# SINTEF REPORT

**SINTEF Building and Infrastructure**
COIN – Concrete Innovation Centre

Address: NO-7465 Trondheim
NORWAY
Location: Richard Birkelands vei 3
Telephone: +47 73 59 52 24
Fax: +47 73 59 71 36

Enterprise No.: NO 948 007 029 MVA

TITLE

**COIN P1 Advanced cementing materials**
**SP 1.1 F Reduced $CO_2$ - emissions**

**Separate grinding versus intergrinding**

**State of the art**

AUTHOR(S)

Klaartje De Weerdt

CLIENT(S)

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS, Veidekke ASA and The Research Council of Norway

| REPORT NO. | CLASSIFICATION | CLIENTS REF. | |
|---|---|---|---|
| SBF BK A07022 | Unrestricted | Terje F. Rønning | |
| CLASS. THIS PAGE | ISBN | PROJECT NO. | NO. OF PAGES/APPENDICES |
| Unrestricted | 978-82-536-0986-7 | 3D006010 | 30 |
| ELECTRONIC FILE CODE | | PROJECT MANAGER (NAME, SIGN.) | CHECKED BY (NAME, SIGN.) |
| | | Harald Justnes | Hara ld Justnes |
| FILE CODE | DATE | APPROVED BY (NAME, POSITION, SIGN.) | |
| | 2007-07-17 | Tor Arne Hammer, Centre Manager | |

ABSTRACT

The main difference between intergrinding and separate grinding of a multi-component cement is that during intergrinding the different components interact with one another. The interactions between the constituents are mostly due to the relative difference in grindability.
When discussing the grindability and the particle size distribution (PSD) of blended cements, one should be careful with comparing results. Grindability can be expressed in different ways and the PSD is strongly dependent on the type and size of the mill. During grinding the PSD changes progressively, hence results can differ a lot at different finenesses, energy consumption levels or grinding times.
In a two-component system some general trends have been observed. In the early period of grinding (at low fineness), the harder component will enrich in the coarser fraction and the softer will dominate the finer fraction of the PSD. The harder component stays coarser and abrades the softer one. The softer component will get a wider PSD and the harder one will get a narrower PSD.
Upon progressed grinding the breakage of the harder component starts and it approaches gradually the smaller and softer ones. As a result, it has been seen that after a considerable time of grinding or at a high fineness, the difference between intergrinding and separate grinding is less than when compared in the early stage of grinding or at low fineness.
Some remarkable interactions have been observed for example softer components shielding the relatively harder components and thereby preventing them from further grinding, or agglomeration of the finer particles upon continuous grinding leading to a sudden decrease in Blaine fineness.
Easier grindable compounds develop a wider PSD and have a beneficial effect on the water demand of the blended cement due to improved particle packing.
Whether separate or intergrinding is preferred depends on which mineral admixtures are used, at which replacement levels, how fine or how long they are ground and what strength and durability properties are required. However, when a constituent of the multi-component cement can not reach its required fineness by intergrinding due to preferential grinding of another easier grindable component, it is clear that the separate grinding technique should be applied.

| KEYWORDS | ENGLISH | NORWEGIAN |
|---|---|---|
| GROUP 1 | Materials technology | Materialteknologi |
| GROUP 2 | Concrete | Betong |
| SELECTED BY AUTHOR | Grinding | Maling |
| | Cement | Sement |
| | Blended | Blandet |

# Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.sintef.no/coin

# TABLE OF CONTENTS

# 1 Introduction

Blended cements are made out of clinker and mineral additions such as: GBFS, fly ash, pozzolan, limestone, burnt clay, etc. Replacing part of the clinker causes not only a reduction in the consumption of natural resources, fossil fuel and in the gas emissions, but can also contribute to better concrete properties in both fresh and hardened state..

The properties and performance of blended cements are affected by the proportions and the reactivity of the mineral additions but also to a large extend by the particle size distribution (PSD). The different components of the blended cement each need to obtain certain fineness in order to be hydraulically, latent hydraulically or pozzolanically effective [3]. The PSD of blended cements also plays an important role in optimizing the water demand and the workability of concrete. By adapting the PSD of the mineral additions and clinker to each other, the packing can be optimized and the void space between the cement particles can be minimized. The water, formerly filling the voids between the cement particles, can act as lubricant and coat the particles with a film of water so that the constituent particles can move freely. Consequently the workability is improved for a given w/c ratio and alternatively the water demand required to produce a desired slump is reduced.

Blended cements can be produced in two ways: by intergrinding the components or by separate grinding and mixing them. With the intergrinding process all components of the blended cement are ground together. In that way the cement is homogenized during the grinding, and at the concrete plant only one silo is needed. Because of interactions between the different cement components due to differences in grindability, the PSD of the blended cement and the different components is difficult to control [3].The second technology consists of separate grinding and storing of the components and finally mixing according to the desired proportions. This process has several advantages: the PSD of each component and of the blended cement can be controlled and, according to the components hardness and required fineness, appropriate grinding equipment can be used for each component. But in this case several silos for storage are needed at the concrete plant.

The PSD of the interground blended cement is, in addition to the chemical and physical properties of the materials, controlled by the grinding equipment and on the duration of the grinding.

Grinding of cement is an important topic when it comes to energy consumption. The clinker grinding is responsible for around 40% of the total energy usage during cement production [21]. Therefore intergrinding is a potential way of saving considerable amount of energy since some mineral admixtures have a clear positive influence on the grindability of clinker.

# 2 Background

When comparing intergrinding and separate grinding, the difference in grindability between the components plays an important role. But grindability can be expressed in many different ways. The same goes for the characterisation of the fineness of the blended cement which can be given as a PSD or as specific surface area, each based on different measurement principles. One must be careful when comparing results, hence a short overview is given.

## 2.1 Fineness

The fineness of cement is often expressed as specific surface area. The specific surface area is however not a definitive feature for fineness since powders with different PSD can still have the same specific surface area. The preferred characterisation of the powder blend is thus given by the PSD.

### 2.1.1 Particle size distribution

There are different methods to determine the particle size distribution (PSD), each of which giving different results [36].

The weight percentage passing *sieves* can be applied to describe the fineness but this technique can only be used for the particles coarser than about 45 µm. Air jet sieves can be used for finer fractions.

Other widely used methods, which measure a broader size range, are based on either sedimentation of particles in liquid or by diffraction of light. In the *X-ray sedigraph*, sedimentation is monitored by the absorption of an X-ray beam. The PSD is calculated from these measurements using Stokes's law. For an older method, the *Andreason pipette*, also based on Stokes law, samples are taken from a suspension at a certain depth at various times and their solid content is determined. In *laser granulometry*, based on the principle of Fraunhofer diffraction, the PSD is calculated from the dispersion pattern formed by a laser-beam after passing through the suspension.

Yet another technique is based on the *electrical sensing zone method* [40]. The particles are suspended in a weak electrolyte solution. As the particles pass through an aperture, they momentarily increase the impedance of the aperture. From this change in impedance, which is proportional to the three dimensional volume of the particle, the number, volume, mass and surface area size distribution can be calculated.

*Light microscopy* and *SEM* can give additional information on the both particle size and shape.

The PSD of cements can be described to a good approximation by a two parameter mathematical model, the *Rosin-Rammler* (RR) *distribution function* also called *Rosin-Rammler-Sperling-Bennet* (RRSB) distribution function [35],[36]:

$$R(x) = \exp\left[\left(\frac{x}{x'}\right)^{n}\right]$$

R(x) is the weight fraction of the particles larger than x, x is the particle diameter in mm, x' is the position parameter also called characteristic diameter wherefore R(x') = $e^{-1}$ =0.368 and n is the uniformity index. The RRSB granulometric diagram with a ln ln 1/R(x) scale on the ordinate and a ln x scale on the abscissa, gives a straight line with slope n as can be seen in Fig. 1. The characteristic diameter x' characterizes the fineness of the RRSB distribution and the slope n of the RRSB straight line is a measure of the width of the distribution. The larger the value of n, the narrower is the distribution.

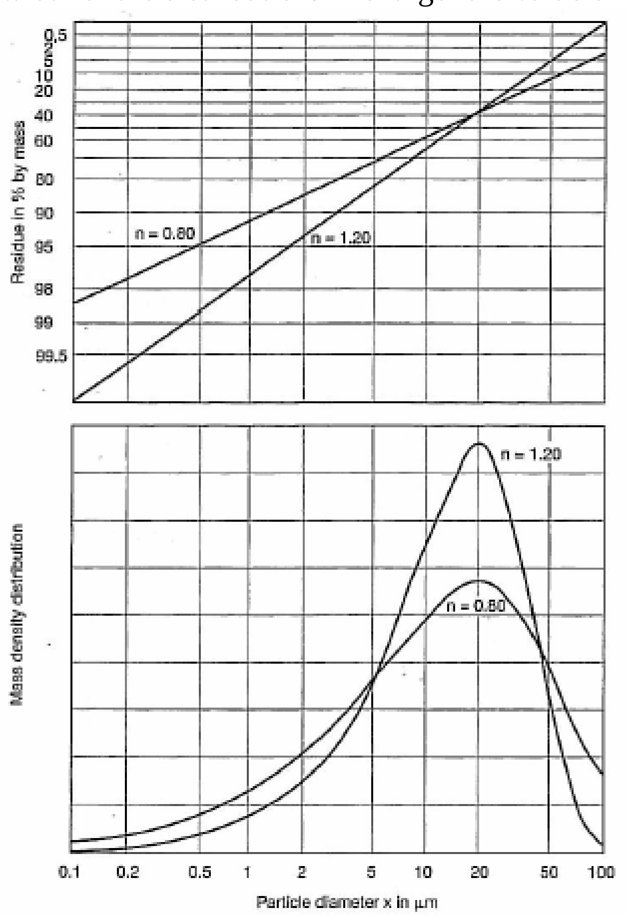



Fig. 1: Particle size distribution; top: cumulative mass distribution in the RRSB granulometric diagram; bottom: mass density distribution in the coordinate system with logarithmic scale on the abscissa.

