Development of strength and heat of hydration of young concrete at low temperature - influence of granulated blast furnace slag, silica and limestone

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DEVELOPMENT OF STRENGTH AND HEAT OF HYDRATION OF YOUNG CONCRETE AT LOW TEMPERATURE

Influence of granulated blast furnace slag, silica fume and limestone filler

Monica Lundgren

Report TVBM-3129 Lund 2005

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ABSTRACT

Mineral additions and fillers are useful and sometimes even essential in concrete. Improved durability, increased strength, lowered permeability or better workability are often achieved through using materials such as silica fume, fly ash, blast furnace slag or limestone filler with Portland cement. The use of additions/fillers in concrete also gives environmental benefits when replacing parts of Portland cement. Additions are widely used in many European countries, either added to the mixture at the construction site or as a constituent in blended cements CEM II and III.

The use of mineral additions/fillers in Sweden has been until recently comparatively limited, even though additions/fillers such as blast furnace slag and limestone filler are readily available. The main explanation for this is that in Sweden, additions and fillers are considered to delay the development of strength at early ages, particularly when curing temperatures are low. Temperatures around 5°C occur frequently on Swedish construction sites. Additions are therefore today avoided, to maintain safety when forms are removed and maintain efficiency during construction. This is due to a lack of knowledge on the behaviour of young concrete at low temperatures when additions/filler are used as part of the binder.

To improve our understanding and increase the data available, the present study investigated the development of compressive strength and heat of hydration while curing at 5°C compared with curing at 20°C. Heat and strength development were investigated for mixtures with silica fume, ground granulated blast furnace slag and limestone filler during the first week of hydration. The addition/filler was included as a part of the binder and replaced parts of the cement. Compressive strength tests were carried out on mortars and isothermal calorimetrical measurements on pastes. The study was carried out on laboratory to ensure isothermal conditions during the tests and accurate temperature control. A wide range of mixture alternatives were tested to investigate the influence of type of addition, percentage of cement replacement, water-binder ratio, age and temperature on concrete properties.

The test results were used to calculate the early-age efficiency, the k-value, of the additions. An efficiency approach for heat of hydration is also introduced. Efficiency values for strength and for heat are discussed in relation to parameters such as age and temperature. Efficiency values for compressive strength and heat of hydration are compared. Possible explanations of the filler effect are presented.

Key words: *compressive strength, early age, granulated blast furnace slag, heat development, isothermal calorimetry, k-value, limestone filler, silica fume, temperature.*

PREFACE

The work presented in this licentiate thesis has been conducted at the SP Swedish National Testing and Research Institute in Borås, Sweden, the Department for Building Technology and Mechanics, and at Lund Institute of Technology (LTH), Sweden, the Division of Building Materials. The experiments have been carried out at SP and the academic studies at LTH.

Financial support for the project was provided by

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- The Swedish Agency for Innovation Systems Vinnova AB
- Cementa AB
- SP

This is gratefully acknowledged here.

My supervisor Professor Per-Erik Petersson, head of the Department for Building Technology and Mechanics at SP and adjunct Professor at LTH, has initiated this project. He encouraged me to move towards new issues in the field of young concrete. I would like to express here my appreciation for his constructive advice and efficient support during my work. I also wish to thank him for giving me encouraging confidence and wise rational solutions.

I wish to thank my supervisors at LTH: to Professor Emeritus Göran Fagerlund for introducing me to the interesting world of concrete structural development, for his enthusiasm in raising questions and presenting ways towards an answer, and to Professor Lars-Olof Nilsson for very interesting discussions and valuable feed-back. I also thank associated Professor Lars Wadsö at LTH for him meticulously introducing the interesting field of isothermal calorimetry to me.

The strength tests would not have been possible without laboratory technician Sten Johansson (SP) backing me up. I am grateful for his careful and jovial assistance, especially during the sometimes not so comfortable tests in the 5°C-laboratory.

Thanks to Catrin Magnusson (SP) for her prompt professional help, a very good eye for the manuscript layout and for tidying up in stubborn documents.

Borås, December 2005

Monica Lundgren

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Proceedings 8th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, May 2004, Las Vegas, USA. pp. 439-454.

Appendix 2

Paper II Limestone Filler as Addition in Cement Mortars: Influence on the Early-Age Strength Development at Low Temperature

Nordic Concrete Research, Publication No 31, 1/2004. Oslo, Norway. pp. 50-63.

Appendix 3

Paper III Cement Pastes with Mineral Additions and Fillers: Heat of Hydration at Early Age and Low Temperature

Manuscript, to be published 2006.

Appendix 4

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Marcus Vitruvius Pollio, in his treatise *De Architectura*
written for the future Roman Emperor Augustus Caesar

stated that buildings should exemplify *firmitas, utilitas, venustas,*
that is buildings should be *safe, useful* and *beautiful.*

SUMMARY

In many countries all over the world, mineral additions and fillers have been used for many years in the production of cement and concrete. In Sweden, however, there has not been any large scale use of additions and fillers until recently, despite the positive effects this may have on the environment and also on concrete properties. The level of resources allocated to research and development in this field has therefore been low compared with many other countries. To increase the use of mineral additions in Sweden and to ensure this usage is safe requires better knowledge, not least where Swedish mineral additions are used under Nordic climatic conditions.

Concrete construction productivity is strongly dependent on how long after casting forms can be stripped. In Sweden, we have extensive experience with structures produced using ordinary Portland cement concrete. Safe and effective form stripping can therefore be performed using this concrete quality, including under severe climatic conditions. Conditions may though be very different where additions/fillers are used. Additions/fillers are normally considered to prolong the time to form stripping, particularly at low temperatures.

The aim of the project presented in this report, is to improve knowledge of the properties of cement and concrete produced using mineral additions/fillers at early age (during the first week after casting) and low temperatures. This will promote efficient, safe, reliable and increased use of these types of materials, particularly under winter conditions.

The work comprised two main activities: (i) determination of strength development/k-values at low temperature in young mortars with mineral additions/fillers and (ii) studying the heat of hydration in young pastes with mineral additions/fillers at low temperature and determining relationships between this and strength development.

Compressive strength tests were carried out on mortar prisms following the procedure in EN 196-1. Values of the coefficient of efficiency (the k-value for strength) were calculated based on the test results.

The development of the heat of hydration was studied on pastes by using isothermal heat conduction calorimetry. Efficiency values (k-values for heat development) were calculated from the test results, at the same age as for the k-values for strength.

Strength test ages were mainly 2 and 7 days but some 28 day values were also measured. The curing temperatures used were 5°C and 20°C.

The study was carried out using Swedish ordinary Portland cement (CEM I 52.5 R) as the main binder and the following mineral additions/fillers:

- Ground granulated blast furnace slag (*BFS*): Swedish Merit 5000 from Oxelösund.
- Silica fume (*SF*): Norwegian undensified Microsilica 940-U from Elkem.
- Limestone (*LL*): high purity $CaCO_3$ rock from the Orgon limestone deposit, France. Three different particle sizes were tested.
- Chalk (*CH*): high purity $CaCO_3$ rock from the Stevns chalk deposit, Denmark.
- Marble (*MA*): high purity $CaCO_3$ rock from the Gummern marble deposit, Austria.

The additions replaced part of the cement at a ratio of 1:1 by mass. The following replacement combinations were used:

- Slag: 20%, **35%**, 65%.
- Silica fume: 5%, **10%**.
- Limestone, Chalk, Marble: 12%, **24%**.

Most attention was focussed on the combinations in bold font. They were tested for water/binder ratios ranging from 0.4 to 0.7. The other combinations were mainly tested for a water/binder ratio of 0.5.

Based on the results presented in appended *Papers I and II*, the following conclusions can be drawn for the *strength tests*:

- The results show that *k*-values for slag and silica fume are significantly lower in young mortar than the values given in standards, both when hydrated at 5°C and at 20°C. This means that the calculated strength for young concrete will be overestimated if standard *k*-values are used. An example of this would be at the point in time of form removal. It is therefore not sufficient in standards to give a single *k*-value for mineral additions. Different values should be stipulated and the values should be dependent on factors such as age and temperature.
- The efficiency of slag does not appear to develop significantly until after seven days, especially for low temperature hydration. The *k*-value for slag in 2-day old mortars appears to be independent of temperature. In 7-day old mortar, there is however a clear tendency for the *k*-value to increase with temperature, from about 0.2 at 5°C to almost 0.4 at 20°C.
- At 2 days, there is a clear tendency for the k-value for silica fume to decrease with increasing temperature, from about 1.3 at 5°C to about 0.5 at 20°C. At 7 days, however, the *k*-value is about 0.8 and appears to be more or less independent of temperature.
- All the limestone filler types used demonstrated a positive effect on mortar compressive strength, compared with values expected for a completely inert material. For the limestone fillers, the *k*-values were normally in the range of 0.2–0.5, the highest values being observed when cured at low temperatures. A very fine-grained limestone filler showed a *k*-value as high as 1 for young mortar cured at 5°C.
- The *k*-value is strongly influenced by the fineness of the limestone filler, particularly at low temperature and young age.
- The type of carbonated rock used for producing the limestone filler does not appear to significantly influence the *k*-value. This is relevant for at least the three types of carbonated rock used in this investigation.
- As expected, traditional type II additions such as silica fume and ground granulated blast furnace slag show higher *k*-values than limestone filler, at 20°C and 28 days. At young ages (below 7 days) the *k*-value of the limestone fillers used in this study are comparable or even higher than the corresponding values for slag. These limestone fillers show also lower k-values than silica fume at early ages. However after longer curing at low temperature limestone maintains its efficiency for compressive strength while the efficiency of silica fume is decreasing.

The following conclusions can be drawn from the results from the *calorimetric studies* presented in appended *Paper III*:

- Isothermal conduction calorimetry is a useful tool for evaluating properties of young mortar and concrete. There is a close relationship between the efficiency coefficients, *k*-values for heat development and corresponding *k*-values for strength.
- Inert fillers are known to contribute to the development of heat and strength of mortar and pastes – the so called filler effect. The following possible explanations are identified in this investigation:

  One is a dilution effect, based on a paste or mortar with filler being less dense and more permeable than paste or mortar without filler. This leads to a higher availability of water for the hydration process, which contributes to a higher rate of strength growth. This can be regarded as being a filler effect.

  The other is that the fine grained filler particles act as nuclei for the initiation of the reaction between cement and water. This accelerates the process, which supports previously reported findings. This filler effect seems to be most pronounced at low degrees of hydration.
- The *k*-value for heat development in granulated blast furnace slag increases slowly from about 0.2 to about 0.4 when curing changes from 2 day/5°C to 7 day/20°C. The reason for this is that the slag is chemically active and takes part in the hydration process. The amount of slag used as replacement in this investigation (20 to 65%) does not seem to influence the *k*-values.
- The *k*-values for silica fume are uncertain due to the low percentage (5 or 10%) of addition used in the pastes, but they seem to vary mainly within 0.4–0.8. The highest *k*-values are relevant for the lowest degree of hydration, which probably can be explained by the nucleation effect. For 2 day/5°C and for low water/binder ratio the *k*-values are as high as 1.2–1.5.
- The *k*-values for heat development in limestone filler vary in this investigation between 0.2 and 0.5. The highest values are, due to the nucleation effect, relevant for short curing times and low temperatures. The values appear in most cases to be independent of the water/binder ratio. However, the *k*-value for 7 day/20°C becomes higher for lower water/binder ratios. This can be explained by the dilution effect.

There does not seem to be any effect of limestone filler content on the *k*-value. The differences between filler produced from chalk, limestone or marble also seem to be more or less negligible.

1 INTRODUCTION

1.1 Short history

Vitruvius wrote about the naturally occurring pozzolana cement:

"There is also a kind of powder which produces astonishing results ... This substance, when mixed with lime and rubble not only lends strength to buildings but even when piers of it are constructed in the sea they set hard under water ...; the water taken in makes them cohere so that they set into a mass which neither the waves nor the force of the water can dissolve."

Today, concrete is the world's most widely used building material. More than 10 billion tons of cement are produced each year worldwide. Cement and concrete are however not modern inventions – their history can be traced back at least 5,000 years! But starting not so long ago ...

800 BC: The Ancient Greeks were the first to use hydraulic mortars which could set both in air and in water. They used these in the construction of waterproof tanks and in the construction of palaces and villas.

300BC–476AD: The Romans further refined the use of hydraulic mortars and are also believed to have discovered concrete, which they made from broken brick aggregate embedded in a mixture of lime putty with brick dust or volcanic ash. Many surviving examples of Roman construction work can still be seen today, over 2,000 years later. These include the Appian Way, the Coliseum, the Pantheon, the Great Roman Baths, the Basilica of Constantine, and the Pont du Gard aqueduct. Archaeologists have found that the Roman Forum had concrete foundations of up to almost 3.5 m deep in places.

Figure 1 *Pantheon, with its wide concrete dome, is an impressive structure from the ancient Roman Empire. The building was erected about 2000 years ago.*

476–1800: Following the fall of the Roman Empire, all development of cement and use of concrete as a construction material ceased completely. It was not until the 18th century that further development of cement took place.

By 1760–1783: Construction of "Smeaton's Tower", the first concrete structure since the Roman era. It was built by John Smeaton in England. He used hydraulic lime to rebuild the Eddystone Lighthouse in stone. He used a mixture of quicklime, clay, sand and crushed iron slag to try to reproduce a "Roman cement" that could withstand the force of the waves.

1818: The first concrete bridge (unreinforced) was built in Souillac, France.

1824: In England, the mason, bricklayer and inventor Joseph Aspdin patented Portland cement. He burnt ground chalk with finely divided clay in a limekiln until the carbon dioxide was driven off. The sintered product was then ground to a fine powder. He called it Portland cement because, when turned into concrete, it resembled the stone quarried on the Isle of Portland.

Portland cement has continued to be the name of common structural cements, which are mixtures of mainly dicalcium silicate, tricalcium silicate and tricalcium aluminate.

Concrete, cement and additions have a long history. The many remarkable buildings that, despite their age, stand today in good condition is proof of concrete's ability to combine good utility with durability. However, before concrete becomes old and proves its durability, it starts life by being *young*, with an unstable structure and rapidly changing properties. This licentiate thesis deals specifically with the development of properties of young concrete and how this development is influenced by the use of mineral additions and fillers such as ground granulated blast furnace slag, silica fume and limestone filler.

1.2 Background of the present project

1.2.1 Use of mineral additions/fillers in Sweden

There are several mineral additions and fillers that are useful as replacements for part of the traditional ordinary Portland cement as binder in mortars and concrete. The additions can be industrial by-products such as granulated blast furnace slag, pulverized fly ash and silica fume or it can be filler in the form of ground limestone. The additions/fillers can be a part of the cement or can be added directly to the mixer. Increased use of additions/filler may lead to significant positive environmental effects, not least to a reduction in carbon dioxide release to the atmosphere.

Additions/fillers have been used in cement and concrete production in many countries around the world for many years. In Sweden, however, they were not used until recently. This is despite Sweden having access to suitable additions and fillers such as blast furnace slag and limestone filler. Mineral additions have had a bad reputation in Sweden. It has been generally believed that the use of industrial by-products and other additions in cement and concrete almost always results in poorer product quality than that achieved where the only binder is ordinary Portland cement. Compared with many other countries, very few resources have been allocated to research and development in this field in Sweden. There is therefore a great need to increase our knowledge of additions/filler, to ensure safe use of mineral additions in Sweden, specifically where Swedish mineral additions are used in Nordic climatic conditions.

Interest in using mineral additions and fillers has increased considerably in Sweden in recent years. New regulations and standards /1, 2/ allow increased use of additions and fillers, particularly for indoor applications. For example, CEM II/A-LL (cement with limestone filler) is today the most commonly used cement in the Swedish market, silica fume is often used for concrete structures exposed to severe climatic conditions and limestone filler is used in high quantities for producing self-compacting concrete.

There are several reasons why mineral additions should be focussed on:

- The move towards environmentally friendly construction is strong. The use of industrial by-products and fillers in the concrete sector can contribute significantly to *sustainable construction.*
- *European harmonisation* gives free trade of products within the EU. Mineral additions and cements containing additions will therefore become increasingly available on the Swedish market. Our competence in this field must however be increased if these products are to be used in a correct and safe way. Our climatic conditions are different and so, in many cases, are Swedish production techniques. These products cannot therefore be uncritically introduced in Sweden without incurring considerable risk, particularly where additions/fillers influence productivity and durability/service life.
- The construction sector continuously strives to reduce costs. Additions/fillers may give cheaper building materials, particularly where large concrete volumes are used such as in the production of residential buildings. It is however important that the use of additions/fillers does not negatively effect quality and *productivity.*
- Additions/fillers can in many cases contribute to improved *concrete quality.* Silica fume improves the durability/service life and limestone filler makes it possible to produce self-compacting concrete. However, other types of usage can impact negatively. For example, high contents of slag strongly reduce salt frost resistance /3/.

1.2.2 Influence of mineral additions/fillers on the properties of young concrete

Concrete construction productivity is highly dependent on how long after casting forms can be removed. Productivity is therefore dependant on the strength growth rate of young concrete. In Sweden, we have many years of experience in strength classes up to 50 MPa with structures produced using ordinary Portland cement concrete. Our experience allows us to accurately calculate the safe form stripping time for this type of concrete. Our experience also allows us to carry out safe and efficient form stripping under severe climatic conditions, for example during winter periods. However, the time to safe stripping may change when additions/fillers are used. Mineral additions are considered to negatively affect strength development rates, particularly at low temperatures.

Early form stripping to promote high productivity is one of the most critical points in production and one of the highest accident risk factors on building sites. This risk becomes even greater where new types of binders, which maybe have lower rates of strength growth, are used.

Environmental demands, European harmonisation, new technical developments and demands on higher productivity will influence the concrete construction sector in the future. Some of these influences are described below:

- Additions/fillers will be more frequently used in cement or mixed directly into the mixer. These materials have in most cases a slower rate of strength growth during the first week after casting than ordinary Portland cement. This will negatively affect productivity. The effect is illustrated in figure 2, where the efficiency (k-value) of a type of ground granulated blast furnace slag is shown as a function of concrete age, for various water/binder ratios /4/. A k-value of 1.0 means that the slag and ordinary Portland cement are equally efficient, a lower or higher value means that the slag is less or more efficient than the cement.

  As shown in the figure, the slag and cement are approximately equally efficient in 28 day old concrete, at least for W/B-values 0.5 and 0.85. However, the slag is considerably less efficient at lower ages. The k-value at 1–5 days, when form stripping normally takes place, is less than 0.6, which is the k-value stated in SS 13 70 03 /2/ for slag. Strength growth in these types of materials is normally considered to be more sensitive to temperature than OPC. This would further reinforce the effect seen in figure 2. It is therefore important that experience is gained on the behaviour of these types of materials, particularly in the harsh and severe Swedish winter conditions.

- Higher strength concrete will be developed and will become more widely used. High performance concrete normally contains silica fume, which may give slow strength growth at low temperatures. High dosages of plasticizing or water reducing admixtures may also be used for such concrete qualities, which may extend the time to stiffening and hence the time to form stripping. These effects must be taken in to consideration if the positive environmental effects of mineral additions are to be utilised whilst simultaneously achieving high productivity.

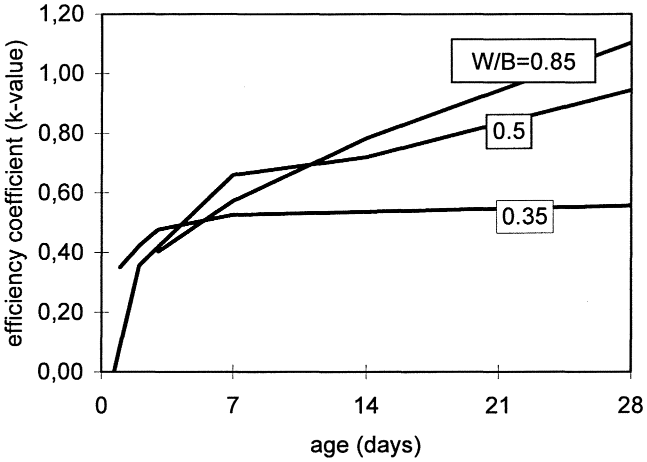


Figure 2 *Efficiency coefficient (k-value) for a quality of ground granulated blast furnace slag as function of age for various values of W/B /4/.*

- Strength growth for young concrete must be able to be correctly calculated if safe early form stripping and high productivity are to be achieved. Calculation tools exist, but there is a lack of input data for the calculations, particularly for mineral additions and fillers used at low temperatures.

1.3 Aim of the project

The work presented in this licentiate thesis was carried out within the project task Use of industrial by-products and filler in concrete, part Early-age strength development at low temperatures in concrete with mineral additions/fillers.

The aim of the project is:

to improve the knowledge of the properties of cement and concrete produced using industrial by-products/fillers at early age, i.e. during the first week after casting. This will promote efficient, safe, reliable and increased use of such types of materials, especially under winter conditions, which often is considered to be crucial for the usefulness of concrete with mineral additions.

Increased use of mineral additions/fillers can have considerable positive environmental effects in the form of reduced carbon dioxide pollution, reduced volumes of non-recyclable waste material and reduced energy consumption. This must however be achieved without adversely affecting productivity and safety at building sites.

This project studied ground granulated blast furnace slag, silica fume and several qualities of limestone filler. The work consisted of two main activities:

- Determination of strength development/k-values at low temperatures for young mortars with mineral additions/fillers
- Study of the heat of hydration for young pastes with mineral additions/fillers at low temperature and the determination of relationships with strength development.

1.4 Co-operation with other projects

Better understanding of the properties of mineral additions/fillers is required for safe and increased use of these materials. There is a lack of knowledge particularly in the areas of (a) concrete rheology, (b) properties of young concrete and (c) long-term properties/durability.

This work focused on issue (b), while cooperating with projects investigating the two other issues:

- *The use of industrial by-products and fillers in concrete - Influence on the properties of fresh concrete.* Project leader Oskar Esping, Building Materials, Chalmers University of Technology /5/.
- *The use of industrial by-products and fillers in concrete – Influence durability/long-term properties.* Project leader Dimitrios Boubitsas, SP Swedish National Testing and Research Institute /6, 7, 8/.

2 YOUNG CONCRETE

2.1 Introduction

Standards have generally accepted 28 days as the age where concrete can start to be considered to be mature. 28 days is the most common age used when testing a large number of properties of concrete for standardised material description. The term young relates to the age prior to this, not only in terms of time but also in terms of vulnerability of the developing properties to a range of factors. *Early-age* and *young concrete* are terms that are used liberally, irrespective of whether a study relates to the first hours or the first few days of hydration, or one to several days, to one week or even longer. Neither early-age nor young concrete can be defined based on material properties. This is because they are not stable. Therefore, in addition to time intervals, the attainment of specific property levels is often suggested. References in the literature are vaguer when it comes to specifying an upper limit for young concrete. However, they often refer to a concrete that cannot yet be considered for full service load.

Both terms often mean that the concrete is *no longer fresh* to be worked with and is *much younger than 28 days*. Young also implies that a solid *structure starts developing* and that the *rate of this development is fast*. In /9/ it is suggested that the period of time of 1–3 days or a degree of hydration up to 50% characterizes young concrete. However, more recent literature on new types of concrete such as high-performance concrete points out that many properties of young concrete continue to change at a significant rate during a longer period of time than 3 days /10/. Neither time nor degree of hydration directly indicates the state of early age concrete. Another interesting proposal made in /9/ is that the *upper limit for young* concrete could be defined as being when the *influence of the external climatic conditions no longer has a decisive influence* on the development of structure.

Wittman /11/ proposed the following approach to describe young concrete. Only a few hours after mixing cement with water, the mixture starts turning from a plastic into a solid phase with properties rapidly changing in time. Fresh concrete, which can be regarded as a low cohesive moist granular material, whose workability is one of the most important properties, starts stiffening and then hardening. A time dependant solidification process of the composite material takes place as the hydration of the cement proceeds. If fresh concrete is often linked to a concrete needing to be mixed, placed, consolidated and finished, then young concrete could start with *concrete that no longer needs to be workable*. Wittman suggested that the lower boundary for young concrete could be the end of workability, or even better the *end of viscosity as a more quantitative measure* to distinguish between fresh and young concrete.

When mobility is no longer important, more attention is paid to the hardening of the concrete and its *ability to build up strength*. Concrete in which there are *sufficient hydration products to form a weak but coherent solid* is often referred to as young concrete. In the literature, young concrete is often referred to as being after the mixture has set, however with no fixed boundaries.

When considering an upper limit for young concrete, it is questionable whether a strict limit should be stated. Studies on the development of the chemical, physical or mechanical properties of the material structure at early ages show that changes are rapid during the first hours and up to several days. The rate of change after 1 week is significantly lower. This would suggest that *young concrete* could be defined as being *a solid material in which ageing* *effects are predominant.* The age when further ageing is of secondary importance in the solidification process could be considered as an upper limit for young concrete.

As can be seen, no strict definition of young concrete can be found in the literature. However, in this report the following four phases are used for defining different stages in the hardening process of concrete, see also /9/:

- Fresh concrete
- Young concrete
- Hardening concrete
- Hardened concrete

A definition of the four phases is shown in figure 3. The figure is relevant for a temperature of 20°C. At lower temperatures, the horizontal axis scale must be changed such as at 5°C the age axis figures must be doubled.

An extensive introduction to young concrete and property development is presented in /12/. Section 2.2 and 2.3 below present some of the aspects studied in this research.

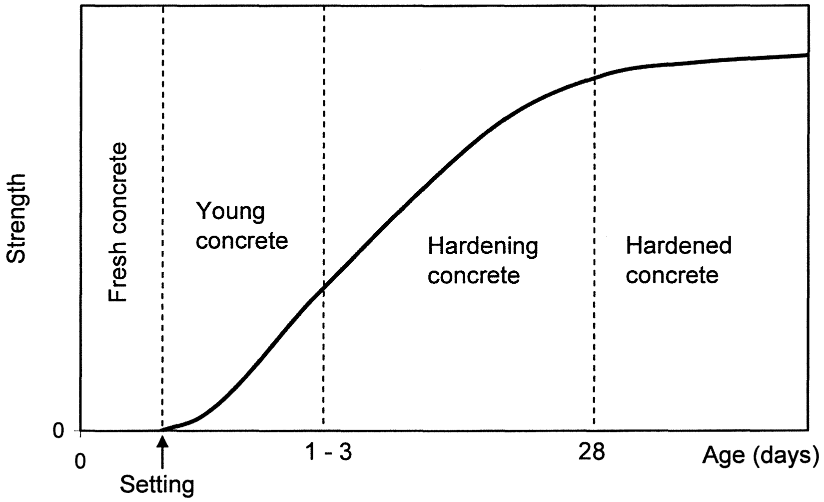


Figure 3 *Principal description of the different phases during the hardening process of concrete.*

2.2 Development of young structure and the solidification process

When the first hydration products are formed, plate-like $Ca(OH)_2$ crystals and long needle-shaped ettringite crystals precipitate around the cement grains as a coating. The mixture is in a plastic, workable phase with high deformability. After 1 to 3 hours, hydration of the calcium silicates begins. First long-fibred and then short-fibered calcium silicate hydrates, C-S-H, break up the coating and grow outward from the grain surface. Needle-like hydration products start building a three dimensional network in the mixture, so hindering the mobility of the cement paste components. Weak links develop between the cement grains and the mixture gradually becomes stiff. A very detailed microstructure formation and hydration study of cementitious materials is given in /13/.

Over a time interval of some hours, the mixture *sets*. After setting, the mixture starts *hardening*, when the amount of hydration products increases and the linking forces become stronger. Figure 4 shows the development of the hydration products and microstructure during different hydration stages.

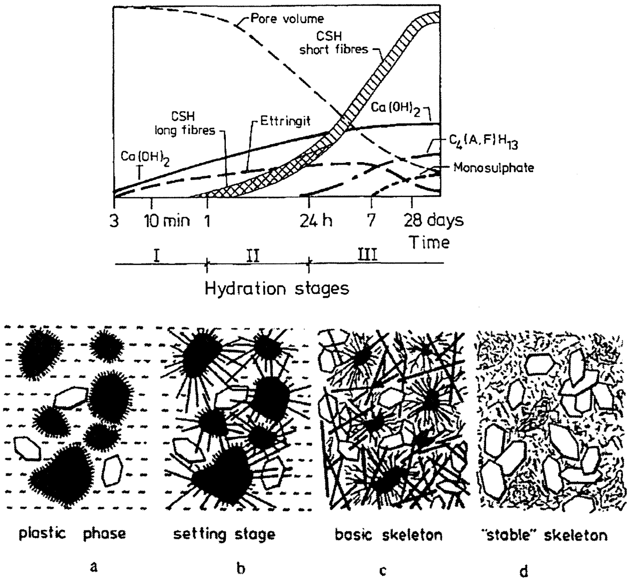


Figure 4 Formation of hydration products and development of microstructure /14/.

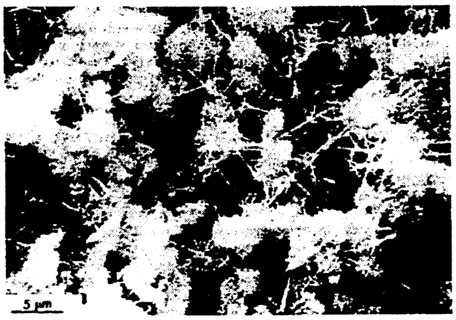


Figure 5 Picture of a cement paste after 1 day of hydration, using a scanning electron microscope /15, from Young J.F 1982/.

Formation of more solid ligaments provides the mixture with a rigid, stable skeleton which enables strength to develop. The first part of stage III in figure 4 corresponds to a *basic* skeleton in the very early hardening stage. In a later hardening stage, a more *stable* skeleton develops and the linking forces grow stronger.

The scanning electron micrograph in figure 5 shows a cement paste after 1 day of hydration, with short and long needles growing from the cement grains. The picture shows the basic skeleton from the early hardening stage and shows that the microstructure is still open.

Figure 6 shows the formation of a solid structure and how this is accompanied by chemical shrinkage. Chemical shrinkage is a reduction of the total volume of the phases involved in the chemical reactions of the hydration. It gives internal and external volume changes. For an unloaded cementitious system sealed against drying, bulk deformation under isothermal conditions can be measured, an external shrinkage called autogenous shrinkage.

