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Survey of Recent Cementitious Materials Research in Western Europe

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ABSTRACT

This report summarizes recent research on cementitious materials in western Europe, based on a perspective gained during a six-month stay at the Centre Scientifique et Technique du Batiment in Grenoble, France. During this period, the author visited sixteen laboratories in seven European countries. Numerous publications, all included in the reference list of this report, were obtained during these visits. Research is grouped into topical areas with a brief description of separate activities at each institution. Emphasis has been placed on those research topics of interest to the Building Materials Division of the National Institute of Standards and Technology. A list of researchers working on cementitious materials in western Europe is also provided for those readers wishing to obtain further information on specific topics.

Keywords: building technology, cement, fracture mechanics, high-performance concrete, hydration, microstructure, shrinkage, transport properties.

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1. INTRODUCTION

During a six-month guest researcher assignment at the Centre Scientifique et Technique du Batiment (CSTB) in France between October 1993 and April 1994, the author visited sixteen laboratories conducting research on cement-based materials and collected recent publications on this topic. This information should be useful in the NIST program on high-performance construction materials, specifically high-performance concrete (HPC). Thus, this report is intended to provide a concise summary of the information collected during this stay and to indicate the relevance of past and present NIST research in this overall framework. Since an exhaustive search would be impractical, this document is only intended to summarize those areas of research that the author encountered during this six month period. Key research topics and results, from the viewpoint of the author, are highlighted in bold type to emphasize their importance. A key to abbreviations used throughout this report can be found in section 5.

2. RESEARCH BY TOPICS

2.1 Analytical Measurements

Microscopy

At EPFL, A. Tolou (1) is heading a group of researchers who are constructing a database of images of concrete from the micro to the macro-level. Optical microscopy of successive cuts through a specimen and subsequent three-dimensional reconstruction have been utilized to produce three-dimensional representations of the aggregate particles in concrete; the technique is currently limited to about 20 particles. The X-ray micro-tomography technique, being employed in a NIST/ Schlumberger/Exxon (2) joint effort, is potentially a much more direct method for obtaining this three-dimensional information for real concrete specimens at a resolution comparable to the time-consuming microscopy technique. In addition, the group at EPFL is using confocal microscopy to study fracture surfaces, cracking, and pore structure in concretes.

Thermogravimetric Analysis (TGA)

Atlassi at the Chalmers University of Technology (3,4) has developed a "standard" thermogravimetric technique for studying cement hydration with and without the addition of silica fume. Using a special TGA, she is able to analyze 19 samples at one time using a program consisting of five temperature steps. Evaporable water is determined by raising the temperature from room temperature to 105 °C and waiting until a constant weight is obtained. Hydration water from the C-S-H gel and calcium aluminate hydrates is determined by the second temperature step to 380 °C. A further increase to 450 °C indicates mainly the calcium hydroxide present in the specimen. An increase to 600 °C is used to determine carbonation products other than calcite while the final increase to 975 °C is used to analyze for calcite (mainly in the range of 600-750 °C) and some secondary hydration products. The developed technique has been utilized to study the effects of silica fume on the evolution of calcium hydroxide and evaporable water in cement paste.

2.2 Curing and Hydration

Two research groups in Sweden are studying the effects of curing conditions on hydration by measuring the effects of relative humidity on the degree of hydration achieved in cementitious materials. Molina at the Swedish Cement and Concrete Research Institute (5) has conditioned specimens to various internal RH's and measured subsequent hydration rates as characterized by non-evaporable water content and X-ray diffraction analysis. For w/c ratios between 0.35 and 0.70, she observed the hydration to nearly cease at an internal RH of about 80%, in general agreement with the value determined by Powers many years ago (6).

The topic of hydration vs. relative humidity is also a major area of the Ph.D. thesis research of Kristina Norling-Mjörnell at the Chalmers University of Technology (7). Her goal is to develop a "self-drying" concrete for use in floors to be covered by carpets, etc. As part of her study, she too has assessed the hydration rate of cement paste as a function of internal relative humidity. She measures the internal relative humidity by placing a crushed sample of the hydrated cement paste in the bottom of a sealed test tube, inserting a relative humidity probe, and measuring the RH achieved at equilibrium. While it is difficult to eliminate carbonation effects, her results are also in agreement with those of Powers, which show a substantial drop in hydration rate at 80% RH and no hydration below about 60% RH.

