

VOLUME 1

**CREEP, SHRINKAGE
AND DURABILITY MECHANICS
OF CONCRETE AND CONCRETE STRUCTURES**



**T. Tanabe, K. Sakata, H. Mihashi, R. Sato, K. Maekawa and H. Nakamura
EDITORS**

 **CRC Press**
Taylor & Francis Group
A BALKEMA BOOK

CREEP, SHRINKAGE AND DURABILITY MECHANICS OF CONCRETE
AND CONCRETE STRUCTURES

PROCEEDINGS OF THE EIGHTH INTERNATIONAL CONFERENCE ON CREEP, SHRINKAGE
AND DURABILITY OF CONCRETE AND CONCRETE STRUCTURES, ISE-SHIMA, JAPAN,
30 SEPTEMBER–2 OCTOBER 2008

Creep, Shrinkage and Durability Mechanics of Concrete and Concrete Structures

Edited by

Tada-aki Tanabe

Chubu Regional Institute of Infra-Technology Evaluation and Support (CRIIES), Japan

Kenji Sakata

Okayama University, Japan

Hirozo Mihashi

Tohoku University, Japan

Ryoichi Sato

Hiroshima University, Japan

Koichi Maekawa

The University of Tokyo, Japan

Hikaru Nakamura

Nagoya University, Japan

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CRC Press

Taylor & Francis Group

Boca Raton London New York Leiden

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

A BALKEMA BOOK

Taylor & Francis
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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Version Date: 20131004

International Standard Book Number-13: 978-0-203-88295-5 (eBook - PDF)

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Preface

During the past five years, two major bridge accidents have occurred in Japan. One was Toki-Messe Bridge in Niigata Pref., a five-span continuous pedestrian bridge, which collapsed two years and four months after the completion of construction. It had been in practical use at the time of the collapse. The other was Tarui Bridge, in Wakayama Pref., a seven-span continuous highway bridge with a box section, which suffered severe cracking damage a year after the completion. It was fortunately not in practical use yet. The research committee of the collapse of the pedestrian bridge concluded that it occurred due to creep failure at the anchorage part in the concrete slab of the mixed structural systems of steel and concrete, though there exist arguments about its justification. The highway bridge was found to have many cracks in the box sections in all seven spans. The JSCE concrete committee to investigate its cause and to advise remedies has concluded that they were due to excessive concrete shrinkage of over 1000 microns. The collapse of the Koror Bridge in the Palau islands two months after the completion of rehabilitation is also well known. The bridge has been deflecting continuously since the completion in 1977. Since its values exceeded several times of design deflection, rehabilitation was carried out in 1996. All these examples tell us that after over a half century of extensive use of pre-stressed concrete in bridge construction, creep and shrinkage including durability problems are gradually revealing their true technical importance through the form of serious social infrastructural damage.

IA-CONCREEP held its eighth international conference from September 30 to October 2, 2008, at Ise-Shima, Japan with cosponsor of JAPAN CONCRETE INSTITUTE. IA-CONCREEP has nowadays become the main forum for discussion and dissemination of research results on creep, shrinkage and other time dependent characteristics of concrete and concrete structures through the consecutive seven international conferences, the first of which was organized by Professor H. Ruesch at Technical University of Munich in 1958.

In two volumes of the proceedings, five invited papers, three technical committee reports and 188 contributed research papers on the topics from micro-mechanics of concrete creep, shrinkage and durability to the regulatory topics such as design standards for those problems are included. It is a well known fact that accurate prediction of long-term behavior of concrete is extremely difficult. However, it is also undeniable that the unexpected collapses of structures are often related to these characteristics. We wish the conference and its proceedings will benefit researchers and engineers who are concerned with concrete and concrete structures. Finally we wish to express our utmost gratitude to the board and advisory board members who initially set the conference framework, scientific committee members who have reviewed the greater-than-expected number of contributed papers and the organizing committee members who have given consideration to even minor details of the three-day schedule of the conference. They are listed in the following pages.

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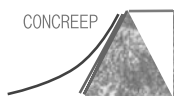
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*Micro structural characterization and micro-mechanics
of creep and shrinkage*

KEYNOTE LECTURE

Heresies on shrinkage and creep mechanisms

F.H. Wittmann

Aedificat Institute Freiburg, Germany

ABSTRACT: First of all it is outlined that shrinkage as measured on drying concrete is not a simple material property but the complex response of a given specimen to long lasting time-dependent internal stresses. Then the physical basis of two frequently cited approaches to explain the origin of hygral shrinkage is briefly described: capillary action and disjoining pressure. The predictions of the two concepts are compared with experimental findings. The following examples have been selected for a critical comparison: (1) direct observation of the interaction of water in a narrow gap, (2) sorption and length change isotherms of different materials, (3) capillary shrinkage of fresh and young concrete, (4) shrinkage of water repellent concrete, and (5) influence of ion concentration on shrinkage. From the presented results it can be concluded that capillary action plays a minor role in the process of shrinkage of cement-based materials.

1 INTRODUCTION

We may consider shrinkage and swelling of concrete to be the volume change imposed by a change of moisture content and by chemical and physical reactions of the solid skeleton with the pore solution. From this definition follows that several mechanisms may act simultaneously or consecutively to generate macroscopically observed volume changes. This complexity is probably one of the reasons, why no general agreement could be found up to now on dominant shrinkage and swelling mechanisms.

In this contribution we will essentially concentrate on drying shrinkage. Drying can be due to loss of water to an environment, which is drier than the pore space of the drying material, or it can be due to water consumption by hydration of cement (autogenous drying). Although the underlying mechanisms are the same, the development of shrinkage under water loss differs in a characteristic way from autogenous shrinkage under water consumption (Alvaredo & Wittmann 1995, Wittmann 2008). Drying shrinkage is provoked by time dependent moisture gradients. In most cases the stress distribution in drying specimens overcomes the tensile strength. As a consequence drying shrinkage is accompanied in most cases by strain softening and surface crack formation.

A multitude of mechanisms have been proposed for hygral shrinkage. Some are simplistic and based on phenomenological observations exclusively. They

cannot be verified nor can they be falsified; therefore they are of limited significance.

Two approaches, however, are based on physical fundamentals. Some authors tried to establish a link between drying shrinkage and capillary action (Coussy et al. 2004, Baroghel-Bouny et al. 1999, Hua et al. 1995). An alternative approach is based on the change of surface energy and disjoining pressure as function of moisture content (Wittmann 1968, Wittmann 1973, Wittmann 1976a, Wittmann 1977, Setzer 1991, Setzer 2008, Churaev & Derjaguin 1984, Weimann & Li 2003). In the following predictions of the two different approaches shall be critically compared with experimental findings.

2 INFINITESIMAL SHRINKAGE

Drying is at the origin of shrinkage. But drying is an extremely slow process. In many concrete structures a hygral gradient exists for many years. That means the outer layers have reached hygral equilibrium with the relative humidity (RH) of the environment quickly while the inner part may remain water saturated for decades. Shrinkage of the infinitesimal thin surface near layers, however, is hindered in the monolithic material. Under high imposed tensile strain, cracks are formed after damage of the material due to strain softening in the surface near zone. This situation is schematically shown in Fig. 1.

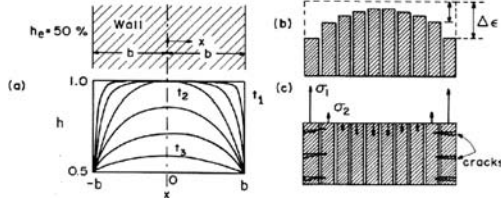


Figure 1. (a) Moisture distribution as function of drying time, (b) infinitesimal shrinkage at one selected time step, and (c) stress distribution and crack formation (after Bažant 1982).

In order to check the validity of predictions of a shrinkage model, results ought to be compared with infinitesimal shrinkage, the only characteristic material property in this context, and not with the measurable response of a drying material. The immediate response depends on infinitesimal shrinkage but also on the dimensions, time-dependent moisture gradient, creep, elastic modulus, tensile strength, strain softening and crack formation. The long lasting internal stress distribution is modified by creep and stress relaxation. In addition it has been shown that shrinkage depends strongly on the simultaneously acting stress (Wittmann 1993) and in practice stress free shrinkage does not exist.

But we are confronted with a basic problem; infinitesimal shrinkage cannot be determined directly by experiments. It has to be determined by inverse analysis from experimental data. A suitable model is now being developed and first results can hopefully be presented soon. In the meantime drying in small hygral steps until hygral equilibrium is reached, in order to avoid crack formation, may be considered as a first approximation for infinitesimal shrinkage. In thin specimens made of hardened cement paste this can be and has been measured. But the moisture diffusion coefficient of cement-based materials is very low, in particular at low RH, and therefore the time to reach hygral equilibrium for a representative volume element of concrete for one step may be in the order of magnitude of one year. That means to measure a length change isotherm may take 20 years and more. This is unrealistic and has never been tried so far.

As a conclusion we may state that the only physical meaningful value in this context, the infinitesimal shrinkage, has never been measured on concrete for obvious reasons. This is certainly a major reason for basic differences of concepts to describe shrinkage. Nevertheless we can carefully compare some predictions, or at least trends, with reliable experimental results.

We cannot but mention creep mechanisms briefly in this contribution because of page limitations. This

shall be dealt with in greater detail elsewhere. But it can be shown that the underlying concept is the same for shrinkage and creep mechanisms.

3 TWO DIFFERENT CONCEPTS TO DESCRIBE SHRINKAGE OF CONCRETE

3.1 Capillary action

Water condenses on a plane surface when the saturation water vapour pressure p_0 is reached in the surrounding air. In a capillary with radius r water condenses at a lower vapour pressure p . The relation between the radius r and the relative vapour pressure p/p_0 is given by the Kelvin equation:

$$r = -\frac{2\gamma V}{RT \ln(p/p_0)} \quad (1)$$

In equation (1) γ stands for the surface tension of water, V for the molar volume, R for the molar gas constant, and T for the temperature.

The Laplace equation describes the pressure change Δp in a liquid under a meniscus with radius r as follows:

$$\Delta p = \frac{2\gamma}{r} \quad (2)$$

If we combine the two equations (1) and (2) we obtain an equation for the pressure change in the water held in capillaries, which are filled at a relative humidity p/p_0 :

$$\Delta p = \frac{RT \ln \frac{p}{p_0}}{V} \quad (3)$$

Essential questions are, is the Kelvin equation and Laplace equation valid in the dominating range of pore radii in hardened cement paste and can the capillary pressure according to equation (3) be considered to have a significant influence on shrinkage of cement-based materials as predicted by poroelasticity (Coussy et al. 2004, Baroghel et al. 1999, and Hua et al. 1995). Comparison with experimental results shall help us to answer these questions.

3.2 Surface energy and disjoining pressure

A droplet having a radius r is under a hydrostatic pressure p given by Laplace equation (2). This pressure becomes significant and can be measured in very small solid particles as well. Surface energy γ of solids is at maximum in vacuo. With increasing water vapour pressure a water film with increasing thickness Γ is adsorbed. It can be shown that the interfacial energy

decreases under the influence of an adsorbed water film:

$$\Delta\gamma = \gamma_0 - \gamma = RT \int_0^p \Gamma d(\ln p) \quad (4)$$

Combining equation (4) with the Laplace equation (2) leads to the well-known Bangham equation:

$$\frac{\Delta l}{l} = \lambda \Delta\gamma \quad (5)$$

λ in equation (5) can be expressed in terms of mechanical properties of the colloidal particles. Equation (5) can be applied to describe quantitatively the length change in the low humidity range where vapour adsorption prevails.

Above 50% RH surface energy does not change significantly with further increase of RH. In this high humidity range water penetrates into small gaps and there it exerts disjoining pressure. The term disjoining pressure is used to describe the complex interaction between water and two solid surfaces. The measurable disjoining pressure Π is generated by a superposition of attractive and repulsive forces. In a simplifying way it can be expressed as follows:

$$\Pi = \Pi_m + \Pi_e + \Pi_s \quad (6)$$

The attractive dispersive or molecular forces Π_m are in the first place van der Waals forces. The van der Waals attraction is weakened by adsorbed water films. The diffuse electric double layer is at the origin of a repulsive component Π_e . The diffuse electric double layer in hardened cement paste depends among other influences on the ion concentration and the pH value. The third term, the structural term, includes the effect of solvation or hydration shells Π_s (Churaev and Derjaguin 1985, Setzer 2008). For a given type of cement the disjoining pressure Π has to be determined experimentally, and must be considered to be a characteristic material property.

In Fig. 2 the action of disjoining pressure is shown schematically: (a) if two surfaces are in close contact in vacuo an attractive force dominates the interaction and

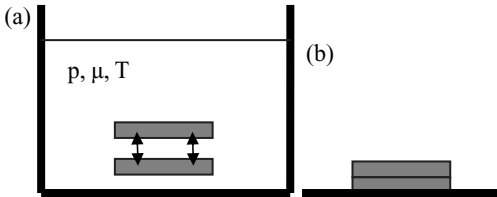


Figure 2. Action of disjoining pressure, schematic.

(b) if the two particles are placed in an aqueous solution water will penetrate into the gap and separate the two surfaces. The pressure, which will be generated in this way, depends on the change of surface energy, the electric double layer and the ion concentration in the liquid (Beltzung 2004, Beltzung & Wittmann 2005).

4 COMPARISON WITH EXPERIMENTAL RESULTS

4.1 Direct observation of interaction of water with a narrow gap

In order to study the interaction of adsorbed and capillary condensed water in a narrow gap a thin quartz plate was placed on a polished quartz block as shown in Fig. 3 (Splittgerber 1971, Splittgerber & Wittmann 1974, Wittmann et al. 1971, Wittmann 1977). From the bending of the quartz plate in the dry state the van der Waals attractive force could be determined. As the relative humidity of the surrounding air has been increased, the van der Waals attractive force decreased because of adsorbed water films. Above 55% RH capillary condensed water separated the thin plate from the supporting block by disjoining pressure. From this observation it is obvious that under these conditions disjoining pressure over-compensates capillary pressure. The height of the separation gap as observed as function of RH is shown in Fig. 4. The typical hysteresis of length change isotherms is reflected by experimentally determined disjoining pressure.

4.2 Sorption and length change isotherms

Precise sorption and length change isotherms have been measured on hardened cement paste by Feldman 1968. More recently Setzer 2008 has published similar results. A typical first desorption branch followed by

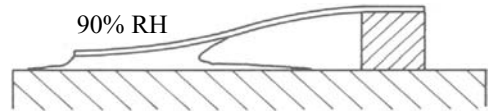


Figure 3. Experimental set up for investigating the interaction of water with a narrow gap.

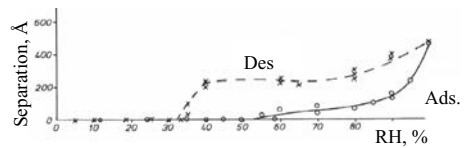


Figure 4. Height h of the separation as function of RH.

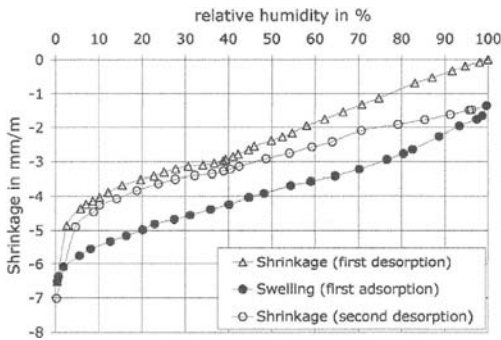


Figure 5. First and second shrinkage and intermediate swelling of hardened cement paste (Setzer 2008).

rewetting and second desorption branch is shown in Fig. 4.

As usual one recognizes a slightly convex first desorption branch between 100% and 40% RH. Between 40% and 30% RH hardly any shrinkage can be observed. The coefficient of hygral dilatation becomes nearly zero. Further drying leads again to a convex branch of shrinkage as function of RH. The adsorption branch has a marked inflection point at about 45% RH. It has been shown elsewhere that shrinkage between 45% and 0% can be predicted quantitatively by means of the Bangham equation (5) (Wittmann 1982, Weimann & Li 2003). Swelling and shrinkage in the higher humidity range can be attributed to the action of disjoining pressure (Ferraris & Wittmann 1987). We will see later that the disjoining pressure is particularly sensitive with respect to the ion concentration of the pore solution.

There are other materials with a distinct pore radius and with reduced interaction between water and the inner surface as for instance porous glass, charcoal, and activated carbon rods (Amberg & McIntosh 1952, Haines and McIntosh 1947). On these materials a pronounced contraction, which generally is attributed to capillary action, can be observed. A typical example is presented in Fig. 6.

During drying capillary action contracts these materials until the pores are emptied then an expansion is observed. Length change isotherms of hardened cement paste have never shown this characteristic behavior. More recently Schiller et al. 2008 have investigated volume changes due to variations in porous materials by means of a meso-scopic model. They came to the conclusion that capillary action may influence hygral volume changes of vycor glass but not shrinkage or swelling of cement-based materials. The striking difference between the materials on which capillary action has an influence on shrinkage and hardened cement paste is the lack or the existence of nano-pores.

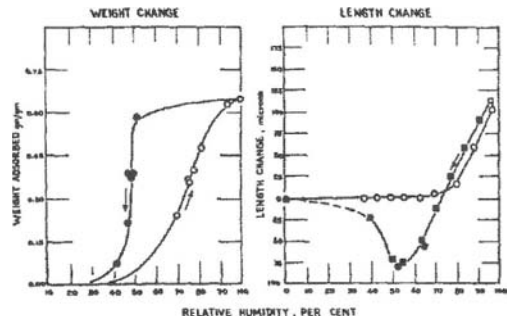


Figure 6. Sorption and length change isotherm of activated carbon (Haines & McIntosh 1947).

4.3 Capillary shrinkage of young concrete

When young concrete is placed and compacted it is usually covered by a thin water film (bleeding). Under these conditions there exists no capillary pressure in the continuous pore solution. When the water film has evaporated, menisci are formed between the small particles at the surface. The higher the cement content and the higher to content of fines, the higher will be the resulting capillary shrinkage.

Capillary pressure can be measured in the pore solution of the fresh concrete (Wittmann 1976b, Wittmann 1975). Typical results are shown in Fig. 7. In this case the surface started to dry after about one hour. As a consequence the capillary pressure increases. Simultaneously the capillary shrinkage has been measured and it can be seen, that capillary shrinkage follows closely the evolution of the capillary pressure in fresh concrete. After a certain pressure has been reached, the surface has been rewetted by spraying water on it. Capillary pressure as well as capillary shrinkage is immediately reduced until the sprayed water has been evaporated again. At this moment both capillary pressure and capillary shrinkage increase again. The surface has been rewetted in this experiment four times. Then the surface was allowed to dry continuously. As can be seen from Fig. 7, after seven hours the capillary pressure rises to very high values but the capillary shrinkage does not follow any more.

We can conclude that fresh concrete reacts like a humid soil and high capillary shrinkage can be observed, which often leads to early cracking of concrete structures. As soon as a solid skeleton is formed, however, capillary shrinkage becomes negligible.

This behavior can be explained in the following way. When the surface has dried, rearrangement of the water in the porous structure takes place. Water retreats into the narrow gaps as shown in Fig. 8. At the same time air is entrained into the young concrete. It has been shown that once the water is captured in the narrow

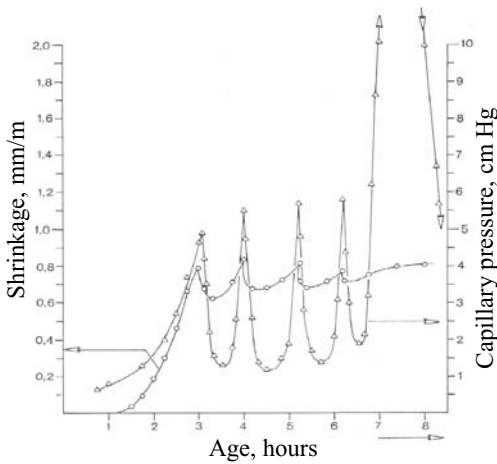


Figure 7. Evolution of capillary pressure and capillary shrinkage in young concrete during drying and rewetting.

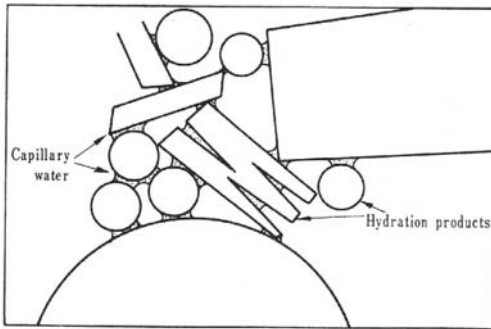


Figure 8. Narrow gaps in which capillary water retreats after rearrangement due to drying and hydration (Chujo & Kondo 1968).

gaps further drying has hardly any influence on the attractive force between two particles. The capillary pressure p increases but the surface on which it acts becomes smaller and smaller. That means the attractive force F_a between neighboring particles remains practically constant. This is a clear indication that capillary action cannot be dominant in the process of shrinkage of cement-based materials.

4.4 Shrinkage of water repellent concrete

Concrete can be made water repellent by surface impregnation with liquid silanes. Silane polymerizes in the porous material and forms a network of silicon resin on the internal surface. Silicon resin is water repellent. The effective diameter of a silane molecule

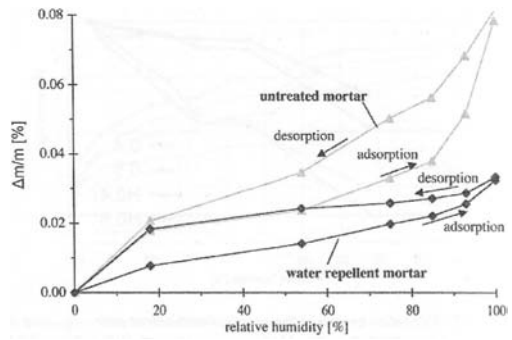


Figure 9. Sorption isotherms of untreated and water repellent mortar.

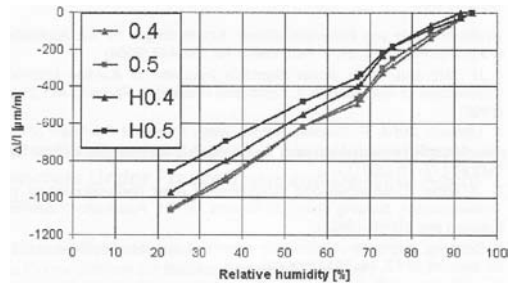


Figure 10. Shrinkage of neat mortar with $W/C = 0.4$ and 0.5 and of identical but water repellent mortar (H0.4 and H0.5).

may be estimated to be 3.5 nm. Therefore pores with a radius smaller than 5 nm cannot be made water repellent by impregnation with silane. Shrinkage of neat and water repellent mortar with $W/C = 0.4$ and 0.5 has been measured (Wittmann, Beltzung & Meier 2005). Relevant results are shown in Figs. 9 and 10. As can have been expected, the sorption isotherms differ a great deal as capillary condensation is hindered. But most important, shrinkage of neat and water repellent mortar is nearly the same. As can be seen from the sorption isotherm in the water repellent mortar there is hardly any capillary water and still strong shrinkage is observed. Therefore capillary pressure can play a marginal role among different shrinkage mechanisms only.

4.5 Influence of alkali content

Several authors have found that shrinkage of concrete increases with increasing alkali content. We have added different amounts of alkali (Na and K) to cement

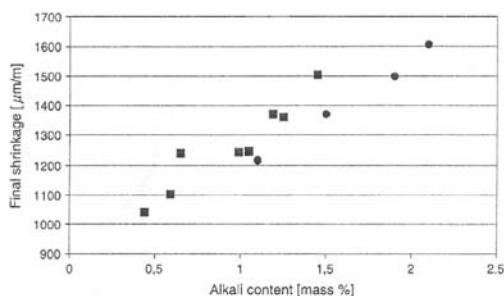


Figure 11. Final shrinkage of cement mortar as function of alkali content.

mortars (Beltzung & Wittmann 2005). Then shrinkage has been measured. Results are shown in Fig. 11. As can be seen, shrinkage increases nearly linear with increasing alkali content. The surface tension of the pore solution has not changed but the alkali ions in an aqueous solution are surrounded by hydration shells so they are at the origin of a strong component of the disjoining pressure. In contrast, if the surface tension is changed significantly, shrinkage remains practically the same (Beltzung 2004).

5 CONCLUSIONS

Based on the results presented above we may summarize essential conclusions in formulating obvious but widespread heresies.

Heresy No. 1: Shrinkage can be measured by following the volume or length change of drying elements.

In reality we observe the complex response of a specimen imposed by drying. Shrinkage as a material property has to be determined by inverse analysis. Then a direct link with underlying physical mechanisms becomes possible.

Heresy No. 2: Capillary pressure is at the origin of hygral shrinkage.

In young concrete high capillary pressure can be observed without any noticeable shrinkage and in concrete without capillary water shrinkage is nearly the same as in concrete with capillary water. Disjoining pressure over-compensates in cement-based materials the influence of capillary pressure.

Heresy No. 3: Shrinkage can be reduced significantly by lowering the surface tension of the pore solution.

Experimental results show, however, that a significant reduction of the surface tension has hardly any influence on shrinkage.

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KEYNOTE LECTURE

Can nano-models lead to improved concrete? Materials science as the intersection of chemistry and mechanics

H.M. Jennings

Civil and Environmental Engineering, Materials Science and Engineering Northwestern University, Evanston, Illinois, USA

J.J. Thomas & I. Vlahinić

Civil and Environmental Engineering, Northwestern University, Evanston, Illinois, USA

ABSTRACT: The highly successful materials science paradigm uses a detailed understanding of the relationships between processing and microstructure, and between micro structure and properties, to design and improve materials. In the case of cement-based materials, processing is controlled by formulation and curing conditions, while most of the key properties are well-defined by mechanics. These are known to be linked by the nanostructure, but a quantitative understanding of nanostructure that would enable a materials science approach to concrete is still lacking. This can be attributed to the complexity of the main hydration product in cement paste, the calcium-silicate-hydrate (C-S-H) gel, which forms with an internal nanopore system that dominates the properties but is difficult to analyze and model. This paper reviews strategies for quantitatively describing the nanostructure of cement paste such that it can be used as input to mechanics models that will be more flexible and reliable than present models. It also illustrates how changes to the nanostructure have a corresponding influence on the complex properties of creep and shrinkage. A key thesis of this paper is that the nanostructure of C-S-H gel is granular, or particulate. The strategy of applying specific concepts related to nanogranular or colloidal materials to cement-based materials holds significant promise for linking processing and properties according to the precepts of materials science.

1 INTRODUCTION

Materials science is a relatively new field of study at the boundary of two disciplines, applied mechanics and chemistry, focusing on relations between the mechanical behavior of materials and their microstructures. Cement chemistry is a mature field that is concerned with the mechanisms that control the rate of reaction between cement minerals and water, the composition and distribution of hydration products, and the resulting properties of the hardened paste over time. There is an associated massive literature, much of which predates the field of materials science, yet the goals of relating processing to microstructure, and microstructure to properties, are clearly those of materials science.

Contemporary research related to cement based materials incorporates advanced mechanics topics including multiscale modeling and poro and chemo mechanics. However, relationships that directly connect measurable features in the microstructure to

properties are lacking. In metals, as an example of materials science, the famous Hall-Petch relationship relates grain size, d , to yield stress according to:

$$\sigma_v = \sigma_i + kd^{-1/2} \quad (1)$$

where σ_i is the yield stress of a single crystal. This is an important, albeit simple, relationship in part because the dependent variable (grain size) is directly measurable. The problem for cement science is that the microstructure has not been quantitatively evaluated in a way that provides direct, easily measurable inputs to models. The difficulty in doing this is illustrated by Fig. 1, which is a backscattered electron micrograph of a neat C_3S paste. The black phase is porosity and the intermediate gray phase is C-S-H, which itself contains nanopores too small to be seen at this magnification. The critical issue is how to capture the distribution in size and space of each of the phases such that they can be used as input into mathematical formulations of properties based on mechanics. With the

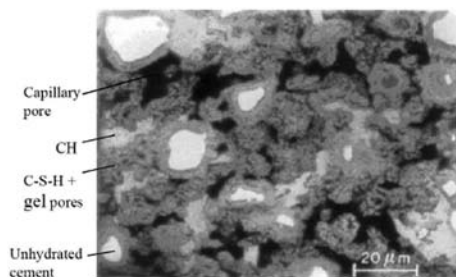


Figure 1. Micrograph of C_3S paste, $w/c = 0.5$, 28 days old. While some of the larger “capillary” pores are easily identified, the smaller pores, sometimes referred to as gel pores, are intermixed with C-S-H. These latter pores, and their associated surfaces, control properties such as creep and drying shrinkage, but they have eluded quantitative characterization in a way that can be related to these properties.

possible exception of relationships between the larger capillary pores and compressive strength, quantitative relationships between measurable features in the microstructure and properties such as drying shrinkage, creep, and permeability are not yet available in a form that has been generally accepted. These shortcomings can be overcome by establishing a quantitative model of the nanostructure of cement paste that provides a link between chemistry and mechanics. This paper discusses recent experimental and theoretical advances that are leading toward models of the nanostructure of C-S-H that will enable the materials science approach. Examples are given of how a model of the nanostructure is influencing the formulation of constitutive laws based on mechanics, and of how chemistry can influence the nanostructure, and in turn properties. This approach can lead to many breakthroughs.

2 QUANTITATIVE NANOSTRUCTURE FOR MECHANICS

The paradigm of materials science is that microstructure provides a mechanistic link between processing and properties. Microstructure thus becomes both a design and an evaluation tool. A nanostructure model is discussed here that is designed to predict elastic, as well as creep and shrinkage properties. This approach was started by Powers and Brownayard (1948) with their extensive evaluation of micro and nano structure and associated attempts to explain creep and shrinkage of concrete. Powers’ model was sophisticated, granular in nature, and provided a platform for predicting properties, but by his own detailed comparison to measurements, the model did not predict all properties successfully (Powers 1968). This model was

soon followed by the “Canada model,” first introduced by Feldman and Sereda (1964), which treated C-S-H as a continuous material that deforms by changing the structure of the interlayer spaces. Recently, starting with concepts rooted in both of these schools of thought, a series of papers (Jennings 2000; Jennings et al. 2007; Jennings 2008a; Jennings et al. 2008) has described a model of the nanostructure of C-S-H, now referred to as the colloid model, or CM-II. A schematic of information incorporated into, and output from the model is shown in Fig. 2. This is an evolving model which is presented here as a strategy for research and not as a finished work.

This paper describes progress in the area of modeling the microstructures of increasingly complex formulations of cement based materials which serve as links between processing on the one hand and properties on the other, as shown in Fig. 3.

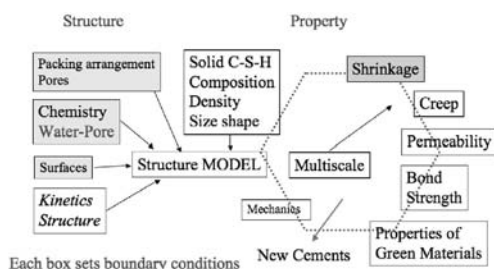


Figure 2. Conceptual illustration of the development and scope of the colloid model of C-S-H gel now known as CM-II (Jennings 2008). The first version of the model reconciled densities and surface areas of C-S-H as determined from sorption of various gases, small-angle neutron scattering, and other techniques. The model was refined by comparing the model to predictions of elastic properties obtained from nanoindentation. The model is presently being refined to incorporate kinetics of reaction and viscous properties.

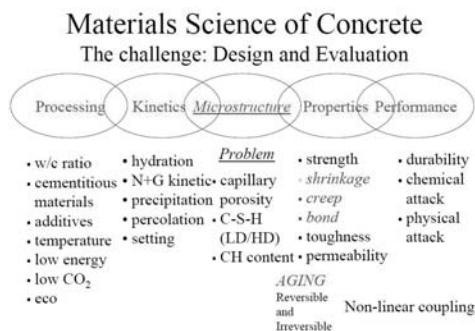


Figure 3. The materials science paradigm, as it applies to cement based materials. Microstructure includes both physical distribution of solids and chemical description of surfaces and liquid.

As described recently in a review of pores and surfaces in cement based materials (Jennings et al. 2008), a critical and under-researched aspect of microstructure is the quantitative description of the changes that occur during deformation, reversible and irreversible, primarily due to drying and loading, as well as the combined effects of both. Only with this quantitative description will it be possible to develop detailed models of properties for the broad spectrum of materials in the near future.

2.1 Particle vs. continuous nanostructure

One of the longest standing debates in the cement literature concerns the basic structure of C-S-H at the nanoscale. On the one hand, Powers and his colleagues argued that the specific surface area of C-S-H was accurately measured using water adsorption, a method that gives extremely high values, on the order of 300 m²/g of C-S-H. They argued that this very high surface area implies that C-S-H is composed of small particles and is granular (particulate) at the nanoscale. The Canada model proposes a continuous layered structure for C-S-H with gel pores existing where adjacent layers match imperfectly. Its proponents noted that the surface area as measured by nitrogen produces a well behaved isotherm that results in a much lower surface area, between 20–100 m²/g, a value strongly dependent on the method used to dry the sample before the measurement. The Canada model emphasizes the importance of interlayer spaces between the sheets of C-S-H, arguing that the high surface areas obtained from water sorption resulted from water reentering these interlayer spaces.

The CM-II model incorporates features of both of these earlier models, as it is based on solid building block particles of C-S-H that are layered in their interior. In this way the surface areas measured by both water vapor and nitrogen sorption can be rationalized, along with much other historical data. Quite recently, Allen et al. (2007) measured accurately for the first time the size, density, and composition of these basic solid particles. Using small angle neutron scattering measurements that take advantage of the large scattering isotope effect when hydrogen is replaced with deuterium, the chemical formula (CaO_{1.7}–SiO₂–H₂O_{1.80}) and mass density (2604 kg/m³) of the solid C-S-H nanoparticles that form in normal portland cement paste and also in pure C3S paste were determined. These values include water contained in the interlayer spaces of the particles in their natural saturated condition, but exclude all liquid and adsorbed water on the surface of the particles, a boundary that is illustrated by the black lines in Fig. 4.

Taking these values as a well-established fixed point, a detailed model of the water isotherm (incorporated into the CM-II model) has finally resolved

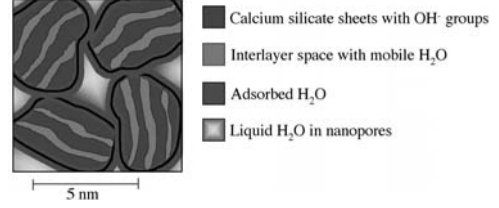


Figure 4. Schematic of the layered C-S-H particles used to interpret the density and composition values (see text) determined from neutron scattering experiments, adapted from Allen et al. (2007). The measured values include all water and solid material contained within the black lines around the surface of the particles.

controversial measurements of density vs. water content of C-S-H published in the 1970's (Feldman and Sereda 1968; Feldman 1973). The core of this argument is shown in Fig. 5.

The density of the globule is modeled as follows. Water contained in different types of spaces has a unique effect on the measured C-S-H density (Jennings 2008a; Jennings 2008b). If f_H is volume fraction of water in either the interlayer space or on the outside surface (both of which expand the volume of solid) the density of the particle is:

$$\rho_{CSH+H} = \rho_{CSH} - (f_H(\rho_{CSH} - \rho_H)) \quad (2)$$

where ρ_{CSH+H} is the density of C-S-H including any water on the surface or in the interlayer space and ρ_{CSH} is the density of C-S-H without any surface or interlayer evaporable water, and ρ_H is the density of water. Note that since the term in parenthesis is always positive (water is always less dense than C-S-H), the addition of water into either of these sites always decreases the overall density of the particle. As water is removed the associated volume is removed and not included in the overall density.

On the other hand, if water is added to a preexisting internal pore, the density of the particle is given by

$$\rho_{CSH+H} = \rho_{CSH} + f_H \rho_H \quad (3)$$

The measured density must always increase as internal pores are filled with water, since the mass increases with no increase in volume. Thus any pore, regardless of its size or shape, can be assigned a volume and free surface with specific thermodynamic characteristics. Various possible densities for C-S-H are described in CM-II with the conclusion that the observed hysteresis at relative humidities (rh) less than 50% are accounted for quantitatively. In other words, removal of water down to 50% rh simply involves the removal of water from outside the particles leaving several layers of water. This involves normal evaporation from

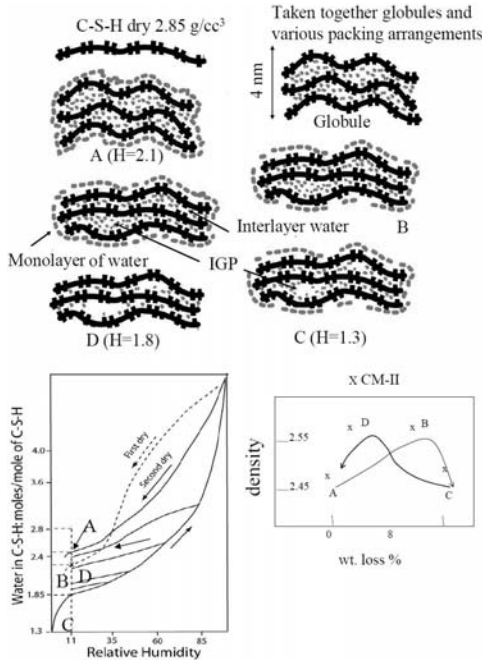


Figure 5. Top: Schematic of the C-S-H nanoparticles according to the CM-II model, showing water content associated with various drying states. Bottom: Water vapor isotherm (left) and density measured by He inflow experiments (Feldman and Sereda 1968; Feldman 1973) (right), as a function of drying. The four points A-D on the lower diagrams are depicted at the water content in moles of water per mole of C-S-H specified on the top schematic. The predicted density at each water content are indicated by points x, plotted against water removed with reference to water content at 11% rh (adapted from Jennings (2008)).

the capillary and gel pores, which is the fundamental basis for models of drying shrinkage.

2.2 Particle packing

Particles with a characteristic size close to 5 nm are central to modeling density and water content below 11% rh. The density and surface area at a coarser scale was modeled by packing these particles into two arrangements, known as high density (HD) C-S-H and low density (LD) C-S-H (Jennings 2000; Tennis and Jennings 2000). Depicting the particles as roughly spherical (the shape may not be that important to mechanical properties (Ulm and Jennings 2008) the major features of the two packing densities are shown in Fig. 6.

The average pore volume of LD and HD expressed in percent, 37 and 24, excludes the smallest water filled spaces within the particles, the interglobular

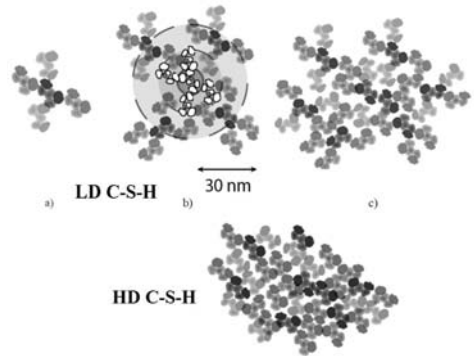


Figure 6. Proposed formation of C-S-H gel, after Jennings (2007). a) One relatively small volume fractal region, formed from contacting 5 nm particles of C-S-H. b) The same volume fractal region (shown in white) has grown into a larger, self-similar structure with a reduced packing density. c) Adjacent fractal regions have grown into each other to form a relatively uniform structure with a range of gel pore sizes. The largest pores are greater than 10 nm across. Upon drying these pores collapse to form a structure with a packing density of about 0.64. The fractal structure of LD C-S-H is depicted at scales between 5 and 100 nm. The volume fraction of pore in LD is on average 37% and the surface area as measured by nitrogen sorption, or SANS, is the surface area exposed to the pores greater than a few nm. The HD structure contains on average 24% porosity and, as measured by nitrogen or SANS, has essentially no surface area. Cement paste contains a mixture of these two structures, and the higher the measured surface area by N₂ the greater the percentage of LD.

pores, and the interlayer spaces. Surface area as measured by sorption, especially nitrogen, and SANS is directly related to the amount of LD present as these techniques are not sensitive to structure contained within the tightly packed HD C-S-H. Thus high water/cement can be correlated with high surface area and therefore a high percentage of LD. This important point is referred to in Section 4.5. Sorption experiments with different gases (Mikhail and Selim 1966) show that both surface area and density are inversely related to molecular size (equivalent to length scale). This suggests that LD C-S-H particles are packed together into a fractal structure, and SANS measurements (e.g. Allen et al. 1987) also give more direct evidence of a fractal nanostructure.

The LD and HD structures can be loosely associated with outer and inner product, but because the location of HD C-S-H is not always exclusively in the space originally occupied by the cement grains, and LD not exclusively in the original water filled space, especially when mineral admixtures are present, the terms LD and HD are preferred here. The neck between two adjacent HD regions is also HD, as shown in Fig. 7. Jennings et al. (1981) argued that the morphology, now

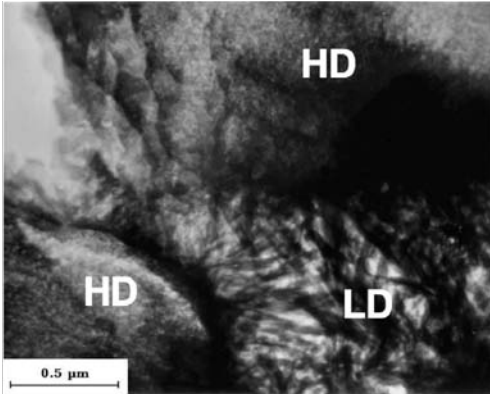


Figure 7. A transmission electron micrograph (Jennings et al. 1981) of a mature C_3S paste, showing LD and HD product.

LD and HD, is a function of the space available for the product to form.

Several important recent results show that the nanostructure is granular (synonymous with colloidal), and, at the atomic scale, has a layered structure. Evidence for the granular structure comes from comparing the behavior of C-S-H to both colloids on the chemistry side and granular (often geotechnical) materials on the mechanics side. The fundamental nanogranular nature of C-S-H on the basis of mechanics has been discussed extensively recently (Constantinides and Ulm 2007; Jennings 2008a). Elastic properties are best described by the self-consistent scheme, as shown in Fig. 8, which is thought to be an indication of granular structure.

2.3 Colloid chemistry

Many concepts of the structure and properties of gels, and how they may be applied to cement based materials, were summarized in a review by Scherer (1999). From this point of view, C-S-H is a colloidal precipitate that can rearrange with time, generally leading to a denser structure. Many of the chemical and physical changes known to occur in gels have also been observed in cements. Notably, the volume of solid and the contained pores shrinks during precipitation, which is often accompanied by polymerization of the silicates as the number of interparticle contacts increases. The results shown in Fig. 9 (adapted from data in Thomas and Jennings 2002) broadly support the possibility that C-S-H is best described as a colloid. The results also suggest that deformation is the result of rearrangement of the colloid particles, and, like other colloids, this rearrangement can be accelerated by heat. In this case the heat causes the particles to rearrange but without the stress e.g. caused by capillary

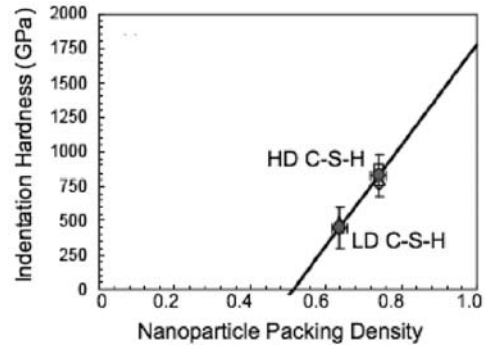


Figure 8. Values of the indentation hardness for LD and HD C-S-H obtained from nanoindentation, along with the micromechanical prediction for an aggregation of particles based on the self-consistent scheme, versus the packing fraction of the particles. The predicted percolation threshold at 50% packing is consistent with a granular material (after Constantinides and Ulm 2007; Ulm and Jennings 2008).

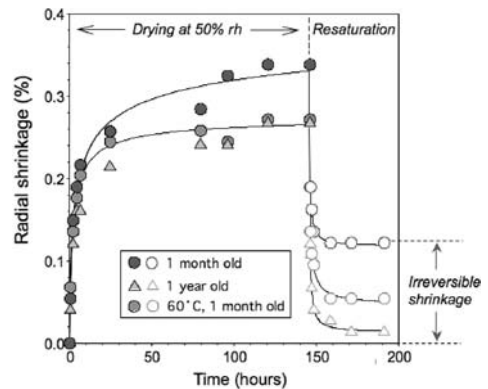


Figure 9. Effect of heating on drying shrinkage, after Thomas and Jennings (2002). Data are for pastes hydrated for 1 month and 1 year at room temperature, and for 1 month at room temperature followed by 24 hrs at 60°C. The large reduction in irreversible shrinkage that results from long term aging between 1 month and 1 year is largely reproduced by just 1 day at 60°C.

forces or external load (which force many particles to rearrange) the C-S-H densifies without causing bulk shrinkage. In other words, heat accelerates aging of the gel.

Fig. 10 shows some results acquired by a deformation mapping technique (DMT) that uses image analysis to determine the deformations that occur in the microstructure (Neubauer et al. 2000), in this case as the result of drying from 85% rh down to 50% rh (Neubauer and Jennings 2000). Two digital images of the same location are required for each analysis,

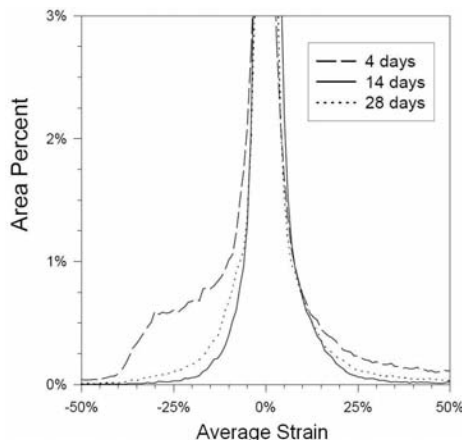


Figure 10. Histogram of the strain magnitudes calculated for the individual pixels of two images of cement paste taken before and after drying from 85% rh to 50% rh (see text). Note the large compressive and tensile strain values in some pixels corresponding to large local deformations in the microstructure.

one for the reference state and one for the deformed state. Once the locations of the corresponding pixel pairs are determined, DMT employs an algorithm that “pulls” the center of each pixel in the micrograph of the deformed material over the reference micrograph such that the deformed image shadows exactly its reference counterpart. This allows the displacements of the nodes of quadrilateral finite elements to be calculated; the elements are formed by discretizing the image according to the locations of the pixels. At this time, any number of finite strain or deformation measurements could be reported. The data displayed in Fig. 10 is a histogram plot of local average strain values in the pixels.

As expected, a macroscopic strain average, i.e. the integration of all the rarefactions (expanding pixels) and compactions (shrinking pixels) across the image, shows that the bulk shrinkage strains are of same magnitude as those measured experimentally (Neubauer and Jennings 2000). What is surprising is that the magnitude of the strains locally is much greater than can be associated with an elastic continuous material, particularly for the compactions. The issue then is how to explain the large magnitude of the local shrinkage, which is an unphysical result if C-S-H is envisioned as a continuous porous matrix. However, when C-S-H is modeled as a collection of colloidal particles that can undergo significant local rearrangement in response to applied stress, the large local deformations are an expected result. This important observation influenced the original development of the colloid model of C-S-H.

Currently, one of the most important and active areas of cement research is understanding the mechanisms that govern the creep and shrinkage of cement paste. Viewing C-S-H as a colloidal, or nanogranular, material is so intellectually rich, in terms of how to structure experiments and associated models, that it offers an avenue to major progress in understanding many properties of cement and concrete, in particular the mechanisms of shrinkage and creep.

3 MODELS OF SHRINKAGE AND CREEP

As was briefly discussed in the last section (see Fig. 9), cement paste experiences both reversible and irreversible deformation under the influence of drying. A similar phenomenon occurs with mechanical loading, which induces both reversible (elastic) deformation and irreversible (plastic) deformation known as creep. Interestingly, when loading and drying are applied at the same time, there is nonlinear coupling such that the deformation is greater than the sum of the expected individual deformations (Pickett 1942), an observation that has defied verifiable explanation for decades.

3.1 Elastic modulus

Statistical analysis of nanoindentation measurements of cement paste (Constantinides and Ulm 2004) has shown that elastic modulus values associated with C-S-H gel are grouped around two values: 22 and 29 GPa. These values remain fixed even if the sample is heat cured (Jennings et al. 2007), a variable that is known to change the porosity. Using the observation that LD has 37% porosity and HD has 24%, and the self consistent approach to scaling, a computed elastic modulus for the globule is about 62 GPa in both cases (Constantinides and Ulm 2004). This strongly supports the idea that the only difference between HD and LD C-S-H is the packing arrangement with the building blocks being the same in both cases.

The successful prediction of modulus and hardness at different scales by the use of the self-consistent approach can be taken as support for the nanogranular nature of C-S-H. However, many aspects of the consequences of viewing C-S-H as a granular material are still under investigation.

3.2 Drying shrinkage

By modeling C-S-H as an assemblage of solid particles with known water content and mass density, the exact amount of water in the interlayer and in-traglobular pore space can be determined (see Jennings (2008a) and Fig. 5). This allows the entire water isotherm to be modeled. In particular, the low pressure (<50% rh)

hysteresis can be attributed to the removal and re-introduction of water into the interlayer spaces and intraglobular porosity.

Of importance here, (see also section 2.1), is that during evaporation from saturation down to 50% rh, there is no evidence for a change in the specific energy of evaporation (Roper 1966). This means that only capillary forces are required to account for the shrinkage throughout this relative humidity range. Below around 50% rh the air-water menisci become unstable (the tensile strength of liquid water starts to be exceeded) and capillaries break down. Within the capillary stress range (above 50% rh) shrinkage is entirely reversible after the first drying (Helmuth and Turk 1967; Verbeck and Helmuth 1968), and thus it should be possible to predict the measured deformations using the available tools of poromechanics.

A linear theory of poroelasticity is firmly rooted in the works of Biot (1941) that date back more than half a century and has long been used to model the behavior of porous media infiltrated by a single fluid. Since then, it has been extended to include three-phase porous materials, e.g. partially saturated porous materials undergoing drying. In fact, one form in particular, initiated by Bishop (1959) and deduced in simpler form by Lewis and Schrefler (1987), Hutter et al. (1999) and others, has been widely used to model deformations in geomaterials, and more recently cementitious materials as well. This classic theory yields the following prediction for the shrinkage strain, ε_{sh} , in a drying porous medium:

$$\varepsilon_{sh} = 1/3 S_w p_c [1/K_b - 1/K_s] \quad (4)$$

where S_w is the volume fraction of water in the pore space, p_c is the capillary pressure, and K_b and K_s are the drained bulk modulus of the porous medium and the bulk modulus of the solid skeleton, respectively. Because the volume fraction of water retained at a specific rh (easily determined from the measured weight loss on drying) depends on the particular pore size distribution of the material and thus on its microstructure, the shrinkage predictions based on Eq. 4 are very much material-specific.