For low water/cement pastes, the formation of a self-supporting skeleton can be observed by changes in the development of the total chemical versus the external chemical shrinkage (autogenous), see figure 7. The transition from suspension to solid occurs when the two

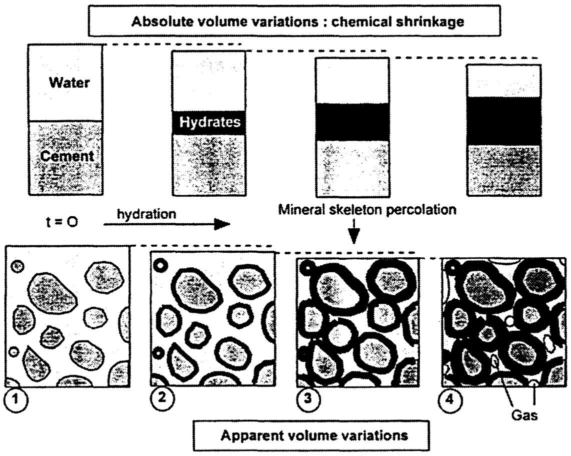


Figure 6 *Principle illustration of the transition from liquid to solid phase. Self-desiccation as a consequence of chemical shrinkage /16/.*

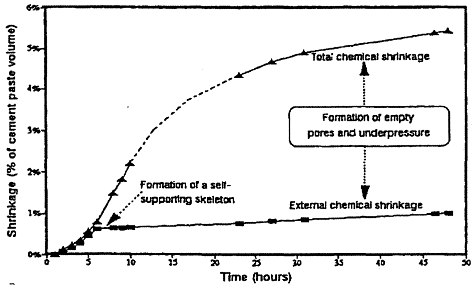


Figure 7 *Total chemical shrinkage and external chemical shrinkage (autogenous) measured for the same cement paste. Sellevold et al.1994, from /10/.*

curves start to diverge. The explanation is that zones appear within the material where the volume variations imposed by the hydration reaction are locally hindered by the newly created solid contacts. The rate of autogenous shrinkage therefore decreases and becomes less than the total chemical shrinkage.

2.3 Factors influencing the hydration process

The chemical process during early hydration involves temperature changes (heat is produced) and relative humidity changes (water is consumed). This clearly indicates that the evolution of the properties of the young structure is not only dependent on the materials involved in the reaction, but also on factors related to the ambient environment – *climate*, *loads*, *restraints*.

Water is vital to the hydration reactions. Young concrete is very sensitive to drying, both internally and at the surface of the concrete structure. Early drying due to evaporation from unprotected concrete surfaces can lead to plastic shrinkage cracking and crazing. Early drying can also lead to poor hydration and hardening, higher permeability and inferior mechanical properties.

Temperature plays a very important role during cement hydration, influencing the rate at which hydration proceeds and the degree of hydration that is reached after a given hydration time. Temperatures above room temperature usually speed up the hydration. However, this does not guarantee that higher temperatures always lead to the highest ultimate strength. Each cement has its own optimum temperature, which will lead to the highest ultimate strength /17/. For example, Portland or modified cements have temperatures around 13°C or for rapid hardening cement around 4°C.

When comparing this with laboratory temperatures of 20–24°C, higher ambient temperatures can speed up setting times, cement hydration and the overall hardening process. Concreting in hot weather, without appropriate protection of the concrete surface, can lead to problems related to evaporation of water from the surface layers, *problems caused by drying,* to problems related to high internal temperature rise in the structure and *increased thermal stresses and deformations*.

If the water needed for the hydration process evaporates instead of participating in the chemical reactions, the solid structure in the drying zones develops differently. Moisture gradients and hindered hydration alter the development of the basic skeleton, i.e. the strength and stiffness of the microstructure. Different mechanical property development inside the same structure acts as *internal restraint*.

The heat of hydration together with high ambient temperatures intensifies the thermal effect on the development of the young structure. Thermal stresses and deformations are increased and the overall cracking sensitivity of the structure is higher.

Low ambient temperatures have a slow-down effect on the hydration process. Cold weather concreting without protection from the ambient temperature leads to *delayed setting* time, a *slow rate of hardening* of the young concrete and therefore a *retarded development of the mechanical properties*. The sensitivity of the young concrete to low temperatures is said to be even greater when mineral additions are used /9/. At low temperatures, they enhance the retarding *effect of the additions* on the development of strength.

Slow development of strength has a negative effect on production rates at construction sites, as longer waiting times before a safe removal of forms are required. The hardening structure has to gain certain strength before the casting procedure can continue without collapse. Since reaching a safe concrete strength takes longer when casting in cold weather, the risk of failure at early ages is greater. A more careful monitoring of strength development is therefore required, having detailed information about the hydration mechanism of the actual mixture at the actual temperature.

2.4 Hydration at low temperature

Temperature plays a very important role during cement hydration, for the rate at which the hydration proceeds, as well as for the degree of hydration that is reached after a given hydration time. Temperatures above room temperature usually speed up the hydration, but there is not a guarantee that a higher temperature always leads to the highest ultimate degree of hydration. Different types of cement have been shown to behave differently with temperature (increase or decrease). The presence of different additions, e.g. slags, pozzolanas or fillers, has proved that the effect of the temperature is even more complicated. If e.g. a higher temperature than room temperature may increase the initial rate of hydration of C_3S and C_2S it may also lead to lower degree of hydration at late ages. On the contrary at lower temperatures a crossover phenomenon can be observed: lower early degree of hydration but higher values of ultimate degree of hydration.

Some of these aspects are discussed in /65, 66/ where the influence of temperatures between 10°C and 60°C was investigated. The results on two different plain Portland cements showed significant differences between the hydration of the four cement phases C_3S, C_2S, C_3A and C_4AF /65/. Generally the degree of hydration was lowest at 10°C. But the different temperatures gave also important differences in the rate of hydration. Especially for C_3S and C_4AF the early rate of hydration was higher at 10°C and 20°C compared to 30–60°C. However a lower degree of hydration was found at ages below 28 days and higher after 90 days. Hydration of C_4AF at 10°C showed a significant catch-up compared to 20°C. The hydration of C_2S was strongly inhibited by lower temperatures.

Some of the results for 10°C and 20ºC for a Portland cement are shown in figure 8: the compressive strength vs. age for the cement and the degree of hydration vs. age for its constituents alite (C_3S), belite (C_2S) and tricalcium aluminate C_3A.

2.5 Influence of mineral additions on strength development

Only brief information is outlined here. Some aspects on strength development in concrete containing additions are treated in e.g. /9, 10, 17/.

Figure 9 shows compressive strength development after 1 and 28 days as a function of curing temperature for concrete produced with a binder consisting of pure OPC or 50% OPC and 50% slag respectively /19/. For 1 day old concrete, the strength is always lowest for concrete with slag irrespective of the curing temperature. The same is true for 28 day old concrete at a

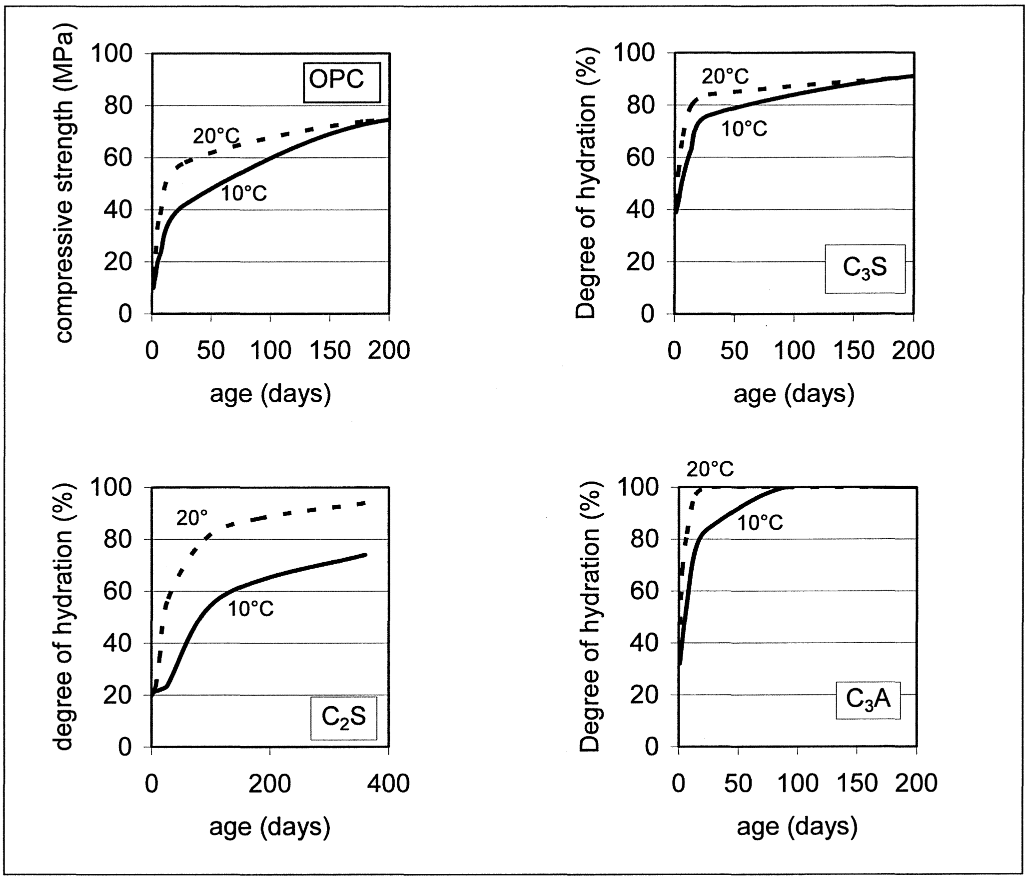


Figure 8 Degree of hydration vs. age for a Portland cement and its constituents /65/.

curing temperature of 5°C. At higher temperatures, the difference between the two types of concrete decreases and for temperatures higher than 25°C the concrete with slag shows the highest strength.

The efficiency factor, the k-value, is used to characterize the efficiency of a mineral addition. At k = 1.0 the mineral addition and the cement are equally efficient. Lower or higher k-values show that the addition is less or more efficient.

In SS 13 70 03 /2/ the k-value for slag is 0.6 and in /9/ the interval 0.6–1.0 is given. Both these are relevant for 28 day old concrete cured at a normal laboratory temperature, i.e. 20°C. According to the results in figure 9, the k-value is lower for lower ages and lower temperatures. However, no k-values for these conditions can be found in the literature or in standards.

The positive effect of silica fume on concrete strength after 28 days is not relevant for young concrete /9/. The difference increases with increasing silica fume content and is most significant at low temperatures. k-values of 1.0–2.0 are given in SS 13 70 03 and in /9/ values as high as 2.0–5.0 are given. These values are, however, relevant for 28 day old concrete at 20°C. For younger concrete and lower temperatures the k-value is probably much lower.

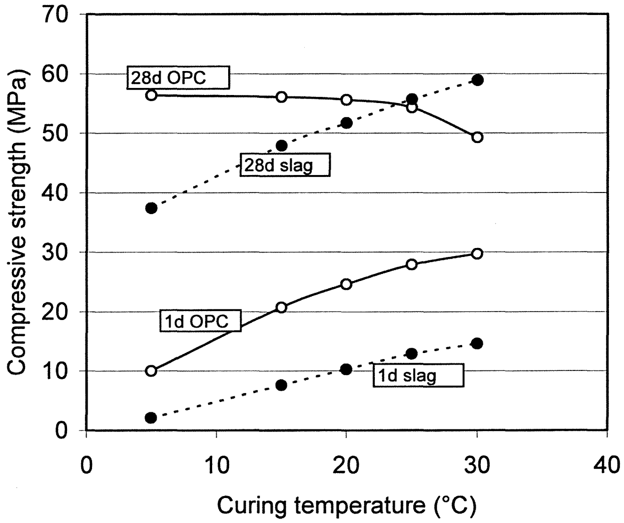


Figure 9 *Influence of the curing temperature and age on the compressive strength for concrete without and without granulated blast furnace slag (OPC/Slag = 50/50). The results are relevant for a water/binder ratio of 0.40 /19/.*

3 MINERAL ADDITIONS AND FILLERS

3.1 Ground granulated blast furnace slag

3.1.1 Properties and use

Ground granulated blast furnace slag is a waste product from the manufacture of pig iron. There are many varieties of slag, including non-ferrous slag. However, the experiments in the present research only use ground granulated blast furnace slag as an addition. Only this type of slag will therefore be described here.

Ground granulated blast furnace slag has been used for producing concrete for more than a century. It is included in cement as a constituent or is added directly into the concrete mixer. However, slag has rarely been used in Sweden in concrete.

Cements and concrete containing slag have been used in many countries to achieve good durability under a variety of conditions. This includes improving durability through improved sulphate resistance, lower alkali aggregate reactivity, higher resistance to chemical attack and higher ultimate strength.

The chemical composition of blast furnace slag is a mixture of lime (CaO), silica (SiO_2), alumina (Al_2O_3), MgO and small amounts of other oxides that are found in Portland cement, but not in the same proportions. Chemical and physical properties of slag can vary widely, depending on the process used and the method of cooling.

Slag is formed as a liquid at high temperatures and therefore has to be cooled. If the slag is cooled slowly, the slag develops a crystalline structure and no or almost no cementing properties. For the slag to become the required reactive, latent hydraulic material, it has to be quenched rapidly so that it solidifies as a glass. Rapid water cooling is achieved by a granulator breaking up the molten slag mass which is then sprayed with high pressure water jets. The result is a granulated amorphous material. After being dried and ground, a ground granulated blast furnace slag is achieved which, due to its latent hydraulic properties, can be used as an inorganic constituent in cements and concrete. Very high temperatures during granulation improve hydraulicity. The glass content has to be high.

Chemical composition is not the only factor that determines slag reactivity. Hydraulic moduli, such as the CaO/SiO_2 or $(CaO + Al_2O_3 + MgO)/SiO_2$ ratios also indicate the level of hydraulicity. The higher the ratio, the higher the reactivity. Using this type of moduli to indicate hydraulicity is a rather simplified approach and is primarily used to give a rough classification of blast furnace slag. However, the moduli do demonstrate that hydraulic activity increases with increased composition alkalinity /20, 21/.

According to European cement standard EN 197-1: 2000 /22/. Portland slag cement CEM II/A contains 6–20% and CEM II/B contains 21–35% slag. Blast furnace slag cements CEM III/ A, B, C have a content of between 36% (A) and 95% (C).

Slag cements are manufactured by intergrinding Portland cement clinker with slag. Slag grindability varies considerably, but is usually harder to grind than Portland cement clinker. Intergrinding can therefore produce cements in which slag can be too coarsely and clinker too finely ground. Cements are therefore sometimes manufactured by separately grinding Portland clinker and slag.

Ground granulated slag particles have irregular, sometimes acicular, shapes. Particle surfaces are smooth and adsorb little water during mixing. This improves the workability of the mix. The typical fineness of most common slag powders is 300–500 m^2/kg (Blaine).

To ensure that the slag is suitable for use as a cementitiuos material, irrespective of whether it is to be used as a constituent in composite cements or as a mineral addition to concrete, many parameters need to be taken into consideration. High glass content is one property. However, the degree of disorder of the glassy structure also has a significant influence on the reactivity of the slag. The higher the degree of disorder is, the more reactive the slag /21/. Other important parameters include chemical composition, undesirable components, the fineness of grinding, the complex structure of the amorphous phase and the content of crystalline phases (although in small proportions compared with the amorphous phases).

A detailed characterisation of the material lies outside the scope of this work. It therefore will not be described further here. More details are available in the literature presented in the reference list.

3.1.2 Blast furnace slag and cement hydration

The main hydration product of a mix of ground granulated blast furnace slag and Portland cement is essentially the same as the main hydration product formed when only Portland cement hydrates. The main hydration product in both cases is calcium silicate hydrate (C-S-H) /23/. Slag hydrates are, however, generally more gel-like than Portland cement hydration products and therefore add denseness to the paste /17, 24, 25/.

Although ground granulated blast furnace slag has an inbuilt hydraulicity, it uses the calcium hydroxide and alkali from the cement as an activator and takes part in early microstructural development. When slag alone is mixed with water, there is a small but immediate reaction releasing calcium and aluminium to the solution. This reaction is however limited until additional alkali or calcium hydroxide are available /24/.

The hydration process is also controlled by the availability of active sites in the glass. Hydration requires a continuous alkaline environment to develop, such as that provided by the reaction of Portland cement with water. This also provides a temperature increase which activates the hydration of the slag component /26/.

Scrivener describes /27/ observations from backscattered electron (bse) images of cement-slag pastes, noting the influence slag has on the distribution of the calcium hydroxide. Bse images of pastes hydrated for one day, which show large accumulations of calcium hydroxide around the slag particles, after 8 months of slow hydration show a decrease in the amount of calcium hydroxide. Bse images show rims of hydration products around the slag particles with different characteristics than those shown by the hydration products around cement particles. This indicates differences in both chemical composition and the type of the C-S-H formed.

Research by /25/ on the nature of the C-S-H showed that the C-S-H changed from fibrillar into more foliated as the slag content increased. The capillary pore structure also became less well connected, explaining the lower permeability of cement pastes which contain slag.

The hydration mechanism of slag in combination with Portland cement is generally described as a two stage reaction. During early hydration, the predominant reaction is with alkali hydroxide. Later in the reaction it is with calcium hydroxide. From calorimetric measurements of heat production rates at room temperature, this two stage effect was observed as a delayed "shoulder" during the main peak of hydration by /24, 28/. In /29/ a model of superposition of the cement reaction and the slag reaction is proposed.

Measurements made at different temperatures show that the delay was shorter at higher temperatures (tests at 15–27–35–60°C) /26/. The authors observed that the effect of increased temperature (60°C compared to 27°C) on early hydration (25 hours) was greater for cement containing slag. They concluded that lowering the temperature leads to the opposite effect. Slag cement is more affected by a lowered temperature due to a lowered benefit from the thermal activation of the cement component hydration.

3.1.3 Strength development and the influence of low temperature

The initial hydration of cement containing slag is slow. This is partly due to the need for the glass to be broken down by the hydroxyl ions released by the hydration of Portland cement, which in some ways is similar to reactions in cements containing pozzolanas. However, the progressive release of alkali by the slag and the formation of calcium hydroxide by the Portland cement lead to the reaction continuing across a long time period. Strength development is therefore slower in young mixtures. As the rate of reaction accelerates at later ages, there is also a faster gain in strength. The 2 day compressive strength is in general lower in mixtures containing slag /17, 21/, even at 7 days (depending on parameters such as slag content, reactivity, fineness, w/c and curing conditions). However, values at 28 days and later generally are at least as high if not higher than for plain cement mixtures.

Strength and strength development is determined by the chemical composition of the cement and the slag, and by the hydraulic reactivity of the cement and slag blend. However, as the hydration reactions between slag and cement are very complex, each slag may behave differently for different mixes /30/ and observations are not always generally valid. A factorial approach carried out by /31/ showed that for a single cement type, the mix parameters dominant for the 1 day compressive strength are cement content, type of slag and replacement level.

Factors such as fineness, particle size distribution (slag and cement) and water-binder ratio also play a significant role. In /32/, fineness is discussed separately for slag and for cement. It is, referring to earlier research that suggests that cement clinker fineness affects early mechanical properties while slag fineness affects late mechanical properties, showed how one slag twice as fine as another slag lead to increased compressive strength and flexural strength (two to three times higher after 6 h and 24 h). Research in /33/ also showed that slag fineness accelerates compressive strength at early ages. Comparing blends of 50% slag with Blaine values of approx. 450, 800 and 1200 m^2/kg, showed that the higher the fineness, the higher the rate of compressive strength gain. This was most pronounced before 3 days for water-binder ratio 0.3 and between 3 and 7 days for water-binder ratio 0.4. The rate of gain after 28 days was similar irrespective of fineness. The positive effect of adding slag was greater for the mixtures with lower water-binder ratios. At high replacement levels, the effect of the fineness on the slag is more pronounced at later age /34/.

The general view adopted is that that the presence of slag leads to early age strength levels, that are too low. Slag containing mixtures are therefore seldom used if low curing temperatures are expected and if no other additions and admixtures are used to counteract the retardation effect. The behaviour of slag cement mixtures at low temperatures has not, however, been thoroughly studied and the retardation effect of slag at low temperatures has therefore not been quantified. An interesting observation was made by Regourd /32/. Regourd found that doubling slag fineness could compensate for the loss in flexural strength resulting from lowering the temperature from 20°C to 5°C, at the age of 7 days.

There are few studies on the development of early strength and heat developed in hydration. There are even fewer studies that have attempted to develop a correlation between strength and heat development. An interesting parameter study was however carried out by /35/, in which strength, microstructure and heat of slag with different glass contents, fineness mixtures and different slag replacement levels were analysed. For the strength-heat relationship, the study concluded that the compressive strength at ages 3 and 7 days did not correlate well with total heat developed at the same ages.

3.2 Silica fume

3.2.1 Properties and use

Many names are used for this material, including microsilica, silica dust, condensed silica fume, fumed silica. However, the term "silica fume" is now generally adopted by standards. It is regarded as a relatively recent addition to the list of supplementary cementitious materials /36/, as a pozzolan which in itself has little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cementitious properties. Its potential for use in concrete as addition was identified by researchers in Norway as early as 1948, who were searching for a use for the industrial waste product silica fume. It was shown to be an addition that improved concrete properties, such as giving increased strength and reduced permeability. It therefore resulted in a denser concrete, with lower diffusivity of chloride ions, providing better protection against corrosion of the embedded steel.

Silica fume is a by-product of the reduction of high-purity quartz with coal or coke and wood chips in an electrical arc furnace during the production of silicon metal or ferrosilicon alloys. The gases escaping from the furnaces have a high content of SiO, which oxidizes and condenses as superfine spherical particles of amorphous silicon dioxide SiO_2.

The industry can today supply high quality silica fume with constant properties. Silica fume generally has a low bulk density (200–300 kg/m^3) and a specific gravity of approximately 2200 kg/m^3 (as opposed to cement 3150 kg/m^3). The particles are very fine, most of them having diameters ranging from 0.03 µm to 0.3 µm. The specific surface is approximately 20000 m^2/kg (BET $_{N2}$), which is 13 to 20 times higher than the values for other pozzolanic materials determined using the same methods /17/.

Silica fume is today used in nearly all industrialized countries, as it seems to make concrete a more sustainable material. High-strength and high-performance concrete are normally produced by using additions of silica fume, which has been shown to mitigate alkali-silica reactions (ASR). However, its role in the ASR is controversial, mitigating or inducing, /37, 38/.

Good dispersion in the mix, well defined requirements for a proper curing and a maximum content of silica fume are often pointed out as essential parameters. The fineness and the pozzolanic effect also lead to changes in the overall porosity of the concrete, the pore size distribution of the capillary pores becoming finer and the gel porosity increasing /39/.

A shortcoming that is frequently discussed arises in the transportation and handling of such a fine material. Silica fume is often delivered densified, as micropellets (agglomerates of individual particles produced by aeration) with a bulk density of 500–700 kg/m^3 or as slurry (water and powder, generally in equal mass) with a bulk density of 1300–1400 kg/m^3. All forms can be successfully used and there is in general no substantial support for claiming that one form has a more beneficial effect upon the resulting concrete than any other /40/. Many researchers do however point out that there may be a degree of agglomeration of silica fume in concrete. It is therefore important that the mixing technologies used ensure good re-dispersion into the mixture to avoid ASR related damage. The agglomeration process to obtain densified silica fume is supposed to be "reversible". However, some research results indicate that the breakdown of the agglomerates in conventionally mixed concrete is sometimes incomplete /41, 42/ and that undispersed agglomerations can participate in alkali-silica reactions.

It has also been suggested that differences between the densified and undensified state may also influence the early age reactivity of the powder. Studies by /43/ shows that densified powder has lower reactivity levels than undensified powder, expressed by the heat of hydration and free lime fixation methods. This aspect should not be overlooked when there is a need for high early strength levels.

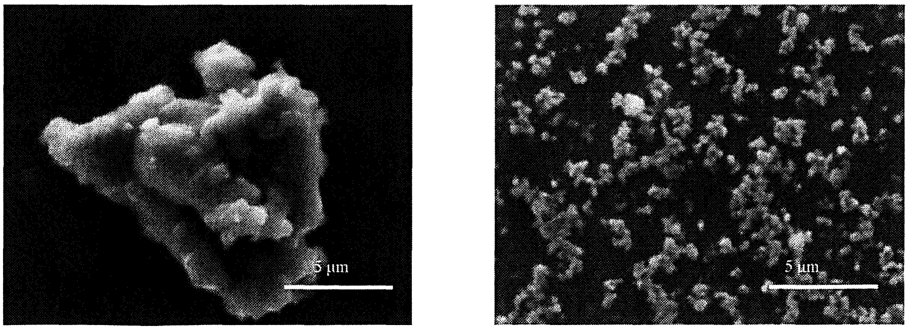


Figure 10 Cement particle to the left and silica fume particles to the right /44/.

3.2.2 Silica fume and cement hydration

Silica fume (SF), typically with over 90% amorphous SiO_2 powder, has a twofold function in concrete, a chemical one and a physical one. It was however initially introduced as a pozzolan. It does not react as a hydraulic material, that is directly with water, but as a pozzolan which requires alkali in the solution as activator. The amorphous SiO_2 reacts with the calcium hydroxide in the saturated solution of calcium hydroxide $Ca(OH)_2$ which is produced during the hydration of the Portland cement (OPC), so producing more calcium silicate hydrate (C-S-H). The fineness of the particles, which are much smaller than the cement particles, also has a packing effect through filling spaces. This speeds up the chemical reaction by providing nucleation centres for hydration. This latter effect is briefly explained below.

The fine silica fume particles in the saturated solution create sites in which material in the solution can centre ("nucleate"), so helping it to precipitate earlier than it might otherwise do. Once it precipitates, the concentration of the material in the solution is reduced, which allows more material from elsewhere to be brought into solution, so speeding up the process.

In a system water-cement-silica fume, cement hydration first produces calcium hydrate. Silica fume then starts reacting with the calcium hydrate produced from the cement hydration. When sufficient Portland cement has hydrated to saturate the pore water, calcium hydroxide, forms on the surface of the silica fume particles. Silica fume is highly reactive at room temperature. It dissolves in a $Ca(OH)_2$ saturated solution within a few minutes /17/.

Cement hydration products and pozzolanic reaction products start filling the water occupied space. The physicochemical reaction proceeds as briefly described below /45/.

- Attack of alkali on SF surface: OH^- is adsorbed on the surface which is then attacked to form a silica-rich amorphous thin film.
- Dissolution of SF into pore solution by the alkali in the pore solution. Rate of dissolution depends on the diffusion process through the reacted layer. Rate determining stage.
- Dissolution of the crystal $Ca(OH)_2$ in the pore solution. $Ca(OH)_2$ crystallizes and dissolves in a reversible process: Crystallized $Ca(OH)_2$ produced by cement hydration may dissolve in the pore solution to achieve chemical equilibrium while $Ca(OH)_2$ is consumed by the pozzolanic reaction.
- Reaction of SF with $Ca(OH)_2$: After the dissolution of silica, Ca^+ and OH^- in the pore solution become chemically adsorbed by silanol groups to form C-S-H.
- $Ca(OH)_2$ or SF is consumed: Below a certain level of $Ca(OH)_2$ content the consumption of $Ca(OH)_2$ due to the pozzolanic reaction is reduced as pH and Ca^+ concentration becomes lower. Or if SF is consumed, the pozzolanic reaction stops.

It has been suggested by /45, 46/ that the pozzolanic reaction of SF is diffusion controlled. Temperature and moisture conditions should not be therefore neglected. The reaction is also influenced by other physical and chemical parameters. A high glass phase content leads to high reactivity, as does a high powder fineness. For high rates of pozzolanic reaction, silica fume from agglomerates (if densified or pelletized) needs to be re-dispersed to a high-fineness powder with a high specific surface. A high degree of agglomeration in concrete is too frequently associated with silica fume. The silica fume in this case does not act as a fine particle cementitious material but as a large-diameter material with an even more complex action, with a long-term reaction to outer chemical attack and volumetric instability.

Zelić et al /47/ studied the early hydration kinetics and how silica fume would act to accelerate the reaction. The authors analysed the hydration process from the point of view of the stage of nucleation and growth, phase-boundary interaction and diffusion (details described in /20/), to study the rate-determining parameters. They suggested that the presence of silica fume would increase the rate of hydration during the first hours by a nucleation effect, when it still exists as inert filler, and not by a pozzolanic reaction. This latter reaction would start, according to the authors, after three days or later.

The hydration mechanism aspects presented here are far from exhaustive. This is only intended to provide an insight into a complicated process. One must also keep in mind the complexity of the chemical reactions at hydration. Silica fume not only affects the amount but also the size of the $Ca(OH)_2$ crystals. In Portland cement, large crystals increase with time and continue to grow at the expense of smaller crystals. In systems with 10–20% SF, they however decreased /48/. All the parameters relating to the cement and SF used, proportion in the water-cement-SF system, moisture conditions and temperature at different hydration stages influence the chemical and volumetric changes during the chemical process. This is reflected in the nature and amount of the developing cement gel which builds up a porosity and strength, two highly valued parameters for the estimation of the quality of the resulting concrete.

3.3 Limestone filler

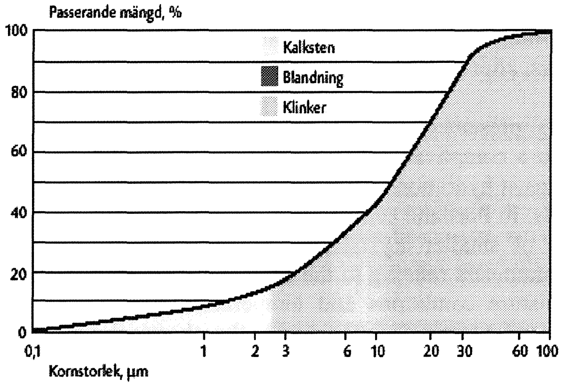
3.3.1 Properties and use

Although the main use of limestone is as a raw material in cement production, it is today also a standard constituent in the European standard cements CEM I (up to 5%), CEM II/A (6% to 20%) and CEM II/B (21% to 35%). By 2001, approximately 19% of all cement sold in Europe contained between 6% and 35% limestone /49/. In 1999, a Portland-limestone cement classified as CEM II/A-LL42.5R containing 12–15% limestone filler became the basic cement in Sweden.

