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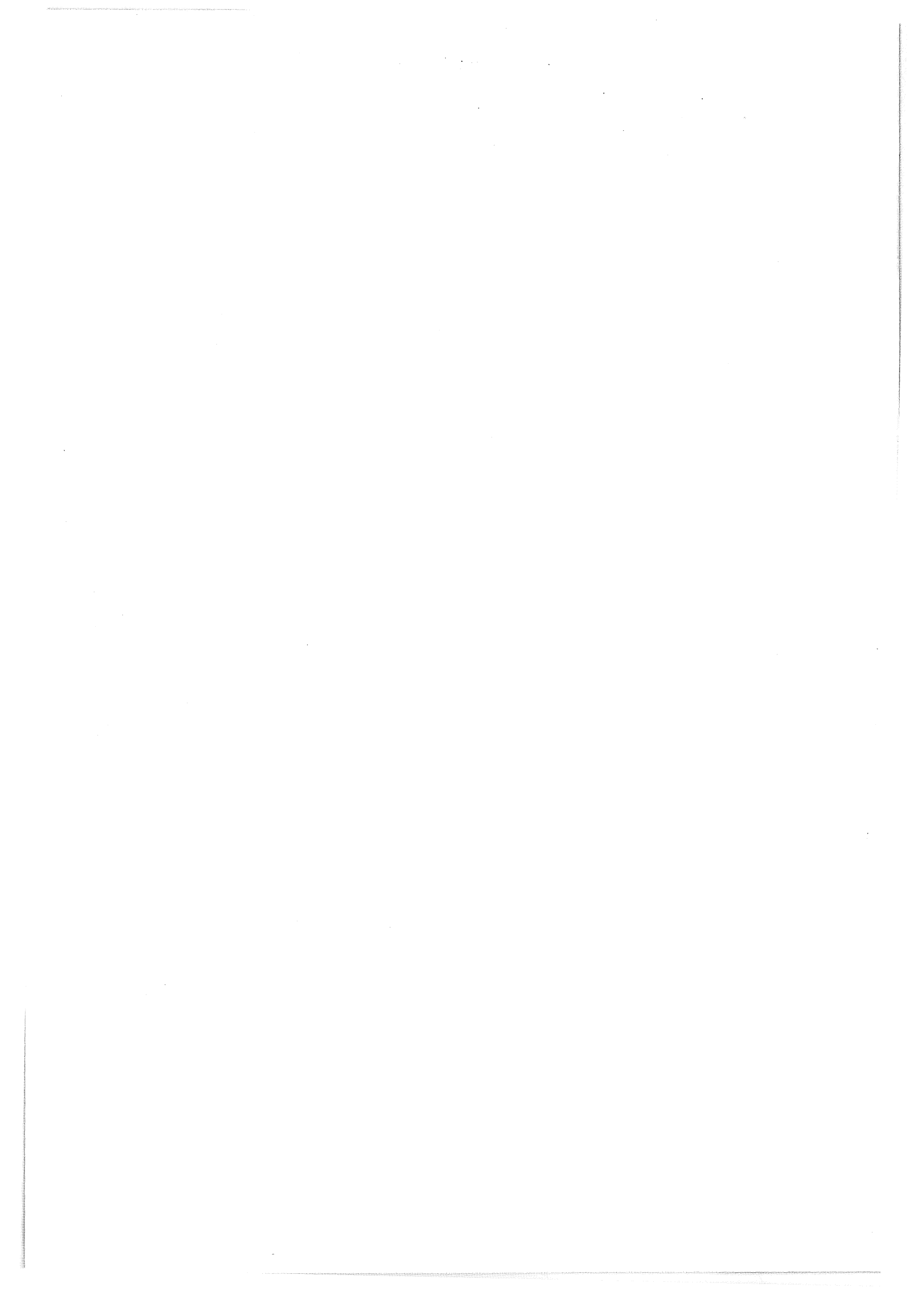
Division of Building Materials

# **Studies of the Efficiency of Granulated Blast Furnace Slag and Limestone Filler in Mortars**

Long-term Strength and Chloride  
Penetration

Dimitrios Boubitsas





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Penetration

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**LUND INSTITUTE  
OF TECHNOLOGY**  
Lund University



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## ABSTRACT

Concrete is, by volume, by far the most widely used construction material. Even small environmental improvements in the production and use of concrete will therefore have significant and positive effects on both the local and the global environment.

The chemical process involved in the production of cement clinker includes decalcination of limestone, i.e. calcium carbonate. This process produces carbon dioxide which cannot be prevented from spreading to the atmosphere by any practical cleaning technique known today. The only way of reducing the impact of the carbon dioxide produced in the decalcination process is to reduce the consumption of cement clinker.

One way of reducing the consumption of cement clinker is to partly replace it with mineral additions such as pulverized fly ash, granulated blast furnace slag, silica fume, limestone filler, etc.

The 'Use of industrial byproducts and fillers in concrete – Long-term properties/durability' project was started to improve knowledge of the long-term properties/durability of cement and concrete produced using industrial by-products/fillers, and to promote efficient, safe, reliable and increased use of such types of materials. The work comprises mainly the following activities:

Determination of material parameters/k-values

Study of mechanisms governing the influence of industrial by-products/filler on the long-term properties/durability.

The results presented in this report concentrate mainly on the first of the two activities described above, i.e. determination of material properties.

Durability is an extensive subject, and in this report the work is restricted to long-term strength and diffusion/migration resistance to chlorides. The two types of mineral additions used were granulated blast furnace slag and limestone.

The tests have investigated the influences of the following parameters of the mineral additions on mortar properties: type of mineral addition, i.e. slag or limestone, different water/binder ratios, percentage replacement of cement by mineral addition, different qualities and fineness of limestone.

The main results are presented in three papers, which are attached as Appendices 1-3 to this report. Most of the tests have been performed in the laboratory, but some field exposure results are described as well.

Key words: chloride diffusion, chloride migration, compressive strength, durability, granulated blast furnace slag, k-value, limestone filler



## **PREFACE**

This work has been carried out at the Division of Building Materials at the Lund Institute of Technology. The project was initiated by my supervisor, Per-Erik Peterson, of SP - Swedish National Testing and Research Institute and Visiting Professor at the Division of Building Materials, whom I wish to thank for his help and support.

I also wish to express my gratitude to all my colleagues at the Division of Building Materials.

The financial support from the KK-foundation, FORMAS and CEMENTA is gratefully acknowledged.





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## SUMMARY

Many countries have a long tradition of using different types of mineral additions and fillers when producing cement and concrete. Examples of materials used are pulverized fly ash, granulated blast furnace slag, silica fume, limestone filler, etc, although such materials have not been used very much in Sweden. As a consequence, little research has been done on mineral additions and fillers in Sweden, and the level of knowledge is low when compared with the situation in many other countries. Above all, it is necessary to increase knowledge about how to use Swedish mineral additions and fillers under Swedish climatic conditions.

It must be pointed out, however, that the situation is changing. Today, a quality of cement with limestone filler is the most commonly used cement on the Swedish market. Silica fume is frequently used in Sweden, especially for concrete in aggressive environments, etc.

There are many reasons today for promoting the use of mineral additions/fillers in cement and concrete, such as: more environmentally friendly building materials; perhaps lower material costs; improved properties of fresh and hardened concrete; etc.

This report is the first part of the project *Use of industrial by-products and filler in concrete – Long term properties/durability*. The aim is to *improve the knowledge of long-term properties/durability of cement and concrete produced using industrial by-products/fillers in order to promote an efficient, safe, reliable and increased use of such types of materials*. The results presented in the report concentrate mainly on determination of material properties of mineral additions/fillers. The next step of the project will be to study the mechanisms governing the influence of mineral additions/fillers on the long-term properties/durability.

The main results are presented in three papers, which are attached as Appendices 1-3 to this report. A short summary of each paper is presented below.

PAPER I: Boubitsas, D, *Long-term Performance of Concrete Incorporating Ground Granulated Blast Furnace Slag*. Proceedings, 8<sup>th</sup> International Conference on Fly Ash, Slag and Natural Pozzolans in Concrete, Las Vegas, 2004, pp. 265-279.

The coefficient of efficiency, the k-value, quantifies the part by weight of Portland cement that can be replaced by one part by weight of mineral addition without changing the concrete properties. The aim of this paper is to introduce a method for determining the k-value as far as chloride penetration is concerned. Results are presented for ground granulated blast furnace slag, and are compared with traditional k-values for compressive strength. Some recommendations on how to use the k-values, and how to improve standards and regulations, are given.

Standards normally give a single k-value for each type of addition, regardless of what environment the concrete will be exposed to. The results in this investigation, however, clearly indicate that this is an excessive simplification. For chloride migration, for example, the k-value is three times higher for slag than it is for compressive strength.

For a reliable service life prediction of concrete structures produced with concrete containing additions, it is therefore necessary to find relevant k-values for different types of degradation mechanisms.

PAPER II: Boubitsas, D, *Replacement of Cement by Limestone Filler. Effect on Strength and Chloride Migration in Cement Mortars*. Accepted for publication in Nordic Concrete Research, 2005.

The paper describes studies carried out to examine the effect on 28-day strength and chloride migration for cement mortar when limestone filler replaces a certain amount of the cement as binder. Fillers produced from three different calcareous carbonates were used, and fillers with three different mean particle sizes were included in the study. The amount of replacement of cement with filler varied between 12 and 24 %, and mortars with different water/binder-ratios were used.

The efficiency of limestone filler as a replacement for cement in mortar and concrete is higher for moderate replacement (12 %) than for higher replacement (24 %). This is relevant both for 28-day compressive strength and for chloride migration.

According to the results in the paper, the mean particle size has little effect on the efficiency of limestone filler. There is, however, a tendency that the filler with the finest mean particle size is slightly more efficient than the coarser fillers as far as compressive strength is concerned. The opposite, however, is the case for chloride migration, for which the coarsest filler seems to be the most efficient.

There is a slight tendency for fillers produced from older calcareous carbonates with large crystals (marble) to be less efficient as far as compressive strength is concerned, compared with the situation where it is produced from younger materials with finer crystals (chalk). For chloride migration, however, the situation seems to be the opposite, i.e. marble is slightly more efficient than chalk.

PAPER III: Boubitsas, D, *Replacement of Cement by Limestone Filler or Ground Granulated Blast Furnace Slag: The effect on Strength and Chloride Diffusion in Cement Mortars. Laboratory and Field Studies*. Manuscript to be published, 2005.

This paper describes laboratory and field trials carried out to examine the effect on the strength and chloride migration/diffusion of cement mortar when a certain amount of the cement binder is replaced by limestone filler or granulate blast furnace slag.

It is shown in the paper that the reliability of measured k-values improves considerably with increasing content of addition/filler.

The k-values for 1-year compressive strength for limestone filler is normally found to be in the interval 0.2-0.5, although a single value is as high as 0.8. The

1-year values for limestone fillers are about the same as were found at 28 days. The 1-year k-value for slag is found to be 1.0-1.5, and about 0.3-0.4 higher than at 28 days.

The results indicate that the chloride migration coefficient is about the same for 28 days and one year for mortar containing limestone filler. The coefficient of migration, however, decreases for the mortars containing slag when the age increases from 28 days to one year. This implies a continuing chemical process in the mortar, leading to a more dense concrete. The one-year k-values are high (2.1-4.3), which is much higher than the k-value of 0.6 given in Swedish standard SS 13 70 03.

The diffusion coefficients calculated from field exposure test results are uncertain, as each result is based on tests on single specimens. However, the k-values for limestone filler seem to be within the range  $0.3 \pm 0.3$ . This is higher than corresponding migration coefficients from the laboratory tests, which are normally about 0.

The k-values for the field diffusion coefficient for slag are high, 3.0-4.3. They correspond well with the values from the migration test, which are in the range 2.1-4.3.



# 1 INTRODUCTION

## 1.1 Background

### 1.1.1 *Concrete construction and environmental impacts*

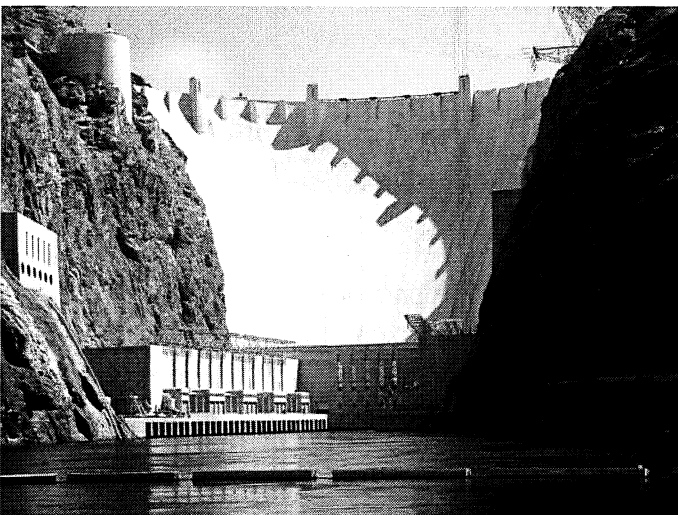
Concrete is a unique building material. In most applications, it cannot be replaced with any other material. In fact, the sustainable society could not be built without using concrete. Hydro power dams built in concrete produce renewable electric energy. Concrete for tunnels, bridges, harbours, railways, etc. contributes to efficient and environmentally friendly transports of people and goods. Waste water treatment plants could hardly be built without using concrete. The list of examples can be made long.

However, the production of concrete and concrete structures leads to environmental impact, as does the production of all other building materials as well. For concrete, the impact is mainly due to:

- energy consumption in connection with production of cement and transportation of raw material, ready-mixed concrete and concrete products
- emission of substances harmful to health and environment from cement production
- consumption of finite natural resources, such as natural gravel.

Concrete is, by volume, by far the most used construction material. Even minor environmental improvements in the production and use of concrete will therefore have significant and positive effects on both the local and the global environment.

Successful efforts have been made to minimize the environmental impact from the use of concrete in the construction sector. Modern transport vehicles reduce the impact from the transport of concrete and its constituent materials, such as gravel, cement and so on. Efficient filtering and cleaning of flue gases from clinker



*Figure 1 - Concrete is used for building the sustainable society. This photo shows a hydro power station on the Colorado river, USA, in concrete, producing renewable electric power.*



production at cement kilns considerably reduces pollution from harmful substances. Using alternative, renewable fuels for clinker production contributes to a substantial reduction in carbon dioxide emissions, and so on.

### *1.1.2 Mineral additions and fillers reduce the environmental impact*

The chemical processes involved in the production of cement clinker include decalcination of limestone, i.e. calcium carbonate. This process produces carbon dioxide which cannot be prevented from spreading to the atmosphere by any practical process known today. The only way of reducing the impact of the carbon dioxide produced in the decalcination process is to reduce the consumption of cement clinker.

One way of reducing the consumption of cement clinker is to partly replace it with mineral additions such as pulverized fly ash, granulated blast furnace slag, silica fume, limestone filler, etc. For many years now, different types of additions and filler have been used around the world when producing cement and concrete. However, such materials have not been used very much in Sweden in spite of the fact that potential supply resources are good, at least as far as blast furnace slags and limestone fillers are concerned. A consequence of this is that very little research into mineral additions and fillers has been done in Sweden and, consequently, the level of knowledge is low when compared with the situation in many other countries. If we are to increase the use of additions and fillers in Sweden, we need to improve our knowledge of them, not least as far as the use of Swedish additions and fillers under Swedish (Nordic) climatic conditions is concerned.

It must be pointed out here that the interest in using mineral additions and filler in cement and concrete is increasing in Sweden. The implementation of EN 206-1 [1] in Sweden opens up for the use of different types of cement with mineral additions and fillers, as well as the use of such mineral additions directly mixed into the concrete. A quality of cement with limestone filler has been developed and introduced in Sweden, and is today the most commonly used cement on the Swedish market. The use of silica fume is relatively well spread in Sweden, especially for concrete in aggressive environments, etc.

### *1.1.3 Mineral additions and filler in concrete – many advantages*

There are many reasons today for promoting the use of mineral additions and fillers in cement and concrete:

- There is a strong focus on reduced environmental impact from construction. The use of mineral additions and fillers in concrete technology may significantly contribute to reaching stipulated environmental goals: for example, where carbon dioxide pollution is concerned.
- European harmonization has opened up free trade of building materials within the EU and, consequently, different types of binders, mineral additions and fillers will be available on the Swedish market. We need to improve our knowledge of materials in these fields in order to be able to use these new materials (as far as Sweden is concerned) in a correct and safe way. Climatic conditions and methods of producing concrete differ from many other countries. We cannot, therefore, directly use these new

products without running a considerable risk of introducing problems. This may affect productivity and safety on the building site, durability/service life of concrete structures, etc.

- Much effort is put into producing cheaper building structures. Using mineral additions/fillers may lead to reduced material costs, not least due to the large quantities of concrete used in the construction sector.
- Mineral additions may, in some cases, contribute to improved properties of fresh or hardened concrete. This is well known where silica fume is concerned, but other additions may also contribute to improved material quality. In Denmark, for example, a certain quantity of fly ash is specified to be used in concrete subjected to severe weather conditions. In Sweden, on the other hand, this is not recommended due to the risk for poor durability! We do not know which of these points of view is the correct one. Probably the two standpoints represent two different ways of producing concrete structures with good durability properties. This is, however, a good illustration of how different the views on mineral additions are in different countries, even in countries with similar climatic conditions and building techniques, such as Sweden and Denmark.

#### *1.1.4 Mineral additions and the Swedish and European building codes*

The usefulness of mineral additions as binders is often defined by the coefficient of efficiency, also known as the k-value. This value quantifies the part by weight of Portland cement that can be replaced by one part by weight of mineral addition without changing the concrete properties. If half a part by weight of cement, for example, can be replaced by one part by weight of a certain mineral addition, the k-value is therefore 0.5.

EN 206-1 [1] gives k-values of 1.0-2.0 and 0.2-0.4 for silica fume and fly ash respectively. No value is given for granulated blast furnace slag in the European standard, but the Swedish application document, SS 13 70 03 [2], stipulates a value of 0.6 for slag. These k-values can be used for calculating an equivalent water/cement ratio:

$$(W/C)_{eq} = W/(C+kR) \quad (\text{eq 1.})$$

where  $W$  = water ( $\text{kg/m}^3$ )  
 $C$  = cement ( $\text{kg/m}^3$ )  
 $R$  = addition ( $\text{kg/m}^3$ )  
 $k$  = coefficient of efficiency or k-value

The intention is that  $(W/C)_{eq}$  can replace  $W/C$  when mineral additions are used. The problem is, however, that the k-values given in standards are normally based on 28 days compressive strength, while building regulations do not specify any requirements for  $W/C$  as far as strength is concerned. Strength is normally checked by testing. There are, however, requirements for the water/cement ratio where durability is concerned; for example, for frost resistance and reinforcement corrosion. No well-documented k-values exist for these parameters.

This paradox, that k-values based on 28 days compressive strength have been used for predicting long-term properties for concrete, has caused confusion and probably contributed to

the scepticism in Sweden about the usefulness of mineral additions. There is an obvious need for better understanding and knowledge.

There are many things indicating that the k-values for long-term properties often differ considerably from the values given in standards. A few examples are given below:

- Slag may have a strongly negative influence on the salt-frost resistance for air-entrained concrete [3], which means that the k-value is normally substantially lower than 1.0. However, the situation is the opposite for concrete without entrained air and tested without salt, i.e. slag improves the resistance, which means that the k-value is higher than 1.0.
- Fly ash often contributes to a lower chloride permeability [4], i.e. the k-value exceeds 1.0 while a value 0.2-0.4 is stated in the European standard. There is, however, considerable uncertainty when calculating the total effect of the risk of reinforcement corrosion, as what is known as the threshold value has to be considered as well. The threshold value, which defines the concentration of chlorides that must be reached close to the reinforcement in order to start the corrosion process, depends, among other things, on the content of mineral additions.
- Slag is able to bind chlorides in its structure, which leads to a lower chloride permeability for concrete produced with slag cement compared to the case where Portland cement is used [4]. The k-value for this property therefore exceeds 1.0. On the other hand, the influence of the threshold value is probably negative, and it is hard to predict the total effect on the risk of reinforcement corrosion. Normally, slag also has a positive effect, i.e. the k-value exceeds 1.0, as far as chemical attack, alkali-silica attack, etc. are concerned, while a k-value of 0.6 is prescribed in Swedish Standard [2] regardless of the type of attack.

In many cases, the way of classifying the efficiency of additions used so far seems to be incorrect. This has created uncertainty of how to use such materials, which in turn has hindered optimum use of additions in cement and concrete. There is therefore a need for a new system with more nuances for classifying additions (and fillers), not least where long-term properties/durability are concerned. To be able to develop such a system, we need more knowledge of the properties and effects of additions and also more material data.

## 1.2 The aim of this investigation

This report comprises the first part of the project *Use of industrial by-products and filler in concrete – Long term properties/durability*.

The aim is:

*to improve the knowledge of long-term properties/durability of cement and concrete produced using industrial by-products/fillers in order to promote efficient, safe, reliable and increased use of such types of materials.*

This may have positive environmental effects: reduced carbon dioxide pollution; reduced deposition of waste materials; reduced energy consumption; etc. This is to be achieved without adversely affecting good long-term properties/durability.

The work comprises mainly the following activities:

- Determination of material parameters/k-values
- Study of mechanisms governing the influence of industrial by-products/filler on the long-term properties/durability.

The results presented in this report concentrate mainly on the first part of the two activities described above, i.e. determination of material properties.

### **1.3 Co-operation with other projects**

Knowledge of how to use mineral additions and fillers in concrete in Sweden is lacking, especially within three areas: a) concrete rheology, b) properties of young concrete and c) long-term properties/durability.

The research project described in this report concerns subject c), long-term properties/durability. The project has been carried out in close cooperation with two other projects dealing with the other two subjects:

*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 on the early strength development, with special focus on winter conditions.* Project leader Monica Lundgren, SP Swedish National Testing and Research Institute [6, 7].



## 2 CONTENTS OF THE REPORT

### 2.1 Introduction

Durability is an extensive subject, and the work described in this report has been restricted to long-term strength and diffusion/migration resistance to chlorides.

The main results are presented in the following three papers, which are enclosed as Appendices 1-3 to this report:

- I Boubitsas, D, *Long-Term Performance of Concrete Incorporating Ground Granulated Blast Furnace Slag*. Proceedings, 8<sup>th</sup> International Conference on Fly Ash, Slag and Natural Pozzolans in Concrete, Las Vegas, 2004, pp. 265-279.
- II Boubitsas, D, *Replacement of Cement by Limestone Filler. Effect on Strength and Chloride Migration in Cement Mortars*. Accepted for publication in Nordic Concrete Research, 2005.
- III Boubitsas, D, *Replacement of Cement by Limestone Filler or Ground Granulate Blast Furnace Slag: the Effect on Strength and Chloride Diffusion in Cement Mortars*. Laboratory and field studies. Manuscript to be published, 2005.

The parameters tested and the materials used are briefly described in Sections 2.2 and 2.3 below.

### 2.2 Parameters studied

The results in this report and in papers I-III are based on laboratory tests and field exposure experiments.

The laboratory tests investigated the influence of mineral additions and fillers on the compressive strength and the chloride migration coefficient. Results for 28 days and 1-year-old mortars are presented. The compressive strengths were measured on mortar prisms in accordance with EN196-1 [8] and the migration coefficient in accordance with NT BUILD 492 [9].

The migration coefficient is used in the laboratory investigations for defining the chloride penetration properties. Migration is defined as the movement of ions under the action of an external electrical field, while diffusion is defined as the movement of ions under a concentration gradient. Normally the value of the migration coefficient determined in accordance with NT BUILD 492 is very comparable with the diffusion coefficient [10].

Diffusion coefficients were determined in the field exposure experiments carried out at the Träslövsläge site on the Swedish west coast. The chloride profiles were measured on mortar specimens that had been submerged in sea water. This report presents preliminary results after 1 year's exposure in sea water. The type of chloride ingress model chosen to estimate the diffusion coefficient in this study is the frequently used empirical model based on the error function solution to Fick's 2<sup>nd</sup> law.

## 2.3 Materials

The tests have investigated the influences of the following parameters of the mineral additions on mortar properties for:

- Type of mineral addition, i.e. hydraulic and inert mineral addition
- Different water/binder ratios
- Percentage replacement of cement by mineral addition
- Fineness of the inert mineral addition
- Different types of the inert mineral addition

The two types of mineral additions used are: granulated blast furnace slag and limestone.

The physical and chemical properties of the materials used throughout the experimental program, as given by the producers, are shown in Tables 1 and 2. The aggregate used was CEN standard sand in accordance with EN 196-1 [8], and the cement was a CEM I 52.5 R product conforming to EN 197-1 [11].

The natural calcium carbonate ( $\text{CaCO}_3$ ) qualities used in this investigation can be divided into chalk, limestone and marble. Chalk originates from the shells of fossil protozoans. It comes from the most recent geological deposits formed in the Cretaceous era, and has very fine crystals. Limestone is also of biogenic origin, but more compact than chalk. Its constituents are seashells and coral, which have been subjected to pressure and were formed in the Carboniferous era. The size of the crystals ranges between those of chalk and marble. Marble is formed when chalk or limestone recrystallise under high heat and pressure and form coarse crystals. The calcium carbonate powder quality, termed limestone, was supplied in three different particle sizes: LL, LLF and LLC (see Table 2). The calcium carbonate content of all three calcium carbonate qualities was  $\geq 98\%$  by mass.