While Eq. 4 is a great improvement over purely empirical methods that are often used to predict shrinkage strains in cement paste and concrete alike, there are significant drawbacks. Historically, experiments have shown that a plot of shrinkage strain vs. humidity yields a straight line and thus a phenomenological relationship of the form $\varepsilon_{sh} = kh$, where k is a constant and h is a relative humidity, is encountered throughout the mechanics community and design profession. Yet, when the shrinkage predictions of the classical poromechanics formulation are compared to data for cement paste (see Fig. 11, dashed line) it can be seen there is poor agreement, even at high values

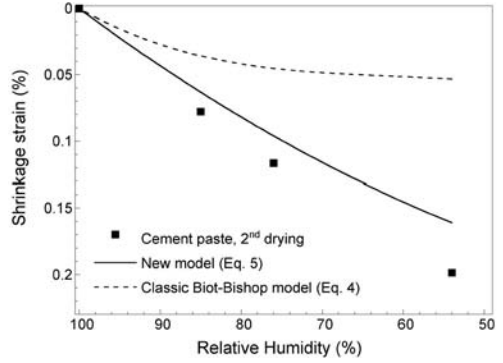


Figure 11. Drying shrinkage strains during the second (reversible) drying cycle of hardened cement paste, along with predicted values from the classic poromechanics model (Eq. 4) and the new formulation of Eq. 5.

of rh. The prediction of the classic model is highly nonlinear regardless of the values of the elastic constants K_b and K_s , as is evident from the form of Eq. 4.

Recently, a new constitutive model for a partially saturated porous media (Vlahinic et al., submitted) was derived. Physically, the key idea advanced by the model is that the pore spaces vacated by the escaping water weaken the ability of the surrounding solid skeleton to resist load. The new formulation yields the following expression for the shrinkage strain:

$$\varepsilon_{sh} = 1/3 p_c [1/K_b - 1/\bar{K}] \quad (5)$$

where $\bar{K}$ describes the effective bulk modulus of the weakened solid. Remarkably, despite the highly nonlinear form of Eq. 5, the shrinkage strain predictions appear nearly linear on a strain vs. rh graph and are able to capture the magnitude of the deformations in hardened cement paste (see Fig. 11) as well as in Vycor™ glass, a much-studied material with an elastic drying response and a pore size distribution very different from that of cement paste. These results also further reinforce the argument that capillary forces are overwhelmingly responsible for the shrinkage strains above 50% rh.

The physics of drying of cement paste becomes more complicated at relative humidities below 50%, as capillary stresses disappear and a number of new processes start to occur: 1) The last few layers of water are removed from the surfaces of solids, 2) inter-layer water is removed, and, 3) according to the CM-II model, water is removed from the intraglobular pores. The first process changes the surface energy of the solid, causing shrinkage as stress is introduced to the particles, and the second causes direct collapse

of the particles, both of which lead to particle shrinkage, and therefore to overall shrinkage. However, these processes have not been expressed mathematically in a form that allows shrinkage data in the lower humidity regime to be accurately modeled.

Without specific reference to the mechanisms above, Coussy et al. (2004) sought to quantitatively establish a link between the surface energy, i.e. the energy of the interfaces between the adjacent phases in a medium, and a macroscopic expression of the drying shrinkage strain. Supposing an open thermodynamic system of reversible nature, Coussy et al. found that changes in energy of the interfaces, in addition to any changes in energy of the solid skeleton itself, provoke the contraction of the solid skeleton during drying (or conversely the expansion during wetting). The results led the authors to propose a modification to Eq. 4. In particular, the authors argued that the term denoting the averaged pore pressure¹, $-S_w p_c$, in Eq. 4 should be replaced with the *equivalent pore pressure*, π , where,

$$\pi = -S_w p_c - \int_{S_w}^1 p_c(S) dS \quad (6)$$

The work of Coussy and coworkers is a pioneering effort in relating the macroscopic properties of cementitious materials, particularly in the intermediate range of and possibly below 50% relative humidity, to the measurable microstructural features of cementitious and other porous materials.

4 VISCOUS BEHAVIOR: CREEP, SHRINKAGE AND AGING

Historically, the mechanisms for irreversible creep and shrinkage have been expressed in mostly empirical terms, and there is little agreement in the literature. This is due in part to the complexity of the observed behavior. Both shrinkage and creep have reversible and irreversible components, and creep has an additional time-dependent component when the load is removed (creep recovery).

It is well-accepted that the irreversible deformation due to either drying or load must involve a permanent rearrangement of the structure of the C-S-H gel. There are several possibilities suggested in the literature, but none are detailed enough to explore experimentally. One of the few measurable quantities that has been

correlated with creep and shrinkage is the degree of silicate polymerization (Parrott and Young 1981), but it is not clear whether this is a cause or an effect.

Here we divide the possible driving forces for irreversible deformation into two categories: 1) internal driving forces such as reduction in energy by densification of gel structure encouraged by heat and drying, and 2) the application of external load. Both contribute to the overall aging process, which reduces the rate and magnitude of viscous flow. We further define the aging process as time-dependent changes to the hydration products after their formation; thus, in this work, aging does not include the hydration itself, a process that stiffens the paste as hydration product fills the pore space.

The colloid model of C-S-H provides a framework for an explicit description of irreversible deformation through rearrangement of the nanoscale C-S-H particles, a process for which there is direct evidence from SANS (Jennings et al. 2007; Thomas et al. 2008). In general, the particles become more tightly packed and specific pores become less numerous or smaller in size with time, a process that is accelerated by heating and drying (Jennings et al. 2007). It is hypothesized that mechanical loading has a similar effect but this is only now being explored experimentally. It was argued recently (Jennings et al. 2008) that studies of the microstructure, and now nanostructure, should focus on changes that take place during deformation, as this is the key to developing constitutive laws based on microstructure.

4.1 Changes in structure due to internal driving force

As previously mentioned, the LD C-S-H exhibits characteristics of a mass fractal structure, which forms the basis for analyzing small angle neutron scattering data (Allen et al. 1987). Application of a fractal microstructure model to the SANS data provides values for several parameters with physical meaning, including the characteristic size of the building-block particles, the surface area per unit specimen volume, the mass fractal exponent, and the correlation length. A consistent observation from SANS studies is that the size of the C-S-H particles does not change during the aging process, whether driven by heat or drying. The specific surface area and the fractal dimension also exhibit only modest changes.

The parameter that is strongly affected by aging is the correlation length, loosely defined as the maximum length scale over which the fractal scaling applies, which decreases with all types of aging. Individual fractal regions within the nanostructure approach each other, overlapping and intertwining. This process lowers the correlation length as it increases the average packing density, allowing the

¹ The expression for averaged pore pressure, i.e. $p_{avg} = S_w p_w + (1 - S_w) p_a = -S_w p_c + p_a$ with $p_c = p_a - p_w$, reduces to $p_{avg} = -S_w p_c$ when the influence of the air/gas phase is assumed inconsequential.

packing density to eventually approach a random-jammed value of 0.64 associated with LD C-S-H. It follows that the gel pores associated with the larger interparticle spaces between or within the fractal regions are reduced in number and average size by this process.

4.2 Evaluating nanoporosity by equilibrium drying

A simple yet powerful method of characterizing the gel pore system of cement paste is to measure the weight loss of a specimen as it is subjected to step-wise drying to progressively lower rh values. Since the size of the pores that are emptied decreases as the rh decreases, this method provides a measure of nanopore volumes in different size ranges. This “equilibrium drying” measurement was first performed by Roper (1966), and we have performed it recently on specimens cured in different ways (Gevrenov 2005; Jennings et al. 2007). Based on this data, the primary change associated with aging is a reduction in the volume of pores with diameters between about 5 and 15 nm, which are some of the gel pores in the LD C-S-H (see Fig. 12). This is accompanied by an increase in the number of interparticle contacts (Jennings 2004), which could explain the increase in degree of silicate polymerization and associated interparticle bonding.

The dramatic drop in pores in the size range 5–15 nm caused by initial drying and by heat curing is consistent with the reduction in correlation length as fractal regions approach each other. The reduction in porosity in this size range is the result of rearrangement of regions of particles and is here proposed as an important physical manifestation of the aging

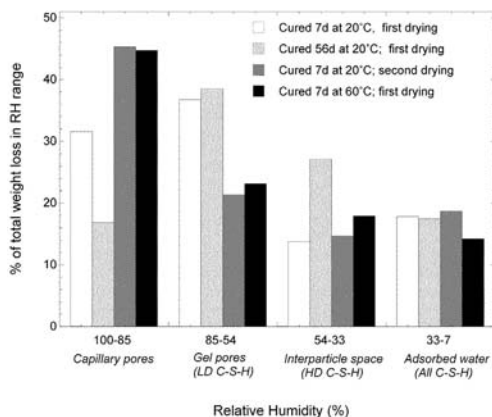


Figure 12. Weight loss on drying to different rh values, which can be associated with specific pore size regimes in the C-S-H gel structure (see axis labels—the pores that empty between 85–54% rh are very approximately between 15–5 nm across).

process. It is entirely possible that these pores decrease with time, drying, and other variables according to a decay function such as the aging term in the constitutive equations proposed by Bažant et al. (1997). Indeed the logarithmic-type creep response encountered in cement-based materials is consistent with the creep behavior of granular materials (Lambe and Whitman 1969) And if the pores in this size range are directly related to aging then equilibrium drying provides a way to probe the nanostructure directly to evaluate the aging process. This may open the door to evaluating the influence of chemicals and other processing variables on the nanopore system and the aging process in general, and could lead to new ways of controlling the nanostructure and properties.

4.3 Changes in structure due to external forces

Very little is known about the changes that occur in the nanostructure of C-S-H due to external mechanical loading. However, there is an extensive literature that suggests that the mechanisms of viscous flow are similar to the mechanisms of irreversible shrinkage outlined above. The concept of C-S-H as a nanogranular material therefore meshes well with many existing theories of creep, and opens some interesting new lines of inquiry.

One of the more intriguing possibilities comes originally from the field of discrete particle physics where Mueth et al. (1998), Hinrichsen and Wolf (2004), and others have shown that when a uniaxial load is applied to granular materials only a fraction of the grains in the assembly sustain the load. These highly-stressed grains tend to form chains or columns across the sample, while the remaining grains provide stability and prevent buckling of the load-bearing chains. Such mechanism of load resistance may also be the root cause of the non-unique relationship between porosity and modulus, as has been observed for sand (Oda 1972). Some of these ideas are incorporated into Fig. 13.

4.4 Nonlinear coupling of creep and shrinkage

The observation that the simultaneous application of load and drying results in a much greater deformation than the sum of the two when applied separately, known as the Pickett effect (Pickett 1942), has been the subject of only a couple of tentative explanations in the literature. It is well known that drying gradients can cause cracks in cement-based materials, a consequence of which is an apparent reduction in shrinkage. A compressive load could then close the cracks in addition to creeping the specimen, making the combined response appear greater than the sum of their individual parts. While this mechanism is logical and correct, its magnitude was shown to be much less than the

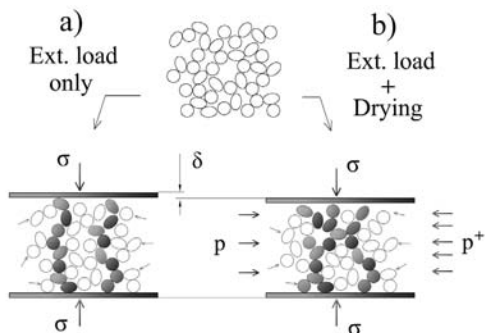


Figure 13. Grain assembly reacting to load. a) Externally applied load is carried by columns of particles, and b) Internal forces from drying or changes in temperature generate local (pressure) gradients that cause the load-bearing columns of particles to buckle.

observed additional deformation caused by the Pickett effect (Bažant 1988). More recently, Bažant has offered the concept of micropre-stress between particles at close proximity to mathematically explain long-term aging due to drying and external loading. Microprestress is postulated to facilitate shear slip between nanoparticles, and also to decay with time gradually diminishing the viscous flow. However, microprestress cannot be measured directly as it is by definition an average macroscopic quantity and is only deduced from macroscopic data via model by Bažant and coworkers.

Here we propose a possible new physical interpretation of the Pickett effect, albeit only a qualitative one at present. In this regard, we note that drying experiments of hardened cement paste have established that the time necessary to achieve near-equilibrium at a specific relative humidity is very long even for small samples. This indicates that diffusion of water out of the gel pores is very slow. Gel pores, therefore, present ideal locations for the development of local pressure gradients during drying, as described by Scherer (1999).

The results of experiments by Bažant et al. (1976) further highlight the importance of gradients in the aging process. The authors measured the creep and drying response of hollow cement paste cylinders with extremely small wall thickness (<1 mm). The thin samples were cast using a novel technique that exploited the differences in the thermal contraction of outer and inner mold surfaces (Bažant et al. 1973). Even for such small wall thicknesses, a nearly uniform moisture equilibrium with the environment was estimated to take slightly less than one day. What Bažant and coworkers noticed, among other observations, is that while drying greatly accelerated the rate of creep,

the creep rate returned to normal within a day, i.e. once the moisture equilibrium with the environment was established. Moreover, the same pattern of behavior was measured during rewetting of the specimens. These observations suggest that not only is the Pickett effect independent of the direction of water movement, i.e. wetting or drying, but that the presence of local pressure gradients, or non-equilibrium, is also a prerequisite for the Pickett effect.

That granular materials resist axial loads by forming columns of highly-stressed grains was discussed in the previous section. The addition of a gradient across such load-bearing columns, caused by a change in humidity or temperature, can upset the local stability and thus contribute to buckling of the columns that carry the load (see Fig. 13). Naturally, such mechanism would be independent of the direction of the gradient and would also be influenced by the magnitude of the rate of drying. The latter also agrees well with the concept of stress-induced shrinkage (Bažant and Chern 1985) and its subsequent refinement, known as micro-prestress theory (Bažant et al. 1997). Both theories were able to quantitatively capture the Pickett effect by including a flow element whose viscosity depends on the time rate of relative humidity, and thus on the rate of drying, in their mathematical description.

Moreover, the effect of temperature change on the microstructure of cement paste may be very similar to that of drying. As indicated by Scherer (1999), the thermal coefficient of water is nearly thirty times greater than that of cement. Thus a faster expanding liquid, if constrained in the pore network with low permeability such as that of gel pores, gives rise to local pressure gradients. Curiously, it is also well-understood that temperature couples with external load in non-linear fashion (transitional thermal creep). Therefore, a view of nanostructure as granular has not only the potential to explain the mechanisms that have escaped explanation for decades, but also to unify the influence of seemingly different effects under a common roof.

4.5 Control of nanostructure

We have observed that LD C-S-H forms primarily during the nucleation and growth stage of cement hydration (Thomas et al. 1998). We have also found ways of accelerating the early reaction rate using C-S-H as a nucleation seed, which also increases the amount of LD C-S-H. This has led to the beginnings of an ability to “control” the nanostructure, and has also led to some counterintuitive observations which can be reconciled by the material science approach described in this paper. For example, consider the response to drying of two cement pastes of the same age (14 days) and water-cement ratio (0.5) but one made with C-S-H

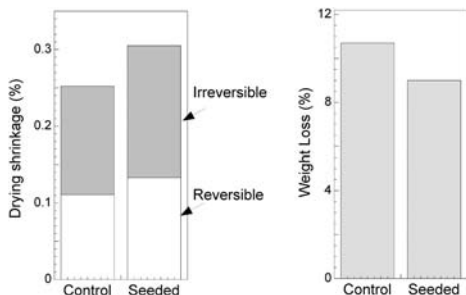


Figure 14. Effect of seeding a cement paste with C-S-H on drying shrinkage behavior. Both specimens were 14 days old at the time of drying and were dried to 76% rh. The larger drying shrinkage and smaller weight loss of the seeded paste is interpreted as a greater amount of LD C-S-H.

seed. As shown in Fig. 14, on drying to 76% rh, the sample with the seed has more shrinkage, but less weight loss.

This counter-intuitive observation can be explained using a poroelastic theory that suggests two opposing influences on strain²: the increased stiffness (bulk modulus) reduces the strain while the increased degree of saturation at a given pressure augments the strain. Since both samples are equally stiff and are dried to the same rh, such that the remaining pore water is under the same capillary pressure, the differences in their shrinkage strains stem from the increased amount of LD C-S-H in the seeded sample, which results in an increased degree of saturation, S_w , of the pore network (i.e. less weight loss).

Another interesting observation is that the sample with the greater amount of LD C-S-H has the greater irreversible component of shrinkage. As discussed earlier, the irreversible strain component on drying is largely the result of the collapse of pores in the approximate size range of 5–15 nm, which are associated with the internal structure of LD C-S-H. These examples show that quantitative micro structure property relationships have the potential of being generalized.

5 SUMMARY

The paradigm of materials science can be applied to concrete, with the potential of improving properties. The core of this approach is to apply nanogranular or colloid concepts to the structure of C-S-H. This establishes solid links between processing and structure and

between structure and properties that can employ all of the advanced tools of chemistry and mechanics. The advantage of using a colloid model is that specific measurable parameters can be visualized as changing as a result of aging.

Perhaps the most urgent future challenge is to establish the nanostructure of C-S-H that forms in blended cements, generally with a lower calcium/silicon ratio than in portland cement. Here the structure at the critical length scale of 5–100 nm is not clear, and it is not certain that the concept of packing particles applies. This requires intense research.

Some of the nanogranular properties discussed in this paper are governed by the granular (particulate) structure and are independent of the size of the particles, while others depend on the colloidal (nanoscale) size of the individual particles. It is useful to list some of the characteristics unique to granular or colloidal materials:

- They can exhibit very large volume change on drying without changing the particles.
- Strength and modulus may not have a unique dependence on the overall porosity, but can depend on packing arrangement.
- The mechanism for creep and shrinkage is sliding at particle contacts and the movement of particles into empty spaces.
- The changes in surface area and volume on drying can depend on the rate of drying.
- An externally applied load can be carried by a relatively small number of particles, forming chains or columns.
- Colloids tend to strengthen with time due to aging processes.

These and other characteristics of granular/colloid materials provide a fertile framework for studying cement-based materials. This approach has already facilitated a reinterpretation and deeper understanding of a large amount of data in the literature and it shows every sign of structuring experiments and theory to make more progress in the future.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation under grant CMS 0409571.

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² Both the classic Eq. 4 and more recently proposed Eq. 5 exhibit the same trend in this regard, although the two are clearly different in terms of the magnitude of their predictions.

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Quantitative microstructural characterisation of cement paste submitted to different moderate temperature and loading conditions

M. Ben Haha, P. Le Bescop & B. Bary

Commissariat à l'énergie atomique Saclay, Gif/Yvette, France

E. Gallucci & K. Scrivener

Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

ABSTRACT: The temperature is known to influence the strength and durability of concrete. Temperature has also a great influence on the creep of cementitious materials. Previous investigations have not provided a complete understanding of these effects; in particular, no quantitative relation between microstructural and macroscopic changes has been developed. In this paper, a combination of macro and micro characterisation has been adopted to further a comprehensive and quantitative understanding of the development of the mechanical and microstructural properties under different loading conditions and moderate temperatures ($<100^{\circ}\text{C}$). Different approaches including both qualitative and quantitative microstructural analysis with SEM, EDS, XRD and TGA were used. A study on different cement pastes has been carried out, to relate microstructural properties such as degree of hydration, CSH composition, relative density and capillary porosity to macroscopic observations. The chemistry of CSH is examined with temperature. the quantity of bound water for different curing conditions was investigated.

1 INTRODUCTION

The properties of concrete can be adversely affected by hot temperatures which may create problems in mixing, placing, hardening etc. Most of these problems are related to increase of porosity during the hydration of cement.

Until now, much effort has focused on the qualitative description of the microstructural and mechanical variation with the temperature. However, how early microstructural development influences long-term properties is not clearly understood.

To explain the large influence of temperature on transport and mechanical properties of these materials, the microstructural development needs to be better understood, and quantitative analysis needs to be carried out.

A fundamental understanding of physical and chemical effects and how and to what extent the curing temperature influences them should be the foundation upon which further advancements can be made in understanding of long-term properties. Therefore, it is necessary to devise a comprehensive, holistic, and, at the same time, feasible approach for the study. Variables such as hydration time, curing temperature, W/C ratio and cement type have been studied

to give a deeper insight into the relationship between microstructure and properties. The hydration kinetics, microstructure, and mechanical behaviour have been investigated together, to attempt to provide a major contribution to knowledge for improving the current quality and for predicting the further changes in concrete performance.

The quantification of the hydration products is one the goals of this study. Cement pastes with 2 different W/C ratios are used to study the hydration products at different temperature conditions. Chemical composition of inner CSH was analyzed by EDS, X-Ray and TG.

Microstructural characterization, quantification of hydration degree and capillary porosity from back-scattered image analysis is performed. The degree of hydration from cement paste is presented, to explain the hydration mechanisms under different conditions.

Hydrated cement based materials and their interactions with their environment provide a macro and microscopic research for nanostructured materials. Clearly CSH, cement pastes and mortars, are hierarchical structures whose material properties change with changes in scale. These composites are organized. Thus, they must be studied at each scale level, i.e., at the nano-, micro- and macrostructural levels in

order to understand their intrinsic behaviour as well as to determine the appropriate design considerations for the long term behaviour of such composites.

2 MATERIALS AND TECHNIQUES

Two cement types were used in this study namely VAZ and COU. The chemical and mineral compositions were defined in different reports (Commene. J.P., 2000; Mary-Dippe. C., 1999) as well as the physical characteristics, such as density, specific surface area, the particle size distributions.

Cement paste with W/C ratio (0.40 and 0.36) of this mix was used to characterise the hydration products by different experimental techniques. The first technique adapted was the Thermal gravimetric analysis (TGA). TGA measures the loss of weight while the temperature of the substance is increased at a constant rate.

Both qualitative and quantitative characteristics of cementitious samples were detected by a SEM. Studies presented here were performed using a SEM FEI Quanta 200 coupled with EDS chemical micro-analysis using a Li/Si crystal detector from PGT. An accelerating voltage of 15kV was chosen to provide the best compromise between spatial resolution and adequate excitation of the Fe K α peak.

SEM-image analysis is based on the stereology principles that lead to the interpretation of 3D structures using their 2D sections (the 3D volume percentage is equal to the 2D surface area percentage in average).

The image is segmented according to the grey levels of the various phases that are quantified. A large number of images should be used (around 100 images) to statistically represent in a significative way the results. Even if some previous study on SEM-IA (Yang & Buenfeld, 2001) showed that the magnification chosen does not have a large influence on the results, the study of cementitious materials is more complex. Since the images are acquired in 8 bits, 256 grey level values are included in the image, ranging from 0, black (porosity) to 255, white (Anhydrous products).

The SEM-BSE images are analysed quantitatively to get volume fractions of phases in cementitious-materials, based on the principle and segmentation method reported in the literature (Ben Haha et al., 2007; Mouret et al., 2001; Scrivener, 2004). Separation of aggregate as shown by Ben Haha et al., (Ben Haha et al., 2007) is more complicated. It needs the combination of image analysis techniques such as grey-level threshold, filtering, hole filling.

A quantitative study on the hydration degree of cement (nature of hydration product) was performed. Also, capillary porosity volume was obtained. Figure 1

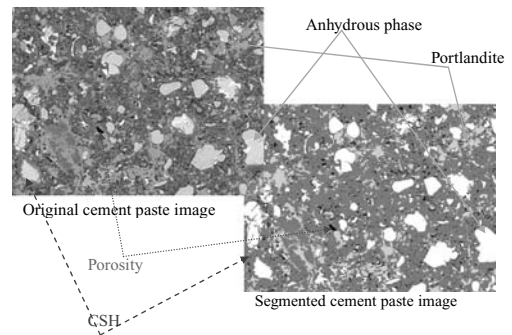


Figure 1. Segmentation of hydrated cement (VAZ) paste, W/C = 0.36.

shows a typical image of cement paste and the corresponding segmented image. The area fractions of anhydrous and aggregate are calculated by comparing their number of pixels to the total number of pixels of the image. According to the stereological principles, this area fraction corresponds to the volume fraction.

3 RESULTS ON HYDRATION PRODUCT

3.1 The combined water in CSH

With C3S paste, the polysilicate content in CSH was found to increase with both time and temperature (important parameter in this study knowing that temperature of nuclear waste disposal could reach 80°C), but decrease as the H/S ratio of CSH. One of the possible explanations of this tendency could be the basis of a condensation reaction. When cement grains are hydrated at elevated temperatures the precipitated, CSH undergoes an increased rate of silicate condensation, causing the decrease of the bound water content and thus the density of this hydration product to be higher. Cong and Kirkpatrick (Cong & Kirkpatrick, 1995) postulated that the increase in the polymerisation of synthesised CSH at elevated temperature was associated with a decrease in its inter-layer spacing.

3.2 Microstructure development

The microstructure of cement paste at 7 days is shown in Figure 2 (low magnification and high magnification). At low temperatures (20°C), the hydration process slows down: inner CSH is not observable, outer CSH has precipitated in the matrix. A few hollow shells ("Hadley" grain), formed from the complete dissolution of small cement grains, are found.

When observing 6 years old samples particularly at those stored at early age during 2 years at 85°C,

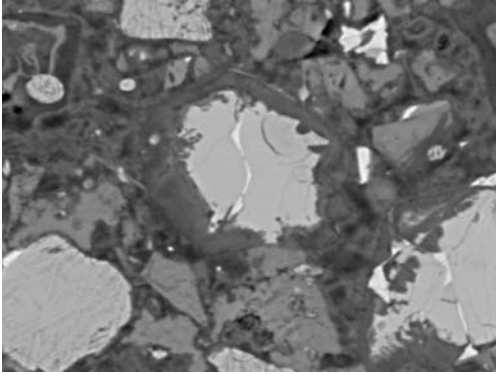


Figure 2. Microstructure of cement (VAZ) paste at 7 day at low temperatures (20°C).

a large amount of visible pores exists. The size and quantity of these pores are much higher than at 20°C, which can be clearly seen even with the images at low magnification. Therefore, high temperature favours the formation of “Hadley” grains.

Compared to 7 day, the degree of hydration at 28 days is higher (Figure 3): less anhydrous product is left and the inner CSH is much thicker. Smaller cement grains are fully reacted and only the biggest ones are left, with a surrounding inner CSH about 5–10 μm thick. The porosity was reduced by the continuous growth of CH and outer CSH products formed within initially water filled space.

A large quantity of calcium hydroxide can be observed in all temperature cases. It should be however noticed that the individual phases at 20°C are much larger. At 85°C, the quantity of visible CH in the matrix is much lower than at the other curing temperatures. The quantity is even much lower than that at 20°C at 7 days, although the degree of hydration is much higher than the latter. This is due mainly to the following reasons:

At higher temperatures, the increase in the grey level of CSH is almost non differentiable from CH phase.

The solubility of $\text{Ca}(\text{OH})_2$ decreases with temperature so at higher temperatures we expect more finer particles of CH to form.

No AFm clusters can be seen at 85°C. As confirmed by subsequent quantitative analysis, the degree of hydration is very similar at all temperatures at later ages. However, the microstructure is coarser due to the nature of the hydration products that are less homogeneously distributed in the matrix at the highest temperatures.

The free volume at low temperatures is better filled, while at higher temperature the hydration products are

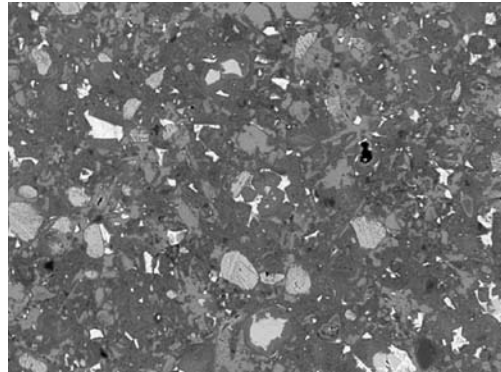
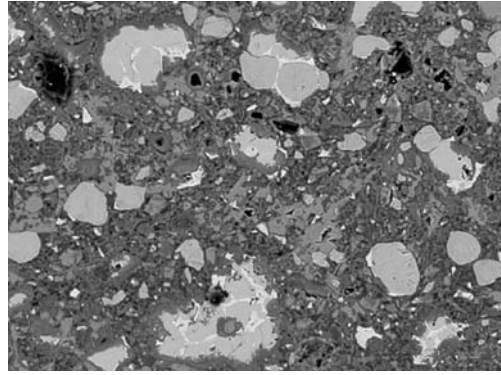


Figure 3. Microstructure development of cement (VAZ) paste at 7 and 28 days at 20°C, W/C = 0.4 (difference on porosity and development of inner CSH within the different samples).

mainly distributed around the anhydrous grains. Consequently, the quantity and size of porosity increases with temperatures. It was however reported in the literature (Famy et al., 2002) that from 7 days to older ages, the shape and size of porosity at high curing temperatures are quite similar.

For all mixes, high temperature results in the fast formation of hydration products; however, a coarser microstructure is observed at later ages. The space at lower temperatures is better filled; but at 85°C, most of the hollow shells normally formed at early ages are still empty at later ages.

3.3 Conclusion on CSH Microstructure, gel porosity and density

Temperature influences the morphology and composition of CSH. In BSE images, the rims of CSH formed around the cement grains are brighter for the pastes cured at lower temperatures (Kjellsen

et al., 1990; Kjellsen et al., 1990; Verbeck & Hel-muth, 1968). The CSH particles at 85°C are more closely packed than those at 20°C (Bentur & Berger, 1979).

A recent study (Jennings et al., 2007) indicates that the hydration of cement paste at 20°C forms a low-density CSH gel structure with a wider range of gel pore sizes and a relatively low packing fraction of solid pores. This fine structure may persist indefinitely under saturated conditions. However, for cured cement paste (85°C or greater), the structure collapses towards a denser and more stable configuration with fewer large gel pores.

The microstructural development of cementitious materials that were initially hydrated at elevated temperature and subsequently stored at ambient temperature has also been widely reported. The rims of CSH surrounding the larger cement grains are normally much thicker after heat curing than those found in pastes hydrated at normal temperature, and are brighter when observed by backscattered image. The inner CSH for this kind of storage has typically a two-tone appearance and the layer formed latter is darker than the layer formed at early ages (Famy et al., 2002; Scrivener, 1992; Taylor et al., 2001). The difference is attributed to the different nanoporosity, and therefore different densities and backscattered electron coefficient.

3.4 Conclusion on calcium hydroxide

It was reported in the literature that at elevated temperatures a greater proportion of portlandite was found to form dense clusters as opposed to the more usual lamellar-type morphology observed under ambient conditions (Kjellsen et al., 1991) With C₃S, Berger et al., (Berger & McGregor, 1973) found that the temperature increase is accompanied by an increase in the number of Ca (OH)₂ nuclei and a decrease in nucleation time and crystal size.

4 EFFECT OF TEMPERATURE ON THE DEGREE OF HYDRATION

The effect on the degree of hydration is discussed in cement paste cases since the comparison between different techniques can be made. The same features were observed for the 2 types of cement (VAZ, COU) at the 2 different W/C ratios (0.36, 0.40).

At later ages, the degree of hydration at all temperatures is very close. From a quantitative point of view, this verifies what is qualitatively observed on the micro structure: the effect of high temperature is only in the kinetics. It accelerates the hydration of the

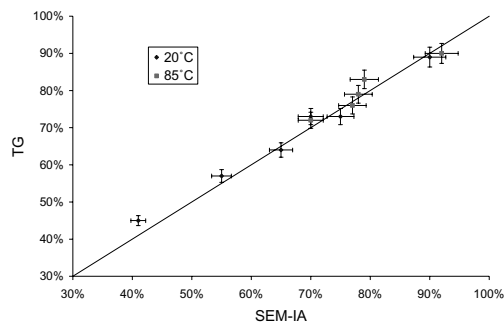


Figure 4. relationship between the degrees of hydration calculated from DTG and SEM image analysis, (VAZ), W/C = 0.4.

cement pastes at early ages, but it does not limit the degree of hydration at late ages.

The degrees of hydration from DTG analysis, calculated from the sum of percentage of the hydration products detectable from this technique, present the same trend as observable on the results obtained from SEM image analysis. Figure 4 shows the relationship between the degree of hydration calculated from DTG and SEM image analysis.

The degrees of hydration presented here are obtained via two different techniques and calculation methods. The results from DTG use the weight fraction of phases, while the one from the SEM image analysis is calculated from the volume change of anhydrous phases observable in SEM images. These two methods show very consistent results. The difference observed is within the error of the measurement. This leads to attest that the SEM image analysis technique is also reliable to quantify the degree of hydration.

5 EFFECT OF TEMPERATURE ON THE CAPILLARY POROSITY

The pores here are measured by image analysis, normalised to the volume of cement paste. The pixel resolution is 0.37 µm. Figure 5 shows the capillary porosity at several ages.

Temperature has the same impact on all mixes, i.e., at early ages, a lower porosity is expected at higher temperature because of higher degree of hydration.

Between different mixes, the capillary porosity is more affected by the W/C. As is expected, cement paste with W/C = 0.36 has lower porosity than mix2 with W/C = 0.4 even at 3 days.

At 28 days, 3 months and 6 year, more porosity is present in the cement pastes at 85°C (Figure 6).

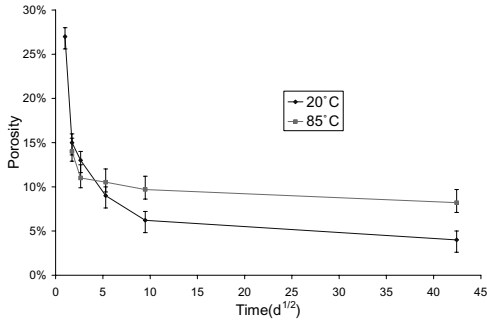


Figure 5. Capillary porosity calculated from SEM image analysis of cement (VAZ) paste at several ages, W/C = 0.4.

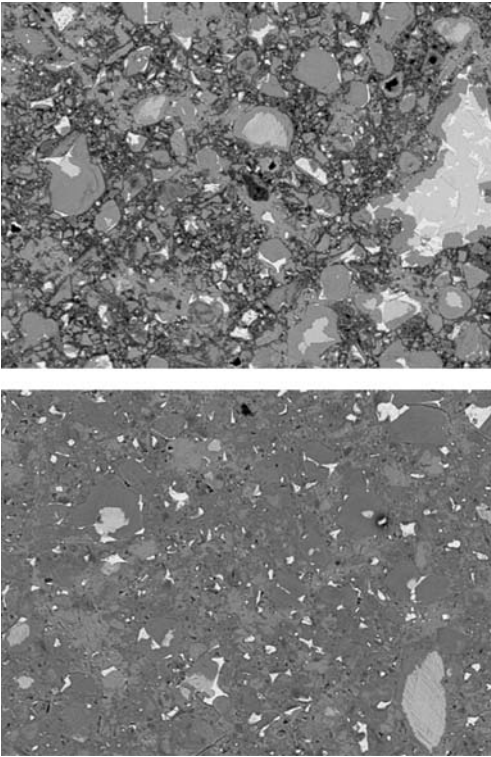


Figure 6. Micro structure development of cement paste (VAZ) at 85°C (Up) and 20°C (dawn), W/C = 0.4.

However the difference with 20°C is not so great, which could be related to the small porosity beyond the range of measurement. All cement pastes with higher W/C (W/C = 0.4) show larger quantity of porosity. However, as shown in the section before, the degree of

hydration is almost the same in different curing conditions. The only difference concerns the quantity of capillary porosity. This could be interpreted as equality between the mass of hydration products. The only change concerns the volume of hydration products that is much higher at low temperature.

To conclude, at early age, due to the higher reaction rate, cement pastes cured at 85°C show lower capillary porosity. However, an inverse trend is seen from 28 days up to 6 years. Capillary porosity is lower at 20°C. At 6 years, the porosity of the samples stored only 3 days at 85°C is close to those iso-thermally cured at 20°C. The short curing at early age with high temperatures has little influence on the capillary porosity.

6 CHEMICALLY BOUND WATER IN CSH

The chemically bound water in cement pastes can be understood as the amount of water needed for cement to react, which includes water in CSH, CH, AFm, and Aft phases (Taylor, 1997).

The complex structure of CSH makes the definition of chemically bound water arbitrary. The bound water in CSH (Taylor, 1997) includes the interlayer water in CSH and adsorbed water, but not water in micropores or in large pores.

Several different methods to determine the bound water are described in the literature (Koster & Odler, 1986) (which is defined as non evaporable water by Taylor (Taylor, 1997)). The bound water defined in different ways gives different results, but comparison can be made on the values determined from the same method. In mature OPC and C₃S pastes at 20°C, it was found to be significantly higher than in the same pastes hydrated at 90°C (Koster & Odler, 1986; Odler et al., 1987).

In CSH, usually, the H/S ratio is used to express the water content. Since the reacted Si in the C₃S and C₂S are known from SEM image analysis and it only exists in the CSH, the content of silica in CSH can be thus calculated using the mass balance of the material.

Thus, H/S molar ratio in CSH is obtained using the amount of combined water and SiO₂. The results

Table 1. Calculation of chemically bound water Data at 6 years, percentage in cement (VAZ) paste, temperature range in TG: 50–1150°C.

	20°C	85°C	Measurement
W _{CSH} (%wt)	8.53	7.79	TG and XRD
Reacted SiO ₂ (%wt)	12.89	12.59	XRD
H/S in CSH (molar ratio)	2.82	2.24	

are shown in Table 1. It should be noticed that when temperatures increase from 20 to 85°C, the chemically bound water in CSH decreases, from 2.8 to 2.2.

7 CSH RELATIVE BRIGHTNESS IN BSE MODE

In BSE images of well polished cementitious sample, several sources of grey level contrast appear. The differences are related to a dominant factor that is the atomic number contrast. For compounds, the brightness is determined by the weighted average of the backscattered coefficients of its elementary components. However, the backscattered coefficient is also affected by microporosity in a way that is not clearly understood. Thus the apparent brightness of CSH in a backscattered image is determined by the microporosity and the composition of CSH, i.e., C/S and H/S ratio.

In a first step, the relative brightness under different curing conditions is investigated. Then all factors linked to the CSH microstructural variation are checked to have a better understanding of temperature effects.

As discussed in section before, a two-tone inner CSH rim (Figure 7) has formed in cement pastes cured at high temperature for different periods. These phenomena have been reported elsewhere (Famy et al., 2002). The difference in grey level has been attributed mainly to a different nanoporosity of CSH formed at normal and elevated temperatures, the latter having a lower nanoporosity, and therefore, higher density and higher backscattered electron coefficient.

The backscattered coefficient of CSH increases when chemically bound water proportion decrease. Thus, at higher temperatures, the CSH appears to be brighter.

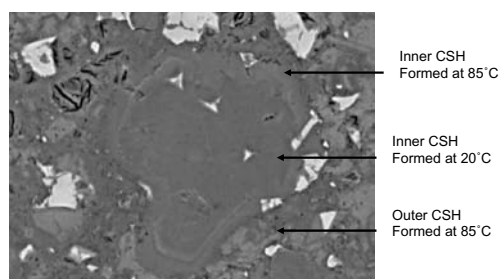


Figure 7. CSH rim formed in cement (VAZ) pastes cured at 2 different temperature (3 days at 85°C followed by 6 years at 20°C, 2 different grey levels).

8 CONCLUSION

Temperature influences the relative brightness, density, and composition of CSH.

The relative brightness of CSH in BSE images is mainly due to its composition and nanoporosity. Indeed, the Ca/(Si+Al) ratio does not almost change over the time and under different curing temperatures. The increase in relative brightness of CSH with temperature can be attributed to the increase in density and decrease in chemically bound water.

For nonisothermally cured cement pastes, a two-tone microstructure is found, which shows similar relative brightness to that isothermally cured at corresponding high temperatures and 20°C, respectively.

Temperature has a kinetically effect that allows the acceleration of the hydration. However it doesn't limit the hydration in the long term. This is probably due to the effect of the temperature on the diffusion of ions and water that dominates the hydration process. At higher temperatures, the density of CSH increases and the gel porosity decreases, but the diffusion rate of water increases that leads consequently to the continuous formation of inner CSH instead of outer CSH.

This was reflected in previous studies (Scrivener, 1992) at lower temperatures from the continuous increase in inner CSH thickness and no change in capillary porosity.

The previous study will be continued in order to determine the effect of loading and relative humidity on CSH and thus to include these parameters in the modelling. Indeed the determination of the different physical parameters that could influence the CSH viscoelastic parameters will be the most important part of future study.

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Pore and nano-structural changes in C-S-H during drying at 50°C

Y. Aono, F. Matsushita & S. Shibata

Sumitomo Metal Mining Siporex Co., Ltd, Tokyo, Japan

Y. Haina

Muroran Institute of Technology, Muroran, Japan

ABSTRACT: Changes in specific surface area of hardened cement pastes and silicate anion structures in C-S-H, subjected to drying and wetting/drying cycles, were studied by means of gas sorption and NMR to clarify the reasons of coarsening of pore structure observed with MIP after drying at 50°C. Decrease in specific surface area due to drying was observed with nitrogen adsorption, and water vapor adsorption associated with Excess Surface Work (ESW) analysis suggested a development of cohesive structure in C-S-H. NMR confirmed polymerization of silicate anion chains. The drying-induced coarsening of pore structure is probably attributed to polymerization of silicate anion chains and development of cohesive structure in C-S-H.

1 INTRODUCTION

Pore structure of hardened cement paste (HCP) is believed as a decisive factor determining properties, such as durability, of cement-based materials. Authors reported that pore structures around 100 nm of diameter of hardened cement paste (HCP) obtained by MIP were coarsened with wetting/drying cycles or drying at 50°C, while frost resistance of HCP (Aono et al. 2007, 2008). In the mean time, the true density of HCP obtained by under-water weighing increased, namely the true specific volume decreased. Change in pore structures of HCP probably connects with change in nano-structures of C-S-H, the main constituent of HCP.

Gas adsorption method is a useful technique that has been applied to nano-structural analysis of C-S-H by many authors (Powers 1947, Brunauer 1962 and Feldman 1968). Specific surface area obtained on the basis of BET method have been mainly discussed, while recently, nano-structure of C-S-H was discussed referring to the difference in BET specific surface areas obtained using nitrogen and water vapor (Odler 2003, Jennings & Thomas 2004). Bentur et al. (1979) pointed out that BET specific surface area is significantly affected by the prerequisite drying of HCP. However, because the applicable relative pressure range of the BET method is lower than 0.35, nano-structure identification of C-S-H by BET method is limited, and information based on entire relative pressure range is not available, which is nevertheless important to identify pore structure and nano-structure of C-S-H. Adolphs & Setzer (1996a, b,

1998) proposed Excess Surface Work (ESW) model capable of covering entire relative pressure range while no attempt has been made to analyze HCP subjected to drying with the ESW model.

Silicate anion chains of C-S-H are also affected by drying, while according to the review of Thomas & Jennings (2006), some different opinions have been reported regarding the polymerization of silicate anions with Trimethylsilylation (TMS) technique (Bentur et al. 1979, Parrot & Young 1981, Milestone 1980). Recently, ²⁹Si-NMR, which is more reliable than the TMS, is widely used for analysis of silicate anion structures (Grimmer 1994, Klur et al. 1998).

As mentioned above, the drying of HCP poses an impact not only on the pore structure but also on the specific surface area and polymerization of silicate anions, while systematic studies of this issue are very few. In this paper, we focused on the relationships between pore structural change in HCP, subjected to wetting/drying cycles or drying, obtained by MIP and nano-structural change in C-S-H, the major constituent of HCP, by means of ²⁹Si-NMR, H₂O and N₂ adsorption.

2 EXPERIMENTS

2.1 Specimen preparation

Specimens of HCP were same as the report of authors in this proceeding (Aono et al. 2008) or previous report (Aono et al. 2007). Curing conditions are listed in Table 1.

Table 1. Curing conditions.

Sample	W/C	Water curing	Environmental change condition
35W20	0.35	2 weeks	Water curing for 4 weeks at 20°C
35DW30		at 20°C	[Air curing for 5 days at 30°C ↔ water curing 2 days at 20°C] × 4 cycles
35DW50			[Air curing for 5 days at 50°C ↔ water curing 2 days at 20°C] × 4 cycles
35D50			Air curing for 4 weeks at 50°C

Table 2. Test methods.

Item	Method
Specific surface area	N ₂ sorption isotherm (Quantachrome NOVA1000) H ₂ O sorption isotherm (BEL Japan, BELSORP 18 PLUS-T)
Silicate anion structure	²⁹ Si-NMR MAS (Bruker, Biospin Avance 400)

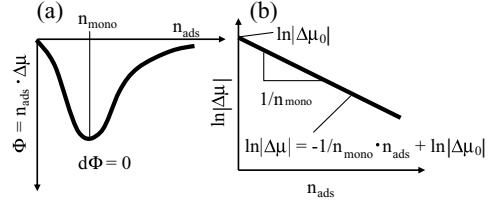
After environmental change curing, specimens were crushed into particles with a diameter of approx. 2.5 to 5 mm, treated with acetone to suspend hydration and kept under the D-dry, carbonation-free, condition until the test. Specimens for nitrogen and water vapor sorption isotherms and for NMR were finely ground in a mortar.

2.2 Test method

Test methods are summarized in Table 2.

Nitrogen sorption isotherm was determined after degassing for two hours using Quantachrome NOVA1000. Specific surface area was calculated using BET (Brunauer-Emmett-Teller) method (Brunauer et al. 1938) and pore size distribution was obtained according to DH (Dollimore-Heal) method (Dollimore & Heal 1964). A nitrogen molecular area of 0.162 nm² was adopted for the specific surface area calculation (McClellan & Harnsberger 1967).

Water vapor sorption isotherm was determined at 25°C after a prerequisite drying in vacuum at 20°C for 24 hours using Bell Japan's BELSORP P18-Plus.

Figure 1. Plots of ESW model (a): ESW (Φ) vs. amount adsorbed (b): plots of logarithm method.

Analysis was performed not only with BET method but also with the ESW model proposed by Adolphs & Setzer (1996a, b, 1998). ESW Φ is defined with the following Equations,

$$\Phi = n_{\text{ads}} \Delta\mu \quad (1)$$

$$\ln |\Delta\mu| = -\frac{1}{n_{\text{mono}}} \cdot n_{\text{ads}} + \ln |\Delta\mu_0| \quad (2)$$

where n_{ads} is the amount adsorbed and $\Delta\mu$ is a change in chemical potential defined as $\Delta\mu = RT \ln(p/p_s)$. Figure 1 shows the plots of Eqs. (1) and (2) represented with the ESW model, where a minimum is shown in Figure 1(a). ESW has a physical content of the adsorption energy of molecule per unit mass of adsorbent and shows a minimum at monolayer adsorption n_{mono} . A line with a negative gradient is shown in Figure 1(b) where the inverse of the gradient gives n_{mono} . Specific surface area can be obtained multiplying n_{mono} by the molecular area of gases. Moreover with Figure 1(b), changes in the specific surface area with an increase in n_{ads} , i.e. with changes in adsorption state at multilayer adsorption, can be discussed (Adolphs & Setzer 1998). A water molecular area of 0.114 nm² was adopted for the specific surface area calculation (Brunauer & Greenberg 1962).

NMR measurement was performed according to ²⁹Si-NMR (MAS) method at a frequency of 79.45 MHz, acquisition time of 10 seconds and number of points of 5000 using Bruker Biospin AVNCE400. The obtained spectrum was subjected to deconvolution using Gaussian/Lorentzian scheme of the dedicated software Bruker WinFit. When ²⁹Si nuclei are subjected to NMR, silicate anions (SiO₄⁴⁻) in a calcium silicate compound show Q₀ to Q₄ peaks in the spectrum representing their chain structures. In C-S-H, the major constituent of HCP, Q₁ (chain end) and Q₂ (within chain) are the major chain configuration and neither Q₃ (branching chain) nor Q₄ (networked chain) can be observed (Grimmer 1994). Klur et al (1998) separated Q₂ peaks into three types by ligand ions: Q_{2p} (H⁺ coordination), Q_{2i} (interlayer Ca²⁺ coordination) and Q_{2Ca} (CaO layer coordination), but the separation is normally difficult because

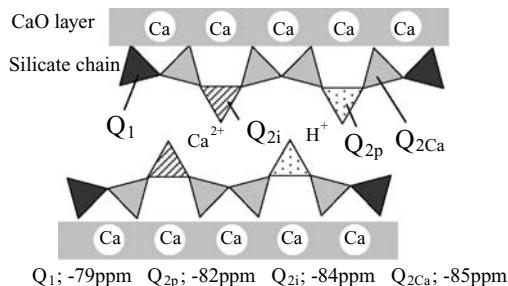


Figure 2. Schematic structure of C-S-H and assignment of Q_n (redrawn of Klur et al. 1998).

Q_{2i} peak is not intensive and overlapping with Q_{2Ca}. Figure 2 shows the schematic silicate anion structure with coordination of Q₁, Q_{2Ca} and Q_{2p}.

Because silicate anion chain of C-S-H resulting from cement hydration is a straight chain, the geometrical relation gives averaged polymerization degree N using Equation (3).

$$N = 2 \times Q_{2\text{total}}/Q_1 + 2 \quad (3)$$

where $Q_{2\text{total}} = Q_{2p} + Q_{2Ca}$ is assumed. According to the method of Parry-Jones et al. (1989), peak intensity ratio I_{Q_0} of Q_0 originated from unreacted cement is determined and the degree of cement hydration α was obtained using Equation (4).

$$\alpha = 1 - I_{O0} \quad (4)$$

3 RESULTS AND DISCUSSIONS

3.1 MIP and under-water weighing

Figure 3 shows the comparison of specific volume of pore and solid in HCP (Aono et al. 2007, 2008). With an increase in degree of drying, v_{tr} decreases and V_{Hg} increases, and $V_{total} - V_{Hg}$ decreases accordingly. This implies that the solid part of HCP shrunk with a development of cohesion and increase in large pores with a diameter greater than 8 nm.

3.2 Nitrogen adsorption

Nitrogen sorption isotherms for HCP are shown in Figure 4 where specific surface areas determined with BET method are also shown. Compared to the non-treated specimen (35W20), amount of nitrogen adsorption, hysteresis and BET (N_2) specific surface area generally decreased according to the drying condition. The decrease of hysteresis implies changes in pore structure of HCP or nano-structure of C-S-H.

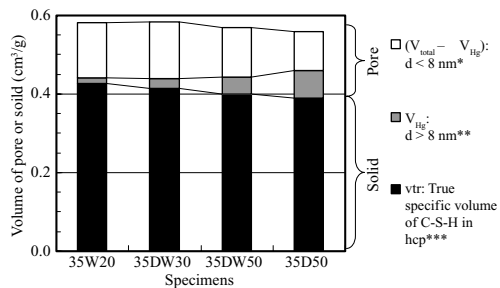


Figure 3. Comparison of specific volume of pore and solid in HCP (Aono et al. 2007, 2008).

Note: *; ($V_{\text{total}} - V_{\text{Hg}}$): Pore volume less than 8 nm in pore diameter (d). H₂O can enter, Hg can not.

**: V_{Hg} : Cumulative pore volume evaluated by MIP, more than $d = 8$ nm.

***; v_{tr} : Volume of solid (C-S-H in hcp) corresponding true specific volume.

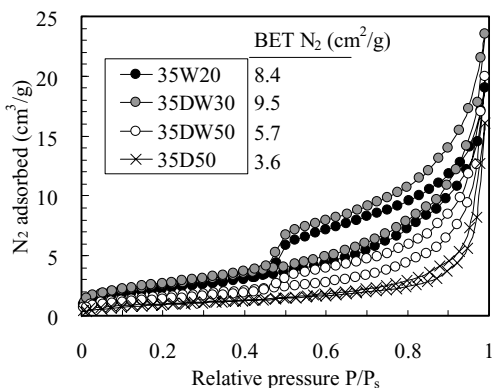


Figure 4. N₂ sorption isotherm of HCP.