Another major use of limestone is as a filler in self-compacting concrete, where limestone filler acts to improve the flow and the filling ability of the concrete. Heavily reinforced concrete elements or structures with complicated geometry can be cast, although they do not allow full compaction. No or very little compaction means an important improvement in the working environment at construction sites. Limestone addition also increases strength, e.g. due to improved particle packing, especially at early ages.

The topics of a state-of-the-art report presented in /49/ cover many factors from manufacture to durability, for workability, hydration and microstructure of cements. The research results show that the main factors, other than rock chemistry, that influence the behaviour of a concrete with cement containing limestone are physical factors such as fineness, particle size distribution, amount compared to the amount of cement or other fines and surface properties. These are important not only for the workability and the interaction with other additions and chemical admixtures, but also for the development of mechanical properties.

In the production of Portland-limestone cement, limestone is added in lumps and is ground together with the clinker. Limestone is in general softer than the clinker. After grinding, the limestone therefore dominates the finer fractions while the cement clinker dominates in the coarser particle sizes. Figure 11 shows a typical particle size distribution for the Swedish CEM II/A-LL42.5R cement.



"Klinker": Clinker
"Kalksten": Limestone
"Blandning": Mixture

Figure 11 Typical particle size distribution for Swedish "Byggcement" CEM II/A-LL 42.5R. Vertical axis: passed amount, %. Horizontal axis: particle size, µm. /50/.

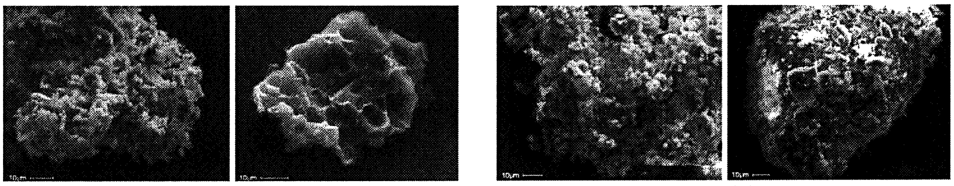
There are special requirements for limestone depending on its field of use. For use as constituent in cements, the requirements in the European standard EN 197-1 /22/ specify the content of $CaCO_3$, clay and total organic carbon. However, the quality requirements set by cement plants may be more rigorous. It is not unusual for limestone to be supplied from one single deposit. Stable chemistry and physical properties are important to achieve long-term uniformity of the cement property.

For use as filler, properties such as fineness and surface area of the powder are important. Porosity, surface texture and F-shape play a crucial role in water demand, interaction with chemical admixtures and the overall rheological properties of the fresh concrete.

Limestone is a carbonated rock which forms as a sediment across millions of years and in different environments. Each deposit therefore has different mineralogical properties. Age, temperature and pressure can result in rocks having different crystal morphologies despite identical chemistry. Crystal sizes, hardness and porosity therefore also differ. When ground the powders from different deposits may have fairly different particle shapes and surface textures.

Figure 12 below shows SEM pictures of limestone from different deposits /51/. Ignaberga is a "young" deposit with small fossils still visible in the sediments. The rock has very fine crystals and an uneven and partly high porosity. In contrast, Pargas is a much older rock with a clearly visible crystalline rhomboedrical structure. The crystals are larger and have smooth surfaces. The age of the sediments in Orsa and Boda/Kullsberg is between these two. Both

have small crystal sizes, Orsa being more fine grained and with more uneven surfaces, Boda/Kullsberg showing a higher compactness of the crystals.
Limestone deposits are classified as being sedimentary, metamorphic or crystalline. In all three cases the rock began formation as sediment. Some sediments are much older than others, and the environment in which different sediments formed can be very different.


Ignaberga, Sweden, ~70 mill. years. Orsa, Sweden, ~450 mill. years.

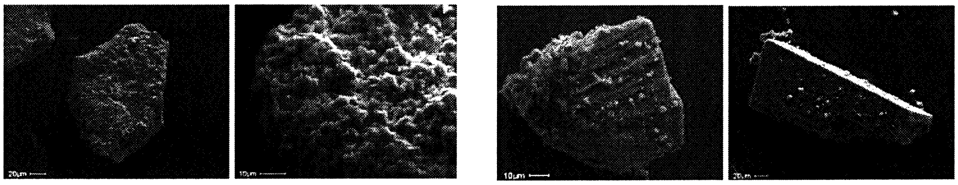

Boda/Kullsberg, Sweden, ~400 mill. years. Pargas, Finland, ~1900 mill. years.

Figure 12 SEM images of different types of limestone. Approximate age in million years /51/.

There can also be changes in temperature or pressure during the rock's lifetime (metamorphosis). The result of this is displayed in the size, shape and surface structure of the crystals, degree of structure ordering and the packing of the rock. A rough classification into chalk/limestone/marble can be used when these characteristics are of interest. Marble is a metamorphosed limestone, showing a clear crystalline structure usually with large crystal sizes. Chalk and limestone are both sedimentary and both have small but different crystal sizes. Chalk is microcrystalline, often rather porous, while limestone is more compact.

The effect of origin, particle size distribution and fineness on different limestone fillers was studied in /51/ for a large number of properties. Rheology and water demand were particularly affected. However, the influence on the compressive strength of pastes after seven days was small. For the use of limestone filler in self-compacting concrete, a more complex particle shape study of rheological properties is found in /5/.

3.3.2 Limestone filler and cement hydration

When used as addition, limestone filler is normally considered to be inert. There are however results /52/ that show that limestone filler takes part in the early hydration, see figure 13. The figure shows that heat development from pastes containing limestone filler is higher during the first 1000 minutes (16 hours). Mixtures with 50 % $CaCO_3$ and W/B = 0.5 are compared, through heat development as voltage output for the entire sample, 300 mg.

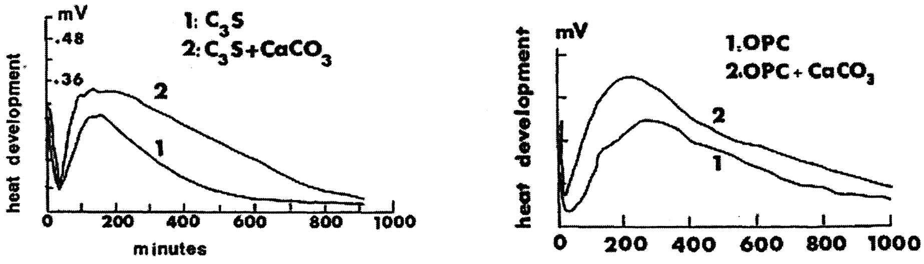


Figure 13 Isothermal calorimetry data for cement pastes containing limestone filler /52/.

The effect may be due to a chemical reaction of the fillers. However, a more probable explanation is that the filler particles act as an accelerator for the cement hydration process. It may also be a combination of the two /53, 54, 55, 56/.

4 TEST METHODS

4.1 Introduction

The influence of mineral additions and low temperature on early strength has been approached by testing *compressive strength* and *heat development* at *5°C* during the first week of hydration. Tests have also been carried out at *20°C* to provide systematic comparison. All tests were carried out in the laboratory under isothermal conditions, to allow the influence of a single temperature throughout mixing, sample preparation, curing and testing to be assessed. The experimental program was structured to allow the influence of the following *parameters* to be identified:

- type of addition/filler (silica fume, blast furnace slag, three types of limestone)
- amount of addition (5%–10% silica fume, 20%–35%–65% slag, 12%–24% filler)
- fineness of limestone filler (three fractions/finenesses of same type of limestone)
- water-binder ratio (0.4–0.5–0.6–0.7)
- age
- temperature

Given the number of test alternatives, the compressive strength was tested on prisms of *cement mortars* with test ages of mainly 2 days and 7 days. Reference values for some mixtures were also determined at 28 days. The heat of hydration for *cement pastes* was determined using isothermal heat conduction calorimetry. Heat development was monitored continuously up to the age of 7 days.

Both test methods are described in the two sections below. The materials and mixtures are described in chapter 5. Details are also found in Papers I–II (strength) and Paper III (heat).

4.2 Compressive strength

The compressive strength tests were generally carried out following the procedures specified in EN 196-1 /57/. Mortar prisms 40 x 40 x 160 (mm) were first tested for flexural strength, using a three-point flexural test. The resultant prism halves were then tested for compressive strength. Three prisms per test alternative were used, giving three values for the flexural and six for the compressive strength. This thesis only discusses the compressive strength.

Some deviations from the standards for mixture proportions, binders and temperatures, were necessary to adapt the procedure to this study. These include:

- Paste:sand proportions were changed to achieve mortars with similar consistence. The sand amount was kept constant (1350 g norm sand per batch).
- The binder was either cement (in plain mortars) or cement plus mineral addition/filler (in blended cement mortars). In blended cement mortars, parts of the cement were replaced with addition at a ratio of 1:1 by mass.
- The temperature was either 5°C or 20°C throughout the entire test chain (material curing, mortar and specimen preparation, cutting, testing).

4.3 k-value for compressive strength

Existing standards specify efficiency coefficients, *k*-values, for reactive additions up to which rate cement can be replaced by addition, without the properties of the concrete being changed. For example at $k = 1$, one part cement can be replaced with one part addition, by mass. According to EN 206-1 /1/, silica fume has a k-value of 1 or 2. It is therefore assumed that one part of silica fume can replace one or two parts of cement depending on environment class, without changing the properties of the concrete. The Swedish application of EN 206-1 (SS 13 07 03, /2/) specifies k = 0.6 for blast furnace slag. This shows that slag is less efficient than cement and one part can only replace 0.6 part of cement.

Limestone fillers are considered to be non-reactive ingredients. They are included as inert components of the fine aggregate. The k-value concept is normally only used for reactive additions. But in this study it is also used for limestone filler to allow the efficiency of limestone fillers of different quality and different fineness to be compared.

The k-values specified in standards are determined from relationships between the water-cement ratio and the compressive strength. It is stipulated that these k-values apply to several properties. This assertion is being studied in a parallel project /6/. The values specified in the standards are established using mature concrete (≥ 28 days) cured at standard laboratory temperatures (20–23°C). The present study is an attempt to establish values for young concrete, age 7 days and below, and to determine whether these values also apply if curing takes place at 5°C instead of 20°C.

The method used for determining k-values is described in figure 14, eq (1a) and eq (1b). By using the relationship between the f_c^{plain} and *W/C* for plain cement mixtures, the equivalent water-cement ratio $(W/C)_{eq}$ for a blended mixture giving the same strength ($f_c^{\text{plain}} = f_c^{\text{blend}}$) can be determined.

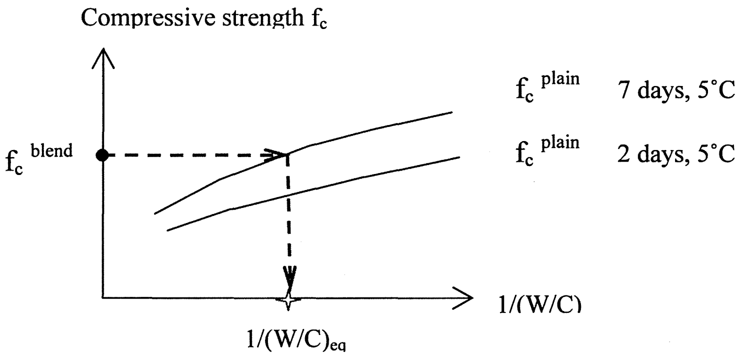


Figure 14 Establishing the equivalent water-cement ratio $(W/C)_{eq}$ for a blended mixture from the relationship between compressive strength and W/C for plain mixture. The figure shows the relationship f_c vs 1/ (W/C).

The equivalent water cement ratio is defined in eq (1a):

$$(W/C)_{eq} = \frac{W}{C + k \cdot R} \tag{1a}$$

where: C = cement (kg) R = addition (kg)
W = water (kg) k = efficiency coefficient.

From eq (1a) the k-value can be calculated as:

$$\mathrm{k} = \left(\frac{W}{(W/C)eq} - C\right)/R \tag{1b}$$

In /6/ it is shown that the evaluation of k-values becomes more accurate at higher addition contents, i.e. it is less sensitive to small variations in the measured f_c-value, see figure 15. The figure also shows that accuracy is also affected by the water/binder ratio. The higher the ratio, the lower the accuracy.

Small variations in measured compressive strength can lead to high variations in k-values. If, for example, measured strength deviates from the true value by 1.0 MPa for a water/binder-ratio of 0.5 and an addition content of 12%, then the k-value deviates from the true value by 0.08. If the addition content is increased to 24%, the k-value deviates from the true value by only about 0.04. This explains why the main series in the tests are carried out with mortars containing relatively high amounts of additions/fillers – 24% for limestone filler, 35% for granulated blast furnace slag and 10% for silica fume.

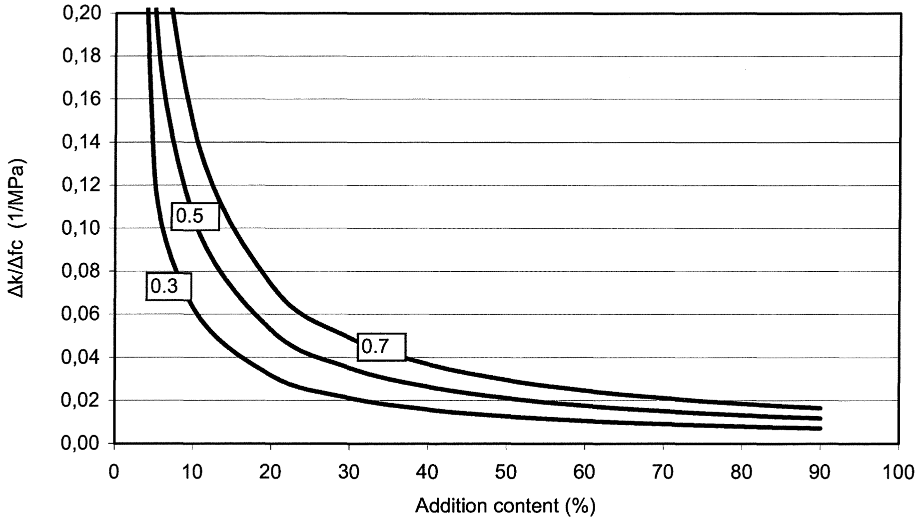


Figure 15 Relationship between $\Delta k/\Delta f_c$ and the additions content for different water/binder-ratios /6/.

4.4 Isothermal heat conduction calorimetry

For the purpose of this study, isothermal heat conduction calorimetry was considered to be the most suitable calorimetrical method for monitoring the heat of cement hydration. The method is considered to be suitable due to the following reasons:

- Using this method, the hydration process is monitored while progressing at an essentially constant temperature.
- Neither the activation energy at different temperatures nor the exact heat capacity of the sample needs to be known.
- The heat production rate dQ/dt is measured from the temperature difference ΔT between the sample and a stable thermostat controlled system (dQ/dt is proportional to ΔT). Heat Q is calculated by a simple integration with time t.
- Modern isothermal calorimeters are stable and have high levels of sensitivity.

The equipment used in this project was an 8-channel TAM Air (Thermal Activity Monitor) isothermal heat conduction calorimeter working in the mW range. The equipment manufacturer is Thermometric AB, Sweden. This equipment can operate within the temperature range 5˚C–60˚C, has good temperature stability (air thermostat stability ±0.02°C) and high sensitivity (limit of detectability 2 μW).

The equipment consists of eight twin calorimeter units, see figure 16, each being composed of two calorimeters (a sample and a reference) placed on a large metal block (aluminium) which acts as a heat sink. The sample is placed into an ampoule (usually a disposable glass vial) and the ampoule is inserted into the ampoule holder. The heat developed in the sample flows through the ampoule holder, through a temperature sensor, to the heat sink whose temperature is kept constant by an air thermostat. A reference calorimeter, which contains an inert sample, is used in parallel with the sample calorimeter. Its role is to compensate for disturbances due to differences in heat capacity between the sample and calorimeter. For a balanced measurement, the reference needs to have a heat capacity equivalent, but not identical, to that of the sample.

A temperature gradient ΔT arises due to the heat transfer between the sample and the heat sink, which produces a voltage signal U (Volt) proportional to the heat flow through the temperature sensor. The direct measurement is of a continuous voltage signal over time, $U_{(t)}$, for the entire sample.

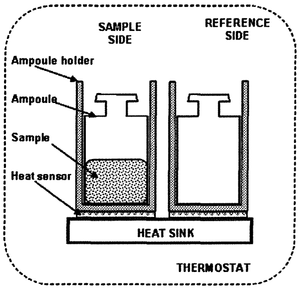


Figure 16 Schematic representation of a twin calorimeter unit. The thermostat is larger and surrounds all eight calorimeter units inside the TAM Air calorimeter.

The voltage signal and the thermal power $P_{(t)}$ (Watt or Joule/s) are directly proportional. $P_{(t)}$ is the measure of the rate of heat development dQ/dt. The proportionality between P and U depends on the construction of each instrument. This is usually described by a calibration coefficient ε and needs to be determined at each specific operating temperature.

A sequence of the steps used in calorimetrical measurements is given below and in figure 17:

$U \sim \Delta T$		voltage is *measured*
$P = \varepsilon\, U = dQ/dt$	[W], [J/s]	thermal power is *calculated* thermal power = rate of heat production
ε	[W/V]	calibration coefficient is *determined* checked at each operating temperature checked for stability over time
$Q = \int P\, dt$	[J]	heat is *calculated* by integrating P

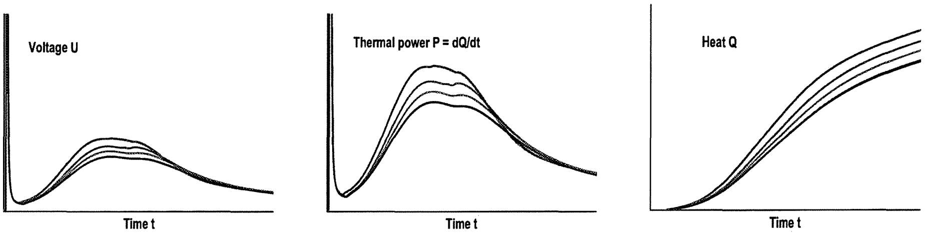


Figure 17 Example of voltage signal (measurement), thermal power and heat (calculated).

Measurements can be made on mortar or paste samples. When testing mortars, it has to be taken into consideration that sand does not participate in the hydration process. It therefore has to be excluded from the heat evaluation per unit of sample. This means that the exact amount of sand in each sample needs to be known or needs to be exactly the same in all the samples for the results to be compared. This can sometimes be a source of calculation error.

The measurements in the present study were carried out on *pastes*. Heat monitoring was made within the *600 mW range* on samples with a mass around *10 g*, at temperatures of *5°C* and *20°C,* using sand in the reference calorimeter for a balanced measurement.

The samples were prepared outside the calorimeter from hand-mixed batches. The mixing order was cement plus addition, then water was added. This was then charged into the calorimeter 5 ± 1 minutes after the water was added. *Two samples* were tested for each alternative (see chapter 5), both samples being taken from the same batch.

Exact times of mixing and sample charging were recorded for each individual sample (in seconds). This time delay was added to the monitored heat measurements to obtain a real time "zero" of the reaction start for each sample. More details are found in Paper III.
Heat development was recorded for a total time of 168 hours (7 days) from the time of the reaction started, i.e. when water was added.

Small samples and the 600 mW recording range allowed the first peak of hydration to be measured, the time of mixing outside the calorimeter being excluded. Evaluations which include the first peak were possible as the data logging interval was 20 seconds. However, the first peak was not included in the result evaluation discussed in this thesis. *Thermal power* and *heat* have therefore only been calculated for the *main peak of hydration.*

Material storage, sample preparation and tests were carried out at a constant temperature, the temperature being the temperature of the calorimetrical measurement. The calorimeter was operated at 5°C and 20°C respectively, placed in a climatic chamber at these temperatures. Hand mixing of pastes, sample preparation and charging into the calorimeter followed careful and identical procedures for all samples, to ensure identical sample handling, to avoid heating materials, ampoules and calorimeter at charging and to reduce the reaction time outside the calorimeter. More information on the calorimetrical method and test procedure can be found in /58, 59, 60, 61/.

4.5 k-value for heat development

Using the heat development results, the efficiency coefficients for heat were assessed in such a way that they would allow a comparison with the values for compressive strength. This evaluation was made for the hydration age of 2 days and 7 days, for comparison with the results for compressive strength.

The total heat development of the sample Q_{C+R} was assumed to be the sum of the heat of reaction of the cement Q_C and the heat of reaction of the addition Q_R.

Q_C and Q_R are expressed as the product of the specific heat of the material, q, and the amount of material, cement and addition respectively. A coefficient of efficiency for heat *k* has been defined as the ratio between the specific heat of the addition and the specific heat of the cement eq. (2) to (4).

$$\frac{Q_{C+R}}{C} = \frac{Q_C + Q_R}{C} = \frac{C \cdot q_C + R \cdot q_R}{C} \tag{2}$$

$$q_R = \frac{C}{R}\left(\frac{Q_{C+R}}{C} - q_C\right) \tag{3}$$

$$k = \frac{q_R}{q_C} \tag{4}$$

Where: $\frac{Q_{C+R}}{C}$ = total sample heat per mass unit of cement (J/g $_{\text{cement}}$)

$\frac{Q_{C+R}}{C} = \frac{Q_C}{C} = q_C$ for plain cement mixtures

$Q_{C+R} = Q_C + Q_R$ = total sample heat (J)

$Q_C = C \cdot q_C$ = heat of the cement reaction (J)

$Q_R = R \cdot q_R$ = heat of the addition reaction (J)

q_C = specific heat of the cement (J/g $_{\text{cement}}$)

q_R = specific heat of the addition (J/g $_{\text{addition}}$)

C = amount of cement (g)

R = amount of addition (g)

k = efficiency coefficient, or k-value, for heat (–)

5 MATERIALS AND MIXTURES

5.1 Cement, additions and fillers

The study was carried out using the Swedish ordinary Portland Cement CEM I 52.5 R from Slite as main binder (*OPC*). This is currently the only CEM I available on the Swedish market. A CEM I was required to enable the effect of each addition to be studied separately. The cement + addition/filler combinations were therefore blended in the laboratory.

The following additions and binder materials were studied:

- Ground granulated blast furnace slag (*BFS*): Swedish Merit 5000 from Oxelösund, certified product.
- Silica fume (*SF*): Norwegian undensified Microsilica 940-U from Elkem, certified product.
- Limestone (*LL*): high purity $CaCO_3$ rock from the Orgon limestone deposit, France. Three fractions were tested (fine *LLF*, medium *LL*, coarse *LLC*).
- Chalk (*CH*): high purity $CaCO_3$ rock from the Stevns chalk deposit, Denmark.
- Marble (*MA*): high purity $CaCO_3$ rock from the Gummern marble deposit, Austria.

Tables 1 and 2 show the chemical and physical properties of these materials. Figure 18 shows the particle distribution of the powders as stated in the material specifications provided by the producers.

Pastes and mortars were manufactured using *deionized water* as mixing water. The mortars were manufactured with *CEN standard sand,* as required by EN 196-1 /57/.

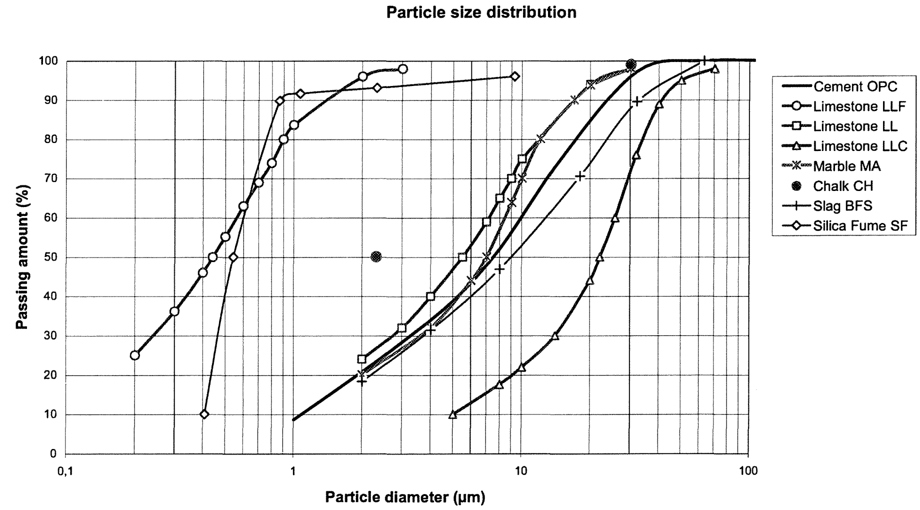


Figure 18 Particle size distribution, according to product specifications.

Table 1 Chemical composition of the powders.

Chemical composition									
	SiO_2 %	CaO %	Al_2O_3 %	Fe_2O_3 %	MgO %	Na_2O %	K_2O %	SO_3 %	L.o.i. %
Cement	20.9	64.1	3.8	2.7	2.8	0.3	1.1	3.4	1.1
Slag	34.0	31.5	12.0	0.3	17.0	0.6	0.6	3.5	1.1
Silica fume	≥ 90	< 0.7	< 1.5	< 3.0	< 2.0	< 1.0	< 3.0		< 3.0
Limestone Chalk Marble	$CaCO_3 \geq 98\%$								
Cement clinker composition (Bogue)						C_3S %	C_2S %	C_3A %	C_4AF %
						62.8	12.4	5.5	8.3

Table 2 Physical properties of the powders.

	Particle size (µm)		Specific surface (m^2/kg)		Particle density
	Top cut $d_{98\%}$	Mean $d_{50\%}$	BET	Blaine	(kg/m^3)
Cement (**OPC**)	~ 32	~ 7.2	1760	541	3114
Slag (**BFS**)	~ 60	~ 9		470	2907
Silica fume (**SF**)	~ 11	~ 0.5	~ 20000		2246
Chalk (**CH**)	~ 30	~ 2.3	2200		2696
Marble (**MA**)	~ 30	~ 7	1500		2722
Limestone medium fraction (**LL**)	~ 30	~ 5.5	1000		2710
Limestone, coarse fraction (**LLC**)	~ 70	~ 22	700		2711
Limestone, fine fraction (**LLF**)	~ 3	~ 0.44	15000		2678

Different types of $CaCO_3$ rock were used to determine whether differences in internal crystal morphology (chalk, limestone and marble) influence strength or heat development. More comments on this subject are found in chapter 3 and Papers II, III.

5.2 Mortars and pastes

Mortars and pastes were manufactured in the laboratory. Slag, silica fume and the different types of limestone were all added as part of the binder, replacing part of the cement at a replacement ratio of 1:1 by mass. The following replacement combinations were tested.

- Slag: 20%, **35%**, 65%.
- Silica fume: 5%, **10%**.
- Limestone, chalk, marble: 12%, **24%**.

Most attention was given to the combinations marked in bold. They were tested for water-binder ratios *W/B* 0.4, 0.5, 0.6 and 0.7. The remaining combinations were mainly, but not exclusively, tested at *W/B* 0.5. Tables 3 and 4 show the test mixtures used.

The *W/B* is in fact the water-powder ratio. The total powder amount includes cement and mineral addition/filler. Plain cement mixtures with *W/B* = *W/C* 0.4 to 0.7 were tested as reference.

Table 3 *Mortar mixtures tested for strength. Test age: 2 and 7 days (all alternatives shown), 28 days (underlined alternatives).*

Mixture	**% OPC**	**% Addition**	**W/B Tested at 5°C**	**W/B Tested at 20°C**
OPC	100	—	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
BFS-20	80	20	0.4, 0.5, 0.6, 0.7	0.5
BFS-35	65	35	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
BFS-65	35	65	0.5	0.5
SF-5	95	5	0.5	0.5
SF-10	10	10	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
LL-12	88	12	0.5	0.5
LL-24	76	24	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
LLC-12,LLF-12	88	12	0.5	
LLC-24,LLF-24	76	24	0.5	0.5
CH-12, MA-12	88	12	0.5	
CH-24, MA-24	76	24	0.5	0.5

Table 4 *Paste mixtures tested for heat development.*

Mixture	**% OPC**	**% Addition**	**W/B Tested at 5°C**	**W/B Tested at 20°C**
OPC	100	—	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
BFS-20	80	20	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
BFS-35	65	35	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
BFS-65	35	65	0.5	0.5
SF-5	95	5	0.5	0.5
SF-10	10	10	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
LL-12	88	12	0.5	0.5
LL-24	76	24	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
LLC-12,LLF-12	88	12	0.5	
LLC-24,LLF-24	76	24	0.5	0.5
CH-12, MA-12	88	12	0.5	
CH-24, MA-24	76	24	0.5	0.5

Ordinary replacement levels for slag and silica fume were used. For limestone, a replacement level of 12% is equivalent to a Portland-limestone cement type CEM II/A, while a 24% replacement is high in comparison with levels normally used in cements. This replacement level was nevertheless used, as it makes observing the differences due to filler content easier, see section 4.3.

All mixtures, both mortars and pastes, were manufactured without chemical admixtures. This was to ensure that supplementary material parameters, which would operate in combination with the additions, would not affect results.

Mortar was prepared by mixing the amount required for three prisms 40 x 40 x 160 (mm) in one batch as specified in EN 196-1. The amount of sand in each batch was held constant at 1,350 g. However, the amount of paste (water, cement and addition) was altered to obtain mortars of similar consistence. Detailed mixture compositions are presented in Paper I (mixtures with slag and silica fume) and II (mixture with limestone, chalk and marble).

The pastes for heat development were prepared by hand-mixing small batches. Two samples of around 10 g per batch were required for the measurements. The pastes with the addition were prepared by first dry mixing the cement and the addition until a homogenous powder is formed. Water was then added. Powder and water were mixed together energetically to break lumps and achieve good, uniform wetting of the powder particles.

Mortars and pastes were prepared and cured at the same the temperatures as for the actual test, 5°C and 20°C respectively. Batches of all materials needed for the tests were therefore stored at each of these two test temperatures.

6 RESULTS AND DISCUSSION

6.1 Introduction

The test results from compressive strength testing and isothermal calorimetry are presented in appendices 4 and 5. The results are discussed in *appended papers I, II and III.* Below are presented supplementary comments and information on *test result precision.*

6.2 Precision of test results

6.2.1 Strength tests

Six specimens were used for measuring the compressive strength for each combination of mortar quality, test age and curing temperature. The mean results for all test series are presented in *appendix 4* with the standard deviations.

