control of AFR is usually more complex and strongly depends on the type of fuel. It can range from exerting practically no control, such as for tires, up to elaborated control schemes in the context of AFR preparation in platforms. In addition to the classical parameters (calorific value, volatiles, ash content, sulfur content), characteristics relevant to OH&S and to the environment need to be determined (flash point, compatibility, toxic organic compounds, heavy metals and others). The quality control can be made both at the site of a platform and at the site of the cement plant. The extent of control at a cement plant will, again, depend on the type and source of material, as well as on the permit conditions for the use of each specific material.

It is highly advisable, specifically in situations of high TSR and use of different AFR qualities, to carry out a regular monitoring of the properties of the AFR streams upon firing. This serves to maintain a stable heat and ash input to the process, as well as for carrying out accurate balances of heat input and CO₂ generation from different types of fuels (e.g. including biomass).

Reference is made to the application in (at least) one cement plant (Höver) of a continuous moisture measurement of fluff fed to the kiln by means of a microwave detector, providing a parameter which strongly correlates with the calorific value of the product. Equipment for continuous, direct determination of the calorific value is under evaluation.

For further details on quality control of alternative fuels (AFR) refer to the Holcim Waste/AFR Quality Control Manual.

The following refers to quality control of coal and petcoke at the stage of grinding and firing.

Objectives

- Provide information for process control of coal mill operation (e.g. separator adjustments), and thus ensure optimal fuel preparation
- Adjustment of fuel mix in case different fuel types are used

Sampling and sample transport

- Fine coal is typically sampled with a screw sampler or piston sampler, installed in a chute after the coal mill, before the fine coal silo. The sampler has to be compliant to applicable safety standards (e.g. ATEX, "Atmosphère explosible").

- Sample transport can be done manually or by pneumatic tube system. During manual transport, samples should be covered and protected from moisture. For automated transport, proper cartouches should be used to avoid opening during transport and explosion risks. At least one example of pneumatic sample transport of fine coal is operating successfully in Holcim.

Parameters and control frequency

Parameter	Frequency
Fineness, moisture	Every 2 to 8 hours / as required
Calorific value	Daily composite sample
SO ₃	As required
Proximate analysis (volatiles, fixed carbon, ash content)	As required / on unloading / per batch
Ash composition	As required / on unloading / per batch

Analytical methods (see also Part VIII)

- Fineness: dry sieving (with or without air-jet apparatus, dedicated set of sieves)
- Calorific value: Bomb calorimeter
- SO₃: Sulfur analyzer (e.g. LECO)
- Proximate analyzer: Muffle furnace, automatic proximate analyzer apparatus

4.9 Kiln dusts

In raw mill/kiln systems, dusts are generated and collected in different locations, which are either extracted from the system or re-introduced to it. The following dust types are distinguished:

- *Main filter dust from preheater/precalciner kilns:*
Dust from the main system filter, which in compound operation, is a combination of dust from the grinding system and from the top cyclones of the preheater, and, in direct operation made up of dust from the top cyclones of the kiln only. In compound operation, the dust is continuously re-introduced to the raw mill/kiln system; in direct operation, it may either be re-introduced to the kiln feed or be extracted from the system and used as cement constituent in small quantities.
Filter dust, particularly in direct operation, can be enriched in highly volatile heavy metals, such as mercury, thallium and cadmium. Kiln dust extraction and addition to cement serves to relieve the kiln system from such heavy metal enrichment and to prevent excessive emissions.
- *Bypass dust:*
Dust collected from a preheater/precalciner kiln bypass system. It is either used as cement constituent or is disposed in different ways (special products, landfilled, treated to eliminate volatile components).
Bypass dust is strongly enriched in the volatile elements Cl (up to 15% has been observed), alkalis and SO₃. Extraction serves to alleviate the kiln systems from these elements and/or to produce low alkali clinker. Bypass dust can also be enriched in moderately volatile heavy metals (e.g. Pb).
- *Kiln dust of long kilns and grate preheater kilns (Lepol kilns):*
Dust collected at the exit of long (dry or wet) kilns, or from cyclones of a grate preheater (it is proposed to use the term CKD only for such kiln dusts).
Such dusts can be partially or entirely re-introduced to the kiln system. Extracted dust is used as cement constituent, sold for different applications or landfilled.
CKD's are moderately enriched with Cl, alkalis and SO₃, as well as with heavy metals.

Quality control of such kiln dusts is normally limited to occasional determination of their chemical composition. In addition to the overall composition, focus can either be to monitor the levels of

volatile minor elements (Cl, alkalis, SO₃), e.g. in context of overall balances of these elements, or to assess the heavy metal concentrations, which can be important for specific applications and for disposal of the dust.

Objectives:

- Filter dust: Assessment of difference between filter dust and raw meal, particularly in terms of lime saturation (important for dust handling during direct operation); determination of enrichment of highly volatile heavy metals
- Bypass dust: Concentration of volatile minor elements (influences stickiness and hence handling properties; determines maximum rate of addition to cement to respect e.g. Cl limits). Assessment of environmental risks for other ways of disposal
- Dust from long kilns (CKD): As for bypass dust

Sampling and sample transport

- Fixed installation for manual spoon or screw sampler.
- Manual transport

Parameters and control frequency

Material	Parameter	Frequency
Filter dust	Total chemical composition, chemical moduli (LS, SR, AR) Cl	As required
	Hg, Ti, Cd, other heavy metals	As required
Bypass dust, CKD	Total chemical composition, Cl, alkalis, SO ₃	Weekly or as required
	Heavy metals	As required

4.10 Set regulators and mineral components (MIC) (11)

Set regulators, mineral components and cement additives are dosed together with the clinker to the cement mill for finish grinding. In case of separate MIC grinding (slag, puzzolan, burnt oil shale), cement and ground MIC are blended in a cement blender to give the final product.

Set regulators are CaSO₄-materials of different type and origin: Their proportion in cement typically ranges between 2 and 6%. They either are of natural origin (gypsum, natural anhydrite) or by-products from industrial processes (i.e. flue gas desulfurization gypsum, phosphor-gypsum, fluoro-gypsum, etc). As the latter may contain impurities affecting setting time, a careful initial assessment and repeated control is recommended.

Mineral components (MIC's) are added to the cement as they can contribute to strength development and develop certain specific cement properties (e.g sulfate resistance, low heat of hydration, etc). Furthermore, they can significantly contribute to the reduction of CO₂ generation per ton of cement. For the above, as well as for economic reasons, it is in the interest of Holcim to maximize clinker substitution by MIC's. Composite cements are specified in practically all national cement standards, and MIC can account for up to 90% of the cement composition. Examples for MIC are blast-furnace slag, silica fume, natural pozzolanas, industrial puzzolanas, SiO₂-rich fly ash, CaO-rich fly ash, burnt oil shale and limestone (as per EN 197-1). Properties of MIC are also subject to specifications in Cement Standards (e.g. EN 197-1) or in specific MIC Standards, which also specify the testing methods.

For detailed information on different MIC types, on their properties and on testing methods, refer to the Product Optimization Manual and references stated therein (e.g. PozzoTech Working Papers).

Quality control of MIC has to start with an initial material source qualification to completely characterize the material (chemical and mineralogical composition), to verify conformity with Standards, and to assess relevant desired performance characteristics (e.g. reactivity). Routine quality control of set regulators and MIC has on one hand to ensure Standard conformity of the material and on the other hand to monitor and, if possible, influence specific important properties. The extent of this control (frequency and parameters tested) has to be defined case by case, considering type, source and volume of the material. Focus has to be on delivery control.

Objective:

- Verify conformity with applicable Standards
- Verify quality of received set regulator or MIC to contract specifications (in case of externally purchased material) or to internal quality specifications (in case of using own source)

Sampling and sample transport

- Sampling should be done upon delivery, preferentially during conveying.
Concerning coarse materials, mechanical samplers should be installed (hammer sampler, bucket sampler at a discharge chute), as manual sampling from conveyor belts should be prohibited for safety reasons. Where this is not possible, sampling from stockpiles has to be applied.
- Powdered materials (fly ash) can be sampled by means of screw samplers, or by special samplers designed for pneumatic transport pipes (sampling under pressure).
- Occasional sampling can also be done at the stage of feeding to the mill system (weight-feeder, silo outlet (fly ash), under due consideration of safety aspects.
- Sample transport is usually done manually.

Parameters and control frequency

(For test methods of MIC see also the Product Optimization Manual)

Type	Parameter	Frequency
Set Regulator		
Natural Gypsum	Moisture	On delivery
	SO ₃ (or total chemical composition)	On delivery
	LOI (indication on gypsum/anhydrite ratio)	On delivery
Industrial Gypsum (Phospho-gypsum)	As above, plus • total P ₂ O ₅ , F • soluble P ₂ O ₅ , F	On delivery/required
	Setting time of laboratory test cements	On delivery/required
Mineral components		
General	Moisture	On delivery
	Total chemical composition, LOI	On delivery
Blast furnace slag	Glass content	On delivery/as required
	Derived from chemical composition: CaO/SiO ₂ , Al ₂ O ₃ ; TiO ₂	On delivery
Natural pozzolan	Chemical comp. (SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , SO ₃ , LOI); ASTM C618	On delivery
	Reactive SiO ₂ (EN 197-1)	On delivery/as required
	Pozzolanicity (Ca(OH) ₂ test); EN 197-1	On delivery/as required
Fly ash	Mineralogic composition (amorphous phases)	On delivery/as required
	Reactive SiO ₂ , reactive CaO (EN 197-1)	On delivery/as required
	Glass content	On delivery/as required
Limestone	Carbon content	On delivery/as required
	Total organic carbon (EN 197-1)	On delivery/as required
	Clay content (EN 197-1)	On delivery/as required
Silica fume	LOI	On delivery
	Specific surface (BET) (EN 197-1)	Initial / as required

(Ground) Burnt oil shale	SO ₃	On delivery
	Fineness	On delivery
	Mortar strength (EN 197-1)	On delivery/as required
	Soundness (EN 197-1)	On delivery/as required

Table III- 4: Quality control requirements for different types of mineral components

4.11 Additives

Different types of chemical additives can be used in the cement grinding process, with the objectives of increasing production rate (grinding aids), of improving flowability (grinding aids) or of improving strength development (quality improvers). Their use can be subject to Cement Standard Specifications (certification, quantity etc.). Refer also to Holcim Product Optimization Manual and Handbook for Optimized Use of Cement Additives.

The quality control of such additives is strongly recommended, and primarily serves to check with relatively simple means the consistency of the product and the possible presence of contaminations. More detailed analyses requiring the use of IR spectrometers or gas chromatographs is beyond the scope of a plant laboratory and would have to be done externally if deemed necessary.

Objectives

- Delivery control to check consistency and agreement with specifications or initial product testing

Sampling and sample transport:

- Liquid samples have to be drawn from the delivery containers, or from the dosing unit at the mill
- Manual transport

Parameters and control frequency

Parameter	Frequency
Density and water content (concentration of active material)	On delivery
pH and Cl content (corrosion potential)	On delivery
Foam formation (see Figure III- 3) (potential for undesired air-entrainment)	On delivery

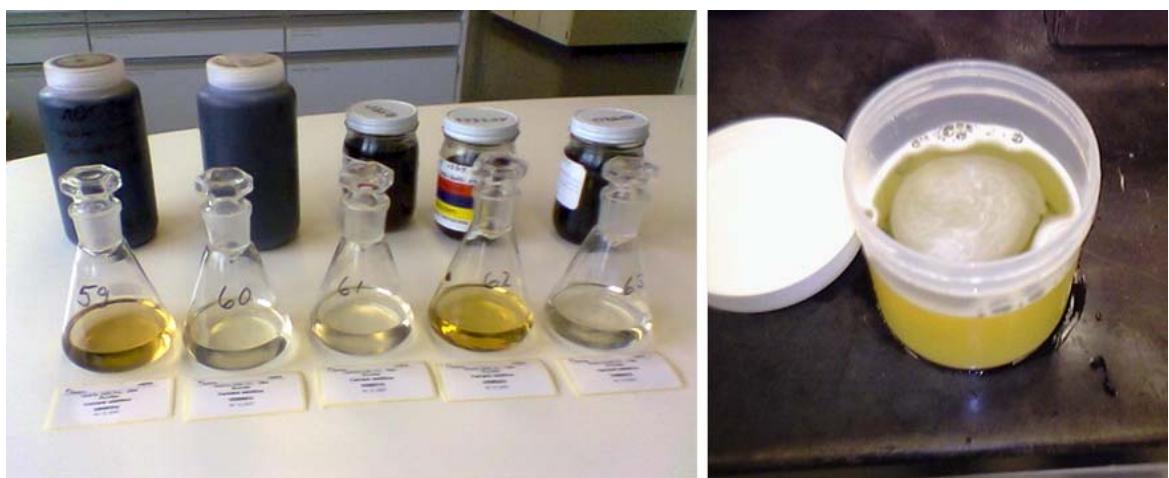


Figure III- 3: Foam test for additives. Left side no foam (ok), right side with foam formation (not ok)

4.12 Cement ex mill (12)

Cement grinding is the last process stage where the final product quality can be controlled. Dosing of the cement constituents (including additives), grinding to a certain fineness, and maintenance of a certain grinding temperature are – along with the clinker properties – decisive for the cement and concrete properties. This applies both for conventional co-grinding of all constituents and for separate grinding and subsequent blending of individual constituents.

As outlined in chapter 2.2, an empirical relationship between proportioning of cement constituents, fineness characteristics and grinding temperature with the physical and mechanical cement properties has to be established as a basis for the process-related quality control.

The quality control at the stage of cement grinding therefore aims on one hand to support the operation of the mill system to maintain correct dosing, fineness and temperature based on short-term testing (hourly or 2 hourly), and, on the other hand, to verify physical and mechanical cement and concrete properties, typically on composite samples of a day or a certain production lot.

- Dosage control

The key to correct dosage is the availability of an accurate, reliable dosing system for each single constituent. Pre-blending of different constituents (e.g. gypsum with a MIC, or two different MIC's) is bad practice and needs to be avoided.

Control parameters on cement to verify/control dosage include:

- SO₃: For set regulator (gypsum) control. (Be aware of the SO₃ content of clinker)
- LOI or CO₂: For limestone control
- Guide-element control of blast furnace slag or other MIC's
(Guide element: selected element that occurs in clinker and MIC in a constant, but very different concentration, e.g. SiO₂, Mn₂O₃, MgO, etc.)
- XRD/Rietveld: For MIC and gypsum control (based on mineralogical composition or glass content; new method with so far limited application and experience.)

Different to the situation at a raw mill, the quality control at the cement mill does not primarily serve to adjust the proportioning of a component to its variable composition, but rather to verify that the proportioning is stable. For this reason, it has to be critically evaluated if automatic, on-line proportioning of cement constituents should be implemented, for example in context of an automated central laboratory system (see Part VI). In many cases, it is preferred not to do so and to leave the decision for feeder adjustment with the operators.

- Fineness control

The conventional fineness parameter for cement, also specified in standards or in supply specification, is the specific surface according Blaine. While is correlation with strength is usually adequate for OPC, it is often not the case for composite cements. It is therefore recommended to apply sieve residues or particle size fractions – as determined by sieving or laser granulometry – for the fineness control of composite cements.

Similar to above, adjustment of the separator settings can be made on-line if a frequent or even continuous (in-line laser granulometer) fineness measurement is available. This is done in some plants, but again, benefits over personnel decision and manual adjustment need to be evaluated

- Temperature control

The temperature of cement during grinding influences the extent of dehydration of gypsum and hence of the setting characteristics of the product. The control has primarily to be done by means of fixed installed temperature probes. The determination of the actual degree of gypsum dehydration in cement is typically done on occasional specific investigations (thermo-analytical investigations, staggered LOI). XRD-based methods in principle also allow this to be done as part of the routine short-term control (see above).

- Verification of cement/concrete physical and mechanical properties:

Traditionally, physical and mechanical properties of cement are tested on daily composite samples or samples of a certain grinding lot, for individual cement types. This is still recommended practice, as it allows relating physical cement properties to the production conditions. It is also a practice specified or recommended by cement standards, notably ASTM (mill certificates).

This practice has partially or completely been abandoned by some European plants, particularly plants producing a high number of different products, as a consequence of the testing work load imposed by the EN 197-1 standard on cement from dispatch, which requires testing of main products from dispatch twice per week. They are relying on the stability of their production process and limit the control of the cement ex mill to the above mentioned chemical and fineness parameters.

Objectives:

- Process control of cement mill operation (e.g. separator adjustments)
- Ensure correct proportioning of cement components (weigh feeder adjustments)
- Ensure cement quality and compliance to pertinent cement standards
- Ensure and evaluate product uniformity (PQM indicator)

Sampling and sample transport

- Recommended is automatic sampling by screw samplers (air slide samplers less preferred) during the transport between the mill and the storage silo. Collection of a composite sample is recommended.
- Depending on the degree of automation the sample is transported either manually or via pneumatic tube system to the laboratory. Sufficient sample needs to be collected (also in case of pneumatic transport to the laboratory) for physical testing

Parameters and control frequency

Parameter	Frequency
Chemical composition (mainly SO ₃ , but also all other elements)	Every 1-2 hour (composite sample)
Fineness (specific surface and/or sieve residues, particle size distribution)	Every 1-2 hour (composite sample)
LOI	Every 1-2 hour (composite sample)
Free lime	Optional / On demand
Color	Optional / On demand
Mineralogical composition	On demand
Physical testing (strength performance, setting times, pack set, etc)	On demand or as required by standards (typically on a daily composite sample)
Cement temperature ex mill	Continuous

Analytical methods

- Chemical composition: XRF, SO₃ also with S-analyzer
- Fineness:
 - Blaine: Manual or semi-automated Blaine apparatus
 - Residue: Sieves (45µm or 32 µm, depending on cement fineness); manual or with air-jet apparatus
 - Particle size distribution: Laser granulometer
 - Free lime: Wet chemical method according standards, semi-automated free lime analyzers (application of XRD with caution only, i.e. both the CaO and Ca(OH)₂ need to be considered, as hydration of original CaO_f in clinker may have occurred)
- Color: Colorimeters (manual or integrated in laboratory automation systems), see Part V

- Mineralogical composition: XRD (Rietveld)
- Physical testing: according to cement testing standards (see also Part V); for special test (e.g. pack set) see also Holcim Product Optimization Manual

4.13 Cement ex dispatch silo (13)

The cement leaving the plant and shipped to the customer needs to be in compliance with the internal product specifications and the applicable cement standard specifications. The testing scope, procedures and frequency depend on the local cement standard, but also on local habits and on specific agreements with customers.

The control of dispatched cement does not allow for any short-term process adjustments.

Objectives:

- Verification of conformity to standards and internal product specification
- Meeting requirements of product certification schemes (e.g. acc. EN 197-1)
- Meeting contract agreements with specific customers
- Detect deterioration of product during storage
- Retain samples for potential customer complaints

Sampling and sample transport

- The samples are collected between silo extraction and the loading spout, preferably by means of a screw sampler (chamber piston sampler is the second choice alternative). Approximately 5kg per sample are needed.
- In the context of product conformity specification, the EN 197-1 cement standard explicitly specifies that the sample has to be a spot sample and not a composite sample. Holcim recommends applying this practice everywhere. It can be assumed that the variability from testing of spot samples better reflects the product variability experienced by customers. Compositing samples at dispatch (e.g. daily composite from several increments) levels out quality variations.
- Manual transport to the laboratory
- Samples may or have mandatorily to be retained over a certain time (e.g. ASTM standards).

Parameters and control frequency

Parameter	Frequency
Chemical composition	
Fineness	
LOI	
Color	As required by the local cement standards
Mineralogical composition	
Physical testing (strength performance, setting times, pack set, etc)	

It was mentioned before that the frequency of physical and mechanical testing of cement from dispatch varies widely according to local practices and standards. To comply with the product certification scheme according EN 197-1, main cements have to be tested twice per week on spot samples from dispatch, which is adopted practice in basically all European cement plants. In the USA, routine testing of dispatched cement is done at low frequency, if at all, but samples have to be retained for 3 months, to be used for testing in case of failures or disputes. In other areas, testing on a daily basis of cement from dispatch is practiced.

5. Uniformity

Uniformity is one of the most important prerequisites for smooth and efficient kiln operation. Excessive fluctuations can easily upset the often less than robust balance of appropriate burning behavior and give rise to operational disturbances. Since the clinker should always be adequately burnt, unnecessarily hard burning is practiced for much of the production time. Consequences are:

- High fuel consumption
- Increased tendency to ring and build-up formation
- Reduced brick lifetime
- Fluctuations in product quality

Uniform cement quality is highly desirable from a customer point of view and can be a competitive advantage on the market.

Holcim has defined several target values for uniformity which are discussed in the following section.

5.1 Raw meal, kiln feed and clinker uniformity

The Holcim uniformity targets for excellence for the key intermediate products are shown Table III-5.

		Short term Average of daily stdev	Long term Stdev of daily average
Kiln feed (or clinker)	LS	< 1.2	< 1.0
	SR	< 0.04	< 0.03
	AR	< 0.04	< 0.03
Raw meal (tentative)	LS	< 3.6 (*)	< 1.0

Table III- 5: Holcim uniformity targets for excellence. (*) For plants with pre-blending systems

The raw meal uniformity target is derived from the kiln feed/clinker uniformity target by assuming a blending effect of 3 in the homogenization silo. It is understood as a guideline for plants with a raw material pre-blending system.

The figures in Table III- 5 indicated standard deviations (absolute values) and have to be determined in the following way:

- Short term: Average of the daily standard deviations over one month.
- Long term: Standard deviation of daily averages over one month

Good short term uniformity is a precondition for stable kiln operation and thus reduced stress on mechanical equipment. Good long term uniformity is a precondition for producing uniform cement quality.

In the following some practical guidelines for evaluation of the uniformity are given:

- Regarding short term uniformity the daily standard deviation should only be calculated if at least 4 samples per day are analyzed.
- Determination of raw meal and kiln feed uniformity should be based on a 1 hourly composite sample. Composite sampling over periods of 2 or more hours will hide the actual process variability and is not recommended for evaluation of uniformity.
- Clinker uniformity is typically based on low frequent (e.g. hourly) spot samples. Again, composite sampling of clinker during longer periods (> 2 hours) will not give a clear picture on clinker variability and is not considered appropriate.

Further clinker uniformity targets exist for the elements SO₃ and K₂O. As a rough guidance value, the coefficient of variation (over one month) of those elements should be < 10.

It has to be pointed out that despite all efforts to produce a uniform kiln feed the clinker uniformity is decisive at the end, as it includes also effects from coal ash absorption and effects from internal dust cycles.

Clinker uniformity is a key indicator in the Product Quality Management (PQM) model. However, for PQM the uniformity is not evaluated on the basis of standard deviation but on compliance with acceptance ranges. A clinker sample is considered compliant when lime saturation is within ±2.5 of the specified target and when free lime is within -0.5 to +1 of the specified free lime target.

5.2 Cement uniformity

Uniformity targets for cement are usually specified for compressive strength performance on mortar. Targets for excellence according to the PQM model are given in Table III- 6 below. The targets are given in terms of coefficient of variation (COV) due to the wide range of compressive strength for different products.

	Excellent	Moderate	Poor
2d strength COV	≤ 7	7 – 10	≥ 10
3d strength COV	≤ 5	5 - 8	≥ 8

Table III- 6: Holcim uniformity targets for excellence (PQM)

In the same way a uniformity target had been defined for 28d strength performance (COV < 3% excellent, 3%- 6% moderate, > 6% poor). This is not part of PQM model, as it is considered to have less market relevance. It can, however, still serve as a guidance value for certain applications.

Part IV: Sampling and Size Reduction

1. Introduction

Sampling is the first step in a series of activities for material testing (see Figure IV- 1). Yet it is a very crucial step. Errors generated by sampling are typically 10 - 1000 greater than the analytical error [Lit 2 and [Lit 3]. One has to consider that the information obtained from a few grams of material is extrapolated to quantities of several tons. Information obtained from biased samples may result in wrong decisions with unpleasant or even severe consequences (for example in assessment of raw material deposits).

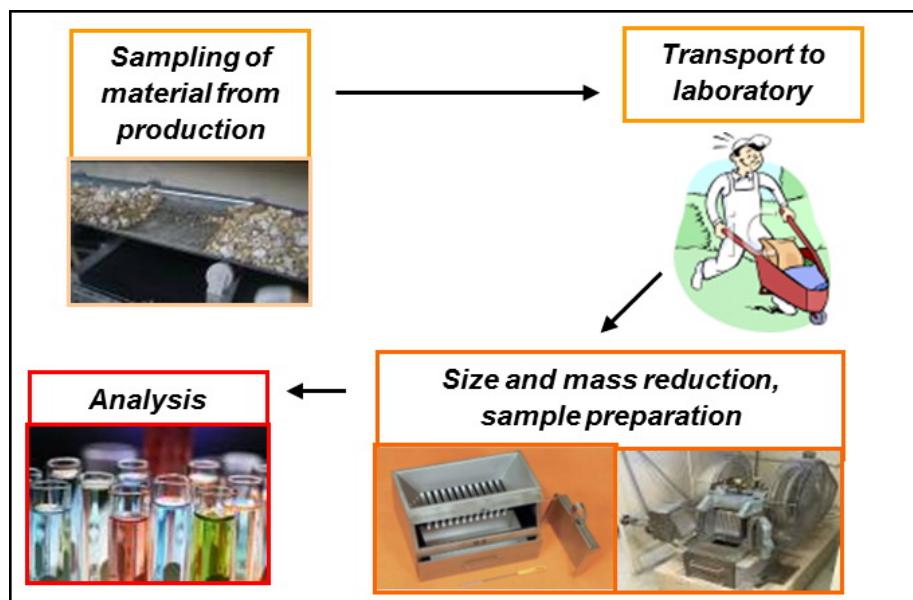


Figure IV- 1: Testing activities for materials from production

Sampling needs to be seen in its context. Basic questions such as

- What do we want to know?
- Why do we need the information and what happens to the results?
- Which actions are triggered?

can guide through the process of designing or assessing sampling procedures.

In the cement industry, the following situations are typically encountered:

- Prospective sampling: In context of geological investigations in order to characterize raw material deposits (decision to acquire a deposit or continue with a project)
- Acceptance control sampling: Sampling of incoming materials (e.g. fuels, AFR, raw materials) at the plant in order to verify compliance to specifications and to support accept/reject decisions.
- Sampling for process control: Sampling during cement manufacturing of key intermediates (raw meal, clinker, cement) in order to control the process on a routine basis (direct interaction).
- Conformity sampling: Sampling of cement in order to prove conformity to applicable standards (basis for certification).

This chapter focuses on routine sampling for process control and acceptance control. For information about prospective sampling refer to the Raw Materials Management Manual. Conformity sampling is described in the applicable (national) cement standards.

2. Theoretical aspects

The objective of this section is to highlight a few basic aspects of sampling. Detailed discussion of sampling theory is beyond the scope of this manual – the interested reader can refer to a list of books and papers at the end of this chapter.

2.1 Representativeness

Sampling yields always an estimation of the true value (μ) of a certain property of the sampled bulk material. A sample is representative when the property value (\bar{x}_s) of the sample differs from the true value (μ) only by a defined amount (Δx). Δx needs to be chosen in advance. It is typically a value that it is not considered relevant for the decision (e.g. LS: $\Delta x = 1$).

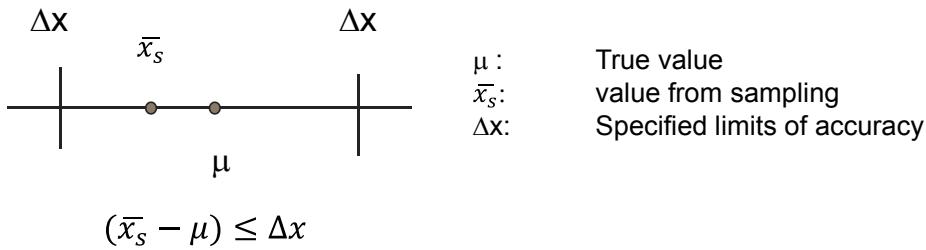


Figure IV- 2: Illustration of a sampling experiment

This definition of representativeness means that for each sample a confidence limit can be calculated that can be compared with the specified limits. However, in order to calculate the confidence limit, the sample must be an outcome of a random experiment; otherwise the statistical methods do not work. In other words, if the sample is biased (shows a systematic error) limits of confidence cannot be calculated, and the result from the sample should not be used for decisions.

The objective of each sampling process is thus to obtain an unbiased sample where all particles in the sampled material stream have the same probability to get into the sample. The following sampling rules help to achieve this objective:

- Always sample a falling material stream (all particles are accessible)
- Sample the whole cross section of the stream
- Combine single samples into a spot sample (rule of thumb: 15 spot samples for one composite)

It follows directly that sampling of stationary material (such as stockpiles) can never give a representative sample and should be avoided and replaced by sampling during loading or discharge over conveyor systems.

2.2 Sample size

In case the sampling installation allows obtaining non-biased, random samples, sampling theory provides models to determine the sample size, which is required for a representative sample. One sampling model that is often encountered assumes the total sampling variance $s^2(t)$ as

$$s^2(t) = \frac{s^2(c)}{\Delta M \cdot N} + \frac{s^2(d)}{N} + s^2(a)$$

In the equation above, ΔM [kg] indicates the mass of one sample increment, and N the number of increments to be combined (hence, total sample mass: $\Delta M \cdot N$). $s^2(a)$ is the analytical variance resulting from sample preparation and analytical measurement. $s^2(c)$ and $s^2(d)$ are the variances which result from composition heterogeneity (small scale heterogeneity) and distribution heterogeneity (large scale heterogeneity), respectively. They are inherent properties of the bulk material at given state of dispersity (granulometry) and can be obtained from (labour-intensive) sampling experiments [see [Lit 8]. Subsequently ΔM and N can be calculated in order to obtain the

desired sampling variance, which is needed to achieve the specified sampling accuracy (see Figure IV- 2).

From the formula above, it can be noted that the required sample mass is a function of

- The heterogeneity of the material, described by the composition and distribution heterogeneity. More heterogeneous (e.g. when fine and coarse particles differ largely in the characteristic of concern) materials require higher sample mass.
- The maximum particle size of the bulk material. As a very rough approximation a third power relationship between sample mass and maximum grain size is assumed. Figure IV- 3 shows this relation in a linearized way. Considering a typical grain size of about 80 mm (e.g. VRM feed size), the required mass for 1 sample increment is about 70 kg.

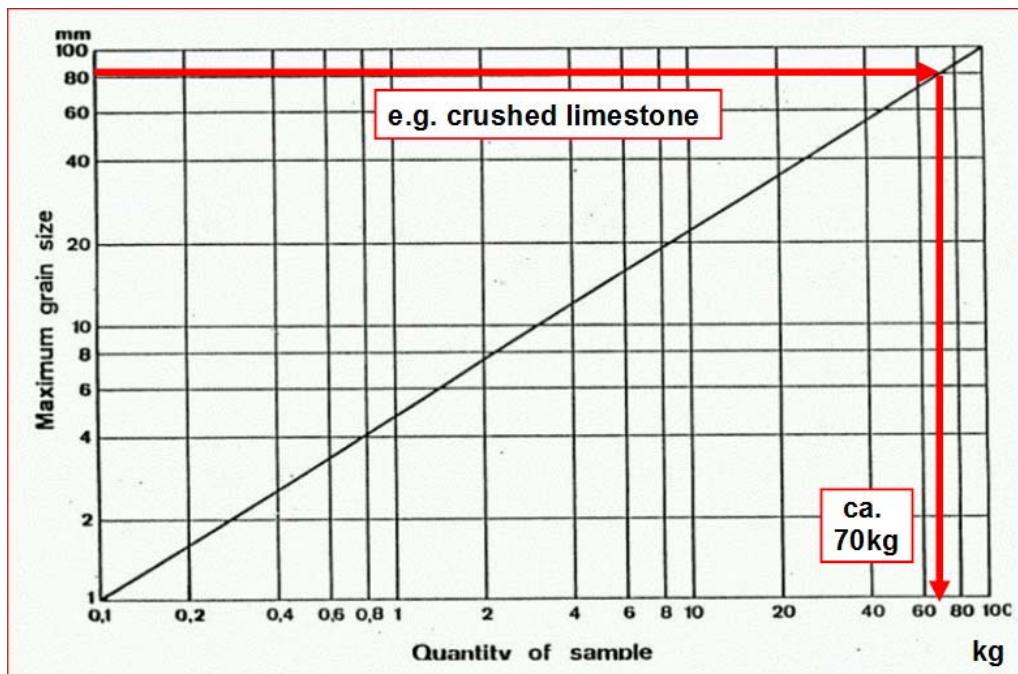


Figure IV- 3: Correlation between maximum grain size and required sample amount

Sample size also depends on the parameter of interest, e.g. moisture determination may require a significantly different sample size than chemical analysis or granulometry.

Generally, sampling of coarse bulk material easily generates sample masses of 500 kg and more. Such large sample masses require big efforts in terms of handling and sample preparation, and are in practice avoided whenever possible. For powdered materials, such as raw meal or cement with top particle size of typically less than 500 µm, sample mass is less problematic.

As a direct outcome of sampling theory, each subsequent step of sample size reduction (crushing, grinding, splitting) represents a further sampling step with its own inherent error. It is important that, on sample size reduction, crushing/comminution always occurs before sample splitting or subsampling.

3. Sampling of coarse grained material

As explained in the section above, representative sampling of coarse bulk material is extremely difficult and results in large sample size. Materials with a broad particle size range tend to segregate, i.e. fines concentrate on the bottom of a material heap. Separation effects also occur when materials are dropped from heights (building of stockpiles) or from one conveyor belt onto a second one running in perpendicular direction. The situation becomes even more difficult with

stratified materials, e.g. due to sequential deposition of different materials. In case of stationary materials such as stockpiles, ships or truck loads, representative sampling is normally not possible as a matter of principle because large parts of the material are not accessible.

On a routine basis, coarse bulk materials need to be controlled in the following situations:

- Blast hole material in the quarry (to ensure correct quality sent to the plant and to schedule mining)
- Raw materials after crushing (to control correct stockpile composition)
- Raw mix after weigh feeders before entering the raw mill (to ensure correct raw mix composition): Usually replaced by raw meal sampling after raw mill.
- Clinker after cooler (to ensure adequate burning)

3.1 Blast hole sampling in the quarry

Detailed information on techniques and equipment for blasthole sampling can be found in the Raw Materials Management Manual.

In most places, blasthole sampling is still done manually by using different mixing and sample splitting procedures. Automation of these procedures is possible to some extent (i.e. by automated sampling systems mounted on drill rigs), but has still not found wide-spread application in Holcim plants. Recent developments towards real-time analysis of drill hole dust (see chapter 6) have shown to be partially successful, but are not yet commercially available.

3.2 Raw materials sampling for stockpile or raw mix control

PGNA analysers (see Part VI chapter 1) have completely eliminated the need to sample material streams for stockpile or raw mix control. PGNAAs analyse the full material stream on a minute by minute basis and have become the standard tool for routine process control.

Sampling towers, still found in some Holcim plants, were mainly used to control stockpile composition in the era before PGNAAs. They comprise of a high frequent sampling device and extensive equipment for sample preparation (drying, crushing, grinding, splitting and dispatch), able to handle the sample size required for representativeness in a fully automated way. Due to their mechanical complexity, they were relatively expensive, both in terms of investment and operational costs (electricity, maintenance). Sampling towers are not recommended for new plants or plant upgrades.

For process control, any manual sampling procedures are not practical due to the large sample mass. However, in some situations, sampling may be required for non-routine testing. Examples can be equipment performance tests (e.g. verification of crusher output as a function of feed moisture, [Lit 6 and [Lit 7] or calibration procedures of PGNAAs equipment. In such cases, sampling can take place either by manual stopped belt sampling or with automated cross-belt sampling equipment (further described below).

Stopped belt sampling:

A section of defined length is completely removed from the stopped conveyor belt (see Figure IV-4). Sampling frames matching the shape of the belt are used to ensure that the full cross section is removed. The length L of the section can be estimated as $L=1.5 d + 100 \text{ mm}$, where d is the maximum particle size of the material being sampled. Stopped belt sampling only works on horizontal belts, not on inclined belts. If done properly, stopped belt sampling provides a bias free sample.

Stopped belt sampling is not very convenient because the stopped belt causes production interrupts. Furthermore, frequent start-stop sequence can result in damages to the belt drive.



Figure IV- 4: Illustration of stopped belt sampling

Stopped belt sampling can potentially be of use for calibration of stockpile PGNA analyzers, when back calculation of stockpiles from raw meal composition is not possible. The belt is crash-stopped, the material in the PGNA tunnel is marked (spray cans) and analyzed for approx. 2 h, then the belt is moved a few meters and all of the marked material is removed from the belt (see Figure IV- 5).

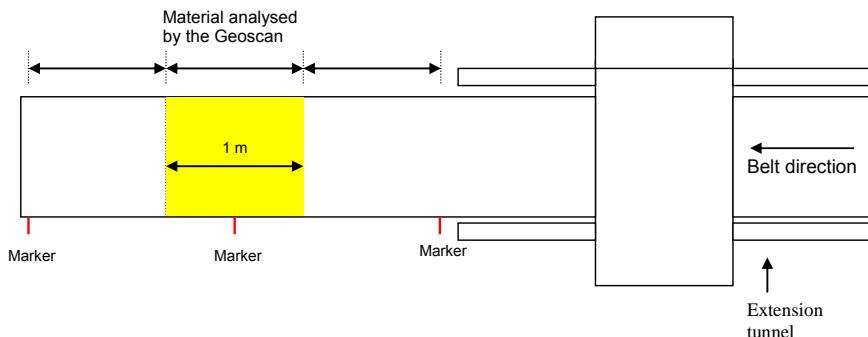


Figure IV- 5: Stopped belt sampling for PGNA calibration (Scantech proposal)

Sampling from moving belts

Sampling from moving belts is only possible with suitable (cross-belt) sampling equipment. Manual sampling from a running conveyor must be strictly avoided. It is a serious safety issue and, from a representativeness point of view, provides meaningless samples.

Technically acceptable are hammer sampler (or cross-belt sampler), which remove cross sections of material from the belt with a rotating cutter/hammer (see Figure IV- 6). They are available from a large number of suppliers. Typically, 20 to 50 kg of material is removed from the belt per stroke, depending on the material load on the belt. Sample preparation equipment (crusher, splitter) is needed to process the sampled material. The sampler must be specifically selected for the material stream (width of cutter, rotational speed, belt geometry) and properly adjusted in order that the whole cross section is removed. Examples in Holcim plants: Ste. Genevieve (monitoring quality of corrective and fuels on unloading, not used frequently), Garadagh (monitoring of limestone quality on delivery from quarry), Hermosillo (MIC's on unloading), Guayaquil (limestone monitoring)

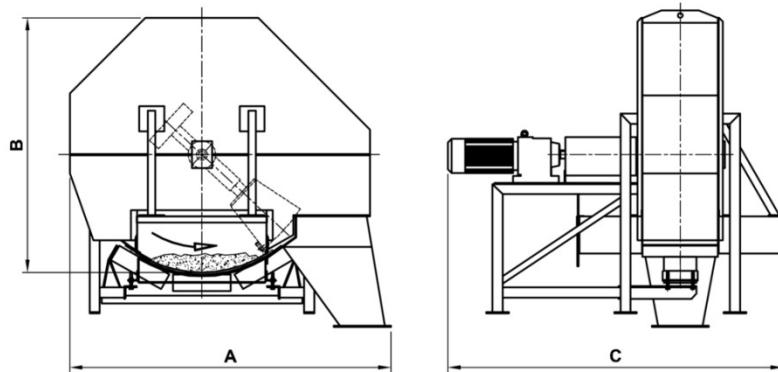


Figure IV- 6: Drawing of hammer sampler (M&W design)



Figure IV- 7: Linear cross stream sampler (Essa design)

An alternative to hammer samplers are linear cross stream samplers which cut through a stream of falling material. They are typically placed at discharge points of conveyor belts (see Figure IV-7). This type of sampler is often used in mining industry and can handle large material streams of up to 16'000 t/h. No application in Holcim plants is known.

3.3 Clinker sampling

Clinker is a coarse grained but rather homogeneous material from a chemical point of view. Sample quantity of 2 - 5 kg is usually considered sufficient for routine analysis (free lime, chemistry). For non-routine analysis (clinker microscopy, clinker reactivity) larger samples may be required. For free lime determination broken out coating, pieces of refractory material or oversized clinker granules (soft burnt core) may have a significant impact on the results (causing outliers) when not sorted out before analysis. Visual inspection of the clinker sample helps to recognize the presence of such disturbances. In most automated sampling equipment size classification takes place removing oversized grains.

Clinker can be sampled at several locations. Selection of the sampling locations often takes available space and time delay between kiln discharge and sampling point into account. If sufficient space is available, clinker sampler are best placed in the chute after the clinker crusher behind the clinker cooler. For wide chutes, more than one sampler may be considered (example GV, two samplers). An alternative location would be transfer points after the pan conveyor on top of the clinker storage, however, with the disadvantage of more time delay. With the objective to sample the clinker as early as possible after discharge from the kiln (fast information for kiln control), cooler grate sampler and high temperature samplers were developed (see below).

While manual sampling from pan conveyors is still practiced in a number of Holcim plants, it is strongly recommended that mechanical sampling systems are used, either operated manually or automatic. A few systems are described in the following sections.

In case the falling clinker stream is sampled, the sampler must approach the material stream from the front, not from the side.

3.3.1 Spoon sampler

The sampler is mounted in a transfer chute. For sampling the spoon or arm is moved downwards into the material stream and diverts partly the material flow into the sampler housing (Figure IV- 8). Oversized particles do not fall through the grate and are returned to the process. Principal technical characteristics are:

Particle size:	Max. 100 mm
Temperature:	Max. 250°C
Sample quantity:	app. 15 dm ³ / pass
Frequency:	< 20 cycles / h

This device is mainly designed for clinker sampling but can also be applied to other material streams.

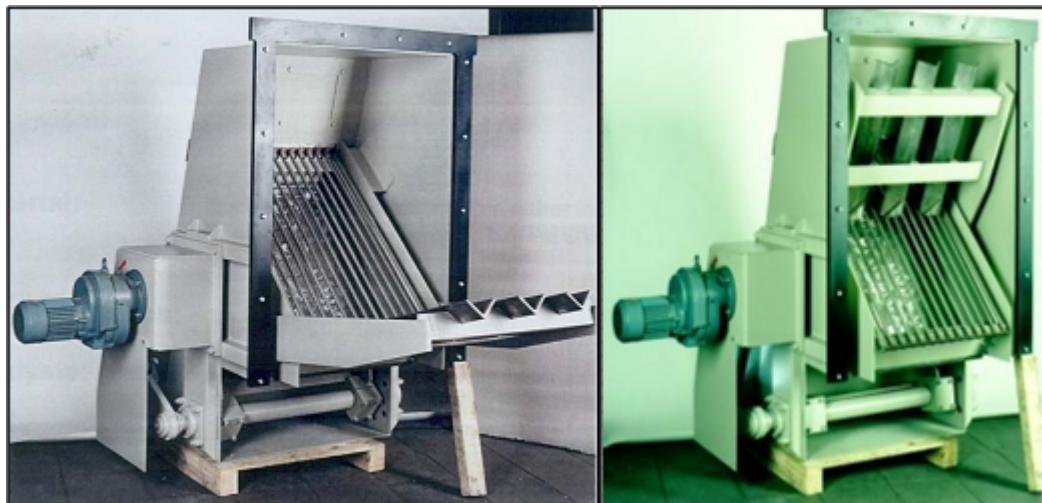


Figure IV- 8: Spoon sampler in sampling (left) and non-sampling (right) positions (Pfaff/FLS design).