Decrease in BET (N_2) surface area due to drying may be explained by the Colloid Model proposed by Jennings (2000), where unit particles, the basic building blocks with a diameter approx. 1 nm, are forming a colloidal particle, a higher-order structure called Globule. C-S-H can be classified in LD C-S-H and HD C-S-H according to the cohesive structure of Globules, where LD C-S-H allows nitrogen gas to enter while HD C-S-H does not. When C-S-H is subjected to drying, LD C-S-H becomes more cohesive and prevents nitrogen gas molecules from entering in the structure resulting in the decrease in BET (N_2) specific surface area. This implies the drying-induced densification of C-S-H and corresponds to the decrease in the true specific volume of HCP as shown in Figure 3.

Pore size distributions for HCP calculated with DH method (Dollimore & Heal, 1964) are shown

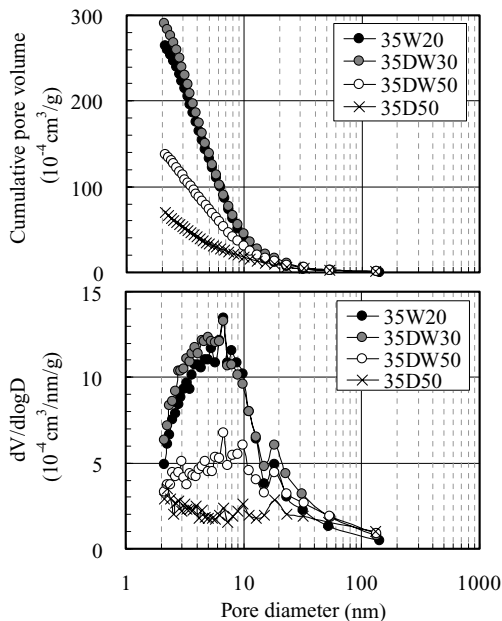


Figure 5. Pore size distribution of HCP with N_2 by DH method.

in Figure 5. Compared to the non-treated specimen (35W20), total pore volumes measured with nitrogen decrease according to the drying condition, i.e. in an order of 50 °C drying and wetting (35DW50) and 50 °C drying (35D50). A marked decrease in pore volume can be found at a pore volume with a pore diameter around 7 nm showing good agreement with the decrease in pore volume with a diameter less than 8 nm ($V_{total} - V_{Hg}$) measured with under-water weighing as shown in Figure 3.

3.3 Water vapor adsorption

Water vapor sorption isotherms of specimens are shown in Figure 6. Compared to the non-treated specimen (35W20), amount of adsorption and hysteresis decreased according to the drying condition, also BET (H_2O) specific surface areas decrease with an extent of drying. Applicable relative pressure range of BET method is limited between 0.05 and 0.35 and the resulting specific surface area is based on the monolayer adsorption, while the difference in water vapor sorption isotherms as shown in Figure 6 occur at higher relative pressure range implying that the drying-induced structural changes are represented at multilayer adsorption states.

This assumption was verified with ESW model proposed by Adolphs & Setzer (1996, 1998) using Equations (1) and (2). The results are shown in Figure 7

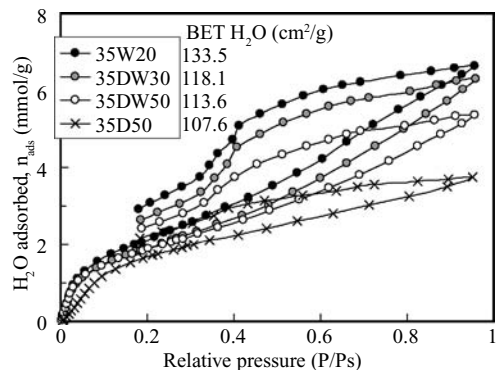


Figure 6. H_2O sorption isotherm of HCP.

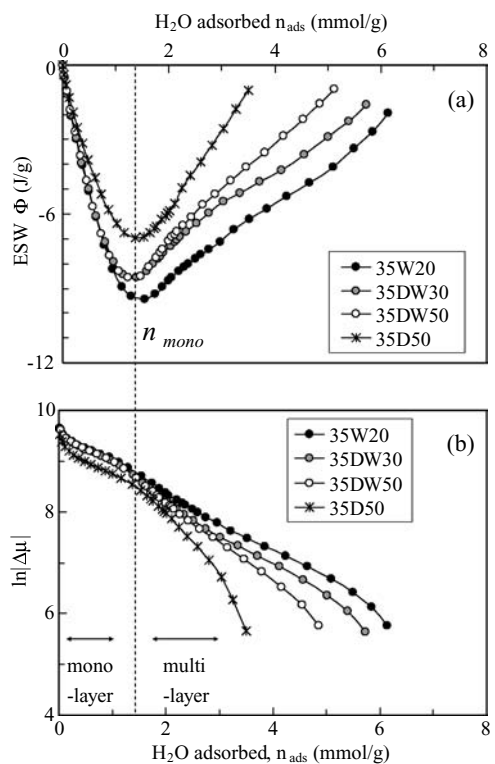


Figure 7. ESW analysis of water vapor adsorption isotherms of HCP, (a): ESW (Φ) vs. amount adsorbed (b): plots of logarithm method.

where the ESW minima at the monolayer adsorption show positive increase due to drying implying the lowering of adsorption energy at the monolayer adsorption as shown in Figure 7(a). It is also shown in Figure 7(b)

Table 3. Specific surface area.

Specimen	Nitrogen adsorption (m ² /g)	Water vapor adsorption (m ² /g)		
	BET BET N ₂	BET BET H ₂ O	ESW S1 H ₂ O*	S2 H ₂ O**
35W20	8.4	133.5	124.8	118.2
35DW30	9.5	118.1	112.5	105.8
35DW50	5.7	113.6	117.7	88.0
35D50	3.6	107.6	109.6	52.7

*: ESW S1 H₂O; mono-layer.

**: ESW S2 H₂O; multi-layer.

that a knick point is present at the monolayer adsorption state and the gradient, corresponding to a specific surface area, increases with an intensity of drying, implying the lowering of the specific surface area of C-S-H at multilayer adsorption states.

Specific surface areas at monolayer and multilayer adsorption states can be calculated using Equation (2). The results of analysis of specific surface area obtained by N₂ and H₂O adsorptions are shown in Table 3. BET-N₂ shows a single digit smaller specific surface area than those using water vapor. Drying-induced changes in specific surface areas with water vapor are almost equal to those with BET-H₂O and ESW S1-H₂O while that of ESW S2-H₂O is much larger.

Jennings (2000) attributed the drying-induced changes in specific surface areas of BET-H₂O to an aggregation of LD C-S-H while the result of ESW S2-H₂O further suggests that the specific surface area at multilayer adsorption decreases significantly.

Conventional knowledge showed that specific surface areas of HCP with BET-H₂O is almost constant regardless of water-cement ratio, age and prerequisite drying condition and is always greater than that with BET-N₂ (Feldman 1968, Odler 2003). This is a consequence of calculating the specific surface areas using monolayer capacity. Because water molecules can access to the nano space of HCP, ESW analysis of changes in specific surface area at multilayer adsorption is likely to figure out the aggregation of C-S-H. The result of ESW analysis may also attribute the coarsening of pore structure observed with MIP (Aono et al. 2007, 2008) the drying-induced aggregation of C-S-H.

3.4 Nuclear Magnetic Resonance

NMR output was analyzed following the chemical shifts shown by Klur et al (1998) and Q₂ was separated into Q_{2p} and Q_{2Ca}. Drying-induced changes in peak intensity are compared in Figure 8 where Q₁ decreases

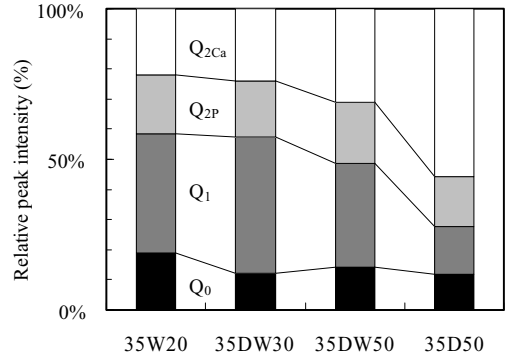


Figure 8. Comparison of relative peak intensity of C-S-H in HCP by ²⁹Si NMR MAS.

Table 4. Degree of polymerization N and degree of hydration α.

Specimen	Degree of polymerization N (Eq. (3))	Degree of hydration α (Eq. (4))
35W20	4.1	81.1
35DW30	3.9	87.7
35DW50	5.0	85.8
35D50	11.2	88.1

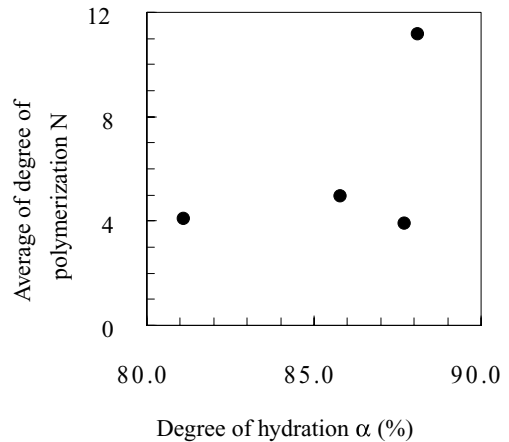


Figure 9. Average of degree of hydration N vs. degree of hydration α.

and Q_{2Ca} increases. The average of the degree of silicate anion polymerization and the degree of hydration calculated with Equation (3) and (4) are shown in Table 4. As shown in Figure 9, the polymerization of silicate anion does not depend on the degree of

cement hydration. This is supported by the report of Brough et al. (1994) showing that Q_2 increased with decrease in Q_1 after the fully hydrated ages of more than 100 days. This implies that polymerization of silicate anions coordinated with CaO layer developed when C-S-H was subjected to drying.

3.5 Pore structure and nano-structural changes due to drying

Above results show that pore structural changes in HCP during drying can be attributed mainly to changes in C-S-H structure at nano levels. Relationship between specific surface area with BET- N_2 and degree of polymerization of silicate anions (Q_{2total}) is shown in Figure 10. With an increase in Q_{2total} , BET- N_2 decreases significantly implying that the drying-induced changes in specific surface area with BET- N_2 is associated with polymerization of silicate anions, which was also noted by Jennings (2000, 2004).

Relationship between specific surface area with BET- H_2O , ESW S1- H_2O and ESW S2- H_2O , and Q_{2total} is shown in Figure 11. Change in specific surface area at monolayer adsorption state (BET- H_2O and ESW S1- H_2O) with an increase in Q_{2total} is slight while at multilayer adsorption (ESW S2- H_2O), it decreases significantly. This also implies an aggregation of C-S-H as seen in BET- N_2 .

Relationships of pore volumes (V_{total} and V_{Hg}) and specific volume of solid (v_{tr}) with respect to Q_{2total} are shown in Figure 12, where V_{total} shows no or slight increase but V_{Hg} tends to increase. This leads to a conclusion that the drying-induced pore coarsening was caused by the development of polymerization of silicate anion chains resulting in a formation of new pore spaces.

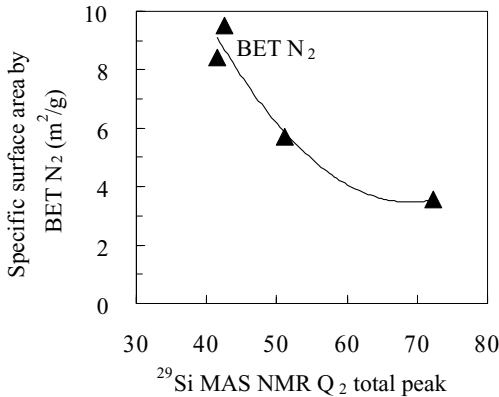


Figure 10. Relationship between specific surface area of BET N_2 and Q_{2total} by NMR.

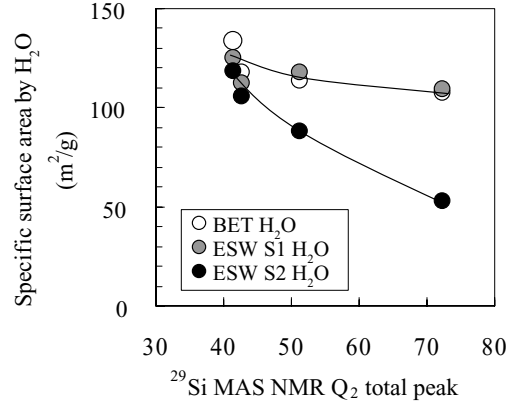


Figure 11. Relationship between specific surface areas at mono- and multi-layer adsorption state by ESW (H_2O) and Q_{2total} by NMR.

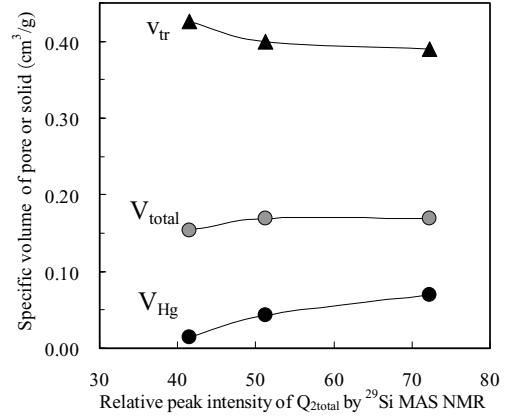


Figure 12. Relationship between pore volumes and Q_{2total} .

4 CONCLUSIONS

When HCP was subject to drying at 50°C , pore structure and C-S-H nano-structure changed in the following manner:

1. Pore volume with a diameter greater than 8 nm increased as measured by MIP.
2. True specific volume measured by the underwater weighing decreased and pore volume with a diameter smaller than 8 nm decreased while the total pore volume remained unchanged.
3. Specific surface area measured with BET- N_2 decreased significantly.
4. Specific surface area measured with BET- H_2O showed good agreement with that obtained by ESW model at monolayer adsorption state (ESW

S1-H₂O) and decreased slightly by drying, while that at multilayer adsorption state (ESW S2-H₂O) decreased significantly in the same manner as in BET-N₂.

5. Polymerization of silicate anion chain was induced by drying as observed in ²⁹Si-NMR and no correlations between silicate anion polymerization and degree of hydration of HCP were recognized.
6. Specific surface area measured with BET-N₂ and ESW S2-H₂O decreased significantly with an increase in polymerization of silicate anions in C-S-H, implying that the drying was responsible to the polymerization and the development of cohesive structures of C-S-H.
7. The drying-induced pore coarsening of HCP, as measured with MIP, was attributed to the formation of cohesive structures resulting from the polymerization of silicate anion chains in C-S-H.

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Carbonation shrinkage mechanism of a tobermorite-based material

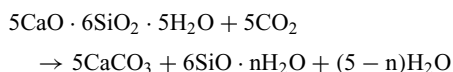
F. Matsushita, Y. Aono & S. Shibata

Sumitomo Metal Mining Siporex Co., Ltd, Mie, Japan

ABSTRACT: A tobermorite-based material (autoclaved aerated concrete) sometimes shows carbonation shrinkage, resulting in the durability problems such as deflection and cracking. In this study, carbonation shrinkage mechanism was studied by the changes of micro-pore structure and silicate-chain structure. A carbonated tobermorite-based material shows no shrinkage at a carbonation degree approximately less than 20%, and, however, shows shrinkage gradually at a carbonation degree from approximately 20% to 60%. The ^{29}Si MAS NMR spectrum showed that, at a carbonation degree less than 25%, the typical double-chain silicate anion structure of tobermorite-1.1nm was well maintained and interlayer Ca ions were exchanged with protons. It corresponded to the absence of carbonation shrinkage at a carbonation degree less than 20%. When carbonation degree exceeded from 25% to 60%, double-chain silicate anion structure of tobermorite-1.1nm was decomposed and Ca ions in the Ca-O layers was dissolved, showing a possible mechanism of carbonation shrinkage.

1 INTRODUCTION

One of the most harmful factors affecting the durability of autoclaved aerated concrete (AAC) is carbonation, in which tobermorite-1.1 nm ($5\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$), the principal binding mineral of AAC, reacts with atmospheric carbon dioxide gas in the presence of moisture, and decomposed to silica-gel and calcium carbonate as shown below.



Carbonation leads to degradation such as the decrease of strength, the increase of deflection and the growth of lattice-like cracking (Goodier & Matthews 1997, Matsushita & Shibata 2000). They are mainly caused by the carbonation shrinkage.

In the microstructure change of AAC during carbonation (Matsushita et al., 1999), the planer particle shapes of tobermorite-1.1 nm and the associated inter-particle pores were not changed significantly, although the double-chain silicate anion structure of tobermorite-1.1 nm was decomposed to silica-gel-like structure and drying shrinkage increased with carbonation.

Numerical values of carbonation shrinkage of AAC were reported from 0.1 to 1.0% for laboratory carbonation though it varied according to the raw materials, carbon dioxide concentration and relative humidity

(Fedin et al., 1970, Sauman 1972, Novikova et al., 1978, Nireki et al., 1990, Ochiai 1993).

However, the relation between carbonation shrinkage and change of tobermorite-1.1nm crystal structure as well as microstructure of AAC has not been reported. We studied the mechanism of carbonation shrinkage of AAC, carbonated under an accelerated condition, with ^{29}Si MAS NMR spectroscopy.

2 EXPERIMENTAL

2.1 Specimens

AAC blocks made by Sumitomo Metal Mining Siporex Co., Ltd. were used for laboratory carbonation. They were shaped in $40 \times 40 \times 160$ mm and dried at 105°C for 2 hours. After that, a pair of 20 mm-brass pins was fixed on both ends by an adhesive for the length change measurement. A surface part from 0 to 10 mm was used for determining the carbonation degree and analyses.

2.2 Carbonation

Laboratory carbonation samples were pre-treated at a temperature of 20°C and relative humidity of 90% for 1 week. Subsequently, they were carbonated under conditions of CO_2 concentration of 3 and 0.3 vol.% at a temperature of 20°C and an ambient relative humidity of 90%.

2.3 Carbonation degree

The amount of combined carbon dioxide and calcium oxide were measured to determine the carbonation degree. TG-DTA was used for determining the amount of combined carbon dioxide except for the amount of adsorbed carbon dioxide gas and carbonated salt other than calcium carbonate. The amount of combined carbon dioxide was measured as the weight loss during heating from 600 to 800°C corresponding to the decomposition of calcium carbonate. The amount of calcium oxide was analysed by ICP. The carbonation degree (Dc) can be given by

$$Dc(\%) = [(C - C_0)/(C_{\max} - C_0)] \times 100, \quad (1)$$

where C , C_0 and $C_{\max}$ are the amount of combined carbon dioxide in a sample, that of an untreated AAC and that when all calcium oxide transformed to calcium carbonate (Matsushita et al., 2000).

2.4 Carbonation shrinkage

Shrinkage strain δ due to carbonation can be given by,

$$\delta = [(l - l_0)/l_0] \times 100, \quad (2)$$

where l and l_0 were current length and initial length after pre-treatment under conditions of 20°C and 90% R.H. for 1 week. Measurement was always done in the carbonation chamber under conditions of 20°C and 90% R.H.

2.5 Analysis of crystalline phases

Crystalline phases were analyzed by XRD using RIGAKU RINT 1000 with CuK α radiation under the conditions of 40 kV and 30 mA.

2.6 Analysis of microstructure

The microstructure was analyzed by mercury porosimeter, EPMA and SEM. Mercury porosimetry was measured with Shimadzu Autopore-9200. EPMA cross-section analysis of Si and Ca were measured with Shimadzu EPMA-2300. Jeol JSM-5410 was used for SEM observation. The specimens measured were untreated AAC and laboratory-carbonated AAC under conditions of CO₂ concentration of 3 vol.% and field-carbonated AAC with various carbonation degrees up to 60%.

2.7 Analysis of silicate-chain structure

Silicate-chain structure was analyzed by ²⁹Si MAS NMR. ²⁹Si MAS NMR spectra was recorded by the Jeol JNM-A-400 WB with an observation frequency

of 79.42 MHz, a repeating time of 7.0 s, a contact time of 6.4 μ s is and a cumulative number of 3000 to 12000 scans. The specimens measured were untreated AAC and laboratory-carbonated AAC under conditions of CO₂ concentration of 3 vol.% with carbonation degrees of 25, 50 and 60%.

3 RESULTS AND DISCUSSION

3.1 Carbonation degree

Carbonation degree as a function of treated time is shown in Figure 1. The higher the carbon dioxide concentration, the faster was the increase in carbonation degree. Carbonation degree reached saturation approximately at 60% after 35 days under a CO₂ concentration of 3 vol.% and 120 days under a CO₂ concentration of 0.3 vol.%.

3.2 Carbonation shrinkage

Carbonation shrinkage reached approximately 0.25% after 40 days for 3 vol.% CO₂ and 160 days for 0.3 vol.% CO₂ showing that a higher CO₂ concentration led to a quicker shrinkage (Figure 2). The maximum value of carbonation shrinkage was approximately 0.27% for 3 vol.% CO₂ and approximately 0.25% for 0.3 vol.% CO₂.

Length change during carbonation as a function of carbonation degree is shown in Figure 3. Regardless of carbonation conditions, the relation between carbonation degree and carbonation shrinkage showed nearly the same tendency. Carbonation shrinkage didn't occur when carbonation degree was less than 20%. When carbonation degree ranged from 20% to 50%, carbonation shrinkage occurred gradually and reached approximately 0.1%. When carbonation degree ranged from 50% to 60%, carbonation shrinkage occurred significantly and reached approximately 0.25%.

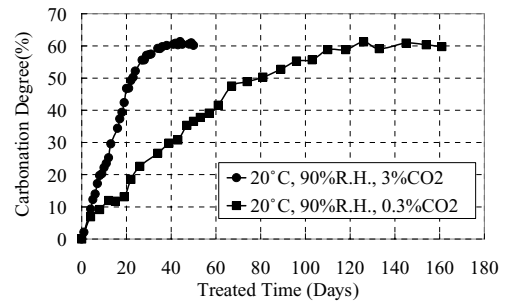


Figure 1. Carbonation degree as a function of treated days.

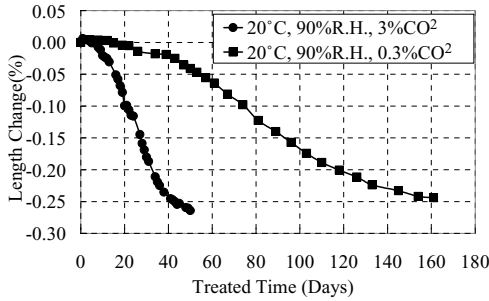


Figure 2. Length change during laboratory carbonation as a function of treated days.

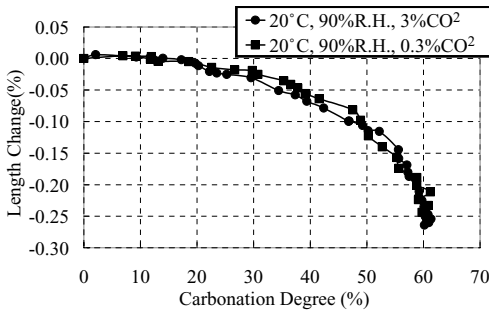


Figure 3. Length change during laboratory carbonation as a function of carbonation degree.

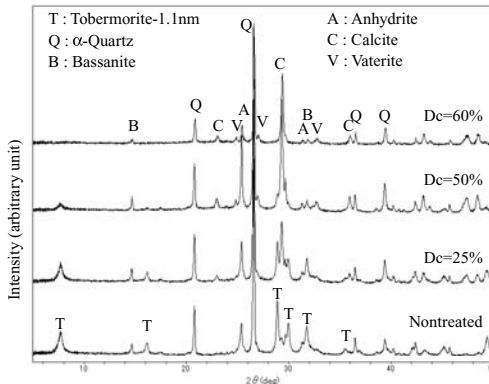


Figure 4. XRD patterns for untreated and laboratory-carbonated AAC.

3.3 Crystalline phases

The XRD patterns for the untreated and laboratory-carbonated AAC at various Dc are shown in Figure 4. For untreated AAC, tobermorite-1.1 nm, α -quartz, anhydrite (CaSO_4) and bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$)

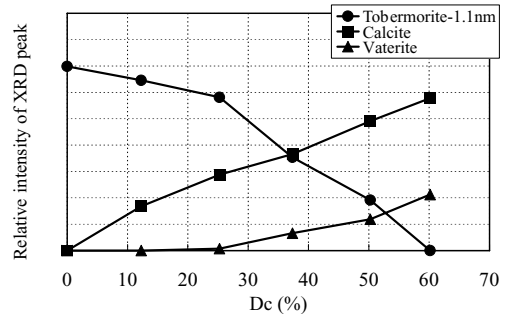


Figure 5. XRD peak intensities of tobermorite-1.1 nm, calcite and vaterite as a function of Dc.

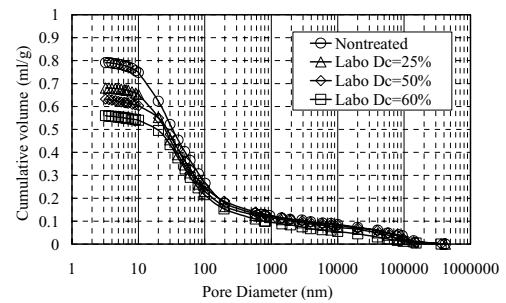


Figure 6. Pore size distributions of untreated and laboratory-carbonated AAC.

were found. Calcium carbonate was found as calcite and vaterite in laboratory-carbonated AAC. The XRD peak intensities of tobermorite-1.1 nm ($002, 2\theta = 7.8^\circ$), calcite ($110, 2\theta = 35.95^\circ$) and vaterite ($102, 2\theta = 32.71^\circ$) as a function of Dc are shown in Figure 5. Tobermorite-1.1 nm decreased and calcite increased with an increase of Dc, and vaterite began to increase at a Dc approximately 30%.

3.4 Microstructure

Pore size distributions of the untreated and laboratory-carbonated AAC with different Dc by mercury porosimeter are shown in Figure 6. The total pore volume decreased from 0.8 ml/g to 0.5 ml/g by carbonation, particularly in the characteristic pores of AAC of approximately 10 to 100 nm that correspond to the inter-particle pores of tobermorite-1.1 nm (Prim and Wittmann 1983).

Figure 7 shows Ca and Si distributions by EPMA cross-section analysis for the untreated and laboratory-carbonated AAC. In these figures, "A" represents air pores, where both the Si and Ca distributions are shown in dark, and "Q" represents α -quartz particles,

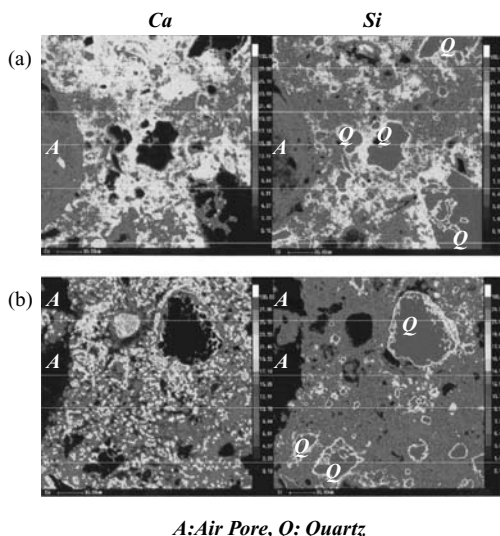


Figure 7. Ca and Si distributions by EPMA cross-section analysis: (a) untreated AAC and (b) laboratory-carbonated AAC (Dc = 50%).

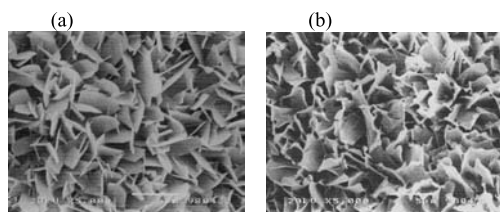


Figure 8. SEM images in air pores for (a) untreated AAC and (b) laboratory-carbonated AAC (Dc = 60%).

where the Si and Ca distributions are shown in bright and dark, respectively. For the untreated AAC, the Si distributions and Ca distributions might represent the distribution frequencies of tobermorite platy particles as the distributions of these shows a resemblance. Therefore, Ca atoms and Si atoms were considered to be distributed homogeneously in the matrix unlike for α -quartz particles. The homogeneous distribution of Ca atoms in untreated AAC changed to uneven distribution in the laboratory-carbonated AAC, which suggest that Ca atoms were deposited cohesively in the matrix during carbonation. On the other hand, the distribution of Si atoms in the matrix was unchanged in the laboratory-carbonated AAC. It was obvious that Ca ions were deposited from tobermorite-1.1 nm and reacted with carbon dioxide, while Si ions remained.

From the SEM images in Figure 8, inter-particle pores by geometrical arrangement of tobermorite

particles are not changed significantly during carbonation.

Therefore, it is most likely that the decrease in pore volume during carbonation was the deposition of calcium carbonate into the inter-particle pores at a pore diameter of approximately 10 to 100 nm. The reason for the absence of swelling during carbonation was attributed to the deposition of calcium carbonate into the inter-particle pores.

3.5 ^{29}Si MAS NMR spectrum

^{29}Si MAS NMR spectra of untreated AAC and laboratory-carbonated with carbonation degrees of 25, 50 and 60% are shown in Figures 9 (a) to (d). The ^{29}Si MAS NMR chemical shifts by peak separation are shown in Table 1.

When carbonation degree ranged from 0% (untreated) to 25%, ^{29}Si MAS NMR spectra were almost unchanged, which implied the double-chain silicate anion structure of tobermorite-1.1nm was well maintained, however at peaks around -100 ppm a little change was observed at a carbonation degree of 25%. On the other hand in the same progress of carbonation degree of 25%, ^{29}Si MAS NMR spectra of specimens with a carbonation degree ranging from 25% to 50% changed considerably. Furthermore, when carbonation degree ranged from 50% to 60%, ^{29}Si MAS NMR spectra changed remarkably in spite of only 10% advance of the carbonation degree. During this process, double-chain silicate anion structure of tobermorite-1.1 nm (Q_2 and Q_3) was supposed to be rearranged to 3-dimensional silica-gel like structure (Q_4).

3.5.1 Untreated specimens

For untreated AAC, signals at -80.6 , -85.3 , -92.0 , -96.0 and -107.4 ppm were observed, which corresponded to Q_1 , Q_2 , Q_3 (1Al) Q_3 (0Al) and Q_4 ,

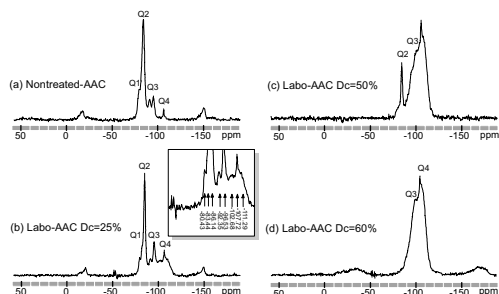


Figure 9. ^{29}Si MAS NMR spectrum for untreated-AAC and laboratory-carbonated AAC.

Table 1. ^{29}Si MAS NMR chemical shifts of samples.

ppm from TMS (Relative Intensity)	Q ₁	Q ₂		Q ₃			Q ₄	
	Q ₁	Q _{2p}	Q _{2i}	Q _{2Ca}	Q ₃ (1Al)	Q ₃	Q ₃ (1OH)	Q ₄ (Quartz)
Untreated	-80.6 (28)			-85.3 (100)	-92.0 (16)	-96.0 (17)		-107.4 (4)
Labo Dc = 25%	-80.4 (15)		-83.4 (51)	-86.1 (100)	-92.4 (23)	-96.5 (42)	-102.7 54	-111.3 (48)
Labo Dc = 50%		-82.8 (5)		-86.1 (21)		-98.0 (60)	-102.3 (90)	-111.1 (100)
Labo Dc = 60%							-102.8 (100)	-110.3 (68)
								-107.5 (5)

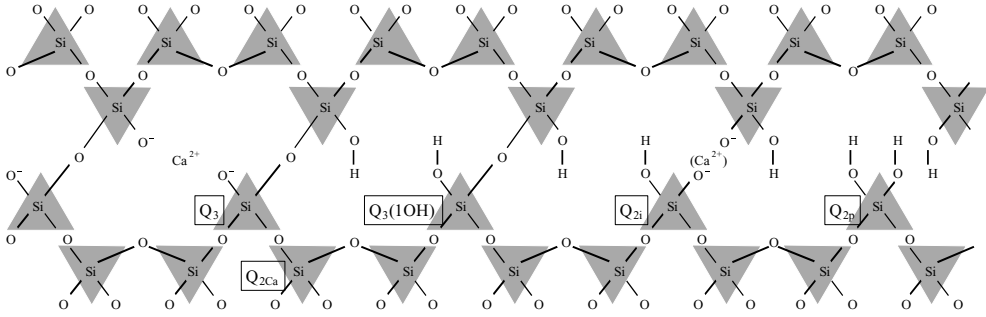


Figure 10. The silicate structure model in tobermorite-1.1 nm including Q₃ (1OH), Q_{2p}, Q_{2i} and Q_{2Ca} bonds.

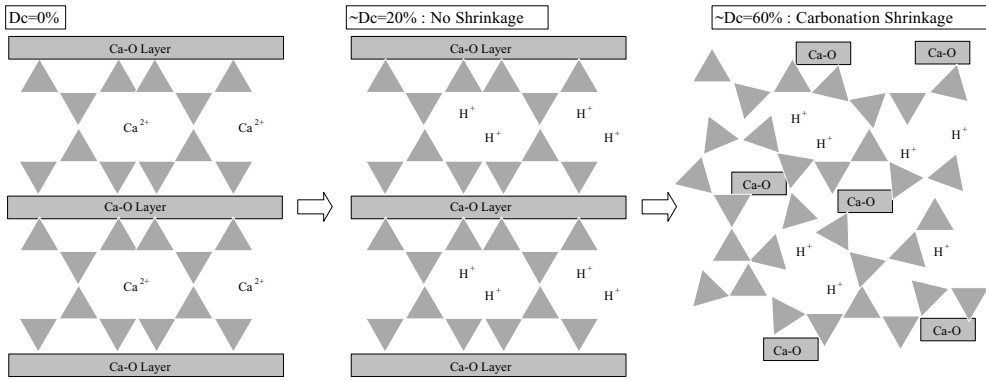


Figure 11. Change of silicate structure and mechanism of carbonation shrinkage.

respectively (Wieker et al., 1982, Komarneni et al., 1985). Q₄ signal at -107.3 ppm corresponded to α -quartz, one of the raw materials of AAC. The value of Q₃/Q₂ of the untreated specimen was approximately 1/3, although the theoretical value is 1/2. Therefore the bridging tetrahedra were supposed to comprise approximately 25% of Q₂ and approximately 75% of Q₃.

3.5.2 Carbonation degree of 25%

When carbonation degree reached 25%, signals at -83.4 ppm, -102.7 ppm and -111.3 ppm appeared in the laboratory-carbonated specimen. The signal at -111.3 ppm corresponds to Q₄ of silica-gel (Grimmer et al., 1982), which differs from Q₄ of α -quartz (-107 ppm). Sato et al., (1992) and Sasaki et al., (1996) concluded from ^{29}Si MAS/CPMAS NMR

spectrum that the signal around -82 ppm corresponded to the protonated silicate ions in the silicate chain. Klur et al., (1997) proposed to attribute -482.1 ppm to bridging tetrahedra bonded to two protons " Q_{2p} ", -83.9 ppm to bridging tetrahedra bonded to one proton and one calcium ion " Q_{2i} ", and -85.3 ppm to silicate tetrahedra coordinated to the calcium ions " Q_{2Ca} ". In short, Q_{2Ca} called by Klur et al., (1997) means the ordinary Q_2 . -83.4 ppm for laboratory-carbonated specimen corresponded to Q_{2i} . A signal at -102.7 ppm corresponds to the bridging tetrahedra bonded to one proton and one silicate ion, " Q_3 (1OH)" (Cong et al., 1993). The silicate structure model in tobermorite-1.1 nm including Q_3 (1OH), Q_{2p} , Q_{2i} and Q_{2Ca} bonds is shown in Figure 10. The appearance of Q_{2i} and Q_3 (1OH) including the protonated silicate ions during the early carbonation periods signified the exchange of calcium ions by protons in the interlayer space of tobermorite-1.1 nm.

3.5.3 Carbonation degree more than 50%

When carbonation degree reached 50%, Q_1 disappeared, Q_2 peaks around -82 ppm to -86 ppm got relatively lower and Q_3 and Q_4 appeared or got higher in carbonated specimens. Q_{2i} (-83.4 ppm) disappeared, a slight signal of Q_{2p} (-82.8 ppm) appeared and the highest signal changed from Q_2 to Q_4 .

When carbonation degree reached 60%, Q_3 (1OH) and Q_4 were detected for laboratory-carbonated specimens. Therefore, double-chain silicate anion structure of tobermorite-1.1 nm was finally decomposed, shrunk and polymerized to a silica-gel-like structure in the final stage of carbonation.

3.6 Mechanism of carbonation shrinkage

During the early carbonation periods at a carbonation degree less than 25%, double-chain silicate anion structure of tobermorite-1.1 nm maintained well and protonated silicate ions in the silicate chain appeared. Komarneni & Tsuji (1989) studied the ion exchange properties of Ca ions in the interlayer space of tobermorite-1.1 nm. The Ca ions in the interlayer and the Ca-O layer occupied 20% and 80% of Ca atoms in tobermorite-1.1 nm, respectively (Taylor 1964). Carbonation shrinkage didn't occur when carbonation degree was less than 20%. Therefore, the absence of carbonation shrinkage until the carbonation degree of 20% may be attributed to the retaining of the main structures of tobermorite-1.1 nm, the double-chain silicate anion structure and the Ca-O layer, as shown in Figure 11.

During the carbonation periods of carbonation degree from 25 to 60%, Ca ions dissolved from the Ca-O layer and the double-chain silicate anion structures

was decomposed, shrunk and polymerized to silica-gel structure. This is the most likely mechanism of carbonation shrinkage of a tobermorite-based material, as shown in Figure 11. It can also support the relation that both of the progress of carbonation shrinkage and the change of silicate anion structure during carbonation degree ranged from 50% to 60% were more remarkable than that during carbonation degree ranged from 20 or 25% to 50%.

4 CONCLUSION

1. For laboratory-carbonated specimens under CO_2 concentrations of 3 and 0.3 vol.%, the relation between carbonation degree and carbonation shrinkage was nearly the same. Carbonation shrinkage was not observed when carbonation degree was less than 20%. Carbonation shrinkage reached approximately 0.1% and 0.25% at a carbonation degree of 50% and 60%, respectively.
2. Tobermorite-1.1 nm decreased and calcite increased with an increase of Dc and vaterite began to increase at a Dc of approximately 30%.
3. The total pore volume decreased from 0.8 ml/g to 0.5 ml/g by carbonation at approximately 10 to 100 nm that correspond to the inter-particle pores. Ca ions were deposited from tobermorite-1.1 nm and reacted with carbon dioxide, while Si ions remained. The reason for the absence of swelling during carbonation was attributed to the deposition of calcium carbonate into the inter-particle pores.
4. When carbonation degree was less than 25%, ^{29}Si MAS NMR spectrum suggested that the double-chain silicate anion structure of tobermorite-1.1 nm was maintained well and calcium ions were exchanged by protons. It was suggested that the reason for the absence of carbonation shrinkage until the carbonation degree of 20% was the retaining of the double-chain silicate anion structure and the Ca-O layer, the main structures of tobermorite-1.1 nm. When carbonation degree ranged from 25 to 60%, Ca ions dissolved from the Ca-O layer and the double-chain silicate anion structures were decomposed, shrunk and were polymerized to silica-gel-like structure. This is the most likely mechanism of carbonation shrinkage of AAC, a tobermorite-based material.

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Drying shrinkage mechanisms of hardened cement paste

C. Duckheim & M.J. Setzer

Institute of Building Physics and Materials Science, University of Duisburg-Essen, Essen, Germany

ABSTRACT: Drying shrinkage has been experimentally investigated by means of a newly developed laser-supported measuring principle. Further—mainly novel—methods have been applied for examining sorption behaviour as well as inner volume and density change. Divided into de- and adsorption, different sections of relative humidity are found with each varying dominating mechanisms. In the lower humidity range shrinkage and swelling are proportional to change in surface free energy. However, an energy reduction during adsorption does not lead to an expansion as assumed up to now (Munich Model), but to a contraction of csh-particles, while pore volume increases simultaneously (and vice versa during desorption). For this reason the influence of surface energy has to be attributed to the dispersive component of disjoining pressure which prevails in the lower humidity range, whereas in the range of condensation repulsive components and capillary tension dominate the processes in hcp.

1 INTRODUCTION

As far as design and optimisation of new kinds of concrete are concerned, but also with regard to modelling the characteristics of this building material, the exact understanding of chemical and physical relations in hcp which significantly determines the material attributes, is of fundamental relevance. However, due to its hygroscopic character, many hcp-properties vary extensively depending on the water content of the pore system. Furthermore, with its highly dispersed microstructure, mainly consisting of nanosized csh-particles and its large internal surface area hcp has features of a colloidal material so that surface interactions play a prevailing role. Precise experimental data of hygric properties as drying shrinkage/swelling or density change are necessary to explain the underlying mechanisms such as disjoining pressure, surface energy change and capillary tension. For this reason detailed measurements regarding various hygric characteristics of the so-called solid-liquid gel-system are conducted at the Institute of Building Physics and Materials Science at the University of Duisburg-Essen. With a high resolution drying shrinkage is measured using a newly developed laser-supported method, a magnetic suspension balance allows the dynamic determination of sorption isotherms and inner volume changes are detected by helium pycnometry.

2 THEORETICAL BACKGROUND

In the past hygric strains of hcp have been explained by means of several different mechanisms. The most important certainly are

- disjoining pressure Π
- surface energy F and
- capillary tension p_c .

The *disjoining pressure* is defined as the difference between the pressure in a liquid under undisturbed bulk conditions and the pressure in an interphase (here pore solution between csh-particles). Following Derjaguin et al. (1987) it is combined of two repulsive components (only active in water filled pores) - the electrostatic part Π_e , which is attributed to the electrical double layer of the adsorbed water molecules and the structural term Π_s due to solvation effects -on the one hand and an attractive interaction force, the molecular or dispersive component Π_m , which is based on the electromagnetic dipole-dipole interaction on the other hand:

$$\Pi = \Pi_m + \Pi_e + \Pi_s \quad (1)$$

Here the molecular component, which leads to a strong attraction in gas filled pores, but only to low attraction forces in water filled pores, has a negative sign. An increase of disjoining pressure due to the adsorption

of water increases the distance between particles and therefore leads to a structural swelling of hcp.

In the lower humidity range shrinkage and swelling are often explained by means of *surface free energy change* ΔF due to the de-/adsorption of water on the surfaces of csh-particles:

$$\Delta F = - \int_{\mu_0}^{\mu} \eta_{\text{ads}} d\mu \quad (2)$$

Here η_{ads} is the ad-/desorbed amount of water, μ the chemical potential with

$$\mu = -R \cdot T \cdot \ln(p/p_0) \quad (3)$$

and μ_0 the chemical potential where adsorption starts. Further details regarding the interpretation of this energy change (modification of particle size due to surface tension) as described in the Munich Model (Setzer 1977, Wittmann 1977) can also be found in Setzer (2008).

The *capillary tension* p_c of pore water is another effect which can explain hygric strains in porous solids. During drying in narrow pores a meniscus is formed at the interface between vapour and liquid so that the pore water is in a state of tension (depression). With decreasing humidity the radius of curvature is reduced and tension rises:

$$p_c = \rho_{\text{H}_2\text{O}} \cdot R_D \cdot T \cdot \ln(p/p_0) \quad (4)$$

Here $\rho_{\text{H}_2\text{O}}$ is the density of water, R_D the specific gas constant of water vapour, T the absolute temperature and p/p_0 the relative humidity. This tensile stress is balanced by compressive stress of the solid matrix, which results in shrinkage. Following Equation 5 which is based on a theory of Mackenzie (1950) these hygric strains ε can be estimated by means of a coefficient S which represents the degree of saturation (here: normalised sorption isotherm) and the bulk moduli of porous hcp K and of pure solid K_s :

$$\varepsilon = \frac{\Delta l}{l_0} = p_c \cdot S \cdot \left[\frac{1}{3 \cdot K} - \frac{1}{3 \cdot K_s} \right] \quad (5)$$

3 EXPERIMENTS

Drying shrinkage of filigree hcp samples is dynamically measured by means of a new laser-supported measuring principle. In this setup the thin sample is placed—approximate stress-free—between a special measuring lever at the bottom and a micrometer screw at the top (Fig. 1). A length change of the specimen results in a corresponding lever inclination (α). This inclination is detected with a laser beam which is

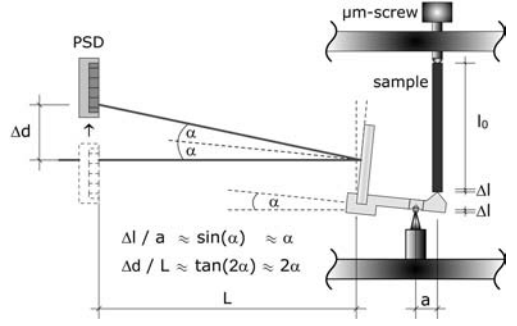


Figure 1. Principle of measuring hygric strains.

reflected by a mirror attached at the other end of the lever and measured by means of a position sensible detector (PSD).

From this position change (Δd) the length change of the specimen (Δl) is calculated subjected to the system geometry:

$$\Delta l = \Delta d \cdot \frac{a}{2 \cdot L} \quad (6)$$

The current setup affords the simultaneous measurement of four samples with a resolution of 20 nm and a random error of measurement $< 1\%$. In order to verify and to complete the results shrinkage strains of seven more specimens are determined using feather touch digital probes.

Sorption isotherms are detected with a magnetic suspension balance which affords the dynamic measurement of ten specimens in an enclosed climate with a resolution of 10 μg .

Relative humidity and temperature inside the measuring chambers are precisely controlled over the complete range between about 0% r.h. and 100% r.h. by a climate generator which adjusts a dewpoint accuracy and a temperature stability of ± 0.15 K. A purge-gas-generator reduces the CO_2 -concentration of the carrier gas to values < 1 ppm (v) so that carbonation of the thin samples is completely avoided.

Inner volume change of hcp can be analysed using helium pycnometry. Pressure differences of the monoatomic gas between a reference chamber and the measuring chamber allow the determination of the pure volume of the solid-liquid gel-system, since helium intrudes even smallest pores in hcp. Further explanations concerning these only shortly presented experimental methods can be found in Duckheim (2008).

4 MATERIALS AND SAMPLE PREPARATION

For the experiments filigree hcp specimens consisting of a CEMI 32.5 R with w/c-ratios of 0.35, 0.4, 0.5, and 0.6 are used. Slabs with dimensions 120 mm × 80 mm × 5 mm are produced for this purpose. After casting the slabs remain in the formwork for 48 to 72 hours, afterwards they are stored in a saturated calcium hydroxide solution for more than twelve months. In this way side-effects due to further hydration and chemical shrinkage during the course of the measurement can be reduced to a negligible amount. A few days before the start of the testing the slabs are cut to strips with a cross-section of 5 mm × 1.4 mm using a precision saw during constant wetting. For drying shrinkage measurements these strips are cut to a length of 50 mm, sorption and density measurements are carried out with samples of various lengths. Till the beginning of the analyses the specimens are stored in the solution further on so that they are completely saturated when measurements start.

5 RESULTS

Hygic strains plotted versus relative humidity are shown in Figure 2 (first cycle, all w/c-ratios) and Figure 3 (both cycles, w/c = 0.40), the corresponding sorption isotherms in Figures 4–5. While desorption has to be subdivided into three parts (100% – 35%, 35% – 25%, 25% – 0%), two different ranges can be found during adsorption (0% – 60%, 60% – 100%).

When drying starts, the upper humidity range features a distinct linearity, followed by a stagnancy or even a slight swelling at 30%, although here sorption isotherms show a markedly mass loss. Further drying leads to moderate water loss and shrinkage at first, but results in considerably increasing values at a humidity below 5%. Concerning adsorption both sorption isotherms and swelling strains are characterized by a declining range till 60%, where water is adsorbed on the internal surface and a following progressive range,

where the pore system is filled successively due to capillary condensation.

The influence of w/c-ratio becomes obvious in Figures 2 and 4. The higher the w/c-ratio the higher are water content and length change of the hcp specimens; but also irreversible shrinkage and mass loss rise with increasing w/c-ratios. First desorption and adsorption form an open hysteresis over the entire humidity range with an irreversible shrinkage of 2 mm/m—3 mm/m and an irreversible mass loss of 1% – 8%, whereas the second cycle forms a closed loop. This applies for hygic strains as well as for sorption isotherms. However, hysteresis nearly completely vanishes if hygic strains are plotted against water content of the structure (Fig. 6). Here we also find a distinct linearity in the upper humidity range, which correlates with a decrease during desorption or an increase during adsorption respectively of the repulsive (electrostatic and structural) components of disjoining pressure, which is the driving force regarding shrinkage in this range. Furthermore, capillary tension in the pore solution increases during drying and thus induces an additional deformation. Noticeable is the stagnancy or little swelling in the transition range between 35% and 25%. This phenomenon can be explained by a capillary tension effect. Due to the high water loss at 30% where the rest of the remained condensate leaves

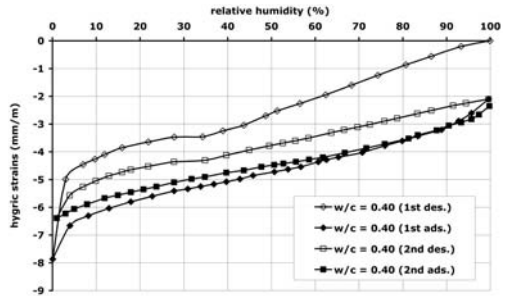


Figure 3. Hygic strains, both cycles of w/c = 0.4.

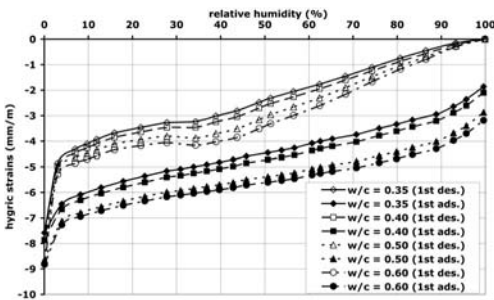


Figure 2. Hygic strains against relative humidity.

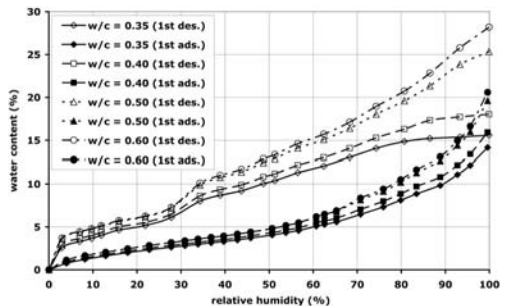


Figure 4. Water content against relative humidity.