The standard deviations for the tests performed at 2 days/5°C are plotted in figure 19 against compressive strength. The standard deviation appears to increase approximately linearly with increasing strength. The coefficient of variation (cov), i.e. the standard deviation divided by the mean value, can be assumed to be independent of age and should therefore be a useful measure of the precision of the test results. This assumption ought to be relevant also for other curing regimes.

Mean cov values for different ages and curing temperatures are presented in table 5. The values are low, 1.6–2.1%, and no significant differences between the values for the different curing conditions and ages are evident.

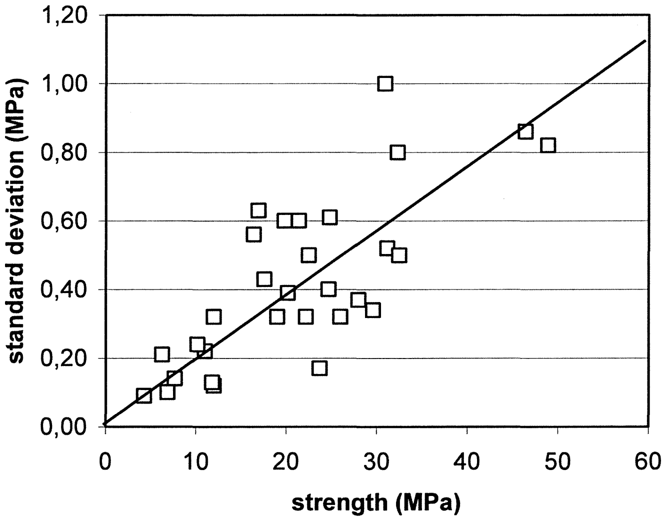


Figure 19 Standard deviation vs. strength for mortars cured for 2 days at 5°C.

Table 5 Coefficient of variation for compressive strength (%) for different ages and curing temperatures.

	5°C	**20°C**
2 days	2.1	1.6
7 days	1.8	1.6

6.2.2 Calorimetry tests

The calorimetry test results are presented in *appendix 5.* For the tested mixture qualities and curing conditions heat values are shown for the ages of 2 days and 7 days. Each test result is the mean of two measurements. The difference between the two values is presented as well.

The method below for estimating standard deviation can be found in most statistical handbooks.

The standard deviation (s) can be calculated from:

$$s^2 = \frac{\sum (x_i - x_m)^2}{n-1} \qquad (5)$$

s = standard deviation
n = number of test results
x_i = individual test results
x_m = mean of the individual test results

For a series of only two test results, the standard deviation formula becomes:

$$s = \frac{x_1 - x_2}{\sqrt{2}} \qquad (6)$$

This is of course an uncertain estimation of the standard deviation. However, if there are many pairs of observations, a fair estimation can be obtained by using the following relationship:

$$s^2 = \frac{\sum (s_i)^2}{n} \qquad (7)$$

where values of s_i are the estimated standard deviations from the individual pairs of observations.

The mean value of the heat of hydration for most pastes, at a specific age, is approximately the same when cured at the same temperature, with one exception: pastes with a content of 65% slag. It is therefore reasonable to use all pairs of observations (except those with 65% slag) for the estimation of an overall standard deviation for each combination of age and temperature These estimated standard deviations are, together with the mean values, used for the calculated coefficient of variation presented in table 6.

Table 6 Coefficient of variation for heat development (%).

	5°C	**20°C**
2 days	0.5	0.3
7 days	1.0	0.8

The cov values are low, between 0.3 and 1.0%. However the values appear to be higher for seven days than for two days. This can be explained by the heat production rate (dQ/dt) being low after two days, as also the output signal from the calorimeter. Even if the differences between specimens are low at early age, when integrating heat over a long time, small differences accumulate. This means that the result (Q) becomes more sensitive to small measurement errors.

6.3 Results in Paper I and II – strength development and k-values at low temperature

The results in appended Papers I and II show that temperature strongly influences the efficiency of mineral additions/fillers. This is illustrated in figures 20 and 21, which are also found in Paper II.

The coefficient of efficiency or k-value increases with age at 20°C for silica fume and blast furnace slag. However, the k-value for limestone filler appears to be more or less independent of age. See figure 20. This agrees with conventional opinion on how these materials behave. At 28 days, the k-value is almost 2.0 for silica fume and around 0.8 for blast furnace slag. These values are close to those stipulated in standards such as EN 206-1 and SS 13 70 03.

The materials however behave completely differently at 5°C, see figure 21. Blast furnace slag appears to be more or less chemically inactive, with a k-value of around 0.2–0.3 which is independent of test age. On the other hand the k-value for silica fume decreases strongly from 1.2 at 2 days to 0 at 28 days. Results in /62, 63/ have also suggested that low temperatures may reduce the efficiency of silica fume. This behaviour is not fully explained or understood.

The results of this investigation clearly show that k-values for mineral additions, hydrated at both 5°C and 20°C, are significantly lower for young mortar (and hence concrete) than the normal values given in standards. This means that the calculated strength for young concrete, such as at the time of form stripping, will be significantly overestimated if normal, standardized k-values are used. It is therefore not sufficient for standards to state a single k-value for slag and silica fume. Different values should be stipulated which should be dependent on factors such as age and temperature.

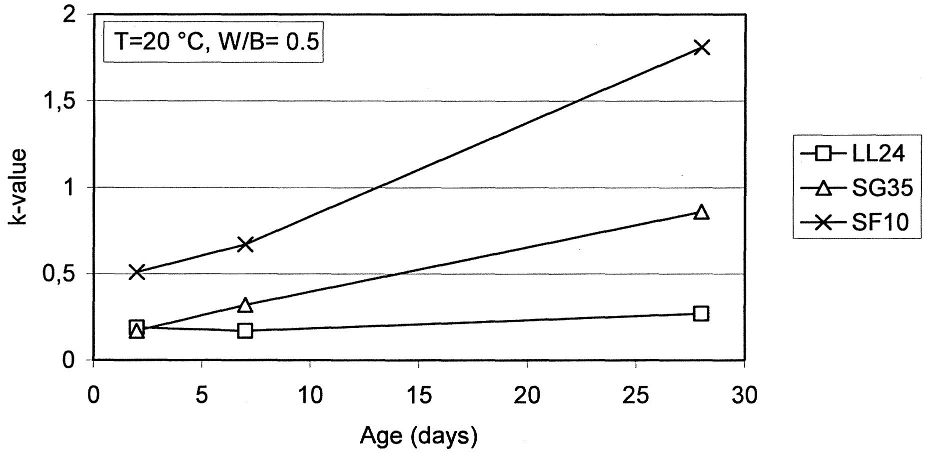


Figure 20 *Coefficient of efficiency (k-value) as a function of age at 20°C for mortars containing granulated blast furnace slag, silica fume or limestone filler.*

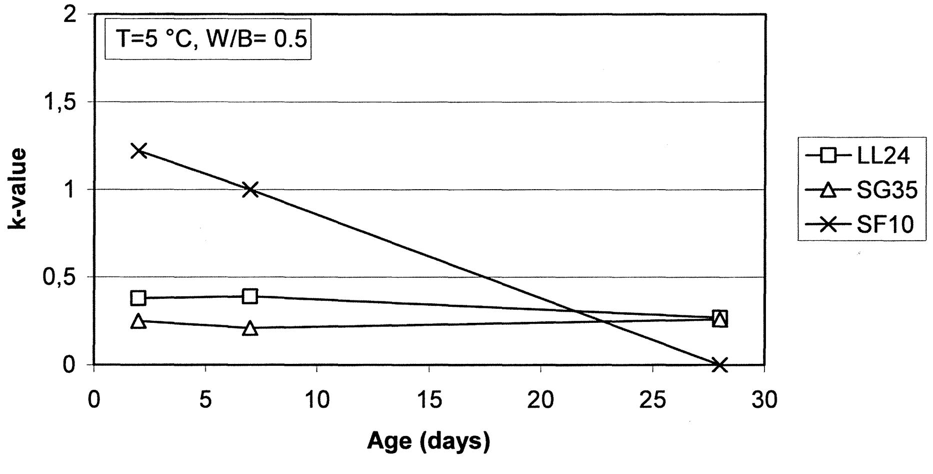


Figure 21 *Coefficient of efficiency (k-value) as a function of age at 5°C for mortars containing granulated blast furnace slag, silica fume or limestone filler.*

6.4 Results in Paper III – heat development and k-values at low temperature

The results in Paper III show that isothermal calorimetry may be a useful tool in the evaluation of strength properties at early age and low temperatures. There is good agreement between k-values for compressive strength and those for heat development, see figure 22 which is also presented in Paper III.

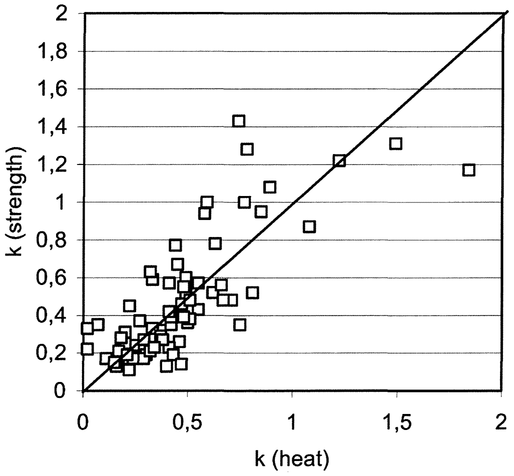


Figure 22 *k-values for compressive strength vs. k-values for heat development for the different additions/fillers and curing conditions tested in this investigation.*

The scatter is relatively wide. This can be partly explained by many of the test results being based on measurements made on pastes and mortars with low amount of addition/filler, which leads to poorer estimation of k-values.

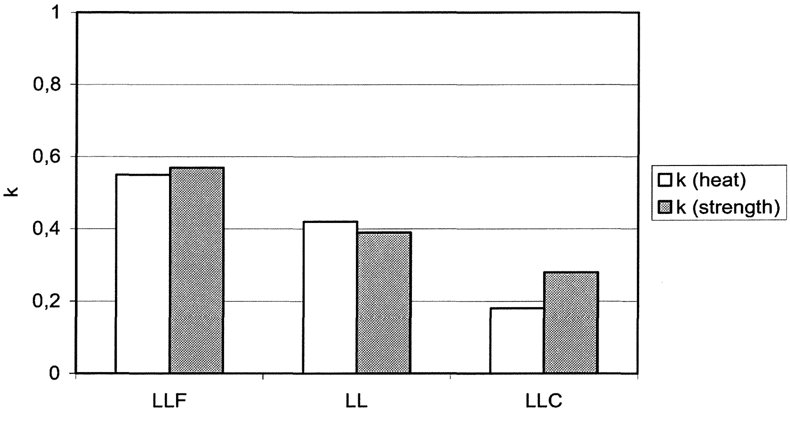


Figure 23 *k-values for heat development and compressive strength for limestone filler of three different fineness (d_{50} is 0.44, 5.5 or 22 µm for LLF, LL and LLC resp.). Values at W/B=0.50, filler content of 24% and curing 7 days at 5°C.*

A more distinct relationship between k-values for strength and those for heat development is presented in figure 23, which shows these values for limestone fillers with different fineness. The k-values increase with increasing fineness and the k-values for heat development and strength are almost identical. This shows that measuring heat development using isothermal heat calorimetry can be a suitable and simple tool for evaluating the efficiency of additions and fillers in pastes, mortar and concrete.

6.5 Heat versus strength at early age

Investigations reported in the literature on the correlation between the kinetics of heat development and the development of mechanical properties show that, at a fixed water-binder ratio, there is a certain relationship between the heat of hydration and compressive strength, see for example /64/.

The results of this study, which are not presented in the appended papers, confirm that the heat of hydration is indicative of the structural changes. The dots in figure 24 sum up the results for two different ages, two temperatures and several combinations of cement and addition. As shown, there is a close relation between the strength and the heat developed per gram powder.

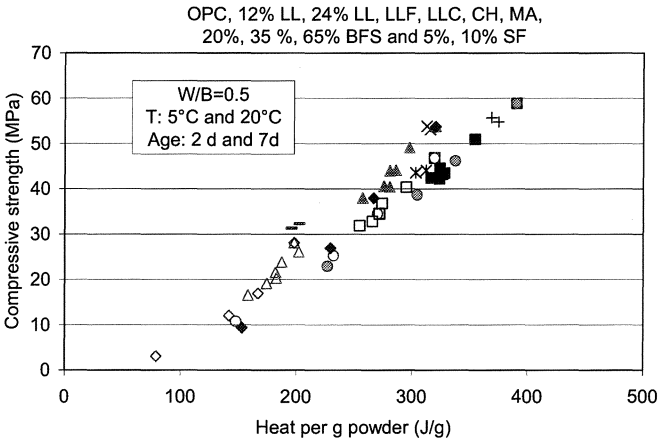


Figure 24 Heat of hydration vs. compressive strength for mortars with W/B = 0.5 containing mineral additions/filler.

7 FUTURE INVESTIGATIONS

As result of the investigations carried out in the present project following objectives for the future research are suggested:

- continued study of the mechanisms behind the "filler effect";
- combined structural and chemical investigations at early age, development of the porosity and pore size distribution, study of the mechanism of hydration and water binding at temperatures below room temperature;
- systematic contextual investigation between microstructure, temperature and age on pastes, mortars or concrete with additions;
- investigations on further fillers used today as chemically inert material.

For the mechanism research carried out in this project it was important to identify the distinct influence of a certain addition. One addition was studied at a time and the investigation has so far not included chemical admixtures. A continuation of the research can therefore consider:

- the influence of chemical admixtures;
- combinations of additions or/and filler.

To increase the range of knowledge within the parameters studied to this point the following continuation of the tests is recommended:

- development of strength and heat of hydration at temperatures within the interval of 5°C–20°C and determination of the temperature sensitivity of mixtures with additions;
- tests of the compressive strength at lower strength levels, close to 5 MPa ;
- refinement of the relationships between compressive strength and W/B; increased amount of tests to allow for reliable curve-fitting and statistical evaluation of the k-values.

Isothermal calorimetry is an effective tool for the study of the hydration rate of cementitious materials. It can be used to further investigate time of induction of the main peak of hydration, depending on temperature and addition used, in combination with methods for determination of setting point or other methods for monitoring the hardening.

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APPENDIX 1

Paper I

Early-Age Strength Development at Low Temperatures in Concrete with Mineral Additions–Efficiency Coefficients for Slag and Silica Fume

by M. Lundgren

Synopsis: The efficiency coefficients, *k*-values, given in standards for some types of mineral additions have normally been determined on mature concrete cured at a laboratory temperature of about 20 °C. It is unlikely that the same values apply also to young concrete, particularly if cured at temperatures below 20 °C. Countries with long periods of cold weather wishing to promote the use of mineral additions in concrete without jeopardizing the safety on the construction site, e.g. at form removal, need more knowledge on the consequences of low temperatures at hydration and realistic data for the estimation of the early-age strength.

This paper presents the development of compressive strength up to 7 days and discusses 2-day and 7-day *k*-value with respect to strength for ground granulated blast-furnace slag and silica fume. Mortar mixtures with water-binder ratio W/B=0.4–0.7 were cured and tested at 5 °C and at 20 °C, in order to study the influence of the temperature, age, type and amount of mineral addition.

2-day and 7-day results show that the *k*-values given in standards overestimate the efficiency of both slag and silica fume. The two mineral additions also show different temperature dependencies. Therefore it is recommended that the standards should specify more differentiated values for each of these additions, dependent on among other things age and temperature.

Keywords: compressive strength, early age, granulated blast-furnace slag, *k*-value, low temperature, silica fume.

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BACKGROUND

One of the results of the attempt to reduce the environmental impact of the concrete industry is the use of mineral additions in concrete. The manufacture of portland cement is an energy-consuming process. It is also responsible for large emissions of CO_2 into the atmosphere. About 1 tonne of CO_2 is produced for each tonne of cement, with the calcination of the limestone and the combustion of fuels each being responsible for about half of these emissions. After overall modernization of the production processes, introduction of alternative fuels for the kilns and more effective cleaning of the smoke gases, in 1997 it was estimated that the calcination process still produced an amount of about 0.54 tonne of CO_2 per tonne cement (1). A more environmentally-friendly concrete industry can, therefore, be attained by replacing a part of the portland cement clinker with alternative binders.

Different qualities of slag, fly ash and silica fume are today valuable industrial by-products used as mineral additions in concrete. They are accepted main constituents, replacing portland clinker, in standard type CEM II and type CEM III cements in accordance with European Standard EN 197-1 (2). Mineral additions have been commonly used in many countries for a long time. Some additions are specifically used because they help to improve certain properties of the concrete: lower permeability, higher resistance to chemical attack, etc. Some additions are have become essential constituents of new types of concrete: silica fume in high-performance concrete, limestone filler in self-compacting concrete.

In Sweden, as in most of the Nordic countries, normal portland cement has been the dominant binder in concrete. Alternative binders are often viewed with suspicion and avoided because of, among other things, the uncertainties related to early-age strength development at low temperatures. Additions are considered to be responsible for retarding the hydration process and for increasing the sensitivity of concrete properties to temperature, particularly to low temperatures. However, it is somewhat unclear in what way and by how much mineral additions affect the early-age behaviour of concrete at low temperatures, which would jeopardize safe form removal and may unnecessarily reduce the construction rate during periods of cold weather.

Three projects were started in Sweden between 2001–2002 for the study of mineral additions in concrete (3, 4, 5). The objective of one of these projects was to improve knowledge of the early-age behaviour of mixtures containing blast-furnace slag, silica fume and several types of limestone filler at low temperatures, by studying the heat of hydration and the early-age development of strength between 5 °C and 20 °C on mixtures with different water-binder ratios (4).

INTRODUCTION

This paper describes the first part of the study on the early-age development of strength: the 2-day and 7-day compressive strength tested at 5 °C and 20 °C on mixtures of mortars with ground granulated blast-furnace slag or silica fume as replacement for portland cement. The tests were carried out to study the compressive strength in relation to different water-binder ratio (*W/B*), different type and amount of addition, curing temperature and age. From empirical relationships between the compressive strength and the water-binder ratio this paper presents an attempt to estimate the efficiency coefficients for some additions. The term *binder* is used throughout this paper as short name for the *total mass of cementitious materials* in a mixture, i.e. cement and addition. *W/B* designates the ratio between *water* and the sum of *cement and addition.*

Efficiency coefficient, *k*-value

The efficiency coefficient *k* for a certain addition shows how many parts by mass of cement that can be replaced by one part of addition without changing the properties of the concrete. One of the main factors governing concrete properties such as strength or permeability is the water-cement ratio *W/C*. When additions are used together with the cement as binder in a mixture, the *W/C* is often replaced by an equivalent water-cement ratio $(W/C)_{eq}$. The equivalent water-cement ratio is defined as:

$$(\mathrm{W/C})_{\mathrm{eq}} = \frac{W}{C+kR} \qquad \text{(Eq 1a)}$$

where W = water content, by mass
C = cement content, by mass
R = addition content, by mass
k = efficiency coefficient

From Eq. (1a) the *k*-value can be calculated as:

$$\mathrm{k} = \frac{\dfrac{W}{(W/C)_{eq}} - C}{R} \qquad \text{(Eq 1b)}$$

k-values discussed in this research are calculated from estimations of $(W/C)_{eq}$ with respect to compressive strength.

European Standard EN 206-1 (6) gives *k*-values for silica fume (*k*=1 or 2 depending on the exposure environment), but not for slag. The Swedish application of EN 206-1, SS 13 70 03 (7), recommends *k*=0.6 for slag. These values originate from tests on 28-days old concrete cured at 20 °C. It is very unlikely that these values apply to young concrete manufactured in cold weather. New *k*-values need to be determined for early-age concrete cured at low temperatures.

EXPERIMENTS

Materials and mixtures

Swedish rapid hardening portland cement CEM I 52,5 R, Swedish ground granulated blast-furnace slag *Merit 5000* and Norwegian undensified silica fume *Microsilica 940-U* (Table 1) were used for the manufacture of mortar mixtures, together with CEN Standard sand with grain size 0-2 mm and deionised water. Mixture proportions are shown in Table 2.

The proportions of the basic mixtures, C-40 to C-70, were set up with consideration to the consistence of the fresh mortar determined in accordance with EN 1015-3 (8). For the purpose of this research it was considered suitable, for each *W/C*, to use the same mixture at 20 °C and at 5 °C and to use mixtures with comparable consistence regardless *W/C*. Starting with a mixture of W/C=0.5, with the proportions water:cement:sand 1:2:6 by mass in accordance with EN-196-1 (9), which yielded a consistency on the flow table of 197 mm at 20 °C, mixtures were designed for the rest of the W/C. The paste amount needed to be slightly increased in order to reach the same consistence at 5 °C. For the purpose of this research, however, it was more suitable that the same mixture proportions were used at both temperatures. Therefore, several mixtures were tested at both temperatures for each W/C in order to find appropriate ones not leading to heavy bleeding or aggregate separation and having comparable consistence.

In mixtures with additions part of the cement was replaced by slag or silica fume on a basis of percentage by mass. All mixtures were manufactured without chemical admixtures to avoid introducing another influencing parameter, other than the type and amount of addition.

Tests

In principle compressive strength tests were carried out on mortar prisms in accordance with EN 196-1 (9), but with other mortar compositions. A batch of mortar sufficient for the manufacture of three 40 mm x 40 mm x 160 mm prisms was prepared at a time, by mechanical mixing. In the case of the mixtures with additions the dry cementitious materials were mixed together by hand prior to adding them to the water, to ensure homogeneity. Specimen compaction was performed on a vibrating table, for 2 x 60 s at a frequency of 50 Hz and an amplitude of 0.75 mm, in moulds fastened with clamps on the table. The prisms were cured in moulds during the first day (22–24 hours), covered to prevent evaporation, as specified in EN 196-1. From day two they were stored in lime-saturated water until the time for testing.

The tests were carried out at two temperatures, 20±1 °C and 5±1 °C, in climate chambers where the temperature was maintained constant throughout preparation, curing and testing.

Each test age involved first a three-point flexure test of three prisms per series. Then the six halves were tested for compressive strength at the exact age of 48 h ±10 min or 168 h ±10 min, counting from the time of mixing the binder with water.

RESULTS

Test results for different mixtures at different ages and different temperatures are given in Tables 3–5. The discussions in this paper focus on the *k*-values with respect to compressive strength.

The compressive strength f_c in Tables 3–5 is the calculated mean value for six test results per mixture. All mixtures were manufactured without air entraining agent and the natural air content in the mortar was low. It was not considered necessary for this analysis to apply any correction for air content. The air content was calculated as the difference between the bulk volume of each prism, determined at the actual test age by weighing the prism in air and in water, and the compact volume, calculated from the mass of the prism at demoulding, mixture proportions and compact density of each of the ingredients.

Fig. 1 shows the variation of strength versus $1/(W/C)$ at 5 °C and at 20 °C, for mortars with portland cement as the only binder. For W/C ranging from 0.4 to 0.7 there seems to be a good correlation between the test results and a linear regression within this interval. The same was found for the mixtures with additions, where linear regression analysis for results of strength versus $1/(W/C)$ yielded equations with correlation factors $R^2 > 0.98$. This indicates that empirical relationships, e.g. the linear equation proposed by Bolomey (10), can be found for the type of binders studied.

The calculation of the *k*-values is very sensitive to variations of the value of $(W/C)_{eq}$, particularly when the amount of addition is small. Even small deviations from Bolomey's relationship may, consequently, influence the result of the *k*-value significantly.

The k-values shown in this paper were therefore calculated without using Bolomey's relationship for the portland cement mixtures. The actual curves, connecting the test values (Fig. 2), were used instead. $(W/C)_{eq}$ was determined graphically, at each age and for each test temperature, by entering the strength of the mixture with addition in the actual curve for the mortar without additions. k-values were then calculated according to Eq. (1b). For calculating k-values for mortars with low compressive strength, the curves for the portland cement mortars were extended graphically downwards, with a slope defined by the line between the results for W/C=0.6 and 0.7 (dashed lines in Fig. 2). These k-values are uncertain and are shown in brackets in Tables 3–5. Low strength values were obtained especially for mortars with high W/B and high amounts of slag, low temperatures and low age at testing.

DISCUSSION

The k-value for mortar containing slag as a function of W/B is shown in Fig. 3. The values are representative for mortars up to seven days old and for temperatures of 5 °C and 20 °C. For these young mortars the k-value seems to be normally around 0.2–0.4, with the highest values being for seven days old mortar tested at 20 °C. According to the results the k-value seems to be more or less independent of the value of W/B.

In a project on durability carried out in close co-operation with the present research Boubitsas (11) found a k-value for slag within 0.7-1.1 at 28 days and 20 °C, by testing the same materials and using the same test methods. This value is on the safe side in comparison to k=0.6 for slag in SS 13 70 03. The early-age results clearly show that the k-value is significantly lower for young mortar, both when cured at 5 °C and at 20 °C. This means that the calculated strength for young concrete, for example at the time of form removal, will be significantly overestimated if conventional standard k-values, such as in the Swedish standard, are used. Therefore, in standards it should not be sufficient to give a single k-value for slag. Different values should be specified dependent on, among other things, age and temperature.

Fig. 4 shows the k-value as a function of age. W/B is 0.5 and the slag content 35% by mass. At 5 °C the k-value seems to be constantly low, around 0.2, up to 7 days. At 20 °C the k-value seems to increase slightly with age, from 0.2 at 2 days to about 0.3 at 7 days. All these values are, however, low. Consequently, the efficiency of slag will develop primarily after seven days of curing, particularly at low temperatures.

Fig. 5 shows the k-value as a function of temperature, for 2-days old mortars with a slag content of 35%. For two out of three different W/B, the k-value is constantly low, about 0.2, within the temperature range 5 °C to 20 °C. For a W/B of 0.6, however, there is a tendency that the k-value decreases with increasing temperature, but this tendency may be dependent on the uncertainties at the calculation of the results. Based on these results there seems to be no significant dependency on curing temperature for the 2-day k-value.

On the other hand, for 7-days old mortars (Fig. 6) there is a clear tendency for the k-value to increase with temperature, from about 0.2 at 5 °C to almost 0.4 at 20 °C. The value is, however, much lower than the corresponding value mentioned above, 0.7–1.1 at 28 days and 20 °C (11).

Fig. 7 shows the k-value at 5 °C as a function of the slag content. The k-value seems to increase with higher slag content. Dashed lines indicate, though, less reliable values for mortars with 65% slag content, due to the fact that the calculated value of $(W/C)_{eq}$ is uncertain as the corresponding value for compressive strength is very low and outside the range (Fig. 2).

Results at 28 days and 20 °C (11) also indicated certain dependency on the replacement percentage, although different for 65% slag content compared to the values in this investigation. The values in Fig. 7 are low and the tendency cannot be considered to be significant, but it is supported by other research showing dependency of k-value on the replacement percentage, age, type of cement and type of addition (12, 13).

The *k*-value for silica fume is shown in Figs. 8–11. EN 206-1 gives a *k*-value for silica fume 1.0 or 2.0 depending on the environment the concrete will be exposed for. The results show that no *k*-value at early age reaches 2.0, while many values are far below 1.0. This means that, as for slag, the values in standards must be much more differentiated compared with the present specifications. The *k*-values in standards should also be related to temperature and age.

Fig. 8 shows that the *k*-value is more or less independent of the *W/B*. *k*-value as a function of age (Fig. 9) shows a tendency for the *k*-value to decrease with age at 5 °C, but to increase with age at 20 °C. These tendencies are weak and cannot be considered to be significant.

Figs. 10 and 11 show the *k*-value as a function of temperature at two different ages. The 2-day results show clearly a decrease of the *k*-value with temperature, for all *W/B,* from about 1.3 at 5 °C to about 0.5 at 20 °C. At 2 days silica fume shows to be more efficient than the cement used ($k > 1$) when the curing temperature is 5 °C, but not at 20 °C. At 7 days the *k*-value seems to be more or less independent of the temperature and mostly lower than the values given in EN 206-1.

CONCLUSIONS

Based on the results obtained in this investigation, the following conclusions can be drawn:

- The results clearly show the that *k*-value for slag is significantly lower in young mortar, both when hydrated at 5 °C and at 20 °C, than the usual value given in standards. This means that the calculated strength for young concrete will be significantly overestimated if a usual, standardized *k*-value (e. g. 0.6) is used. Therefore, in standards it should not be sufficient to give a single *k*-value for slag. Different values should be specified, among other things dependent on age and temperature.
- The efficiency of slag does not seem to develop significantly until after seven days, especially for hydration at low temperatures.
- The *k*-value for slag in 2-days old mortars seems to be independent on temperature, while in 7-days old mortar there is a clear tendency for the *k*-value to increase with temperature, from about 0.2 at 5 °C to almost 0.4 at 20 °C.
- The *k*-values for silica fume in young mortar cured at low temperatures are often much lower than corresponding values given in standards. This means, as for slag, that the values in standards should be much more differentiated compared with the situation today. The k-values in standards should be related also to temperature and age.
- At 2 days there is a clear tendency for the k-value for silica fume to decrease with temperature, from about 1.3 at 5 °C to about 0.5 at 20 °C. At 7 days, on the other hand, the *k*-value is about 0.8 and seems to be more or less independent of the temperature.

ACKNOWLEDGEMENTS

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Table 1 - Description of the cementitious materials, as reported by the producer

	Cement CEM I 52.5 R	Slag GBFS	Silica Fume SF
SiO_2 %	20.9	34.0	min 90
CaO %	64.1	31.5	max 0.7
SiO_2 %	20.9	34.0	min 90
Al_2O_3 %	3.8	12.0	max 1.5
Fe_2O_3 %	2.7	0.3	max 3.0
MgO %	2.8	17.0	max 2.0
Na_2O %	0.3	0.6	max 1.0
K_2O %	1.1	0.6	max 3.0
SO_3 %	3.4	3.5	
L.o.i. %	1.1	1.1	max 3.0
Spec. surf. m^2/kg	541 (Blaine)	470 (Blaine)	~ 20000 (BET)
ρ kg/m^3 1)	3114	2907	2246

1) Particle density (compact), determined at our laboratory on the actual batch.

