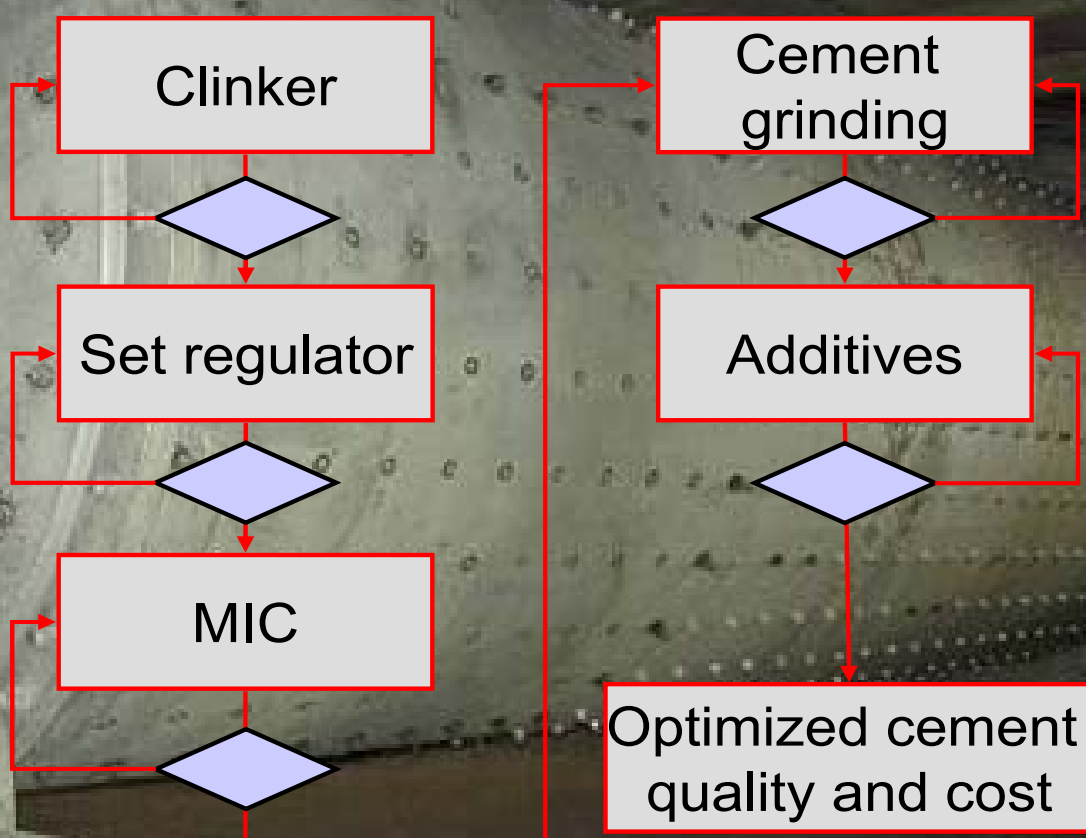


Product Optimization Manual

Holcim Group Support Ltd
Cement Manufacturing Services



Product Optimization Manual

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Introduction

Product optimization is an important element for the Holcim mindsets Better Cost Management (BCM), Permanent Marketing Innovation (PMI) and Sustainable Ecological Performance (SEP). A key indicator for product optimization is the clinker factor in the cement. Lowering the clinker factor contributes to cost reduction, permits product differentiation and is one of the best measures to minimize the specific CO₂ emissions.

Between the years 1990 and 2005, the clinker factor within the Holcim group decreased significantly from 83 % to 75 %, whereas in the last years limited further reduction occurred. There are several reasons for the recently slow progress of clinker factor reduction such as availability and cost of Mineral Components (MIC), standard requirements, market perception of composite cements and low clinker reactivity and uniformity (e.g. due to use of AFR).

An important pre-requisite for product optimization is the proper definition of the product mix and requirements between marketing and manufacturing, which sets the framework for the optimization of the individual products. The product optimization process should be based on a systematic approach, addressing in consecutive steps the optimization in the following five areas: clinker, set regulator, MIC, cement grinding and cement additives. Successful action in all these steps should allow to achieve the required cement quality at lowest possible cost.

The product optimization process shall start with the adaptation of the clinker properties, as clinker is still the major component in most cements and controls important cement properties like setting and strength development. The main objectives of the clinker optimization are the maximization of the clinker strength potential and clinker uniformity.

The set regulator impacts both the setting behavior and strength development and has to be adjusted accordingly to achieve optimum performance. Industrial gypsum offers a cost-effective alternative to natural gypsum. However, attention must be paid to the negative impact of some minor constituents.

Since MICs are also main cement constituents, their quality must be well-controlled and carefully selected, through specification of certain quality characteristics as well as the establishment of a reliable quality control system for the MIC delivery. Upgrading and/or pre-homogenization must be considered if quality and uniformity are not appropriate.

The grinding process is decisive for the particle size distribution (PSD) of the cement and hence for the strength potential as well as for the gypsum dehydration and related impacts on setting behavior and storage stability. In order to achieve an optimum PSD, separate grinding offers of course the highest flexibility for the production of composite cements, but also for compound grinding a consistent optimization of the grinding circuits can help to improve the cement PSD and performance.

The use of cement additives is the last step in the product optimization process. While grinding aids serve in first instance to increase the mill throughput, quality improvers can help to improve the setting and strength performance of the cement.

The present manual describes in detail the state-of-the art knowledge for the five mentioned optimization steps and contains as well chapters on performance prediction and on test methods for the evaluation of the cement components and cement properties.

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1. **INTRODUCTION**

It lies in the responsibility of Manufacturing to achieve the product quality targets at minimum costs by optimization of the production processes, improvement of intermediate and final products and optimum cement design. The benefits of product optimization are manifold and are in line with the Holcim strategy for

- better cost management (BCM)
 - reduction of production costs
 - increase of production capacity
 - lower or delayed needs for investments
- permanent market innovation (PMI)
 - improvement of product quality
 - product differentiation
- sustainable ecological performance (SEP)
 - reduction of CO₂ output
 - extension of raw material resources

A key indicator for product optimization is the clinker factor in the cement. The potentials to manufacture economical and market conform composite cements with higher clinker substitution are not always fully recognized. There are several reasons for the slow progress of clinker factor reduction such as:

- availability and cost of Mineral Components (MIC)
- standard requirements (prescriptive instead of performance oriented)
- market tendencies (quality race, tendency to high early strength cements)
- market perception of composite cements
- low clinker reactivity and uniformity (e.g. due to use of AFR) and reluctance to clinker mineralization
- traditional grinding technology (compound instead of separate grinding)

Between the years 1990 and 2005 the clinker factor within the Holcim group decreased from 83 % to 75 %. A further decrease of 1.5 – 2 % was achieved in the years 2006 and 2007, which is partially related to the inclusion of the Indian plants in the Holcim group but also the further progress of the development of composite cements.

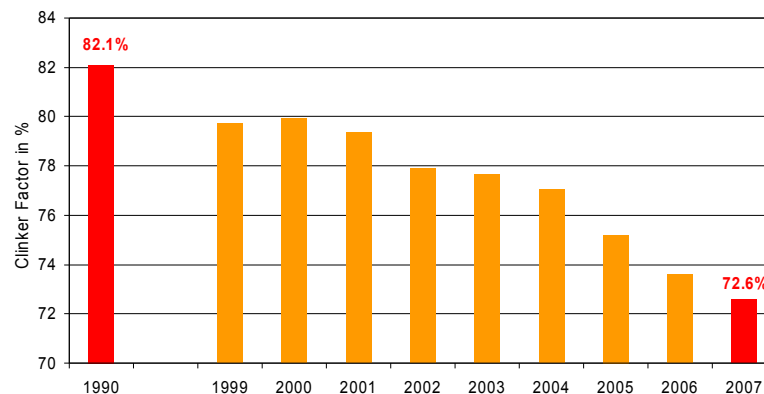


Figure 1: Development of clinker factor in the Holcim Group 1990 – 2007, India included in the years 1990 and 2006

The development of the clinker factor is strongly depending on the regions, which is related to the local standards but also to customer acceptance towards composite cements. A clinker factor of 70 % was achieved in 2005 in the European and Latin American plants. Highest potential for further clinker factor reduction has North-America. The ASTM allows since 2008 the addition of 5 % limestone in the cement. However, the use of composite cements is there substantially restricted by the tradition to add mineral components to the concrete (ground granulated blast furnace slag, fly ash).

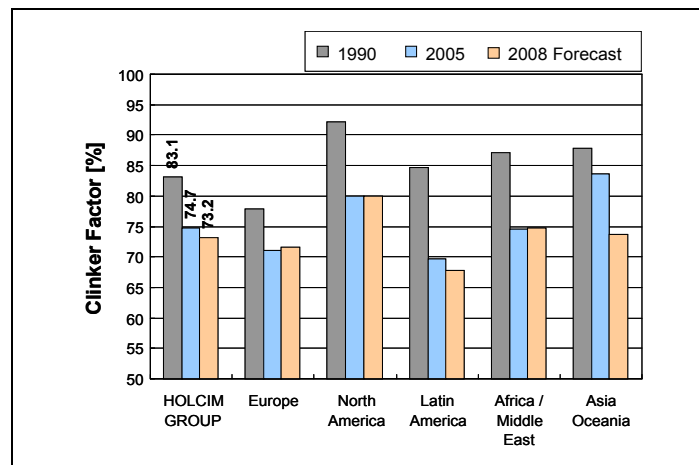


Figure 2: Development of clinker factor in the Holcim Group 1990 - 2005

Lowering the clinker factor is one of the best measures to reduce CO₂ emission. A clinker factor reduction of 1 % reduces the specific CO₂ emissions by 7 – 9 kg CO₂/t cement and should hence be in the focus of cement manufacturing. Furthermore, composite cements can provide in many respects advantages in application compared to OPC (e.g. improved durability with slag cements).

Table 1: Influence of clinker factor reduction on CO₂ emission compared to other measures

| Measure | | Effectiveness (kg CO ₂ / t cement) |
|----------------------------|-----|--|
| Clinker factor reduction | 1 % | 7 - 9 |
| Increased use of AFR | 1 % | 2 - 3 |
| Improved energy efficiency | 1 % | 1 - 2 |

An important pre-requisite for product optimization is a good alignment between marketing and manufacturing, which have to agree upon appropriate product mix and quality targets. The definition of product mix and quality targets should consider the market requirements and marketing strategy as well as the production circumstances. Indicators for the product optimization potential are the following parameters:

- product costs
- compliance to internal product specifications
- compliance to manufacturing quality targets (e.g. coefficient of variation of early/late strength)
- product performance against competitors (benchmarking)
- customer complaints on product quality

These parameters (except of “costs”) constitute basically the quality KPIs, which form the basis for the Product Quality Index used for the performance monitoring of the Holcim plants. The details of the quality KPIs are described in the “Holcim Product Quality Management Reference Manual”.

2. DECISION TREE FOR PRODUCT OPTIMIZATION

In order to exploit the complete optimization potential, the product optimization process should follow some systematic approach. For this purpose, a corresponding decision tree has been established, which is shown in the Figure 3 below. It focuses on five major optimization steps addressing: clinker, set regulator, mineral components (MIC), cement grinding and additives. Successful action in all of these steps should allow to achieve the required cement quality at lowest possible cost (e.g. through maximum reduction of clinker factor).

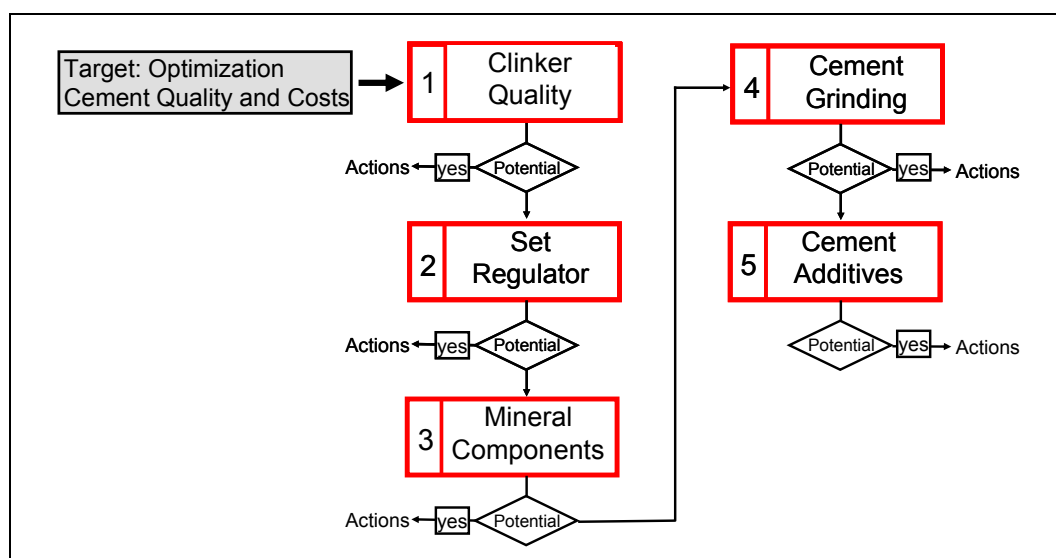


Figure 3: Product Optimization Decision Tree

1. The product optimization process shall always start with the adaptation of the clinker properties as clinker is the major component in most cements. It is controlling important cement properties like setting and strength development, in particular early strength. Due to the lower clinker content composite cements show in general a lower early strength than Portland cements, which often hinders further clinker factor reduction. Main objectives of the clinker optimization are therefore the maximization of the clinker strength potential and clinker uniformity. Mineralization offers additional potential for clinker strength development, but should always be considered as second step of the clinker optimization.
2. The set regulator has to be adjusted to the targeted cement properties (gypsum/set retarder optimization). Only at an adjusted gypsum dosage, the maximum strength and optimum setting time can be achieved. Therefore, a gypsum optimization should be carried out regularly for all cements and of course after every major change in clinker design and cement production. Industrial gypsum offers a cost-effective alternative to natural gypsum. However, attention must be paid to the negative impact of some minor constituents (e.g. P_2O_5 , F).

3. Since MICs are main cement constituents their quality must be well-controlled and carefully selected. Upgrading and/or pre-homogenization must be considered if quality and uniformity are not appropriate. This includes the specification of appropriate ranges for certain quality characteristics in the supply contract as well as the establishment of a reliable quality control system for the MIC delivery.
4. As a general rule for composite cement production, clinker is preferably ground to a high fineness with a narrow particle size distribution (PSD) and MIC to a low to medium fineness with a wide PSD. Adequate residence time and grinding temperature allow for a good control of gypsum dehydration and uniform cement properties. Important is also a consistent optimization of the grinding circuits. Separate grinding offers a higher flexibility than compound grinding when considering the different grindabilities of the cement constituents and the required PSDs for them.
5. About 60 % of the Holcim plants use cement additives. While grinding aids serve in first instance to increase the mill throughput, quality improvers increase early strength by accelerating clinker hydration. Of particular interest are tailor-made quality improvers, which are usually less expensive and at least as effective as commercially available products.

For all of the above mentioned optimization steps, the uniformity of intermediate and final products is the key factor for the maximum exploitation of the optimization potential. At high standard deviation the production targets have to be kept further away from the limits than at low standard deviation. E.g., cement with low uniformity (high std-dev) has to be ground with higher fineness or higher clinker factor to achieve the early strength at a confidence level of 95 % than cement with high uniformity (low std-dev). Hence non uniformity creates additional production costs, but also increases the number of constraints and leaves less opportunity for optimizations in the production process.

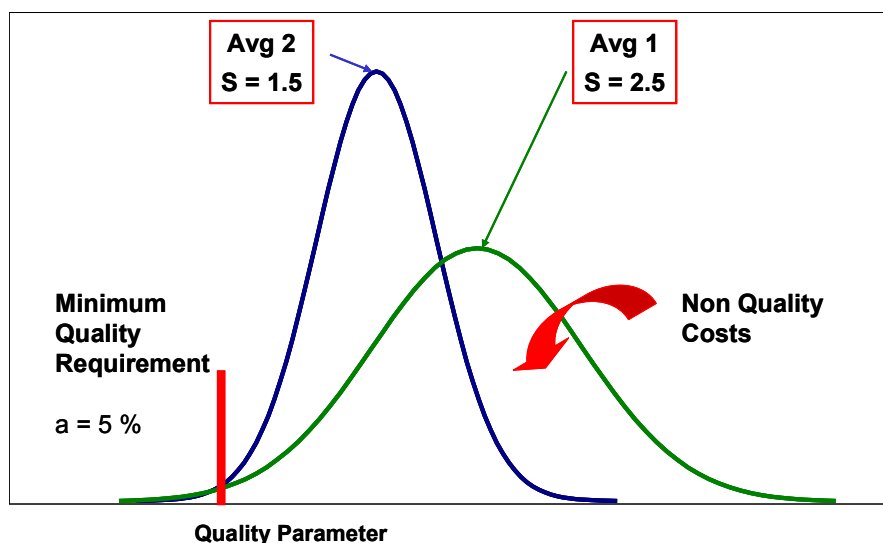


Figure 4: Influence of standard deviation on target selection and quality costs

3. CLINKER

3.1 Chemical composition

3.1.1 General

The chemical composition of Portland cement clinker lies in a comparatively narrow range, which is illustrated as yellow triangle in the graph below. Only if the clinker composition is located in this triangle the minerals required for setting and hardening can be formed.

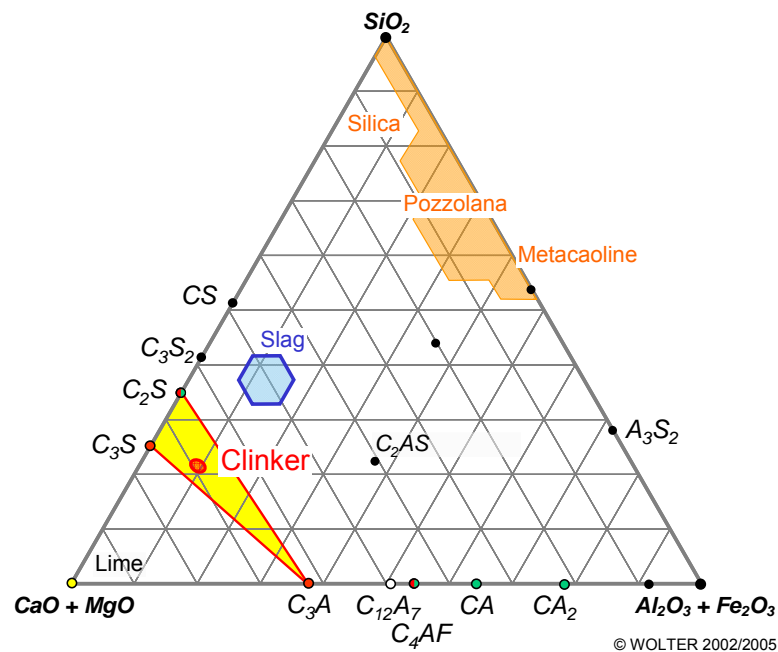


Figure 5: Range of Portland cement clinker composition (yellow triangle)

The following table shows the average composition of all Portland cement clinkers in the Holcim group. According to the narrow range of possible compositions the range for the different oxides is as well quite close.

Table 2: Composition of Holcim Portland cement clinker, source ATR 2008

| | Unit | Average | Min | Max | n |
|--------------------------------|------|---------|------|-------|-----|
| LS | | 95.7 | 85.1 | 103.1 | 169 |
| SR | | 2.50 | 1.85 | 3.13 | 169 |
| AR | | 1.55 | 0.48 | 2.70 | 169 |
| LOI | | 0.28 | 0.00 | 0.95 | 141 |
| SiO ₂ | % | 21.4 | 19.4 | 25.3 | 169 |
| Al ₂ O ₃ | % | 5.1 | 2.8 | 6.6 | 169 |
| Fe ₂ O ₃ | % | 3.5 | 2.2 | 6.8 | 169 |
| CaO | % | 65.4 | 61.3 | 68.1 | 169 |
| MgO | % | 1.9 | 0.6 | 5.2 | 169 |
| SO ₃ | % | 0.8 | 0.01 | 2.1 | 168 |
| K ₂ O | % | 0.68 | 0.09 | 1.36 | 158 |
| Na ₂ O | % | 0.24 | 0.00 | 0.79 | 156 |
| TiO ₂ | % | 0.26 | 0.00 | 0.58 | 72 |
| P ₂ O ₅ | % | 0.17 | 0.00 | 0.52 | 73 |
| F | % | 0.15 | 0.00 | 0.30 | 34 |
| CaO _f | % | 1.37 | 0.42 | 3.4 | 164 |

The main oxides CaO, SiO₂, Al₂O₃ and Fe₂O₃ provide about 95 % of the total chemistry. The major portion of the remaining 5 % consists of MgO, alkalis, sulfur and other minor elements (see section 3.3). Furthermore clinker contains trace elements such as heavy metals, which are not discussed in detail in this manual.

For the evaluation of the clinker quality as well as the raw mix composition, the main oxides are translated into the so called moduli, which provide more meaningful values than the single oxides alone. In general, the quality targets for a clinker are expressed in terms of lime saturation, silica ratio and alumina ratio (refer to sections below), which are commonly in the following ranges:

Lime saturation: 85 – 100, typical range: 94 – 98

Silica ratio: 1.8 – 3.6, typical range: 2.3 – 2.6

Alumina ratio: 1 – 3, typical range: 1.4 – 1.8

The moduli of all main Portland cement clinker in the Holcim group are shown in the figure below.

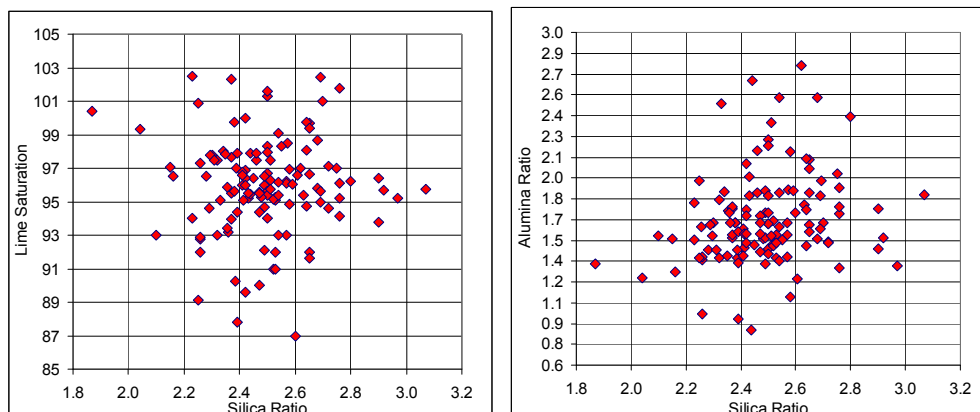


Figure 6: Moduli of Holcim Portland cement clinkers, source ATR 2008

The target moduli for the different plants strongly depend on the conditions of the deposit as well as the availability of corrective materials. Furthermore, it has to be taken into account that a change of the moduli influences the burning behavior of the raw meal. The sections below describe the correlation between moduli, clinker quality and burning behavior.

3.1.2 Lime saturation

The Lime saturation (LS) describes the CaO content actually present relative to the maximum CaO, which can be combined with the SiO_2 , Al_2O_3 and Fe_2O_3 (C_3S , C_3A , $\text{C}_2(\text{A},\text{F})$ or C_4AF) without the necessary presence of free lime. In non mineralized clinker free lime will unavoidably be present at $\text{LS} > 100$ even if the clinker is heavily burnt. In mineralized clinkers, the lime saturation can exceed 100 (see section 3.4) without free lime being present.

$$\text{LS} = (\text{CaO} \times 100) / (2.80 \times \text{SiO}_2 + 1.18 \times \text{Al}_2\text{O}_3 + 0.65 \times \text{Fe}_2\text{O}_3)$$

The lime saturation is the most relevant parameter for the clinker strength potential, since it is more or less correlating with the C_3S content. With increasing lime saturation the C_3S content increases and enhances both the early and late strength potential of the clinker.

3.1.3 Silica ratio

The silica ratio (SR) describes the ratio between solid (silicates) and liquid (aluminates) phases at sintering temperature and is calculated by the following formula:

$$\text{SR} = \text{SiO}_2 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$$

The silica ratio is an indicator for the amount of liquid phase in the clinker, which decreases with increasing SR. Clinker with high SR tend to be dustier than clinker with a low silica ratio. Furthermore the burning behavior is improved with higher amounts of liquid phase, viz. low SR, since the sintering reactions are facilitated.

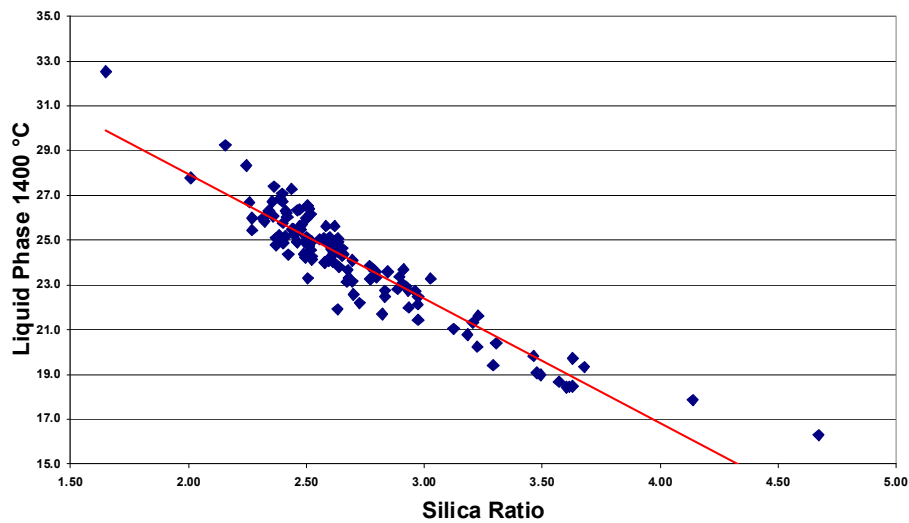


Figure 7: Correlation between silica ratio and liquid phase content

Although the liquid phase is correlated to the silica ratio, other formulae elaborated by Lea and Parker [Lea 70] are used traditionally for the calculation of the amount of liquid phase (LP) at sintering temperature:

- (I) 1338 °C AR < 1.38 LP = $8.50 \text{ Al}_2\text{O}_3 - 5.22 \text{ Fe}_2\text{O}_3 + \text{MgO}^* + \text{K}_2\text{O} + \text{Na}_2\text{O}$
 AR > 1.38 LP = $6.10 \text{ Fe}_2\text{O}_3 + \text{MgO}^* + \text{K}_2\text{O} + \text{Na}_2\text{O}$
- (II) 1400 °C LP = $2.95 \text{ Al}_2\text{O}_3 - 2.20 \text{ Fe}_2\text{O}_3 + \text{MgO}^* + \text{K}_2\text{O} + \text{Na}_2\text{O}$
- (III) 1450 °C LP = $3.00 \text{ Al}_2\text{O}_3 - 2.25 \text{ Fe}_2\text{O}_3 + \text{MgO}^* + \text{K}_2\text{O} + \text{Na}_2\text{O}$

* for MgO > 2 %, the MgO content in the formula is fixed to 2

The figure below shows the development of the liquid phase for different SR and AR in relation to the temperature.

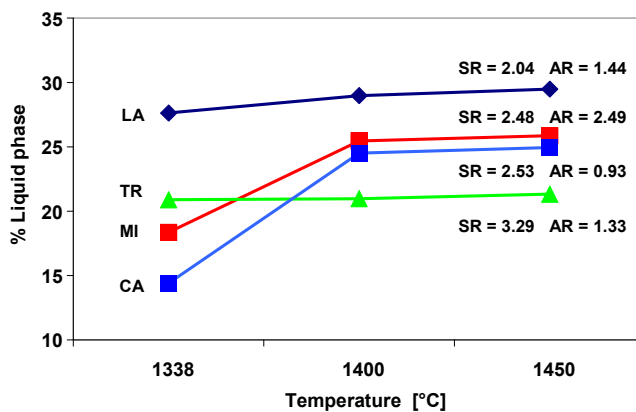


Figure 8: Liquid phase content calculated on basis of Lea and Parker formulae

Most Holcim plants refer to formula II (LP at 1400 °C). Using that formula, a liquid phase content between 23 and 27 % is considered normal. In this range about 80 – 100 % of the pore volume is filled with liquid phase, allowing for adequate granulation and burning behavior. Clinker with lower liquid phase content is considered dry (dusty), above 27 % wet clinker.