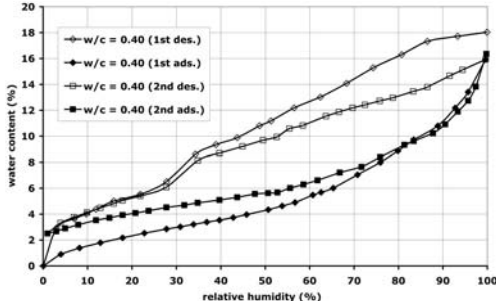


Figure 5. Water content, both cycles of $w/c = 0.4$.

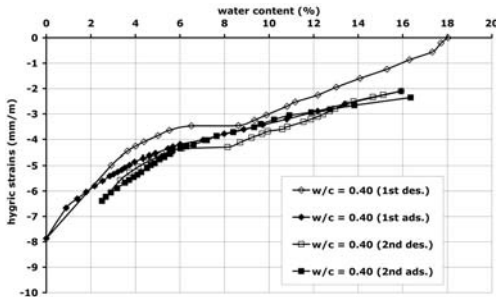


Figure 6. Hygric strains versus water content.

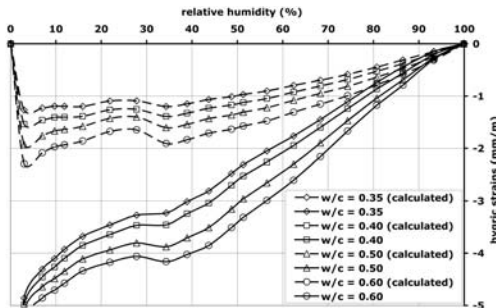


Figure 7. Estimated and measured hygric strains.

the pore system, a basic fraction of this low-pressure vanishes. Since the main part of shrinkage deformation is caused by the decrease of disjoining pressure, the structure only expands slightly instead of a complete reversion. A corresponding estimation following Equation 5 can be seen in Figure 7. A distinct qualitative agreement of calculated and measured strains is obvious.

In the lower humidity range the rest of pore water is basically existent in the form of adsorbed layers on the

internal surface. Here shrinkage and swelling are proportional to surface free energy change ΔF (Fig. 8) calculated from sorption isotherms (Equation 2) as shown before in the Munich Model. However, in the following it will be demonstrated, that an energy reduction during adsorption does not lead to an expansion of csh-particles because of a reduction of surface tension as assumed up to now, but to a contraction of particles, while simultaneously pore volume increases significantly and vice versa during desorption. For this reason the influence of surface energy has to be attributed to the dispersive (attractive) component of disjoining pressure. Results of helium pycnometry confirm this assumption. With increasing humidity capillary condensation in the gel pores leads to an increasing swelling due to rising repulsive forces of disjoining pressure during adsorption in the upper range from 60% on (Fig. 2 and Fig. 4).

Pure density of hcp consisting of solid and water, shown in Figure 9, increases with decreasing w/c -ratio. Values between 1.8 g/cm^3 and 2.4 g/cm^3 can be found. Density rises distinctly due to loss of water in the course of first desorption to about 20% r.h. and remains nearly constant during the following drying.

Wetting only causes marginal changes in density up to 60% r.h. With beginning capillary condensation of water in pores density decreases significantly, but

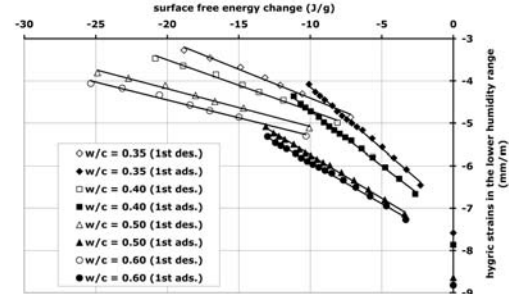


Figure 8. Hygric strains versus energy change.

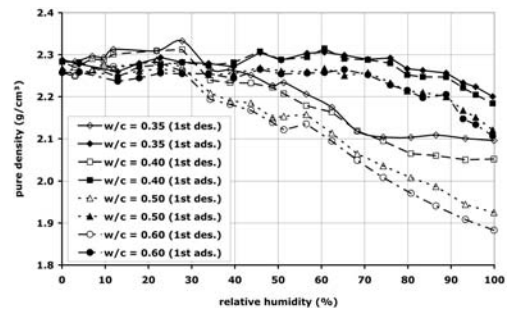


Figure 9. Pure density versus relative humidity.

does not reach the initial values. If at a first approximation the measured volume changes are attributed to the desorption and adsorption of pore water only and thus a deformation of the matrix is neglected, density of pore water can be estimated (slope of the regression line in Figure 10). In case of a w/c-ratio of 0.60 the bulk density of 1.00 g/cm^3 is found at first drying, but a significantly higher value of about 1.19 g/cm^3 for the following adsorption. This applies for the other w/c-ratios as well, pore water densities between 1.10 g/cm^3 and 1.20 g/cm^3 have been found primarily for all drying and wetting cycles, first desorption—in all cases the bulk density of water has been calculated—excepted (see Table 1). These elevated values are due to the intense interaction of the condensate with the large internal surface and affirm the structuring of the pore solution and therefore the existence of the structural component of disjoining pressure.

Considering the range of low humidities and hence of low volume and mass changes we find a distinct deviation. The relation between mass change and volume change would mean a pore water density of 2.0 g/cm^3 and higher, which is impossible. For this reason the solid matrix must change its volume in this range. A calculation of the density of the pure solid phase ($2.2 \text{ g/cm}^3 - 2.6 \text{ g/cm}^3$) shows a considerable decrease during drying from 30% to 0% and an increase during rewetting up to 60% (Fig. 11). This means an expansion of csh-particles during desorption and a contraction during adsorption as stated above. In combination with the external shrinkage

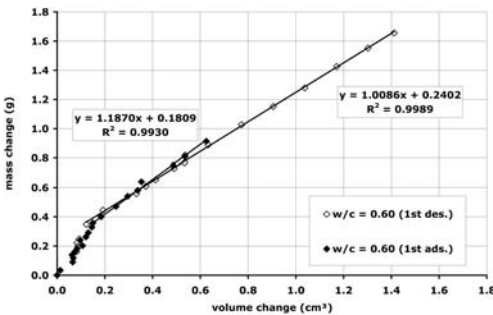


Figure 10. Calculation of pore water density.

Table 1. Pore water density in g/cm^3 .

w/c	1 st des.	1 st ads.	2nd des.	2nd ads.
0.35	0.99	1.30	1.19	1.17
0.40	0.98	1.27	1.17	1.20
0.50	1.00	1.22	1.13	1.15
0.60	1.01	1.19	1.14	1.13

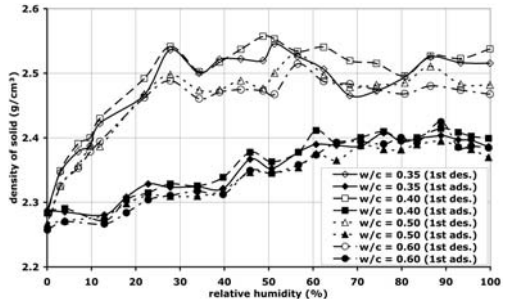


Figure 11. Density of solid versus relative humidity.

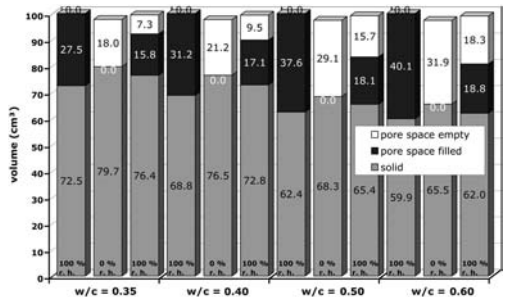


Figure 12. Volume change and water-cement-ratio.

the simultaneous swelling of particles leads to a pronounced decrease of pore volume due to drying and vice versa in case of rewetting. The volume differences of solid as well as of filled and empty pore space—estimated by means of a combination of outer shrinkage and inner volume change data—depending on the w/c-ratio of the hcp-samples between the situation at the beginning of the measurement (100% r.h.) and the end of first de- (0% r.h.) and adsorption (100% r.h.) are demonstrated in Figure 12 (starting volume $V_0 = 100 \text{ cm}^3$).

6 CONCLUSIONS

Precise measurements of drying shrinkage by means of a new laser-supported method and of inner volume change by means of helium pycnometry are the basis of some new cognitions regarding drying shrinkage mechanisms of hardened cement paste. The application of a humidity generator which provides exactly controlled climatic boundary conditions and the use of very thin specimens allow the determination of the hygric changes as an approximate material behaviour in a comparatively short time. By varying w/c-ratios the influence of different hcp-structures could be detected. The results of the conducted experiments can

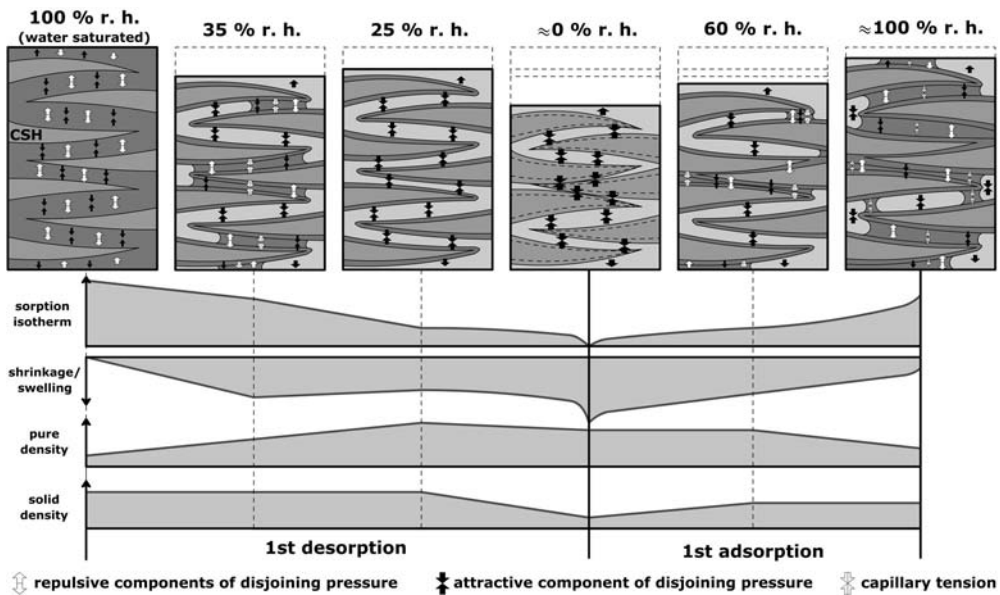


Figure 13. Drying shrinkage mechanisms.

be summarized as follows: Both shrinkage strains and sorption isotherms form a hysteresis over the complete range of humidity. Irreversible parts are due to first drying exclusively, following desorption-adsorption cycles form closed loops. However, hysteresis vanishes if shrinkage and swelling are plotted against water content of the structure. Therefore, hygric strains of the solid-liquid gel-system are closely associated with the pore water contained in the hcp matrix. In the range from 0% r.h. to 100% r.h. desorption and adsorption must be divided in different sections with each varying dominating mechanisms. Starting with fully hydrated water saturated specimens, during first drying we find a linear shrinkage strain down to about 35% due to decreasing disjoining pressure and increasing capillary tension with the desorption of condensate. From 35% to 25% the rest of this condensate is abruptly desorbed and the structure slightly expands since the low-pressure due to capillary tension is reduced. In the lower humidity range shrinkage as well as swelling are proportional to change in surface free energy. However, the influence of this change has to be attributed to the dispersive component of disjoining pressure. This increasing attraction between the surface of particles leads to a significant reduction of pore volume and an expansion of the csh-particles during desorption between 25% and 0% and vice versa during adsorption in a range from 0% to 60%. Above this point pores are filled due to capillary condensation and the repulsive components (electrostatic and structural term) of disjoining pressure now

	water content	1st shrinkage	2nd shrinkage	swelling	irreversible parts	pure density	solid density	pore water density
w/c = 0.35								
w/c = 0.40								
w/c = 0.50								
w/c = 0.60								

Figure 14. Influence of water-cement-ratio.

again are the dominating mechanisms. The structuring of pore water is affirmed by its elevated density. Figure 13 shows a schematic delineation of the above described relations, the influence of w/c-ratio of the structure on the analysed properties can be seen in Figure 14.

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Study on influence of the alkali contents on volumetric change of cement paste due to dry and wet change

Tomohiro Koyanagi & Hideki Oshita

Chuo University, Tokyo, Japan

ABSTRACT: The hydration product in the hardened concrete is made by a layer structure, and the pore surface takes on a positive electric charge. In the case of high R_2O density in concrete, the electric repulsion occurs between the surface and the alkali ion and then it seems to be thought that the alkali contents are influence on the dry shrinkage behavior. However, the qualitative and quantitative evaluation has not been performed. In this study, the measurement of the volumetric change of cement paste due to dry and wet change was performed as a parameter of W/C, the atmospheric temperature and the alkali contents and then the influence of the alkali contents on the volumetric change behavior was evaluated. As a result, it is noted that the alkali contents influence on volumetric change of cement paste due to dry and wet change.

1 INTRODUCTION

The influence of drying shrinkage is an important problem in a concrete structure that is a typical porous material. The factors effected on a mechanism of volumetric change due to dry and wet change of concrete are relative humidity, atmospheric temperature, pore structure, migration of capillary water and gel water etc. Until now, a lot of studies on that mechanism have been performed in the past.

The concrete structure which is under the actual environment possesses a different alkali contents by scattering antifreezing admixture, carbonation and a kind of cement. However, a study on (hereinafter, R_2O density) influence of alkali contents on volumetric change of concrete due to dry and wet change has been scarcely performed in the past research. F. Beltzung pointed out that the hydration product in hardened concrete is made by a layer structure and these surfaces take on a high electric charge.

And then when R_2O density of concrete is high, the electric repulsion occurs between hydration products surface which takes on a electric charge and the alkali ion. Therefore, it seems that the volumetric change due to wet and dry change is influenced by electric repulsion.

In this study, the measurement of volumetric change of cement paste due to drying and wetting was performed with a parameter of W/C, atmospheric temperature and alkali contents and then the influence of alkali contents on the characteristic of volumetric change was discussed.

2 EXPERIMENTAL

2.1 *Used materials and experimental parameter*

In experiments, an ordinary Portland Cement is used (density: 3.16 g/cm^3 , surface area: $3290 \text{ cm}^2/\text{g}$) that contains the amount of alkali 0.51% in R_2O density ($\text{Na}_2\text{O} + 0.658\text{K}_2\text{O}$). The mix proportion of cement paste was shown in Table 1, and NaOH was used for the adjustment of R_2O density. W/C of cement paste is 30, 50 and 60%, and the atmospheric temperature is 20 and 40 degrees Celsius. NaOH which is amounted to 0, 2 and 4% of cement weight was added to mixing water. The example of specimen name is shown in Figure 1.

A mixing is performed by mortar mixer and NaOH is added to. The mortar mixer is moved at low speed for 60 seconds and after that moved mixing water, at high speed for 90 seconds.

The prismatic specimen of which size is $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$ is used. Three specimens for the measurement of length change were made and the temperature the center of specimen was measured for each parameters. The specimen's surface is protected by glass plate to prevent water dissipation. The specimen was removed from the form at 24 hours after placing and then cared in water with the temperature of 20 degrees Celsius for 6 days. And then, the specimen is cared with the atmospheric temperature of 20 degrees Celsius and R.H. 60% for 20 days and then the experiment was performed at the age of 28 days.

Table 1. Mix proportion (No. 1).

Atmospheric temperature (°C)	W/C (%)	Unit content (kg/m ³)		Chemical admixture	Amount of NaOH addition	Specimen
		Water	Cement			
20	30	469	1621	$C \times 0.01$	0	M-30-0-20
					$C \times 0.02$	M-30-2-20
					$C \times 0.04$	M-30-4-20
					0	M-50-0-20
	50	602	1227	1227	$C \times 0.02$	M-50-2-20
					$C \times 0.04$	M-50-4-20
					0	M-60-0-20
					$C \times 0.02$	M-60-2-20
					$C \times 0.04$	M-60-4-20
	60	645	1090	$C \times 0.01$	0	M-30-0-40
					$C \times 0.02$	M-30-2-40
					$C \times 0.04$	M-30-4-40
					0	M-50-0-40
40	30	469	1621	$C \times 0.01$	$C \times 0.02$	M-50-2-40
					$C \times 0.04$	M-50-4-40
					0	M-60-0-40
					$C \times 0.02$	M-60-2-40
	50	602	1227	1227	$C \times 0.04$	M-60-4-40
					0	M-30-0-20
					$C \times 0.02$	M-30-2-20
					$C \times 0.04$	M-30-4-20
	60	645	1090	$C \times 0.01$	0	M-50-0-20
					$C \times 0.02$	M-50-2-20
					$C \times 0.04$	M-50-4-20
					0	M-60-0-20
					$C \times 0.02$	M-60-2-20
					$C \times 0.04$	M-60-4-20

2.2 Measuring method

Measuring method of length change was shown in Figure 2. The length change is measured by 1/1000 mm displacement sensor. Two teflon seats of 0.2 mm in

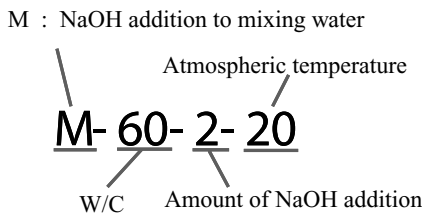


Figure 1. The specimen name of an example.

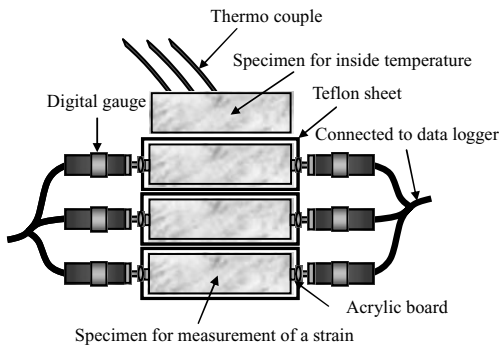


Figure 2. Measuring method of length change.

Table 2. The relative humidity of each region.

Stage	Wet stage			Dry stage		
	I reg- ion	II reg- ion	III reg- ion	I' reg- ion	II' reg- ion	III' reg- ion
Relative humidity %	40→60	60→80	80→95	95→80	80→60	60→40
time (hour)	24	28	28	28	28	28

thickness were paved under the specimen to decrease the friction.

Relative humidity was controlled by three regions in the process of wet and dry stage as shown in Table 2. Measurement was performed with the order of drying stage after wetting stage. In wet stage, I~III regions correspond to the R.H. region of 40% → 60%, 60% → 80% and 80% → 95% respectively. In dry stage conversely, I'~III' regions correspond to the R.H. region of 95% → 80%, 80% → 60% and 60% → 40% respectively. The measurement was begun when the length change of specimen has disappeared and the temperature of specimen becomes uniform under cared in 40% and 95% of R.H. at the wetting stage and drying stage, respectively.

The measurement of mass change due to dry and wet change was performed. The setting of time on

measurement mass change was same as measurement of length change. The rate of mass change was showed by the percentage of mass at each measurement time based on mass of the specimen during the early stages of dry.

2.3 Measurement of pore size distribution

The measurement of pore size distribution was performed by mercury porosimeter. The sample was adjusted to particle size of 2.5~5 mm. The pre-processing was done at -45 degrees Celsius for 3 days by using the freeze-drying machine.

3 RESULTS

3.1 Length change of cement paste NaOH addition to mixing water

Figures 3 and 4 shows the strain history in the wetting and drying stage, respectively. The strain increases with the increase of amount of NaOH addition in each W/C as shown in Figures 3 and 4.

Figure 5 shows the relationship between the final drying shrinkage strain shrinkage strain is larger with the increase of R_2O density at each W/C. The tendency is more remarkable in case of large W/C

Figure 6 (a) and (b) shows the relationship between the strain and mass change rate at W/C 60% and Figure 6 in wet stage, the expansion strain increases in proportion with the increase of the mass rate. In dry stage, it seems that the increase rate of dry shrinkage strain to the rate of mass reduction is small in the early stage and then the increased rate becomes large gradually at each additional amount of NaOH. Moreover, the less amount of NaOH addition, the increased rate is the more sharply. From above all, it seems that NaOH addition makes internal pore organization of cement paste sparse and then the enough capillary tension does not occur by waters in relatively large pore being dissipate.

3.2 The pore size distribution of cement paste NaOH addition to mixing water

Figure 7 shows the pore size distribution of cement paste with W/C of 60%. It seems that the pore with

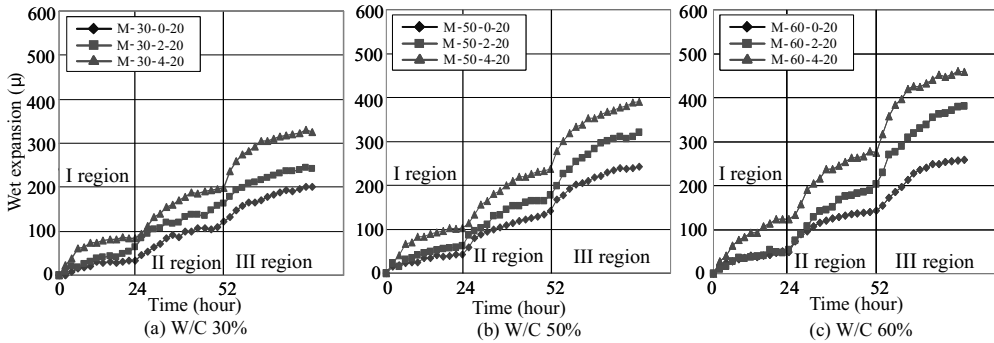


Figure 3. Relationship between wet expansion and time.

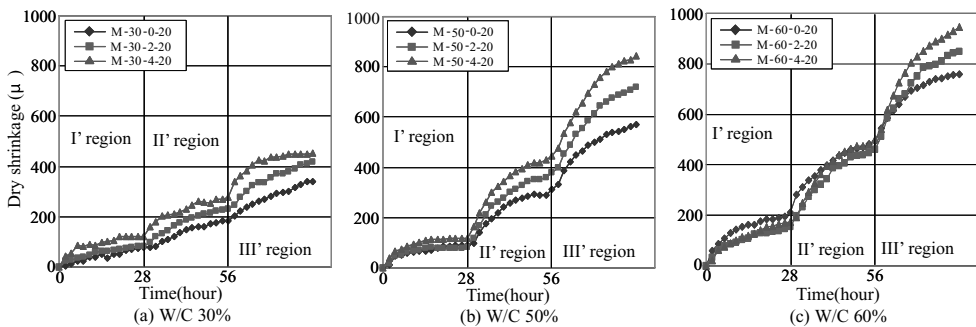


Figure 4. Relationship between dry shrinkage and time.

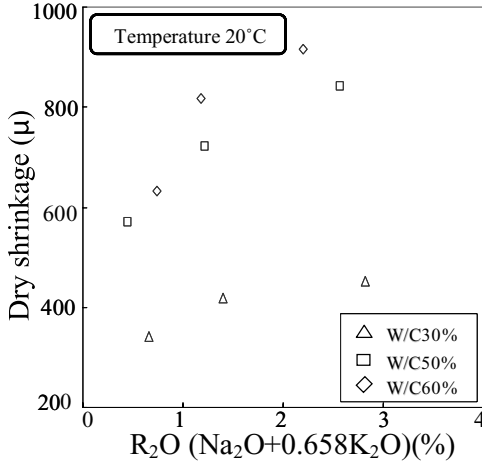


Figure 5. Relationship between dry shrinkage and R_2O density.

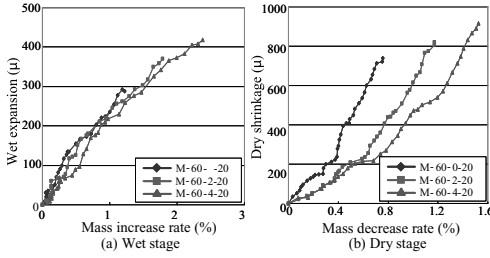


Figure 6. Relationship between strain and mass change rate (%).

large diameter increases with the increase of NaOH addition as shown in Figure 7.

Figure 8 shows the relationship between the R_2O density ($Na_2O + 0.658K_2O$) and the total pore volume. It can be seen that the total pore volume increase as R_2O density becomes larger in W/C 30% cement paste. This tendency appears remarkably in case of high W/C. This phenomenon is thought that the hydration reaction at the early stage was promoted by added NaOH in mixing water. In liquid phase of high R_2O density, the C-S-H gel with high density is generated on the surface of cement particle by a rapid hydration reaction. Therefore, the hydration reaction is restrained in the unhydrate cement part for a long terms and then growth of $Ca(OH)_2$, C-S-H and Ettringite is prevented. As a result, the pore structure with relation large diameter occurs. Moreover, the phenomenon is discussed bases on the viewpoint of solubility product. Ca^{2+} exists in the minute pore solution and then its density is kept by

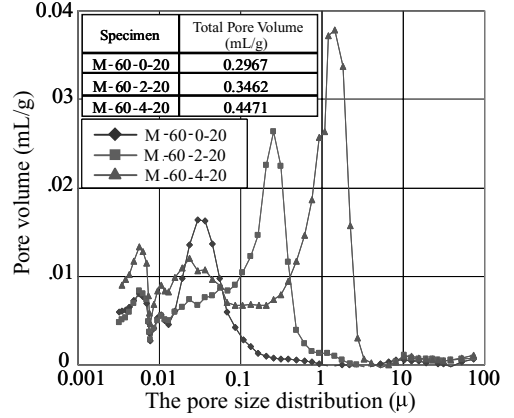


Figure 7. The pore distribution of W/C 60% cement paste.

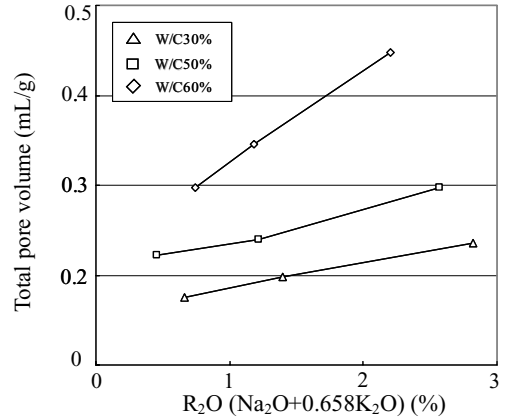
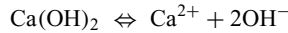


Figure 8. Relationship between total pore volume and R_2O density.

equilibrium state as shown in Eq. (1).



$$K_{sp} = [Ca^{2+}][OH^-]^2 = \text{const} \quad (1)$$

Namely, Ca^{2+} density decreases with increase of OH^- density and then the hydration reaction of cement is prevented. As a result, it seems that pore structure becomes porous.

In the past research, it is reported that the change of pore structure greatly influence on volumetric change due to dry and wet change. Therefore, the R_2O density is not the sole cause of length change because the change of pore structure influence on length change of cement paste. In the next chapter, the specimen of which pore structure is identical and only the R_2O

density is different was made and then the influence of R_2O density on volumetric change of cement paste was discussed.

4 EXPERIMENT OF LENGTH CHANGE IN CEMENT PASTE WITH SAME PORE STRUCTURE

4.1 Experimental outline

The specimen, of which pore structure is identical and only the R_2O density is different, was made. The making method is that the specimen was made at same batch and then the specimens were soaked into the aqueous sodium hydroxide of which concentration was 0, 2 and 4%. Table 3 shows a soaking period. The soaking period of low W/C cement paste was long, on the other hand, soaking period of high W/C cement paste was short. Table 4 shows the concentration of aqueous sodium hydroxide and mix proportion. The example of specimen name is shown in Figure 9. The measuring

Table 3. Period to soak.

W/C (%)	Aqueous sodium hydroxide soaking period (Day)
30	16
50	28
60	36

Table 4. Mix proportion (No.2).

Atmospheric temperature (°C)	W/C (%)	Unit content (kg/m ³)				Specimen
		Water	Cement	Chemical admixture	Concentration of aqueous sodium hydroxide (%)	
20	30	469	1621	$C \times 0.01$	0	P-30-0-20
					2	P-30-2-20
					4	P-30-4-20
					0	P-50-0-20
	50	602	1227		2	P-50-2-20
					4	P-50-4-20
					0	P-60-0-20
					2	P-60-2-20
	60	645	1090		4	P-60-4-20
					0	P-30-0-40
					2	P-30-2-40
					4	P-30-4-40
40	30	469	1621	$C \times 0.01$	0	P-50-0-40
					2	P-50-2-40
					4	P-50-4-40
					0	P-60-0-40
	50	602	1227		2	P-60-2-40
					4	P-60-4-40
					0	
					2	

method of length change, material age, size of specimen and method of mixing are same as shown in 2.1 section.

4.2 R_2O density and pore size distribution of cement paste

Figure 10 shows a pore size distribution of cement paste with the 60% of W/C and then Table 5 shows R_2O density of cement paste with the 50 and 60% of W/C. It is noted that the pore structure of W/C 60% cement paste is identical without the concentration of aqueous sodium hydroxide. Therefore, there is no influence of R_2O density on the change of pore structure at each parameter.

4.3 Length change of cement paste

Figures 11 and 12 show the strain history of cement paste with the 50 and 60% of W/C at the temperature of

P : Soak a specimen in aqueous sodium hydroxide

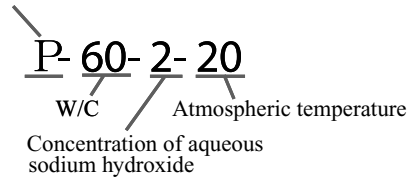


Figure 9. The specimen name of an example.

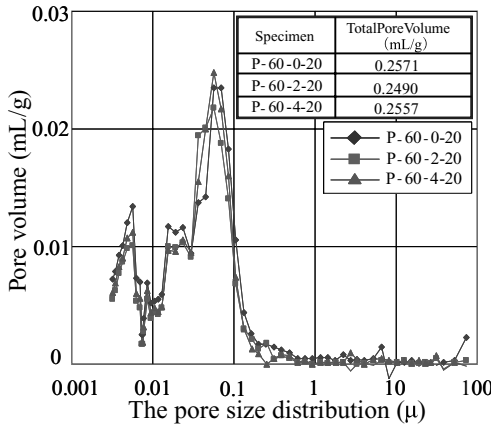


Figure 10. The pore size distribution of W/C 60% cement paste.

Table 5. R_2O density of cement paste.

Specimen	R_2O ($Na_2O + 0.6258K_2O$) (%)
P-50-0	0.48
P-50-2	1.10
P-50-4	2.87
P-60-0	0.49
P-60-2	1.27
P-60-4	2.39

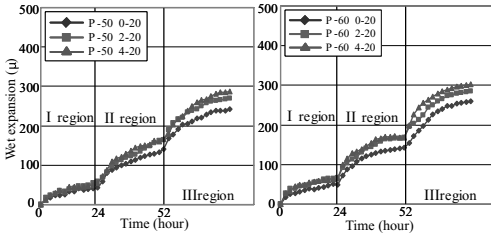


Figure 11. Relationship between wet expansion and time at 20 degrees Celsius.

20 degrees Celsius in wetting and drying stage, respectively. The strain is increasing with the increase of R_2O density in each W/C as shown in Figures 11 and 12.

The charge model on surface of hydration product is shown in Figure 13. The surface of hydration product is charged and then it seems that the alkali ion that is attracted with a negative electric charge for existence of SiO^- is adsorbed. As a result, the outside edge of the hydration product takes on positive electric charge in appearance. To discuss the increase of strain based on this model, the electric repulsion occurs between

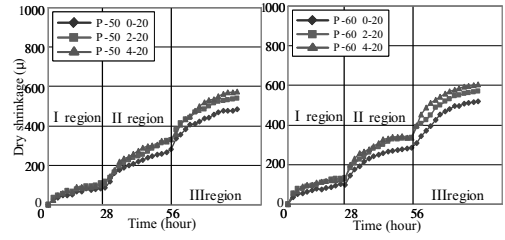


Figure 12. Relationship between dry shrinkage and time at 20 degrees Celsius.

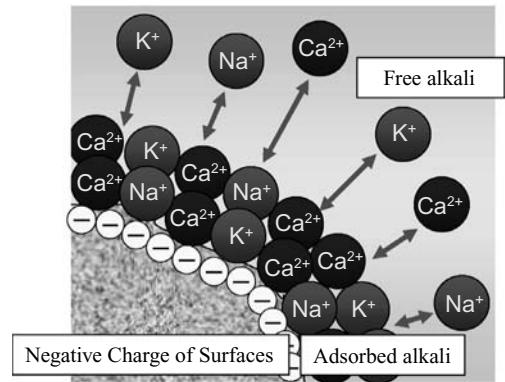


Figure 13. The charge model on the surface of hydration product.

free alkali and the adsorption alkali and then it seems that this electric repulsion promote length change of cement paste.

4.4 Relationship between length change due to R_2O density and atmospheric temperature

Figures 14 and 15 show the strain history of cement paste with the 50 and 60% of W/C at the temperature of 40 degrees Celsius in wetting and drying stage, respectively. In wet stage, the strain is increasing with the increase of R_2O density in each W/C as shown in Figures 14 and 15.

Table 6 shows the increasing rate of a final strain with the increase of atmospheric temperature calculated by the following Equation.

$$\frac{\varepsilon_{f-40} - \varepsilon_{f-20}}{\varepsilon_{f-20}} = \Delta \varepsilon_T \quad (2)$$

ε_{f-40} : The final strain at 40 degrees Celsius
 ε_{f-20} : The final strain at 20 degrees Celsius
 $\Delta \varepsilon_T$: Increase of the strain with increase of atmospheric temperature

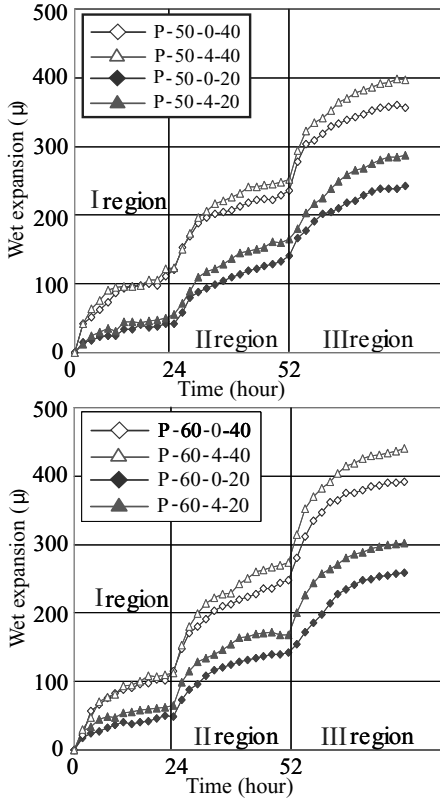


Figure 14. Relationship between wet expansion and time at 20 and 40 degrees Celsius.

In dry stage, the increasing rate of increase of a final strain is constant without the temperature. However, in wet stage, the atmospheric temperature has a considerable influence on the rate of increase of a final strain.

Table 7 shows the increasing rate of the strain of unit alkali, calculated by Eq. (3).

$$\frac{\varepsilon_{fD} - 4^{-\varepsilon} fD - 0}{R_2O} = \Delta\varepsilon_A \quad (3)$$

$\varepsilon_{fD}-4$: The final strain which is sorbed 4% aqueous sodium hydroxide
 $\varepsilon_{fD}-0$: The final strain which is sorbed 0% aqueous sodium hydroxide
 $\Delta\varepsilon_A$: Increase of the strain of unit alkali

In both dry and wet stage, the higher W/C is the larger the increasing rate of the strain of unit alkali. Moreover, the same tendency occurs remarkably in the condition that is atmospheric temperature is high. It seems that the solubility product of alkali ion such

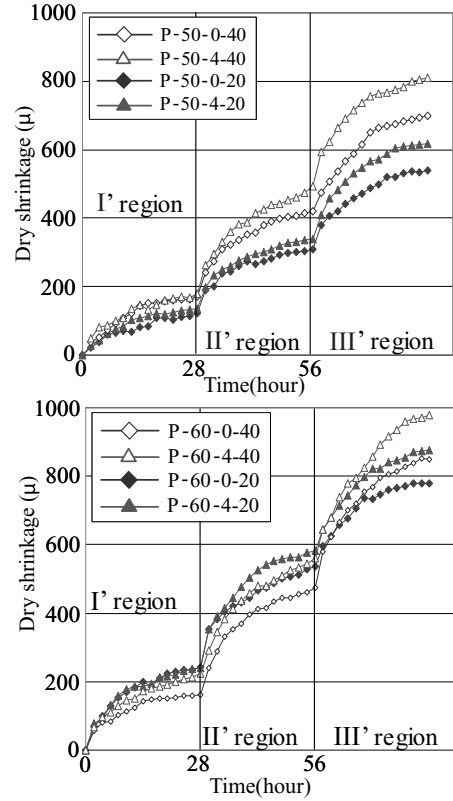


Figure 15. Relationship between dry shrinkage and time at 20 and 40 degrees Celsius.

Table 6. The rate of increase of a final strain with increase of atmospheric temperature.

Specimen	Wet stage	Dry stage
P-50-0	1.46	1.29
P-50-4	1.38	1.31
P-60-0	1.51	1.10
P-60-4	1.45	1.12

as Na^+ and K^+ was changed by atmospheric temperature. The solubility product of alkali ion increases under the high atmospheric temperature and then the dissolution of alkali ion in pore solution is activated. The electric repulsion which occurs between free alkali and the adsorption alkali grow up with increase of R_2O density. As a result, it seems that the rise of electric repulsion contributes to promote length change of cement paste. Moreover, when W/C is high, the surface area of hydration product is large and then the

Table 7. The ratio of increase of the strain of unit alkali.

Stage	W/C (%)	Atmospheric temperature (°C)	Increase of the Strain of unit alkali
Wet stage	50	20	18.4
		40	17.2
		20	22.6
		40	25.3
Dry stage	50	20	33.1
		40	46.0
	60	20	51.6
		40	68.9

amount of adsorption alkali grows up. Therefore, the electric repulsion power grows up with increase of R_2O density. However, it will be necessary to examine it in the future because this mechanism is not enough to be clear yet.

5 CONCLUSIONS

The finding obtained in this study is shown below.

1. It is clear that the pore with large diameter tends to increase by adding NaOH to mixing water and then the change of pore structure greatly influence on volumetric change due to dry and wet change.

2. Measurement of length change was performed by using the specimen of which pore structure is identical and only the R_2O density is different and then it is clear that length change of cement paste tends to increase with increase of R_2O density. Moreover, this tendency appeared remarkably at high atmospheric temperature.

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Stress induced shrinkage of concrete in tension

H.W. Reinhardt & T. Wüstholtz

University of Stuttgart, Stuttgart, Germany

ABSTRACT: The paper deals with shrinkage and creep experiments under tensile loading on three types of self-compacting concrete. The experiments have been conducted on specimens which were wrapped in foil in order to simulate the interior of a mass concrete structure. The superposition of creep and shrinkage turned out to be questionable. The results could not be explained without assuming a stress-induced shrinkage component which is the largest for low-strength concrete and the smallest for high-strength concrete.

1 INTRODUCTION

Creep and shrinkage are time-dependent phenomena which have been investigated many times. Most investigations concern the compressive behaviour where shrinkage strain and creep strain follow the same direction. There are some theories which claim that shrinkage of a loaded specimen is different from shrinkage of a non-loaded specimen due to suppression of microcracks (Alvaredo 1994). Bazant and Wittmann postulate other causes of stress induced shrinkage (Bazant & Yunping 1994, Wittmann 1993). If stress induced shrinkage is independent of the loading direction does it also occur under tensile loading? That was the question which will be looked into in the following.

2 EXPERIMENTAL

2.1 *Material*

Three concrete compositions have been investigated which are given in Table 1.

All mixes had self-compacting properties. Therefore, the fresh properties are given in detail. The mix of strength class C30/37 contains limestone powder as addition, the C45/55 had a mixture of limestone powder and flyash as additions, and the C60/75 had only flyash as a second binder component.

The cement was in all three cases a portland composite cement CEM II/A-LL which contains limestone powder up to 20%. The equivalent water to cement ratio taking account of 0.4 for the k -value of the flyash varied between 0.70 and 0.34. The volume of the cementitious paste which is responsible for shrinkage and creep varied considerably. With 3.05 g/cm^3 the density of cement, 2.30 g/cm^3 the

density of flyash, and 1.00 g/cm^3 the density of water the cementitious paste volume of C30/37 amounted to 245.4 litres/m^3 , of C45/55 306.7 litres/m^3 , and of C60/75 405.1 litres/m^3 . The mechanical properties are listed in Table 1.

2.2 *Free shrinkage measurement*

There were three types of free shrinkage measurement: one on prisms of $100 \times 100 \times 530 \text{ mm}^3$ starting at an age of 1 day in 20°C and 65% RH. The second and third measurement type was performed on dog-bone shaped specimens with a central prismatic portion of $80 \times 100 \text{ mm}^2$ cross-section. In both cases the specimens were stored up to an age of 7 days moist, then wrapped into foil and stored in 20°C and 65% RH until the shrinkage measurement started on the 29th day in a room with 20°C and 50% RH. The specimens prepared for the second type of shrinkage measurement remained inside the wrapping during the whole observation period. The specimens of the third measurement type have been unwrapped at an age of 29 days. The wrapping should simulate a thick-walled structural element which dries only very slowly.

2.3 *Sustained loading*

Sustained loading was performed on dog-bone shaped specimens with a central prismatic portion of $80 \times 100 \text{ mm}^2$ cross-section. The specimens were wrapped in foil in the same manner as some shrinkage specimens. A lever type loading frame was used. Details are described in (Wüstholtz & Reinhardt 2007).

2.4 *Humidity sensing*

The humidity around the specimens inside the foil wrapping was measured continuously by a sensor.

Table 1. Mixture proportions and concrete properties.

Strength class			C30/37	C45/55	C60/75
Cement content	m_c	[kg/m ³]	239	298	495
Cement type			CEM II/A-LL 32.5R		CEM II/A-LL 42.5R
Total water content (incl. water from superplasticizer)	m_w	[kg/m ³]	167	166	188
Equivalent water-cement ratio $(w/c)_{eq}$ ¹⁾	$\frac{m_w}{m_c + 0.4 \cdot m_{FA}}$	[-]	0.70	0.49	0.34
Superplasticizer (type: PCE)	%SP	[% by mass of cement]	1.25	1.25	1.45
Fly ash	m_{FA}	[kg/m ³]	0	99	126
Limestone powder	m_{LS}	[kg/m ³]	337	133	0
Aggregates: rounded river sand and gravel	m_{agg}	[kg/m ³]	1601	1640	1510
Powder content (cement + filler)	m_p	[kg/m ³]	576	530	621
Paste volume (inclusive 15 litres of air)	V_{Paste}	[litres/m ³]	385	370	420
Water-powder ratio (by volume)	V_w/V_p	[-]	0.82	0.87	0.86
Fresh properties					
Slump flow	sf	[mm]	750	770	770
V-funnel flow time	tv	[s]	10.5	12.9	12.0
J-ring:	sf _J	[mm]			
Slump flow	t _{500,J}	[s]	750	700	730
Flow time			5	7	8
Hardened properties					
(age of 28 days)					
Compressive strength (cubes of 150 × 150 × 150 mm ³)	$f_{cc,150}$	[MPa]	41.1	60.2	77.6
Modulus of elasticity (compression)	E_c	[MPa]	29770	34720	38900
Tensile strength	f_{ct}	[MPa]	3.2	3.9	4.7

¹⁾ With max. $m_{FA} = 0.33 \cdot m_c$, according to DIN 1045-2.

This measurement turned out to be important when evaluating the results.

3 RESULTS

3.1 Free shrinkage

Figure 1 summarizes the shrinkage measurement results. The left plot shows the results received with the wrapped specimens, the middle one the measurements starting on the 29th day, and the right plot the measurements starting on the 1st day.

The wrapped specimens show a slow increase of shrinkage with time which has been expected since drying is hindered by the wrapping foil. The middle plot shows a rapid increase of drying during the first 100 days of measurement. Thereafter, there is only a small increase of shrinkage. One should mention

that the specimens were wrapped in foil up the 29th day. Then, the measuring instruments (LVDT) were attached and the specimens could dry. The right plot is the picture of prisms which were placed in a climate controlled room on the 1st day. The shrinkage is very fast up to almost 100 days, decelerates then, and comes to an end on 500 days. The specimens, which could dry after 29 days are closest together. Thinking in terms of autogenous shrinkage and drying shrinkage (Carbonation shrinkage is thought to be negligible) the autogenous part had developed in moist condition before the measurements started. What can be seen is that the drying shrinkage part is very similar. This picture changes drastically looking to the plot of prisms which could dry from the 1st day (right plot). There, autogenous and drying shrinkage are superimposed. The lines deviate strongly from each other.

Most shrinkage is observed at the high strength concrete C60/75, least shrinkage at the C30/37. The same

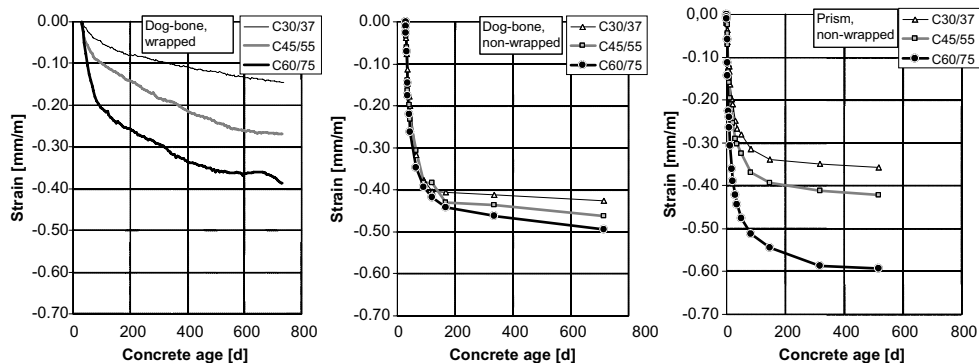


Figure 1. Shrinkage measurement results. Left: Wrapped dogbone shaped specimens in 20°C 50% RH starting on 29th day, Middle: Non-wrapped prisms in 20°C 50% RH starting on 29th day, Right: Non-wrapped prisms in 20°C 65% RH starting on 1st day.

order is seen also with the wrapped specimens where the C60/75 shrinks the most and C30/37 the least.

There must be reasons for this behaviour. First, C60/75 has the largest autogenous shrinkage. However, using the prediction of Model Code 90 (Müller et al. 1999) the autogenous shrinkage part of C60/75 is only 0.15 mm/m and of C 30/37 it is 0.05 mm/m. This can explain the difference between the shrinkage of the middle and the right figure. But it cannot explain that C60/75 shrinks more than the other two concrete mixtures. The reason for that must be the different cementitious paste content of the mixtures. According to Grube (Grube 1991) the cementitious paste content is the key parameter for the extent of shrinkage. He has found an almost linear relation between paste content and shrinkage of concrete. If we assume a shrinkage amount of unity for C45/55 then C30/37 should have a reduction factor of 0.80 and the C60/75 should have an increase factor of 1.32. If we analyse the data such that only the drying part (total shrinkage minus autogenous shrinkage calculated acc. to (Müller et al. 1999) is considered then the ratios from the measurements read 0.87 and 1.32, i.e. the agreement is rather good. It is difficult to predict a comparative ratio for the wrapped specimens since the final shrinkage is not yet reached. There is only a strong trend that the samples shrink more the more cementitious paste is in them.

3.2 Total strain in creep test

Figure 2 shows the total measurement of the sustained loading test. The loading ratio was 69% of the mean short time loading strength. Although the tensile loading should lead to a tensile strain one can observe that the total strain tends to a negative strain, i.e. the shrinkage strain prevails. After 50, 100, and 150

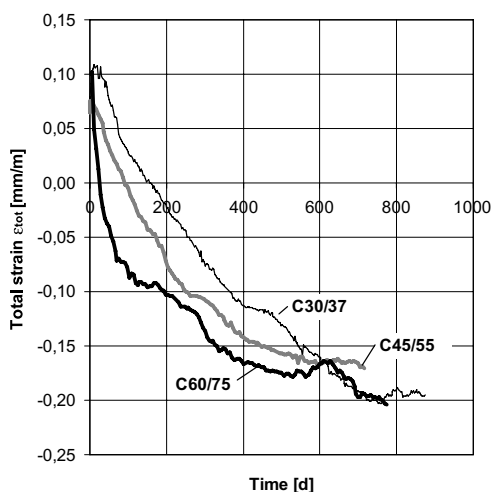


Figure 2. Total strain from an age of 29 days. The load ratio is 69% ($r = 0.69$).

days, resp., the C60/75, C45/55, and C30/37 intersects the zero strain value. So, shrinkage strain has compensated creep strain. After 600 days of loading, all concrete types showed a negative strain of 0.17 mm/m. Thereafter, they deviate a little from each other.

The usual assumption is that concrete with a high water to cement ratio creeps more than a concrete with a low water to cement ratio. This is also postulated by the Model Code (Müller et al. 1999) but one should keep in mind the amount of cementitious material which is different from each other as always discussed in chapter 3.1. So, the total strain is mainly determined by the shrinkage strain rather than by the creep strain.

3.3 Humidity around the specimens

The humidity inside the foil wrapping has been measured continuously. It was obvious that the humidity decreases as a function of time because the wrapping is not absolutely air tight and the concrete consumes water during hydration. The outside humidity was kept constant at 50% RH. But it was also obvious that the loaded specimens were surrounded by a relative humidity that is lower than the humidity of the load-free specimens. Although the scatter is considerable the trend is clear. This phenomenon has been found already by others (Alexandrovsky & Desov 1968). The difference is the largest with the C30/37 and is almost negligible with the C60/75. The reason for that is that the supply of free water is the highest with the C30/37 whereas most of the water is consumed with the low water to cement ratio concrete C60/75. This aspect will play a mayer role in the analysis of the creep results.

4 DISCUSSION OF RESULTS

4.1 Superposition of strain components

In order to specify creep, usually, one measures the total strain in a sustained loading experiment and subtracts the instantaneous strain and the shrinkage strain which is simultaneously measured on load-free specimens, from the total strain. The carbonation shrinkage is neglected since the experiments do not last long and the carbonation influences only the surface of the specimens. Micro-cacking of concrete is also neglected. Shrinkage has then two components: autogenous and drying shrinkage, and, as supposed in the creep tests, the stress induced shrinkage. As creep is concerned there is basic and drying creep which cannot be separated in the experiments.

4.2 Free shrinkage

The shrinkage strain has been predicted by the Model Code (Müller et al. 1999) and compared with the test results. Figure 3 shows the experimental and calculated curves. The full lines belong to the calculation and the lines with symbols belong to the experimental results. One can observe that the measured shrinkage strain of C30/37 is much smaller and that the measured strain of C60/75 is much larger than the predicted ones. The values for the C45/55 is in good agreement with the prediction. The deficiency of the model is that the composition of the concrete is not taken into account, the only parameter is the compressive strength.

The model allows to separate autogenous from drying shrinkage. The high-strength concrete exhibits the largest autogenous shrinkage and the smallest drying shrinkage, whereas the low-strength concrete shows

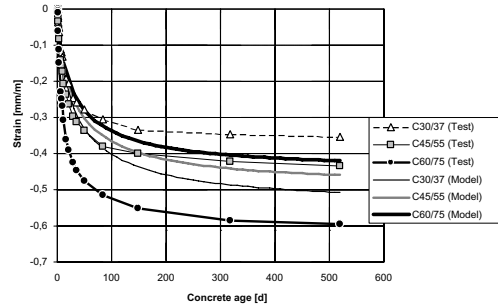


Figure 3. Experimental and calculated shrinkage strain for unwrapped specimens from an age of 1 day at 20°C and 65% RH.

