SYMPOSIUM FF

Materials Science of High-Performance Concrete

November 28 - 30, 2000

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* Invited paper

SESSION FF1: MICROSTRUCTURE AND RHEOLOGY OF HIGH-PERFORMANCE CONCRETE Chair: Mette Geiker Tuesday Morning, November 28, 2000 Room 301 (Hynes)

8:30 AM *FF1.1

MICROSTRUCTURE OF HIGH-PERFORMANCE CONCRETE. Paul E. Stutzman, Inorganic Building Materials Division, National Institute of Standards and Technology, Gaithersburg, MD.

An improved understanding of the relationships between composition and structure and the performance properties of high-performance concretes (HPC) may be developed through microstructural characterization. Microscopical analysis using the scanning electron microscope has been invaluable in characterizing the development of microstrucure and the influence of mineral admixtures on the cement paste and the paste / aggregate transition zone. Microstructural features of selected high-performance concretes will be explored to demonstrate these capabilities.

9:00 AM FF1.2

COOLING STRAINS IN HARDENED CEMENT PASTE THROUGH DIFFERENTIAL THERMAL CONTRACTION: CH VS C-S-H. Erland Schulson, Thayer School of Engineering, Darmouth College, Hanover, NH; Ian Swainson, Tom Holden, Neutron Program for Materials Research, National Research Council of Canada, Chalk River Laboratories, Chalk River, ON, CANADA.

When cooled, hardened cement paste is subject to the development of internal stresses. One type, which is well recognized, originates from the freezing of pore water. This type is caused by crystal pressure and/or by hydraulic pressure. Another type, which appears to be less well recognized, may originate from differential thermal contraction between crystalline Portlandite (of the hexagonal crystal system) and the gel-like C-S-H matrix. It is the latter type that is considered here. Along the crystallographic *a*-direction the contraction coefficient is smaller than it is within the matrix ($\sim 10 \times 10^{-6} \mathrm{K}^{-1}$ vs $\sim 18\times 10^{-6} {\rm K}-1$ at temperatures around 250K). Along the c-direction, it is larger (~ 28 \times 10-6K-1). This implies that upon cooling CH platelets become compressed in the a-direction and, provided that cohesion is maintained between the platelets and the matrix, extended in the c-direction. Correspondingly, stresses should develop within the platelet and the matrix. To investigate this point, neutron diffraction experiments have been performed on hardened cement paste (w/c = 0.36) which was cooled in increments of 5 K from 298 K to 20 K. (Heavy water was used in place of light water.) The aand c lattice parameters of CH were calculated from the diffraction spectra. The results showed that, as expected, compressive strains were registered within CH along the a-direction and tensile strains, along the c-direction. At 200 K, for instance, the a-compressive strain relative to room temperature is $\sim 2 \times 10^{-4}$ and the c-tensile strain is $\sim 1 \times 10^{-3}$. Correspondingly, compressive and tensile stresses of

about -5 MPa and 14 MPa are estimated from the elastic stiffness constants for CH.

 $9{:}15~\text{AM}~\overline{\text{FF1.3}}$ QUASI-ELASTIC NEUTRON SCATTERING STUDIES OF THE HYDRATION KINETICS IN TRICALCIUM AND DICALCIUM SILICATE PASTES. Jay C. McLaughlin, Dan A. Neumann, NIST Center for Neutron Research, Gaithersburg, MD.

Quasi-elastic neutron scattering (QENS) has proven to be a useful tool in examining the hydration reaction in cement systems. QENS is able to measure the fraction of water that is 'free' or liquid like, and the amount of water that is 'constrained' in the solid phases, $Ca(OH)_2$ and the C-S-H gel. Thus, the ratio of the bound water to the total water is a measure of the extent of the hydration reaction. Tricalcium silicate (C_3S) is the primary constituent of cement and the hydration reactions are similar. Our current studies have focused on two aspects of the hydration reaction, the effect of particle size distribution (PSD), and effect of adding dicalcium silicate (C_2S) . For the PSD experiments, four C_3S powders from the same batch, but ground to different fineness, were measured by laser diffraction and found to have PSD's peaked at 1-5 $\mu m,$ 10-12 $\mu m,$ 25-30 $\mu m,$ and 100-300 μ m. The most apparent change in the hydration reaction is the amount of bound water increases as the PSD becomes smaller. Little change is seen in the length of the induction period or the rate of reaction in the diffusion limited regime. For the $C_3S:C_2S$ systems five compositions where examined, pure C_3S , 80:20, $\overline{60:40}$, 30:70 C₃S:C₂S mixtures and pure C₂S. Two changes are apparent, the length of the induction period increases, and the rate of reaction in the diffusion limited regime increases as C_2S is increased.