3.3.2 Cooler grate sampler

The sample is collected from through holes in one of the cooler grate plates (see Figure IV- 9). During the times when no clinker is sampled, a fan provides positive pressure to the sample transport via the steel tube through the cooler grate plate and thus generates an air lock to prevent from clinker falling through the holes. The system is provided by the ITECA company and operates successfully at the Holly Hill plant (US).

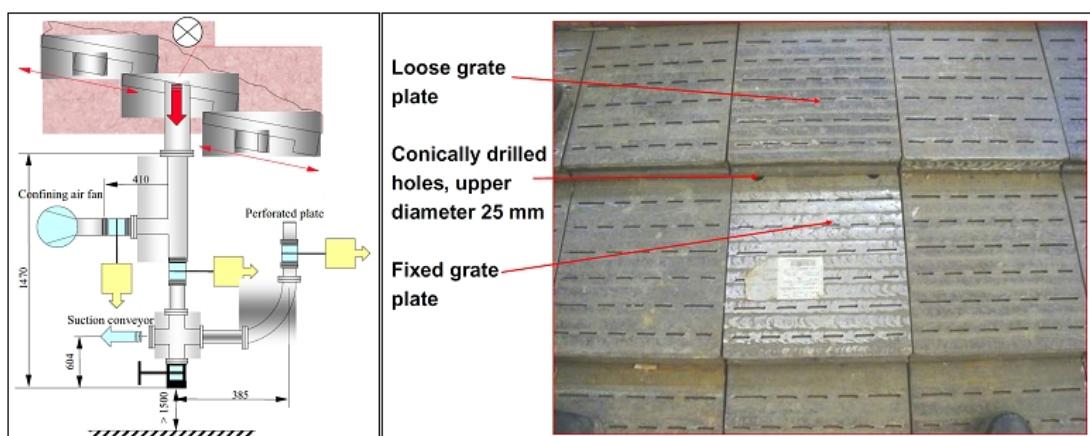


Figure IV- 9: Schematics and picture of a cooler grate sampler

3.3.3 High Temperature Clinker Sampler

The ITECA sampling device is composed of a horizontal arm, which is driven into the clinker stream falling from the rotary kiln into the cooler by 2 pneumatic jacks. Two sampling grids located at the end of this arm perform the 0 – 15 mm granulometry selection. The inverted V shape of the upper part of this bucket facilitates material flow. The sampler is exposed to very high clinker temperatures and is made of heat resistant refractory steel.

In the “sampling” position, the arm moves into the clinker flow. In the “resting” position, the front end of the sampler is covered with the wall of the hopper and serves as a plug. The clinker sample is evacuated from the collector tube by means of a metallic plunger fixed on the end of a transversal pneumatic jack. The material then falls into a selection hopper, which eliminates fine particles (<2 mm), and then into a spout.

The ITECA high temperature clinker sampler is installed at the Portland and Midlothian plants (Holcim US), working well according to plant information.

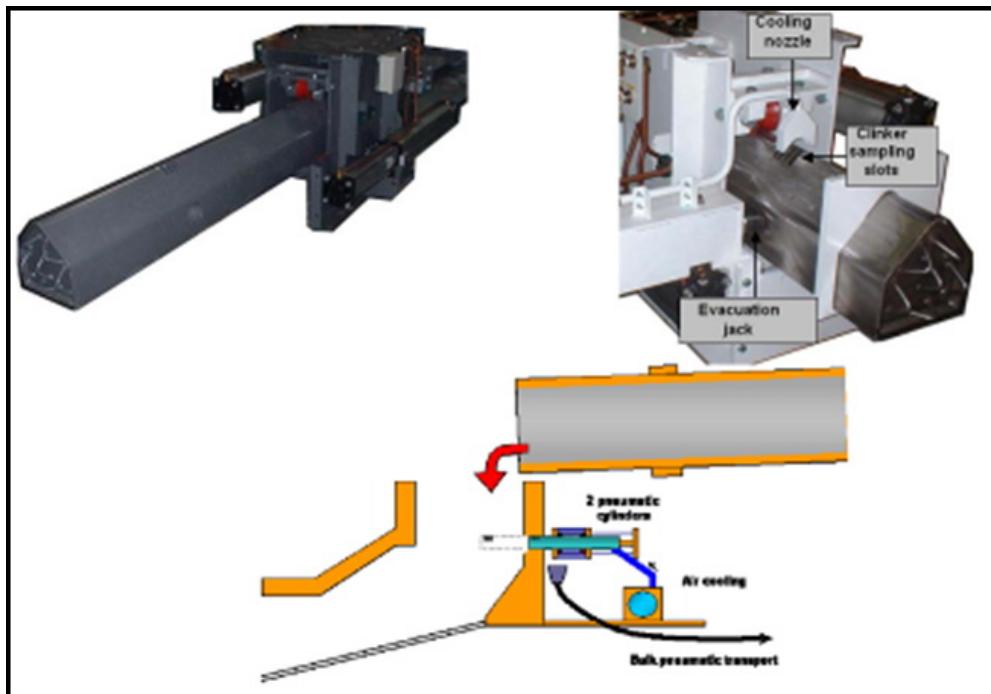


Figure IV- 10: High Temperature Clinker Sampler at the outlet of a clinker cooler.

3.3.4 Bucket clinker sampler

The bucket clinker sampler consists of a small bucket attached to an axis, which is driven manually or by a cylinder (see Figure IV- 13). It is a very simple construction, and can be made at the plant site. Such a system is for example operated at the Polpaico plant (Chile).

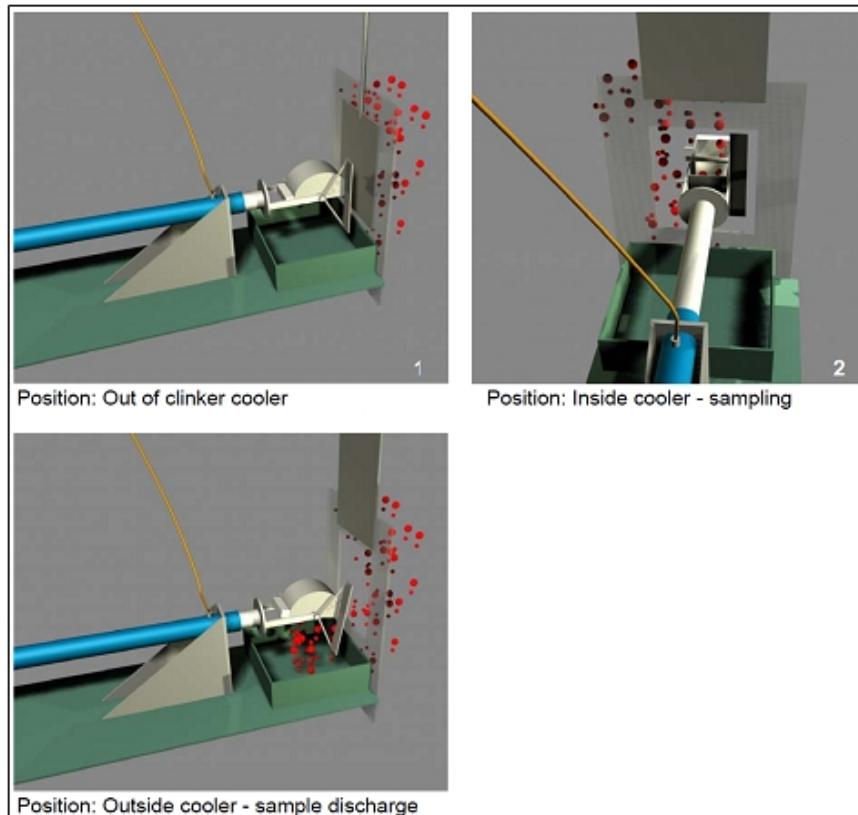


Figure IV- 11: Sketch illustrating the sampling procedure using a clinker bucket sampler

4. Sampling of powder materials

Sampling of powders does not require large sample volumes and involves less preparation work as for coarse materials. However, biases can readily be introduced when basic aspects regarding installation of sampling devices are not considered:

- The sampler needs to be correctly positioned with respect to material flow.
- Installation just below a de-dusting point should be avoided. De-dusting can lead to a loss of fine particles in the sample, e.g. affecting fineness of the cement sample.
- The sampler must be air-tight. Any air flow through the sampling system leads to segregation and can create biased samples.
- Sufficient distance of the sampler to intervening material streams, such as baghouse dust, must be provided to allow proper mixing.
- Sampler need to be maintained properly and protected from exposure to heavy rain / moisture (clogging).
- Large drop heights (> 10 m) between the sampler and the sample container must be avoided due to potential segregation.

Furthermore, the sampler should be easily accessible, especially when not connected automated sample transport (motivation of personnel).

The ideal powder sampler would access the whole material stream and thus provide a completely random sample (see section 2.1 above). The Vezin type sampler design shown in Figure IV- 12 fulfils this criterion. The sampler consists of a rotating cutter (or cup), which crosses the whole stream of falling material. It is flanged directly into the vertical chute. Such type of samplers is common in mining industry but so far rarely used in cement industry (no known application in Holcim plants). Negative aspects are the space requirement (4 m drop height in the chute) and relatively high costs (budget price for the ITECA rotating cup sampler: 80 k€). It thus needs to be included into the plant design from the beginning.

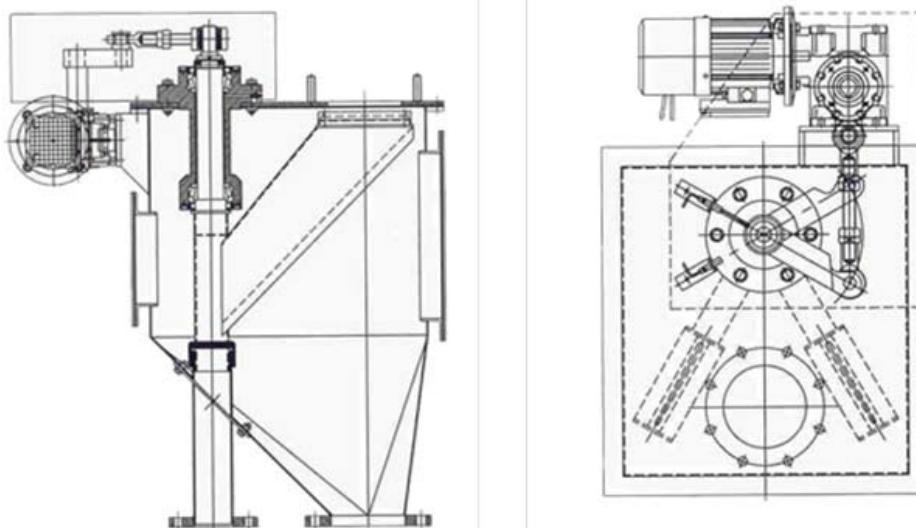


Figure IV- 12: Vezin type sampler (rotating cup sampler), ITECA design. Left: side view; Right: top-view.

All samplers presented below, which are common in cement industry, cannot access the whole material stream.

4.1 Screw sampler

Screw samplers are frequently applied for sampling powders out of a free falling material flow, e.g. in a transfer chute. They are typically applied for materials with < 2 mm particle size. The sampler consists of a transport screw across the material flow, embedded in a perforated tube. The screw transports the extracted material to a discharge outlet chute where the material falls into the sample container or subsequent sample preparation equipment. Common screw samplers resist temperatures up to 150°C; they are not suitable for sticky materials. Up to 50 kg per hour can be collected with these samplers.

Automated screw samplers have a geared motor coupled to the transport screw (see Figure IV-13). Screw speed (rpm) and extraction time can be adjusted allowing for flexible sampling frequencies. To obtain a one hour average sample, the screw can either turn continuously at slow speed or spot samples can be withdrawn at given time intervals (e.g. every 5 minutes 2 minutes of extraction). Automated samplers often discharge into a mixing drum where the sample is homogenized before it is transported to the laboratory.

Depending on the dimensions of the chute, the sampler has to be selected accordingly. Screw samplers with two or three screws in parallel are available.

Design of the screw differs between suppliers. Most suppliers apply equally pitched screws. ITECA claims that their design of variably pitched screw leads to more representative samples. In reality the difference is probably not significant, but systematic studies are missing.

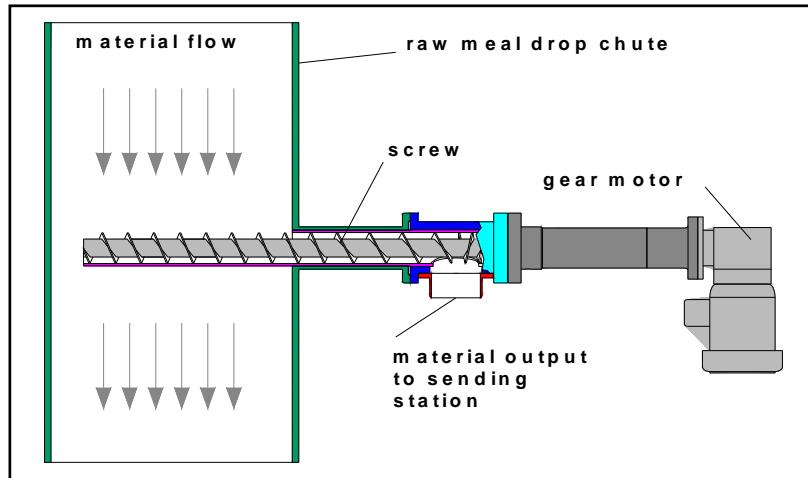


Figure IV- 13: Left picture: General screw sampler arrangement

Manual screw samplers operate with the same principle but the screw is turned manually with a crank (see Figure IV- 14) They are not recommended where high sampling frequency is needed but can be used e.g. at cement silo outlets or filter dust discharge.



Figure IV- 14: Manual screw sampler

Due to segregation effects in falling stream, the sampler must be placed across the material stream, as shown in Figure IV- 15.

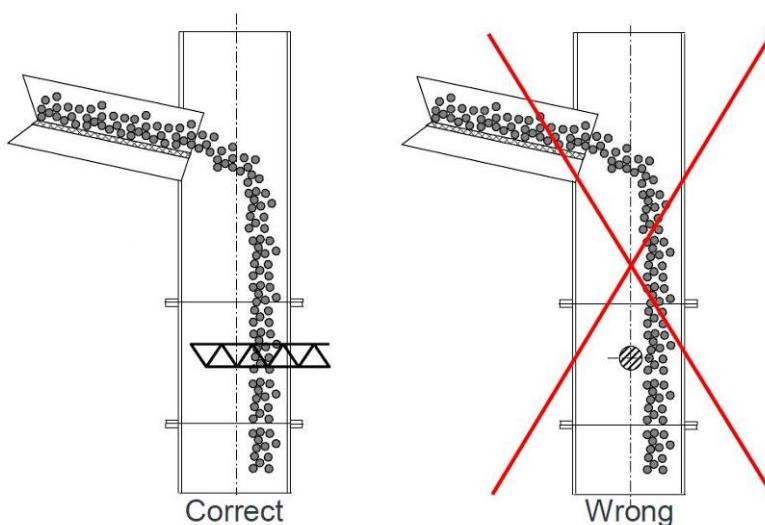


Figure IV- 15: Installation of screw samplers across the material stream

4.2 Air slide sampler

Air slide sampler are used to sample fine material (< 2 mm) at temperatures <120°C from air slides.

They consist of a rotating tube with a longitudinal slot (see Figure IV- 16). The tube is fastened in the hollow axle gear in way that the extracted sample will fall directly into the sample bottle. By intermittent extraction, the rotating tube is parked between the sampling periods with the slot into the protective guard (opposite the material flow). The longitudinal slot can be driven pneumatically or electromechanically.



Figure IV- 16: Air slide sampler

Due to horizontal segregation of material in air slides, the sampler must be vertically positioned. However, also lateral segregation can occur in air slides and thus biased sample cannot always be avoided. Air slide sampler should only be installed if there is no possibility (i.e. space restrictions) to install screw sampler.

4.3 Tube samplers

Automated tube piston sampler: The chamber is generally mounted in chutes, hoppers or at conveyor belt drop offs. When activated, a slotted sample tube enters the product stream with the slot facing down. While fully extended, the sample tube rotates 270 degrees, taking a sample through the product stream. The sample tube then retracts out of the product stream, into the sampler housing and deposits the sample into discharge. Sample tube can be driven hydraulically or pneumatically.

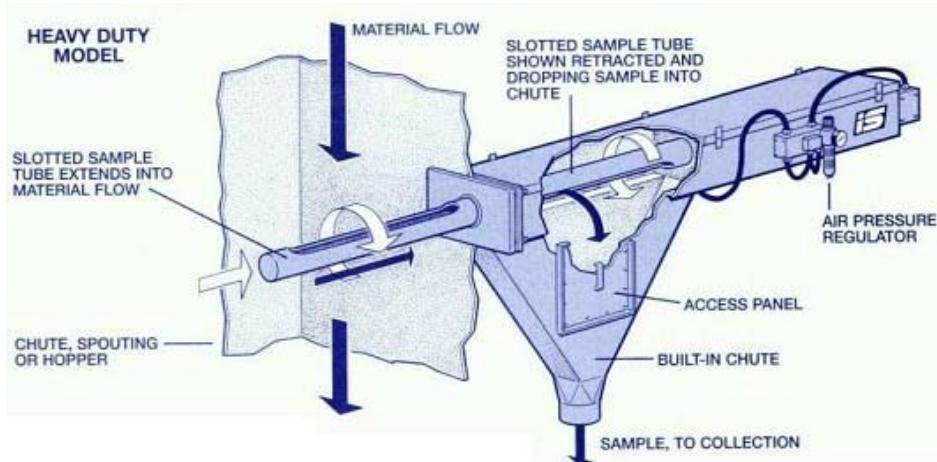
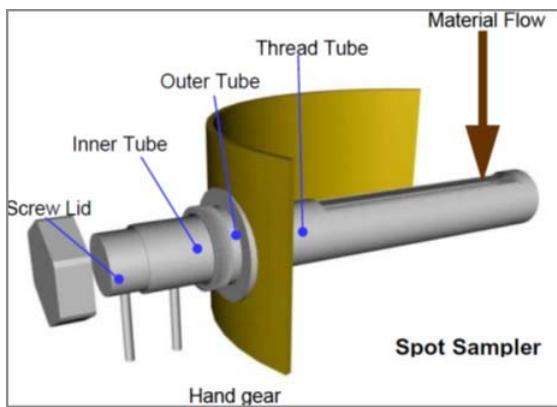


Figure IV- 17: Schematics of a piston sampler (interysystems design)



Manual tube sampler: The principle of operation of a manual piston sampler is the same as described above. However, the piston is hand driven. This can be used for sampling campaigns where a manual reference sample is required. A dedicated opening in the chute to access the material stream must be provided.

Figure IV- 18: Manual tube sampler

4.4 Hot meal sampling

Hot meal sampling is a potential safety risk. Contact with hot meal in case of overpressure at the sampling point can cause severe burns. The sampling installation for hot meal must be designed in a way that contact with hot material is avoided. Safe designs of hot meal samplers exist both for manual and automatic hot meal sampling.

The hot meal sampler must be positioned at the meal chute to the kiln inlet, after the bottom preheater cyclone. The sampling spoon must be made from heat resistant material to resist temperatures of up to 1100 °C.

Automated hot meal sampler: Automated hot meal samplers consist of a sampling piston and a cooling device, either water or air cooling, to cool down the hot meal (typically below 100°C). At sampling time the sampling piston moves into the meal duct, collects the hot meal and retracts out of the duct (spot sample). The sample is cooled and then sent to the laboratory by pneumatic transport.

The major sampling equipment suppliers (FLS, Polysius, ITECA) offer differently designed hot meal sampling systems. The Polysius design is shown below.

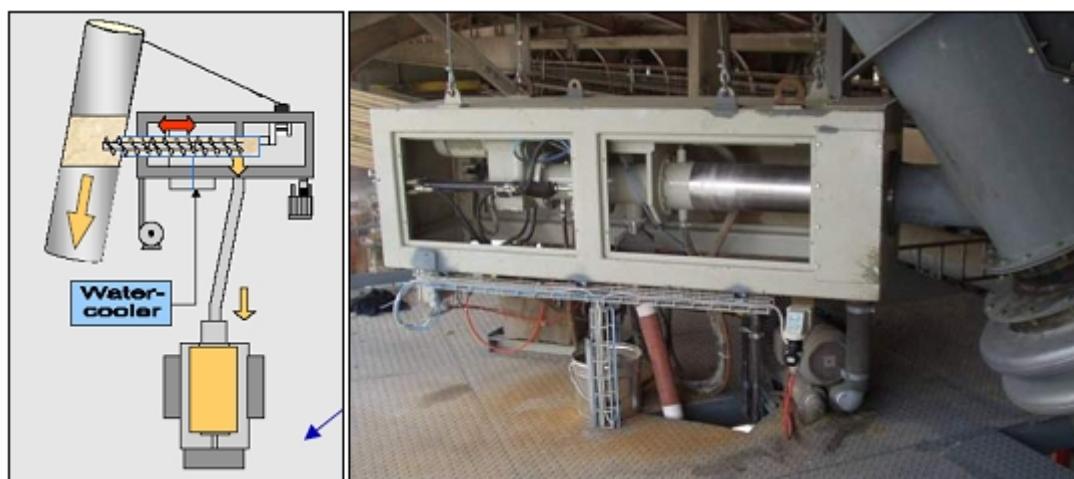


Figure IV- 19: Automated hot meal sampler (Polysius design, approx. 70'000 Euro)

Manual hot meal sampler: The sampler is based on the principle of a gate valve and is permanently attached to the preheater. The sampling spoon is located in an extended insertion muff that is fully enclosed. The spoon is inserted into the material stream and retracted through a gate valve system. Subsequently, the sample can be safely removed, because there is no longer

an open connection with the hot stream of process material. This design refers to a ZKG publication.



Figure IV- 20: Example of manual hot meal samplers. Left: Cilacap (Indonesia), right FLS design at St. Genevieve (USA)

5. Sample transport

Once the sampling has taken place, the sample is transported to the lab where it will be analysed. The samples can either be transported by hand or via an automated device.

As a general consideration, any alteration of the sample during transport (e.g. loss of dust or moisture, cross contamination) has to be avoided.

5.1 Manual transport

Samples, collected at locations requiring only low frequency control, can be transported manually to the laboratory. Before and during the transport, the following precautions should be taken:

- The sample should be enclosed in a sturdy bag or container, and clearly labelled, at different places, in such a way that the label is not lost during transport, and that no confusion will occur.
- The bag / container should be sealed to avoid any contamination by dust or liquids during transport.
- If the moisture has to be determined, it is particularly important that the sample is completely sealed and brought as fast as possible to the lab.
- If Mercury (Hg) has to be determined, the sample must not be exposed to temperatures above 45°C.

5.2 Automated transport

Automated sample transport devices allow to save time and resources. They are particularly useful where high sampling frequency is required, such as at the raw mill (raw meal), the kiln/cooler outlet (clinker) or the cement mill. For new plants, automated sample transport for raw mill and cement mill samples should be included by default.

5.2.1 Pneumatic tube conveying system

Pneumatic tube conveying systems connect the sampling stations in the plant with the central laboratory. The sample material is enclosed in special capsules (or cartridges), which are transported through steel tubes over distances of up to several 100 meters. One or more rotary blowers integrated in the tube network generate a slight over- or under-pressure, allowing the cartridges to move at transport speeds typically between 8 and 20 m/s.

A pneumatic transport system consists of a sending station, a receiving station at the laboratory, the transport tubing incl. diverters, blowers and sample capsules.

The sending station has typically the following functions:

- Fill the transport capsule with the sample material and lock the capsule
- Dispatch the filled capsules to the laboratory
- Receive the empty capsules from the laboratory
- Dispatch capsules introduced manually

The receiving station has typically the following functions:

- Receive capsule from the transport and open (de-cap)
- If connected to an automated laboratory, empty sample at the dosing device
- Dispatch empty and cleaned capsules back to the sending stations

The integral capsule orientation monitor and the turning device enable the capsule to be dispatched and received in either direction as desired. Several sampling stations are connected to the pneumatic transport with a number of tube diverters. Only one capsule can be transported through the system at the time. Scheduling of capsules is a main task of the control system.



Figure IV- 21: Illustrations of sample capsules (left), and a receiving station at the laboratory (right picture, Herzog design).

Critical aspect of a pneumatic tube transport system is the correct alignment and installation of the transport tubes. Misalignment can easily cause blockage of the sample capsules. Pipefitting work should be done by a qualified and proven company. In addition, clean and dust free compressed air is absolutely required for correct operation.

Different suppliers use different tubing diameters and closing mechanisms for pipes and capsules. Table IV- 1 below lists typically found suppliers and solutions in cement industry:

Supplier	Tube outside/ inside diameter [mm]	Cartridge volume [cm ³]	Cartridge
FLS	80 / 75	600	Steel ringed plastic tube, closed with cap
Polysius	80 / 75	350	Steel ringed plastic cylinder, closed with cap (Vulkollan plug)
Herzog	80 / 75	Ca. 350	Steel ringed plastic tube, closed with cap
ITECA	80 / 75	200	Plastic tube with bronze runners (replaceable), closing with spring mechanism

Table IV- 1: Pneumatic transport solutions from different suppliers

5.2.2 Cable transport system

As an alternative to pneumatic sample transport, cable transport systems with a disk chain are available. The disk chain drags the sample material through a transport tube (see Figure IV- 22). This system is offered in combination with automated (de-centralized) container laboratories from the ITECA and the FKV Company.

The systems connects single or multiple sample points at up to 150 m distance. The transport system will generate a continuous flow of material, going from the samplers to the container laboratory and then back to the process. The throughput of the transport system is approximately 100 kg/h. Discharge rotating valves are installed along the transport tube where it is needed to drop material.



Cable transport system allow for flexible tube layout including sharp bends (up to 180 degrees). However, the disk chain needs to be replaced periodically (at least yearly) due to abrasion. There are currently no applications in Holcim plants.

Figure IV- 22: Cable transport system

6. Reduction of sample mass

Mass reduction methods are used to reduce the size of the samples – from kilograms sampled in the process to a few grams needed for analytical purpose. Mass reduction plays an important role in the sample preparation process, as it represents an additional sampling step with its own inherent error.

The most common tools and methods to reduce sample mass are presented in this section. Any of these methods is considered superior to “grab sampling” (Figure IV- 23), where the required sample mass is just arbitrarily removed from the primary sample. For more theoretical aspects on representative mass reduction in sampling refer to the study of Esbensen. [Lit 2]

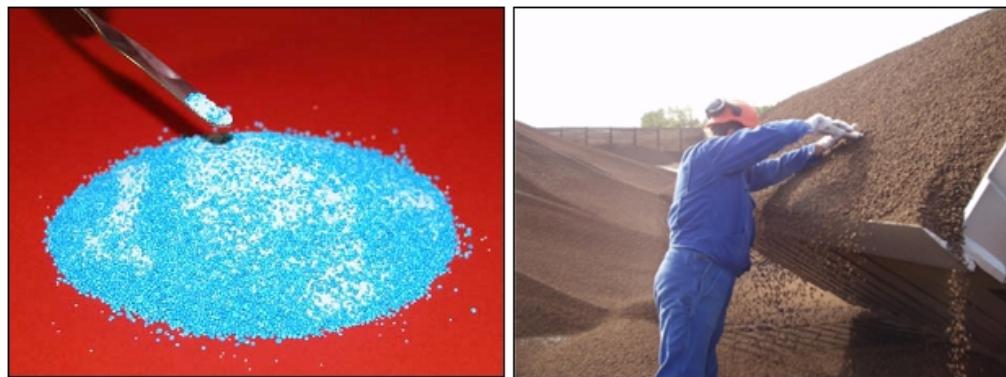


Figure IV- 23: Illustrations of grab sampling. To be avoided in practice.

6.1 Coning and quartering

The coning and quartering method (Figure IV- 24) can be used to reduce/ divide piles of different size using simple equipment (blade knife, etc). The lot produced by the sampling is placed on a surface (soil, ground, table) covered by a clean plastic sheet and reduced by incremental splitting. This method can be used as a first step to reduce large piles, mostly for large bulk samples in the quarry (see [Lit 7] as an example). The material is then further reduced using riffler or rotary separator. The coning and quartering works well for materials with poor flow characteristics (i.e. contaminated soil) and low segregation.

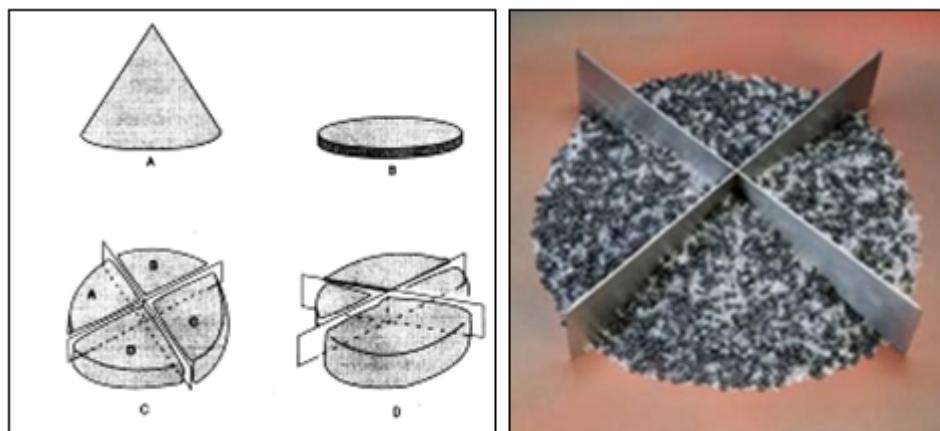


Figure IV- 24: Example of coning and quartering

6.2 Riffle type sample splitters

A more reliable method for mass reduction is splitting with riffle type splitters. If designed and used correctly it provides a reliable and inexpensive method for mass reduction with reasonable speed. Riffle splitters can be applied to free flowing materials only; they can't be used for sticky and or wet materials such as clay. Riffle type splitters are often applied in the quarry for drill hole material or in the laboratory for large clinker samples.

Riffle splitters divide the sample into two equal parts. They consist of a hopper and a series of equally spaced chutes (or slots) that alternately discharge in opposite directions into the two separate trays (see Figure IV- 25). The distance between the blades forming the chutes is a function of the top grain size of the sample material. As a rule of thumb blade spacing should be at least 2.5 to 3 times greater than the diameter of the largest particle. Typical blade spacing in commercial systems is 5 to 75 mm. Blade spacing less than 5 mm should not be used.



Figure IV- 25: Examples of riffle splitter

Following points should be considered when using riffle splitters:

- Use a container matching the length of the hopper to feed the splitter.
- Pour material onto the centre line in an even flow.
- Avoid dust loss

6.3 Rotary splitters

Rotary splitters are based on the same principle as riffle splitters. The revolving feeder distributes the sample material equally (in time) over a number of radial chutes, assuming constant rotational speed. These devices are very easy to use, since one only needs to pour the material to be divided into a hopper, thereby getting one or several reduced splits. They also require very little preparation and clean-up and split the sample very fast. The latter depends on the rotating speed as well as the influx velocity of the material through the feeding funnel.

The essential principle is that every second radial chute contributes to one of the two alternative collecting reservoirs. Since a larger number of sub-samples in this context give more representative samples it can be desired to increase the total number of revolutions. This can be done by using a smaller outlet size of the hopper. Also, size, slope and rotation speed of the inlet tube can be altered to change the outlet speed.



Figure IV- 26: Rotary splitters

This type of splitter can only be applied to free flowing powders. They are mostly used in laboratories to split large cement samples.

Part V: Quality Control Laboratories and Equipment

1. Quality control laboratories

1.1 Basic requirements

The performance of the quality control tasks at a plant requires the availability of laboratory and office facilities with appropriate space and room conditions. The specific needs depend to a certain extent on the quality control concept, i.e. on the degree of automation, and control and monitoring systems installed locally (such as PGNA analyzers).

The rooms typically required, their functions and approximate space requirements are compiled in the Table V- 1 and Table V- 2. Table V- 1 compiles the room needs applicable to most cement plants; it includes the main function or type of laboratory, with indications on how the rooms could be sub-divided. This sub-division is being done in different ways, according to the needs and the architectural design of the laboratories. Table V- 2 compiles additional room requirements depending on the specific needs of individual plants.

The net total room requirements for the quality control department varies in the order of 250 to 450 m²; the gross total room requirement (overall footprint), comprising corridors, toilets, coffee corners etc, amounts to 350 to 600 m².

1.2 Location and layout

There is a fair degree of freedom for the architectural design of the laboratories, their location and layout, in such a way that laboratory layouts look quite different from plant to plant. The design of a laboratory layout should, however, pay due attention to the following aspects:

- In case of a quality control concept with centralized automated laboratory, this automated laboratory should be located adjacent to the central control room. This permits supervision of, and minor interactions with the system by CCR operators.
- The layout of all other parts of the laboratory facilities should take in consideration the work flow of sample preparation and testing (see also below).
- Sample reception room and preparation of coarse samples (drying, crushing, and splitting) should preferentially be located on ground floor level, with separate entrance, to minimize dust contamination of the rest of the building.
- Physical testing rooms, applying heavy equipment (hydraulic presses), are also preferentially located on ground floor level.
- In case of a central, automated laboratory on higher floor levels (same as CCR), the chemical laboratories are best located on the same level. This allows direct interaction of laboratory personnel with the automated system, such as for manual sample introduction, and for systems supervision, support (calibration, cross-checking) and maintenance.
- A separate room for handling and testing of fuels, particularly coal and petcoke, is advisable to minimize contamination and facilitate housekeeping.

Room	Possible sub-divisions	Function	Space requirement [m ²]
Offices			20 - 40
	QA-Manager office	Documentation, data management, reporting	15
	Technician office	Documentation, data management, supervision on-site systems (PGNAA)	20
Sample preparation			30 - 50
	Sample reception	Sample reception, intermediate storage	10
	Sample preparation	Weighing, drying, sieving, crushing, splitting, (grinding)	30
	Mill room	Preparation laboratory cements	10
Chemical laboratory			50 - 100
	"Wet" laboratory	Free lime, insoluble, titration, special elements, reference methods	25 - 40
	Instrument laboratory	Instrumental analyses (photometer, S/C-analyzers, calorimeters, proximate analyzers, particle size distribution, AAS,)	25 - 35
	Balance room	Weighing (analytical balances)	10
	Furnace room	Loss on ignition, fusing	10
	Microscopy room	Microscopical examination (clinker)	10
	Fuel room	Sieving, calorific value, proximate analysis	15 - 20
XRF/XRD room			30 - 50
	Sample preparation	Pressed tablet and / or fused bead preparation	15 - 35
	XRF/XRD room	XRF and XRD measurement	15 - 35
Physical laboratory			40 - 70
	Physical laboratory	Cement fineness, cement paste and cement mortar preparation and testing	30 - 50
	Curing room	Curing of mortar specimen	15 - 20
	Autoclave room	Autoclave testing	10
Storage			25 - 40
	Sample storage	Mortar sand, general sample storage, cement retained sample storage	10 - 20
	Chemicals storage	Storage of chemicals; separate storage of specific classes of chemicals acc. OH&S rules	10 - 15
	Glassware / equipment storage	Glassware, spare parts of testing equipment	10 - 15

Table V- 1: Basic room requirements

Room	Possible sub-divisions	Function	Space requirement [m ²]
Automated laboratory	Sample preparation / testing	Pneumatic tube reception, sample preparation, compositing, testing	40 - 50
	XRF/XRD room	Separate room for XRF/XRD spectrometers for easier manual access	30
	Operator room	Control and supervision of system, possibly including on-site systems (PGNAA)	20
	Auxiliary room	Dedusting, air compressors, water cooling, etc, for automated laboratory equipment	15
Shift room			20 - 30
	Shift room	Separate room for main shift-related tasks (fineness, free lime, etc)	25
AFR laboratory			45 - 65
	Sample preparation	Drying, grinding, splitting of AFR	15
	AFR laboratory	Determination of specific properties of AFR	30 - 40
	Storage		10
Concrete laboratory			100 - 150
	Storage bins sand and gravel	Storage / conditioning of concrete aggregates	30
	Concrete laboratory	Concrete preparation, aggregate sieving	40
	Curing	Concrete specimen curing	30
	Mill room	Preparation of laboratory cements	5
	Storage (samples/equipment)		30

Table V- 2: Complementary room requirements

1.3 General room conditions

1.3.1 OH&S related installations

Operational health and safety has highest priority in the area of the quality control laboratories, and all necessary features to eliminate risks and to ensure rapid help in case of incidents have to be provided, according to the kind of activities performed in the different rooms and in line with local regulations. Such features shall include – but not be limited to – the following items:

- Appropriate **signalization** has to be applied as necessary with regards to
 - *Warnings* of risks (fire, toxic substances, etc.)
 - *Prohibition* of entrance, smoking, use of electronic equipment, etc.
 - *Personal Protection Equipment* directions, e.g. use of safety glasses, mouth protection, etc.
 - *Rescue facilities*, e.g. showers, eye-wash, rescue direction, meeting points, etc.

- **Safe rescue routes** have to be ensured, e.g. doors of the chemical laboratory and of storage rooms opening to the outside
- **Showers and eye-wash facilities** have to be provided in the chemical laboratory
- **Fire extinguishers** must be mounted in each laboratory as well as in the storage rooms for chemicals.
- At least one **fume cupboard** should be available in the chemical laboratory (dimensions 200 x 150 cm). A mobile bench top fume cupboard (dimensions 120 x 80 cm) is recommended for the XRF sample preparation room (cleaning of crucibles/moulds with acids). Furthermore, hot air extract ventilation in the furnace area and a proper ventilation system in the storage rooms for chemicals should be provided (Note: this may interfere with air conditioning).
- An effective **dedusting system** has to be installed in the sample preparation room (crushers, mills, sieves etc.). Generally, dust, noise and vibrations should be eliminated as far as possible in all rooms.
- Use **closed cupboard with proper ventilation** to separately store highly toxic chemicals. The floors should be sealed by coatings in order to prevent leakage and groundwater contamination. Storage rooms for chemicals should be equipped with cupboards and shelves resistant against aggressive chemicals.
- **Waste water** with hazardous chemicals must be collected in dedicated containers in the laboratory rooms. Acidic and alkaline solutions must be stored separately.

1.3.2 Service installations

Service installations (power supply, water, gas etc.) should be arranged in accordance with equipment, location and requirements.

- **Power supply** (voltage, current) has to conform to the equipment specifications. Transformers may be required. In the laboratories, a sufficient number of plug sockets should be provided in addition to the power supply ports dedicated to specific instruments. For example, working tables could be equipped with plug sockets at regular distances.
- **Water supply** is required in all laboratories and rooms, except for the storage rooms. In the chemical laboratory at least two sinks should be available. If a HF induction furnace is used for fused bead preparation in the XRF sample preparation room, water supply must be provided for cooling of the furnace. It is recommended to install a specific filter system for the external cooling water supply of the XRF equipment (only if a cooler is needed in case of water/water cooler).
- **Gas supply** is indispensable in the chemical laboratory and in the XRF sample preparation room. Fixed gas taps should be mounted both on the working tables and in the fume cupboards. It is recommended to use locally installed gas cylinders which have to be mounted to walls or placed in the sub-construction of the fume cupboards.

1.3.3 Installation requirements

- **Sinks** must be installed in the chemical and physical laboratories. In the chemical laboratory, two sinks should be available.
- The **water basins** in the curing room should be separated in three independent units instead of one large basin.
- **Special base constructions** (rubber layers etc.) should be applied to absorb noise and vibrations from specific equipment such as laboratory mills, laboratory crushers, sieve machines, etc.
- In the physical laboratory, the vibrating table and sufficient space for storage of the moulds should be integrated into the central working table.

1.3.4 Ambient conditions

- **Dust infiltration** through doors and windows to laboratory rooms has to be strictly prevented to ensure proper functionality of analytical instruments.

- **Temperature and humidity** in the chemical laboratory and in storage rooms for chemicals should not vary too much. For that purpose, the laboratory area is usually integrated in a centralized air conditioning system for the whole building.
- **Controllable air conditioning** (temperature, humidity) has to be provided in the XRF/XRD-room and in other rooms with sensitive analytical equipment (instrument laboratory room) to ensure analytical stability.
- **Strict control and recording of ambient conditions** (temperature, humidity) are required in the physical laboratory and curing room, in order to comply with the corresponding specifications in the standards for physical testing of cement and mortar.

2. Main laboratory equipment

2.1 Introduction

This chapter provides a compilation of major equipment used in plant laboratories and corresponding supplier companies. It is basically grouped along the functional laboratories, as listed in Table V- 1. Not included here are furniture requirements and minor equipment.

Descriptions of methods and procedures (SOP's) of important analytical methods are not given here, but in Part VIII of this manual.

2.2 Sample preparation

Main equipment for this area is:

2.2.1 Drying

Drying ovens are required to dry (coarse) rock or coal samples. Recommended dimensions are approx. 80x60x80 cm (internal dimensions), providing about 400 l internal space. This allows to dry materials in quantities of up to 40 kg. Maximum temperature should be 250 – 300 °C. Connection to an exhaust-air venting system should be considered.

Suppliers are large laboratory equipment suppliers such as:

Cole Palmer USA: <http://www.coleparmer.com/>

Fisher Scientific, USA: www.fishersci.com

A&P Instruments, Hong Kong: www.anp.com.hk

Or specialized manufacturing companies such as

- ThermoScientific (Heraeus), USA: <http://www.thermoscientific.com/>
- Binder, Germany: www.binder-world.com/
- Salvislab, Switzerland: www.salvislab.com/

2.2.2 Weighing

2 – 3 precision balances should be available to cover following maximum loads:

- 60 -150 kg; readability 10 or 20 g; this balance could be placed on a trolley to be mobile (see Figure V- 1)
- 3-5 kg (optional) readability 0.01 or 001 g)
- 500 g, readability 0.001 g

Major manufacturers and global suppliers are (further local suppliers may also be available):

- Sartorius, USA: <http://sartorius.balances.com>
- Mettler Toledo, Switzerland: <http://ch.mt.com>
- Ohaus, USA: <http://us.ohaus.com>
- Kern & Sohn GmbH, Germany: <http://www.kern-sohn.com/>

2.2.3 Sieving

Sieves are used to determine the granulometry of coarse materials, such as crushed raw materials or clinker, and for powders, such as raw meal or cement.

Sieve openings are standardized by international (ISO) and national standards. Annex V-1 provides a comparison table of standardized sieves.

For coarse material, a set of sieves with following sieve openings is recommended (or a selection thereof):

1, 2, 4 10, 20, 31, 40, 63, 90, 125 µm

For powdered materials, a set of sieves with following sieve openings is recommended
32, 45, 63, 90, 200, 500 µm

For cleaning of sieves < 1mm opening, ultrasonic bathes need to be available.

For powder sieving, the application of an **air-jet sieving apparatus** is recommended. Maximum sieve opening is 4 mm, smallest sieve opening is 20 µm. The most frequently used brand in the cement industry is Hosokawa Alpine, but also other suppliers offer such equipment (e.g. Retsch).

For coarse sieving, particularly when frequently used (e.g. for concrete aggregates), sieve shaker racks can be applied.