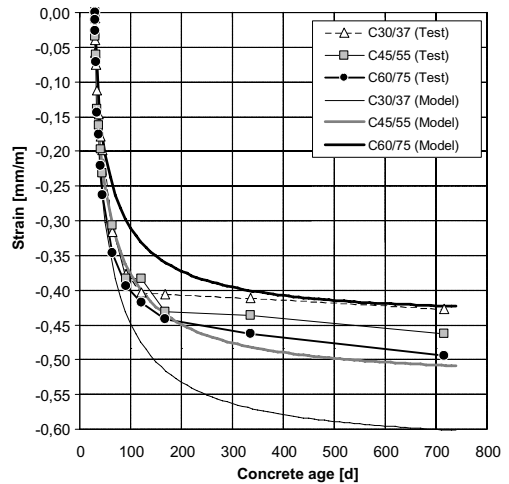


Figure 4. Shrinkage strain from experiments and calculation from an age of 29 days at 20°C and 50% RH.

the opposite. The results will be used later when creep is discussed. The results of the tests which started only after 29 days are compared in Figure 4. The impression is the same as before, namely that the shrinkage strain of C60/75 is greatly underestimated and the shrinkage strain of C30/37 is overestimated. One should mention that the climatic conditions of the results of Figures 3 and 4 are different.

The shrinkage after 500 days of drying has been also calculated according to (Bazant et al. 1993). This model takes account of the cement content, the aggregate content, the water to cement ratio, the compressive strength, and the humidity. The outcome of shrinkage for the specimens wrapped in foil were 0.56 mm/m for C30/37, 0.57 mm/m for C45/55, and 0.81 mm/m for C60/75. These values are much larger than the measured results. They are also larger than

the values received on those specimens which were not wrapped in foil (see Figure 1, middle diagram).

The B3 Model (Bazant 1995) has been applied to the specimens which were not wrapped in foil and which could dry in a 50% RH atmosphere. The shrinkage after 500 days of drying was predicted as 0.51 mm/m for C30/37, 0.48 mm/m for C45/55, and 0.53 mm/m for C60/75. The prediction is rather close to the measured values. An evaluation of numerous shrinkage results came also to the conclusion that the B3 Model leads to the best fit (Fernandez-Gomez & Landsberger 2007).

4.3 Creep and shrinkage

The Model Code (Müller et al. 1999) has also been used for the prediction of creep. Since the humidity inside the foil wrapping was not constant the calculations have been made for 50, 65, and 80% RH. Figure 5 contains various lines: the line with the designation ϵ_{tot} represents the total measured strain in the creep experiment, the black line which crosses the line of the total strain represents the free shrinkage as measured on companion specimens, the dotted line shows the instantaneous or elastic strain, the three almost parallel lines on top are the calculated creep strains, and the three lines at the bottom are the shrinkage strains which should occur in order to explain the total behaviour. There is one line in between which

represents the free shrinkage as measured on companion specimens, the dotted line shows the instantaneous or elastic strain, the three almost parallel lines on top are the calculated creep strains, and the three lines at the bottom are the shrinkage strains which should occur in order to explain the total behaviour. There is one line in between which represents the total minus free shrinkage strain. This should, if superposition were valid, be conventionally the creep strain. But the line tends to negative values which is physically not possible. That means that the shrinkage of the loaded specimens must be larger than the shrinkage of the load free specimens. There is one aspect which may have led to the difference, i.e. the local humidity. As discussed in 3.3 the humidity around the loaded specimens was about 10% RH lower which leads, according to the model, to a difference of 22%. That means that the line for shrinkage would shift by 22% downwards but this is by far not enough to explain the decreasing line of the total strain minus shrinkage strain. Therefore, one must assume that an extra amount of shrinkage is present which is called stress induced shrinkage.

A similar behaviour has been found with C45/55 which is shown in Figure 6. The humidity difference between loaded and load free specimens is here only 5% RH and, thus, the correction term of shrinkage according to the model (Müller et al. 1999) is only 2% which is within the scatter of experimental results. So, also here, stress induced shrinkage can be recognized.

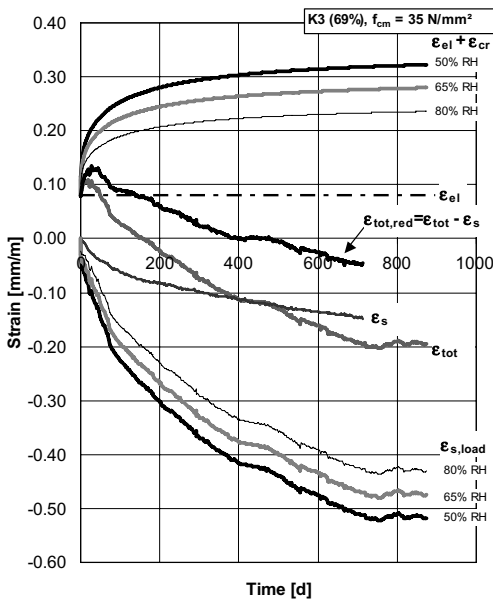


Figure 5. Strain components of creep experiments on C30/37 with loading ratio of 69%.

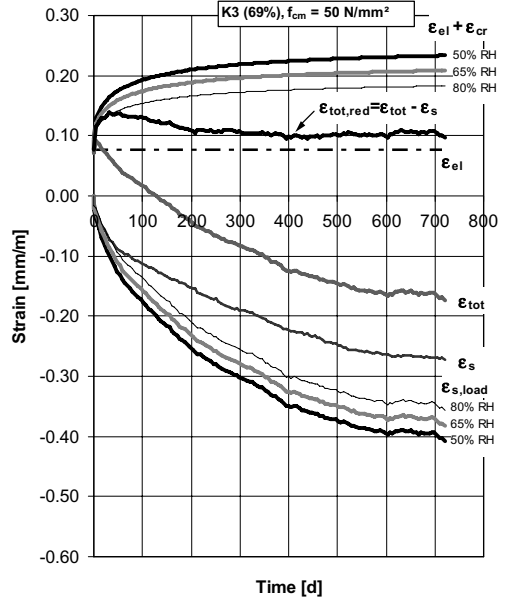


Figure 6. Measured and calculated strain for strength class C45/55.

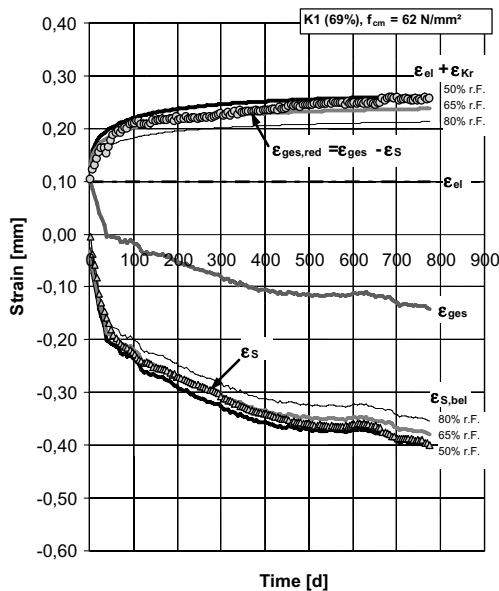


Figure 7. Measured and calculated strain for strength class C60/75.

The last example concerns the concrete C60/75 which can be found in Figure 7. As stated in chapter 3.3 there was a small difference in humidity and Figure 7 shows almost no stress induced shrinkage because the measured line of total minus shrinkage strain coincides with the predicted creep curve. It can be concluded from Figures 5 to 7 that stress induced shrinkage exists and that it is larger with lower strength class.

One should recall the test conditions. The loading ratio was quite high, it amounted to 69% of the mean tensile strength as measured at the time of load application. Tests have also been performed with 75% loading ratio, but the specimens failed after a few days (Wüstholtz & Reinhardt 2007). That means that the stress was very close to the sustained tensile strength. The specimens were wrapped in foil in order to simulate the interior of a mass concrete structure. The tests do not allow to extrapolate the results to other humidity conditions, for instance to specimens which dry quicker than the ones tested. Comparing the three concrete types it is not only the strength class which makes them different but also the composition. C30/37 had a large amount of limestone powder whereas C60/75 had a large quantity of flyash. C45/55 contained both types of fillers. Flyash is a pozzolanic addition whereas limestone powder is inert. It seems that the inert addition led to more stress induced shrinkage.

Bazant (Bazant & Yunping 1994, Bazant & Chern 1985) has postulated stress induced shrinkage which is due to microdiffusion from capillary pores to gel

pores. He has validated the hypothesis with creep tests. During our experiments, one could observe that the moisture around the specimens which were wrapped in foil was lower for those which were loaded compared to those which were load-free. This could mean that moisture is more consumed in the loaded specimens. This could be due to microdiffusion. The water which diffuses into the gel pores react with unreacted cement and causes chemical shrinkage and self-desiccation which in turn produces autogenous shrinkage. A second effect which has been reported is that specimens which were loaded for long time show a higher tensile strength after unloading compared to specimens which were load-free (Reinhardt & Rinder 2006). This would support the idea of continued hydration. It could also happen that microcracks appear which enhance diffusion and cause the same effect as microdiffusion does.

5 CONCLUSION

Shrinkage and sustained tensile loading tests have been carried out on three types of concrete: a low-strength concrete C30/37, a medium-strength concrete C45/55, and a high-strength concrete C60/75. All were self-compacting. The specimens were wrapped in foil in order to simulate the interior of a mass concrete structure. The main conclusions are:

- The results show a great influence of concrete composition on shrinkage which could not accurately be predicted by current prediction models.
- The usual method to determine creep from sustained loading tests by subtracting elastic and shrinkage strain from the total strain showed a further component which is called stress-induced shrinkage.
- The stress-induced shrinkage was the largest for low-strength concrete and the smallest for high-strength concrete.
- The phenomenon of stress-induced shrinkage deserves more attention and research.

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Relationship between creep and chemical potential of concrete

M. Ozawa, M. Kasuya & H. Morimoto

Gifu University, Gifu, Japan

ABSTRACT: In this study, in which the internal moisture is treated as changes in the internal relative humidity, uni-axial creep tests are conducted to determine the relationship between the creep and the changes in the internal humidity. The chemical potential of water is focused as one of the properties of internal moisture, and migration of internal moisture is evaluated in terms of changes in the chemical potential of water. The linkage between such changes and the compressive and tensile creep is then elucidated. The relationship between creep development and changes in the chemical potential associated with moisture migration was investigated from the aspect of thermodynamics. As a result, linear correlations were recognized between them. This indicates a possibility of formulating a creep prediction equation using the chemical potential of water in concrete as a parameter.

1 INTRODUCTION

The creep behavior of concrete, which strongly affects early cracking, is also strongly affected by moisture migration in concrete. It is therefore vital for elucidating the creep mechanism of concrete to treat creep as the deformation behavior of concrete involving moisture migration, thereby grasping the relationship between creep and moisture migration. Despite the wide variety of studies on the creep of concrete in the literature, few have given sufficient consideration to the relationship between internal moisture and creep deformation. Vigorous discussion has been conducted on the drying creep of concrete since the report by Pickett (Pickett, G. 1947) that the sum of the basic creep strain and the drying shrinkage strain is always smaller than the creep strain under air-dry conditions (the Pickett effect). Bazant reported that the Pickett effect can be explained by the micro prestress-solidification theory (Bazant, Z.P. et al., 1997). Wittmann pointed out in regard to the Pickett effect that the drying shrinkage strain evaluated as the difference between the drying creep and the basic creep is not identical to the drying free shrinkage strain (Wittmann, F.H. 1982). Asamoto reported that internal moisture is related to the creep behavior of concrete. This study aims to experimentally elucidate the linkage among the creep of concrete, water migration in concrete, and the properties of such water, thereby obtaining fundamental data for formulating a creep prediction model (Asamoto, S. et al., 2000). In this study, in which the internal moisture is treated as changes in the internal relative humidity, uniaxial creep tests are conducted to determine the relationship between the creep and the changes

in the internal humidity. The chemical potential of water is focused as one of the properties of internal moisture, and migration of internal moisture is evaluated in terms of changes in the chemical potential of water. The linkage between such changes and the compressive and tensile creep is then elucidated.

2 EVALUATION OF MOISTURE MIGRATION IN CONCRETE

Moisture migration in concrete was evaluated as changes in the chemical potential of water (Tada, S., 2005) (Gordon, M. et al., 1999). A chemical potential is evaluated as the Gibbs free energy per mol of a substance.

Equation (1) gives the chemical potential of water, μ_w . The term μ_w° represents the standard generated chemical potential. This study focuses on the amounts of chemical potential associated with changes in the vapor pressure of water, μ_w^* . In Eq. (1), which describes the chemical potential of pure liquid, the second term of the right side, μ_w^* is focused in this study as the chemical potential of water in concrete.

$$\mu_w = \mu_w^\circ + \mu_w^* = \mu_w^\circ + RT \ln(RH) \quad (1)$$

$$\mu_w^* = RT \ln(RH) \quad (2)$$

where μ_w = chemical potential of water (J/mol), μ_w° = standard generated chemical potential (J/mol), μ_w^* = chemical potential associated with changes in the vapor pressure of water (J/mol), R = gas constant, T = Temperature (K), RH = Relative Humidity.

3 OUTLINE OF CREEP TESTS

3.1 Specimen fabrication

Table 1 gives the specified mixture proportions of concrete. Normal portland cement with a specific surface of 3,360 cm²/g and density of 3.15 g/cm³ was used as the cement at a water-cement ratio (W/C) of 57%. The fine and coarse aggregates were river sand with a density of 2.62 g/cm³ and a fineness modulus of 2.63 and crushed stone with a density of 2.61 g/cm³ and maximum size of 25 mm, respectively, both from Nagara River. Table 2 gives the as-mixed slump, air content, and temperature. Table 3 gives the types of specimens. Two types of specimens were prepared for creep tests to be subjected to compressive and tensile loads. The factors of experiment included dry and sealed conditions. Free deformation specimens, sealed and dry, were also prepared for correcting the measured strain. Figures 1 and 2 show the geometries of compressive and tensile creep specimens, including the locations of strain gauges and humidity sensors. The compressive creep specimens measured 150 by 150 by 300 mm, whereas the tensile creep specimens measured 100 by

100 by 400 mm, with a loading plate on each end to transfer the tensile stress via four deformed bars (diameter: 10 × 80 mm) embedded in the specimen. The free deformation specimens were of the same size as the specimen to be loaded. The measurement items included the strain in the longitudinal direction of specimens and the relative humidity and temperature within specimens. Embedded strain gauges manufactured by T company were used for measuring the longitudinal strain. Non-heating-type ceramic humidity sensors manufactured by N company were used for measuring the internal humidity of specimens. These were placed in the cross-sectional centers of sealed specimens and at 5, 10, and 75 mm (cross-sectional center) from the surfaces of dry specimens. After being demolded (placing after 1day), specimens were wet-cloth-cured in a thermo-hygrostatic room at a temperature of 20°C ± 3°C and relative humidity of 80 ± 5%. Loading and drying began at an age of 28 days. Table 4 gives the compressive strength, elastic modulus in compression, tensile strength, and elastic modulus in tension at 28 days. The tensile strength was determined by uni-axial tension tests using specimens of the same size as those used for tensile creep tests.

Table 1. Mix proportion.

Water cement ratio (%)	s/a (%)	Unit weight (kg/m ³)		Fine aggre- gate	Coarse aggre- gate	Admix- ture
		Water	Cement			
57	44.2	180	316	851	926	3.16

Table 2. Properties of fresh concrete.

Slump (cm)	Air (%)	Temperature (°C)
17	5.4	22

Table 3. Category of specimens.

Type of loading	Load- ing	Drying condi- tion	Size of specimen (mm)	Num- ber
Compression	Yes	Sealed	150 × 150 × 300	1
	No	Unsealed		
Tension	Yes	Sealed	100 × 100 × 400	
	No	Unsealed		

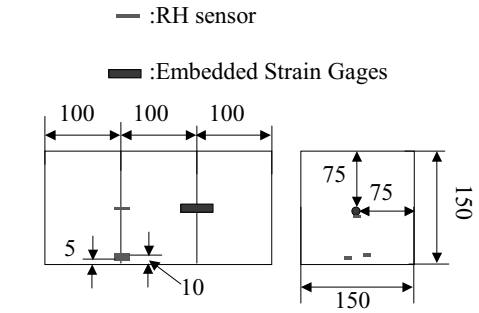


Figure 1. Size and shape for Creep specimens of compressive tests (Unit: mm).

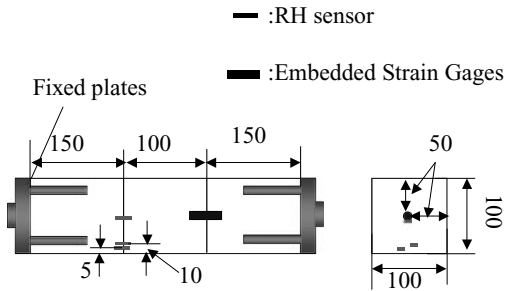


Figure 2. Size and shape for Creep specimens of tensile tests (Unit: mm).

3.2 Creep testing apparatus

In this study, hydraulic compressive and tensile creep testing apparatuses shown in Figures 3 and 4, respectively, were used. Their maximum capacities were 500 and 200 kN, respectively. After loading the specimens using load cells, the strain and load were recorded using data loggers at every 2 hours. The specimens were re-loaded when the reduction in the load due to creep has become approximately 5% of the initial load. Meanwhile, the shrinkage strain of free deformation specimens placed under the same environmental conditions was measured to correct the strain measured in the creep tests. Figure 5 shows the preset humidity history of the creep testing room. As shown in the figure, the relative humidity of the atmosphere in the room

Table 4. Strength and elastic modulus at age of 28 days.

Fc N/mm ²	Ecc kN/mm ²	Ft N/mm ²	Ect kN/mm ²
35.9	28.1	2.68	29.6

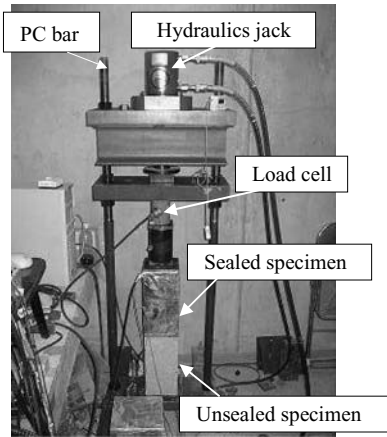


Figure 3. Compressive creep test apparatus.

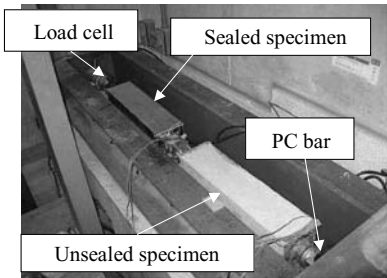


Figure 4. Tensile creep test apparatus.

was set at $80 \pm 5\%$ for the first 40 days and reduced to $40 \pm 5\%$ thereafter. The air temperature was set at $20 \pm 2^\circ\text{C}$. Figure 6 shows the loading stress histories for the compressive and tensile creep testing. Compressive and tensile stresses of 6.0 and 0.80 N/mm², respectively, were adopted in consideration of the strength test results at 28 days and the capacities of the loading apparatuses.

3.3 Method of measuring relative humidity in concrete

3.3.1 Non-heating ceramic humidity sensor (Nan-to. Y. 2000)

Figure 7 shows the sensing element of the non-heating-type ceramic humidity sensor (HLD5AT manufactured by N company) used in this study. The humidity sensor consists of a humidity sensing element (ceramic), and resistance thermometer for temperature correction of measurement values. Its ranges of humidity measurement in air and sensitivity are 20 to 90% and $\pm 3\%$, respectively. In order to confirm the operation of these sensors in concrete (an alkaline solid), a humidity preconditioning test was conducted by embedding them in concrete to determine the calibration line.

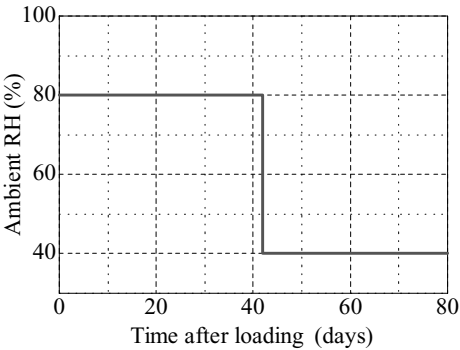


Figure 5. Ambient RH during tests.

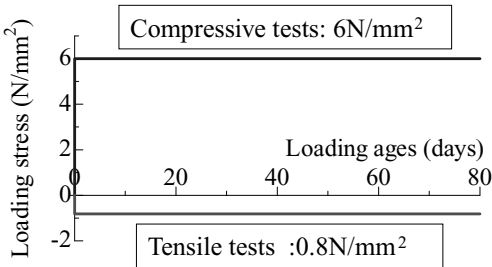


Figure 6. Loading pattern.

3.3.2 Humidity preconditioning test (Nanto, Y. 2000)

The measured values with the humidity sensor in atmospheric air and in concrete under a same humidity condition may be different. For this reason, a humidity preconditioning test was conducted to confirm the operation of the humidity sensor in concrete. Table 5 gives the salts used in the test and the preset relative humidities. Three salts were used, with the preset humidities being 85%, 59%, and 33%. The specimens encasing the sensors were cylinders 50 mm in diameter and 100 mm in height. A ceramic humidity sensor and measuring resistor were embedded in the cross-sectional center of each specimen. Three specimens were prepared for each preset humidity (nine in total). A concrete was proportioned similarly to Table 1 and wet-screened after mixing using a 5 mm sieve to obtain the mortar phase. Specimens were fabricated with this

mortar, demolded one day after placing, and water-cured for a month. These specimens were then placed in desiccators containing saturated salt solutions in the bottom space until the specified humidity equilibrium is attained. We had run the humidity preconditioning test for 400 days. We judged the equilibrium condition by confirming a static state of the internal humidity together with the ambient humidity. The humidity and temperature were monitored once every day. Figure 8 shows the state of the humidity preconditioning test.

4 TEST RESULTS

4.1 Humidity measurement in concrete

Figure 9 shows the results of the humidity preconditioning test on humidity sensors. The relationship between the humidity in concrete and the ambient air humidity in equilibrium was approximated by a linear function (Eq. (2)), which was used as a calibration function.

y = 1.45x - 26.1 (3)

where y = calibrated humidity in concrete (%) and x = measured humidity in concrete (%).

4.2 Compressive creep tests

4.2.1 Time-related changes in strain and internal humidity of free deformation specimens

Figure 10 shows the time-related changes in the strain and internal humidity of free deformation specimens. The fluctuation range of ambient humidity is shown in the figure. The same goes for the following figures 11

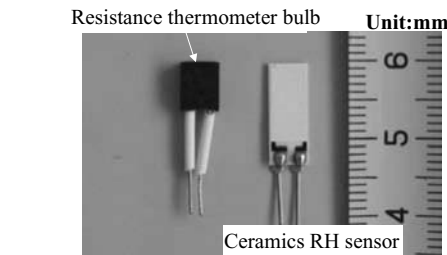


Figure 7. RH sensor.

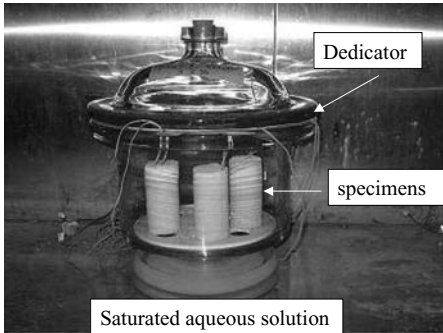


Figure 8. RH sensor calibration test.

Table 5. Setting up for RH sensor.

Salts	RH(%)	
	Reference values	Measured values
KCl	85	86
NaBr	59	66
MgCl ₂ · 6H ₂ O	33	40

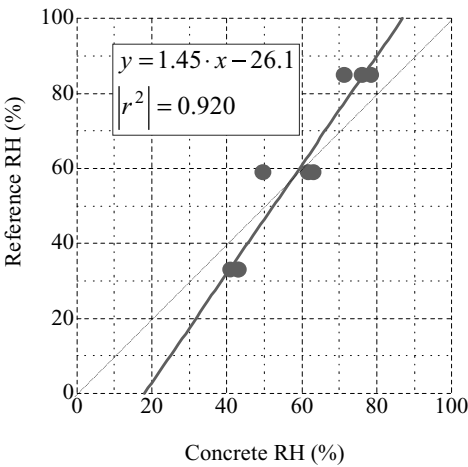


Figure 9. RH calibration line.

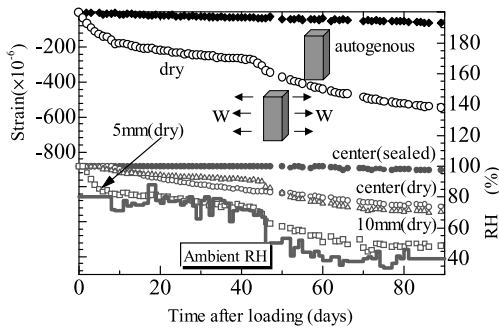


Figure 10. Relationship between shrinkages strains and internal RH (Compression).

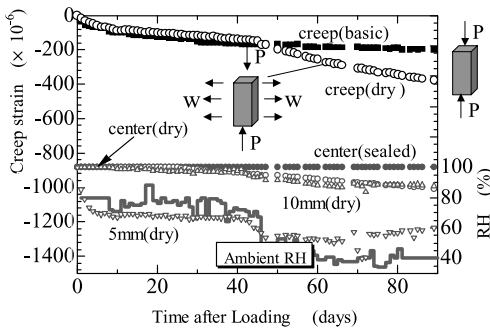


Figure 11. Relationship between creep strains and internal RH (Compression).

to 13. This figure reveals an autogenous shrinkage of around 50×10^{-6} in sealed specimens at the end of a 90 day test period. Also, the internal relative humidity of sealed specimens was as high as 97% after 90 days. In regard to dry specimens, a shrinkage of around 273×10^{-6} occurred after 40 days, during which the ambient humidity was 80%. After the ambient humidity was lowered to 40%, the strain ended up at around 546×10^{-6} at the end of 90 days. The relative humidity at a depth of 5 mm was around 82% after the first 8 days, which then decreased to 73% (42nd day, at which the ambient humidity was reduced to 40%) and then to 48% (90th day). The relative humidity at 10 mm from the specimen surface and cross-sectional center slowly decreased from the beginning of drying, ending up being around 70% after 90 days.

4.2.2 Time-related changes in compressive creep strain and internal humidity

Figure 11 shows the time-related changes in the strain and internal humidity of creep specimens. This figure reveals that the basic creep strain was around $200 \times$

10^{-6} at the end of the 90 day test period, whereas the internal relative humidity remained 100% even after 90 days. On the other hand, the drying creep strain was 140×10^{-6} after 40 days with an ambient humidity of 80% but progressed further after the ambient humidity was reduced to 40%, being around 375×10^{-6} at the end of the 90 day test period. The relative humidity at a depth of 5 mm began to decrease from the beginning of drying, reaching around 70% after 7 days. The reduction was slower thereafter, being 65% at the 42nd day. After the ambient humidity was reduced to 40%, the humidity at 5 mm tended to level off at a level similar to the ambient humidity. The relative humidities at a depth of 10 mm and in the center slowly decreased from the beginning of drying, reaching around 87% at the end of the 90 day test period. In creep specimens, the rate of humidity reduction near the surfaces tended to be higher than that of free deformation specimens during 7 days. Acceleration of water migration due to loading pressure can be regarded as another possible factor for the difference in the rate of internal humidity between creep specimens and free specimens.

4.3 Tensile creep tests

4.3.1 Time-related changes in strain and internal humidity of free deformation specimens

Figure 12 shows the time-related changes in the strain and internal humidity of free deformation specimens. This figure reveals that the autogenous shrinkage strain of sealed specimens was around -53×10^{-6} 80 days after the beginning of measurement. The shrinkage strain of dry specimens was around 311×10^{-6} after the first 40 days, during which the ambient humidity was 80%. Following the subsequent reduction in the ambient humidity to 40%, the strain further progressed to around -663×10^{-6} at the 80th day. The internal humidity at the cross-sectional center of sealed specimens remained nearly 100% throughout 80 days, whereas that at a depth of 5 mm of dry specimens decreased to 91% during the first 10 days in an environment with an ambient humidity of 80%. The humidity decreased more slowly thereafter, being around 91% after 40 days of testing. Drying further progressed after the relative ambient humidity was reduced to 40%, with the humidity reaching 67% after 80 days of testing. The internal humidity at a depth of 10 mm began to change on the third day from the beginning of testing, decreasing to around 100% 7 days later, but leveled off thereafter. Drying at 10 mm from the surface progressed again after the ambient humidity was reduced to 40%, with the humidity reaching 80% at the 80th day. The internal humidity at the cross-sectional center remained 100% for the first 70 days but gradually decreased thereafter, being 96% after 80 days of testing.

4.3.2 Time-related changes in the tensile creep strain and internal humidity

Figure 13 shows the time-related changes in the tensile creep strain and internal humidity. This figure reveals that the basic creep strain was around 18×10^{-6} after 80 days from the beginning of loading. In regard to the drying creep, a strain of around 18×10^{-6} occurred after loading for 40 days at an ambient humidity of 80%. The drying creep further progressed thereafter, with the ambient humidity being reduced to 40%, ending up with a strain of 130×10^{-6} at the end of 80 days. The relative humidity at the cross-sectional center of sealed specimens was retained nearly at 100% until 80 days from the beginning of testing, showing that the internal humidity was generally kept high. The relative humidity at a depth of 5 mm of dry specimens rapidly decreased to 81% during the first 7 days of testing in an environment with an ambient humidity of 80%. The relative humidity decreased more slowly thereafter, reaching 79% by the 40th day, but the reduction in the ambient humidity to 40% accelerated the drying again, reducing the internal humidity to end up at around 61% at the 80th day. At a depth

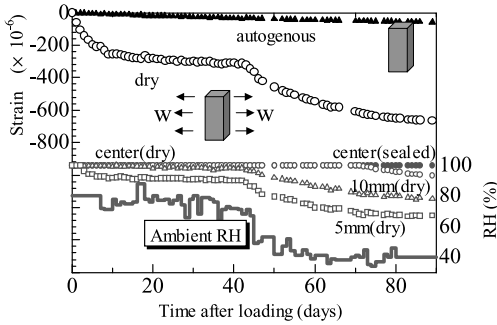


Figure 12. Relationship between shrinkages strains and internal RH (Tension).

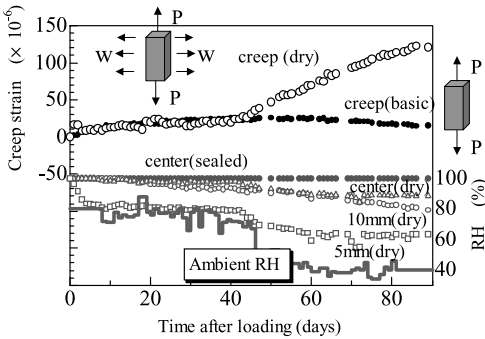


Figure 13. Relationship between creep strains and internal RH (Tension).

of 10 mm, the internal humidity began to change on the third day from the beginning of testing, decreasing to around 100% at the 10th day, but leveled off thereafter at around 100%. When the ambient humidity was reduced to 40%, the drying rate gained again, to a humidity of 80% after the 80th day. The relative humidity at the cross-sectional center remained 100% for the first 5 days but gradually decreased thereafter, reaching 98% at the end of the 40th day. With a reduction in the ambient humidity to 40%, the humidity in the center decreased further to 88% at the end of the 80th day. In regard to the difference in the moisture migration rate between free deformation specimens and creep specimens, the migration rates near the surfaces tended to be higher during 7 days, similarly to the case of compressive creep.

5 RELATIONSHIP BETWEEN DRYING CREEP AND CHEMICAL POTENTIAL

Figure 14 shows the relationship between the compressive and tensile drying creep and cross-sectional average chemical potential. Figure 12 reveals that both the compressive and tensile drying creeps linearly increase with the changes in the average chemical potential of the cross-section (reduction in the humidity). Equations (4) and (5) give the relational expressions between the chemical potential and the compressive and tensile creeps determined by least squares.

$$\varepsilon_{\text{crc}} = 0.702 \cdot \mu_{\text{ave}} \quad (4)$$

$$\varepsilon_{\text{crt}} = -0.193 \cdot \mu_{\text{ave}} \quad (5)$$

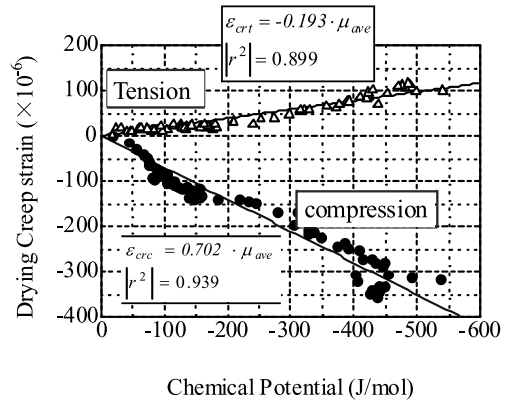


Figure 14. Relationship between drying creep strain and average chemical potential.

where $\varepsilon_{\text{crc}} =$ compressive drying creep ($\times 10^{-6}$), $\varepsilon_{\text{crt}} =$ tensile drying creep ($\times 10^{-6}$), $\mu_{\text{ave}} =$ average chemical potential (J/mol).

The relationship was found to be linear correlation both in compression and in tension. This suggests that the development of creep is closely related to the moisture migration phenomenon, namely, changes in the chemical potential. Moreover, the obtained relationship between the creep and the changes in the chemical potential suggests a possibility of formulating a creep prediction equation using the chemical potential of water in concrete as a parameter.

6 CONCLUSIONS

1. Humidity measurement in concrete was attempted using non-heating ceramic humidity sensors for measurement in air. As a result, the internal humidity of concrete was found to be measurable with a practical accuracy.
2. Whereas the basic creep was scarcely affected by the ambient humidity, the drying creep changed in response to changes in the ambient humidity. It is therefore inferred that drying creep is significantly affected by the internal moisture migration.
3. The relationship between creep development and changes in the chemical potential associated with moisture migration was investigated from the aspect of thermodynamics. As a result, linear correlations were recognized between them. This indicates a possibility of formulating a creep prediction equation using the chemical potential of water in concrete as a parameter.

ACKNOWLEDGEMENT

This study is supported by the Grant-in-Aid for Young Scientists (B) of the Japan Society for the Promotion of Science 2007, No. 18760334, to "A study on the effect of moisture migration phenomenon on the creep properties of early-age concrete." The authors express their gratitude to the organization for their financial support.

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Modelling creep by microstructural changes

E.A.B. Koenders, H.W.M. van der Ham & K. van Breugel

Microlab, Delft University of Technology, Delft, The Netherlands

S.J. Lokhorst

Movaris, Utrecht, The Netherlands

ABSTRACT: Models for creep have been developed in many different directions in the last decades. Every special purpose or every detailed influence that affects the creep or shrinkage have been tried to fit into a model in one way or another. The final result of all this work is that there still exists no real consensus about how creep should be modelled properly and taken into account objectively. The current trend towards nano-level modelling could be a serious attempt to improve creep models or to come up with a completely new approach on how creep models should work. The model presented in this paper is based on the work as published by Lokhorst in 1998. He developed a creep model which is based on the evolution of the volumes of hydration products during hardening of the concrete. In this model, the so-called “hollowshell” concept has been embedded and the simulations show very good agreement with experimental results. The model has shown to have the potential to calculate creep directly from the microstructural changes. In order to show this potential, results of this microstructure-based creep model will be compared with other existing creep models which are frequently used in creep calculations. The paper will show results of the microstructure-based creep model versus other existing creep models and the pros and cons of the models will be identified. It might provide an overview of the gaps where creep models could be improved either by means of introducing advanced modelling technologies or by means of further development of currently used modelling concepts.

1 INTRODUCTION

In this paper, a model will be presented that describes how the development of creep can be related to the development of the microstructural changes. This microstructure is described schematically as a system of expanding cement grains that come into contact while hydrating. The different stages where the growing particles are going through are indicated as: initial stage, early hydration, “clustering” and “bridging”. An overview of these stages is provided schematically in Figure 1.

The deformational behaviour of the microstructure, associating with the different stages of the particle

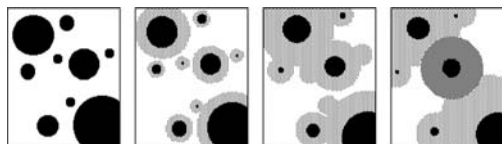


Figure 1. Development of microstructure; schematic representation of the particle expansion process; from left to right: initial stage, early hydration, “clustering” and “bridging”.

growth, will strongly depend on the performance of these contacts between the grains. These contacts, indicated as inter-particle bonds, depend on the morphological properties of the microstructure determined by the water cement ratio and the particle size distribution. In the early beginning, all cement grains are surrounded by water and hydration has not yet commenced. During hydration, these grains will gradually dissolve under formation of an expanding shell (cement gel) subdivided into an inner and an outer product (Breugel 1991). The expanding borders of the original grain progressively grow in outward direction with strong increase of the expanding volume. Gradually, with elapse of time, the hydrating grains come into contact, become ‘embedded’ and form a load bearing structure under the formation of “clusters” (Figure 1). With the ongoing inclusion of the smaller particles embedded in the shell of the bigger particles, contacts are being formed between these growing cluster formations, called “bridging”. The bridging volume can therefore be applied as a measure for the formation of structure of an evolving microstructure. With progress of the bridge volume more and more contacts are being formed that associate with the strength gain of the cementitious

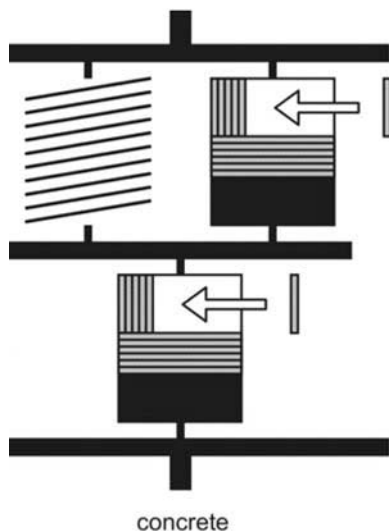


Figure 2. 'Bar-model' for the deformational behaviour of hardening concrete (Lokhorst, 2001).

material. The strength and stiffness will only be determined by those particles, which are partly embedded and which are able to bridge the gaps to their neighbouring particles.

Figure 2 provides an abstract illustration of the structure of hardening cement paste and aggregates of concrete. The model for the cement paste is split up into an un-hydrated cement volume and volumes that mimic the growth of the cement gel. The smallest volume is the 'contact gel', representing those grains that have the ability to 'bridge'. The stiffness of the model can be calculated from a series system build up from these three components as shown in Figure 2. The volumetric ratios and the local stiffness of the anhydrous cement and gel provide the necessary data to calculate the modulus of elasticity of the system. If the cement gel has, besides elastic, also time dependent properties, the effect of the hardening process, i.e. change of the three volumes, on the creep behaviour of the model, can be determined as well.

2 MATURING CREEP

If the model, represented by the cement matrix in Figure 2, is loaded, an elastic deformation will occur initially. After this loading stage, the strain in the gel will progressively increase in time due to creep effects. During this deformation enhancement, new hydration products will be formed that add additional load bearing capacity to the system. At formation,

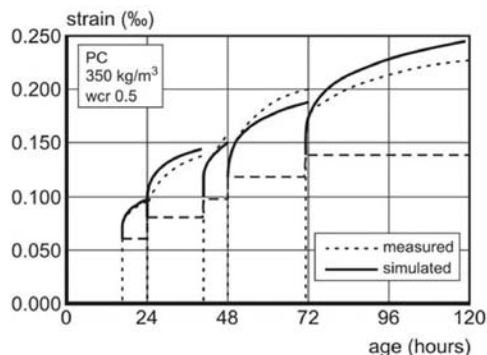


Figure 3. Measured and calculated deformations of creep on hardening concrete.

the newly formed gel products are stress-free, however, because of compatibility requirements, these gel products will gradually start to carry a certain part of the load. In the model, the development of the new formed hydration products (gel) will be imitated by gradually adding new "bars". These bars associate with the volumetric increase of the hydration products and enhance the load bearing capacity of the microstructure proportionally. The bars all have the same microstructural properties and vary in age only. The deformational behaviour is determined by simple constitutive relations and by the change of the microstructures' morphology. The deformational behaviour of the concrete is simulated by schematizing the elastic deformation of the aggregates, modelled as a spring, and both the parallel and serial systems embedded in the cement matrix model (Figure 2). In Figure 3, five short creep experiments are simulated by the Bar-model for hardening concrete (At five different ages (16, 24, 40, 48 and 71 hours after casting) specimens are loaded up to 30% of their ultimate compressive strength. Throughout the experiments the load is kept constant. The specimens are hardened at 20°C. In order to avoid drying shrinkage, the specimens were sealed with foil after casing and during testing. With the simulations, the total deformation consisting of the elastic and shrinkage deformation $\varepsilon(t)$ of the bars is calculated by the formula:

$$\varepsilon(t) = \frac{\sigma}{E} + at^n \sigma \quad (1)$$

in which:

- t = time in hours;
- E = 30,000 N/mm² (elastic modulus, similar for cement gel loaded in compression and tension);
- a = 1.5 · 10⁻⁵, aging factor;
- n = 0.3, power factor.

The influence of the loading history on the deformations of the bars is taken into account by assuming the superposition principle to be valid. In the model, the anhydrous cement and the aggregates exhibit elastic behaviour only and have assigned a modulus of elasticity of $60,000 \text{ N/mm}^2$ (both in compression and tension). The age dependency, which is commonly used in creep formulas, is solely related to a change of the microstructure, i.e. the growth of the hydration products in time. In Figure 3, the measured and calculated total deformations (elastic deformations plus creep deformations) are plotted against time. The elastic deformations are plotted by a dashed horizontal line. The results show that the elastic deformations as well as creep deformations increase with increasing age at loading. From the figure, it can be seen that those trends can be simulated with the model quite well.

3 TOWARDS A HOLLOW SHELL MODEL

The ‘Bar-model’ is a refinement of the creep formula as proposed by van Breugel (Breugel, 1980). Based on this version of this Bar-model, the presence of hollow shells in the cement paste’s micro-structure is considered to play a dominant role in the early-age deformational behaviour of concrete. The hollow shell concept is based on microstructural observations conducted by Kjellsen et al. (1996). With microscopic imaging he discovered hollow spaces in between the anhydrous hydrating cement core and the already formed hydration products (Figure 4). The progressively hydrating cement particle withdraws itself under the formation of the hydration products. This implicitly leads to the occurrence of a thin intermediate layer which doesn’t contain hydration products and, therefore, exhibit a low local paste density. The presence of the hollow shell suggest a weak physical interaction,

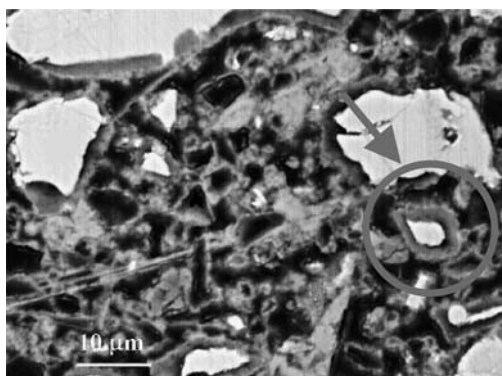


Figure 4. Microscopic image of a micro structure with indicated a hollow shell around the anhydrous cement particles.

or even an absence of physical interaction, between the anhydrous cement grain and the surrounding shell of hydration products. With elapse of time, hydration products are commencing to be formed and the anhydrous cement core withdraws itself continuously. Whenever applying the load to the concrete specimen, these hollow shells might be subject to additional stress that promotes creep deformations. This mechanism implicates that the load applied to the specimen can be transferred throughout the micro-structure somewhere in-between a fully connected non-hollow shell model and a model where a hollow shell is present. In Figure 5, the two concepts for transferring load are provided schematically. To investigate the contribution of the anhydrous cement grains inside a hollow shell concept to the elastic modulus of a system, in this section, a modified version of the Bar-model will be considered. In this model the anhydrous cement is surrounded by a cement shell of hydration products (gel) and where the load can be transferred either through the anhydrous cement core or this core does not participate in the load-bearing capacity of the system (see Figure 6). The model includes the volumes occupied by the capillary pores, anhydrous cement and volumes of cement that are already hydrated. The figure gives an impression of how the volumetric contributions change with elapse of time. The anhydrous part will reduce and the volume of hydration products will be enhanced under a simultaneous reduction of the capillary pore volume. The model indicates that the shell volume capturing the anhydrous cement grains act as “bridges” and are able to carry the load imposed to the specimen. The changes of the volumetric components during hydration can be calculated with the numerical simulation model Hymostruc. In this model, these changing volumes are calculated as a function of the water cement ratio, the particle size

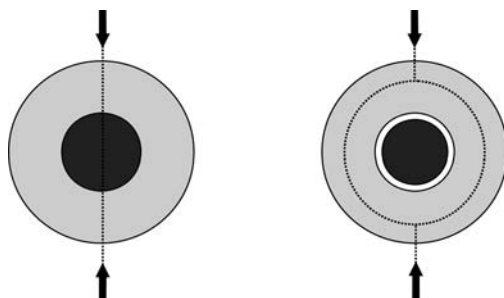


Figure 5. In case full interaction exists between the anhydrous cement grain and the surrounding shell of cement gel a load will be transferred via the shell and the grain (left). In case no interaction exists, a load can only be transferred via the shell of the hollow-shell model (right).

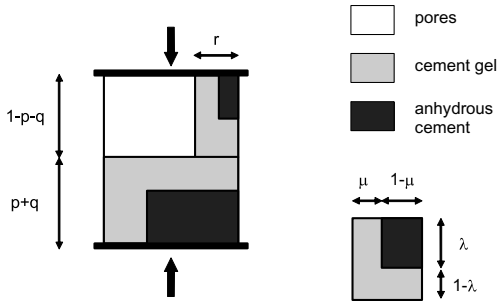


Figure 6. Modified composite Bar-model for hardening cement paste; a model where the anhydrous cement is surrounded by cement gel.

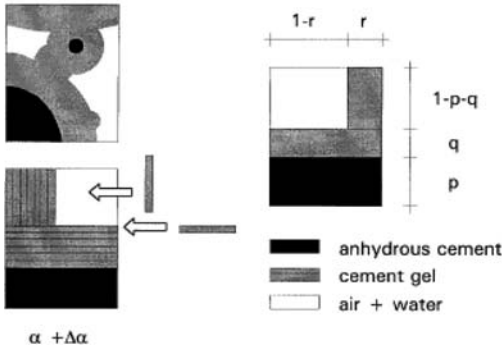


Figure 7. Schematic representation of the volumetric changes of the microstructural model.

distribution, the temperature, and the chemical composition of the cement. In (Lokhorst, 2001), it can be observed that the volumetric parameters p , q and r are defined as (see also Figure 7):

$$\begin{aligned} p(\alpha) &= \frac{(1 - \alpha) \cdot V_{\text{cem}}}{V_{\text{paste}}} \\ q(\alpha) &= \frac{V_{\text{cluster}}(\alpha) - V_{\text{bridge}}(\alpha) - (1 - \alpha)V_{\text{cem}}}{V_{\text{paste}}} \\ r(\alpha) &= \frac{1}{(1 - p(\alpha) - q(\alpha))} \cdot \frac{V_{\text{bridge}}(\alpha)}{V_{\text{paste}}} \end{aligned} \quad (2)$$

where: V_{cem} = initial cement volume
 V_{paste} = initial paste volume
 V_{cluster} = actual cluster volume
 V_{bridge} = actual bridge volume
 α = degree of hydration

Table 1. Values of k used for determination of the effective elastic modulus.

Type of cement	Compression	Tension
Blast Furnace Slag cement	$k_c = 1.0$	$k_t = 0.7$
Portland cement	$k_c = 0.85$	$k_t = 0.5$

From the model as shown in Figure 6, the effective elastic modulus E_{eff} is determined using a serial alignment of the elastic modulus for E_c and the hollow shell elastic modulus H_c :

$$E_{\text{eff}} = k \cdot H_c + (1 - k) \cdot E_c \quad (3)$$

where k is a weighing factor between 0 and 1, E_c the elastic modulus of concrete and H_c the hollow shell elastic modulus, excluding the stiffness of the anhydrous cores of the cement particles in the stiffness of the system. For $k = 1$ the cement grains are completely ineffective in the stiffness of the cement paste and the effective elastic modulus E_{eff} is equal to the hollow shell elastic modulus H_c . Indicative k values for Portland cement and Blast furnace slag cement are provided in Table 1.

4 TOWARDS A STRAIN ENHANCEMENT FACTOR FOR EARLY-AGE CONCRETE

Based on the model as presented in Figure 6, a general proposal is postulated for the development of a model for the simulation of creep strains of early-age loaded concrete. The model is based on the “regular” modulus of elasticity of concrete E_c and the effective elastic modulus E_{eff} (see eq. 3). In this paper, the strain enhancement factor mimics the ultimate creep strain for concrete loaded at early-ages. For the strain enhancement factor e_h it holds:

$$e_h = \frac{E_c - E_{\text{eff}}}{E_{\text{eff}}} \quad (4)$$

The strain enhancement factor, in fact, represents the ultimate strain that is to be expected due to the creep effects. From the strain enhancement factor provided in eq. (3) the ultimate creep can be calculated according to

$$\varepsilon_c = e_h \cdot \varepsilon_e \quad (5)$$

where ε_e is the elastic strain at loading. The ultimate creep strain ε_c also includes the effect of the maturing microstructure. While deforming, the microstructure of the early age loaded concrete will still

prolong its hydration, which leads to the generation of newly formed (stress free) hydration products that will become load bearing after the moment of formation. This process, the evolving and maturing microstructure will participate in bearing the load that act on the concrete and contribute to a decline of the developing creep.

With progress of the hydration process, the volumetric contributions p, q and r , representing the change of the cement, paste, cluster and bridge volume, will gradually change. While hydrating, the initial cement volume will decrease where the cluster and bridge volumes will increase. The cluster volume is the volume that is defined as the total volume of the remaining anhydrous cores of the cement grains plus the volume of the cement gel for all fractions. The bridge volume, on the other hand, is considered to be equal to the volume of those particles that are embedded in the outer shell of a free particle in a cluster that are able to act as a bridge with the neighbouring clusters (see also Figure 1). With these definitions, the change of the volumetric contributions within an evolving microstructure can be calculated. For the mixture used in this paper (350 kg/m³ Portland cement, wcr 0.5), the results of the changing volumes are provided in Figure 8.

From the figure it can be observed that the initial cement volume (p) reduces linearly with elapse of the hydration process (see eq. 2) and that both the cluster and bridge volumes increase with progress of the hydration process. From these results, the development of the regular E_c and the hollow shell modulus H_c can be calculated. The results of this calculation is provided Figure 9 and show that, due to the lacking contribution of the stiffness of the anhydrous cement cores, the stiffness of the hollow shell modulus is significantly less in comparison with the regular elastic modulus. The results also show that the hollow shell

modulus starts to gain its stiffness at a higher value of the degree of hydration.