**Table 1. Chemical composition of the cement and slag.**

Chemical composition	Cement (%)	Slag (%)	Mineralogical composition of cement	(%)
CaO	64.1	31	$\text{C}_3\text{S}$	62.8
$\text{SiO}_2$	20.9	34	$\text{C}_2\text{S}$	12.4
$\text{Al}_2\text{O}_3$	3.8	13.1	$\text{C}_3\text{A}$	5.5
$\text{Fe}_2\text{O}_3$	2.7	0.2	$\text{C}_4\text{AF}$	8.3
$\text{SO}_3$	3.4	1.41		
MgO	2.8	17.0		
$\text{K}_2\text{O}$	1.1	0.52		
$\text{Na}_2\text{O}$	0.3	0.54		
Cl	0.02	0.01		

**Table 2. Physical characteristics of the cement and limestone fillers used**

Material	Designation	Mean particle size ( $\mu\text{m}$ )	Specific Surface, BET ( $\text{m}^2/\text{kg}$ )
Cement	CEM	8	1760 (550 Blain)
Limestone (fine)	LLF	0,44	15000
Chalk	CH	2,3	2200
Limestone (medium)	LL	5,5	1000
Marble	MA	7,0	1500
Limestone (coarse)	LLC	22,0	700
Slag	BFS	8	470 (Blain)

The ground granulated blast-furnace slag (GBFS) used in the tests was a commercially available Swedish product.

Five different mortar mixtures were cast with Ordinary Portland Cement as the only binder, and with a range of water/binder ratios between 0.4 and 0.8. Another five different mortar mixtures were cast where part of the Ordinary Portland Cement was replaced with limestone filler (binder = OPC + limestone), and four different mortar mixtures were also cast later on, with part of the Ordinary Portland Cement being replaced this time with slag (binder = OPC + slag). The mixture compositions are shown in Table 3.

**Table 3. Mortar mix proportions used in the experimental study.**

Mortar	W/B	Cement (kg/m <sup>3</sup> )	Limestone filler (kg/m <sup>3</sup> )	Slag (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	Aggregate (kg/m <sup>3</sup> )	Air (%)	Consistence (mm)
<i>Cement</i>								
OPC-0.4	0.40	702			281	1263		169
OPC-0.5	0.50	500			250	1500	4.9	170
OPC-0.6	0.60	413			248	1593		176
OPC-0.7	0.70	345			242	1666		168
OPC-0.8	0.80	319			255	1654		172
<i>Cement and limestone filler</i>								
CH24-0.5	0.50	380	120		250	1500	4.8	173
LL12-0.5	0.50	440	60		250	1500	5.0	175
LL24-0.5	0.50	380	120		250	1500	4,7	180
LL24-0.7	0.70	262	83		242	1666	5.4	164
MA24-0.5	0.50	380	120		250	1500	6.0	178
<i>Cement and slag</i>								
BFS20-0.5	0.50	400		100	250	1500	5.3	185
BFS35-0.5	0.50	325		175	250	1500	6.0	184
BFS35-0.7	0.70	224		121	242	1666	8.1	170
BFS65-0.5	0.50	175		325	250	1500	5.3	195





## 3 LITERATURE REVIEW

### 3.1 Ground Granulated Iron Blast-furnace Slag

#### 3.1.1 Introduction

This section is not intended to be a state-of-the-art description of the use of iron blast-furnace slag: instead, its purpose is to provide some background on the use of iron blast-furnace slag as a cementing material (in combination with Portland cement), and to elucidate some relevant properties concerning this investigation. Although there are many types of ferrous and non-ferrous slag, for brevity in this section, iron blast-furnace slag will be referred to as slag.

Blast-furnace slag is formed as a liquid at 1350-1550 °C in the manufacture of iron. The blast furnace is filled from the top with a mixture of ore, coke, and limestone. Each kilogram of iron produced requires about 1.75 kg of ore, 0.75 kg of coke, and 0.25 kg of limestone. The limestone, which is primarily calcium carbonate, undergoes thermal decomposition to calcium oxide and carbon dioxide. The calcium oxide helps to remove the siliceous, aluminous, and other oxide impurities from the ore. This mixture of products, which is known as slag, is molten in the blast furnace and floats on the denser molten iron. Both molten materials are drawn off at regular intervals from continuous furnace processes. The slag rate tapped from the slag furnace is about 300 kg per tonne of iron [12].

If the slag is allowed to cool slowly after drawing off from the furnace, it crystallizes to give a material with actually no cementing properties. However, if cooled sufficiently rapidly to 800 °C, it forms a glass that is latent hydraulic. Cooling is most often achieved by spraying droplets of the molten slag with high pressure jets of water. This gives a wet, sandy material which when dried and ground is called ground granulated blast-furnace slag [13].

The suitability of slag for use in cement depends primarily on its reactivity (hydraulicity) The properties of slag that have been general accepted as influencing its reactivity are [14]:

- The degree of vitrification (glass content)
- The chemical composition
- The mineralogical composition
- The fineness of grinding
- The activation of slag glasses

The following sections provide a brief summary of each of these properties, and their influence on hardened concretes, mortars and cement pastes.

#### 3.1.2 Degree of vitrification (glass content)

Glasses can be described as “the product of fusion of inorganic materials, which have cooled to a rigid condition without crystallizing”, hence lacking long-range interatomic order [15]. The degree of disorder in a glass can be observed by the way in which it diffracts X-rays to form a diffraction pattern. Figure 2 illustrates diffraction patterns of: (a) ordered, crystalline SiO<sub>2</sub> (cristobalite); and (b) non-crystalline SiO<sub>2</sub> (glass). As can be seen in Figure 2, for the

non-crystalline state, diffraction of X-rays results in a broad diffuse halo rather than sharp diffraction peaks.

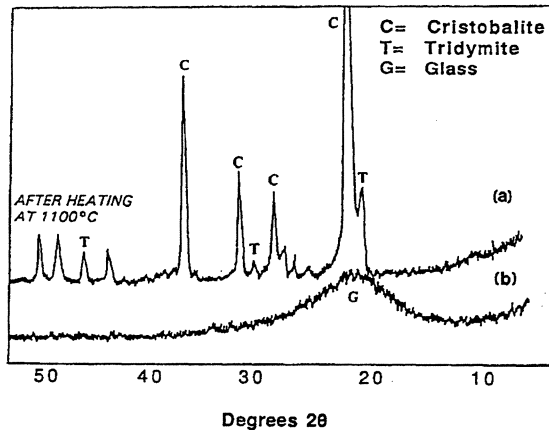


Figure 2 - X-ray diffractograms of (a) crystalline silica and (b) glassy silica [15].

A feature of glass-forming oxides, such as pure  $\text{SiO}_2$ , is that although the integral structure lacks long-range interatomic order, there is continuity in the chains of constituent atoms (Figure 3a). The disorder results from randomness in the size of the rings into which these chains are linked to form a structural network. When more complex glasses are formed, for example by introducing sodium ions into silicate structures, a greater level of disorder results. Not only are the rings of the glass-forming component disordered, but many are also broken to form non-bridging oxygen atoms (Figure 3b). Further levels of disorder result as more constituents are introduced into the glass, e.g. random chemical disorder may be caused by the replacement of Si by Al or Fe (Figure 3c). Most of the glasses of practical interest to the cement industry are disordered, both by chain breaking through the presence of modifier cations such as Na, K, and Ca, and by chemical disordering of the chains (Al, Fe) [15].

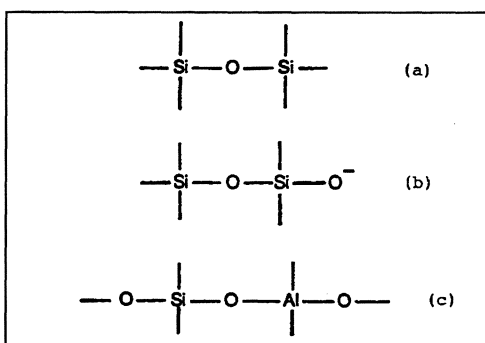


Figure 3 - Structures of silicate glass, (a) typical Si-O chain with oxygen bridging in simple glasses, (b) non-bridging oxygen in complex glasses containing  $\text{Na}^+$  ions, (c) random chemical disorder resulting from substitution of Si by Al [15].

The degree of vitrification (glass content) achieved during quenching depends on several factors: furnace tapping temperature, slag chemistry, slag viscosity, and the rate of cooling achieved by the quenching method. The first three factors are optimised for blast-furnace operations, the primary function being to produce iron with consistent properties. As a result of modern furnace practice, coupled with uniform sources of iron and limestone flux, slags

now are consistent in chemistry. As long as the tapping temperature is high enough, and a standard quenching process is used, the resulting glass contents should be fairly constant [14].

The latent hydraulicity of the quenched slag is generally considered to result from the perched energy level of its amorphous structure (glassy) in comparison to the crystalline structure of the same composition [14, 16, 17]. That implies that the glassy phase is thermodynamically metastable, and when the energy barrier ( $\Delta G$ ) see Figure 4, is overcome, hydration can proceed.  $\Delta G$  can be overcome by alkaline, sulphate, or temperature activation.

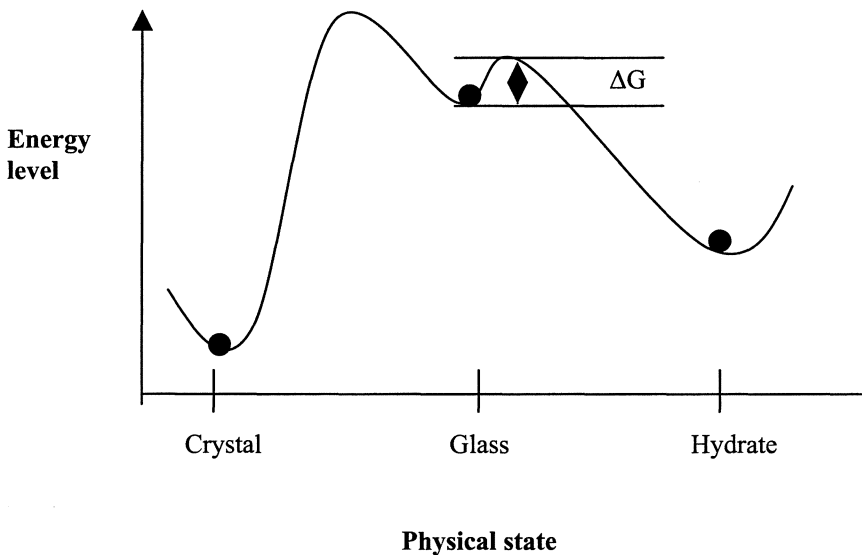


Figure 4 – Schematic free energy diagram for slag [3].

Roy and Idorn [16] stated, that, “. . . whether or not slag cement hydration is a true activated chemical reaction may be academic”, and the thermodynamic concept was suggested to be appropriate for developing an understanding of this relatively complex process.

In spite of the fact that a mainly glassy structure is essential to slag hydraulicity, conflicting results about the glass content have been reported. Schröder [18], in his comprehensive review, has presented results showing roughly linear relations between strength and glass content. Smolczyk [17] and Taylor [13], on the other hand, quoted several investigations reporting that a small proportion of crystalline material in the glassy slag has a beneficial effect on the reactivity. In his survey, Hooton [14] found contradictory opinions regarding the minimum acceptable glass content. Minimum levels such as 90 % have been quoted, while others have suggested that 30-40% glass was acceptable, and some proposals in between. Hooton [14] stated, that, although a glassy structure is essential to reactivity, high glass content does not guarantee a highly reactive slag.

### 3.1.3 Chemical composition

The chemical composition is also of great importance to slag hydraulicity. It can vary over a wide range, depending on the nature of the ore, the composition of limestone, the coke consumption and the kind of iron being made. Because of the carefully controlled processes to give consistent iron production, the range of slag chemical composition is fairly narrow for

a specific ore and furnace operation. Examples of chemical compositions of blast-furnace slag from different countries are given in Table 4 [19]. Other minor components are  $\text{TiO}_2$  (<4 %), and  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  (<2 %).

**Table 4. Chemical composition (per cent) of blast furnace slags [19].**

Source	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	MnO	S
France	43	35	12	8	2	0.5	0.9
Germany	42	35	12	7	0.3	0.8	1.6
Japan	43	34	16	5	0.5	0.6	0.9
Sweden*	31	34	13.1	17.0	0.2	0.7	1.4
South Africa	34	33	16	14	1.7	0.5	1.0
USA	41	34	10	11	0.8	0.5	1.3

\* From chemical analyses of the slag used in this investigation.

The general state of knowledge of the influence of the major elements on the hydraulic activity of slags, is that the hydraulic activity increases [14, 17] with increasing content of CaO and Al<sub>2</sub>O<sub>3</sub> and with decreasing content of SiO<sub>2</sub>. With a few exceptions, the influence of MgO on hydraulicity is said to be beneficial. The effect of minor elements on reactivity is more unclear [17].

To predict the hydraulic reactivity of a blast furnace slag, many studies have been concentrated on the chemical composition. A lot of compositional moduli have been proposed to predict optimal slag composition. Some common moduli used in the prediction of hydraulic reactivity of slag (or compressive strength of blended cement mortars) include the main oxides of the slag (Table 5) [20]. Other moduli also include correlation coefficients, minor elements and glass content, all of which produce a more complicated analysis.

**Table 5. Formulas proposed for assessment of hydraulicity of GGBFS [20].**

	Formula	Requirement for good performance	The value for the GGBFS used in this investigation
1	$\frac{\text{CaO}}{\text{SiO}_2}$	1.3-1.4	1.0
2	$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2}$	>1.4	1.4
3	$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$	1.0-1.3	1.0
4	$\frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2}$	>1.0	1.8

In his investigation, Mantel [20] confirmed (among others'), Hooton's [14] and Smolczyk's [17] findings, that the various chemical formulas proposed in the literature are not adequate for predicting the hydraulic activity of slag and therefore the compressive strength development of mortars or concretes incorporating slag as binder.

### 3.1.4 Mineralogical composition

Crystallized slag contains melilite as the main constituent. Melilite is a solid solution of gehlenite  $C_2AS$  and akermanit  $C_2MS_2$ . Some other minerals that may occur are dicalcium silicate  $C_2S$ , merwinite  $C_3MS_2$ , pseudo-wollastonite  $CS$ , and others similar minerals [19].

The constitution of glassy slags can be simplified by regarding granulated slags as super cooled liquid silicates, and by considering the glassy silica in which some Si-O-Si are broken and neutralised by metal cations called structure modifiers. Silica tetrahedral is isolated or polymerised with bridging oxygen atoms (Figure 5). The negative charges of these anionic groups are neutralised by cations such as,  $Ca^{2+}$ ,  $Mg^{2+}$ , or aluminium ions [19]. The crystalline phases found in glassy slag are merwinite, melilite, and others.

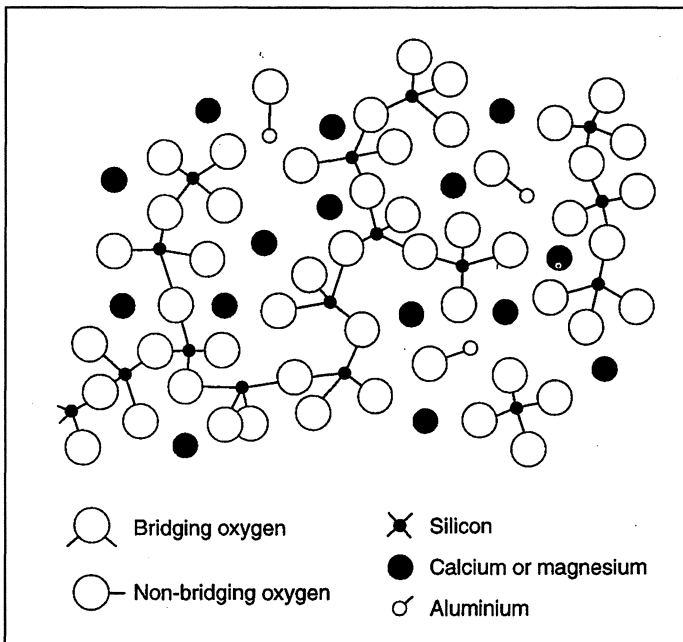


Figure 5 - Schematic structure of a glassy slag [19].

Opinions on the influence of the glass composition on the hydraulic properties of slag are not always in agreement [13, 14, 16, 17]. The effect of the glass composition on hydraulic activity is therefore unclear.

### 3.1.5 Fineness of grinding

Slag has been reported to be less easily ground than Portland cement [14, 19]. Intergrinding, to produce blended cements, thus produces Portland cement clinker which is more small-grained than the slag fraction. As for all cements, an increase in the fineness of the grinding in cements incorporating slag, also results in an increase in reactivity and, therefore, an increased strength.

The influence of fineness of the two constituents is reported to vary depending on their relative proportions. Figure 6 shows the strength development for mortars, where the clinker and slag were ground separately, and mixed afterwards, with a slag content of 75%.

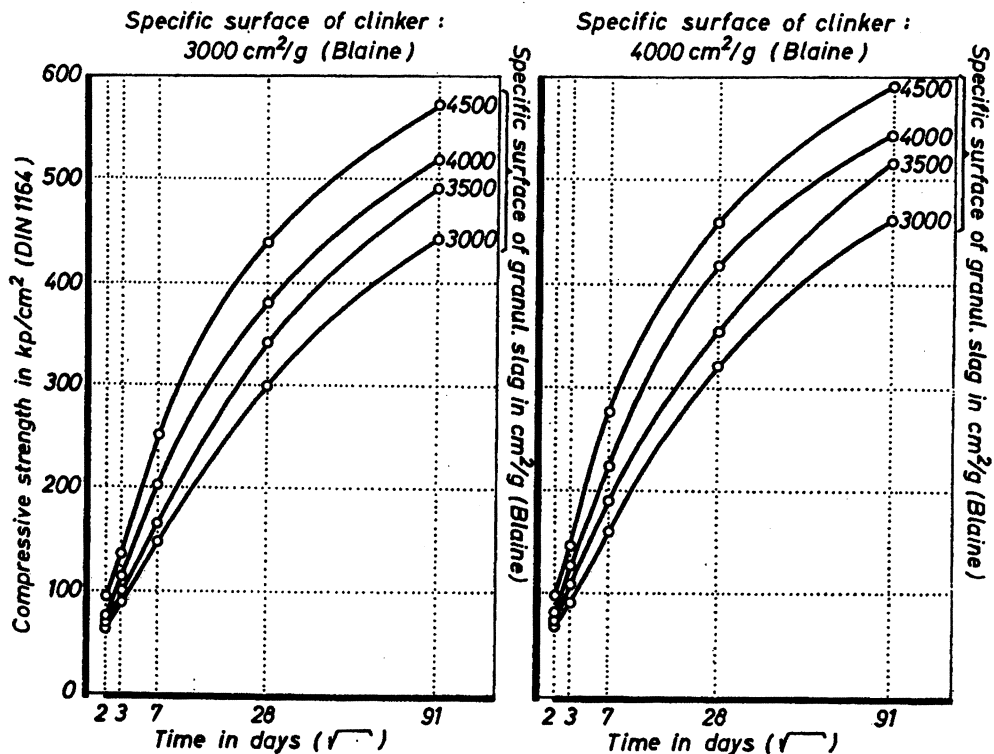


Figure 6 – Compressive strength versus time as a function of fineness [18].

As Figure 6 indicates, the fineness of slag is of major importance at all ages in cements with high slag content. On the other hand, with slag contents up to about 50-60 %, the early strength is reported to depend mainly on the fineness of the clinker fraction, and the later strength on that of the slag fraction [18, 19].

According to ACI-recommendations [21], separate grinding of slag and Portland cement, with the materials combined in the mixer, has two advantages over the interground blended cements: 1) each material can be ground to its own optimum fineness, and 2) the proportions can be adjusted to suit the particular project needs. In their research into to what degree the strength of mortars and concretes is affected by the way slag is added, Longo and Torrent [22] found that the differences observed between intergrinding, separate grinding followed by dry mixing, and separate grinding and separate batching into the mixer, were generally insignificant.

### 3.1.6 Activation of slag

Granulated blast-furnace slag alone is normally not hydraulic at room temperature, but if some suitable activator is present, it shows pronounced cementitious properties. Activators can include lime ( $\text{Ca(OH)}_2$ ), Portland cement, caustic soda ( $\text{NaOH}$ ), or gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) [14]. This section describes a general view of the activation of slags by the calcium hydroxide liberated from the Portland cement hydration.

If slag is placed in water, it dissolves to a slight extent, but no hydration products can be observed. However, a protective film is quickly formed, and inhibits further reaction. It is suggested that this protective film is dissolved in the presence of  $\text{Ca(OH)}_2$ , allowing further reaction to occur [23]. The reaction continues if the pH is kept sufficiently high, and thus the

pore solution of Portland cement is a suitable medium [24]. Figure 7 shows the change in the amount of combined water (chemical bound) during the hydration of slag with  $\text{Ca(OH)}_2$  as an activator. The curves in Figure 7 show that the slag hydration was not very dependent on the  $\text{Ca(OH)}_2$  content when it exceeded 5 % [24].

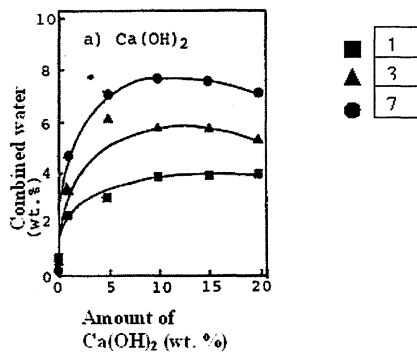


Figure 7 - Amount of combined water during the hydration of granulated blast furnace slag with  $\text{Ca(OH)}_2$  as an activator [24].

Taylor [13] quotes many studies about slag cement hydration, that have shown that the principal hydration products are essentially similar to those given by pure Portland cement, except that the quantities of  $\text{Ca(OH)}_2$  found are in varying degrees lower than those which are produced solely by Portland cement.

Although several hypotheses have been proposed, the mechanism of the attack (hydration) on the glass is not established [13].

## 3.2 Properties of Portland cement activated slag

### 3.2.1 Introduction

Cements incorporating blast-furnace slag have somewhat different properties from those of Portland cement. These differences have been well known for a long time, and include; low heat of hydration, increased setting time, increased creep and shrinkage, increased resistance to chloride attack, and delayed strength development. The rest of this section presents a brief review of the two last-mentioned properties.

### 3.2.2 Strength

Compressive and flexural strength gain of cements containing slag can vary over a wide range. The extent to which slags affect strength depends on the particular slag's hydraulic activity, the ratio in which it is used in the mixture, water-cementitious materials ratio, physical and chemical characteristics of the Portland cement and curing conditions. In this short overview of the strength development, the focus will be upon the effect of replacement ratio of cement by slag in a mixture, and the effect of the water-cementitious materials ratio.



As can be seen in Figure 8, the strength achieved with a certain slag is greater in concrete mixtures with high water-cementitious materials ratios than in those with low water-cementitious materials ratios [21].

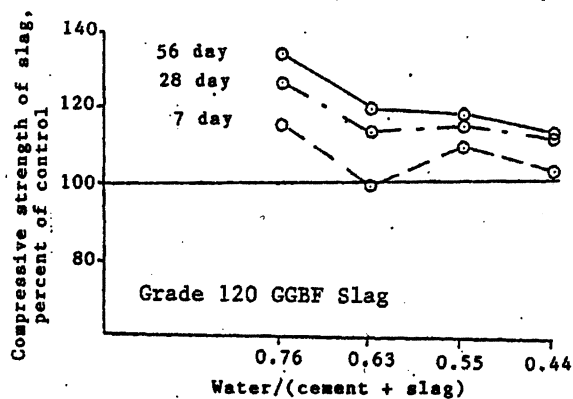


Figure 8 – Influence of water-cementitious materials ratio on compressive strength, expressed as a percentage of mixture made with Portland cement [21]

Hwang and Lin [25], conformed in their extensive investigation the results of Hogan and Meusel [26] that the optimum slag content for strength development, depends upon the age of the mortar. The influence of slag replacement on mortar compressive strength is shown in Figure 9. The highest 28 days' strength is found with a slag replacement rate of 40 percent. According to the same results, early strength (3 days) seems to be inversely proportional to the amount of slag in the mixture.

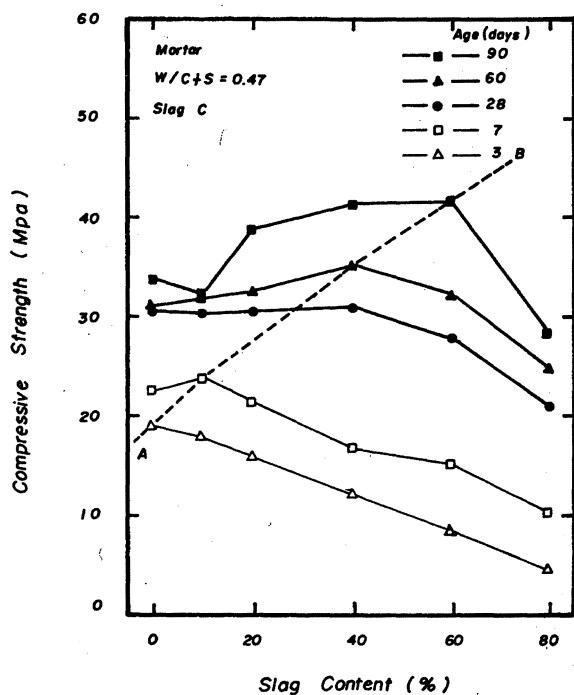


Figure 9 – Effect of slag replacement on mortar compressive strength [25]

### 3.2.3 Chloride ion penetration

The high resistance to diffusion of chlorides, in mortars and concretes including blast-furnace slag as a part of the binder is well known, and has been reported in many references [15, 17, 27, 28]. Because of the vast variety of the ways to measure and report the resistance to chlorides, some estimation of the resistance to chlorides are presented in this section, with the purpose of giving a general view of the effect of slag.

Smolczyk [17] showed how the diffusion resistance of concrete bars made from blast-furnace slag cement increases considerably with an increasing slag content (Figure 10). These results show that the composition of the cement has a greater influence than does the w/c-ratio.