Manufacturers or suppliers for sieving equipment are:

- Siebtechnik, Germany: <http://www.siebtechnik-gmbh.de/>
Sieves, shaker racks, air-jet sieving apparatus (SLS 200)
- ELE, UK: <http://www.ele.com/>
ELE has taken over took over Soiltest, which is a “classical” manufacturer and supplier of sample preparation equipment, such as sieves, shaker racks etc
- Haver & Boecker: <http://www.haverboecker.de/>
Manufacturer of sieves, shaker racks, etc (see annex 1)
- Hosokawa Alpine, Germany: <http://www.alpinehosokawa.com/>, or <http://www.luftstrahlsieb.de/>
Manufacturer of air-jet sieving apparatus (e.g. 200 LS-N) and corresponding sieves
- Retsch, Germany: <http://www.retsch.com/>
Air-jet sieving apparatus and corresponding sieves
- Testing Bluhm & Feuerhardt, Germany: <http://www.testing.de/>
Sieves, shaker racks, air-jet sieving apparatus
- Matest, Italy: <http://www.matest.com/>
Sieves, shaker racks, air-jet sieving apparatus
- Humboldt, USA: <http://www.humboldtmfg.com/>
Sieves, shaker racks, etc
- and others

2.2.4 Crushing

Crushers have to be available for size reduction of coarse material samples, e.g. from quarries or from external material supplies (correctives), as well as of clinker samples.

For rock samples (and clinker), jaw-crushers are recommended, with feed opening min. 100x100 mm, and variable slit (2- 30 mm).

For clinker or coal, cross-beater mills are recommended, with internal grate for fineness < 20 mm. A typical model is the Retsch SK 1.

Major suppliers and typical equipment models are:

- Retsch, Germany: <http://www.retsch.com/>
E.g. jaw crusher type EB 10/8 or EB15/10; cross-beater mill type SK 1

- Siebtechnik, Germany: <http://www.siebtechnik-gmbh.de/>
- Fritsch, Germany: <http://www.fritsch.de/>
E.g. cross-beater mill type Pulverisette 16

2.2.5 Grinding

2.2.5.1 Small samples

For fine-grinding of material for wet-analytical purposes or for pressed tablets for XRF analyses, **disk mills** are recommended. The mill body should be noise-damping.

Typical vessel size is 100 cm³. The alloy of the grinding vessel and rings is determining the wear resistance, tungsten carbide (WC) being the most resistant, followed by "Colomonoy" and hardened steel. For the analyses of trace concentrations of heavy metals, special steel vessels can be applied which do not give raise to contamination with alloy metals of the grinding vessel. It is recommended to have two or more grinding vessel sets available dedicated to different material types (to minimize cross contamination).

Major suppliers and typical models are:

- Herzog, Germany: <http://www.herzog-maschinenfabrik.de>
Type HSM 100
- Siebtechnik, Germany: <http://www.siebtechnik-gmbh.de/>
Type TS 1000
- Retsch, Germany: <http://www.retsch.com/>
Type RS 200
- FLS, Denmark: <http://www.flsmidth.com>
FLS has incorporated former Pfaff AQS GmbH with the entire product range of sampling, pneumatic tube sample transport and sample preparation
Typical disc mill (manual): PAL M100M

2.2.5.2 Large samples

For fine grinding of larger samples, i.e. 5 to 8 kg, particularly for grinding of **laboratory cements**, a drum mill with suitable ball charge is required. The system used at HGRS-MT-laboratory, which can be recommended also for plant laboratories or central laboratories is the following:

- Siebtechnik, Germany: <http://www.siebtechnik-gmbh.de/>
Drum mill type TTS 50, drum volume 50 liter, ball charge 80 kg

Steel balls with diameters of 20, 30, 40, 50, and 60 mm are used, as well as steel-cylpebs of dimensions 12x12 mm and 15x15 mm.

The practice at the HGRS-MT laboratory for laboratory cement grinding involves changing of the ball charge in the course of finer grinding; the following steps are applied:

Step 1: < 32 mm to approx. 50 % R90 μ m:

30 kg ø 60mm; 25 kg ø 50 mm; 25 kg ø 40 mm

Step 2: to approx. 20 % R90

44 kg ø 30mm; 36 kg ø 20 mm

Step 3: to target fineness (e.g. Blaine 4500 cm²/g; 10 % R45mm)

44 kg steel cylpebs 15x15 mm; 36 kg steel cylpebs 12x12 mm

2.2.6 Homogenization

For the mixing of finely crushed or ground materials, three-dimensional shaker-mixers should be available.

The best known systems are of the Turbula-type (registered trade mark). They are available in versions for 2, 17, or 55 liter homogenizing vessels, of which the first, and optionally the second should be available in a cement plant preparation laboratory.

Supplier/Manufacturer:

- W.A. Bachofen AG, Switzerland: <http://www.wab.ch>
E.g. Turbula T2F; Turbula T10F

2.2.7 *Splitting*

Splitting of coarse samples, i.e. samples with maximum size > 50 mm, is usually done manually, by homogenizing (shoveling) coning and quartering.

For samples with maximum grain size of < 50 mm, splitting with riffle-splitters is the appropriate method (see Figure V- 1). Riffle splitters are further described in chapter 4. They are available with blade spacing between 6.5 and 75 mm. The blade spacing should be about 3 times the top grain size of the sample material.

Main suppliers:

- Siebtechnik, Germany: <http://www.siebtechnik-gmbh.de/>
Blade spacing 20, 30 and 40 mm; different numbers of slots
- Retsch, Germany: <http://www.retsch.com/>.
Types RT 6.5 to RT 75; blade spacing 6.5, 12.5, 25, 37.5, 50, 75 mm; different numbers of slots
- ELE, UK: <http://www.ele.com/>
- Humboldt, US: <http://www.humboldtmfg.com/>
- Essa, Australia: <http://www.labtechessa.com.au>
- and others

2.3 XRF sample preparation

2.3.1 *Weighing*

An analytical balance is needed, independent on whether pressed tablet or fused bead preparation is applied.

Capacity: 0 – 200g accuracy 0.1 mg

Suppliers (see also chapter 2.2.2):

- Sartorius, USA: <http://sartorius.balances.com>
- Mettler Toledo, Switzerland: <http://ch.mt.com>

2.3.2 *Pressed tablets*

Fine grinding for pressed tablet preparation is usually done with disk mills (see chapter 2.2.5.1).

For tablet pressing, hydraulic presses are applied. It is recommended to use the typical standard models of the below-mentioned main suppliers, rather than smaller, or even hand-operated equipment. Usually, steel rings are applied for tablet pressing; alternatively aluminum cups can be used.

In addition to the stand-alone presses, major suppliers also offer combined grinding/pressing units with integrated cleaning of used steel rings. These models have the advantage – in addition to substantial reduction of labor work - of very reproducible sample preparation. The two most common systems (FLS and Polysius) are described in part VI of this manual.

Major suppliers:

- Herzog, Germany: <http://www.herzog-maschinenfabrik.de>
For stand-alone: type HTP 40; combined mill/press: HP-MT
- FLS, Denmark: <http://www.flsmidth.com>
For stand-alone: e.g. PAL 40M; Combined mill/press: Centaurus type
(Note: FLS has taken over Pfaff AQS GmbH with their product range for sample preparation)

- Polysius, Germany: <http://www.polysius.com/de/>
Combined mill/press type APM

Additional suppliers

Besides the above listed suppliers, also ITECA, France offers a combined mill/press unit, usually part of a full laboratory automation, with special designed (very heavy) mill and with tablet pressing using boron oxide as sample support instead of steel rings. No such system is in operation in Holcim plants.

- Iteca, France: <http://www.iteca-socadei.com/>

2.3.3 Fused beads

Preparation of fused beads can be done with different furnace types and degree of automation. In most cases, platinum/gold crucibles and moulds are needed; alternatives are graphite moulds (Herzog only).

High temperature muffle furnace

Bench-top high temperature muffle furnaces are used for fully manual bead preparation, either as the standard method or as back-up for more automated systems. Maximum temperature: 1150 – 1200 °C; Chamber size min. 20x20x20 cm.

Manufacturers/suppliers for muffle furnaces:

- Nabertherm, Germany: <http://www.nabertherm.com/>
- ThermoFisher, USA: <http://www.thermoscientific.com/>
Range of muffle furnaces from type Heraeus (part of ThermoFisher) or type Lindberg
- Linn: <http://www.linn-high-therm.de/>
- Herzog, Germany: <http://www.herzog-maschinenfabrik.de/>
Type HAG 12; fully automated

Induction furnace

Induction furnaces are used for semi-automatic to fully automatic fused bead preparation. Usually, one sample at a time can be prepared. Induction furnaces provide good temperature control and short melting time (3-6 min). Cooling water may be required.

Suppliers and typical models:

- Linn, Germany: <http://www.linn-high-therm.de/>
Type Lifumat 2.0,Ox
- Claisse: <http://www.claisse.com/>
Type The Bee
- Panalytical, Netherlands: <http://www.panalytical.com/>
Type Perl'X 3 or Eagon 2
- Herzog, Germany: <http://www.herzog-maschinenfabrik.de/>
Type HAG-M:HF

A fully automated system based on electrical furnace and cooling facility, attachable to a sample magazine is available from Herzog (HA HF-16, described in part VI). Very recently also FLS has introduced units for automated fused bead preparation (DCF series, 10-20 beads per hour, can be integrated into automated laboratories).

Gas burner furnaces

Gas burner furnaces provide the advantage of simultaneous preparation of several beads. In addition costs are generally lower than for an induction furnace system. Flame temperature stability and mechanical reliability were problems encountered in the past, modern equipment,

however, proves to be more reliable and are successfully applied in many plants (including HGRS-MT laboratory). Still, these furnaces need good and stable gas quality.

Suppliers and typical models:

- Claisse, Canada: <http://www.claisse.com/>
Type M4 fluxer
- Chemplex Industries: <http://www.chemplex.com>
- Fluxana, Germany: <http://www.fluxana.de/>
Type Vulcan 2MA, 4MA, 6MA, with 4 to 6 positions respectively

2.4 XRF/XRD spectrometers

The methodology of XRF and XRD is described in Part VII and VIII, including characterization of different spectrometer types.

Here, reference is only made to the major suppliers of such instruments:

- Bruker, German: <http://www.bruker.com/>
Complete range of WDXRF- and XRD-Spectrometers
- PANalytical, Netherlands: <http://www.panalytical.com/>
Complete range of WDXRF- and XRD-Spectrometers
- ThermoFisher/ARL, USA/Switzerland: <http://www.thermoscientific.com/>
Complete range of WDXRF- and XRD-Spectrometers
- Oxford, UK: <http://www.oxford-instruments.com/>
Low-power WDXRF spectrometer (MDX1000) and benchtop EDXRF (Lab-X- 3500)
- Spectro, Germany: <http://www.spectro.com/>
EDXRF spectrometer (e.g. XEPOS)
- Rigaku, Japan: <http://www.rigaku.com/>
Wide range of WDXRF and EDXRF, as well as XRD spectrometers; few (if any) applications in Holcim group

2.5 Analytical equipment

2.5.1 Introduction

The analytical / instrumental laboratory has to be equipped for all analytical task required in addition to the XRF analyses. This can involve:

- Analyses required by standards that cannot be done by XRF (L.o.I, free lime, acid insoluble residues, etc.)
- Performance of reference analyses according to the methods defined in the cement testing standards; these usually require “wet-chemical” analyses (titration, gravimetric analyses, spectrometric analyses)
- Determination of specific components, additional or in complementation to XRF analyses (sulfur, chloride, fluoride, trace elements, etc.)
- Determination of specific non-chemical properties (e.g. color)

For this purpose, the laboratory has to be equipped with general glassware, plastic-ware, accessory tools and chemicals, as well as with specific measuring instruments.

Reference is made to the description of important analytical methods in part VIII.

In this chapter, a summary is given on the required general equipment and on specific instrumentation and pertinent suppliers thereof.

2.5.2 General laboratory equipment

Annex V-2 provides a generic list of glassware, plastic ware and accessories typically used in cement plant analytical laboratory. It may serve as a guideline / check list, in particular in case of equipping a new laboratory. Adaptations have to be made for each individual case.

Annex V-3 provides a very basic list of chemicals needed in a cement plant analytical laboratory. Globally operating major suppliers for general laboratory equipment, chemicals, and partly also laboratory furniture are:

- Fisher Scientific (part of Thermo Fisher), USA: <http://www.fishersci.com/>
- Cole-Palmer, USA: <http://www.coleparmer.com/>
- A & P Instruments, Hong Kong: <http://www.anp.com.hk>
- Sigma-Aldrich, USA: <http://www.sigmaaldrich.com/>
(incorporates Fluka chemicals company)

Specific for glassware:

- Schott, Germany: <http://www.schott.com/>
- Duran, Germany: <http://www.duran-group.com> (chemically and thermally highly resistant)

Specific for chemicals:

- Merck, Germany: <http://www.merckgroup.com/>
- Johnson Matthey, USA: <http://www.matthey.com/>
- Riedel de Haën, Germany: <http://www.riedeldehaen.com>

2.5.3 Special instrumentation

2.5.3.1 Instruments for titration and element specific electrodes

It is generally required to be equipped for wet chemical analyses for free lime determination, CaCO₃ titration, pH-measurement and in specific cases for chloride or fluoride determination. It is recommended to do this with partially automated titration equipment and appropriate electrodes.

Leading suppliers for such equipment are:

- Metrohm, Switzerland: <http://www.metrohm.com/>
- Mettler-Toledo, Switzerland: <http://ch.mt.com/>
- WTW, Germany: <http://www.wtw.de>

For illustration, the HGRS MT laboratory uses following instrumentation:

pH-measurement:

- Metrohm Titroprocessor Titrando 808 (or Titroprocessor 686); combined pH glass electrode

CaCO₃-titration:

- Metrohm Titroprocessor 686, Dosimat 665
- Metrohm combined pH glass electrode

Cl-titration

- Metrohm Titroprocessor Titrando 808 (or Titroprocessor 686 and Dosimat 665)
- Metrohm Ag Titrode, Ag/AgCl reference electrode

Fluorine-determination

- Metrohm Dosimat 775
- Metrohm pH/Ion Meter 692
- Metrohm ion-selective F-electrode, Ag/AgCl reference electrode

2.5.3.2 Flame photometer

Flame photometry (Figure V- 1) is the reference method for determination of K₂O and Na₂O according to EN 196-21 and ASTM C 114. Note that ASTM also refers to atomic absorption spectrometry (AAS) as a reference method.

Major suppliers of cement testing equipment and general laboratory equipment also supply flame photometers (often not clear what the original manufacturer is) e.g.:

- Toni Technik: <http://www.tonitechnik.com>
Type 9130.145
- Cole-Palmer: <http://www.coleparmer.com/>
- ThermoFisher (Fisher Scientific): <http://www.fishersci.com>

2.5.3.3 Free lime

In addition to the wet chemical free lime determination (reference methods in testing standards) and the XRD-based method, a benchtop laboratory equipment for semi-automated free lime determination is available based on conductivity measurement. In a few Holcim plants this equipment is applied, though it is certainly not a widely applied instrument.

Suppliers and instruments:

- Toni Technik: ToniLIME: <http://www.tonitechnik.com/>
(instrument originally developed by Acmel as FLA 1)
- Acmel, France: <http://www.acmel.com/>
Since 2006 daughter company of Toni Technik, but operating as individual company specifically in francophone countries: Developed and produces FLA1 analyzer (application e.g. in Jerez, Joliette)

2.5.3.4 Sulfur and carbon

Related to the involved common technical concept of sulfur and carbon analyzers (inductive furnace for combustion, infrared detection of CO₂ and SO₂), combined analyzers are often applied.

Price of such an analyzer is in the region of 25 to 40 k€. Major suppliers and equipment are:

- LECO, USA: <http://www.leco.com/>
Sulfur/carbon analyzers SC 144DR (basic instrument), SC 632 (increased degree of automation), CS 230 Series
- Eltra: <http://www.eltragmbh.com/>
Sulfur/carbon analyzers CS 580, CS-2000
Sulfur/carbon/hydrogen analyzer: CSH 580 (application e.g. Hermosillo)
- Horiba Scientific, Japan: <http://www.horiba.com/scientific/>
Sulfur/carbon analyzers EMIA-8100 series
- Analytik Jena, Germany: <http://www.analytik-jena.de>
C/S analyzer 'multi EA' series

2.5.3.5 Trace elements

Determination of trace elements may be a task for normal cement plant laboratory, or it may require the implementation of a specific AFR laboratory, with extended facilities and instrumentation, in particular to deal with different types of alternative fuels.

AAS

The methodology is described in Part VIII of this manual.

Price for an AAS system is starting from 45k€ but can be as high as 80 k€, depending on configuration. Major spectrometer suppliers are:

- Agilent Technology, USA: <http://www.home.agilent.com/>
Took over Varian Inc. and their AAS spectrometer line; actual model series comprise: 55 B AA, 245 FS AA, 240 Z AA (Zeeman; equipment used at HGRS-MT laboratory)
- Perkin Elmer, USA, <http://www.perkinelmer.com/>
PinAAcle product series

- Analytik Jena, Germany: <http://www.analytik-jena.de/>
novAA-series
- ThermoScientific, USA: <http://www.thermoscientific.com/>
Actual models are iCE series (3300, 3400, 3500)
- Shimadzu, Japan: <http://www.ssi.shimadzu.com/>
Actual models are: AA-6200; AA-7000

ICP-OES

The methodology is described in Part VIII of this manual.

Price for an ICP-OES system is roughly 80 – 120 k€. Major suppliers are:

- Agilent Technology, USA: <http://www.home.agilent.com/>
Took over Varian Inc. and their ICP spectrometer line
Actual model series comprise: 710 and 720/730 series ICO-OES; 7700 series ICP-MS
- Horiba Scientific, Japan: <http://www.horiba.com/scientific/>
Took over the Jobin Yvon ICP spectrometer series
Actual models are: Activa and Ultima ICP-OES series
- Perkin Elmer, USA, <http://www.perkinelmer.com/>
Actual models are Optima 7300 and Optima 8x00 ICP-OES series
- Spectro, Germany: <http://www.spectro.com>
Actual models are: Genesis, Spectroblue- and Arrcos- ICP-OES series
- ThermoScientific, USA: : <http://www.thermoscientific.com/>
Actual models are iCAP ICP OES series
- Shimadzu, Japan: <http://www.ssi.shimadzu.com/>
Actual models are: ICPE-series (7510, 9000 and 8100)

2.5.3.6 *Color*

Color meters are used in several cement plant laboratories to monitor the whiteness of white cements or the color shades of grey cement. Instruments are used as stand-alone bench-top instruments or integrated in automated laboratory system. Some suppliers also offer instruments for on-line applications, i.e. to be installed e.g. above conveyor belts.

Major suppliers of colorimeters are:

- Konica-Minolta, <http://www.konicaminolta.com/>
Typical models for cement industry: CM3610A (used at HGRS-MT laboratory); CM-5 (used at Untervaz plant)
- X-Rite, USA [http://www.xrite.com/](http://www.xrite.com)
Typical model for cement industry, used as benchtop instrument or integrated in automated laboratory: SP 62 (applied in lab automation Ste. Genevieve, Lägerdorf, Eclépens)
Model for continuous color monitoring, installation above belt conveyor: TeleFlash

2.5.3.7 *Thermal analysis*

Main suppliers of TGA and/or DSC equipment are:

- Mettler-Toledo, Switzerland. <http://www.mt.com>
Actual models: DSC 1 or combined TGA/DSC 1 (about 60 k€ for basic equipment)
- Perkin Elmer, USA: <http://www.perkinelmer.com>
Actual models DSC 4000, Pyris 1 TGA
- Setaram, France: <http://www.setaram.com>
Actual models: Labsys evo (combined TGA/DSC), Sensys evo DSC

DSC and TGA systems should be checked monthly with special Indium and Aluminum samples (available from supplier). These samples have well known melting temperatures and melting enthalpies (e.g. Indium 156.6 °C, 3.252 kJ/mol). Indium is also used for calibration, if necessary.

2.6 Fuel testing

Instrumentation for testing of traditional fuels – in addition to sample preparation, sieving, weighing (see corresponding chapters) typically involves equipment for determination of gross calorific value and – though less frequently applied in cement plant laboratories - for elemental analyses and moisture/volatiles/ash (sulfur see chapter 2.5.3.4).

Major suppliers and equipment are:

Combustion calorimeter:

- IKA, Germany: <http://www.ika.de/>
Typical model: IKA C 2000 (applied at HGRS_MT laboratory)
- Parr, USA: <http://www.parrinst.com/>
Typical model: Parr 6400
- LECO, USA: <http://www.leco.com/>
Model AC-350

Elemental analyzers; moisture, volatiles, ash

- LECO USA: <http://www.leco.com/>
Wide range of analyzers, notably CHN-900 for carbon, hydrogen and nitrogen, and TGA-601 for moisture, volatiles and ash

2.7 Physical testing

Equipment for physical and mechanical testing of cement, cement paste and mortar properties specified in national cement standards is to a large extent specified in corresponding national standards for cement testing. Usually, they are based or refer to one of the two major standard families, i.e. ASTM- or EN-standards. These standards define the essential, minimum requirements of equipment; furthermore, they may also explicitly allow the use alternative equipment, provided that prove is made that results are matching those from the standard testing equipment (e.g. use of vibrating table versus jolting table for mortar compaction in EN 196-1 and ASTM C 109)

Manufactures and suppliers of testing equipment usually indicate to which standards the testing equipment corresponds, and the may offer basic, reference equipment for certain test, as well as equipment with increased degree of automation, facilities for multiple testing and modern way of data processing and management.

Several companies are manufacturing and supplying equipment for physical and mechanical cement and concrete testing. It is not always transparent for a specific company as to which equipment is actually manufactured by them and for which equipment they are just a distributor, in order to be able to offer a complete range of equipment for testing of cement, concrete, aggregates, rocks, soils etc.

Major manufacturers/suppliers

- (1) Toni Technik (Zwick/Roell Group), Germany: <http://www.tonitechnik.com/>
Globally operating, highly reputed manufacture of wide range of cement and concrete testing equipment; high price segment, but also recognized high quality. Widely applied in Holcim group.
- (2) ELE, UK: <http://www.ele.com/>

Globally operating manufacturer of complete range of cement and concrete testing equipment. Lower price segment. Widely applied in Holcim group, though both with satisfactory and unsatisfactory feedback on quality.

- (3) Humbold, USA: <http://www.humboldtmfg.com/>
Highly reputed supplier/manufacturer of complete range of cement and concrete testing, with focus on ASTM standard testing, mainly covering market of US other ASTM-oriented countries.
- (4) Walter und Bai, Switzerland: <http://www.walterbai.com/>
Supplier of complete range of cement and concrete testing equipment, manufacturer of reputed, high quality hydraulic presses. Presses fairly wide applied in Holcim group
- (5) Testing Bluhm & Feuerterdt GmbH, Germany: <http://www.testing.de/>
Relatively new company (spinoff from Toni Technik), also elaborating taylor-made solutions.
Supplier of complete set of cement and concrete testing equipment.
- (6) Ibertest, Spain: <http://www.ibertestint.com/>
Globally operating supplier/manufacturing of complete range of cement and concrete testing equipment. Limited application in Holcim group
- (7) Matest, Italy: <http://www.matest.com/>
Supplier/manufacturer of complete range of cement and concrete testing equipment.
- (8) LBG srl Testing Equipment, Italy: <http://www.lbgsrl.com/>
Supplier/manufacturer of complete range of cement and concrete testing equipment.
Manufacturer of automatic penetrometer for paste and mortar
- (9) Controls, Italy: <http://www.controlsgroup.net/>
Supplier/manufacturer of complete range of cement and concrete testing equipment.
- (10) ZEB Zündерwerke Ernst Brüm GmbH, Germany: <http://www.zeb-maxam.com/>
Supplier of automated Blaine apparatus PC-Blaine-Star

Major supplier of laser granulometers are:

- (11) Malvern, UK: <http://www.malvern.com/>
Manufacturer of benchtop laser granulometers (e.g. Mastersizer 2000) and of in-line laser granulometers (Insitec).
- (12) Sympatec, Germany: <http://www.sympatec.com/>
Manufacturer of benchtop laser granulometers (HELOS systems) and “industry” versions (MYTOS systems) for on-site installation or for laboratory automation systems
- (13) Cilas, France: <http://www.cilas.com/>
Manufacturer of benchtop laser granulometers (wet- and dry-dispersing), e.g. model 1090
- (14) Fritsch, Germany: <http://www.fritsch.de/>
Manufacturer of benchtop laser granulometers (wet- and dry-dispersing), Analysette models

The following tables presents a list of major equipment used for physical and mechanical testing of cement, cement paste and mortar. Minor equipment is not listed here, but in Annex V-2 a generic list – prepared on courtesy by ELE – for a complete set of equipment and tools is presented.

Blaine specific surface	Manual Blaine apparatus	EN 196-6; ASTM C 204	1, 2, 3, 4, 5, 6, 7, 8, 9
	Automated Blaine apparatus Widely applied and recommended equipment to facilitate operation and data handling. Instruments are available that are built according to standard specifications (using small sample quantity) and instruments using larger sample volumes, more convenient for routine applications (Dyckerhoff system)		1, 2, 4, 5, 6, 7, 8, 9

	Ex.: ToniPerm; built according EN and ASTM standards (see Figure V- 1) ToniPerm Dyckerhoff, not strictly standard conform, as larger cement volumes are used. Widely applied for routine application PC-Blaine-Star	EN 196-6; ASTM C 204	10
	Wagner turbidimeter	ASTM C115	3
Setting time	Vicat apparatus, manual	EN 193-3; ASTM C187/191/472	1, 2, 3, 4, 5, 6, 7, 8, 9
	Vicat apparatus, automated, for single measuring cell Vicat apparatus, automated, for 6 – 8 measuring cells, circular set-up (e.g. ToniSET Compact Proven, widely applied equipment. Further options: Equipment with 6 or up to 12 measuring cells, linear set-up (e.g. ToniSET Classic; built by Acmel; see chapter 2.5.3.3)	EN 193-3; ASTM C187/191/472	1, 2, 3, 4, 5, 6, 7, 8, 9
	Gillmore apparatus	ASTM C 141/266	1, 2, 3
Workability	Flow table	ASTM C 230/1437	1, 2, 3
Soundness	Le Chatelier mold and Le Chatelier water bath	EN 196-3	1, 2, 4, 5, 6, 7, 8, 9
	High pressure autoclave	ASTM C 151	1, 2, 3, 4, 5, 6, 7, 8, 9
Mortar preparation	Mortar mixer (basic)	EN 196-1; ASTM C 305	1, 2, 3, 4, 5, 6, 7, 8, 9
	Mortar mixer with extended facilities (automated dosage of sand and water, etc) E.g. ToniMIX		1, 2, 4, 5, 6, 7, 8, 9
Molds	Triple molds, prisms	EN 196-1	1, 2, 5, 6, 7, 8, 9
	Triple molds cubes	ASTM C 109	1, 2, 4, 5, 8, 9
Compaction	Jolting apparatus (reference method EN 196-1)	EN 196-1	1, 2, 4, 5, 6, 7, 8, 9
	Vibration table (accepted alternative EN 196-1)	EN 196-1	1, 2, 4, 5, 6, 7, 8, 9
Storage	Climatic storage chamber (humidity cabinet) Chambers for storage of mortar prisms at controlled temperature and humidity acc. Standard requirements. Different sizes for storage of 16 and more triple molds	EN 196-1	1, 2, 4, 5, 6, 7, 8, 9
	Wet storage tanks	EN 196-1	1, 2, 4, 5, 7, 8, 9
Mortar strength	Hydraulic press for compressive strength testing Basic models Equipment with different capacities are offered, typically 200, 250, 300 kN (300 kN is recommended) E.g. ToniZEM (typical for EN 196-1) Humbold HMC-1000 series (for ASTM C 109)	EN 196-1 ASTM C 109	1, 2, 4, 5, 6, 7, 8, 9
	Hydraulic press for compressive strength testing Various models with extended facilities, e.g. bend testing, different control systems etc E.g Toni Technik ToniPRAX		1, 2, 4, 5, 6, 7, 8, 9,

Heat of hydration	Calorimeter (solution method)	EN 196-8; ASTM C186	1, 2, 3, 5, 6, 7, 8, 9
Laboratory furniture			1 2, 4

Table V- 3: Equipment for standardized testing

Balances	Precision balances for 0 – 400 g 0 – 6 kg 0 – 15 kg		See chapter 2.2.2
Thermohydrograph	Thermohydrograph to record temperature and humidity in laboratory		
Setting/workability	Flow table		1, 2, 3, 5, 6, 7, 8, 9
	Automatic Penetrometer The equipment allows to continuously measuring the progressive consistency increase of cement paste (or similar material). This is a very useful, non-standard method providing valuable information on the setting behavior of cement. Only manufactured and supplied by LBG; model M028		7
	Holcim cone Method to determine mortar flow		HGRS
Heat of hydration	Differential calorimeters E.g. ToniCal		1
Particle size distribution	Laser granulometers Laser granulometers are widely applied for cement optimization purposes, but increasingly also for routine quality control of cement fineness, both as stand-alone equipment or integrated into central laboratory automation systems. Furthermore in-line systems for quasi real-time psd-monitoring are available and applied in several Holcim group companies. Today, primarily dry-dispersing laser granulometers are used; the alternative is the wet-dispersing system with ethanol or water as dispersing medium		

Table V- 4: Non-standardized methods and additional equipment

 A stainless steel mobile balance with a digital control panel and a weighing platform.	 A stainless steel riffle splitter with multiple parallel blades used for sample division.
Mobile balance	Riffle Splitter
 A white flame photometer unit with a digital display showing '-000' and several control knobs.	 A grey-toned free lime analyzer unit with a red control panel and a small display screen.
Flame photometer	Free lime analyzer ToniLIME

Figure V- 1: Various laboratory equipment

Part VI: Automated Quality Control Systems

Automated analyzer systems have become increasingly important for process control in recent years. Systems for nearly all stages in the cement production process have been developed (and are still under development). The objective of this chapter is to give an overview on applied techniques, suppliers and their available products.

The terms on-line, at-line, etc. are not always consistently used. The following definition is based on the proximity of the test method to the production process in space and time [Lit 10]. It is used throughout this manual:

- *At-line*: Fully automated analysis in the central plant laboratory with manual or automated sampling. Example: Particle size analysis of cement in central, automated laboratory.
- *On-line*: The measuring device is placed close to, but not in, the production line. Fully automated sampling and sample transport. Example: Particle size analysis with laser granulometer installed at the cement mill.
- *In-line*: Continuous (real-time) measurement of material properties, the measurement device is directly placed in the process. No sampling required. Example: PGNAA, emission monitoring

1. Automated bulk material analysis with PGNAA

Analyzers based on Prompt Gamma Neutron Activation (PGNA) technology have become the state-of-the-art tool for real-time elemental analysis of bulk materials. While first commercial systems were available already in 1985 (chute-type analyzer from GammaMetrics, now Thermo Fisher) they suffered from high investment costs, large space requirements and cumbersome calibration procedures. Only after introduction of cross-belt arrangements in 1995 the PGNA units gained widespread acceptance. As of 2012 a total of 76 units were in operation in Holcim plants (see Figure VI- 1), 51 for stockpile control and 25 for raw mix control.

PGNAA units in Holcim

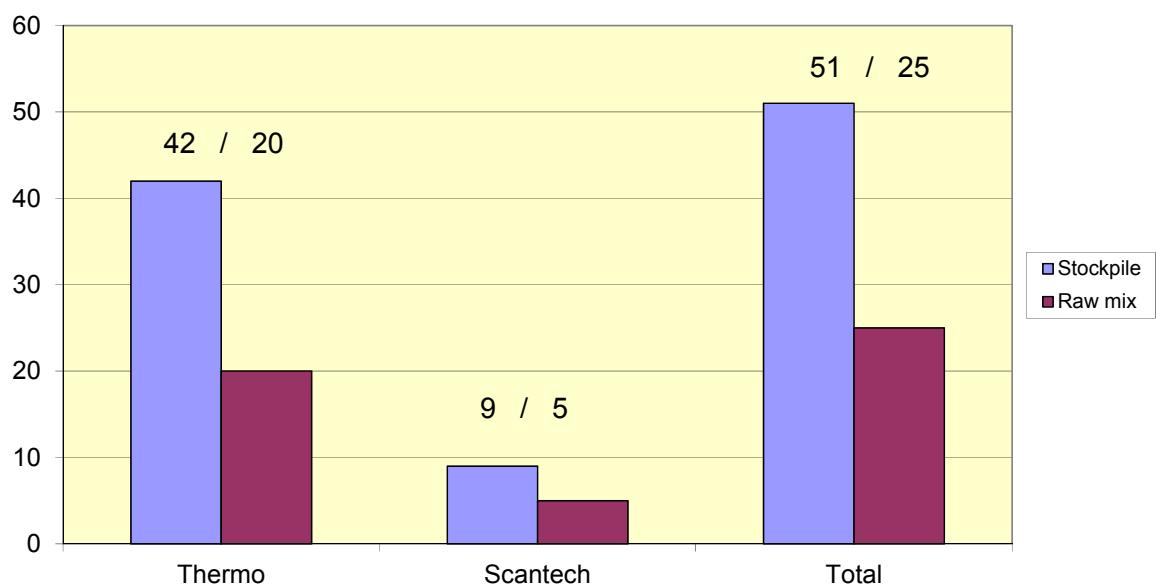


Figure VI- 1: Installed PGNAA units in Holcim plants as of 2012 (suppliers: Thermo and Scantech)

PGNA technology allows measuring the elemental composition of bulk materials such as raw materials, minerals and coal. In contrast to XRF analysis, it can analyze the full material stream in real-time and does not need sampling nor sample preparation.

1.1 PGNAA principles

The bulk material is irradiated with neutrons from an appropriate source. The neutrons interact with nuclei of the elements leading to excited, unstable states which release gamma radiation on decay (Figure VI- 2). The emitted gamma radiation is characteristic for each individual element. The predominating physical process with commercial PGNAA systems is called thermal neutron capture; it requires thermal neutrons with an energy of less than 1 eV.

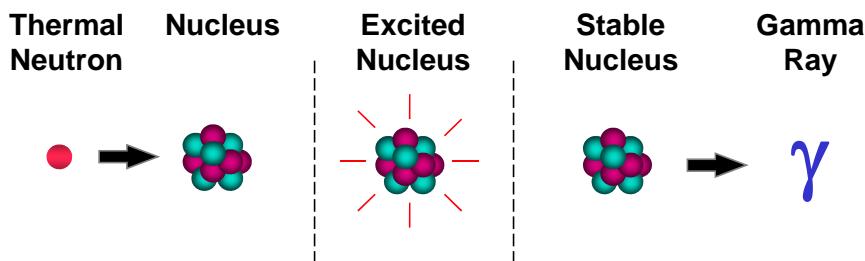


Figure VI- 2: Generation of characteristic gamma-rays by neutron activation

Due to the highly penetrating nature of neutrons and gamma radiation, the full material depth is analyzed. Not every element has the same efficiency in absorbing thermal neutrons; the efficiency is a function of the Barnes cross section. This results in different detection levels for the individual elements. Sensitivities of elements relevant to cement industry are given in Table VI- 1.

Sensitivity in weight%	Elements
< 0.01%	Cl
0.01 – 0.1%	S, Fe
0.1 – 0.3%	Na, Al, Si, K, Ca
0.3 – 1.0%	Mg, P

Table VI- 1: Three sigma detection limits in 10 minutes within an elementally simple rock matrix > 150 mm thick.

Note the low sensitivity for Phosphorus. In the cement industry concentrations of usually lower than 0.5% P_2O_5 are observed. PGNAA technology is presently not the appropriate choice for controlling this element. On the other hand sensitivity of Cl is extremely high and leads to large signals (already at low concentrations) interfering with other elements. Therefore Cl containing materials (e.g. PVC) have to be avoided for conveyor belts running through the PGNAA installation.

1.2 Suppliers

Holcim has three officially approved suppliers for PGNAA's. A compilation of their current systems is shown in Table VI- 2 below:

- *ThermoFisher Scientific*: Thermo is the main supplier of PGNAA's in Holcim (2012: 63 out of 77 units, see Figure VI- 1). Formerly named GammaMetrics and later Thermo Electron, the company has been integrated into the international Fisher Scientific group in 2008. ThermoFisher developed and brought to market the first analyzer based on neutron activation in 1985. Headquarters are located in San Diego, CA while the analyzers are manufactured in Adelaide, Australia. Service and development is supported by around 100 employees. In 2006, Thermo Electron acquired ASYS which was a competing supplier of PGNAA's. Holcim purchased 7 units from ASYS before the merger; these units are now supported by Thermo.
- *Scantech*: Scantech is a relatively small company based in Adelaide, Australia where they also manufacture their analyzers. They sold 13 units to Holcim plants, mainly in the eastern European region. Scantech employs around 25 people for development and support of PGNAA. Most of Scantech PGNAAs have been sold to coal industry.

- Sodern:** Sodern is part of the EADS Company being the largest aerospace company in Europe. Headquarters and production are located in Limeil-Brévannes near Paris. Sodern uses neutron generation tubes instead of ^{252}Cf as a neutron source. To this date there is no Sodern analyzer in operation in Holcim plants, but two systems were recently sold to Holcim group plants (2012, Costa Rica and Mexico). Since 2010 Panalytical is the global distributor for Sodern systems and also provides technical support.

	ThermoFisher	Scantech	Sodern
First sell to cement market	1985	1994	1998
Installation worldwide (2009)	> 320	Ca. 80	Ca. 30
Latest generation (2012)	CB-OMNI	GEOSCAN-C UCG (MK IV)	CNA Gen III
Neutron source	^{252}Cf / Neutron tube possible	^{252}Cf	Neutron generation tube
Detector type	Nal	BGO	BGO
Weight (1200 mm belt)	3.8 t	3.4 t	5.5 t
Conveyor belt sizes	600 – 1800 mm	600 – 2020 mm	650 – 2000 mm
Price (approx.)	300'000 Euro	250'000 Euro	250'000 Euro

Table VI- 2: Comparison of different PGNAA suppliers and their current systems

Sabia is a fourth supplier of PGNAA analyzer offering with ^{252}Cf source. Sabia is mainly present in North America and has only few systems installed in cement industry (7 as per end of 2010), but considerably more in coal industry. There are no installations in Holcim plants; however, a supplier evaluation at HGRS has been initiated. SMA (ScanMin Africa) is a fifth supplier of PGNA analyzers (using an Am-Be neutron source) who recently appeared, but they seem to be more focused on mining industry.

1.3 PGNAA hardware

A typical configuration of a PGNA analyzer is shown below (Figure VI- 3). Details can vary between the different suppliers.

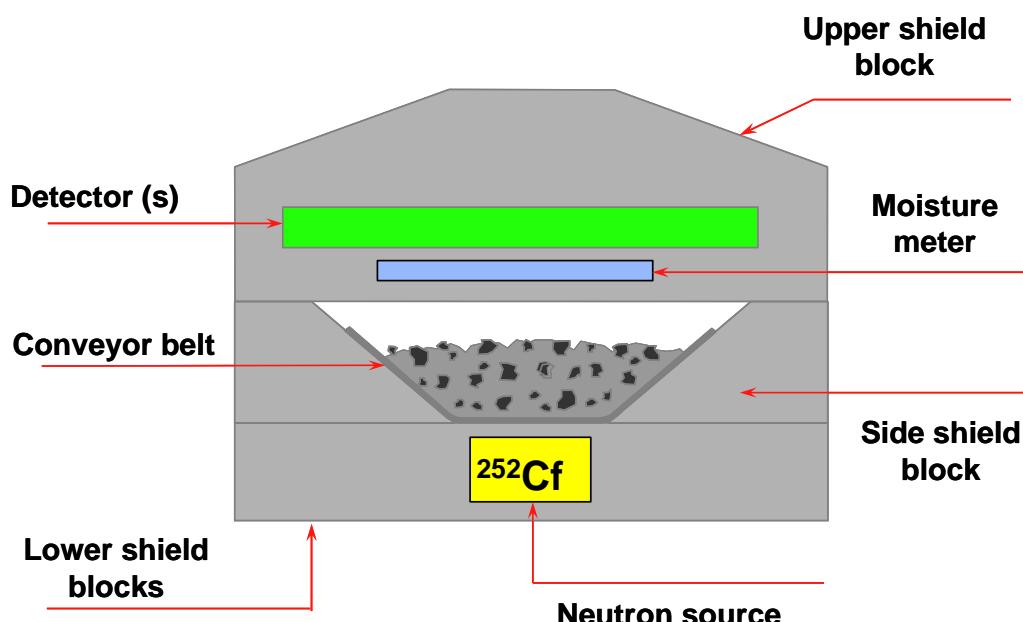


Figure VI- 3: Typical components of a PGNA

A description of the most important parts is given below:

Neutron source:

Two types of neutron sources are mostly applied in PGNA analyzers:

- **252-Californium isotope:** The radioactive 252 isotope of Californium is synthetically produced in nuclear reactors. Spontaneous fission of ^{252}Cf atoms produces relatively slow neutrons of 2.1 MeV energy. The half life time of this isotope is 2.65 years. Thus, about every 2.5 years a source top-up of half the amount installed is required. For a typical application between 30 and 70 μg ^{252}Cf are installed. As of 2012, the price for a 19 μg source top-up is in the range of 21 to 30 kUSD (source: Thermo).
- **Neutron tubes:** By accelerating Deuterium (^2H) onto a Tritium (^3H) target highly energetic neutrons (approx. 14MeV) are generated. In contrast to ^{252}Cf this process is not continuous but can be controlled (on/off feature). Sodern (see Table VI- 2) uses exclusively neutron tubes for their analyzer. The latest generation of the Thermo analyzer is now also available with neutron tubes. The lifetime of a tube used to be around 8000 h, the latest generation tubes (from Sodern) are claimed to last more than 15'000 h. Price of a neutron tube is around 35'000 Euro.

Also the combination of $^{242}\text{Americium}$ and Beryllium is used as neutron source for neutron activation (only reference: ScanMin analyzer). This source has a much longer half-life time than ^{252}Cf (about 430 years) and would thus not need any source top-up. However, the initial amount of source to get the same neutron flux as ^{252}Cf is about 10 times higher (and makes the equipment more expensive).

Detectors:

The detection system converts the gamma radiation into an electronic signal which is processed with a computer to yield the elemental composition. Detectors consist of scintillation crystals and photomultiplier tubes. There are two types of materials used for scintillation crystals:

- Sodium Iodide (NaI), used by ThermoFisher (and Sabia)
- Bismuth Germanate (BGO), used by Scantech and Sodern

NaI crystals are bigger in size than BGO crystals. Both types are acceptable. A typical PGNAA has 2-4 NaI detectors (Thermo) or 4-8 BGO detectors (Scantech), depending on the required analytical performance.

Shielding blocks

Shielding is required to protect the environment from harmful radiation. The shielding blocks are usually made from polyethylene or polypropylene, sometimes modified with boron compounds. In addition, the blocks act as neutron moderator in order to slow down neutrons for efficient neutron capture. The blocks make significant contributions to the total weight of the analyzer. This is particularly the case for systems using neutron tubes (Sodern), which produce higher energetic radiation.

The shielding blocks come in different modules, making on-site assemblage relatively easy. Installation of a modern PGNA unit does not require cutting of the conveyor belt.

ThermoFisher applies wear plates between the lower shielding blocks and the conveyor belt which need to be replaced periodically. In Scantech systems, there is no contact between conveyor belt and analyzer, but the gap between belt and lower shielding blocks needs to be periodically cleaned from dust.

Moisture meter

The PGNAA suppliers use different technologies for moisture determination. Scantech uses microwave technology which is a separate unit and not integrated into the analyzer. ThermoFisher includes a Helium-3 neutron detector in the analyzer (He-3 detectors count thermalized (slow) neutrons; the count rate is directly proportional to moisture). Sodern bases moisture analysis directly on the Hydrogen (γ -ray) signal. The moisture meter in Scantech and ThermoFisher systems is an optional feature.

Electronics

The electronics cabinet provides means for data accumulation and processing as well as communications with the operator consoles. It is a separate unit installed close to the analyzer.