From the results provided so far, strain enhancement factor for estimating the magnitude of the ultimate creep of early age loaded concrete can be calculated. According to the definition provided in equation 5, and the k -values for compression as provided in Table 1, the strain enhancement factor is calculated for the Portland cement-based mixture as used before (see Figure 10).

The results are validated with creep data determined from creep tests conducted by Lokhorst (see Figure 3 and/or Lokhorst, 2001). It should be noted that the results represent the creep only. In order to achieve the total creep deformation ε_{tot} , the following formula should be adopted (see also eq. 5):

$$\varepsilon_{tot} = \varepsilon_e + \varepsilon_c = \varepsilon_e (1 + e_h) \quad (6)$$

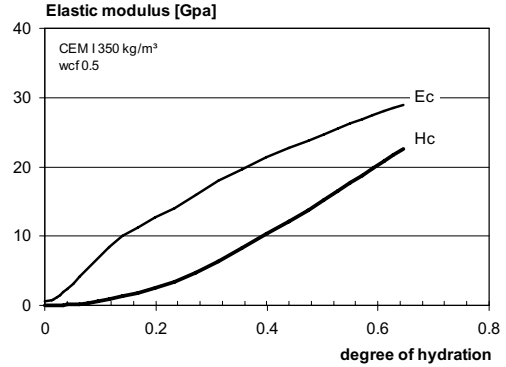


Figure 9. Elastic modulus of concrete E_c and the hollow shell modulus H_c .

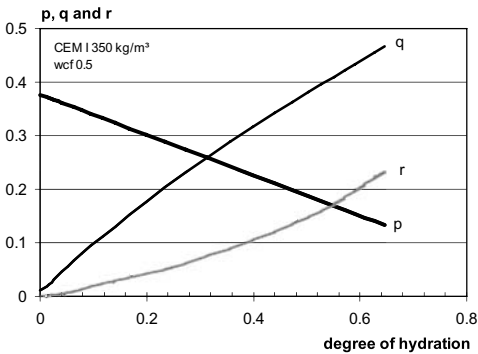


Figure 8. Change of the volumetric parameters p, q and r as a function of the degree of hydration.

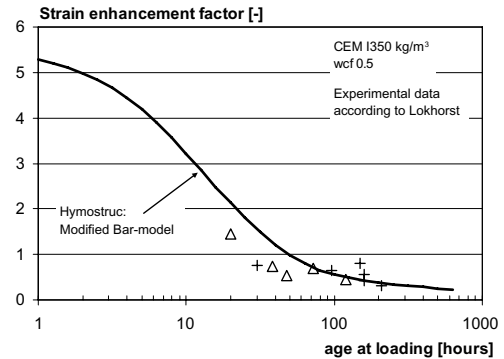


Figure 10. Strain enhancement factor for the Portland cement-based concrete 350 kg/m³ and a water/cement ratio of 0.5.

The strain enhancement factor e_h can be compared with the creep coefficient ϕ . The advantage of the strain enhancement factor is that it is directly related to the development of the microstructure and with this to the composition of the mix. The model provided in this paper is implemented in the Hy-mostruc model, which makes its usage very convenient. Whenever a designer wants to estimate the order of magnitude of the creep that is to be expected for a given mix composition, a simple calculation will supply a clear insight in this phenomenon.

5 RECENT DEVELOPMENTS

With respect to the development of visco-elastic models based on microstructural changes, at TU Delft research is being conducted where the effect of water inside the hollow shell is taking into account as well (Ham et al. 2008). The availability of water inside the shell between the remaining anhydrous cement core and the already generated shell of hydration products will affect the development of the creep in general and the development of the rate of loading in particular. When considering the hollow shell model shown at the right hand side of Figure 5, it can be observed that water might accumulate inside the hollow shell and that it will have a share in the load bearing mechanism to simulate creep. In Figure 11, a schematic impression is provided of the background of this model. Left, the hollow shell model is shown with water available insight the hollow shell of a single hydrating cement particle. Whenever load will be applied to this particle, the transfer of load will occur via the shell built-up from hydration products, but also via the remaining anhydrous cement core, where the intermediate water layer act as a load transferring layer. Due to this confined water layer, pressure differences will develop between the water confined in the water accumulated shell and the surrounding capillary water in the paste system. These pressure differences will alter whenever the paste is loaded and induce

the confined water to become under an inclined pressure. Pressure differences between the confined shell water and the capillary water will drive this confined water to move from the shell towards the surrounding capillary water while passing through the hydrated shell layer that surrounds the cement particle. The principle is schematically shown in Figure 11, in the middle. Water withdrawn from the shell will force the system to redistribute its load, causing more load to be transferred through the hydrated shell. This additional load will enhance the actual stress level in the hydration products and lead to an additional deformation of this shell that surrounds the hydrating cement particle. Whenever applying this principle to the particles in all fractions, the total deformation of hardening load bearing cement paste system can be simulated. The mechanism behind this model is schematically shown in Figure 11, right. The inter-particle movement of the confined water in the shell is modelled in Hymostruc using a FEM schematisation (Ham et al. 2008).

6 DISCUSSION AND CONCLUSIONS

Modelling creep by means of the volumetric changes that occur in the microstructure during hydration is the main principle addressed in this paper. In 2001, Lokhorst published the first ideas about this mechanism to model creep and showed the potential of this method by postulating a model to simulate the relaxation of concrete, and validated this model by a series of experiments for the stress development in early age concrete, conducted with the TSTM. The model turned out to be very promising.

Based on similar principles, in this paper the potential of a creep model is provided. The model shows that taking into account the volumetric changes of a cementitious microstructure, i.e. cement, cluster and bridge volume, enables the possibility to identify the governing processes necessary to model the visco-elastic properties. Encouraging results have been achieved so far from the strain enhancement factor enabling the potential of simulating the ultimate creep of early-age loaded concrete. The results clearly show the effect of early loading and the reduction of the strain enhancement with progress of the hydration process. The maturing microstructure demotes the creep rate and declines the actual creep strain to develop. The models shows good agreement with experimental data achieved from laboratory tests conducted in Delft. Extending the potential of the model with the hollow shell to be a water accumulated load bearing intermediate layer will provide the opportunity to take into account rate effects and other time dependent stiffness variations into the creep calculations as well. The final result will be a microstructural-based model that enables the calculation of the visco-elastic properties

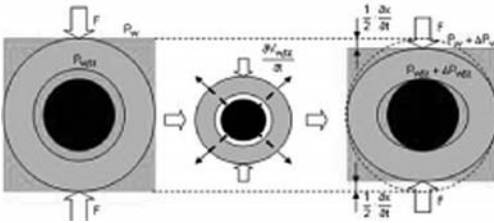


Figure 11. Schematic representation of the hollow shell model for visco-elastic properties of the developing micro structure.

of hardening cementitious materials. The model can also be utilized to simulate the hardening stresses in early age concrete elements.

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Study of micromechanical behavior of cement paste by integration of experimental nanoindentation and numerical analysis

Petr Kabele, Denis Davydov, Petr Jůn, Jiří Němeček & Milan Jirásek

Faculty of Civil Engineering, Czech Technical University in Prague, Prague, Czech Republic

ABSTRACT: In the present study, we use the finite element method to examine the ability of various constitutive relations to reproduce the response of a hydrated phase of hardened cement paste measured in a cyclic nanoindentation experiment. It is found that the linear viscoelastic model, which fits very well a single loading-dwell-unloading cycle, does not properly describe the subsequent cycles. Qualitatively the best results are obtained with a combined viscoelastic and plastic constitutive law. A finite element model is also employed to analyze the effect of material inhomogeneity in the vicinity of the indent. The results of the numerical study provide a valuable feedback to experiments by helping to select appropriate indentation depths and loading histories. The study also extends the knowledge about the micromechanical behavior of cement paste.

1 INTRODUCTION

Understanding and description of mechanical behavior of hardened cement paste at the scale of its microstructure may, in conjunction with multiscale modeling (e.g. Šmilauer & Bittnar 2006), facilitate the development of new cement-based materials with properties tailored to specific structural requirements.

Nanoindentation, since it allows measuring mechanical properties of a very small material volume, appears to be a suitable experimental technique to identify the behavior of individual phases of hardened cement paste (e.g. Constantinides et al. 2003). The principle of nanoindentation, which was originally developed for materials with homogeneous microstructure and for films, consists in pressing an accurately-shaped hard tip (indenter) into the tested material, while simultaneously recording the applied force P and the displacement of the indenter against the tested specimen h . Standard processing of the measured P - h relation is based on the analytical solution of a contact problem involving an indenter and a semi-infinite solid body (Oliver & Pharr 1992) and provides the hardness and Young's modulus. However, material properties obtained by this method may be contaminated by various nonlinear phenomena. For example, results of nanoindentation commonly exhibit a size effect (e.g. Wei et al. 2004). Creep of the tested material was found to be one of the factors contributing to the size effect. Ignoring creep in the evaluation of nanoindentation results can lead to an overestimation of the size effect on hardness and to a spurious size effect on elastic properties.

Application of nanoindentation to materials such as cement paste faces particular challenges arising from the inhomogeneity and porosity of the material microstructure as well as from the nonlinear response of its individual phases.

Complementing nanoindentation with a finite element (FE) analysis may further enhance this experimental technique and address many of the challenges mentioned above. On one hand, results of numerical simulations can provide a valuable feedback to experiments by helping to select appropriate loading histories and indentation depths (e.g. with regard to the topology of the material microstructure). On the other hand, by using more advanced nonlinear material models to fit the response obtained from a nanoindentation test, it can become possible to retrieve characteristics describing plastic and viscous behavior of the material phases.

In the present paper, we focus on testing the ability of various constitutive relations to qualitatively reproduce the response of a hydrated phase of hardened cement paste measured in a cyclic nanoindentation experiment. We also numerically analyze various aspects of the nanoindentation experiments.

2 SPECIFICS OF NANOINDENTATION OF CEMENT PASTES

Cement paste is a heterogeneous material with the major constituents being hydrated phases (e.g. C-S-H gels and portlandite), unhydrated phases (rest of clinkers) and porosity. Due to its fine resolution,

nanoindentation can be employed to measure micro-mechanical properties of these individual phases. To this end, a large number of indents is produced and subsequently separated into specific phase groups with the aid of electron microscope (ESEM). Since the results usually exhibit a significant scatter (even for one single phase), they are treated statistically (Constantinides & Ulm 2004, 2007).

An example of an indented cement paste sample is shown in Figure 1. The typical pyramidal shape of indenter imprints is formed by the Berkowich indenter tip.

Figure 2 shows a typical result of a single indent in terms of applied force P and penetration depth h .

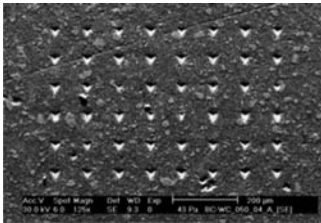


Figure 1. ESEM image of indented cement paste—matrix with large indents (5500 nm in depth).

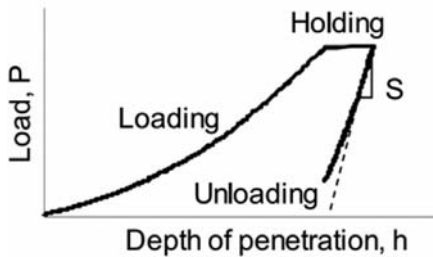


Figure 2. Typical result of nanoindentation test.

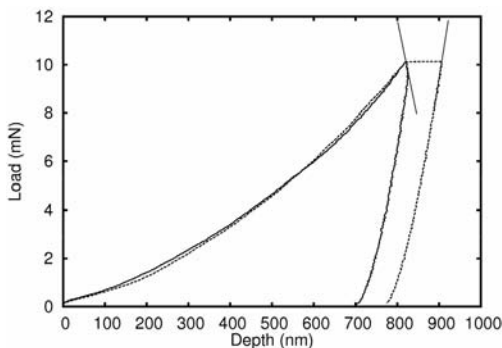


Figure 3. Experimental results of nanoindentation tests on cement paste without and with dwell period before unloading.

The response during loading involves nonlinear phenomena, such as plastic yielding and creep. The holding (or dwell) period is sometimes included to let the material creep before unloading. In the standard evaluation procedure, it is assumed that the unloading curve involves solely elastic deformations. Then the elastic modulus is determined from the initial slope S of the unloading branch by the method proposed by Oliver & Pharr (1992).

Figure 3 shows the response of cement paste samples when loading was immediately followed by unloading and when the load was kept constant for 120 s before unloading. In the former case the unloading branch has initially a negative slope (because h increases due to creep, even at decreasing P) while in the latter case most of the creep takes place during the holding period and the unloading response is almost elastic. This clearly shows the significant effect of creep.

3 EXPERIMENTAL PART

Samples of white cement paste (CEM-I 52,5 White, Holcim, SK) with water/cement ratio of 0.5 were prepared and stored in water for 28 days. Before testing, a 4 mm thick slice from the bulk material was cut and polished on coarse to very fine emery papers to achieve a smooth and flat surface. The specimens were washed in an ultrasonic bath to remove dust. The resulting surface roughness, which was verified by atomic force microscopy (AFM), was in the range of several tens of nm.

Indentation was performed with Nanotest (Micro Materials, UK) nanoindenter equipped with Berkowich type indenter. Each indent was performed under force control, with the loading history shown in Figure 4. After identifying by ESEM those indents that hit exclusively the hydrated phase, a cluster of P - h curves was obtained. From these curves a typical one was selected for the forthcoming numerical reproduction.

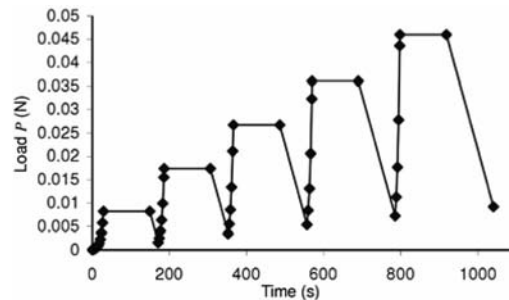


Figure 4. Nanoindentation loading history.

4 NUMERICAL ANALYSIS PART

4.1 Performance of various constitutive models

In order to find a constitutive model that would be able to represent the experimentally obtained behavior of the hydrated phase, a series of numerical simulations of the nanoindentation experiment was carried out. Nanoindentation was modeled as a contact problem of a deformable body (specimen), which was pushed against a rigid conical indenter. Large deformations and large displacements were taken into account. Note that the constitutive relations discussed hereafter were applied to the Cauchy stress and logarithmic strain. The problem was reduced to two dimensions by assuming axial symmetry. Figure 5 shows the FE mesh and boundary conditions used. The analyses were carried out with the general-purpose FE program ADINA.

4.1.1 Linear viscoelastic model

Vandamme & Ulm (2006) examined the ability of several linear viscoelastic models to reproduce the nanoindentation tests on cement paste. For a loading and dwell period they derived analytical solutions of the problem, which makes it possible to determine parameters of the viscoelastic model directly from the history of indenter displacement measured during the dwell period at which P is kept constant. The best results were obtained with a 5-parameter combined Kelvin-Voigt-Maxwell deviator creep model. The model was based on the assumption that the creep behavior is associated with shear and employed the functional formulation:

$$e_{ij}(t) = \int_0^t C^d(t - \tau) \dot{s}_{ij}(\tau) d\tau \quad (1)$$

where t = time; e_{ij} = deviatoric strain tensor; s_{ij} = deviatoric stress tensor; the overdot denotes differentiation with respect to time; and

$$C^d(t) = \frac{1}{G_0} + \frac{1}{G_V} \left(1 - e^{-\frac{G_V}{\eta_V} t} \right) + \frac{t}{\eta_M} \quad (2)$$

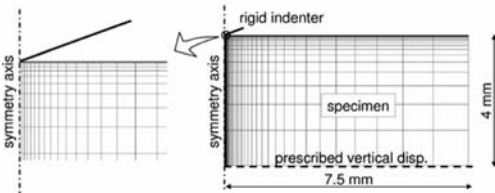


Figure 5. Axially symmetric FE model of nanoindentation experiment.

is the shear creep function with material parameters G_0, G_V, η_V, η_M . The volumetric behavior was considered as purely elastic, with bulk modulus K_0 .

For our FE simulation we evaluated Young's modulus E_0 from the first unloading branch by the standard Oliver & Pharr (1992) method, and we derived the corresponding moduli G_0 and K_0 assuming that Poisson's ratio is 0.196. Then we determined the creep parameters G_V, η_V, η_M by fitting the experimental response (h - t curve) measured during a 240 s long dwell period that followed the indenter loading up to 10 mN.

Interestingly, the simulation captured very well not only the first dwell period, on which the parameters had been fitted, but also the first loading period; see Figure 6. However, in the second loading cycle, only the later stage was accurately reproduced. A significant deviation from the experimental curve occurred during the unloading and reloading periods. Namely, the analytical results exhibited a strong hysteresis. This suggests that in the model significant viscous deformation was taking place even during the unloading period, whereas in reality this effect was much less pronounced.

4.1.2 Nonlinear viscoelastic model

For the nonlinear viscoelastic model we used the creep potential based formulation. The stress-strain relationship involved the decomposition of strain tensor into elastic and viscous parts:

$$\sigma_{ij} = D_{ijkl}^{\text{elast}} (\varepsilon_{kl} - \varepsilon_{kl}^C) \quad (3)$$

where σ_{ij} = stress tensor; ε_{ij} = strain tensor; ε_{ij}^C = creep strain tensor; D_{ijkl}^{elast} = elastic stiffness tensor. The evolution of creep strain was governed by a flow rule with the Mises type potential, which again implied

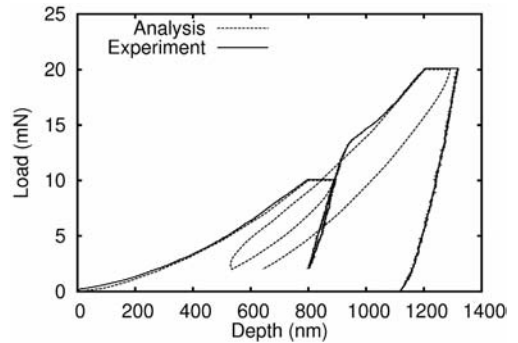


Figure 6. Response calculated with the 5-parameter linear viscoelastic model.

association of the viscous behavior with shear:

$$\dot{\varepsilon}_{ij}^C = \dot{\gamma}; s_{ij} \quad (4)$$

The scalar parameter γ was determined such that, under constant stress, the equivalent creep strain $\bar{\varepsilon}^C$ was linked to the equivalent stress $\bar{\sigma}$ and to the time by the power creep law:

$$\bar{\varepsilon}^C = a_0 \bar{\sigma}^{a_1} t^{a_2} \quad (5)$$

where a_0, a_1, a_2 = material parameters. Strain hardening creep was assumed.

The main difference between this model and the linear viscoelastic model consist in the nonlinear dependence of the creep strain on the stress. The dependence on time is given by a power function instead of the combination of an exponential function with a linear one but, for the present applications, this is not so important since the time range remains limited to a few minutes.

A parametric study was carried out to find the model parameters such that the results of the FE simulation provided the best fit of the first cycle of loading-dwell-unloading. Figure 7 shows that this goal was satisfactorily meet. However, the subsequent loading cycles showed a significant deviation from the experiment. In particular, the subsequent loading branches lacked the typical kink that occurred shortly after exceeding the maximum load from the previous cycle. This resulted in the total displacement at the end of the analysis lower than that obtained from the experiment. On the other hand, the behavior during unloading was matched fairly well.

Figure 8 shows the calculated distribution of residual effective creep strain after complete unloading following the fifth cycle. It is obvious that intense straining affected a core under the indenter with radius of about $3 \mu\text{m}$.

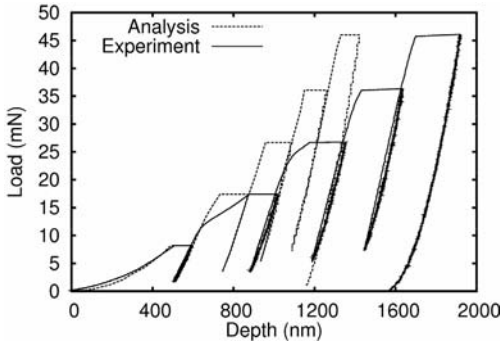


Figure 7. Response calculated with the nonlinear viscoelastic model.

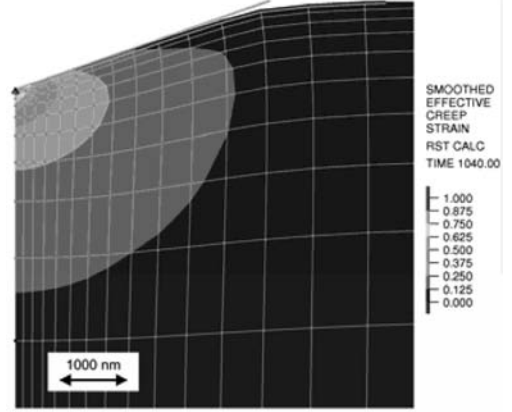


Figure 8. Residual effective creep strain after complete unloading (nonlinear viscoelastic model).

4.1.3 Combined nonlinear viscoelastic and plastic model

As a next step, the nonlinear viscoelastic model was enhanced by a plastic element, assuming that the kink during loading could be attributed to plastic yielding. The stress-strain law was then extended as:

$$\sigma_{ij} = D_{ijkl}^{\text{elast}} (\varepsilon_{kl} - \varepsilon_{kl}^C - \varepsilon_{kl}^P) \quad (6)$$

where ε_{ij}^P = plastic strain tensor. The evolution of plastic strain was controlled by the associated flow rule:

$$\dot{\varepsilon}_{ij}^P = \dot{\lambda}; \frac{\partial f}{\partial \sigma_{ij}} \quad (7)$$

where λ is the plastic multiplier and

$$f = \frac{1}{2} s_{ij} s_{ij} - \frac{1}{3} \sigma_Y^2 \quad (8)$$

is the Mises yield function, with σ_Y = yield stress. A perfectly plastic behavior was assumed.

The present model involves two nonlinear phenomena: creep and plasticity. These phenomena cannot be simply separated in the force-controlled nanoindentation test, since even under a constant force (dwell period) the material creeps, which results in a variable contact area with the indenter and therefore a variable stress field under the indenter. Consequently, the parameters were determined by a trial and error approach, which probably did not provide the optimum values. Nevertheless, this deficiency does not prevent us from examining some general features of the model.

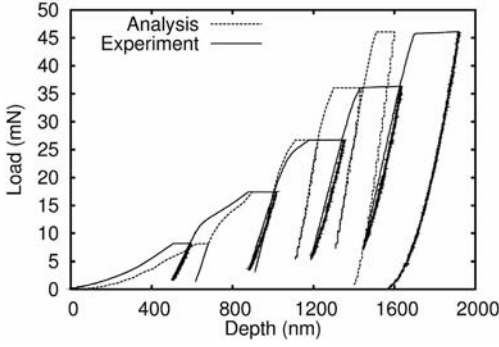


Figure 9. Response calculated with the combined nonlinear viscoelastic and plastic model.

Figure 9 shows that the combined nonlinear viscoelastic and plastic model qualitatively reproduced all the characteristic features of the measured nanoindentation curve. As opposed to the previous models, the present one did not exaggerate the hysteresis during unloading-reloading and properly captured the kink during the subsequent loading.

4.1.4 Viscoplastic model

In an attempt to reduce the number of model parameters, yet maintain the features of the combined model (in particular, existence of the yield stress), the viscoplastic constitutive law was implemented. The stress-strain law was written as:

$$\sigma_{ij} = D_{ijkl}^{\text{elast}} (\varepsilon_{kl} - \varepsilon_{kl}^{VP}) \quad (9)$$

where ε_{kl}^{VP} = viscoplastic strain tensor. The evolution of viscoplastic strain was described by the associated flow rule:

$$\dot{\varepsilon}_{ij}^{VP} = \dot{\lambda} \frac{\partial f}{\partial \sigma_{ij}} \quad (10)$$

with the Mises yield function (8).

For the viscoplastic model, the stress is allowed to be outside the yield surface. The power relationship between the norms of the overstress $\sigma_{ij}^{VP} = \sigma_{ij} - \bar{\sigma}_{ij}$ and of the viscoplastic strain rate $\dot{\varepsilon}_{ij}^{VP}$ was prescribed as:

$$\|\sigma_{ij} - \bar{\sigma}_{ij}\| = \sigma_Y (t_{ch} \|\dot{\varepsilon}_{ij}^{VP}\|)^m \quad (11)$$

where $\bar{\sigma}_{ij}$ = projection of the stress on the yield surface; t_{ch} = characteristic time; m = rate sensitivity parameter. Equation 11 is known as Norton's power law.

The viscoplastic model differs from the viscoelastic ones by the existence of an elastic domain in which the

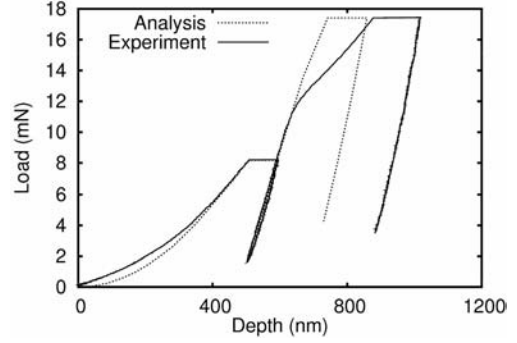


Figure 10. Response calculated with Norton's viscoplastic model.

behavior is elastic and thus time-independent. Creep or relaxation can occur only if the stress level exceeds the yield limit. For simplicity, no plastic hardening was considered; otherwise the number of material parameters to be identified would be too high.

To find the best fit with the current model trial and error procedure was utilized. As seen in Figure 10, this model could capture the first loading-dwell-unloading cycle. However for the second cycle there was a significant mismatch and the response resembles that of the nonlinear viscoelastic model. A possible explanation, which we still have to verify, is that the response was governed by the behavior of an intensively strained and yielded core under the indenter (Fig. 8). Since hardening was neglected in the viscoplastic model, the nonlinear viscoelastic model and the viscoplastic model beyond yield gave a similar response.

4.2 Effect of material inhomogeneity on the evaluation of Young's modulus by nanoindentation

As we have pointed out previously, one of the difficulties when nanoindentation is applied to cement paste is due to inherent inhomogeneity and porosity of the substrate. Then a sensible question to be asked is whether it is appropriate to use the method based on the assumption of a homogeneous elastic halfspace (Oliver & Pharr 1992) to evaluate Young's modulus. To clarify this point, a series of numerical analyses was carried out. The linear elastic material model was used; however the indent was performed into a hemispherical inclusion with Young's modulus different from that of the surrounding matrix (Fig. 11). The value of Poisson's ratio was assumed to be the same in the inclusion and the matrix.

The simulation involved a single loading cycle. Different ratios between the elastic moduli of inclusion

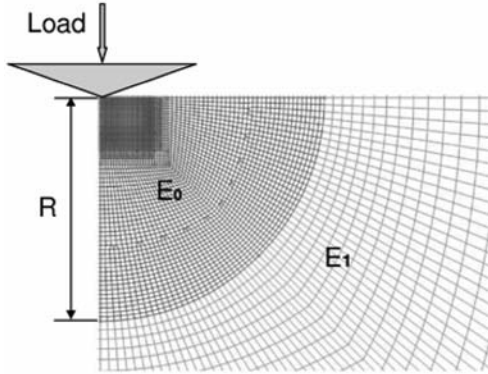


Figure 11. Axially symmetric FE model for the study of the effect of inhomogeneity on Oliver & Pharr procedure.

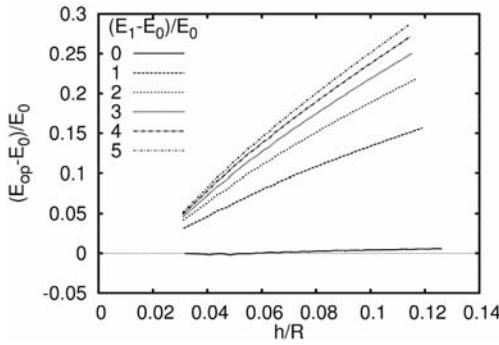


Figure 12. Normalized difference between the elastic modulus evaluated by Oliver-Pharr procedure (E_{op}) and the actual modulus of inclusion (E_0) for different normalized indentation depths (h/R) and different ratios between matrix and inclusion moduli ($E_1 - E_0$)/ E_0 .

and matrix were studied. Young's modulus was calculated by the Oliver & Pharr (1992) method at different penetration depths. Figure 12 shows the dependence of the error in the resulting modulus on the penetration depth for different ratios of matrix and inclusion elastic moduli.

As seen in Figure 12, when $E_0 = E_1$, the elastic modulus evaluated by the Oliver & Pharr procedure from the FE analysis result was almost equal to the elastic modulus of inclusion regardless of the penetration depth, as expected. Note that the small deviation resulted from a numerical error of the FE calculation. However, the presence of matrix with a different elastic modulus distorts the results of the Oliver & Pharr procedure. The error increases with increasing penetration depth and increasing difference between elastic moduli of matrix and inclusion (Fig. 12).

As found by Constantinides & Ulm (2007) and Miller et al. (2008), the elastic moduli of C-S-H and the surrounding unhydrated grains in cement paste are in the ranges of 20–40 GPa and 110–120 GPa, respectively. Then the ratio $(E_1 - E_0)/E_0$ falls in the range of 1.75–5. Considering that the typical size of the hydrated phase inclusions is several μm , it follows from Figure 12 that reasonable values of Young's modulus (and perhaps other properties) are obtained by indents with h in the order of few hundreds nm.

5 CONCLUDING REMARKS

In the present paper, we examined the ability of several constitutive models to reproduce the response of a hydrated phase of hardened cement paste measured in a cyclic nanoindentation experiment. The model that combined nonlinear viscoelastic and plastic elements provided the best qualitative match to the experimentally measured response, which suggests that both instantaneous yielding and creep are phenomena that significantly affect the microscale behavior of the hydrated phase. On the other hand, it was found that identification of the model parameters poses certain difficulties. Although it is not elaborated in this paper, attempts were made to find the parameters through rigorous mathematical optimization. Nevertheless, this effort did not yield satisfactory results since it was not possible to separate the viscous and plastic behavior from the measured data. Presently, we are developing a test method that uses a modified loading history and exploits the depth-sensing ability of a recently acquired nanoindenter to overcome this difficulty.

By analyzing the sensitivity of the evaluation of microscale Young's modulus to the size of the indented inclusion we were able to estimate the appropriate indentation depth. The depths used in the present study (up to 2 μm) appear to exceed the optimum value, which means that the results may not represent purely the behavior of the hydrated phase. However, our recent tests with indentation depth up to 300 nm show behavior which is qualitatively consistent with that presented.

ACKNOWLEDGMENTS

The presented research has been supported by the Ministry of Education, Youth and Sports of the Czech Republic under Research Plan MSM6840770003, by the European Union under Marie-Curie Research and Training Network NANOCER, and by the Czech Science Foundation under project 103/06/1856.

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Determination of the static elastic constant of concrete derived from the elastic constant of cement paste

T. Endo & M. Ishikawa

Tohoku Gakuin University, Sendai, Japan

M. Kawasumi

Concrete Material Physics Research Association, Tokyo, Japan

ABSTRACT: Static Young's modulus of concrete is an important factor as well as creep in order to evaluate the long-term internal stresses on a concrete dam. Therefore, in this paper, the prediction method of Young's modulus of the dam concrete using moderate-heat Portland cement is discussed. Supposing that the concrete is two phase material which is composed of cement paste and aggregate, Young's modulus of the concrete is calculated based on the compound theory. Here, the Young's modulus of hardened cement paste is evaluated from the experimental equation considering unbound water affected by the degree of hydration of cement and the Young's modulus of aggregate is estimated from the amount of water absorption. Measured static Young's moduli of concrete in existing dams are compared with those of concrete which are calculated based on the compound theory, and it is shown that the both give a good agreement.

1 INTRODUCTION

In order to support electric power energy demand after the World War II, many concrete dams for the hydroelectric power generation were constructed in Japan. More than 40 years have passed already after construction of these dams and for appropriate maintenance it is expected to establish the safety evaluation method reflecting the present state of a dam. That is, to verify the long-term safety of the existing dam, the mechanical characteristic of the concrete which composes a dam must be correctly evaluated. For this purpose, concrete creep-tests have been carried out and the reports already accomplished, however, research works on the long-term evaluation of Young's modulus of the concrete have been hardly performed. Therefore, in this paper the prediction method of the Young's modulus of dam concrete was investigated based on the compound theory for contributing to the safety of concrete dams.

2 ESTIMATION METHOD OF YOUNG'S MODULUS OF CEMENT PASTE, AGGREGATE AND CONCRETE

2.1 Overview

To predict the static Young's modulus of concrete, the concrete was considered to be two phase material

composed of cement paste and aggregate. The Young's modulus of hardened cement paste was derived from Kawasumi's evaluation method and the Young's modulus of aggregate was estimated based on the absorption coefficient of aggregate. Details are described below.

2.2 Estimation method of Young's modulus of the cement paste

Kawasumi showed the evaluation method of Young's modulus of hardened cement paste cured in the water using moderate-heat Portland cement. At the first step in this method the velocity of P- wave and S- wave of the hardened cement paste is measured. Then a pulse Young's modulus and a pulse Poisson's ratio are calculated from these velocities. Moreover in the last the static Young's modulus and Poisson's ratio of the cement paste are evaluated by proposed experimental equation.

2.3 Kawasumi's research overview

Using cement paste specimens with w/c values of 0.25, 0.30, 0.35, 0.40, 0.45, 0.50 and 0.55 made with moderate heat Portland cement and cured in water, their P- and S-wave velocities were measured at ages of 3, 7, 14, 28, 91 days, 6 months, 1 year, and 2 years. One average value was calculated from 9 specimens' data. Each of the P- and S-wave velocities was expressed as

a linear function of unbound water content and air content. As these contents are calculated by the expression of cement hydration with any w/c and at any age which was derived by S. Seki et al. and Kamasumi, P- and S-wave velocities in cement paste with any w/c at any age can be calculated. From the calculated P- and S-wave velocities, the pulse Young's modulus and pulse Poisson's ratio can be taken. As the relation between pulse and static Young's moduli and the relation between pulse and static Poisson's ratios have been obtained by Kamasumi, it can be calculated the values of static Young's modulus and static Poisson's ratio of moderate heat Portland cement paste cured in water with any w/c at any age. Thus these values were calculated with the w/c prescribed above, at the ages between 3 and 805 days.

2.4 Pulse velocity in cement paste

Kamasumi showed the pulse velocity in the cement paste made with moderate heat Portland cement and cured in water by the following equations.

$$V_p/\text{COEF} = 4924.18 - 5729.98 \phi_1 - 4283.04 \phi_g \text{ (m/s)} \quad (1)$$

$$V_s/\text{COEF} = 2610.15 - 3513.92 \phi_1 - 1927.00 \phi_g \text{ (m/s)} \quad (2)$$

$$\text{COFE} = \left[1 + \left(\frac{1-D}{1+\gamma} \right) \left(\frac{\gamma - W/C}{D + W/C} \right) \right]^{\frac{1}{2}} \quad (3)$$

$$D = \frac{\rho_w}{\rho_c} \quad (4)$$

$$\begin{aligned} \phi_1(t) &= \frac{W - W_B}{\rho_w} = \frac{W - \gamma \cdot C_H(t)}{\rho_w} \\ &= \frac{W - \gamma \cdot R_H(t) \cdot C}{\rho_w} \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{C_H(t)}{C} &= R_H(t) \\ &= \frac{1 - \exp\{\gamma \cdot C - W\} k_0 t^{1-m}}{1 - \gamma(C/W) \exp\{(\gamma C - W) k_0 t^{1-m}\}}, \\ &\quad (W/C \neq \gamma) \end{aligned} \quad (6)$$

where, V_s = P- wave velocity (m/s); V_c = S- wave velocity (m/s); γ = assumed perfect bound water content to cement (this value is assumed to be 0.37) (kg/kg); W = water content per 1 m³ cement paste (kg/m³); C = cement content per 1 m³ cement paste (kg/m³); ρ_w = density of water (kg/m³); ρ_c = density of cement (kg/m³); $W_B(t)$ = bound (or combined) water content per 1m³ cement paste (kg/m³); ϕ_l = volume of unbound water per 1m³ cement

paste (m³/m³); ϕ_g = volume of air per 1m³ cement paste (m³/m³); $Ch(t)$ = hydrated cement content per 1m³ cement paste (kg/m³); $Rh(t)$ = rate of hydration of cement (kg/m³/kg/m³); and k_0, n = experimental constant.

2.5 Pulse Young's modulus of cement paste

From the pulse velocities, pulse Young's modulus and pulse Poisson's ratio are obtained by the following equations.

$$E_d = 2(1 + \nu_d) \rho V_s^2 \times 10^{-7} \quad (7)$$

$$V_d = \frac{\left(\frac{V_p}{V_s} \right)^2 - 2}{2 \left\{ \left(\frac{V_p}{V_s} \right)^2 - 1 \right\}} \quad (8)$$

where, E_d = pulse Young's modulus (N/mm²); ρ = density of medium (g/cm³); ν_d = pulse Poisson's ratio; V_p = P- wave velocity (cm/s); V_s = S- wave velocity (cm/s).

2.6 Static Young's modulus of cement paste

According to Kamasumi, Static Young's modulus (E_{sp}) and Static Poisson's ratio (ν_{sp}) in the cement paste are obtained by the following equations from the pulse Young's modulus and the pulse Poisson's ratio.

$$E_{sp} = 0.001628 \times (E_d/0.0981)^{1.315} \quad (9)$$

$$\nu_{sp} = \nu_d/1.212 \quad (10)$$

where, E_{sp} = static Young's modulus of cement paste (N/mm²); and ν_{sp} = static Poisson's ratio.

2.7 Young's modulus of aggregate

In order to evaluate the Young's modulus of fine-aggregate and coarse-aggregate, following equation based on the absorption coefficient was adopted.

$$\left. \begin{matrix} E_{sa} \\ E_{ga} \end{matrix} \right\} = \frac{5.89}{\mu^{0.22}} \times 10^4 \quad (11)$$

where, E_{sa}, E_{ga} = Young's modulus of fine-aggregate or coarse-aggregate (N/mm²); μ = water absorption of fine-aggregate or coarse-aggregate (%).

The equation to calculate the Young's modulus of whole aggregate is shown below as a function of sand-coarse aggregate ratio.

$$E_a = S_a E_{sa} + (1 - S_a) E_{ga} \quad (12)$$

where S_a = sand-coarse aggregate ratio, E_a = the Young's modulus of whole aggregate (N/mm²).

2.8 Young's modulus of concrete

There are many equations to evaluate a Young's modulus of compound materials. In this study following equation that was basically developed by Hashin-Hansen and improved later was selected referring to the investigation of Kiyohara et al. That is, in this equation K factor is introduced to evaluate the influence of the micro crack occurred at the phase boundary between the cement paste and the aggregate and the boundary-layer of the aggregate.

$$E_c = E_{sp} \cdot \frac{(1 - V_a) E_{sp} + (1 + V_a)(k \cdot E_a)}{(1 + V_a) E_{sp} + (1 + V_a)(k \cdot E_a)} \quad (13)$$

where, E_c = static Young's modulus of concrete (N/mm²); E_{sp} = static Young's modulus of cement paste (N/mm²); E_a = static Young's modulus of aggregate (N/mm²); V_a = volume of aggregate per 1 m³ concrete (m³/m³); and k = compensation coefficient.

3 CALCULATION OF YOUNG'S MODULUS OF EXISTING DAM CONCRETE

3.1 Mix proportion of dam concrete and physical properties

For calculation of Young's modulus of dam concrete Kurobe and Tonoyama dam were selected because of using a moderate heat Portland cement. Calculated Young's modulus based on the compound theory was compared with the value obtained from experiment and the validity of this technique is discussed.

The specified mix proportion of the concrete which was used for Kurobe and Tonoyama dam is shown in Table 1. Mix proportion of 40 mm wet-screened concrete is also shown in Table 2. Moreover, the physical properties of the hardened concrete and aggregate are shown in Table 3. and Table 4.

3.2 Calculation of the static elastic modulus of cement paste and aggregate

Based on these data, the calculation result of P- and S-wave velocity of cement paste is shown in Table 5. The density of the cement paste is also shown in

Table 1. Mix proportion of full mix concrete.

Name of dam	Kurobe	Tonoyama
Max size of aggregate (mm)	180	80
Air (%)	3-4	4-5
W/C (%)	47.2	42.9
Water (kg/m ³)	85	105
Cement (kg/m ³)	180	245

Table 2. Mix of 40 mm wet-screened concrete.

Name of dam	Kurobe	Tonoyama
Water (kg/m ³)	143	119.4
Cement (kg/m ³)	304	285.5
W/C (%)	47.2	41.8
Cement paste (volume)		
Water (%)	14.3	12.1
Cement (%)	9.48	9.00
Paste (%)	23.78	21.1
Air (%)	5.9	2.6

Table 3. Physical properties of concrete (Mix of 40 mm wet-screened concrete).

Name of dam	Kurobe		Tonoyama	
Age days	E_c^* N/mm ²	σ_c^{**} N/mm ²	E_c^* N/mm ²	σ_c^{**} N/mm ²
7	17,100	20.4	18,500	25.5
28	22,000	33.4	24,100	37.3
91	25,300	43.4	32,000	49.0
183	26,900	46.1	—	—
365	29,700	48.6	—	—

* Young's modulus, ** Compressive strength.

Table 6. Moreover, calculated dynamic and static elastic constants of cement paste are shown in Table 7. For the calculation of Young's modulus of concrete using Equation 13 Young's modulus of the aggregate, absolute volume of the cement paste and the aggregate per 1 m³ concrete are shown in Table 8.

Incidentally, here, V_m , V_a is the capacity ratio of the base material (cement paste) and the aggregate to the whole product (concrete), respectively.

3.3 Calculation of static Young's modulus of dam concrete

Although the static Young's modulus of dam concrete can be estimated from Equation 13, in the equation k value isn't decided. According to a investigation of Kiyohara et al. $k = 0.87$ was proposed. Using this

Table 4. Physical properties of aggregate.

Name of dam	Kurobe	Tonoyama
Fine aggregate		
Water absorption (%)	0.6	2.6
Specific gravity	2.59	2.56
Lithology	Granite	*
Coarse aggregate		
Water absorption (%)	0.7	1.5
Specific gravity	2.64	2.60
Lithology	Granite	*

* Sandstone, shale and granule conglomerate.

Table 5. Calculation results of P- and S-wave velocity of cement paste.

Kurobe			
Age days	R _H (t)	V _p m/s	V _s m/s
7	0.5716	3131.7	1497.1
28	0.7155	3534.5	1744.1
91	0.8201	3827.3	1923.7
183	0.8708	3969.4	2010.8
366	0.9121	4084.9	2081.6
730	0.9441	4174.5	2136.6
Tonoyama			
Age days	R _H (t)	V _p m/s	V _s m/s
7	0.5438	3279.4	1594.5
28	0.6818	3686.0	1843.9
91	0.7837	3986.4	2028.2
183	0.8344	4135.8	2119.8
366	0.8768	4260.7	2196.3
730	0.9118	4363.7	2259.5

Table 6. Density of cement paste.

Name of dam	Kurobe	Tonoyama
Water (kg/m ³)	600.84	571.56
Cement (kg/m ³)	1277.30	1366.72
Density (g/cm ³)	1.878	1.938

value and Equation 13 the Young's modulus of dam concrete was calculated and the results are shown with experimental data in Figure 1 and Figure 2. From the figures considerable differences between them can be seen. It seems that calculated values are larger than experimental ones and the k value is not to be constant.

As a parameter reflecting to the Young's modulus of concrete E_{sp}/E_a and V_p/V_a are considered,

Table 7. Calculation results of dynamic and static elastic modulus of cement paste.

Kurobe				
Age days	ν_d	E_d N/mm ²	E_{sp} N/mm ²	ν_{sp}
7	0.3519	11,390	7,450	0.2903
28	0.3391	15,310	11,000	0.2798
91	0.3310	18,520	14,120	0.2731
183	0.3274	20,180	15,800	0.2701
366	0.3246	21,580	17,270	0.2678
730	0.3225	22,660	18,440	0.2661
Tonoyama				
Age days	ν_d	E_d N/mm ²	E_{sp} N/mm ²	ν_{sp}
7	0.3452	13,270	9,100	0.2848
28	0.3331	17,590	13,190	0.2748
91	0.3254	21,160	16,810	0.2685
183	0.3219	23,050	18,820	0.2656
366	0.3191	24,690	20,600	0.2632
730	0.3168	26,080	22,170	0.2614

Table 8. Calculation results of Young's modulus of aggregate.

Name of dam	Kurobe	Tonoyama
E_{sa} (N/mm ²)	64,600	46,800
E_{sg} (N/mm ²)	62,500	52,900
V_{sa} (m ³ /m ³)	0.322	0.319
V_{sg} (m ³ /m ³)	0.376	0.446
S_a	0.4613	0.4170
E_a (N/mm ²)	63,500	50,300
V_m (m ³ /m ³)	0.238	0.209
V_a (m ³ /m ³)	0.762	0.791

however, the latter may be constant in every concrete. Then the relationship between k values obtained from Equation 13 taken account of measured data of concrete and parameter E_{sp}/E_a was investigated. A regression is shown below.

$$k = 0.075 + 2.017 \cdot \frac{E_{sp}}{E_a} \quad (\text{Krobo}) \quad (14)$$

$$k = 0.231 + 1.168 \cdot \frac{E_{sp}}{E_a} \quad (\text{Tonoyama}) \quad (15)$$

Calculated static Young's moduli using Equation 13 with k values estimated from Equation 14 and 15 and measured ones are presented in Table 9, Figure 3 and Figure 4, respectively.

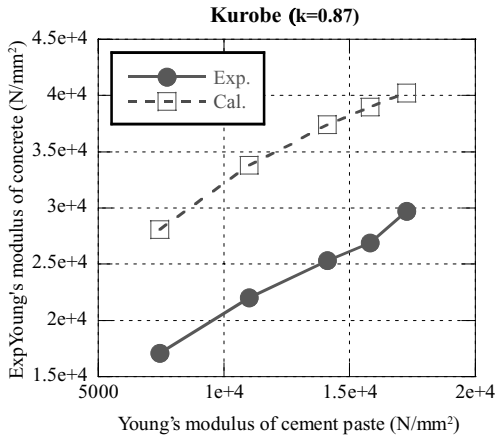


Figure 1. Young's modulus of dam concrete and cement paste (Kurobe Dam).

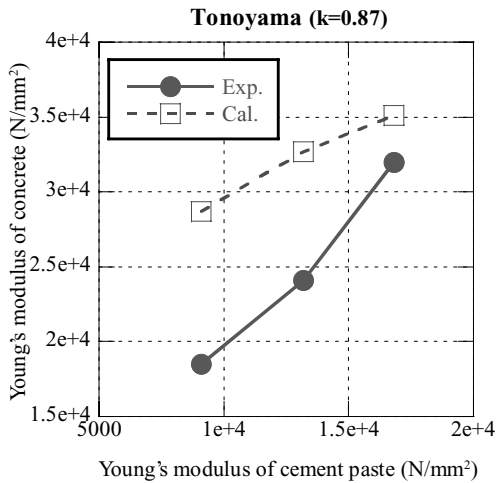


Figure 2. Young's modulus of dam concrete and cement paste (Tonoyama Dam).

These show a good agreement between calculated values and actual measured ones of static Young's moduli of concrete.

As a result, if we have measured values of static Young's modulus of a dam concrete, the possibility that the variation of long-term static Young's modulus can be estimated in this way was shown. Using a described method calculated long-term Young's moduli are shown in Figure 5 and Figure 6 with measured ones.

Table 9. Calculation of static elastic modulus of concrete.

Kurobe				
Age days	E_{sp} N/mm ²	$E_c(c)$ N/mm ²	$E_c(e)$ N/mm ²	$E_c(c) / E_c(e)$
7	7,450	17,200	17,100	1.01
28	11,000	21,700	22,000	0.99
91	14,120	25,500	25,300	1.01
183	15,800	27,500	26,900	1.02
366	17,270	29,200	29,700	0.98
730	18,440	30,600	—	—

Tonoyama				
Age days	E_{sp} N/mm ²	$E_c(c)$ N/mm ²	$E_c(e)$ N/mm ²	$E_c(c) / E_c(e)$
7	9,100	18,100	18,500	0.97
28	13,190	25,200	24,100	1.04
91	16,810	31,400	32,000	0.98
183	18,820	34,900	—	—
366	20,600	38,000	—	—
730	22,170	40,700	—	—

* $E_c(c) = E_c(\text{calculation})$, $E_c(e) = E_c(\text{experiment})$

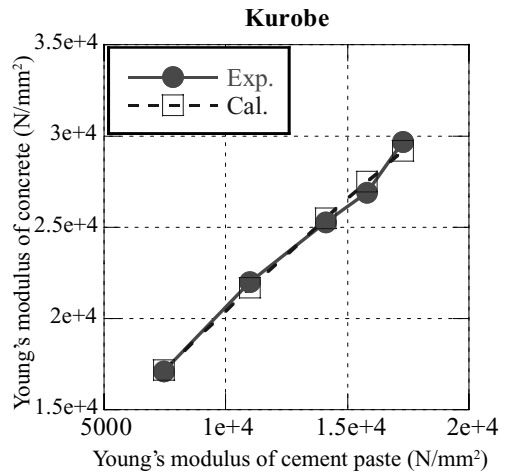


Figure 3. Young's modulus of dam concrete and cement paste.

4 CONCLUSIONS

For contributing to the safety of existing concrete dams the prediction method of Young's modulus of the dam concrete using moderate-heat Portland cement was discussed. In the investigation the concrete was considered to be two phase material which was composed of cement paste and aggregate, the Young's modulus

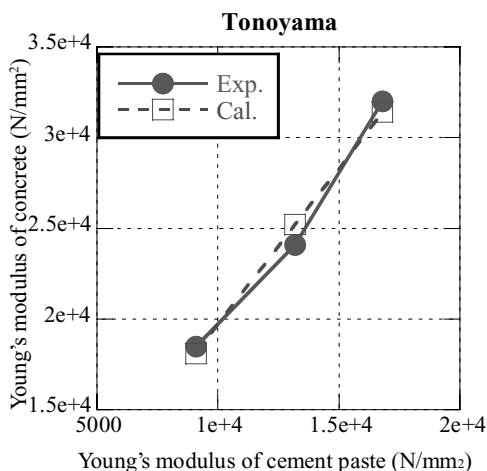


Figure 4. Young's modulus of dam concrete and cement paste.

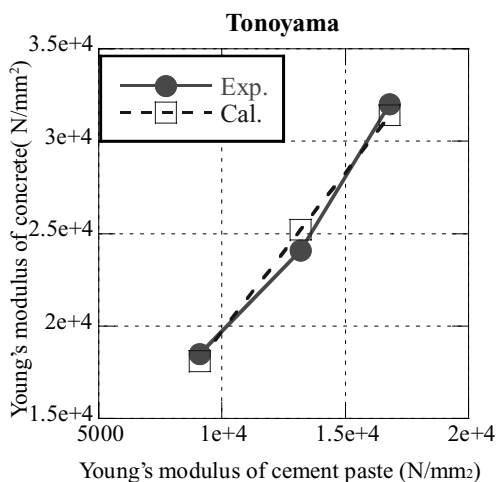


Figure 5. Young's modulus of dam concrete dependent on time (Krobe Dam).

of the concrete was calculated based on the compound theory. Also the Young's modulus of hardened cement paste was evaluated from the experimental equation considering unbound water affected by the degree of hydration of cement and the Young's modulus of aggregate was estimated from the amount of water absorption.