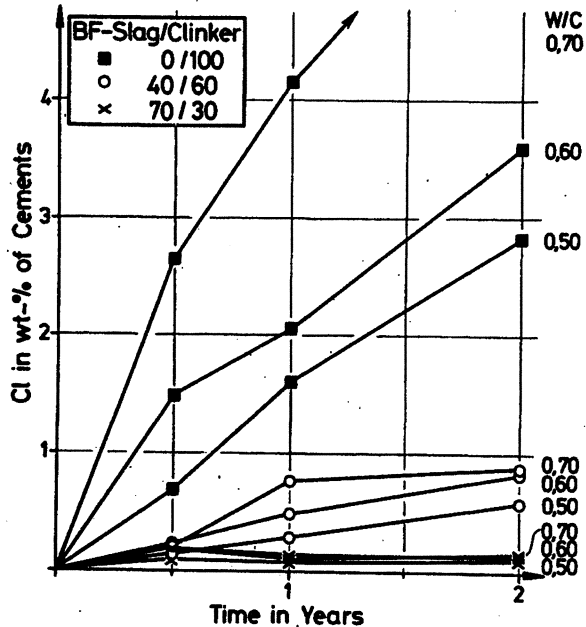


Figure 10 – Chloride content in 20.3-40.6 mm deep layers in concrete bars stored in 3.0 molar solution of NaCl [17].

Decter et. al. [27] measured the chloride ion diffusivity in pastes with different binders, using a steady-state (thin disc) method. The binders used included a sulphate-resisting Portland cement (SRPC), an ordinary Portland cement (OPC), and blended cements prepared from OPC and 40%, 50% or 70% of ground granulated blast-furnace slag. Their results, of the diffusion coefficients (D), are illustrated in Figure 11.

The SRPC had by far the highest D value, followed by the OPC. The slag cements had greater resistance to chloride diffusion than OPC, and their diffusion coefficient decreased as the percentage in the blends increased. In the same investigation, concrete slabs containing similar cements were regularly immersed in NaCl solution. The chloride concentration profiles from this test are shown in Figure 12. Similar trends are found on comparison of the resistances to chloride penetration, but the differences are much less pronounced.

Wee et. al. [28] showed (Figure 13), with a different kind of soaking test, the superior resistance of slag mixtures to chloride penetration compared with ordinary Portland cement mixtures. The pattern in this study, too, was the same, with the diffusion coefficient decreasing as the percentage of slag in the blends increased.

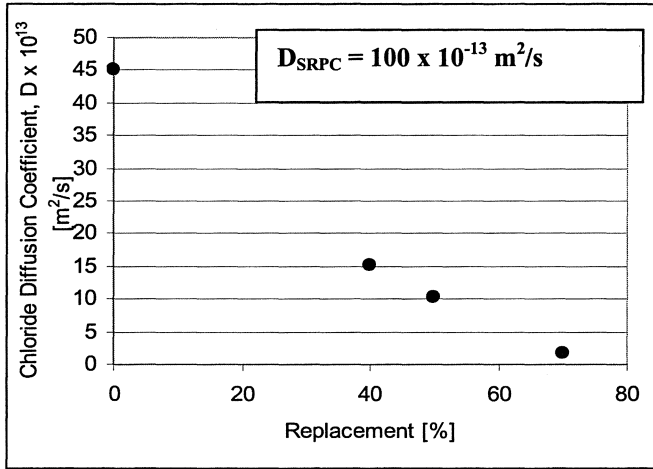


Figure 11 – Diffusion coefficient versus slag replacement rate [27].

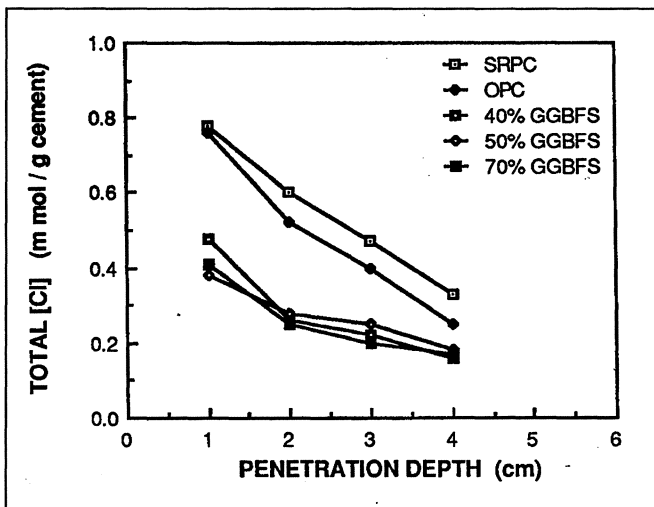


Figure 12 – Concentration profiles of total chloride for various mixes after 48 weeks' ponding [27]

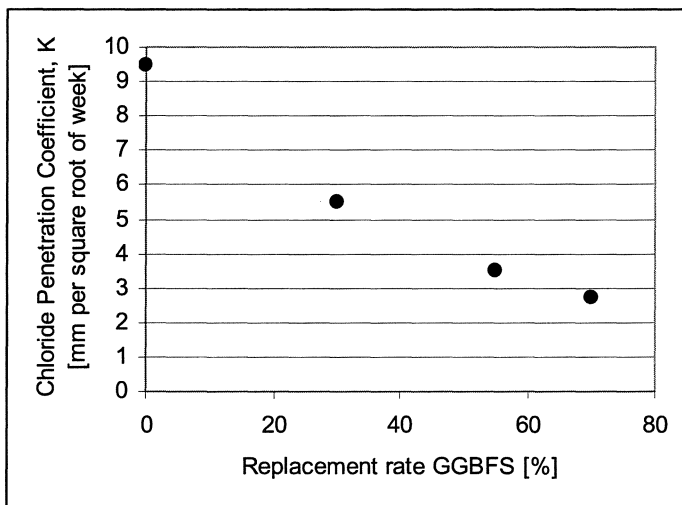


Figure 13 – Relationship between chloride penetration coefficient  $K$  and replacement rate of OPC with slag [28].

### 3.3 Limestone filler

#### 3.3.1 Introduction

This section provides an introduction to limestone ( $\text{CaCO}_3$ ) as a main constituent of cement, and continues by describing the properties of such cements relevant for this investigation. For simplicity, cements incorporating limestone ( $> 5\%$  by weight) as one main constituent and clinker as the other will be referred to as limestone-blended cements, regardless of the exact manner of production, or the proportion of limestone and clinker etc. Further on, ground limestone for inclusion in blended cements is referred to as limestone filler.

Use of Portland cement containing small quantities of about 5 to 10 % by weight of limestone is common practice in many European countries. In some countries, such as Germany and France, blended cements with a limestone content up to 20 % by weight have been employed in building construction and structural engineering since the mid 1980s. European Standard EN 197-1 [11] identifies cements that may contain limestone as one main constituent from 6 to 35 % by weight.

European Standard EN 197-1 specifies that limestone shall meet the following requirements for approval as a main constituent in cements;

- a) The calcium carbonate content ( $\text{CaCO}_3$ ) shall be at least 75 % by mass
- b) The clay content, determined by the methylene blue test, shall not exceed 1,20 g/100 g
- c) Limestone with a total organic carbon (TOC) content up to 0.50 % by mass can be accepted

The effects of limestone filler in blended cements have not yet been completely explained, and for a long time ground limestone was considered as an inert filler. Nowadays, it is generally accepted that limestone participates in the hydration reaction, and several studies have pointed out the following phenomena:

- The interaction of  $\text{CaCO}_3$  from the limestone with  $\text{C}_3\text{A}$  from the clinker, to form calcium aluminate monocarbonate hydrate ( $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot x\text{H}_2\text{O}$ ) (monocarbonate) [29, 30, 31]
- Transformation effects of the calcium carbonate on the ettringate-monosulphate system by the formation of monocarbonate [29, 30, 31]
- There is an interaction between calcium silicate ( $\text{C}_3\text{S}$ ) and calcium carbonate, resulting in acceleration of the hydration of  $\text{C}_3\text{S}$  and modification of the Ca/Si ratio of C-S-H [32, 33]

Many investigations of the hydration behaviour of limestone, pointing out the above phenomena, have been carried out on pure compounds in order to simplify and understand the complex hydration of limestone-blended cements: for example, hydration of pure synthesized  $\text{C}_3\text{A}$  in the presence of  $\text{CaCO}_3$  mixed in small vials. Not much has been published about the influence of these phenomena on the behaviour of mortars and, more importantly, of concretes.

Bonavetti et. al. [31] concluded that calcium carboaluminate hydrate is the final hydration product of  $\text{C}_3\text{A}$  in limestone-blended cements, and is an unstable compound in sulphate and chloride environment, and presumably can introduce durability problems. Ranc et. al. [34]

reported research in progress showing that, compared with quartz filler, the 28-day strength contribution of calcareous filler may be more than 5 MPa, and this could be due to the formation of monocarbonate.

### 3.4 Properties of limestone-blended cement/mortar/concrete

#### 3.4.1 Introduction

One of the most important issues in the use of limestone-blended cement is the question of the maximum replacement proportion of clinker by limestone filler. In this respect, there is no general agreement. The rest of this section is devoted to the issue of the replacement rate and some other issues concerning the compressive strength and chloride penetration of pastes, mortars and concretes.

#### 3.4.2 Strength

A wide-ranging program established by the British Building Research Establishment and the British Cement Association has investigated the properties of limestone-blended cements containing 5 % and 25 % limestone filler. In his paper reporting the results from this program, Matthews [35] summarises: “The results indicate that the performance of cements containing 5 % limestone is, overall, indistinguishable from that of Ordinary Portland Cement without additions” and that “The performance of cements containing 25 % limestone is akin to what would be expected from a cement with only 75 % cementitious materials.

In general, cements with 5 % limestone addition were prepared by grinding a mixture of clinker, gypsum and limestone to a slightly greater fineness than the Ordinary Portland Cement (OPC), or by blending OPC with limestone filler. The cements with 25 % limestone were usually prepared by blending rapid-hardening Portland cement with limestone filler, or by intergrinding clinker, gypsum and limestone to a significantly greater fineness than is usual for OPC. Some randomly chosen, general results for concrete compressive strength from this investigation are shown in Figure 14.

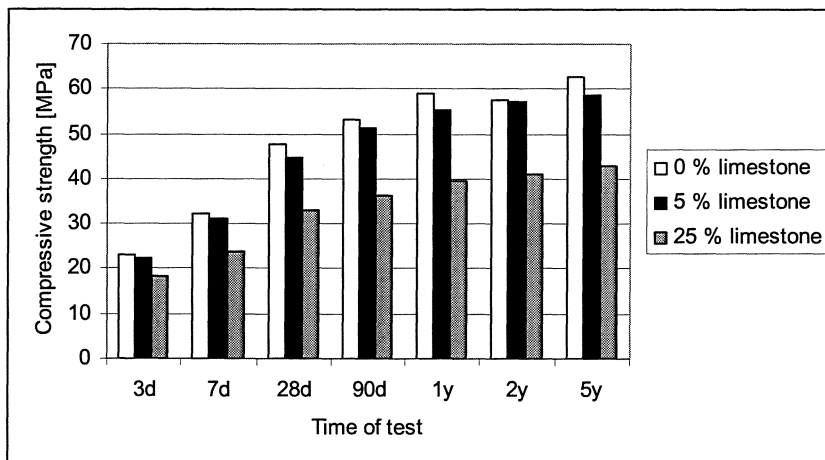


Figure 14 – The compressive strength at different testing times of Ordinary Portland Cement concrete, and with OPC replaced by 5 % and 25 % limestone filler (Binder content 300 kg/m<sup>3</sup>, w/c~0.60) [35].

As indicated in Figure 14, the compressive strength of cement with 5 % limestone addition is slightly lower than the corresponding OPC control, while cement with 25 % addition has substantially lower strength. Durability results from this investigation are presented later on in this section.

That cements with a low replacement rate, such as 5 % of limestone filler, have indistinguishably performance, and sometimes better performance, than that of OPC-based concrete, at least as far as compressive strength is concerned, is widely known, and in many countries it is common practice to intergrind limestone in the cements.

Vuk et. al. [36] investigated the influence of clinker type (cements with different  $C_3S$  content), and fineness of cement, on compressive strength and heat of hydration, for plain cements and for cements with 5 % interground limestone additive. Clinker A had a lower  $C_3S$  content than clinker B, of 35 % and 46 % respectively. 5 % gypsum was also interground in each cement. Their results on compressive strength tests on mortars are shown in Figures 15 and 16.

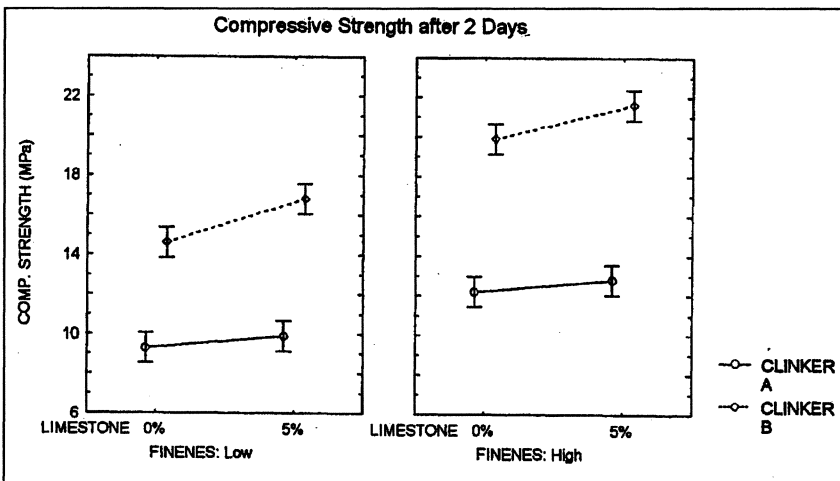


Figure 15 – The effect of limestone addition on the compressive strength after two days [36].

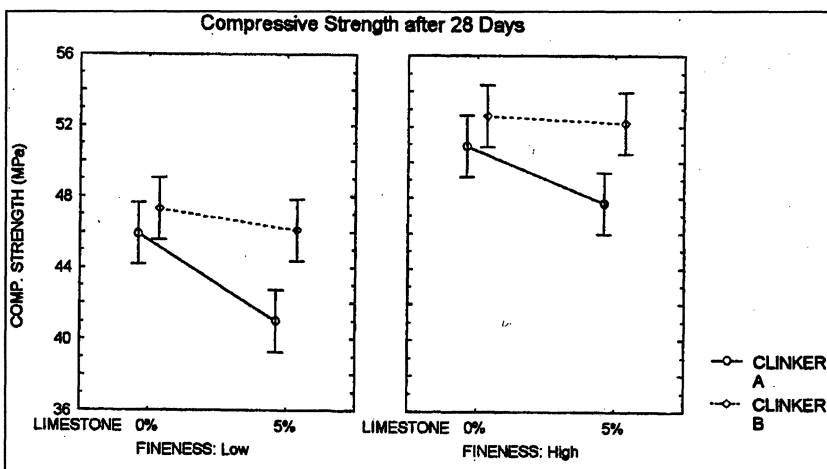


Figure 16 – The effect of limestone addition on the compressive strength after 28 days [36].

Figure 15 and 16 show that, initially, the addition of limestone increased the compressive strength, but after 28 days the effect was the reverse. It can also be seen that the cement with a higher  $C_3S$  content, that the 5 % limestone cement had a more pronounced increase in compressive strength at the early age strength (two days), while the decrease in compressive strength is much less for the same cement after 28 days. The fineness of the cement does not seem to be a decisive factor for the interaction of limestone filler in the compressive strength development, other than for the absolute values of compressive strength.

It is often reported that limestone-blended cements, having up to 10 % limestone content and more or less the same fineness, develop almost the same compressive strength as corresponding pure cements [37]. To reach the same 28-day compressive strength of concrete with higher limestone replacement rates, and otherwise identical composition, the fineness of the clinker has to be increased [38]. Increasing the fineness of the limestone without also increasing the clinker fineness has no significant influence on the compressive strength: see Figure 17.

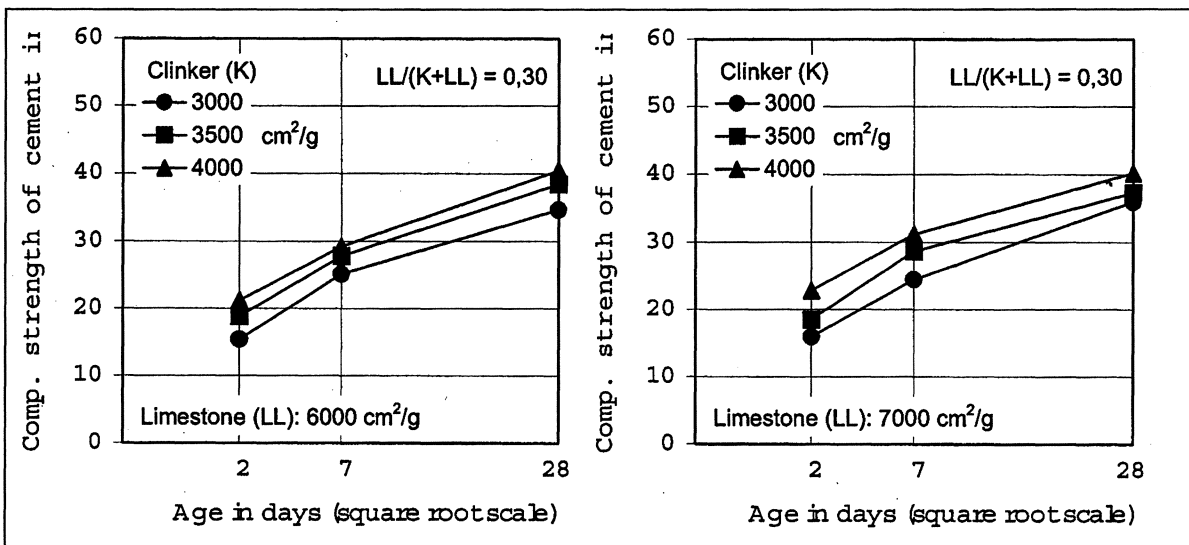


Figure 17 – Compressive strength of limestone-blended cement, with 30 % limestone content, and its dependency on the fineness of clinker and limestone [38].

### 3.4.3 Chloride ion penetration

Ranc et al. [34], pointed out that the general criticism of blended cement incorporating mineral additions considered to be inert, such as limestone filler or quartz filler, are that, when a pure Portland cement and a blended Portland cement are mixed with the same quantity of water, the water/clinker ratio of the blended cements is higher than that of the pure Portland cements, so the porosity of the hydrated paste is greater, and the durability less.

According to the authors, this reasoning is false when the cements are in the same strength class, because the mechanical strength depends on the porosity, and it is obvious that, to achieve the same 28 – day mechanical strength, i.e. the same quantity of hydrates with a lower clinker content, the clinker must be finer in a blended cement than in a pure OPC.

Their study compared artificial cements, without mineral additions, and blended Portland cements containing 15 to 25 % filler, within the same strength class. It was found that for the same mechanical strength class, the durability properties tested of blended cements with fillers is identical to that of pure Portland cements without additions.

Cochet et. al. [39] studied the diffusion of chloride ions in mortars with three different kind of binders. The binders used were OPC, blended Portland cement with calcareous filler, and a blended Portland cement with siliceous filler. All cements were produced from the same clinker quarry, but the fineness of the cements was set to obtain cements with the same compressive strength (strength grades) at 28 days. Two blended cements were produced, with 15 % and 27 % by weight of limestone filler replacement, and two quartz filler cements with 12 % and 20 % replacement rate (% wt.). Otherwise the mortars had the same constituents and the same water-cement ratio ( $w/c = 0.5$ ).

The two cement strength grades achieved had compressive strengths of 55 MPa and 45 MPa at 28 days. The higher cement grade was obtained with one of the OPCs and with the two blended cements with the lower fillers replacement ratio. The lower cement grade was also obtained by one of the OPCs (coarser than the first one), and with the blended cements with higher filler replacement ratio.

At the age of 28 days, the mortars were tested in a steady-state diffusion cell, to measure the chloride ion diffusion. The diffusion coefficient was estimated from this test, with the results showing that the diffusion of chloride ions for the blended cement with the low replacement ratio was equivalent to that of Portland cement without mineral additions in the same strength grade. However, the diffusion coefficient for the blended cements with higher replacement rate was about 50 % higher than the diffusion coefficient for the ordinary Portland cement in the same strength grade.

The authors' conclusion that the diffusion of chloride ions in Portland cement with limestone or siliceous addition is equivalent to that of Portland cement without mineral additions, provided that the cements considered are in the same strength grade, do not seem to agree with their results when the replacement rate of Portland cement by mineral additions is increased to levels over 20 %.

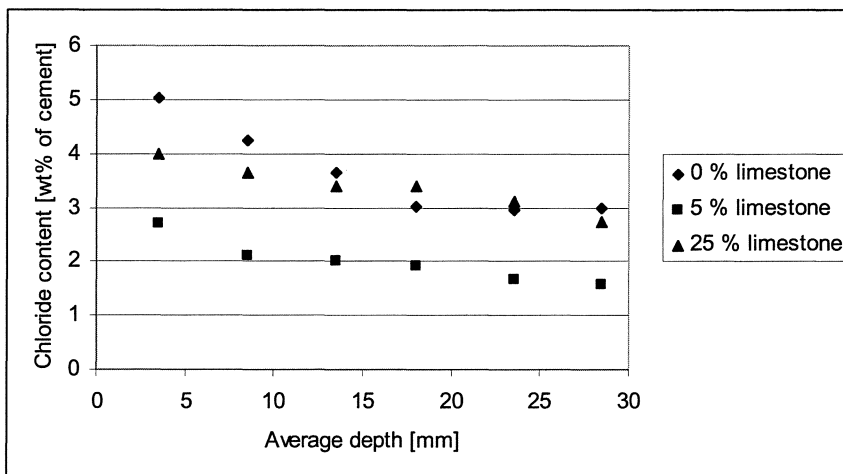


Figure 18 – Chloride content at an average depth of 5 mm, versus penetration depth [35].



The previously mentioned investigation by Matthews [35] also examined the chloride penetration. Specimens with the same mixture as for the compressive strength (see Figure 14) were exposed in the tidal zone at a marine exposure site for five years. Chloride profiles were obtained by drilling at 5 mm depth intervals: some of the results are shown in Figure 18. These results reveal only small differences between cement with 0 % and 25 % limestone filler, but an obvious improvement for the 5 % cements.

## 4 COMMENTS ON THE PAPERS

### 4.1 Introduction

A short introduction and summary of the three papers included in this licentiate report is presented in the following, together with some new reflections regarding the results from the papers.

### 4.2 Paper I: Long-term Performance of Concrete Incorporating Ground Granulated Blast Furnace Slag

The aim of this paper is to introduce a method for determining the coefficient of efficiency, the k-value, for mineral additions (in this case, ground granulated blast-furnace slag) as far as chloride penetration is concerned. The requirements for the chosen method were; to be fairly acknowledged (specified in a standard), easy and fast to perform, and with a good precision. A round-robin test [40] carried out in the Nordic countries has confirmed Nordtest method NT-Build 492 [9] as fulfilling these requirements, Streicher et. al. [41] also pointed out this method's suitability for rapid chloride tests on the basis of simplicity, duration of test, and theoretical basis.

NT-Build 492 is a non-steady-state migration method, where an external electrical potential is applied axially across the specimen and forces the chloride ions on the outside to migrate into the specimen. After a certain test duration, specified in the standard, the specimen is axially split and a silver nitrate solution is sprayed on to one of the freshly split sections. The chloride penetration depth can then be measured from the visible white silver chloride precipitation, after which the chloride migration coefficient can be calculated from this penetration depth as specified in the standard.

The results for the mortars with normal Portland cement as the only binder, plotted against w/c ratio, give a linear relationship between the migration coefficient and the w/c ratio, i.e. the migration coefficient seems to be proportional to the w/c ratio, when varying over the range 0.4 - 0.8 (see Figure 19a).

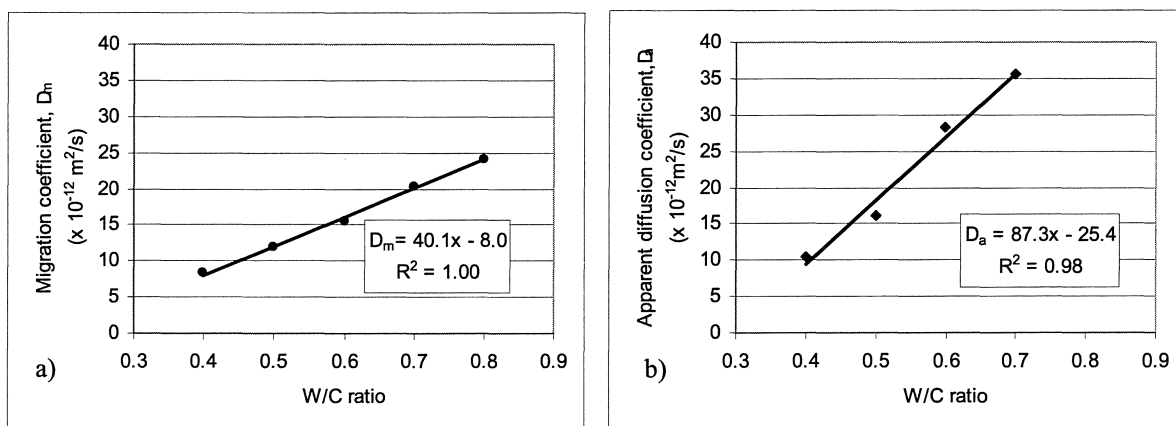


Figure 19 – a) The migration coefficient as a function of W/C for mortar with CEM I 52.5 R as binder (from appendix I). b) The diffusion coefficient as a function of W/C for concretes with a CEM I 42.5 as binder [42].

This proportionality was also reported by Frederiksen et. al. [42], when the tested concretes were made with ordinary Portland cement, both by the same method, and by using a conventional immersion test (NT-Build 443). The conventional immersion test involves: immersing concrete specimens in sea water or in a solution with a high concentration of chlorides for a certain time, measuring the profile of total chloride content in the specimen, and determining the chloride diffusion coefficient using Fick's Second Law and curve fitting.