1.4 PGNAA performance

Following tests are established to measure the performance of a PGNAA (see Annex VI-1 for detailed description):

- *Static repeatability*: A synthetic standard is analyzed over 300 min, the minute by minute elemental analyses are combined to 10-min block averages. The standard deviation of these 30 values (for each element) is a measure of the signal stability of the analyzer.
- *Static accuracy*: Compares PGNAA results (1 hour block average) of the synthetic calibration standards (typically five standards) to the actual chemical composition of the standards, as given by the supplier.
- *Dynamic accuracy*: Compares PGNAA results from actual production with the plant laboratory XRF analyses of the same material. This requires representative sampling of raw meal and an appropriate back-calculation to the material which has passed the analyzer (considering time delay, added correctives, kiln dust, etc). Typically 7 piles or 48 h of stable kiln/raw mill operation is required for dynamic accuracy testing. Depending on the type of PGNAA application the dynamic accuracy is also called stockpile accuracy and mill feed accuracy respectively.
- *Dynamic Blending Accuracy*: Although not strictly a PGNAA performance guarantee, this parameter measures the ability of the control software in use to convert the results of the PGNAA into controlled material feeding set-points to desired chemical targets. For details see section VI-9 below.

The PGNAA suppliers are requested to provide guarantee figures for each of these performance tests. The guarantees will be verified on commissioning. Before the dynamic accuracy guarantee can be verified, a dynamic calibration is required (see below).

The repeatability performance is specific for each element. The following factors have an impact on the repeatability:

- Barns cross section: Given for each element, cannot be influenced.
- Amount of installed ^{252}Cf : More ^{252}Cf gives better repeatability. Due to decrease of source strength, the repeatability deteriorates over time. This is not the case for neutron tubes.
- Number of installed detectors and detector efficiency (type of detectors).
- Tunnel opening (distance between detectors and material surface): The tunnel opening is selected as a function of the granulometry of the material on the belt. Smaller particle size allows for lower tunnel opening and better repeatability.
- Belt load: The material thickness is expressed in kg/m and results from mass flow (t/h) and belt speed (m/s). The higher the belt load the better the repeatability (see Figure VI- 4).
- Acquisition time: Longer acquisition time improves repeatability; e.g. an increase from 1 min to 10 min acquisition time improves repeatability by a factor of 3.2.

Experiences have shown that sufficiently high belt load is crucial for good PGNAA performance. A belt load of 50 kg/m is considered as the absolute minimum requirement for PGNAA operation. The loss on repeatability is not a linear function of the belt load (see Figure VI- 4).

Besides a minimum belt load, also a uniform distribution of the material on the belt is required (i.e. constant belt loading and distribution). Some supplier (ThermoFisher, Scantech) can compensate for belt load fluctuations using special calibration procedures. Asymmetric (lateral or longitudinal) distribution of material on the belt can also impact performance.

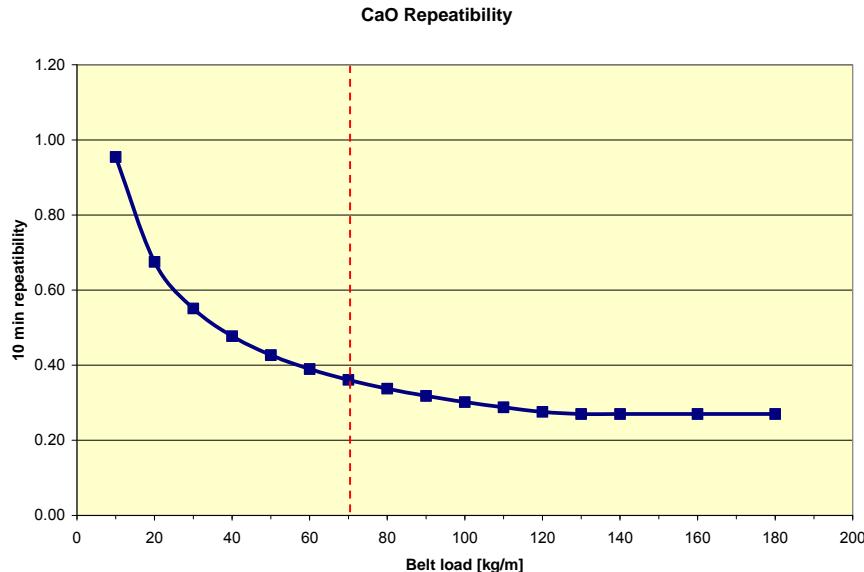


Figure VI- 4: CaO 10 min repeatability as a function of belt load.

Special attention is needed when the material on the belt is present in different layers. If these layers differ in moisture content (difference > 15%), biased chemical analyses will result and a pre-homogenization of the bulk material is required (e.g. through a vertical drop or chute).

The accuracy is mainly a function of the calibration range. The larger the requested calibration ranges the lower the accuracy. A stockpile application needs generally a larger calibration range than a raw mix application. However, also layering and belt load variations will affect accuracy.

1.5 Calibration

On delivery PGNAA analyzers are pre-calibrated in the requested elemental range. On-site procedures include a static and a dynamic calibration:

- *Static calibration* is actually not a real calibration, but only a verification or gain/offset correction of the factory calibration. Static calibration includes verification of static repeatability and static accuracy. Synthetic calibration standards (manufactured by the supplier) are used; they are typically packed in plastic bags, each containing around 2-3 kg (see Figure VI- 5). The bags are placed in the tunnel of the analyzer and then measured while the belt is stopped. Different belt loads can be simulated by variation of numbers of bags placed on the belt. Besides the (typically five) synthetic calibration standards, it is recommended to prepare and use two additional standards from plant specific material.
- *Dynamic calibration* adjusts PGNAA analysis to the plant own XRF analysis (back calculated from raw meal analysis) using the concept of dynamic accuracy testing (see previous section). Dynamic calibration is often more complex for a stockpile application than for a raw mill application. Reference procedures for both stockpile and raw mill applications are given in Annex VI-1. Under certain circumstances PGNAA and XRF results cannot be correlated, e.g. when the material flow cannot be tracked due to complicated transport, which makes dynamic calibration very difficult.



Figure VI- 5: Calibration standards used for static calibration

Calibrations should be verified regularly (approximately every 2 months, or upon experience), since analyzer drifts can occur.

1.6 Applications

PGNAA analyzers are either used for stockpile control (analyzing the material stacked on the pre-blending stockpile) or for raw mix control (analyzing the raw meal feed). The majority of PGNAA installations in Holcim are for stockpile control (see Figure VI- 1), but with the improved analytical performance available today, raw mill applications are becoming equally important.

1.6.1 PGNAA for stockpile control

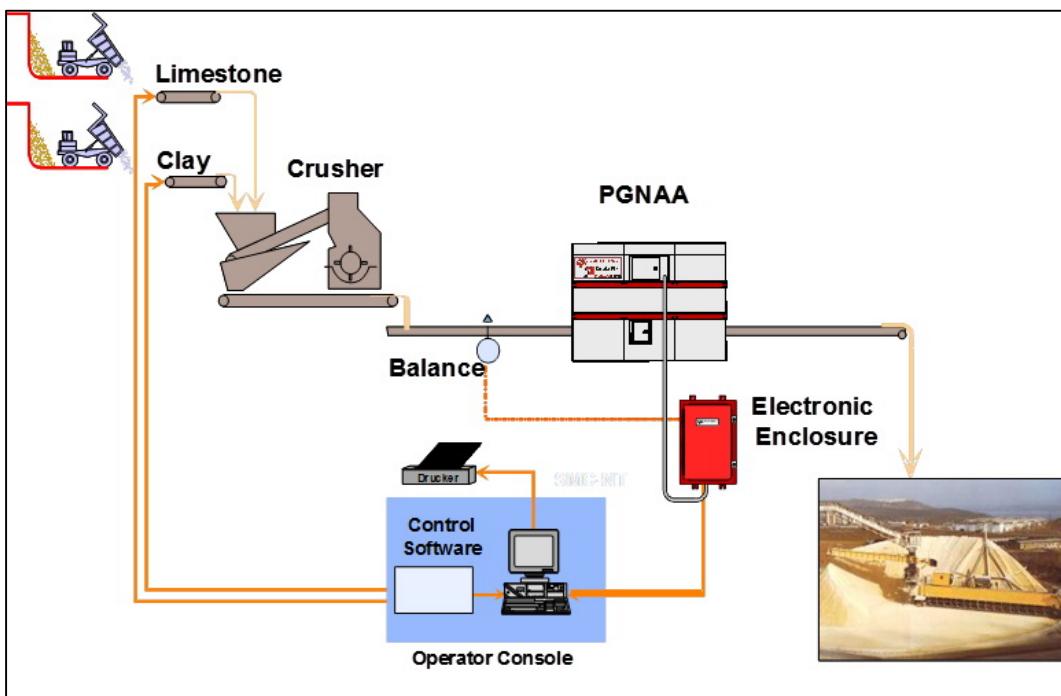


Figure VI- 6: PGNAA controlling the feeder settings at the crusher

The PGNAA is installed between the crusher and the pre-blending bed. The two common setups are:

- Monitoring: The PGNAA continuously monitors the stockpile composition. Depending on the results, the crusher/quarry operator can schedule the subsequent dump trucks with appropriate material quality.
- Control: Different raw materials (e.g. limestone and clay, see Figure VI- 6) can be dosed to the crusher with separate apron feeders. Blending software reads the PGNAA results and calculates the optimal feeder settings to achieve the desired stockpile composition.

Compared to raw mix analyzer, stockpile analyzers typically are operated with lower ^{252}Cf amounts (30-40 μg), but with higher belt loads (100 kg/m and more).

1.6.2 PGNAA for raw mix control

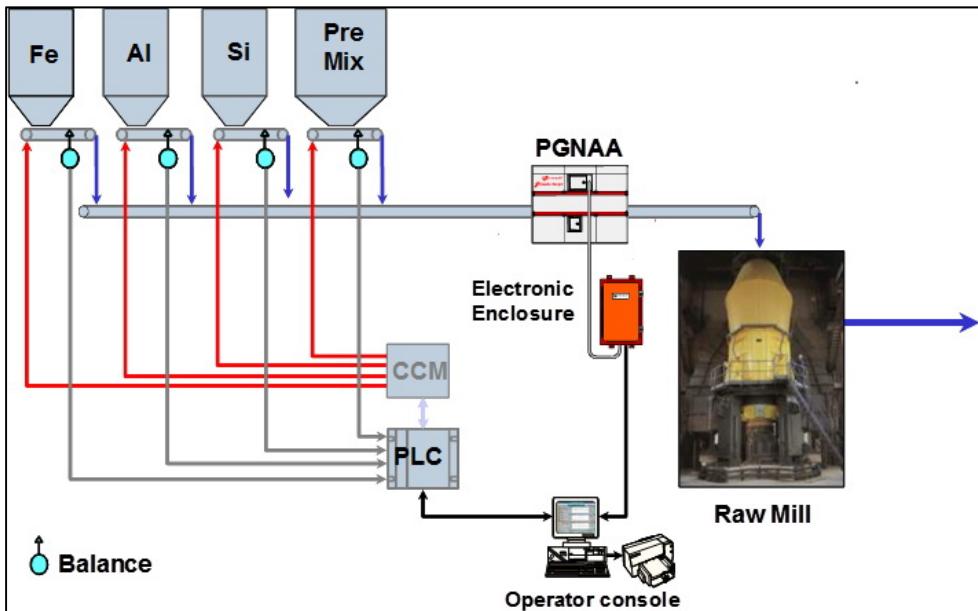


Figure VI- 7: Raw mill PGNAA application

The raw mix analyzer is installed on the conveyor belt feeding the raw mill, shortly after the weight feeders. The feeder setpoints are directly controlled by the PGNAA with blending software (see paragraph 9. Blending software) to achieve the desired raw meal composition.

1.7 ^{252}Cf : Safety and supply aspects

^{252}Cf is a radioactive element and thus presents a safety hazard in the plant. Industrial PGNAA's are designed to protect plant personnel from hazardous radiation levels. Shielding blocks reduce dose levels to typically <20 $\mu\text{Sv/h}$ in accessible areas. Special attention is needed when the area below the analyzer is accessible, where the radiation levels are higher. The analyzer tunnel must not be entered by plant personnel when the source is installed. Manipulation of sources (e.g. on replacement) must only be done by trained service engineers from the PGNAA supplier.

Even though approaching the analyzer during operation is safe, it is still highly recommended to control the accessibility to the analyzer area (e.g. with a housing that can be locked). This is mandatory when the analyzer is located in publicly accessible areas, such as quarries.

Special permits are required from local environmental authorities to operate a PGNAA analyzer. Transport of radioactive material also needs special permits and is normally carried out by special transportation companies. In addition, clearance at customs (on importing ^{252}Cf) often requires special documents. It is noted that the administrative tasks related to ^{252}Cf have become more

complex and time-consuming in recent years – depending heavily on the country. The process of ordering, delivery and installation of a ^{252}Cf source top-up typically takes 2 – 6 months.

Systems with neutron tubes should in principle provide less administrative hurdles, but according to experiences from competitors (Italcementi, Schwenk) this is not the case (see [Lit 13]).

2. New technologies for automated analysis of bulk material

2.1 Automated analysis of blast hole dust with LIBS

In May 2009, Thermo Scientific announced a device to analyze drill cuttings from blast hole drilling in real-time. The system is based on the technique of laser induced breakdown spectroscopy (LIBS). A short laser pulse focused on the material stream creates a local plasma which emits upon cooling element-specific radiation. The emitted radiation is detected and analyzed with a built-in spectrometer to give the elemental composition of the material passing the laser beam. Apart from the excitation method by laser pulses the technique is similar to other emission spectroscopy (e.g. ICP-OES). The laser pulse is triggered several times per second. Signals are accumulated over several laser pulses in order to obtain a better signal to noise ratio.

The analyzer is directly mounted on the drill rig. The spectral data is transmitted over a wireless connection to the data processing/ analysis unit (located for example in the quarry office). A schematic drawing is given in Figure VI- 8 below. Figure VI- 9 shows a test installation mounted on a drill rig.

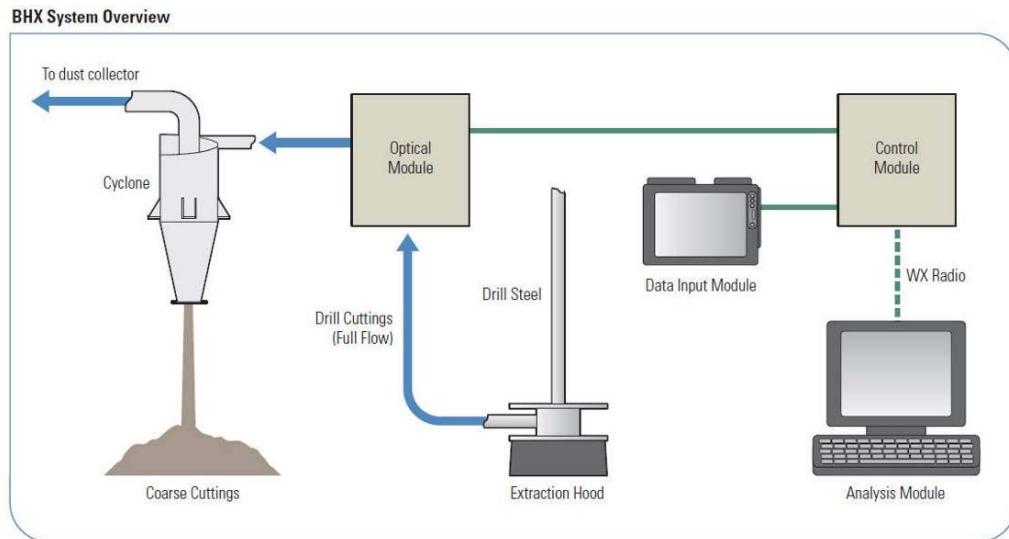


Figure VI- 8: BHX schematics

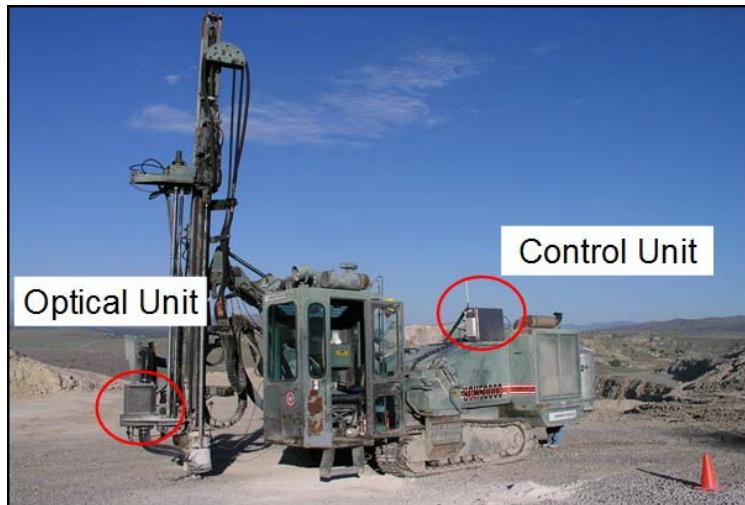


Figure VI- 9: BHX installation on drill rig

The equipment is technically well advanced and has been tested extensively at a site of Holcim US. Some feedback that was received on the analyzer performance:

- Analyzed elements are SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O and Na₂O
- Accuracies in the range of 0.02 to 0.8 % RMSD were achieved, depending on the element. (SiO₂ being one of the weakest elements)
- Concerns still exists on
 - Efficiency of the homogenizer (mixing air, dust and drill chips), which is crucial in order to have a representative material flow passing the laser beam
 - Ability to handle moist and sticky material (clogging of optical window and homogenizer)
 - Handling of inhomogeneous materials with different hardness: Drilling through hard material takes more time than drilling through soft material; the analytical regime is, however, time sensitive and not mass flow sensitive.

ThermoFisher stopped development of the BHX system and put the project on-hold in mid-2011. It is currently not commercially available. Due to the weak economy, ThermoFisher was not able to sell the equipment. Economic feasibility is thus not yet proven.

A very similar analyzer has independently been developed by the University of Aachen together with the Fraunhofer Institute [Lit 11]. It is available through Atlas Copco. The equipment was tested at the Dotternhausen quarry showing reasonable correlation between online analyzer and XRF [Lit 12].

In summary, LIBS is not an established technology, but considered promising for the future.

2.2 Automated bulk material analysis with infrared

In 2007, ABB has presented a new product called SpectraFlow for inline analysis of bulk materials. The technology is called SOLBAS, meaning 'Safe OnLine Bulk Analysis System'. Main driver for the development was to provide an alternative to PGNA technology which does not use radioactive components and thus can be installed without special permits. The analyzer is installed above a conveyor belt (see Figure VI- 10)

The analytical measurement is based on Near Infrared (NIR) technology. The bulk material passing the analyzer is irradiated with bright light. The resulting reflectance spectrum contains information on chemical bonds within the analyzed minerals. The relation between reflectance spectrum and the elemental composition of the bulk material is established with a series of up to 30 plant-specific calibration samples by multiple linear regressions.

Weaknesses arising from IR technology are:

- Non-penetrating radiation, i.e. only the surface of the material stream is analyzed. This renders the technology unsuitable when layers of different material qualities are present on the belt.
- Robustness of calibration in case the mineralogical composition of the bulk material varies.

Test installations were evaluated at Untervaz (UV) and Devil's Slide (DS) for stockpile control. The UV installation has been removed due to insufficient analytical performance. The analyzer at the DS plant performed satisfactory, but was not purchased since DS already has a PGNA installed.

The technology can in principle be used for coarse raw materials, taking the mentioned weaknesses into account, and also for powdered materials (raw meal, kiln feed, cement) or clinker. Since 2011, the "SpectraFlow for Airslides" is available for real-time analysis of powders in airslides. Potential application is control of raw meal (after raw mill, existing) or control of cement after cement mill (under development by ABB).

The SOLBAS technology is not recommended for coarse bulk material and cannot replace PGNA systems. Application to powdered and homogeneous materials is however considered more promising. Price-wise the SOLBAS system is equal or more expensive than PGNA (e.g. SpectraFlow for Airslides: CHF 400'000 budget price).

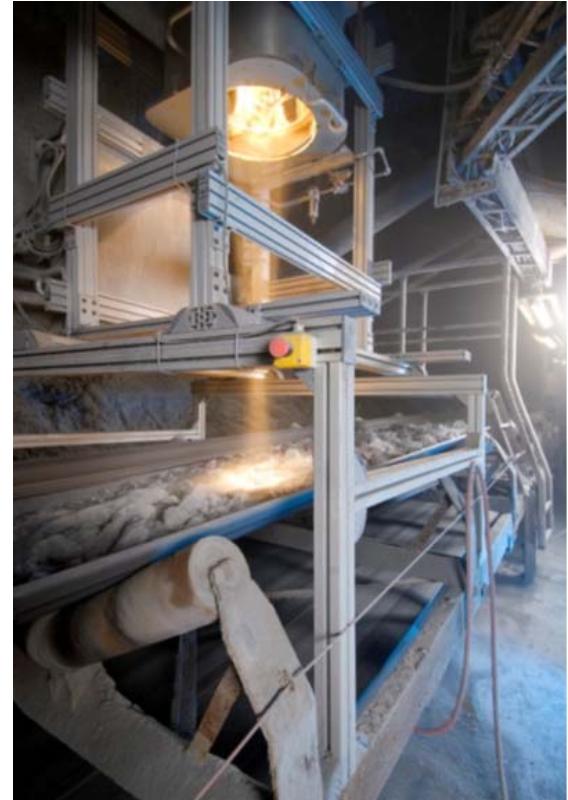


Figure VI- 10: SpectraFlow testing installation for stockpile control in Untervaz

3. On-line XRF for raw mill control

On-line XRF systems are locally (i.e. close to the raw mill) installed XRF spectrometers with an automated sampling and sample preparation system. The systems provide raw meal analyses in high frequency. A sample throughput of around 6-7 samples per hour can be achieved. Blending software then uses the analyses to control the set-points of the raw mill weigh feeders. On-line XRF systems are part of a decentralized quality control setup (refer to part III of this manual). Figure VI- 10 shows a typical setup.

On-line XRF systems typically employ low powered EDXRF systems, which are less accurate than laboratory WDXRF systems.

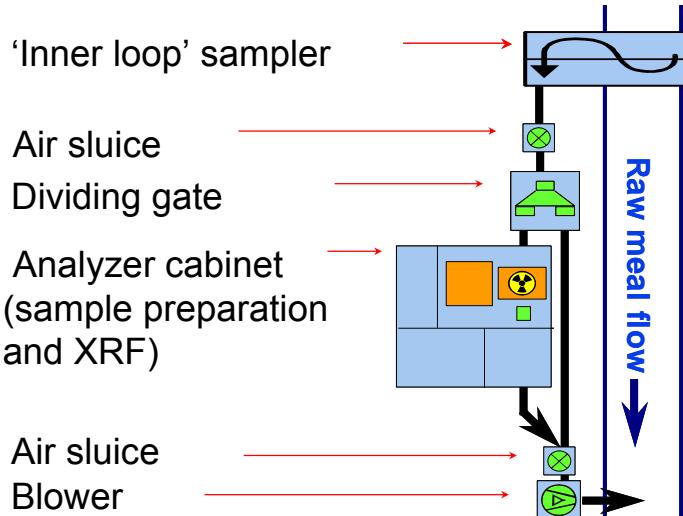


Figure VI- 10: Schematic drawing of an on-line system for raw meal analysis

Different systems from different suppliers with different capabilities and features have appeared and disappeared over the past 20 years. Only a few systems were installed in Holcim plants and even less systems are still in operation today. The most known systems are:

- **AOT (Polysius):** Includes a sampling device, a grinding unit, a tablet press and an EDXRF spectrometer. Polysius AOT systems are installed in Holly Hill (HH) and Joliette (JO). The HH system is still in operation (with good experiences); the JO system was never running properly. Polysius has stopped further development in 2009; the AOT is no longer produced.
- **QCX/OnStream (FLS):** Modular system consisting of a sampling unit and the analytical module OLX900 (tablet press and a Panalytical EDXRF spectrometer). A grinding module is optionally available. FLS systems are installed at the Moni (Cyprus, no longer part of Holcim) and the Rohoznik (RN) plant.
- **FX3500 (ITECA):** Includes a grinding unit (ring mill), vibratory compaction and an Oxford EDXRF spectrometer. ITECA systems are installed at the Theodore and Mason City plants. The installation at the Altkirch (AL) plant was removed due to unreliable mechanics of the system.

The investment for an online XRF system costs around 250 to 500 k€, depending on the configuration, type and supplier.

Online XRF systems for raw meal control were never very popular and are not widely applied in Holcim. For new plants, PGNAA control in combination with a central laboratory is the recommended solution. A central laboratory is much easier to maintain and supervise than (several) local analytical units in the process. Online XRF analyzers may be considered when application of PGNAA is not possible (e.g. due to space restrictions in existing plants).

4. On-line free lime analysis

The French company ITECA offers a system for on-line free lime analysis of clinker. The system consists of an automated clinker sampler, a sample preparation unit (grinding with a vibration mill) and an analytical unit (see Figure VI- 11 below). The analytical unit consists of a balance, an electrode and a robot arm moving the sample/beakers between different positions.



Preparation unit

Analysis unit

Electrical Unit

Figure VI- 11: Automated free lime analyzer from ITECA (front view). System dimensions 2m x 0.9m x 1.9 m.

The free lime determination is based on conductivity of a suspension of ground clinker in heated ethylene glycol (80°C). According to the supplier, up to five analyses per hour can be performed. Experience from Holcim installations has shown that around three analyses per hour are realistic.

There are around 10 ITECA units in operation in Holcim plants, mostly in the European region (in particular France and Spain) and in Morocco. Some feedback from the plants:

- The analytical accuracy of the free lime analysis is considered good, provided that a proper calibration is established and maintained.
- Mixed experiences were made with mechanical reliability. Most problematic parts are the clinker sampling and transport system.
- Operational costs (glycol) are relatively high. Spare parts are expensive.
- Regular maintenance and cleaning is necessary to avoid clinker dust and glycol accumulation.

A very similar free lime analyzer based on the same analytical principle is also available from FLS (FL 800, formerly produced by Autec), without installations in Holcim.

5. On-line XRD analysis

FCT ACTech offers a system for on-line XRD and Rietveld analysis called 'Continuous On-Stream Mineral Analyzer' or COSMA. The locally installed analyzer can be applied for finish mill control (e.g. online determination of gypsum minerals, limestone and other MIC content) and/or clinker analysis (free lime analysis and quantification of clinker minerals).



Figure VI- 12: On-line XRD system

The system consists of an automated cement or clinker sampler, a grinding unit (if required, e.g. for clinker) and the analytical XRD unit. The powdered material is presented as a flat, continuously moving target bed on a rotating table. Opposite to the table the XRD tube is installed. Analysis integration time is 1 minute.

Until present, there are no installations within Holcim plants. Systems for cement analysis have been sold to Lafarge, Heidelberg, Buzzi Unicem and other, smaller cement companies. The price of the system is around 350'000 Euro for cement application and 450'000 Euro for clinker application.

6. On-line particle size distribution (PSD)

Systems for on-line particle size distribution (PSD) analysis are mainly used for control of cement and slag grinding. Potential benefits are:

- Improved product uniformity due to high analysis frequency
- Reduced energy consumption by optimized grinding process (separator control)
- Maximized throughput and less overgrinding
- Shortened transition period between different products

Different systems are available from different suppliers. The systems typically consist of a sampling unit and the analytical unit using laser diffraction technology.

- **Malvern/Insitec:** Online particle size analyzer based on laser diffraction, requires a sampling unit which can be provided but is not manufactured by Malvern. Such systems are installed in about 20 Holcim plants (e.g. Camden, Jerez, Höver, Devils Slide, Grand Couronne, Altkirch). According to plant experiences, the system is mechanically simple and requires little maintenance. Critical part is the optical window, which blurs after a certain time. Measurements are taken every 20 seconds, but typically a rolling average (1-2 min) is used. Installation costs around 100'000 Euro.
- **Sympatec/MYTOS:** The MYTOS particle size analyzer is available as an in-line version (directly integrated into the chute, $T < 60^{\circ}\text{C}$) for chute diameters from 100 mm to 200 mm, and an online version (separate sampling) for chutes up to 800 mm diameter. Sympatec provides its own sampling unit called TWISTER.
- **KIMA OPS:** 'Online Particle Sizer' from the German company KIMA. The system was installed at the Siggenthal plant in 2003. The plant has reported good performance. However, the system is no longer in operation due to the installation of an automated central laboratory with integrated laser granulometer.

Online PSD measurement is a very powerful tool, offering complete fineness characterization of the product in a very short time. Data should be used in high-level mill control systems, if available. However, in case several mill systems are operated in parallel each mill would require a separate device, which renders the concept expensive.

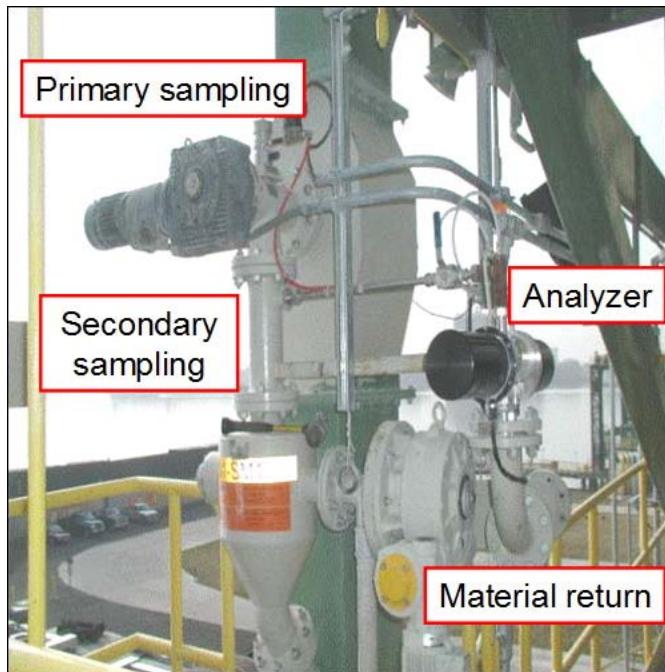
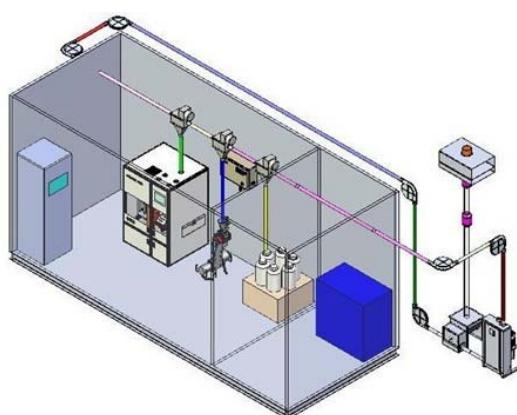


Figure VI- 13: On-line particle size analyzer from Malvern, installed at Camden (slag grinding).

7. Container laboratories

Container laboratories (“plug and play cabins”) present an intermediate solution between an automated central laboratory and decentralized online analyzers. Different analytical equipment are integrated into a container, which is placed relatively close to the sampling points. The automated sampling installations are connected to the container via automated transport. For reasons of flexibility and costs mostly cable transport is used and not pneumatic transport. Analysis in the container laboratory is fully automated and does not require human intervention.

Available systems are mostly designed for cement mill control. Systems for clinker and raw meal control are also available but less frequently sold, according to supplier information. Suppliers offering such systems are ITECA, FCT and FKV (list may not be complete). Holcim has no experience with such systems.



Configuration of a container laboratory is flexible. As an example, a system dedicated to cement (mill) control may contain a particle size analyzer (laser granulometer), a Sulfur/Carbon analyzer for SO₃ determination and optionally XRD equipment. The COSMA on-line analyzer (see chapter 5) is often encountered in combination with container laboratories. Systems for clinker analysis need to contain a sample preparation unit and can be extended with automated free lime analysis.

Figure VI- 14: Container laboratory for cement control (incl. particle size analyzer, S/C analyzer) from FKV

Container laboratories can be a solution for very specific cases (e.g. upgrade of existing plants), but are in general not the preferred concept for Holcim.

8. Automation in central laboratories

Principles of centralized and automated quality control systems are presented in part III of this manual. This section shall give an overview on available solutions and specific features.

8.1 Automated sample preparation systems

Automated sample preparation modules rationalize the process of sample preparation for XRF and XRD analysis. Systems for pressed tablet and fused bead preparation exist. Samples can be prepared within a short period of time (< 5 min) and without human intervention. The very consistent sample preparation process leads to good reproducibility of analytical results.

Particularly for XRD analysis with Rietveld refinement, sample preparation can significantly impact the results. In such cases, automated pressed tablet preparation with one of the systems described below is highly recommended.

Grinding and pressing conditions can be programmed for different types of materials. Optional are links with a transport belt to the XRF or XRD-spectrometers. Combined mill/press units can be integrated in fully automated laboratory systems.

8.1.1 Polysius (APM)

The Polysius APM (Automatic Preparation Module) is a relatively compact module (footprint 600 x 550 mm) consisting of a grinding unit and a pressing unit. After manual sample input the system proceeds through all the subsequent steps in a fully automated way:

- Fine grinding in disk mill (grinding time adjustable)
- Dosing of grinding aid
- Tablet pressing
- Tablet cleaning
- De-dusting and cleaning cycle

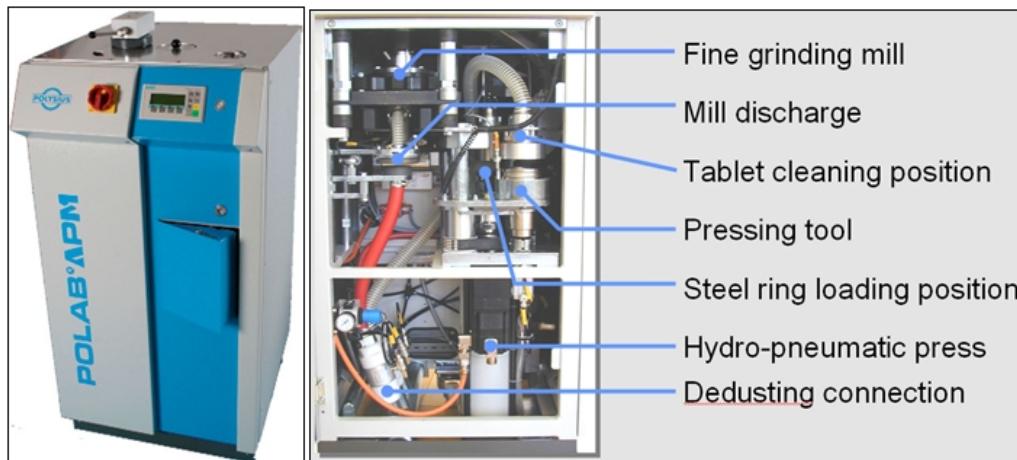


Figure VI- 15: Polysius APM system for automated tablet pressing

As an option the module can be equipped with a sample magazine (APMplus) and connected with the XRF/XRD analyzed via small conveyor belt. The sample throughput is between 10 and 20 samples per hour. The system is considered proven and reliable. The price for the basic version is about 70 k€, the version with sample carousel and connection to XRF (for automation) is about 120 k€.

8.1.2 FLS (Centaurus)

The FLS Centaurus system was introduced in 2008. It is also a combination of mill and press for automated pressed tablet preparation and offers very similar features as the Polysius APM. The system is a bit larger than the APM system. It offers full remote control and is designed for

integration into automated laboratories. Sample throughput is around 8-10 samples per hour. Price of the Centaurus system is about 100 to 120 k€.



Figure VI- 16: Centaurus sample preparation module connected to a Panalytical XRF spectrometer (installed in GV)

8.1.3 Herzog

Herzog also offers modules for automated preparation of pressed tablets (HP-MP) with similar capabilities as the two systems already mentioned.

In addition a system for automated fused bead preparation is available from Herzog (HA-HF16). It consists of a rotating table with 16 positions, each holding a crucible for fluxing, and an inductive furnace. The system automatically proceeds through

- Weighing and dosing of sample and flux
- Heating and fusing
- Casting and cooling with air jet

The system is capable of fully automated sample input and output. It does, however, not include a grinding unit; the sample input must be already ground to < 0.1mm. Price of the system is relatively high (about 140 k€). It is especially suited for integration into automated laboratories with high fused bead throughput.

References in Holcim: Gador (Spain), Obourg (Belgium)



Figure VI- 17: Automated fusion machine (Herzog)

8.2 Automated, central laboratories

Fully automated laboratories perform the routine sampling and testing activities in a cement plant without human intervention. The systems usually consist of:

- Automated samplers connected to a sample sending station
- Pneumatic (or mechanical) sample transport system
- Sample receiving station in the laboratory

- Sample racks or carousels for intermediate sample storage
- A robot (or similar) which distributes the sample to the sample preparation and analytical equipment
- Sample preparation equipment (typically mills and tablet presses)
- Analytical equipment, such as
 - XRF
 - XRD
 - Particle size analyzer (laser granulometer)
 - C/S analyzer
 - Colorimeter
- Various software modules for system control, process optimization (such as blending software) and data management; Interfaces to the process control system (PCS)

Major suppliers that offer complete automated laboratories are

- FLS: QCX/RoboLab. Consists of a robot placed in the center of a circular arrangement of sample preparation and analytical equipment (see Figure VI- 18). Arrangement of the different units is flexible. The robot arm is relatively powerful and needs to be stopped when human interaction with the machines is required.
- Polysius: POLAB Series. Two different versions are available (ACT: compact version for small applications, AMT bigger version for higher sample throughput), which also use a central robot for sample distribution. The arrangement is more compact than the RoboLab (see Figure VI- 19) but a bit less flexible. Most recent development of Polysius is the POLAB Shuttle system, where a small robot arm is moving on rails, allowing a very flexible design (installation at the Lägerdorf plant).
- ITECA: The ITECA system does not employ a central robot, but connects the different units through small conveyor belts and several small robot arms. The price is comparatively lower than for the FLS and Polysius systems, but design appears also less rugged. For evaluation of a ITECA laboratory see [Lit 14]
- ROMIX (KHD): The ROMIX family is the solution offered by KHD for laboratory automation and employs as well a central robot. No experience within Holcim.

Alternatively to the described systems above, automation can also be implemented by local engineering companies who combine the different individual components (mills, presses, robot arms) into one automated system. The Untervaz plant for example operates a laboratory where Herzog components were combined into one automated laboratory by ABB.



Figure VI- 18: Example of the Robolab at GV (USA). The robot is weighing a sample. Visible (clockwise) are two grinding units and one sample press. Receiving station, sample rack and connection to XRF/XRD equipment are not visible.

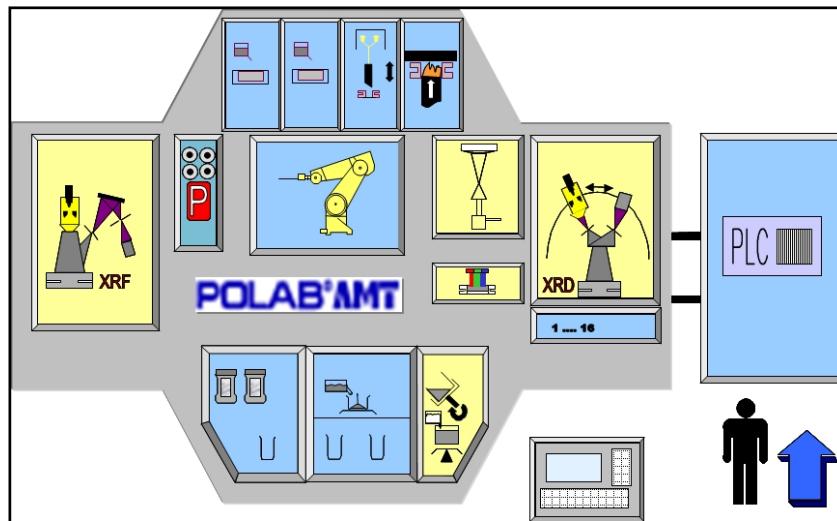


Figure VI- 19: Typical POLAB AMT setup. The system is enclosed in a container.

Costs are very much dependent on the configuration. As a very rough estimate one can expect the investment costs of an automated laboratory between 2 to 4 million Euro.

Examples of installations within Holcim (list may not be complete):

Rochefort (France)	FLS Robolab
SCCC (Thailand)	FLS Robolab
Cilacap (Indonesia)	FLS Robolab
Midlothian (USA)	FLS Robolab
St. Genevieve (USA)	FLS Robolab
Untervaz (Switzerland)	ABB/Herzog
Höver (Germany)	KMI/Herzog
Dotternhausen (Germany)	KMI/Herzog
Obourg (Belgium)	FLS (Pfaff)
Höver (Germany)	FLS (Pfaff)
Merone (Italy)	Herzog
Eclepens (Switzerland)	POLAB AMT (Polysius)
Ternate (Italy)	POLAB AMT (Polysius)
Holly Hill (USA)	POLAB AMT (Polysius)
Siggenthal (Switzerland)	POLAB AMT (Polysius)
Lägerdorf (Germany)	POLAB Shuttle
Portland (USA)	ITECA

9. Blending software

Automated systems produce analytical data at high frequency. In order to make optimal use of this data, dedicated software modules are needed. The software to control the chemical composition of the raw meal, stockpile feed, or other materials by adjusting feeder set points is called blending software or simply control software. It is an important and integral part of online systems.

Different software products are available, which apply different optimization algorithms (e.g. Model Predictive Control) and show different grades of complexity. PGNA analyzer can mostly communicate with any of the software. Some software is especially designed for PGNA systems, other software can also work with XRF data or a combination of both XRF and PGNA data. A list of software and their supplier in use at Holcim plants is given below:

- **QCX/ Blendexpert (FLS):** Very comprehensive and powerful, but also quite complex. Good experience made for example at Cartago, Midlothian, St.Genevieve. For stockpile control the

QCX/PileExpert module is available. The software is rather expensive, about 100'000 €, depending on configuration. Works with PGNAAs, XRF or combination of both.

- **ACQnet (Polysius)**: Available with Polysius (e.g. Polab) products. Applied with good experience at Holly Hill, Ternate and Siggenthal. Provides modules for raw mix and stock pile control. Works with PGNAAs and/or XRF analyses. Roughly 80 to 100 k€.
- **RMP (ABB)**: Proven software applied at Oujda and Merone. If an ABB environment is already installed at the plant, this can be advantageous. Pricewise similar to QXC. Works with PGNAAs and/or XRF analyses.
- **PREBOS/RAMOS (Thermo)**: Proven and widespread software from Thermo which is exclusively available with ThermoFisher PGNAAs (does not work with XRF analyses). PREBOS is used for stockpile control, RAMOS is the module for raw mill control. Applied e.g. at Portland, Midlothian, Guyaquil, Mississauga, Ternate. The software is not further developed, but can still be purchased on request for about 40'000 €.
- **O-Blend / Blendscan (Scantech)**: Applied at Alesd, Campulung, Beli Izvor and Garadagh in combination with Scantech PGNAAs (does not work with XRF data). This software was originally developed by Online Automation (based in Lausanne, Switzerland), but is meanwhile distributed by Scantech under the name Blendscan. It costs about 45 k€ Euro. Satisfactory performance is reported by the plants using it.
- **RMCS (Process solution)**: Low-cost product applied at Kandos and Theodore: Works with XRF analysis, mixed experiences.

Software suppliers are requested to provide guarantee figures for the blending performance. The blending performance is a measure of how good the software can control the feeders to achieve the required targets (e.g. LS). Blending control performance is made by each hour calculating a rolling 2 hour average of PGNAAs results over 72 hours (71 data points). The result should be within 2% of the setpoint for the control parameters (eg. LS, SR, AR etc).