Comparing particle size distributions can then be limited to comparing the Rosin-Rammler parameters: x' and n. During grinding x' decreases continuously. In the early stage of grinding n increases but at a certain specific surface n starts to decrease after having reached a maximum. At that point aggregation occurs. From Fig. 2, one can see that the uniformity index n of the clinker sample has a maximum value at about 320 $m^2$/kg specific surface area. It then begins to decrease due to interaction of particles (aggregation). Slag on the other hand can be ground without aggregation up to 400 $m^2$/kg.

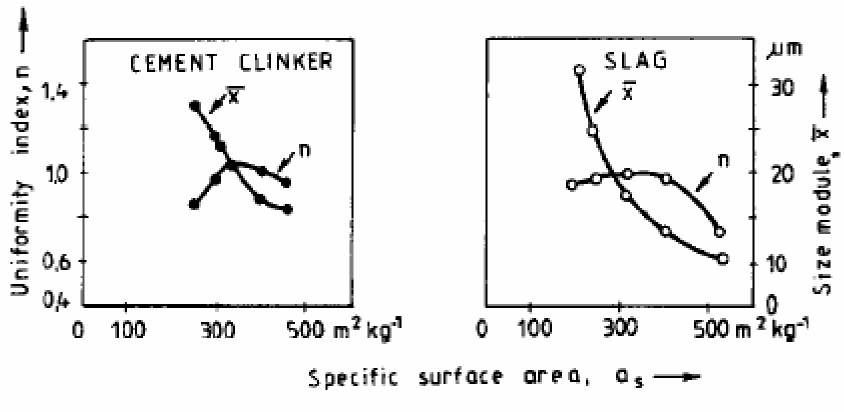



Fig. 2: The RRSB characteristics of clinker and slag: C, clinker, S, slag [2].

### 2.1.2 Specific surface area

In the cement industry, the specific surface area of cement is most often determined with the *Blaine air permeability* apparatus. The time necessary to get a fixed amount of air through a bed of cement under defined conditions is measured. And the specific surface is calculated from the air permeability of the bed of cement, its porosity, its density and the viscosity of the air.

Another method to determine the specific surface area is the *BET (Brunauer-Emmet-Teller) gas adsorption*. By measuring the amount of adsorbed nitrogen gas at -196°C for different $N_2$ partial pressures, one can calculate the monolayer capacity and then the specific surface area. The BET method gives between two and three times higher values than the air permeability method, since it measures all surfaces including that of the pores that are only open at one side, internal surfaces and micro-cracks.

The relative difference between the specific surface determined with the Blaine method and according to BET can give relevant information concerning agglomeration and formation of flakes [9].

## 2.2 Grindability

Grindability has been defined in many different ways. It can for example be the energy consumed to grind to a certain fineness, specified by weight fraction below a certain cut (kJ/kg) or by specific surface area (kJ/$m^2$). It can also be the rotational frequency of the mill per specific surface area (kg/$m^2$), or the specific surface formed during unit time ($m^2$/kg min), and even the Bond index related to unit surface area (J/$m^2$) [2].

The three commonly used methods are described by: Zeisel [35], Bond [34] and Hardgrove [34]. A short description of these methods will be given. One should always be aware of the limits of these methods for estimating the amount of energy needed for industrial cement grinding, since the tendency of the fine fraction to agglomerate and hinder further comminution is greater in the test equipment than in industrial ball mills [35].

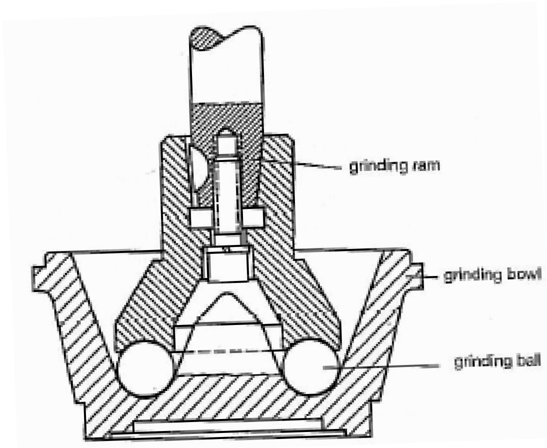



Fig. 3: Grinding bowl and grinding ram of the Zeisel grindability test equipment [35].

The equipment for the *Zeisel grindability test* is shown in Fig. 3. It consists of a grinding bowl and eight circulating grinding balls which are loaded and driven by a grinding ram. In the original process 30 g of material to be tested with a particle size between 0.8 mm and 1.0 mm is comminuted. The specific surface area is used as a measure of the progress of comminution, and the deflection of the rotatable grinding bowl acting against the force of a torsion spring is used to measure the energy expended for grinding. After a given number of rotations of the grinding ram, a sample is taken from the grinding bowl and the specific surface is determined and then ground again. After several such grinding steps the relationship is obtained between the quantities of specific energy in kWh/ton which have to be expended to generate specific levels of fineness. In the modified test the fines which have been generated with a particle size less than 0.125 mm are removed from the grinding bowl after each grinding step and replaced by the same quantity of fresh material. The number of grinding ram rotations is set so that each grinding step generates a proportion of fines to be removed of 50%. The test is concluded when equilibrium has been established. This occurs when the proportion of fines removed, the grinding time, the ratio $K_i$ of the mass of fines produced to the number of grinding ram rotations and the measured power consumption per grinding step remained constant for three grinding steps in succession. A parameter for grindability of the mill feed is obtained from the ratio $K_i$ of the last grinding step, the specific surface area calculated from the PSD and the power consumption required. The Zeisel grindability $W_t$ is expressed in kJ/kg.

The *Bond grindability test* has been widely used for the predictions of ball and rod mill energy requirements. According to Bond, the specific work demand of in-plant grinding ($W_B$) is [33],[34]:

$$W_B = W_i \cdot \left( \frac{10}{\sqrt{x_{80}}} - \frac{10}{\sqrt{X_{80}}} \right) \text{, kWh/t}$$

where $X_{80}$ is the 80% particle size (µm) of the feed and $x_{80}$ is that of the mill product; $W_i$ is the Bond work index which is the specific work demand (kWh/t) for grinding from infinite particle size to 100 µm. Bond developed a measuring method for determining the $W_i$ material characteristic. The work index ($W_i$) can be determined from laboratory measurements using the following formula:

$$W_i = \frac{4.9}{x_{\max}^{0.23} \cdot G^{0.82} \cdot \left( \frac{1}{\sqrt{x_{80,m}}} - \frac{1}{\sqrt{X_{80,m}}} \right)} \text{, kWh/t}$$

where $x_{max}$ is the grinding fineness (hole size of the checking screen used at the laboratory grinding, usually 100 µm), $X_{80,m}$ is the 80% particle size (µm) of the feed of the laboratory mill, and $x_{80,m}$ is that of the mill product; G is the grindability factor (g/revolution), i.e., the mass of material with particle size $<x_{max}$ produced by the laboratory mill during 1 revolution. The purpose of the laboratory measurements is to determine the G factor. As for the Zeisel grindability a multistage closed-circuit dry grinding process is carried out until equilibrium is reached. For determination of the Bond grindability 700 $cm^3$ of bulk material <3.3 mm is fed into the laboratory mill. At the end of each grinding cycle the entire product is discharged from the mill and screened on a test sieve. The oversize fraction (>100 µm) is returned to the mill for a second run together with fresh material to make up the original weight corresponding to 700 $cm^3$. The weight of product per unit of mill revolution, called the ore grindability of the cycle, is then calculated and used to estimate the number of revolutions required for the second run, equivalent to a circulating load of 250%. The process is continued until a constant value of grindability is achieved, which is the equilibrium condition. The average value of the last three cycles is taken as the standard Bond grindability (G), which is the net grams of undersize produced per mill revolution.

The *hardgrove process* was developed in the US for grindability tests of coals. The essence of the process is as follows [34]: a 50g 590-1190 µm coal sample is ground in a ASTM D409 type bearing mill for up to 60 revolutions and then the mill product is screened through a 74-µm screen for 20 min using a Retsch screening machine. Hardgrove-index:

$$H = 13 + 6.93m_H$$

where H is the Hardgrove index and $m_H$ the mass (ing) of the particles smaller than 74 µm. One always has to carry out two parallel measurements, the relative deviation of which cannot exceed 3%.