2.3 Drying and Shrinkage

Plastic Shrinkage

At the Chalmers University of Technology, Dr. Radocea (8,9) has done his Ph.D. thesis on the mechanism of plastic shrinkage of cement-based materials. His general viewpoint is that plastic shrinkage is due to the capillary forces produced as larger surface pores empty during drying of fresh concrete. As concrete dries when exposed to air and wind, water evaporates from its surface. If this water cannot be sufficiently replaced by "bleed" water from the inside of the concrete, the largest capillary pores in the concrete will empty, creating an internal capillary pressure which will in turn cause plastic shrinkage of the concrete. The developed model has been validated by illustrating that plastic shrinkage does indeed depend on the rate of surface evaporation (ambient temperature, RH, and wind speed), sample thickness, the geometry of surface pores, and the elastic modulus of the concrete in its plastic state. Experimentally, the capillary pressure is measured by inserting a water-filled syringe into the specimen and monitoring the change in signal of a pressure transducer attached to the top of the syringe.

Self-Desiccation and Shrinkage

Self-desiccation shrinkage measurements are being made at the Laboratory for Building Materials in Denmark (10). Cylindrical samples are cast and constantly rotated slowly during one day of curing to avoid settling. The specimens are then sealed and placed in a constant temperature oil bath, and the ensuing shrinkage is continuously monitored. **These researchers feel that in HPC, the shrinkage strains due to water "removal" during self-desiccation may be sufficient to cause extensive micro-cracking.** The major difference between drying shrinkage and self-desiccation shrinkage is that the latter occurs much earlier in the life of the concrete, before its elastic properties have had a chance to develop fully.

Shrinkage under Field Conditions

At the field level, Granger et al. (11) have related measured shrinkage to environmental conditions, specifically the ambient relative humidity. By assuming a linear relationship between shrinkage and weight (water) loss, they were able to adequately predict observed shrinkage based on the ambient relative humidity, a measured sorption isotherm for concrete, and a non-linear diffusion model. Measurements made over the course of several years indicate that the shrinkage varies by about $200*10^{-6}$ as the relative humidity changed between 100 and 60% in a cyclical manner. This research emphasizes the effects of environmental conditions on materials performance, a subject which has been an integral part of NIST research for several years (12).

At LCPC, Acker has reviewed shrinkage and cracking of field concrete and concluded that there are three primary mechanisms which need to be considered: self-desiccation, thermal effects, and drying (13). Calculations indicate that the shrinkage potential of concrete is on the order of $1750 * 10^{-6}$, a value larger than that usually measured (see value in above paragraph), due the effects of surface cracking, etc.

Sorption Isotherms

Several groups in Europe are making fundamental measurements of the sorption isotherms of cement-based materials. This includes personnel at LCPC in France (14,15), Chalmers University of Technology in Sweden (16,17), and the Laboratory for Building Materials in Denmark (10). Currently, all measurements are being made by the desiccator method using salt solutions to control humidity, with several years required to reach a "true" equilibrium. However, LCPC is in the process of installing equipment for a vacuum gravimetric apparatus, which includes a microbalance with 10^{-6} gram sensitivity, to generate continuous sorption isotherms. **In general, the measurements suggest that the nanopore structure of the C-S-H gel is similar in cement pastes with and without silica fume.** The fineness of the cement influences the higher RH portions of the sorption isotherms as would be expected, i.e., a finer cement results in a finer capillary pore structure.

At the Laboratory for Building Materials in Denmark, Lauge Nielsen has developed analytical techniques for predicting the shrinkage/swelling behavior of cement-based materials based on sorption isotherms and the resultant stresses which develop in porous materials (18). The sorption isotherm is first analyzed to determine a pore size distribution which is in turn used to determine the "global" capillary stresses to be expected at a given relative humidity. Finally, shrinkage/expansion is calculated based on these stresses and the elastic properties (Poisson's ratio and Young's modulus) of the solid phase of the porous material. This analytical approach is similar in some ways to the digital-image-based approach currently being developed for this problem at NIST, where these calculations are performed directly on computer representations of the microstructure of the porous materials (19).

2.4 Expansive Reactions and Cracking in Concrete

A review of this topic has recently been provided by researchers at G.M. Idorn Consult (20). In this review, cracking due to alkali-silica reaction, freezing and thawing, sulfate attack, and steam curing are discussed. Inherent differences between laboratory and field concrete often inhibit the application of laboratory results to predicting field performance.

Alkali-Silica Reactions

Lagerblad and Utkin (21) have studied the propensity of undispersed silica fume to undergo alkali-silicate reactions in concrete. The larger undispersed silica fume particles may not participate in the rapid pozzolanic reactions, so that the alkali ions present in the pore solution may react with them to form an alkali silicate. This reaction product is then slowly converted over time to C-S-H gel via reaction with calcium hydroxide. They have found that these reactions are not always expansive and that the worst situation is when the alkalis are from an external source and the concrete is under some type of mechanical loading. In concretes containing alkali susceptible aggregates, the reaction of alkali ions with the silica fume may actually be beneficial as it will remove or reduce one component of the alkali-silica reaction. In effect, the reaction is dispersed to many very small sites (the silica fume) as opposed to fewer local sites (the aggregate surfaces) so that any expansive stresses generated due to the reaction will also be dispersed. In support of this, Geiker and Thaulow (22) have observed that silica fume and fly ash can be very effective in preventing or at least delaying the expansion of mortar bars exposed to alkali solutions, a result seen previously by other researchers. At LCPC, DeLarrard and Larive have hypothesized that alkali-silica reaction may not be a problem in high-performance concretes due to their diminished internal relative humidity (23). Because of these materials' low w/c ratio, the amount of pore water may be insufficient to provide transport for the deleterious alkali ions to the reactive aggregate sites. This hypothesis is now being addressed in a fairly extensive experimental study.