Table 2 - Mixture composition. Amounts per batch used for the manufacture of three mortar prisms 40 mm x 40 mm x 160 mm

Mixture	W/C	W/B 1)	Water g	Cement g	GBFS g	SF g	Sand g
C-40	0.40		288	720	-	-	1350
C-50	0.50		240	480	-	-	1350
C-60	0.60		217.5	362.5	-	-	1350
C-70	0.70		210	300	-	-	1350
BFS20-40		0.40	288	576	144	-	1350
BFS20-50		0.50	240	384	96	-	1350
BFS20-60		0.60	217.5	290	72.5	-	1350
BFS20-70		0.70	210	240	60	-	1350
							1350
BFS35-40		0.40	288	468	252	-	1350
BFS35-50		0.50	240	312	168	-	1350
BFS35-60		0.60	217.5	235.6	126.9	-	1350
BFS35-70		0.70	210	195	105	-	1350
BFS65-50		0.50	240	168	312	-	1350
SF10-40		0.40	288	648	-	72	1350
SF10-50		0.50	240	432	-	48	1350
SF10-60		0.60	217.5	326.25	-	36.25	1350
SF10-70		0.70	210	270	-	30	1350

1) Water-binder ratio, i.e. water/(cement+addition), by mass

Table 3 - Test results for mortars with portland cement as the only binder

Mixture	W/C	Age *days*	Temp °C	Air 1) *%*	f_c mean 2) *MPa*	f_c std. dev. *MPa*
Age 2 days T 5 °C						
C-40	0.40	2	5	1.7	46.4	0.9
C-50	0.50	2	5	2.3	28.0	0.4
C-60	0.60	2	5	2.5	17.6	0.4
C-70	0.70	2	5	2.5	11.0	0.2
Age 7 days T 5 °C						
C-40	0.40	7	5	1.7	71.6	1.2
C-50	0.50	7	5	2.2	53.7	0.4
C-60	0.60	7	5	2.6	38.5	0.6
C-70	0.70	7	5	3.2	26.2	0.6
Age 2 days T 20 °C						
C-40	0.40	2	20	1.6	62.4	1.0
C-50	0.50	2	20	2.2	46.8	1.2
C-60	0.60	2	20	2.1	34.8	0.7
C-70	0.70	2	20	1.7	25.0	0.4
Age 7 days T 20 °C						
C-40	0.40	7	20	1.7	71.6	1.0
C-50	0.50	7	20	1.9	58.8	0.6
C-60	0.60	7	20	1.9	45.2	0.8
C-70	0.70	7	20	1.5	33.8	0.3

1) Natural air content in the mortar at test age. Mean of three values, 2) Mean of six values

Table 4 - Test results for mortars containing silica fume

Mixture	W/B	Age *days*	Temp *°C*	SF *% by mass*	Air 1) *%*	f_c mean 2) *MPa*	f_c std. dev. *MPa*	k mean
Age 2 days T 5 °C								
SF10-40	0.40	2	5	10	1.8	48.9	0.8	1.31
SF10-50	0.50	2	5	10	2.7	32.3	0.8	1.22
SF10-60	0.60	2	5	10	3.2	19.8	0.6	1.43
SF10-70	0.70	2	5	10	3.4	12.0	0.1	1.28
Age 7 days T 5 °C								
SF10-40	0.40	7	5	10	1.4	69.9	0.8	0.78
SF10-50	0.50	7	5	10	1.6	53.8	0.7	1.00
SF10-60	0.60	7	5	10	2.4	37.7	0.5	0.94
SF10-70	0.70	7	5	10	2.8	26.4	0.2	1.00
Age 2 days T 20 °C								
SF10-40	0.40	2	20	10	1.9	59.2	0.8	0.48
SF10-50	0.50	2	20	10	2.6	43.6	0.9	0.51
SF10-60	0.60	2	20	10	3.0	31.9	0.5	0.60
SF10-70	0.70	2	20	10	3.2	23.1	0.6	0.59
Age 7 days T 20 °C								
SF10-40	0.40	7	20	10	2.0	71.6	2.6	0.95
SF10-50	0.50	7	20	10	2.8	55.7	2.1	0.67
SF10-60	0.60	7	20	10	3.1	42.7	0.7	0.77
SF10-70	0.70	7	20	10	3.0	31.7	0.4	0.63

1) Natural air content in the mortar at test age. Mean of three values, 2) Mean of six values

Table 5 - Test results for mortars containing ground granulated blast furnace slag

Mixture	W/B	Age *days*	Temp *°C*	GBFS *% by mass*	Air[1] *%*	f_c mean[2] *MPa*	f_c std. dev. *MPa*	k mean[3]
Age 2 days T 5 °C								
BFS20-40	0.40	2	5	20	2.1	30.9	1.0	0.17
BFS20-50	0.50	2	5	20	2.9	16.9	0.6	0.11
BFS20-60	0.60	2	5	20	2.9	10.2	0.2	0.22
BFS20-70	0.70	2	5	20	2.5	6.3	0.2	(0.45)
Age 7 days T 5 °C								
BFS20-40	0.40	7	5	20	2.1	58.2	0.7	0.26
BFS20-50	0.50	7	5	20	2.9	37.9	1.2	0.13
BFS20-60	0.60	7	5	20	2.9	25.3	0.6	0.24
BFS20-70	0.70	7	5	20	2.2	17.9	0.6	0.45
Age 2 days T 5 °C								
BFS35-40	0.40	2	5	35	2.4	22.5	0.5	0.23
BFS35-50	0.50	2	5	35	3.0	12.0	0.3	0.25
BFS35-60	0.60	2	5	35	2.5	6.9	0.10	(0.37)
BFS35-70	0.70	2	5	35	2.2	4.3	0.09	(0.53)
Age 7 days T 5 °C								
BFS35-40	0.40	7	5	35	2.5	42.1	1.4	0.13
BFS35-50	0.50	7	5	35	2.9	26.9	0.5	0.21
BFS35-60	0.60	7	5	35	2.3	18.0	0.3	(0.35)
BFS35-70	0.70	7	5	35	1.9	12.1	0.4	(0.47)
Age 2 days T 5 °C								
BFS65-50	0.50	2	5	65	2.7	3.0	0.04	0.35
Age 7 days T 5 °C								
BFS65-50	0.50	7	5	65	2.7	9.3	0.12	0.31
Age 2 days T 20 °C								
BFS35-40	0.40	2	20	35	2.2	40.5	0.4	0.23
BFS35-50	0.50	2	20	35	2.7	25.2	0.2	0.17
BFS35-60	0.60	2	20	35	2.2	17.5	0.4	0.25
BFS35-70	0.70	2	20	35	1.3	12.6	0.2	(0.36)
Age 7 days T 20 °C								
BFS35-40	0.40	7	20	35	2.5	55.8	0.4	0.35
BFS35-50	0.50	7	20	35	2.4	38.7	0.1	0.32
BFS35-60	0.60	7	20	35	2.3	27.4	0.6	0.37
BFS35-70	0.70	7	20	35	1.6	19.9	0.2	0.40

1) Natural air content at test age. Mean of three values

2) Mean of six values

3) Values in brackets are uncertain because they are calculated for low strength levels, below the strength range of experimental values for the neat portland cement mixtures (Figs. 1, 2)

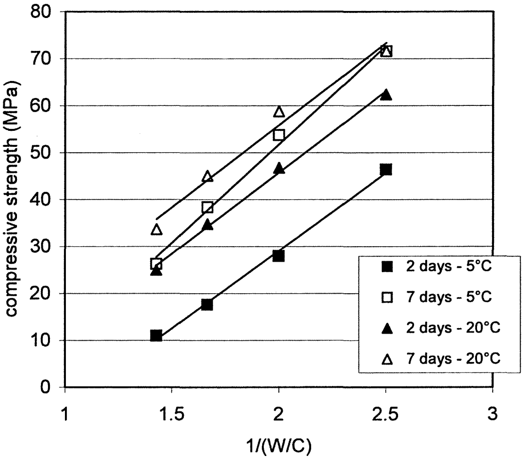

Fig. 1. Compressive strength vs 1/(*W/C*) for mortar with portland cement as the only binder. There is a good correlation between the test results (dots) and Bolomey's equation (lines).

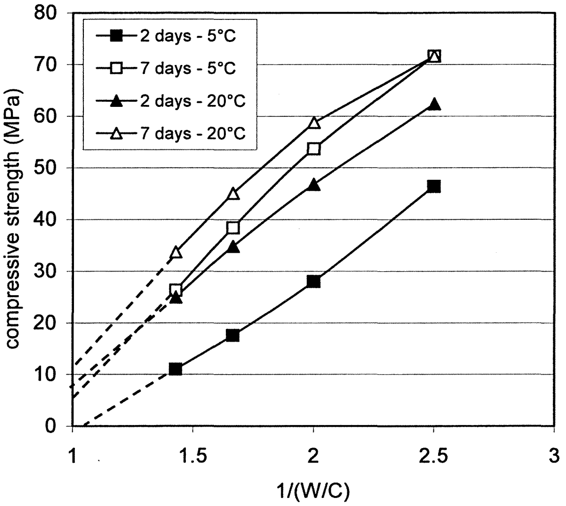

Fig. 2. The relationship between compressive strength and 1/(*W/C*) used for the calculation of $(W/C)_{eq}$. Results for mortar with portland cement as the only binder.

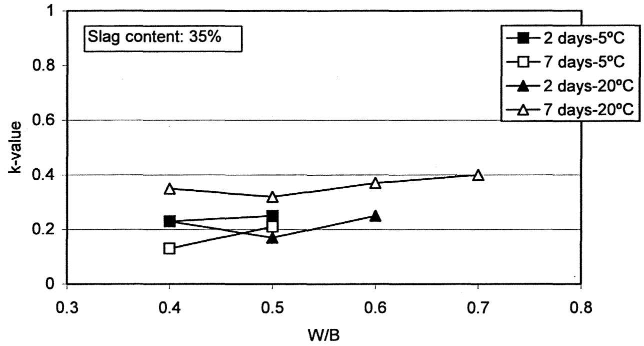

Fig. 3. The *k*-value for mortar containing slag, as a function of *W/B*. Results at slag content 35% by mass.

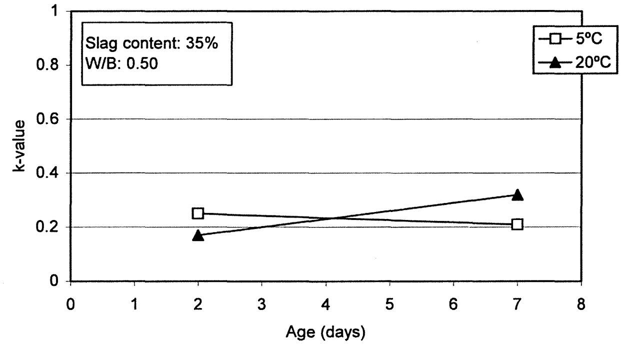

Fig. 4. The *k*-value for mortar containing slag, as a function of age.

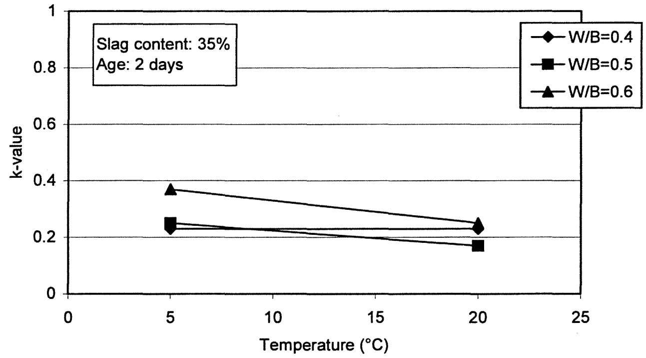

Fig. 5. The *k*-value for mortar containing slag, as a function of temperature. 2-days old mixtures.

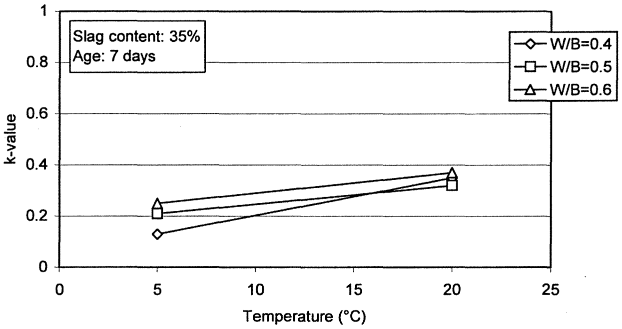

Fig. 6. The *k*-value for mortar containing slag, as a function of temperature. 7-days old mixtures.

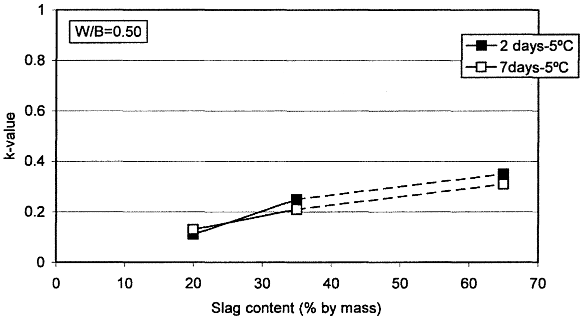

Fig. 7. The *k*-value as a function of slag content for mortars with *W/B*=0.50 tested at 5 °C. Results at different test ages.

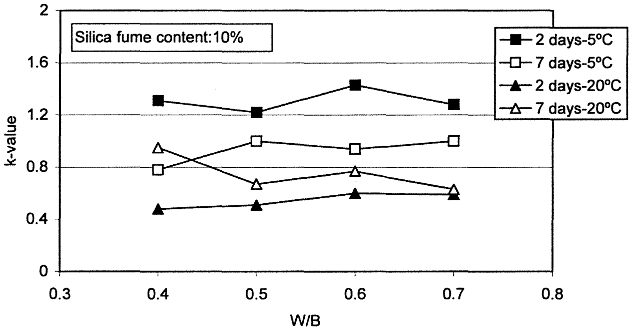

Fig. 8. The *k*-value for mortar containing silica fume, as a function of *W/B*. Results at different test ages and different temperatures.

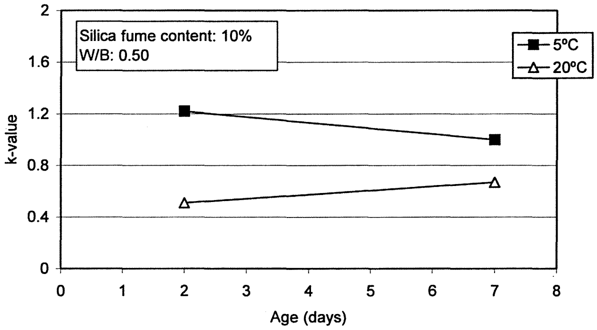

Fig. 9. The *k*-value for mortar containing silica fume, as a function of age. Mixtures with silica fume content 10% by mass and *W/B*=0.50.

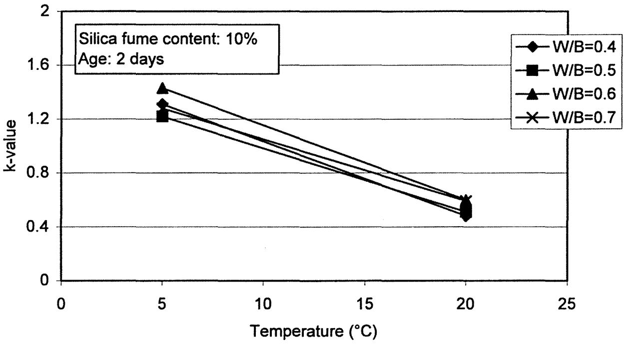

Fig. 10. The *k*-value for mortar containing silica fume, as a function of temperature. 2-days old mixtures.

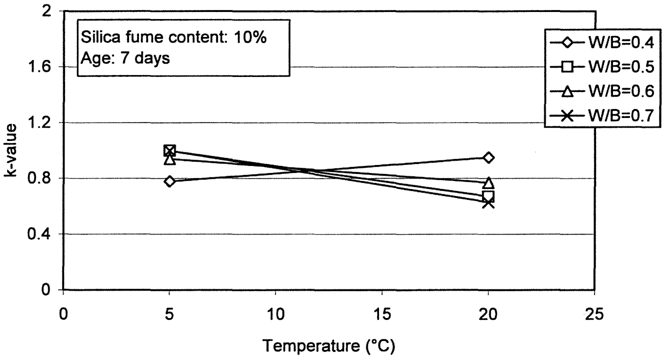

Fig. 11. The *k*-value for mortar containing silica fume, as a function of temperature. 7-days old mixtures.

APPENDIX 2

Paper II

Limestone Filler as Addition in Cement Mortars: Influence on the Early-Age Strength Development at Low Temperature

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ABSTRACT

Limestone filler is increasingly used, among other things as replacement for clinker in cement and as addition to self-compacting concrete. There are research results presented in the literature on how limestone filler affects the material properties of concrete but still much knowledge is lacking. This is relevant not least for young concrete used at low temperatures under winter conditions. This paper presents results from an investigation aiming to increase knowledge on the performance of limestone filler under cold, severe climatic conditions. The main focus is on the strength development of young concrete.

The results clearly indicate that curing temperature significantly influences the efficiency of limestone filler. The efficiency increases with decreasing temperature.

Key words: cement, early-age, efficiency, limestone filler, low temperature, strength.

1. INTRODUCTION

1.1 Background

The use of limestone filler in concrete has increased considerably during the last decade. Limestone is partly used as replacement for clinker in cement. In Sweden, for example, the most common cement today is a Portland-limestone cement with a limestone content of about 15 %, corresponding to CEM II/A-LL in EN197-1 [1]. Limestone filler is also used in self-compacting concrete (SCC) in order to improve the rheological properties and the stability. Typical quantities for SCC are about 100 kg limestone filler per m^3 of concrete.

It has been observed that limestone filler sometimes has a positive effect on strength and strength development. A so-called "filler effect" is given as reason for this influence. The mechanisms behind this effect are not fully understood but they are mostly considered to be of a physical nature, e.g. by filling voids between grains of cement clinker. Goldman and Bentur [2] suggest that a fine filler, with particle size smaller than 0.073 µm, even though inert, increases strength in concrete because the transition zone between the paste and the aggregates becomes denser. According to the authors this effect of physical nature, called “microfiller effect”, is present also when reactive fillers are used, e.g. silica fume, and can be at least as significant as the pozzolanic effect on the development of strength in concrete.

Limestone filler is normally considered to be an inert material, although its effects may also be of chemical nature [3], implying among other things increased rate of reaction of the C_3S. A chemical activity of the limestone filler when used in cement and concrete is also sustained by some more recent studies. Bonavetti et al [4] indicated an increased degree of hydration in cement pastes due to the presence of limestone filler. Tsivilis et al [5] found increased amount of CH and of non-evaporable water in limestone cement paste, which would imply an improved hydration of the alite. Studies by Péra et al [6] suggest an accelerating effect of limestone on the hydration of cement and show that different hydration products are formed due to the presence of $CaCO_3$. A general observation is that transformation of ettringite into monosulfate is delayed by the calcium carbonate [3, 7, 8].

Although a number of studies have been dealing with limestone as filler in concrete it is still not fully understood how the use of limestone filler influences the concrete strength, or which are the mechanisms behind the effect of limestone filler on the strength development in concrete. Almost all the studies presented in the literature are carried out at room temperature and at an age of about a month. Very little, if anything, is presented about the effect of limestone filler on the strength development at temperatures below 20 °C and at early age.

This paper presents results from a project where the early-age strength development at low temperature has been studied for concrete containing limestone filler. Limestone filler produced of carbonated rocks from different quarries and with different finenesses have been studied, in combination with parameters like the water-binder ratio of the mixture, age and temperature.

In EN 206-1 [9] the efficiency of type II additions, i.e. reactive ones such as most fly ashes and slags, is given by the *k*-value. The *k*-value defines how many parts by weight of ordinary Portland cement can be replaced by one part of a specified mineral addition without changing the concrete properties, especially where durability aspects are concerned. In this paper, however, the *k*-value concept is used also for limestone filler in order to be able to compare quantitatively the efficiency of different types and qualities of fillers and how they influence the early-age strength development at low temperature.

Tests have been carried out at two different temperatures: 5 °C as the main low temperature and 20 °C as a reference. The reason is that for structures in many regions, for example in the Nordic countries, the temperature at casting and curing lies many degrees below the standard laboratory temperature 20–23 °C. In order to perform efficient and safe construction it must be possible to estimate the strength development at early ages and low temperatures for all types of concrete, also for those containing limestone filler and other types of materials substituting cement and aggregates in concrete.

2. EXPERIMENTAL PROGRAMME

2.1 Materials

Ordinary Portland cement (**OPC**) of type CEM I 52.5 R was used as main binder in cement mortars, manufactured with Portland cement as the only binder, and in blended mortars, manufactured with cement and limestone filler. Limestone filler was studied as an addition to the mortar. It was included as part of the total amount of binder, replacing part of the cement on the basis of percent by mass of the total amount of binder. The binder content is defined in this paper as the total mass of cement and limestone filler.

Mortar mixtures were manufactured with CEN standard sand and deionised water, in principle according to EN 196-1 [10]. No chemical admixtures were used. The cement and the limestone filler qualities used are described in Tables 1 and 2.

Table 1 – Cement: clinker composition and physical properties.

					Particle size		Specific surface	
Cement	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	Top cut $d_{98\%}$ (μm)	Mean $d_{50\%}$ (μm)	Blaine (m^2/kg)	BET (m^2/kg)
CEM I 52.5R **(OPC)**	62.8	12.4	5.5	8.3	~ 32	~ 7.5	541	1760

Limestone is a sedimentary calcium carbonate rock formed through sedimentation. Despite identical chemical composition, rocks from different deposits may vary considerably. Crystal shape and size, porosity, hardness and reactivity during processing may be very different in rocks formed in different environments. A characterization of some of these parameters is given in [11]. There are three distinct types of limestone:

- chalk, a younger, microcrystalline rock, produced by the sedimentation of shells of small fossils
- limestone, a more compact sedimentary rock, with a crystal size between that of chalk and that of marble
- marble, a metamorphic rock with coarse crystals, formed when chalk or limestone recrystallised under conditions of high temperature and high pressure.

In order to analyse if differences in mineral properties have any influence on the early-age strength development, blended mortars were manufactured with cement and each of these types of limestone, as addition. Powders of high-purity chalk **(CH)**, limestone **(LL)** and marble **(MA)**, with a particle size distribution close to the particle size distribution of the cement used **(OPC)**, were used for a comparison independent on fineness.

Table 2 – Limestone: chemical composition and physical properties.

		Particle size		Specific surface
Limestone	$CaCO_3$ (%)	Top cut $d_{98\%}$ (μm)	Mean $d_{50\%}$ (μm)	BET (m^2/kg)
Chalk **(CH)**	≥ 98%	~ 30	~ 2.3	2200
Marble **(MA)**	≥ 98%	~ 30	~ 7	1500
Limestone **(LL)**	≥ 98%	~ 30	~ 5.5	1000
Limestone, coarse fraction **(LLC)**	≥ 98%	~ 70	~ 22	700
Limestone, fine fraction **(LLF)**	≥ 98%	~ 3	~ 0.44	15000

For the study of the influence of the fineness of the limestone two more powders were studied:
- a very fine fraction (**LLF**), comparable with the limestone fraction found in the Swedish Portland-limestone cement of type CEM II/A-LL, and a coarse fraction (**LLC**) comparable with the particle size distribution of a common limestone filler used in self compacting concrete. The two fractions LLC and LLF are of same type and from the same quarry as limestone LL.

2.2 Mixtures and tests

The use of limestone as addition was studied primarily on mortar mixtures with 24% limestone, tested for compressive strength at the age of 2 days and 7 days, at 5 °C and 20 °C respectively. Limestone type LL was studied over a range of water-binder ratio of 0.4 to 0.7. Comparison was made between cement mortars with $W/C = 0.4$–0.7 and blended mortars manufactured with the same amounts of water, sand and binder, but by using a mixture of cement and limestone filler as binder.

Comparisons between limestone (LL) and marble (MA) or chalk (CH) and the influence of the fineness (LL versus LLF and LLC) were made on mixtures with $W/B = 0.5$. This comparison between different type and fineness of limestone filler was also made at 12% limestone content, however only limited at the test temperature of 5 °C.

A content of 12% limestone filler is comparable with the amount of limestone in the Swedish Portland-limestone cement CEM II/A-LL 42.5 R. 24% limestone is slightly higher than the amount of limestone allowed in a cement CEM II/A-L, but the reason for studying this amount was based on the assumption that, at a higher amount, the efficiency of limestone addition could be better recognized due to a smaller scatter of the results, see for example [12].

Mortar prisms, 40 x 40 x 160 (mm), were manufactured and tested in principle by following the procedures in EN 196-1 [10]. However, some deviations from the standard procedures were made, to adjust to the purpose of this investigation:

- mixture proportions were changed, to be able to test mixtures with $W/B = 0.4$–0.7 and having similar consistence,
- the temperature at manufacture, curing and test was 5 °C and, for some test alternatives, also 20 °C for comparison,
- the binder consisted of cement and limestone (parts of the cement replaced by limestone, 1:1 by mass).

The proportions of the mixtures were chosen with consideration to the consistence of the fresh mortar. This was measured on a flow table according to EN 1015-3. Starting with the consistence obtained at 20 °C for a standard mortar with the proportions water:cement:sand 225:450:1350 (g), new mixtures were set up to reach similar consistence at $W/C = 0.4$, 0.6 and 0.7. Then new mixture proportions were determined at 5 °C, to obtain mortars with same consistence for these W/C.

However, for the purpose of this research it was more suitable to use the same proportions at both 5 °C and 20 °C for each W/C. Therefore the intermediary proportions shown in Table 3 were chosen, yielding not the same but comparable consistence. Blended cement-limestone filler mixtures with $W/B = 0.4$–0.7 were manufactured with the same proportions water:powder:sand as the mixtures, but with parts of the cement replaced with limestone.

Table 3 shows the mixture composition of the tested mortars. Cement mixtures were labelled according to the rule *binder-W/C*. Blended mixtures were labelled according to the rule *limestone type and amount - W/B*. The type of limestone filler was coded LL, LLF, LLC, MA or CH and the amount of filler (12 or 24) as percent of the total amount of binder.

Table 3 – Mixture composition. Amounts per batch needed for the manufacture of three mortar prisms 40mm x40mm x160mm.

Cement mortars	W/C	Water (g)	Cement (g)	Sand 1) (g)	Blended mortars	W/B 2)	Cement (g)	Limestone (g)	W/C
OPC-0.4	0.4	288	720	1350	LL24-0.4	0.4	547.2	172.8	0.53
OPC-0.5	0.5	240	480	1350	LL12-0.5, LLF12-0.5, LLC12-0.5, MA12-0.5, CH12-0.5	0.5	422.4	57.6	0.57
					LL24-0.5, LLF24-0.5, LLC24-0.5, MA24-0.5, CH24-0.5	0.5	364.8	115.2	0.66
OPC-0.6	0.6	217.5	362.5	1350	LL24-0.6	0.6	275.5	87	0.79
OPC-0.7	0.7	210	300	1350	LL24-0.7	0.7	228	72	0.92

1) Same amount of sand was used in both cement mortars and blended mortars.
2) Water/binder ratio = water/(cement + limestone), by mass.

All the constituent materials were pre-stored at 5 °C or 20 °C before starting manufacturing the specimens. The prisms were manufactured, compacted, stored and tested in climate rooms with constant temperatures, 5 °C or 20 °C respectively. After mixing, the prisms were compacted while in mould, on a vibrating table: 2 times 60 s, at a frequency of 50 Hz and an amplitude of 0.75 mm. The prisms were cured in moulds for one day, sealed against evaporation, and then stored in lime-saturated water until testing.

The main test temperature was 5 °C, but most mixtures were tested at 20 °C as well, for comparison with the standard laboratory temperature. The test alternatives are shown in Table 4.

Table 4 – Test alternatives: type of binder and W/B per test age and test temperature.

Temperature	Binder	Test age 2 days	Test age 7 days	Test age 28 days
5 °C	OPC	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
	OPC 88% Limestone 12%	LL, LLF, LLC, MA, CH 0.5	LL, LLF, LLC, MA, CH 0.5	LL 0.5
	OPC 76% Limestone 24%	LL 0.4, 0.5, 0.6, 0.7 LLF, LLC, MA, CH 0.5	LL 0.4, 0.5, 0.6, 0.7 LLF, LLC, MA, CH 0.5	LL 0.5
20 °C	OPC	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7	0.4, 0.5, 0.6, 0.7
	OPC 88% Limestone 12%	LL 0.5	LL 0.5	LL 0.5
	OPC 76% Limestone 24%	LL 0.4, 0.5, 0.6, 0.7 LLF, LLC, MA, CH 0.5	LL 0.4, 0.5, 0.6, 0.7 LLF, LLC, MA, CH 0.5	LL 0.5

Strength was determined according to EN 196-1. Three prisms per mixture were tested by three-point flexure test, followed by compressive strength testing on the resulting six half-prisms. The test ages were 2 days and 7 days, ± 10 minutes. Tests at 28 days were beyond the purpose of this research. However, for a comparison with the standard age, cement mixtures and blended mixtures LL24-0.5 and LL12-0.5 were tested at 28 days as well. See Table 4.

3 RESULTS

This paper presents the test results of the compressive strength (f_c). Based on the compressive strength, the efficiency coefficients (*k*-values) for the different types of limestone fillers were calculated.

Table 5 shows the compressive strength for the cement mortars, as mean of six values per mixture, and the variation between the lowest and highest test values.

Table 5 – Test results: compressive strength for cement mortars.

Cement mortars	W/C	Air[1)] %	f_c mean value (MPa)	f_c min-max (MPa)	Air[1)] %	f_c mean value (MPa)	f_c min-max (MPa)
			2 days 5°C			**2 days 20°C**	
OPC-0.4	0.4	1.7	46.4	44.7-46.9	1.6	62.4	62.1-63.7
OPC-0.5	0.5	2.3	28.0	27.5-28.6	2.2	46.8	44.7-47.5
OPC-0.6	0.6	2.5	17.6	17.0-18.3	1.8	34.8	33.6-35.5
OPC-0.7	0.7	2.5	11.0	10.7-11.2	1.7	25.0	24.4-25.6
			7 days 5°C			**7 days 20°C**	
OPC-0.4	0.4	1.7	71.6	70.4-73.2	1.7	71.6	70.1-73.1
OPC-0.5	0.5	2.2	53.7	53.1-54.2	1.9	58.8	58.3-59.6
OPC-0.6	0.6	2.6	38.5	38.5-39.1	1.9	45.2	44.4-46.2
OPC-0.7	0.7	3.2	26.2	25.6-27.1	1.5	33.8	33.2-34.1
			28 days 5 °C			**28 days 20°C**	
OPC-0.4	0.4	2.5	84.0	80.7-86.2	1.7	83.2	81.8-84.2
OPC-0.5	0.5	2.6	67.4	66.6-68.1	2.2	65.45	64.9-66.2
OPC-0.6	0.6	2.4	52.7	50.9-53.7	2.3	50.40	48.9-51.7
OPC-0.7	0.7	1.9	39.3	38.7-39.7	1.8	40.33	39.3-41.2

1) Natural air content in the mortar.