Results from the investigation by Frederiksen et. al. [42], are shown in Figure 19b, when the immersion method was used. The chloride penetration coefficients obtained from these different tests should not be expected to be identical, even if performed on the same kind of specimen, because they are by definition different. One is a migration coefficient, and the other is a diffusion coefficient (apparent). In spite of the differences, parallel tests have shown that the value of the migration coefficient determined using NT-Build 492 corresponds well with the diffusion coefficient obtained with the conventional immersion test, NT-Build 443 [10, 42]. The close correlation between the two methods can be utilised for either method to obtain a diffusion coefficient. NT-Build 443 seems to be closest to reality, but for the reasons mentioned earlier. NT-Build 492 was decided most suitable for the ongoing investigation.

The k-values obtained in this investigation for the 28 day compressive strength were in the range of 0.7- 1.1, with small differences concerning the replacement quantity. These results were also in good agreement with the recommended k-value of 0.6 in the Swedish Standard [2], if it is remembered that standards should be on the safe side.

The results from the chloride migration, however, show that the effectiveness of slag in preventing chloride diffusion will be greatly underestimated. The k-values from the migration test for slag were three times higher than the corresponding k-values for compressive strength.

At first sight, the chloride migration method used in this investigation seems suitable for predicting k-values for chloride ingress when mineral additions are included, but must be verified by field exposure tests.

#### **4.3 Paper II: Replacement of Cement by Limestone Filler: The Effect on Strength and Chloride Migration in Cement Mortars**

Normally, the k-value concept is used only for EN 206-1 Type II additions, i.e. reactive additions such as most fly ashes, and silica fumes. However, in this paper, the k-value concept has been applied also for limestone in order to be able quantitatively to compare the efficiency of different types, qualities, and fineness of limestone, when used as cement replacement in binders. Most of the research investigations have concentrated on the effect of limestone filler on the hydration reaction and strength development. There are, however, very few references describing the durability effects of limestone addition. This article presents results for chloride penetration (chloride migration), and compares k-values obtained from the migration test with k-values obtained from traditional compressive strength testing.

The results from the compressive strength test revealed that the amount of replacement has a significant effect on the compressive strength. 12 % replacement gives a k-value of 0.85, while the corresponding value for 24 % replacement is 0.2. These results are in accordance with earlier reported results. Betrandy et. al [43], reported k-values varying from 0.2-0.4 for

cement pastes of 75 % Portland cement and 25 % limestone filler blend by mass. It is often reported that limestone-blended cements, having a moderate replacement of about 10 % limestone content, and more or less the same fineness, develop almost the same compressive strength as corresponding pure cements [37]. The results did not indicate any tendency for the k-value to vary as a function of the fineness, nor were any significant differences in compressive strength efficiency reported when different types of calcareous carbonates were tested.

If the results from the compressive strength were somehow expected, the results from chloride migration test were not. The amount of replacement still had a significant effect on the k-value; the lower replacement rate of 12 % limestone produced a k-value of 0.1, meaning that very little cement could be replaced by limestone as far as chloride penetration was concerned. The higher replacement rate of 24 % limestone produced negative k-values for all the tested limestone filler proportions. The negative k-value means that the chloride penetration for 24 % replacement rate with limestone filler is higher than for a situation where 24 % of the cement is removed from the mortar without any replacement. This detrimental effect of limestone could not be explained at the time.

Additional work revealed some unexpected results, shown in Figure 20, where the migration coefficient for mortars with pure cement as binder, at different ages, is plotted against the water/cement ratio. It can be seen from the figure that the migration coefficient at various w/c-ratios is lower at 28 days than for 1 and 2 years. It seems as if the chloride migration coefficient is lower at 28 days - also confirmed by control measurements - and then increases after one year and stabilizes, possibly with exception for the 0.8 water/cement ratio. These results are difficult to explain, but a similar tendency can be seen in Figure 21 [10]. For concretes without addition, and for water/binder ratios of 0.4 and 0.7, Figure 21 shows how the chloride diffusivity decreases with early age and, after a certain age, increases slightly, and then stabilises.

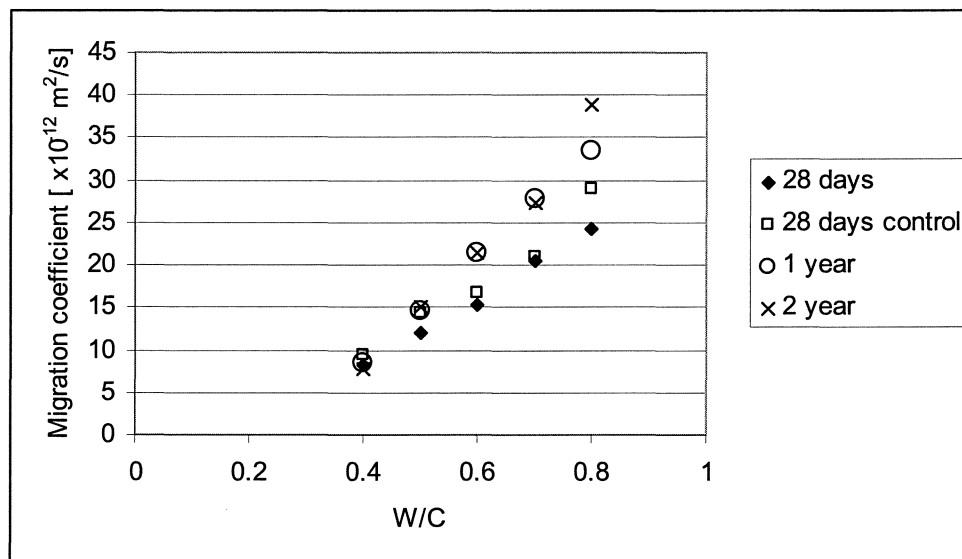


Figure 20 – Chloride migration coefficient at different ages as a function of water/cement ratio.

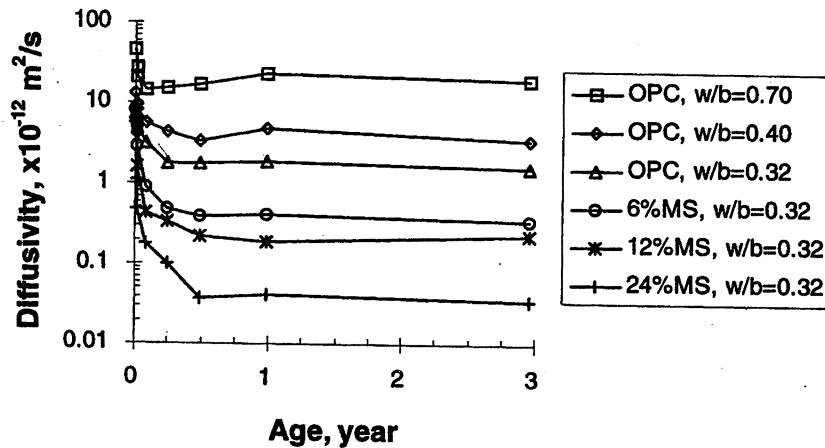


Figure 21 – Diffusivity versus age [10].

Therefore the reason for the negative k-values seems to be due to the very low migration coefficients of the OPC mortars at 28 days. After one year the mortars with limestone filler replacement had k-values of around 0 (see appendix 3), which is much more expected.

#### 4.4 Paper III: Replacement of Cement by Limestone Filler or Ground Granulate Blast Furnace Slag: the Effect on Strength and Chloride Diffusion in Cement Mortars. Laboratory and Field Studies.

This paper describes a first trial to investigate how well the k-values from the accelerated laboratory test correlate with results obtained in field exposure, as far as chloride penetration is concerned. Another important reason for this investigation is to acquire experience and to work out a procedure for the more extensive field exposure investigation, which is to follow in the near future.

Figures 22a and 22b show results (for one-year-old mortars) for chloride migration (laboratory testing) and chloride diffusion (field testing).

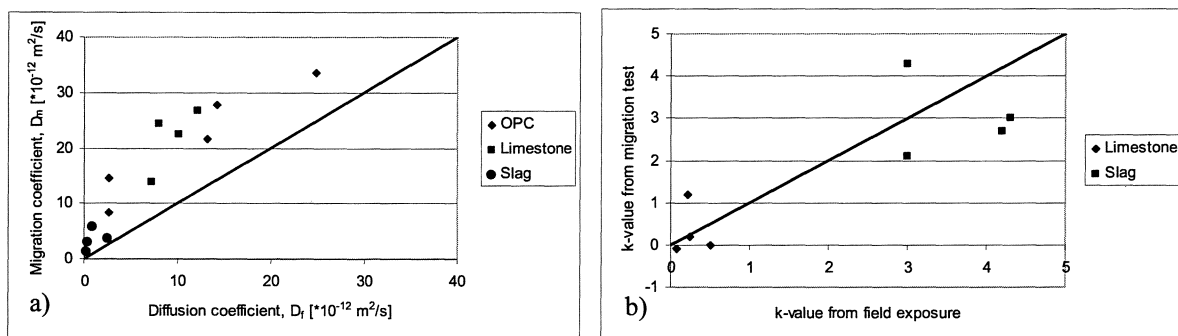


Figure 22 – a) The migration coefficient versus the diffusion coefficient. b) k-values from migration testing versus k-values from diffusion testing.

The comparison in Figure 22a between the migration coefficient (laboratory testing) and diffusion coefficient (field testing) reveal that the first one is higher for all mortars tested. Figure 22b shows a tendency for the k-values obtained from field testing to be higher than from laboratory testing, except in two cases. It is too early to draw any conclusions about the correlation between the results from the accelerated laboratory test and those obtained from

field exposure. One reason may be that the chloride diffusion coefficients in the field test are gained from a single chloride profile, and additional work is required for statistically verifying the results. The other reason may be that one year seems to be short time for gaining results from field exposure, especially when concerning dense mortars.

The paper also presents some general results found when comparing tests performed at 28 days with those performed at one year.

As far as compressive strength development is concerned, mortars with slag replacement had a more pronounced improvement than mortars with limestone replacement. For chloride migration, for all mortars with slag replacement, the chloride migration coefficient had decreased after one year, while for the mortars with limestone replacement the chloride migration coefficient was about the same for 28 days and one year.

One unexpected outcome from this investigation was the increase of the migration coefficient for the mortar with only Ordinary Portland Cement, when comparing the results from 28 days with the results from one year. This strange outcome will be investigated in more detail further on.

As far as the results from the field exposure are concerned, the same trends as for the migration test could be discerned, despite the uncertainties: for example, the increase of the apparent diffusion coefficient with increased water/cement ratio for OPC mortars, the influence of the amount of limestone replacement rate on the apparent diffusion coefficient, and also for slag mortars in the field tests showing the best resistance against chloride ion penetration.



## **5 FUTURE INVESTIGATIONS**

The first part of the project, presented in this report, has concentrated on determination of material parameters/ $k$ -values for compressive strength and chloride penetration when cement is replaced by mineral additions.

The second part of the project will collect and statistically verify more material parameters in connection with the above properties, and also for other properties concerning reinforcement corrosion, such as threshold values of chlorides for initiation of corrosion and for propagation of carbonation.

Looking further ahead, it is the intention to investigate combined mechanisms, such as testing the chloride penetration on carbonated specimens.

As with the first part of the work, the second part will also involve both laboratory tests and corresponding field tests. It will also include studies of mechanisms governing the influence of mineral additions on some of the above-mentioned properties.

Questions arising from the present studies, such as the strange development of the migration coefficient for Ordinary Portland Cement mortars will be looked at.





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## **PAPER I**

**Title:** *Long-Term Performance of Concrete Incorporating Ground Granulated Blast Furnace Slag.*

**Author:** Boubitsas, D.

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# Long-Term Performance of Concrete Incorporating Ground Granulated Blast Furnace Slag

by D. Boubitsas

## Synopsis:

The aim of this paper is to introduce a method for determining the coefficient of efficiency, the k-value, with respect to chloride migration in concrete. Some results for ground granulated blast furnace slag are presented and compared with traditional k-values for compressive strength. Finally, some recommendations on how to use the k-values and how to improve standards and regulations are given.

Standards normally give a single k-value for each type of addition, regardless of what environment the concrete will be exposed to. The results in the investigation, however, clearly indicate that this is too great a simplification. For chloride migration, for example, the k-value is three times higher for slag than is the corresponding k-value for compressive strength.

For a reliable service life prediction of concrete structures produced with concrete containing additions, it is, therefore, necessary to find relevant k-values for different types of degradation mechanisms. The most important mechanisms are corrosion induced by carbonation, by chlorides from the sea or by other chlorides, freeze/thaw attack with or without chlorides and perhaps also chemical attack.

**Keywords:** chloride migration; compressive strength; concrete; durability; granulated blast furnace slag; k-value



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## INTRODUCTION

Concrete is a green construction material for building a sustainable society. Concrete for harbours, railways, tunnels, etc. leads to efficient and environmentally friendly transport. Concrete for hydro power stations is the basis for the production of renewable energy. Wastewater treatment plants can hardly be built without using concrete, and so on. The list of examples is very long.

However, the production and use of concrete also has an environmental impact, as have all other building materials. For concrete the impact is mainly contributed by:

- Energy consumption in connection with cement production, and transportation of raw materials, ready-mixed concrete, and concrete products.
- In connection with cement production, emission of substances harmful to health and the environment.
- Consumption of finite natural resources, such as natural sand, gravel, and crushed rock.

Many of the environmental problems have been or can be solved by using alternative fuels for cement kilns, more efficient transports, modern production processes, effective cleaning of flue gases, etc. One major problem, however, is the carbon dioxide emission during cement clinker production. The manufacture of normal portland cement contributes to some five to seven percent of the total manmade carbon dioxide emissions. The production of carbon dioxide is a part of the process and there are no realistic methods to remove the carbon dioxide from the flue gases. The only way of reducing the carbon dioxide emissions is to replace parts of the portland cement clinker in cement with alternative cementing materials, such as fly ash, silica fume, and granulated blast furnace slag.

In many countries alternative materials have been used for long time for replacement of Portland cement. In other regions, such as Sweden and most of the Nordic countries, normal portland cement has been the only or at least the completely dominant binder in concrete. Consequently the knowledge of the properties of alternative binders and of how to use them is limited in these regions. This is not least relevant where long-term properties and durability in the cold and harsh Nordic climate is concerned.

In order to increase the knowledge of and the use of alternative binders, three research projects were started in Sweden in 2001 (1, 2, 3). One of these deals with long-term properties and durability of concrete with mineral additions, and results from the project are presented in this paper. The results

mainly concern chloride permeability for concrete containing ground blast-furnace slag, but some data on compressive strength are presented as well.

The aim of this paper is to introduce a method for determining the coefficient of efficiency, the k-value, where chloride migration is concerned. Some results for ground granulated blast-furnace slag are presented and compared with traditional k-values for compressive strength. Finally, some recommendations on how to use the k-values and how to improve standards and regulations are given.

### **THE COEFFICIENT OF EFFICIENCY FOR MINERAL ADDITIONS**

The coefficient of efficiency, the k-value, for mineral additions defines how many parts by weight of normal portland cement can be replaced by one part of a specified mineral addition without changing the concrete properties.

In many cases W/C is assumed to be the dominant factor defining the concrete properties; for example where strength and permeability are concerned. When additions are used in concrete, the equivalent water/cement ratio  $(W/C)_{eq}$  is used instead of W/C. The equivalent water-cement ratio can be calculated by using the k-value:

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

- W = water content by weight ( $\text{kg/m}^3$ )
- C = cement content by weight ( $\text{kg/m}^3$ )
- R = content of addition by weight ( $\text{kg/m}^3$ )
- k = k-value

The k-value can thus be calculated as:

$$k = (W/(W/C)_{eq} - C)/R \quad (\text{Eq 1b})$$

Take the following steps to calculate the value of k for a given addition:

1. Determine the relationship between the property to be studied (strength, permeability, frost resistance, etc.) and W/C for the cement used, see Fig. 1.
2. Determine the value of the property to be studied for a given concrete mixture containing the addition to be investigated.
3. By using Fig. 1 and the result from step 2,  $(W/C)_{eq}$  can be determined.
4. By using the known values of C, R and W and the value of  $(W/C)_{eq}$  determined in step 3, the k-value can be calculated using Equation 1b.

Values of  $k$  are given in regulations and standards. European Standard EN 206-1 (4) gives  $k$ -values for type II additions, i.e. reactive additions. The values are 0.2-0.4 for fly ash and 1.0-2.0 for silica fume. No values are given for slag but Swedish Standard SS 13 70 03 (5) gives, for example, a  $k$ -value of 0.6 for ground blast furnace slag. Standards relevant in other regions or countries give other values, see for example (6).

The  $k$ -values are used for calculating  $(W/C)_{eq}$  which in turn is used, among other things, for predicting the long term performance of concrete structures where strength, frost resistance, reinforcement corrosion and other durability properties are concerned. The problem is that almost all  $k$ -values presented in regulations and standards are based on results from strength testing of 28 days old concrete. These values are therefore not relevant for predicting the long-term properties and durability of concrete structures. More representative values can only be obtained from results derived from long-term or durability testing. This paper presents such results for chloride permeability/chloride migration and compares them with  $k$ -values obtained from traditional compressive strength testing.

## TEST METHODS

### Consistence and Air Content

The consistency was measured for each batch according to European Standard test method EN 1015-3 (10). The principle is that a flow value is measured in terms of the mean diameter of a test sample of the fresh mortar. This has been placed on a defined flow table disc by means of a defined conical mould, and given a number of vertical impacts by raising the flow table and allowing it to fall freely through a given height. The aim was to reach about the same consistency for all the mixtures. The air content, which varies between 5.3 and 8.1%, was measured by using an air meter with a volume of 1 litre in accordance with Swedish Standard SS 13 71 24 (11).

### Compressive Strength Testing

In principle, strength testing was carried out in accordance with European Standard test method EN 196-1 (7), but with other mortar compositions than as stated in the standard. The mortars for the strength testing were produced in small batches, about 2 litres per batch, and the mortars for the migration testing in larger batches, about 50 litres per batch. The method specifies that prismatic mortar specimens, of size 40 mm x 40 mm x 160 mm, are to be used. The mortar is prepared by mechanical mixing and is compacted in a mould using a vibrating table for compacting. Each mould contains three specimens. During the first 24 hours the specimens are stored in the mould tightly covered with a lid to prevent evaporation. After the specimens are demoulded they are stored

under lime-saturated water at a temperature of  $+20 \pm 2$  °C. At the required age, here 28 days, the specimens are taken from their wet storage, broken in flexure into two halves and each half is tested for compressive strength. In the experiments described in this paper, three prisms, i.e. six specimens, were used for determining the compressive strength for each mortar quality.

### **Chloride Migration Testing**

The migration coefficient is used in this paper for defining the chloride permeability properties. Migration is defined as the movement of ions under the action of an external electrical field while diffusion is defined as the movement of ions under a concentration gradient. Normally the value of the migration coefficient determined using this method is very comparable with the diffusion coefficient. A detailed investigation of the relationship between migration and diffusion is presented in (8).

Chloride migration testing was performed in accordance with Nordtest method NT BUILD 492 (9). An external electrical potential is applied axially across the specimen and forces the chloride ions on the outside to migrate into the specimen, see Fig. 2. After a certain test duration, specified in the standard, the specimen is axially split and a silver nitrate solution is sprayed on to one of the freshly split sections. The chloride penetration depth can then be measured from the visible white silver chloride precipitation, after which the chloride migration coefficient can be calculated from this penetration depth as specified in the standard.

450 mm long cylinders with a diameter of 100 mm were cast in steel moulds. After demoulding the cylinders were stored under water until the time for testing at 28 days. Immediately before testing, 50 mm thick specimens were sawn from the cylinders, excluding 50 mm at each end of the cylinders.

After sawing any burrs were brushed and washed away from the surfaces of the specimens and excess water was wiped off. When the specimens were surface-dry they were placed in a vacuum container for vacuum treatment. The vacuum (1-5 kPa) was maintained for three hours and then, with the vacuum pump still running, the container was filled with saturated  $\text{Ca}(\text{OH})_2$  solution so that all specimens were immersed. The vacuum was maintained for another hour before allowing air to re-enter the container. The specimens were then kept in the solution for  $18 \pm 2$  hours, after which the testing started.

## **MATERIALS**

The ground granulated blast-furnace slag (GBFS) used in the tests is a commercially available Swedish product called Merit-5000. The chemical composition is shown in Table 1 and the particle size distribution in Fig. 3. The specific surface area is  $470 \text{ m}^2/\text{kg}$  and the compacted density is  $2900 \text{ kg/m}^3$ . All the information is taken from the product data sheet for the product. The

cement used was a commercially available rapid-hardening normal portland cement with a chemical composition shown in Table 2, and having a specific surface area of  $550 \text{ m}^2/\text{kg}$ . The aggregate used was a CEN standard sand according to (7), i.e. a siliceous sand consisting of rounded particles. The largest particle size is 2.0 mm. Tap water was used for all the mixtures. No admixtures were used.

The compositions of all the mixtures are presented in table 3. As can be seen, the consistency is almost the same for all the mixtures, between 169 and 195 mm with a slight tendency to increase when cement is replaced by slag.

The cement content for some mixtures is high. For the mortar with a W/C of 0.40, for example, the cement content is  $702 \text{ kg/m}^3$ . The reason for this is the fine graded aggregate and the fact that no plasticizer was used.

## TEST RESULTS

### Compressive Strength

The results from the compression strength tests are shown in Table 4. Each mean value is calculated by using the results for six individual specimens.

The results for the mortars with normal portland cement as the only binder are plotted against  $1/(W/C)$  in Fig. 4. There is a linear relationship, with good correlation, between compressive strength and  $1/(W/C)$ , i.e. Bolomey's formula (12) is relevant for the type of cement used. This relationship is used in this investigation for determining the k-values for the mortars containing additions.

The k-values for compressive strength at 28 days vary between 0.67 and 1.07, i.e.  $0.87 \pm 0.20$  for the slag used in the tests. There is a tendency for the k-value to be higher for mortar containing 35% slag than for higher or lower slag content, see Fig. 5. However, this tendency can not be considered as being significant due to the scatter in the test results. Nor it is possible, from the results in this investigation, to conclude that the k-value for mortar containing blast furnace slag depends on the W/C.

### Chloride Migration

The results from the chloride migration tests are shown in Table 5. Each mean value is calculated from the results for three specimens.

The results for the mortars with normal portland cement as the only binder are plotted against W/C in Fig. 6. There is a linear relationship, with good correlation, between the migration coefficient and W/C, i.e. the migration coefficient seems to be proportional to W/C for the type of cement used in this investigation. This relationship is used in this investigation for determining the k-values representing migration for the mortars containing slag.

From the results found in this investigation, the 28 days k-value for the ground blast-furnace slag used is 2.10-2.34, as far as chloride migration is concerned. The value seems to be more or less independent of both the slag content, see Fig. 7, and the water-binder ratio.

## DISCUSSION

Values of k are given in European Standard EN 206-1 for fly ash and silica fume but not for granulated blast furnace slag. A recommended k-value of 0.6 for slag, however, is given in the SS 13 70 03, which is the Swedish application document for EN 206-1. This recommended k-value is in good agreement with the value for slag representing the 28 days compressive strength found in this investigation, which is 0.67-1.07. The k-value in the Swedish standard seems to be on the safe side, as it should be in a standard.

EN 206-1 classifies the environment by using 17 different exposure classes representing different types of degradation mechanisms, such as reinforcement corrosion initiated by carbonation, by chlorides from the sea or by other chlorides, by freeze/thaw attack or by chemical attack. W/C is the most important factor when choosing concrete for the different types of exposure environments. When additions are used W/C is replaced with  $(W/C)_{eq}$  which in turn is strongly dependent on the k-value.

EN 206-1 and SS 13 70 03 give a single k-value, or sometimes two alternative values, for each type of addition for all exposure classes. The results in this investigation, however, clearly indicate that this is too great a simplification. For chloride migration, for example, the k-value is three times higher for slag than the corresponding k-value for compressive strength. The most probable explanation for the high k-value is the high chloride binding capacity of slag (13). By choosing the k-value as given in existing standards, the effectiveness of slag in preventing chloride diffusion will be greatly underestimated. In other cases, for example where scaling resistance is concerned, slag contributes adversely to durability (14). This means that the k-value is lower than for compressive strength and it can even be negative.

The chloride migration coefficient is one of several parameters influencing the risk of corrosion attack. Other important parameters are the chloride threshold value and the corrosion rate. A useful k-value for predicting the ability of an addition to prevent corrosion attack should reflect all these parameters. More research is necessary in order to make it possible to determine such relevant k-values.

For a reliable service life prediction of concrete structures produced by concrete containing additions it is necessary to find relevant k-values for different types of degradation mechanisms. The most important ones are those mentioned above, i.e. corrosion induced by carbonation, by chlorides from the sea or by other chlorides, by frost with or without chlorides and perhaps also by chemical attack. Such values should be included in standards and

regulations in order to improve the ability to design for durability, also for concrete containing additions.

### **CONCLUSION**

The following conclusions can be drawn from the results obtained in this investigation:

- The k-value obtained for 28 days compressive strength for the granulated blast furnace slag used in this investigation is about 0.7-1.1. This is in good agreement with values normally used in standards and regulations.
- The 28 days k-value for the migration coefficient was about 2.1-2.3, which is about three times higher than for k-values for compressive strength.
- For a reliable service life prediction of concrete structures produced with concrete containing mineral additions, it is necessary to find relevant k-values for different types of degradation mechanisms. The most important mechanisms are corrosion induced by carbonation, by chloride ingress from seawater or by other sources, cycles of freezing and thawing with or without chloride ingress, and chemical attacks.

### **ACKNOWLEDGEMENT**

This paper describes some results from a five-year investigation of the long-term properties/durability of concrete containing additions. The project is financially supported by The Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS) and Cementa Ltd.