Secondary Ettringite Formation

Secondary ettringite formation is often linked to high temperature curing of concrete. The ettringite decomposes at temperatures above 60 °C and later reforms when the concrete cools down. Because of its expansive nature, this secondary formation often leads to cracking of the concrete. It has often been assumed that this cracking is due to the crystallization pressure exerted by the forming ettringite as it deposits in porous regions such as the interfacial zones surrounding each aggregate. However, researchers at G.M. Idorn Consult in Denmark (24) now feel that this is not the case and that the cracking is due to a process in which the paste portion of the concrete is uniformly expanding. As evidence of this, they have measured the gap width around each aggregate particle in representative mortars and concretes and observed that this value is larger for the larger aggregates, supporting a uniform expansion of the paste. They feel that after these gaps form, the secondary ettringite deposits in them and is thus a result and not a cause of the damage (expansion).

Unfortunately, they are not at this time sure as to why the paste undergoes a uniform expansion, but it apparently involves the uptake of water from the ambient environment. Other unexplained observations include the fact that no expansion is observed when very fine sand is used and that entrained air prevents the expansion.

Researchers at the Swedish Cement and Concrete Research Institute have also investigated the effects of mix design and curing temperature on delayed ettringite expansion of mortars (25). While low w/c ratios and the inclusion of silica fume can delay or reduce the expansion, if reaction temperatures exceed 60 °C, the only way to avoid delayed ettringite formation is to utilize a cement with a low aluminate content.

2.5 Fillers- Effects on Hydration and Performance

Three groups are conducting researchin this area: the groups of Dr. Nonat and Dr. Pera in France and researchers at the Swedish Cement and Concrete Research Institute. By studying pastes and suspensions, Dr. Nonat's group (26) has shown that certain fillers (calcium and barium carbonate and titanium dioxide) accelerate the hydration while others (quartz and α-alumina) retard it. They attribute these effects to the dispersion/ coagulation of the cement particles present when each of the fillers is incorporated into the mix. If a filler increases the number of interparticle contacts, which act as possible nucleation and growth sites in the early hydration, the hydration is accelerated and the set time is reduced.

Similar studies are being conducted at the Swedish Cement and Concrete Research Institute (27). While many fillers have been found which accelerate the hydration, wollastonite gives the most improvement in mechanical properties, perhaps due to its fibrous nature.

Researchers at INSA in Lyon have studied the use of metakaolin in blended cements (28). Metakaolin is produced by calcining kaolin at temperatures between 700 and 800°C. Similar to silica fume and fly ash, metakaolin reacts with calcium hydroxide to produce C-S-H gel, and also produces a calcium aluminate silicate hydrate product. Thus, in these blended cements, calcium hydroxide content is reduced and the pore size distribution is shifted to smaller sizes (since the metakaolin particles are all typically smaller than 20 μm in size), with no detrimental effects on compressive strength. The use of this material in concrete has also been investigated at the CSTB near Paris.

2.6 Fire Resistance of HPC

While no publications were obtained on this topic, two research programs are now underway. The first is at Lund Institute of Technology in Sweden and is part of Sweden's national program on HPC. The second will be a collaborative effort between CSTB and LCPC and will investigate the fire resistance of HPC from both a material and a structural viewpoint. During fire tests, HPC specimens often exhibit intense spalling or explode, but the exact causes of this phenomenon remain to be proven. Current theories are based on thermally induced stresses due to mismatches in thermal expansion coefficients or stresses induced by the internal pressure which develops when liquid and bound water is converted to steam. This steam cannot easily escape because of the low permeability of HPC, so that large pressure gradients may develop, causing rapid cracking and "explosive" damage.

2.7 Freeze-Thaw (Frost) Resistance

As would be expected, the northern European countries are much more concerned with the freeze-thaw performance of concrete materials than those in southern Europe. Dr. Fagerlund of Lund Institute of Technology is one of the leading researchers in this area. For HPC, he feels that several degradation mechanisms must be considered, including water in pores, aggregate, interfacial regions, and cracks and self-desiccation (or the removal of water) effects (29). His theoretical calculations indicate that 1% freezable water is sufficient to cause considerable damage during freeze/thaw cycling. This freezable water content is a function of w/c ratio and degree of hydration and varies more significantly for the lower w/c ratios commonly employed in HPC. Thus, the effect of specimen age prior to freeze/thaw testing is much more critical for HPC than for conventional concrete, as supported by recent results generated at NIST (30). Because smaller air pores may absorb water, air-entrained HPC may not necessarily perform in a manner superior to non-air-entrained HPC. The modelling of this absorption process is outlined in a separate publication (31).