10. List of equipment supplier

PGNAA:

Supplier	Country	Webpage
Thermo Scientific	USA	http://www.thermoscientific.com
Scantech	Australia	http://www.scantech.com.au/
EADS Sodern	France	http://www.sodern.com
Sabia	USA	http://www.sabiainc.com/

Automated sampling and sampler preparation; laboratory automation

Supplier	Country	Webpage
FLS (Pfaff, Autec)	Denmark	http://www.flsmidth.com
Polysius	Germany	http://www.polysius.com
Herzog	Germany	http://www.herzog-maschinenfabrik.de
ITECA	France	http://www.iteca.fr
FCT	Australia	http://www.fct-actech.com
KMI	Germany	http://www.kmi.info
FKV	Italy	http://www.fkv.it

Part VII: XRF

1. Introduction

X-Ray fluorescence (XRF) is nowadays almost universally employed for routine analysis in the cement industry. It is a fast method to obtain elemental composition of material samples for controlling almost all stages of production. Both solid and liquid samples can be analyzed. XRF spectroscopy is capable to detect and quantify nearly all elements of the periodic table, with exception of very light ones such as Lithium.

The importance of XRF spectroscopy for daily quality control in cement industry is reflected in this separate chapter. Some theoretical aspects of XRF are given below. However, the main purpose of this chapter is to provide practical information on XRF for cement applications. For more theoretical information on XRF, a list of literature is given in the Annex Part VII-1 at the end of this document.

2. Related standards

The ISO/DIS 29581-2 standard describes a method for chemical analysis of cement (and related materials) using XRF. This standard can be used as basis for plant procedures. Limits for accuracy and repeatability of the method are shown below for reference. They have to be fulfilled for each of the measured elements.

Content of element species % mass fraction absolute	Accuracy limit for "normal" performance % mass fraction absolute		Accuracy limit for "expert" performance % mass fraction absolute
0 to 0,49	0,05		0,02
0,50 to 0,99	0,08		0,03
1,00 to 6,99	0,20		0,08
7,00 to 14,99	0,30		0,12
15,00 to 29,99	0,38		0,15
30,00 to 49,99	0,50		0,20
50,00 to 79,99	0,63		0,25
80,00 to 100	0,75		0,30

NOTE All values of accuracy are expressed on the basis of fused, i.e. loss-on-ignition-free, samples.

Table VII- 1: Accuracy limits according to ISO/DIS 29581-2, as the closeness of agreement between a test result and the reference value for a certified reference material

Element mean value % mass fraction	Repeatability limit for "normal" performance % mass fraction absolute	Repeatability limit for "expert" performance % mass fraction absolute
0 to 0,49	0,057	0,023
0,50 to 0,99	0,080	0,032
1,00 to 1,99	0,110	0,044
2,00 to 3,99	0,135	0,054
4,00 to 4,99	0,155	0,062
5,00 to 6,99	0,172	0,069
7,00 to 9,99	0,202	0,081
10,00 to 14,99	0,240	0,096
15,00 to 19,99	0,290	0,116
20,00 to 24,99	0,335	0,134
25,00 to 29,99	0,372	0,149
30,00 to 34,99	0,405	0,162
35,00 to 39,99	0,437	0,175
40,00 to 44,99	0,465	0,186
45,00 to 49,99	0,492	0,197
50,00 to 54,99	0,517	0,207
55,00 to 59,99	0,542	0,217
60,00 to 64,99	0,565	0,226
65,00 to 69,99	0,587	0,235
70,00 to 74,99	0,610	0,244
75,00 to 79,99	0,630	0,252
80,00 to 100	0,650	0,260

NOTE All values of repeatability are expressed on the basis of fused, i.e. loss-on-ignition-free, samples.

Table VII- 2: Repeatability limits according to ISO/DIS 29581-2, as difference between two results of the same sample by the same operator within a short period of time. Note that repeatability as referred to in this table includes sample preparation.

An ASTM standard similar to ISO/DIS 29581-1 is under development (WK13067). The ASTM C-114 standard specifies the permissible variations in results for chemical analysis of cement which also apply to XRF analysis (see Table VII- 3). The standard is element specific and widely applied but does, however, not take into account elemental concentrations. Requirements of ASTM C-114 are relatively easy to achieve with modern spectrometers, if only variations from the analytical measurement (spectrometer stability) are considered. If variations from sample preparation are included, then the requirements are more challenging (see also VII 7.2).

TABLE 1 Maximum Permissible Variations in Results^A

(Column 1) Component	(Column 2) Maximum Difference Between Duplicates ^B	(Column 3) Maximum Difference of the Average of Duplicates from SRM Certificate Values ^{C,D,B}
SiO ₂ (silicon dioxide)	0.16	±0.2
Al ₂ O ₃ (aluminum oxide)	0.20	±0.2
Fe ₂ O ₃ (ferric oxide)	0.10	±0.10
CaO (calcium oxide)	0.20	±0.3
MgO (magnesium oxide)	0.16	±0.2
SO ₃ (sulfur trioxide)	0.10	±0.1
LOI (loss on ignition)	0.10	±0.10
Na ₂ O (sodium oxide)	0.03	±0.05
K ₂ O (potassium oxide)	0.03	±0.05
TiO ₂ (titanium dioxide)	0.02	±0.03
P ₂ O ₅ (phosphorus pentoxide)	0.03	±0.03
ZnO (zinc oxide)	0.03	±0.03
Mn ₂ O ₃ (manganese oxide)	0.03	±0.03
S (sulfide sulfur)	0.01	E
Cl (chloride)	0.003	E
IR (insoluble residue)	0.10	E
Cx (free calcium oxide)	0.20	E
CO ₂ (carbon dioxide)	0.12	E,F
Alk _{sol} (water-soluble alkali) ^G	0.75/w	E
Chl _{sol} (chloroform-soluble organic substances)	0.004	E

Table VII- 3: Performance requirements for chemical analysis of cement according to ASTM C-114

3. Theory of XRF

3.1 Basic Principle

The sample is irradiated by X-Rays produced by an X-Ray source (X-Ray tube). On irradiation, the elements present in the sample emit element-specific X-Ray radiation. By measuring the intensity of the emitted radiation it is possible to determine how much of each element is present in the sample (quantitative analysis). By measuring the energy (or the wavelength) of the emitted radiation, one can identify the elements present in the sample (qualitative analysis).

3.2 Generation of fluorescence radiation

When X-Ray radiation from the source hits the sample three main processes take place:

- Fluorescence
- Compton Scatter (scattering with loss of energy)
- Rayleigh Scatter (elastic scattering without loss of energy)

These processes compete with each other as a function of thickness, density and chemical composition of the sample material. Fluorescence is the key for XRF spectroscopy. It results from interaction of incoming X-Ray radiation with the electron shell of atoms. Incoming X-ray radiation expels inner shell electrons from atoms, producing a 'hole' in the electron shell. The process of filling this hole with electrons from the outer shell creates the fluorescent radiation (see Figure VII-1). Depending on the energy level (shell) of the expelled electron and on the energy level of the electron 'filling the hole', different energy levels of the emitted fluorescence radiation are observed. This corresponds to the different lines of a chemical element (e.g. $K\alpha_1$, $L\beta_2$, etc.; for nomenclature of the lines see literature). For routine applications mostly the K lines ($K\alpha_1$, $K\beta_1$, $K\beta_2$) are used. Lines from the L or M series can be important for heavy elements or when severe line overlapping occurs.

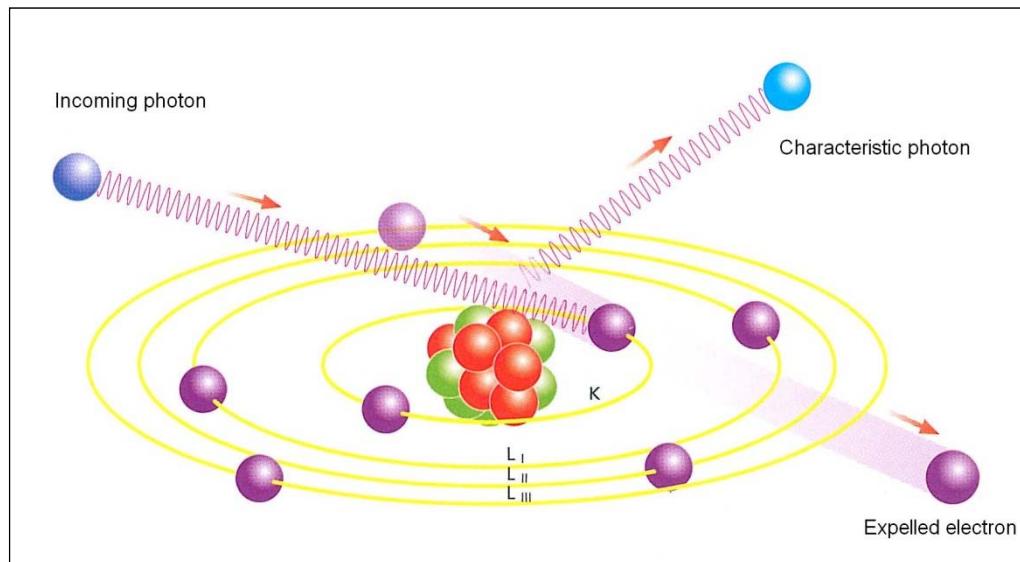


Figure VII- 1: Characteristic fluorescence radiation

The efficiency of the fluorescence process depends on the energy of the incoming photon. The highest yield of fluorescence radiation is reached when the energy of the incoming photon is just above the binding energy of the electron to be expelled. When the energy becomes lower, the electron cannot be removed, leading to the so called *absorption edges*. If on the other hand the energy of the incoming photon increases, the fluorescence also becomes lower, as absorption of the X-Ray photons becomes less effective.

Other processes to 'fill holes' in the electron shell can occur (e.g. emission of Auger electrons). The *fluorescent yield* indicates the ratio of the emitted fluorescence photons to the number of initial holes. For elements with low atomic number the fluorescent yield becomes very low. This explains why these elements are very difficult to measure by XRF. Elements down to Fluorine can be quantified with XRF instruments typically applied in cement industry. Analysis of Carbon is possible with special crystals, but rarely applied for routine analysis.

3.3 Absorption and enhancement effects

The primary X-Ray radiation is absorbed on its way through the sample. At the same time the fluorescence radiation produced inside the sample is as well absorbed on its way out of the sample. The absorption increases as the path length, density and atomic number of the elements in the sample increase and as the energy of the x-ray radiation decreases. Fluorescence radiation produced inside the sample at a certain distance from the sample surface is no longer able to leave the sample. This so called *analysis depth* again depends on the energy of incoming x-rays and the chemical composition and density of the sample. Table VII- 4 below shows approximate analysis depths in various materials for three different lines. It can be seen that XRF is clearly a surface analysis method; only the outermost layer (μm to mm) is analyzed.

Matrix	Mg K α	Cr K α	Sn K α
Iron	0.7	4.5	55
SiO ₂	1	35	290
Li ₂ B ₄ O ₇	13	900	4600
H ₂ O	16	1000	5300

Table VII- 4: Analysis depth in μm for three different lines in three different matrices

The energy of the emitted fluorescence radiation is in the range of 0.1 – 100 keV (corresponding wavelength 12 – 0.01 nm). Fluorescence radiation itself can have enough energy to expel electrons from other elements in the sample, leading to *secondary fluorescence* (see Figure VII-2). The contribution of secondary fluorescence can be in the order of 20%. Hence the primary fluorescence radiation of one element is absorbed and the (secondary) fluorescence of another element is enhanced. Likewise also tertiary or higher order fluorescence can occur. A spectrometer measures the sum all fluorescence radiation and one cannot distinguish between individual contributions. The proportions of contributions depend on the matrix of the sample. In quantitative analyses, these effects of absorption and secondary enhancement may have to be corrected. Modern software packages offer a selection of correction models (matrix correction or inter-element correction, see 6.5) for this purpose.

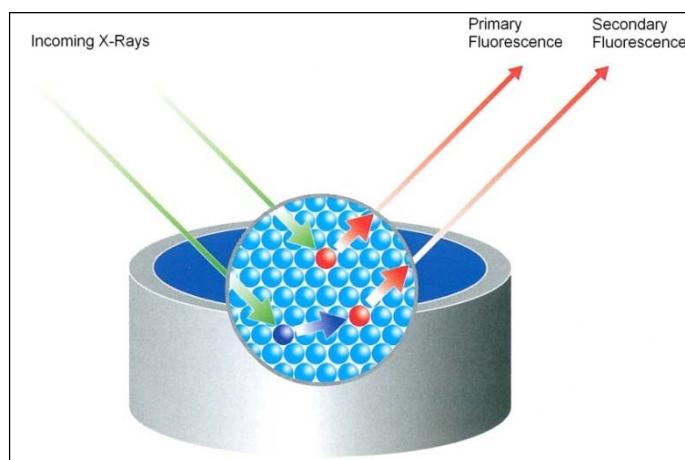


Figure VII- 2: Primary and secondary fluorescence

3.4 Matrix effects

The term “matrix effects” stands for all influences on the fluorescence of a particular element arising from its surroundings, i.e. the matrix. The matrix consists of everything in the sample but the element itself. There are two classes of matrix effects

- Those arising from chemical composition of the matrix
- Those arising from the physical properties of powders (particle size effects, mineralogical effects, surface effects, segregation effects)

Matrix effects from chemical composition (also referred to as “inter-element effects”) are caused by absorption and enhancement effects and are described in section 3.3 above. These effects can be reduced by diluting the original matrix with elements of low atomic numbers (e.g. fusion with Lithium-borates) and application of mathematical corrections.

Matrix effects of the second category result from the fact that powders with particles of different composition (e.g. raw meal) are normally heterogeneous on the scale of penetration depth of fluorescence radiation. An illustration of the particle size effect is shown in Figure VII- 3. Effects from mineralogy occur when elements are present in different mineralogical phases and when the different phases do not have the same absorption coefficients. Problems occur for instance with Silicon, which can be present in quartz or in clay minerals.

Particle size and mineralogical effects can be reduced by fine grinding. With pressed tablets these effects always occur as the process of fine grinding is limited. Fusion eliminates these effects completely.

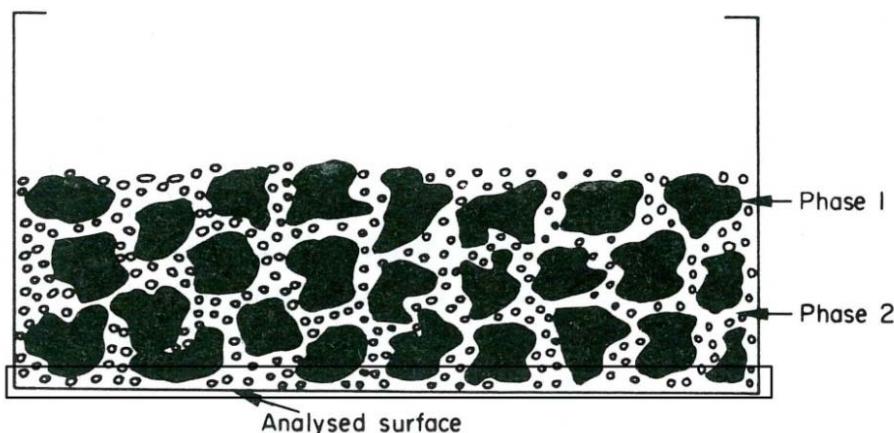


Figure VII- 3: Illustration of particle size effect. Phase 2 would be over-represented in the analyzed surface of the sample.

In cement industry problems from matrix effects are often circumvented by using ‘matrix matched’ calibrations standards, i.e. the matrix is kept as constant as possible. It means that for each individual material type (e.g. raw meal, clinker, cement, correctives) a separate calibration curve is established.

4. Equipment

There are two basic types of XRF spectrometers:

- Wavelength dispersive spectrometers (WDXRF)
- Energy dispersive spectrometers (EDXRF)

The spectrometer types differ only in the way the polychromatic fluorescence radiation from the sample is separated into the element specific components.

4.1 Wavelength dispersive spectrometers (WDXRF)

The fluorescence radiation from the sample falls on a crystal and is spatially separated according to Bragg's law (Diffraction, see part VIII) into its monochromatic components of different wavelengths. Different types of crystals for different elements are available. A detector placed at a certain angle (*often referred to as 2θ*) measures the intensity of X-rays with the corresponding wavelength. A schematic setup of a WDXRF spectrometer is shown in Figure VII- 4. Two different setups need to be distinguished here:

- *Fixed channels or multichannels (monochromators):* As the name implies, these instruments have a set of fixed detectors mounted at the angle of interest. Each detector measures one specific element. Since all intensities of all elements are measured at the same time, these spectrometers are also called *simultaneous spectrometers*. Modern spectrometers can accommodate 20 or more channels.
- *Goniometer:* These instruments use one moving detector on a goniometer which is moved through an angular range. They are called *sequential spectrometers* as they measure intensities at different wavelengths one after the other.

Simultaneous spectrometers offer short measurement times in combination with high precision, because crystals and detectors can be selected in an optimal way for each element. The elemental range is limited to the selected elements. This configuration is particularly suited for fast routine analysis in a plant laboratory. Investment costs are generally higher compared to sequential spectrometers.

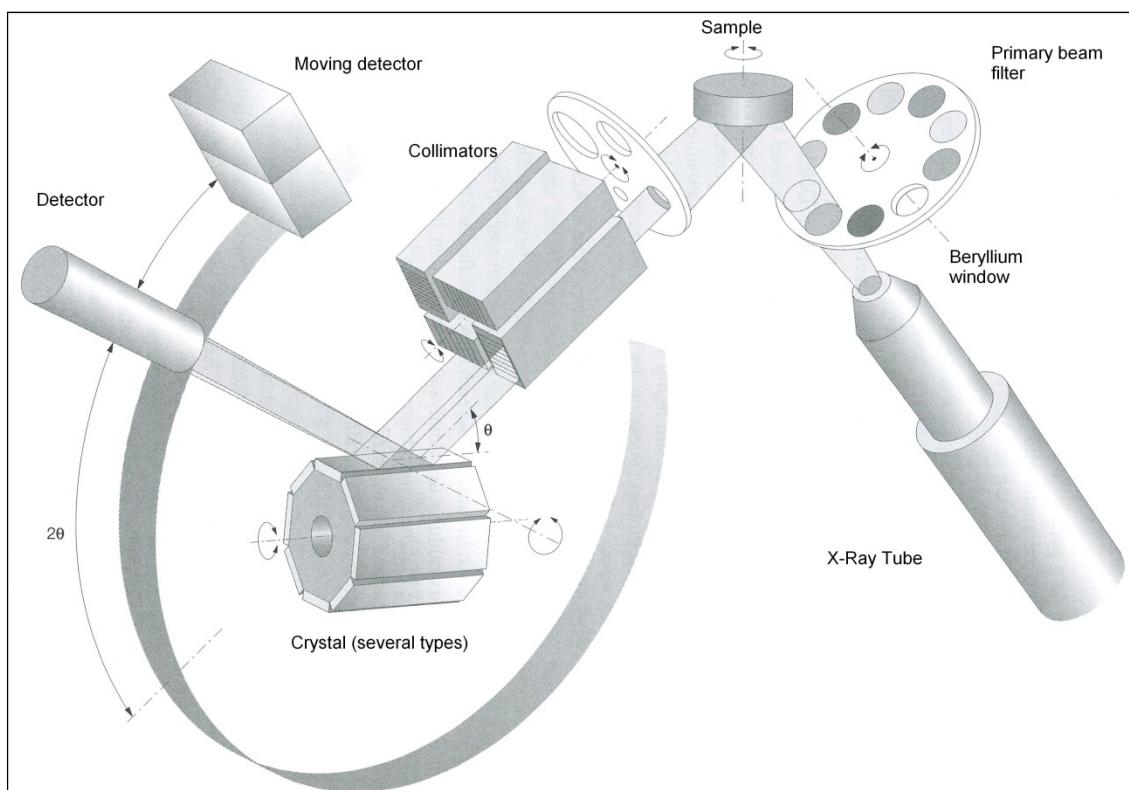


Figure VII- 4: Schematic setup of a WDXRF spectrometer [Source: Kläntschi et al, Elementanalytik, 1996, Spektrum Akad. Verlag, p.155]

Sequential spectrometers offer the full elemental range to be measured and thus a high degree of flexibility. Disadvantage used to be a longer measurement time as compared to fixed channels spectrometers, but in modern spectrometers the difference in measurement time is negligible.

It is possible to combine these two arrangements into one spectrometer to profit from both fast and accurate analysis and the flexibility. Typical application would be a fixed channel for fluorine or sodium determination.

4.2 Energy dispersive spectrometers (EDXRF)

In energy dispersive XRF the emitted fluorescence radiation falls on an energy dispersive detector, which can directly measure the energy of the individual photons. All elements are simultaneously detected.

The sample can be irradiated directly by the X-ray tube. Alternatively, a secondary target can be placed between the tube and the sample. The sample is then irradiated with almost monochromatic fluorescence radiation of the secondary target, leading to better sensitivity. However, disadvantage is that energy (intensity) is lost. The excitation process in EDXRF is generally more efficient than WDXRF, because no intensity is lost at the diffraction crystal and because of shorter optical path lengths.

A further technique to improve EDXRF performance is the usage of 3D optics (also referred to as polarizing EDXRF), which also uses a secondary target. The X-Ray path (X-ray tube -> secondary target -> sample -> detector) is not in one plane but in two perpendicular planes. With this arrangement scattered radiation from the X-Ray tube will not reach the detector and thus will reduce the spectral background and lead to lower detection limits.

The EDXRF concept is relatively simple and the instruments are compact and relatively non-expensive. Major drawback is the low sensitivity for elements with low atomic weight such as Na, Al, Si. On the other hand, EDXRF has a good sensitivity for heavy elements.

Handheld EDXRF devices weighing less than 2 kg are available. They may be applied to fast acceptance control of AFR (heavy elements screening) but also show poor performance for the lighter elements (< Cl).

4.3 Comparison of EDXRF and WDXRF

Both techniques have their advantages and disadvantages. The table below summarizes a few key aspects:

	WDXRF	EDXRF
Elemental range	Be – U	Na - U
Detection limit	Good for all elements	Good for heavy elements, less for light elements
Spectral resolution	Good (ca. 5-20 eV)	Ca. 150 – 200 eV
Costs	Typically > 100 k€	Typically < 65 k€
Power consumption	200 – 4000 W	5 – 1000 W
Measurement	Simultaneous / Sequential	Simultaneous
Critical moving parts	Crystal, Goniometer	None

Table VII- 5: Comparison of WDXRF and EDXRF technique

For routine analysis in a cement plant WDXRF (> 1 kW tube) is standard, as they provide sufficient accuracy on the light elements. EDXRF spectrometers have found application for analysis of trace (heavy) elements in AFR but also as backup solution for the main (WDXRF) spectrometer. However, also low powered WDXRF can serve as backup equipment as they are not a lot more expensive than good EDXRF devices.

4.4 Important components of XRF spectrometers

4.4.1 X-Ray tube

X-ray tubes generate the required X-ray radiation to provoke fluorescence in the sample. In X-ray tubes, electrons emitted from the cathode (heated filament) are accelerated towards the Anode target. When the electrons strike the anode target X-ray radiation is emitted. The anode target is made of elemental metal (e.g. Rhodium or Gadolinium). X-rays leave the tube through a Beryllium window.

X-ray tubes can be classified according to the power applied to the tube. WDXRF usually operates with 1kW to 4 kW tubes (max. voltage 50-60 kV and max. ampere 50 – 170 mA). High powered tubes (> 3 kW) require external water cooling and thus makes the equipment heavier and more expensive. EDXRF uses low powered XRF tubes in the range of typically 50 to 500 W.

X-ray tubes deteriorate over time and need to be replaced after a certain time. Deterioration of the tube should be monitored by drift correction standards (see also 7.3.2). Depending on the operation conditions the tube lifetime is about 2-4 years. Due to their high price (roughly 25 k€), they contribute considerably to the operational cost of an XRF spectrometer.

4.4.2 Detectors

WDXRF and EDXRF use different type of detectors. WDXRF has only to count pulses as the crystal has already discriminated between different energies, whereas an EDXRF detector needs to distinguish between different energy levels.

WDXRF uses gas proportional counters (for the lighter elements F – Zn) and/or scintillation counters (for heavy elements ~Ti - U) as detector systems. For design and functionality of these detector systems refer to literature. Gas proportional counters require P-10 gas (mixture of argon and methane) for operation. Often a combination of both detector types is found in modern spectrometers.

For EDXRF accuracy several detector systems are available for EDXRF, depending on the required detection limit and accuracy:

- Proportional counters: Low performance (resolution) but relatively cheap; used in portable devices
- Semiconductor based detectors (PIN diode, Xflash drift chamber): mid-price and performance, used in bench top analyzers
- Si(Li) detector: High performance and price, require liquid nitrogen cooling. Used in stationary laboratory systems.

4.5 Supplier and available equipment

There are three major suppliers offering proven XRF equipment:

- Bruker AXS (formerly Siemens): Head office in Germany
- Panalytical (formerly Philips): Head office in the Netherlands
- Thermo Scientific (ARL): Head office in Switzerland

All the suppliers above have a large number of units delivered to Holcim plants and provide their services on a worldwide basis.

The two companies Rigaku and Shimadzu, both based in Japan, also offer XRF equipment but have no or very few units supplied to Holcim plants.

For special applications, also the manufacturers Spectro and Oxford may be considered. Spectro offers only EDXRF equipment but has been very active in the development of these

spectrometers. Oxford provides both handheld devices (EDXRF) and stationary laboratory equipment.

The table below summarizes the product portfolio of the mentioned supplier as per 2011. Prices, where indicated, only include the spectrometer, without spare parts, installation and training.

Total costs for purchase and installation of a new WDXRF equipment in a cement plant are typically around 200 – 250 k€, depending on the configuration.

	Bruker AXS	Panalytical	ThermoFisher (ARL)	Spectro
WDXRF; sequential	S8 Tiger 1, 3, 4 kW tube below sample 140 – 200 k€	Axios Series 2.4, 3, 4 kW, tube below sample Ca 200 k€	ARL ADVANT'X 1.2, 2.5, 3.6, 4.2 kW, tube below sample	None
WDXRF seq. and simultan. combined	none	none	ARL 9900 1.2, 2.5, 3.6, 4.2 kW tube above sample Up to 32 fixed channels, limited or full XRD capability (Workstation) 200 – 500 k€ ARL OPTIM'X 50W tube below sample 80 k€	None
WDXRF; simultaneous (fixed channels)	S8 Lion 3, 4 kW tube above sample; free lime channel possible 120 – 220 k€	CubiX XRF	ARL PERFORM'X 1.2 – 4.2 kW tube below sample; includes small spot analysis and mapping 200 – 250 k€	None
EDXRF	S2 Ranger 50 W tube, XFlash detector, 60 – 70 k€	MinPAL 9 W tube, SDD detector ca. 60 k€ Epsilon 5 0.6W tube, 3D optics, solid state detector, ca 120 k€	ARL QUANT'X 50 W tube, SDD detector Ca. 60 k€	IQ II 50 W tube, SDD detector ca. 45 k€ XEPOS 50 W tube, SDD detector ca. 60 k€
Handheld EDXRF	S1 Tracer 30 k€	none	NITON series 20 – 30 k€	xSort 30 k€

Table VII- 6: Product portfolio of main XRF supplier

ARL offers high flexibility on combining of simultaneous and sequential features in one spectrometer (9900 Series).

As the only supplier, ARL can combine full XRF (WDXRF, simultaneous and sequential) and XRD capabilities into one spectrometer (9900 Workstation), hence the large price range. ARL was the first supplier to integrate (limited) XRD capability into their XRF, which is used to measure the intensity of the free lime peak (free lime channel). This feature is now also available with the Bruker S8 Lion spectrometer. It is recommended for plants that do not need full XRD capabilities (required for Rietveld analysis), but want to have an easy and fast possibility to analyze free lime.

5. Sample preparation

The sample preparation procedure has a significant influence on the measured count rates. Two different sample preparation methods are commonly used in cement plants:

- Fusion (fused beads)
- Tablet pressing (pressed powder tablets or pellets)

These two methods can be applied to powdered solids and will be presented in the following sections. Sample preparation for liquids will not be discussed in this document.

In order to reduce the (human) sample preparation error automated sample preparation equipment is highly recommended. Examples are shown in the Part VI.

5.1 Fusion

5.1.1 Preparation of fused beads

Powdered material mixed with a fluxing agent is melted at 900 – 1200°C to form a glass sample (bead). During fusion the sample is decomposed and completely dissolved in the flux.

Essentially a fusion procedure consists of:

- Accurate weighing of sample and flux (typically 1g of sample and 5-7 g of flux)
- Heating the mixture until it melts and the sample dissolves into the molten flux
- Agitating to homogenize the melt
- Pouring liquid into a hot mould
- Cooling to obtain a solid glass disk (fused bead)

The sample must be ground and sieved to analytical fineness (< 63 µm) before fusion. Cross-contamination from both grinding vessels (e.g. steel to influence Fe and/or Cr/V) and sieves (e.g. brass to influence Cu/Zn) can occur during sample preparation. This contamination is, however, only relevant if accurate analysis of trace elements (< 0.1%) are of interest.

The flux to sample ratio and fusion temperature depends on the nature of the sample that needs to be analyzed. Examples are given in Table VII- 7 below (source: HGRS laboratories). Each flux has a loss on ignition (LOI) which needs to be taken into account to determine the exact quantity of flux. On opening a new bottle of flux, the LOI has to be determined. The weight of flux is calculated by multiplication of the basis weight (e.g. from Table VII- 7) with the factor [100/(100-LOI)].

Material	Flux type ^{*)}	Flux + sample ratio	Sample [g]	Flux [g]	Fusion temp.[°C]
Limestone, clay, sand, raw meal, clinker, cement, MIC	A 10	1 + 5	1.1000	5.5000	1130
	A 1000	1 + 5	1.5000	7.5000	1050
Iron corrective, slag with Fe ₂ O ₃ > 22%	A 1000	1 + 10	0.6000	6.0000	1130
Refractory samples with MgO > 35%	A 10	1 + 8	0.7500	6.0000	1130
Gypsum	A 14	1 + 5	1.1000	5.5000	900
Hot meal (total composition)	A 1000	1 + 5	1.2000	6.0000	900

Table VII- 7: Fused bead preparation programs for different materials. ^{*)} see Table VII- 8

Accurate weighing and clean working practice (washing, drying, handling of Pt/Au ware, etc.) are the key factors for preparation of fused beads with a good reproducibility. Weighing of sample and flux should be performed to four decimal digits precision (e.g. 1.5000 g). It is recommended to

weigh the flux and the sample directly into the crucible. Weigh first about one half of the flux, then the sample and then the rest of the flux on the top.

5.1.2 Fluxing agents

Flux agents should be selected with respect to mechanical behavior of the bead (crystallization) and hygroscopic properties. The most commonly used fluxes are di-lithium tetraborate and lithium metaborate.

- **Di-Lithium Tetraborate, ($\text{Li}_2\text{B}_4\text{O}_7$)** is a commonly used flux in XRF analysis. It is barely hygroscopic, but shows some tendency to crystallization and cracking of the bead. Its melting point being 930°C is relatively high.
- **Lithium Metaborate, LiBO_2** is even more susceptible to crystallization than tetraborate, but has a better solubility for several elements. Its melting point is 845°C and it has a low viscosity. It is the preferred flux for the preparation of fused beads, but it is the most expensive one.
- **Sodium Tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$** is very hygroscopic. Fused beads have no tendency to crystallize or crack but must be kept in a desiccator to prevent formation of a white hydroborate layer. The melting point is 741°C . Sodium cannot be determined. This flux is rarely used at cement plants.

A combination of borates is useful in certain applications. Especially the addition of lithium metaborate to lithium tetraborate may help prevent crystallization and cracking of the fused beads. Some companies offer mixtures designed for different applications. As an example, Table VII- 8 shows a selection fluxing agents from Merck (Spectromelt series). Claisse offers a 50:50 mixture of Li-Tetraborate and Metaborate (with 0.5% LiBr), which can be applied for almost any material in the cement industry.

Flux agent	Merck designation
Di-lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$)	Spectromelt A 10
Mixture of $\text{Li}_2\text{B}_4\text{O}_7$ with 0.07% LiBr (lower surface tension of flux)	Spectromelt A 1000
Mixture of $\text{Li}_2\text{B}_4\text{O}_7$ and LiBO_2 66:34	Spectromelt A 12
Mixture of $\text{Li}_2\text{B}_4\text{O}_7$ / $\text{LiBO}_2/\text{La}_2\text{O}_3/\text{LiF}$ 51:27:12:10	Spectromelt A 14
Lithium metaborate (LiBO_2)	Spectromelt A 20
Mixture of $\text{Li}_2\text{B}_4\text{O}_7$ and LiBO_2 12:22	Spectromelt A 22

Table VII- 8: Merck fluxing agents

Due to electrostatic forces, dusty fluxes stick to the weighing pan, the funnel, the spatula and the crucible wall, resulting in a loss of flux. Granular fluxes do not stick to any surface and are easier to handle, thus recommended.

Borate melts can show strong tendency to stick to the crucibles and moulds and can break when they are removed from the mould. In most cases the use of a non-wetting agent is beneficial. Iodide and bromide salts are known to be most efficient for that purpose. They can be added into the mix before or during the fusion. For practical reasons, is recommended to use a flux that already includes the non-wetting agent (e.g. Spectromelt A 1000).

Other chemicals commonly added to the fluxes are:

- **LiF** is added to the mix to ensure a better transfer of the melt into the mould
- **NH_4NO_3 or NaNO_3** can be added to oxidize small amounts of organic material or partially oxidized elements, to prevent corrosion of the crucible.
- **La_2O_3 or BaO_2** were added to decrease the matrix effects by increasing the X-ray absorption of the flux, these additives are, however, no longer required.
-

5.1.3 Preparation equipment

5.1.3.1 Manual preparation (minimum requirement)

For the manual preparation of fused beads the following equipment is recommended:

- 2 muffle furnaces (see chapter 5)
- 2 Bunsen burners
- 1 small blower
- 2-5 Pt/Au crucibles
- 2-5 Pt/Au molds

Advantages:

- Minimum investment
- Easy to implement

Disadvantages:

- Operator is exposed to heat during removal of crucible
- Slow and prone to human errors (lower repeatability)

5.1.3.2 Automated and semi-automated preparation

Automated equipment for preparation of fused bead improves reproducibility of the sample preparation process. In addition the operator is not exposed to heat or hot material. Different types of automated fusion machines are available, differing in type of heating (electrical or with gas burners) and sample throughput. For types and suppliers see part V of this manual.

5.1.4 Care of crucibles and moulds

Crucibles and moulds used for fused bead preparation are made out of a Pt/Au alloy (5% Au typically). They can make a significant contribution to operating costs of an XRF equipment. The life of these consumables can be extended by considering some fundamental rules:

- Place hot platinum crucible or mould on a clean refractory material. They should never be placed on a cold metallic or dirty surface.
- Heat the crucible and mould under oxidizing conditions. When heating over a Bunsen burner avoid smoky flame because the free carbon will embrittle the platinum.
- Residue from a crucible should not be scraped by means of hard tool, e.g. screwdriver. Scratches on the crucible retain more residues in subsequent operation.
- Cleaning crucibles: Put about 2g of flux and 0.2g of KI (potassium iodide) in the crucible, heat until fused, then cast. An alternative way is to let the crucible stand in 2 % nitric or hydrochloric acid overnight. Never use the mixture of the 2 acids.
- When fusing in a muffle furnace the crucible and mould should not be placed directly on furnace refractory. The bottom of the crucible or mould will be deformed and the platinum becomes brittle. Take an alumina brick and cut furrows into it. Place magnesia rods into the furrows and place the crucible on the magnesia rods, so that will not touch the brick itself (see Figure VII- 5).
- Avoid unnecessary long heating of platinum as it tends to promote crystal growth that eventually produces cracks. Fusion temperature should be kept low (ideally < 1050 °C).
- When a crucible has lost its lustre and more residue sticks to the surface, it can be polished again with wet fine abrasive paper (e.g. p 800). Moulds should not be polished but replaced. The quality of the mould surface influences the analysis results.

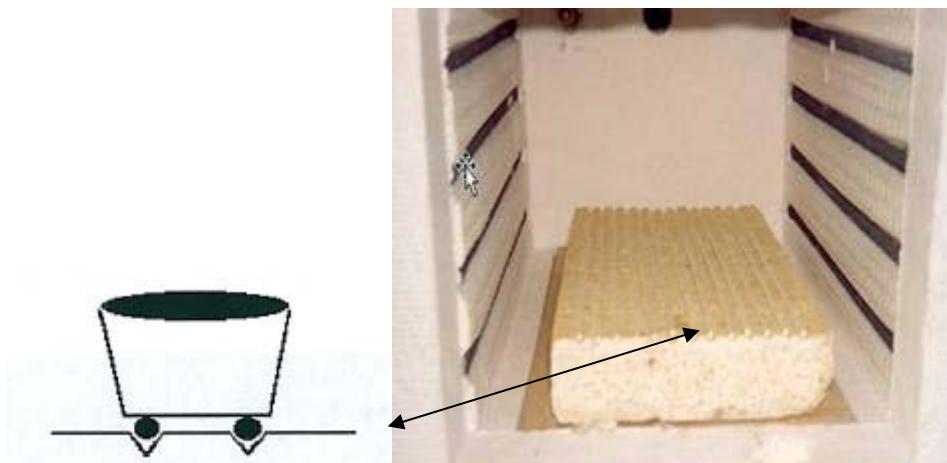


Figure VII- 5: Cut alumina brick with magnesia rods to protect the crucible

5.2 Pressed powder tablets

5.2.1 Preparation of pressed tablets

The powdered material is simply pressed under high pressures, typically 150 to 200 kN during 10 to 30 seconds, to form a tablet. Samples can be pressed into steel rings or alumina cups. ITECA uses boric acid as sample support. Sample preparation equipment is described in part V of this manual.

The sample first needs to be ground sufficiently fine to achieve homogenization and eliminate large and/or inconsistent grain sizes. Ideally the particle size should be much smaller than the analysis depth (see Table VII- 4). All particles must at least pass the 63 µm sieve, particle size < 30 µm would be desirable. It is essential to maintain constant and controlled conditions for grinding and pressing. The optimum grinding time needs to be experimentally determined (see example below). In order to achieve a good reproducibility, weighing should be performed to one decimal digit precision (e.g. 10.0 g).

Grinding aids are used to improve the grinding efficiency, prevent sticking, easy cleaning of the grinding vessel and as a binder improving the stability of the tablets. There is a large number of binding agents available, such as wax, cellulose powder or stearic acid.

To avoid cross contamination, it is recommended to take the ground sample to be pressed directly from the grinding vessel. Do not empty and clean the vessel with the brush first.

The surface of the pressed tablet should be smooth and uniform. This may not be the case when deformed pressing tools or too much/too little material was used to press the tablet. Tablets may break when stored over longer periods of time due to absorption of moisture or CO₂ (e.g. hot meal samples).

A simple test to check the stability of a pressed tablet: Drop the tablet (including steel ring) from 1m height onto a rubber mat. An adequately prepared tablet should stay intact and not lose any material.

5.2.2 Determination of the optimum grinding time

For the determination of the optimum grinding time, grinding tests have to be carried with each of the materials (e.g. raw meal, clinker, etc.). As an example, the following procedure can be used to prepare the tablets (for a vibratory disk mill with a 100 ml Tungsten-carbide grinding vessel):

Grinding:

Weight: 15.0 g sample (e. g. raw meal)
 Grinding aid: 3 - 5 tablets (e.g. Herzog HMPA 20)
 Grinding time [sec]: 30, 90, 120, 150, 180, 210, 240

Tablets Pressing:

Weight: 10.0 g
 Pressure: 120 kN
 Pressure retaining time: 10 sec

Data evaluation:

Measure the intensities/elemental concentrations and plot them as a function of the grinding time (see Figure VII- 6). The optimum grinding time is the time after which only small changes in the intensities occur (typically of SiO₂ and CaO).

Once optimum grinding time has been found also the fineness ($R_{45\mu\text{m}}$) should be measured, recorded and monitored over time. Changed fineness indicates changed sample preparation conditions (equipment or material grindability).

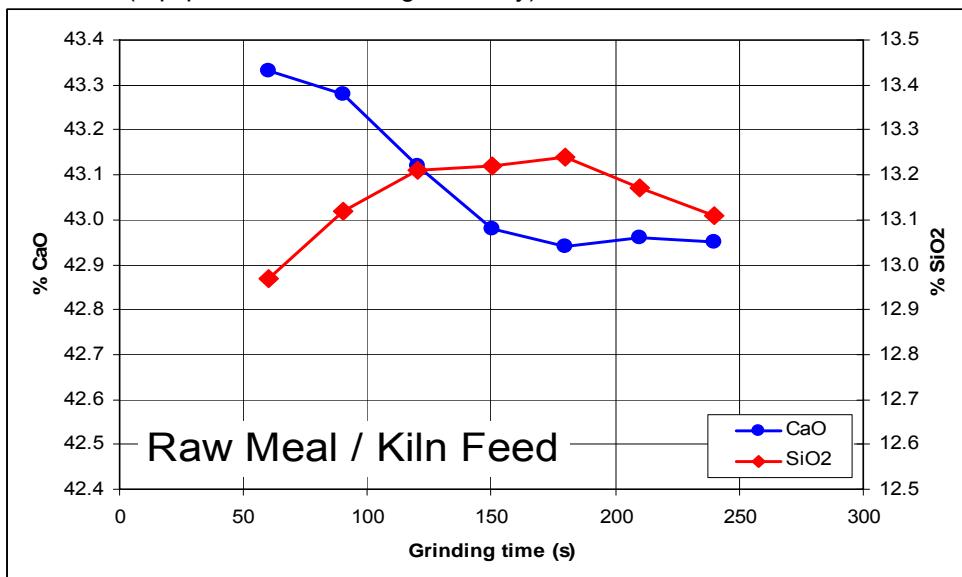


Figure VII- 6: Determination of optimum grinding time for raw meal. Optimum grinding time is in the region of 150 sec.
 [Source: CMS-MT 02/13550.]

5.2.3 Cleaning of grinding tools

For manual sample preparation, the vessels should be cleaned with a brush between samples of the same type. Good cleaning results are achieved by grinding about one piece A4 size white paper, together with 3 grinding aid tablets for 120 sec. Alternatively, sand can be used for cleaning.

Cross contamination can be reduced considerably by grinding a cleaning sample consisting of the same material as the next sample to be ground. Good practice is to use different grinding vessels for different materials (e.g. raw meal/ kiln feed and clinker/cement).

5.3 Sample preparation reproducibility

Sample preparation has considerable influence on the reproducibility of the total analytical result. For illustration, Table VII- 9 shows the standard deviation of XRF analyses based on 9-10 beads or 9-20 pressed tablets from the same sample.