9:30 AM FF1.4

HIGH STRENGTH CONCRETE PREPARED WITH SPECIALLY

STRUCTURED WATER. J. Uchrin, Interactive Technology, Reno, NV; R. Uchrin, U.R.F. Technology Development, Reno, NV

Water has distinctive properties with a unique structure. This structure allows water to manage the electric charge of another molecule. The detailed structure of liquid water (unlike ice, with tetrahedral geometry) can be random and irregular. The necessity of maintaining a tetrahedral, hydrogen bond structure gives water an open, loosely packed structure, compared to most of the other liquids. Therefore, changing the physical and chemical properties of the water result improvements in technological process. It is well known that with the hardening of the cement paste the solution and hydration of cement minerals concurrently take place: - producing supersaturated solution - with spontaneous dispergation of minerals, up to colloid particles - with formation of thixotrope coagulant structure developing and growing simplified crystal structure. The use of structured water allows managing the electric charge of other molecules. The hydration of cement paste in a higher degree takes place than it would be possible in normal cement paste hardening procedure. We have conducted a series of experiments to confirm this fact. In our results the compressive strength of the concrete increased by 20 /%. Measurements were made on the 3rd and on the 28th day. After the 3rd day the cement paste was examined with electron microscope, where our samples showed significantly reduced grains. Our technological process provides new physical and chemical characteristics, significantly increasing the watertight quality, freezing resistance and chemical resistance.

10:15 AM *FF1.5

RHEOLOGY OF HPC. Chiara F. Ferraris, National Institute of Standards and Technology, Gaithersburg, MD.

In the world of concrete, the word rheology is seldom if not at all used. Instead words such as "ease of placement" and "compaction without segregation" are commonly used to describe concrete flow. The term, ease of placement, covers various other properties of fresh concrete that are called: workability, flowability, compactibility, stability, finishability, pumpability, and/or consistency. None of these words are defined, yet, in term of fundamental entities commonly used in rheology, such as viscosity or yield stress. Most engineers measure workability with the slump cone proposed by Abrams almost a century ago, even if the test was never designed to specifically measure workability. Nevertheless, in the last 10-20 years, several researchers introduced into the concrete world methods developed for other materials. Their research lead to several new tests, to methods to predict concrete flow from its parts (cement paste, mortar), and to computer simulation methods to predict concrete flow from its composition. In this paper, an overview of the state of the art will be presented. Emphasis will be on the new measurement methods and the research that is being conducted today in various laboratories around the world. The links between rheology and "ease of placement" will also be discussed. A vision of the needed future research will be presented.

10:45 AM <u>FF1.6</u>

APPLICATION OF DISSIPATIVE PARTICLE DYNAMICS FOR MODELING CEMENT BASED MATERIALS. Nicos S. Martys, James Sims, National Institute of Standards and Technlogy, Gaithersburg, MD.

Dissipative particle dynamics (DPD) is emerging as a powerful computational tool for the modeling of complex fluid flow like that of suspensions. In this talk, results from a numerical study to validate the DPD method will be presented. Tests include: recovery of Einstein's prediction of the viscosity of a dilute sphere suspension, motion of an ellipsoid under shear, and the dependence of a sphere suspension viscosity on solid fraction and Peclet number. The application of DPD for modeling the flow of cement-based materials will be discussed.

11:00 AM FF1.7

RHEOLOGICAL AND DIELECTRIC PROPERTIES OF FRESH CEMENT PASTES WITH HIGH SILICA FUME CONTENT. Giovanni Dotelli, <u>Marinella Levi</u>, Politecnico di Milano, Dept of Industrial Chemistry and Chemical Engineering, Milano, ITALY.