2.8 Hydration Chemistry, Mechanisms, and Models

In France, the premier public laboratory for fundamental studies on hydration and setting is in the Laboratoire de Recherches sur la Réactivité des Solides under Dr. Nonat at Dijon. In fact, Dr. Nonat was awarded the 1993 RILEM Robert L'Hermite medal for his research in this area (32). In Dijon, they are using a variety of experimental techniques to investigate fundamental relationships between hydration and setting in cement-based materials (33). Specifically, their research is focused on the kinetics of C_3S hydration (34-36). Typically, they measure particle size distribution (to assess coagulation), pore solution conductivity, heat evolution via microcalorimetry (37), and shear strength as a function of time and mix design.

They observe an initial reversible coagulation of the cement particles followed by a true set, which they attribute to the development of a continuous network of hydration products linking together the initially isolated or loosely connected cement particles. They often observe that less than 1% hydration is required to initiate the setting process (38). These results would be in general agreement with the insights that have been gained at NIST using our three-dimensional cement microstructural development model (39) and are also supported by measurements at ENS/Cachan which show a physical set due to the formation of C-S-H gel.

When a superplasticizer is added to the mix, two effects are observed (40) which tend to increase the set time. First, the superplasticizer increases the dispersion of the cement particles so that more hydration is required to achieve setting. Additionally, the induction period is prolonged (although once the hydration begins, it does occur at an accelerated rate).

Similar to the studies being conducted within the ACBM Center by Prof. Kirkpatrick at the University of Illinois, the Dijon group is using solid state NMR to investigate C_3S hydration (41,42). This enables an assessment of the polymerization of the silicate species as a function of time and mixture proportions. They only observe silicate polymerization when they start with monomeric silicate units. When starting with dimers or higher, the Ca++ ions simply form bridging units with no observable further polymerization.

At EPFL, Dr. Navi and one of his Ph.D. students (43) have implemented a version of the computer model for cement hydration originally developed by Hamlin Jennings at NIST (44). They model a system size of about 2000 grains, considering the cement particles between 7.5 and 60 μm in size, and hope to study the effects of particle size distribution and assumed kinetics on the hydration and setting of cement paste. Their efforts were still in the very early stages when I visited their laboratory in December of 1993.

At Delft University of Technology, Dr. van Breugel has developed a model called HYMOSTRUC for the hydration and formation of structure in cement-based materials, based on stereological analyses (45). His model accounts for the embedding of smaller particles in the hydration products of the larger particles and the consumption of water throughout the hydration process. He is now hoping to use this model in the study of the creep and relaxation properties of early-age concrete, which is being modelled using a simple beam and spring model (46). The number of beams is dependent on the degree of hydration (provided by HYMOSTRUC) and each beam has a separate creep history described by a power law with the appropriate time lag. Experimentally, they have constructed a large test rig for measuring the strains which develop in concrete at early ages due to removal of water via drying and self-desiccation.

2.9 Mechanical Properties

Fracture Mechanics

Goltermann and Holm (47) have reviewed the fracture mechanisms present in concrete from the point of view of two basic scenarios: expansion of the paste/shrinkage of the aggregate and expansion of the aggregate/shrinkage of the paste. The former is characterized by tangential concentric ring cracking around each aggregate while the latter exhibits cracks radiating outward from the aggregate surfaces. Since these mechanisms exhibit distinctly different cracking patterns, thin section analysis of crack patterns in deteriorated concrete can provide useful insight into the ongoing degradation processes and contribute to the development of a repair/maintenance strategy.

Many groups in Europe and the U.S. are applying a probabilistic approach to fracture processes in concrete. The group of Dr. Breysse at ENS/Cachan is one such group (48-51), utilizing a combination of experiments and computer models. All of these stochastic models attempt to account for the heterogeneity of concrete systems and its effects on measurements made at the structural level. The Cachan group has used multi-scale network models and finite element codes to develop links between "micro-cracking" and "macro-response". Implications for size effects (fracture energy increases with sample size but strength decreases) and strain localization are also explored in this research.