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Table 1 - Chemical composition of the granulated blast-furnace slag used in the tests, percent by mass. Loss on ignition = 1.3%

<b>SiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>CaO</b>	<b>MgO</b>	<b>Na<sub>2</sub>O</b>
34.0	13.1	0.2	31.0	17.0	0.54

<b>K<sub>2</sub>O</b>	<b>V<sub>2</sub>O<sub>5</sub></b>	<b>TiO<sub>2</sub></b>	<b>S</b>	<b>MnO</b>	<b>Cl</b>
0.52	0.11	2.3	1.41	0.7	0.01

Table 2 - Chemical composition of the cement used in the tests, percent by mass. Loss on ignition 1.2%

<b>SiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>CaO</b>	<b>MgO</b>	<b>Na<sub>2</sub>O</b>
20.9	3.8	2.7	64.1	2.8	0.3

<b>K<sub>2</sub>O</b>	<b>V<sub>2</sub>O<sub>5</sub></b>	<b>TiO<sub>2</sub></b>	<b>SO<sub>3</sub></b>	<b>MnO</b>	<b>Cl</b>
1.1	-	-	3.4	-	0.04

Table 3 - Composition of the mortars used in the test

	<b>Cement (kg/m<sup>3</sup>)</b>	<b>GBFS (kg/m<sup>3</sup>)</b>	<b>Water (kg/m<sup>3</sup>)</b>	<b>Aggregate (kg/m<sup>3</sup>)</b>	<b>(W/B)</b>	<b>Air (%)</b>	<b>Consistence (mm)</b>
<b>C-40</b>	702		281	1263	0.4		169
<b>C-50</b>	500		250	1500	0.5	4.9	170
<b>C-60</b>	413		248	1593	0.6		176
<b>C-70</b>	345		242	1666	0.7	7.5	168
<b>C-80</b>	319		255	1654	0.8		172
<b>BFS20-50</b>	400	100	250	1500	0.5	5.3	185
<b>BFS35-50</b>	325	175	250	1500	0.5	6.0	184
<b>BFS35-70</b>	224	121	242	1666	0.7	8.1	170
<b>BFS65-50</b>	175	325	250	1500	0.5	5.3	195

Table 4 - Results from the compressive tests. The mean values are obtained from tests on six specimens. The variation of k shows the highest and lowest individual k-value respectively

Mixture	Water/binder	GBFS % by weight	Compressive strength, $f_c$ MPa	$f_c$ variation MPa	k mean	k variation
C-40	0.40		82.4	80-86		
C-50	0.50		66.7	64-69		
C-60	0.60		48.5	47-50		
C-70	0.70		42.2	40-44		
C-80	0.80		33.2	31-34		
BFS20-50	0.50	20	56.0		0.68	0.5-0.8
BFS35-50	0.50	35	65.9		1.07	0.9-1.1
BFS65-50	0.50	65	57.9		0.87	0.8-0.9
BFS35-70	0.70	35	36.6		0.67	0.5-0.8

Table 5 - Results from the chloride migration tests. The mean values are obtained from tests on three specimens. The variation of k shows the highest and lowest individual k-value respectively

Mixture	Water/binder	GBFS % by weight	Migration coeff., $D_n$ $m^2/s \times 10^{-12}$	$D_n$ variation $m^2/s \times 10^{-12}$	k mean	k variation
C-40	0.40		8.28	8.1-9.0		
C-50	0.50		11.95	11.9-12.0		
C-60	0.60		15.42	14.5-16.2		
C-70	0.70		20.36	20.0-20.7		
C-80	0.80		24.14	23.6-24.9		
BFS20-50	0.50	20	8.49	7.4-9.0	2.10	1.9-2.5
BFS35-50	0.50	35	5.61	5.2-6.0	2.34	2.2-2.5
BFS65-50	0.50	65	2.69	2.2-3.5	2.33	2.1-2.5
BFS35-70	0.70	35	11.48	10.6-12.5	2.26	2.1-2.5

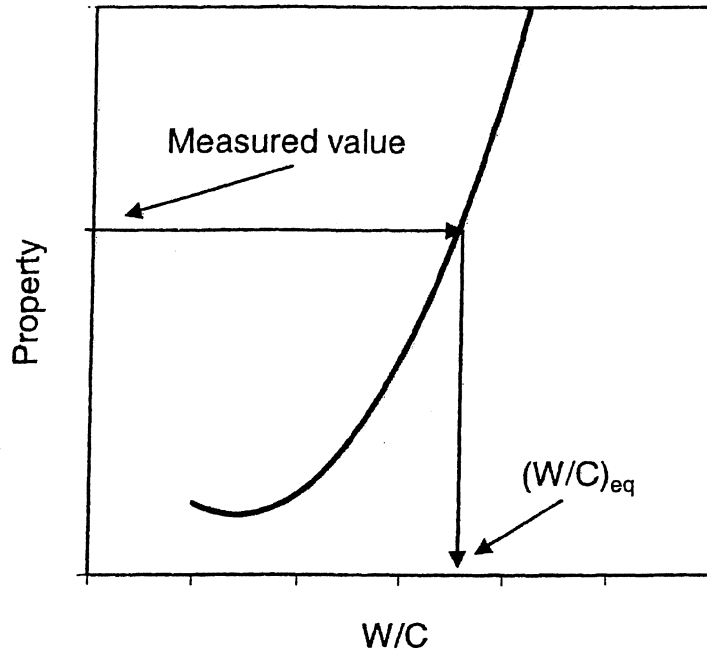


Fig. 1. The relation between w/c and a defined property (strength, migration coefficient, etc.) for normal portland cement. This relation is used for determining the value of  $(W/C)_{eq}$  for concrete and mortar containing mineral additions.

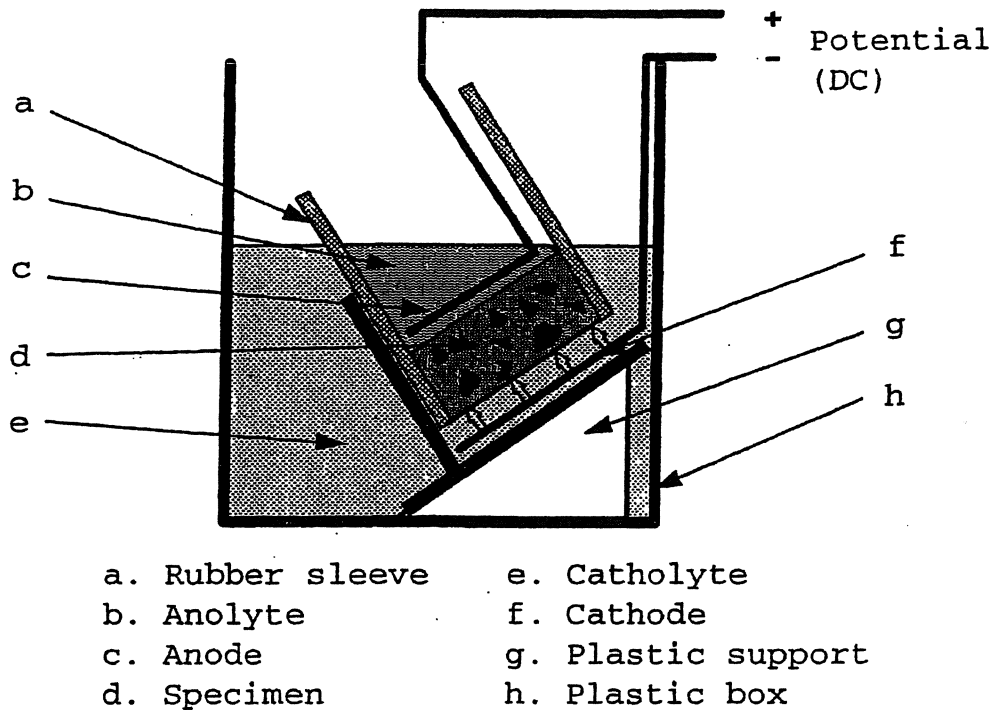


Fig. 2. Test set-up for measuring the chloride migration coefficient (9).

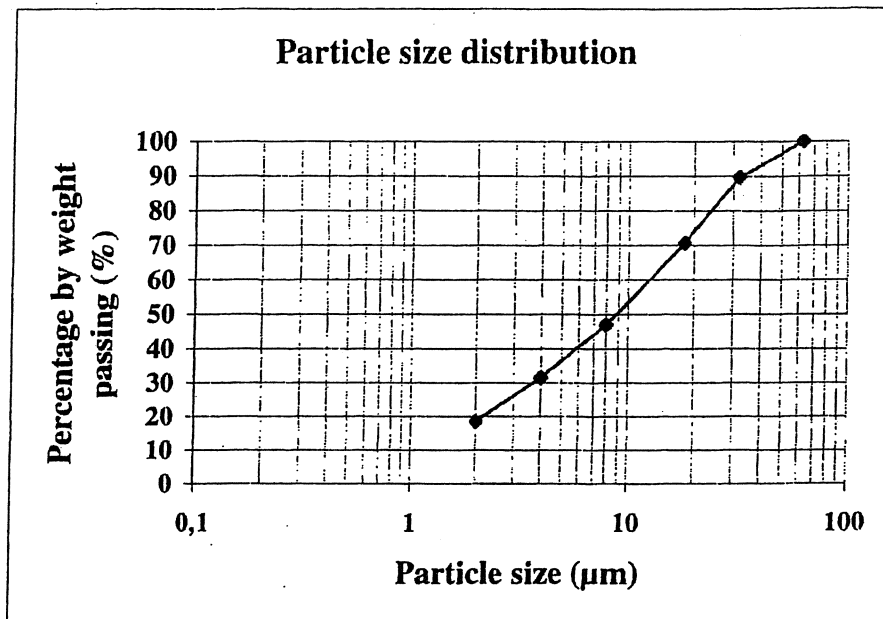


Fig. 3. Particle size distribution for the ground blast-furnace slag used in the tests.

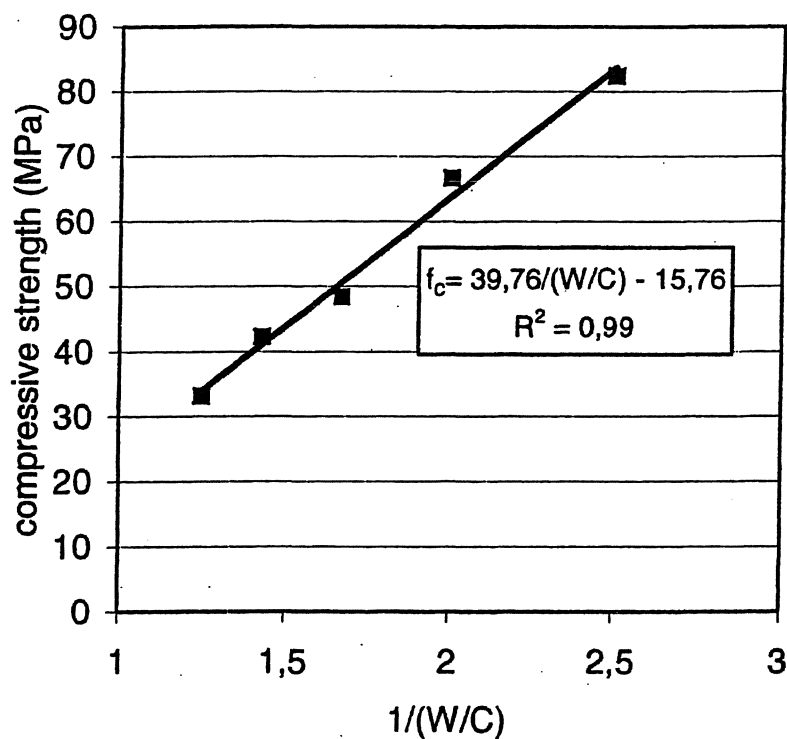


Fig. 4. Compressive strength,  $f_c$ , as function of  $1/(W/C)$  for mortar with normal portland cement as binder.

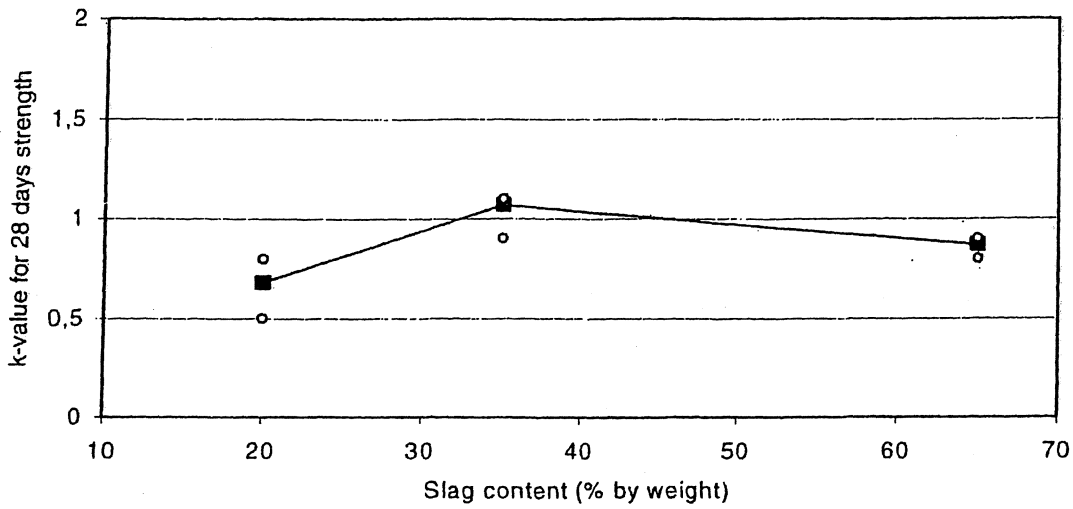


Fig. 5. The k-value for 28 days compressive strength as function of slag content. The results are relevant for a water/binder ratio of 0.5 and for the used slag quality. The black squares represent the mean values for six specimens and the circles the highest and lowest individual value respectively.

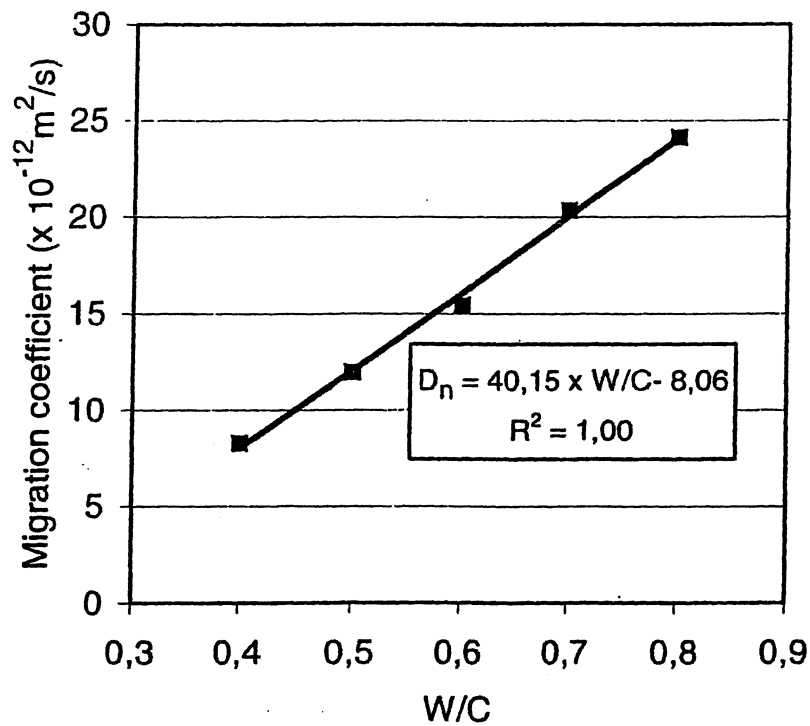


Fig. 6. The migration coefficient,  $D_n$ , as function of W/C for mortar with normal portland cement as binder.

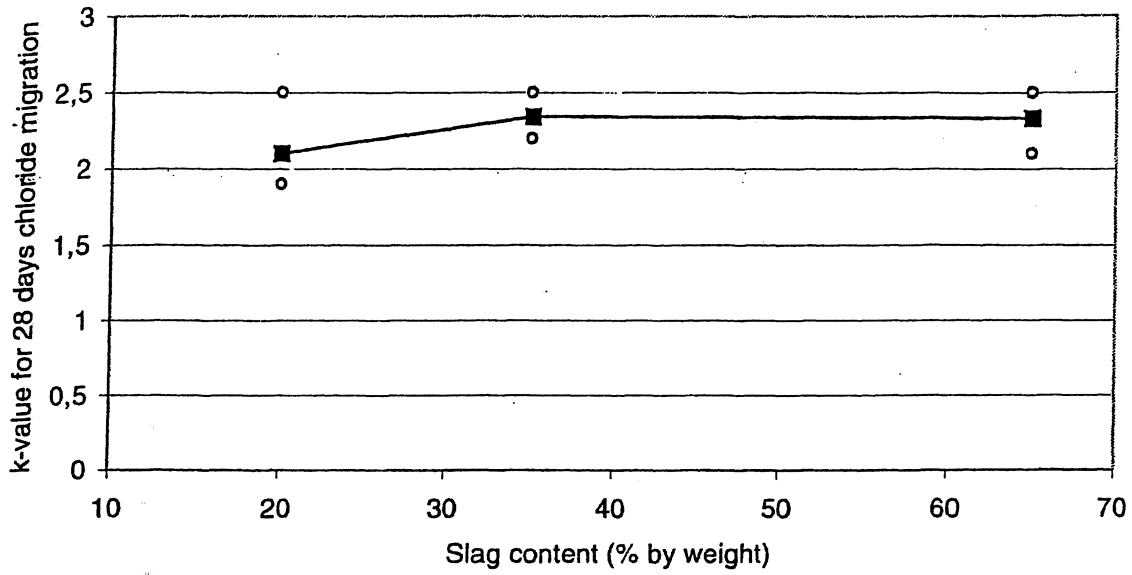


Fig. 7. The k-value for 28 days chloride migration as function of slag content. The results are relevant for a water/binder ratio of 0.5 and for the used slag quality. The black squares represent the mean values for three specimens and the circles the highest and lowest individual value respectively.



## **PAPER II**

**Title:** *Replacement of Cement by Limestone Filler: The Effect on Strength and Chloride Migration in Cement Mortars.*

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# Replacement of Cement by Limestone Filler: The Effect on Strength and Chloride Migration in Cement Mortars.



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## ABSTRACT

This paper describes studies carried out to examine the effect on 28-day strength and chloride migration of cement mortar when a certain amount of the cement is replaced as binder by limestone filler. Fillers produced from three different calcareous carbonates were used, and three different mean particle sizes of the same type of filler were included in the study. The amount of replacement of cement with filler varied between 12 and 24 weightpct. of the total binder, and mortars with different water/binder-ratios were used.

**Key words:** chloride migration, efficiency, k-value, limestone filler, strength.

## 1. INTRODUCTION

Use of limestone filler in combination with Portland cement is common practice in many European countries, in the interest of technical, economical and ecological benefits.

The substitution of parts of the cement by limestone filler have shown to have several effects on the properties of paste, mortar and concrete. In studies of pure compounds of clinker, various authors have reported that the  $C_3S$  hydration rate is accelerated when the amount and fineness of  $CaCO_3$  is increased [1]. Although limestone filler has no pozzolanic properties, several studies indicate that even non-hydraulic fillers enhance the hydration of the major cement phases at early ages [2, 3]. This is due to the fact that they generate a large number of nucleation sites for precipitation of the hydration products [1]. Calcium carbonate may also react with  $C_3A$  to form calcium carboaluminates [4].

The enhanced degree of hydration at an early age has also been reflected by the early age strength. It has been shown that the use of limestone filler as a replacement for cement may improve the strength of both mortars and concretes at early ages (3 and 7 days), but this improvement seems to be less pronounced or has completely disappeared at a later age (28 days) [5, 6].

Most of the research investigations have emphasised on the effect of limestone filler on the hydration reaction and strength development. There are, however, very few references describing the durability effects of limestone addition.

One of the major durability problems of concrete structures is the diffusion of chloride ions through the normal thicknesses of concrete cover causing corrosion of the reinforcing bars. The measuring technique used by most workers to study chloride penetration is the steady-state cell diffusion test, and the samples used are often thin specimens of paste. It is well known that penetration of chlorides is strongly affected by their chemical and physical interaction with the C-S-H phases in the hydrated cement paste. In a steady-state test, most of the interactions will be completed, and their effect on chloride transport will be reduced. During an unsteady-state experiment, these interactions take place and slow down the ion penetration.

In cell diffusion tests of thin mortar specimens, in which cement had been replaced by limestone filler but in which the W/C-ratio had been kept constant (i.e. a reduction of the bulk water), the chloride diffusion coefficient was found to be lower for blended mortars [7]. Cochet et. al. [8] found, also with cell diffusion tests, that the diffusion of chloride ions in mortars with blended cement was equivalent to that of mortars with Portland cement without mineral additions, provided that the cements considered are in the same strength grade.

In pounding tests, where the specimens were immersed in artificial sea water, Moukwa [9] has shown that the addition of limestone filler led to a much higher chloride penetration than in the reference mortar with only OPC.

The objective of the study described in this paper is to determine the coefficient of efficiency (k-value) for mortars with limestone filler addition, based on strength and chloride penetration. The coefficient of efficiency for mineral additions defines how many parts by weight of normal Portland cement that can be replaced by one part of a specified mineral addition without changing the concrete properties. Normally, the k-value is used only for EN 206-1 Type II additions [10], i.e. reactive additions such as most fly ashes, silica fume and vitrified blast furnace slags. In this paper, however, the k-value concept is used also for limestone filler in order to be able quantitatively to compare the efficiency of different types of qualities of limestone.

In most cases, the W/C-ratio is assumed to be the dominant factor defining the concrete properties; for example, when strength and permeability are concerned. When additions are used in concrete, the equivalent water/cement-ratio  $(W/C)_{eq}$  is used instead of W/C. The equivalent water/cement-ratio is calculated by using the equation:

$$(W/C)_{eq} = W/(C+kR) \quad (1a)$$

where:

W = water content by weight ( $\text{kg/m}^3$ )

C = cement content ( $\text{kg/m}^3$ )

R = content of addition ( $\text{kg/m}^3$ )

k = k-value.

The k-value is used for calculating  $(W/C)_{eq}$  which in turn is used, among other things, for predicting the long-term performance of concrete structures in respect of strength, frost resistance, reinforcement corrosion and other durability properties. A problem is that almost all k-values given in regulations and standards are based on results from strength testing of 28-day-old concrete. These values are, therefore, probably not relevant for predicting the long-term performance and durability of concrete structures. More representative values can be obtained only from results derived from durability testing. This article presents such results for chloride

permeability (chloride migration), and compares them with k-values obtained from traditional compressive strength testing.

The project described in this paper is part of a larger program investigating the efficiency of fillers in concrete. Another part of the program deals with the influence of type I additions on early strength development under winter conditions. Results from that part of the program has previously been published in Nordic Concrete Research [11].

## **2. MATERIALS AND METHODS**

### **2.1 Materials**

The physical and chemical properties of the materials used throughout the experimental program, as given by the producers, are shown in Tables 1 and 2. The aggregate used was CEN standard sand in accordance with EN 196-1 [12], and the cement was a CEM I 52.5 R product conforming to ENV 197-1 [13].

The natural calcium carbonate types used as fillers in this investigation can be divided into chalk, limestone and marble. Chalk originates from the shells of fossil protozoans. It comes from the most recent geological deposits formed in the Cretaceous era, and has very fine crystals. Limestone is also of biogenic origin, but more compact than chalk. Its constituents are seashells and coral, which have been subjected to pressure and were formed in the Carboniferous era. The size of the crystals ranges between that of chalk and marble. Marble is formed when chalk or limestone recrystallise under high heat and pressure and form coarse crystals.

Fillers produced from three different qualities of natural calcium carbonate (CH, LL and MA) were used in this study, see Table 2. Type LL is a calcium carbonate powder manufactured from a high-purity white limestone from France, which were supplied in three different particle sizes (LL, LLF and LLC). Type MA is a white marble powder with high purity from Austria, while type CH filler is a Danish calcium carbonate powder from a more recent origin than the two others, and can be defined as a fine microcrystalline sedimentary chalk. The calcium carbonate content of all three limestone qualities was  $\geq 98\%$  by mass.

All materials were received in single bulk deliveries and stored in airtight containers to prevent deterioration with time.

*Table 1 - Properties of the cement*

Chemical composition	(%)	Mineralogical composition	(%)
CaO	64.1	C <sub>3</sub> S	62.8
SiO <sub>2</sub>	20.9	C <sub>2</sub> S	12.4
Al <sub>2</sub> O <sub>3</sub>	3.8	C <sub>3</sub> A	5.5
Fe <sub>2</sub> O <sub>3</sub>	2.7	C <sub>4</sub> AF	8.3
SO <sub>3</sub>	3.4		
MgO	2.8		
K <sub>2</sub> O	1.1		
Na <sub>2</sub> O	0.3		
Cl	0.02		

*Table 2 - Physical characteristics of the cement and limestone fillers used*

Material	Designation	Mean particle size (µm)	Specific Surface, BET (m <sup>2</sup> /kg)
Cement	CEM	8	1760
Limestone (fine)	LLF	0,44	15000
Chalk	CH	2,3	2200
Limestone (medium)	LL	5,5	1000
Marble	MA	7,0	1500
Limestone (coarse)	LLC	22,0	700

Blaine fineness of the cement: 550 m<sup>2</sup>/kg

## 2.2 Test program

Five different mortar mixtures were cast with Cement I 52.5 R as the only binder and a range of water/binder-ratios between 0.4 and 0.8. Another seven different mortar mixtures were cast where a part of the Cement was replaced with limestone filler (binder = cement + limestone). The mixture compositions are shown in Table 3.