3.1.4 Alumina ratio

The alumina ratio (AR) describes the ratio between aluminate (C_3A) and ferrite (C_4AF) and describes hence the properties of the liquid phase.

$$AR = Al_2O_3 / Fe_2O_3$$

With regard to clinker an AR between 1.4 and 1.6 has a positive influence on the burnability since at this ratio the liquid phase is formed at the lowest temperature.

Furthermore the alumina ratio is relevant for the viscosity of the liquid phase. Above 1.6 the viscosity of the liquid phase increases.

3.2 Mineralogical composition

3.2.1 General

Clinker consists of the four main minerals alite, belite, aluminate and ferrite. It furthermore contains free lime, alkali sulfates and sometimes periclase. At very high sulfur contents also sodium sulfate or calcium-potassium sulfates (Ca-Langbeinite) or even anhydrite can occur. Typical ranges of the minerals are listed in the table below.

Table 3: Typical ranges of clinker minerals

| Mineral Name | Chemical formula | Simplified formula | Content in clinker (%) | |
|-----------------|----------------------|--------------------|------------------------|---------------------|
| | | | Normal OPC clinker | Mineralized clinker |
| Alite | Ca_3SiO_5 | C_3S | 60 – 70 | 70 – 80 |
| Belite | Ca_2SiO_4 | C_2S | 10 – 20 | 0 – 10 |
| Aluminate | $Ca_3Al_2O_6$ | C_3A | 7 – 10 | 7 – 10 |
| Ferrite | $Ca_4Al_2Fe_2O_{10}$ | C_4AF | 7 – 10 | 7 – 10 |
| Free lime | CaO | CaOf | 0.5 – 1.5 | 0.5 – 1.5 |
| Periclase | MgO | MgO | 0.6 – 1.2 | 0.6 – 1.2 |
| Alkali sulfates | K_2SO_4 | | 0.6 – 1.2 | 0.6 – 1.2 |

The clinker phases are not pure minerals but contain always some minor elements due to the (geological or industrial) source of the raw materials [Bha 95, Kri 77a,b]. Typical contents of minor elements in the main clinker phases are shown in the table below.

Table 4: Typical ranges of minor elements and mineralogical parameter of clinker minerals

| | Alite | Belite | Aluminate | Ferrite |
|-----------|------------|------------|------------|-----------|
| Formula | C_3S | C_2S | C_3A | C_4AF |
| SiO_2 | | | 2.9 – 7.1 | 1.8 – 4.3 |
| Al_2O_3 | 0.4 – 1.8 | 0.5 – 3.0 | | |
| Fe_2O_3 | 0.2 – 1.9 | 0.4 – 2.7 | 4.8 – 11.4 | |
| MgO | 0.3 – 2.1 | | 0.4 – 2.2 | 1.9 – 4.5 |
| SO_3 | 0.01 – 0.1 | 0.01 – 0.5 | 0.01 – 0.1 | |
| K_2O | | 0.1 -1.9 | 0.1 – 3.1 | |
| Na_2O | | 0.1 - 0.8 | 0.3 – 4.6 | |
| TiO_2 | | | | 3.5 |

3.2.2 Correlation between clinker moduli and clinker phases

The proportion of the minerals depends in first instance on the chemical composition of the clinker and can hence be influenced by an adjustment of the different moduli. The relation between the moduli and the clinker phases is sketched in the following graphs. The below figures assume a total of 100 % from the main oxides (CaO , SiO_2 , Al_2O_3 , Fe_2O_3).

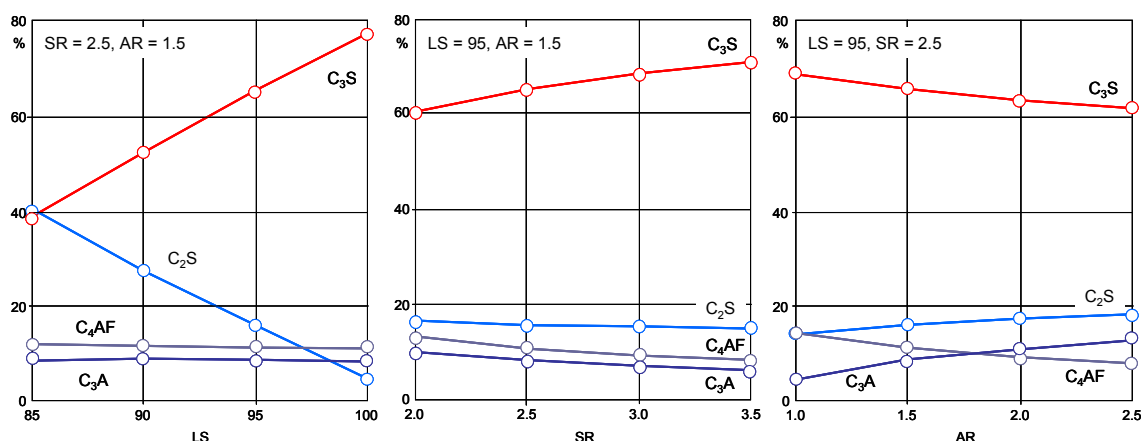


Figure 9: Correlation between clinker moduli and clinker phases

Keeping all parameters constant, the most important influences of the different moduli can be summarized as follows:

- With increasing lime saturation the C_3S strongly increases.

- An increase of the silica ratio results in an increase of the silicate phases and reduced content of liquid phase (C_3A , C_4AF). In particular the C_3S content is fostered, however the effect is minor compared to an increase of lime saturation.
- With increasing alumina ratio mainly the C_3A content increases at the expense of C_4AF , but also - at a minor extent - of C_3S .

3.2.3 Properties of clinker minerals

The clinker performance can be influenced by adjusting the clinker moduli and hence the clinker phases. The most relevant properties of the different clinker minerals are listed in the table below and can be summarized as follows:

Table 5: Influence of clinker minerals on cement properties

| Clinker phase | Early strength | Final strength | Setting time | Water demand | Soundness |
|-----------------|----------------|----------------|--------------|--------------|-----------|
| Alite | ↑ | ↑ | - | - | - |
| Belite | ↓ | ↑ | - | - | - |
| Aluminate | ↑ | ↓ | ↓ | ↑ | - |
| Ferrite | (↓) | (↑) | - | (↓) | - |
| Free lime | - | - | ↓ | - | negative |
| Alkali sulfates | ↑ | ↓ | ↑ | ↑ | - |
| Periclase | - | - | - | - | negative |

Simplified, the influence of the clinker phases can be summarized as follows.

- The overall strength development of the cement is determined in first instance by the silicates.
- With the exception of C_3S , all phases that help to increase early strength have always a negative effect on the late strength.
- The clinker phases C_3A and alkali sulfates tend to increase the water demand.

The contribution of the main clinker phases to the strength development is shown schematically in the figure below.

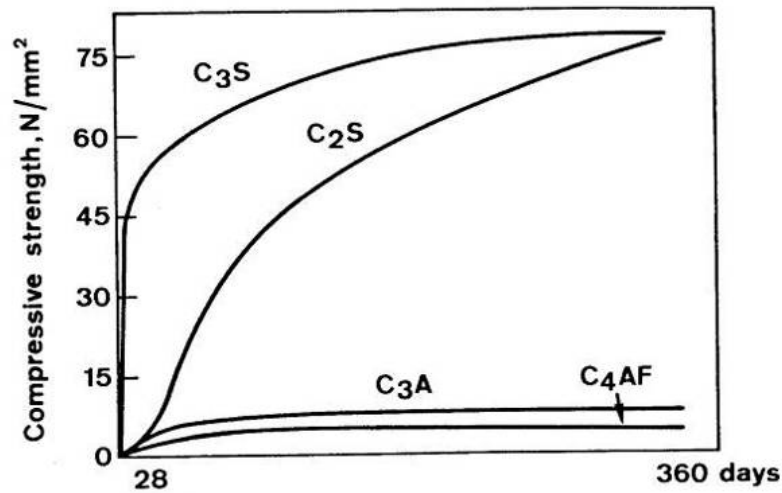


Figure 10: Strength contribution of different clinker phases

3.2.3.1 Alite

Alite is the main mineral in Portland cement clinker and is the phase, which produces the most relevant cement property. It reacts fast and reaches high strength in a short time. Alite improves both early and late strength potential of the clinker.

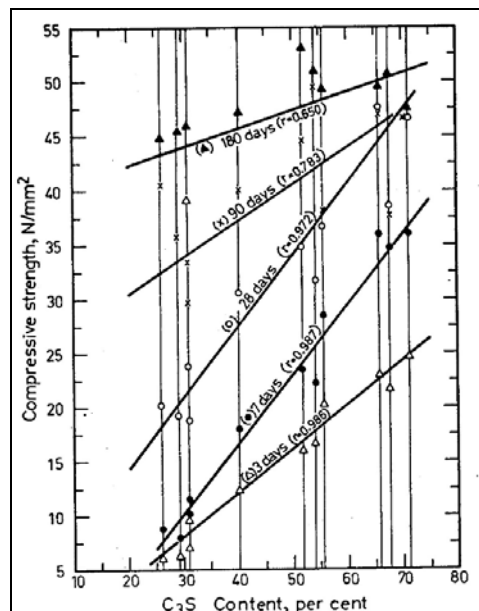


Figure 11: Correlation between alite content and strength development

Thermodynamically alite is not stable at ambient temperature, however it is stabilized by the impurities in its crystal structure. Seven alite modifications are known in the meta-stable temperature range below 1250 °C. In industrial clinker, it

occurs predominantly in the monocline (MII) or tricline modification. Differences in the reactivity of the different modifications are rarely analyzed and considered negligible.

Alite can take up several elements in its crystal structure (see Table 4). Most relevant for practical purposes is the uptake of MgO, which can be incorporated up to 2 % in the crystal structure, replacing CaO (refer to section 3.3.3).

3.2.3.2 Belite

Belite is less reactive than alite and contributes to late strength (> 28 d), it does not contribute to early strength.

Belite occurs in five modifications. In industrial clinker it occurs in its β -modification. High temperature modifications of belite are known to have a higher reactivity than β -belite, which was used for “belite clinker” production. However, the stabilization requires extremely high cooling rates, which are technically not achievable.

In clinker that was burnt under strongly reducing conditions, belite can also occur in its γ -modification. This modification does not react hydraulically. It can be identified by clinker microscopy or by XRD analysis. The transformation of β -belite into γ -belite can make the clinker granules to crumble due to the related volume increase.

3.2.3.3 Aluminate

Aluminate is the mineral with the highest influence on the setting of the cement. The reaction of aluminate starts directly after water addition and in the presence of soluble sulfate (from gypsum) needlelike ettringite is formed, a phase very rich in water. The linkage of these needles causes the setting of the cement (see also section 4). Due to the formation of these water rich minerals, the C_3A content shows a positive correlation to the water demand. Furthermore C_3A contributes to early strength up to 1 d.

In industrial clinker aluminate occurs in its cubic or orthorhombic modification, the change in the crystal structure is induced by the uptake of alkalis. Therefore the orthorhombic aluminate is also called alkali-aluminate. The formation of alkali-aluminate is directly related to the alkali-sulfur ratio of the clinker. At sintering temperature the alkalis combine with the sulfur and form alkali sulfates. If the alkali-sulfur ratio is higher than 1, the excess alkalis – in particular sodium – are taken by the aluminatic liquid phase and during cooling they are fixed in the aluminate.

Of practical relevance is the change in reactivity that is evoked by the change of modification. Orthorhombic aluminate has a higher reactivity than cubic aluminate. Therefore clinker with high content of orthorhombic aluminate tends to fast setting and may also affect negatively the compatibility with admixtures (more erratic setting behavior).

Even without the presence of orthorhombic aluminate fast setting can also occur when the aluminate as such is very high. It is recommended to keep the aluminate level below 10 % in OPC in order to guarantee proper set control. For composite cements, a high C_3A might however be beneficial with regard to 1 d strength.

In sulfate resistant clinker, the amount of aluminate is limited, typically to 5 % (high sulfate resistance) or 8 % (moderate sulfate resistance). Below an AR of 0.638 theoretically no C_3A should be present any more. However, in practice C_3A was recognized until an AR of 0.55.

Orthorhombic and cubic aluminate can be differentiated by microscopical analysis or XRD analysis.

3.2.3.4 Ferrite

Ferrite ($C_2(A,F)$ or C_4AF) is reacting much slower than aluminate and has therefore no significant influence on the setting behavior and early strength. Ferrite rich cements (like high sulfate resistant cement) are in general slower setting than aluminate rich cements.

Ferrite is a solid solution between C_2A and C_2F , viz. it can contain varying concentrations of aluminum and iron. A correlation between its composition and its reactivity was not proven so far.

The ferrite content is significant for the cement color. Like most iron containing minerals pure ferrite has a brownish discoloration. However, in industrial clinker the phase contains always some Mg that substitutes Fe in the crystal structure. This substitution turns the brownish into a grayish discoloration.

3.2.3.5 Alkali sulfates

Most clinker contain about 0.5 – 1.0 % alkali sulfates, in particular potassium sulfate. However, other alkali-sulfur minerals are as well formed depending on the alkali sulfur ratio and the level of the two elements.

Table 6: Common alkali-sulfate phases in clinker

| Alkali compound | Chemical formula | Melting temperature / °C |
|---------------------|----------------------------|------------------------------|
| Arcanite | K_2SO_4 | 1074 |
| Calcium langbeinite | $2 Ca_2SO_4 \cdot K_2SO_4$ | 1011 |
| Aphthitalite | $(K, Na)_2SO_4$ | 968 |
| Thenardite | Na_2SO_4 | 884 |
| Anhydrite | Ca_2SO_4 | 1450 (decomposes at 1200 °C) |

Excess alkalis are mainly taken up in the aluminate phase but also by belite.

Although alkalis reduce the melt temperature, there is no positive effect on alite formation because alkali sulfate melt and clinker melt (aluminate, ferrite) are immiscible phases. In the absence of sulfates, high contents of alkalies inhibit the formation of C_3S from C_2S and free lime by stabilizing lower energy C_2S .

The influence of alkali sulfates on product properties is described in section 3.3.

Too high concentrations of alkalis – independent if present as alkali sulfates or bound in aluminate - are not desirable, because they can cause deleterious alkali-silica reaction with reactive aggregates. Internationally clinker with $\text{Na}_2\text{O}_{\text{equ}} < 0.60 \%$ are accepted as low alkali cement and can be used in combination with alkali sensitive aggregates. High alkali sulfate contents can also cause efflorescence by deposition on the surface of Na_2SO_4 , as observed at the Tecomán plant [Sch 01].

The amount of alkali sulfates can be estimated on basis of the total amount of alkalis and sulfate taking into account the alkali sulfur ratio. Experimentally it can be determined by the content of soluble alkali content according to ASTM C 114.

3.2.3.6 Free lime

Clinker contains always some free lime. At a given clinker composition this mineral is an indicator for the burning degree, i.e. it is a measure for the development of the alite formation.

The optimum range for the free lime content is somewhere in the range between 0.5 and 1.5 %. Lower free lime content is indicative of hard burning conditions and hence energy waste. Furthermore it is correlated with a decrease in early strength (due to strong alite growth under hard burning conditions).

Free lime contents higher than 1.5 % can be a sign of insufficient burning (soft burning) or of inadequate raw meal preparation or composition. As a rule of thumb (Bogue formula) each percent of free lime lowers the C_3S content by 4.0 % and consequently the strength potential. Furthermore too high free lime contents might cause expansion problems due to portlandite formation.

Above the limit of 1.5 – 1.8 % a shortening of setting time, a lower late strength, expansion problems and storage problems (prehydration, disintegration) can occur.

Principally, excessive free lime is present when:

- The lime saturation is too high, which leads to more or less evenly distributed free lime crystals.
- Reaction in the kiln is not complete due to insufficient burning temperature or too rapid passage through the sintering zone.
- Carbonate grains are too coarse in the kiln feed, which gives relict clusters.
- The kiln feed was insufficiently homogenized, which results in free lime clusters with large distances in between.
- Alite decomposition into belite and free lime occurs due to too slow cooling or incorporation of foreign ions. In practice, this source of free lime usually does not result in large quantities.

Clinker microscopy provides an adequate tool for the clarification of the sources for excessive free lime. Free lime determination can be carried out by wet chemistry or by XRD analysis.

It has to be stated that the liter weight and free lime content often show only poor correlation. Hence the liter weight is in most cases no adequate analysis for the

determination of the burning degree and priority should always be given to the free lime analysis.

3.2.3.7 Periclase

Periclase is critical with regard to expansive reactions taking place. Its influence on the soundness depends on the crystal size of the periclase and its distribution. Finely distributed periclase is considered less critical than coarse periclase crystals. A coarsening of the periclase can be avoided in first instance by sufficient fine grinding of the raw meal, to reduce the original dolomite grain size. During clinker burning, an adequate length of the sintering zone (avoid too long sintering zone) and fast cooling helps to avoid coarsening of the periclase crystals.

MgO in the cement clinker derives predominantly from dolomite, which is occurring in several limestone deposits. Furthermore MgO can origin from clay, which can contain MgO in the range of 0.5 to 5.0 %. During sintering a part of the MgO is solved in the liquid phase, another part is taken up in solid by the silicate phases, in particular alite. Up to 2 – 2.5 % MgO can be taken up by the silicate and aluminite (ferrite) phase without the necessary presence of periclase (see also section 3.3.3).

3.2.3.8 Anhydrite

In clinker with high sulfur excess also anhydrite (CaSO_4) can occur. This anhydrite is so called “dead burnt”, since it is hardly soluble in water and has hence no direct influence on the setting and strength development.

With regard to clinker quality it is of interest due to the fact that it binds some of the calcium so that it is missing for the formation of alite.

3.2.4 Determination of mineralogical composition

The mineralogical composition is traditionally calculated by the Bogue formula. In modern cement plants nowadays XRD is used for the routine control of the clinker composition. Furthermore the clinker phase composition can be determined by microscopy and point counting.

The methods are described in more detail in section 9.1.1.

3.3 Minor elements

3.3.1 General remarks

There is no strict definition for minor elements in clinker. In the present context, minor elements are understood as elements (or elements oxides respectively) other than CaO , SiO_2 , Al_2O_3 and Fe_2O_3 occurring in concentration ranges between 5 % and 0.01 %. They typically comprise MgO , SO_3 , K_2O , Na_2O , TiO_2 , P_2O_5 , Mn_2O_3 , Cl , F , BaO and SrO . Elements occurring at lower concentrations are referred to as trace elements. Trace elements, in particular heavy metals in clinker are not dealt with in

detail in this manual and reference is made to [Ste 05] for typical concentrations in clinker. It can be added that in general heavy metals do not affect the product quality as such but they have to be monitored with regard to health and safety (e.g. for CrVI in the cement).

An overview of the contents of minor elements in Holcim Group clinkers is given in Table 7.

Table 7: Concentrations of minor elements in Holcim Group clinkers (source: ATR 2008 and [Hol 04], for SrO and BaO: MT Laboratory data base, limited number of data)

| | Average | Median | Min | Max | Ideal | Recommended limit |
|--------------------------------------|---------|--------|------|------|----------------------------|-------------------|
| K ₂ O [%] | 0.70 | 0.68 | 0.12 | 1.36 | | |
| Na ₂ O [%] | 0.24 | 0.22 | 0.02 | 0.69 | | |
| Na ₂ O _{equ} [%] | 0.70 | 0.65 | 0.18 | 1.26 | 0.60 – 1.00 < 0.60 (LA) | < 1.3 |
| SO ₃ [%] | 0.80 | 0.75 | 0.07 | 2.10 | | < 2.0 |
| Alkali sulfur ratio | 1.51 | 1.12 | 0.34 | 7.01 | ~ 1 | |
| MgO [%] | 1.88 | 1.70 | 0.39 | 5.02 | < 3.5 | 4.8 |
| P ₂ O ₅ [%] | 0.18 | 0.14 | 0.01 | 0.52 | < 0.3 | < 0.5 |
| Mn ₂ O ₃ [%] | 0.12 | 0.06 | 0.03 | 1.10 | | < 1.0 |
| TiO ₂ [%] | 0.27 | 0.27 | 0.05 | 0.58 | | |
| SrO [%] | 0.10 | 0.07 | 0.02 | 0.30 | | |
| BaO [%] | 0.09 | | 0.04 | 0.32 | | |

Minor elements can influence the clinker properties in several respects, including strength development, setting behavior, soundness, color, and others. Controlling their concentration in clinker can therefore potentially be useful to optimize clinker properties. Due to potentially deleterious effects, concentrations of some of the minor elements in cement (and hence in clinker) can be limited by Cement Standards.

Minor elements are unavoidably introduced with traditional and alternative raw materials, as well as with fuels. The range within which they can be controlled is often quite limited, and therefore also the range by which clinker properties can be optimized.

Possibilities to control the content of minor elements in clinker can be as follows:

- Selective quarrying of raw components to reduce or enhance certain minor elements
- Preblending of raw components to achieve uniform levels of minor elements in the raw mix

- Substitution of raw components with similar materials but with different contents of minor elements
- Addition of specific materials to selectively increase the contents of certain minor elements (e.g. gypsum to increase SO_3 , puzzolan or waste glass to increase alkalis, fluorspar to increase F)
- Modification of fuel mix

In the following sections, impacts of minor elements are reviewed. Further information on the role of minor elements in clinker and cement can be found in text books ([Lea 76], [Lea 01], [Tay 97]) and overview papers ([Bha 95], [Bha 06], [Hol 04], [Moi 92]).

3.3.2 Alkalis and sulfur

The impacts of alkalis – K_2O and Na_2O – and of sulfur (SO_3) on clinker properties are strongly related, and are best discussed in an integrated way.

3.3.2.1 Alkalis and sulfur occurrence and limits

Data on alkali and sulfur concentrations in Holcim Group clinkers is given in Table 7. It is evident that K_2O is usually present in higher concentrations than Na_2O . Although K_2O and Na_2O have similar effects, it is usually preferable to have the alkalis predominantly present as K_2O . In general, the alkali content is expressed as sodium equivalent ($\text{Na}_2\text{O}_{\text{equ}}$), which is calculated by the following formula:

$$\text{Na}_2\text{O}_{\text{equ}} [\%] = \text{Na}_2\text{O} [\%] + 0.658 \times \text{K}_2\text{O} [\%]$$

The form, in which alkalis and sulfur occur in clinker, depends mainly on the alkali sulfur ratio, which is calculated by the following formula:

$$\text{A/S-ratio} = (\text{Na}_2\text{O} [\%] / 62 + \text{K}_2\text{O} [\%] / 94) / (\text{SO}_3 [\%] / 80)$$

In a first approximation, alkalis and sulfur occur in clinker as alkali-sulfates, to the extent possible by the molar ratio of these elements. In case of a molar excess of alkalis over sulfur, excess alkalis are preferentially incorporated in the aluminat phase (C_3A) forming alkali-aluminates. This entails a change in modification from cubic to orthorhombic aluminat [Shi 82]. In case of an excess of sulfur, sulfur can be present in the double salt calcium langbeinite, can be incorporated in belite, and in extreme cases, can be present as calcium sulfate (anhydrite, CaSO_4). Typical alkali sulfate phases are listed in Table 6.

Alkalis and sulfur are volatile to a certain extent during clinker burning and can therefore give rise to operational problems in form of build-up and ring formation. Critical are in particular high intakes of sulfur und situations of a molar excess of sulfur over alkalis. Furthermore, cement kiln dust of long kilns and by-pass dust are enriched in alkalis and sulfur (and chloride).

Alkalis and sulfur have a strong influence on cement properties, notably on strength development, setting time and water demand and can therefore effectively be used to optimize cement quality. Furthermore, alkalis can have a deleterious impact in hardened concrete in presence of “reactive” aggregates: through the so-called alkali-aggregated-reaction expansive products are formed that can lead to concrete cracking.

Tentative, practical limits that should in general not be exceeded without careful assessment of impacts on cement and concrete quality are:

- $\text{Na}_2\text{O}_{\text{equ}}$ 1.3 %
- SO_3 : 2.0 %

For situations where alkali-aggregate reactions are of concern, the use of low-alkali cements can be specified. On a world-wide basis, the limit for alkalis in low-alkali cement given in cement standards is usually 0.60 % $\text{Na}_2\text{O}_{\text{equ}}$. The production of such cements implies an equal or similar limit in clinker.

Cement standards do not specify SO_3 limits in clinker. Limits for SO_3 are, however, specified for cements.

3.3.2.2 Influence on product performance

Strength development

Alkalis and sulfur have a strong impact on the reactivity of clinker and can effectively be used to optimize the strength development; in particular to enhance early strength. Alkali sulfates are readily soluble in the mixing water of mortar or concrete. They have a significant accelerating effect on the rate of early hydration and therefore enhance the early strength development. However, this goes usually along with a reduction of late (28 d) strength.

This relationship can be seen both when comparing clinker from different origin (Figure 12) and when comparing clinker samples from one and the same plant (Figure 13). The results in displayed in Figure 12 were measured on laboratory cements made from industrial clinkers. The alkali sulfate content was calculated from the Na_2O , K_2O and SO_3 content of the clinker taking into account the alkali sulfur ratio.

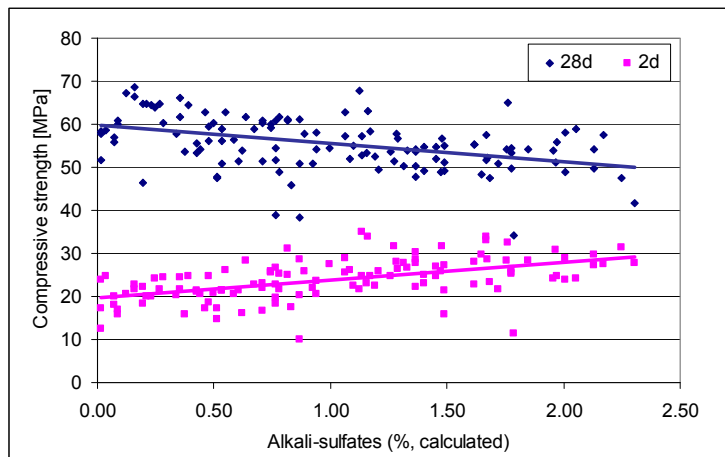


Figure 12: Mortar 2d and 28 d strengths vs. calculated alkali-sulfate content in clinker (Data source: Product Handbook 2004; Laboratory cements made from industrial clinkers; “ Na_2SO_4 ” calculated from concentrations of SO_3 , K_2O and Na_2O in clinkers, taking in account the molar alkali-sulfur ratio)

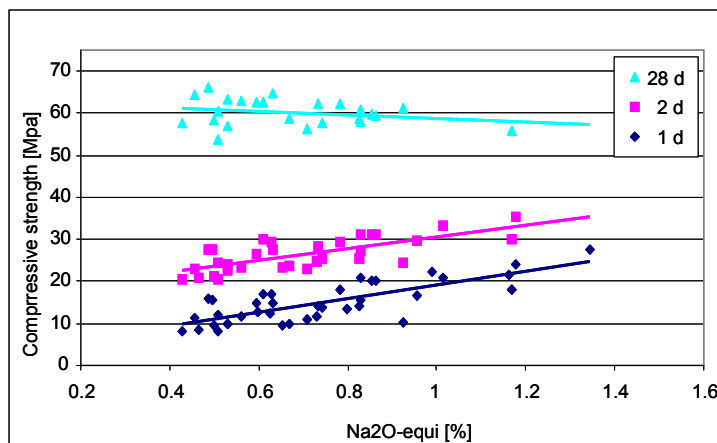


Figure 13: Strength versus clinker Na_2O -equi from specific plant (Source: Höver REACT Data Analysis, Tianhe Yang 2008)

The control of the amount of alkali sulfates – i.e. of the alkali and sulfur concentrations and the resulting molar ratio – is therefore one of the most effective ways to optimize the strength development characteristics of clinker, e.g. in order to achieve:

- high early strength characteristics (“reactive” clinker), beneficial for composite cements
- cements matching strength requirements at 2 d and 28 d (e.g. sub-class “R” in the European Cement Standard EN 197-1)
- cements with high late strength

Setting time

Alkalis and sulfur can influence the setting behavior through two effects:

- Soluble alkali-sulfates contribute to the availability of dissolved sulfate-ions in the mixing water and hence to the ettringite formation, which has a retarding effect. Recent practical experience re-confirmed this effect, whereas some earlier studies had also reported setting time reduction due to the acceleration of early hydration by the dissolved alkalis.
- Orthorhombic alkali-aluminate present in case of molar excess of alkalis over sulfur exhibits a very rapid rate of hydration. It thus accelerates setting and in extreme situations can lead to disturbed setting behavior (early stiffening).