As a result, the actual measured values and the calculated values of the Young's modulus of the concrete were approximate well and the long-term Young's modulus of dam concrete would be calculated by this method was shown.

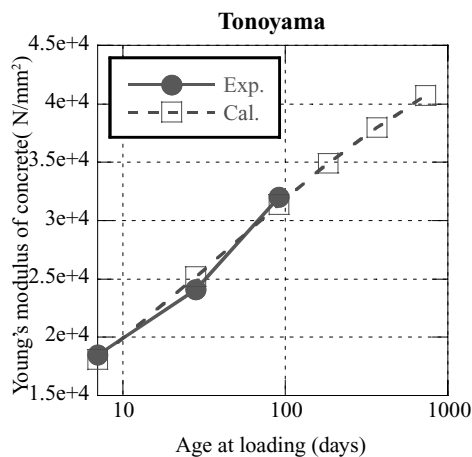


Figure 6. Young's modulus of dam concrete dependent on (Dam).

Incidentally, it is necessary to clarify the estimation method of Young's modulus of aggregate and the influence of parameter E_{sp}/E_a on Young's modulus of concrete.

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Micro elastic modulus of blended cement pastes

K. Kurumisawa, T. Nawa & Y. Hirukawa

Hokkaido University, Sapporo, Japan

ABSTRACT: For improving the properties of concrete, fly ash and Blast furnace slag (BFS) is mixed with ordinary Portland cement (OPC). These blended concrete has a high resistance to chloride ingress by reducing large pores at later age. This is because fly ash and BFS is reacted with calcium hydroxide and then produce calcium silicate hydrate (C-S-H) gel which expand in cement matrix. It was well known that blended concrete has advantages such as low porosity and low calcium hydroxide content. However, the properties of C-S-H in blended concrete are not cleared well because its structure is changed with mineral admixtures. To understand the structure of C-S-H is important for predicting the properties of concrete. Recently, to determine the mechanical property of C-S-H, nano-indentation method is applied for hardened cement paste by Ulm et al. In their study, this method is only applied for OPC only or degraded OPC until now. Therefore, we applied this method for measuring the elastic modulus of blended hardened cement paste and also measured compositions of blended cement paste by backscattered electron image. As a result, the elastic modulus of HCP mixed with fly ash is lower than that of HCP only. It is indicated that the elastic behavior of C-S-H in blended cement is different from that in OC.

1 INTRODUCTION

For improving the properties of concrete, fly ash (FA) and Blast furnace slag (BFS) is mixed with ordinary Portland cement (OPC). These blended concrete has a high resistance to chloride ingress by reducing large pores at later age. This is because fly ash and BFS is reacted with calcium hydroxide and then produce calcium silicate hydrate (C-S-H) gel which expand in cement matrix. It was well known that blended concrete has advantages such as low porosity and low calcium hydroxide content. However, the properties of C-S-H in blended concrete are yet not understood because its structure is changed with addition of mineral admixtures. To understand the structure of C-S-H is important for predicting the properties of concrete. Recently, to determine the mechanical property of C-S-H, nano-indentation method is applied for hardened cement paste by Bernard and Ulm (2003). In their study, this method is only applied for OPC or degraded OPC until now (Ulm, 2004). Therefore, we applied this method for measuring the elastic modulus of blended hardened cement paste and also measured component compositions of blended cement paste by backscattered electron image analysis. However, we are faced with the problem that when the nano-indentation method is applied, it is difficult to identify each phase in cement paste at nano level. Hence we adopted

the micro-indentation method that can measure the elastic modulus of component at micro level where each phase can be easily determined by SEM.

2 EXPERIMENTAL

2.1 Sample preparation

Ordinary Portland cement (OPC) and Eco-cement (ECO), Fly ash (FA) and Blast furnace slag (BFS) were used in this study. Properties of cements and chemical composition of cements is shown in Table 1, 2, respectively.

The water to binder ratio of the cement paste is 0.5 by weight. EC were also mixed with FA or BFS from 0 to 0.7 by weight. Replacement ratio of FA is 0.1, 0.2, and 0.3 (EF10, EF20 and EF30), and that of BFS is 0.3, 0.5 and 0.7 (ES30, ES50 and ES70). Mixing time was 3 minutes. Cement pastes were cast in cylindrical moulds. Each of them was sealed and left in the room at 20°C for 1, 3, 7, 28, 91 and 365 days. The hydration degree of each paste was determined by using the ignition loss technique (105–950°C).

2.2 Backscattered Electron Image (BEI) measurement

Specimens of 5 millimeters cubic of pastes were prepared and immersed in acetone for approximately

Table 1. Properties of materials.

Sample	Blaine surface area (cm ² /g)	Density (g/cm ³)	Ig. loss (%)
OPC	3450	3.16	0.83
EC	4310	3.17	1.02
FA	3530	2.27	1.6
BFS	6000	2.89	—

Table 2. Chemical composition of cements.

	Chemical composition (%)					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
OPC	20.93	5.16	2.97	64.16	2.48	2.11
EC	17.01	7.42	3.72	61.63	2.24	4.09

24 hours to remove most of the water by solvent exchange. D-dry was applied to specimens to remove most of the acetone. They were immersed in low viscosity epoxy resin under vacuum at room temperature. After the impregnated resin was hardened, the surface of specimens was polished with sand paper and then with diamond paste. Finally, carbon was coated. The specimens were examined at 500 × at 15 KeV by SEM with BSE detector. Observation area is 150 × 200 μm and each pixel size is 0.32 μm. And degree of hydration α_c is determined by following equation,

$$\alpha_c = 1 - \frac{V_{ci}}{V_{c0}} = 1 - \frac{A_{ci}}{A_{c0}} \quad (1)$$

where V_{ci} , V_{c0} , A_{ci} and A_{c0} are volume of cement at time i , volume of cement at initial, area fraction of cement at time i and area fraction of cement at initial respectively.

2.3 Energy Dispersive X-ray analysis (EDX) measurements

The measurement condition of EDX is the same as BEI measurement except for measuring pixel size. The measuring pixel size is 256 × 256. In this study, the elements of Na, Mg, Al, Si, P, S, K, Ca and Fe are detected. Threshold value of each element is determined by measuring each phase using point count analysis. The decision algorithm of the phase in hardened cement paste is not reported, though *Bentz (1999)* reported on the decision algorithm of distribution of phases in the cement particle. Firstly, when the pixel in BEI is brighter than that of Aluminate in unhydrated

cement particle, the pixel is unhydrated cement. When it is darker than Aluminate, it is pore (Pore), C-S-H, FA or other hydration products (C-S-H), Ca(OH)₂ (CH) or BFS. When the pixel of unhydrated cement contains Al and Fe in unhydrated cement, it is Ferrite phase. When the pixel does not contain Fe, it is Aluminate phase. It is Alite phase in case the Ca/Si ratio of the other pixels is high. The rest of pixels in unhydrated cement are Belite phase. The pixel that does not indicate the value of Ca is pore ($\geq 0.32 \mu\text{m}$), and the pixel that shows no value of Si and high value of Ca is calcium hydroxide and the other pixels are C-S-H or other hydration products including fine pores ($< 0.32 \mu\text{m}$).

2.4 Compressive strength measurement

The measurement of compressive strength was determined by using cylindrical specimen with a 100 mm height and a 50 mm diameter.

2.5 Mercury intrusion method

Mercury intrusion method (MTP) is applied for measuring pore size distribution. 5 mm cubic specimens after drying were used for measurement.

2.6 Elastic modulus measurement by indentation

A loaded indenter was applied to the same sample as in the above section 2.2 to measure the indentation. Once a pre-determined load was achieved, the load was removed. The elastic modulus can be calculated based on the inclination measured upon removing the load by *Oliver (1992)*. The maximum load was 20 mN and the loading speed was 1.0 mN/s. Once the maximum load was achieved, it was held for five seconds. Then, the load was removed at the same speed as reaching the maximum load. Measurement conducts at 100 points with 10 μm intervals. In the study, a Fisher's scope H100C was used. After the pushdown, there remain the indentations, which are available for observation by EDX and then determined component composition such as C-S-H, CH and so on.

3 RESULTS

3.1 Compressive strength

Changes in compressive strength of paste with age are shown in Figs. 1 and 2. The strength of all specimens except the EC increased with time. In other words, addition of fly ash and BFS had enhanced strength at the long-term age. Therefore it is important to clarify the mechanism on the improvement of strength development due to mineral admixtures.

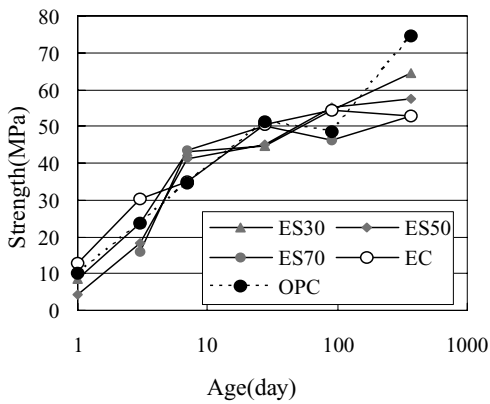


Figure 1. Compressive strength with age.

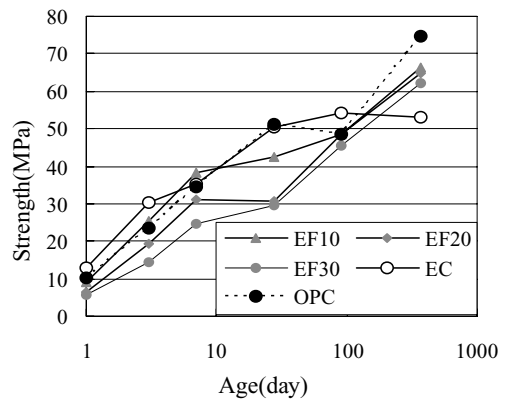


Figure 2. Compressive strength with age.

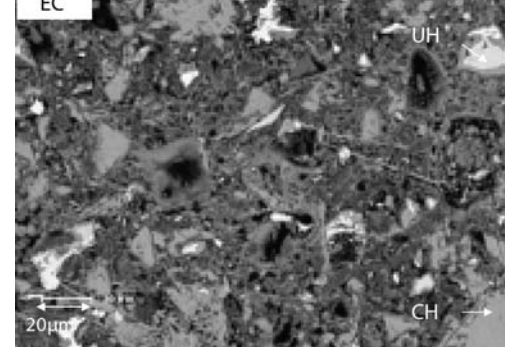
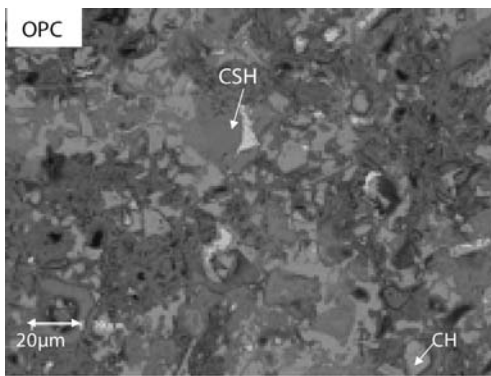


Figure 3. Backscattered electron image.

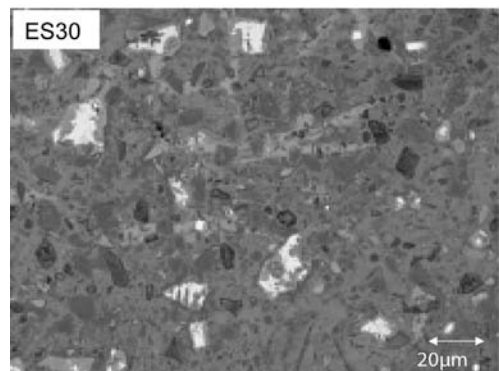
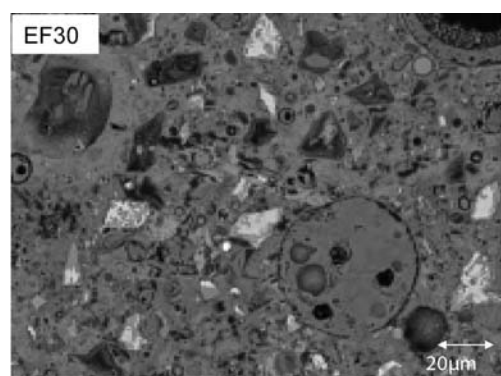


Figure 4. Backscattered electron image of EC with FA of Slag.

3.2 BEI observation

BEI at 1 year curing are shown in Figs. 3 and 4. Black, dark gray, light gray, white pixel show Pore, C-S-H or Fly ash, CH or BFS, and UH, respectively. It is evident

that many pores are left in the EC, but a pore is hardly left with the case of OPC and ES30.

This leads to the change in microstructure of cement pastes due to addition of mineral admixtures.

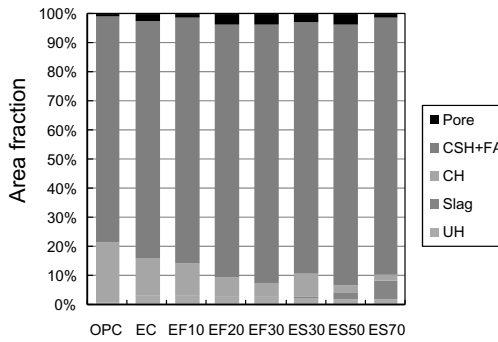


Figure 5. Area fraction measured by BEI.

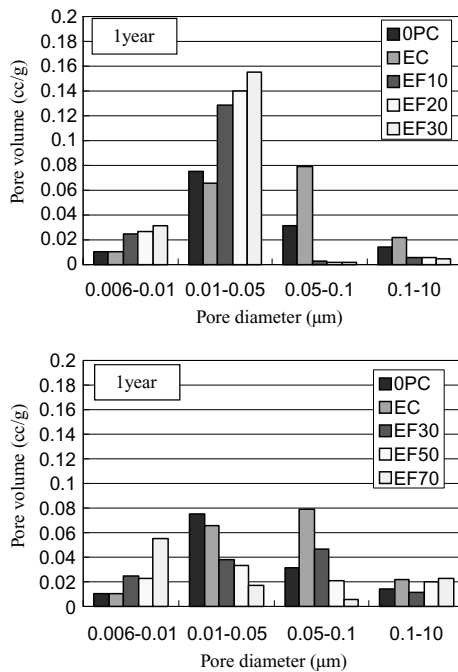


Figure 6. Pore size distribution at 1 year.

The fraction in area of each phases (Pore, C-S-H, CH, Slag and UH) of 1-years old paste, which calculated by BEI is shown in Fig. 5. Most of phases are hydration products, and few unhydrated component remain. In addition, there are not the coarse pores that can observe by BEI.

3.3 Pore structure measured by MIP

Pore size distribution of specimens at 1 year from the MIP measurement is shown in Fig. 6. Coarse pore ($>0.05 \mu\text{m}$) is existed in EC, but not in specimens mixed with mineral admixtures. It is confirmed that

Table 3. Porosity at 1 year measured by MIP (cc/g).

OPC	EC
0.130	0.177

EF10	EF20	EF30
0.162	0.174	0.194

ES30	ES50	ES70
0.121	0.098	0.100

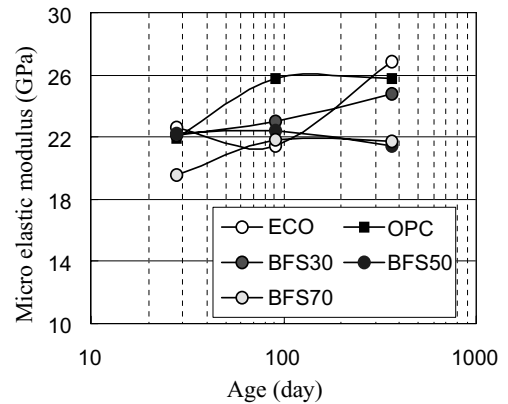
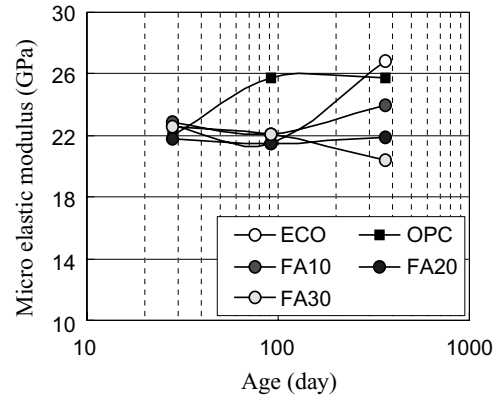


Figure 7. Micro elastic modulus with age.

pore structure changed greatly by mineral admixtures. There are a lot of fine pores in ES70 compared with the other samples.

Porosity at 1 year measured by MTP is shown in Table 3. As for the specimens with BFS, porosity decreased greatly. The porosity in mixed with or without FA was almost the same, but it was shown that pore size distribution was different.

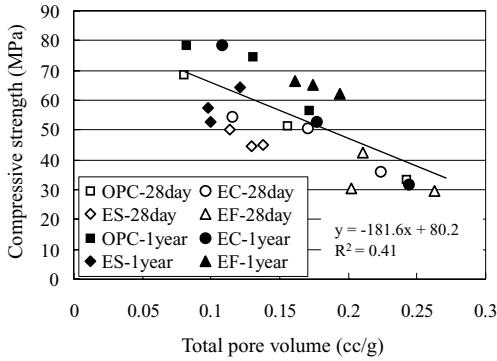


Figure 8. Effect of porosity on compressive strength.

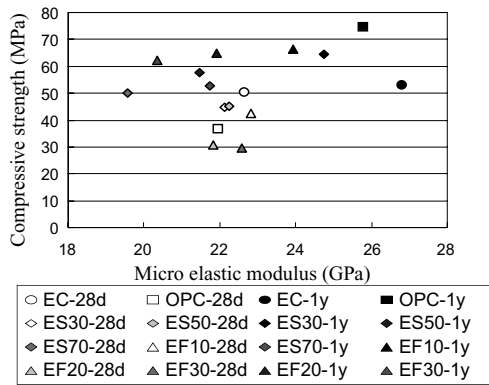


Figure 9. Effect of micro elastic modulus on compressive strength.

3.4 Micro elastic modulus

Micro elastic modulus measured by indentation method was shown in Fig. 7. Elastic modulus measured in this study and results from nano-indentation (Oliver, 2003) was almost the same. Micro elastic modulus of OPC and EC increased with age, but that of specimens with high replacement ratio did not increase with age.

4 DISCUSSIONS

Effect of porosity on compressive strength is shown in Fig. 8. It was shown that relationship between porosity and strength is almost linear, but the coefficient of correlation is not so high. The effect of porosity on strength is influenced by a kind of cement and mineral admixtures. Therefore it is difficult to estimate the compressive strength only by porosity. Relationship between of micro elastic modulus on compressive

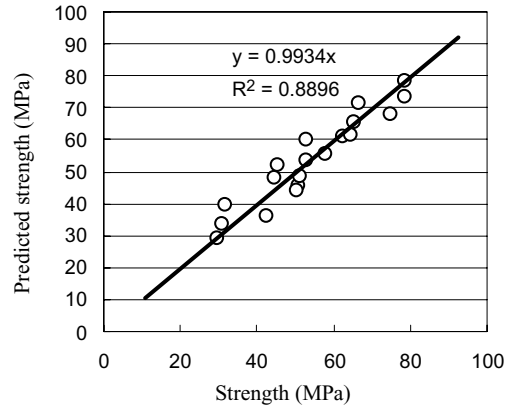


Figure 10. Relationship between measured and predicted strength.

strength is shown in Fig. 9. It is clear that the bulk elastic modulus is related to compressive strength. This is consistent with the previous reports (Klink, 1992 and Boumiz, 1996). However, the relationship between micro elastic modulus and compressive strength was not good. In other words the prediction of the compressive strength is not possible only by a micro elastic modulus. Therefore, we cannot explain the compressive strength by porosity or micro elastic modulus of matrix independently. Accordingly, we try to estimate the compressive strength as a function of both coarse porosity and the micro elastic modulus. Following equation is obtained,

$$\sigma_c = 3.1 \times E_m - 257 \times P \quad (2)$$

where σ_c = compressive strength (MPa); E_m = elastic modulus (GPa); and P = porosity (cc/g). As shown in Fig. 10, there is a good relationship between measured and predicted strength. Therefore it is possible that compressive strength development can be explained by these two parameters.

5 CONCLUSIONS

In this study, we investigated the effect of micro elastic modulus of cement paste matrix on strength. It was cleared that pore structure and micro elastic modulus of matrix changed by adding mineral admixtures.

It is possible to predict the compressive strength with considering both of coarse porosity and micro elastic modulus. That is, it is indicated the compressive strength is influenced by not only porosity but also micro elastic modulus of matrix.

ACKNOWLEDGMENT

A part of this study is partially supported by the Japan cement association. Eco-cement that used in this study is offered from Taiheiyo Cement Corporation. We would like to thank to Mr. Konno and Mr. Matsushima at Hokkaido Industrial Research Institute for their cooperation.

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Study of the hydration process of quaternary blended cements and durability of the produced mortars and concretes

M. Katsioti & P. Pipilikaki

School of Chemical Engineering, National Technical University of Athens, Athens, Greece

K. Pavlou & E. Chaniotakis

Titan Cement Company S.A., Department of R&D and Quality, Elefsina, Greece

M. Fardis, E. Karakosta & G. Papavassiliou

NCSR Demokritos, Institute of Material Science, Ag. Paraskevi, Athens, Greece

ABSTRACT: This study aims to clarify the effect that quaternary blended cements have on the hydration process and durability of concrete. Therefore, blended cements with two different proportions of high calcium fly ash, natural pozzolana and limestone have been produced and have been compared with CEM I type cement. Compressive strength was measured at different ages and the hydration kinetics was studied by means of Proton Nuclear Magnetic Resonance (NMR-¹H). Furthermore, the above mentioned cements have been used to produce mortars and concretes and their durability have been determined. The aspects of durability that has been determined are: pore size distribution by means of NMR-¹H and mercury intrusion porosimetry, chloride penetration, carbonation and resistance to sulphates attack. The conclusion of the present study is that quaternary blended cements can perform as well as CEM I cement as far as compressive strength are concerned and they produce durable mortars and concretes.

1 INTRODUCTION

Clinker production is an energy intensive process associated with the emission of large amounts of CO₂, hence amplifying greenhouse effect. Cement production is also an energy intensive process, as well as demanding from the raw materials perspective. Technical improvements by the cement industry to decrease the environmental impact of the latter processes are reaching their limit. One of the remaining options could be the reduction of the clinker content in cement. One way to achieve this is the production of blended cements, through the use of supplementary cementing materials such as granulated blastfurnace slag (GGFS), fly ashes from power plants, natural and industrial pozzolanas or limestone. The production of blended cements results in lower emission and lower energy consumption since less clinker is used. [ECOsolve, Taylor (1995)].

Different kind of additives have been used around the world but the role of each additive and its effect on the hydration process and durability of concrete is not clearly understood especially in ternary and quaternary systems. This study aims to contribute clarifying the effect that blended cements with four components have on the hydration process and durability of concrete.

2 MATERIALS AND METHODS

Two different blended cements (QBC1) and (QBC2) and a CEM I cement of the same class as given in the European Standard EN197-1 were produced using a laboratory ball mill whose composition and specific area are presented in Table 1.

The compressive strength of mortars was measured according to the European Standard EN196-1 at 1, 2, 7, 28 days while the hydration process was monitored in cement pastes with water to cement ratio of 0.5 by means of Proton Nuclear Magnetic Resonance (¹H-NMR).

Table 1. Composition and specific area of produced cements.

	CEM I	QBC1	QBC2
Fly ash (%)	0	6	15
Pozzolana (%)	0	17	12
Limestone (%)	0	8	15
Clinker (%)	95	66	55
Gypsum (%)	5	4	3
Blaine (cm ² /g)	2660	4660	5240

Moreover, the above mentioned cements have been used to produce mortars and concretes and their durability was determined. In order to estimate the durability the following aspects have been measured:

- pore size distribution by means of NMR-H and mercury porosimetry in cement pastes with water to cement ratio of 0.5 at the age of 6 months when the hydration of the cement is almost complete,
- penetration of chlorides measured according to ASTM C1202-05 performed at the age of 28 days in concrete with effective water to cement ratio of 0,5,
- carbonation measured in concrete with effective water to cement ratio of 0,6 that remained one day in the mould and six days in a $\text{Ca}(\text{OH})_2$ saturated solution and then kept inside a carbonation chamber that had concentration of CO_2 1%, temperature $\sim 20^\circ\text{C}$ and RH $\sim 70\%$ for 28d, 56d, 90d, 180d, 365d (1 year) and 730 days (2 years) using the method of phenolphthaleine.
- resistance against sulphates attack by measuring the expansion of mortars with water to cement ratio of 0,5 made according to the European Standard EN196-1, that were first cured for 14 days in a saturated lime solution and then immersed in a 5% Na_2SO_4 solution for 18 months (1,5 year).

3 RESULTS AND DISCUSSION

3.1 Compressive strength

The results of the measurements of the compressive strength of the cements are presented in Table 2. It is obvious that quaternary blended cements exhibit satisfactory strengths both in the early and later ages that are similar to those of the CEM I.

In fact quaternary blended cements present higher early compressive strengths than the CEM I. On the other hand, the compressive strength at the age of 28 days is approximately the same for all three cements. This behaviour can be attributed either to an acceleration of the hydration reaction deriving from the use of the additives or from the action of the additives as fillers which contribute to the early strength evolution. In order to determine which mechanism is more accurate a study of the hydration kinetics is essential.

Table 2. Compressive strength of the cements.

Cement	1 day (MPa)	2 days (MPa)	7 days (MPa)	28 days (MPa)
CEM I	8,0	12,5	23,3	41,4
QBC1	12,5	19,4	30,3	41,4
QBC2	10,0	16,3	27,1	40,1

3.2 Study of the hydration process by means of nuclear magnetic resonance (^1H -NMR)

Proton Nuclear Magnetic Resonance (^1H -NMR) studies of porous systems such as cement monitors the evolution of surface to volume ratio as function of time. The ^1H -NMRT₁ spin-lattice relaxation time of the water that takes part in the hydration process is shown as a function of hydration time in Figure 1. On these diagrams the basic periods of the hydration reaction have been marked: the dormant period, the acceleration period and the diffusion period.

The start of the acceleration period has been plotted as a function of the clinker amount in the cement which is the main component that hydrates and is presented in Figure 2. Furthermore it a linear line has been fitted in these data. From the diagrams presented in Figure 1 and 2 it is evident that the dormant period is longer in the case of the quaternary blended cements. Respectively longer is the acceleration period. Thus,

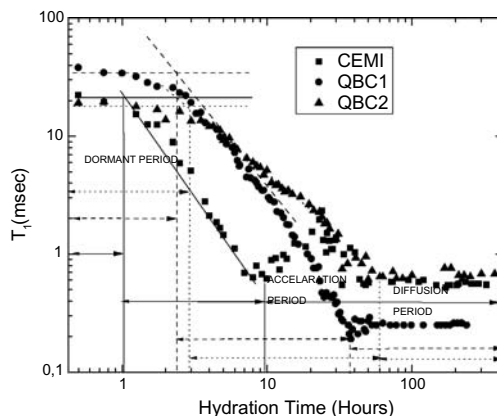


Figure 1. T_1 relaxation time as a function of hydration time.

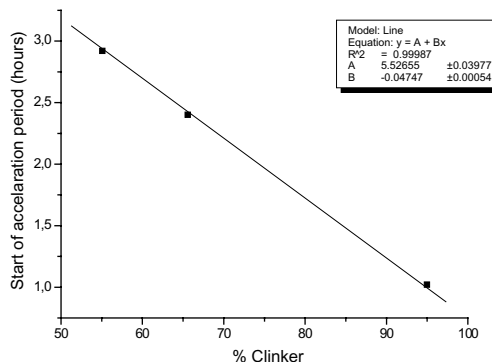


Figure 2. Correlation of the start of acceleration period with the amount of clinker in the cement.

quaternary blended cements present a delay in the hydration reaction that can be attributed to the fact that the clinker which is hydrated is less in the blended cements.

Therefore, it is obvious that the hydration rate of the quaternary blended cements is lower than that of the CEM I.

It is possible to fit sigmoid curves in the hydration kinetics data. The result of this adjustment is presented in Figure 3.

The fitted curves help to estimate the derivatives of the hydration kinetics and present the hydration rate as a function of time. The derivatives are shown in Figure 4. They must be examined only according to the location of the peak and their width.

It is noticeable that a) the maximum of the hydration rate shifts in later time in the case of the quaternary blended cements and b) the width of the peaks increases significantly in the case of the quaternary

blended cements which means that hydration process take a lot more time in comparison to the reference cement.

From the above it is obvious that partial substitution of the clinker of cement by additives delays significantly the acceleration period of the hydration of cement which is characterized by the creation of the majority of the C-S-H gel through homogeneous nucleation and growth. This information can only be derived by the study of the hydration kinetics by means of Proton Nuclear Magnetic Resonance.

3.3 Mercury intrusion porosimetry (MIP)

In this study the cumulative intruded volume curve (Figure 5) and the incremental intrusion volume vs radius curve (Figure 6) are presented in order to estimate and evaluate the pore structure of the hardened blended cements.

A parameter of particular interest that can be determined from the cumulative porosity curve is the critical pore size.

The critical pore size (d_{cr}) corresponds to the steepest slope of the cumulative porosity curve. The critical

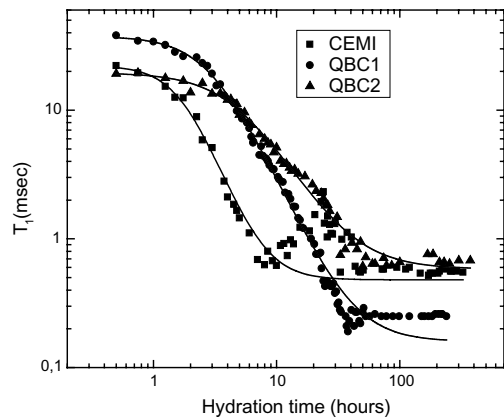


Figure 3. Fit of sigmoid curve on the hydration kinetics data.

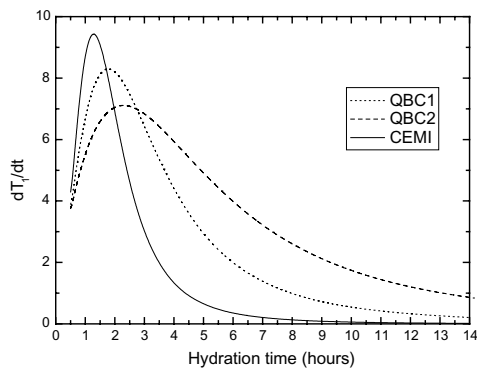


Figure 4. Diagrams of the derivatives of the hydration kinetics versus time of hydration.

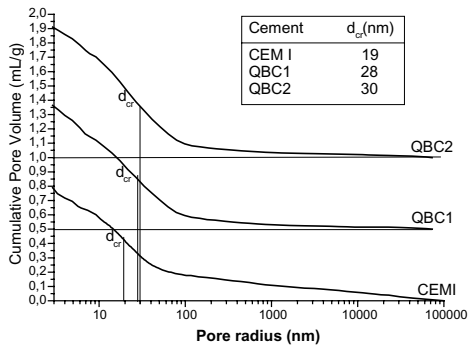


Figure 5. Cumulative intruded volume vs. radius curve.

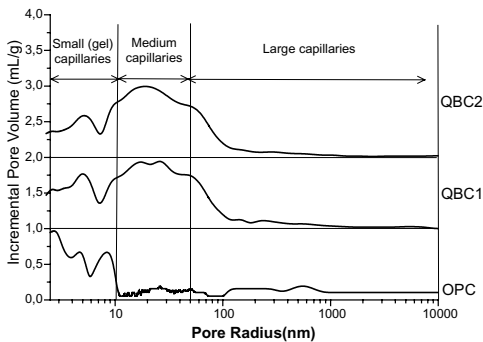


Figure 6. Incremental intrusion volume vs. radius curve.

pore size controls the transmissivity of the material. [Aligizaki 2006] The critical pore diameter is the most frequently occurring diameter in the interconnected pores that allows maximum percolation. [Winslow and Diamond 1970] The critical pore size of each cement cumulative porosity curve is marked on Figure 5.

From the results of the mercury intrusion porosimetry tests it is obvious that when additives are introduced in cements their critical diameter increases meaning that additives presence in cement produce larger interconnected pores in the cement paste. It must be noted that in the case of the quaternary blended cement that has a larger quantity of clinker (QBC1) the critical diameter is slightly smaller and that indicates that the pore structure of the cement is controlled mainly by the quantity of clinker. Finally, it is very important that the critical diameter of all three cements is of the same magnitude.

Classification of pore sizes is marked on Figure 6, performed according to S. Mindess et al., (2002). Pores sized from 50 to 10000 nm are called large capillaries. Capillary porosity is assumed to have a major effect on transport processes but only a minor effect on hydration rates. [Brown and Shi (1991)] Large capillaries sized more than 100 nm decrease as content of additives increases. Pores sized from 10 to 50 nm are called medium capillaries. These pores affect permeability and they appear as a result of mineral admixtures addition. [Brown and Shi (1991)] As it was expected the existence of additives created a larger amount of pores of this size. In fact, the vast majority of pores of quaternary blended cements are presented in this area. Pores sized from 2,5 to 10 nm are called small (gel) capillaries. These pores are not connected with permeability but they affect shrinkage. Pore of this size exist in all examined hardened cements. The majority of pores of the CEM I are presented in this area.

3.4 Nuclear magnetic resonance (NMR) cryoporometry

The pore size distribution obtained by NMR cryoporometry is presented in Figure 7.

Firstly, as far as small (gel) pores are concerned NMR cryoporometry investigation is in accordance with the above mentioned Mercury Intrusion Porosimetry results.

Pores sized from 0,5 to 2,5 nm that are examined with this method, are called micropores and they are part of the gel porosity of the cement paste. [S. Mindess et al., (2002)] The C-S-H gel is a colloidal amorphous gel, which contains pores of approximately few nanometers. Due to the small size of the gel pores, which are only an order of magnitude greater than the size of the water molecules and due to the great affinity of water molecules to the gel surfaces, the movement of water in gel pores does not contribute much to

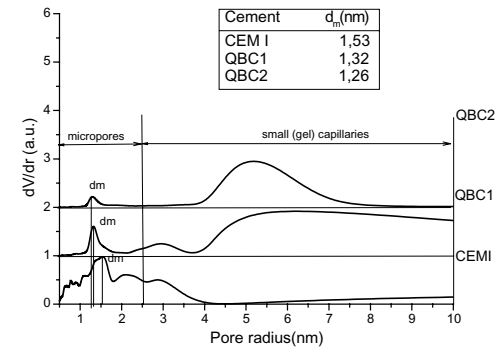


Figure 7. Pore size distribution of cement mortars obtained by NMR cryoporometry.

Table 3. Results of chloride penetration test according to ASTM C1202.

Cement	Charged passed (C)	Permeability class
CEM I	5907	High
QBC1	2368	Medium
QBC2	5160	QBC2

cement paste permeability. [Hearn et al. 1994] Gel porosity has a major effect on hydration rates, because gel pores exist inside the hydration products that accumulate between the liquid phase and the anhydrous cement grains. All hardened cements present a peak (dm) in their pore size distribution at around 1,5 nm which moves towards smaller radius as additives content increases. This means that quaternary blended cements have smaller gel pores.

3.5 Chloride penetration

The of the rapid Chloride penetration tests results are presented in Table 3. These results clearly show that quaternary blended cements have a better performance against chloride penetration. Specifically, CEM I has half of the resistivity of QBC1.

In order to explicate this result the porosity results mentioned above must be taken in consideration. Quaternary blended cements present a distribution of pores in the are of 10 to 50 nm in which transport processes are controlled by electrostatic interactions between the pore walls and the pore liquid that extend over a significant fraction of the pores' cross-sectional area; for this reason, electrostatic effects may hinder transport processes through these pores. [Brown and Shi (1991)] Chloride penetration is controlled by transport phenomena and therefore influenced by this effect. Furthermore, quaternary blended cements have

smaller interlayer micropores and there is evidence for the binding of chlorides in CSH gel, possibly in inter-layer space. [Papadakis (2000)] Lastly, it must be taken in consideration that the rapid test is a measurement of the electrical conductivity of concrete, which depends on both pore structure and composition of the pore solution. The addition of additives changes greatly the chemical composition of the pore solution, which has little to do with the pore structure itself. [Papadakis (2000)].

In order to experimentally support the above mentioned assumptions, investigation is still in process.

3.6 Carbonation

The results of the carbonation test are presented in Figure 8. The diagram shows that during the first period (until 180 days) of exposure in CO₂ all three concretes presented approximately the same depth of carbonation while after that age quaternary blended cements presented higher carbonation than CEM I.

In order to better estimate the rate of carbonation of the concretes the experimental data that are presented in Figure 8 were fitted in the equation $D = K \cdot t^{0.5}$, where D = depth of carbonation in mm, K = carbonation coefficient in mm/y^{0.5} and t = time of exposure in days, [Neville (1995)] and the value of K was estimated for each concrete and are presented in Table 4.

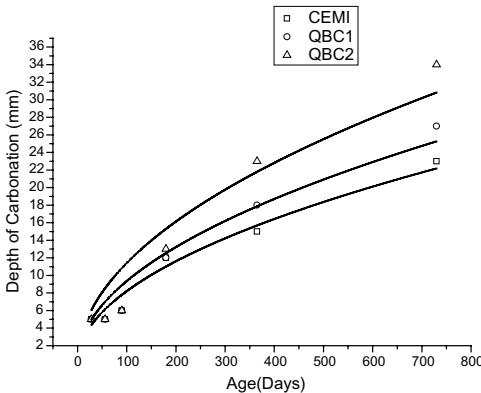


Figure 8. Progress of carbonation of concretes with time of exposure.

Table 4. Estimated carbonation coefficients K of the concretes.

Cement	K (mm/y ^{0.5})
CEM I	15,67
QBC1	17,96
QBC2	21,77

The results of Table 4 verify that CEM I has a lower carbonation rate than quaternary blended cements. It is noticeable that QBC1 has a carbonation rate very similar to that of CEM I.

When pozzolanic additives substitute clinker there is a reduction of the amount of portlandite due to the pozzolanic reaction. Literature [Neville (1995)] mentions that the depth of carbonation is greater when the amount of portlandite present is lower. It follows that the presence of fly ash results in a more rapid carbonation. This is the case of the blended cements used in this study and as pozzolanic additives amount increase carbonation is higher.

3.7 Resistance against sulfate attack

The results of the expansion measurements of the three mortars are presented in Figure 9.

In the data derived by the expansion measurements first order exponential growth ($y = y_0 + A_1 \cdot e^{x/t_1}$) was fitted and the curves are presented in Figure 9. The detailed results of the fitting are presented in Table 5.

It is obvious that CEM I has a greater expansion; the y_0 value which represents the final expansion of the cement is higher than quaternary blended cements.

This is due to the fact that blended cements have a lower amount of C₃A due to the reduction of clinker. This is the first factor that controls sulfate resistance.

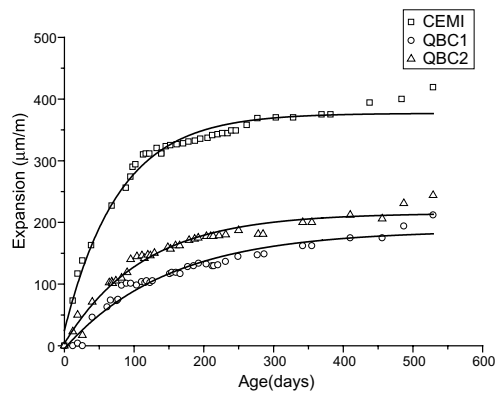


Figure 9. Progress of expansion of mortars in sulfate environment with time of exposure.

Table 5. Results of the fitting of first order exponential growth in the expansion versus time results.

Cement	Y_0	A_1	t_1
CEM I	377	-352	-78
QBC1	187	-192	-149
QBC2	215	-211	-112

Furthermore, the blended cements contain pozzolanic additives that react with portlandite reducing it in that way so that it won't react with sulfates.

The two blended cements present approximately the same expansion up to the age of 90 days and after that QBC1 has a better behavior.

4 CONCLUSIONS

Concluding this study, quaternary blended cements can perform as well as CEM I as far as compressive strength is concerned. They display high early strength that as proved by the study of the hydration reaction by NMR- H^1 is due to the filling effect of the materials. They have pore distribution in the area of medium and small capillary pores. As far as durability is concerned quaternary blended cements and especially QBC1 present exhalent behavior against chloride penetration and sulfate attack and a satisfying low carbonation depth, while ordinary blended cement behaves well only against carbonation. The conclusion of the present study is that quaternary blended cements can perform as well as CEM I cement as far as compressive strength are concerned and they produce durable mortars and concretes.

ACKNOWLEDGEMENTS

This work has been funded by the project PENED 2003. The project is cofinanced 75% of public expenditure through EC-European Social Fund, 25% of public expenditure through Ministry of Development-General Secretariat of Research and Technology and through private sector, under measure 8.3 of OPERATIONAL PROGRAMME "COMPETITIVENESS" in the 3rd Community Support Programme.

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*Multiphase and multi-scale approaches to creep,
shrinkage and durability*

JCI COMMITTEE REPORT

Multi-scale modeling to link observed behavior, characterization and analysis

H. Mihashi

Tohoku University, Sendai, Japan

K. Maekawa & T. Ishida

The University of Tokyo, Tokyo, Japan

S. Asamoto

Saitama University, Saitama, Japan

I. Maruyama

Nagoya University, Nagoya, Japan

ABSTRACT: This paper provides an overview of the mathematical modeling for time-dependent behaviour of cementitious materials. Since the cementitious materials have complex and multi-scale structures, the modeling need to bridge a very wide range of the order from nano-scale for material science level to meter-scale for structural analysis. Furthermore the structure of the cementitious materials is formed through chemical reaction and changes with time as a function of the environmental condition. Thus analytical models for observed behaviour in the cementitious materials need to be sufficiently comprehensive and precise characterization for material structure and measurement of the environmental conditions are essential for building up the constitutive models.

1 INTRODUCTION

For durability design and/or prediction of life time of concrete structures, nowadays it is essential to apply some relevant mathematical models to simulate the time-dependent behaviour of concrete.

Cementitious materials such as concrete have complex multi-component and multi-scale structures that first form through chemical reaction and then continue to change with time (e.g. Jennings et al. 2008). As a result, various aspects of the behaviour have been observed but sometimes the real mechanisms are not clarified. If the observed behaviour is just simplified as a material law, the potential of modern numerical methods for computerized structural design is not fully used.

It could be noticed that a lot of information on the cementitious materials exists dealing with the various aspects of formation and development of the micro-structure and strength. In the field of cement chemistry, chemical reaction process, hydration products and micro-pore systems were deeply studied.

Material structure of the heterogeneous composite system, mechanism of crack initiation and propagation, and mass transportation through the internal network of the porous micro-structure and cracks were studied in the field of material engineering. For the analysis and design of buildings and infrastructures, however, those scientific knowledges are limited to be transferred but averaged material laws have been obtained by a large amount of experimental studies.

One way to come to more realistic and more reliable material laws is to link the observed time-dependent behaviour with details of the material structure and with real mechanisms (Wittmann, 1983). However, the observed behaviour of concrete cannot be linked directly each other and a hierarchic system of at least three different levels needs to be introduced. Table 1 shows an example proposed by Wittmann (1983). For combining all of these observed behaviour into a unified system, conceptual modelings are essential to integrate carefully all of the important findings on these different levels into a general computational framework based on mathematical modelling. Here

Table 1. Three structural levels of concrete and corresponding characteristic features, mechanisms and models. (Wittmann 1983).

Structural levels	Characteristic features	Mechanisms	Type of models
Micro-level	Structure of Hardend cement Paste, Xerogel	Particle displacement, Capillary tension, Disjoining pressure, Surface free energy	Materials science models
Mesco-level	Pores, Cracks, Inclusions	Crack formation and Extension, Differential stress	Materials engineering models
Macro-level	Quasi-homogeneous structural elements	Apparent mechanisms	Structural engineering Models Material laws

the modelling of concrete should cover microstructure, hydration, temperature, moisture content, state of equilibrium, and mechanical and volumetric changes. The integration is to be sought in terms of a computational tool that can take into consideration the development of micro-structure and various changes of concrete exposed to any arbitrary environment. Furthermore, for predicting the life time of concrete structures, it needs to predict the structural performance of concrete together with the transport of various external agents into the concrete microstructure (Maekawa et al. 1999).

In this paper, some examples of such mathematical modelling and computational tools together with some experimental technologies to characterize the material structure are overviewed.

2 MATHEMATICAL MODELING FOR TIME-DEPENDENT BEHAVIOR OF CEMENTITIOUS MATERIALS BASED ON MICRO-MESOSCOPIC APPROACH

2.1 Microstructural modeling of concrete

As a starting point for predicting the time-dependent behavior of concrete or concrete structures, i.e. heat production and resultant thermal deformation, autogenous shrinkage, drying shrinkage and creep behavior, microstructural modeling of concrete is discussed. For the initial state of concrete, which is determined by the properties and performance of raw materials, mixture proportion, work operation, and hydration process, a couple of models have been proposed with which the evolution of the initial state of the concrete can be predicted as a function of the mixture composition and curing condition. The five most frequently discussed micro-structural models are the HYMOSTRUC (van Breugel 1991),

CEMHYD3D (Bentz & Garboczi 1993), Navi's model (Navi & Pignat 1999), DuCOM (Maekawa et al. 1999, Maekawa et al. 2003) and CCBM (Maruyama et al. 2007). Regarding, especially deformation phenomenon, HYMOSTRUC, CEMHYD3D, CCBM, and DuCOM are dealing with, and consequently, these models are overviewed here.

HYMOSTRUC predicts the degree of hydration from the data of water to cement ratio, mineral components of cement, particle size distribution, and curing condition (i.e. humidity and temperature). The particle size distribution is represented by Rosin-Rammler function and the particles are uniformly placed in the space in statistical way. Shape of cement particles is assumed to be spherical, and it keeps the geometry during hydration process. Inter-particle contact with each other occurs when the cement particles grow. The effect of inter-particle contact on the rate of hydration is modeled with the concept of 'cell density'.

The rate of hydration is described as a function of basic rate of hydration and coefficients of diffusion process in hydrates with Arrhenius' law for curing temperature effect. The basic rate of hydration is determined by the amount of C_3S and C_2S . The coefficients of diffusion process in hydrates take into account of density of hydrates, residual water and relative humidity in pore structure.

Using HYMOSTRUC, van Breugel & Lokhorst (2001) explained the creep behavior of early age concrete based on the concept proposed by Ghosh (1973). Assuming inherent creep of cement hydrates and strain conservation among cement hydrates, redistribution of stress between old hydrates and new hydration products was mathematically solved in his study.

Koenders & van Breugel (1997) developed a model for autogenous shrinkage based on the HYMOSTRUC. In this model, a simple pore size distribution curve was used, and this pore size distribution, residual water, and adsorption curve gave

the thermodynamic equilibrium, and relative humidity in cement paste matrix. Thermodynamic equilibrium and a similar approach to Munich model (Wittmann 1982), which is based on the surface tension concept, can produce the deformation of cement paste in early age.

CEMHYD3D is using the method of Cell Automaton, and accumulation of reaction in local cells represents the total reaction of cement paste and gives the discrete (or voxel) 3-dimensional cement paste structure. The accumulation is determined by the local chemical reaction rule which is a function of density of substances in target cell and neighborhood cells. This unique model can take into account many chemical reactions at once. But discrete system in size and time, may produce some other problems, such as evaluation of time with changing curing temperature and reaction of fine particles like silica fume. In spite of these problems, combining with statistical approach, CEMHYD3D has been successfully applied to many engineering problems.

Regarding shrinkage problem, combining CEMHYD3D and geometrical algorithm (Bentz et al. 1995) can take into account the thermodynamic equilibrium and relative humidity in the cement paste matrix. Using these parameters, and considering specific surface free energy and Bangham equation (Bangham & Fakhoury 1931) it can simulate the deformation of porous material (Bentz et al. 1998).

Recently, CCBM was proposed by Maruyama et al. in Japan. This model is based on the fundamental kinetic model for Portland cement developed by Tomosawa (1974 & 1997). The kinetic model is expressed as a single equation composed of four rate determining coefficients which represent the rate of surface solution, formation and destruction of initial impermeable layer (for dormant period), and the following diffusion controlled process. This model also assumes that cement is spherical and it keeps its shape during hydration. Aiming for the universality, CCBM introduced the particle size distribution, reaction of each mineral compositions, coefficients for precipitation rate, and difference of density of cement gel which is affected by the temperature history. Model parameters were determined according to the cement reaction data obtained by X-ray/Rietveld method (Hoshino et al. 2006, Matsushita et al. 2007). Phase composition problem was also modeled according to experimental data (Maruyama et al. 2007). Fig. 1 shows the comparison of degree of hydration between the experimental results and calculated results by CCBM. This model focused on the problem of early age cracking in RC members. Heat capacity and coupling of the heat and moisture transport were modeled precisely and succeeded in predicting the temperature history and distribution (Maruyama et al. 2006). Using capillary tension and disjoining pressure approach

for autogenous shrinkage, self-induced stress in RC members coupled with thermal deformation and autogenous shrinkage was evaluated with FE analysis (Maruyama & Sato 2005).

Another Japanese micro-structural simulation model named DuCOM was also developed by Maekawa, Ishida, Kishi and others in the University of Tokyo (Maekawa et al. 1999, Maekawa et al. 2003). The analytical system can simulate hydration reaction, micro-pore structure formation, moisture transport/equilibrium and their system dynamics based on thermodynamics. DuCOM is comprised of mainly the multi-component hydration heat model, microstructure development model and moisture transport and equilibrium model. Each model is briefly explained below.

In the multi-component hydration heat model of DuCOM, the chemical compounds of Portland cement are aluminate (C_3A), alite (C_3S), belite (C_2S), ferrite (C_4AF), and gypsum. Other blending materials, such as blast furnace slag, fly ash or limestone powder, are incorporated into the model as individual components. The total heat generation rate per unit volume of such a blended cement is represented as the sum of the specific heat generation rate of the individual clinker component. The temperature-dependent heat generation ratio of each clinker component is based on the Arrhenius law. The heat generation rate can be idealized by two material property parameters, i.e. the reference heat rate and activation energy, when temperature is constant at 293K. In the heat generation, the following factors are taken into account as mutual interaction: retardation of the cement-slag reaction at an early stage caused by the presence of fly ash and organic admixtures, free water consumption due to hydration progress, heat generation rate change of slag and fly ash based on the amount of calcium hydroxide in the liquid phase, the interdependence between C_3S and C_2S and relative fineness of each mineral component. Finally, the temperature distribution and the degree of hydration of the concrete can be obtained by applying thermodynamic energy conservation to the space and time domain of interest. The hydration degree of hardened cement paste in this model is assumed to be the ratio of accumulated heat Q of hydrated products to final heat generation Q_∞ . According to the hydration model, the hydration reaction process for an arbitrary cement powder can be simulated rationally.