The aim was to reach about the same consistency for all the mixtures, which was accomplished by keeping the water content fairly constant and altering the cement content. The consistency was measured in accordance with European Standard test method EN 1015-3 [14]. The mortars were produced in accordance with European standard EN 196-1 [12], with some modifications (see Table 3). The first modification was that, in some cases, the water/cement-ratio differed from EN 196-1, which specifies a constant 0.5 ratio. The second modification was that the mortar batches were much larger than in EN 196-1. The third modification was that, in those cases where the water/binder ratio was not 0.5, the proportions by mass in the mix differed from those given in the standard (one part of cement, three parts of standard sand and one half part of water).

The air contents are relatively high, as a result of the fine-grained aggregate and the high paste volume. The air content was measured in accordance with Swedish Standard SS 13 71 24 [15]. However, the variation between the different mixtures was small, with the air contents varying from 4.8% to 6.0%. This indicates that variations of the air contents between the mixes do not influence the test results very much.

Table 3 – Mortar mix proportions used in the experimental study

Mortar	W/B	W/C	Cement (kg/m <sup>3</sup> )	Limestone filler (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	Aggregate (kg/m <sup>3</sup> )	Air (%)	Consistence (mm)
<i>Cement</i>								
OPC-0.4	0.40	0.40	702		281	1263		169
OPC-0.5	0.50	0.50	500		250	1500	4.9	170
OPC-0.6	0.60	0.60	413		248	1593		176
OPC-0.7	0.70	0.70	345		242	1666		168
OPC-0.8	0.80	0.80	319		255	1654		172
<i>Cement and limestone filler</i>								
LLF24-0.5	0.50	0.66	380	120	250	1500	4.8	135
CH24-0.5	0.50	0.66	380	120	250	1500	4.8	173
LL12-0.5	0.50	0.57	440	60	250	1500	5.0	175
LL24-0.5	0.50	0.66	380	120	250	1500	4.7	180
LL24-0.7	0.70	0.92	262	83	242	1666	5.4	164
MA24-0.5	0.50	0.66	380	120	250	1500	6.0	178
LLC24-0.5	0.50	0.66	380	120	250	1500	4.8	165

### 2.3 Determination of the k-value

The k-value for mineral additions can be calculated by using Equation (1a), which gives:

$$k = (W/(W/C)_{eq} - C)/R \quad (1b)$$

$(W/C)_{eq}$  can be calculated by using empirical relationships between the studied property (i.e. strength or chloride permeability) and W/C for OPC mixtures, and comparing this relationship with results obtained for mortars containing limestone filler: see Figure 1. By using the known values of C, R and W, and the value of  $(W/C)_{eq}$ , the k-value can be calculated using Equation (1b).

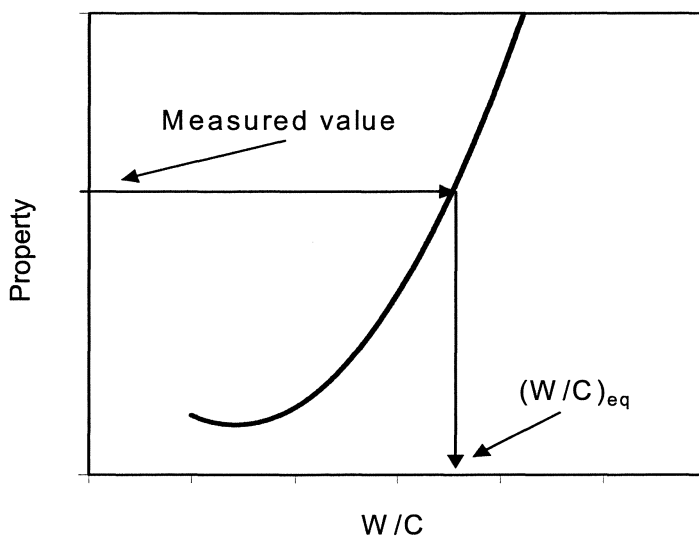


Figure 1- The relation between the w/c-ratio and a defined property (strength, migration coefficient, etc.) for Ordinary Portland Cement. This relation is used for determining the value of  $(W/C)_{eq}$  for concrete and mortar containing mineral additions.

## 2.4 Strength test

Prismatic mortar specimens (40 mm x 40 mm x 160 mm) were cast and water-cured for 28 days. By the end of this period, the flexural and compressive strengths were determined in accordance with European Standard EN 196-1.

## 2.5 Chloride permeability test

This paper uses the migration coefficient for defining the chloride permeability properties. Migration is the movement of ions under the influence of an external electrical field, while diffusion is the movement of ions as the result of a concentration gradient. Normally, the value of the migration coefficient determined using this method is very similar to the diffusion coefficient. A detailed investigation of the relationship between migration and diffusion is presented in [16]. Chloride migration testing was performed in accordance with Nordtest Method NT BUILD 492 [17], which is a non-steady-state method. An external electrical potential was applied axially across the specimen and forced the chloride ions on the outside to migrate into the specimen. After a certain test duration, specified in the standard, the specimen was axially split and a silver nitrate solution was sprayed on to one of the freshly split sections. The chloride penetration depth can then be measured from the visible white silver chloride precipitation, after which the chloride migration coefficient can be calculated from this penetration depth as specified in the standard.

450 mm long cylinders with a diameter of 100 mm, were cast in steel moulds. After demoulding, the cylinders were stored under water until the time for testing at 28 days. Immediately before testing, 50 mm thick specimens were sawn from the cylinders, cutting off 50 mm at each end of the cylinders.

After sawing, any burrs were brushed and washed away from the surfaces of the specimens and excess water was wiped off. When the specimens were surface-dry they were placed in a desiccator for vacuum treatment. The vacuum (1-5 kPa) was maintained for three hours and then, with the vacuum pump still running, the container was filled with saturated  $\text{Ca(OH)}_2$  solution until the specimens were immersed. The vacuum was maintained for another hour before air was allowed to re-enter the container. The specimens were then kept in the solution for  $18 \pm 2$  hours, after which testing started.

### 3. RESULTS

#### 3.1 Compressive strength

The results from the compressive strength tests are summarized in Table 4. Each value is the mean result of six specimens. The table also shows the mean values for the k-value, calculated as described in Section 2.3.

*Table 4 – Results from compression tests*

Binder	W/B	Replacement	Compressive strength, $f_c$	Standard deviation, $f_c$	k-value	Standard deviation, k
		% by weight	(MPa)	(MPa)		
Cement						
OPC-0.4	0.40		82.4	1.9		
OPC-0.5	0.50		66.7	1.7		
OPC-0.6	0.60		48.5	1.5		
OPC-0.7	0.70		42.2	1.5		
OPC-0.8	0.80		33.2	1.3		
Cement and limestone filler						
LLF24-0.5	0.50	24	51.9	1.1	0.38	0.06
CH24-05	0.50	24	49.8	1.1	0.26	0.06
LL12-0.5	0.50	12	62.3	0.8	0.85	0.08
LL24-0.5	0.50	24	48.6	1.0	0.20	0.05
LL24-0.7	0.70	24	31.1	1.3	0.40	0.1
MA24-0.5	0.50	24	47.3	1.4	0.14	0.07
LLC24-0.5	0.50	24	49.9	1.0	0.27	0.04

The results from the compressive strength tests are also shown in Figure 2 for the mortars with Portland Cement as binder. There is a linear relationship, with good correlation, between compressive strength and  $1/(W/C)$ , i.e. Bolomey's Formula [18]. This relationship is used in this investigation for determining the k-values for the mortars containing limestone filler.

Figure 3 shows the case where type LL limestone filler is used, and the only variation is the amount of replacement. It can be seen that the amount of replacement has a significant effect on the compressive strength. 12 % replacement gives a k-value of 0.85, while the corresponding value for 24 % replacement is 0.2. The same tendency was observed by Lundgren [11], although the effect was less pronounced. It seems, however, that there is a tendency for limestone filler content to have an effect; at least in the interval studied here. It should be observed that a limestone filler content of 24 % is very high. In practice, the content is normally below 20 %, and typical contents are 12-16 %.

However, most of the tests in this investigation have been performed with mortars containing 24 % limestone. This may have had a negative influence on the reported k-values, and one must be aware of this fact when the results are analysed.



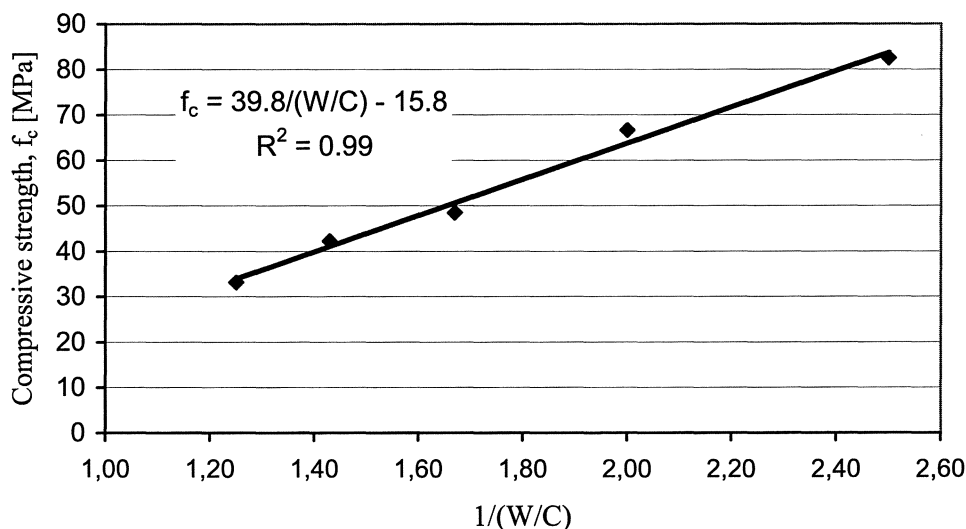


Figure 2 – The 28 days compressive strength,  $f_c$  as a function of  $1/(W/C)$  for mortar with Portland Cement as binder.

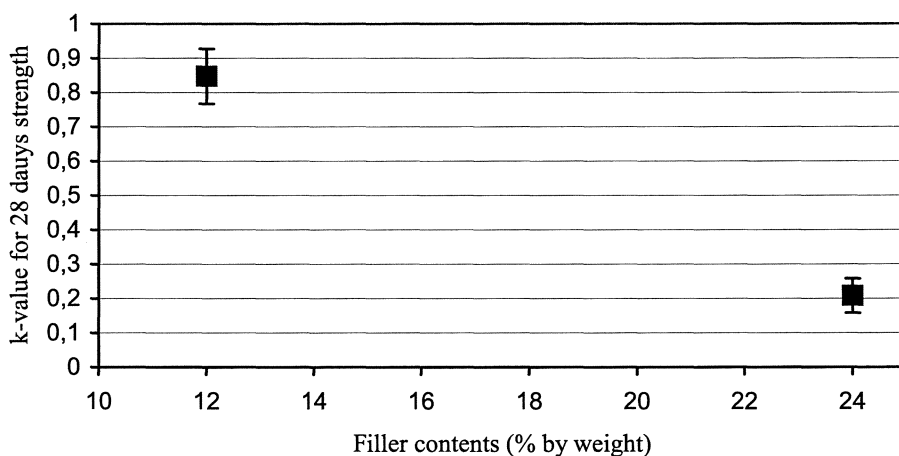


Figure 3 – The  $k$ -value for 28 days compressive strength versus the amount of cement substituted by limestone filler (% by weight of total binder). The results are relevant for mortars with  $W/B$ -ratios of 0.5, and for a filler quality of LL.

Figure 4 shows the compressive strength as a function of the mean particle size of type LL filler. The results do not indicate any tendency for the  $k$ -value to vary as a function of the fineness, except perhaps for the very fine fraction, which has a slight tendency to give a higher  $k$ -value. Regardless of the fineness of the filler, the  $k$ -values seem to be relatively small, between 0.2 and 0.4.

Similar results were reported by Lundgren [11] for tests performed after curing for seven days at 20 °C. However, according to Lundgren, the influence of the fineness on the compressive strength is much greater for lower temperatures and shorter curing times.

Figure 5 shows compressive strength results for fillers produced from different types of calcareous carbonates. There is a very weak tendency for fillers produced from younger materials

with smaller crystals (chalk) to produce a slightly higher efficiency than fillers from older materials with larger crystals (marble). The tendency is very weak and cannot be regarded as significant if based on the results in this investigation.

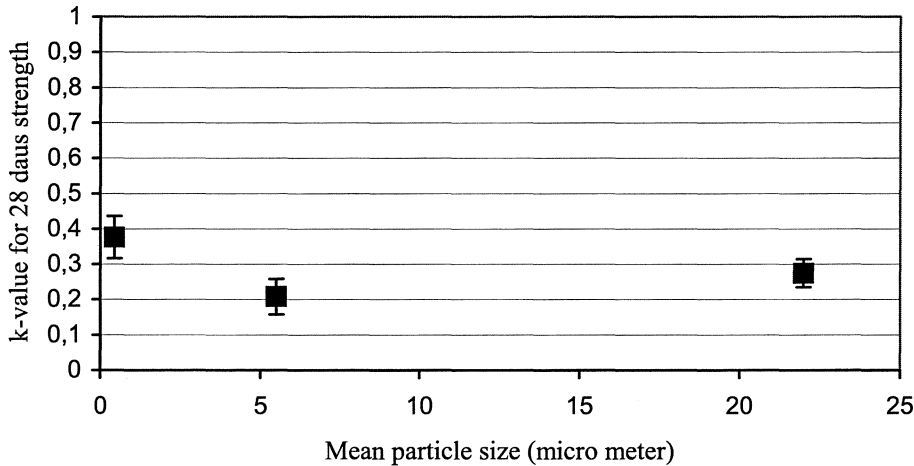


Figure 4 – The k-value for 28 days compressive strength, as a function of the mean particle size for type LL limestone filler. The results are relevant for mortars with W/C-ratios of 0.5.

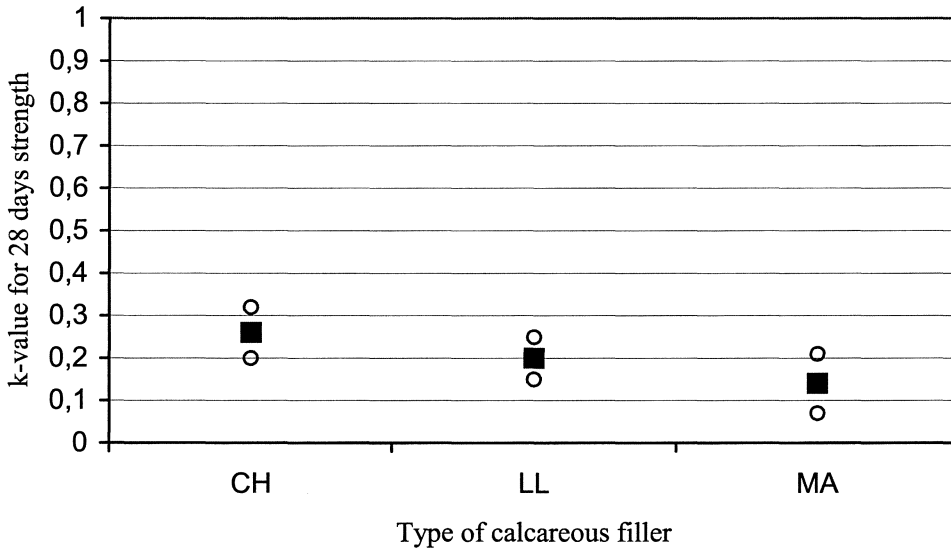


Figure 5 – The k-value for 28 days compressive strength plotted against the different calcium carbonate types. The results are relevant for mortars with W/C-ratios of 0.5.

### 3.2 Chloride migration

The results from the chloride migration tests are summarized in Table 5. Each value is the mean result of tests on three specimens. The table also shows the mean values for the coefficient of efficiency, together with the standard deviation.

Table 5 – Results from chloride migration test

Binder	W/B	Replacement (% by weight)	Migration coefficient, $D_m$ (* $10^{-12}$ m <sup>2</sup> /s)	Standard deviation, $D_m$ (* $10^{-12}$ m <sup>2</sup> /s)	k-value	Standard deviation, k
Cement						
OPC-0.4	0.40		8.3	0.6		
OPC-0.5	0.50		11.9	0.1		
OPC-0.6	0.60		15.4	0.9		
OPC-0.7	0.70		20.4	0.3		
OPC-0.8	0.80		24.2	0.6		
Cement and limestone filler						
LLF24-0.5	0.50	24	23.0	0.4	-0.47	0.03
CH24-0.5	0.50	24	24.5	1.2	-0.60	0.09
LL12-0.5	0.50	12	14.4	0.8	0.10	0.25
LL24-0.5	0.50	24	23.3	1.2	-0.49	0.10
LL24-0.7	0.70	24	38.5	0.2	-0.56	0.01
MA24-0.5	0.50	24	22.7	0.7	-0.44	0.06
LLC24-0.5	0.50	24	19.9	0.6	-0.17	0.06

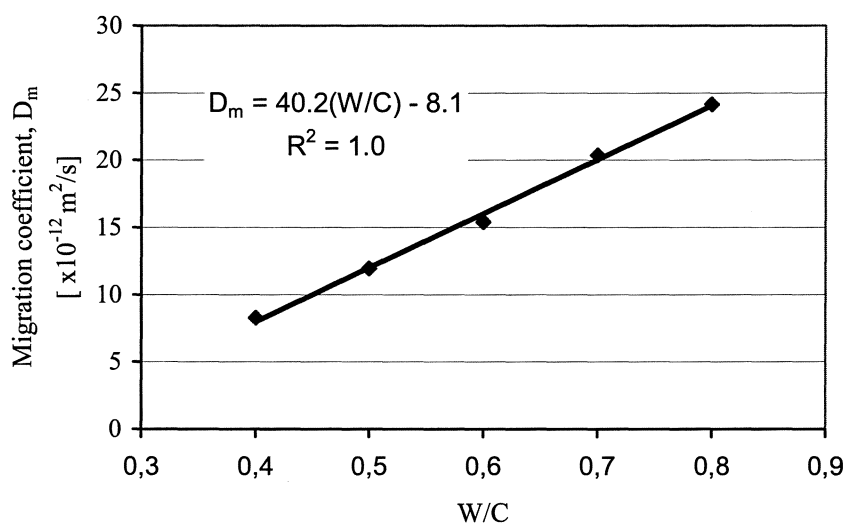


Figure 6 – Chloride migration coefficient as a function of W/C for mortars with ordinary Portland cement as binder.

The migration coefficient ( $D_m$ ) for the mortars with Ordinary Portland Cement as the only binder are plotted in Figure 6 as function of the W/C-ratio. There is a linear relationship between  $D_m$  and W/C. This relationship is used in this investigation for determining the k-values in accordance with the method described in Section 2.3 for the mortars containing limestone filler. Figure 7 shows the k-values for chloride migration for two different amounts of limestone filler in mortar. The scatter is relatively wide, but the tendency is the same as for compressive strength, i.e. the k-value is much higher for 12 % substitution than for 24 % substitution of the cement by

limestone filler. The values, however, are much lower for chloride migration than for compressive strength; 0.1 compared to 0.85 for 12 %, and -0.5 compared to 0.2 for 24 % replacement. This indicates that efficiency values based on strength tests are unusable for predicting chloride penetration for concrete qualities containing limestone filler.

It must be noted that the k-values for chloride migration obtained in this investigation are very low. The k-value for 12 % filler contents is 0.1, which means that the filler has almost no effect at all. This is not completely unexpected, as limestone fillers are normally assumed to be more or less chemically inert. On the other hand, the value for 24 % replacement is surprisingly low at -0.5. A negative value in fact means that the chloride permeability for 24 % replacement is higher than for a situation where 24 % of the cement is removed from the mortar without any replacement.

The results from the tests reported in this paper cannot explain the very low and negative k-values for higher limestone contents. Additional work is required.

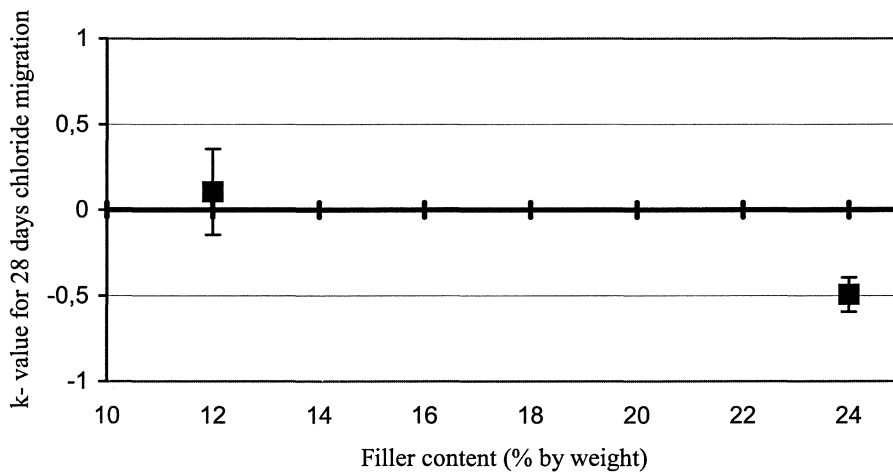


Figure 7 – Compressive strength versus the amount of filler (% by weight of total binder). The results are relevant for mortars with W/B-ratios of 0.5 with type LL filler quality.

Figure 8 shows the k-value for migration as a function of the mean particle size of type LL limestone filler. All the values are negative, with the highest value being observed for the coarsest filler (LLC). This contradicts the results for compressive strength, where there is a tendency for the finest filler to give the highest k-value.

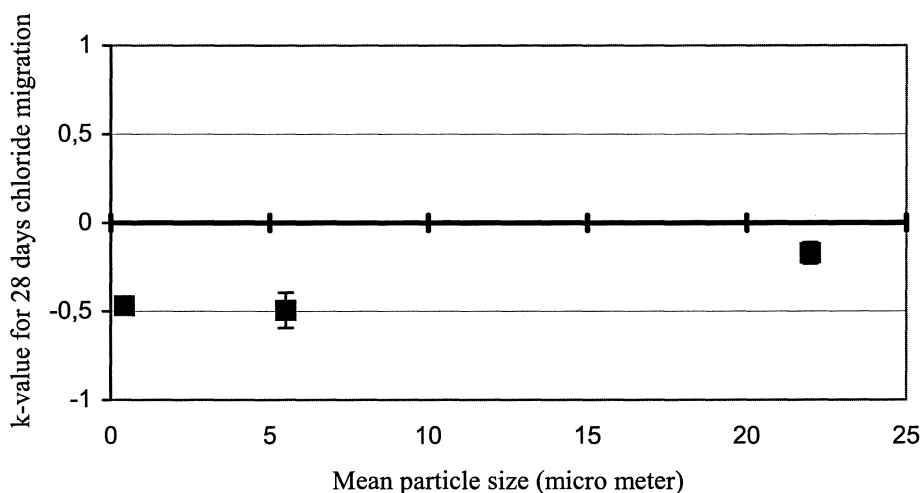


Figure 8 – *k*-values for the Chloride migration coefficient, as a function of the mean particle size of the limestone filler used in the mortars. The results are relevant for mortars with W/B-ratios of 0.5 and type LL filler.

Figure 9 shows the *k*-value for migration as function of the W/B-ratio. The values are similar, about -0.5, for the two ratios tested, W/B = 0.5 and W/B = 0.7.

Figure 10 shows the *k*-value for the migration coefficient for fillers produced from different calcareous carbonates. All the values are negative and there is a tendency for marble (MA) to have a slightly higher value and chalk (CH) to have a somewhat lower value. This contradicts the results from the strength tests, where CH gave the highest values and MA the lowest values. It must, however, be observed that the tendencies are weak, both in respect of migration and of strength.

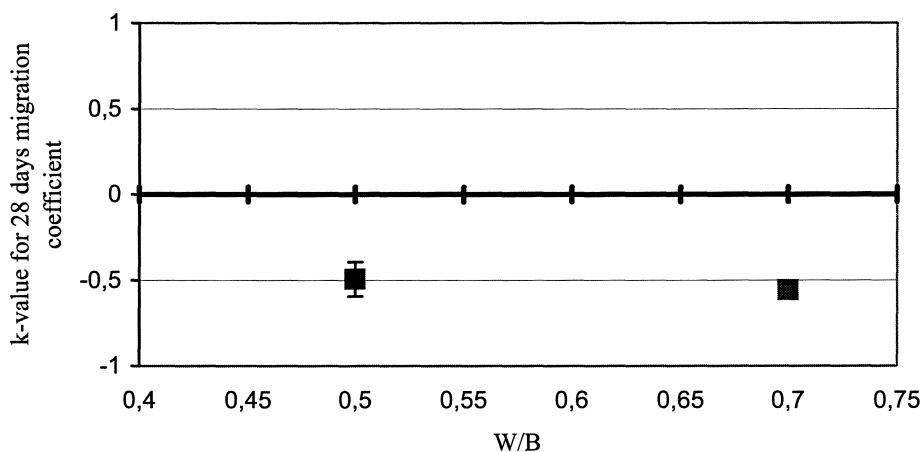


Figure 9 – The *k*-value for 28 days chloride migration coefficient, plotted against the water /binder ratio for the mortar mixes with type LL filler.

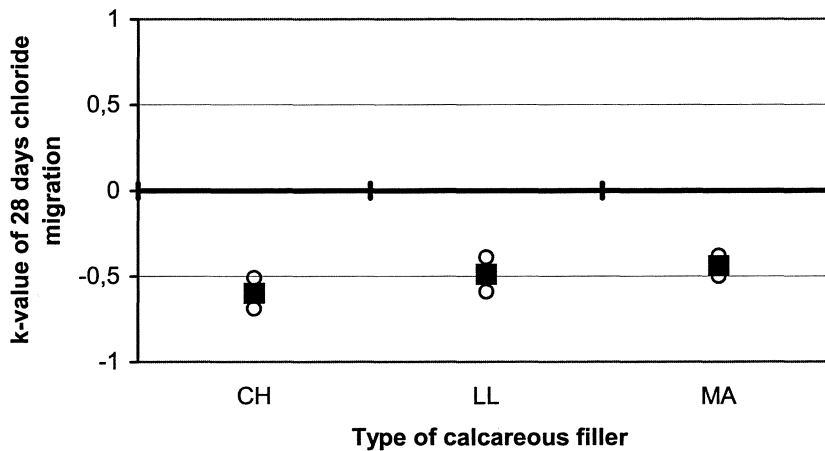


Figure 10 – The  $k$ -value for 28 days chloride migration coefficient, plotted against the different calcium carbonate types.