Water demand

Alkali sulfates tend to increase water demand.

Efflorescence

High levels of soluble alkali sulfates can cause efflorescence in concrete [Sch 01].

Summary

The impact of alkalis and sulfur on the cement performance are summarized in a qualitative way in the table below.

Table 8: Influence of alkali and sulfur on the cement properties

| Na ₂ O _{equ} (%) | SO ₃ (%) | A/S | Low alkali | Early strength | Late strength | Setting time | Efflore- scence |
|---|------------------------|-----|---------------|-------------------|------------------|-----------------|--------------------|
| < 0.60 | < 2.0 | > 1 | Yes | ~ | ~ | ↓ | ~ |
| | | ~ 1 | | ↑ | ↓ | ↑ | |
| | | < 1 | | | | | |
| 0.6 – 1.0 | < 2.0 | > 1 | No | ~ | ~ | ↓ | ~ |
| | | ~ 1 | | ↑ | ↓ | ↑ | |
| | | < 1 | | | | | |
| 1.0 – 1.3 | < 2.0 | > 1 | No | ~ | ~ | ↓ | ~ |
| | | ~ 1 | | ↑ | ↓ | ↑ | |
| | | < 1 | | | | | |
| < 1.3 | > 2.0 | > 1 | ~ | ~ | ↓? | ~ | ↑ |
| | | ~ 1 | | | | | |
| | | < 1 | | | | | |

Conclusively, the following can be said:

- A Na₂O_{equ} between 0.6 and 1.0 % and a balanced molar alkali sulfur ratio are considered optimum for most situations.

- A significant molar excess of alkalis over sulfur results in a reduced early strength potential, along with a risk of problematic setting behavior. It is typically recommendable to take measures for increasing the sulfur content to optimize the clinker quality.
- A significant molar excess of sulfur over alkalis has usually no particular effect on clinker properties up to SO_3 levels of 2.0 %. At SO_3 levels above 2.0 %, the following possible effects may occur
 - Reduction of the late strength potential
 - Dosage of gypsum in cement may need to be significantly reduced (in order to keep total SO_3 within standard SO_3 limits). This can impact the setting behavior and furthermore will increase the clinker factor.

Situations of high sulfur contents and molar excess of sulfur are typically associated with the use of petcoke as main fuel.

Further information on the influence of alkalis and sulfur on cement can be found in [Str 85a], [Str 85b], [Str 86], [Mon 97a] and [zim 04].

3.3.2.3 Measures to influence alkali and sulfur content in clinker

Alkali and sulfur contents in clinker can be optimized through following measures:

Raw mix

- Change of conventional raw components (clay, shale, fly ash, etc)
- Selective quarrying
- Use of high-alkali raw components, traditional or alternative (pozzolan, spent pot liners, waste glass), or even of pure alkali compounds such as sodium bicarbonate NaHCO_3
- Use of high-sulfur raw materials (gypsum)

Fuel

- Change of fuel mix, particularly to control sulfur intake (coal, petcoke, AFR)

Operational measures:

- Dust extraction (CKD, by-pass dust)
- Chlorination and (by-pass) dust extraction: extreme measure to achieve low-alkali clinker

3.3.3 MgO

MgO is a common minor element in clinker, mainly stemming from dolomitic limestones in the raw mix. Other contributing raw mix components can be clay/shales, basaltic components, as well as blast furnace slags.

The present, certainly simplified understanding is that up to 2 % MgO in clinker will be incorporated in the main clinker minerals, notably in alite, while amounts of MgO in excess of 2 % are present as the mineral periclase (MgO).

This assumption is reflected in some of the calculation formulae for clinker liquid phase content, clinker lime saturation, as well as empirical formulae for “corrected” Bogue calculations (see end of chapter). The influence of MgO on cement properties was thoroughly investigated by Dreitzler and al. [Dre 82], [Rot 84].

The 2 % of MgO present in normal clinker minerals basically substitute for CaO, hence it contributes to the quantity of alite and to the strength development. Periclase, on the other hand, is inert with respect to strength contribution or setting time. However, due to the hydration of periclase (MgO) to brucite ($\text{Mg}(\text{OH})_2$) at late stages in hardened concrete, expansion problems leading to cracks in concrete structures can potentially occur.

Contents of MgO in Ordinary Portland Cements or in clinker are limited in all common Cement Standards, due to the risk of expansion. In the European Cement Standard EN 197-1, the limit is 5.0 % in clinker, in the ASTM C-150 it is 6.0 % in cement. Furthermore, performance specifications can be given, notably in ASTM C-150, for the expansion of mortars resulting from the autoclave expansion tests (ASTM C-151). The practical relationship between the autoclave test results and actual concrete field performance, however, is disputed [Wol 93], [Kle 05].

Statistics for MgO contents in Holcim clinkers are given in Table 7. It is evident that for most plant clinkers, the MgO content is well below the standard limit.

Different objectives can exist for optimizing MgO contents in clinker:

Optimal utilization of raw material reserves:

In case of raw material with high MgO content, maximization of MgO in clinker can be an objective. Gains in reserves have to be weighted against negative impacts of high MgO contents, which are risks to fail expansion test limits of Standards, or maximum expansion limits accepted in the market, and a loss in strength potential due to the presence of 1 – 3 % of inert periclase in clinker.

The “comfort” side would be to stay below about 3.5 % MgO in clinker. Highest levels in Holcim Group clinkers are around 4.8 %. It is recommended that this level is not exceeded unless there are very strong reasons to do so, even in areas with cement standards allowing for 6 % of MgO in cement.

The most effective measure to reduce the risk for excessive expansion is to grind the raw meal very fine, i.e. to residues on 90 μm of 10 % or less. This leads to a homogeneous distribution of periclase in clinker (avoidance of clusters), which is less harmful with regard to expansion.

Optimization of strength potential

Generally, the impact of MgO on the strength potential is modest.

As mentioned above, up to 2 % of MgO can be incorporated in the normal clinker minerals, substituting for CaO. This amount therefore contributes to the formation of alite, and hence to the strength potential. A practical consequence of this is, that the lime saturation (calculated with the conventional formula) of MgO-rich clinkers should not be increased above 97. Quantitative determination of alite and belite (e.g. by microscopy) can help to determine an appropriate level of lime saturation for clinkers of high MgO contents. Furthermore, the MgO-corrected lime saturation formula may be applied to calculate the effect of MgO

Some plants have reported negative impacts on 28 d strength development when MgO contents exceed about 2 % in clinker. Also the literature is speculating about negative impacts of MgO on strength [Cla 06], related to its stabilization of the less reactive M3 modification of alite. At the moment, there is not sufficient evidence to fully support these observations and hypothesis.

Improvement of burnability

MgO is reported to have a fluxing impact on the clinker liquid phase and therefore improves burnability. Most probably, the level of MgO in most clinkers is sufficiently high and there is no need to specifically optimize MgO for this purpose.

It may be mentioned that upon burning of clinker with high MgO content more CO₂ is released from the raw mix, because MgO is normally present as carbonate. For fan-limited kiln systems, this can entail a slight reduction in the production rate.

There are some formulas which take into account the effect of MgO on liquid phase content as well as LS and clinker phases. Formulae accounting for the effect of MgO:

Liquid phase (LP) at 1400 °C (Lea and Parker):

$$LP = 2.95 \text{ Al}_2\text{O}_3 + 2.2 \text{ Fe}_2\text{O}_3 + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O} \quad (\text{up to max 2.0 \% MgO})$$

The formula for the LS and clinker phases should only be used for “consultative” purposes, but not for routine application.

$$LS (\text{clinker}) = ((\text{CaO} + 0.75 \text{ MgO}) \times 100) / (2.8 \text{ SiO}_2 + 1.18 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3) \\ (\text{up to max 2.0 \% MgO})$$

Clinker phase composition (Holcim modified Bogue formulae [Kri 77a,b])

$$C_3S_{\text{mod}} = C_3S_{\text{Bogue}} + 4.0 \text{ MgO} + 5.5 \text{ K}_2\text{O}$$

$$C_3S_{\text{mod}} = C_2S_{\text{Bogue}} - 1.5 \text{ K}_2\text{O} - 2.2 \text{ K}_2\text{O}$$

$$C_3A_{\text{mod}} = C_3A_{\text{Bogue}} + 7.8 \text{ Na}_2\text{O} + 1.5 \text{ AR} - 2.1 \text{ SO}_3 - 5$$

$$C_4AF_{\text{mod}} = C_4AF_{\text{Bogue}} - 6.5 \text{ Na}_2\text{O} + 1.7 \text{ AR} + 5.0 \text{ Mn}_2\text{O}_3 + 3$$

3.3.4 P_2O_5

Practical impacts of P_2O_5 on clinker properties are primarily negative, in terms of reducing strength potential and extending setting time.

Intakes of P_2O_5 occur with conventional raw materials, often in association with the limestone, and with alternative fuels, particularly with animal meal and sewage sludge.

Optimization of P_2O_5 in clinker thus usually revolves around establishing acceptable maximum limits in clinker in connection with using above mentioned materials. The experiences within the Holcim Group can be summarized as follows:

Table 9: Influence of different P_2O_5 levels on the cement properties

| P_2O_5 level in clinker [%] | Comments/Effect |
|-------------------------------|--|
| < 0.3 | <input type="checkbox"/> Uncritical <input type="checkbox"/> No significant impact on strength and setting |
| 0.3 – 0.5 | <input type="checkbox"/> Acceptable <input type="checkbox"/> In most cases little impact on strength and setting <input type="checkbox"/> 0.5 % P_2O_5 in clinker is in most Holcim plants (using P_2O_5 bearing AFR) the acceptance limit |
| 0.5 – 1.0 | <input type="checkbox"/> Critical <input type="checkbox"/> Negative effect on strength and setting <input type="checkbox"/> Needs to be investigated case by case |

P_2O_5 in clinker is mainly incorporated in belite, forming a continuous solid-solution between C_2S and C_3P . This entails a reduction of alite formation (C_3S) (and hence of strength potential) through two effects:

- P_2O_5 binds CaO in a “belite”-phase, thus reducing the CaO-content available for C_3S formation,
- phosphorous-containing belite is stabilized and the reaction between belite and free lime at sintering temperatures impeded.

The latter effect can be seen in clinker micrographs, where belite can be in direct contact with free lime, which is impossible in low- P_2O_5 clinkers.

P_2O_5 that is soluble in the mixing water of mortar or concrete is known to retard setting.

Strength-reducing effects of P_2O_5 can be compensated to some extent by raising the lime saturation of the clinker. In the literature it is further reported that the use of F can compensate for losses in strength incurred by P_2O_5 ([Gut 68], [Moi 92]). There is presently no indication that this is practically applied.

A comprehensive investigation of the influence of P_2O_5 on cement properties has recently been published [Pun 08] also including exhaustive literature references.

3.3.5 Mn₂O₃

Mn₂O₃ is typically present in clinkers at low levels.

The statistics for Holcim Group clinkers is given in Table 7. Clinkers with contents above 0.30 % are exceptional.

Unlike many other transition elements, Mn, along with Fe and Ti, is not associated with toxic or environmentally problematic properties. There are also no limits given in any Cement Standards.

At the typical levels encountered (< 0.3%), there are no indications within the Holcim group of relevant effects on clinker or cement properties.

As presented by Moir [Moi 92], Mn₂O₃ is mainly located in the ferrite phase, substituting for Fe₂O₃. If present in large quantities, it will increase the content of ferrite and reduce the content of aluminates, but also of alite, because CaO is used to combine with Mn₂O₃. This can account for a reduction of strength in such situations.

Reasons for optimization of Mn₂O₃ contents in clinker can occur in following contexts:

Optimal utilization of raw material reserves:

In rare cases, plants can be faced with raw components having higher than usual Mn₂O₃ contents. In such cases decisions need to be made concerning the acceptable maximum level, as well as necessary adaptations of other compositional characteristics.

In a Holcim internal investigation [Iml 02] it was shown that levels of up to 1 % Mn₂O₃ in clinker are as such not problematic and could potentially also be increased by adjustments in the clinker composition. It was also confirmed that Mn₂O₃ is predominately located in the ferrite phase, followed by alite, belite and aluminates.

In order to compensate for the incorporation of Mn₂O₃ and the resulting impacts on the clinker phase composition, the overall composition of the raw mix and clinker has to be adapted, primarily, of course, by reducing the Fe₂O₃ content.

Imlach proposes to aim for the usual target values of clinker moduli, but to use formulae corrected for the amount of Mn₂O₃ present. The proposed formulae are as follows (to be applied for design purposes only; not to be used in routine quality control):

$$LS = 100 \text{ CaO} / (2.8 \text{ SiO}_2 + 1.18 \text{ Al}_2\text{O}_3 + 0.65 (\text{Fe}_2\text{O}_3 + 0.62 \text{ Mn}_2\text{O}_3))$$

$$SR = \text{SiO}_2 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + 0.70 \times \text{Mn}_2\text{O}_3)$$

$$AR = \text{Al}_2\text{O}_3 / (\text{Fe}_2\text{O}_3 + 0.62 \text{ Mn}_2\text{O}_3)$$

Darkening of clinker and cement color

Some cement markets appreciate a dark color of cement, and plants can be faced with the objective to darken the clinker and cement color. It is known that Mn_2O_3 has a pronounced darkening effect on clinker color. Holcim internal investigations [Iml 02], [Iml 00b] have shown – perhaps against expectations – that the darkening effect is not stronger but about equal to that of Fe_2O_3 at same increases in quantity.

Further information on the influence of manganese in clinker and cement can be found in the pertaining literature, notably [Kno 83].

3.3.6 TiO₂

TiO₂ is typically present in clinkers at levels around 0.3 % (see Table 7).

TiO₂ is not typically used to optimize clinker properties. Occasionally, with the use of TiO₂-rich raw materials (e.g. iron or silica correctives containing ilmenite FeTiO_3) the question of acceptance of levels of 0.5 % or slightly above may occur. As also confirmed by the literature mentioned below, there is no reported evidence of negative impacts at such levels.

TiO₂ is preferentially located in the ferrite phase, but can be found at lower concentrations in the other main clinker minerals.

With regard to its influence on phase development and compressive strength development [Kno 77] reported that for laboratory produced clinkers increasing the TiO₂ content up to 1 % did cause an increase in strength in spite of a decrease of C_3S , but only at 7 days and more. At 2 days no increase was observed.

3.3.7 Cl

Chloride contents in clinker are typically at levels of $\leq 0.01\%$, rarely up to 0.04 %. This is due both to low Cl inputs with raw materials and fuels, and to the high volatility of chloride at sintering temperatures, rendering it very difficult to attain higher levels in a sustainable way.

According to Holcim experience, chloride inputs up to 300 g/t clinker can be accepted for a preheater/precalciner kiln system without bypass. Higher chloride inputs – as may particularly arise with the use of chloride-containing AFR – require a bypass system and the extraction of chloride enriched kiln dust. This kiln dust can and should be used in the cement (if accepted by the pertaining Cement Standards).

Most, if not all Cement Standards specify a limit for chloride in cements, typically at 0.10 % Cl. This is to prevent corrosion of steel enforcement in concrete. Addition of above mentioned chloride enriched kiln dust to cement has, of course, to respect these limits.

For chloride intakes above 150 g/tg clinker, it is desirable to optimize kiln operation and clinker burnability such that chloride circulation can be reduced and that chloride levels in clinker equal to the input or equal to 0.03 % (at inputs < 300 g/t

clinker) can be maintained in a sustainable way. This minimizes problems with build-up formations.

Chloride in clinker and particularly in kiln dust is present as water soluble potassium (or sodium) chloride, KCl or NaCl respectively.

Soluble chloride in cement has the effect of an accelerator, increasing early strength development. The use of chloride enriched kiln dust as cement constituents therefore modifies cement properties, with respect to a dust free cement, and should therefore be applied with as constant as possible dosage rates.

Impacts on the use of bypass dust in cement have been investigated in a Holcim internal study [Bid 03].

3.3.8 SrO and BaO

BaO and SrO, both earth-alkalis and hence related in their chemical behavior to CaO, are, according Lea [Lea 76] typically present below 0.05 % for BaO and 0.2 % for SrO; with SrO occasionally up to and above 0.5 %. This is in line with the limited data available for clinkers from the Holcim group (see Table 7). Their presence may sometimes be “discovered” due to total chemical analyses being short of 100 % by a few tenths of a percent.

At the mentioned levels, there is no concern about deleterious impacts on clinker and cement properties. It is even reported that BaO may increase 28 d strength when present between 0 and 0.5 % [Lea 01].

In a case reported from outside the Holcim group, the use of limestone with high SrSO₄ contents (up to 11 %) is limited in the raw mix such that the SO₃ content in the raw meal is kept around 1.5 % [ZKG 89]. This would account for a SrO concentration of 2 % in the raw meal (!). Verbal information from this plant was that high amounts of free lime were observed at these SrO concentrations (inhibition of alite formation), and that fluorspar is used in the raw mix to counteract this effect. Taylor [Tay 90] states that the maximum permissible content of SrO in a raw mix of normal lime saturation is 3 %.

3.3.9 F

Fluoride is typically present in clinkers at concentration levels around 0.05 – 0.1 %.

It is well known that at concentration levels above 0.2 %, fluoride exerts a set retarding effect (in particular at low ambient temperatures), which can lead to problems in cement application. Possible measures to mitigate the delay in setting are the adjustment of the C₃A and C₃S content in clinker (see also following chapter 3.4 on clinker mineralization).

On the other hand, fluoride can in a beneficial way be increased to levels of 0.20 – 0.30 % in clinkers optimized for this purpose. Use is made of the fluxing and mineralizing effect of fluoride in clinker, improving the burnability characteristics and facilitating the alite formation. This has traditionally been applied for production of white cement clinkers (to improve the very poor burnability characteristics) or to

maximize production rates of kilns. The modern application is rather to produce so-called mineralized clinker, exhibiting a very high strength potential that can be exploited to reduce clinker factors in cement. This is treated separately in chapter 3.4.

3.4 **Clinker mineralization**

The concept of clinker mineralization is based on the use of CaF_2 (fluorite, also called fluorspar) in the raw mix, which enables the production of clinker with very high lime saturation (LS 101 – 103) and hence very high alite content.

The possible benefits that can be obtained from such very reactive clinker are as follows [Mon 04]:

- Decrease of clinker factor (5 – 10 percentage points) and/or improvement of cement quality
- Increase of production volume (at constant clinker capacity)
- Reduction of thermal energy consumption (albeit to a limited extent and not a primary goal)
- Reduction of specific grinding energy (up to 8 %)
- Reduction of production costs (up to 2.5 USD/t)
- Reduction of CO_2 emissions (7-9 kg CO_2 /t cem per percentage point of clinker factor reduction)

The effect of F is twofold:

- It acts as a flux, enhancing clinker liquid formation at lower temperatures and improving the burnability
- It acts as a mineralizer, rendering alite thermodynamically stable at lower temperatures [Ker 03]

Optimum concentration level for F in mineralized clinker is around 0.25 %. It should not exceed 0.35 %, as the known effect of set retardation could become too severe.

Fluoride is usually added in form of natural fluorite CaF_2 ; an overview of global resources is given by [Ste 07]. It can also be provided as CaF_2 or in other chemical forms through alternative raw materials (e.g. spent pot liners from the alumina industry).

In order to successfully implement clinker mineralization, a comprehensive planning and a thorough supervision of the initial production phase is essential, as many aspects require attention, including cost/benefit analyses, clinker and cement design, materials handling, analytical methods, kiln instrumentation and operation, as well as product testing in mortar and concrete. Reference is made to the “Guide for Clinker Mineralization” [Mon 03], as well as to a status report on clinker mineralization in the Holcim Group made in 2004 [Mon 04].

Concerning clinker design, the “ideal” ranges for chemical and physical parameters as shown in Table 10 are recommended [Mon 04].

Table 10: Ideal ranges for mineralized clinker

| Parameter | Limit/Range |
|--|-------------------|
| Clinker | |
| LS | 101 - 103 |
| SR | 2.8 ± 0.2 |
| AR | 1.8 ± 0.2 |
| C ₃ S (% , acc. Bogue) | > 70 |
| C ₃ S (% , microscopy, Rietveld analysis) | > 75 |
| C ₃ A (% , acc. Bogue) | 8 - 10 |
| Alk / SO ₃ | 0.8 - 1.2 |
| Na ₂ O _{equ} (%) | 0.6 - 1.2 |
| Liquid Phase (at 1400 °C) (%) | 23 - 25 |
| F ⁻ (%) | $0.23 \pm 0.03^*$ |
| Free lime (%) | < 2.0 |
| Kiln feed burnability | |
| HGRS burnability test | moderate to good |

* update 2009

The beneficial impact from a mineralized clinker on the strength development is undisputed (see [Mon 04] and plant references cited therein).

Attention requires, however, the setting retardation effect of F on cement and concrete. This effect is temperature dependant and particularly critical at low temperatures. Measures to control and limit set retardation include:

- Strict control of F-dosage to the raw mix to the above given range. Concentrations above 0.32 % in clinker can be problematic.
- Achievement of a real C₃A content in the above given range. For several mineralized clinkers it has been observed that the real C₃A content, as determined by XRD/Rietveld or microscopy, is significantly less than calculated by Bogue or “expected” from the alumina ratio. In such situations, it is advisable to further increase the alumina ratio.
- Optimization of the gypsum content in cement, usually meaning a reduction as compared to the non-mineralized clinker.

A different approach for clinker mineralization has been proposed and patented by FLS, making use of the addition of F (CaF₂) and SO₃ (gypsum) to the hot part of a precalciner kiln (example Aalborg). Holcim has no experience with this procedure.

On the other hand, successful mineralization at high SO₃ inputs (100 % petcoke firing) has been achieved at the Guayaquil plant of Holcim Ecuador [Pol 04]; [Zim 04].

3.5 Clinker optimization with regard to process requirements

The clinker composition is not only of relevance for the product quality it has also significant influence on the process requirements. Clinker properties that are important with regard to processing are:

- Uniformity
- Burnability
- Clinker granulometry
- Coating tendency

3.5.1 Uniformity

Sufficient uniformity of raw meal and kiln feed are important for process control and consistent production of good clinker. The following table shows guide values for short and long term standard deviations for clinker, kiln feed and raw meal (Holcim uniformity targets).

Table 11: Guide values for excellent uniformity of raw meal, kiln feed and clinker

| Material | Parameter | Daily hourly samples (average of daily standard deviation) | Monthly daily averages (standard deviation of daily averages) |
|----------------------------|-------------|---|--|
| Kiln feed (and clinker) | LS σ | < 1.2 | < 1.0 |
| | SR σ | < 0.04 | < 0.03 |
| | AR σ | < 0.04 | < 0.03 |
| Raw meal | LS σ | < 3.6 ^{*)} | < 1.0 |

^{*)} for plants with pre-blending system

3.5.2 Burnability

The term “burnability” describes the ease of clinker mineral formation in the production process. An optimization of the burnability can hence help to reduce burning costs in clinker production. The burnability of a raw mix depends on physical and chemical parameter of the raw meal/clinker such as:

- Raw mix fineness
- Micro-homogeneity of raw components
- Mineralogical composition of raw components
- Chemical composition of the clinker

For the same chemical composition and raw meal fineness the burnability can vary significantly. Raw mixes containing clay as silica source are in general easier to burn than raw mixes with quartzitic silica source.

With regard to the chemical composition of the clinker, the burnability deteriorates with:

- Increasing lime saturation
- Increasing silica ratio

Furthermore it is likely that the burnability deteriorates with increasing viscosity of the liquid phase, viz. increasing alumina ratio.

The burnability can be determined by laboratory tests, in which a raw meal sample is burnt under defined conditions. The free lime content after cooling is an indicator for the burnability.

Burnability models were developed to evaluate the influence of the different parameters on the burning behavior. Only by knowing these impacts focused optimization of the raw mix composition is possible. Several models were developed, that take into account several of the above mentioned parameters. The Holcim burnability model is based on the following parameters:

- Coarse quartz (quartz > 32 µm)
- Coarse calcite (quartz > 90 µm)
- Lime saturation
- Silica ratio

The procedure of the burnability test and model are described in Annex 1.

3.5.3 Granulometry and coating tendency

The clinker granulometry and the coating tendency in the kiln are in first instance influenced by the SR and AR of the raw meal/clinker, since they determine the content and viscosity of the liquid phase (see Figure 14). 23 - 27 % liquid phase (at 1400 °C) are considered adequate to achieve a good granulation and coating tendency. At lower liquid phase contents the clinker gets dusty.

At alumina ratios higher than 2.0, the viscosity of the liquid phase increases significantly and clinker ball formation and built up formation is becoming likely. At very low ARs (< 1.2) the viscosity contrast is too low so that granulation and refractory coating is impaired. The result is dusty clinker and poor coating. Furthermore, high SO₃ contents cause dust because of a reduction of surface tension.

Besides the chemical composition, the granulation behavior is furthermore influenced by the micro-homogeneity of the raw meal. A fine grained, micro-homogenous material with a subsequent homogenous liquid phase distribution is advantageous, coarse particles impair granulation.

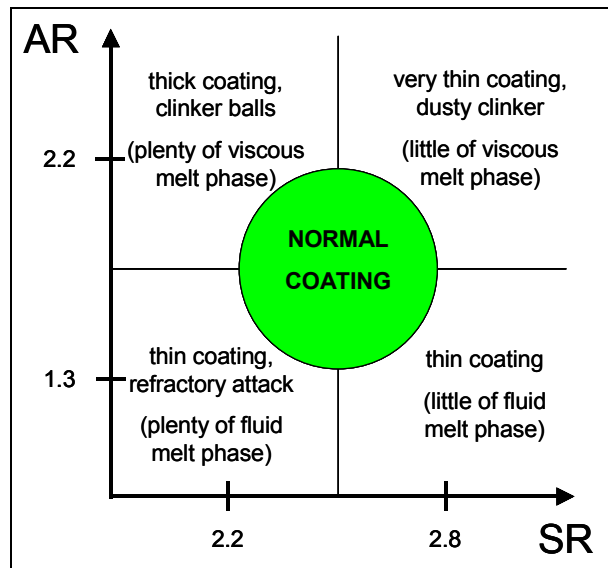


Figure 14: Influence of SR and AR on coating behavior and clinker granulometry

Clinker granulometry can be assessed by means of sieving an adequate quantity (25 – 50 kg) of a representative clinker sample through a set of sieves, e.g. with sieve openings of 1, 5, 8 and 16 mm (or similar).

Clinkers are called “dusty” when more than 25 % are passing the 1 mm sieve.