System	n	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	LS	SR	AR
Automated (ABB Robot)	10	0.05	0.03	0.02	0.06	0.41	0.02	0.02
Automated (ABB Robot)	10	0.09	0.03	0.01	0.19	0.49	0.01	0.01
Automated (FLS Robolab)	10	0.05	0.01	0.01	0.05	0.32	-	-
Automated (POLAB)	10	0.03	0.01	0.01	0.03	0.24	0.02	0.00
Automated (Polysius APM)	-	0.03	0.01	0.01	0.03	0.14	0.01	-
Automated (Pol. Quicklab)	20	0.04	0.02	0.01	0.04	-	-	-
Manual Lab1	9	0.19	0.04	0.02	0.28	1.76	0.02	0.02
Manual Lab 2	10*	0.18	0.07	0.00	0.16	-	-	-
Manual Lab 3	10	0.11	0.03	0.01	0.10	0.60	0.02	0.01
Manual Lab 4	10*	0.07	0.02	0.01	0.18	-	-	-
Manual Lab 5	9	0.16	0.06	0.03	0.55	0.42	0.04	0.03
Manual Lab 6	10	0.06	0.04	0.01	0.06	0.41	0.02	0.02

Table VII- 9: Standard deviation of measured XRF results (raw meal, * indicates cement). Tablets are marked yellow, green entries are fused beads.

It is clearly shown that automated sample preparation (pressed tablets) leads to improved repeatability. Manual sample preparation with fused beads can lead to repeatability close to automated tablet pressing but also similar to manual tablet pressing, if not done carefully. Automated fusion will also lead to better reproducibility.

6. Calibration

The XRF spectrometer measures the intensity of the element specific fluorescence in the form of pulse rates (kilo-counts per second, kcps). Of final interest, however, is the percentage elemental composition of the sample. Calibration is required in order to establish a mathematical relationship between intensity (count rates) and the corresponding concentration. It is based on a series of measurements of samples of known composition.

Due to matrix effects (see VII 3.4), individual calibrations are required for different material types and for different concentration ranges in order to ensure adequate accuracy. Some technical aspects related to calibration are discussed in the following sections. It needs to be understood that XRF is a relative method and that proper calibration is of outmost importance for accurate analytical results.

6.1 Calibration standards

Calibration standards must represent the chemical composition of the samples to be analyzed. Ideally, the calibration samples cover the calibration range equally spaced.

In case of pressed powder tablets, also the mineralogical composition has to be correctly represented. Note that raw materials from the quarry may change mineralogy over time and thus calibration needs to be adapted.

The chosen sample preparation method (fused bead or pressed tablet) has strong influence on selection and preparation of calibration standards.

Standards may be classified as:

- *Primary*: Certified standards from external suppliers shipped with a certificate of analysis. According to terminology of ISO 29581-2, these are referred to as certified reference materials (CRM).
- *Secondary or plant specific*: Selected materials having the same origin as the materials to be analyzed (e.g. raw meal, cement samples). In ISO 29581-2, these are called industrial reference materials (IRM)
- *Synthetic*: Standards by mixing known components (e.g. pure chemical compounds and/or CRM) in the required proportions.

6.1.1 Certified reference materials (CRM)

CRM's can be purchased from dedicated suppliers. A list of suppliers is given at the end of this chapter. CRM's are typically available for cement and cementitious materials such as slag, fly ash or pozzolana.

CRM's can be used to complement the calibration of fused bead programs. It is possible to establish a fused bead calibration curve based on CRM's only. CRM's must not be used for pressed tablet programs, because they will not represent the mineralogical characteristics of the material to be analyzed (and because they are expensive).

Some XRF suppliers now offer sets of CRM's, which were especially selected for cement plant applications. Examples are the CementQuant package from Bruker AXS, the CEMOXI package from Panalytical or the CATS package of Claisse. With these packages, a plant can set up a fused bead reference calibration, which subsequently can be used to analyze plant specific standards for pressed tablet calibrations.

6.1.2 Plant specific calibration standards / industrial reference materials (IRM's)

The objective of plant specific standards is to match the matrix of the material to be analyzed as close as possible. To obtain such a standard, material from the plant is collected, adequately prepared and analyzed by an external reference laboratory (see procedure in Annex Part VII-3). IRM's are required for preparation of pressed tablet programs for routine analysis.

Certified analyses of secondary/synthetic calibration standards can be obtained from reference laboratories such as the HGRS MT laboratory, certified third party laboratories or central laboratories in a Holcim group company or regional cluster.

6.1.3 Synthetic calibration standards

Synthetic standards are prepared by mixing the required constituents (e.g. pure chemical compounds and/or CRM) in adequate proportions.

Hot meal is the only relevant application of synthetic standards in cement industry. Hot meal is not stable over longer periods of time, as it reacts with moisture and CO₂ from the atmosphere. Thus hot meal is 'simulated' by mixing raw meal, clinker and compounds containing the elements Cl, Na, K and S (such as NaCl, KCl, Na₂SO₄, K₂SO₄, etc). The compounds can be mixed in a linear or in a non-linear way. Two examples are shown in Table VII- 10 and Table VII- 11.

The chemical compounds have to be dried and fine ground in a mortar prior to mixing. The clinker used in the mixes has to be ground to < 10% residue on 90 micron sieve. The mixtures must be well homogenized.

The proportions of the mixtures should be selected in a way that the entire expected concentration range of circulating elements in the hot meal is covered. All mixes should be analyzed by an external laboratory.

Mix #	Raw Meal	Clinker	Mix 1	NaCl	K ₂ SO ₄
Mix 1	200 g	800 g			
Mix 2			80 g	10 g	10 g
Mix 3			90 g	5 g	5 g
Mix 4			95 g	2.5 g	2.5 g

Table VII- 10: Example of hot meal calibration standards (linear mixing)

The linear mixes (i.e. simultaneous increase of all characteristic elements) are easy to prepare. However, inter-element effects between these elements (Cl, Na, K, S) are not perfectly accounted for. The example in Table VII- 11 adjusts the LOI by mixing clinker and raw meal in the appropriate proportions and adds different chlorides and sulfates in a non-linear way. Although a bit more complicated, it should lead to a more robust calibration.

Mix #	LOI	KCl	NaCl	CaCl ₂	K ₂ SO ₄	Na ₂ SO ₄	CaSO ₄
HM 1	2 %			2.0 %	1.0 %		
HM 2	2 %			1.4 %			8.0 %
HM 3	7 %				4.0 %	1.0 %	
HM 4	7 %	1.5 %					2.0 %
HM 5	12 %		0.2 %				3.0 %
HM 6	12 %	0.7 %				0.5 %	

Table VII- 11: Example of hot meal calibration samples (non-linear mixing)

6.2 Pressed tablet calibrations

Calibration standards for pressed tablet programs (IRM's) have to be prepared from the specific materials to be analyzed at the plant. Materials from other plants should not be used, and also commercially available reference or calibration samples should not be used. Separate programs have to be established for each type of material. The entire elemental range occurring in the material type should be covered.

A general flow diagram for preparation of the calibration standards is given in the Annex VII-3. Key aspects are:

- Prepare a sufficient quantity of sample, i.e. 2.5 to 5 kg. Each pressed tablet uses up about 10 to 20g of sample material. To optimize measuring programs (sample preparation) and to allow for regular cross-checks, there should be ample sample available.
- Fineness of the calibration sample: The calibration sample should be in the state just before the final fine-grinding for tablet pressing. Powdered materials such as raw meal should be maintained in their original fineness ex mill; coarse materials such as clinker and raw components have to be crushed to a fineness that is adequate for the last fine-grinding step in the disk mill (typically < 1 - 5 mm).
- The final steps in sample preparation to obtain a pressed tablet have to be strictly identical to the way the routine samples will be prepared (quantity of material for final grinding, grinding vessel, grinding time, grinding aid, applied pressure and time for tablet pressing, etc.).

Typical measuring programs and the required number of calibration samples are given below. The number of standards in Table VII- 12 is based on experience. ISO 29581-2 requires at least 7 calibrations standards per program.

Material	Number of samples	Comments
Raw Meal	8	
Clinker	8 per measuring program	Different clinker types (e.g. Type I, Type V) may require separate measuring programs
Cements	6 – 8 per measuring program	Different types of cements (OPC, limestone cements, slag cements etc) require separate measuring programs and a separate set of calibration samples.
Limestone	6 (CaO range approx. 45 – 54 %)	Fused beads preferred Pressed tablets suitable for Cl and S
Marl	6 (CaO range approx. 12 – 44 %)	Fused beads preferred Pressed tablets suitable for Cl and S
Clay / shale	6 (CaO range approx. 0 – 12 %)	Fused beads preferred Pressed tablets suitable for Cl and S
Correctives: Silica, alumina, iron	4 per measuring program	Fused beads preferred
Mineral components: slag, puzzolan, fly ash	6 per measuring program	Fused beads preferred
Gypsum	4	Fused beads preferred Commercial standards preferred

Table VII- 12: Example for pressed tablet programs in a cement plant

6.3 Fused bead calibrations

The application of fused bead measuring programs is far more universal than that for pressed tablets and is as such not limited to a given, specific source of materials ("plant specific" materials).

Calibration standards for fused bead programs can be prepared from materials of different origin (i.e. different plants). Commercially available reference samples from reputed institutes (CRM's) can be used. Last but not least, samples used and analyzed in round-robin tests can be used.

Lower quantity of material needs to be prepared (typically 150 – 500 g), since preparation of one fused bead consumes only around 1g of sample. A flow diagram for fused bead calibration standards is shown in Annex VII-4.

Fused bead programs can be established in the same way as for pressed tablets (see Table VII-12), which means that for each material a calibration curve exists. With the sample preparation procedure described in ISO 29581-2, the calibration range can be extended, which allows for example combining limestone and marl into one single calibration curve.

The sample preparation in ISO 29581-2 takes into account the weight loss of the sample during fusion, which corresponds to the LOI of the sample in good approximation. Before preparation of a fused bead the LOI of the sample is determined and the required mass m of sample is calculated according to

$$m = \frac{m_0}{1 - \frac{LOI}{100}}$$

where m_0 is the standard sample weight according to the desired flux:sample ratio (see for example Table VII- 7). This method ensures that the actual sample concentration in the fused

bead is always constant. It is in principle identical to preparation of a loss free calibration curve, however more convenient from a practical aspect. When applying this method one needs to convert the test results (kcps, % oxide concentration) back to the as received basis by multiplication with $[m_0/m]$. The example below shows a fused bead calibration curve (CaO) for a limestone/marl/clay deposit with very linear behavior over the whole CaO range.

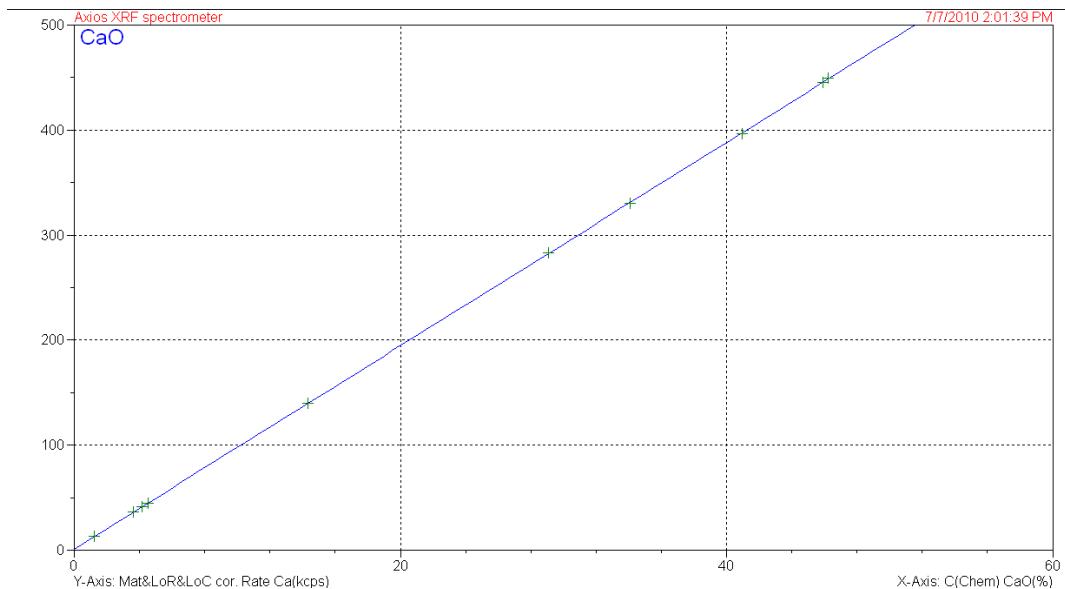


Figure VII- 7: Wide-range CaO fused bead calibration on loss-free basis

It needs to be pointed out that the loss free method described above increases workload and is not recommended for routine applications. It is not required in cases where variation of LOI is small (e.g. raw meal, clinker, cement).

6.4 Advantages / limits of fused bead and pressed tablet programs

Fused beads:

Advantages:

- High accuracy due to elimination of particle size and mineralogical effects and reduced inter-element effects.
- Less restriction with selection of calibration standards. Applicable to materials of different origin (not limited to plant specific materials).
- A relatively wide range of elemental concentrations, also for minor elements, can be covered.
- The same analytical programs with the same calibration standards can be used at several plants.

Disadvantages:

- More time consuming and expensive than pressed tablet preparation
- Lower signal intensity due to dilution of sample (can be relevant for analysis of trace elements).
- Elements with high volatility may be lost during fusion process. This mostly affects chlorine, sulfur and, to some extent, sodium.
- Application in fully automated laboratory systems is more difficult and is typically not done.

Pressed tablets:

Advantages:

- Fast, easy and low cost sample preparation method
- Easy integration into partial and complete automation systems:
 - Automated preparation of pressed tablets

- Automated complete chain from sample preparation to XRF-analyses and up to automatic process control (blending control)
- Less sample dilution and more signal intensity (for analysis of trace elements)
- Analysis of volatile components (chlorides, volatile sulfur components)

Disadvantage:

- Highly susceptible to matrix effects and less accurate than fused bead programs. Subject to significant errors in case chemical, mineralogical and particle size characteristics of the material change.
- Sensitive to changes in the process of tablet preparation (grinding, pressing)
- The element range for minor elements can be very limited and not always be sufficient for a good calibration (e.g. for MgO, alkalis, P₂O₅)

In practice, the pressed powder tablet preparation technique is used for daily routine analysis of production samples. It is, however, strongly recommended to setup fused bead calibration curves, which can be used to cross-check results from tablet analysis, e.g. on a daily basis.

6.5 Matrix correction

Particularly in cases of calibration curves covering a large concentration range, matrix effects can be significant, leading to strongly non-linear relations between intensity and concentration. This can be overcome with mathematical corrections. There are numerous approaches for inter-element corrections, based on either theoretical or empirical considerations. They can be roughly divided into two categories:

- *The influence coefficient methods*: Influence coefficient methods use numerical coefficients that correct for the effect of each matrix element on the element to be determined in a given specimen. These coefficients (sometimes also referred to as “alphas”) are determined empirically. There are different models to determine the influence coefficients (e.g Rasberry-Heinrich model or the more advanced Lachance-Claisse model).
- *Fundamental parameter (FP) method*: The FP method is a fully theoretical approach. It calculates the count rates based on the physical theory of X-Ray production.

The calibration software of modern spectrometers typically comprises several inter-element correction algorithms. For detailed explanations of matrix correction methods refer to literature in the Annex VII-1.

The practical application of matrix correction methods has to be undertaken with care. The main problem is that often only a limited number of standard samples are available, which may not be sufficient to represent the full complexity of the inter-element effects. In consequence the correction coefficients do not fully account for the true inter-element influences, but rather reflect the specific situation of the applied set of standard samples, including sample preparation errors.

For matrix correction using influence coefficients, the following rule of thumb can be applied:

- For the first inter-element correction coefficient, at least 6 calibration samples are required
- For each additional coefficient, at least three more calibration samples are required

In cement industry matrix correction can often be avoided by using narrow calibration ranges and matrix matched calibration standards.

6.6 Standardless XRF

Standardless XRF methods do not use the ‘classical’ approach to establish a calibration based on matrix matched reference materials. Rather they use special software packages to calculate elemental concentrations in unknown samples from a ‘master calibration’ established by the

supplier of the XRF equipment at their laboratories. As such standardless means that the user does not have to look for reference materials. These methods can be useful when

- Matrix matched reference materials are not available. Especially in the field of alternative fuels and raw materials with rapidly changing sample matrix (e.g. contaminated soils), the preparation of calibration standards is often not feasible.
- Elements other than the major ones in the calibration are of interest. For example to investigate concentrations of heavy elements in raw materials.

Standardless methods need a full scan of the 2θ range (WDXRF), thus a spectrometer with goniometer is required. Standardless analysis works also well with EDXRF spectrometers.

All major XRF suppliers offer own software packages for standardless XRF. Most popular are

- *UniQuant 5*: Package developed by ARL (ThermoFisher), the most recent version 5 is only available with ARL spectrometers. It is very flexible and allows complete elemental scans for a huge variety of material types. A scan takes roughly between 5 and 15 minutes. Good experiences made at HGRS.
- *ProTrace*: Package only available with Panalytical AXIOS spectrometers. It is especially suitable for analysis of trace elements in geological samples and cementitious materials. Very good experiences made at HGRS laboratories.
- *Omnian*: Standardless package from Panalytical to work with their sequential WDXRF and EDXRF equipment for completely unknown samples. No experiences at HGRS.
- *SPECTRA^{plus}*: Standardless package for Bruker spectrometers (S8 Tiger and S2 Ranger)
- *TurboQuant*: Standardless package from Spectro for their EDXRF spectrometers (Epsilon 5)

It is clear that not the same accuracy can be expected as with classical calibration methods. Quality of results is variable, depending on the matrix of the sample. Crosscheck with other methods (e.g. ICP-OES, AAS) is necessary. Standardless methods are not used for routine analysis, but are useful to get quickly qualitative elemental information of unknown samples (screening). Reference is also made to the AFR Quality Control manual for applications in the AFR field.

7. Implementation and maintenance of programs

7.1 Implementation of measuring programs

Each X-ray spectrometer supplier has a different philosophy with regard to the measuring conditions:

- Thermo (ARL):
Thermo ARL uses pre-defined settings, e.g. for 3 kW tube rating 30 kV and 80 mA, for 800 W tube rating 20 kV and 30 mA. The counting time is set according to the type of instrument e.g. 60 s for simultaneous spectrometers and 20 – 30 s for sequential spectrometers.
- Bruker:
Bruker determines the optimum measuring conditions for each analytical program at the moment of the implementation of analytical program. The 2θ position and the Pulse Height Analysis (PHA) of all elements are optimized by adjusting the line position to the measurement peak. The optimization of the 2θ is carried out by measuring one calibration sample (e.g. the sample with the highest CaO in the limestone calibration program). An example of the results of such optimization is given in Table VII- 13:

Element	Concentration [%]	kV	mA	kcps	Counting time [s]
Al	0.11	30	80	3.3	20
Ca	54.75	30	30	551	20
Fe	0.10	30	80	15	20
K	0.02	30	80	6	30
Mg	0.30	30	80	5.8	30
Na	<0.01	30	100	1	100
S	0.02	30	80	1	30
Si	0.37	30	80	26	20

Table VII- 13: Optimized settings for Bruker spectrometer (3 kW tube)

- Panalytical

Optimum kV, mA and counting times are established at the factory and are automatically set for every element, but these conditions can be changed according to experience. On first implementation of analytical programs, so called channels are defined for every element of interest, the angel is checked by scanning a sample containing the elements of interest. If the obtained peak is not good, it can be improved by increasing or decreasing the counting time.

7.2 Repeatability of XRF measurements

A simple procedure to evaluate the repeatability of instrument and sample preparation is the following:

- Prepare a batch (approx. 500g) of well homogenized powdered material (cement, raw meal, etc)
- Prepare seven specimens (pressed tablet or fused beads)
- Measure two samples in the following sequence:

1 st sample	2 nd sample
1 st sample	3 rd sample
1 st sample	4 th sample
1 st sample	5 th sample
1 st sample	6 th sample
1 st sample	7 th sample

Standard deviation of the 7 results for the first sample indicates the instrument repeatability.

Standard deviation of all seven specimens indicates instrument and sample preparation repeatability. As a guideline the paired differences between the 7 individual specimens should comply with the limits given in Table VII- 3.

7.3 Maintenance of measuring programs

Various factors can impair the analytical performance of a spectrometer and it is indispensable to check the measuring program periodically. This can simply be done by measuring a reference specimen for instance once per day or once per shift (see procedure below). A good agreement with the known composition of the sample confirms the proper function of the spectrometer. Should deviations occur, it has to be ensured that the sample was intact and the measurement carried out correctly; if so, all applied measuring programs need to be recalibrated. Alternatively a full calibration may be necessary.

7.3.1 Sample procedure for daily check

- Collect a raw meal sample of about 2 kg and homogenize well
- Prepare 10 pressed powder tablets and (or) 10 fused beads and measure them.
- Record all results from the 10 tablets (or 10 fused beads) in an Excel file
- Compute average, standard deviation, minimum and maximum of the 10 values
- Each subsequent day a sample (tablet or bead) is measured. The result should be in the range of the previous measurements.

- If the results are out of the range, prepare a new tablet/bead and repeat the measurement.
(Note: Pressed powder tablets are not stable over longer periods of time)
- If the results are still out of the range:
 - Perform drift correction, repeat measurement.
 - If still out of range, contact service to investigate the reasons for the drift.

7.3.2 Drift correction and recalibration

Despite the high stability of modern spectrometers, long-term drifts are unavoidable. The tube and detector degrade over the time and the response of the other components can also change.

Drift correction occurs by measuring selected specimens (drift correction samples) and calculation of the ratio between observed intensities and those obtained when the calibration was performed. The ratios are then used to correct the measured intensities of the unknown sample; calibration curves are not changed. Drift correction samples do not have to match the matrix of analyzed materials, but they must contain the required elements. Since they need to be stable over long periods of time, mostly glass samples are chosen. They are typically supplied with the spectrometer (e.g. ARL calls them "setting-up samples").

The observed intensity drift should be small and steady over time. A sudden drop in intensities indicates an instrument problem for which the drift correction method is not appropriate. The reasons for the sudden drop of intensities should be investigated with the help of a service engineer. Different elements can drift at different rates. For example a drift of light elements (Na, Mg) only, while heavy elements remain stable, indicates deterioration of the vacuum.

In some situations (e.g. after a major maintenance service) drift correction is not sufficient and recalibration may become necessary. A recalibration consists of an adaptation of the calibration curve (i.e. corresponding mathematical equation) of an element to the new measuring conditions on the basis of one or two recalibration measurements with two calibration standards of high and low concentrations. This procedure is usually foreseen in the software of the measuring program. Since only two measured values are used, recalibration has to be applied with due precaution. Alternatively, all calibration standards can be measured again and completely new calibration curves can be established. This is, however, more time consuming.

Part VIII: Analytical Methods

In this part, some of the fundamental analytical test methods are presented. Where possible, reference is made to the prevalent standards from the standardization institutes (EN, ASTM, DIN). In case a new analytical method has to be implemented in a plant laboratory, it is strongly recommended to refer to these standard methods.

For some methods reference is made to HGRS procedures ("SOP A-xxx"); these methods can be provided on request.

1. Free lime

The free lime content of clinker can be determined with one of the following methods:

- *Manual titration (ASTM C114)*: The method is based on dissolving free lime in a mixture of glycerin/ethanol under reflux and subsequent titration with an alcoholic solution of ammonium nitrate, using phenolphthalein as indicator.
- *Manual titration according to Schläpfer-Bukowski*: Free lime is extracted from the ground clinker sample with ethylene glycol forming a soluble calcium glycolate. The extract is titrated with diluted HCl using phenolphthalein/ naphtolphthalein as indicator. This method is applied in HGRS laboratories (SOP A-006).
- *Conductometry*: Measures free lime as function of the conductivity of a suspension of ground clinker in hot ethylene glycol. Automated titration equipment is available (see Part V). The at-line analyzer from Iteca (including a clinker crushing and grinding unit, see Part VI) is based on the same technique.
- *X-ray diffraction (XRD)*: In principle, there are two methods to analyze free lime by XRD. On the one hand the intensity of the free lime peak at about $37.5^\circ 2\theta$ can be evaluated with a calibration curve; on the other hand, quantification with the Rietveld method is possible. While the calibration method can be applied with XRF spectrometers with a separate free lime channel (limited XRD capabilities), the Rietveld method requires a scan of the full 2θ range and thus a fully capable XRD unit.

Due to the intrinsic instability of calibration samples (hydration of free lime), the recalibration of the analytical program requires a special procedure using green NiO. An example is shown in Annex VIII-1.

Differences between the individual methods exist. Manual titration is considered most accurate, but requires careful manipulation. In particular the quality of the solvents can significantly influence the results; the solvents must be absolutely water-free. Table VIII- 1 shows a comparison of the presented methods regarding time demand and detection limit.

	Time (without sample preparation)	Detection limit	Investment cost
Manual titration	Ca. 45 min	0.1% CaO	Low (< 1k€)
Conductometry	Ca. 5 min	0.2% CaO	Medium (10 k€)
XRD	Ca .5 min	0.4 % CaO	High (> 50 k€)

Table VIII- 1: Comparison of different methods for free lime determination

2. Special methods for selected elements

Elemental analysis of materials in cement industry is usually done with XRF. For certain elements, the detection limit or accuracy of XRF may, however, not be sufficient. In the following special methods for the elements sulfur, carbon, chlorine, fluorine and mercury are described.

Supplier and types of available equipment are given in Part V.

2.1 Sulfur and carbon

The accurate determination of sulfur in cement plant laboratories is of high importance. Also the fast and routine determination of carbon can be a requirement, e.g. to determine limestone contents in cement, or to determine the content of organic carbon in raw materials.

Both sulfur and carbon can easily and accurately be determined with a special S/C analyzer, consisting of a furnace and infrared (IR) detection cells. The sample is burned in pure oxygen atmosphere in which sulfur and carbon compounds are oxidized to gaseous SO₂ and CO₂ respectively. In order to ensure complete oxidation, a catalyst is often added to the sample (e.g. Com-Cat by Leco). SO₂ and/or CO₂ are quantified with IR-cells and allow back calculation of the elemental sulfur / carbon content in the sample.

The analyzers have been proven very versatile, can handle nearly all materials occurring in the cement manufacturing process (raw materials, cement, fuels, etc) and are widely applied. Exceptions are fluoride containing materials (> 1% F), which may damage the equipment.

The lower quantification limit is around 0.02% SO₃. Calibration is based on synthetic calibration standards. Different calibration curves have to be established for different SO₃ concentrations, as linearity is not given over a large concentration range.

A standard operating procedure for determination of sulfur and carbon is available from HGRS/MT (SOP No. A-028).



Figure VIII- 1: LECO S/C analyzer for determination of elemental sulfur and carbon

For raw materials the determination of pyritic sulfur and of organic carbon is often of interest. Both can be easily measured with an S/C analyzer after treating the sample with diluted HCl, in order to dissolve carbonates and sulfates. Standard operating procedures for HCl extraction (A-014) and measurement (A-028) are available from HGRS/MT.

2.2 Chloride

Relevant chlorine concentrations in cementitious materials may range from very low (< 0.01%, e.g. in limestone) up to high (15%, e.g. in bypass dust). The lower quantification limit for XRF (on pressed tablets) is typically around 0.02%. This means the XRF is not sufficiently accurate for evaluation of heat balances and alkali/sulfur balances or for raw material deposit investigations. A frequently used alternative method is potentiometric titration.

Potentiometric titration allows accurate determination of the chloride content in raw materials, raw meal, clinker, cement and fuel samples. The method measures the potential between two electrodes (reference and indicator electrode) as a function of the added reagent volume. Normally the reagent is a silver nitrate solution and the reaction taking place is the precipitation of silver chloride.

The sample needs to be completely dissolved (digested) before it can be analyzed. Possible digestion methods are:

- Treatment with strong (and chloride free) acids such as HNO₃, HF and oxidizing agents such as H₂O₂, possibly in a microwave oven (Example: HGRS A-043)
- Combustion in a calorimeter bomb (works only for combustibles)

The titration can be done manually (burettes), but automated titration equipment is much more convenient and efficient. Different types with different degrees of flexibility and sample throughput are available.

Compared to XRF analysis on pressed tablets, titration offers a lower detection limit (50 ppm Cl) and better accuracy, but requires more time for sample preparation.

A standard operating procedure is given in ASTM C-114. A similar procedure (SOP A-010) is available from HGRS/MT.

2.3 Fluoride

Accurate fluoride analysis is required for plants producing mineralized clinker. Observed fluoride concentrations are typically in a range below 0.3%. In this concentration range, fluoride is best determined by potentiometry using an ion selective electrode (ISE).

Methods using the ISE measure the potential between the ISE and the reference electrode, which is a function of the fluoride concentration in the solution. The measured potential is evaluated either with a calibration curve or with the standard addition method.

- *Calibration (mV vs. F concentration):* A calibration curve can be established with
 - NaF solutions in different concentrations
 - material specific reference standards (e.g. clinker with known F concentration).Since the ISE potential is also affected by other cations in the solution, the second method is preferred.
- *Standard Addition:* After measurement of the sample solution a specific volume of NaF standard solution is added several times and the potentials are recorded. Together with the potential of the blank sample, the unknown F concentration can be determined with linear regression. This method is used at HGRS (SOP A-001). The lower detection limit of this method is around 0.05% F.

All of the three ISE methods are applied within Holcim. HGRS recommends use of either the calibration with material specific reference standards or the standard addition method.

Practical hints for F determination: The sample is fused with solid NaOH pellets and then dissolved in water under addition of citric acid. The measurement solution is buffered with TISAB solution, which is both pH buffer as well as masking agent for cations. Standard glass ware must be avoided, since significant absorption / desorption of fluoride on the glass surface may occur. Instead plastic (TPX, PP) beakers, flasks, etc shall be used. Standard operating procedure from HGRS: SOP A-001

2.4 Mercury

Mercury as environmentally relevant element often needs to be determined in raw materials and fuels. Challenging is the low concentration (sub ppm range), in which it occurs in nature.

Dedicated mercury analyzers based on cold vapor technique have proven to be especially suitable for mercury analysis. The analyzer heats the sample, which liberates the mercury. The gases are swept through a gold coated amalgator, where mercury is selectively trapped by

amalgamation. Then the amalgator is rapidly heated, releasing again the mercury. Detection is based on the AAS technique (see below). The working range of these analyzers is within 5 ppb to 500 ppm, at a repeatability of less than 1.5%.

Most known and widely applied equipment is the AMA-254 (LECO), but other brands are also available (e.g. Analytical Jena). Costs are around 25'000 Euro.

Reference: HGRS SOP A-069; see also EPA Method 7473¹

For higher concentrations levels (> 10 ppm), XRF and ICP-OES can be an alternative method.

2.5 Soluble chromium (hexavalent chromium, Cr⁶⁺)

According to European standards cements must be tested for soluble chromium. It must not exceed 2 ppm.

The official test method is described in EN 196-10. Soluble chromium is extracted from a laboratory mortar during a specified time period. Treatment with diphenylcarbazide solution yields a reddish-purple Cr⁶⁺ complex absorbing at 540 nm which is subsequently quantified with UV/VIS spectrometry. The method should not be applied to clinker samples.

A simple UV/VIS spectrometer can be purchased at relatively low costs (3000 Euro).

3. Spectroscopic techniques for (trace) elemental analysis

The need to determine trace elements may arise in the context of analyzing circulation and enrichment processes in kiln systems, and in the context of using alternative fuels and alternative raw materials. Materials to be analyzed therefore comprise kiln dust, clinker, cement, raw components and fuels, in particular alternative fuels of different nature.

Modern sequential XRF spectrometers allow to measure trace elements and particular heavy elements down to detection limits sufficient for many applications (see standardless analysis in Part VII).

In case lower concentration levels need to be analyzed, or in case sample preparation can only be done by dissolution of the sample, spectroscopic methods using liquids need to be applied, notably AAS (atomic absorption spectroscopy) or ICP-OES (inductively coupled plasma spectroscopy).

3.1 Elemental analysis by optical emission spectroscopy (ICP-OES)

Optical emission spectroscopy can detect all relevant elements (including light elements such as beryllium and boron) and it is suitable for all concentration ranges, i.e. from percentage level down to sub-ppm levels.

Principle: Atoms emit light at characteristic wavelengths, when they are thermally excited. The emission results from electron transitions within the electron shell of the atom. Each emission line results from a particular electron transition in a particular element - in ICP-OES mostly from ionized states. The intensity of the emitted light is proportional to the concentration of the element in the sample.

¹ www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7473.pdf

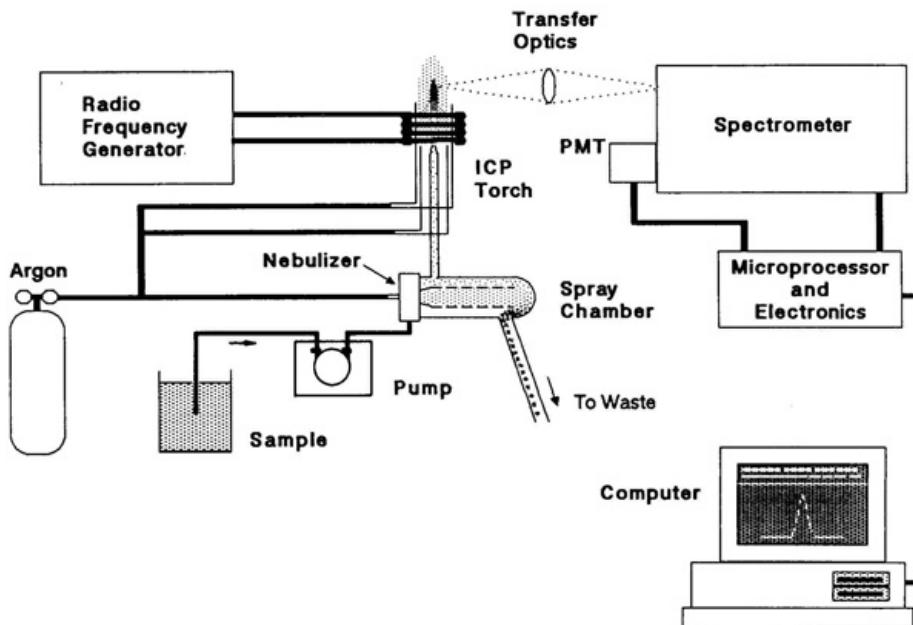


Figure VIII- 2: Schematic setup of an ICP-OES spectrometer

A schematic setup is shown in Figure VIII- 2. Main parts of an ICP-OES equipment are:

- *Pump*: Transfers the liquid sample into the nebulizer/spray chamber
- *Nebulizer*: Transfers the stream of liquid sample into a mist of very fine droplets. Nebulizers work either pneumatically or with ultrasonic. The spray chamber separates large from fine droplets. Fine droplets are then swept with the Argon stream into the plasma torch. Only around 1-2% of the total introduced sample quantity reaches the plasma torch.
- *Plasma torch (ICP – inductively coupled plasma)*: The plasma serves as thermal excitation source. It is a hot (6000 K and more), shining gas consisting of atoms, ions and electrons. The ICP is created and maintained by transferring electrical energy to the Argon gas with a high frequency field induced in the coil. Systems with radial (side viewed) and axial (end-on viewed) plasmas are available. Axial systems usually offer a lower limit of detection.
- *Spectrometer*: The spectrometer isolates the wavelengths of interest (typically in the range of 160 – 860 nm) from the light emitted by the plasma source. This is achieved by diffraction of the emitted light on special gratings.
- *Detector*: The detection system translates the intensity of light of a certain wavelength into an electronic signal which is processed to give the elemental concentration. Most systems employ solid state CCD (charge couple device) type detectors.

Modern systems are able to measure several elements simultaneously, however, sequential spectrometers are still available.

Sample preparation is an important aspect of this technique, since only liquid solutions can be introduced into an ICP-OES system. Solid samples require digestion procedures involving strong acids (e.g. H₂SO₄, HNO₃, HF, etc.) and a designated microwave oven. For examples of digestion procedures see ASTM D5513 or ASTM D5198 (waste materials).

Due to the required sample preparation effort ICP-OES is not necessarily a technique for routine process control. The method requires experiences in set-up and operation, and should only be applied if the low detection limits of trace elements are a requirement for a specific laboratory. Applications in a cement plant can be

- Determination of trace elements (heavy metals) in raw materials, clinker, cement and fuels. The method is typically applied in AFR laboratories of AFR platforms or of cement plants

needing a strict acceptance control of AFR's. Acceptance control is often requested by the environmental authorities and may be part of operating permits.

- Elemental composition of materials where XRF reference materials are not available (e.g. AFR or ashes of fuels). Example: P_2O_5 content in animal meal.
- Reference method for validation of other methods (e.g. XRF)

Supplier: see Part V.

3.2 Atomic absorption spectroscopy (AAS)

AAS is another method to determine the concentration of a specific element in a sample. Approximately 70 elements can be measured.

Principle: AAS makes use of the same (element specific) electronic transitions as emission spectroscopy, but in a reverse manner. A beam of light with the characteristic wavelength is sent through the atomized sample. The higher the loss in intensity of the light beam, the higher the concentration of the element in the sample. A schematic setup is shown in Figure VIII- 3.

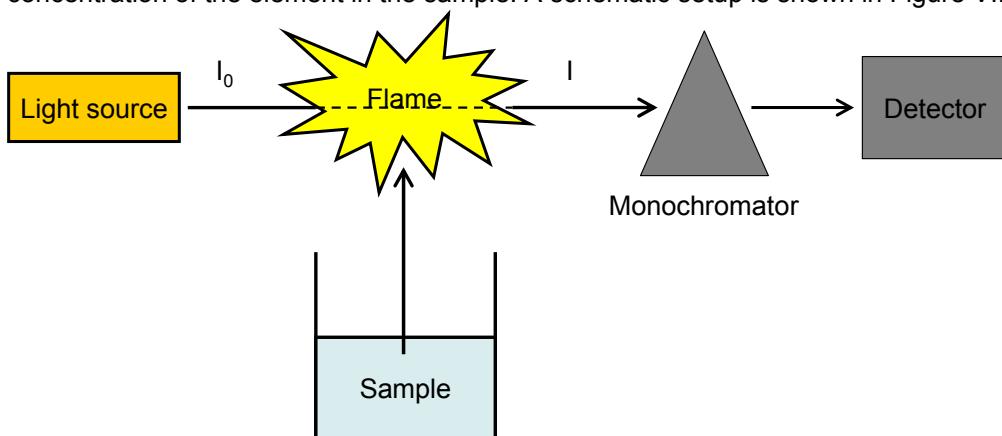


Figure VIII- 3: Schematic setup of a (Flame)-AAS analyzer

Main components of an AAS spectrometer are:

- *Light Source*: Traditional light source for AAS is the hollow cathode lamp (HCL). With a HCL light at the element specific wavelengths can be generated. However, for each element to be analyzed a different HCL is required, which renders AAS a single element method. Latest generation spectrometers use Xenon lamps as continuous light source, which is applicable for nearly all elements.
- *Atomizing unit*: As for ICP OES, the liquid sample needs to be first nebulized and then atomized. Traditional atomizing unit is the air-acetylene flame (temperature around 2500 K) or the nitrous oxide (N_2O)-acetylene flame (temperature around 3000 K). Alternative electro-thermal atomization units are available (ETA-AAS), which mostly consist of a graphite furnace, electrically heated to around 3000K. Compared to Flame-AAS, ETA-AAS offers lower detection limits as no nebulizing unit is needed. Even solid samples can be analyzed.
- *Monochromator*: Acts as a filter and lets only pass light with the desired wavelength.
- *Detector*: Traditionally photomultiplier tubes were employed. In modern spectrometers semiconductor detectors are used.

Different techniques for background absorption compensation are used and are improving the analytical performance. Most common are:

- Compensation with deuterium lamp: A deuterium lamp serves as second light source and is alternating with the HCL. Both signals are used to compensate for background absorption.
- Compensation using the Zeeman Effect: A magnetic field is applied to the atomization unit (mostly for ETA-AAS) and the light from the HCL is passed through a rotating polarizer.

AAS is mainly used for analysis of trace elements. Applications in cement laboratories can be

- Analysis of environmentally relevant elements such as Cd or Ti (ETA-AAS), as it offers lower detection limits compared to ICP-OES.
- Accurate determination of alkalis (Na, K) with flame-AAS. Flame AAS is a reference method for determination of alkalis according to ASTM C 114.
- In combination with the cold vapor technique mercury can be analyzed at very low detection limits (see 2.4).

For suppliers see Part V.

3.3 Comparison of ICP-OES and AAS

In very general words, AAS is less complex, easier to use and cheaper in purchasing and operation as compared to ICP-OES, but less flexible. The decision for a method needs to be taken in view of the application (required elements, detection limits, sample throughput, etc.). The table below shall give a few indications.

	ICP-OES	Flame-AAS	ETA-AAS
Detection limits	Very good for most elements Best for non-metals (e.g. B, S, P), refractories (e.g. Al, Si, Ba, Ti), halogens	Very good for some elements Best for Group I elements (e.g Na, K)	Excellent for some elements Best for all metals (e.g. Cd, Ti)
Elements	73	68+	50+
Sample throughput	1-60 elements per minute Best if > 6 elements per sample	10-15 sec per element	3-4 min per element
Precision Short term Long term (8h)	0.1 – 2.0% 1 – 5%	0.1 – 1.0% 1 – 2%	0.5 – 5% 1 – 10%
Interferences Spectral Chemical Ionization	Many Very few Very few	Very few Many Some	Very few Very many Very few
Sample volume req.	Medium	Large	Very small
Capital cost	High 60 – 140 kU\$	Low 15 – 20kU\$	Medium 30 – 40 kU\$
Operating costs	High	Low	Medium
Unattended operation	Yes	No	Yes

Table VIII- 2: Comparison between ICP-OES and AAS techniques. See also ²

3.4 ICP-MS

The ICP atomization unit is also available in combination with a mass sensitive detector (MS). This technique offers detection limits in the ultra-trace range (sub ppb), which may be required for some environmental analyses. At the same time ICP-MS is very demanding to operator skills and operating conditions. It is not a typical equipment in standard cement plant laboratories and will thus not be further discussed.

² A good overview of spectral elemental analysis is available from Thermo:
http://www.thermo.com/eThermo/CMA/PDFs/Articles/articlesFile_18407.pdf

4. Wet chemical methods for elemental analysis

The traditional “wet” test methods are based on gravimetric, colorimetric or titrimetric techniques. They involve a series of manual operations such as weighing, igniting, dissolving and desiccation. The procedures often require strong chemical reagents, which can be dangerous if not handled properly. An analyst with both scientific education and manipulation skills is required to obtain acceptable results. The methods are time consuming and prone to errors.

Test methods for chemical analysis of cement are described in the standards below. They are not further explained in this manual.

- ASTM C 114
- EN 192-2
- ISO 29581-1

In most of the operating cement plants, these methods are no longer applied for routine analyses, for reasons mentioned above. Still, some of the methods are useful for reference analysis or as a backup method if all XRF equipment fails (e.g. carbonate titration).

5. XRD: Determination of mineralogical composition

X-ray diffraction (XRD) provides information about the atomic arrangement in a crystal. In cement industry, powder diffraction is used to get qualitative and quantitative analysis of crystalline compounds. It is a rapid and non-destructive analysis.

Every crystalline material gives a characteristic diffraction pattern which acts as a unique “fingerprint” (see for example a mixture of calcite and quartz in Figure VIII- 4). The position and intensity information are used to identify the phase by comparing it with patterns from a database, such as the Powder Diffraction File (PDF) or the International Center for Diffraction Data (ICDD).

Only crystalline phases produce a distinct pattern that can be used as a fingerprint in identification. Amorphous phases, as for example occurring in blast furnace slag, are more difficult to qualify and quantify.