# 3 Literature

When discussing the different influence of intergrinding and separate grinding of blended cement, one should always take into account the chemical and physical properties of the ground materials, the grinding time, desired fineness or energy consumption, and the grinding equipment.

## 3.1 Chemical and physical properties of ground materials

The interactions between the different constituents of blended cement during intergrinding strongly depend on their relative grindability. The grindability in its turn depends on the origin of the component and their physical and chemical properties. In Fig. 4 an example of difference in grindability between some commonly used mineral admixtures is shown. It should be noted that though trass is easier grindable than slag, trass needs to be ground much finer than slag in order to be pozzolanically effective [3]. In the following some specific characteristics of clinker, gypsum, limestone, fly ash, slag and natural pozzolan in relation to separate grinding and intergrinding will be discussed.

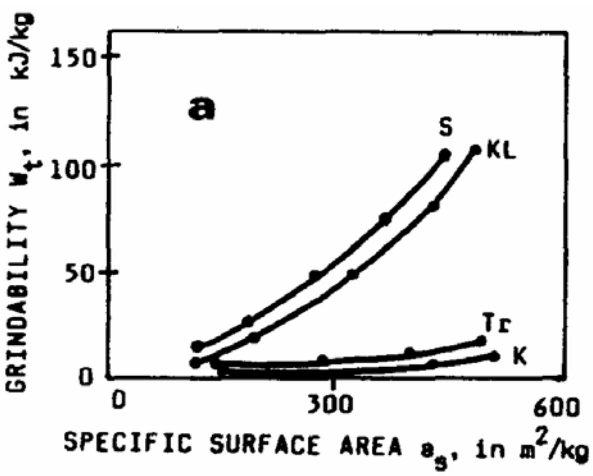



Fig. 4: Grindability (Zeisel) of S = Slag; KL = clinker; Tr = trass and K = limestone [1].

It can be interesting to determine the PSD of the different components, after they have been ground together. In the studies described in the following sections different methods have been used. Generally the ground material is first divided up in to different particle size fractions by means of a Andreasen [3],[5] or Alpine apparatus [1],[3],[5],[31]. The first apparatus is based on the sedimentation method and the second one is a kind of air-classifier. Then the content of the different components in each fraction is determined using heavy liquid centrifugation [3], [32], chemical analysis [1],[3],[31],[32], thermal analysis [5], X-ray analyses or electron microscopy [2].

### 3.1.1 Clinker

The chemical composition and the manufacturing conditions have an influence on the grindability. For example M. Tokyay [25] performed a study on 15 commercial clinkers showing a wide range of chemical composition. He found that the $Al_2O_3$ and the free CaO content, silica modulus (SM), liquid phase ($L_p$) and ratio of silicates to fluxes [($C_3S + C_2S)/(C_3A + C_4AF$)] influenced the grindability. Another example is the beneficial influence of rapid cooling on the grindability [35].

One can influence the clinker grindability by adding transition metal oxides or calcium sulphate to the raw meal [4],[39]. They influence the melt content in the kiln and the porosity of the clinker.

S. Tsivilis et al. [30] investigated the effect of the PSD of cement on the strength development and found that optimal PSD is continuous and steep (high n), has a high content in the 3-32 µm fraction and especially in the 16-24 µm fraction, a low content of very fine particles and a Blaine fineness between 250 and 300 $m^2/kg$.

D.P. Bentz and C.J. Haecker [26] claimed that the effects of the PSD of the cement and the w/c ratio must be considered concurrently when studying hydration kinetics of Portland cements. For low w/c ratios, at long enough times, model results indicate that the effects of PSD on the degree of hydration become insignificant. The difference in degree of hydration between two different cements with a characteristic diameter 5 and 30 µm is negligible at a w/c ratio 0.246 after approximately 80 days of curing.

### 3.1.2 Gypsum

A small quantity of gypsum (<5%) is usually added to the clinker to control setting. It is generally known that gypsum significantly improves the grindability of the clinker. This action has been attributed to its ability to prevent agglomeration and coating of powder on the balls and the mill chamber.

In [17] D. Touil pointed out that the addition of 4.5% gypsum, when grinding cement clinker to a fineness of 250-400 $m^2/kg$, decreases the specific energy (kWh/t) expended by about 30% compared to grinding performed without gypsum.

According to I. Tanaka et al. [24] clinker powder has a positive charge electrical and gypsum powder a negative charge, see Fig. 5. This might be an interesting way of approaching the interactions between the different components of blended cements during intergrinding.

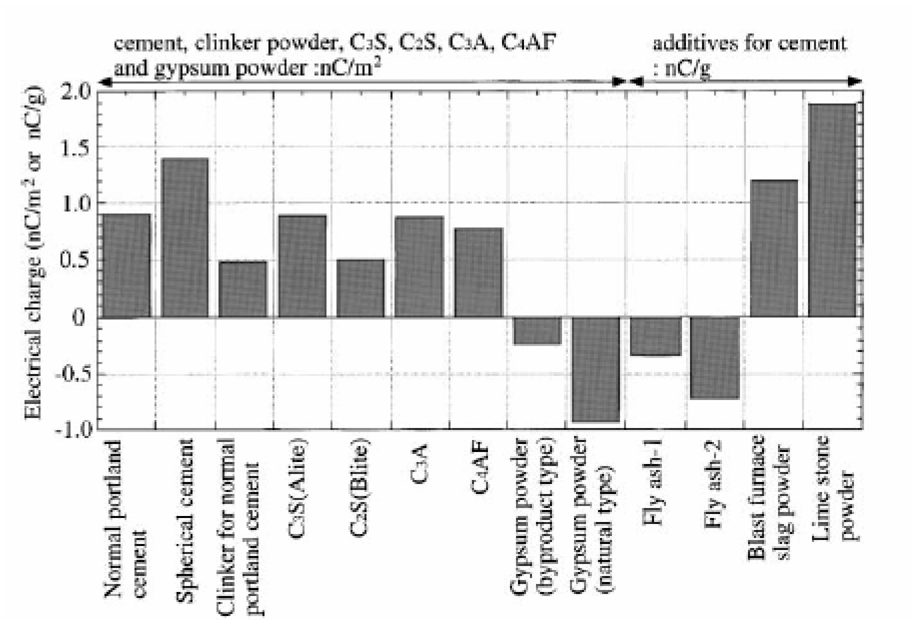



Fig. 5: Electrical charges of cement and its constituent materials [24].

### 3.1.3 Limestone

S. Tsivils et al. [5] and B. Von Schiller and H.G. Ellerbrock [29] studied the intergrinding of clinker and limestone. They found that when limestone was interground with clinker, it widened the PSD of the cement (see Fig. 7). The component which was the hardest to grind, clinker, was found in the coarser fraction whilst the easier to grind one, limestone, was concentrated in the finer fraction (see Fig. 6). The addition of limestone with a wide PSD led to a decreasing water demand per volume dry material and improved the workability.

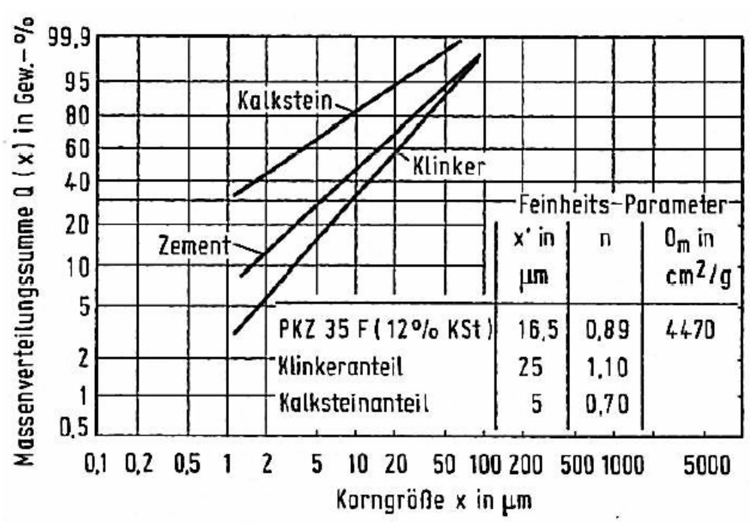


Fig. 6: Cumulative mass distribution of a limestone cement with limestone content of 12wt.% and of its clinker and limestone components after grinding [29].

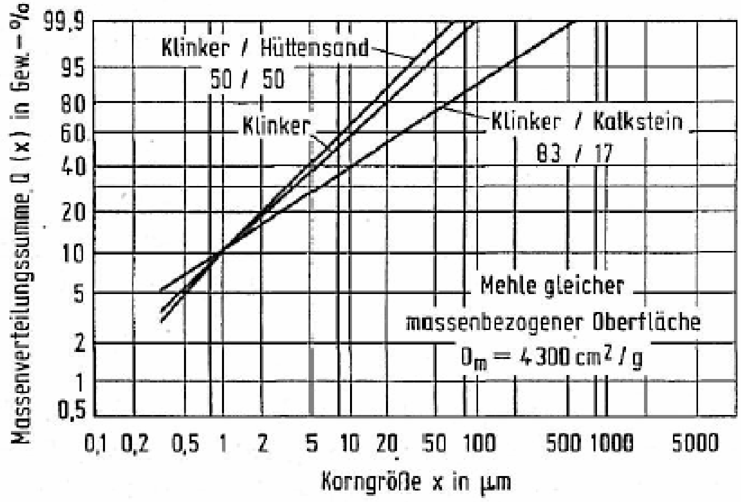



Fig. 7: Particle size distribution of interground clinker/slag and clinker/limestone with equal Blaine specific surface [29].