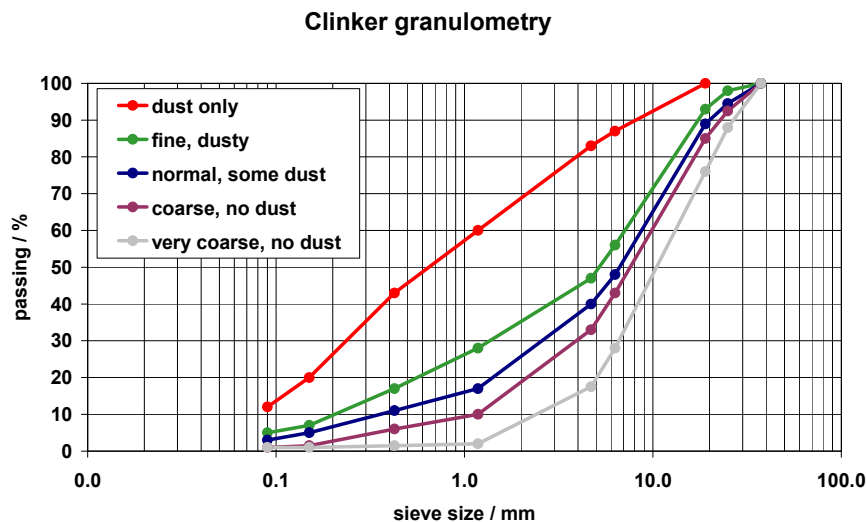


Figure 15: Typical particle size distributions for clinker and the associated classification

3.6 Process influences on clinker quality

The process conditions can, to a greater or lesser extent, influence the clinker performance, as visualized below in a qualitative way.

| Conditions | Early strength | Final strength | Setting time | Water demand |
|---|----------------|----------------|--------------|--------------|
| Reducing conditions (alite decomposition, shift ferrite to aluminat) | ↘ | ↘ | ↘ | - |
| Hard burning (alite growth, low free lime, sulphur volatilization) | ↘ | ↘ | ↗ | - |
| Slow cooling (alite decomposition, coarse crystallization of liquid phase) | ↘ | ↘ | ↘ | - |

↗ increase ↘ decrease - no effect

3.6.1 Reducing conditions

Reducing burning conditions can be caused by a deficiency of oxygen in the kiln gas or oxydizable constituents in the raw mix (e.g. carbon and sulfides). Under these conditions Fe^{3+} is reduced to Fe^{2+} , which cannot be incorporated into C_4AF . Hence more C_3A is formed and consequently the setting times are reduced. Furthermore, C_3S is destabilized by Fe^{2+} and decomposes into C_2S and free lime resulting in a lower strength performance [Scr 95a]. Reducing conditions furthermore enhances the volatilization of sulfates in clinker.

Some of the effects of reducing conditions can partially be reverted upon exposing the clinker to the fresh air in the clinker cooler due to re-oxidation of Fe^{2+} (dark outer part and brown core of clinker nodules) [Scr 95b].

Further information on impacts of reducing conditions can be found in [Syl 81].

3.6.2 Hard burning

Excessive burning generally has a negative effect on clinker reactivity because the alite size increases and imperfections in the alite structure are eliminated. Early strength performance is therefore impaired whereas late strength can be improved. Grindability is generally impaired by hard burning.

3.6.3 Cooling conditions

The clinker cooling rate from sintering temperature down to about 1200°C (crystallization of the liquid phase) can have an effect on strength development and setting behavior. After clinker has passed the burning zone, the rate of clinker cooling is usually around 18 to $20^\circ\text{C}/\text{min}$. Slow cooling produces coarse C_3A and C_4AF crystals, fast cooling gives a fine grain size distribution. Furthermore, slow cooling can cause a resorption of CaO from C_3S into the liquid phase (due to changing phase equilibrium conditions), resulting in belite rims around alite crystals.

A systematic investigation was made by the VDZ in the years 1987 – 1990 [Syl 88] [Sch 88], [Sch 88a]. It was found that:

- Setting is faster for slowly cooled clinker, attributed to the coarseness of C_3A crystals
- Strengths are higher for rapidly cooled clinkers (possible explanation: higher amount of crystal lattice defects in alite, rendering it more reactive)
- The cooling regime is a combination of the cooling taking place still within the rotary part and taking place in the actual cooler. Optimum quality is achieved when the clinker leaves the rotary part at a temperature slightly above the liquid phase crystallization temperature and is then cooled as fast as possible in the cooler.

However, for practical purposes with "normal" cooling rates, the influence of the cooling regime is not a dominant factor for clinker performance.

3.6.4 Process influences by AFR

Due to their generally lower ease of combustion, AFR are more prone to cause problems with burning and cooling conditions as mentioned in the previous chapters.

If the A(F)R have a too coarse granulometry, there is also the risk of insufficient integration of the "ash" particles into the clinker matrix, which can lead to free lime and lower strength.

The process and quality control of AFR is thus essential to ensure the performance and uniformity of the clinker.

3.7 Influence of clinker characteristics on grindability

The grindability of the clinker is determined by its microstructure and the phase compositions. The grindability of a clinker depends on the following factors:

- Alite
 - Alite shows the best grindability among all clinker phases and has a low tendency to agglomeration. Hence clinkers high in alite are easier to grind than low ones.
 - Internal cracks caused by thermal stress release can occur in alite, which are favorable with regard to grinding. However, these cracks are observed often in hard burnt clinker and are hence a sign for overheating.
- Belite
 - Belite is more difficult to grind than alite, tends more to agglomeration and hence impacts the grindability negatively.

- Liquid phase
 - The liquid phase is among the hardest components of the clinker and for sure harder than alite. Nevertheless, the effect of liquid phase content on clinker grindability is not clearly determined.
- Free lime
 - Free lime has a favorable effect on clinker grindability.
- Granulometry, porosity and temperature
 - Large clinker nodules as well as dust are difficult to grind.
 - The total clinker porosity is in first instance important for the coarse grinding of the clinker and has less effect on fine grinding.

A comprehensive literature review is given by [Hil 95]

4. SET REGULATOR

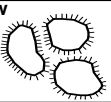
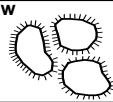
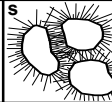
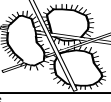
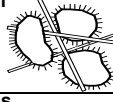
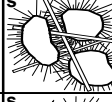
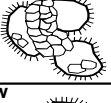
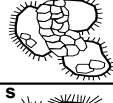
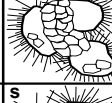
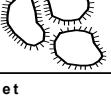
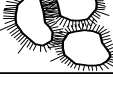
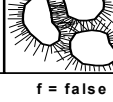
The relevance of gypsum and anhydrite as regulators for the setting of cement is known for a long time. However, fundamental research carried out by Lerch [Ler 46], Kühl [Kuh 61] and Hansen [Han 56] has shown that the sulfate dosage also influences the grindability and storage stability. By optimizing the sulfate dosage also the strength development of the cement can be influenced [Zgr 85].

Most of the plants use natural gypsum sources for set regulation but the amount of industrial gypsum is increasing.

4.1 Set regulation

In order to obtain a normal setting behavior of the cement, the soluble sulfate has to be adjusted to the clinker reactivity. The requirement for sulfur is related in first instance to the C_3A content and modification, viz. its reactivity. Furthermore the setting behavior is strongly influenced by alkalies. Correlations have also been found for the cement alkali content and the cement fineness. However, up to now there is no tool to predict the optimum gypsum dosage and composition, so that a gypsum optimization has to be carried out individually for each cement type.

Unbalanced SO_3 supply causes abnormal setting, which is always related to a drop of workability (see Figure 16, [Loc 80]).

| Clinker reactivity | Sulfate availability in solution | Type of set | Time of hydration | | |
|--------------------|----------------------------------|-------------|---|---|---|
| | | | 10 min. | 1 hour | 3 hours |
| low medium | low medium | regular | w  | w  | s  |
| low | high | false | f  | f  | s  |
| high | low | flash | s  | s  | s  |
| high | high | quick | w  | s  | s  |

w = workable s = set f = false set

Figure 16: Influences on the setting of cement [Loc 80]

Excessive supply of soluble SO_3 results in false set, which is attributed to fast formation of secondary gypsum. The crystals form needles that interlock the cement particles and hence stiffen the cement paste. False set can be overcome by further mixing of the concrete without further water addition.

Flash set occurs if the SO_3 supply is too low and is most critical with regard to product quality. Flash set causes immediate setting and is not reversible by adding water or further mixing, i.e. placing of the concrete is not possible.

Quick set is the designation for setting disturbances resulting from very high C_3A contents ($> 10\%$) and/or high contents of very reactive orthorhombic C_3A (alkali aluminate). Setting takes place so fast that proper placing of the cement is not possible anymore. An efficient set regulation for quick set can only be achieved by reducing the C_3A content and/or balancing the alkali sulfur ratio to avoid formation of alkali aluminate.

The solubility of calcium sulfates is very sensitive towards temperature changes (Figure 17). To figure out the optimum gypsum dosage, the cement should ideally also be tested close to field conditions, if e.g. the temperatures are much different from laboratory conditions. Several other factors like alkali sulfates and cement fineness might also influence the balance [Ric 86, Bur 92].

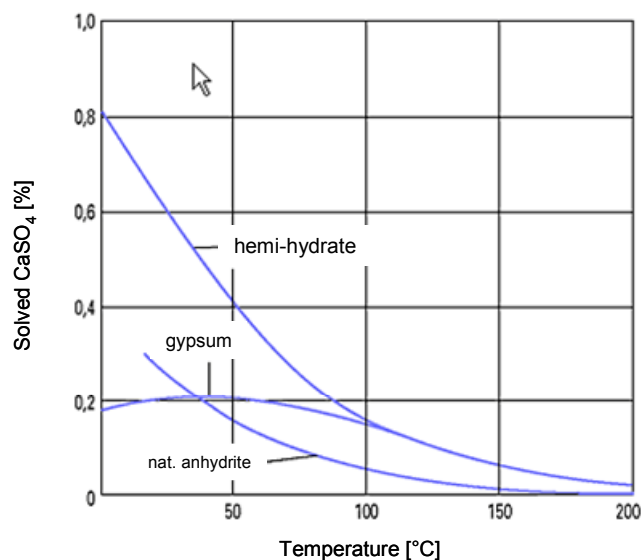


Figure 17: Solubility of gypsum, hemi-hydrate and anhydrite at different temperatures.

Setting disturbances can be tested according to ASTM C 451 (paste method) or ASTM C 359 (mortar method). Basically both tests use the Vicat indentation for the evaluation of the setting behavior. However, it has to be taken into account that these methods cannot address all influencing parameters of the field conditions.

4.2 Types of set regulators

4.2.1 Natural gypsum and anhydrite

Natural calcium sulfates occur in the form of gypsum and anhydrite II. Depending on the purity of the deposit, natural gypsum can contain some amounts of accessorial minerals such as quartz, calcite or clay.

The content of deleterious elements such as P or F is in general negligible.

4.2.2 Industrial gypsum

Industrial calcium sulfates provide potential for cost reduction in cement manufacturing. They derive from industrial processes, in which calcium compounds are transferred into gypsum or anhydrite. In 2008 about 13 % (3.2 Mio t) of the total gypsum in the Holcim group was provided from other industrial processes (source ATR 2008). Some typical industrial gypsum types are shown in the Table 12.

Table 12: Types of industrial gypsum

| Designation | Source – Chemical reaction | Impurities |
|-----------------|---|--|
| Desulpho-gypsum | <u>Flue gas desulphurization (FGD)</u> 1. $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$ 2. $\text{H}_2\text{SO}_3 + \text{CaCO}_3 \rightarrow \text{CaSO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ 3. $2 \text{CaSO}_3 + \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow 2 \text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ <i>Precipitation is also possible with $\text{Ca}(\text{OH})_2$ instead of CaCO_3</i> | SO_3^{2-} , Cl, Na ⁺ , Mg ²⁺ |
| Phospho-gypsum | <u>Fertilizer and phosphoric acid production</u> 1. $3\text{Ca}_3(\text{PO}_4)\text{CaF}_2 + 10 \text{H}_2\text{SO}_4 + 20 \text{H}_2\text{O} \rightarrow 6 \text{H}_3\text{PO}_4 + 10 \text{CaSO}_4 \cdot 2 \text{H}_2\text{O} + 2 \text{HF}$ | P_2O_5 , F ⁻ , Cd |
| Fluoro-gypsum | <u>Hydrofluoric acid production</u> 1. $\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow 2 \text{HF} + \text{CaSO}_4$ | CaF_2 , Be |
| Boro-gypsum | <u>Boric acid production</u> 1. $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5 \text{H}_2\text{O} + 2 \text{H}_2\text{SO}_4 \rightarrow 6 \text{B}(\text{OH})_3 + 2 \text{CaSO}_4$ <i>$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5 \text{H}_2\text{O} = \text{colemantite}$</i> | $\text{B}(\text{OH})_3$ |
| Titano-gypsum | <u>TiO₂ production (widely used in the US)</u> 1. $\text{FeTiO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{TiOSO}_4 + \text{FeSO}_4 + 2 \text{H}_2\text{O}$ 2. $\text{TiOSO}_4 + n \text{H}_2\text{O} \rightarrow \text{TiO}_2 \cdot n \text{H}_2\text{O} + \text{H}_2\text{SO}_4$ 3. $\text{H}_2\text{SO}_4 + \text{CaCO}_3 + 2 \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2 \text{H}_2\text{O} + \text{CO}_2 + \text{H}_2\text{O}$ <i>$\text{FeTiO}_3 = \text{ilmenite}$</i> | TiO ₂ , Fe compounds |
| Organo-gypsum | <u>Citric, formic and tartaric acid production</u> | organic compounds |

For the utilization of industrial gypsum, the following items have to be addressed:

- high moisture contents (handling problems)
- varying amounts of impurities (set retardation)

The content of impurities depends on the production processes and on the downstream purification processes.

FGD gypsum stems from other industries but as well from wet scrubber installations within the cement plant (e.g. Untervaz). It is important that the FGD gypsum is adequately oxidized to avoid sulfite (SO_3^{2-}) in the product, which causes problems with set retardation. Although the chemical composition of FGD gypsum is similar to natural gypsum, some plants experienced admixture incompatibilities in particular with PCE (polycarboxylate ether) and air entrainers. Unburned carbon particles can cause black spots on concrete surfaces. As a rule of thumb the TOC content should be lower than 0.10 %. A simple method to verify the content of unburned particles is by slurring the gypsum in deionized water and evaluating the amount of black spots on the sample surface (G. Bachmann, personal information).

Phosphogypsum provides in many countries the most important source for alternative gypsum. It is known that the impurities contained in phosphogypsum can seriously affect the cement hydration. Water-soluble phosphate or fluorine compounds in concentration of as little as 0.10 % can cause an unacceptable set retardation of cement [Geb 05]. A close correlation was found for the content of impurities and crystal size. In general coarse phosphogypsum contains less water soluble impurities [Geb 05].

Several plants experienced severe problems with admixture incompatibilities when using phosphogypsum, resulting in both strong retardation as well as acceleration [Aqu 04]. The incompatibilities can be at least partially compensated by the utilization of adequate additives, such as accelerators.

There are several more or less effective purification processes (washing, neutralization, recrystallization) reported [Mur 68, Geb 05]. However, each of these processes will increase the cost significantly. Most commonly the phosphogypsum is treated with hydrated lime to convert the impurities into insoluble calcium-phosphate and calcium-fluorite, which do not affect the cement setting. The purification should be controlled on basis of the soluble phosphorous and fluorite content as well as on pH basis.

In most plants industrial gypsum is used in a blend with natural gypsum. The substitution of natural by industrial gypsum should be done stepwise and the effect on setting time and strength development has to be tested in industrial trials [Mon 95]. Furthermore potential admixture incompatibilities should be carefully checked.

Some parameters that should be specified in the supply contract are given in Table 13.

Table 13: Typical quality parameters for desulfo- and phosphogypsum

| | Desulfogypsum | Phosphogypsum |
|--|---------------|--------------------------------|
| Free moisture (%) | < 10 | < 15 |
| CaSO ₄ x 2 H ₂ O (%) | > 95 | > 90 |
| CaSO ₄ x ½ H ₂ O (%) | < 0.5 | |
| Minor components (%) | < 5 | |
| Chloride (%) | < 0.01 | < 0.01 |
| C-Compounds (% C) | < 0.01 | |
| Na ₂ O + K ₂ O | < 0.5 | |
| P ₂ O ₅ (%) | | < 0.5 (total) / 0.05 (soluble) |
| F (%) | | < 0.5 (total) / 0.05 (soluble) |

4.2.3 Sulfate phases in clinker

A part of the soluble sulfur can also be contributed by the clinker. In general, clinker contains some amount of alkali sulfates (refer to section 3.3.2), in case of extreme sulfur excess (alkali sulfur ratios $\ll 1$) also anhydrite I. The latter one is hardly soluble and will not impact the set regulation.

Alkali-sulfates in contrast are readily soluble and hence relevant for the setting time. The content of soluble clinker alkalis can be tested according to ASTM C 114, by dissolving the clinker in deionized water.

The sulfate content of the clinker has also be taken into account for the gypsum dosage in cement since the SO₃ content is limited for nearly all cement types. Therefore clinker with very high SO₃ contents limits the gypsum dosage on cement.

Table 14: Properties of calcium sulfates

| Calcium sulfate | Chemical formula | Crystal water (%) | Density g/cm ³ | Occurrence in nature | |
|-----------------------|---|-------------------|---------------------------|----------------------|---------|
| | | | | Nature | Cement |
| Gypsum | CaSO ₄ ·2 H ₂ O | 20.9 | 2.32 | Yes | Yes |
| Hemihydrate | CaSO ₄ ·0.5 H ₂ O | 6.2 | 2.70 | No | Yes |
| Soluble anhydrite III | CaSO ₄ | - | 2.50 | No | Yes |
| Natural anhydrite II | CaSO ₄ | - | 2.98 | Yes | Yes |
| Anhydrite I | CaSO ₄ | - | - | No | clinker |

4.3 **Behavior of calcium sulfates during grinding**

Since gypsum stability is very sensitive towards temperature it can easily dehydrate during grinding, resulting in either hemihydrate or even anhydrite III. The solubility of these phases is much higher than for gypsum (see Table 15) and hence more sulfate is provided during the first minutes of cement hydration. Therefore increased gypsum dehydration is one of the main reasons for false set (refer to section 4.1) and flowability problems.

Table 15: Solubility of sulfate phases at 25 °C

| Calcium sulfate | Chemical formula | Stability range (°C) | Solubility (g/l) | Dissolution kinetics |
|-----------------------|--|----------------------|------------------|---------------------------|
| Gypsum | $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ | < 40 | 2.4 | faster than anhydrite |
| Hemihydrate | $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ | metast. | 6 | 3-4 faster than anhydrite |
| Soluble anhydrite III | CaSO_4 | metast. | 6 | fast |
| Natural anhydrite II | CaSO_4 | 40 – 1180 | 2.1 | |
| Anhydrite I | CaSO_4 | > 1180 | - | |

Dehydration can be controlled by the reduction of the mill temperature, which can be adjusted through the optimization of the mill ventilation, water injection and shortening of residence time of cement in the mill (by more efficient grinding). Furthermore, the dehydration is influenced by the water pressure in the mill. However, partial gypsum dehydration is generally unavoidable. In order to keep a uniform product quality it is therefore important to keep the level of dehydration constant as soon as the gypsum optimization has been carried out.

Gypsum dehydration can also occur during storage – especially at high cement temperatures (refer to section 6.5). The water released by the gypsum phases reacts with the cement causing lump formation and coating in the cement silos.

Lump formation can be avoided by partial substitution of gypsum by anhydrite or reduction of product temperature (refer to section 6.5.2).

Since the sulfate phases are much softer than the clinker, they concentrate in the fine fraction of the cement (< 20 µm) during grinding. Hence, they contribute significantly to the specific surface of the cement. The grindability of cements with different amounts of gypsum should therefore be evaluated on basis of the residues instead of Blaine.

4.4 **Industrial trials for set regulator optimization**

Optimization of the set regulator dosage should be carried out regularly but in any case after significant changes in the clinker production characteristics (e.g. fuels, clinker composition, burning conditions) or cement grinding (e.g. change of milling temperature).

An optimum gypsum dosage is crucial to achieve the desired setting behavior as well as the maximum strength development at a given age. Each of the reactions responsible for disturbed setting (see section 4.1) causes a bridging/widening of the pore structure and hence a decrease of the strength.

However, to maximize the gypsum content in the cement is also an effective means for clinker factor and cost reduction, provided the gypsum is cheaper than the clinker.

An industrial scale gypsum optimization can be carried out in a four step procedure, which was developed by Holcim France Benelux. The respective paper is attached in Annex 1:

1. Increase addition of set regulator until reaching a cement SO_3 content about 0.5 – 1 % above the standard limit.
2. Stop the feeding of set regulator completely.
3. Take every 5 to 10 min a cement sample of 15 to 20 kg until SO_3 reaches minimum again (takes in general about 1 h).
4. Test samples for selected properties:
 - composition and fineness
 - mandatory: setting time and mortar strength development
 - recommended: concrete workability and strength development, false set test

Strength and setting times are plotted versus the sulfate content and should result in similar graphs as shown schematically in the figures below. It might be useful to test the setting and strength development as well at different temperatures which might reflect the field conditions better than the standard conditions. Due to the gypsum dehydration that might occur in the silo, the tests should also be carried out on dispatch samples or at least it should be clarified that the gypsum phases are identical in the ex-mill and ex-silo samples.

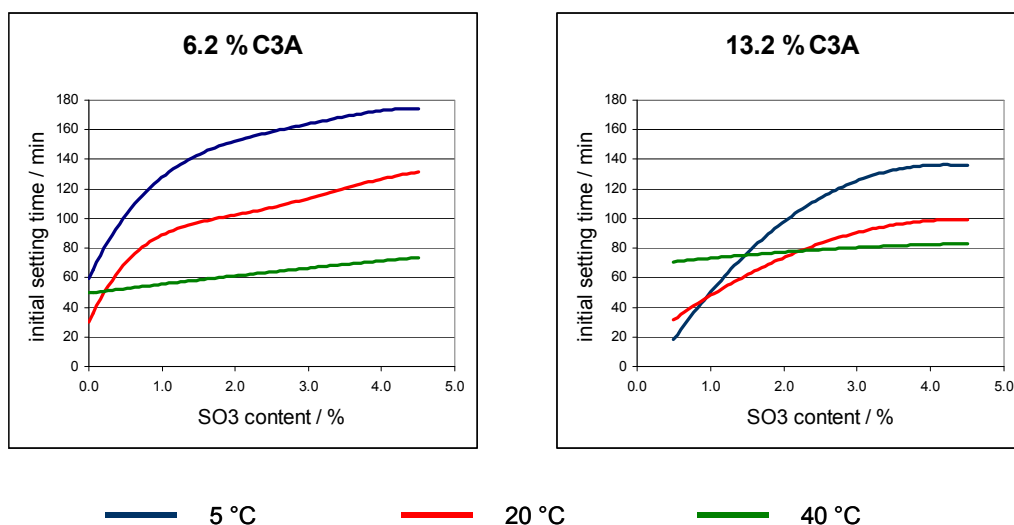


Figure 18: Influence of C_3A reactivity and SO_3 supply on setting behavior

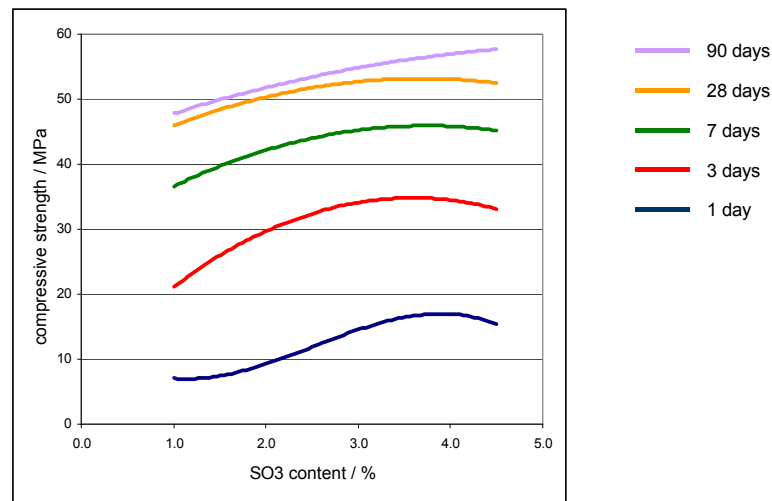


Figure 19: Influence of SO₃ content on the strength (scheme)

ASTM C 563 describes a method for optimum SO₃ determination by adding different amounts of ground gypsum to the cement and measuring the 1 d strength. The optimum gypsum is calculated by an empirical formula. However, this method is not assumed to reflect the practical conditions since the added gypsum is not dehydrated and hence not in the same state as the resulting cement. Furthermore the background of the formula is unclear (personal information L. Roberts, chairman of ASTM subcommittee sulfate content). However, this test provides a possibility to increase the gypsum dosage to SO₃ contents above the general standard limits.

5. **MINERAL COMPONENTS**

5.1 **General**

Mineral components can be divided into three classes, which are based on their reaction process:

- Latent-hydraulic MICs contain sufficient amounts of CaO to form strength relevant hydration products, without external Ca(OH)_2 source. These MICs contribute to strength development already at an early stage of hydration and can hence be used in higher proportions in the cement without extreme loss of early strength. Most prominent example for a latent-hydraulic MIC is granulated blast furnace slag (gbfs).
- Pozzolanic MICs cover a wide range of materials, characterized by siliceous or alumina-siliceous composition and low CaO contents. They originate from industrial (e.g. fly ash, silica fume) as well as natural sources (e.g. volcanic ash, trass). In presence of Ca(OH)_2 from the clinker hydration reaction they form cementitious hydrates, which contribute to strength development. Most pozzolanic materials react quite slowly, so that the early strength is diminished significantly.
- Inert materials (e.g. limestone), which do not take part in the hydraulic reactions or react only to a very small amount. They act as “filler” in the cement stone structure by densifying the space between the clinker particles.

Depending on cement application and national cement standards mineral components are used typically in the ranges given in the table below.

Table 16: Typical ranges of mineral components in blended cements

| MIC | General Purpose | Sulfate Resistance | Low Heat of Hydration | Chemical resistance | Avoidance of AAR |
|-------------------------------|-----------------|--------------------|-----------------------|---------------------|------------------|
| Granulated blast-furnace slag | 25 - 40 | 70 | 50 | 60 | 50 |
| Fly Ash (Class F) | 15 - 30 | 30 | 30 | 40 | 25 |
| Natural Pozzolan | 15 - 30 | 30 | 30 | 40 | 15 |
| Limestone | 10 - 25 | n.a. | n.a. | n.a. | |

Several standards allow the addition of “minor additional constituents”, which do not exceed a proportion of 5 % in the cement mix. In the ASTM 150 for Portland cement, limestone is the only material that can be used. The EN allows for a much wider selection of materials. According to EN standard, minor additional constituents can be natural mineral materials (e.g. limestone), process dusts (e.g. by-pass dust, CKD etc.) but also common MICs (e.g. slag, fly ash, limestone). They might have

inert, pozzolanic or latent-hydraulic properties and shall not influence the cement performance negatively.

Since MICs serve as main cement components they must be carefully selected and well-controlled. Up-grading and/or pre-homogenization must be considered if quality and uniformity are not appropriate. Industrial MICs are in general by-products of other processes and hence the supplier does not focus on up-grading their quality. Improvement of the MIC quality is hence subject to negotiation. Key parameters have to be specified accordingly in the contracts. For natural pozzolans, selective mining in particular with regard to pozzolanic activity should be envisaged.

The following sections describe the properties and most relevant parameters of widely used MICs. More details can be found in the to MICCem documentation on Holcim Portal.

5.2 **Granulated blast furnace slag**

A comprehensive overview on the properties of granulated blast furnace slag is given in [Mat 00] and the SlagTec documentation on Holcim Portal.

5.2.1 **General characteristics**

Blast-furnace slag (bfs) is a by-product of pig iron production. It forms from the accompanying minerals of the iron ore and the added limestone. After leaving the blast-furnace, the molten slag is either air cooled or granulated, i.e. quenched with water.

Air cooled slag (bfs) has no hydraulic properties and is therefore not of interest for cement production, but it can be used as raw material for clinker production. Due to the water quenching, granulated blast furnace slag (gbfs) is mainly glassy and develops hydraulic properties in the presence of an activator. Dry granulation was tested for a granulator project in Mexico in the late 1990ies. The quality (in terms of glass content and activity) of the resulting gbfs was comparable to water granulated bfs, but the product had a very poor grindability, which made it unattractive for production [Mon 97a, Mon 97b, Mon 97c].

Ground gbfs is used as MIC in cements or as additive in concrete. The gbfs particles have a rather smooth surface and show a splintered morphology (see Figure 20).