Table 6 shows the results for the blended mortars. Strength results are shown as mean, lowest and highest test value. The natural air content in the blended mortars was similar, of same magnitude, as the air content in the cement mortars. Therefore these values are not shown, for the sake of simplicity of the table.

Table 6 shows also the efficiency coefficients, *k*-values, of the different fillers in different mixtures.

APPENDIX 5

Results from calorimetric testing

Table B5:1 *Calorimetric test results for pastes with Portland cement as the only binder*

Mixture	**W/C**	**Age** *days*	**Temp** °C	**Q_C/C mean** [1] *J/g_{cement}*	**$\Delta/(Q_C/C)$** [2] *J/g_{cement}*
C-40	0.40	2	5	203.1	4.0
C-50	0.50	2	5	198.0	0.4
C-60	0.60	2	5	202.1	2.2
C-70	0.70	2	5	198.8	1.4
C-40	0.40	7	5	302.3	4.8
C-50	0.50	7	5	320.0	0.6
C-60	0.60	7	5	320.5	1.2
C-70	0.70	7	5	317.1	2.2
C-40	0.40	2	20	301.5	1.2
C-50	0.50	2	20	319.1	0.8
C-60	0.60	2	20	321.7	0.6
C-70	0.70	2	20	323.3	4.8
C-40	0.40	7	20	346.9	0.6
C-50	0.50	7	20	390.0	1.4
C-60	0.60	7	20	409.0	0.4
C-70	0.70	7	20	413.6	11.0

1) Mean of two values

2) Difference between the two individual values

Table B5:2 Calorimetric test results for pastes containing ground granulated blast furnace slag

Mixture	**W/B**	**Age** *days*	**Temp** *°C*	**GBFS** *% by mass*	**Q_{C+R}/C mean** 1) J/g_{cement}	**$\Delta(Q_{C+R}/C)$** 2) J/g_{cement}
BFS20-40	0.40	2	5	20	208.8	1.0
BFS20-50	0.50	2	5	20	209.0	0.6
BFS20-60	0.60	2	5	20	211.3	1.2
BFS20-70	0.70	2	5	20	205.2	4.0
BFS20-40	0.40	7	5	20	336.7	3.4
BFS20-50	0.50	7	5	20	333.1	1.2
BFS20-60	0.60	7	5	20	340.0	4.2
BFS20-70	0.70	7	5	20	334.9	11.8
BFS20-40	0.40	2	20	20	331.8	1.2
BFS20-50	0.50	2	20	20	337.4	2.4
BFS20-60	0.60	2	20	20	336.7	0.8
BFS20-70	0.70	2	20	20	336.0	0.0
BFS20-40	0.40	7	20	20	396.4	0.8
BFS20-50	0.50	7	20	20	421.7	0.2
BFS20-60	0.60	7	20	20	427.2	2.6
BFS20-70	0.70	7	20	20	423.1	0.6
BFS35-40	0.40	2	5	35	223.8	1.4
BFS35-50	0.50	2	5	35	218.5	0.8
BFS35-60	0.60	2	5	35	218.5	2.2
BFS35-70	0.70	2	5	35	211.5	0.0
BFS35-40	0.40	7	5	35	366.6	6.4
BFS35-50	0.50	7	5	35	352.5	1.2
BFS35-60	0.60	7	5	35	362.2	13.0
BFS35-70	0.70	7	5	35	356.2	0.0
BFS35-40	0.40	2	20	35	367.9	0.8
BFS35-50	0.50	2	20	35	356.6	1.0
BFS35-60	0.60	2	20	35	356.7	0.6
BFS35-70	0.70	2	20	35	365.9	0.0
BFS35-40	0.40	7	20	35	487.8	5.0
BFS35-50	0.50	7	20	35	468.1	0.8
BFS35-60	0.60	7	20	35	469.2	4.4
BFS35-70	0.70	7	20	35	511.0	1.8
BFS65-50	0.50	2	5	65	225.0	2.6
BFS65-50	0.50	7	5	65	437.2	10.0
BFS65-50	0.50	2	20	65	422.2	0.8
BFS65-50	0.50	7	20	65	647.1	5.2

1) Mean of two values.
2) Difference between the two individual values

Table B5:4 Calorimetric test results for pastes containing limestone filler

Mixture	W/B	Age *days*	Temp *°C*	GBFS *% by mass*	Q_{C+R}/C mean 1) J/g_{cement}	$\Delta(Q_{C+R}/C)$ 2) J/g_{cement}
LL24-40	0.40	2	5	24	230.4	1.4
LL24-50	0.50	2	5	24	229.7	1.8
LL24-60	0.60	2	5	24	232.4	1.6
LL24-70	0.70	2	5	24	223.8	1.0
LL24-40	0.40	7	5	24	350.0	1.0
LL24-50	0.50	7	5	24	362.7	5.0
LL24-60	0.60	7	5	24	372.0	6.8
LL24-70	0.70	7	5	24	361.8	2.6
LL24-40	0.40	2	20	24	342.5	1.2
LL24-50	0.50	2	20	24	348.9	1.2
LL24-60	0.60	2	20	24	354.7	0.2
LL24-70	0.70	2	20	24	355.5	4.2
LL24-40	0.40	7	20	24	397.9	1.8
LL24-50	0.50	7	20	24	425.4	1.2
LL24-60	0.60	7	20	24	441.5	0.6
LL24-70	0.70	7	20	24	440.9	10.8
LLF24-50	0.50	2	5	24	265.8	0.6
LLC24-50	0.50	2	5	24	208.6	0.8
MA24-50	0.50	2	5	24	240.2	1.4
CH24-50	0.50	2	5	24	239.3	0.0
LLF24-50	0.50	7	5	24	375.8	2.2
LLC24-50	0.50	7	5	24	338.0	4.0
MA24-50	0.50	7	5	24	368.8	7.0
CH24-50	0.50	7	5	24	368.7	1.4
LLF24-50	0.50	2	20	24	360.3	2.0
LLC24-50	0.50	2	20	24	334.5	1.8
MA24-50	0.50	2	20	24	357.1	1.4
CH24-50	0.50	2	20	24	356.8	0.8
LLF24-50	0.50	7	20	24	426.3	2.4
LLC24-50	0.50	7	20	24	415.7	3.2
MA24-50	0.50	7	20	24	431.4	10.4
CH24-50	0.50	7	20	24	429.2	4.4
LL12-50	0.50	2	5	12	212.8	1.2
LLF12-50	0.50	2	5	12	247.6	0.2
LLC12-50	0.50	2	5	12	198.6	0.4
MA12-50	0.50	2	5	12	219.8	0.2
CH12-50	0.50	2	5	12	211.3	1.2
LL12-50	0.50	7	5	12	337.8	6.4
LLF12-50	0.50	7	5	12	358.9	0.6
LLC12-50	0.50	7	5	12	320.8	0.8
MA12-50	0.50	7	5	12	347.0	1.6
CH12-50	0.50	7	5	12	334.6	3.4
LL12-50	0.50	2	20	12	335.1	0.6
LLF12-50	0.50	2	20	12	348.6	0.6
LLC12-50	0.50	2	20	12	325.0	0.0
MA12-50	0.50	2	20	12	336.6	0.0
CH12-50	0.50	2	20	12	339.2	1.2
LL12-50	0.50	7	20	12	402.6	0.6
LLF12-50	0.50	7	20	12	407.2	0.0
LLC12-50	0.50	7	20	12	399.7	1.2
MA12-50	0.50	7	20	12	399.4	2.4
CH12-50	0.50	7	20	12	403.6	2.6

1) Mean of two values

2) Difference between the two individual values

Table B5:3 Calorimetric test results for pastes containing silica fume

Mixture	W/B	Age *days*	Temp *°C*	SF *% by mass*	Q_{C+R}/C mean 1) J/g_{cement}	$\Delta(Q_{C+R}/C)$ 2) J/g_{cement}
SF10-40	0.40	2	5	10	236.7	0.0
SF10-50	0.50	2	5	10	224.8	0.8
SF10-60	0.60	2	5	10	218.8	1.6
SF10-70	0.70	2	5	10	216.0	1.2
SF10-40	0.40	7	5	10	323.3	5.0
SF10-50	0.50	7	5	10	347.4	2.2
SF10-60	0.60	7	5	10	341.2	4.6
SF10-70	0.70	7	5	10	338.0	0.4
SF10-40	0.40	2	20	10	325.3	0.8
SF10-50	0.50	2	20	10	336.6	0.0
SF10-60	0.60	2	20	10	339.3	0.4
SF10-70	0.70	2	20	10	335.1	0.6
SF10-40	0.40	7	20	10	379.9	7.4
SF10-50	0.50	7	20	10	409.4	1.8
SF10-60	0.60	7	20	10	429.0	7.6
SF10-70	0.70	7	20	10	428.3	3.2
SF5-50	0.50	2	5	5	205.8	0.6
SF5-50	0.50	7	5	5	332.1	1.8
SF5-50	0.50	2	20	5	328.3	1.4
SF5-50	0.50	7	20	5	394.3	4.0

1) Mean of two values

2) Difference between the two individual values.

Table 6 – Test results: compressive strength for blended mortars and k-values for limestone.

Blended mortars	W/B	f_c mean (MPa)	f_c min-max (MPa)	k 1) mean	k 1) min-max	f_c mean (MPa)	f_c min-max (MPa)	k 1) mean	k 1) min-max
			2 days 5 °C				**2 days 20 °C**		
LL12-0.5	0.5	23.7	23.5-24.0	0.43	0.37-0.46	40.3	40.1-40.7	0.28	
LLF12-0.5	0.5	29.6	29.2-30.0	1.17	1.12-1.21				
LLC12-0.5	0.5	22.2	21.7-22.6	0.22	0.13-0.25				
MA12-0.5	0.5	24.7	24.3-25.4	0.52	0.49-0.64				
CH12-0.5	0.5	24.8	24.3-26.0	0.55	0.49-0.72				
LL24-0.4	0.4	32.5	31.7-33.1	0.35	0.32-0.39	47.6	46.8-48.7	0.19	0.17-0.28
LL24-0.5	0.5	19.0	18.6-19.3	0.38	0.36-0.42	32.8	32.5-33.1	0.19	0.19-0.23
LL24-0.6	0.6	11.8	11.6-12.0	0.46	0.45-0.49	23.2	22.7-23.8	(0.29)	(0.26-0.33)
LL24-0.7	0.7	7.7	7.6-8.0	(0.64)	(0.63-0.69)	17.1	16.7-17.5	(0.43)	(0.40-0.46)
MA24-0.5	0.5	20.2	19.8-20.7	0.48	0.43-0.51	34.4	33.9-35.2	0.27	0.26-0.32
CH24-0.5	0.5	21.4	20.7-22.1	0.56	0.51-0.60	34.6	33.9-35.1	0.29	0.26-0.32
LLF24-0.5	0.5	26.0	25.5-26.5	0.87	0.84-0.89	36.8	36.0-38.0	0.42	0.36-0.48
LLC24-0.5	0.5	16.4	15.8-17.2	0.21	0.15-0.27	31.8	31.3-32.2	0.15	0.13-0.17
			7 days 5 °C				**7 days 20 °C**		
LL12-0.5	0.5	49.0	47.7-49.7	0.57	0.44-0.62	50.9	50.4-51.7	0.17	
LLF12-0.5	0.5	54.4	53.3-55.6	1.08	0.96-1.21				
LLC12-0.5	0.5	46.3	45.1-47.5	0.33	0.20-0.43				
MA12-0.5	0.5	48.6	47.4-50.0	0.52	0.41-0.65				
CH12-0.5	0.5	50.8	50.3-51.5	0.75	0.70-0.79				
LL24-0.4	0.4	58.5	57.2-59.6	0.36	0.33-0.44	58.6	57.9-60.1	0.14	0.12-0.25
LL24-0.5	0.5	40.5	39.8-40.9	0.39	0.36-0.41	42.3	41.5-43.1	0.17	0.15-0.21
LL24-0.6	0.6	28.2	27.7-28.7	0.48	0.47-0.52	31.5	30.7-32.0	(0.26)	(0.22-0.30)
LL24-0.7	0.7	19.9	19.5-20.5	(0.63)	(0.61-0.66)	22.8	22.1-23.5	(0.30)	(0.26-0.35)
MA24-0.5	0.5	40.4	39.6-41.1	0.39	0.34-0.42	43.5	42.8-43.8	0.23	0.21-0.26
CH24-0.5	0.5	43.9	42.1-45.1	0.55	0.48-0.61	43.2	43.0-44.0	0.21	0.19-0.24
LLF24-0.5	0.5	44.1	43.4-44.9	0.57	0.54-0.60	44.5	43.3-45.9	0.27	0.23-0.34
LLC24-0.5	0.5	37.9	37.1-38.7	0.28	0.25-0.32	42.4	41.6-43.2	0.19	0.15-0.22
			28 days 5 °C				**28 days 20 °C**		
LL12-0.5	0.5	62.2	60.5-64.4	0.50		58.5	57.4-59.4	0.36	0.25-0.43
LL24-0.5	0.5	52.3	51.4-52.7	0.29		49.7	48.7-50.6	0.27	0.21-0.31

1) Values in brackets are uncertain because they are calculated for low strength levels, below the strength range of experimental values for the Portland cement mortars; see Figures 1 to 3.

Figures 1 and 2 show the early-age strength of the limestone mixtures LL24-0.4 to LL24-0.7 and OPC-0.4 to OPC-0.7 mixtures. There seems to be a fairly linear relationship between the compressive strength (f_c) and the inverse of the water-binder ratio for both cement and blended mortars. This indicates that a linear equation as proposed by Bolomey, Eq. (1), could be used for calculations, but with different empirical parameters a and b to be determined for each specific age and temperature.

$$f_c = a\left(\frac{1}{W/B} - b\right) \qquad (1)$$

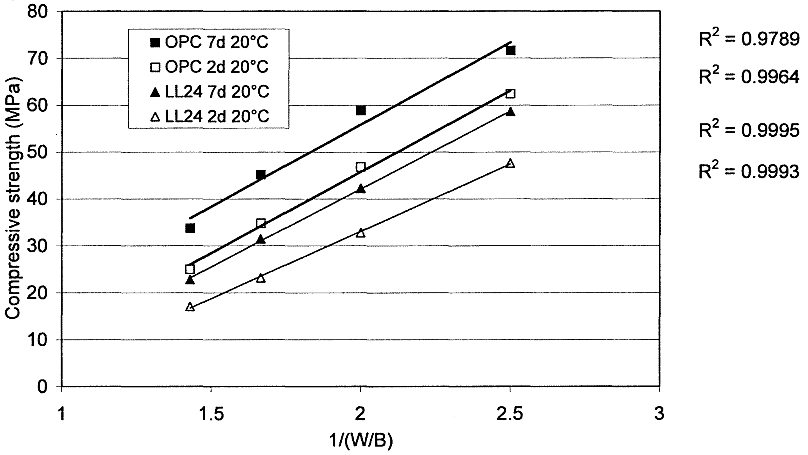


Figure 1 – Mean compressive strength at 20 °C (dots) and relationship versus 1/(W/B) (lines).

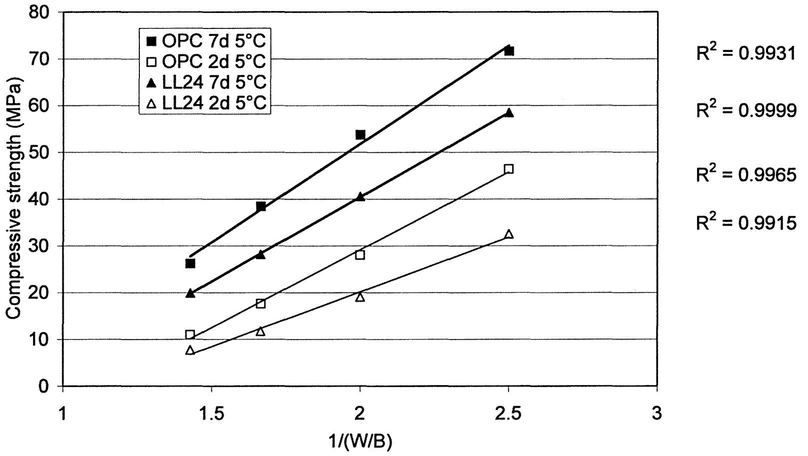


Figure 2 – Mean compressive strength at 5 °C (dots) and relationship versus 1/(W/B) (lines).

The calculation of the *k*-value for an addition is made by finding a replacement for the water/binder ratio – an equivalent water-cement ratio $(W/C)_{eq}$ – that the mixture with addition should have in order to obtain the same compressive strength as the mixture without addition.

The equivalent water-cement ratio is defined as:

$$(W/C)_{eq} = \frac{W}{C + kR} \qquad (2)$$

where:
W = water content, by mass
C = cement content, by mass
R = addition content, by mass
k = efficiency coefficient

From Eq. (2) it should be noted that the calculation of the *k*-value is sensitive to small variations of the $(W/C)_{eq}$, in particular when the amount of addition is small; see [12].

$(W/C)_{eq}$ can be calculated by using empirical relationships between strength and *W/C* for OPC mixtures, as e.g. trend lines according to Eq. (1), or they can be found out graphically from the real experimental data graphs.

In the present attempt to evaluate the efficiency of limestone filler the graphical alternative was used. The reason for this was primarily that the distribution of the results for OPC mortars deviated slightly from a straight trend line, especially at 7 days and 20 °C. See the correlation coefficients in Fig.1.

The *k*-values given in Table 6 were calculated by using Eq. (2) and the $(W/C)_{eq}$ determined from the experimental data graphs shown in Figure 3. A graphical extension, defined by the slope between *W/C* 0.6 and 0.7, was added for the lower strength values.

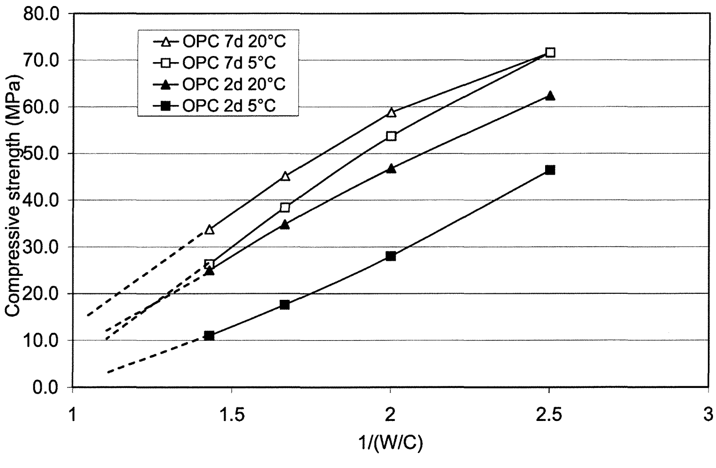


Figure 3 – The relationships between compressive strength and 1/(W/C) for cement mortars, used for the graphical estimation of $(W/C)_{eq}$ for mortars containing limestone filler.

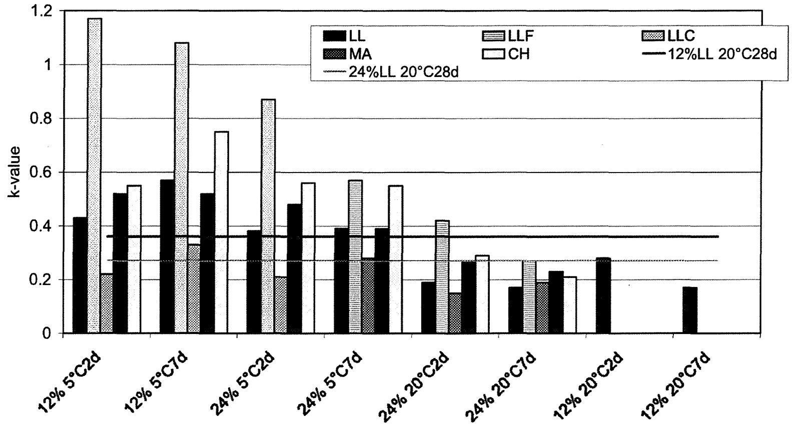
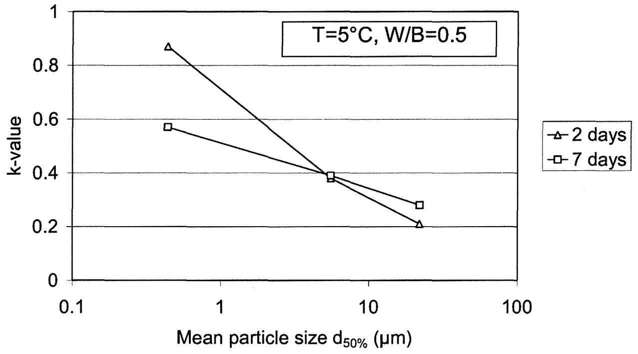
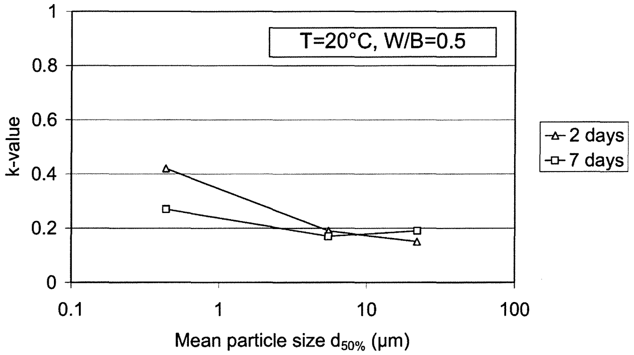


Figure 4– k-values for different qualities of limestone in mortars with W/B 0.5



a)



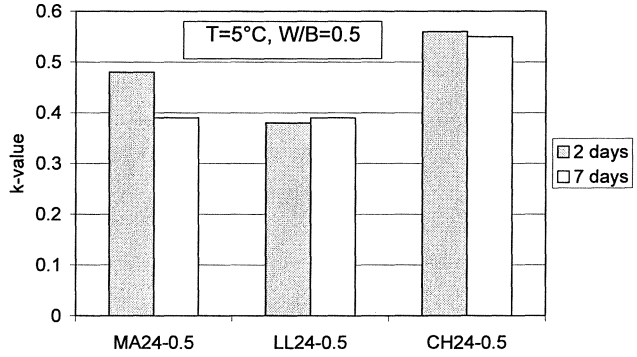
b)

Figure 5 – Influence of the fineness of the filler on the coefficient of efficiency at early age at 5 °C (a) and at 20 °C (b). Values for mortar with W/B 0.5 and 24% limestone filler type LL.

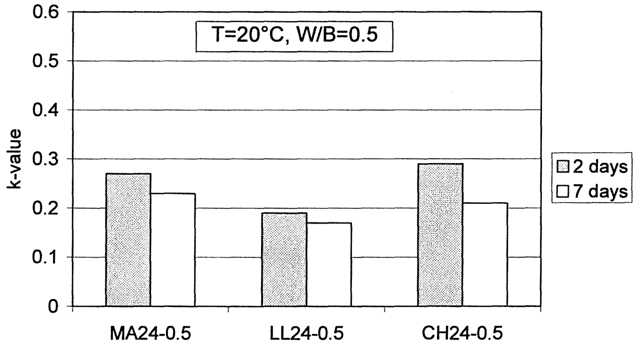
A general indication shown by the results in Table 6 is that efficiency coefficients for strength can be applied to limestone. However, the values are rather low, with the exception of the very fine limestone fraction LLF. An overall comparison of *k*-values for limestone is shown in Figure 4.

The *k*-values as a function of the mean particle size of the filler ($d_{50\%}$), in mortars with 24% limestone filler, are shown in Figure 5. The fineness of the filler seems to be a significant parameter regarding the efficiency coefficient, especially at low temperature. The finest limestone filler in this investigation has a *k*-value of almost 1 at 5 °C and early age, but it decreases to 0.2-0.3 for the coarse filler fraction. The fineness of the filler has an influence on the compressive strength also at 20 °C, at least for two days old mortar, but less significant as at low temperature.

A comparison between *k*-values for limestone fillers produced with different types of carbonated rock, CH, LL and MA, are presented in Figure 6 below.



a)



b)

Figure 6 – Influence of the type of the carbonated on the coefficient of efficiency of the limestone filler. Values at 5 °C (a) and at 20 °C (b) for mortar with 24% limestone and W/B 0.5.

According to the results, there does not seem to be any significant influence of the type of carbonated rock used on the *k*-value of the filler. This can be observed at both 5 °C and 20 °C, for 2 days as well as for 7 days old mortars. The small differences between these three types of carbonated rocks may be due to some differences in finesses. The mean particle size was 2.3, 5.5 and 7.0 respectively for CH, LL and MA. Probably the value for CH24 in Figure 6 would have been slightly lower if its fineness would have been the same as for LL24.

Figure 7 shows a comparison between the *k*-values for limestone filler (LL) and the *k*-values for two qualities of reactive additions – silica fume (SF) and ground granulated blastfurnace slag (SG) – as function of age, at 5 °C and 20 °C.

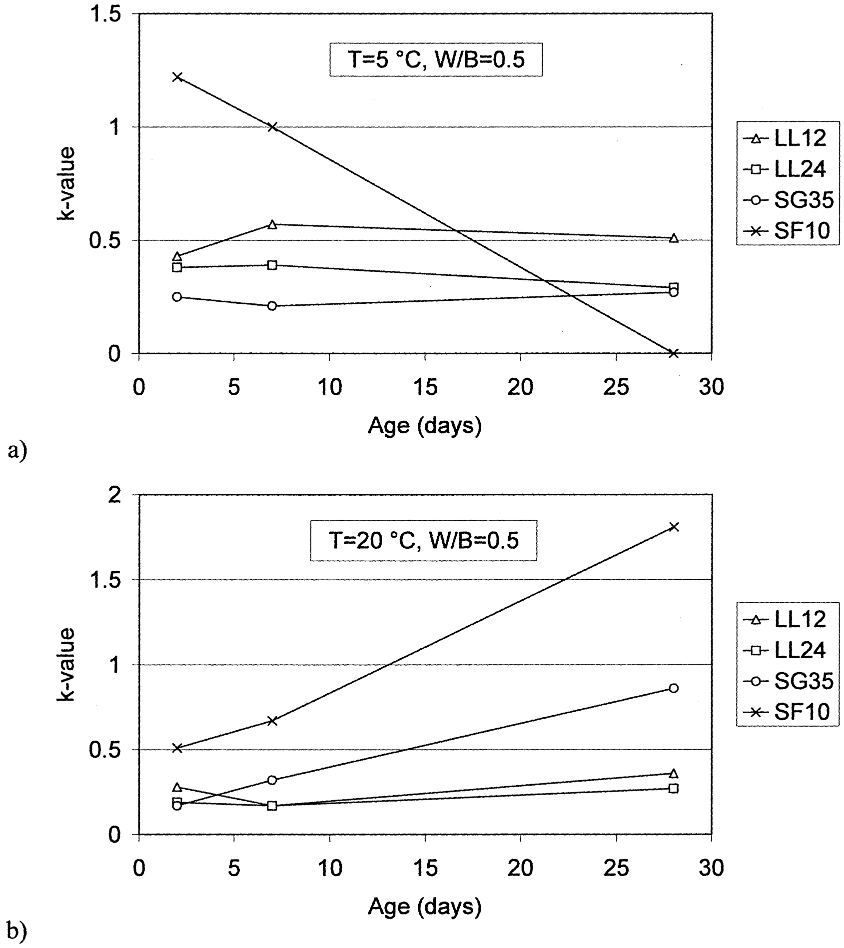


Figure 7 – Coefficients of efficiency as a function of age, for limestone (LL), silica fume (SF) and ground granulated blastfurnace slag (SG), at 5 °C (a) and 20 °C (b). Results for mortars with W/B 0.5 and 12% or 24% limestone, 10% silica fume or 35% slag as part of the binder.

The results for slag and silica fume were determined in a complementary part of the investigation presented in this paper. The tests were performed exactly as the tests presented in this paper, but with the use of silica fume or ground granulated blastfurnace slag instead of limestone filler. Details about the studies on SF and SG can be found in [13].

Considering the *k*-value of silica fume 1 or 2 according to EN 206-1 [9] and the *k*-value for slag 0.6 according to the Swedish Standard SS 13 70 03 [14], this investigation found that the 28-day values for slag and silica fume correspond well with the standard values, if the curing temperature is 20 °C. However, at earlier ages the *k*-values for these two additions are considerably lower, at both 5 °C and 20 °C.

At early age limestone filler and slag have comparable coefficients of efficiency in mortars cured at 20 °C, but in mortars cured at 5 °C limestone shows higher efficiency than slag: *k*-values are about 0.4 or higher, compared to about 0.2 for slag. On the other hand neither limestone nor slag reach the efficiency of silica fume at early age, regardless the curing temperature.

The comparison in Figure 7 shows that if a low temperature can lead to higher early-age coefficient of efficiency compared to 20 °C, not least for limestone, the development up to 28 days is very different at different temperatures. At 20 °C slag shows a significant increase in efficiency, reaching a *k*-value of about 0.8 at 28 days, while limestone only reaches values of about 0.3. At 5 °C on the other hand the efficiency of both slag and limestone seems to remain more or less unchanged after 7 days, though at a higher level for limestone compared with slag. These observations refer to the addition qualities used in this study, in mortars with W/B 0.5.

Limestone compared with silica fume shows significant differences. The early-age *k*-values for silica fume are higher than for limestone, much higher at 5 °C compared to 20 °C. Later at 28 days, where the *k*-values for limestone show small changes compared to early-age values, silica fume shows considerably increased values at 20 °C and an opposite development at 5 °C. After 7 days the efficiency of silica fume in mortars cured at 5 °C decreases rapidly, showing zero efficiency for compressive strength at 28 days.