Low water-to-cement ratios, selected aggregates and the addition of special additives, i.e. silica fume (SF) and superplasticizers, make the hardened cementitious products so special that they are known as High Performance Concrete. In the present work we are mainly interested in the study of their behavior before setting (workability) We have investigated the rheological and dielectric properties of ordinary Portland cement pastes (w/c = 0.3) containing different amounts of silica fume (SF/binder = 0 - 15 wt%) and superplasticizer (1 wt% of dry products) in the first 8 hours after mixing. Rheological measurements were performed under gradual variation of the share rate (in 1/s): plastic viscosity (in Pa s) vs. shear rate and shear stress vs. shear rate are presented at different times. All flow curves are of pseudoplastic type. A simple analysis of this behavior can be performed by hypothesizing a power law relation between plastic viscosity and shear rate. Dielectric measurements were performed with a frequency response analyzer (100 Hz - 100 kHz) and complex permittivity was monitored constantly for the first 8 hours. Permittivity and dielectric loss are studied as a function of both frequency and time. The influence of SF addition on rheological and dielectric properties of fresh pastes is discussed.

11:15 AM FF1.8

PARAMETER STUDY ON THE INFLUENCE OF STEEL FIBERS AND COARSE AGGREGATE CONTENT ON THE FRESH PROPERTIES OF SELF-COMPACTING CONCRETE. <u>S. Gruenewald</u>, J.C. Walraven, Delft University of Technology, Faculty of Civil Engineering and Geosciences, Delft, THE NETHERLANDS.

Self-Compacting Concrete (SCC) offers several economic and technical benefits. Reasons to apply this kind of concrete are increased productivity, improved working conditions and superior concrete quality. The use of steel fibers extends the possibilities of SCC. Fibers are added to cements and concretes because of their benefits in crack control and energy absorption. They bridge cracks and retard their propagation, and they improve several characteristics and properties of concrete, including fire resistance and both plastic and total shrinkage behavior. Fibers are known to affect the workability of concrete. Therefore, an investigation was performed to compare the properties of plain SCC and SCC reinforced by steel fibers. Two mixtures of SCC with different aggregate contents were used as reference. Each of the concretes was tested with four types of steel fibers at different amounts to answer the question to what extent the workability of SCC is influenced. The slump flow, a fiber funnel and the J-ring were used to evaluate the material characteristics. This paper discusses the suitability of the applied test methods and the effect of the coarse aggregate content, the amount and type of steel fibers on the workability of SCC.

11:30 AM FF1.9

RELATION BETWEEN SUPERPLASTICIZER ADSORPTION AND RHEOLOGICAL BEHAVIOUR OF REACTIVE POWDER CONCRETE. <u>Olivier Bonneau</u>, Pierre-Claude Aitcin, CRIB, Universite de Sheirbrooke, CANADA; Christian Vernet, LCR, Lafarge, FRANCE; Micheline Moranville, LMT, ENS de Cachan, FRANCE.

Reactive Powder Concretes (RPC), which form a new generation of Ultra High-Performance Concrete, contain very fine powders: cement, crushed quartz, silica fume. Superplasticizer dosage is optimized with rheological tools to obtain a good workability in such a low water content material (W/C=0.20). Adsorption isotherm measurements of two superplasticizers, a copolymer of acrylic ester (CAE) and a polynaphtalene sulfonate (PNS) have been carried out in each fine powder at a water to solid ratio of 0.35. The SP quantity used to saturate the surface of all reactive powders present in RPC is calculated according to the Langmuirs model and extrapolated at W/C=0.20. A strong correlation is found between the rheological optimum and the saturated value for the two admixtures with R2=0.95. This result shows that rheological behaviour of RPC directly depends on the adsorbed uptake of superplasticizer.

11:45 AM <u>FF1.10</u>

FFFECT OF SILICA FUME, METAKAOLIN AND LOW CALCIUM FLY ASH ON CHEMICAL RESISTANCE OF HIGH PERFOR-MANCE CONCRETE. D.M. Roy and P. Arjunan, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

There is now considerable evidence that certain aspects of concrete durability may be enhanced by incorporating supplementary cementitious materials. Effects of aggressive chemical environments were evaluated on mortars prepared with portland cement and substituted cements including silica, fume, metakaolin, or low calcium fly ash at various replacement levels. The natural adverse chemical environment conditions of acetic or sulfate-rich environments were simulated using sulfuric acid, hydrochloric acid, nitric acid, acetic acid, phosphoric acid and a mixture of sodium and magnesium sulfates. Comparisons were made at equivalent water/cementitious material ratios. Chemical resistance information was used to propose realistic portland cement: supplementary cementitious material proportions. Mechanical properties of the cementitious products were also evaluated.