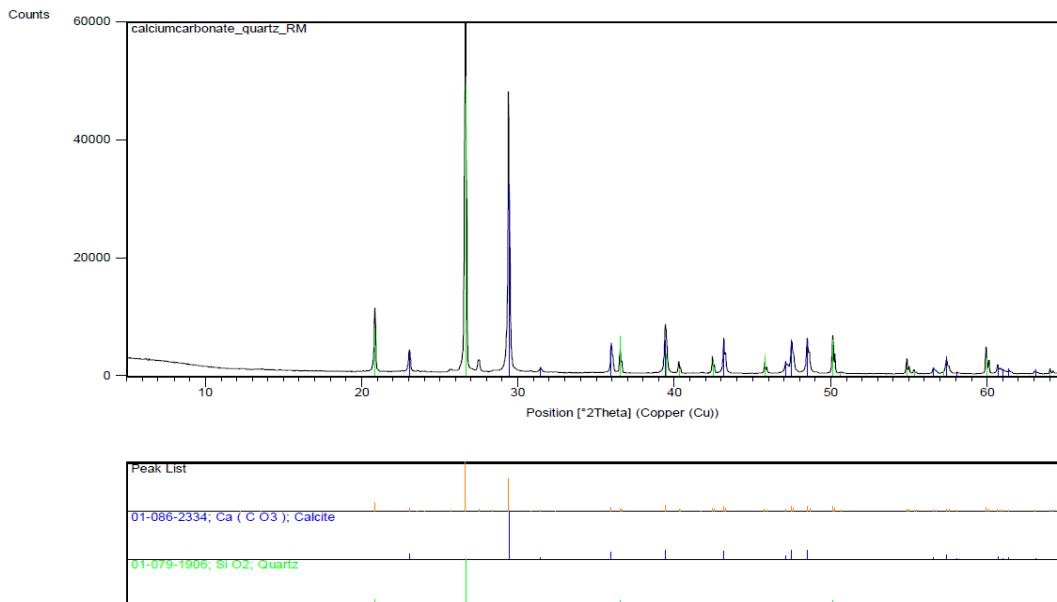


Figure VIII- 4: Powder diffraction pattern of a calcite/quartz mixture (e.g. limestone)

XRD has become an analytical tool for routine analysis in cement plants only in the last 10 years. The number of XRD applications is, however, rapidly growing.

5.1 Principles of XRD

XRD makes use of elastic scattering of X-rays at the electron shells of atoms. In crystalline materials (with periodically arranged atoms), constructive interference of scattered radiation occurs at certain angles. The angle or direction of interference is characteristic for each mineral leading to the characteristic diffraction pattern. The Bragg's law describes the conditions under which constructive interference occurs:

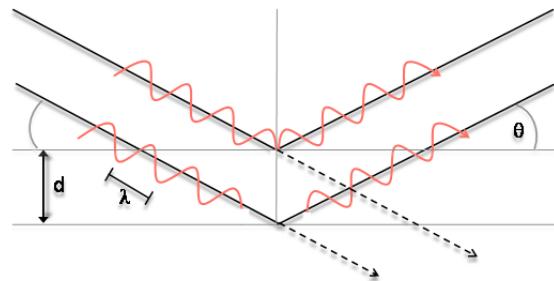
$$n \lambda = 2 d \sin \theta$$

$$n = 1, 2, 3, \dots$$

λ = wavelength of x-ray radiation

d = distance between lattice planes

θ = scattering angle



With known λ (monochromatic x-rays) the diffraction angle θ is measured and the characteristic distance d between lattice planes can be evaluated. On the other hand, if d (and θ) is known the wavelength λ can be determined; this is utilized in WDXRF to discriminate the energy of the fluorescence radiation (see Part VII).

Figure VIII- 5 below shows a typical powder diffractogram of a clinker sample. On the x-axis the diffraction angle 2θ is plotted versus the intensity of the reflections (counts) on the y-axis.

Overlapping of different reflections from different minerals is common. The width of the reflection is a function of the crystallinity of the mineral phase. The reflections tend to get broader with

- Very small crystal size ($<0.1 \mu\text{m}$)
- High defects and disordered crystal structure, e.g. due to incorporation of foreign atoms such as alkalis in Alite

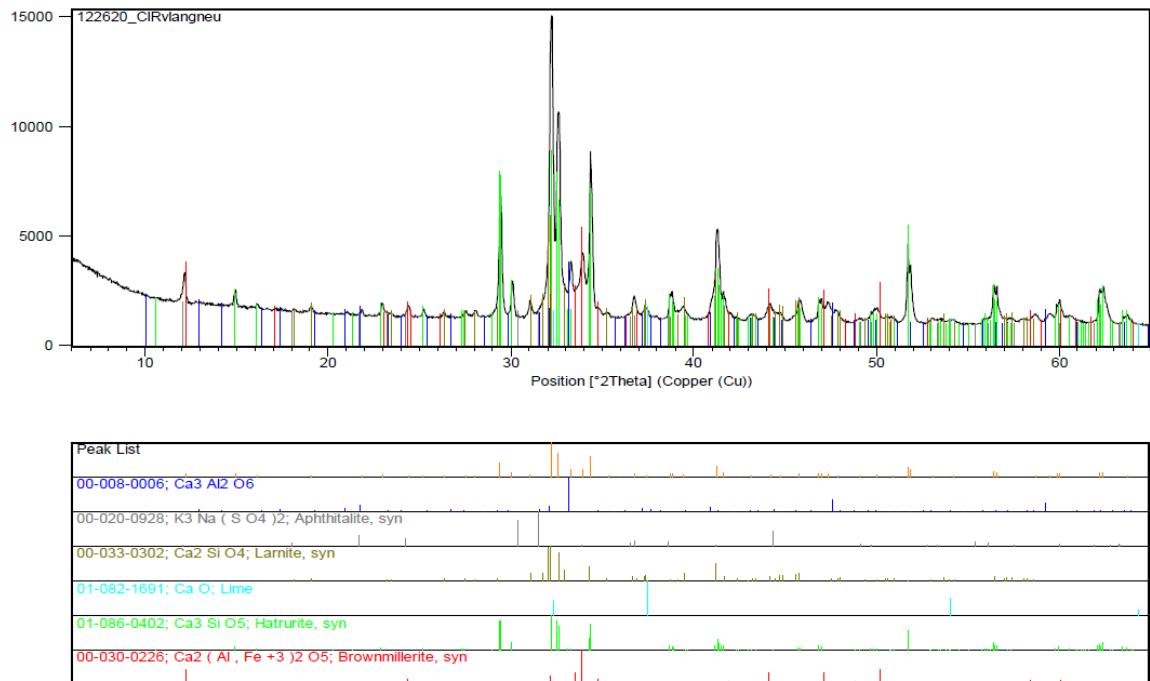
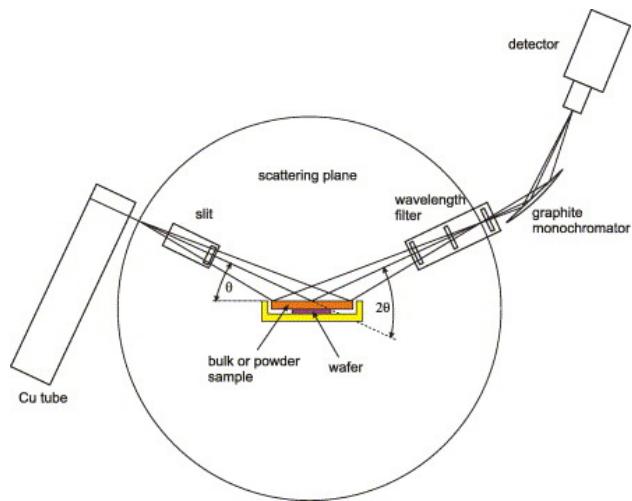


Figure VIII- 5: Powder diffractogram of a clinker sample

5.2 XRD spectrometers

A typical XRD spectrometer consists of an x-ray tube, a sample holder and a moving detector mounted on a goniometer (see Figure VIII- 6). The sample is placed on the central sample holder, the x-ray tube and the detector are arranged peripherally on the focusing circle; this configuration is known as Bragg-Brentano and is used in most commercially available spectrometers. While moving both the sample and the x-ray tube the intensity of the reflected X-rays is measured.



F
Figure VIII- 6: Schematics of an XRD spectrometer [R. Gilles et al, Acta Materialia 2006, 54(5), 1307]

The X-ray tubes for XRD are similar to the ones used for XRF. A typically employed tube would have a copper anode and a power rating of 1 – 3 kW. XRD requires monochromatic x-ray radiation. This is achieved by a monochromator (typically graphite crystal), which is placed between the sample and the detector.

Bruker and Panalytical are the two major supplier of XRD spectrometers. They both offer a range of products for the different application requirements. A good choice for cement plants is the D4 Endeavour spectrometer from Bruker or the Cubix³ spectrometer from Panalytical. These are both designed for routine applications in an industrial environment, i.e. they are compact, offer high sample throughput and can be integrated into automated laboratories. Spectrometers designed for research such as the D8 Advance (Bruker) or the Empyrean (Panalytical) offer more flexibility and possibilities and may be an option for regional laboratories (e.g. on RMSO level).

ARL (ThermoFisher) also offers XRD spectrometers, both as standalone instrument (ARL X'TRA) and combined with XRF (ARL 9900 Series). XRD capabilities in the ARL 9900 come in three versions (free lime channel, compact version for determination of free lime and major clinker phases and the Workstation with full XRD capability). ARL is compared to Bruker and Panalytical relatively new to XRD (first units in 2005) and is still considered lagging behind the two others, especially in terms of Rietveld software.

The trend is to use separate units for XRF and XRD as both equipment can be used simultaneously, whereas the combined XRF/XRD unit can only do one measurement at a time.

5.3 Sample preparation

Sample preparation is an important aspect of quantitative XRD analysis. Samples are always analyzed on pressed tablets as fusion would destroy the crystals in the sample. Grinding is needed to reduce the size of crystallites and randomize their orientation. However, overgrinding will lead to loss of crystallinity and thus has to be avoided. For cement samples, high grinding temperature must be avoided as it changes the content of the different SO₃ containing phases (gypsum dehydration). Cement samples are mostly pressed to tablets without prior grinding.

For routine analysis the process of fine-grinding and pressing should be automated (e.g. by using an automated combination of mill and press, see systems described in Part VI). The usage of pressed tablets, which were prepared for XRF does often not give optimal reflection intensities. It is desirable to have a separate sample preparation program for XRD analysis; however in practice this is often not done due to time constraints.

5.4 Quantitative XRD

While XRD can readily provide qualitative information, it is much more difficult to get quantitative information (i.e. how much of each mineral is present). There are in principle three methods for quantitative XRD:

- *Internal standard method (RIR)*: Used for special applications, very time consuming and not further discussed here.
- *Calibration method*: Reference standards with known concentration of the mineral are used to establish a calibration curve (signal intensity vs. concentration; similar to XRF). This approach requires that the mineral shows characteristic peaks which are not overlapped and that the mineral can be quantified by a reference method. This method is often applied for determination of free lime or limestone (calcite) in cement. It has only limited use for determination of the clinker phases alite and belite, as solid solution effects from foreign cations lead to peak shifts.
- *Rietveld refinement*: Most powerful method for phase quantification, allows quantification of clinker phases on a routine basis. Further described below.

5.4.1 Rietveld refinement

Rietveld refinement is a computational, standard-less method to determine mineral concentrations in material samples from powder diffractograms.

The Rietveld (whole pattern fitting) method fits a theoretically calculated pattern to a practically measured XRD-pattern by a least-square refinement. The theoretical pattern is generated from a list of potentially present phases together with their structural parameters and further information such as lattice dimensions, atom positions, preferred orientation, peak width, etc, which are available from crystallographic databases. All this information is compiled in the control file, which needs to be created for each application. Setting up a control file requires profound expertise in mineralogy and requires support from the XRD supplier. For clinker applications ready-to-use control files are available from the suppliers (and from HGRS). For cement application, a corresponding control file needs to be established for each cement type.

Rietveld refinement requires special software modules, which are delivered with the XRD spectrometer on request. The corresponding software from Bruker is named TOPAS BBQ, Panalytical provides RoboRiet for this purpose.

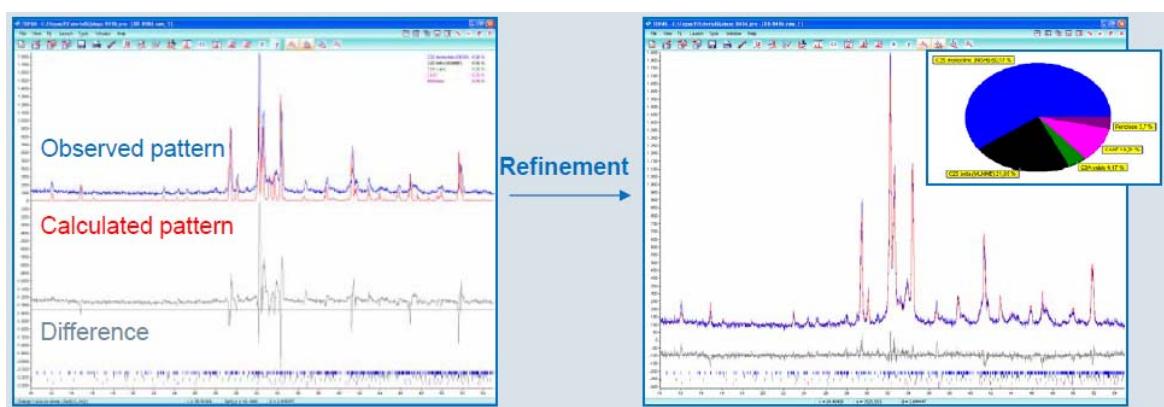


Figure VIII- 7: Process of Rietveld refinement (Source: Bruker AXS presentation)

During the fitting of a measured pattern with the calculated one, parameters are varied in an iterative manner in order to find the best fit (= refinement). Mathematically, the quality of the fit is described with the parameters goodness of fit (GOF), the residual Rp (quantifies difference between observed and calculated patterns), and the weighted residual wRp. As a rule of thumb, Rp and wRp are considered satisfactory when they are less than 10, GOF less than 4, and when these values remain stable in a series of measurements.

The difficulties in the phase quantification with Rietveld occur due to:

- Overlapping peaks (e.g. alite and belite)
- Solid solution effects which alter intensities and positions (e.g. C₄AF)
- Background noise, which limits detection of phases with small quantities (e.g. free lime and periclase)

Limitation of quantitative XRD in terms of precision is illustrated in Table VIII- 3 below. The results result from intra- and inter-laboratory tests (11 different laboratories) using artificial cement composed of NIST SRM clinker [Lit 15]. These numbers are also basis for the standard test method ASTM C 1365.

	Mineral content [%]	Repeatability (within laboratory)		Reproducibility (between laboratories)	
		Standard deviation s	r (d2s)	Standard deviation s	R (d2s)
Alite	52.0%	0.74	2.04	2.23	6.18
Belite	20.5	0.64	1.77	1.41	3.91
Aluminate	5	0.47	1.31	0.74	2.05
Ferrite	13	0.49	1.36	0.95	2.63
Periclase	3.7	0.23	0.63	0.32	0.89
Gypsum	4.4	0.21	0.59	0.58	1.62
Bassanite	1.8	0.39	1.08	0.81	2.24
Anhydrite	2.1	0.27	0.74	0.63	1.75

Table VIII- 3: Repeatability and reproducibility of quantitative XRD; d2s indicates the maximum difference between duplicates

The detection limit of minor mineral phases is generally around 0.5% and varies in function of the mineral. Precise quantification is possible for minerals in concentrations above 1% (rule of thumb).

5.5 Applications and benefits

Phase quantification with XRD/Rietveld has found several applications in cement industry, some of them are listen in Table VIII- 4.

Material	Applications	Benefits
Clinker	<ul style="list-style-type: none"> • Free lime determination • More realistic clinker phases as with Bogue calculation • Potential Identification of different alite modifications (M1/M3) (offered by Bruker only) 	<ul style="list-style-type: none"> • Better kiln control • Detection of deviation from normal production. Most promising in situations with complex AFR utilization. • Sound database for cement optimization and strength prediction
Cement	<ul style="list-style-type: none"> • Determination of sulfate phases • MIC quantification (e.g. limestone, slag) 	<ul style="list-style-type: none"> • Control of gypsum dehydration (strength, setting) • Fast verification of MIC proportioning
Hot meal	<ul style="list-style-type: none"> • Determination of mineral phases 	<ul style="list-style-type: none"> • Reduced cyclone blockages in situations with high Cl and SO₃ input (example SG)
Raw meal / Kiln feed	<ul style="list-style-type: none"> • Potentially: Determination of quartz content 	<ul style="list-style-type: none"> • Control of kiln feed burnability

Table VIII- 4: Application and benefits of phase quantification with XRD/Rietveld

XRD/Rietveld can be integrated into laboratory automation. It is expected that the application of XRD/Rietveld in cement plant laboratories will become more important in the future. Particularly in context of increasing AFR consumption, XRD is believed to provide additional information for better kiln control. Some plants already started to use parameters such as alite for clinker control and no longer use the chemical parameters (LS, SR, etc.). However, XRF will remain the main equipment for process control. XRD should not distract from accessing the basic requirements (good uniformity, stable kiln operation, etc.).

6. Thermal analysis

Main thermal analysis technique used in cement industry is Thermogravimetrical analysis (TGA) and, to a lesser extent, Differential Scanning Calorimetry (DSC). The methods are often complementary. Both methods require very little sample material, typically between 10 and 100 mg.

TGA involves measurement of the mass of a sample in function of temperature, while the sample is subjected to a controlled temperature program. A typical TGA curve shows the mass loss (or gain) of a sample plotted against the temperature (Figure VIII- 8). Any event that causes a change of sample mass (i.e. dehydration, decarbonatization) can be observed.

DSC monitors the heat flow to a sample and to a reference while the entire system is subjected to a controlled temperature program. In other words, sample and reference are maintained at the same temperature and the heat flow to keep both at the same temperature is measured. A DSC plot shows the differential rate of heating (J/s) against the temperature. Any event that results in absorption or evolution of heat (such as phase transitions, decomposition reactions) can be observed. The area under a DSC peak is directly proportional to the heat of reaction.

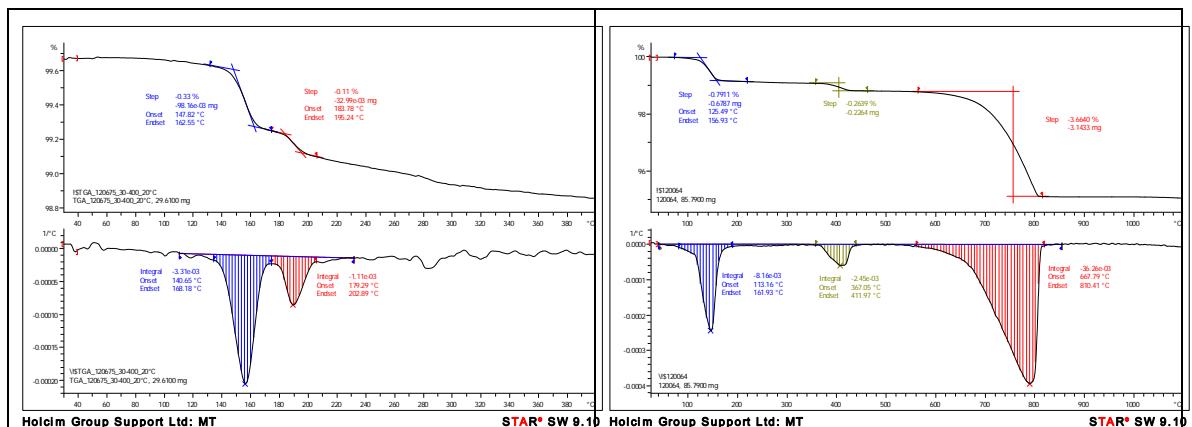


Figure VIII- 8: TGA curve of a slag cement sample (left) and a limestone cement (right). Note the different temperature range.

Applications:

- *Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and hemi-hydrate ($\text{CaSO}_4 \frac{1}{2} \text{H}_2\text{O}$) in cement with TGA:* The conversion of di-hydrate to hemihydrate (at 150 to 160 °C) and hemihydrate to anhydrite (at ca. 200 °C) is evaluated. A typical heating rate for TGA is 20 °C/min (with ca. 40 mg). In order to have separate peaks of the two dehydration steps the crucible must be covered with a perforated lid. For calculation of sulfate phases see instructions in Annex VIII-2.
- *Determination of calcite in cement or raw meal with TGA:* Decarbonatization of calcite (loss of CO_2) occurs at about 700 to 800 °C. Calculation of the amount of calcite in the sample: %_weight_loss x 2.28.
- *Pre-hydration of cement with DSC and TGA:* Only qualitative indications for hydration-phases in cement samples can be obtained. CSH phases appear as broad peaks between 50 and

250°C, ettringite at ca. 110 - 120°C (broad) and monosulfate at about 220°C. Most easily the hydrated free lime peak can be identified at about 450°C.

7. Fineness

7.1 Sieving (sieve residues)

Sieving is a very common method in cement plants to determine material fineness from grinding processes. The sieve openings of the sieves depend on local standards and requirements, but very often the sieves in Table VIII- 5 below are employed:

Material	Fine sieve	Coarse sieve
Raw meal	90 µm (or 75 µm)	200 µm (or 212 µm)
Coal / Petcoke	90 µm (or 75 µm)	200 µm (or 212 µm)
Cement	32 µm or 45 µm	75 µm or 90 µm

Table VIII- 5: Frequently used sieves

Examples for applicable standards are EN 196-6 (dry sieving), ASTM C110, ASTM C430 or ASTM C786 (wet sieving). The standards describe manual procedures. The use of mechanical sieving devices is, however, recommended for powders (e.g. Alpine Air Jet Sieve), as they improve repeatability of the method. Typical sample mass for sieving is 20g (sieves 45 – 75 µm) to 50 g (sieves > 90 µm), which takes around 10 to 20 minutes to be processed on an Alpine AirJet.

Both wet and dry sieving is possible. Dry sieving is mostly used for coarse sieves (> 45 µm), wet sieving for fines sieves (< 45 µm). Note that dry and wet sieving may give significantly different results, depending on the nature of the material. For example raw meals containing chalk limestone give lower residues with wet sieving as the fine chalk particles dis-agglomerate when in contact with water.

7.2 Specific surface area (Blaine)

Fineness of cement is often indicated by its specific surface area (SSA).

The specific surface can be determined by the Blaine air permeability method described in ASTM C204 or EN 196-6. The SSA (or Blaine value) is a calculated value based on the time that a certain amount of air needs to flow through a pad of cement with defined dimensions and compaction degree. Calculation of the Blaine values also requires the density of the cement sample. Blaine values are indicated in cm²/g (in some places m²/kg is used); typical values for cement are between 3000 – 5000 cm²/g (or 300 – 500 m²/kg).

The apparatus to determine Blaine values is relatively simple and can even be self-made according drawings in the referred standards

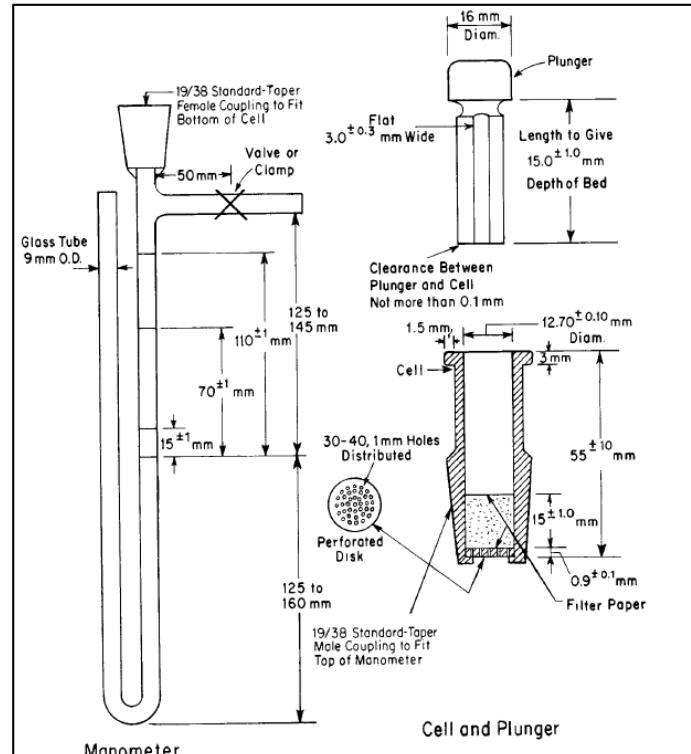


Figure VIII- 9: Schematics of Blaine apparatus, according to ASTM C204

above (see for example Figure VIII- 9). Commercial equipment with different degrees of automation is available from a great number of suppliers (e.g. ToniTechnik, Ele, Acmel). The Blaine measurement is not very precise and suffers from poor reproducibility. ASTM D204 states that two measurements of the same cement by the same operator should not differ by more than 3.4% - resulting in a maximum difference of ca. 140 cm²/g at 4000 cm²/g. A recent inter-laboratory test has shown Blaine values between 4520 and 4940 cm²/g for the same cement sample (23 plants participating, 4730 cm²/g on average, s=118 cm²/g). Significant differences can even occur between different operators at the same plant, in particular when using manual equipment. Automated equipment improves repeatability of the measurement.

It needs to be pointed out that different cement samples with different particle size distributions can yield the same specific surface. As such the Blaine value is not a direct measurement of the cement fineness.

An alternative method for specific surface determination is the BET method (named after the scientists Brunauer, Emmet and Teller). It is based on physical absorption of gas molecules (e.g. nitrogen) on cement particles. The BET method also includes internal surfaces of particles such as micro-cracks or pores. It is, however, not used for routine measurements at cement plants.

7.3 Particle size distribution (PSD) with laser granulometer

The use of particle size analyzer based on laser diffraction (also referred to as laser granulometer) has become widespread in cement industry. The particle size distribution is calculated by comparing the scattering pattern obtained from sample material falling through the laser beam with an optical model. Applied models are the Fraunhofer theory and the Mie theory. A comprehensive description can be found in the ISO 13320-1 Standard.

Both laboratory systems and on-line systems are available. On-line systems are discussed in Part VI. The laboratory equipment typically consists of a

- Feeding unit: Feeds the powder into the dispersing unit (vibratory feeder)
- Dispersing unit: Dry or wet dispersing units are available. For cement applications, dry dispersion is recommended. If wet dispersion is chosen, non-aqueous media (e.g. isopropanol) should be used.
- Optical unit: Different lenses are available, which define the particle size range the analyzer can measure. A typical range for cement applications is 1 – 350 µm.

Good maintenance of the equipment is required for optimal usage. In particular the optical system needs to be cleaned frequently with a good vacuum cleaner. For dry dispersion, high quality compressed air is needed, free of oil and moisture, which requires a separate compressor unit. Total cost of a laboratory system is around 80 – 90 k€.

Main suppliers of laser granulometers are:

- Malvern, UK: Malvern offer the Mastersizer series as laboratory system and the Insitec for online process control (see chapter 6)
- Sympatec, De: HELOS system for laboratory applications, MYTOS for online process control
- CILAS, Fr: Offers laboratory systems only

Laser granulometers give a complete particle size distribution of the sample in a very short time. Typically the PSD is displayed as mass distribution curve with a logarithmic particle size scale (see Figure VIII- 10). The Rosin-Rammler-Sperling-Bennet (RSSB) distribution is often a good approximation for the observed PSD. Thus the PSD can be characterized with the RSSB parameters x' (position parameter, indicating fineness) and n (slope, indicating the width of the PSD). For more details refer to the Product Optimization Manual.

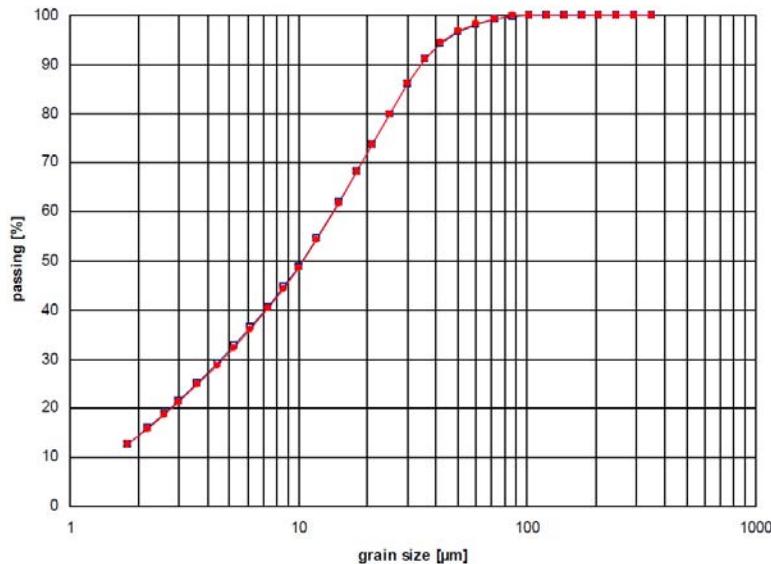


Figure VIII- 10: PSD (cumulative curve) as measured by a laser granulometer

It has to be pointed out that reproducibility of PSD curves between different granulometers (brand and type) is not always given [Lit 16].

7.4 Comparison between different methods

Different techniques of fineness measurement will give different results and cannot always be directly compared. The differences result from the different physical measurement principles, as different dimensions of the particles are measured. They are an inherent problem of particle size analysis. There is not one right or wrong result.

For example the sieve residues as determined by dry sieving and by laser granulometer will always disagree to a certain amount. Laser granulometry will generally report larger particle size (higher residues) compared to sieving. Figure VIII- 11 below shows a comparison of the three discussed techniques on (OPC) cement samples. The two techniques to measure the residue on 32 micron (R_{32}) show the same trend, but there is a significant difference in absolute numbers. Blaine values show the expected inverse trend (higher Blaine – lower sieve residues).

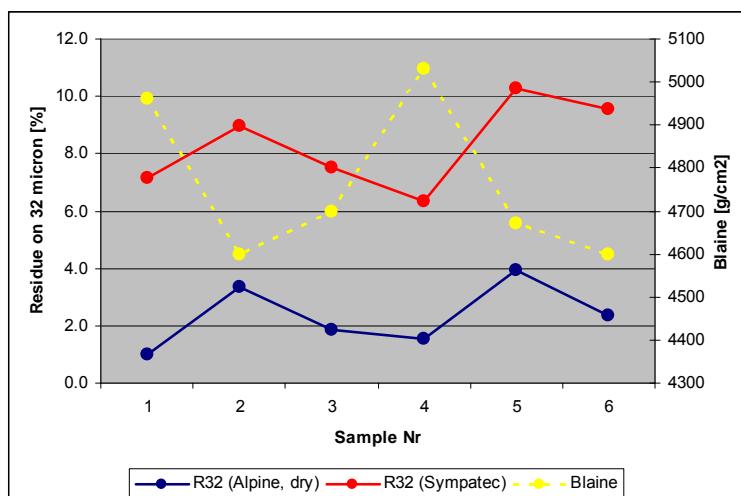


Figure VIII- 11: Comparison of sieve residues by dry sieving and laser granulometer of cement samples (same cement type, same plant but different production periods)

Most supplier of laser granulometer developed methods to calculate the specific surface area (Blaine) value from the particle size distribution. This calculated Blaine can be used for relative

comparison with other samples, but one should be very careful to compare it to actually measured Blaine values with the method described above.

8. Physical testing

Physical testing methods of cement are described in pertinent standards and are not described further in this manual. Table VIII- 6 below shows relevant testing parameters and methods according to ASTM standards and EN standards. Required testing equipment is given in Part V.

	EN	ASTM
Compressive strength	EN 196-1	ASTM C109
Setting time (Vicat needle)	EN 196-3	ASTM C191
Normal consistency (Vicat)	EN 196-3	ASTM C187
Soundness (Le Chatelier)	EN 196-3	
Soundness (Autoclave expansion)		ASTM C151

Table VIII- 6: Standards for cement testing

9. Fuel testing

9.1 Traditional fuels

9.1.1 Analysis of solid fuels (coal and petcoke)

Testing of traditional, solid fuels (i.e. coal and petcoke) may include several parameters.

- **Proximate analysis:** Proximate analysis stands for a group of parameters defined in ASTM D3172:
 - Moisture (104°C – 110°C open crucible) – ASTM D3173
 - Ash content (750°C open crucible) – ASTM D3174
 - Volatile matter (950°C, covered crucible) – ASTM D3175
 - Calculation of fixed carbon
 The methods do not require sophisticated equipment – muffle furnaces with good temperature control and ventilation are sufficient. Depending on the region other procedures (temperature programs) may exist.
- **Ultimate analysis:** Ultimate analysis stands for a group of parameters as defined in ASTM D3176:
 - Moisture – ASTM D3173
 - Ash content – ASTM D3174
 - Total sulfur content – ASTM D3177
 - Total carbon and hydrogen content - ASTM D3178.
 - Total nitrogen content – ASTM D3179
 Determination of S, C, H and N is mostly done with special analyzers based on high temperature combustion (e.g. the S/C analyzer described in 2.1). While S/C analyzers are relatively common in cement plant laboratories, dedicated H and N analyzer are more found in central laboratories.
- **Calorific value:** Determination of the calorific value typically requires a bomb calorimeter. Examples of applicable standards are ASTM D5865 or DIN 51900. One should carefully differentiate between gross calorific value (GCV) and net calorific values (NCV). While the GCV can be directly measured, NCV can only be obtained from calculations. The most accurate method requires determination of the elemental hydrogen content. If elemental hydrogen cannot be determined approximate formulas may be used according to Table VIII- 7.

It is important to indicate the reference state of the analyzed fuel sample (e.g. as received, air dried, as fired), as this has an impact on the GCV. Conversion between different reference states is possible when moisture content of each state is known (see formulas in DIN 51900).

- **Chlorine content:** May be determined according to ASTM D4208.
- **Ash composition:** Ash composition can be determined by XRF using ASTM D4326. Alternatively individual elements of interest can be determined by ICP-OES.

ASTM D5865 (general relationship)		Where:
$Q_{\text{net}} = Q_{\text{gross}} - 215.5 * H$		Q_{net} : Net calorific value [J/g], constant pressure
Approximation for coal:		Q_{gross} : Gross calorific value [J/g], constant volume
$Q_{\text{net}} = Q_{\text{gross}} * 0.983 - (15 * VM) + 60$		H: Total hydrogen content [%], including sample moisture
Approximation for petcoke:		VM: Volatile matter [%]
$Q_{\text{net}} = Q_{\text{gross}} * 0.981$		

Table VIII- 7: Conversion NCV – GCV (according to ATR Guidelines)

9.1.2 Analysis of liquid fuels (fuel oils)

The main properties of fuel oil derived from petroleum are subject to certain standards. For example, Table VIII- 8 shows requirements for heavy fuel oil according to the German Standard DIN 51603.

Requirement			Testing method
Flashpoint in closed cup: min	°C	65	DIN 51758
Kinematic viscosity: max	mm ² /s (cSt)	at 50°C: 450 at 100°C: 40	DIN 51561 DIN 51562
Conradson carbon residue: max	% mass	15	DIN 51 551
Sulfur content: max	% by mass	2.8	DIN 51409
Water content, not removable: max	% mass	0.5	DIN 51786
Sediment content: max	% mass	0.5	DIN 51789
Calorific value: min	MJ/kg	39.8	DIN 51900
Ash (oxide ash): max	% mass	0.15	DIN EN 7

Table VIII- 8: Requirements for heavy fuel oil as per German Standard DIN 51603

Similarly, the Standard ASTM D396 contains specifications for fuel oils and refers to a list of testing methods.

Most of these tests are not carried at the plant laboratory but in specialized laboratories (external laboratory or AFR laboratory). Important parameter to be tested at the plant can be

- Calorific value: Bomb calorimeter, see solid fuels
- Flashpoint: Flash point tester, see AFR Quality Control Manual
- Viscosity: Viscosimeter, see AFR Quality Control Manual

9.1.3 Analysis of natural gas

Most important parameter of natural gas is the calorific value. It this can be determined

- With a continuous recording calorimeter according to ASTM D1826
- By stoichiometric combustion according to ASTM D-4891

9.2 Analysis of alternative fuels

See AFR Quality Control Manual.

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[Lit 16] R. Geurts, *World Cement* **1992**, 51.

Annexes

Annex Part II-1: Quality Manager

Standard Job Description

Job Title:	Quality Manager
Purpose/Mission:	
Ensure that the quality of intermediate and final products comply with authorized specifications and product targets and provide input to ensure that products are competitive in the market	
Dimensions	
Scope of authority:	<ul style="list-style-type: none"> ▪ Quality and Control of finished, semi-finished and input products, including fuels and AFR ▪ Support implementation and maintenance of ISO 9000 ▪ Ensure consistency of management systems (ISO 9000, 14000, 18000, Holcim systems)
Spending authority:	Within budget limit
Report to:	Plant Manager
Functional report	Plant Manager
Location	
Department / Group	
Management level	MML / Line function
Critical Tasks:	Critical Tasks achievement measurement:
1. (Quality lab operations) Plan, organize and manage sampling, measurements and analysis throughout the production process. Ensure calibration and maintenance of equipment is properly done.	Analysis are accurate and precise Planned analysis are completed on time
2. (Quality operations) Carefully analyze quality performance, timely identify any deviation from standards and investigate causes. Collaborate with the Production Manager and Process Performance Engineer / Manager to define corrective and preventive actions.	Deviation from target set for process and product # of customer complains related to quality issues Product uniformity
3. (Standards) Ensure that the appropriate quality system is in place and manage it in line with regulations and in coordination with RMSO Quality Assurance. Prepare and coordinate across departments ISO, EN and central quality certification; ensure correct implementation of the corrective actions identified through audits.	Quality documents alignment with latest regulation and RMSO Quality assurance Achievement of needed certification Norms requirements (internal, EN) fulfillment # of observations in ISO certifications # of legal non compliance Essential PQM elements not in place
4. (People management) Inform and motivate quality personnel, ensure their availability and performance according to plant needs and promote their professional development through coaching, individual development plans and trainings.	Absenteeism rate Dialogue performed with direct reports Achieved individual development plans of direct reports
5. (Management – Planning and cost control) Collaborate with internal and external stakeholders to define product and process requirements. Investigate and propose possible ways to maximize the trade off between benefits and costs of the quality system.	Compliance with internal product and clinker specification Lab budget respect Process and product quality
6. (OH&S and environment) Guarantee and foster compliance with OH&S and environment policies for all quality personnel. Ensure cleanliness within quality premises and contribute to plant cleanliness.	LTIFR and LTISR of team under responsibility Number of environmental issues
7. (Innovation and continuous improvements) Together with the Process Performance Engineer / Manager and Production Manager, consider and propose new techniques and/or technologies to optimize costs and improve quality. Investigate and validate impact of product, production and process changes onto quality.	Product quality improvements Process quality improvements Production quality improvements

Qualifications, including competencies, skill, knowledge:			
Preferred Education:	Chemistry or Chemical Engineering, Material science degree		
Preferred professional memberships:			
Preferred Experience:	3 years experience in laboratories of industrial companies; experience in ISO certifications. Statistical knowledge. Knowledge in cement and possibly experience in cement application		
Computer Skills	Microsoft Office, SAP, TIS/LIMS		
Language requirements:	Local language English	Language Level:	Good written and spoken Good written and spoken
Other	Knowledge of PMA, Solvel preferred		
1. <i>Think the business:</i> Strategic alignment; analysis and problem solving; business and financial acumen 2. <i>Deliver results:</i> Manages execution; customer focus; supports action, change and innovation; leads for performance 3. <i>Energize people:</i> Communication; engages and inspires; develops employees; cultivates relationships and networks; fosters teamwork and cooperation 4. <i>Act as a role model:</i> Adapts and learns; establishes trust and confidence			

Other requirements:

JD written by:	Pier Gribaudi, Beatriz Méndez-Villamil	Version Number:	3.0
JD controlled by:	Jean-Pierre Grozellier, Strategic Cement Manufacturing	Date issued:	December 07

Annex Part II-2

October 12, 2007

LABORATORY SUPERVISOR**GENERAL DESCRIPTION:**

Responsible for overseeing and ensuring efficient laboratory operations including: analysis and quality control of raw mix, clinker and cement, analysis of raw materials, fuels including traditional, alternative and liquid alternative fuels. Supervise plant lab personnel and ensure adherence to quality standards, policies and testing procedures.

SUPERVISION EXERCISED/RECEIVED:

Work is performed with considerable independence with the review of tests and procedures made by the Quality Manager for desired results and conformance to established policies. Exercises supervision over Physical Tester.

DUTIES:

- Ensure continuous improvement of all technical and laboratory operations
- Schedule lab activities to maintain optimum workflow
- Develop and implement QC/QA training programs for lab personnel
- Monitor chemical and physical test results to ensure that quality objectives and targets are met
- Work with the distribution and production departments to investigate out-of-specification results and recommend corrective actions
- Ensure quality programs and procedures, including corporate and ISO guidelines, are strictly followed
- Ensure that the lab maintains CCRL certification and that it complies with applicable regulatory standards and guidelines, e.g. ASTM C 150, AASHTO M 85, DOT requirements, etc.
- Monitor all lab equipment, test procedures, calibration requirements and results
- Maintain all quality data and sample request records
- Actively participate in reviewing and setting quality targets and objectives as a member of the plant's quality council
- Conduct safety training for relevant lab and quality related areas
- Implement lab safety procedures and audits, take corrective action to eliminate safety hazards, ensure that employees receive adequate safety training and facilitate departmental toolbox safety meetings, etc.
- Maintain a clean and orderly work area

PREFERRED QUALIFICATIONS:

Education:

- Bachelor's degree in chemistry desired; engineering or other related field preferred

Experience and Skills:

- Two (2) plus years material handling and/or industrial process experience
- Two to four years QC/QA experience and/or similar training
- Experience with sampling and testing
- Experience with EMS, QMS and H&S processes
- Working knowledge of ASTM and AASHTO test methods and specifications
- Working knowledge of computers, mathematics, and chemistry
- Working knowledge of laboratory equipment operation and calibration
- SAP PP user role experience

Human Resources**QUALITY TECHNICIAN I****GENERAL DESCRIPTION:**

Quality Technician I provides a quality product to the customer by collecting samples and performing tests on raw materials, materials in process, finished products, and competitive products.

SUPERVISION EXERCISED / RECEIVED:

Work is performed with considerable independence with the review of tests and procedures made by the Quality Manager for desired results and conformance to established policies. Exercises no supervision over any other laboratory personnel.

DUTIES:

- Follow all safety policies, procedures, MSDS, and proper use of chemicals
- Able to operate and troubleshoot the automation equipment in order to have all samples analyzed
- Responsible to operate the x-ray equipment and RoboLab automation equipment in manual mode
- Take, prepare and analyze samples from authorized sampling points as per the Quality Control Plan, work instructions and quality procedures, e.g. Blaine, 45-, 90-, 200- μ m fineness, x-ray pellet preparation and analysis, pack set, LOI, split LOI, free lime titration, SO₃ determination by Leco, and calcination degree
- Interpret test results and take actions to production process control as per Quality Control Plan in order to maintain product quality targets
- Enter all data into Laboratory Data Management System (LDMS)
- Understand and follow the Quality Management System (QMS) documents that apply to the Quality Department, e.g. Quality policy, control of non-conforming product
- Must be able to work positively in a team environment
- Additional duties, as required

PREFERRED QUALIFICATIONS:

Education:

- High School diploma or equivalent

Experience:

- Previous experience in the cement industry or laboratory environment

Skills:

- Possess adequate computer skills to run x-rays, automation software, LDMS, and reporting information
- Basic understanding of the cement manufacturing process and the relationship between the chemical and physical properties and their effects on the final product
- Math skills at the algebra level
- Read, write, and speak English
- Communication
- Initiating action
- Good work standards

Rev. Date: April 22, 2009

October 12, 2007

PHYSICAL TESTER

GENERAL DESCRIPTION:

Physical Tester analyzes and reports all physical properties of cement in accordance with ASTM (Section 4.01) and AASHTO Standards.