Similar observations, that a low temperature may with time reduce the strength-increasing effect of silica fume, have been mentioned in other studies [15, 16]. This performance is however not fully explained or understood.

4 CONCLUSIONS

Based on the results found in this investigation, the following conclusions can be drawn:

- All the types of limestone filler used in this investigation showed a positive effect, compared with what could be expected from a completely inert material, on the mortar compression strength. This effect can be quantified by the coefficient of efficiency or *k*-value. For the limestone fillers the *k*-value was normally in the range of 0.2-0.5, with the highest values when cured at low temperature. For a very fine-grained limestone filler, however, a *k*-value of about 1 was found for young mortar cured at 5 °C.
- The *k*-value is strongly influenced by the fineness of the limestone filler, especially at low temperatures and young age.
- The type of carbonated rock used for producing the limestone filler, with regard to the metamorphose level, does not seem to significantly influence the *k*-value. This is relevant at least for the three types of carbonated rock used in this investigation.

- Traditional type II additions such as silica fume and ground granulated blast furnace slag show, as expected, higher *k*-values than limestone filler at 20 °C and 28 days. At young ages (below 7 days), however, the *k*-value of the limestone fillers used in this study are comparable or even higher than the corresponding values for slag. These limestone fillers show also lower *k*-values than silica fume at early ages, but after a longer curing time at low temperature limestone maintains its efficiency for compressive strength while the efficiency of silica fume is decreasing.

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APPENDIX 3

Paper III

Cement Pastes with Mineral Additions and Fillers: Heat of Hydration at Early Age and Low Temperature

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ABSTRACT

Isothermal calorimetry was used to study the heat of hydration of cement pastes with mineral additions and fillers at early age at 5°C and 20°C respectively. It is shown that isothermal calorimetry is a useful tool for evaluating the efficiency of additions and fillers.

Granulated blast furnace slag, silica fume and limestone filler of different fineness and quality were used as part of the binder with normal Portland cement CEM I 52.5R. Values for the efficiency of the additions/fillers and the amount of heat developed were estimated. The results are compared with corresponding efficiency values for compressive strength.

The so called filler effect is analysed and discussed. Two mechanisms that can contribute to the effect are discussed.

Key words: cement, compressive strength, efficiency, heat of hydration, temperature, limestone filler, slag, silica fume.

1 INTRODUCTION

In Sweden, concrete traditionally has been produced by using ordinary Portland cement as binder. Additions and filler were rarely used. This is however gradually changing. Today the most commonly used cement in Sweden contains about 15% limestone filler, silica fume is often used in concrete qualities exposed to severe climatic conditions and large amounts of filler are used in self-compacting concrete. Due to environmental considerations and to an open and expanding European market, the use of cement and concrete containing additions/fillers can be expected to increase in Sweden in the future.

The previous limited use of additions and fillers in Sweden can be explained by lack of knowledge of how these materials affect concrete properties under the harsh and severe Swedish climatic conditions. This particularly applies to properties such as consistency, strength development under winter conditions and durability.

The project presented in this paper is a part of a larger Swedish research program in which the influence of additions and fillers on concrete properties has been studied. The main interest was to study the influence on early strength development under winter conditions /1, 2/. Results on the influence of additions/fillers on consistency are presented in /3/ and on durability/service life in /4/.

This paper reports the study of the heat of hydration using isothermal calorimetry at different curing temperatures, during the first week of hydration of pastes with and without additions and filler. This investigation is closely related to those presented in /1, 2/, the cement qualities, additions and fillers tested being identical. The results from the three investigations are compared in this paper.

2 EXPERIMENTAL PROGRAM

2.1 Measurement principle

The hydration kinetics was studied using an isothermal heat conduction calorimeter, TAM Air, which uses the heat flow principle. In this type of calorimeter, the hydration of a sample takes place in a sealed reaction vessel which is surrounded by a larger metal block which acts as a heat sink. Heat is allowed to flow between the reaction vessel and the heat sink. The heat sink is however kept essentially at a constant temperature (the selected test temperature) by means of an air thermostat. In the exothermal cement hydration process, the role of the heat sink is to take up the heat produced, so keeping the hydration process at the chosen test temperature. A more detailed description of the calorimeter can be found in /5/.

Recording using an isothermal calorimeter gives a continuous measurement of the heat production rate, also called thermal power P. The total heat produced up to a certain age, Q, is calculated as the integral of the thermal power over time. Thermal power recording in the present study was made within the 600 mW range, on small samples (see below) prepared outside the calorimeter and charged into the calorimeter within 5±1 minutes after the addition of water. This allowed the majority of the first peak of the reaction to be recorded. In this work, only the main peak of hydration (the second peak) was however evaluated. More details are given in chapter 4.

Low temperature tests were carried out at 5°C and the heat production rate under isothermal conditions was recorded for up to 7 days. Identical mixtures were also tested at 20°C to give comparable results. To ensure isothermal conditions throughout the test procedure (material storage, sample preparation and measurements) the calorimeter was operated in a climatic chamber where the temperature was 5 ± 1°C and 20 ± 1°C respectively.

2.2 Samples

Given the sensitivity of the equipment (a limit of detectability of 2 μW), the sample size used in the experiments was small. The calorimeter uses 20 ml disposable glass vials and in cement hydration tests the sample volume is usually half this volume or less. A target mass of about 10 g was therefore chosen for the paste samples. The samples were taken from hand mixed batches. The pastes containing addition or filler were prepared by first mixing the cement and the addition/filler into a homogenous powder and then adding water. Each test alternative involved two samples, both being taken from the same batch. To ensure paste homogeneity, both in the batches and in each sample, a thorough mixing, sample preparation and sample handling procedure was followed. Particular care was taken to avoid the warming of the samples and the glass vials before charging them into the calorimeter, above all during the tests at 5°C.

2.3 Materials

Cement, additions and fillers

Swedish ordinary Portland cement CEM I 52.5 R was used as the main binder. Ground granulated blast furnace slag, silica fume and limestone filler were used as mineral additions. The chemical composition of the cement, additions and fillers is presented in table 1.

Blast furnace slag investigations used Swedish Merit 5000 and silica fume investigations used Norwegian undensified Microsilica 940U. Both are certified products and commercially available additions for concrete.

Investigations on limestone fillers were carried out on three types of $CaCO_3$ rock – chalk, limestone and marble – and three different finenesses. Most tests were carried out using powders of chalk, limestone and marble with a grading close to the fineness of the cement used. Limestone powders with coarser or finer fractions were also tested, see table 2.

Powders of chalk, limestone or marble may have different particle characteristics even where they have the same particle size distribution. For the two most common applications of limestone in concrete – as filler in self-compacting concrete and as part of the binder in blended cements – some powder properties greatly influence the powder's effect on concrete. In self-compacting concrete, particle shape, size, porosity, surface texture and particle size distribution are critical parameters for the rheology and flowability of the fresh mix. Where limestone is used as part of the binder, we would expect these particle characteristics to be at least as important, particularly as limestone particles are generally finer than the cement clinker particles. In the Swedish Portland-limestone cement (i.e. CEM II/A-LL) where 12–15% of the total amount of binder is limestone, the limestone is predominantly within the very fine fraction, mainly below 5 μm /6/.

Carbonated rocks, being natural sedimentary deposits formed across millions of years, acquire different properties dependent on the environment of formation. Calcitic chalk, limestone and marble therefore have significant differences in crystalline morphology, hardness and porosity although their chemical compositions are the same. Different qualities of limestone filler and various particle size distributions are therefore included in the investigation.

Paste mixtures

The paste mixtures used are presented in table 3. Plain and blended cement pastes were manufactured using deionised water as mixing water. No chemical admixtures were used, in prder to isolate the influence of the addition/filler.

The blended mixtures were produced using cement and one addition or filler at a time. The addition/filler replaced parts of the cement at a rate of 1:1 by mass and was considered as part of the total amount of binder. Mixtures with 20%, 35% or 65% slag, 5% or 10% silica fume and 12% or 24% limestone filler were tested.

Table 1 – Materials: chemical composition.

Chemical composition									
	SiO_2 %	CaO %	Al_2O_3 %	Fe_2O_3 %	MgO %	Na_2O %	K_2O %	SO_3 %	L.o.i. %
Cement	20.9	64.1	3.8	2.7	2.8	0.3	1.1	3.4	1.1
Slag	34.0	31.5	12.0	0.3	17.0	0.6	0.6	3.5	1.1
Silica fume	≥ 90	< 0.7	< 1.5	< 3.0	< 2.0	< 1.0	< 3.0		< 3.0
Limestone	$CaCO_3 \geq 98\%$								
Cement clinker composition (Bogue)						C_3S %	C_2S %	C_3A %	C_4AF %
						62.8	12.4	5.5	8.3

Table 2 – Materials: physical properties.

	Particle size (µm)		Specific surface (m^2/kg)		Particle density
	Top cut $d_{98\%}$	Mean $d_{50\%}$	BET	Blaine	kg/m^3
Cement (**OPC**)	~ 32	~ 7.2	1760	541	3114
Slag (**BFS**)	~ 60	~ 9		470	2907
Silica fume (**SF**)	~ 11	~ 0.5	~ 20000		2246
Chalk (**CH**)	~ 30	~ 2.3	2200		2696
Marble (**MA**)	~ 30	~ 7	1500		2722
Limestone medium fraction (**LL**)	~ 30	~ 5.5	1000		2710
Limestone, coarse fraction (**LLC**)	~ 70	~ 22	700		2711
Limestone, fine fraction (**LLF**)	~ 3	~ 0.44	15000		2678

Table 3 – Mixtures and test alternatives. Two samples were tested for each alternative.

Mixture	% OPC 1)	% Addition 1) and type		W/B 2)	Temperature
OPC	100	—	—	0.4, 0.5, 0.6, 0.7	5°C, 20°C
BFS20	80	20	slag	0.4, 0.5, 0.6, 0.7	5°C, 20°C
BFS35	65	35	slag	0.4, 0.5, 0.6, 0.7	5°C, 20°C
BFS65	35	65	slag	0.5	5°C, 20°C
SF5	95	5	silica fume	0.5	5°C, 20°C
SF10	90	10	silica fume	0.4, 0.5, 0.6, 0.7	5°C, 20°C
LL12	88	12	limestone, medium	0.5	5°C, 20°C
LLF12	88	12	limestone, fine	0.5	5°C, 20°C
LLC12	88	12	limestone, coarse	0.5	5°C, 20°C
CH12	88	12	chalk	0.5	5°C, 20 °C
MA12	88	12	marble	0.5	5°C, 20°C
LL24	76	24	limestone, medium	0.4, 0.5, 0.6, 0.7	5°C, 20°C
LLF24	76	24	limestone, fine	0.5	5°C, 20°C
LLC24	76	24	limestone, coarse	0.5	5°C, 20°C
CH24	76	24	chalk	0.5	5°C, 20°C
MA24	76	24	marble	0.5	5°C, 20°C

1) Percent by mass of total amount of binder. Binder = cement + addition.
2) Water-binder ratio.

As shown in table 3, the plain cement mixtures (OPC) were tested at water/binder ratios (*W/B*) of 0.4, 0.5, 0.6 and 0.7. These water/binder ratios were also used for the blended mixtures with 20% and 35% slag, 10% silica fume and 24% limestone medium fraction. For the other mixtures, with lower or higher addition contents or different limestone filler types and fineness, the tests were limited to a W/B of 0.5.

2.4 Evaluation of the tests

Heat of Hydration
An isothermal heat conduction calorimetrical test allows the thermal power to be measured while the reaction in the sample continues at a constant temperature. The thermal power P, in Watt (or Joule/s), is a measure of the rate of the reaction. It depends on the reactivity of the powder (cement and mineral addition) with water at a given temperature and a given concentration of the powder/water mixture. A typical measurement shows an immediate reaction peak which starts after water addition. There then follows a dormant period when the reactions rest before the main hydration reactions start. The end of the dormant period and start of the main hydration reactions occurs earlier or later depending on mixture composition factors. These include type of binder, W/B, additions and ambient factors such as temperature. The influence of these factors on the development of the main hydration peak was studied in this paper.

The heat of hydration Q is the integrated thermal power P over time. Graphically it can be seen as the area between measured P and the time axis. The evaluation discussed in this paper only assesses the heat developed during the main peak of hydration, figure 1, left. The main contribution to the first peak appears to be from the hydration of calcium sulphate hemihydrate to the dihydrate gypsum /7/. In practice, when mixing full scale concrete batches, this heat peak occurs in the mixer and has most likely been passed by the time when the concrete is poured into the mould. It is therefore assumed that only the main peak plays a role in the structural development of strength.

The time of the start of the main peak was taken as being the point in time when the dormant period ended and the rate of heat development begins to increase again. This point in time was different for different mixtures, being affected by both temperature and mixture parameters. Consequently, there was an individual start time for the integration for each mixture, marked by arrows in figure 1 to the right. Time "zero" was the time when the water was added.

Figures 2–3 show examples of calorimetrical results at 5°C and 20°C. The graphs are for mixtures with 12% limestone filler. The heat and the heat production rate, here given per gram cement, show how the temperature and the fineness of the filler affect early hydration.

The measurements of thermal power show how significantly the development of heat of hydration at 5°C compared to 20°C differ. At 20°C, the main reactions slowed down after 12 h, while this took twice as long time at 5°C.

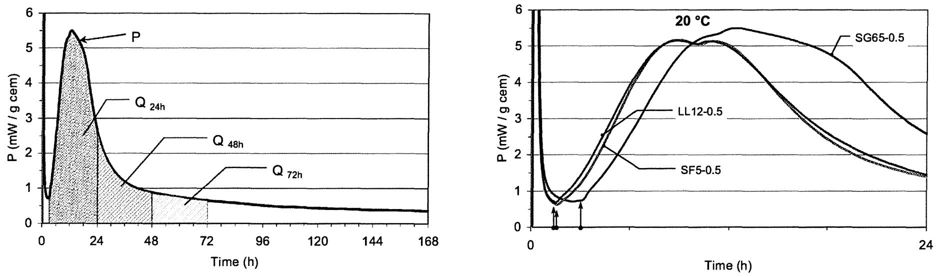

FIGURE 1 *Example: evaluation of the heat of hydration Q from the thermal power P. The thermal power shows the rate of development of the heat of hydration.*

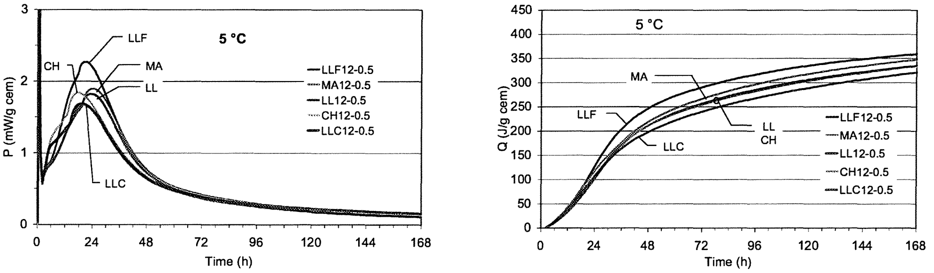

FIGURE 2 *Heat production rate and heat per gram cement at 5°C. Mixtures with 12% filler and W/B 0.5. Comparison between marble, chalk and coarse, medium or fine limestone.*

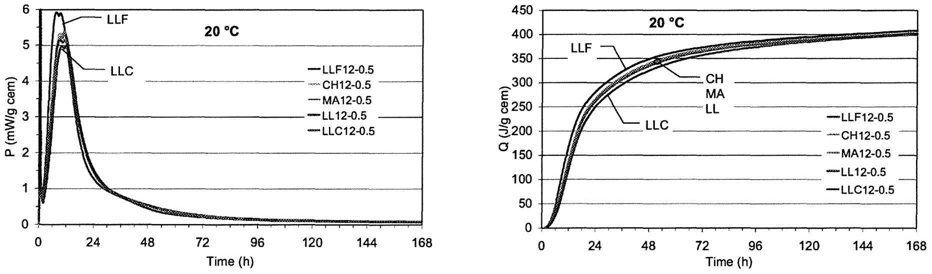

FIGURE 3 *Heat production rate and heat per gram cement at 20°C. Mixtures with 12% filler and W/B 0.5. Comparison between marble, chalk and coarse, medium or fine limestone.*

Efficiency coefficient (k-value) for heat

The total heat of hydration Q_{C+R} developed by a sample, at a specific time and temperature, depends on the total amount of binder and water involved in the reaction. To compare different mixtures, the total sample heat needs to be expressed as the heat development per unit of mass. The heat of hydration can be evaluated per gram sample, gram powder (cement plus addition/filler) or gram cement. Several evaluation methods can be used to study the influence of the addition on the heat of hydration. The method chosen in this paper is presented as follows.

The total heat of the sample Q_{C+R} was assumed to be the sum of the heat of reaction of the cement Q_C and the heat of reaction of the addition Q_R. Q_C and Q_R can also be expressed as the product of the specific heat of the material, q, and the amount of material (cement or addition/filler). Eq. (1) and (2) show the explicit mathematical expression. The coefficient of efficiency, *k,* is defined as the ratio between the specific heat of the addition and the specific heat of the cement, eq. (3).

$$\frac{Q_{C+R}}{C} = \frac{Q_C + Q_R}{C} = \frac{C \cdot q_C + R \cdot q_R}{C} \qquad (1)$$

$$q_R = \frac{C}{R}\left(\frac{Q_{C+R}}{C} - q_C\right) \qquad (2)$$

$$k = \frac{q_R}{q_C} \qquad (3)$$

Where:

$Q_{C+R} = Q_C + Q_R =$ total sample heat (J)

$Q_C = C \cdot q_C =$ heat developed from the cement reaction (J)

$Q_R = R \cdot q_R =$ heat developed from the addition reaction (J)

$q_C =$ specific heat of the cement (J/g $_{\text{cement}}$)

$q_R =$ specific heat of the addition (J/g $_{\text{addition}}$)

$C =$ amount of cement (g)

$R =$ amount of addition (g)

$k =$ efficiency coefficient (–), also referred to as *k*-value

In this paper, the specific heat of the powder q_{C+R} is also used. It is defined as:

$$q_{C+R} = \frac{Q_{C+R}}{C+R} \qquad (4)$$

3 TEST RESULTS

The test results for heat development and calculated k-values are presented in table 4. The heat development is given as the total heat development divided by the cement content, Q_{C+R}/C which can be directly used for calculating the k-value according to eq. (3).

Each heat development value in table 4 is the mean of two separate measurements. The difference between the two values was generally small. For 80% of the measurements the difference was less than 3%. Measurement precision is discussed in more detail in /8/.

Table 4 – Sample heat per gram cement, as the mean of two values. Efficiency coefficients calculated according to eq. (1–3).

Mixture	W/B	$\frac{Q_{C+R}}{C}$ (J/g_{cement}) 1)				k (–)			
		5°C		20°C		5°C		20°C	
		2 days	7 days	2 days	7 days	2 days	7 days	2 days	7 days
OPC-0.4	0.4	203.1	302.3	301.5	346.9				
OPC-0.5	0.5	198.0	320.0	319.1	390.0				
OPC-0.6	0.6	202.1	320.5	321.7	409.0				
OPC-0.7	0.7	198.8	317.1	323.3	413.6				
BSF20-0.4	0.4	208.8	336.7	331.8	396.4	0.11	0.46	0.40	0.57
BSF20-0.5	0.5	209.0	333.1	337.4	421.7	0.22	0.16	0.23	0.32
BSF20-0.6	0.6	211.3	340.0	336.7	427.2	0.18	0.24	0.19	0.18
BSF20-0.7	0.7	205.2	334.9	336.0	423.1	0.13	0.22	0.16	0.09
BSF35-0.4	0.4	223.8	366.6	367.9	487.8	0.19	0.40	0.41	0.75
BSF35-0.5	0.5	218.5	352.5	356.6	468.1	0.19	0.19	0.22	0.37
BSF35-0.6	0.6	218.5	362.2	356.7	469.2	0.15	0.24	0.20	0.27
BSF35-0.7	0.7	211.5	356.2	365.9	511.0	0.12	0.23	0.25	0.44
BSF65-0.5	0.5	225.0	437.2	422.2	647.1	0.07	0.20	0.17	0.35
SF5-0.5	0.5	205.8	332.1	328.3	394.3	0.75	0.72	0.55	0.21
SF10-0.4	0.4	236.7	323.3	325.3	379.9	1.49	0.63	0.71	0.85
SF10-0.5	0.5	224.8	347.4	336.6	409.4	1.22	0.77	0.49	0.45
SF10-0.6	0.6	218.8	341.2	339.3	429.0	0.74	0.58	0.49	0.44
SF10-0.7	0.7	216.0	338.0	335.1	428.3	0.78	0.59	0.33	0.32
LL12-0.5	0.5	212.8	337.8	335.1	402.6	0.55	0.41	0.37	0.24
LLF12-0.5	0.5	247.6	358.9	348.6	407.2	1.84	0.89	0.68	0.32
LLC12-0.5	0.5	198.6	320.8	325.0	399.7	0.02	0.02	0.14	0.18
CH12-0.5	0.5	211.3	334.6	339.2	403.6	0.49	0.33	0.46	0.25
MA12-0.5	0.5	219.8	347.0	336.6	399.4	0.81	0.62	0.40	0.18
LL24-0.4	0.4	230.4	350.0	342.5	397.9	0.42	0.50	0.43	0.47
LL24-0.5	0.5	229.7	362.7	348.9	425.4	0.51	0.42	0.30	0.29
LL24-0.6	0.6	232.4	372.0	354.7	441.5	0.47	0.51	0.33	0.25
LL24-0.7	0.7	223.8	361.8	355.5	440.9	0.40	0.45	0.32	0.21
LLF24-0.5	0.5	265.8	375.8	360.3	426.3	1.08	0.55	0.41	0.29
LLC24-0.5	0.5	208.6	338.0	334.5	415.7	0.17	0.18	0.15	0.21
CH24-0.5	0.5	239.3	368.7	356.8	429.2	0.66	0.48	0.37	0.32
MA24-0.5	0.5	240.2	368.8	357.1	431.4	0.67	0.48	0.38	0.34

1) For the plain OPC mixtures R = 0.

4 COMMENTS ON THE TEST RESULTS

4.1 Filler effect

Introduction
Fillers have been shown to contribute to the development of heat and strength in mortar and concrete, the so called filler effect. The effect is not fully understood or explained. Some results indicate that limestone fillers may be, to some extent, reactive chemically /9, 10, 11/, but this effect is not discussed in this paper. Along with this another common explanation given in the literature is that of the fine grained particles acting as nuclei for the initiation of the cement hydration process and accelerating the reaction between cement and water /11, 12, 13/. This and a further possible explanation of the filler effect are discussed below.

Dilution effect
The specific heat of the cement used in this investigation is shown in figure 4, at different ages and curing temperatures. The curves represent different water/cement ratios.

For short curing times and low temperatures (2 days/5°C), W/C does not influence the specific heat of the cement (q_C). It is around 200 J/g for all the W/C ratios studied. For longer curing times or higher temperatures, the specific heat decreases with decreasing W/C ratio. For example, when cured for 7 days at 20°C, the specific heat is 415 J/g for a W/C ratio of 0.7 but only 350 J/g for W/C ratio of 0.4. A probable explanation is that a higher degree of hydration leads to a denser and less permeable paste. This delays local water transport and the hydration process due to lack of water, especially for low water/binder ratios.

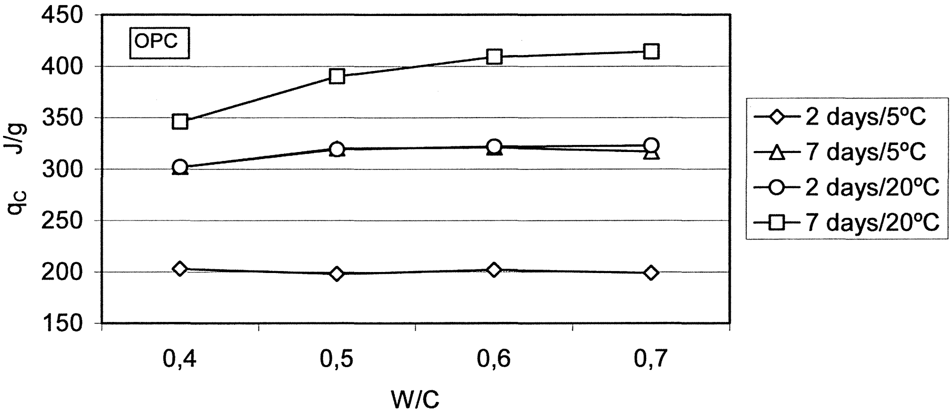

FIGURE 4 *Specific heat of the cement used vs. W/C, at different curing times and temperatures.*

When additions are used as replacement for parts of the OPC, the properties of the mortar are not classified by W/C but by W/C$_{eq}$, which is defined as:

$$W/C_{eq} = \frac{W}{C + k \cdot R} \tag{5}$$

W = water content
C = cement content
R = addition content
k = efficiency coefficient

When OPC is replaced by addition of ratio 1:1 by mass, when k is lower than 1.0, W/C$_{eq}$ becomes higher than the corresponding W/C for mortar or paste with cement as the only binder. This is normally the case for limestone filler and slag, at least at the low temperatures and short curing times in this investigation. A mortar/paste becomes therefore more permeable when inert or low-reactive additions are used and the availability of water to the cement reaction improves. This leads to a higher hydration rate and heat development for the OPC part of the binder than where no addition is used. The contribution from the addition to the specific heat of the paste is thus partly derived from heat development from the reaction of the addition itself and partly from the acceleration of the OPC reaction due to the dilution effect. This dilution effect may, at least partly, explain the filler effect for mortars with low water/binder ratios containing inert fillers or low reactive additions.

The specific heat for 7 days/20°C is shown in figure 5 for OPC paste and for paste containing 24% limestone filler. The specific heat for the OPC paste decreases with decreasing W/B ratio. The specific heat also decreases for paste with limestone filler, but not to the same extent as for the OPC paste.

From equations (2), (3) and (4) it can be shown that k can be calculated from:

$$k = \frac{q_{C+R}}{q_C} \cdot \frac{C+R}{R} - \frac{C}{R} \tag{6}$$

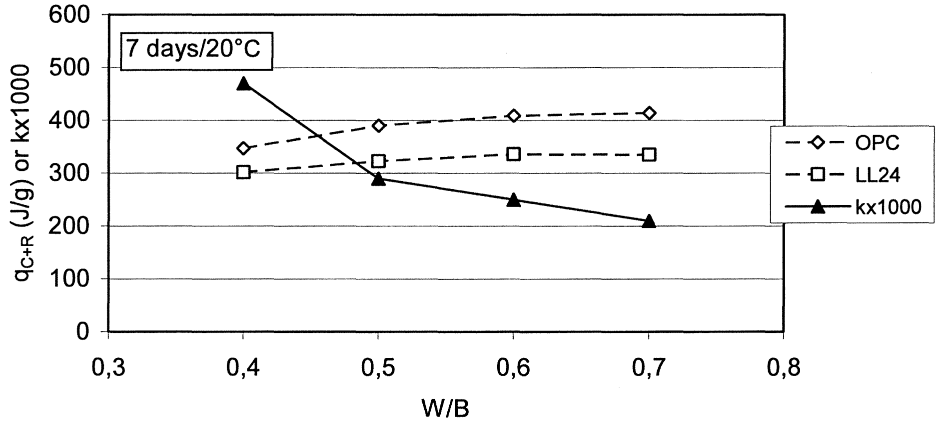

FIGURE 5 Specific heat (q_{C+R}) and efficiency coefficient (k) as a function of W/B for paste containing 0 or 24% limestone cured at 20°C for 7 days.

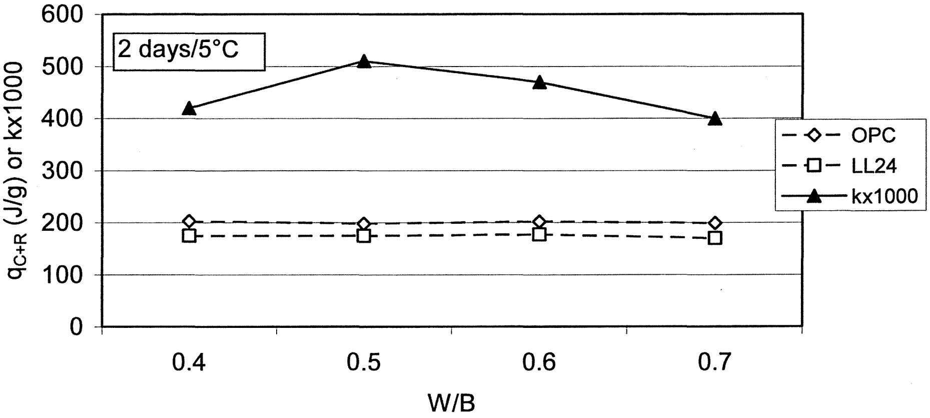

FIGURE 6 Specific heat (q_{C+R}) and efficiency coefficient (k) as a function of W/B for paste containing 0 or 24% limestone cured at 5°C for 2 days.

As can be seen from equation (6), k increases as the ratio q_{C+R}/q_C increases. This explains why the k-value for limestone filler in figure 5 increases from 0.2 for W/B = 0.7 to almost 0.5 for W/B = 0.4.

Figure 6 shows the same relationship as shown in figure 5, but for a curing period of 2 days at a temperature of 5°C. For this curing period, the paste has not become as dense and the specific heat is independent on the W/B ratio. This also applies both to the OPC paste and to the paste containing 24% limestone filler. The k-value therefore is essentially independent of the W/B ratio, as shown in the figure.

The results presented above, showing the k-value for heat development to be higher for dense pastes than for more permeable pastes, explains the high k-values in table 4 for pastes with W/B ratios of 0.4 and in some cases for W/B ratios of 0.5. The effect is most pronounced at high degrees of hydration, i.e. for longer curing times and higher temperatures.