Another group researching this subject is that of Dr. Carpinteri at the Politecnico di Torino in Turin, Italy (52). They are using fractal statistics to characterize fracture surfaces. They explain the trend of increasing fracture energy with increasing sample size to be due to a fracture surface with a fractal dimension greater than 2 and the decrease in strength with increasing sample size to be due to a defect distribution with fractal dimension less than 2 (i.e., like a Cantor set, the larger the sample, the more likely it is to contain a large void). They have contrasted their multi-fractal scaling law (MFSL) results against Bazant's size effects law (SEL) and prefer the former even though over the practical experimental range, there is little difference in the values predicted by the two laws. The two laws do have different concavities so that if a larger experimental range could be investigated, one should prove superior to the other.

While in France, I also came into contact with a professor from the University of Arizona, Dr. George Frantziskonis, who is working in the area of heterogeneity and fracture in brittle materials (53-56). His group is focusing on the effects of spatial correlations on dissipated energy and crack formation in brittle materials, such as concrete, and the use of fractals to describe the observed behavior at a variety of scales. Most recently, he is examining the use of wavelet transforms (57) to describe this multiscale heterogeneity.

These probabilistic approaches are similar to the one being pursued by Dr. Erik Schlangen, of Delft University of Technology, who is currently spending 14 months at NIST in the Building Materials Division (58). He is using a (mainly 2-D) beam model in which the beams can be under torsion as well shear and/or compression. The heterogeneity of the underlying microstructure is either chosen stochastically or based on the generation of a grain structure designed to match that present in a real mortar or concrete. The model has proven invaluable in simulating the effects of loading conditions and boundary conditions on the mechanical response of cement-based materials.

At EPFL, J. Wang is simulating crack propagation in micro-cracked concrete (59). In 2-D, concentric microcracks are placed over a portion of each circular aggregate's periphery, the resulting structure is meshed, and cracking under direct tension loading is predicted. The predicted load-displacement curve contains a snapback after failure which is generally not observed experimentally, perhaps due to inertia effects.

Long Term Performance

In recent years, there has been much controversy surrounding possible strength retrogression of HPC. A possible explanation for this sometimes observed phenomena has now been proposed by researchers at LCPC (60). **They have observed that when an HPC cylinder is dried under normal conditions for several years, a significant moisture gradient develops, with the outer layer of the specimen containing much less water than its inner core.** This is different from conventional concrete, where a nearly uniform distribution of water is achieved at long times. The distribution present in HPC should result in the development of compressive stresses in the interior, prior to any loading of the concrete cylinder, so that the measured compressive strength would be less than that expected during the normal course of strength development. This theory has been further validated by research at the University of Sherbrooke (61), where aged HPC specimens were dryed at low pressure to eliminate the inherent moisture gradient and an increase in compressive strength back to its expected level was observed.

2.10 Microstructure Characterization

As part of the Swedish program on HPC, Dr. Kjellsen at the Swedish Cement and Concrete Research Institute and Dr. Atlassi at Chalmers University of Technology are collaborating to study the effects of w/c ratio, silica fume content, and curing conditions on the microstructure and performance properties of cement pastes (27). In addition to SEM, TGA, and X-ray diffraction studies, they will measure bound water content, silicate polymerization, compressive and bending strength, and sorption isotherms for a series of pastes. Dr. Kjellsen is also collaborating with Dr. Hamlin Jennings of Northwestern University on an environmental SEM study of microcracking in high-performance and conventional cement pastes (27).

Dr. Daniel Quenard, my host at CSTB, is involved in a European Community project on the use of image analysis to characterize cementitious materials. Applications being explored in this project include: automatic characterization of air void systems on polished sections, determination of w/c ratio on thin sections (62), quantification of crack patterns, and overall characterization of the microstructure of hardened cement paste. For w/c ratio determination, the technique is similar to that commonly used in Denmark (demonstrated to me at Idorn Consult A/S) and the Scandinavian countries, utilizing thin sections impregnated with a fluorescent dye. The brighter the dye, the more porous the cement paste and thus the higher the initial w/c ratio. Naturally, the results are also dependent on the degree of hydration of the cement paste so that measurements must be made at a "standard" age or on "fully hydrated" specimens. In general, the measurements are more reliable on paste than on concrete specimens. The overall project is expected to continue through the end of 1994 with a final project report being generated in early 1995.

Dr. Renaud Maggion, currently with Ciments Francais, performed his Ph.D. research on the evolution of microstructure in hydrating C_3S systems (63). Using small-angle x-ray scattering, mercury porosimetry, and TEM, he evaluated the porosity and specific surface of hydrating C_3S paste as a function of w/c ratio and hydration time. Porosity, density, and specific surface were all found to be linear functions of the degree of hydration. The texture of the C-S-H gel was characterized by a fractal dimension very close to 3 for length scales between 2 nanometers and a few micrometers. Over long periods of time, the C-S-H gel undergoes rearrangement at the nanometer scale.