#### 4 Conclusions

The results presented in this paper are relevant for the constituent materials used and where the limestone fillers are added to the mortar directly in the mixer. Other materials or other ways of using limestone fillers, such as a part of the cement, may lead to other results. It must also be emphasized that uncertainties can occur in the results, because in some cases the results are only based on a few measurement points.

Based on the test results presented in this paper, the following conclusions can be drawn:

- The efficiency of limestone filler as replacement for cement in mortar and concrete is higher for moderate replacements, 12 %, than for higher replacements, 24 %. This is relevant both for 28 days compressive strength and for chloride migration
- The  $k$ -values for 28 days compressive strength for the limestone fillers used in this investigation are in the interval 0.2 to 0.9, while the corresponding interval for chloride migration is -0.6 to 0.1. This means that the efficiency for compressive strength, when expressed (for example) as a  $k$ -value, cannot be used for estimating the efficiency as far as chloride migration is concerned. It is reasonable to believe that the  $k$ -value for the limestone filler, as well as for other additions, is unique also for other material properties of mortar and concrete.
- The mean particle size of limestone filler has little effect on the  $k$ -value. There is a tendency, as far as 28 days compressive strength is concerned, for the filler with the finest mean particle size (0.44  $\mu\text{m}$ ) to be slightly more efficient than the coarser fillers. The opposite, however, is the case for chloride migration, for which the coarsest filler is the most efficient (or, in other words, has the least negative effect on the migration properties).
- There is a slight tendency for fillers produced from older calcareous carbonates with large crystals (marble) to be less efficient where 28 days strength is concerned than is the case when the filler has been produced from younger materials with finer crystals (chalk). However, the situation seems to be the opposite for chloride migration, i.e. marble is slightly more efficient than chalk.

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### **PAPER III**

**Title:** *Replacement of Cement by Limestone Filler or Ground Granulated Blast Furnace Slag: The effect on Strength and Chloride Diffusion in Cement Mortars. Laboratory and Field Studies.*

**Author:** Boubitsas, D.

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# Replacement of Cement by Limestone Filler or Ground Granulate Blast Furnace Slag: the Effect on Strength and Chloride Diffusion in Cement Mortars. Laboratory and field studies.



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## ABSTRACT

This paper describes laboratory and field trials carried out to examine the effect on the strength and chloride diffusion of cement mortar when a certain amount of the cement binder is replaced by limestone filler or granulate blast furnace slag. Limestone fillers produced from three different calcareous carbonates were used, and three different mean particle sizes of fillers were included in the study. The amount of replacement of cement by filler varied between 12 and 24 %, and mortars with different water/binder-ratios were used. The ground granulated blast-furnace slag (GBFS) used in the tests was a commercially available Swedish product called Merit-5000, and the replacement varied from 20 to 65% of the binder content.

**Key words:** chloride diffusion, efficiency, ground granulated blast-furnace slag, k-value, limestone filler, strength,.

## 1. INTRODUCTION

This paper describes studies carried out to examine the effect on the strength and chloride diffusion of cement mortar when a certain amount of the cement binder is replaced by limestone filler or granulate blast furnace slag. The paper focuses on laboratory and field exposure tests on one-year-old mortar specimens. Results from corresponding laboratory tests on 28-day-old mortars have been published by the author previously [1, 2].

The W/C-ratio is normally assumed to be the most important parameter defining the concrete properties; for example, when strength and permeability are concerned. The equivalent water/cement-ratio  $(W/C)_{eq}$ , which is used instead of W/C when additions are used in concrete, is defined as:

$$(W/C)_{eq} = W/(C+kR) \quad (1a)$$

where:

W = water content ( $\text{kg/m}^3$ )

C = cement content ( $\text{kg/m}^3$ )

R = content of addition ( $\text{kg/m}^3$ )

$k = k\text{-value}$

The  $k$ -value, or coefficient of efficiency for the mineral addition, can be calculated by using Equation (1a), which gives:

$$k = (W/(W/C)_{eq} - C)/R \quad (1b)$$

$(W/C)_{eq}$  can be calculated by using empirical relationships between the studied property (i.e. strength or chloride permeability) and  $W/C$  for OPC mixtures, and comparing these relationship with results obtained for mortars containing mineral additions: see Figure 1.

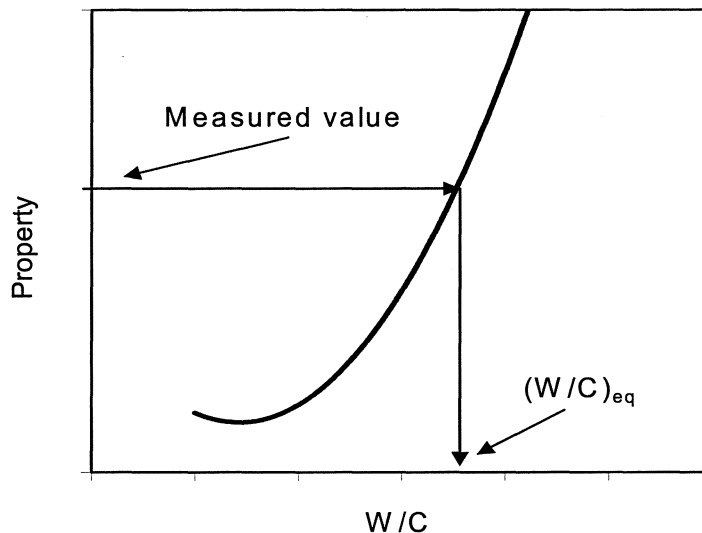


Figure 1- The relation between the  $W/C$ -ratio and a defined property (strength, migration coefficient, etc.) for Ordinary Portland Cement. This relation is used for determining the value of  $(W/C)_{eq}$  for concrete and mortar containing mineral additions.

The  $k$ -value is used for calculating  $(W/C)_{eq}$  which in turn is used, among other things, for predicting frost resistance, reinforcement corrosion and other durability properties. However, almost all  $k$ -values given in regulations and standards are based on results from strength testing of 28-day-old concrete. Consequently, in most cases, these values are not relevant for predicting the long-term performance and durability of concrete structures. More representative results can be obtained only from long-term and durability testing. This paper describes results, for one-year-old mortars, for chloride migration (laboratory testing) and chloride penetration (field testing), and compares them with  $k$ -values obtained from traditional compressive strength testing.

The  $k$ -value concept is normally used for Type II additions as defined in EN 206-1, i.e. reactive ones. However, in this paper the  $k$ -value is used for fillers as well, in order to compare the efficiency of different types of limestone fillers.

The project described in this paper is part of a larger investigation aiming at studying the efficiency of additions and fillers in concrete. Another project is investigating the influence of additions/fillers on early strength development under winter conditions. Results from that part of the investigation have been previously presented in [3, 4].

## 2. MATERIALS

### 2.1 Constituent materials

The physical and chemical properties of the cement/slag/limestones used throughout the experimental program, as given by the producers, are shown in Tables 1 and 2. The aggregate used was CEN standard sand in accordance with EN 196-1 [5], and the cement was a CEM I 52.5 R product conforming to EN 197-1 [6].

Fillers produced from the three different qualities of natural calcium carbonate were used in this study, see Table 2. Type LL is a calcium carbonate filler manufactured from a high-purity white limestone from France. Type MA is a white marble powder with high purity from Austria, while type CH filler is a Danish calcium carbonate powder from a more recent origin than the two others, and can be defined as a fine microcrystalline sedimentary chalk. The size of the crystals is coarsest for the marble calcium and finest for the chalk. The calcium carbonate content of all three limestone qualities was  $\geq 98\%$  by mass.

The ground granulated blast-furnace slag (GBFS) used in the tests was a commercially available Swedish product called Merit-5000.

All materials were obtained in single bulk deliveries and stored in airtight barrels to prevent deterioration with time.

**Table 1 – Chemical composition of the cement and slag**

Chemical composition	Cement (%)	Slag (%)	Mineralogical composition of cement	(%)
CaO	64.1	31	C <sub>3</sub> S	62.8
SiO <sub>2</sub>	20.9	34	C <sub>2</sub> S	12.4
Al <sub>2</sub> O <sub>3</sub>	3.8	13.1	C <sub>3</sub> A	5.5
Fe <sub>2</sub> O <sub>3</sub>	2.7	0.2	C <sub>4</sub> AF	8.3
SO <sub>3</sub>	3.4	1.41		
MgO	2.8	17.0		
K <sub>2</sub> O	1.1	0.52		
Na <sub>2</sub> O	0.3	0.54		
Cl	0.02	0.01		

**Table 2 - Physical characteristics of the cement, slag and limestone fillers used**

Material	Designation	Mean particle size ( $\mu\text{m}$ )	Specific surface, BET ( $\text{m}^2/\text{kg}$ )
Cement	CEM	8	1760
Chalk	CH	2.3	2200
Limestone	LL	5.5	1000
Marble	MA	7.0	1500
Slag	BFS	8	470 (Blaine)

Blaine fineness of the cement:  $550 \text{ m}^2/\text{kg}$  .

## 2.2 Mortars

Five different mortar mixtures were cast with Ordinary Portland Cement as the only binder, with water/binder-ratios ranging between 0.4 and 0.8. Another five different mortar mixtures were cast where a part of the Ordinary Portland Cement was replaced with limestone filler (binder = OPC + limestone). Finally, four different mortar mixtures were cast where a part of the Ordinary Portland Cement was replaced with slag (binder = OPC + slag). The mixture compositions are shown in Table 3.

The mortars were produced in accordance with European Standard EN 196-1 [5], with some modifications. One modification was that the water/cement-ratio for some mixtures differed from the standard, which specifies a constant 0.5 W/C-ratio. Another modification was that the mortar batches were much larger than in EN 196-1. The third modification was that, in those cases where the water/binder (W/B) ratio was not 0.5, the proportions by mass in the mix differed from those given in the standard (one part of cement, three parts of standard sand and one half part of water).

For all the mixes, the aim was to reach about the same consistency. This was accomplished by keeping the water content more or less constant and altering the binder content. The consistency was determined as described in European Standard test method EN 1015-3 [7].

The air contents, which were measured in accordance with Swedish Standard SS 13 71 24 [8], were relatively high although no air entraining agents were used. This is probably a result of the fine-grained aggregate and the high paste volume. The variations between the different mixtures were small, with the air contents varying from 4.8% to 6.0% (except in one case). This indicates that variations of the air contents between the mixes do not influence the test results very much.

**Table 3 – Mortar mix proportions used in the experimental study**

Mortar	W/B	Cement (kg/m <sup>3</sup> )	Limestone filler (kg/m <sup>3</sup> )	Slag (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	Aggregate (kg/m <sup>3</sup> )	Air (%)	Consistency (mm)
<i>Cement</i>								
OPC-0.4	0.40	702			281	1263		169
OPC-0.5	0.50	500			250	1500	4.9	170
OPC-0.6	0.60	413			248	1593		176
OPC-0.7	0.70	345			242	1666		168
OPC-0.8	0.80	319			255	1654		172
<i>Cement and limestone filler</i>								
CH24-0.5	0.50	380	120		250	1500	4.8	173
LL12-0.5	0.50	440	60		250	1500	5.0	175
LL24-0.5	0.50	380	120		250	1500	4.7	180
LL24-0.7	0.70	262	83		242	1666	5.4	164
MA24-0.5	0.50	380	120		250	1500	6.0	178
<i>Cement and slag</i>								
BFS20-0.5	0.50	400		100	250	1500	5.3	185
BFS35-0.5	0.50	325		175	250	1500	6.0	184
BFS35-0.7	0.70	224		121	242	1666	8.1	170
BFS65-0.5	0.50	175		325	250	1500	5.3	195

### 3. TEST PROGRAM

#### 3.1 Compressive strength

The compressive strength test was performed in accordance with European Standard EN 196-1 [5]. The test principle is that prismatic mortar specimens (40 mm x 40 mm x 160 mm) are cast and water-cured until the time for testing, which in this investigation means one year. The prisms were then broken into two halves by flexure. Each half prism was then tested for compressive strength.

#### 3.2 Chloride migration

Chloride migration testing was performed in accordance with Nordtest method NT BUILD 492 [9]. The migration coefficient is used in for defining the chloride penetration properties. Migration is defined as the movement of ions under the action of an external electrical field while diffusion is defined as the movement of ions under a concentration gradient. Parallel tests have shown that the value of the migration coefficient determined using this method corresponds well with the diffusion coefficient obtained with the conventional immersion test [10].

The principal of the method is that an external electrical potential is applied across the specimen and forces the chloride ions on the outside to migrate into the specimen. After a certain test duration, specified in the standard, the specimen is split and a silver nitrate solution is sprayed on to one of the freshly split sections. The chloride penetration depth can then be measured from the visible white silver chloride precipitation, after which the chloride migration coefficient can be calculated from this penetration depth as specified in the standard.

450 mm long cylinders with a diameter of 100 mm were cast in steel moulds. After demoulding, the cylinders were stored under water until the time for testing, i.e. one year later. Immediately before testing, 50 mm thick specimens were sawn from the cylinders, with the 50 mm thick discs at each end of the cylinders being discarded. The specimens were then placed in a vacuum container for vacuum saturation, after which testing started.

#### 3.3 Chloride diffusion (field exposure)

##### 3.3.1 *Specimens and exposure*

The specimens for field exposure were cast in plastic moulds with  $\varnothing$  165 mm, length 250 mm and 10 mm thick, see Figure 2. 20 mm thick slices were cut away from the end sides of the specimens after about one month of water curing. The specimens were then transported to the field exposure site and submerged in the sea in "open" plastic boxes, exposing the two newly cut surfaces to seawater, see Figure 3. The moulds were not removed at any time, which means that chloride penetration was one-dimensional when the specimens were submerged in the sea water.

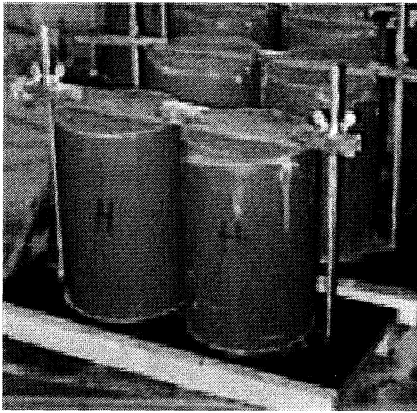


Figure 2 – Specimens for field exposure.

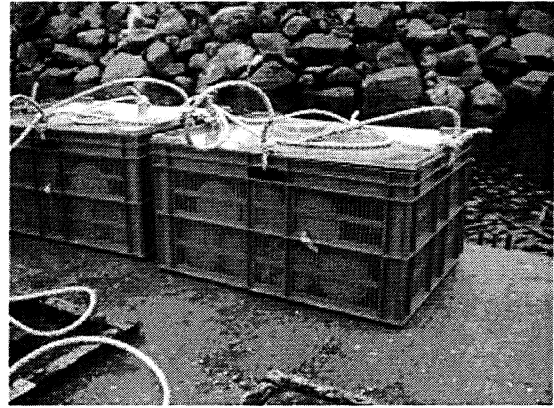


Figure 3 –The arrangement for immersing the specimens in the sea..

The field exposure site is situated in Träslövsläge, in the south-western part of Sweden. The exposure conditions at the Träslövsläge field site are well documented [11]. The chloride concentration in the seawater varies with time from 10 to 18 g per litre, and the water temperature has normally an annual variation ranging between + 20 °C and + 2 °C.

### 3.3.2 Measurement of Chloride Profiles

After about one year submerged in the sea, one specimen of each kind of mortar was brought back to the laboratory for analysis. Each specimen was individually sealed in double, thick plastic bags, and stored at room temperature for no longer than three weeks prior to measurement of chloride profiles. The specimens were sawn in the middle, and one part was used for measurement of chloride profiles and the other piece was used for measurement of moisture profiles and degree of capillary saturation. This paper reports only the chloride profiles.

For the measurement of chloride profiles, powder samples were taken by dry-grinding with a drill gradually from the exposed surface to a certain depth. Powder from each millimetre was taken for the first 5 mm, and then powder was taken for every second millimetre until 20 mm, after which the distance between where powder samples were taken was increased gradually. The depth of each sample was measured manually with a sliding calliper with an accuracy of about 0.5 mm. From each depth, about 10 g of powder was ground, collected and stored in small sealed plastic bags until testing. Before testing, a sample of about 1 g from each depth was dried at 105 °C for 24 h and then tested for chloride content.

The acid-soluble chloride content in each sample was determined principally in accordance with AASHTO T260 [12] using potentiometric titration on an automatic titrator (Metrohm Titrator 716), with a chloride selective electrode and Ag/AgCl reference electrode. This method has shown good repeatability and reproducibility in round-robin tests, and in addition the measured values agree very well with the expected “true” values [13].

### 3.3.3 Determination of the diffusion coefficient

The type of chloride ingress model chosen to estimate the diffusion coefficient in this study is the frequently used empirical model based on the error function solution to Fick’s 2<sup>nd</sup> law. The fundamental principle of this model is that the diffusion coefficient can be estimated, by curve fitting, from the error function to the chloride profiles gained from the field exposure test, see Figure 4.

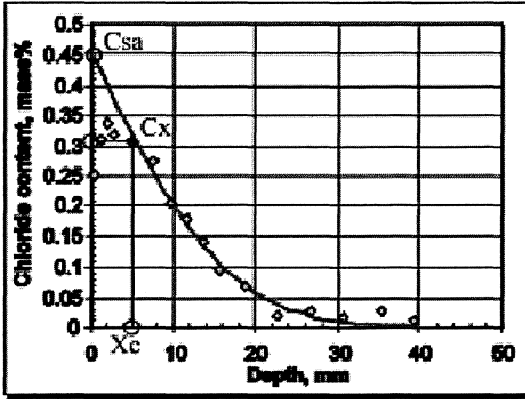


Figure 4-Curve fitting of the measured profiles to the error-function solution to Fick's 2<sup>nd</sup> law.

The mathematical solution to Fick's 2<sup>nd</sup> law used for the curve fitting, when the initial chloride content is negligible, as in this case, is:

$$C(x,t) = C_{sa} \cdot \left(1 - \operatorname{erfc}\left(\frac{x}{2\sqrt{D_a \cdot t}}\right)\right) \quad (2)$$

- $C(x,t)$  = Chloride content at time  $t$  and depth  $x$  from the surface [% by mass of binder]  
 $C_{sa}$  = Apparent surface chloride content [% by mass of binder]  
 $D_a$  = Apparent diffusion coefficient [ $\text{m}^2/\text{s}$ ]  
 $t$  = Exposure time [s]  
 $x$  = Depth from the surface [m]

The curve fitting procedure gives the two regression parameters,  $D_a$  and  $C_{sa}$ .  $D_a$  is the "apparent diffusion coefficient" achieved after an exposure time  $t$ , assuming that the diffusion coefficient  $D_F$  in Fick's 2<sup>nd</sup> law was constant during the whole exposure. Then  $D_a$  equals  $D_F$ .  $C_{sa}$  is the "apparent surface chloride content" achieved after an exposure time  $t$ , assuming that the boundary conditions were constant during the exposure. Then  $C_{sa} = C(x=0, t)$ . The surface chloride content ( $C_{sa}$ ) cannot be taken as the boundary condition for a particular environment, as it depends on the porosity and on the binding capacity of the concrete. Therefore, the effect of the concrete must be considered as well [16].

Curve fitting has been done in accordance with a procedure proposed by Nilsson [15]. The principle of this procedure is that all the points are used for a first curve fitting which leads to a first chloride profile. This procedure is repeated but with successively more and more of the points closest to the surface excluded from the curve fitting. This continues until a chloride profile is found for which the correlation coefficient,  $R^2$ , exceeds 0.98.

Two additional parameters have been read from the curve-fitting graph:  $X_c$  defines the depth from the surface where the first measurement point used in the curve-fitting is situated, while  $C_x$  is the measured chloride content at  $X_c$ .

The chloride profiles reported in this paper are not statistically verified, as the results for the chloride diffusion in the field test are gained from a single chloride profile. Additional work is required for verifying the results.



## 4 RESULTS

### 4.1 Compressive strength

The results from the compressive strength tests after one year are shown in Table 4. Each mean value is the mean result of six specimens. The low/high values correspond to the lowest and highest value for the six individual specimens in each series. The table also shows the mean values for the coefficient of efficiency (the k-value) calculated according to Equation 1b. The table also shows the corresponding low/high values. The low/high values are the lowest and highest values derived when calculating the k-value from the low/high-values of compressive strength.

Table 4 also shows the mean results from tests performed at 28 days (in *italics*) for both the compressive strength and the k-value. These results have been presented previously by the author [1, 2].

**Table 4 – Results from compressive tests**

Binder	W/B	Replace- ment (% weight)	f <sub>c</sub> (MPa)			k-value		
			mean	low-high	<i>mean</i>	mean	low-high	<i>mean</i>
			1 year		<i>28 days</i>	1 year		<i>28 days</i>
Cement								
OPC-0.4	0.40		91.6	89-94	<i>82.4</i>			
OPC-0.5	0.50		69.9	66-75	<i>66.7</i>			
OPC-0.6	0.60		51.1	50-54	<i>48.5</i>			
OPC-0.7	0.70		40.9	39-44	<i>42.2</i>			
OPC-0.8	0.80		33.2	30-36	<i>33.2</i>			
<i>Cement and limestone filler</i>								
CH24-05	0.50	24	54.9	53-57	<i>49.8</i>	0.4	0.3-0.5	<i>0.3</i>
LL12-0.5	0.50	12	66.2	63-68	<i>62.3</i>	0.8	0.5-1.0	<i>0.9</i>
LL24-0.5	0.50	24	57.0	55-58	<i>48.6</i>	0.5	0.4-0.6	<i>0.2</i>
LL24-0.7	0.70	24	28.8	28-30	<i>31.1</i>	0.2	0.2-0.3	<i>0.3</i>
MA24-0.5	0.50	24	50.3	49-53	<i>47.3</i>	0.2	0.2-0.3	<i>0.1</i>
<i>Cement and slag</i>								
BFS20-0.5	0.5	20	71.1	71-72	<i>56.0</i>	1.1	1.1-1.2	<i>0.7</i>
BFS35-0.5	0.5	35	74.2	71-77	<i>65.9</i>	1.2	1.1-1.3	<i>1.1</i>
BFS35-0.7	0.7	35	52.7	50-55	<i>36.6</i>	1.5	1.4-1.6	<i>0.7</i>
BFS65-0.5	0.5	65	68.2	66-71	<i>57.9</i>	1.0	0.9-1.1	<i>0.9</i>

The compressive strength test results are plotted in Figure 5 for the mortars with Ordinary Portland Cement as the only binder. There is a linear relationship, with good correlation, between compressive strength and 1/(W/C), i.e. Bolomey's Formula [17]. This

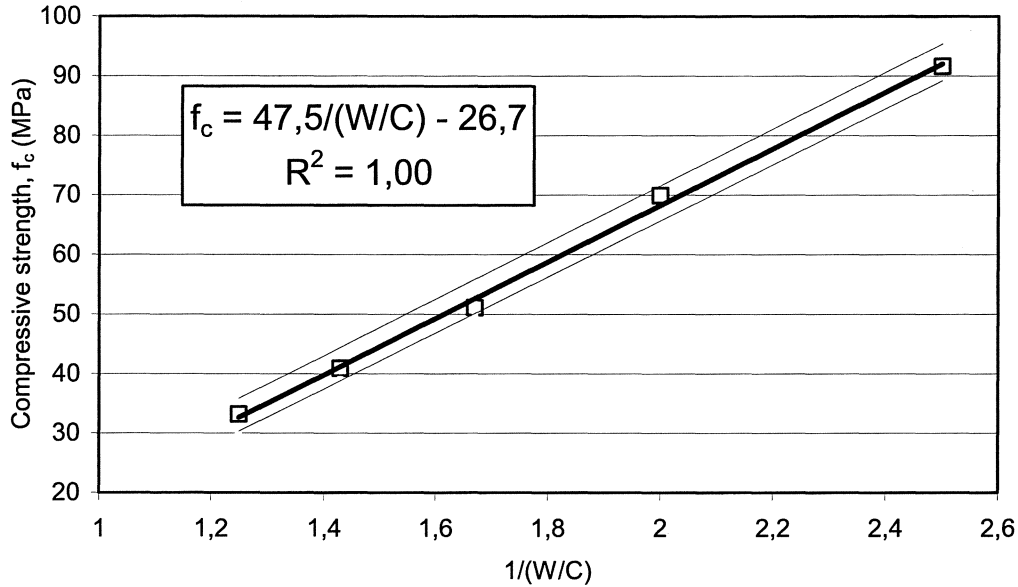


Figure 5 – The one-year compressive strength,  $f_c$  as a function of  $1/(W/C)$  for mortar with Ordinary Portland Cement as binder. The upper and lower limits are based on the high/low values of the compressive strength presented in Table 4.

relationship is used in this investigation for determining the k-values for the mortars containing limestone filler and slag as part of the binder. The upper and lower limits of the curve shown in the figure are calculated based on the low/high compressive strength values presented in Table 4.