S. Tsivils et al. [5] observed a remarkable trend. As the limestone content surpassed 30%, the grinding of both clinker and limestone was inhibited. Samples containing 40% limestone show in spite of a higher Blaine specific surface (due to the higher limestone content) a lower clinker and limestone fineness compared to those containing 30%. B. Von Schiller and H.G. Ellerbrock [29] experienced a similar phenomenon when increasing the limestone content from 12 to 20 wt.%. The fineness of the limestone cement namely decreased and its PSD became narrower.

B. Von Schiller and H.G. Ellerbrock [29] found that to obtain a 50MPa 28 day compressive strength the limestone cement has to be ground increasingly finer as the limestone content augmented. The cement had to have a characteristic diameter x' of 30 µm when no clinker was replaced by limestone, 26 µm for 10 wt.% replacement level, 14 µm for 20wt.% and it is impossible to obtain that strength for a limestone cement containing 30wt.% limestone. This led to the conclusion that for a strength level of 50 MPa not more than 15-20 wt.% limestone should be applied in limestone cement.

N. Voglis et al. [19] compared blended cements produced with 15% limestone, natural pozzolan or fly ash. The limestone cement had the highest energy consumption for grinding, required to obtain the same 28 day compressive strength. It had the highest Blaine specific surface and widest PSD (lowest n). Up to seven days the limestone cement exhibited the highest value of compressive strength, while the fly ash cement showed the lowest value in strength. The reason for this behavior is the filler effect of the fine particles of limestone, the higher clinker fineness in the limestone cement and the low rate of the pozzolanic reaction in the fly ash cement. For the period 28-540 days, the strength development is very significant in case of OPC and the fly ash cement, while the limestone cement showed the lowest rate of strength development.

### 3.1.4 Fly ash

N. Bouzoubaâ [28] and J. Payá et al. [8] both performed a study on the influence of the time of grinding on the properties of fly ash. The former ground the blended cement for 2, 4, 6, 8 and 10 hours and the later ground for 10, 20, 30, 40 and 60 min. Some of the results are shown in Fig. 8 and Table 1. It can be seen that increase in Blaine was most significant at the beginning of the grinding and that further grinding was less effective. The fact that the strong increase in Blaine fineness coincides with an increase in specific gravity at the start of grinding, indicates the presence of cenospheres, plerospheres and irregular particles in the original fly ash. These particles are crushed during the first stage of grinding. Grinding strongly affected the morphology and shape of the fly ash particles, rounded particles are crushed into sharp edged pieces. This on its turn affects the water demand of the concrete as the ball bearing effect of the originally rounded particles is destroyed. The increased fineness on the other hand seems to result in an improved reactivity (i.e. crushing of hollow spheres would increase avaible glassy wall surface to alkaline water).

J. Payá et al. [8] observed a small change in the mineralogical composition of fly ashes caused by the grinding: an increase of the calcium carbonate content in fly ash, due to partial combustion of carbon particles and following reaction with calcium oxide.

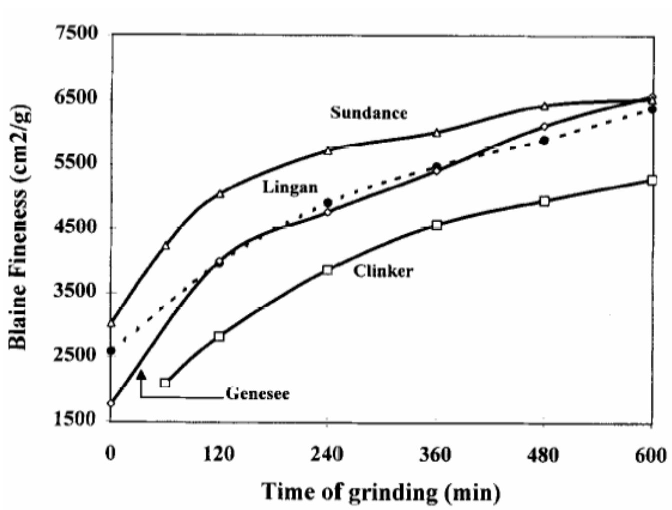



Fig. 8: The effect of grinding on the Blaine fineness of clinker and three different fly ashes [28].

Table 1: Granulometric and fineness parameters for ground fly ash [8].

| Fly ash | Mean diameter $d_m$ * (μm) | Median diameter $d_{50}$ (μm) | Specific gravity ρ (g/cm³) | $S_v$ † ($m^2/cm^3$) | $S_m$ † ($cm^2/g$) | $S_b$ † ($cm^2/g$) |
|---|---|---|---|---|---|---|
| T0 | 32.19 (3.62) | 15.64 | 2.44 | 0.971 | 3980 | 2810 |
| T10 | 13.48 (1.44) | 7.86 | 2.60 | 1.620 | 6230 | 3560 |
| T20 | 9.96 (1.03) | 6.00 | 2.68 | 1.871 | 6980 | 4320 |
| T30 | 8.49 (0.86) | 5.21 | 2.65 | 1.975 | 7450 | 4860 |
| T40 | 6.91 (0.69) | 4.13 | 2.64 | 2.245 | 8500 | 4930 |
| T60 | 5.93 (0.57) | 3.58 | 2.69 | 2.403 | 8930 | 5670 |

* Standard deviation values are given in parentheses

† Specific surface: $S_v$ and $S_m$ are calculated surfaces per volume unit and per mass unit respectively; $S_b$ represents Blaine fineness

When comparing compressive strength of interground and separate ground fly ash cement the results are not consistent. N. Bouzoubaâ [7] found that when fly ash and Portland cement clinker (55:45%) and a small amount gypsum were ground to a Blaine fineness of 450 $m^2/kg$, the interground cement had a lower compressive strength than the separate ground one at all ages (1, 7, 28 and 90 days). This may be attributed, at least in part, to the lower fineness value of clinker in the interground cement. On the other hand, it appeared that after 4 hours of grinding, the compressive strength of the interground fly ash cement was higher than the separate ground one for all recorded ages (1, 7 and 28 days). This may be due to higher homogeneity. F.M. Kilickale and K. Celik [13] replaced 9, 14 and 19 wt.% of Portland cement with fly ash and ground it to Blaine finenesses of 350 and 370 $m^2/kg$. They found that the separate grinding technique leads to a higher 7 and 28 day compressive and flexural strength than the intergrinding technique. The blended cements show lower compressive and flexural strength than the control Portland cement.

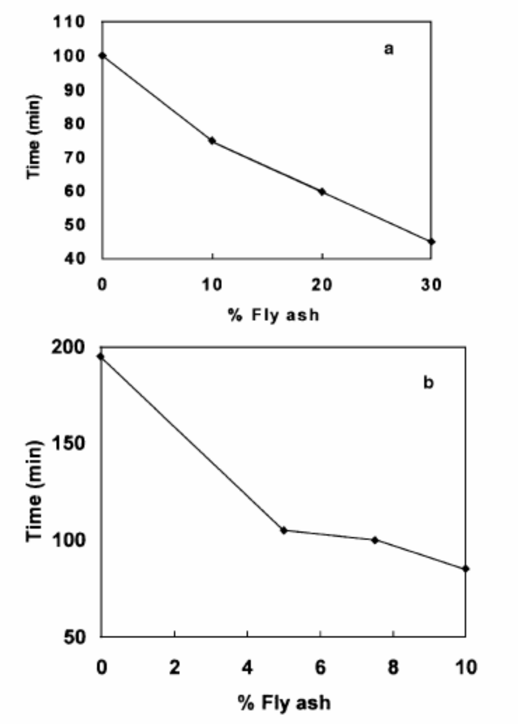



Fig. 9: Effect of fly ash on the grinding time. Replacement of clinker by fly ash in (a) limestone cement, (b) OPC [23].

From the results of the study of I. Elkhadiri et al.[23], shown in Fig. 9, one can see that replacing clinker by fly ash in OPC and in limestone cement (13wt.%) considerably reduced the grinding time to obtain the same weight percentage retained on the 80 µm sieve.

N. Bouzoubaâ [7] composed blended cements with 55% fly ash. Through the addition of the fly ash the time required to obtain the same Blaine fineness as the laboratory cement (400, 450 and 500 $m^2/kg$) was also significantly reduced.

### 3.1.5 Slag

The influence of slag on the grindability of blended cement varies widely.

L. Opoczky [1] composed blended cement by intergrinding clinker, slag and limestone (72.5:17.5:10.0%). The Zeisel grindability (kJ/kg) of this three component system was better than the clinker's grindability.

B. Von Schiller and H.G. Ellerbrock [29] interground 50wt.% slag and 50wt.% clinker. In this case the blended cement had a worse grindability than the clinker and it seemed that it was energetically more advantageous to grind clinker and slag separately.