SESSION FF2: MIXTURE PROPORTIONING AND INTRODUCTION OF POZZOLANS Chair: David Lange Tuesday Afternoon, November 28, 2000 Room 301 (Hynes)

1:30 PM <u>*FF2.1</u>

MIXTURE-PROPORTIONING OF HIGH-PERFORMANCE CONCRETE. <u>Francois de Larrard</u>, Head Methods and Facilities for Road Construction and Maintenance, LCPC Centre de Nantes, FRANCE.

In Europe, High-Performance Concrete is generally considered as a concrete of superior properties, e.g. having a compressive strength at $28 \ \rm days$ more than 60 MPa, and/or a water/binder ratio less than 0.40. In the US, a more general meaning has been adopted by ACI: HPC is something suitable for the proposed application, and not achievable with conventional means. Whatever the continent, there is the same need for designing materials - made up with a growing number of constituents; - fulfilling a growing number of criteria, most of them being specified in terms of performance. There is therefore a great challenge addressed to the research community: i) how to link all important concrete properties with the nature and dosage of components (mix-design) and ii) how to account silmutaneously and scientifically for a vast list of specifications, in order to achieve the most economical mixture for a given application. The paper will present a state-of-the-art of this question, with a special emphasis on the approach carried out at LCPC, France, which has recently lead to a comprehensive theory and a software program for scientific concrete mixture proportioning.

2:15 PM <u>FF2.2</u>

A SIMPLE MIX-DESIGN METHOD FOR SELF-COMPACTING CONCRETE. <u>Nan Su</u>, National Yunlin University of Science and Technology, Dept of Construction Engineering, Yunlin, TAIWAN; Chen-Chang Kao, National Taiwan University, Dept of Civil Engineering, Taipei, TAIWAN; Kung-Chung Hsu, National Taiwan Normal University, Dept of Chemistry, Taipei, TAIWAN ROC.

Self-compacting concrete (SCC), a new kind of high performance concrete with excellent deformability and segregation resistance, was developed in Japan in 1988. The mix-design method of SCC has been established and recommended by Japan Ready-Mix Concrete Association (JRMCA), which requires test procedures on cement pastes and mortars, Apparently, it is too sophisticated to be implemented in practice. This article proposes a new mix-design method, which determines the amount of aggregates first, and then fills the cementituous materials into the voids of aggregates to make the resulting concrete having adequate flowability and other desired SCC properties. Several tests, including the slump flow, V-funnel, Land U-type tests, and compressive strength test, were carried out and the results indicate that SCC could be produced successfully by this method. The type and dosage of superplasticizer, amount and quality of cementitious materials and water content are major factors determining the properties of SCC. Compared to the JRMCA method, this method is simpler, requires less cementitious materials, and more time and cost saving.

3:00 PM <u>*FF2.3</u>

SILICA FUME IN HIGH PERFORMANCE CONCRETE. Erik J. Sellevold, University of Trondheim, Trondheim, NORWAY.

Two main topics will be discussed in this talk: 1) The degree of reaction of silica fume in HPC and consequences for the cement reactions, along with water binding capacity and chemical shrinkage of the pozzolanic reactions. and 2) The crack sensitivity of a given concrete mix at early ages in a given application depends on the following factors: heat generation, autogenous shrinkage, thermal dilation coefficient, elastic modulus, tensile strength, and the creep/relaxation properties. The development of each of these depends strongly on the temperature history. It is the interaction of these factors at any given time and location in the structure that determines the crack sensitivity. The effects of silica fume on these factors and on the overall crack sensitivity for some typical cases will be discussed.

$\begin{array}{l} \textbf{3:30 PM} \hspace{0.1 cm} \underline{\textbf{FF2.4}} \\ \textbf{Transferred to FF1.10.} \end{array}$

3:45 PM <u>FF2.5</u>

OIL CRACKING WASTE CATALYST AS AN ACTIVE POZZO-LANIC MATERIAL FOR SUPERPLASTICIZED MORTARS. Kung-Chung Hsu, Fan-Feng Ku, National Taiwan Normal University, Dept of Chemistry, Taipei, TAIWAN; Nan Su, National Yunlin University of Science and Technology, Dept of Construction Engineering, TAIWAN ROC.