According to Bolomey's formula, the compressive strength,  $f_c$ , is defined as:

$$f_c = A/(W/C) + B \quad (3)$$

By combining Bolomey's formula and Equation 1b, we obtain the following equation for calculating the k-value:

$$k = ((W/A) \cdot (f_{c,add} + B) - C)/R \quad (4)$$

where W = water content  
 C = cement content  
 R = addition content  
 A, B = constants in Bolomey's formula  
 $f_{c,add}$  = compressive strength of concrete with addition

Differentiating Equation 4 gives the following expression:

$$dk/df_{c,add} = W/(A \cdot R) \quad (5)$$

Equation 5 defines how much the k-value is influenced if the measured compressive strength of the concrete with addition is varied with  $df_{c,add}$ . As can be seen, the influence is independent of the value of k.

Equation 5 is illustrated in Figure 6 for different water/binder-ratios  $W/(C+R)$ . It can be seen that the evaluation of the  $k$ -value is more accurate for higher contents of addition, i.e. it is less sensitive for small variations of the measured  $f_c$ -value. The accuracy is also affected by the water/binder-ratio: the higher the ratio, the lower the accuracy.

Small variations of the compressive strength lead to high variations of the  $k$ -value. For example, if the measured compressive strength deviates from the true value by 1 MPa for a mortar with a water/binder-ratio of 0.5 and an additions content of 12%, then the  $k$ -value deviates from the true value by about 0.1. As the individual values of the compressive strength for a series of six specimens often vary over a range of 4-6 MPa (see Table 4), the variations of the calculated  $k$ -values may be considerable.

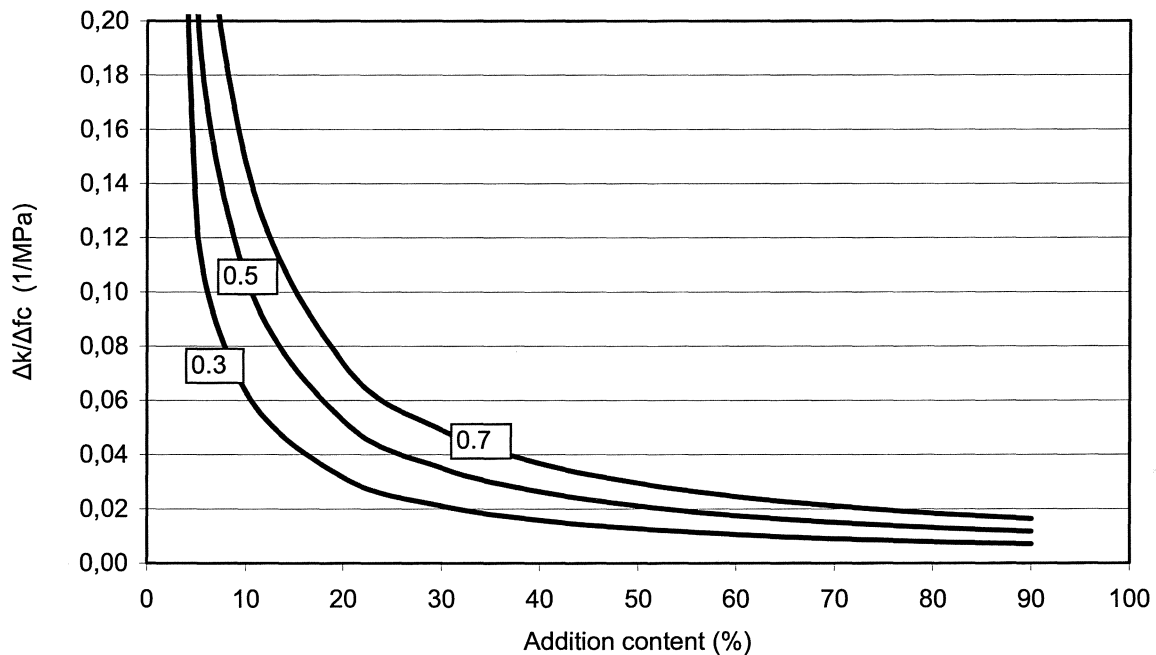


Figure 6 – Relation between  $\Delta k/\Delta f_{c,add}$  and the additions content for different water/binder-ratios

It can be seen from Table 4 that there is a tendency for the  $k$ -value of limestone filler to increase with time. The mean  $k$ -value seems to increase by about 0.1 from 28 days to 1 year. However, the scatter is considerable and the tendency must, therefore, be considered to be weak. However, the tendency is stronger for the  $k$ -value for slag: the mean value increases by about 0.3-0.4 from 28 days to 1 year.

In the case where type LL limestone filler or slag is used, and the only variation is the amount of replacement. The results in Table 4 reveal that the amount of replacement may have an effect on the  $k$ -value for the limestone filler. 12 % replacement gives a mean  $k$ -value of 0.8, while the corresponding value for 24 % replacement is 0.5. However, the scatter is considerable, especially for mortar with a limestone content of only 12 %. For mortar with slag there does not seem to be any strong effect of the slag content on the  $k$ -values.

The magnitude of the W/B-ratio influences the  $k$ -value for one-year strength on different ways, when comparing limestone replacement with slag replacement (see Table 4). For the

slag, the tendency is that a higher W/B ratio results in a higher k-value, and for the limestone the tendency seems to be the opposite.

There is a weak indication given from the results in Table 4, that, the fillers produced from younger materials with smaller crystals (chalk) produce a higher efficiency than the filler from older material with larger crystals (marble).

## 4.2 Chloride migration (laboratory)

Table 5 shows the results from the chloride migration tests after one year. Each mean value is the mean result of three specimens. The low-high values correspond to the lowest and highest value for the individual specimens in each series. The table also shows the mean values for the k-value calculated from Equation 1b, with the corresponding low/high values. The low/high values are the lowest and highest values derived when calculating the k-value from the low-high-values of the chloride migration.

**Table 5 – Results from chloride migration tests**

Binder	W/B	Replacement (% by weight)	d <sub>m</sub>			k-value		
			mean	low-high	<i>mean</i>	mean	low-high	<i>mean</i>
			1 year		<i>28 days</i>	1 year		<i>28 days</i>
Cement								
OPC-0.4	0.40		8.4	7.6-9.5	8.3			
OPC-0.5	0.50		14.5	14.0-14.7	11.9			
OPC-0.6	0.60		21.5	19.3-23.3	15.4			
OPC-0.7	0.70		27.8	27.4-27.9	20.4			
OPC-0.8	0.80		33.5	29.4-35.6	24.2			
<i>Cement and limestone filler</i>								
CH24-05	0.50	24	26.8	25.5-28.1	24.5	-0.1	-0.2- -0.1	-0.6
LL12-0.5	0.50	12	14.0	13.3-14.8	14.4	1.2	1.0-1.4	0.1
LL24-0.5	0.50	24	24.4	22.6-26.0	23.3	0	-0.1-0.2	-0.5
LL24-0.7	0.70	24			38.5			-0.6
MA24-0.5	0.50	24	22.5	22.4-22.6	22.7	0.2	0.2-0.2	-0.4
<i>Cement and slag</i>								
BFS20-0.5	0.5	20	5.7	5.4-5.9	8.5	3.0	2.9-3.1	2.1
BFS35-0.5	0.5	35	2.9	2.8-3.0	5.6	2.7	2.7-2.7	2.3
BFS35-0.7	0.7	35	3.7	3.5-3.9	11.5	4.3	4.2-4.3	2.3
BFS65-0.5	0.5	65	1.3	1.28-1.38	2.7	2.1	2.1-2.1	2.3

Table 5 shows also mean results from tests performed at 28 days (in *italics*) for both the chloride migration and the k-value as well. These results have been presented previously by the author [1, 2].

The results from the chloride migration tests are plotted in Figure 10 for the mortars with Ordinary Portland Cement as the only binder. There is a linear relationship, with good correlation, between the migration coefficient and the W/C ratio. This relationship is used in this investigation for determining the k-values for the mortars containing limestone filler and slag as part of the binder. The upper and lower limits of the curve shown in the figure are calculated based on the low/high chloride migration values presented in Table 5.

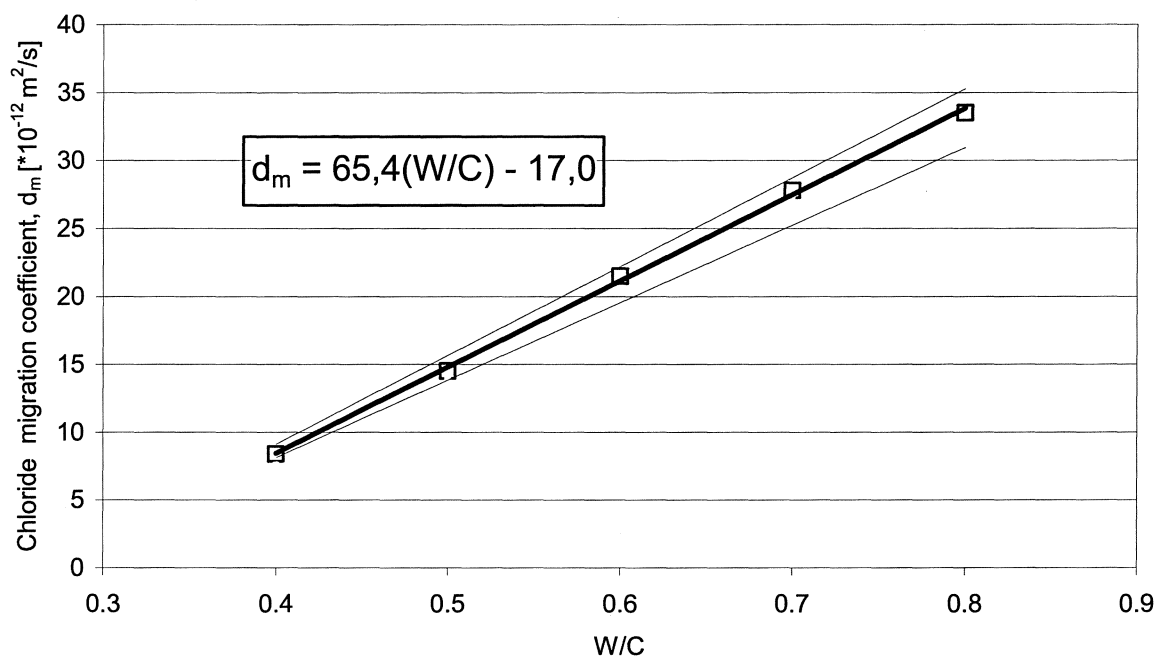


Figure 10 – The one-year chloride migration,  $d_m$ , as a function of W/C ratio for mortar with Ordinary Portland Cement as binder. The upper and lower limits are based on the high/low values of the chloride migration presented in Table 5.

The results in Table 5 show that the k-value for one year old mortar is about 0 for all the mixes with 24% limestone content, but considerably higher (about 1.0) when the limestone content is only 12%. It is not possible to explain this marked influence of the limestone content from the results in this investigation. The same tendency, but much weaker, can also be seen for the k-values based on compressive strength, where the k-value increases from about 0.2-0.5 to about 0.8 when the limestone content decreases from 24 to 12 %, see Table 4.

When comparing the k-values for limestone replacement, from tests performed at 28 days, with the tests performed after one year, significant differences can be observed. The k-values from tests performed at 28 days are negative, while for the tests performed after one year the k-values are about 0. But when the migration coefficients obtained at the different ages are compared, there are no differences. This is due to the unexpected results found for the mortars with only OPC as binder, in Table 5, it can be observed that the migration coefficient is lower for the early age (28 day) then for the later age (one year). This unexpected effect cannot be explained by the results found in this investigation.

The coefficient of migration decreases for the mortars containing slag, when the age increases from 28 days to 1 year, see Table 5. This implies a continuing chemical process in the mortar leading to a denser concrete. Such an effect could not be observed for mortar with limestone filler. This agrees well with the findings regarding the compressive strength, which was improved considerably for mortar with slag but not for mortar with limestone filler (see Table 4). When concerning slag, for both compressive strength and chloride migration, the influence on age was more pronounced for a W/C-ratio of 0.7 than for a W/C-ratio of 0.5.

### 4.3 Chloride diffusion (field)

The results from the field exposure tests at the Träslövläge exposure site are summarized in Figures 11-13 and in Table 6. Figures 11-13 show the chloride profiles for different water/binder ratios, measured after one year of exposure. The chloride content is expressed as percentage by mass of binder (including slag/limestone filler).

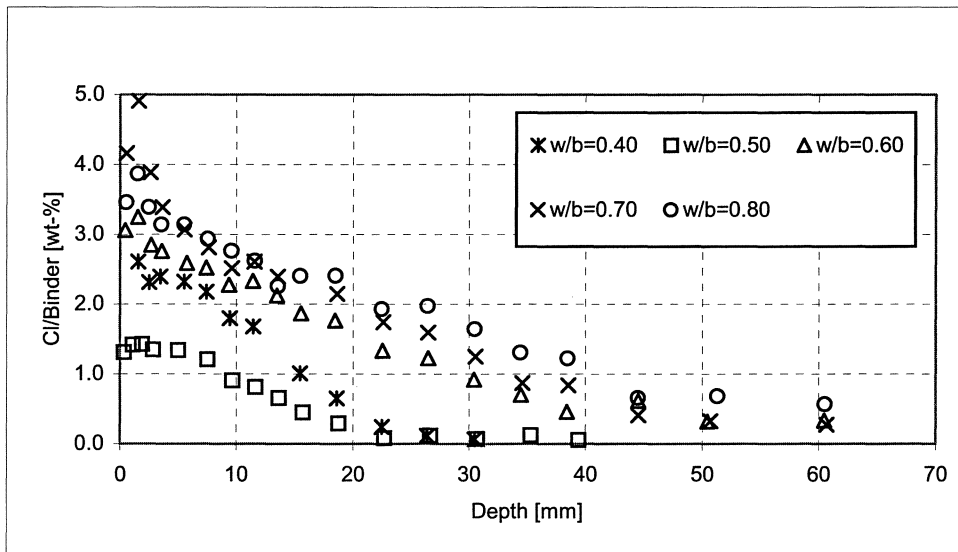


Figure 11 –Chloride profiles after one year exposure time for mortars with OPC as binder and different W/C ratios.

Figure 11 shows the results with OPC as the only binder. The measured chloride profiles correspond to the expected result: the higher the W/C ratio, the more chlorides have diffused into the mortar. There is, however, one exception from the expected results: the chloride profile for the mortar with a W/C ratio of 0.5 is the lowest one, and also lower than the profile for the mortar with a water/cement-ratio of 0.4. One explanation may be that the specimen with a water/cement-ratio of 0.5 has been partly in the bottom sediment, which may have affected chloride transport into the specimen.

Figure 12 shows the chloride profiles for mortars with limestone filler, and Figure 13 for mortars with slag. The penetration depth is much lower for mortar with slag than for mortar with OPC as the only binder (compare with Figure 11). This pronounced ability of slag to improve chloride resistance is well known and in accordance with the results from the migration test, see Table 5.

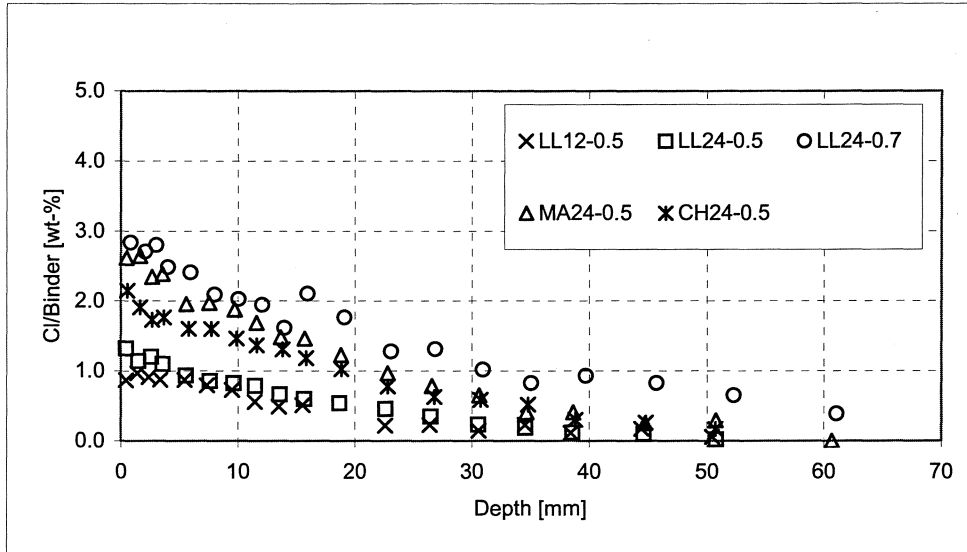


Figure 12 –Chloride profiles after one year exposure time for mortars with OPC and limestone filler as binder.

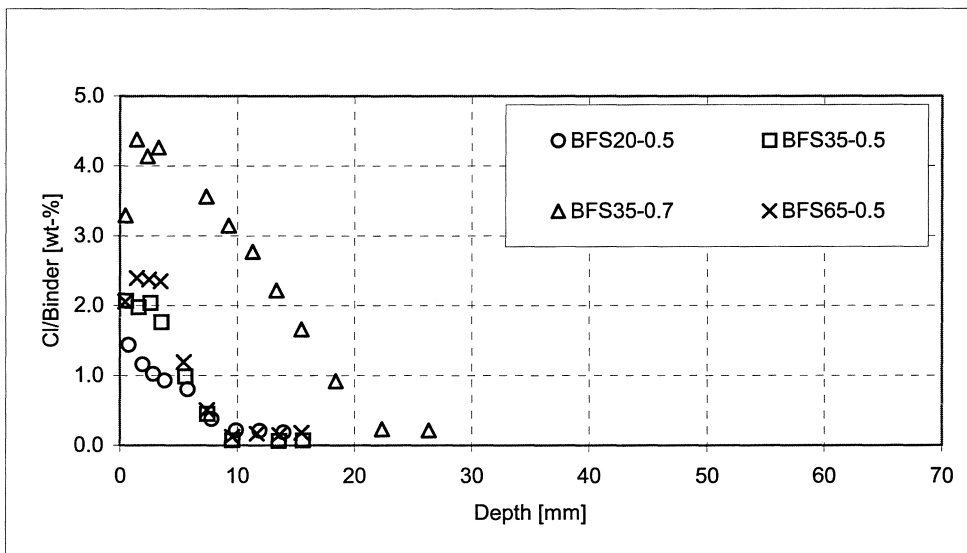


Figure 13 –Chloride profiles after one year of exposure for mortars with OPC and granulated blast-furnace slag as binder.

Table 6 presents the diffusion coefficient and the other regression parameters from the curve-fitting evaluation.

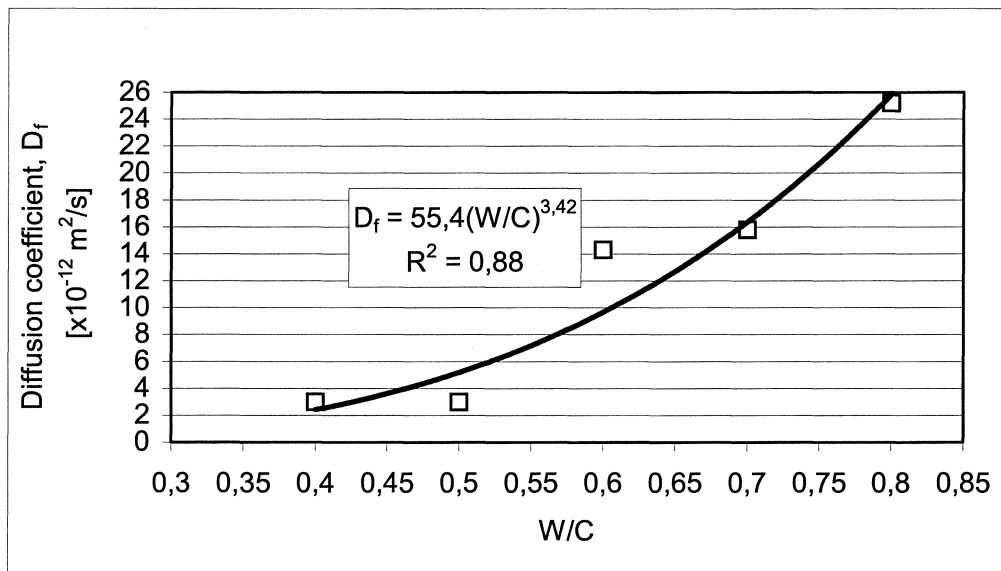
As mentioned before, each result for the chloride diffusion (field) is gained from a single specimen. Despite this uncertainty, an attempt is made to calculate the  $k$ -values according to Equation 1.b.

The diffusion coefficient ( $D_a$ ) for the mortars with Ordinary Portland Cement as the only binder is plotted in Figure 14 as function of the W/C ratio. A linear regression line would lead to a diffusion coefficient of 0 at a water/cement ratio of about 0.4. This seems unrealistic, and

therefore the potential relation shown in the figure is used instead. This relation, in spite of its uncertainty, is used for calculating k-values for slag and limestone fillers, see Table 7.

*Table 6 – Results from chloride diffusion in field exposure*

Binder	W/B	Replacement (% by weight)	Apparent diffusion coefficient, $D_a$ (* $10^{-12}$ m <sup>2</sup> /s)	Apparent surface chloride content, $C_{sa}$ Cl/Binder (wt-%)	Chloride content at $X_c$ , $C_x$ Cl/Binder (wt-%)	Depth from surface, $X_c$ (mm)
<b>Cement</b>						
OPC-0.4	0.40		2.7	3.9	2.2	7.5
OPC-0.5	0.50		2.7	2.0	1.3	5.0
OPC-0.6	0.60		13.3	3.2	3.1	0.4
OPC-0.7	0.70		14.3	3.7	3.9	2.6
OPC-0.8	0.80		24.9	3.5	3.4	2.5
<b>Cement and limestone filler</b>						
CH24-0.5	0.50	24	12.2	2.0	2.2	0.6
LL12-0.5	0.50	12	7.3	1.0	1.0	1.4
LL24-0.5	0.50	24	8.0	1.3	1.3	0.4
LL24-0.7	0.70	24	22.1	2.7	2.8	0.8
MA24-0.5	0.50	24	10.2	2.6	2.6	0.5
<b>Cement and slag</b>						
BFS20-0.5	0.50	20	0.9	1.5	1.4	0.7
BFS35-0.5	0.50	35	0.4	3.5	2.0	2.6
BFS35-0.7	0.70	35	2.6	6.6	3.6	7.4
BFS65-0.5	0.50	65	0.3	5.4	2.3	3.5



*Figure 14 – Chloride diffusion coefficient as function of W/C after one year of field exposure for mortars with OPC as the only binder.*



Table 7– *k*-values based on results from chloride diffusion during field exposure and the curve in Figure 14

Binder	W/B	Replacement (% by weight)	Diffusion coefficient, $D_a$ (* $10^{-12}$ m <sup>2</sup> /s)	<i>k</i> -value
<i>Cement and lime-stone filler</i>				
CH24-0.5	0.50	24	12.2	0.1
LL12-0.5	0.50	12	7.3	0.2
LL24-0.5	0.50	24	8.0	0.5
LL24-0.7	0.70	24	22.1	0.6
MA24-0.5	0.50	24	10.2	0.3
<i>Cement and slag</i>				
BFS20-0.5	0.50	20	0.9	4.3
BFS35-0.5	0.50	35	0.4	4.2
BFS35-0.7	0.70	35	2.6	3.0
BFS65-0.5	0.50	65	0.3	3.0

The *k*-values in Table 7 are uncertain, as they are based on the very uncertain relation in Figure 14. The relation is especially uncertain for diffusion coefficients lower than about  $2-3 \cdot 10^{-12}$  m<sup>2</sup>/s, i.e. for the region relevant for the mortars with slag. However, the *k*-values for limestone filler seem to be within the interval  $0.3 \pm 0.3$ . This is higher than corresponding migration coefficients from the laboratory tests, which are normally, according to Table 5, about 0, although the value is as high as 1.2 for one individual mortar quality. The corresponding *k*-values for compressive strength are in the interval  $0.5 \pm 0.3$ , see Table 4.

The *k*-values for the diffusion coefficient for slag are high, 3.0-4.3. These correspond well with the values from the migration test, which are in the interval 2.1-4.3. The *k*-values for compressive strength, however, are much lower, about 1.0. This clearly indicates the need for different *k*-values for different mortar or concrete properties. It also shows that the *k*-value for slag given in SS 13 70 03 may be much too low, at least as far as chloride penetration is concerned.

## 5 Conclusions

The following conclusions can be drawn from the results from the investigations presented in this paper:

- The reliability of measured *k*-values improves considerably with increasing content of addition/filler.
- The *k*-values for 1-year compressive strength for limestone filler is normally found to be in the interval 0.2-0.5, although a single value is as high as 0.8. The 1-year-values for limestone fillers are about the same as were found at 28 days. The 1-year *k*-value for slag is found to be 1.0-1.5, which is about 0.3-0.4 higher than at 28 days.
- The results indicate that the chloride migration coefficient is about the same for 28 days and one year for mortar containing limestone filler. The one-year *k*-value is about 0 for all the mixes with 24% limestone content, but considerably higher (about 1.0) when the limestone content is only 12%. It is not possible to explain this marked influence of the limestone content from the results in this investigation

- The coefficient of migration decreases for the mortars containing slag when the age increases from 28 days to one year. This implies a continuing chemical process in the mortar leading to a more dense concrete. The one-year k-values are in interval 2.1-4.3, which is much higher than the k-value of 0.6 which is given in Swedish standard SS 13 70 03.
- The diffusion coefficients calculated from field exposure test results are uncertain, as each result is based on tests on single specimens. However, the k-values for limestone filler seem to be within the interval  $0.3 \pm 0.3$ . This is higher than k-values from corresponding migration coefficients from the laboratory tests, which are normally about 0.
- The k-values for the diffusion coefficient for slag are high, 3.0-4.3. These values correspond well with the values from the migration test, which are in the interval 2.1-4.3.
- The k-values for a mineral addition/filler sometimes vary considerably when determined for different material properties. Standards normally give a single value (or sometimes two values) for the coefficient of efficiency for all properties. This is not satisfactory: different values should be used, depending on which property is of interest.

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