Pore Structure Characterization

Dr. Birgit Meng, who spent several months in the Building Materials Division of NIST in 1987 as a guest researcher from the Institut fur Bauforschung in Aachen, Germany, has recently proposed a new method for characterizing pore systems (64,65), based on combining sorption, mercury intrusion, and image analysis measurements. The smallest pores

(1-10 nm) are estimated based on sorption measurements and subsequent analysis using the Kelvin equation. Pores between 10 nm and 1 μm are measured using mercury intrusion porosimetry and application of the Washburn equation. For image analysis assessment of the larger pores (> 1 μm), the pore fraction vs. size is estimated by an analysis of a 2-D image using variable size filters, a technique originally utilized for cement-based systems at NIST (66). The resulting "complete" pore size distribution is analyzed using fractal analysis techniques to determine an effective porosity and a characteristic pore radius for transport. This effective porosity can then be used to estimate fluid permeabilities, diffusivities, and capillary flow coefficients, where better correlation is observed than when total porosity alone is used as the dependent variable.

At Imperial College of Science and Technology in England, Dr. Karen Scrivener has been involved in SEM characterization of cement microstructure for a number of years. She, along with Dr. Quenard of CSTB, is currently part of a European Community science project entitled "Characterization of Microstructure as a Tool for Prediction of Moisture Transfer in Porous Media" (67). In this study, the transport properties of a sandstone, two bricks, and several cement pastes are being examined along with evaluation of each material's microstructure. The ultimate goal is to relate microstructure to transport coefficients in a quantitative manner. Two-dimensional SEM images of pore structures are being characterized by their correlation functions, which can then be utilized to reconstruct a three-dimensional representation of the porous material, as recently demonstrated at NIST (68).

2.11 Mix Proportioning

At LCPC, a computer program, aptly named BETONLAB, has been developed to assist in the mix design of concrete, including HPC (69,70). Given a mix design, the program predicts strength and slump and projects the cost of the mix. Modified versions of Feret's and Hashin's laws are used to predict compressive strength and elastic modulus (at 28 days), respectively (71). The model of Farris is used to predict slump. It basically considers the concrete as a mixture of different particles, each class of particles having an effect on the overall viscosity described by some function of their volume proportion.

Different methods for the proportioning of HPC mixes have been presented in an AFREM (Association Francaise de Recherches et D'Essais sur les Materiaux et les Constructions) group on "Connaissance et Utilisation des BHP" (Knowledge and Utilization of HPC). LCPC has developed the method of flows (or grout method) for mix proportioning of HPC (72). A modified version of this method is being employed by EDF-CEMETE (Electricity of France) to produce HPC with compressive strength greater than 60 MPa, a low heat of hydration to avoid thermal cracking, and a formulation capable of being pumped. The silica fume content of this concrete is 10% of the cement. Fly ash or other filler materials are used to lower the heat produced by the paste portion of the concrete. Being a large producer of fly ash, EDF is interested in producing a very high-performance concrete without the use of silica fume.

2.12 Particle Packing

Idorn Consult A/S was responsible for the development of the packing models used in the SHRP-funded program on concrete materials at Pennsylvania State University (73). In this program, standard packing models were evaluated for their applicability to concrete. While these packing models are generally adequate for monosize spherical particles, concrete aggregates and cement particles are neither spherical or monosize. Nevertheless, the existing models can provide some information on the highest packing densities which might be achievable for a given mix design. The packing density achieved has an effect of many important properties of concrete, such as workability, permeability, and compressive strength, with denser mixes generally exhibiting superior properties.

At the Swedish Cement and Concrete Research Institute, Dr. Anders Lamer is also applying packing models to concrete research (74). He utilizes a modified Fuller curve approach and a packing factor based on the bulk density of the dry mix. He finds that particles less than 250 μm in size are important in achieving a dense packing and that the densest packing also seems to give the best rheological properties.

2.13 Physical Testing

Researchers at LCPC have been studying the effects of different capping techniques on the measured compressive strength of HPC (75). They are proponents of the sand box capping method, originally developed by Purrington and McCormick in 1926 (76), in which the concrete cylinder to be tested is capped on both ends with a box (shell) containing sand to achieve uniform stress transfer between the testing platens and the concrete specimen. They find that the results from the sand-box method are in better agreement with those obtained by surface grinding of the cylinder ends than those obtained using conventional sulfur or epoxy capping compounds for concretes of normal (55 MPa) and high (70 MPa) strength. For very high strength concretes (> 100 MPa), however, the sand-box method gives characteristic strengths about 11% lower than those obtained via surface grinding. Researchers at NIST (76) have recently completed a study on the effects of testing variables on the compressive strength of high-strength concrete cylinders and found that the end preparation (sulfur capping vs. grinding) can have a significant effect on the measured compressive strength for high-strength concretes. Here, it was found that for 90 MPa concrete, grinding often resulted in strengths that were about 6% higher than those obtained using sulfur capping.