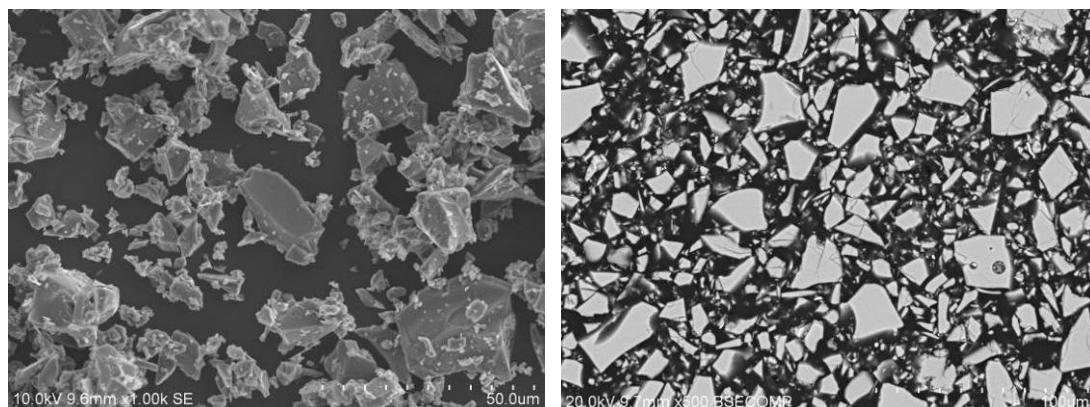


Figure 20: SEM micrographs of gbfs, left: topographical image of unground gbfs powder, right: polished section of unground gbfs powder sample

The chemical composition and variability of the slag/gbfs depends on the nature of the ore, the composition of the limestone flux, the coke consumption and the iron type that is produced in the blast-furnace. The composition controls the viscosity of the melt and hence the amorphous content of the resulting gbfs. Main elements of gbfs are CaO , SiO_2 , Al_2O_3 and MgO (see Table 17), minor components are sulfur (in form of S^{2-}), ferrous and manganese oxides and TiO_2 .

The reactivity of gbfs is mainly related to the glass content and structure. It is generally accepted that the reactivity is improved by increasing contents of CaO , Al_2O_3 and partially MgO and decreasing contents of SiO_2 and TiO_2 . Although the most relevant parameters are known, a prediction of slag reactivity only on basis of a chemical-mineralogical characterization is not possible up to now [Man 94].

The table below summarizes compositional ranges and recommended limits for gbfs. A brief summary of the effect of the different parameters on the slag properties are given in the following sections.

Table 17: Key quality parameter of gbfs (source: SlagCem documentation)

| Parameter | Practical Range | Ideal range/value | Recommended | |
|--------------------------------------|-----------------|-------------------|-------------|------|
| | | | Min | Max |
| Glass content [%] | 65 – 100 | > 95 | > 90 | |
| Basicity – CaO/SiO_2 | 0.85 – 1.4 | 1.3 – 1.4 | 1 | max |
| LOI [%] | 0.2 – 2.5 | Min | < 1.5 | |
| CaO [%] | 30 – 45 | Max | | |
| SiO_2 [%] | 30 – 40 | Min | | |
| Al_2O_3 [%] | 5 – 20 | 11 – 14 | 10 | 15 |
| MgO [%] | 4 – 12 | | | 15 |
| TiO_2 [%] | 0.4 – 2 | 0.4 – 0.5 | | 1 |
| Fe_2O_3 [%] | 0.5 – 5 | Min | | 2 |
| Fe_{met} [%] | 0.1 – 1 | Min | | 0.5 |
| Moisture after storage [%] | 8 – 20 | < 8 | | < 10 |

5.2.2 Quality parameters of granulated blast furnace slag

5.2.2.1 Glass content

The glass (amorphous) phase is the reactive part of gbfs. The crystalline phases, with exception of C_2S occurring at high C/S ratios, are considered inert. The European standard EN 197-1 requires a minimum glass content of 67 %. With respect to slag reactivity such low amounts are not considered beneficial, ideally the glass content should be higher than 90 %, which should be easily achievable with modern granulation processes.

The glass content can be quantified microscopically with plain and cross-polarized light [Dri 94]. Another reliable technique is the glass determination by X-ray diffraction with an internal standard.

5.2.2.2 Basicity

The gbfs basicity is the most important quality parameter for the cement producer. It gives an indication for the rigidity of the glass structure and thus the reactivity of the slag. A loose network is prone to fast reaction, while a rigid structure resists the reaction. Elements loosening the network structure are CaO, MgO and Al_2O_3 , while SiO_2 is the main element strengthening the network structure.

There are numerous formulae to describe the basicity or reactivity of gbfs, which all include the main slag oxides CaO, SiO_2 , Al_2O_3 and MgO. Some of them are refined by the integration of minor components such as TiO_2 , MnO or CaS. However, none of these formulas is appropriate for a generic prediction of the reactivity of gbfs from different blast-furnaces. The most commonly used formulas are given below:

$$CaO/SiO_2$$

$$(CaO + MgO)/SiO_2$$

$$(CaO + MgO)/(SiO_2 + Al_2O_3)$$

The easiest basicity formula for gbfs reactivity is the CaO/SiO_2 ratio, which should ideally be in the range between 1.3 and 1.5.

With respect to the basicity, the interests of pig iron producers and cement manufacturers are contradictory. The pig iron producer aims for minimizing CaO/SiO_2 ratio since high ratios decrease the productivity of the furnace. It is therefore important to specify acceptable ranges for the CaO/SiO_2 ratio in the contracts.

5.2.2.3 Loss on ignition

The loss on ignition is a measure to estimate the alteration of the gbfs. During storage gbfs is in contact with water from the granulation process. Therefore it starts hydrating at the surface, which could also cause lump formation in the stock pile [Lan 07]. Altered gbfs is less reactive than fresh one, since the hydration products do not have hydraulic properties any more.

The European standard limits the LOI of gbfs to 3 %. Ideally it should not be higher than 1.5 %. Some gbfs' show a negative LOI, which is related to the oxidation of reduced elements like sulfide in the slag.

5.2.2.4 CaO and SiO₂

CaO and SiO₂ are the main elements influencing the stability of the gbfs glass structure and are therefore crucial with respect to slag reactivity. The European standard EN 197-1 requires a minimum (CaO + MgO)/SiO₂ ratio of 1.0.

High CaO and low SiO₂ are in general beneficial for high slag reactivity. The ratio between the two oxides should be according to the specifications given in 5.2.2.2.

5.2.2.5 Al₂O₃

Aluminum has a major influence on the gbfs reactivity. It can either strengthen or weaken the glass structure and can hence influence the reactivity in a negative or positive way. Alumina has in first instance a positive influence on cement early strength, but high contents might lower the late strength potential.

Ideally the Al₂O₃ content lies between 11 and 14 % and is not lower than 10 %. It was detected that at very high alumina contents the slag reactivity might be decreased.

5.2.2.6 MgO

Magnesium has an ambiguous effect on gbfs reactivity. MgO contents up to 15 % can compensate for poor reactivity due to low CaO contents. This beneficial effect is also considered in some of the basicity formula. In contrast high MgO concentrations decrease the slag reactivity.

As magnesia is an element of the glass network, it does not occur as periclase even at high MgO contents of 20 %. Nevertheless, the British standard BS 6699 limits slag MgO to 14 %.

5.2.2.7 TiO₂

Titanium originates in general from the iron ore. Periodically TiO₂ is introduced into the blast-furnace for refractory protection, most commonly by the addition of ilmenite (FeTiO₃).

TiO₂ reduces the reactivity and grindability of gbfs. The reasons for its negative impact are not clarified. Ideally the TiO₂ content should be lower than 0.5 %. TiO₂ contents of more than 1 % can be deleterious for reactivity.

The negative impact of TiO₂ can be overcome by finer grinding of the slag or by decreasing the slag content in the cement.

5.2.2.8 Other elements

Metallic iron results from a contamination of the slag stream by the iron melt. Its content is ideally below 0.5 %. It is regarded critical with regard to wear of the slag mills, however it can be separated from the mill feed by magnetic separators.

When seawater is used for the granulation process, gbfs might contain significant amount of chloride. This has no impact on the slag quality but might limit the slag content in the cement due to the applicable chloride limit, which is 0.1 % for most cement standards.

5.2.3 Grindability

Granulated blast furnace slag is in general much harder to grind than clinker. The grindability is influenced by glass content, porosity, LOI (CSH phases), TiO_2 content and content of metallic iron (abrasivity).

Alteration does not affect the grindability to a significant extent [Lan 07, Sch 03]. In cases, where an improved grindability was reported the result was based on specific surface area determination by Blaine (see also section 5.2.7). This result is falsified due to the high specific surface of the reaction product on the slag surface. Hence, slag grindability should always be evaluated on basis of the particle size distribution or residue.

Since slag is accumulating in the coarse cement fraction, it is difficult to achieve the slag fineness required for optimum strength development without over-grinding the clinker component. Separate grinding offers the opportunity to optimize the particle size distribution of the slag and clinker to achieve the required product properties (refer to section 6.3.2). Limiting factors for the slag fineness are economical aspects (grinding costs) as well as product performance criteria.

5.2.4 Influences of GBFS on product quality

Performance of slag cements in concrete is in many respects superior to Portland cement (for detail see SlagTech documentation on Holcim Portal). Compared to Portland cements, slag cements show the following differences:

- Improved workability
- Lower water demand at same slump due to lower slag reactivity and smooth slag surfaces
- Lower heat of hydration
- Higher late strength
- Higher resistance to chemical attack (e.g. chloride, sulfate ingress) due to denser microstructure (less capillary porosity)
- Less tendency to provoke alkali aggregate reaction (less soluble alkalis)

Inferior properties of slag cements are:

- Lower early strength
- Requirement of more curing efforts

The low early strength can partially be compensated by adjusting the overall cement fineness as well as the individual clinker and gbfs particle size distribution (only possible for separate grinding systems) and/or the sulfur content and sulfate type [Ehr 97].

5.2.5 Color of concrete structures made with slag cements

At high slag contents fresh mortar or concrete structures might show a mottled green or green-blue surface which disappears with time. This temporary condition is commonly called “greening” and occurs only on a small percentage of concrete.



Figure 21: Concrete block showing the typical blue-green discoloration, oxidation has started at the block edges and the contact of the molding

The blue-green color is attributed to the presence of iron- or manganese sulfides in lower oxidation states in the slag. The degree and extent of the coloration depends on the rate of oxidation, the percentage of slag, curing condition and the porosity of the concrete.

The concrete performance is not affected by the green color and does not need to be treated. In most cases, the surface becomes light gray or white within a week or even hours, when the concrete is exposed to air and the oxidation proceeds. However, the concrete core will remain green indefinitely. The velocity of core shading is a measure for the density of the concrete structure: the slower the discoloration vanishes, the denser (i.e. better) the concrete structure.

Factors diminishing the oxidation progress include: extended wet curing, cold and wet weather conditions, sealed or otherwise densified surfaces.

5.2.6 Up-grading of gbfs

Since slag is a by-product of the iron and steel producing industry, the improvement of the slag quality for cement production will not be in the focus of the blast furnace operator. Therefore, supply contracts should cover all critical parameters (refer to SlagTec documentation).

In the cement plant, the room for slag quality improvement is limited to the following areas:

- Homogenization of different slag qualities (e.g. different sources, altered and non-altered slag)
- Adjustment of slag fineness to achieve appropriate strength development
- Utilization of cement quality improvers

5.2.7 Alteration of gbfs

The relatively constant production of gbfs is in contrast to the fluctuating seasonal demand for it. Therefore the slag has to be stored. While storage for a short period is actually desirable as the gbfs loses water, long time storage can cause alteration and consolidation of the gbfs and affect its properties (mainly grindability and reactivity). The degree of alteration is not only depending on storage time and conditions, but also on the gbfs itself.

General experience in cement works has shown that fairly long storage does in fact make gbfs easier to grind, but that the gbfs reactivity at the same specific surface is reduced. In a study of [Lan 07] it was shown that in spite of having the same specific surface, altered gbfs are coarser than fresh one. Hence, the loss in reactivity was also related to a loss of reactive fine grained particles. This phenomenon is related to the formation of hydration phases on the slag grains, which contribute significantly to the specific surface but not to reactivity. An evaluation of the grindability and reactivity should therefore always be related to a constant PSD or sieve residue and not to a constant specific surface.

The LOI provides a rough measure for the degree of alteration. However, a direct correlation between strength activity and LOI has not been proven so far. Therefore the hydraulic activity has to be always checked in application tests. In order to avoid fluctuations in the product quality, long-term stored gbfs should always be blended with fresh slag and in an adequate proportion.

5.3 Metallurgical slag

Metallurgical slag is a by-product of the steel making process. It is often confused with blastfurnace slag although they are in fact completely different materials. Steel slags are designated according to the type of producing furnace they originate from: Basic Oxygen Furnace (BOF), Electric Arc Furnace (EAF) and Open Hearth.

In contrast to blast-furnace slags their importance as cement component is low. Due to their comparatively poor reactivity they can only be used in low proportions in the cement [Loc 06]. The predominant part of steel slags is used as aggregates in road construction. High phosphorous steel slags can also be used as fertilizer.

The slags are usually air cooled, forming solid, lumpy rock type material. They consist from a mixture of calcium silicates (C_2S) and calcium ferrite (C_4AF) with fused and combined oxides of iron, magnesia and manganese.

5.4 Fly ash

5.4.1 General characteristics

Fly ashes are obtained from the flue gas de-dusting systems of coal firings. Due to the high temperature reached during combustion, most of the minerals contained in the coal melt and form small fused drops. The subsequent sudden cooling transforms these drops partly or entirely into spherical glass particles. The resulting product is a heterogeneous mixture of spherical glassy ((0) 50 – 80 %) and crystalline (50 – 20 %) particles and unburned carbon.

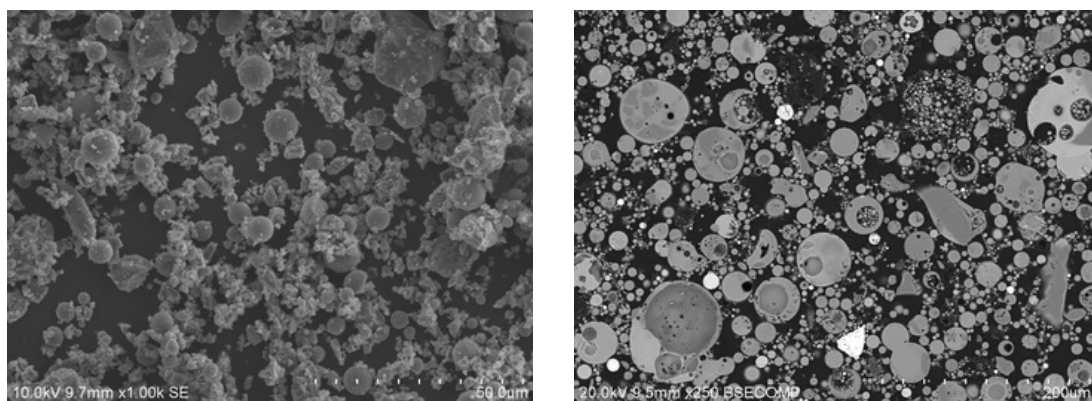


Figure 22: SEM micrographs of fly ash, left: topographical image of fly ash powder, right: polished section of fly ash powder sample

Due to their specific morphology (see Figure 22) and high fineness, fly ashes act as a filler and ball-bearing, reducing the water demand and improving the workability. The morphology, glass content and fineness are directly related to the temperature of the combustion process. Depending on coal type, ash content and coal accompanying minerals, fly ashes show a great variety in their chemical composition (see table below). As rule of thumb anthracite or bituminous coals result in low

calcium fly ashes (class F acc. to ASTM), sub-bituminous coal and lignite in high calcium ashes (class C).

Table 18: Chemical composition of siliceous and calcareous fly ashes

| Parameter | Coal Type | |
|------------------------------------|--------------------------|--------------------------|
| | Anthracite Bituminous | Lignite Subbituminous |
| SiO ₂ [%] | 40-55 | 20-70 |
| Al ₂ O ₃ [%] | 23-35 | 1-20 |
| Fe ₂ O ₃ [%] | 4-17 | 1-15 |
| CaO [%] | 1-8 | 8-40 |
| MgO [%] | 1-5 | 0.5-7 |
| SO ₃ [%] | 0.1-2 | 1-15 |
| Na ₂ O [%]* | 0-4 | 0-6 |
| K ₂ O [%]* | 0-3 | 0-4 |
| LOI [%]* | 0-5 | 0-5 |
| CaOf* | 0-0.5 | 1-20 |

Differences between class C and class F fly ashes concern the chemical and mineralogical composition as well as the amount, composition and reactivity of the glass. Class F fly ashes show exclusively pozzolanic properties attributed to the glass reaction, while class C fly ashes possess as well hydraulic properties in addition.

The reactive part of class F fly ashes is the alumo-siliceous glass, which makes up between 50 and 80 % depending on the type of coal firing. The glass structure is rather rigid and therefore it is a slowly reacting material. Typical mineral phases in class F fly ashes are: quartz, mullite, hematite and magnetite, which are all considered inert. Anhydrite can be present in small amounts.

The glass of class C fly ashes is more reactive than that of class F ashes with glass contents in the same order as for class F ashes (50 – 80 %). The possible mineral phases are more widespread than for class F ashes: quartz, free lime, periclase, aluminat, belite, anhydrite, ferrite, spinel, merwinite, alkali sulfate, melilite, sodalite and hematite.

Comprehensive reports on fly ash specifications and their effect on concrete properties are given in [ACI 96, RIL 91].

5.4.2 Quality parameters of fly ashes

In many countries, fly ashes are used as concrete addition in first instance and hence most fly ash specifications are related to this application. However, the limits can also be applied for fly ashes used as cement constituent. Nevertheless, the

utilization of fly ashes in cement grinding gives more room for adjusting/improving the fly ash properties to the targeted cement properties.

Key performance indicators for fly ash are as follows:

Table 19: Quality parameter of fly ashes (source: FlyAshTech)

| Parameter | Ideal | Limits | Indicator for / Influence on cement performance |
|---|-------|--------------------------|---|
| Typical indicators for fly ash reactivity | | | |
| Total CaO (%) | > 20* | | Content of active minerals/phases |
| Reactive SiO ₂ (%) | max | < 25 (EN) | SiO ₂ in glass phase |
| Reactive CaO (%) | > 15* | < 10 10 15* | CaO in glass phase |
| SO ₃ (%) | < 3 | | Set retardation Conflict with SO ₃ cement standard limits |
| Parameters influencing the cement performance | | | |
| LOI (%) | < 2 | < 5/7 (EN) < 2 (ASTM) | Water demand Admixture incompatibilities Creation of discolorations and pop ups |
| R ₄₅ (%) | < 10 | < 20 | Water demand Reactivity |
| Free CaO (%) | < 1 | < 2.5 | Soundness |

* *calcareous fly ashes*

5.4.2.1 Fineness

The fly ash fineness is the most important indicator for the amount of glass particles in the fly ash and hence for the fly ash reactivity. It also indicates the amount of spherical particles in the fly ash, which is an important parameter for the fly ash influence on workability.

Furthermore a high fineness is beneficial with respect to the filler effect of the fly ash in the cement. For a “ready to use” fly ash the fineness should be similar to that of Portland cement or finer. Ideally the fineness is less than 20 % R_{45µm}. Fly ashes with R_{45µm} of less than 10 % are outstanding.

Due to the high porosity of the coke and the open spheres, the determination of the specific surface is not very meaningful. However, it is a requirement in some standards (e.g. India, Japan, Russia).

5.4.2.2 Loss on ignition

The loss on ignition is a measure for the content of unburned carbon contained in the fly ash and has severe impact on the product properties.

High amounts of unburned coal affect (darken) the cement color or create pop-ups (black spots) on the mortar/concrete surface. Furthermore organic carbon is known to impair the effectiveness of concrete admixtures, especially air entrainers. High contents of unburned carbon contribute to an increase of the water demand, due to the comparatively high porosity of the coke particles.

Most standards limit the LOI to some extent. According to EN 197-1, the LOI should not exceed 5 % but contents up to 7 % are acceptable if the durability is not affected. ASTM limits the LOI for fly ash additions (in concrete) to 2 % due to the expected admixture incompatibilities.

5.4.2.3 Glass content

In low calcium fly ashes, the glass is the only active phase showing pozzolanic properties. High calcium fly ashes contain hydraulic phases in addition.

The glass content can be determined according to EN 196-2 by solving the fly ash in HCl and KOH (acc. to EN 196-2), the glass content is considered to be the soluble part. Visual determination with an optical microscope fails to determine the fly ash glass content satisfactorily.

5.4.2.4 Reactive silica

The term “reactive silica” describes the amount of silicon that is entrapped in the glass phase. It is a measure for the fly ash reactivity and grinding activation potential. According to EN 197-1, the reactive silica must be higher than 25 %.

Reactive silica can be determined indirectly by calculating the difference between total SiO₂ on the dried fly ash and the SiO₂ content in the insoluble residue in HCl and KOH (EN 196-2).

5.4.2.5 Reactive CaO

The term “reactive CaO” describes the amount of calcium that is entrapped in the glass phase. As reactive SiO₂ it is an indicator for the glass reactivity. High contents of reactive CaO are indicative of high glass reactivity.

According to EN 197-1, the content of reactive CaO has to be less than 10 % for low calcium fly ashes and above 10 % for high calcium fly ashes.

Reactive CaO can be determined by titration after selective dissolution in ethyl aceto-acetate and isobutanol (EN 196-2).

5.4.2.6 Free lime/periclase

Lignite ashes might contain free lime or periclase, which are considered critical with respect to soundness.

According to EN the soundness of fly ash has to be tested in a mixture of 70 % OPC and 30 % fly ash. The expansion shall not exceed 10 mm.

5.4.2.7 SO₃

SO₃ is often present in lignite fly ashes in form of anhydrite. Small amounts can also occur in hard coal fly ashes from flue gas desulfurization.

SO₃ as such is not regarded as critical with respect to cement quality. However, it influences the setting behavior and has therefore to be taken into account for sulfate optimization. Furthermore high amounts of sulfur might conflict with the cement SO₃ limits.

5.4.2.8 Alkalis

Most fly ashes show a comparatively high alkali content. High alkali contents might conflict with respect to the standard limits for low alkali cements, which consider the total alkali content and not the soluble part of the alkalis.

The predominant part of the alkalis are entrapped in the glass phase, making the glass more reactive. Since most of the fly ash glass does not react even after long times, the predominant part of the fly ash alkalis can be considered insoluble. Hence they do not contribute to alkali aggregate reaction nor serve for the acceleration of the cement hydration.

5.4.3 Grinding of fly ash cements

Most low calcium fly ashes are so-called “ready to use” MIC’s. In general they can be added to the separator or be blended with the OPC without further preparation.

The fly ash fineness is key parameter for the potential of blending fly ash directly into the cement. For coarse fly ashes, the fly ash content in the cement should not exceed 10 % R_{45μm} otherwise significant decrease of the early strength has to be expected. Fly ashes with less than 10 % R_{45μm} can be added up to 30 %.

The effect of grinding on the fly ash reactivity is widely discussed. Unambiguously intergrinding of fly ashes offers a certain potential for fly ash beneficiation and leaves hence more room for optimization than using fly ash as concrete addition only. Furthermore the cement properties can be influenced to a certain extent by gypsum optimization and the utilization of additives

Grinding causes an activation of coarse fly ashes [Mon 83], especially when they have high amounts of reactive SiO₂ and CaO. But also for fine fly ashes certain activation can be achieved by grinding due to the destruction of oversized particles.

The predominant part of the glass spheres is not destroyed during grinding and hence the fly ashes’ positive influence on water demand (filler effect) and workability (ball-bearing effect) is not affected.

5.4.4 Influences of fly ashes on product quality

Fly ash cements offer proven technical benefits with regard to workability, long term strength development and concrete durability. Compared to Portland cement, fly ash containing cements show in general:

- Improved workability (ball bearing effect)
- Less water demand in the range of 5 – 10 % (filler effect, ball bearing effect)
- Less heat of hydration (less risk of early age cracking)
- High late strength gain (proper curing provided)
- High resistance to chemical attack (chloride, sulfate) and alkali aggregate reaction

Most of the benefits are related to the lubrication effect of the fly ash's spherical particles. The pozzolanic reaction is responsible for the high ultimate strength, low permeability and resistance to chemical attack [Geb 92].

Inferior properties of fly ash cements are:

- Lower early strength (partially compensated by reduced water demand and filler effect)
- More curing effort required

5.4.5 Up-grading of fly ash

Up-grading the fly ash quality is mainly limited to the power plant operator. Reduced LOI and higher finenesses can be achieved by optimization of the combustion process and coal preparation (reduction of unburned carbon) or by classification of the fly ash.

Furthermore there are several technologies available for the beneficiation of fly ashes with high carbon content and/or low fineness [Gu 98]. Beneficiation of fly ash by electrostatic separation was recently reported determined for some applications [Laf 08].

Measures for fly ash up-grading in the cement plant are limited to homogenization of different fly ash qualities and activation by grinding.

5.5 Natural pozzolans

5.5.1 General

The term "pozzolana" was originally used for a volcanic tuff located in Pozzuoli close Naples. Nowadays it is used in a more technical way for siliceous or silico-aluminous materials with low CaO contents and the ability to react with calcium

hydroxide to form strength developing phases (CSH, CAH). The composition and properties of these phases are similar to those formed during clinker hydration.

A strict classification is difficult since the term covers materials extremely different in origin, chemical and mineralogical composition. A very detailed overview over different types of pozzolans is given in [Kru 04]. Pozzolan properties can either be present in natural materials (natural pozzolans) or be induced to them by thermal treatment. According to the European Standard EN 197-1, the latter ones are designated as natural calcined pozzolans since the pozzolan reacting phases are formed during the thermal treatment. Most prominent material of that class is perhaps metakaoline, which consists basically of thermally destructed (amorphous) clay minerals.

Pozzolans can be of biological (e.g. diatomite, see Figure 23) or volcanic origin (e.g. trass, volcanic glass etc). Also by-products of industrial processes like silica fume and fly ashes can be considered as artificial pozzolans¹.



Figure 23: SEM micrograph of diatomite

Pozzolans consist of varying proportions of active, inert but also harmful components. Amorphous phases (volcanic glass, amorphous clay) and zeolithes are considered reactive, while well crystallized minerals (e.g. quartz, feldspar, pyroxene) are considered inert. Harmful components include organic substances and clays, which negatively affect the performance of the pozzolan cement.

Due to their inhomogeneous nature, it is not possible to establish universally applicable requirements for the composition of pozzolans. Some typical figures are listed in the table below.

¹ EN 197-1 does not classify fly ash and silica fume as artificial pozzolans but in separate clauses

Table 20: Quality parameter of pozzolans

| Parameter | Limit | Standard | Evaluation |
|--|--------|-----------|------------------------------------|
| Chemical composition | | | |
| SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ [%] | > 70 | ASTM C618 | Minimum content of reactive phases |
| Reactive SiO ₂ [%] | > 25 | EN 197-1 | |
| LOI [%] | < 10.0 | ASTM C618 | Critical elements |
| SO ₃ [%] | < 4 | ASTM C618 | |
| Moisture [%] | < 3 | ASTM C618 | |
| Mineralogical composition | | | |
| Glass content [%] | > 50 | | Reactive phase |
| Zeolithes [%] | > 20 | | Impact on water demand |
| Clay [%] | < 10 | | |
| Mortar performance | | | |
| Strength activity | > 75 | ASTM C311 | Strength contribution |
| Pozzolanicity test Ca(OH) ₂ | | EN 196-5 | Reactivity |

5.5.2 Quality parameters of pozzolans

5.5.2.1 Chemical requirements

The chemical composition of natural pozzolans varies over a wide range. Key parameter for the suitability as MIC is their amount of reactive silica, alumina and iron. Therefore most of the standards require a minimum content of these elements (e.g. ASTM C 618 > 70 %). However, the chemical composition provides little value in judging its quality.

It is generally agreed that a pozzolan should have a substantial portion (> 25 % acc. to EN 197-1) of amorphous silica ("reactive silica"), which cannot be identified by XRF analysis only. EN 197-1 requires a minimum of 25.0 % reactive silica, which is defined as the amount of silica that is solved in HCl and boiling KOH (refer to EN 196-2).