Superplasticized mortars containing waste catalyst (FCC) have been characterized. The waste catalyst, comes from catalytic crackers of oil companies, consists mainly of silicon oxide and aluminum oxide, and shows amorphous structure. The tested results indicate that mortars with FCC exhibit greater compressive strength than plain mortars. The strength improvement could be attributed to high pozzolanic activity of the waste catalyst. One evidence is that higher

temperature rise was observed in FCC mortars than plain mortars. Besides, the XRD and SEM analyses indicate that a significant amount of ettringite was produced in the early curing period. It is clear that this temperature rise is due to the exothermal reaction of FCC and released calcium oxide from cement hydration.

> SESSION FF3: CONCRETE AS A POROUS MATERIAL Chair: Della M. Roy Tuesday Afternoon, November 28, 2000 Room 301 (Hynes)

4:00 PM *FF3.1

CONCRETE AS A POROUS MATERIAL. <u>George Scherer</u>, Princeton University, Princeton, NJ.

This paper reviews what we know and what we need to know about the porosity of concrete. The pores of interest include nanometric spaces within the structure of C-S-H, micron-scale capillaries created by excess water of hydration, macroscopic voids entrapped or deliberately entrained during mixing of concrete, the interfacial transition zone between paste and aggregate, and porosity within the aggregates. Pores control transport of water in the form of liquid and vapor, and transport of ions by diffusion or advection. Movement of water and ions permits deterioration of concrete by a variety of mechanisms including freezing/thaw (F/T) cycles, alkali-silica reaction (ASR), external sulfate attack, delayed ettringite formation (DEF), and corrosion of rebar. Moreover, moisture permits stress corrosion at crack tips, which increases the susceptibility of concrete to stresses. This talk focuses on several areas of ignorance: evolution of porosity during processing; coupled flow, diffusion, and precipipation involved in ASR and DEF; influence of pore size on crystallization pressure (pertinent to the possibility that ettringite needles create significant stresses in gaps around aggregates); relative importance of hydraulic pressure and crystallization stress in F/Tdamage; influence of water on the response of concrete to applied strains (including temperature changes).

4:45 PM FF3.2

DIRECT OBSERVATION OF ICE FORMATION AND WATER CONTENT IN THE PORE SYSTEM OF HARDENED PORTANDITE CEMENT PASTES DURING FREEZE-THAW. Ian P. Swainson, Neutron Program for Materials Research, NRC, Chalk River, Ontario, CANADA; Erland M Schulson, Thayer School of Engineering, Dartmouth College, Hanover, NH.

0.5mm radius cylinders of deuterated hardened portlandite cements pastes (hcp's) with water-to-cement ratios w/c = 0.36 and w/c = 0.40were made. Neutron diffraction measurements were performed while the saturated hcp's were subjected to freezing and thawing over -43° to +20°C, at average rates of 2°C/hr. The structure of ice forming inside the pores of hcp appears to be ice Ih at these temperatures. Broadened ice "Bragg" peaks grew as a continuous function of temperature. On thawing, ice melts at a higher temperature yielding a hysteresis in ice content inside the pore structure. The degree of hysteresis during freeze-thaw is a function of pore size (determining the freezing point), pore shape (spheres should show no hysteresis), and possibly water migration. The w/c = 0.40 hcp was subjected to two freeze-thaw cycles. Irreversible ejection of liquid water from the pore system into the environment was observed during the first freeze, above ca. -23° C, after which the two cycles appear identical. This evidence of water migration through the pore system may explain the shape of the ice hysteresis near the bulk melting point, which is slightly wider than predictable solely by pore size/shape. There is no evidence of large scale modification of pore size/shape from brittle or plastic failure of the pore walls. Approximately twice the amount of ice formed in the w/c = 0.40 sample as in the w/c = 0.36 sample by -43°C. However, the hysteresis loops are very similar when ice content is scaled independently to unity at -43° C in both hcp's, indicating a similar pore size and shape distribution in both samples.