The grindability difference between interground and separate ground slag cement is, besides the composition of the blended cement, strongly dependent on the replacement level, as shown in Fig. 10 by L. Opoczky [2] and in Fig. 11 by M. Öner [10]. L. Opoczky [2] found that when producing slag cement the Bond grindability W and the work index $W_s$ are more advantageous at lower and at higher slag contents (<25wt.% and >75wt.%) in case of simultaneous grinding, while in the central part of the curve (>25wt.% and <75wt.%) they are more advantageous in separate grinding. Whereas the experiments of M. Öner [10] pointed out that the grindability, specific grinding energy per specific surface, of a mixture of slag and clinker was better than the weighed average of the grindability of the components, for all slag additions.

One can clearly see from Fig. 10 and Fig. 11 that the energy consumption for grinding increases as the slag content increases. To obtain the same 28 day compressive strength (50MPa) for slag cement (50:50wt.%), a coarser slag (x'=30.9) requires to be blend with a finer clinker (x'=12) than a finer slag (x'=21,2/17). To obtain the same compressive strength, it is energetically more advantageous to compose slag cement with a coarser slag and a finer clinker than with a finer slag with a coarser clinker [27].

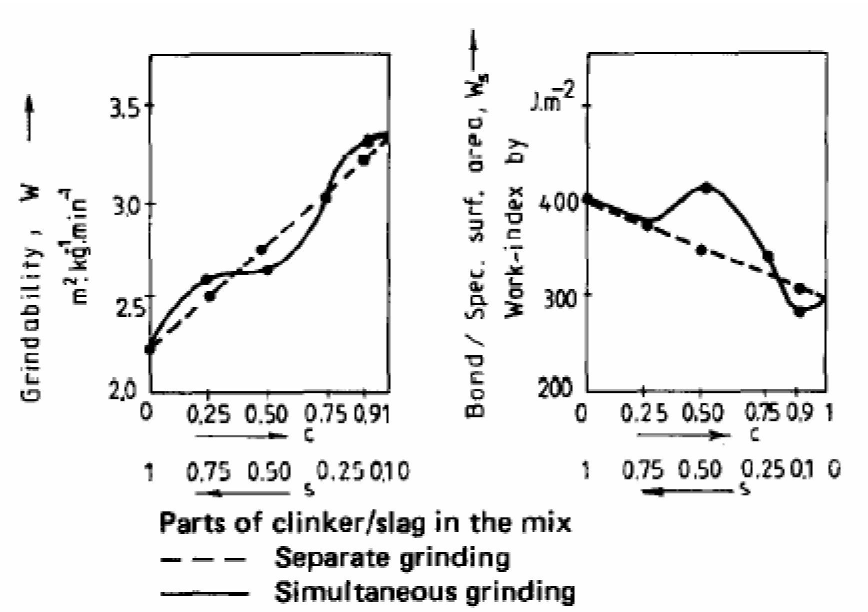



Fig. 10: Grindability and Bond index of clinker + slag mixtures. C, clinker; S, slag [2].

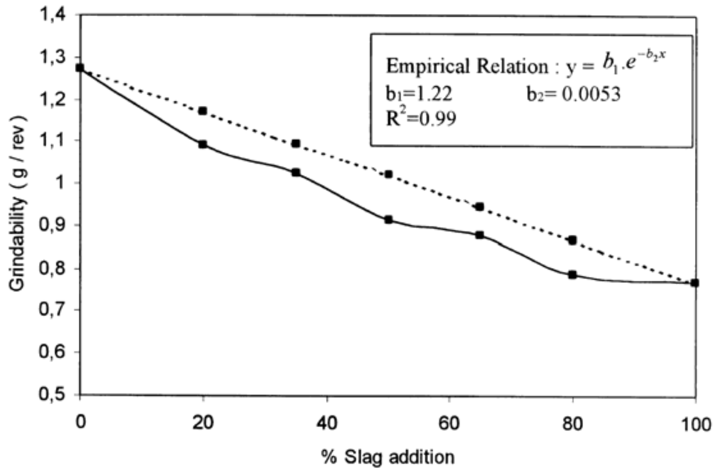



Fig. 11: Variation of grindabilities of clinker, slag and their mixtures [10].

Simultaneous grinding leads to an enrichment of clinker particles in the finer fractions and slag particles in the coarser fractions [2][10][11][14][29]. The PSD of the interground slag cement is narrower than the reference Portland cement (see Fig. 7).

Comparing Fig. 6 and Fig. 13, it can be seen that when clinker is interground with slag the clinker has a finer (smaller x') and wider (lower n) PSD than to when it is interground with limestone.
From these results it can be concluded that during intergrinding the PSD of the softer to grind component becomes finer and wider and the PSD of the harder to grind one becomes coarser and narrower [29].

The enrichment of slag particles in the coarser fraction can have a detrimental effect on the strength development of slag cement since slag requires a certain fineness (400-450$m^2$/kg) to have an appropriate hydraulic activity, see Fig. 12. According to the experiments in [2] the fineness requirements for slag can not be fulfilled through simultaneous grinding at a 40wt.% slag content and thereby result in a significant loss of hydraulic activity of the latter.

In [10] the interground slag cement (50:50%) has lower strength values, particularly at late curing ages (28 day) compared to separate ground slag cement with the same composition and the same Blaine fineness (300 $m^2$/kg). Separate grinding leads to finer cement at the same Blaine fineness because of a different PSD. The slag particles are finer in the separate ground slag cement.

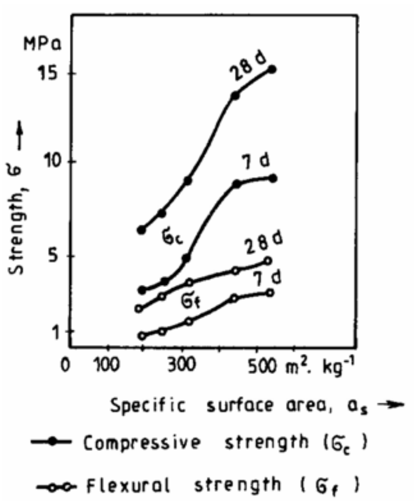



Fig. 12: Hydraulic activities of ground slag [2].

B. Li et al. [11], F.M. Kilickale and K. Celik [13], H. Binici et al. [14][18] and B. Von Schiller and H.G. Ellerbrock [29] made blended cements with a slag content ranging from 5% to 30 % and a Blaine fineness between 250 $m^2$/kg and 500 $m^2$/kg with or without other mineral admixtures (fly ash, natural pozzolan, limestone). They all found that separate grinding led to superior strength development compared to intergrinding. The fine ground slag cements could even exceed the 28 day compressive strength of the reference Portland cement. Separate grinding seemed to be advantageous according to sulfate resistance and gave rise to a lower heat of hydration [14].

During intergrinding or separate grinding to a Blaine fineness of 320 $m^2$/kg, the water demand of the cement decreases as the replacement level of slag increases (30-70wt.%). For an equal 28 day compressive strength (52MPa) and increasing slag content the water demand stays more or less constant during intergrinding [27].

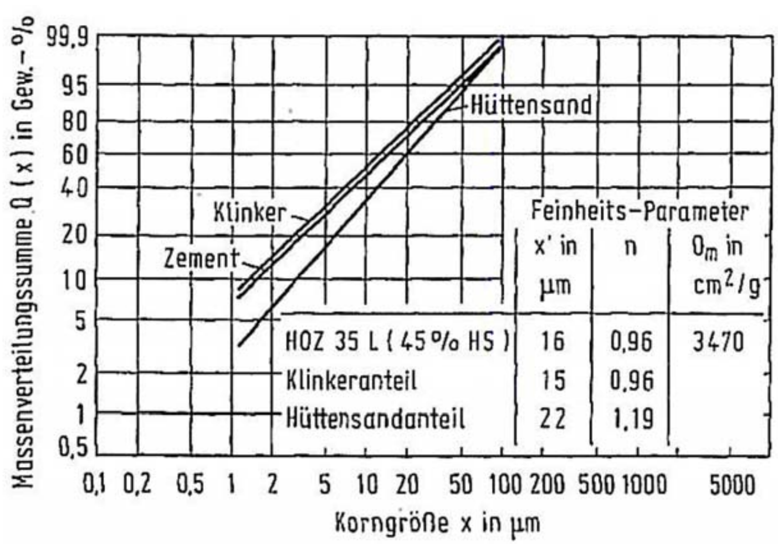


Fig. 13: Cumulative mass distribution of a slag cement with slag content of 45wt.% and of its clinker and slag components after grinding [29].

### 3.1.6 Natural pozzolan

The impact on the grindability and the PSD of cement by replacing part of the clinker by a pozzolan can differ widely due to the great range of possible chemical and physical properties of natural pozzolans.