Furthermore pozzolans can contain significant amounts of alkalis which enhance the pozzolan reactivity (improved glass reactivity) on one hand, but might be critical with regard to alkali aggregate reaction on the other hand.

5.5.2.2 Mineralogical composition

As mentioned above, the chemical composition of a pozzolan cannot be used independently in judging the quality of a pozzolan. Only in combination with mineralogical analysis it will give indication of the pozzolanic potential. Most natural pozzolans owe their activity to volcanic glass, opal, cristobalite and zeolithes.

A mineralogical analysis of the pozzolans and determination of the glass content should be carried out by XRD with Rietveld refinement (refer to 9.2.1). However, the analysis is not trivial in particular when the pozzolan contains clay minerals as well as amorphous phase. Indirectly, the amount of active phases can be determined by the EN 196-2 method for soluble silica.

5.5.2.3 Clay content

A good means for the measurement of the clay content is the methylene blue test according to EN 933-9, which was originally developed for determination of clay minerals in limestone. The test measures the amount of methylene blue taken up by a sample ground to a specific fineness. The result indicates the amount of swellable clay minerals only; non-swellable clay minerals like illite or chlorite are not detected by this test.

5.5.3 Grinding of pozzolan cements

Due to their large inner surface, the grindability should always be checked on residue basis and not on Blaine. The result of the latter analysis would be falsified by the contribution of the inner surface.

In general, pozzolans are easier to grind than the clinker and will hence be concentrated in the fine fraction of the cement influencing water demand and strength development. Also pozzolans might tend to agglomeration when containing high amounts of clay minerals.

Good experiences were made with the production of pozzolan cements with narrow particle size distribution with high efficiency separators [Geb 87, Tor 88, Jor 89] and separate grinding has also shown some potential for the improvement of cement performance [Bre 94].

5.5.4 Performance tests

The only safe way to determine the suitability of any given pozzolan is to test it in mortar and concrete mixes in order to judge its influence on strength development and water demand. All of these tests are based on a comparison between an OPC mortar and a mortar, in which a defined amount of OPC is replaced by pozzolan. The tests are ideally carried out on industrial cements, however for an orientation also laboratory cements can be used.

The Holcim activity test is based on a clinker substitution rate of 30 % and a pozzolan fineness of 6 – 8 % $R_{45\mu m}$. The strength activity is evaluated after 28 d (refer to 9.2.4).

EN 196-5 describes an indirect activity test on the final pozzolan cement, which compares the quantity of calcium ions present in an aqueous solution in contact with pozzolan cement sludge after 8 or 15 days with calcium ion saturation concentration of a solution with the same alkalinity (refer to 9.2.3).

5.5.5 Influence of pozzolans on product properties

In general, pozzolans tend to increase the water demand of the concrete significantly, which is related to the amount of zeolithes and clay minerals. Compared to Portland cements, pozzolan cements show in general

- Higher water demand (high inner surface)
- High late strength gain (adequate curing provided)
- Improved durability (resistance to chemical attack, alkali aggregate reaction)

5.5.6 Up-grading of natural pozzolans

Beneficiation of natural pozzolans is limited basically to the homogenization of the different qualities occurring in a quarry, which also provides optimum use of the pozzolan reserves. However, one of the key issues for the upgrading of pozzolans is to find a conclusive key parameter to determine the pozzolans activity. The definition of these key parameters is quite complex for pozzolans since their reactivity can often not be connected to a single chemical parameter.

A successful optimization of pozzolan quality and reserves was achieved in the 1990ies by Nobsa plant. The plant switched the quality control of their pozzolans from chemistry based control (Al_2O_3 limit) to a mineralogy based control (clay content) and pre-blending of different pozzolan qualities. This measure helped to achieve a better pozzolan and cement uniformity and to reduce the clinker factor by 2 %. Furthermore the pozzolan reserves could be increased by 25 % whereas the waste was reduced by 30 % [Oss 00].

5.6 Natural calcined pozzolans

The term “natural calcined pozzolans” is used for materials that are activated by some kind of thermal treatment. The properties (chemical and mineralogical) of the final product are similar to pozzolans.

The most prominent material of this type might be metakaolinite, which is produced by several suppliers from high quality clays (kaolinite). The thermal treatment between 600 and 800 °C destroys crystal structure of the kaolinite, resulting in a highly reactive, amorphous MIC.

Further materials in the class of calcined pozzolans are listed below [Kru 04].

- Calcined oil sand (calcined fine tailings, calcined drill cuttings)
- Calcined laterite
- Rice husk ash (Rice hull ash)
- Calcined paper sludge

5.7 **Burnt shale**

Burnt shale, specifically oil shale, is produced from shales with 5 – 65 % organic matter. The shale is calcined for steam or electrical energy generation in bottom furnaces or fluidized beds at approximately 800 °C. From this process, an ash is obtained, which is called burnt oil shale.

Burnt oil shales contain a mixture of pozzolanic, hydraulic and inert phases. In line with the composition of the starting materials and the production process, they consist of clinker phases like belite (C_2S) and monocalcium aluminate (CA), larger amount of amorphous clay and small amounts of calcium sulfate and free lime.

Within the Holcim group burnt oil shale is produced at Dotternhausen, which uses the oil shale as raw mix component, fuel and also in a fluidized bed reactor, which generates electrical energy. The ash of the shale, the burnt oil shale, is used as MIC in cement production in a proportion of up to 35%. The plant produces also special products, which consist almost entirely of burn oil shale.

Burnt shale can develop strength without further activation due to the hydraulic minerals (C_2S , CA) that it contains. A key parameter for oil shale quality is hence the compressive strength, which has to be at least 25.0 MPa after 28 days (acc. EN 196-1). Attention has to be paid to the oil shale influence on expansion, which is related to the rather high free lime content. The high sulfur content of burnt oil shales has to be taken into account for the manufacture of cement by adjusting the gypsum dosage.

5.8 **Silica fume**

5.8.1 **General**

Silica fume (microsilica) is a by-product from the smelting process in the silicon metal and ferrosilicon industry. The reduction of quartz to silicon at temperatures up to 2000 °C produces SiO vapor, which oxidizes and condenses in the low-temperature zone to tiny spherical particles consisting of non-crystalline silica (Bradley-Williams, 1986, PCA p. 20).

Main features of silica fume are a high content of amorphous silica (> 85 %) and a very high specific surface area, ranging from 200 000 to 300 000 cm²/g. The average diameter of the condensed silica fume is about 0.1 µm (see figure below) and is therefore 100 times smaller than the cement particles. These characteristics account for the substantial pozzolanic activity of silica fume but also for handling problems. Furthermore the strong agglomeration tendency can cause problems with the silica fume dispersion in the mortar or concrete.

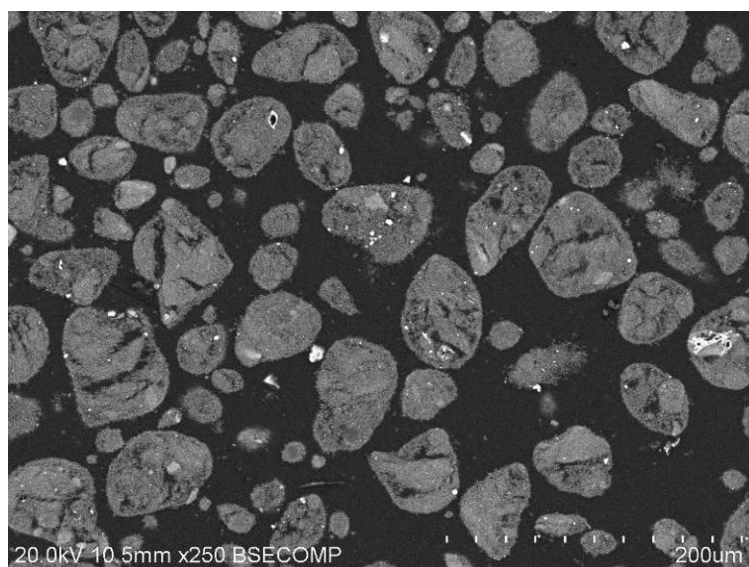


Figure 24: SEM micrograph of silica fume (polished section) showing small agglomerates made up of numerous μm -scale silica fume particles.

Depending on the production process, the chemical composition of silica fume varies within the ranges given in the table below.

Table 21: Chemical ranges of silica fume [Lea 01]

| | Silicon metal | Ferro silicon |
|------------------------------------|---------------|---------------|
| SiO ₂ [%] | 94-98 | 86-90 |
| Al ₂ O ₃ [%] | 0.1-0.4 | 0.2-0.6 |
| Fe ₂ O ₃ [%] | 0.02-0.15 | 0.3-1.0 |
| CaO [%] | 0.08-0.3 | 0.2-0.6 |
| MgO [%] | 0.3-0.9 | 1.0-3.5 |
| SO ₃ [%] | 0.25-0.75 | 0.5-0.1 |
| Na ₂ O [%]* | 0.1-0.4 | 0.8-1.8 |
| K ₂ O [%]* | 0.2-0.7 | 1.5-3.5 |
| LOI [%]* | 0.8-1.5 | 2.0-4.0 |
| C [%] | 0.2-1.3 | 0.8-2.3 |

Silica fume acts in the cement as a filler (reduction of pore space) but shows also a very high pozzolanic activity, i.e. it reacts already within the first days of hydration and is therefore – in contrast to other MICs – contributing to early strength. However, due to its high specific surface silica fume increases the water demand extremely and is therefore limited to 10 % in the European standard. It also tends very much to agglomeration in the mortar or concrete. In concreting it is in general used in combination with plasticizers.

Due to its high price, it is only used for special cements for high performance concretes, which require high strength and density.

5.8.2 Quality parameters of silica fume

Key quality parameters of silica fume are its content of reactive SiO_2 and the specific surface, which should exceed certain values. Furthermore the silica fume should not contain too high amounts of organic substances (i.e. LOI).

Table 22: Quality parameter of silica fume

| | Silicon metal |
|--|---------------|
| SiO_2 [%] | > 85 |
| Specific Surface [m^2/g] | > 15 |
| LOI [%] | < 4 |
| Moisture [%] | < 3 |

Blaine surface measurement is not appropriate, therefore specific surface should be determined by an external laboratory the by BET-method.

5.8.3 Handling of silica fume

The high specific surface of undensified silica fume is the reason for its low bulk density (about 200 - 300 kg/m^3), high transportation cost and dust formation. The handling problems can be overcome by using densified (> 500 kg/m^3) or pelletized (> 600 kg/m^3) silica fume. Silica fume slurry is not appropriate for cement production and should only be used directly in concrete.

Also on account of its fineness, silica fume has a high tendency to agglomerate. As a result, special care needs to be taken to disperse it when incorporated into the cement.

5.8.4 Influences of silica fume on product quality

Silica fume containing cements are quite rarely produced and only for high strength applications. Most of the silica is added to the concrete. Actually only three cement plants within the Holcim group are using silica fume in amounts of up to 5 %.

Fresh concrete properties are influenced by huge increase of the specific surface by the silica fume addition and hence increased cohesiveness. This is one important reason why silica fume should be used with super-plasticizers or water reducers. During pumping or vibration the particles act as ball bearings, lubricating the mix and giving it a greater mobility. Silica fume containing cements are less susceptible to segregation and bleeding. The missing bleed water requires more efforts in curing. Setting behavior is similar to OPC.

As silica fume is more reactive than other MICs, e.g. fly ash or slag, it contributes to early as well as to late strength. The filler effect and high pozzolanic reaction densify the microstructure and reduces permeability significantly.

With regard to durability, silica fume containing concrete structure are less susceptible to alkali silica reaction, leaching and efflorescence. The dense microstructure is beneficial with respect to chloride and sulfate ingress.

5.9 Limestone

5.9.1 General

Limestone is used in many countries as main cement component (e.g. Europe) or as minor constituent with up to 5 % in the cement [Det 96]. The EN 197-1 allows for up to 35 % limestone addition. ASTM has now accepted the addition of up to 5 % limestone.

Limestone is considered inert, since it only reacts to a very small extent and is not actively increasing strength by formation of strength relevant phases. The practical effect of limestone as mineral component is related to physical influence, improving particle packing and increasing early hydration rate of clinker particles.

Suitable for cement production are basically all limestones that exceed a certain content of calcium carbonate. Critical components for cement quality in limestones are clay minerals and organic carbon. The EN 197-1 specifies limits for the above mentioned parameters (see Table 23), if the limestone proportion in the cement exceeds 5 %. Although these key figures are quite strict for limestone additions up to 5 %, they provide useful guide values.

Table 23: Key quality parameter of limestone

| Parameter | Practical Range | Ideal range/value |
|--------------------------------|-------------------------|-------------------|
| Calcite content [%] | > 75 | > 95 |
| TOC content [%] | < 0.5 (L) < 0.2 (LL) | minimum |
| Methylene blue value [g/100 g] | < 1.2 | minimum |

5.9.2 Quality parameters of limestone

5.9.2.1 Calcite content

A minimum calcite content is demanded by almost all standards to guarantee the inert properties of this cement component. The minimum calcite content (calculated on basis of CaO) should be at least 75 %, but in general higher than 85 %.

5.9.2.2 MgO content

MgO in limestone deriving from dolomite is as such no sign of bad quality limestone. It is, however, restricted due to the standard limits of MgO in cement (note: the EN considers a MgO limit only for the clinker not for the total cement). Often these limits are in the range of 5 % MgO on cement basis. Moreover, most standards require a minimum content of calcite in the limestone that is used for cement production, which consequently also reduces the potential amount of dolomite.

Furthermore, dolomite is sometimes discussed with regard to the so called de-dolomitisation (often this reaction is mixed up with the alkali silica reaction). This reaction is, however, related to much coarser dolomite, which can occur in aggregates. If the dolomite is finely dispersed like in cement, then no deleterious reaction is expected. In practice, no negative impact of dolomite on the cement performance has been encountered so far.

5.9.2.3 Organic matter

Organic matter might reduce the effectiveness of air entrainers in the concrete. Furthermore, limestones with high TOC contents seem to reduce the frost resistance of concrete (Sprung/Siebel 1991).

The European standard limits the limestone TOC content to 0.5 % (index L) or even below 0.2 % (index LL).

5.9.2.4 Clay content

Elevated clay content increases the water demand and can be deleterious with respect to concrete frost resistance.

The European standard limits the expansive clay minerals to 1.20 %. The clay content is determined by the methylene blue test in accordance with EN 933-9. It is important that the limestone is ground to an adequate fineness of 5000 cm²/g for this test.

5.9.3 Properties of limestone cements

As limestone is in general easier to grind than clinker, it concentrates in the fine fraction reducing the pore space between the clinker particles. This so called filler effect improves the cement properties in such a way that limestone cements have in general a lower water demand than OPCs and lower tendency for bleeding.

The densifying effect of the limestone particles helps also to keep the strength level. The strength loss due to reduced clinker content can be compensated by optimizing the cement PSD, so that for small contents of limestone the strength can be the same as for OPC. However, the optimum limestone content and PSD have to be determined for each clinker. In contrast to pozzolanic or latent-hydraulic MICs, limestone cements do not show a great strength gain at higher ages.

5.10 Minor additional constituents

5.10.1 Definition

The term “minor additional constituents” covers materials that can be added to the cement in amounts of up to 5 %. These might be inorganic mineral materials derived from the clinker production process such as filter dust, kiln dust or by-pass dust. The use of process dusts in the cement contributes to resolve or avoid disposal problems with this type of material.

According to the European standard, this term can also cover specially selected inorganic natural mineral materials or other materials like slag, fly ash, pozzolans, limestone provided they are not used as main constituents in the cement. Their content in the cement is limited to 5 % maximum.

5.10.2 Filter dust and kiln dust

Filter dust of preheater kilns can be extracted and added to the cement, if allowed by the applicable standards.

The composition of filter dust is in general similar to raw meal composition. In small dosages it should not be detrimental with regard to clinker properties. However, a dosage of 5 % should not be exceeded due to the negative impact of clayish material on the water demand.

Kiln dust from long kilns (often called CKDt) is much more decarbonated than suspension preheater dust and contains more chloride, alkalis and sulfur, as well as free lime. It can also be added up to 5 % to cement as long as chloride or alkali limits are not violated. Due to the alkali salts and free lime it is more reactive with positive influence on early strength.

5.10.3 By-pass dust

Bypass dusts are characterized by high amounts of alkalis, SO₃ and chlorine. Typical ranges are given in the table below.

In most cases, the maximum allowed dosage of 5 % cannot be reached due to the chlorine limit of 0.1 %, which is applicable to most cement types (exceptions: road binders, slag cement CEM III according to EN).

Furthermore, bypass dusts can significantly contribute to the alkali content of the cement. Hence their dosage has to be carefully controlled, if specific alkali limits have to be fulfilled in the cement.

Since bypass dusts have significant influence on the setting and strength development, the dosing of the by-pass dust should be kept constant and an adequate stock for kiln downtimes must be guaranteed.

Table 24: Characteristics of bypass dust

| Parameter | Average | Maximum |
|-----------------------|---------|---------|
| K ₂ O [%] | 10.5 | 25.0 |
| Na ₂ O [%] | 2.5 | 4.0 |
| SO ₃ [%] | 8.5 | 16.5 |
| Cl ⁻ [%] | 5.5 | 9.5 |

Due to their high content of alkali sulfates and chlorides, bypass dusts influence the setting behavior and strength development. In general, the addition of bypass dusts tend to reduce setting times and to improve early strength of the cement. The effect of by-pass dust addition to the cement has always to be tested with the by-pass dust itself. A simulation with chemical grade alkali sulfates and alkali chlorides is not possible and might lead to the wrong conclusions [Bid 03].

The highly hygroscopic nature of bypass dust can cause severe handling problems due to stickiness. To avoid sticking, the bypass dust can be blended with ground limestone.

6. **CEMENT GRINDING**

The cement performance depends basically on the properties of the main components and their proportions. For a given cement composition, the fineness has decisive influence on the cement performance in mortar and concrete. The purpose of the mill system is to provide a product fineness that will result in the required workability (water demand, setting time, bleeding tendency) and strength development. However, the effects of the mill system on the product quality are more complex and influence the particle size distribution (PSD) of the cement as well as the degree of gypsum dehydration. Hence, an optimized grinding process is an effective measure for the economic production of market oriented cements.

6.1 **Characterization of cement fineness**

The most common parameter to characterize the cement fineness is the specific surface according to Blaine. However, this parameter gives misleading results for the comparison of cements with different design and cements containing MICs with a high inner surface like fly ashes or pozzolan. Therefore it is better to determine the fineness on basis of sieve residues or by laser granulometry, which is considered the state of the art method (refer to 9.5.1).

Graphically the PSD can be depicted as cumulative %-residue or %-passing (Figure 25, top) or in probability density functions, which describe the incremental frequency of occurrence (Figure 25, bottom).

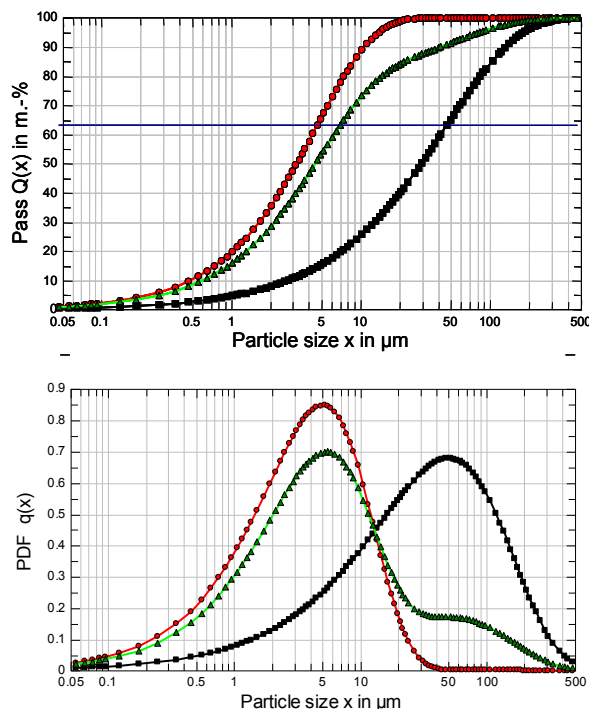


Figure 25: Graphical plot of the particle size distribution of three cements, top: cumulative distribution, bottom: probability density function (frequency graph)

The diagrams illustrate the meaning of the terms steep/flat or narrow/broad, which are often used to describe a PSD. From the cumulative curve one can conclude on the steepness of the curve, from the weight fraction per particle size on the wideness. For example in the top graph, the steeper red curve can be distinguished from the flatter darker curves. In the lower graph the red curve shows a narrower peak than the other two curves.

Characteristic values for the particle size distribution (wide – narrow) and fineness (μm) can also be evaluated by using the Rosin-Rammler-Sperling function (RRSB) and plotted in RRSB diagrams (see Figure 26). The residues at different particle sizes are plotted in this diagram, which has a double logarithmic y-axis and a logarithmic x-axis. By linear regression the slope n and the characteristic diameter x' are calculated:

Slope n of the straight line describes:

- indicator for the wideness of particle size distribution
- with increasing n the PSD gets steeper

Characteristic diameter x' [μm]:

- Indicator the fineness; x' is defined as the particle size at which 63.2 % of particles are passing (viz. 36.8 % residue)

At the same specific surface, cements with a high n tend to have a higher water demand than cements with a low n .

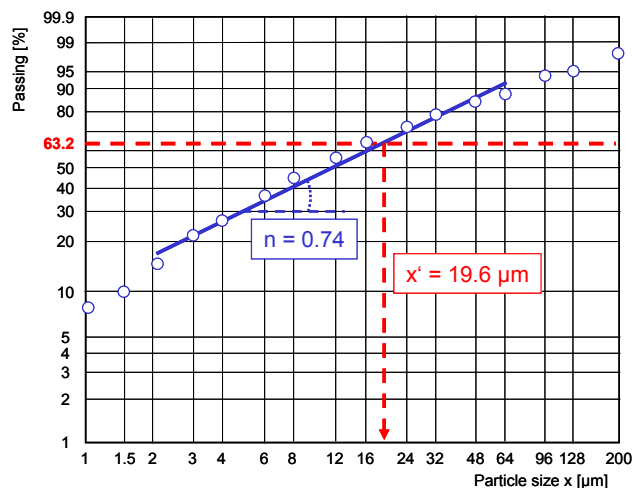


Figure 26: RRSB particle size distribution graph and characteristic values

6.2 Influence of the grinding system on the cement properties

6.2.1 Cement grinding in ball mill and VRM systems

The two-compartment ball mill operating in a closed circuit with high efficiency separator is still the most common arrangement for cement grinding [Jor 05]. A wide particle size distribution (PSD), which is advantageous with regard to workability and water demand, can be achieved by the adjustment of the quantity of separating air. Typical n -values for the different grinding systems are given in the diagram below.

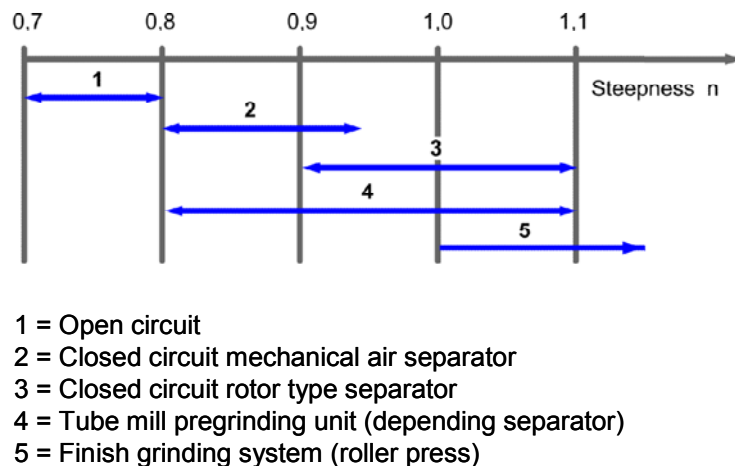


Figure 27: Typical n -values for cements ground in various grinding systems (source: grinding manual)

Vertical Roller Mills (VRM) are established in raw grinding for several decades due to their high grinding efficiency. However, their establishment for cement grinding took until the 1990ies. At the beginning, a main disadvantage of VRM systems in finish grinding was the very steep PSD with the respective consequences for the cement quality. However, with the actual vertical roller mills it is not a problem anymore to get a PSD similar to the ball mill and nowadays VRM's are well established in finish grinding [Bue 03, Fis 03, Jor 05].

The influence of the grinding system is not limited to the particle size distribution, but influences the gypsum dehydration as well. In VRM, the energy consumption and residence time are lower, and hence the product will not be heated up to the same level as in ball mills. Hence, the degree of gypsum dehydration will be lower than in ball mill systems with the known effects on sulfate solubility (refer to section 4) and storage stability (refer to sections 6.5.2).

As also indicated also in Figure 27, the finish grinding with roller presses still leads to a very narrow PSD and the application of such finish grinding systems is thus so far limited from the point of view of cement quality.

6.3 **Grinding of OPC and composite cements**

6.3.1 **Grinding of OPC**

The specific surface of the clinker minerals is decisive for the reaction kinetics since the hydration reactions start from the surface of the clinker particle. OPC's of different strength classes are commonly achieved by increasing the fineness, which is in general in the range between 2500 and 5000 cm²/g. The influences of the OPC fineness can be summarized as follows:

- Early strength increases with cement fineness significantly, while the effect on 28 d strength is less pronounced.
- Finenesses above 3000 cm²/g increase the water demand slightly.
- The tendency towards bleeding decreases with increasing fineness.

For OPC's, the slope of the PSD for Portland cement is of particular importance with respect to workability. At a constant specific surface, OPC's with steeper PSD tend to show increased water demand and early stiffening. The latter problem was in particular experienced in VRM systems, when highly reactive clinker (high C₃A) is ground at low temperatures together with gypsum. The gypsum is not transformed to highly reactive hemi-hydrate and as a consequence there is a lack of sulfate in the system. For such clinkers, the PSD and sulfate source have to be carefully adjusted.

The effect of the PSD on the Portland cement performance is not fully understood. It is generally accepted that the fraction of particles < 8 µm fosters the early strength development. Since the specific surface is proportional to this fraction, the Blaine value gives good indication of the early strength potential. The 28 d strength is mainly controlled by the particles between 2 and 24 µm, which can be characterized by the steepness of the PSD. At a given Blaine, the 28 d strength can be improved by increasing the steepness of the PSD.

6.3.2 **Grinding of composite cements**

The performance of composite cements depends, besides cement proportioning and quality of the cement constituents, decisively on fineness and PSD of the individual cement constituents and the total cement. The optimum cement performance can only be achieved, if fineness and PSD of the individual cement constituents are in their optimum range.

6.3.2.1 **Compound versus separate grinding**

Fineness and PSD are pre-determined by the selected grinding process and the grindability of the cement constituents. For a given grinding system and fineness (x'), soft materials yield in general a wider PSD than hard materials [Alb 93]. This relation is illustrated in the figure below, where the grindabilities of typical MIC's and clinker are plotted vs. the slope of the RRSB curve.