> SESSION FF4: TRANSPORT IN HIGH-PERFORMANCE CONCRETE Chair: Dale P. Bentz Wednesday Morning, November 29, 2000 Room 301 (Hynes)

8:30 AM *FF4.1

TRANSPORT IN HIGH PERFORMANCE CONCRETE. Lars-Olof Nilsson, Chalmers University, Dept of Building Materials, Gothenburg, SWEDEN; Jean-Pierre Ollivier, INSA, Laboratoire Materiaux et Durabilité des Constructions, Toulouse, FRANCE. HPC can be designed to be highly impermeable against ingress and leaching of various species in order to significantly improve the performance and service life, compared to normal concrete. Such a design is frequently based on controlling the transport properties by applying a material science approach. The paper deals with steady state and non-steady state transport of selected species, mainly moisture (water) and chloride. Transport properties, as well as chemical and physical binding properties, from early age to mature HPC are shown with a continuous comparison with normal concrete. Concrete mix designs include water-binder ratios from 0.4 and below and the effect of additives, especially silica fume. The state-of-the-art is summarised and some new results are added and discussed. The material science approach is mainly on a macro-level. Additionally, for moisture transport the significant differences between HPC and normal concrete, concerning moisture level dependency of the transport properties and the relation between transport and the state of moisture, as shown by sorption isotherms, are discussed. For chloride transport the effect of age, the significance of the high concentration of alkalis in HPC and the effect of moisture are especially analysed.

9:00 AM <u>FF4.2</u>

BEAM-BENDING METHOD FOR MEASURING PERMEABILITY OF CEMENT AND MORTAR II. RESULTS. <u>Wilasa Vichit-Vadakan</u> and George W. Scherer, Princeton University, Engineering Quad, Princeton, NJ.

When a saturated rod of Portland cement paste is bent, a pressure gradient is created in the liquid. As the liquid flows to eliminate the gradient, there is a decrease in the force required to sustain a constant deflection. By measuring the kinetics of force relaxation, it is possible to obtain the permeability of the sample, as well as its elastic modulus and creep function. We are reporting the evolution of permeability, elastic modulus, and creep function for Portland cement pastes with water-cement ratios varying from 0.4 to 0.7. The results show that the permeability can vary by as much as two orders of magnitude, depending on the water-cement ration and the age of the samples. The permeability results for w/c = 0.6 are compared with measurements made by the conventional method of pushing water through a plate. Both rods and plates were cast at the same time and permeability tests were performed a the same ages. The elastic modulus results are verified using pulse velocity measurements.

9:15 AM FF4.3

EFFECT OF CONDITIONING ON MOISTURE PROFILES IN HIGH PERFORMANCE CONCRETE. <u>Mette Geiker</u>, Technical University of Denmark, DENMARK; Peter Laugesen, Dansk Beton Teknik A/S, DENMARK.

The moisture content of concrete has a significant effect on the durability of concrete. Thus, the initial moisture content should be controlled in accelerated durability tests. As part of the evaluation of selected methods of testing the freeze/thaw resistance of high performance concrete (HPC), the effect of selected conditioning (drying and re-saturation) and freeze/thaw exposure on the moisture profile has been investigated. The work is based on testing moisture parameters in concrete specimens at various levels from the exposed surfaces after various combinations of drying, re-saturation, and freeze/thaw testing, mainly according to the so-called Bors method. The samples applied were 117 concrete prims (30 mm x 30 mm x 70 mm) and 20 slices (50 mm thick), all cut from cast concrete cylinders (150 mm). Most tests have been performed on a three powder concretes with an equivalent w/c ratio at 0.39. Selected testing has also been performed on three other concretes, ranging from $0.\bar{3}7$ to 0.45 in equivalent w/c ratio. The high w/c-ratio concretes were non-air entrained. When initiating the investigations it was expected that the low permeability of HPC would limit the moisture movements taking place The investigations showed that re-saturation of HCP is generally slow, causing the original water content (from before drying) not to be reached during the limited time available for conditioning samples prior to testing.

10:00 AM <u>FF4.4</u>

ANALYSIS OF IONIC TRANSPORT MECHANISMS IN HYDRATED CEMENT SYSTEMS DURING A DIFFUSION EXPERIMENT. <u>Eric Samson</u>, Yannick Maltais, Jacques Marchand, CRIB-Dept of Civil Engineering, Laval University; James J. Beaudoin, IRC-National Research Council, Ottawa, CANADA; Kenneth Snyder, National Institute of Standards and Technology, MD.