Researchers at ENS/Cachan are utilizing a large triaxial compression machine for testing HPC in true triaxial compression (77). A sample with an uniaxial compressive strength of 120 MPa can have a triaxial compressive strength greater than 200 MPa.

2.14 Rheology and Mixing

In the area of rheology (or workability), many countries are conducting research and development activities on new rheometers. Major efforts have been made in Scotland, Norway, and France. There is also a RILEM task group entitled "Workability of Special

Mixes" which addresses this topic.

In Scotland, the group of Dr. Bartos at the University of Paisley has developed the "ORIMET" test to assess the properties of underwater and other special concretes (78). The test consists of measuring the flow time of a sample of concrete (about 7.5 liters) from a 80 mm diameter (maximum aggregate size of 20 mm) casting pipe.

In Norway, the group of Dr. Gjorv at Trondheim developed the **BML viscometer** in the early 1990s (79). This equipment consists of a coaxial cylinders viscometer which records the torque needed to achieve different angular velocities. As is typical, the flow is characterized by a yield stress and a plastic viscosity. A recent evaluation of this equipment (80) has shown it to be inadequate for concretes with slump values less than 100 mm and that significant plug flow occurs for slump values less than 200 mm.

In France, LCPC is in the process of developing a commercial rheometer for field use (81,82). The device is called **B.T. RHEOM** and is intended to measure the rheological properties of fluid concretes, including HPC mixes. The device is basically a parallel plate torsional viscometer with the added capability of applying a homogeneous vibration during the test. The plates are separated by a distance of about 100 mm, considered an adequate separation for mixes with a maximum aggregate size of 20 mm. Measurement time is on the order of five minutes. Commercialization of this apparatus is expected in 1995.

In Sweden, a standard method for evaluating necessary mixing time has been developed (83). Satisfactory mixing is indicated by a coefficient of variation less than some critical value (e.g. 6%) for the cement content of a series of 2-liter samples. The cement content of each sample is determined by a pycnometer method in which the sample is weighed in air and water and then wet screened to remove the coarse aggregates.

2.15 Service Life Prediction

Corrosion

A key value for predicting the service life of concrete in which the reinforcing steel is susceptible to corrosion is the chloride threshold concentration necessary to depassivate the steel. At the Swedish Cement and Concrete Research Institute, Karin Pettersson (84,85) has conducted studies on this parameter as a function of w/c ratio and silica fume addition. Corrosion is assessed using polarization resistance measurements while chloride content is evaluated using standard chemical techniques. The critical chloride content is seen to vary with w/c ratio and additives such as silica fume and fly ash. **The addition of silica fume generally reduces the chloride diffusion coefficient to an extent that offsets the fact that the critical chloride concentration to initiate corrosion is also reduced.**

Frost Attack

Dr. Fagerlund of Lund Institute of Technology has conducted studies on the effects of frost attack on the service life of concrete, with regards to both reinforcement corrosion and general cracking (86,87). The report concerning reinforcement corrosion considers the effects of salt scaling on penetration of the chloride ion and carbonation fronts, as well as the subsequent influence on the corrosion of the reinforcing steel. Formulas are provided for calculating the residual service life. The report concerning general cracking considers the critical air content required to avoid freeze/thaw damage depending on the mix design and the wetness and salt content of the environment.

In addition, Dr. Fagerlund has recently completed a general report on the principles and methods for evaluating the durability and service life of construction materials (88) and a detailed report on the calculation of time-dependent moisture distributions in field concrete (89).

2.16 Transport Properties

Conductivity/Diffusivity

A member of Dr. Nilsson's group at Chalmers University of Technology, Tang Luping, has been working extensively in the area of measuring the diffusion coefficient of chloride ions in concrete (90-95). They have developed a modified version of the AASHTO/ASTM Rapid Chloride Permeability Test (96) in which the diffusion of chloride ions is accelerated by a smaller voltage (30 Volts vs. 60 Volts in the AASHTO test) and the intrusion of chloride ions into the specimen is directly measured as opposed to being inferred from the total coulombs passed through the system in a given period of time. Diffusion coefficients that they have calculated based on an analysis of diffusion with an applied electric field are in reasonable agreement with those measured using conventional diffusion cell techniques. This accelerated technique is similar to that recently employed by Pavla Halamickova in the joint University of Toronto/NIST project (97).

The group at Chalmers have also studied the effects of slag and fly ash on the chloride diffusion coefficients of blended cement pastes. These additives have been found to reduce chloride diffusion both by modification of the pore structure and by increasing the chloride chemisorption capacity of the paste. Similarly, the addition of silica fume has been found to drastically reduce the chloride ingress into concrete specimens at a given age. The replacement of 24% of the cement with silica fume can reduce the chloride ion diffusion coefficient by an order of magnitude or more at ages beyond 28 days compared to a control system without silica fume. For such systems, proper curing is necessary to achieve these desirable properties as curing in air or at high temperatures may result in much higher diffusion coefficients.