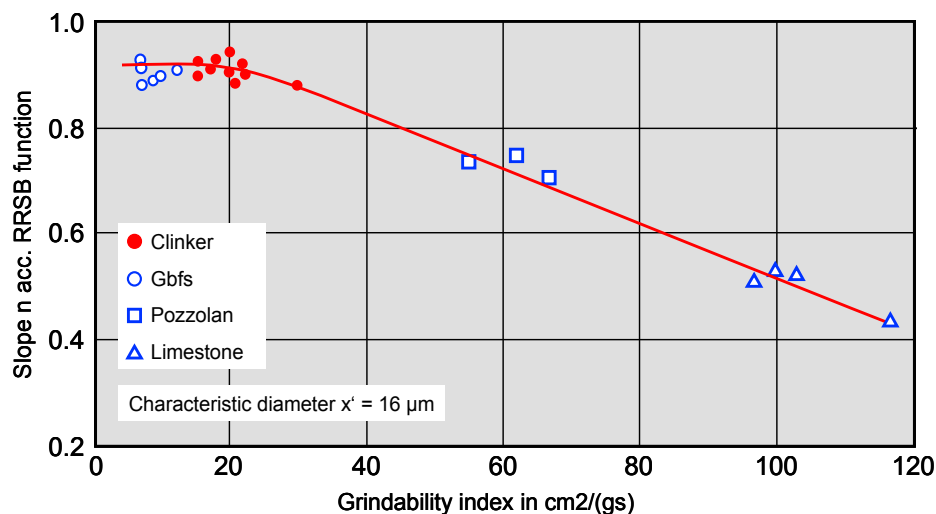


Figure 28: Slope of clinker and MIC with same characteristic diameter versus grindability index [Alb 93]

Compound grinding systems are still the most common systems for the production of composite cements. However, the PSD of the different components cannot be influenced individually and independently in this process. Hence, the different grinding behavior of the cement constituents is reflected in the PSD of the resulting cement. Cements containing softer materials than clinker (e.g. pozzolan, limestone) have wider PSD's, whereas the addition of harder materials (e.g. gbfs) results in a somewhat steeper PSD than ground clinker alone, although its grindability is worse than clinker. Additionally, the soft and coarse material fractionate: the soft material accumulates in the fine fraction while the hard materials concentrate in the coarse fraction of the cement.

This lack of flexibility with compound grinding limits the optimization potential for composite cements. With soft MIC the clinker will always concentrate in the coarse fraction, so that its early strength potential cannot be fully exploited (refer to section 6.3.2.2). For slag cements, the clinker will be enriched in the fine fraction.

Separate grinding systems offer higher flexibility than compound grinding considering the different grindabilities of the cement components on one hand and the different fineness/PSD requirements on the other hand. This allows fine tuning of the cement quality, in particular with regard to strength development. There are several examples of group plants which have reduced clinker factor by changing from compound to separate grinding [Bre 94, Mon 95a, Mon 95b]. Nevertheless, the potential for fine tuning is limited if the same grinding energy is applied as for compound grinding [Mon 96].

6.3.2.2 Optimum fineness of cement constituents

Due to the lower clinker factor, composite cements require in general a higher grinding fineness than OPC to achieve a similar strength development (in particular early strength). Furthermore, the PSD and fineness of the individual constituents must be optimum to yield the best cement performance. It is obvious that the

optimization of the individual finenesses of the clinker constituents can only be achieved by separate grinding.

The Holcim concept for the optimum grinding of blended cement is illustrated in the figure below. According to this concept, the clinker should be ground to high fineness with narrow PSD. Since the small clinker particles are the main contributors to early strength, this allows for maximum exploitation of the clinker strength potential. The MIC should be coarser than the clinker and show a wider PSD. However, the fineness of the MIC should still be high enough that they can be activated and contribute to late strength. For very active MIC's, like gbfs, also a very high fineness might be beneficial with regard to strength development. In any case, the PSD of clinker and MIC should be complementary to yield a beneficial PSD for the whole cement.

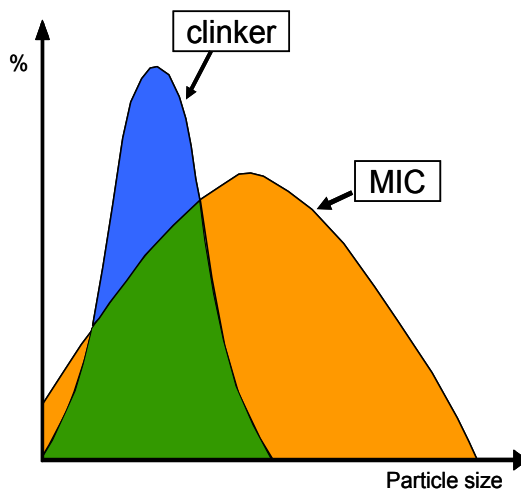


Figure 29: Scheme of optimum particle size distribution of clinker and MIC in blended cement

6.3.2.3 Concepts for optimum grinding of different blended cement types

The advantages of separate grinding differ significantly depending on the cement type. A comprehensive overview on the advantages and disadvantages is given in [Mon 96].

Gbfs cements

- It is in principle possible to improve the strength development of gbfs by separate grinding. However, at the same energy input separate grinding offers only little improvement potential for clinker factor reduction. On industrial scale, the reduction was in the order of about 5 %.
- In general, the early strength of gbfs cements is determined by the clinker fineness whereas late strength depends on the slag fineness.
- Certain gbfs might also contribute to early strength when ground to a very high fineness. Gbfs activation by very fine grinding might offer an interesting

potential to improve the early strength, though this is combined with high grinding energy [Mon 95, Lan 95].

- Positive influence was also experienced by fractionating the gbfs into a very fine and coarse fraction [Ehr 03]. This concept resulted in a considerable increase of early strength while late strength remained on the same level. However, a fraction of gbfs had to be ground to a very high fineness of about 5000 cm²/g so that the economical relevance of this concept is doubtful.

Fly ash cements

- Fly ashes as such show already a fineness which is close to cement. Therefore, the addition of fly ashes to the separator is the most appropriate way for fly ash cement production, provided the fly ash is of adequate fineness.
- Grinding is only necessary for coarse fly ashes, but also for fine ashes grinding might be beneficial. Several studies have shown that fly ash grinding causes certain activation since oversized particles are destructed [Par 91, Heu 94]. The fly ash spheres are not destroyed during grinding and hence the workability is not impacted [Mon 83].
- Separate grinding is not applied for fly ash cements. One study carried out by FLS indicated some potential for late strength tuning by separate grinding [Als 83].

Pozzolan cements

- For pozzolan cements, separate grinding provides a potential to improve the cement performance. The independent control of the clinker and pozzolan fineness allows for an adaptation of the strength development with regard to increased early and lower late strength.
- In compound grinding of pozzolan cements, the clinker remains rather coarse and the pozzolan is overground. A certain beneficiation of the cement properties can be achieved by the installation of high efficiency separators. Those systems reduce the overgrinding of the pozzolan to some extent and the clinker is ground more efficiently. However, the fine grinding of the clinker is paid by higher energy consumption. In the Holcim studies, a clinker factor reduction of about 5 % was obtained [Geb 93, Bre 94, Mon 95b].

Limestone cements

- Limestone as such has no influence on the strength development but can improve the workability considerably. In general, for limestone cements a wide PSD (viz. wide PSD of the limestone) is more favorable than a steep one (filler effect).
- In combined grinding, the limestone is ground to the favorable wide PSD. At least for limestone dosages up to 20 % separate grinding offers no advantage.

6.4 **Grinding trials for cement optimization**

In a first step, the cement proportioning and fineness should be evaluated on laboratory scale. These trials can be rather extensive and cover a variety of compositions.

However, it has to be kept in mind that the laboratory trials do not reflect the PSD of the industrially ground cement. Furthermore, the degree of gypsum dehydration and hence setting and strength development might be influenced. Therefore, industrial trials are mandatory to evaluate the optimum cement design.

For the industrial trials, the most promising points from the laboratory program are selected. During the trials, the following points should be fulfilled:

- The mill should run in a stable condition
- The duration of the trials should be sufficient. In general, the duration of an industrial scale grinding trial should be around 8 h minimum.
- All relevant parameters, like mill throughput, energy consumption, fineness should be documented (see Annex 4).

For further information refer also to section 9.4.3.

6.5 **Influence of the grinding temperature on product performance**

6.5.1 **Dehydration of gypsum phases**

The energy consumed in the grinding process is nearly totally converted into heat causing an appreciable increase of the cement temperature. The product temperature is depending on the mill system (ball mill, VRM), mill ventilation, as well as the temperature (in particular clinker) and moisture of the materials entering the mill. Typically, the product temperature is in the range of 90 - 120 °C. At this temperature, the gypsum will dehydrate partially, forming easily soluble hemi-hydrate and/or anhydrite III. The degree of dehydration depends on the temperature and residence time of the product in the mill. If the amount of dehydrated gypsum gets too high, the workability of the cement will be impaired (false set, refer to section 4).

A constant product temperature is crucial to achieve a uniform degree of gypsum dehydration and hence a uniform product performance. The degree of gypsum dehydration is mainly influenced by the following parameters, which should be kept as constant as possible:

- Mill ventilation
- Clinker temperature (avoid alternate utilization of cold and hot clinker)

Water injection is frequently used in ball mills to reduce the cement temperature and thus to limit gypsum dehydration. This can, however, result in lower cement reactivity due to pre-hydration of the cement. This tendency is especially pronounced for high aluminate and high alkali cements.

Water injection should always be considered as last measure after all other steps for mill optimization have been carried out (e.g. mill venting, separator venting...). The amount of water should be carefully controlled and be adjusted such that the product temperature is reduced to about 110 °C. If the product temperature is reduced to lower temperatures (in particular when injecting water into the 2nd compartment and not evaporated completely due to low dew point temperatures), inherent moisture might remain in the cement, causing pre-hydration and loss of strength. In order to control the product temperature, it is therefore important to install a thermo couple in the material stream and not only in the gas stream. For details of mill operation and optimization refer to "grinding manual" (in preparation).

Due to the lower grinding temperatures and residence times, the dehydration is not that pronounced in VRM systems. Hence, cements produced in VRM's contain in general more gypsum than ball mill produced cements. Setting disturbances related to lower gypsum dehydration, viz. less soluble sulfur, are comparatively seldom. However, an increase of the soluble sulfur can be achieved by:

- increasing of gypsum dosage, in order to provide more sulfur at the same level of dehydration
- adding more heat to the mill system (i.e. higher mill outlet temperatures), in order to increase gypsum dehydration

6.5.2 Influence of the grinding temperature on storage stability

Gypsum that is not dehydrated during grinding might dehydrate in the silo. The water liberated from the gypsum particles diffuses to the cooler parts of the silo where it reacts with the cement. Coatings and bridging may form as consequence of a pre-hydration of aluminates. Consequently, the cement loses flowability or lumps and/or build-ups are formed. Typical minerals found in the lumps are ettringite ($C_3A \times 3 CaSO_4 \times 32 H_2O$) and syngenite ($K_2Ca(SO_4)_2 \times H_2O$).

Since the lump formation is mainly related to a reaction of the aluminates, cement with high contents of C_3A and in particular highly reactive alkali (orthorhombic) C_3A prone to pre-hydration. The pre-hydration results in set retardation and loss of strength development. Furthermore, the cement contains more easily soluble hemihydrate formed due to gypsum dehydration during silo storage, which might cause setting disturbances.

Preconditions for the above described reactions are a high temperature (above 80/90 °C) and water release from the gypsum. Measures to prevent lump formation [Sch 01] are indicated in Table 25.

Table 25: Measures to prevent lump formation [Sch 01]

| Purpose | Measure |
|--|---|
| Avoid water penetration in silo | <input type="checkbox"/> Control silo roof, walls and aeration for potential water ingress <input type="checkbox"/> Reduce storage time |
| Keep cement temperature < 75 °C at silo entrance | <input type="checkbox"/> Avoid grinding of hot clinker <input type="checkbox"/> Optimize mill air ventilation <input type="checkbox"/> Inject water into one or both grinding chambers <input type="checkbox"/> Installation of cement cooler |
| Reduce water input via gypsum | <input type="checkbox"/> Partial or complete substitution of gypsum by anhydrite <input type="checkbox"/> Gypsum optimization for each cement type (to avoid overdosing of gypsum) |
| Adjust clinker properties | <input type="checkbox"/> Balance alkali/sulfur ratio (~ 1) to avoid formation of highly reactive C ₃ A <input type="checkbox"/> Reduce K ₂ O content to avoid syngenite formation <input type="checkbox"/> Adjust adequate free lime level to provide “water absorbent” |
| Improve cement flowability | <input type="checkbox"/> Adjust cement fineness (flowability gets better with higher fineness) <input type="checkbox"/> Use cement additives to improve flowability |

6.5.2.1 Analysis of lump formation

The flowability loss can be evaluated by the pack set (ASTM C 1565) or similar test like the Holcim pack set test, which evaluates the tendency to agglomeration of the cement (refer to section 9.5.5).

To identify the degree of gypsum dehydration before and after silo, an easy test based on staggered LOI (70, 240 and 600 °C) can be applied (section 9.5.3). By this method, free water (moisture), water bound in sulfate phases (gypsum and hemihydrate) and water in portlandite (Ca(OH)₂) can be evaluated. The test should always be carried out on a comparative basis for a sample from ex mill/silo inlet and silo outlet.

Differential scanning analysis (DSC) or thermo gravimetric analysis (TGA) are more sophisticated methods to determine the sulfate phases and hydrates. These methods allow for distinguishing between the amount of gypsum and hemi-hydrate very accurately. Determination of anhydrite is only possible by XRD analysis.

7. CEMENT ADDITIVES

7.1 Introduction

Cement additives are added in small quantities to the cement mill to improve the manufacture or the properties of cement. The two main groups of additives are the processing additions (often also called grinding aids) and the functional additions (often also called quality improvers).

In many countries, the cement standards refer to the required quality tests and the limits for dosing of cement additives. Both quality and dosage have to be optimized for each mill and product combination.

The guarantee that the product complies with the national standards has to be given by the supplier of the products as remark in the technical data sheet. The required remark is: The product fulfills the requirements of the "national cement standards" (with reference number).

In addition, as a control, spot check testing has to be carried out periodically as well by the plant (refer also to section 9.4.2 "Quality control of additives in the cement plant").

7.2 Standard specifications

For the use of cement additives, the compliance with the requirements of the standards is of course mandatory. A short reference is given in the following paragraphs.

7.2.1 European Standard EN 197-1

The total quantity of additives shall not exceed 1.0 % by mass of the cement (except for pigments). The quantity of organic additives on a dry basis shall not exceed 0.5 % by mass of the cement. These additives shall not promote corrosion of the reinforcement or impair the properties of the cement or of the concrete or mortar made from the cement. When admixtures for concrete, mortar or grouts conforming to the EN 934 series are used in cement, the standard notation of the admixture shall be declared on bags or delivery documents.

7.2.2 ASTM Standards

The ASTM standards use the term "additions" in place of the European Standard definition "additives". An addition is a material that is inter-ground or blended in limited amounts into a hydraulic cement during manufacturing, either as processing addition to aid in manufacturing and handling the cement or as functional addition to modify the use properties of the finished product.

Table 26: Classification of cement additives

| Designation | Definition |
|-------------------------|---|
| Functional addition | An addition introduced to modify one or more properties of a hydraulic cement. |
| Air-entraining addition | A functional addition that will entrain air in mortar or concrete. |
| Processing addition | An addition introduced to aid in the manufacture or handling, or both, of a hydraulic cement. |

ASTM 465 (processing additions)

This specification pertains to the criteria and tests to be used for determining whether a processing addition, when used in the recommended amount at the option of the cement producer in the manufacture of hydraulic cements, meets the requirements as prescribed by definition in Specifications C 150, C 1157 and C 595.

ASTM C 226

Specification for Air-Entraining Additions for use in the Manufacture of Air-Entraining Hydraulic Cement.

ASTM C 150 (“5 Additions” and “12. Manufacturer’s Statement”)

- 5.1.2 Processing additions may be used in the manufacture of the cement, provided such materials in the amounts used have been shown to meet the requirements of Specification C 465.
- 5.1.3 Air-entraining Portland cement shall contain an interground addition conforming to the requirements of Specification C 226.
- 12.1 At the request of the purchaser, the manufacturer shall state in writing the nature, amount, and identity of any air-entraining addition and of any processing addition used, and also, if requested, shall supply test data showing compliance of such air-entraining addition with Specification C 226 and of such processing addition with Specification C 465.

7.3 Types and dosage of cement additives

Table 27 gives an overview on the different types of cement additives, their usual dosage and the most common ingredients. It is of course also possible to have multifunctional additives, which combine several different ingredients (e.g. combination of water reducer with accelerators).

Table 27: Types of additives, usual dosage and most common ingredients

| Type / Class | Usual dosage (kg/t of cement) | Ingredients / chemically active materials |
|------------------------|-------------------------------|--|
| Grinding aids | 0.1 – 0.3 | Glycols (e.g. diethylene glycol), amine-acetate, triethanolamine |
| Strength enhancers | 1.5 – 2.5 0.3 – 0.6 | Mineral salts: Chlorides, alkali salts (early strength!) Amines: Triisopropanolamine, (other alkanolamines) |
| Chromium (VI) reducers | 3 – 5 0.5 – 0.8 | Fe(II)sulfate Sn(II)sulfate |
| Water reducers | 0.5 - 3 | Lignosulfonates, polynaphthalene sulfonates (NFS), polycarboxylates, polyacrylates |
| Set control | 0.2 – 0.5 1 – 2 0.2 - 2 | Retarders: Gluconates, sugar derivates, phosphates, phosphonates Accelerators: Alkali salts |
| Air entrainers | 0.5 - 5 | Rosin soaps, fatty acids (soaps), synthetic surfactants |
| Water retention | 1 - 2 | Cellulose ethers, Welan Gum or other polysaccharides |

The typical cost for a grinding aid is 1.0 to 1.5 USD/kg, which corresponds to 0.1 to 0.5 USD per tonne of cement. The cost for the other cement additives (functional additions) depends strongly on the selected raw materials.

7.4 **Applications of cement additives and benefits**

In Table 28, the typical applications of cement additives for the different cement types are shown.

The following specific benefits can be obtained by the use of cement additives:

- Grinding aids:
 - Reduction of specific grinding energy consumption
 - Increase of mill output (or achievement of higher fineness at same production rate)
 - Improvement of flowability of cement (reduction of pack set)
- Functional additions:
 - Improvement of strength performance (chemical activation of clinker or other hydraulic components of the cement) or reduction of clinker factor at constant quality
 - Reduction of water demand (reduction of the required amount of mixing water by better dispersion of particles)
 - Adjustment of the setting time with chemically active components (retarder, accelerator)

- Air entrainment for cement to be applied in freeze-thaw resistance concrete
- Water retention to prevent bleeding and water separation in mortar and concrete
- Reduction of soluble Cr VI (through the reducing agent added to the cement).

Table 28: Typical and possible applications of cement additives

| Cement type | Grinding aid | Strength enhancer | Water reduction | Set control | Air entrainer | Water retention |
|-------------------------------------|--------------|-------------------|-----------------|-------------|---------------|-----------------|
| OPC | typical | possible | | | | |
| OPC white | typical | | | possible | | |
| Limestone cement | possible | typical | | | | |
| Masonry cement | | | | possible | possible | typical |
| Fly ash / Pozzolan | possible | possible | possible | | | |
| Blast furnace slag cement | possible | typical | | | | |
| Cement for self compaction concrete | possible | | typical | possible | | typical |

For the grinding aids, the potential reduction in specific grinding energy consumption depends strongly on the cement fineness and the grinding system. For ball mills with separator, the typical potential savings that can be expected are as follows:

| Blaine Cement (cm ² /g) | Spec. energy reduction (%) |
|------------------------------------|----------------------------|
| 3000 | 0 - 5 |
| 3500 | 5 - 10 |
| 4000 | 10 - 15 |
| 4500 | 15 - 20 |
| 5000 | 20 - 30 |

For the functional additives, the potential for strength enhancement and/or clinker factor reduction varies significantly depending on the actual situation. The selection of suitable additives and the fine tuning of the cement design has thus to be usually done on a plant-specific basis.

For the Cr VI reducers, further details on their usage and effects can be found in the reference [Mon 03a].

7.5 **OH&S**

It is the responsibility of all users of additives to establish appropriate safety and health practices. All persons who are responsible for handling and storage of chemicals must read the instructions in the material safety data sheet (MSD), to take the right measure for personal protection and for actions in case of spillage or fire.

7.6 **Recommendations and procedure for testing of cement additives**

It is recommended to take the test procedures and requirements of ASTM C 465 as best practice for all countries, not just for ASTM regions.

The application of cement additives should be considered if one or several of the following points applies:

- Cement additive applications were not evaluated within the last years, a cost saving potential is likely
- Bottlenecks in cement grinding capacity, unfavorable electricity tariffs
- Evaluation of clinker factor reduction (utilization of cheaper materials)
- High specific grinding energy consumption (e.g. more than 40 kWh/t)
- Solving of “pack set” problems, problems with cement handling
- Cement setting problems
- Production of special cements/binders (masonry cement, road binder ...)

For the industrial testing of cement additives, the conditions as indicated in chapter 6.4 are to be applied. Typically three dosages are to be tested per additive and to be compared against the reference without additive. The duration of a grinding trial at a certain dosage should be around 8 hours.

In Annex 4, a reference list of parameters that should be collected during the industrial testing of cement additives is given, in order to have a clear basis for the evaluation of the obtained results.

8. **STRENGTH PREDICTION**

8.1 **Strength prediction on basis of clinker properties**

In 1980 [Geb 80] investigated the influence of clinker quality upon the properties of cement concrete. The objective was to develop a model to predict the cement strength potential from the clinker composition. The main findings of this investigation confirmed the commonly known influences of the clinker minerals:

- An increase of C_3A and alkalis is associated with an elevated water requirement and enhances the setting time
- An increase of C_3S is related to a higher compressive strength up to 28 d
- An increase of C_3A is associated with a higher early strength
- The rate of strength developments or the reactivity of a clinker is influenced almost exclusively by C_3A , C_3S , alkalis and sulfates
- Amongst these, the alkalis represent the strongest single factor influencing the rate of strength development
- An increase of alkalis implies a higher early and lower late strength

These relations reflected in the regression formula for the 2 d (CS_2) and 28 d (CS_{28}) strength of mortars and the ratio between the 2 and 28 d strength ($R_{2/28}$):

$$CS_2 \text{ (MPa)} = 1.42 + 0.19 C_3S + 0.35 C_3A + 0.85 K_2O_{sol}$$

$$CS_{28} \text{ (MPa)} = 39.9 + 0.28 C_3S - 7.6 K_2O_{sol}$$

$$R_{2/28} = 2.1 + 0.3 C_3S + 0.6 C_3A + 10.4 (K_2O + Na_2O + SO_3)$$

The formulas should be understood as general indication on influence of clinker parameters on the strength development and not as an accurate prediction of strength, since the formulas do not include crucial parameters like cement fineness or gypsum content.

8.2 **Application of strength prediction models in the plant**

The market demands for a constant cement quality are continuously increasing, but the physical testing of cement – in particular with respect to the 28 d strength - takes in general place when the cement is already applied. The factors influencing the strength development are known for a long time. However, the computerized databases of recent years facilitated the interpretation of strength variations significantly. Over the last years, several tools have been developed for the prediction of the cement strength, which help to

- take appropriate actions in handling and cement application
- take appropriate actions in the cement production process (cement grinding, clinker burning, raw mix preparation)

- optimize quality control procedures and methods
- supply customers with actual data of the product

Potential tools for that purpose are mathematical multiple correlation models.

The models should be based on multiple variable regression systems that take into account chemical and physical parameters that are known to influence the strength development:

- Clinker minerals: C_3S , C_3A , free lime
- Chemical parameter: Na_2O_{equ} , SO_3 , LOI
- Fineness parameter: specific surface area, R_{45}

The number of parameters in such models should always be kept as low as possible. As global model, the above eight parameters should always be included in the regression system. This approach allows that all influencing parameters are integrated although they might not vary to great extent (and would hence not appear as statistically relevant by applying a multiple regression).

For special cases, the basis could be extended by certain minor constituents such as MgO , F or P , which are known to influence the strength development. For the prediction of late strength also the results of early strength are included in the calculation. It has to be stated that the regression must be carried out for each plant and cement type individually. A generic formula that fits for all plants, types of clinker and cement does not exist so far.

Strength prediction models are today applied in several Holcim companies, e.g. Holcim US, Cement Australia, Holcim New Zealand (ICM card 01991), Holcim Apasco, Holcim Western Europe.

The regression coefficients in the different plants are based on historical chemical, physical and strength data of the respective cements. The time span included has to be long enough to have an adequate number of samples to secure a stable database, but must exclude samples that were produced before major changes in the production process. It is hence mandatory to update the coefficients on regular basis (e.g. every week/month) and to find a representative time span for the calculation of the regression factors. A control/recalculation of the regression coefficients is carried out once per week at Holcim US and Holcim New Zealand including a historical data of 16 weeks (Holcim New Zealand) or several years (Holcim US).

At present, a strength prediction tool cannot replace physical testing but serves more as a supportive tool to guarantee the product consistency and to understand the process influences on the strength development. Sudden deviations between the predicted and measured strength can help to identify factors, which have a strong influence on the strength development.

With an appropriate data set, the accuracy of the prediction is reported to be in the range of the accuracy of the testing method (personal information Holcim NZ). However, also larger deviations were experienced (see figure below). Poor

correlation might in most cases be related to an insufficient number of historic data for the current production conditions.

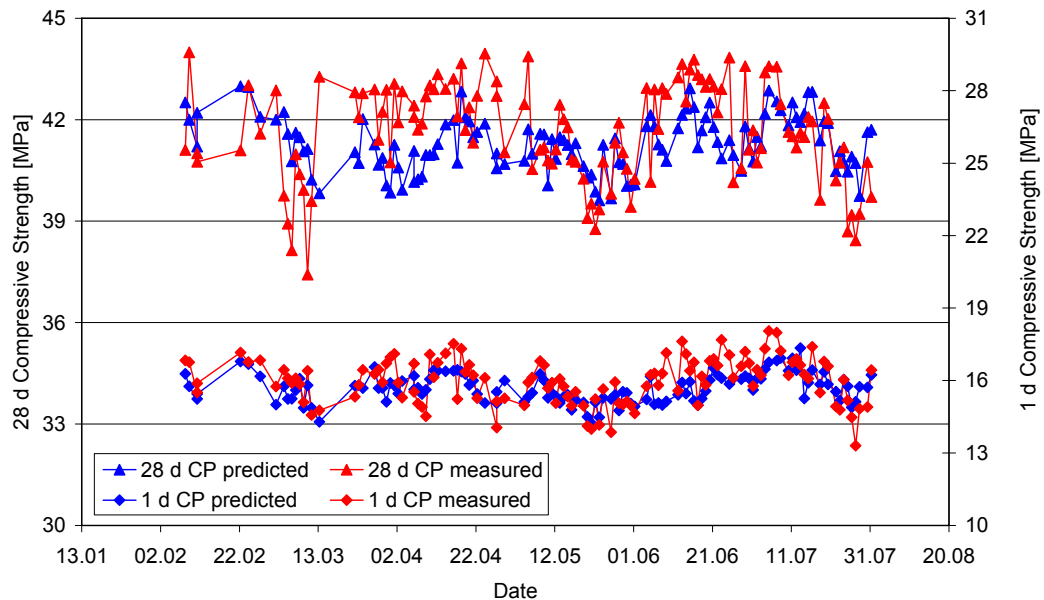


Figure 30: Correlation between predicted (blue curves) and measured strength. Source Holcim US.

A rather sophisticated tool was developed by the Virtual Cement and Concrete Testing Laboratory (VCCTL) consortium that was founded in 2001. The consortium is a US government/industry collaboration headquartered at the National Institute of Standards and Technology (NIST). Besides strength calculation, the tool simulates other physical properties of the cement paste like heat of hydration, hydration degree, pore solution composition etc., which are relevant for the cement application or the durability [Hae 03]. The tool is rather complicated and requires numerous input data. For the time being this tool is not considered applicable on plant level. Version 1.1 of the software can be downloaded at <http://vcctl.cbt.nist.gov>.

9. **TEST METHODS AND PROCEDURES**

The following section lists some specific or important test methods which should be applied in the quality assessment of clinker, MIC, cement, set regulators and cement additives. Common techniques like e.g. cement analysis by XRF are not covered in this manual but will be described in detailed in the Quality Control Manual (in preparation).

9.1 **Clinker**

9.1.1 **Mineralogical composition**

The mineralogical composition of the clinker can be determined either by

- Bogue calculation
- X-ray diffraction with Rietveld refinement
- clinker microscopy

The clinker phase determination by Bogue is well known and established for a long time. It gives a rough estimate of the true clinker phase contents. However, it is based upon equilibrium conditions and does not take into account the influence of minor elements on phase formation. As long as raw materials and fuels are kept on a constant level, the Bogue calculation provides sufficient information as the difference between the true values and the calculated ones stays on a constant level. However, at high Thermal Substitution Rates (TSR) and fluctuating fuel mixes, the determination of the true phase composition by Rietveld is advisable.