K. Erdogdu et al. [6] replaced 25% of the clinker with a natural pozzolan and T.K. Erdem et al. [15] used 20% and 30% of perlite, also a natural pozzolan.
Their experiments pointed out that intergrinding led to a finer PSD than separate grinding for the same energy consumption (around 40 kWh/t), or that grinding to certain Blaine fineness (in the region of 350 $m^2/kg$) required less energy by intergrinding. The separate grinding yielded coarser particles compared to intergrinding. This refinement can be explained by the fact that during intergrinding the natural pozzolan was ground not only by the steel charges in the laboratory ball mill but also by the clinker particles. These interactions eliminated the relative coarser pozzolan particles and yielded a finer PSD for interground cements. For a given Blaine fineness and composition, the compressive strength of the mortars prepared with interground cement was generally higher than those prepared with separately ground cements. The higher compressive strength of the interground cement was due to its more beneficial PSD and higher homogeneity.
It should be noted that the difference in strength between intergrinding and separate grinding decreases with curing time of the concrete.
In Fig. 14 D. Touil et al. [17] show that besides gypsum, the natural pozzolanic additive tuff at a replacement level of 10% has a significant beneficial effect on the grinding of cement clinker by decreasing the specific energy for a given Blaine fineness, especially at high levels of fineness (400-600 $m^2/kg$).

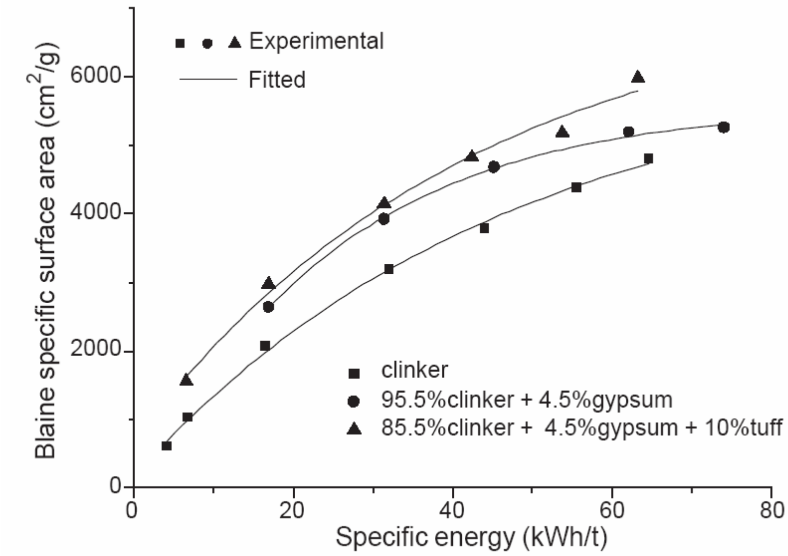



Fig. 14: Blaine specific surface of crude cement clinker feed using additional compounds versus specific energy [17].

F.M. Kilickale and K. Celik [13] replaced 9, 14 and 19 wt.% of Portland cement with trass and grinding it to Blaine finenesses of 350 and 370 $m^2$/kg. They found in contradiction to the previous authors that the separate grinding technique led to a higher 7 and 28 day compressive and flexural strength than the intergrinding technique. The blended cements show lower compressive and flexural strength than the control Portland cement.

C. Hosten and C. Avsar [12] noticed a remarkable interaction between trass and clinker during intergrinding. The clinker had a greater Bond's work index than the trass. This indicates that clinker requires more energy than trass to grind to have 80% of the material passing the 200 mesh (74 µm). But on the other hand it was found that the Bond grindability of the clinker-trass mixtures (trass content of 17 and 31 wt.%) was worse than the individual grindability of the clinker. This is probably due to the presence of relatively soft trass particles shields harder clinker particles from being ground, leading to an unfavorable effect on the mixtures grindability.
The Blaine specific surface of trass (352 $m^2$/kg) was more than double that of clinker (170 $m^2$/kg). The addition of trass to the feed proportionally increases the surface area of the ground composite product. This shielding effect, where further grinding is prevented by the softer component, has also been observed for other mineral blends like kaolin with quartz or feldspar [33].

B. Uzal and L. Turanli [22] and L. Turanli [20] composed blended cement by replaced 55% of the clinker by natural pozzolan. Different types of pozzolan and clinker were tested. They interground the components for 90 and 120 min or to a Blaine fineness of approximately 470 $m^2$/kg and made a comparison with the reference Portland cement.

For the same grinding time, a higher Blaine value was obtained and for certain Blaine fineness less time was required, when the pozzolan was interground. So according to the grinding time and the Blaine fineness values, it seemed that blended cements were easier to grind than Portland cements. This is however not true according to the percentage of material coarser than 45 μm, another fineness parameter. According to that parameter, the blended cements were coarser than the reference Portland cement. This confirms that the Blaine specific surface by itself is inadequate as a measure of fineness and should always be used together with other fineness parameters. The compressive strength of the blended cement was lower than the reference Portland cement at all ages except for 91 day compressive strength.
The different types of pozzolan used, varied in hardness. The relative hardness of the natural pozzolan and the clinker significantly affected the PSD of the high-volume natural pozzolan blended cement. The harder pozzolans contributed to a finer grinding of the clinker, whereas the softer pozzolan resulted in a relative coarser grinding of the clinker phase.

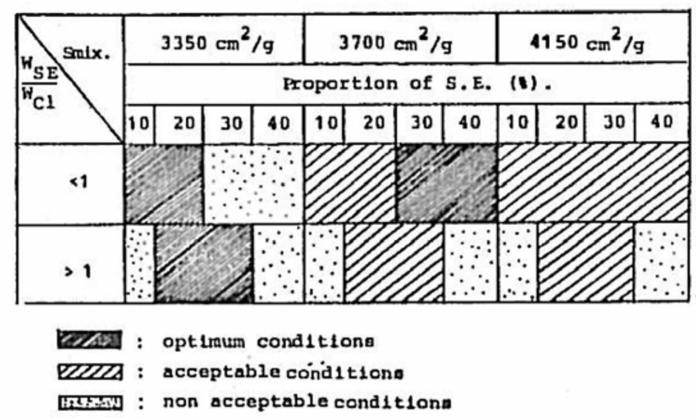
S. Tsimas et al. [32] performed a very interesting study on three component blended cements. Three different sets of blended cements were prepared. For the first set they replaced 10, 20, 30 and 40% of clinker with pozzolan. For the second sequence, 5, 10, 15 and 20% of the clinker was substituted by fly ash in a 80% clinker and 20% pozzolan blend and for the last set 5, 10, 15 and 20% of the clinker was substituted by slag in a 80% clinker and 20% pozzolan blend. All blended cements were ground to 335, 370 and 410 $m^2$/kg Blaine fineness. Intergrinding an increasing amount of pozzolan with clinker leads to a decrease of specific surface for both clinker and pozzolan. A 30-40% clinker replacement by pozzolan causes insufficient specific surface of both clinker and pozzolan. The addition of fly ash reduces considerably the specific surface of both clinker and pozzolan but gets ground fine enough itself (700 $m^2$/kg). Comparing the time required for separate grinding and intergrinding to obtain a certain Blaine fineness, it is found that for a replacement level of 10-20% pozzolan the time necessary for co-grinding is shorter than for separate grinding. Whereas for 30-40% replacement levels separate grinding is energetically favorable. Slag serves as a grinding medium for clinker and pozzolan but does not get ground fine enough itself (<250 $m^2$/kg). Slag addition has only a minor effect on the grinding time and no clear conclusion can be drawn concerning the grinding method.

S. Tsimas et al. [31] studied the effect of intergrinding Santorin earth (SE) with clinker. The SE has a special feature: it consists of a light and heavy fraction. The light fraction, rich in $SiO_2$, $Al_2O_3$ and CaO, is easy to grind while the heavy fraction rich in $Fe_2O_3$ is harder to grind. SE was added at replacement levels of 10, 20, 30 and 40% and the blended cements were ground to Blaine finenesses of 335, 370 and 415 $m^2$/kg. Depending on the Bond work index (kWh/t) of the SE (amount of hard and soft fraction) only certain replacement levels were allowed to make sure that clinker and SE were ground fine enough to be sufficiently effective (see Table 2).

The fact that the SE consists of a softer and harder phase considerably complicated the interactions during intergrinding.

Table 2: Specific surface of clinker and SE after intergrinding [31].

| Wi (KWh/st) | S.E. % | 3350 $cm^2/g$ Clinker | S.E. | 3700 $cm^2/g$ Clinker | S.E. | 4150 $cm^2/g$ Clinker | S.E. |
|---|---|---|---|---|---|---|---|
| $\frac{Clinker}{SE_1}:\frac{13.4}{14.3}$ | 10 | 3710 | 1850 | 4430 | 2600 | 5030 | 3870 |
| | 20 | 2730 | 6220 | 3070 | 6420 | 3600 | >10000 |
| | 30 | 2720 | 6380 | 2850 | 7480 | 3180 | >10000 |
| | 40 | 1800 | 6370 | 2350 | 7880 | 2640 | >10000 |
| $\frac{Clinker}{SE_2}:\frac{14.0}{12.2}$ | 10 | 2980 | 7100 | 3500 | 7680 | 3830 | 8200 |
| | 20 | 2840 | 5820 | 3280 | 6800 | 3630 | 6950 |
| | 30 | 2680 | 5650 | 3170 | 5600 | 3380 | 5900 |
| | 40 | 2600 | 5070 | 3030 | 5450 | 3210 | 5700 |




### 3.2 Duration of grinding and desired fineness

K. Erdogdu et al. [6], H. Binici et al. [14] and T.K. Erdem et al.[15] studied the difference in PSD between the product of intergrinding and separate grinding of blended cements. They used slag and/or natural pozzolan at different replacement levels (5-30%) and ground until a fixed level energy consumption or a fixed Blaine fineness. The difference in PSD decreases as the particle size considered gets smaller. This is attributed to fewer interactions between the ingredients for interground cement at small particle size. Thus, it can be stated that the interactions between the ingredients of interground blended cements mostly occur between larger particle sizes.