Nucleation effect

Figure 7 presents k-values for pastes containing 24% limestone of different finenesses. The results show that the k-value becomes higher the finer the limestone grading is. This is most pronounced at low degrees of hydration, i.e. at low temperatures and short curing times. For 5°C and 2 days, the k-value is over 1.0 for the finest limestone (d_{50} = 0.44 μm), but less than 0.2 for the coarsest limestone (d_{50} = 22 μm). This supports the theory that the limestone particles act as nuclei for initiation of the hydration process. As the number of particles per unit mass is proportional to $(\text{diameter})^3$, the number of particles can be estimated to be more than 100,000 times higher for the fine grained limestone than for the coarser. The fine grained limestone can therefore be supposed to contain much more efficient nuclei for the chemical process.

The nucleation effect seams to decrease with increasing degree of hydration. For 20°C and 7 days there seems to be almost no nucleation effect, at least not at the grain sizes used in this investigation. The k-value is 0.2–0.3 for all the three grain sizes used.

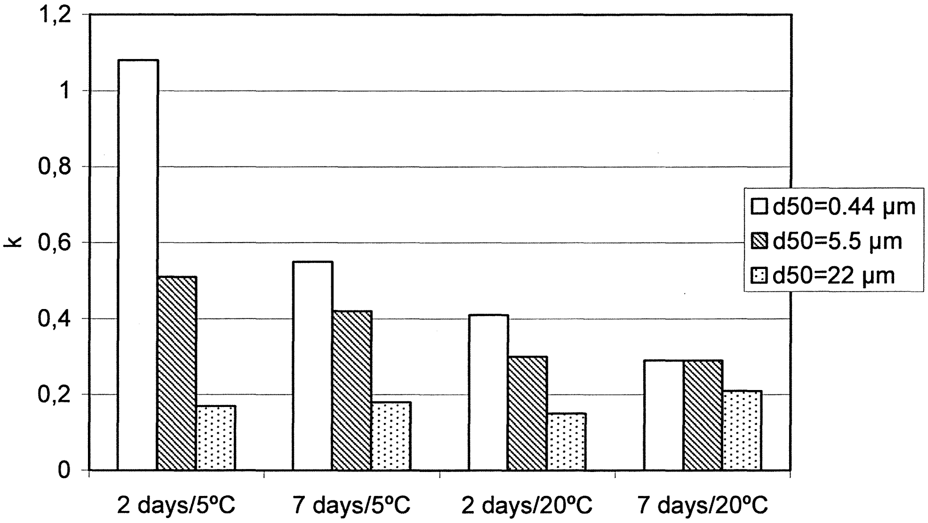

FIGURE 7 k-values for different curing conditions for paste containing 24% limestone of different fineness. W/B = 0.5.

This nucleation effect for young paste cured at a low temperature can also be seen for the very fine-grained silica fume. The k-value is 0.8–1.5 at 2 days and 5°C, see table 4, but decreases to about half this value at 7 days and 20°C.

4.2 k-values for the additions/fillers used

Introduction

The k-values found for heat of hydration in the tests are presented in table 4. Some of the results for the additions/fillers used are discussed below.

Granulated blast furnace slag

The k-value for granulated blast furnace slag increases slowly from about 0.2 to around 0.4 when curing conditions change from 2 days/5°C to 7 days/20°C, see figure 8. This is explained by slag being chemically active and by it taking part in the hydration process, at least at 20°C. The high values for paste with low water/binder ratios can be explained by the dilution effect discussed above.

Figure 9 presents the k-values determined for pastes containing different amounts of granulated blast furnace slag. The test results show negligible differences between k-values determined for pastes with different slag contents.

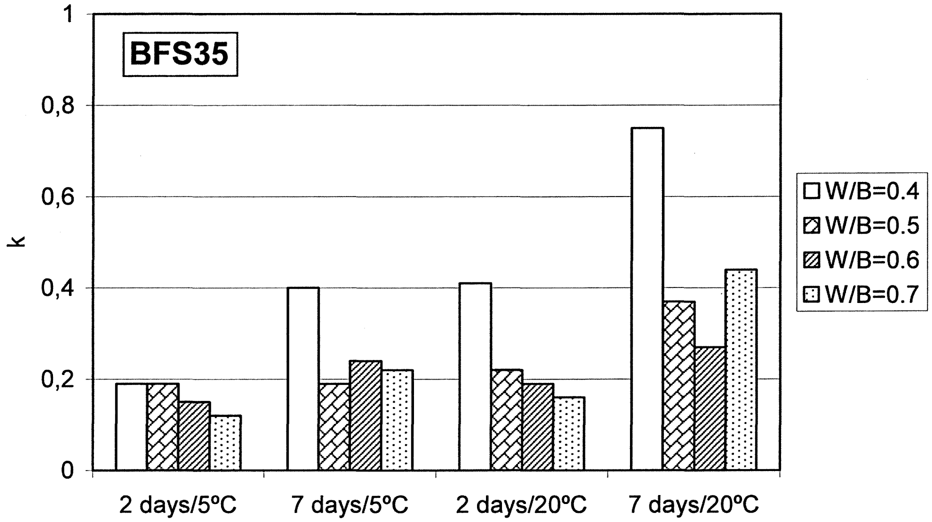

FIGURE 8 *k-values for different curing conditions and different water/binder ratios for paste containing 35% granulated blast furnace slag.*

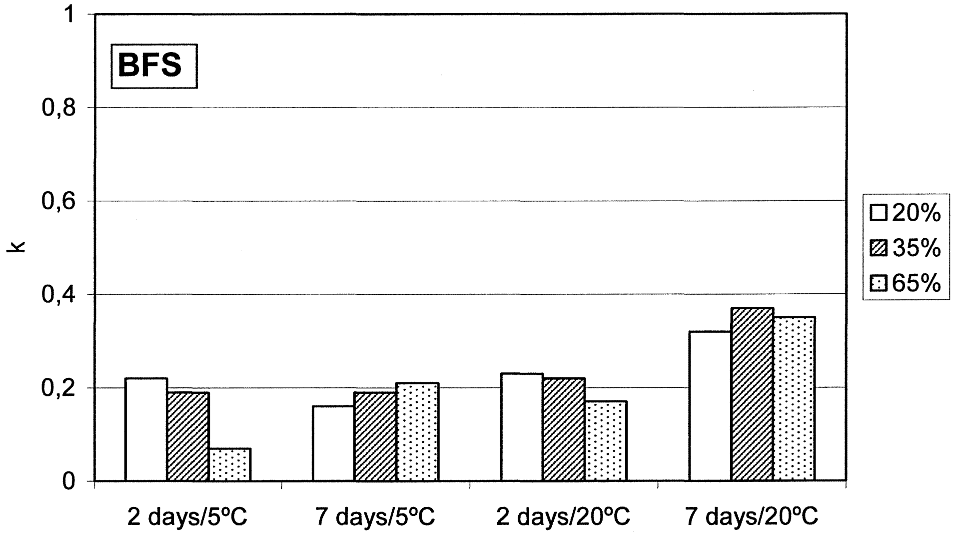

FIGURE 9 *k-values for different curing conditions for paste with W/B = 0.5 containing different contents of granulated blast furnace slag.*

Silica fume

The k-values for silica fume are uncertain due to the low percentage of addition (5 or 10%) used in the pastes. The values however appear in most cases to vary between 0.4 and 0.8, see figure 10. The highest k-values are found for the lowest degree of hydration, which probably can be explained by the nucleation effect. The k-values for 2 days/5°C and for low water/binder ratios are as high as 1.2–1.5.

The k-value seems in most cases to be higher at lower values of water/binder ratio. The results of this investigation cannot explain this effect. It is probably not caused by the dilution effect, as the k-values are relatively high and addition levels are low.

Limestone filler

The k-values for limestone filler vary between 0.2 and 0.5, see figure 11. Due to the nucleation effect, the highest values are for short curing times and low temperatures. The values appear, in most cases, to be independent of the water/binder ratio. However, the k-value for 7 days/20°C becomes higher at lower water/binder ratios. This can be explained by the dilution effect.

Limestone filler content does not appear to have any effect on k-value, see figure 12. The effect of filler quality, whether it is produced from chalk, limestone or marble, also appears to be negligible, see figure 13. The k-values for the limestone filler do, however, show a tendency to be slightly lower than for the other two qualities.

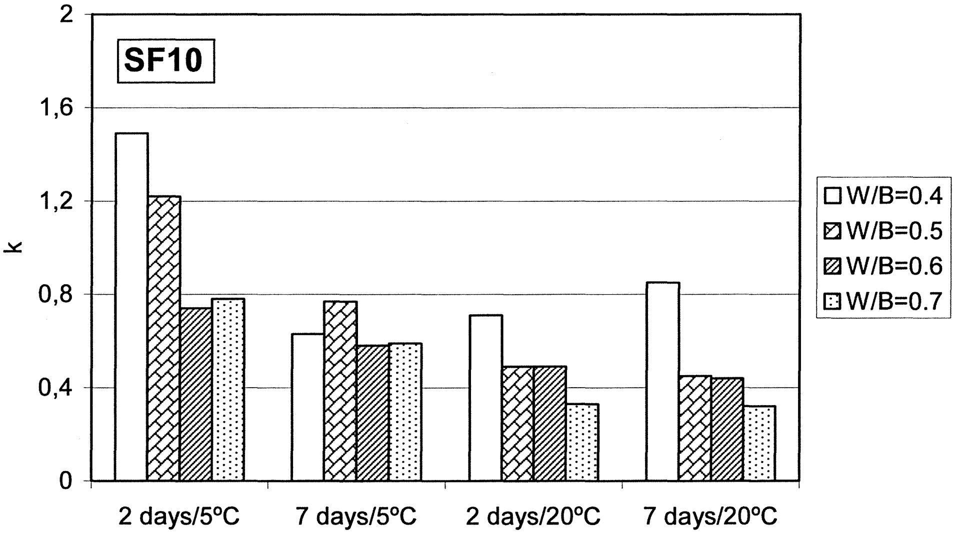

FIGURE 10 k-values for different curing conditions and different water/binder ratios for paste containing 10% silica fume.

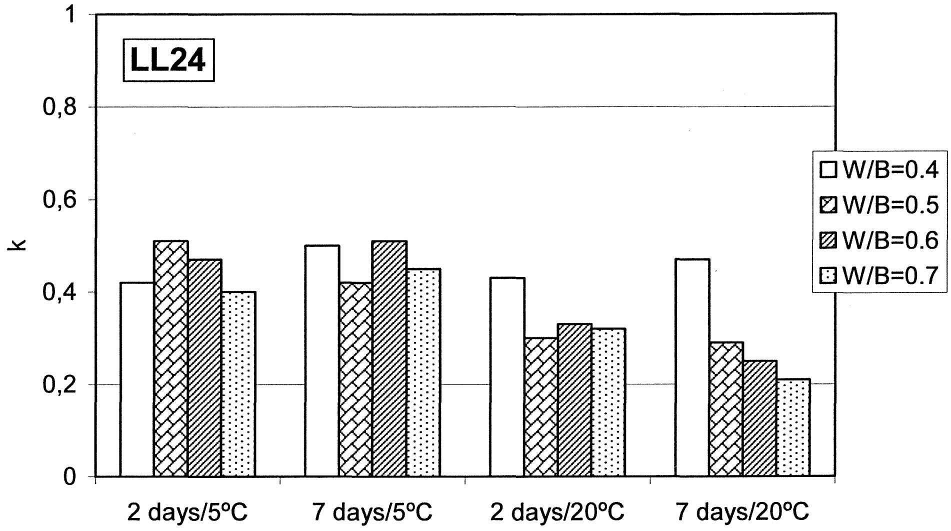

FIGURE 11 *k-values for different curing conditions and different W/B for paste containing 35% granulated blast furnace slag.*

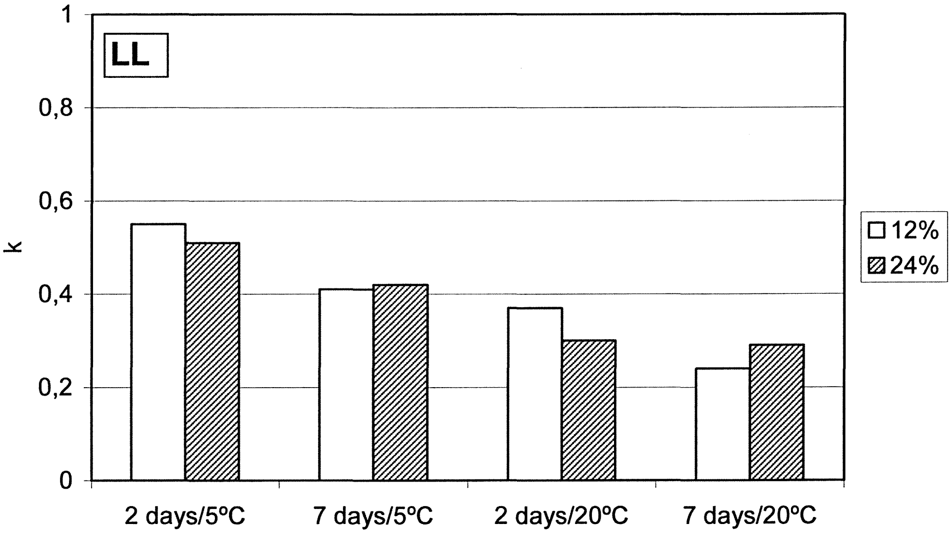

FIGURE 12 *k-values for different curing conditions for paste with W/B = 0.5 containing different contents of limestone filler.*

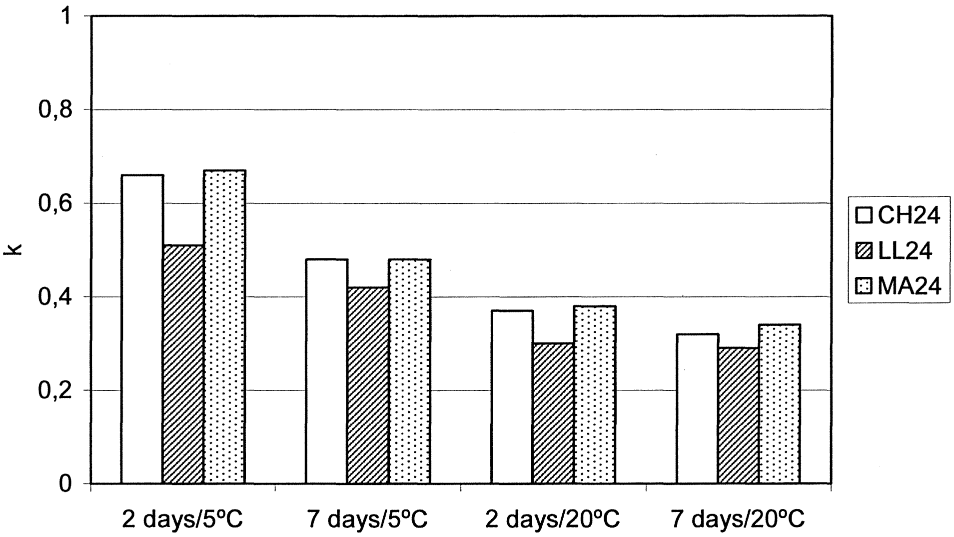

FIGURE 13 k-values for different curing conditions for filler produced from chalk, limestone or marble. Paste with 24% filler content.

4.3 k-values for heat of hydration vs. k-values for strength, a comparison

k-values for compressive strength have been determined for most of the mixtures and curing conditions used in the calorimetrical investigation. The results were published in /1, 2/. In figure 14, the k-values for compressive strength are compared with corresponding k-values for heat development. The values include results for limestone filler of different fineness and mineralogical composition, ground granulated blast furnace slag and silica fume, different curing conditions, different water/binder ratios and different addition or filler contents.

The results in figure 14 show, as expected, a good agreement between k-values for strength and k-values for heat. The scatter is however relatively wide. This can be partly explained by many of the test results being based on measurements on mixtures with low addition/filler contents, which leads to poorer estimation of k-values.

In many cases the results showed close relationships between k-values for strength and those for heat development. This is illustrated in figure 15, which shows the k-values for limestone fillers with different fineness. The k-value increases with increasing fineness and the k-values for heat development and strength are almost identical. This shows that measuring heat development using isothermal calorimetry can be a suitable and simple tool for evaluating the efficiency of additions and fillers in cement, mortar or concrete.

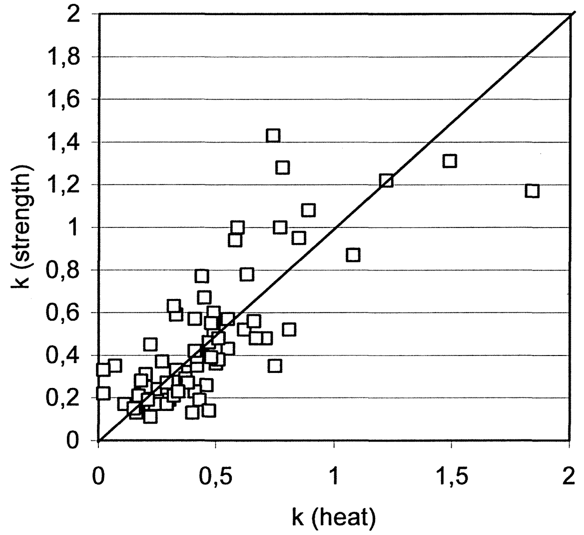

FIGURE 14 *k-values for strength vs. k-values for heat development for the different additions/fillers and different curing conditions used in this investigation. The k-values related to strength are presented in /1, 2/.*

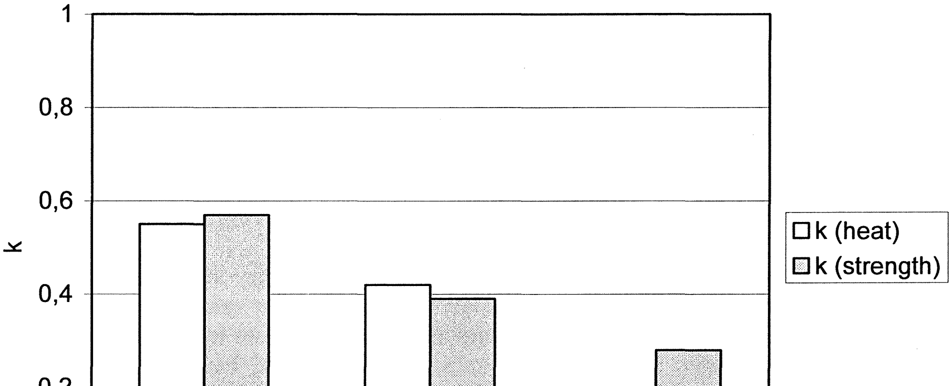

FIGURE 15 *k-values related to heat development and strength for limestone filler of three different finenesses (d_{50} is 0.44 µm for LLF, 5.5 µm for LL and 22 µm for LLC). Pastes with W/B = 0.50, 24% filler content and curing for 7 days at 5°C.*

5 CONCLUSIONS

Based on the results of this investigation, the following conclusions can be drawn:

- *Isothermal calorimetry* is a useful tool for evaluating the properties of young paste, mortar or concrete. This investigation found a close relationship between the efficiency coefficients, k-values, for heat development and corresponding k-values for strength reported elsewhere.

- Inert fillers have been shown to contribute to the development of heat and strength in paste and mortar – the so called *filler effect*. The following two possible explanations are identified in this investigation:

  One is a dilution effect, based on a paste or mortar with filler being less dense and more permeable than paste or mortar without filler. This leads to enhanced water availability for the hydration process. This contributes to a higher rate of strength growth, which can be regarded as a filler effect.

  The other is that the fine grained filler particles, acting as nuclei for the initiation of the reaction between cement and water, accelerate the hydration process. This supports previously reported findings. This filler effect appears to decrease with increasing degree of hydration.

- The k-value for heat development for granulated *blast furnace slag* increases slowly, from about 0.2 to about 0.4, as curing conditions change from 2 days/5°C to 7 days/20°C. This can be explained by the slag being chemically active and by it taking part in the hydration process. The amount of slag replacement used in this investigation is 20 to 65%, which does not seem to influence k-values.

- The k-values for *silica fume*, although uncertain due to the low content levels (5% or 10 %), appear to vary in most cases within 0.4–0.8. The highest k-values are for the lowest degrees of hydration, which can be explained by the nucleation effect. The k-values for 2 days/5°C and for low water/binder ratios are as high as 1.2–1.5.

- The k-values for heat development for *limestone filler* vary in this investigation between 0.2 and 0.5. Due to the nucleation effect, the highest values are for short curing times and low temperatures. The values appear in most cases to be independent of the water/binder ratio. However, the k-value for 7 days/20°C becomes higher at lower water/binder ratios, which can be explained by the dilution effect.

  Limestone filler content does not appear to have any effect on the k-value. The difference between filler produced from chalk, limestone or marble also seems to be negligible.

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APPENDIX 4

Results from compression strength testing

Table B4:1 Compressive strength test results for mortars with Portland cement as the only binder

Mixture	**W/C**	**Age** *days*	**Temp** °C	**Air** [1)] *%*	$\mathbf{f_c}$ **mean** [2)] *MPa*	$\mathbf{f_c}$ **std. dev.** *MPa*
C-40	0.40	2	5	1.7	46.4	0.86
C-50	0.50	2	5	2.3	28.0	0.37
C-60	0.60	2	5	2.5	17.6	0.43
C-70	0.70	2	5	2.5	11.0	0.22
C-40	0.40	7	5	1.7	71.6	1.2
C-50	0.50	7	5	2.2	53.7	0.36
C-60	0.60	7	5	2.6	38.5	0.64
C-70	0.70	7	5	3.2	26.2	0.58
C-40	0.40	28	5	2.5	84.0	2.1
C-50	0.50	28	5	2.6	67.4	0.58
C-60	0.60	28	5	2.4	52.7	1.1
C-70	0.70	28	5	1.9	39.3	0.43
C-40	0.40	2	20	1.6	62.4	1.04
C-50	0.50	2	20	2.2	46.8	1.15
C-60	0.60	2	20	2.1	34.8	0.73
C-70	0.70	2	20	1.7	25.0	0.39
C-40	0.40	7	20	1.7	71.5	1.05
C-50	0.50	7	20	1.9	58.8	0.59
C-60	0.60	7	20	1.9	45.2	0.76
C-70	0.70	7	20	1.5	33.8	0.30
C-40	0.40	28	20	1.7	83.2	0.99
C-50	0.50	28	20	2.2	65.5	0.53
C-60	0.60	28	20	2.3	50.4	1.12
C-70	0.70	28	20	1.8	40.3	0.62

1) Natural air content in the mortar at test age. Mean of three values.

2) Mean of six values.

Table B4:2 Compressive strength testt results for mortars containing ground granulated blast furnace slag

Mixture	W/B	Age *days*	Temp *°C*	GBFS *% by mass*	Air1) *%*	f_c mean 2) MPa	f_c std. dev. MPa
BFS20-40	0.40	2	5	20	2.1	30.9	1.0
BFS20-50	0.50	2	5	20	2.9	16.9	0.63
BFS20-60	0.60	2	5	20	2.9	10.2	0.24
BFS20-70	0.70	2	5	20	2.5	6.3	0.21
BFS20-40	0.40	7	5	20	2.1	58.2	0.67
BFS20-50	0.50	7	5	20	2.9	37.9	1.22
BFS20-60	0.60	7	5	20	2.9	25.3	0.64
BFS20-70	0.70	7	5	20	2.2	17.9	0.61
BFS20-50	0.50	2	20	20	2.5	34.5	0.60
BFS20-50	0.50	7	20	20	2.6	46.8	0.56
BFS35-40	0.40	2	5	35	2.4	22.5	0.50
BFS35-50	0.50	2	5	35	3.0	12.0	0.32
BFS35-60	0.60	2	5	35	2.5	6.9	0.10
BFS35-70	0.70	2	5	35	2.2	4.3	0.09
BFS35-40	0.40	7	5	35	2.5	42.1	1.44
BFS35-50	0.50	7	5	35	2.9	26.9	0.55
BFS35-60	0.60	7	5	35	2.3	18.0	0.35
BFS35-70	0.70	7	5	35	1.9	12.1	0.38
BFS35-40	0.40	28	5	35	2.8	62,0	1.3
BFS35-50	0.50	28	5	35	3.2	42.6	0.27
BFS35-60	0.60	28	5	35	2.3	29.1	0.41
BFS35-70	0.70	28	5	35	2.2	19.5	0.56
BFS35-40	0.40	2	20	35	2.2	40.5	0.44
BFS35-50	0.50	2	20	35	2.7	25.2	0.16
BFS35-60	0.60	2	20	35	2.2	17.5	0.43
BFS35-70	0.70	2	20	35	1.3	12.6	0.20
BFS35-40	0.40	7	20	35	2.5	55.8	0.37
BFS35-50	0.50	7	20	35	2.4	38.7	0.15
BFS35-60	0.60	7	20	35	2.3	27.4	0.63
BFS35-70	0.70	7	20	35	1.6	19.9	0.18
BFS35-50	0.50	28	20	35	2.6	61.5	0.52
BFS65-50	0.50	2	5	65	2.7	3.0	0.04
BFS65-50	0.50	7	5	65	2.7	9.3	0.12
BFS65-50	0.50	2	20	65	1.8	10.7	0.14
BFS65-50	0.50	7	20	65	2.0	22.9	0.18

1) Natural air content at test age. Mean of three values.

2) Mean of six values.

Table B4:3 Compressive strength test results for mortars containing silica fume

Mixture	W/B	Age *days*	Temp *°C*	SF *% by mass*	Air[1] *%*	f_c mean [2] MPa	f_c std. dev. MPa
SF10-40	0.40	2	5	10	1.8	48.9	0.82
SF10-50	0.50	2	5	10	2.7	32.3	0.80
SF10-60	0.60	2	5	10	3.2	19.8	0.60
SF10-70	0.70	2	5	10	3.4	12.0	0.12
SF10-40	0.40	7	5	10	1.4	69.9	0.83
SF10-50	0.50	7	5	10	1.6	53.8	0.69
SF10-60	0.60	7	5	10	2.4	37.7	0.53
SF10-70	0.70	7	5	10	2.8	26.4	0.20
SF10-40	0.40	2	20	10	1.9	59.2	0.78
SF10-50	0.50	2	20	10	2.6	43.6	0.90
SF10-60	0.60	2	20	10	3.0	31.9	0.54
SF10-70	0.70	2	20	10	3.2	23.1	0.55
SF10-40	0.40	7	20	10	2.0	71.6	2.6
SF10-50	0.50	7	20	10	2.8	55.7	2.1
SF10-60	0.60	7	20	10	3.1	42.7	0.69
SF10-70	0.70	7	20	10	3.0	31.7	0.44
SF10-50	0.50	28	5	10	3.2	58.3	0.99
SF10-50	0.50	28	20	10	2.9	71.4	1.4
SF5-50	0.50	2	5	5	2.5	31.2	0.52
SF5-50	0.50	7	5	5	2.3	53.1	0.85
SF5-50	0.50	2	20	5	2.8	44.1	0.86
SF5-50	0.50	7	20	5	2.9	54.8	0.78

1) Natural air content at test age. Mean of three values.

2) Mean of six values.

Table B4:4 Compressive strength test results for mortars containing limestone filler

Mixture	W/B	Age *days*	Temp *°C*	GBFS *% by mass*	Air1) *%*	f_c,mean 2) MPa	std. dev. MPa
LL24-40	0.40	2	5	24	1.6	32.5	0.50
LL24-50	0.50	2	5	24	1.8	19.0	0.32
LL24-60	0.60	2	5	24	1.3	11.8	0.13
LL24-70	0.70	2	5	24	0.50	7.7	0.14
LL24-40	0.40	7	5	24	1.8	58.5	0.85
LL24-50	0.50	7	5	24	1.9	40.5	0.42
LL24-60	0.60	7	5	24	1.7	28.2	0.39
LL24-70	0.70	7	5	24	0.9	19.9	0.35
LL24-50	0.50	28	5	24		52.3	0,49
LL24-40	0.40	2	20	24	2.2	47.6	0.70
LL24-50	0.50	2	20	24	2.2	32,8	0.20
LL24-60	0.60	2	20	24	1.8	23.2	0.38
LL24-70	0.70	2	20	24	1.1	17.1	0.34
LL24-40	0.40	7	20	24	2.0	58.6	0.86
LL24-50	0.50	7	20	24	2.2	42.3	0.63
LL24-60	0.60	7	20	24	1.7	31.5	0.71
LL24-70	0.70	7	20	24	1.1	22.8	0.70
LL24-50	0.50	28	20	24	2.0	49.7	0.94
LLF24-50	0.50	2	5	24	2.6	26.0	0.32
LLC24-50	0.50	2	5	24	1.4	16.4	0.56
MA24-50	0.50	2	5	24	2.9	20.2	0.39
CH24-50	0.50	2	5	24	2.3	21.4	0.60
LLF24-50	0.50	7	5	24	2.6	44.1	0.64
LLC24-50	0.50	7	5	24	1.4	37.9	0.56
MA24-50	0.50	7	5	24	3.2	40.4	0.52
CH24-50	0.50	7	5	24	2.3	43.9	1.1
LLF24-50	0.50	2	20	24	2.9	35.8	0.75
LLC24-50	0.50	2	20	24	1.2	31.8	0.41
MA24-50	0.50	2	20	24	3.2	34.4	0.46
CH24-50	0.50	2	20	24	2.6	34.6	0.50
LLF24-50	0.50	7	20	24	2.7	44.5	0.89
LLC24-50	0.50	7	20	24	1.1	42.4	0.56
MA24-50	0.50	7	20	24	3.0	43.5	0.44
CH24-50	0.50	7	20	24	2.6	43.2	0.24
LL12-50	0.50	2	5	12	2.2	23.7	0.17
LLF12-50	0.50	2	5	12	2.7	29.6	0.34
LLC12-50	0.50	2	5	12	1.9	22.2	0.32
MA12-50	0.50	2	5	12	2.9	24.7	0.40
CH12-50	0.50	2	5	12	2.4	24.8	0.61
LL12-50	0.50	7	5	12	2.2	49.0	0.78
LLF12-50	0.50	7	5	12	2.0	54.4	0.90
LLC12-50	0.50	7	5	12	2.1	46.3	0.84
MA12-50	0.50	7	5	12	3.1	48.6	0.87
CH12-50	0.50	7	5	12	2.4	50.8	0.48
LL12-50	0.50	28	5	12		62.2	1.45
LL12-50	0.50	2	20	12	2.1	40.3	0.23
LL12-50	0.50	7	20	12	1.9	50.9	0.55
LL12-50	0.50	28	20	12	2.2	58.5	0.70

1) Natural air content at test age. Mean of three values.

2) Mean of six values.

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