XRD with Rietveld refinement is a relatively new technique for the quantitative determination of the clinker phase composition, but is nowadays well accepted and established in the routine quality control of many cement plants. The development of new detector systems enabled the utilization of this technique on industrial level. In cement plants, this technique can be automated and be included in the quality control of the clinker.

Clinker microscopy has a long tradition in clinker evaluation. It gives information on the clinker microstructure as well as on the quantity of the different clinker phases. However, it requires well trained personnel and the analysis takes quite a long time, since at least 4000 points have to be counted. Therefore this method is not suitable for a regular quality control basis. Nevertheless, it is the only direct method to determine the clinker phases.

9.1.2 **Free lime analysis**

Free lime determination according to the ASTM standard or Schläpfer-Bukowski is one method for wet chemical analysis. Finely ground clinker is dispersed in ethylene glycol, where free lime forms calcium glycolate. The amount of calcium glycolate is analyzed by titration with hydrochloric acid. For the analysis it is important that the clinker is finely ground ($< 63 \mu\text{m}$) and the ethylene glycol is absolutely anhydrous.

The method covers both free lime and Ca(OH)_2 , so that the uptake of moisture in these samples is not that critical.

In most modern cement plants, the free lime is controlled by XRD either in stand alone instruments or in combined XRF/XRD instruments. The analysis can be carried out on the same pressed pellet used for XRF analysis. The method uses a single peak of the free lime XRD spectrum to determine the free lime content in the clinker. Fresh clinker samples have to be taken for the set up of the calibration curve. Hydrated free lime (portlandite) is not determined by this method. Hence, it is unavoidable to carry out the analysis immediately after sampling. The accuracy of the method has to be checked on regular basis by wet chemistry (at least once per week).

Another online method for free lime determination is conductometry. The basis is similar as for wet chemical analysis. The clinker is dissolved in glycol, which causes a shift in the conductivity, which is proportional to the amount of calcium glyconates in the solution. However, the experience showed that the systems need quite high maintenance. Cross contaminations were experienced when the system was connected with two kiln lines.

9.1.3 Clinker Microstructure

Clinker microscopy is the only method to get information on the clinker microstructure. It is a valuable tool to detect process impacts related to raw material and fuel preparation, the kiln temperature profile during burning and cooling as well as on reducing conditions. The preparation of the clinker samples as well as the analysis is rather time consuming and hence this method cannot be applied on a high frequent routine control basis. Furthermore it requires intensive training for the operator to familiarize with the specific features of the clinker microstructure and their interpretation.

A basis for the proper set-up and application of clinker microscopy at plant or central laboratories is given by the Holcim "Clinker Microscopy Manual" (refer to Sch 07).

9.1.4 Determination of fluoride

The determination of fluoride clinker is measured with an ion selective electrode after digestion. The finely ground material is placed in a nickel crucible covered with NaOH pellets and heated with a lid to red color at 700 - 800 °C. The cooled residue is dissolved and neutralized with citric acid solution and diluted with water to a known volume. Low fluoride concentrations are measured with the triple addition method.

Based on these results, it is possible to setup as well a plant specific XRF pressed pellet program for automated measurement in process control system.

9.2 Mineral components

9.2.1 Mineralogical composition

The mineralogical composition can either be determined by semi-quantitative XRD or by XRD with Rietveld refinement. For the latter, the structures of all mineral phases occurring in the sample have to be available and it requires some experience when dealing with unknown materials.

9.2.2 Determination of slag glass content

The glass content of slags is in general determined by microscopic point counting [Dri 94]. The slag is ground to a fineness of 40 – 60 µm and the glassy and crystalline particles are counted under the microscope.

Rietveld analysis with internal standard offers a fast and reproducible alternative to the classical point counting method.

9.2.3 Strength activity tests for pozzolanic materials

The reference document for testing pozzolanic materials according Holcim standard is: PozzoTech Working Paper 13.

For this test, the pozzolan is ground to a fineness of 6 – 8 % R₄₅. A MIC proportion of 30 % is added to a reference OPC. For the evaluation of the activity, the strength after 28 d is compared to the reference OPC.

9.2.4 Slag activity test

Slag activity shall be evaluated by determining the compressive strength of both Portland cement mortars and corresponding mortars made with the same mass of 50-50 mass combinations of ground granulated blast furnace slag and Portland cement.

The reference method to be followed is ASTM C989.

9.3 Set regulator (gypsum/anhydrite)

For total chemical analysis of gypsum, the test methods of ASTM 471 can be taken as reference methods.

In most cases, the following quick testing methods are preferred:

9.3.1 Determination of the combined water and CO₂ from carbonates

Crystal water can be quantified most accurate by differential scanning calorimetry (DSC). Crystal water and CO₂ (carbonates) can be quantified as well by thermogravimetry (TG). In case the respective equipment is not available, the weight loss gives sufficient information.

- 1) Weight loss at 45 °C indicates the moisture
- 2) Weight loss between 45 °C and 230°C indicates the crystal water
- 3) Weight loss between 230 °C and 900 °C indicates the CO₂ (carbonates)

9.3.2 Total chemical analysis

The most recommended and fast testing method is testing by X-ray fluorescence spectrometer (XRF). Fused beads (glass disks) and pressed powder pellets are possible.

9.3.3 Determination of sulfur content

Sulfate is precipitated from an acid solution of the gypsum with barium chloride (BaCl₂). The precipitate is filtered and weighed as barium sulfate (BaSO₄) and the sulfur trioxide (SO₃) equivalent is calculated (ASTM C471).

Instrumental methods are a fast and reliable alternative to the wet testing. In some cases, notably scrubber gypsum or industrial gypsum, significant levels of sulfite may be present. In such cases, analytical test methods shall be chosen so that sulfate and sulfite (probably as well sulfide) can be reported separately.

9.3.4 Critical parameter of industrial byproduct gypsum

Depending on the origin and industrial process where the byproduct gypsum is produced, the following elements or contaminants are present in higher or lower concentrations:

- Fluoride
- Phosphorous
- Sulfites
- Citric acid
- Surfactants (air entrainers)

The most recommended quality control of such by-product gypsum is the application test in laboratory cement mixes by controlling the Vicat setting time. This test has to be made as well with each delivery of new batches.

Remark: In case, the retardation is significantly higher compared to standard gypsum or in case, the quality of the by-product gypsum is expected to have relevant variations in above parameters, the blending of standard gypsum and by-product gypsum can be the preferred way for co-processing.

9.4 Cement additives

9.4.1 Quality control of additives by the manufacturer statement (certificates)

Test certificates with results for ASTM C 465 and IR-Spectra for quality control have to be delivered with the first batch. This is not only required for regular production, the same documentation is required for pretesting. This ASTM test certificate should be given by the supplier in addition to the confirmation that the product qualities fulfill the requirements of the national cement standard.

9.4.2 Quality control of additives in the cement plant

The plant is responsible to elaborate a suitable quality control concept for the additives used in cement production. As a general recommendation, the following parameters should be tested from every new batch delivered to the stock in the plant:

- Density and water content: gives information on active material
- pH and chloride content: gives information on corrosion potential (tanks, pipes, pumps)
- Foam formation, bottle test: gives a first information on the risk potential of forming undesired air
- IR-Spectra (delivered periodically from the producer of the additives)

Additional tests according ASTM 465 are carried out by the plant in case of admixture from new or different sources are used or if targets values from above testing are outside the plant specifications.

9.4.3 Application tests (cement optimization)

9.4.3.1 Running time of tests

Adjusting time depends on mill type: ball mills 2-3 h and vertical mills 1-2 h.
8 h of stable production are required at the minimum after the adjusting time.

9.4.3.2 Mill feed

The mill feed mix is kept stable in composition during a test. The specific feed [m³/h] usually rises during a test. Target is to achieve a fixed target fineness by selection of an optimum sieve, laser granulometry or less favorable, the Blaine value.

9.4.3.3 Energy consumption

Energy consumption of the complete grinding system is recorded (mill, separator, mill ventilation). Specific savings (kWh/t) are in most cases a result of a higher mill feed.

9.4.3.4 Testing of cement

In the first part, every 30 minutes fineness/screen-residues and mill conditions are optimized. As soon as the production runs stable (after 2 - 4h), samples are taken every hour and mixed to a homogeneous sample.

- Fineness (Blaine) ; optionally laser granulometry
- Residue 45 µm sieve
- Pack set test or HGRS cement flow test (Annex 3)
- Setting time (start and final setting, including water demand)
- Standard strength including fresh density and raw density on hardened mortar
- Concrete test at standard conditions at fixed slump (3") or fixed DIN table flow (50 cm); to be compared with internal targets and competitor cement

9.5 Cement

9.5.1 Particle size distribution

The fineness of cements is often characterized by the specific surface according to Blaine (SSB). The determination of the Blaine is also required by some of the standards (e.g. ASTM). It is based on the air permeability of a powder that indirectly measures the specific surface. However, it does not uniquely characterize the particle size distribution (PSD): at the same SSB the cement can have a different PSD, in particular when comparing cements with different compositions. The specific surface gives also misleading values for blended cements, which contain MIC's with a high inner surface like fly ashes and pozzolans.

A more reliable parameter to describe the cement fineness is provided by the PSD. It can be measured by sieve analysis or by laser granulometry. Typical particle size ranges, sample weights and measuring times for the different analyzing method are summarized in the table below.

Table 29: Methods for determination of PSD

| Method | Particle size (µm) | Sample weight (g) | Time (min) |
|--------------------------|--------------------|-------------------|------------|
| Mechanical (dry sieving) | 33 – 2000 | 15 | 60 |
| Air jet sieving (Alpine) | 33 - 2000 | 50 | 60 |
| Laser granulometry | 1 - 200 | 50 | 20 |

The PSD of a cement is commonly characterized by the Rosin-Rammler-Sperling function (RRSB) and the by the parameters d' (position parameter) and n (slope).

The parameter d' describes the particle diameter corresponding to a residue of 36.8 % and n the slope of the straight RRS line.

Small d' -values describe a high fineness and large n -values a narrow PSD. At the same d' , the specific surface is lower for narrower n . For a constant Blaine, d' is lower for cements with steeper PSD.

The particle size distribution can be also be determined by measuring the residue on defined sieves (R_{45} , R_{90}). For cement sieve analysis air jet sieves are preferred, since on mechanical sieves the cement particles tend to agglomerate and falsify the result. In some cases also wet sieving is applied. However, due to the starting hydration reactions, wet sieving is considered very critical. The smaller the sieve mesh size intervals, the more accurate the PSD can be depicted.

Laser granulometry provides the state of the art technology for determining the PSD. This method gives the whole particle spectrum in a range between 1 and 200 μm . To avoid pre-hydration, the analysis for cements should always be run in a dry state or – for wet laser granulometer – with alcohol. Wet laser granulometer run on water basis are not considered adequate for cement analysis.

9.5.2 Sulfate optimization

The optimum sulfate content should be determined in an industrial trial. It consists basically of 4 steps (for more details refer to section 4.4be determined in an industrial trial. It consists basically of 4 steps (for more details refer to section 4.4 and Annex 2):

- Increase addition of set regulator until reaching a cement SO_3 content about 0.5 -1 % above the standard limit
- Stop the feeding of set regulator completely
- Take every 5 to 10 min a cement sample of 15 to 20 kg until SO_3 reaches minimum again (takes in general about 1 h)
- Test samples for selected properties:
 - mandatory: setting time and mortar strength development
 - recommended: concrete workability, strength development

9.5.3 Degree of gypsum dehydration

The easiest way to estimate the degree the gypsum dehydration is to determine the LOI in the following temperature ranges:

| Temperature range | Type of moisture | Formula |
|-------------------|-----------------------------------|---|
| 20 - 70 °C | Inherent moisture | |
| 70 – 240/250 °C | Gypsum water Hemihydrate water | Gyp = 4.78 x LOI HH = 16.1 x LOI |
| 240/250 - 600 °C | Portlandite | $\text{Ca(OH)}_2 = \text{LOI} \times 4.113$ |

The method does not allow for distinguishing between water coming from gypsum and hemihydrate, respectively. Therefore, the exact content can only be estimated by the formulas given above. Furthermore, anhydrite cannot be determined by this method. It is recommended, in particular for the analysis of lumps, to go up to 600 °C to evaluate the Portlandite content, since this gives an indication on the hydration degree of the lump.

DSC analysis offers the possibility to distinguish exactly between gypsum and hemihydrate. Anhydrite can not be detected by this method.

Rietveld analysis is also capable of determining the gypsum phases. However, due to the rather small amount of these phases, the analysis is not very exact.

9.5.4 Cement proportioning

Quantitative determination of cement constituents is a rather sophisticated issue. For all methods, calculations are based on several assumptions, which might over- or underestimate the proportion of one or the other cement component.

The easiest but also most error-prone way to evaluate the cement proportioning is by the application of linear regression systems using specific oxides that are contained in significant concentrations in one cement component only (e.g. MgO or TiO₂ for slag determination, LOI for limestone). For the effective utilization of this method, the composition of the cement components needs to be known. Since some MICs do not contain such elements and also the content of the indicative elements might change, the calculation is not very accurate. Therefore, it should only be used as a rough evaluation of the cement composition. For multiple blend cements, this method comes to its limits (e.g. pozzolan – slag – clinker blends).

Another way of determining the cement composition is by Rietveld analysis with internal standard. The spiking of the sample is, however, related to a high preparation effort. It was shown that for slag cements (with one slag source) also Rietveld analysis without internal standard is possible [Sch 05]. For this, all minerals contained in the cement components must be identified.

The prEN 196-4 describes a method for the determination of gbfs, fly ash, natural pozzolans, siliceous fly ash, limestone, silica fume and set regulators by selective dissolution in EDTA and HNO₃. The method is not suitable for cements containing calcareous fly ash, burnt shale and all other components that contain clinker type hydraulic minerals. The method shows a very good reliability, but is very time consuming (about 1.5 days per sample) and hence not suitable for routine control.

In Germany, a method was developed to evaluate the slag proportion by microscopical point counting of the slag and clinker particles on a cement fraction (32 – 45 µm) [VDZ 75]. A chemical correction based on CaO has to be applied afterwards, since the counted fraction is never identical with the total cement composition. This method works very well for cements that were produced by compound grinding where the particles are randomly distributed in all fractions. For separately ground cements, the representativeness of the counted fraction is rather poor.

9.5.5 Flowability testing

The flowability or tendency of a cement powder to consolidate can be measured by ASTM pack set test (ASTM C 1565) or the Holcim flowability test.

The ASTM method measures the mechanical force needed to overcome the cohesive forces. For the test, the cement is placed into a flask. The cement is consolidated on a vibrating table for a defined period. After that, the flask is rotated in 180 °C increments until the bed collapses. The number of half turns is a relative indication of the force required to overcome the consolidation and is designated as pack-set index (P.S.I.). The higher the number of turns the stronger is the tendency of the cement towards consolidation.

A simple method was developed by HGRS, which requires only equipment that is commonly available in plant laboratories. 100 g of cement is put with a funnel on a 0.50 mm sieve (200 mm diameter), which is fixed with two rubber rings on a shock table. The test measures the amount of cement that pass through the sieve after ten shocks.

9.5.6 Concrete testing

The laboratory cement is made at a fixed consistency close to the typical national multi purpose concrete mix.

Adjust the water content to obtain a slump of $3\frac{1}{2} \pm \frac{1}{2}$ inches [90 \pm 15 mm]. The workability of the concrete mixture shall be suitable for consolidation by hand rodding and the concrete mixture shall have the minimum water content possible. Achieve these conditions by final adjustments in the proportion of fine aggregate to total aggregate or in the amount of total aggregate, or both, while maintaining the yield and slump in the required ranges.

10. **REFERENCES**

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Annex 1

Holcim Burnability Test



HOLCIM BURNABILITY TESTS

The burnability of a raw mix is defined as the ease of formation of the clinker minerals and is - by convention - expressed as the content of uncombined lime (CaO_f) in the clinker remaining after heating under given conditions. The following methods can be employed to determine the burnability of a raw meal.

1. HOLCIM BURNABILITY TEST

A 10 g sample of raw mix - nodulized with a small quantity of water and then dried at 60 °C for 24 hours - is heated in a platinum crucible at 1400 °C for 15 minutes. After rapid cooling of the sample, the uncombined lime is determined according to the Schlöpfer-Bukowski method.

As supported by experience, the uncombined CaO left gives a reliable, however, relative indication of the ease of burnability of a raw mix to be expected under plant conditions.

The test also does not allow an assessment of the individual contributions of different raw mix parameters to the total free lime content, nor indicate the free lime that will be encountered in practice.

The evaluation of the "Holderbank" burnability test results is made on the following basis:

| <u>range CaO_f</u> | <u>burnability</u> |
|--|--------------------|
| 0 - 2 % | very good |
| 2 - 4 % | good |
| 4 - 6 % | moderate |
| 6 - 8 % | poor |
| above 8 % | very poor |

2. PHYSICO-CHEMICAL BURNABILITY MODEL

This model allows the calculation of the CaO_f -content as expected to result from the above mentioned burnability test - provided that the lime saturation (LS), the silica ratio (SR), the percentage of coarse calcitic grains (Cc) larger than 90 microns, and of coarse quartz (Q) larger than 32 microns have been previously determined - according to the formula:

$$\text{CaO}_f = 0.5611 Q_{>32 \mu\text{m}} + 0.1663 \text{Cc}_{>90 \mu\text{m}} + 0.3557 \text{LS} + 0.8041 \text{SR} - 33.8859$$

The coefficients for this formula were derived from a multiple regression analysis carried out in HMC/TC and based on a considerable amount of experimental data.

As can be realized, the possibility of differentiation between the influence of chemical composition (LS, SR) and fineness on the CaO_f -content, as determined by the burnability test, allows useful information to be obtained for an effective optimization of raw mixes with regard to these parameters.

Annex 2

Sulfate Optimization in Cement

Method to optimize SO₃ in the cement

(according to procedure of Holcim France / Benelux)

1. OPTIMUM SO₃ IN THE CEMENT

The SO₃ determined in the cement is the sum of SO₃ of the different constituents:

- Clinker
- MIC
- Calcium sulfate added for finish grinding

The SO₃ from the different constituents does not react in the same manner. This reaction can considerably influence the cement properties:

- Setting
- Rheology of the cement paste
- Kinetics of hardening
- Dimensional variations
- Compatibility of admixture-cement in the fresh concrete

In case of clinker the SO₃ is integrated in the crystal lattice. The contribution of sulfur by the raw meal or by the fuels, influences the final SO₃ content in the clinker.

The SO₃ of clinker varies mainly as a function of the fuels used during the burning process. Attention has to be given to obtain sufficient SO₃ in form of alkali sulfates in order to avoid fast setting of the cement.

It is not possible to calculate in a quantitative manner the effect of all these phenomena without a purely experimental study applied to the cement. This is even more indispensable since not all the cements have exactly the same composition, the same burning conditions, the same MIC, the same particle size distribution, etc....

There are certain mathematical models to determine the optimum SO₃ in the cement. None of them gives satisfactory results, as the effect of particle size distribution is not taken into account.

2. METHOD TO OPTIMIZE THE SO₃ IN THE CEMENT

The optimization exercise has to be realized on an industrial scale for all different cement types produced.

Once the cement mill is in a stable condition, deliberately increase the dosage of calcium sulfate in order to produce cement out of norm for a short period. The cement should be directed to a transition silo or directly "diluted" in the normal silo.

Notes: Foresee to take a clinker sample in order to determine its SO₃ content.
The Blaine might increase a little bit, but do not touch the grinding system!

At a certain moment, the cement analysis will detect an elevated SO_3 , for instance 5%.

This will be the $\text{SO}_3 t_0$

Then: Stop the weigh feeder for calcium sulfate (or divide the weigh feeder dosage by two or three to avoid a too strong effect) and every 5 minutes take a sample of 5 - 10 kg (quantity depends on set of tests to be realized).

$\text{SO}_3 t_5$

$\text{SO}_3 t_{10}$

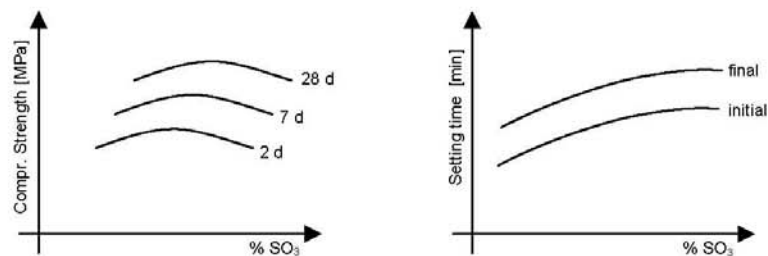
$\text{SO}_3 t_{15}$

$\text{SO}_3 t_{\dots}$

You will observe that the SO_3 of the cement will decrease rapidly.

Usually the exercise is finished within one hour. Put the weigh feeder back on its original set point.

It only remains to test the set of cements with different SO_3 on the different properties (setting, strength, shrinkage) and to establish the corresponding curves of values as a function of the SO_3 content (e.g. Compr. Strength = $f(\text{SO}_3)$).



Note: The fact to test cement with SO_3 out of norm will allow examining what happens if one day you are really in this situation.

Recommendation:

The optimum SO_3 can help you to gain a lot in fineness, strength, workability and other cement properties.

Every time you change:

- > the composition of clinker (or clinker factor)
- > the composition of MIC (or percentage of addition)
- > the fineness
- > the type of calcium sulfate

=> Make an optimum SO_3 !

... it does not cost you a lot and it can give you a great benefit!

Annex 3

Pack Set Test

Flowability of Cement (Pack Set Test)

Testing Method

In order to express the flowability of a powder numerically with the aid of a simple apparatus, the principle is utilized whereby shearing forces of definite magnitude are applied to a powdered material, which is positioned on a sieve. The quantity that flows through will vary according to the magnitude of the cohesive forces and constitutes a measure for the flowability of a powder.

The test apparatus comprises a shock table (conforming to ASTM C-230), on which a standard test sieve of 200 mm diameter is fixed by means of two rubber rings.

For performing the test, 100 g of the material is placed carefully in the center of the screen by means of a funnel and an o-ring.

Then ten shocks are applied, and the quantity of material that has passed through the sieve is measured. The sieve with mesh sizes of 0.50 mm has been proved most suitable for the investigation of cement. The accuracy of the measurements is quite sufficient for practical requirements (5.0 % relative).

Equipment

- ⇒ Shock table hand operated (see ASTM C230)
- ⇒ Standard Sieve, mesh size 0.50 mm, 20 cm diameter
- ⇒ Balance (accuracy $\pm 0.1\text{g}$)
- ⇒ Funnel with an outlet of 4 cm, or o-ring and funnel
- ⇒ A 20 cm sieve collector to catch the passing material

Procedure

1. Weigh 100.0 g of cement
2. Put the sieve bottom and the testing sieve on top of each other
3. Place the cement with the funnel / o-ring in the center of the sieve
4. Fix the sieve well on the vibrating table using the rubber rings
5. Apply 10 shocks on the shock table, not more than one shock per second
6. Weigh the screened matter in collector bottom
7. Repeat measurement (double check) and take the average

Evaluation

The target value is fixed by the plant requirements: typically 40-50% passing (0.5mm sieve) is the optimum range. But it depends strongly on local needs!

Flowability of cement (pack set test)



1



2



3



4

Annex 4

Reference List for Grinding Trials

Cement Additive Evaluation for Product and Process Optimization



| Plant | | Date | |
|--------------------|-------------------------------------|--------------|---------|
| Cement data | Brand / norm | | unit |
| | Holcim Product code | | |
| | Cement additive dosing | | |
| | | | |
| Cement Composition | | Moisture [%] | |
| | Clinker | | [%] |
| | Gypsum | | [%] |
| | Gbfs | | [%] |
| | Fly Ash | | [%] |
| | Limestone | | [%] |
| | Pozzolan | | [%] |
| | Other MIC: | | [%] |
| | CKD | | [%] |
| Mill data | Grinding system | | |
| | Mill type (ball mill, VRM) | | |
| | Separator type | | |
| | Pregrinding | | |
| | Mill Main drive power | | kWh/t |
| | Grinding system | | kWh/t |
| | Production rate | | t/h |
| | Rejects | | t/h |
| | Recirculation bucket elevator power | | kW |
| | Mill Vibration (ONLY FOR VRM!) | | mm/s |
| | Mill Sound signal (ONLY FOR BM) | | % |
| | time till stable conditions | | [min] |
| | supplier | | |
| Cement additive | cement additive brand | | |
| | Dosage | | [g/t] |
| | purpose | | |
| | Additive cost | | [USD/t] |

| | | | | | | | | | |
|--|--------------------------------------|--|--|-----------|----------------------|----------------------------|--|------------|--|
| Cement Fineness | Fineness / Blaine | | | | cm ² /g | | | | |
| | Residue 45 µm | | | | [%] | | | | |
| | Residue µm | | | | [%] | | | | |
| | x' (RRSB) | | | | [µm] | | | | |
| | d(50%) | | | | [µm] | | | | |
| Physical tests | RRSB-slope (n) | | | | [-] | | | | |
| | norm consistency / water demand | | | | [%] | | | | |
| | Set testing Vicat initial set | | | | [min] | | | | |
| | Set testing Vicat final set | | | | [min] | | | | |
| | Test method / Standard | | | | | ASTM/ EN / BIS / ISO / ... | | | |
| Chemical tests | compr. strength 1d | | | | [MPa] | | | | |
| | compr. strength 2d | | | | [MPa] | | | | |
| | compr. strength 3d | | | | [MPa] | | | | |
| | compr. strength 7d | | | | [MPa] | | | | |
| | compr. strength 28d | | | | [MPa] | | | | |
| Material handling properties | SO3 (for gypsum optimization) | | | optional | [%] | | | | |
| | LOI | | | | [%] | | | | |
| | ... | | | | | | | | |
| | flowability (Sieve: mm) | | | | [%] | | | | |
| | pack set | | | | [revolutions] | | | | |
| additional observations | others ... | | | | | | | | |
| | Process | | | | | | | | |
| | Products | | | | | | | | |
| | Holcim cone water/cem. ratio | | | optional | | | | | |
| | Holcim cone sand/mortar volume ratio | | | | [%] | | | | |
| Application based testing Holcim cone | Holcim cone flow 10 min | | | | [mm] | | | | |
| | Holcim cone flow 45 min | | | | [mm] | | | | |
| | Holcim cone compress. strength 1d | | | | [MPa] | | | | |
| | Holcim cone compress. strength 28d | | | | [MPa] | | | | |
| | mortar temperature 10 min | | | | °C | | | | |
| | mortar temperature 45 min | | | | °C | | | | |
| | cement content in concrete | | | | [kg/m ³] | | | | |
| | Aggregate size [max. grain size] | | | | [mm] | | | e.g. 16 mm | |
| | water / cement ratio | | | | [-] | | | | |
| | Slump 10 min | | | | [mm] | | | | |
| Concrete tests | Slump 45 min | | | | [mm] | | | | |
| | fresh unit weight | | | | [kg/m ³] | | | | |
| | air content | | | | [%] | | | | |
| | fresh concrete temperature 10 min | | | | °C | | | | |
| | fresh concrete temperature 45 min | | | | °C | | | | |
| | compr. strength 2d | | | mandatory | [MPa] | | | | |
| | compr. strength 7d | | | | [MPa] | | | | |
| | compr. strength 28d | | | mandatory | [MPa] | | | | |
| | | | | | | | | | |
| | | | | | | | | | |

Cost Calculation

| e.g. | | | | | Off | Dosage 1 | Dosage 2 | Dosage 3 |
|----------------------------|--|--|--|---------|-----|----------|----------|----------|
| Clinker | | | | [CHF/t] | | | | |
| Gypsum | | | | [CHF/t] | | | | |
| Gbfs | | | | [CHF/t] | | | | |
| Fly Ash | | | | [CHF/t] | | | | |
| Limestone | | | | [CHF/t] | | | | |
| Pozzolan | | | | [CHF/t] | | | | |
| Other MIC: | | | | [CHF/t] | | | | |
| CKD | | | | [CHF/t] | | | | |
| Additive cost | | | | [CHF/t] | | | | |
| Energy cost | | | | [CHF/t] | | | | |
| Total cost cement produced | | | | [CHF/t] | | | | |