L. Opoczky [1] developed a theory on the interactions in a two component system during the intergrinding process. In the early period of grinding, meaning at lower fineness, the components do not interact that much and the properties of the easier grindable ones (limestone, trass) will prevail. In this period the harder grindable component is still present in an “unground state”. Upon progressed grinding the breakage of the harder component e.g. blast-furnace slag particles is starting but simultaneously that of the small ones is slowing down (due to the reduction of defects the resistance to breaking increases and particle interactions occurs). Consequently the harder larger particles gradually approach the smaller ones. In this period the positive effect of the particles upon one another (abrading effect, inhibition of particle interaction) is already effective and as a consequence of this – as well as of the better fitting together of the different morphologies of the particles next to one another – a “more compact” structure is formed.

B. Uzal and L. Turanli [22] observed a similar phenomena. They composed two blended cements with two different clinkers, natural pozzolans, and gypsum in the proportions 42:55:3 wt.% by intergrinding for 90 and 120 min and compared them to their reference Portland cement. They stated that after 90 min of grinding the amount of material retained on the 15 µm sieve was larger for blended cements than for the reference Portland cement. These coarser particles in the blended cements were attributed to the clinker component which was harder to grind than the pozzolans. However after 120 min of grinding, no coarser phase in blended cements was observed in PSD with respect to the reference Portland cement. It can be concluded that relatively low grinding times may result in coarser clinker phase for blended cements containing high volume of natural pozzolans.

It should be mentioned that during grinding the surface properties of the particles are modified. The impacts create microdefects in the structure of the material and thereby increase their surface energy and chemical reactivity. This principle is known as mechano-chemical activation.
Energetically modified cement (EMC) is based on this principle and is produced according to a special procedure of high intensive grinding of ordinary Portland cement together with different types of fillers. H. Justnes et al. [9] applied fly ash and quartz as fillers at replacement levels of 50%. The EMC treatment improved the performances of the blended cements considerable: the setting time was reduced by half, substantial strength gain was obtained (150-400% relative to untreated), and the pore structure was significantly refined. Concrete prepared with EMC cement made containing 20% and 50% quartz sand performed as in line with ordinary Portland cement with respect to production properties (setting time, workability) and compressive strength. Furthermore it showed enhanced durability properties accept for carbonation. The improved performance of EMC is attributed to an increased early hydration, better distribution of hydration products and an enhanced reactivity of the filler resulting in an extensive pore size refinement of the hardened binder [41].

### 3.3 Grinding equipment

The change of PSD during grinding strongly depends on the grinding equipment used, ranging from what type of mill e.g. ball mill, high pressure roller press or a combination, recirculation system, to the mills dimensions e.g. laboratory mill or full scale mill. Also the chemical composition of the ground cement seems to fluctuate between different mills as the temperature within the mill, caused by friction, tends to differ, giving rice to different ratios in calcium sulphate hydrates. Therefore, comparing results obtained with different equipment should always be done with care (Fig. 15).

Products from roller grinding mills and high-pressure grinding rolls have narrower particle size distributions than those from ball mills [36][38].

T.I. Fredvik [37] compared the PSD of cements ground in a full-scale mill and a laboratory mill. The results are shown in Fig. 16. There are only minor differences for the fine and coarse fractions but when focusing on the "½-value width[1]" significant differences are observed. The differences increase as the cements are ground finer: the full-scale ground cement mainly get a parallel displacement from right towards left when the cements are ground finer, whereas the laboratory ground cements in addition get a significantly wider distribution density (illustrated with the arrows in Fig. 16).

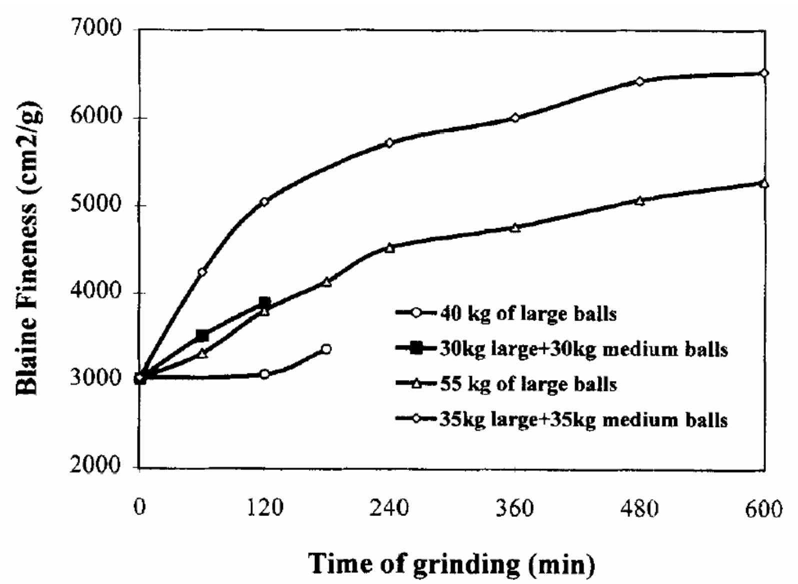



Fig. 15: The effect of the amount of grinding balls in the mill on the Blaine fineness of fly ash (10kg fly ash was in the grinding mill) [28].

[1] The 1/2 –value width refers to the width of the distribution density curves at 50% of the maximum value.

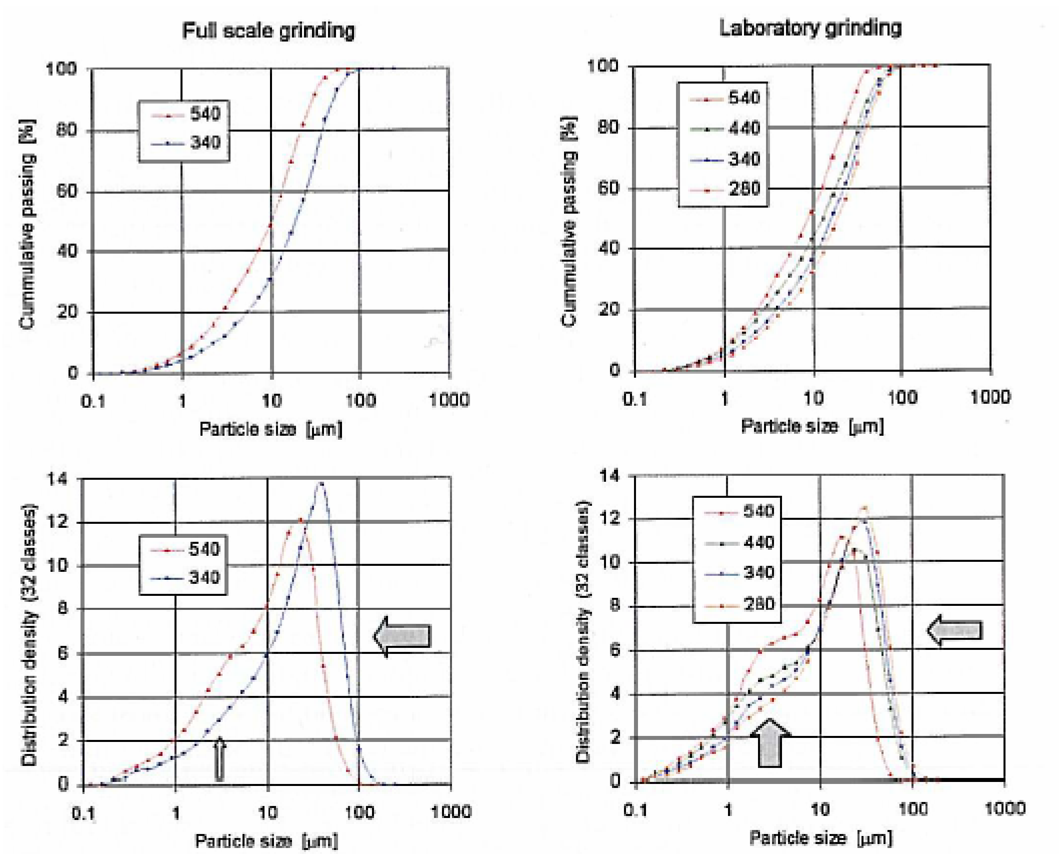



Fig. 16: Particle size distribution of cements grinded in full-scale and laboratory mill [37].

# 4 Conclusions

Whether separate or intergrinding is preferred depends on the following three criteria:

- *Technically:*
  The separate grinding process has the advantage that the PSD of the different components can be controlled, an appropriate technology can be applied for each component and that the cements can be composed according to what is wanted.
  The intergrinding process is technically simpler and homogenization takes place in the grinder. However the PSD of the different components is mainly depending on their relative difference in grindability.