SUPERVISION EXERCISED/RECEIVED:

Work is performed with considerable independence with the review of tests and procedures made by the Laboratory Supervisor for desired results and conformance to established policies. Exercises no supervision over any other laboratory personnel.

DUTIES:

- Follow all safety policies and procedures.
- Composite cement production; run ASTM C 150 / AASHTO M 85 tests including: Blaine, 325, Vicat initial and final set time, false set, flow, air, autoclave, mortar bar, makes and breaks cubes
- Run ASTM C 917 test for customer information
- Keep Blaine and 325 screen verification and calibration up to date
- Check moist cabinet for sufficient water, temperature, and humidity
- Keep monthly lab sheet current
- Run ASTM C 150 / AASHTO M 85 test methods on monthly samples for all state lab requests
- Run ASTM C 150 / AASHTO M 85 test methods on competitor samples
- Run ASTM C 563 optimum SO₃ and ASTM C 1038 mortar bar expansion
- Maintains work area in clean and orderly condition
- Performs calibrations and verifications of assigned equipment
- Maintains LDMS update for both, physical tests and calibration records
- Assist and perform such other duties as directed by the Laboratory Supervisor

PREFERRED QUALIFICATIONS:

Education:

- High School diploma or equivalent
- Associates degree or specialized training in relevant field preferred

Experience and Skills:

- Two (2) to four (4) years of relevant work experience
- Previous experience in the cement industry or laboratory environment
- Math skills at the algebra level

Human Resources**MAINTENANCE TECHNICIAN I (LABORATORY)****GENERAL DESCRIPTION:**

Under the direction of the Laboratory Supervisor, the Mechanical Maintenance Technician I (Laboratory) is responsible for trouble shooting equipment, preventative maintenance inspection, installation of equipment, and improvement of the RoboLab. Good mechanical aptitude is required for this position.

SUPERVISION EXERCISED / RECEIVED:

Work performed with considerable independence with the review of maintenance repairs and procedures made by the Laboratory Supervisor for desired results and conformance to established policies. Exercises no supervision over any other laboratory personnel.

DUTIES:

- Follow all safety policies and procedures
- Timely repair of RoboLab equipment and auxiliaries so as to maximize availability of the RoboLab to the Quality Technicians
- Operate forklift, man lift, light crane, drill press, cut-off saw, pipe threader, hydraulic press, iron worker, and various hand tools
- General layout, welding and cutting skills with ability to work from blueprints, sketches, or detailed instructions
- General rigging knowledge
- Have a basic understanding of hydraulics and be able to read schematics
- General knowledge of installation and care of bearings (roller, ball, and sleeve oil)
- Coupling alignment knowledge
- Make preventative maintenance inspections and complete necessary forms and reports
- Track and document RoboLab performance on daily basis
- Make estimates of material requirements and prepare requisitions and reports
- Maintain work area in clean and orderly condition
- Respond to call-outs during non-work hours as needed
- Perform such other assignments as directed by the supervisor

PREFERRED QUALIFICATIONS:

Education:

- High School diploma or equivalent
- Completion of trade school or training program preferred.

Experience:

- Two (2) plus years industrial maintenance experience

Skills:

- Use of Microsoft Office
- Good computer skills
- Read, write, and speak English
- Communication
- Decision making
- Initiating action
- Good work standards

Rev Date: April 22, 2009

Annex Part IV-1: Supplier of sampling equipment

Supplier, country	Website	Products
FLSmidth, Danmark (acquired Pfaff AQS)	http://www.flsmidth.com	Various (automated and manual) samplers for powders. Special clinker, hot meal designed for cement industry. Pneumatic sample transport.
Polysius, Germany	http://www.polysius.com	Various (automated and manual) samplers for powders. Special clinker, hot meal designed for cement industry. Pneumatic sample transport.
Herzog, Germany	http://www.herzog-maschinenfabrik.de	Various (automated and manual) samplers for powders. Special clinker, hot meal designed for cement industry. Pneumatic sample transport.
ITECA, France	http://www.iteca.fr	Various (automated and manual) samplers for powders, clinker and hot meal designed for cement industry. High temperate clinker sampler, below grate sampler. Vezin type sampler. Pneumatic sample transport.
M&W Jawo, Danmark	http://www.m-w.dk/	Samplers for powders and coarse materials, cross-belt samplers. Sample splitting equipment
Intersystems, USA	http://www.intersystems.net	Samplers for mining industry, cross belt samplers. Sample splitters.
Essa, Australia	http://www.essa.com.au	Samplers for mining industry (large volumes), cross stream samplers

Annexe Part V-1: International Test Sieve Comparison Table

International Test Sieve Comparison Table 2011 TEST SIEVES, NOMINAL SIZES OF OPENINGS					125-1 mm TABLE 1		Internationale Analysensieb-Vergleichstabelle 2011 SIEBBÖDEN FÜR ANALYSENSIEBE (Prüfsiebe) Maschen- bzw. Lochweiten				
1	2	3	4	5	6	7	8	9	10	11	
ISO 565 · ISO 3310 Table 1, Millimetre sizes		DEU	FRA	GBR	NLD	USA		CAN	TYLER®		
Principal sizes Hauptreihe	Supplementary sizes Nebenreihen	DIN	NF	BSI	N	ASTM E 11 #, 2004 ASTM E 323 ②, 1980 (2004)		CGSB	T		
R 20/3	R 20 R 40/3	DIN ISO 3310	AFNOR NF ISO 3310	BS 410 ISO 3310	NEN 2560	ASTM E 11 #, 2004 ASTM E 323 ②, 1980 (2004)		CAN/CGSB-8.2-M88 metric	TYLER Screen Scale		
2000	2001	2000	2000	1998				1988	1910		
ISO 3310-1	Woven Wire Cloth #	125-1	125-1	125-1	125-1	125-1	125-1	125-1	26,5-1		
ISO 3310-2	Round Holes ●	125-1	125-1	125-1	125-1	125-1	125-1				
	Square Holes ■	125-4	125-4	125-4	125-4	125-4	125-3,35				
w	w	w	w	w	w	w	w	No.	w	Mesh	
125	125	125	125	125	125	125	125	5 in.	125		
	112		112	112	112	112			112		
		106	106	106	106	106		4,24 in. 4 in. (b)	100		
	100		100	100	100	100		3,1/2 in.	90,0		
90	90	90	90	90	90	90	90		80,0		
	80		80	80	80	80		3 in.	71,0		
		75	75	75	75	75					
	71		71	71	71	71					
63	63	63	63	63	63	63	63	2,1/2 in.	63,0		
	56		56	56	56	56			56,0		
		53	53	53	53	53		2,12 in. 2 in. (b)	50,0		
	50		50	50	50	50					
45	45	45	45	45	45	45	45	1,3/4 in.	45,0		
	40		40	40	40	40			40,0		
		37,5	37,5	37,5	37,5	37,5		1,1/2 in.			
	35,5		35,5	35,5	35,5	35,5			35,5		
31,5	31,5	31,5	31,5	31,5	31,5	31,5	31,5	1,1/4 in.	31,5		
	28		28	28	28	28			28,0		
		26,5	26,5	26,5	26,5	26,5		1,06 in. 1 in. (b)		1,05 in.	
	25		25	25	25	25		25,0 (b)	25,0		
22,4	22,4	22,4	22,4	22,4	22,4	22,4	22,4	7/8 in.	22,4	.883 in.	
	20		20	20	20	20			20,0		
		19	19	19	19	19		3/4 in.		.742 in.	
	18		18	18	18	18			18,0		
16	16	16	16	16	16	16	16,0	5/8 in.	16,0	.624 in.	
	14		14	14	14	14				.525 in.	
		13,2	13,2	13,2	13,2	13,2		0,530 in. 1/2 in. (b)			
	12,5		12,5	12,5	12,5	12,5		12,5 (b)	12,5		
11,2	11,2	11,2	11,2	11,2	11,2	11,2	11,2	7/16 in.	11,2	.441 in.	
	10		10	10	10	10			10,0		
		9,5	9,5	9,5	9,5	9,5		3/8 in.		.371 in.	
	9		9	9	9	9			9,0		
8	8	8	8	8	8	8	8,0	5/16 in.	8,0	2,1/2	
	7,1		7,1	7,1	7,1	7,1				7,10	
		6,7	6,7	6,7	6,7	6,7		0,265 in. 1/4 in. (b)		3	
	6,3		6,3	6,3	6,3	6,3		6,3 (b)		6,30	
5,6	5,6	5,6	5,6	5,6	5,6	5,6		3,1/2	5,60	3,1/2	
	5		5	5	5	5				5,00	
		4,75	4,75	4,75	4,75	4,75		4		4	
	4,5		4,5	4,5	4,5	4,5				4,50	
4	4	4	4	4	4	4	4,00	5	4,00	5	
	3,55		3,55	3,55	3,55	3,55				3,55	
		3,35	3,35	3,35	3,35	3,35		3,35		6	
	3,15		3,15	3,15	3,15	3,15				3,15	
2,8	2,8	2,8	2,8	2,8	2,8	2,8	2,80	7	2,80	7	
	2,5		2,5	2,5	2,5	2,5				2,50	
		2,36	2,36	2,36	2,36	2,36		8		8	
	2,24		2,24	2,24	2,24	2,24				2,24	
2	2	2	2	2	2	2	2,00	10	2,00	9	
	1,8		1,8	1,8	1,8	1,8				1,80	
		1,7	1,7	1,7	1,7	1,7		1,70	12		
	1,6		1,6	1,6	1,6	1,6				1,60	
1,4	1,4	1,4	1,4	1,4	1,4	1,4	1,40	14	1,40	12	
	1,25		1,25	1,25	1,25	1,25				1,25	
		1,18	1,18	1,18	1,18	1,18		1,18	16		
	1,12		1,12	1,12	1,12	1,12				1,12	
1	1	1	1	1	1	1	1,00	18	1,00	16	

Woven Wire Cloth # Drahtgewebe

Round Holes ● Rundlochung

Square Holes ■ Quadratlochung

(b) ASTM Supplementary values

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International Test Sieve Comparison Table 2011 TEST SIEVES, NOMINAL SIZES OF OPENINGS				900–5 µm TABLE 2			Internationale Analysensieb-Vergleichstabelle 2011 SIEBBODEN FÜR ANALYSENSIEBE (Prüfsiebe) Maschen- bzw. Lochweite				
1	2	3	4	5	6	7	8	9	10	11	
ISO 565 · ISO 3310 Table 2, Micrometre sizes		DEU	FRA	GBR	NLD	USA		CAN	TYLER®		
Principal sizes Hauptreihe	Supplementary sizes Nebenreihen	DIN	NF	BSI	N	ASTM E 11 #, 2004 ASTM E 161 Ø, 2000 (2004)		CGSB	M	CAN/ CGSB- 8.2-M88 metri	TYLER Screen Scale
R 20/3	R 20 R 40/3	2000	2001	2000	1998			1988		1910	
ISO 3310-1	Woven Wire Cloth #	900-20	900-20	900-20	900-20	850-20	850-20	900-32		850-20	
ISO 3310-3	Electroformed Ø	500-5	500-5		500-5	500-5					
w	w	w	w	w	w	w	w	No.	w	Mesh	
	900		900	900	900			900		20	
	800		850	850	850	850	850	20	800		
710	710	710	710	710	710	710	710	25	710	24	
	630		630	630	630	630	630		630		
		600	600	600	600	600	600	30	560	28	
500	500	500	500	500	500	500	500	35	500	32	
	450		450	450	450	450	450		450		
		425	425	425	425	425	425	40	400	35	
355	355	355	355	355	355	355	355	45	355	42	
	315		315	315	315	315	315		315		
		300	300	300	300	300	300	50		48	
250	250	250	250	250	250	250	250	60	250	60	
	224		224	224	224	224	224		224		
		212	212	212	212	212	212	70		65	
180	180	180	180	180	180	180	180	80	180	80	
	160		160	160	160	160	160		160		
		150	150	150	150	150	150	100		100	
125	125	125	125	125	125	125	125	120	125	115	
	112		112	112	112	112	112		112		
		106	106	106	106	106	106	140		150	
90	90	90	90	90	90	90	90	170	90	170	
	80		80	80	80	80	80		80		
		75	75	75	75	75	75	200		200	
63	63	63	63	63	63	63	63	230	63	250	
	56		56	56	56	56	56		56		
		53	53	53	53	53	53	270		270	
45	45	45	45	45	45	45	45	325	45	325	
	40		40	40	40	40	40		40		
R'10	36	36	36	36	36	36	36		36	400	
32			32	32	32	32	32	450	32	450	
25			25	25	25	25	25	500		500	
20			20	20	20	20	20	635		635	
16 Ø			16 Ø	16 Ø	16 Ø	16 Ø	15 Ø				
10 Ø			10 Ø	10 Ø	10 Ø	10 Ø	10 Ø				
5 Ø			5 Ø	5 Ø	5 Ø	5 Ø	5 Ø				
Woven Wire Cloth # Drahtgewebe				Electroformed Ø Elektrogeformte Siebfolie				© Copyright 2011 by HAVER & BOECKER			

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Annex Part V-2: General Laboratory Equipment

1. Glassware

Standard volumetric flasks, burettes, and pipettes should be of precision grade or better. Wherever applicable, the use of special types of glassware, such as colored glass for the protection of solutions against light, alkali-resistant glass, and high-silica glass having exceptional resistance to thermal shock is recommended.

Funnels, various size and top diameters	10 of each size
Burettes, normal, semi-automatic and automatic type; 10, 25 and 50 ml; readability 0.05 and 0.1 ml	3 of each size
Beakers, high form, Jena glass; 50, 100, 250, 400, 600, 800 and 1000 ml	10 of each size
Erlenmeyer flasks, Jena glass; 100, 250, 300, 500 and 1000 ml	10 of each size
Reflux condenser; length 300 mm min.	2 pieces
Measuring glass cylinders, graduated, round foot; 10, 50, 100, 250, 500 and 1000 ml	10 of each size
Volumetric pipettes; 5, 10, 20, 50 ml	10 of each size
Graduated pipettes; 10, 20 and 50 ml	10 of each size
Pipette Filler, rubber bulb with 3 air valves	10 pieces
Test tubes, AR glass	100 pieces
Wash bottles, flat bottom flask, Jena glass; with rubber stopper and glass tubes; 250, 500 and 1000 ml	5 of each size
Watch glasses, Jena glass; various diameters (40, 100, 125, 150 and 175 mm)	10 of each size
Volumetric flasks, graduated; 250, 500 and 1000 ml	5 of each size
Wide-neck bottles, with screw lids (sample bottles for powder); 100, 250 ml	300 pieces of each
Wide-neck bottles, with screw lids (sample bottles for powder) 500, 1000 and 2000 ml	50 pieces of each
Thermometers, centigrade scale - 20 to 150 °C and from - 5 to 400 °C	5 each

2. Polyethylene containers

Polyethylene containers (bottles etc.) are recommended for all aqueous solutions of alkalis and for standard solutions where the presence of dissolved silica or alkali from the glass would be objectionable. Such containers shall be made of high-density polyethylene having a wall thickness of at least 1 mm.

PE bottles, wide-neck and narrow-neck; 100, 250, 500 and 1000 ml	10 each
Narrow-neck bottles, polypropylene; 10 and 20	10 each
PE beakers; 50, 100, 250 and 500 ml	10 each
Funnels, polypropylene; various diameters	10 each
Wash bottles, plastic; 500 ml	10 pieces
Pipette supports, plastic	6 pieces
Test tube supports, plastic	6 pieces
Plastic bags different sizes	1000 pieces each
Sample containers, plastic; 500	500 pieces
Sample containers, plastic; 1000, 2500 and 5000 ml	50 pieces

3. Various accessories

Weighing scoops	10 pieces
Weighing boats, aluminum	6 pieces
Agate mortars, with pestle, standard quality; inner diameter approx. 100 mm	2 pieces
Porcelain mortars, with pestle; various diameters	2 pieces
Porcelain dishes, glazed; various diameters	10 pieces
Evaporating dishes, porcelain, with spout; 100 and 150 ml	20 of each
Crucibles, porcelain; various size and diameter	20 each
Buchner funnels, porcelain; diameter 65 mm	10 each
Filter paper, coarse-textured, medium-textured and retentive paper	20 pks of each
Indicator paper, universal; incl. color scale	5 pks
Tripod supports, steel; for gas burners	5 pieces
Plate supports, with iron plate and steel tube	5 pieces
Filtering funnel supports, steel or plastic	5 pieces
Support clamps, angular; steel, corrosion proof; various clamp widths	5 pieces
Spatula spoons, alumina and nickel; various size	5 each
Crucible tongs, steel or nickel; various size	5 pieces
Brushes, various types; for cleaning of burettes, pipettes etc	10 each
Rubber hose, 1a quality; various diameters	5 m
Vacuum hose; various inner diameters (5, 10 mm) and wall thickness (3,5 mm)	5 m
Rubber stoppers, assorted	100 pieces
Rubber gloves	12 pairs
Water jet pumps, chromium plated brass and plastic	2 pieces
Glass cutter	2 pieces
Stop watches	4 pieces
Glass wool	2 kg
Stopcock grease	100 g
Tool box; containing hammers, screw drivers, saws, wrenches, etc.	1 set

Annex Part V-3: List of Chemicals

Reagent grade chemicals shall be used in all tests (designation of chemicals as "p.a." or "a.r.").

5 l	Ammonia solution, min. 25%
1 kg	Ammonium acetate
1 kg	Ammonium chloride
0.5 kg	Ammonium molybdate
1 kg	Ammonium nitrate
0.5 kg	Ascorbic acid
2 kg	Barium chloride
1 kg	Borax
30 l	Ethanol
20 l	Glycol
20 l	Hydrochloride acid, 36%
15 g	Methyl orange indicator
2 l	Nitric acid, 65%
1 kg	Potassium hydroxide
2 kg	Potassium carbonate
20 g	Phenolphthalein indicator
1 kg	Sodium hydroxide (pellets)
0.50 kg	Sodium chloride
2 kg	Sodium carbonate (anhydrous)
0.50 kg	Sulphosalicylic acid
0.20 kg	Silver-II-nitrate
1 l	Sulphuric acid, 95-97%

Annex Part VI-1: PGNAA guarantees static, dynamic, blending performance

TYPICAL REQUIRED PGNAA PERFORMANCE GUARANTEES

1. PGNAA ANALYZER FOR STOCKPILE CONTROL

1.1 Static Performance Guarantee (Stockpile)

Description	Guarantee Values	Remarks
1.1.1 Static Precision (repeatability)		
- Dry basis - LOI incl. - 5 h; 300 values - Reduction to 30 values, each as average of 10 consecutive values	One Standard Deviation	Oxide SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ CaO MgO SO ₃ K ₂ O Na ₂ O Cl
1.1.2 Static Accuracy		
Procedure - Dry basis - LOI incl. - RMSD (root mean squared deviation) - 1 h	Guaranteed Maximum RMSD	Range *) Oxide (4% - 25%) SiO ₂ (0% - 6%) Al ₂ O ₃ (0% - 6%) Fe ₂ O ₃ (25% - 50%) CaO (0% - 5%) MgO (0% - 1%) SO ₃ (0% - 2%) K ₂ O (0% - 2%) Na ₂ O (0 - 0.05%) Cl
Performance verification of static accuracy is conducted with five reference standards. Performance is verified by comparing known values for each oxide in each reference standard with corresponding one-hour analyses of each standard reported by the analyser.	X _{REF} = Reference value X _{CBA} = CBA hourly analysis value n = Number of cal. standards = 5	$RMSD = \sqrt{\frac{\sum_{i=1}^n (X_{REF_i} - X_{CBA_i})^2}{n}}$
The performance verification calculations are performed for each oxide.	*) To be adjusted according to the specific application	

1.2 Dynamic Performance Guarantee (Stockpile)

1.2.1 Stockpile Accuracy (1 RMSD)	
LS	
SR	To provided by the supplier
AR	
<p>The stockpile accuracy expresses the maximum tolerable deviation (root mean square deviation) of the PGNAA analyzer from X-ray fluorescence analysis. The test comprises the evaluation of min. 7 individual, completed stockpiles. The average value of each quality parameter from the individual stockpiles, determined by the PGNAA, is compared with the related recalculated quality parameter value, determined by the laboratory based XRF system. The difference between the recalculated figure and the PGNAA value is calculated.</p> <p>According to the below-mentioned equation the RMSD of the 7 stockpile comparisons is calculated for each quality parameter.</p>	
$RMSD = \sqrt{\frac{\sum_{i=1}^n (X_{\text{recal}_i} - X_{\text{CBA}_i})^2}{n}}$ <p style="text-align: right;">$X_{\text{recal}} = \text{recalculated stockpile value}$ $X_{\text{CBA}} = \text{CBA stockpile value}$ $n = \text{Number of observations} = 7$</p>	

2. CROSS BELT ANALYZER RAW MILL FEED (PGNAA RAW MILL FEED)

2.1 Static Performance Guarantee (Raw Mix Control)

Description	Guarantee Values	Remarks
2.1.1 Static Precision (repeatability)		
- Dry basis - LOI incl. - 5 h; 300 values - reduction to 30 values, each as average of 10 consecutive values	One Standard Deviation	Oxide SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ CaO MgO SO ₃ K ₂ O Na ₂ O Cl
2.1.2 Static Accuracy		
Procedure - Dry basis - LOI incl. - RMSD (root mean squared deviation) - 1 h	Guaranteed Maximum RMSD	Range *) Oxide (12% - 15%) SiO ₂ (2% - 5%) Al ₂ O ₃ (2% - 5%) Fe ₂ O ₃ (38% - 47%) CaO (0% - 1.5%) SO ₃ (0% - 4%) MgO (0% - 2%) K ₂ O (0% - 2%) Na ₂ O (0 - 0.05%) Cl
Performance verification of static accuracy is conducted with five reference standards. Performance is verified by comparing known values for each oxide in each reference standard with corresponding one-hour analyses of each standard reported by the analyser.	X _{REF} = Reference value X _{CBA} = CBA hourly analysis value n = Number of observations = 5	RMSD = $\sqrt{\frac{\sum_{i=1}^n (X_{REF_i} - X_{CBA_i})^2}{n}}$
The performance verification calculations are performed for each oxide.	*) To be adjusted according to the specific application	

2.2 Dynamic Performance Guarantee (Raw Mix Control)

2.2.1 Mill Feed Accuracy (dynamic)		
Parameter	Mill Feed Accuracy Guaranteed values (One RMSD)	Remarks
SiO ₂		
Al ₂ O ₃		
Fe ₂ O ₃		
CaO		
MgO		
SO ₃		
K ₂ O		
Na ₂ O		
Cl		

The mill feed accuracy expresses the maximum tolerable deviation (root mean square deviation) of the cross belt analyzer from X-ray fluorescence analysis. It shall be determined by comparing the laboratory (XRF) results of 48 consecutive 1 hour composite raw meal samples with the corresponding 1 hour mill feed averages of the cross belt analyzer.

The RMSD shall be calculated as follows:

$$\text{RMSD} = \sqrt{\frac{\sum_{j=1}^n (X_{\text{REF},j} - X_{\text{CBA},j})^2}{n}}$$

X_{REF} = XRF value of 1 hour raw meal sample
 X_{CBA} = CBA value of 1 hour measuring time
 $n = 48$ = Number of observations

2.2.2 Blending Control Performance

Deviation from control target for the rolling average of 2 hours should be smaller 2% of the control target:

$$| X_{\text{analyzer}} - X_{\text{target}} | < 0.02 * X_{\text{target}}$$

for 95 % of all calculated averages over a test period of 72 hours (equal to 71 data sets).

X control parameter (max. 3 out of LSF, SR, AR; C₃S, C₃A or equivalent)

X_{analyzer} rolling average over 2 hours raw meal production (analyzer results)

X_{target} control target value

Annex Part VII-1: LiteratureBooks:

- J. P. Willis, A. R. Duncan, Understanding XRF Spectrometry, Panalytical B. V, 2008
P. E. Bertin, Principle and Practice of X-Ray Spectrometric Analysis, Springer Verlag GmbH, 1988.
Ron Jenkins, X-Ray Fluorescence Spectrometry, Second edition, John Wiley & Sons, 1999.
R. E. Van Grieken, A. A Markowicz (Eds), Handbook of X-Ray Spectrometry, Second Edition, Marcel Dekker Inc. New York, 2002.

Internet Resources:

- <http://www.learnxrf.com>
http://www.bruker-axes.de/fileadmin/user_upload/xrfintro/index.html
<http://www.horiba.com/scientific/products/x-ray-fluorescence-analysis/tutorial/>

Annex Part VII-2: Selected suppliers of XRF calibration standardsNIST (NBS) (<http://www.nist.gov>):

National Institute of Standards and Technology
Gaithersburg, MD 20899
USA

Offers a series of standard reference materials (SRM) for clinker, Portland cement and some raw materials (e.g. limestone, clay, sand)

BAS EURO (<http://www.basrid.co.uk/bas.htm>)

Bureau of Analysed samples Ltd.
Newham Hall, Newby
Middlesbrough,
England, TS 89 EA
Offers CRM's for cement, slag and some raw materials (e.g. limestone, sand, iron ore, fluorspar)

MBH Analytical (<http://mbh.co.uk>)

Holland House, Queens Road
Barnet, Herts, EN 5 4DJ
England
Offers a series of CRM's for cement, clinker (also for XRD), coal and coal ashes, rocks and soils

Breitlaender (<http://www.breitlander.com>)

Eichproben und Labormaterial GmbH
Postfach 8046
D-4700 Hamm
Germany
Offers XRF fused beads (setting up samples, monitors)

Keller (<http://www.keller-mannheim.de>)

Max. F. Keller GmbH
Einsteinstr. 14a
Friesenheimer Insel
D-6800 Mannheim 1, Germany
Offers coal and coke reference materials

Brammer Standard (<http://www.brammerstandard.com/>)

Brammer Standard Company, Inc.

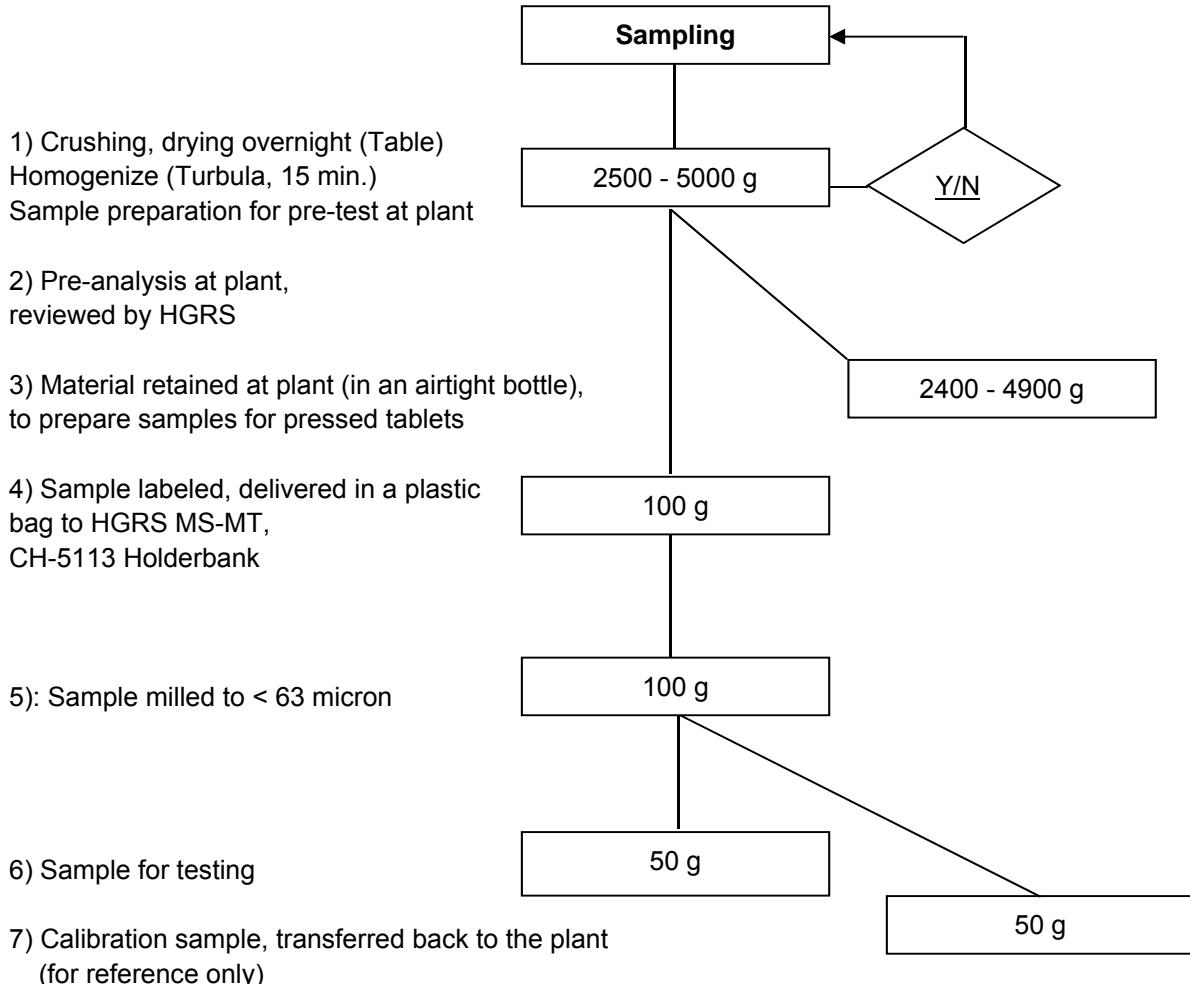
14603 Benfer Rd

Houston, TX 77069-2895 USA

Reseller of CRM's, wide range of cements, clinker, MIC's and raw materials, including the Domtar Gypsum standards

Annex Part VII-3: Preparation of calibration standards for pressed tablet programs

For each material type, a certain number of very well homogenized samples should be prepared, which cover the complete range of chemical composition encountered for the respective type of material. The samples should be prepared according to the subsequent procedures.

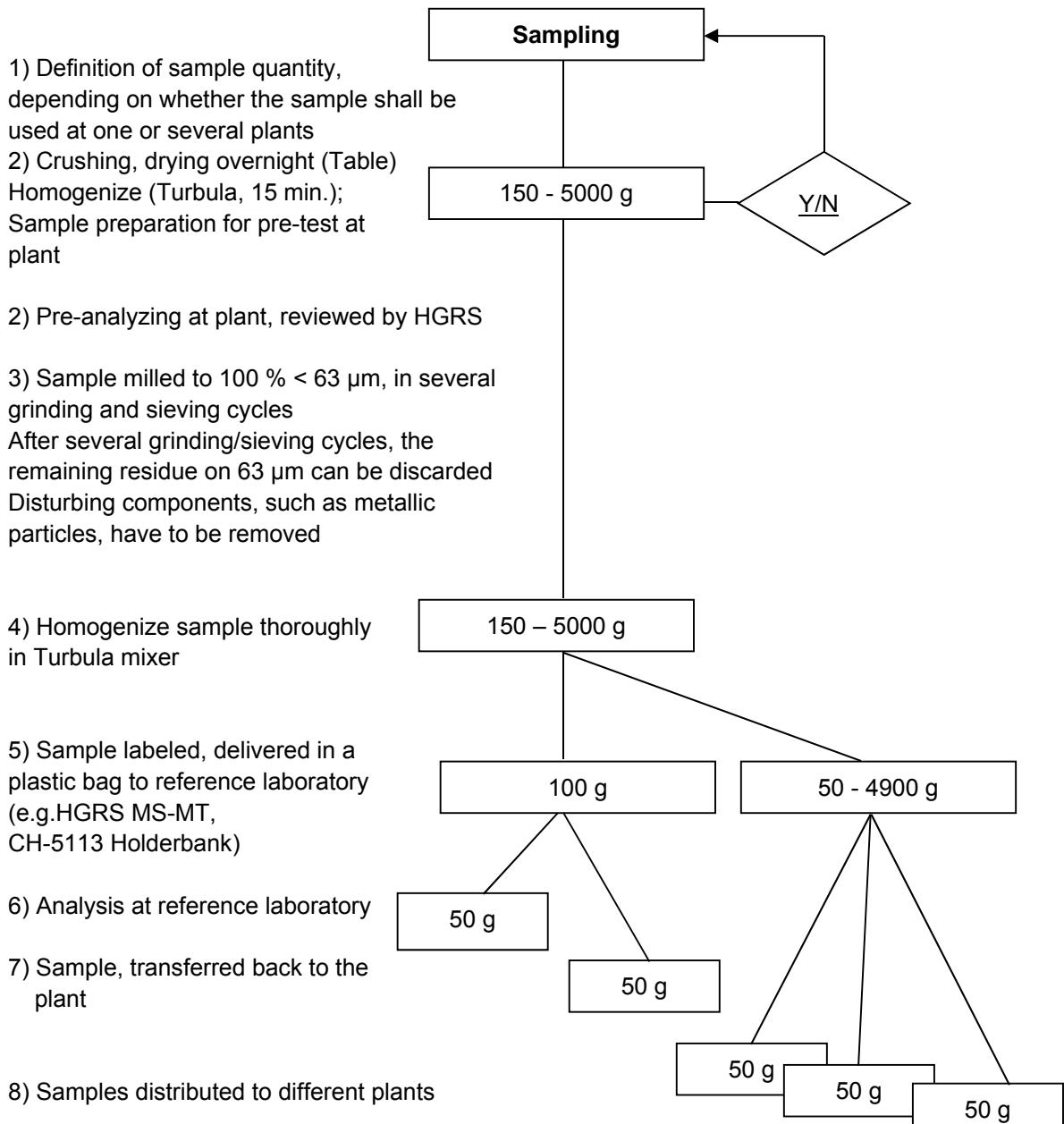


Material	Drying	Fineness
Limestone, Clay/Shale	105 °C	crushed ≤ 2 mm
Correctives: Silica, Iron	105 °C	crushed ≤ 2 mm
Raw Meal	105 °C	unchanged
Clinker	non	crushed ≤ 2 mm
Cements	non	unchanged
Gypsum	45 °C	crushed ≤ 2 mm

Table: Specifications for step 1)

Annex Part VII-4: Preparation of calibration standards for fused bead programs

For each material type, a certain number of samples should be prepared, which cover the complete range of chemical composition encountered for the respective type of material. The samples can have different origins.



Material	Drying	Fineness
Limestone, Clay/Shale	105 °C	crushed < 2 mm
Correctives: Silica, Iron	105 °C	crushed < 2 mm
Raw Meal	105 °C	unchanged
Clinker	non	crushed < 2 mm
Cements	non	unchanged
Gypsum	45 °C	crushed < 2 mm

Table: Specifications for step 1)

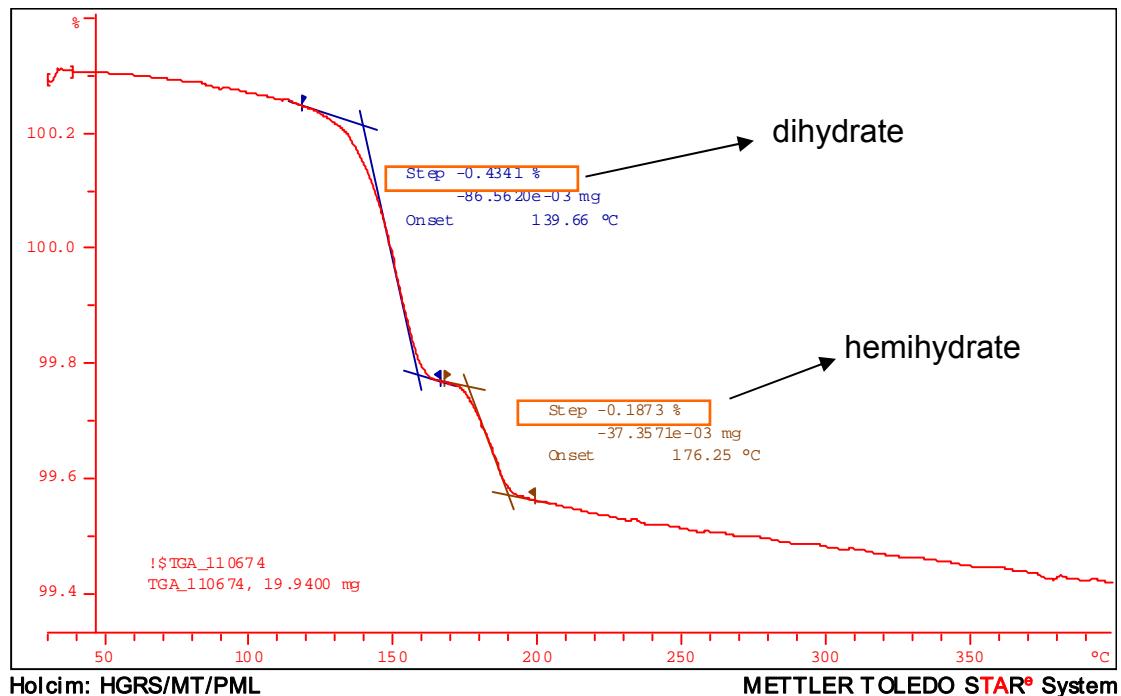
Annex Part VIII-1: Free determination by XRD: Calibration Method

- Preparation of calibration standards:
About 6 clinker samples covering a free lime range between 0.5 and 3.5 % CaO free are required. The samples should be as fresh as possible. The selected samples are crushed to < 5 mm, homogenized and the free lime is determined by manual titration method at the plant laboratory.
- Preparation of pressed powder tablets:
The crushed clinker samples are homogenized and reduced to about 100g, then 20.0 g clinker sample are weigh and ground together with 5 grinding aids tablets for one minute in a disc mill. 10 g of the ground sample are then weigh and press into a steel ring or Al-cup at 200 kN for 20 seconds.
- Calibration of XRD spectrometer
Prior to start the calibration the real 2 theta of the free lime peak has to be determined and entered into free lime analytical program. To measure the free lime intensities of the calibration samples the following measuring conditions are applied for a 3 kW equipment:
 - Counting time 100 seconds
 - kV: 30
 - mA: 100
- Recalibration of the free lime analytical program
Free lime is not stable and it is not possible to keep a clinker sample long enough to be used as recalibration sample. Instead NiO (green, because NiO black has other angle) is used to simulate the free lime peak in proximity. Prior to measure the recalibration samples the real 2 theta of the NiO peak has to be determined and entered in the line library.

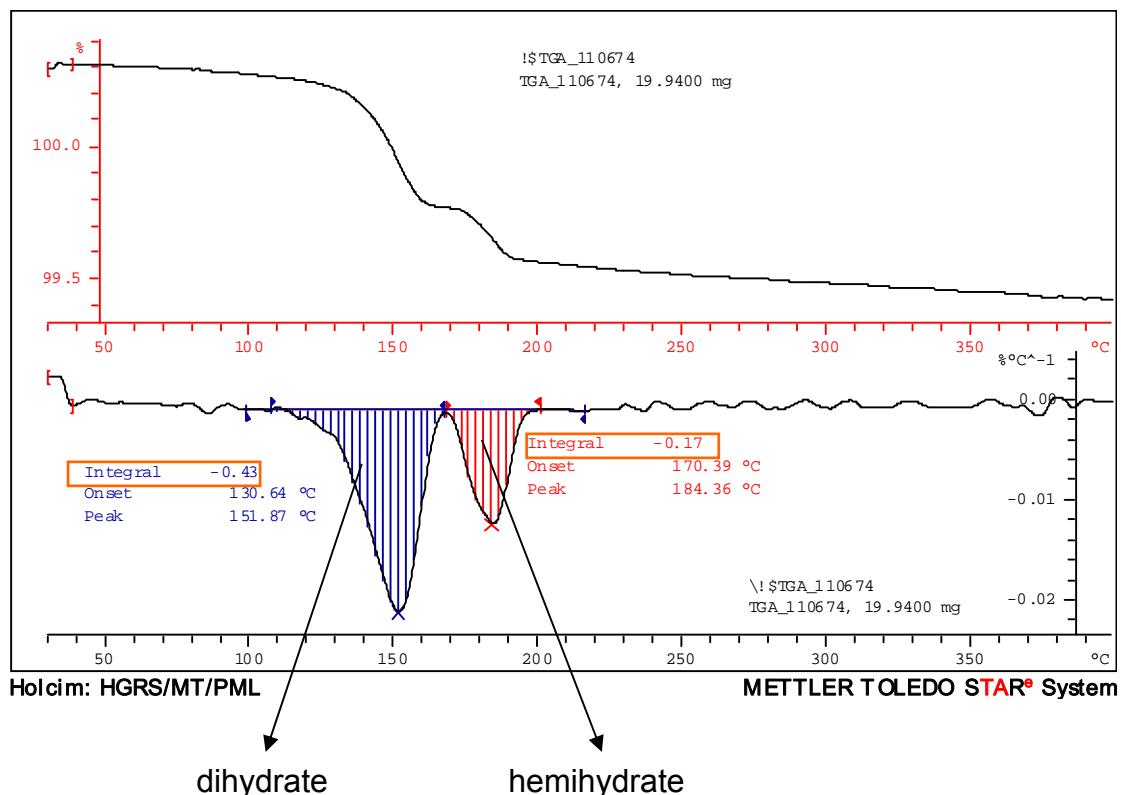
For the recalibration of the free lime analytical program two samples are required, one containing NiO representing the high point and one without NiO for low point of the curve. The sample preparation applied for the free lime recalibration samples is as follows:
 - Preparation of the high point tablet
 - Weigh 2 g NiO
 - 20.0 g of raw meal
 - Grind the mix together with 5 grinding aid tablets for 20 seconds in a disc mill
 - Weigh 10.0 g of ground mix and press into a steel ring or Al-cup at 200 kN for 20 seconds
 - Preparation of the low point
The same as above but without NiO.

Annex Part VIII-2: TGA Quantification of dihydrate (gypsum) and hemihydrate (bassanite)

Tangential (normalized to sample weight)



Derivation (normalized to sample weight)



Reaction:

	<i>formula</i>	<i>molecular weight</i>
dihydrate	$\text{Ca}_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$	172.17 g/mol
hemihydrate	$\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$	145.14 g/mol
water	0.5 H ₂ O	9.0 g/mol
water	1.5 H ₂ O	27.0 g/mol

From “Thermal Analysis” (Mettler Toledo) – User Com 26 (2/2007)

From stoichiometric considerations, dehydration of the dehydrate is expected to give a total mass loss of 20.9 %, made up of steps of

- 15.7 % (dihydrate → hemihydrate)
- 5.2 % (hemihydrate → anhydrous form, based on the mass of dihydrate)

The dehydration of the hemihydrate is expected to give a mass loss of 6.2 %.

dihydrate => hemihydrate

$$172.17 \text{ g/mol} = 100 \%$$

$$27.00 \text{ g/mol} = 15.68 \%$$

$$= 15.68 / 100 = 0.157$$

hemihydrate => anhydrous

$$172.17 \text{ g/mol} = 100 \%$$

$$9.00 \text{ g/mol} = 5.23 \%$$

$$= 5.23 / 100 = 0.052$$

hemihydrate

$$145.14 \text{ g/mol} = 100 \%$$

$$9.00 \text{ g/mol} = 6.20 \%$$

$$=> 6.2 / 100 = 0.062$$

Calculations

Integration (area under the curve) for dihydrate: = 0.43 (x_1)

Integration (area under the curve) for hemihydrate: = 0.18 (y_1)

$$x_1 / 0.157 = 2.7 \text{ wt \% dihydrate}$$

$$\frac{y_1 - ((0.052/0.157) * x_1)}{0.062} = 0.6 \text{ wt\%}$$

Result:

2.7 wt % dihydrate and 0.6 wt % hemihydrate are present in the measured sample



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