Johansson (98) at the Swedish Cement and Concrete Research Institute has studied the relative contributions of absorption (wet/dry cycling) vs. diffusion to chloride ingress in concrete. The cyclic exposure consisted of 7 days in 3% NaCl solution followed by 14 days drying at 50% RH, 20°C. The basic finding is that when wet/dry cycles are present, their contribution to chloride ingress far outweighs that due to diffusion, especially in concretes with a high w/c ratio.

Dr. Houst (99), at EPFL, has studied the diffusion of carbon dioxide and oxygen in cement mortars. **He has observed a rapid increase in the diffusion coefficients of both gases as the sand content of the mortar is increased from 49 to 55%.** This increase could be due to the increased connectivity of the interfacial zones as more sand is added to the mix, supporting the results of mercury intrusion experiments recently published from a joint Purdue University/NIST project (100). The NIST modelling in this area has been extended by a group in France who have utilized mercury intrusion porosimetry curves and their own version of a NIST model to compute the porosity of the interfacial zones (relative to that of the bulk paste) in mortars (101).

Liquid Permeability

Two groups are applying renormalization techniques to predict permeability based on pore size distribution information. Dr. Breysse (102) at ENS/Cachan has developed a simple one-dimensional network approach and must correct the computed permeabilities by a factor of porosity to the eighth power to obtain reasonable agreement with experimental data. A Ph. D. student at CSTB is performing similar analysis, but using a three-dimensional approach (103). **Starting with a mercury intrusion porosimetry curve for a porous material, he estimates the true pore size distribution and calculates permeability on a 3-D multi-scale tube network. For a variety of cement pastes and mortars, good agreement has been observed between computed and previously measured (104) values.** Experimentally, Dr. Breysse is evaluating the effects of microcracking on permeabilities, by monitoring the liquid permeability of a thin specimen loaded in tension (77).

Moisture Permeability

Dr. Hedenblad of Lund Institute of Technology (105) has performed extensive experimental measurements on the moisture permeability of cement-based materials. Moisture flow through a specimen under a controlled relative humidity gradient is obtained by a gravimetric method. Transport at low relative humidities is relatively insensitive to w/c ratio but w/c ratio is significant for transport at higher relative humidities. **For concretes at high relative humidities (normal field conditions), much of the transport takes place through the interfacial zones between cement paste and aggregates, as the measured transfer rate actually increases with increasing aggregate content.**

The simulation of partially saturated flow is quite complex. Recently, lattice-gas automata simulations have been applied to this problem by researchers at the École Normale Supérieure in Paris. Their published results (106-109) are very preliminary in nature and they are using the same basic code that Nicos Martys, of the NIST Building Materials Division, has obtained from the original developers at MIT.

3. SUMMARY

While far from being inclusive, the previous section should provide a valid frame of reference for current cement and concrete research in western Europe. More recently, emphasis is being placed on research on high-performance concrete. Key topics for this research include mix design, rheology and mixing, self-desiccation shrinkage and cracking (including proper curing), and long-term performance. Another issue being addressed simultaneously is the upgrading of construction codes and practices to allow for the efficient use of these new materials and systems. For example, France has only recently approved the use of 60 MPa concrete in construction design, even though compressive strengths greater than 100 MPa can now be routinely achieved.

The past and current research programs of NIST seem to be well focused on areas considered important in the European research community. Relating microstructure to properties is seen as a key area, as evidenced by the ongoing European community science project on relating microstructure to transport in building materials such as bricks and cements. Modelling has turned out to be the critical activity in this project as it offers the best hope for establishing quantitative relationships between microstructure and transport properties. On both sides of the Atlantic Ocean, the overall goal is to develop the technical basis to predict the performance of cement-based materials in a given environment.

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5. ABBREVIATIONS

ACBM - National Science Foundation Science and Technology Center for Advanced Cement-Based Materials
C_3A - Tricalcium Aluminate
C_3S - Tricalcium Silicate
C-S-H - Calcium Silicate Hydrate
CSTB - Centre Scientifique et Technique du Batiment
EDF - Electricité de France
ENS - École Normale Supérieure
EPFL - Ecole Polytechnique Federale de Lausanne
HPC - High-Performance Concrete
INSA - Institut National des Sciences Appliquées de Lyon
LCPC - Laboratoire Central des Ponts et Chaussées
MIT - Massachusetts Institute of Technology
NIST - National Institute of Standards and Technology
SEM - Scanning electron microscopy
SHRP - Strategic Highway Research Program
TEM - Transmission electron microscopy
TGA - Thermogravimetric analysis
w/c - Water-to-cement ratio

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