- *Energy or time advantage:*
  Depending on the properties of the fillers, the amount which is added, how long and how fine they are ground and the strength and durability properties required, either separate grinding or intergrinding has an advantage (expressed in time or energy). This indicates that components can have a beneficial

influence on each other (grinding aid) or can prevent each other from being ground (e.g. shielding by softer components) whilst interground.

- *Feasibility:*
  It is possible that a constituent of the multi-component cement can not reach its required fineness by intergrinding due to preferential grinding of another easier grindable component. In that case it is clear that the separate grinding technique should be applied

# 5 Suggestions for further research

Grinding in a laboratory mill, whether separate grinding or intergrinding, will give a significantly wider PSD than in a full scale mill. The different PSD in their turn will give rise to different water demand and different strength development. Therefore in order to be representative for full scale production, the grinding tests must be carried out in full scale mills.

For concrete applications at lower temperatures, the development of sufficient early strength is crucial. Blended cements with large percentages of mineral admixtures (fly ash, trass, limestone, etc.) generally have a lower early strength. This can be attributed to a higher water/clinker ratio, the “dilution effect”, as well as the normally slower reaction of additions.
Fine grinding of the alternative raw materials has a significant effect on the initial strength development, and a well designed PSD gives rise to a lower water demand. Therefore it is clear that the optimization of the fine grinding process of clinker and mineral admixtures is of major importance for the development of an “all-round” blended cement.

# 6 References

[1] L. Opoczky, Grinding technical questions of producing composite cement, Mineral Processing, 44-45 (1996) 396-404.

[2] L. Opoczky, S. Verdes and K. Mrákovics Török, Grinding technology for producing high-strength cement of high slag content, Powder Technol., 48 (1986) 91-98

[3] S. Tsivilis, S. Tsimas and A. Moutsatsou, Contribution to the problems arising from grinding of multicomponent cements, Cem. Concr. Res., 22 (1992) 95-102

[4] S. Tsivilis and G. Kakali, A study on grindability of Portland cement clinker containing transition metal oxides, Cem. Concr. Res., 27 (1997) 673-678

[5] S. Tsivilis, N. Voglis, J. Photou, Technical note: a study on intergrinding of clinker and limestone, Minerals Engineering, 12 (1999) 837-840

[6] K. Erdogdu, M. Tokyay, P. Turker, Comparison of intergriding and separate grinding for the production of natural pozzolan and GBFS-incorporating blended cements, Cem. Concr. Res., 29 (1999) 743-746

[7] N. Bouzoubaa, M.H. Zhang, A. Bilodeau, and V.M. Malhotra, Laboratory produced high-volume fly ash blended cements: physical properties and compressive strength of mortars, Cem. Concr. Res., 28 (1998) 1555-1569

[8] J. Paya, J. Monzo, M.V. Borrachero and E. Peris-Mora, Mechanical treatment of fly ashes. Part I: physico-chemical characterization of ground fly ashes, Cem. Concr. Res., 25 (1995) 1469-1479

[9] H. Justnes, L. Elfgren, V. Ronin, Mechanism for performance of energetically modified cement versus corresponding blended cement, Cem. Concr. Res., 35 (2005) 315-323

[10] M. Oner, A study of intergrinding and separate grinding of blast furnace slag cement, Cem. Concr. Res., 30 (2000) 473-480

[11] Beixing Li, Wenquan Liang, Zhen He, Study on high-strength composite protland cement with a larger amount of industrial wastes, Cem. Concr. Res. 32 (2002) 1341-1344

[12] C. Hosten and C. Avsar, Grindability of mixtures of cement clinker and trass, Cem. Concr. Res., 28 (1998) 1519-1524

[13] F.M. Kilickale and K. Celik, Comparison between properties of separately grinded and intergrinded blended cements, 9$^{th}$ CANMET/ACI supplementary papers Warsaw, Poland 2007

[14] H. Binici, O. Aksogan, I. H. Cagatay, M. Tokyay, E. Emsen, The effect of particle size distribution on the properties of blended cements incorporating GGBFS and natural pozzolan, Powder Technol., 177 (2007) 140-147

[15] T.K.Erdem, C. Meral, M. Tokyay, T.Y. Erdogan, Use of perlite as a pozzolanic addition in producing blended cements, Cem. Concr. Comp., 29 (2007) 13-21

[16] L.M. Tavares, M.C. Cerqueira, Statistical analysis of impact-fracture characteristics and microstructure of industrial Portland cement clinker, Cem. Concr. Res., 36 (2006) 409-415

[17] D. Touil, S. Belaadi, C. Frances, Energy efficiency of cement finish grinding in a dry batch ball mill, Cem. Concr. Res., 36 (2006) 416-421

[18] H. Binici, O. Aksogan, Sulfate resistance of plain and blended cement Cem. Concr. Comp., 28 (2006) 39-46

[19] N. Voglis, G. Kakali, E. Chaniotakis, S. Tsivilis, Portland-limestone cements. Their properties and hydration compared to those of other composite cements, Cem. Concr. Comp., 27 (2005) 191-196

[20] L. Turanli, B. Uzal, T. Bektas, Effect of material characteristics on the properties of blended cements containing high volumes of natural pozzolans, Cem. Concr. Res., 34 (2004) 2277-2282

[21] A. Jankovic, W. Valery, E. Davis, Cement grinding optimization, Minerals Engineering, 17 (2004) 1075-1081

[22] B. Uzal, L. Turanli, Studies on blended cements containing a high volume of natural pozzolans, Cem. Concr. Res., 33 (2003) 1777-1781

[23] I. Elkhadiri, A. Diouri, A. Boukhari, J. Aride, F. Puertas, Mechanical behavior of various mortars made by combined fly ash and limestone in Moroccan Portland cement, Cem. Concr. Res. 32 2002 1597-1603

[24] I. Tanaka, M. Koishi, K. Shinohara, A study on process for formation of spherical cement through an examination of the changes of powder properties and electrical charges of the cement and its constituent materials during surface modification, Cem. Concr. Res., 32 (2002) 57-64

[25] M. Tokyay, Effect of chemical composition of clinker on grinding energy requirement, Cem. Concr. Res., 29 (1999) 531-535

[26] D.P. Bentz, C. J. Haecker, An argument for using coarse cements in high-performance concretes, Cem. Concr. Res., 29 (1999) 615-619

[27] A.A. Jeknavorian, E.F. Barry, F. Serafin, Determination of grinding aids in Portland cement by pyrolysis gas chromatography-mass spectrometry, Cem. Concr. Res., 28 (1998) 1335-1345

[28] N. Bouzoubaa, M.H. Zhang, A. Bilodeau, V.M. Malhotra, The effect of grinding on the physical properties of fly ash and Portland cement clinker, Cem. Concr. Res., 27 (1997) 1861-1874

[29] Von B. Schiller and H.-G. Ellerbrock, Mahlung und Eigenschaften von Zementen mit mehreren Hauptbestandteilen, Zement Kalk Gips, 45 (1992) 1951-1956

[30] S. Tsivilis, S. Tsimas, A. Benetatou and E. Haniotakis, Study on the contribution of the fineness on cement strength, Zement Kalk Gips, 43 (1990) 26-29

[31] S.Tsimas, A. Moutsatsou, S. Tsivilis, Study of the homogeneity of Santorin earth and its consequences on the cogrinding with clinker, Ciments Betons Platres Chaux, 770 (1988) 43-45

[32] S. Tsimas, S. Tsivilis, G. Parissakis, Interaction of the constituents of the mixture during a co-grinding process, Ciments Betons Platres Chaux, 748 (1984) 147-150

[33] H. Ipek, Y. Ucbas, C. Hosten, The bond work index of mixtures of ceramic raw materials, Mineral Engineering, 18 (2005) 981-983

[34] B. Csóke, Z. Hatvani, D. Papanastassiou and K. Solymár, Investigation of grindability of diasporic bauxites in dry, aqueous and alkaline media as well as after high pressure crushing, Int. J. Miner Process, 74 (2004) 123-S128

[35] F. W. Locher, Cement: principles of production and use, Verlag Bau+Technik GmbH, Dusseldrof, 2006

[36] H.F.W. Taylor, Cement Chemistry 2nd edition, Thomas Telford Publishing, London, 1997

[37] T. I. Fredvik, Initial strength development of fly ash and limestone blended cements at various temperatures predicted by ultrasonic pulse velocity, Doctoral theses at NTNU 2005:112

[38] H. Roseman, H.-G. Ellerbrock, Grinding technology for cement production – development, current situation and outlook, Zement Kalk Gips, 2 (1998) 51

[39] I. Odler, N. Zhang, Possible ways of producing Portland cement clinker which is particularly easy to grind, Zement Kalk Gips, 1 (1997) 36

[40] http://www.beckmancoulter.com/products/instrument/partChar/pc_multisizer3.asp

[41] H. Justnes, P.A. Dahl, V. Ronin, J.-E. Jonasson, L. Elfgren, Microstructure and performance of energetically modified cement (ECM) with high filler content, Cem. Concr. Composites, 29 (2007) 533-541