Next, the microstructure development model is summarized. The model can simulate the microstructure formation process of the hardening cement paste matrix for any mix proportion under arbitrary environmental conditions based on the information from the above multi-component hydration model. In the microstructure model, micro-pores in the concrete are classified into three types: capillary pores, gel pores,

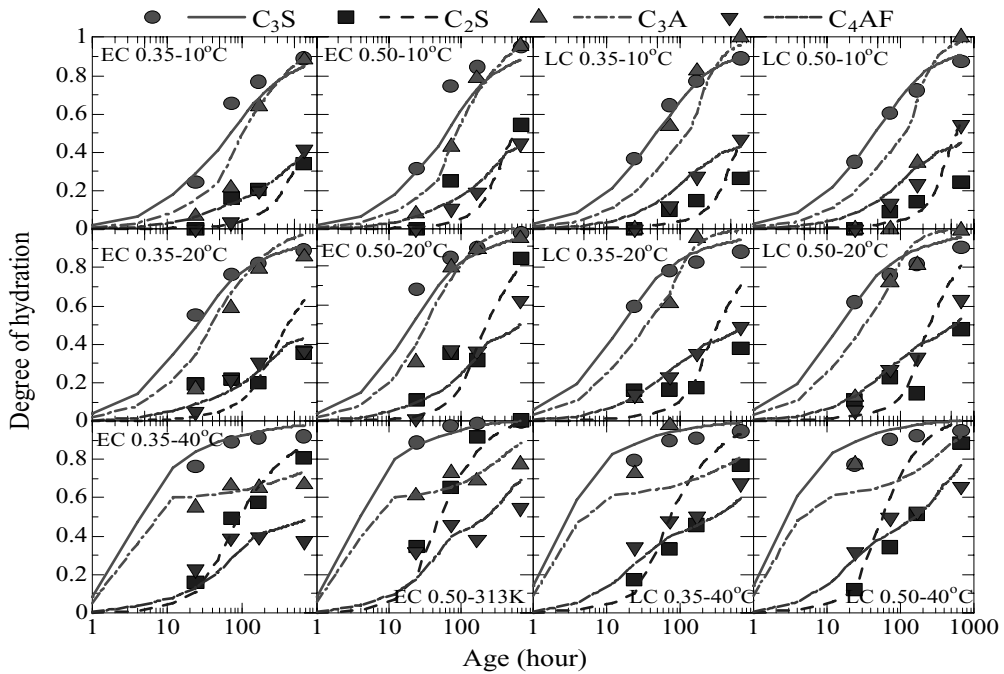


Figure 1. Experimental results of degree of hydration of C_3S , C_2S , C_3A , and C_4AF (dots), and calculated ones by CCBM using fitted parameters (lines).

and interlayer pores. The capillary pores are located in the relatively large interparticle spaces between the powder particles; they act as free space for the precipitation of hydrate products. The gel pores are thermo-dynamically defined as the spaces where new C-S-H gel grains conditionally precipitates only when the temperature rises (Nakarai et al. 2007). The interlayer pores are located between the layer structures of the C-S-H gel grains; the layer thickness is defined as $2.8 \text{ \AA}$ corresponding to water molecular size. From the average degree of hydration and the weight of chemically combined water computed in the hydration model, the volume of gel products and porosity of capillary pores, gel pores and interlayer pores are calculated in the model. The entire micro-pore structure is idealized as the total porosity of the above-mentioned capillary pores, gel pores and interlayer pores. The pore distribution of each pore is represented by a simple Raleigh Ritz function, postulating that the pores are cylindrical in shape.

Moisture in the cementitious microstructure can be presented in both liquid and vapor phases in the moisture transport and equilibrium model. The vapor and liquid phase transports are formulated based on mass conservation laws. The pore moisture is classified as adsorbed water, condensed water in capillary pores

and gel pores, and interlayer water in the interlayer pores in the model.

Firstly, the moisture equilibrium model is explained. Considering the surface equilibrium between the vapor and liquid phases in fine pores, the relationship between the radius r_s of pore where the meniscus is formed and pore humidity can be obtained from Laplace equation and Kelvin's equation, when the interface is a part of an ideal spherical surface. The amount of water in the microstructure at a given ambient relative humidity can be calculated because the porosity distribution of the microstructure is known from the above mentioned microstructure development model. Pores of radius less than r_s would be completely filled, while the other pores would be empty. Thus, the model gives the saturation of pores by integrating the total pores volume from zero to r_s . The pores include physically adsorbed water in their solid walls. In the model, the adsorbed layer is idealized based on the modified BET theory (Hillerborg 1985). The degree of moisture saturation in concrete is then given as the total of saturation in micro-pores consisting of capillary pores, gel pores and interlayer pores, and the volume of adsorbed layer. The adsorption-desorption hysteresis is explained as the inkbottle effect in the model. It is assumed that moisture can be

trapped in inkbottle-shape pores owing to the complex geometrical characteristics of the microstructure. During the wetting stage, as relative humidity increases, liquid water can gradually condense in the smaller pores. On the other hand, during the drying stage, evaporation of moisture occurs from larger pores. During virgin drying, the evaporation of trapped water in larger inkbottle-shaped pores can be inhibited due to connection to smaller pores. The result is an apparent adsorption-desorption hysteresis. In the model, the saturation in monotonic drying is idealized based on the inkbottle effect. Since the stability of the condensed water in inkbottle-shaped pores is strongly dependent on the ambient temperature according to experimental findings, the temperature sensitivity in saturation-humidity paths is implemented (Ishida et al. 2007). The hysteresis of interlayer water is also modeled based on the experiments that revealed the hysteresis has a temperature dependence, too (Ishida et al. 2007).

Next, the moisture transport model is described. Moisture transport in a porous body is driven by the pore pressure gradient and the temperature gradient. Ishida et al. (2007) proposed a formulation of vapor flux that can be applied to arbitrary temperature conditions. The model takes into account of factors reducing the apparent diffusivity of vapor, such as the complexity of the pore network. The vapor flux is driven by the gradient of absolute vapor density ρ_v of the system, instead of by relative humidity.

2.2 Mesoscopic modeling for time-dependent behaviour of concrete

Recently, a project has been in progress, which couples the mesoscopic thermo-physical information obtained from DuCOM with macroscopic structural information such as stress, strain, deformation, cracking and others computed by a 3D FEM structural system named COM3 (Maekawa et al. 2003). One of the targets of this project is the development of a multi-scale constitutive model that can simulate the time-dependent deformation of concrete such as shrinkage and creep based on the hydration reaction, pore structure and moisture state in the pores (Maekawa et al. 2003, Zhu et al. 2004, Asamoto et al. 2006). Outline of the multi-scale constitutive model is described below.

In the model, concrete is idealized as a two-phase composite with aggregate and hardening cement paste. The aggregates are modeled as elastic particles with a stiffness determined by their density, while the hardening of cement paste is expressed by the progressive formation of finite fictitious clusters as the hydration proceeds based on solidification theory (Bazant & Prasannan 1989). The number of clusters is dependent on the degree of hydration as obtained from

DuCOM. The stress in the hardening paste is given as the summation of stresses applied to all clusters. Both volumetric terms and deviation of stress and strain are computed, taking into account of interactions between aggregate particles and the cement paste matrix.

According to the model, the mechanical behavior of a fictitious cluster is associated with the thermodynamic state of moisture in micro-pores such as capillary pores, gel pores and interlayer pores. Recently, moisture migration in gel pores was divided into moisture transport through the internal pores of C-S-H gel grains and water in motion within the inter-particle spaces of hydrate micro-products (Asamoto et al. 2006). The motion of moisture in capillary and gel pores is idealized based on seepage theory, which describes moisture in the pores migrating gradually under sustained stress.

Since the rate of motion depends on pore size, it takes longer for moisture in smaller pores to reach the equilibrium. The moisture in interlayer pores diffuses and causes the volumetric change only at high temperature. Each component is composed of an elastic spring, a dashpot and a slider whose parameters are determined by temperature, moisture saturation, pore size distribution and other factors of the hardening cement paste.

The driving force behind volumetric change in the model is assumed to be related to capillary pressure and solid surface energy. These phenomena are computed, coupling with the thermodynamic state of moisture in the micro-pores. The capillary force is calculated based on the Laplace equation, the Kelvin equation and the degree of saturation of capillary and gel pores subjected to pore pressure. Shrinkage under a relatively high humidity condition is caused mainly by the capillary force in the model. On the other hand, in the case of a relatively low humidity condition, the increase in the solid surface energy of gel particles due to desorption of water is idealized as the main mechanism to drive the shrinkage. By coupling the above volumetric stress depending on moisture states in pores with the C-S-H skeleton stress, the equilibrium between skeleton stress and external loading can be satisfied. Thus, the time-dependent deformation can be computed according to the boundary conditions without conventional classification such as autogenous/drying and basic/drying creep. Currently, the model is able to reasonably simulate the time-dependent deformation of cementitious composites under arbitrary boundary conditions (Zhu et al. 2004, Asamoto et al. 2006). Fig. 2 summarizes DuCOM and multi-scale constitutive model concept.

2.3 Experiments for verifying models

Some of model components, especially related with the phenomena in micro-pores, are dependent on

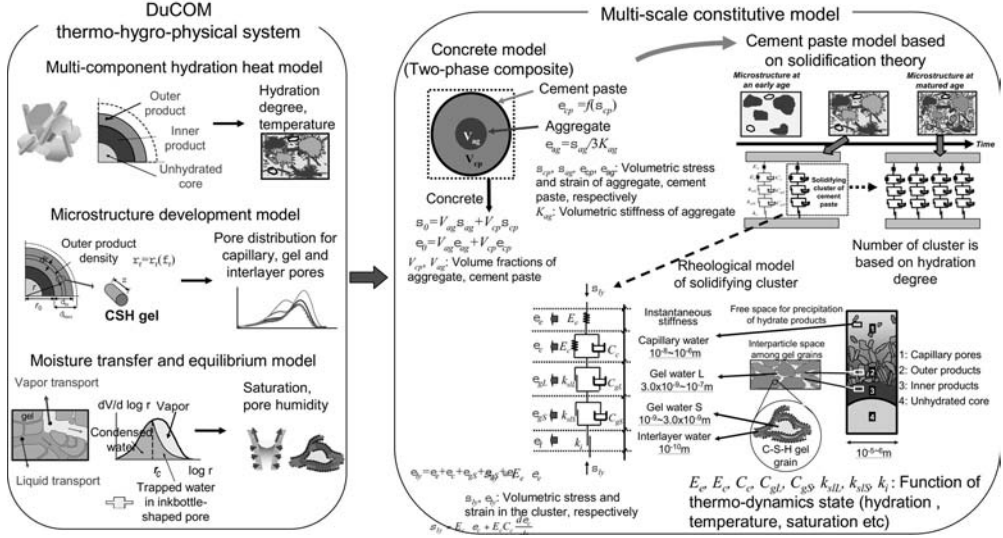


Figure 2. DuCOM and multi-scale constitutive model.

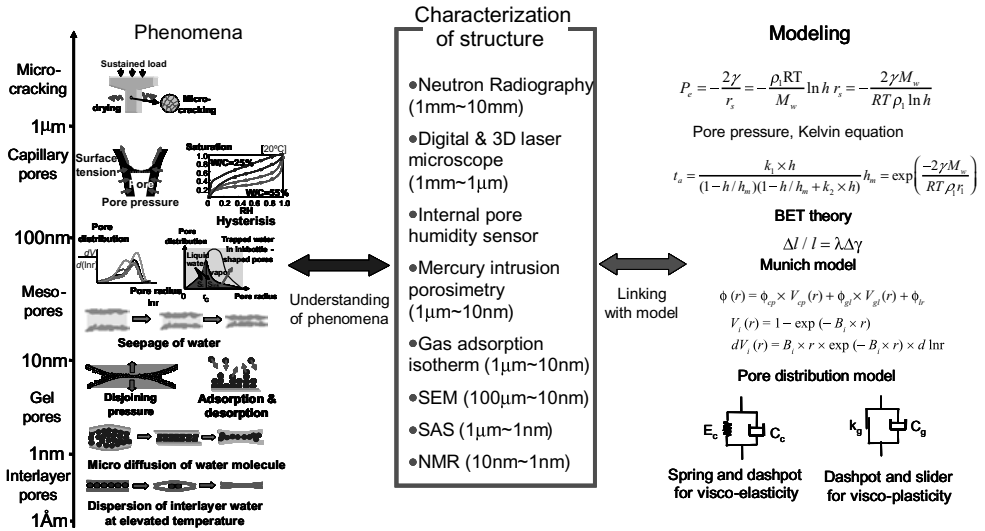


Figure 3. Schematic illustration of the linkage of phenomena, characterization of structures and modeling.

various macroscopic assumptions arising from experiments. Regarding CCBM, model parameters of hydration process are determined according to the experimental data of X-ray/Rietvelt analysis, DSC, and MIP with several assumptions for amorphous phase component. And the accuracy of the model is discussed with experimental data of ig. loss, calorimeter, and X-ray/internal standard method. In the case of

DuCOM, the modeling of the temperature-dependent hydration process and microstructure formation of gel pores is based on indirect information obtained from the adiabatic temperature test and the thermo-gravimetric analysis. The hysteresis and the temperature sensitivity of moisture such as trapped water in inkbottle-shaped pores and interlayer water are simply idealized according to macroscopic experimental

findings. The ultimate recoverable and irrecoverable time-dependent deformation in the model is also based on the various experimental data of shrinkage and creep. The hydration, microstructure, moisture states, and time-dependent deformation in fine pores have been extensively studied over several decades, but it has been difficult to directly observe the phenomena and verify the theories, particularly at nanometer scale. Thus, the modeling must be postulated from macroscopic information and remain empirical. According to the model, the computational prediction can give a good agreement with the phenomena that have been experienced, while the unusual extending conditions and phenomena in the far future are hardly predicted at convincing level. In order to predict the long-term durability of RC structures and to utilize a variety of cementitious materials for various structures, the intrinsic micro information from experimental analysis is necessary.

Recent remarkable development of the experimental technique is expected to reveal the above unclear microphysical phenomena. It may enable us to investigate the microstructure and moisture behavior at micrometer and nanometer scale. Directly observing the time-dependent behavior of cement hydrates in fine pores, each phenomenon can be clarified and the various theories assuming from macroscopic information can be verified. Since the molecule behavior is dominant at nanometer scale and should be modeled not only by classical thermodynamics but also by molecular dynamics, statistical theories and others, the experimental studies are useful for idealizing the phenomena at nanometer level. Identifying the dominant phenomenon and physics in each scale for the time-dependent behavior at macro-scale, the modeling of the time-dependency of cement hydrate at the multi-scale is possible and enables to predict the deterioration process of RC structures under arbitrary boundary conditions. Thus, as shown in Fig. 3, the linkage between the phenomenon, experimental analysis and modeling based on theories at each scale is quite important. In the next chapter, the state-of-the-art of experimental techniques to verify the theory at each scale will be described.

3 EXPERIMENTAL TECHNOLOGY AND METHODOLOGY TO MEASURE MICROSCOPIC INFORMATION OF CEMENTITIOUS MATERIAL

3.1 *Propagation and distribution of micro-crack and moisture transport in micro-crack (1 mm~1 μ m level)*

3.1.1 *Time-dependent behavior in micro-crack*

The behavior of microcracks in cementitious materials has been extensively studied because the micro-

cracks can affect the diffusivities of chloride ion, CO₂ and other harmful agents in concrete and they lead to the reduction of the durability. Gran (1995) reported an impregnation technique based on fluorescent ethanol that can be slowly replaced with the pore water. This technique is called as Fluorescent Liquid Replacement (FLR) technique and does not need traditional preparation procedures such as drying and evacuation that may induce microcracks. The FLR technique gives impregnation depths that are several orders of magnitude larger than the measurable impregnation obtained with traditional procedure using epoxy. According to him, the FLR technique can be used to observe the crack development due to loading, freezing/thawing, corrosion etc., even in the case of low W/C concrete with dense porosity (Gran 1995). Ammouche et al. (2000 & 2001) proposed an image analysis technique for the quantitative assessment of microcracks in cement-based materials. The highlighted microcracks and other microdefects of the polished samples were observed by using an optical microscope. The various micro information such as porosity, air bubble and microcracks was extracted from the observed image conducting a pretreatment of the color image and an automatic thresholding on the gray level histogram. The characteristics of the crack network were quantified using classical stereological methods. The technique enabled to determine the specific crack length, the degree of orientation and other crack pattern characteristics and seemed to lead to the basis of the micromechanical discussion.

Recently, the development of laser microscopes and digital microscopes has been progressive. The advantage of these technologies is to observe the phenomenon in micro-pores with high resolution and color under arbitrary conditions such as wetting conditions, while SEM, X-ray diffraction and others need some preprocessing of samples, for example, vacuum drying and evaporation coating. In the case of laser microscopes, 3D laser scanning technology has been advanced and enables us to examine the surface roughness of specimens at high resolution of nm level (http://www.keyence.co.jp/microscope/laser/vk_9700/index.jsp). The observable 2D range of 3D laser microscopes and latest digital microscopes is about from 1 μ m to 1 mm. Although these technologies are not applicable for studying phenomena at nanometer scale, it is expected that the propagation of micro-crack under sustained stress and the meniscus formation in micro-meter pores are observable because they are able to continuously measure such behavior. An example of observation on the surface of hardened cement paste by using the above mentioned 3D laser microscopes is shown in Fig. 4.

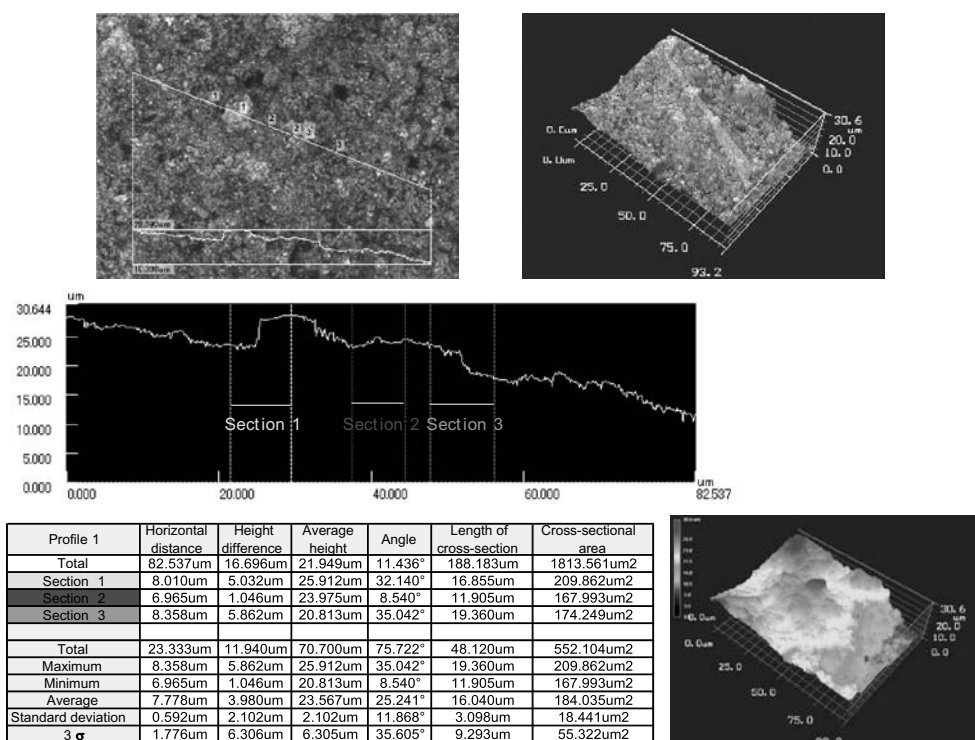


Figure 4. Observation of cement paste surface by 3D laser microscopes.

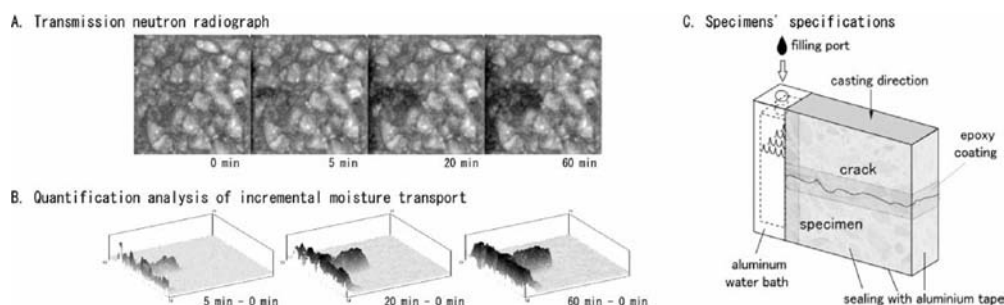


Figure 5. W/C = 50%, crack width 0.05 mm, relative water content 30% (Kanematsu et al. 2007).

3.1.2 Moisture transport around crack and between aggregate and cement paste matrix

Recently, Neutron Radiography (NR) technique was adopted for the observation of moisture transport behavior around crack. Kanematsu et al. (2007) observed moisture behavior in different crack width ranging from 0.05 to 0.3 mm in the specimen whose size was $100 \times 100 \times 20$ mm. Relative water content in the concrete was also the one of parameters. According to the experiment, it was confirmed that the speed

of penetration of moisture in the crack is affected by the relative water content in the concrete. The typical figure of NR is shown in Fig. 5.

For mitigation of autogenous shrinkage, recently saturated porous aggregate was applied to the concrete of low water to binder ratio. For the performance-based design of these kinds of material and evaluation of concrete performance, effect of water in porous aggregate on the reduction of shrinkage of concrete should be evaluated. Regarding this aspect,

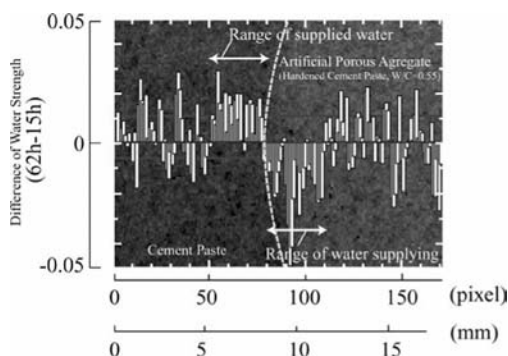


Figure 6. Moisture transfer between different porous media during hydration process.

Lura (2003) used ink for the observation of the effective distance from the aggregate surface, and this experiment revealed that the range within 1mm from the cement paste matrix to the aggregate surface was colored, and, at least, 1mm distance from the aggregate was supplied water from the aggregate. Bentz et al. (2006) used the X-ray tomography technique for getting the information of water distribution around saturated light weight aggregate. From this experiment, water was supplied to the position of 2 mm away from the aggregate surface. Maruyama et al. (2007) also carried out a similar experiment using NR, which is shown in Fig. 6. In this experiment, porous aggregate was limited by hardened cement paste with $W/C = 0.55$, and W/C of cement paste matrix was 0.30. Subtraction of water strength obtained by NR test, that the range of supplied water in hardening cement paste was 4 mm from the surface of imitated aggregate was detected. Fig. 6 shows the distribution of water strength of NR around cement paste matrix—aggregate interface.

3.2 Microstructure and moisture state in micro-pores ($1 \mu\text{m} \sim 10 \text{ nm}$ level)

3.2.1 Pore distribution and volume

The mercury intrusion porosimetry has been widely used to study the microstructure of hardened cement paste. It measures the volume of mercury which infiltrates into sample pores according to injection pressure. By converting the injection pressure of the test results into the cylindrical pore radius, and assuming the mercury intrusion volume as volume of the pores which corresponds to the cylindrical shaped pores, the relationship between the pore radius and volume can be obtained. This relationship is said to be the cumulative pore capacity curve and is the most basic

relationship which describes the distribution characteristics of pores in the microstructure. The specific surface area of sample pores is also evaluated from the mercury intrusion porosimetry results. Based on the modeling which assumes the geometry as the cylindrical shape, specific surface area is evaluated as a total sum of pore surface of cylindrical shape.

A gas adsorption test is also an accepted methodology to examine the pore structure. It measures the specified volume of gas adsorption to adsorbent which it balances in relative humidity under an isothermal environment, that is, the test measures the adsorption isotherm. In the gas adsorption test, as well as the mercury intrusion porosimetry, the volume of gas adsorption corresponds to sample pore volume. There are various gases that can be used in the gas adsorption tests. From a viewpoint of microstructure evaluation, nitrogen is often used because it is an inert gas. Kelvin equation is generally used to analyze the pore size distribution from the adsorption isotherm. Applying the Kelvin equation to the results of the adsorption isotherm relationship, the accumulated pore capacity curve similar to the mercury intrusion porosimetry is gained. The adsorption volume is obtained with the volumetric method, while the mercury intrusion volume in the mercury intrusion porosimetry directly corresponds to the volume of pores.

The BET theory is used for evaluating the specific surface area based on the adsorption isotherm. The theory is expanded from the Langmuir theory and multilayer adsorption state is considered, assuming the adsorption site on the adsorbent. The adsorption isotherm expressed with the BET theory nearly corresponds to the II type adsorption isotherm. The range of relative humidity in which the BET theory is accepted is about from $h = 0.05$ to 0.35 in the case of hardened cement paste. The monolayer adsorption volume and interaction constant are determined from the results of the BET plot within this range. In Fig. 7, the solid line in the graph is the fitting results of the relative humidity range of $h = 0.05$ to 0.35 in a straight line. The monolayer adsorption volume, specific surface area and interaction constant are calculated based on the fitting results and are marked in each graph.

Davis (1984) showed the correlation of the BET specific surface area using nitrogen adsorption isotherm and the mercury intrusion porosimetry by targeting a variety of samples. Davis pointed out that the mercury intrusion porosimetry gives a larger specific surface area than the BET methods does. However, the results in both methods are not so different and they can be directly compared for practical purposes. Fig. 8 shows the comparison of the specific surface of hardened cement paste measured with these two different methods. In these results, the mercury intrusion methods tend to give larger specific surface area than the BET method does.

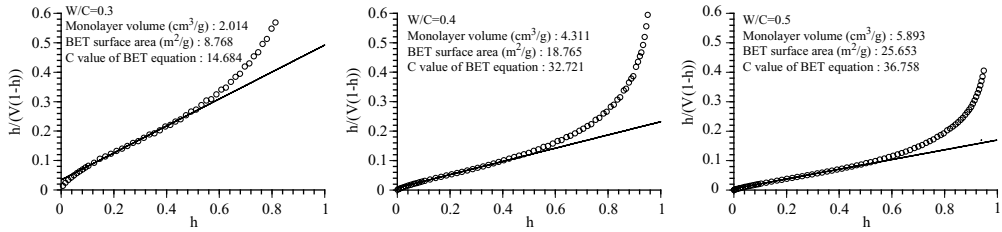


Figure 7. BET plot of hardened cement paste; N₂ adsorption (Chiba Institute of Technology, Utsumi Lab).

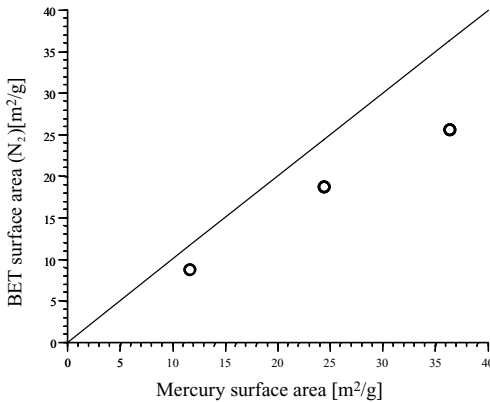


Figure 8. Comparison of surface area of hardened cement pastes with W/C = 0.3, 0.4 and 0.5 obtained from N₂ adsorption isotherms and mercury intrusion porosimetry (Chiba Institute of Technology, Utsumi Lab).

Samples to be used in the mercury intrusion porosimetry and gas adsorption tests need to be dried before the tests. Gallé (2001) studied porosity obtained in the mercury intrusion porosimetry results at the maximum injection pressure of 413 MPa by targeting the dried sample using each drying method. It was found that samples executed in an oven-drying at 105°C have the highest porosity in the mercury intrusion porosimetry. Juenger et al. (2001) deliberated the differences of the BET specific surface area and the pore volume based on the drying conditions targeting the nitrogen adsorption test. According to their experimental results, the oven drying at 105°C has the lowest BET specific surface area compared to that of D-dry and a combination of methanol elution and D-dry in the nitrogen adsorption. The measured porosity is dependent on not only test method but also pre-drying conditions.

Odler (2003) deliberated on the difference of the BET specific surface area depending on each type of adsorbate. Fig. 9 shows the summarized results of the BET specific surface of H₂O adsorption and

N₂ adsorption described in references (Odler 2003, Mikhail & Abo-El-Enel 1972, Mikhail & Selim 1966). From these results, it is found that water vapor adsorption evaluates the higher specific surface area than that of the nitrogen adsorption. Feldman and Sereda (1968) explained the difference in the specific surface area between water vapor adsorption and nitrogen adsorption in terms of the filling of interlayer pores only by water. Daimon et al. (1977) pointed out that the only water could absorb into intercrystallite pore of C-S-H gel and interlayer pores, while nitrogen cannot enter such small pores. Recently, Jennings and his co-workers (Thomas et al. 1999, Jennings 2000, Tennis & Jennings 2000) suggested that the calcium silicate hydrate (C-S-H) in cement paste is classified into two types: a high density C-S-H (HD C-S-H) and a low density C-S-H (LD C-S-H). HD C-S-H is made of densely packed particles into which nitrogen cannot penetrate. Particles of LD C-S-H are not packed as tightly as those of HD C-S-H, and nitrogen can penetrate partially into this structure. On the other hand, water can infiltrate into both types of C-S-H and as a result the difference in the specific surface area by vapor adsorption from nitrogen adsorption arises. There is, however, no unified explanation about the variation of surface area due to adsorbents.

Due to the characteristic and theory of each test method, the range of pore size of the analysis target is specified. In the case of mercury intrusion porosimetry, the pore radius in which mercury can be infiltrated shall be specified depending on the injection pressure. Currently, equipment which can pressurize up to 400 MPa is widely used, and the minimum pore radius which the mercury can infiltrate during pressurization is about $r = 1.8 \times 10^{-9}$ [m] according to Washburn equation. That is, based on the maximum injection pressure of the equipment to be used, the minimum limit value of the theoretically evaluable pore radius in mercury intrusion porosimetry is specified.

On the other hand, the evaluable minimum pore diameter in the gas adsorption test is the minimum value of pore diameter whose molecule diameter to be used can be detected from the gas adsorption tests. Generally, since adsorption potential of micro pores

with less than 2.0×10^{-9} [m] is extremely large, it is thought that Kelvin equation is not approved in such fine pores. Dubinin equation (Dubinin 1960) is also used for evaluating micro pore size. In gas adsorption test, the maximum value of pore diameter is theoretically infinitely large. At the area close to saturated vapor pressure, however, the experimental error is perceptively sensitive to temperature control and pressure control, and practically, pore radius range which can

be evaluated with Kelvin equation is assumed to be about from 1 to 100 nm (see Fig. 10).

3.2.2 Internal humidity

Grasley et al. (2007 & 2006) developed a new internal relative humidity measurement system and proposed a model to predict drying stress gradient in concrete. The system involved embedding of a small, and digital, RH and temperature sensor in a small plastic tube with Gore-Tex caps into fresh concrete. The sensors were a capacitive type RH sensor and used a thermistor to measure temperature. In the system, the internal humidity could be measured at the accuracy of $\pm 1.8\%$ (when RH is less than 80%) and the temperature sensor had an accuracy of $\pm 0.3^\circ\text{C}$ (at 20°C). Using the system, the potential free shrinkage strain based on Kelvin-Laplace equation was calculated and the drying stress induced by internal and external restraint at any point across the cross-section was determined. The model revealed that the tensile stress in the surface layer routinely exceeded the tensile strength of concrete in drying concrete, even in the case of free shrinkage.

Ceramic humidity sensor is also used to measure internal pore humidity in concrete. When water vapor within a porous ceramic material diffuses and is adsorbed on its crystal surface, moisture dissociates into hydroxyl and proton on the surface, reducing the electric resistance of the ceramic. The humidity-sensing mechanism of a humidity sensor utilizes this phenomenon, ionic conduction by water adsorption. Among the wide variety of ceramic humidity sensors

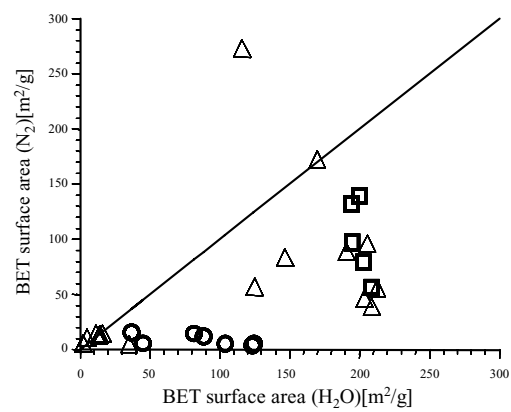


Figure 9. Comparison of BET surface area obtained from H₂O adsorption and N₂ adsorption isotherms Δ : Odler 2003, $\circ$: Mikhail & Abo-El- Enel 1972, $\square$: Mikhail & Selim 1966).

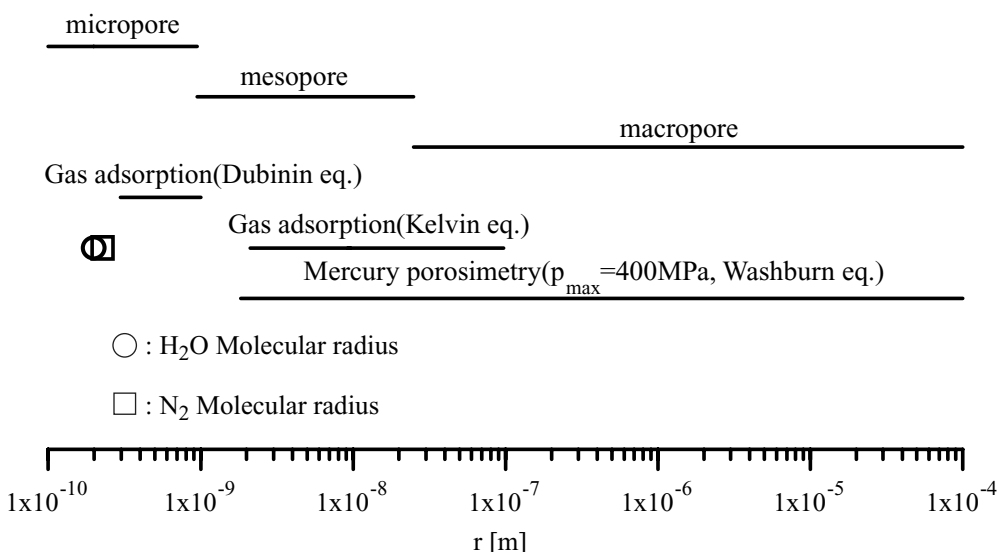


Figure 10. Measurement range of mercury porosimetry and gas adsorption.

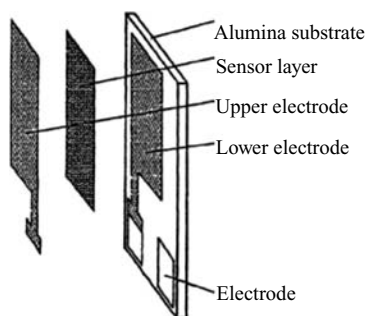


Figure 11. Configuration of sensor element.

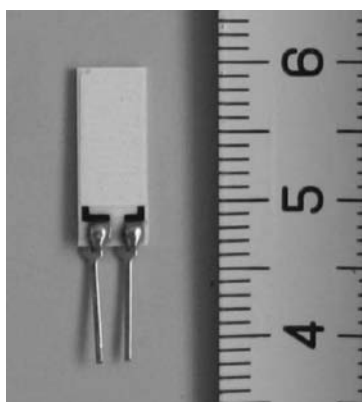


Figure 12. Sensor element.

available with various materials, sensors made with NASICON ceramic materials have the potential to be used as humidity sensors for concrete, as they show a high ionic conductivity while having relatively high durability and long-term stability (Yagi & Saiki 1991, Ozawa et al. 2007). Fig. 11 shows the configuration of a sensor element, which consists of an alumina substrate on which a ceramic moisture-sensitive film is deposited between two electrodes. With its body being small and thin ($5 \times 13 \times 0.8$ mm) as shown in Fig. 12, this type of sensor embedded in concrete allows measurement of humidity in concrete without significantly disturbing the humidity profile of concrete.

The measurement range and accuracy of this sensor are 20 to 90% RH and ± 3 to 5%, respectively, within the effective temperature range of 0 to 50°C. When embedding this sensor in concrete, it is necessary to calibrate its sensing characteristics beforehand by conducting controlled humidity testing, as various ions contained in the moisture in concrete can affect the ion conduction. Fig. 13 and Fig. 14 show typical

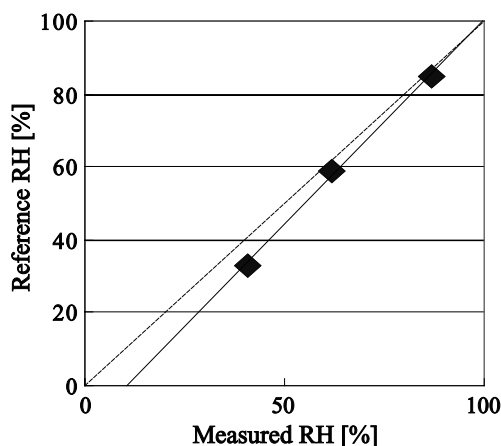


Figure 13. Characteristics of sensor in air.

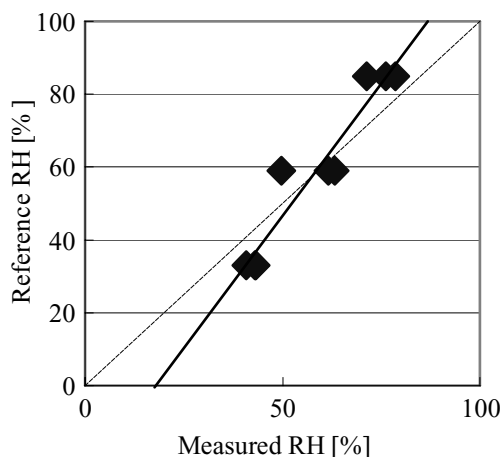


Figure 14. Characteristics of sensor in concrete.

sensing characteristics of this sensor in air and in concrete, respectively, obtained from controlled humidity testing for 400 days. Fig. 13 reveals that the measurement error tends to increase as the humidity decreases in air. In concrete, however, the measurement error tends to increase both in the high and low humidity ranges as shown in Fig. 14. When using this sensor, the measured data should be corrected accordingly based on the recognized sensing characteristics.

Fig. 15 shows typical humidity measurements at depths of 5, 10, and 50 mm from the surface of a concrete specimen with a cross-sectional size of 10 by 10 mm.

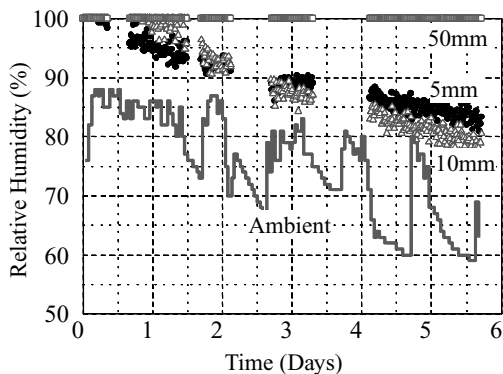


Figure 15. Typical humidity measurements.

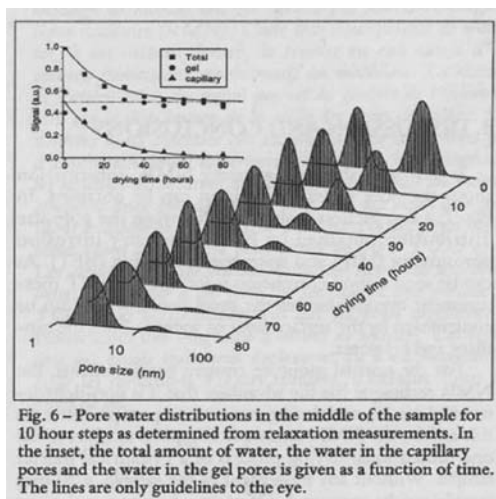


Figure 16. Pore water distribution during drying (Valckenborg et al. 2001).

3.3 Measurable information in nano-pores

The microphysical information in nano-pores is considerable to evaluate the durability of concrete structures because it is known that the moisture in fine pores greatly affects long-term creep, shrinkage under low humidity and others. It has been, however, very difficult to measure or observe the structure and the moisture behavior in nano-pores because the pre-process, for example, vacuum drying and evaporation coating for experimental technologies such as SEM, X-ray diffraction and others can cause the destruction of the nano-pores structure and dispersion of moisture in nano-pores. Recently, the study focusing on the microstructure and the moisture behavior in pores of nanometer scale has been progressive using latest experimental technologies.

Nuclear Magnetic Resonance (NMR) is one of interesting technologies to be able to investigate the time-dependent behavior in fine unsaturated and saturated pores. Valckenborg et al. (2001) examined the drying process and the pore water distribution of saturated mortar by means of NMR. It was found that the moisture cannot be extracted from gel pores (< 10 nm) until the water in capillary pores (10–1000 nm) is drained as shown in Fig. 16. Hazrati et al. (2002) measured water content profiles using proton nuclear magnetic resonance imaging (NMRI) technique during the capillary absorption of water in unsaturated mortar samples. The water diffusivity coefficient obtained in the experiment is strongly dependent on the water content and can be approximated by the sum of two exponential functions. Heijden et al. (2007) built a dedicated NMR setup in order to study the moisture transport in heated concrete. One-dimensional moisture profiles in fire-clay brick, calcium-silicate brick and concrete during heating were measured and compared with their model. Aono et al. (2007) investigated the change of microstructure of hardened cement paste due to drying and drying-wetting cycle using MIP, Archimedian method and Si^{29} -NMR. It was found that the pore distribution is coarser due to drying because the condensation polymerization of silicate anion is progressive during drying. Small-angle scattering techniques (SAS) using neutrons (SANS) or X-rays (SAXS) are also powerful method to study the microstructure of hardening cement paste. The angular profile of the small-angle scattered intensity from the sample is effectively a Fourier transform of the microstructure and can in principle be analyzed to determine the size distribution, volume fraction, and shape of the scattering features (Jennings et al. 2008). The advantage of the technique is also to examine the microstructure in saturated state. Thomas et al. (1998) reported the variation on the surface area of OPC with aging by SANS (Allen & Thomas 2007). They found that the surface area increases slightly with long-term curing and is greater in the case of higher water-to-cement ratio. In addition, it was suggested that the dense and inner product of C-S-H cannot be observed by SANS or SAXS and they interpreted the experimental findings as evidence for two-different morphologies of C-S-H. Allen et al. (2007) investigated the mean formula and mass density of the nanoscale C-S-H gel particles in hydrating cement by combining SANS and SAXS data and by exploiting the hydrogen/deuterium neutron isotope effect both in water and methanol. They have established a C-S-H formula $(\text{CaO})_{1.70}(\text{SiO}_2)(\text{H}_2\text{O})_{1.80}$ with a mass of density 2.604 Mg m^{-3} and a water mass fraction of 0.174.

Studies by NMR and SAS techniques on microstructure and moisture behavior in micro-pores

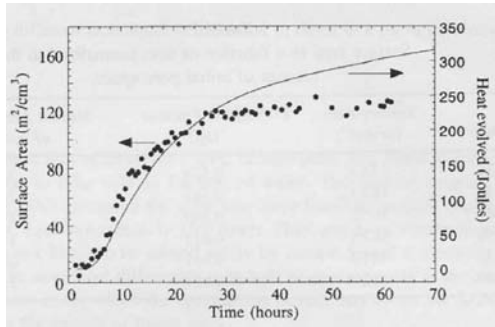


Figure 17. surface area (solid circles) and heat evolved (line) for OPC/H₂O at 30°C and W/C = 0.4 (Thomas et al. 1998).

have been in progress recently. The nanoscale information may lead to further modeling of time-dependent behavior of cementitious materials under arbitrary conditions.

3.4 Summary of current technologies and future prospects

As described above, recent development of experimental techniques to study microphysical information has been remarkable and progressive. It is expected that the development enables us to reveal the classical assumption about time-dependent behavior of cementitious materials and to enhance the numerical models. Some of techniques, however, show different results even in the same measuring target. Since these differences appear to be caused by the characteristic and limitation of each test method, it is indispensable to understand the technique correctly and to analyze the varying test results comprehensively.

In order to verify various theories about micromechanics of cementitious materials, study on the microstructure related with moisture behavior in micro-pores is essential because hydration process, microstructure formation, transportation of ion, shrinkage and creep are strongly affected by moisture state in pores. Currently, NMR or SAS seems to be one of the effective techniques to examine such time-dependent behavior under various conditions. For further investigation for microphysical information, the application of various experimental techniques should be taken into account. Thus, the collaborative studies with researchers in other scientific fields such as chemical engineering, biotechnical engineering, nano-technology and others are necessary.

4 MATHEMATICAL MODELING FOR TIME-DEPENDENT BEHAVIOR OF CONCRETE COMPOSITES BASED ON MESO-MACROSCOPIC APPROACH

4.1 Effect of aggregates and interaction with cement paste phase ($1\mu\text{m}\sim 1\text{--}10\text{mm}$ level)

Aggregates are used to reduce the shrinkage of concrete by restraining the shrinkage of the matrix paste. The roles of the type and amount of aggregate to reduce shrinkage were addressed by Pickett (1956), Roper (1959), and Hansen & Nielsen (1965) as shown in Fig. 18. They also indicated that some types of aggregates often exhibit a large degree of shrinkage. Consequently, the selection of the type of aggregate can have a significant effect on the long-term behavior of a concrete structure. The water absorption of aggregates is directly related to the shrinkage strain of concrete in the same types of rocks. However, this correlation decreases when different types of rocks are used (Snowdon & Edwards 1962). It is well known that artificial lightweight aggregate does not exhibit so much large shrinkage strain in spite of its large water absorption ratio. Fujiwara (1984) found that internal specific surface areas (SSAs) of coarse aggregates measured by the BET method using nitrogen were in close agreement with the shrinkage strains, as shown in Fig. 19. Larger SSA will be associated with a greater surface energy or disjoining pressure (Powers 1965), resulting in a higher shrinkage (or expansion) strain. On the other hands, a previous research showed that the measured SSAs vary with the adsorbates used (Brunauer et al. 1938). Hence, BET surface area of the shrinking aggregate using water vapor will be reasonable information. Fig. 20 shows that the SSAs using water vapor have a good agreement with concrete shrinkage strains with various kinds of

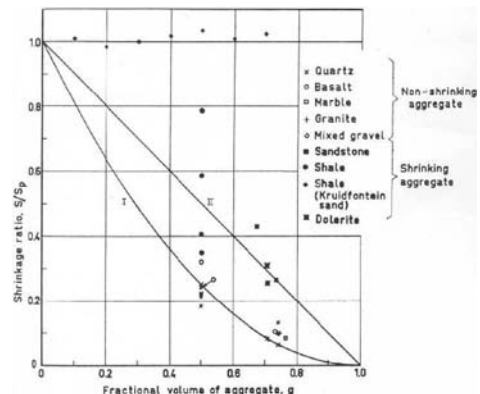


Figure 18. Volume of aggregates versus shrinkage strain ratios (Hansen & Nielsen 1965).

aggregates (Imamoto & Arai 2007). Furthermore, the evaluation of the shrinkage behavior from the viewpoint of the SSA will provide a perspective for new mixture design methodologies for concrete.

Recently, it was reported that a prestressed reinforced concrete (PRC) bridge in Japan had suffered severe cracking of RC member surfaces even though only three years had passed after the construction. A number of cracks were found on the surface of the RC members and vertical cracks were observed in the web even though it was horizontally prestressed. According to the emergency committee set up by JSCE, one of the reasons for this serious damage

might have been excessive shrinkage of the concrete (JSCE Concrete Committee 2005). Since such serious concrete shrinkage was thought to be associated with aggregate properties, the committee studied the influence of aggregate properties on concrete shrinkage. Shrinkage experiments of three types of concretes with different types of aggregates were conducted. The aggregates for mix A were from the same source as used for the bridge concrete, while the aggregates for mix B were standard ones extracted from a different site. The sand in mix C was standard but the gravel was the same as that in mix A. The test results are shown in Fig. 21. The concrete with the same type of aggregates as that of the PRC bridge exhibits extremely large shrinkage, about twice larger than that of concrete containing standard aggregates. Although little attention has been paid to the characteristics of aggregates themselves in the design process considering concrete mix proportion, structure size and boundary conditions, the above mentioned findings suggested that the effect of each property on mechanical behavior of concrete should be studied and taken into account in the design.

Asamoto et al. (2008) investigated quantitatively the influence of various aggregate properties on concrete shrinkage behavior using the multi-scale constitutive model described in Section 2.2. One of the aggregate properties could be possibly responsible for the large shrinkage of the bridge concrete. For example, the targeted aggregate had relatively softer elastic modulus in comparison with normal aggregate, (JSCE concrete committee 2005). According to the numerical simulation, however, such large shrinkage due to the soft stiffness of aggregate takes place only in the case of extremely low Young's modulus (1.0 GPa) as shown in Fig. 22. Since aggregate shrinkage appeared to be

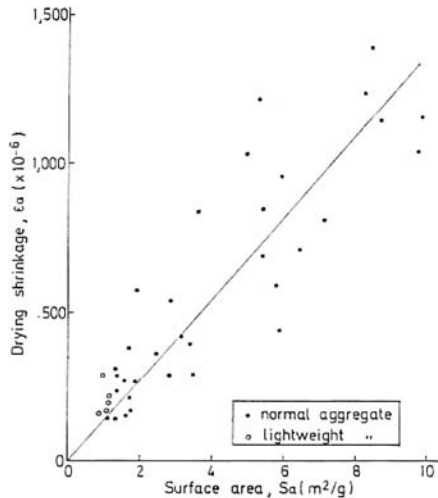


Figure 19. BET(N₂) versus aggregate shrinkage strain (Fujiwara 1984).

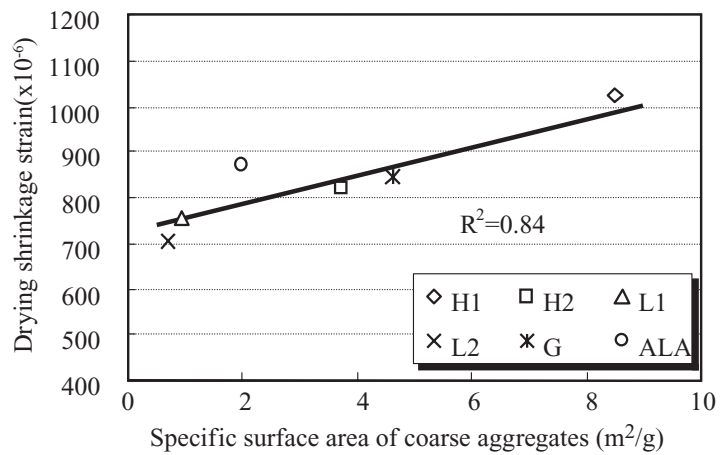


Figure 20. BET(H₂O) versus concrete shrinkage strain (constant aggregate volume) (Imamoto & Arai 2007).