The mechanisms of ionic transport in hydrated cement systems during a simple diffusion experiment were investigated using a numerical model called STADIUM. The model accounts for the coupling between the various ionic fluxes, chemical activity effects and the chemical interaction of ions with the solid matrix. During the numerical simulations, the behavior of seven different ionic species and five solid phases were considered. The influence of various parameters (such as the reactivity of C4AF and the microstructural alterations induced to the solid by the various chemical reactions) were investigated. Numerical results are compared to experimental data obtained for well-cured paste and mortar samples.

10:15 AM <u>FF4.5</u>

PREDICTING ION DIFFUSION COEFFICIENTS OF HYDRATED CEMENT SYSTEMS. <u>Yannick Maltais</u>, Jacques Marchand, Eric Samson, CRIB-Dept of Civil Engineering, Laval University, Quebec, CANADA; Dale Bentz, Edward J. Garboczi, National Institute of Standards and Technology, MD.

In order to study the influence of cement composition on the ionic transport properties of hydrated cement systems, seven different paste mixtures and six different mortar mixtures were prepared. Test variables included type of cement (ASTM Type I, ASTM Type V and a white cement) and water/cement ratio (0.40, 0.60 and 0.80). All samples were cured in sealed conditions (wrapped in an adhesive aluminum foil) for six months. Pore solution extraction and chloride migration experiments were performed on all mixtures. The total porosity and the degree of hydration of all samples were also determined. In order to calculate the ionic diffusion coefficient of each mixture, all migration test results were analyzed using a numerical model called STADIUM. Diffusion coefficients were compared to the values predicted by the NIST hydration model (CEMHYD3D). Good agreement was found between the two series of data. The influence of the cement mineralogical composition on the ionic transport properties of paste and mortar mixtures is discussed based on the numerical results yielded by the CEMHYD3D model.

10:30 AM FF4.6

MAGNETIC RESONANCE IMAGING OF CONCRETE MATERIALS. <u>Bruce Balcom</u>, Department of Physics, University of New Brunswick, Fredericton, CANADA; Ted Bremner, Department of Civil Engineering, University of New Brunswick, Fredericton, CANADA.

The local water content in concrete materials is well known to effect the durability and strength of the material. A series of new magnetic resonance imaging (MRI) techniques have been developed in our laboratories over the last several years which have permitted studies of concrete freeze/thaw, concrete drying and local water redistribution between the cement paste matrix and porous light-weight aggregates. These MRI techniques permit flexible, non-invasive visualization of water content with sub mm resolution with image acquisition times of less than one minute in their latest implementations. This presentation will concentrate on the basis of our MRI techniques with their application to dynamic phenomena such as water redistribution in light-weight concrete and the propagation of freezing fronts in normal and light weight concrete as a function of cure time.

10:45 AM FF4.7

EXPERIMENTS AND SIMULATIONS OF CONCRETE MICROSTRUCTURE PERMEABILITY. <u>Eric N. Landis</u>, Shan Lu, University of Maine Dept of Civil & Environmental Engineering, Orono, ME; Nicos S. Martys, John G. Hagedorn, National Institute of Standards and Technology, Gaithersburg, MD.

In this study we are exploring concrete permeability and related durability issues by combining a high resolution three-dimensional scanning technique called x-ray microtomography with a lattice Boltzmann method for simulating fluid flow through a. porous media. Microtomographic scans produce three-dimensional images of concrete microstructure at spatial resolutions approaching one micron. This microstructural data can then be used as input data for flow simulations. Three dimensional image analysis is required to measure the pore network, and the connectivity of that network to the specimen boundaries. Experiments were conducted on concrete specimens with varying microstructure. Microtomographic scans were conducted at two different spatial resolutions (1.2 microns and 6 microns) in order to capture effects at different length scales. Simulations of fluid flow were carried out on this data. Results will be presented comparing experiment and simulation.

11:00 AM FF4.8

USING STATISTICAL DESCRIPTIONS OF MICROSTRUCTURE TO ESTIMATE DIFFUSIVE TRANSPORT COEFFICIENTS IN POROUS RANDOM MATERIALS. K.A. Snyder, Building Materials Division, NIST, Gaithersburg, MD; J. Marchand, Département de Génie Civil, Université Laval, Sainte-Foy, CANADA; D.P. Bentz, E.J. Garboczi, Building Materials Division, NIST; R.A. Cook, Department of Civil Engineering, University of New Hampshire, Durham, NH; P.E. Stutzman, Building Materials Division, NIST.

Accurate estimates of ionic transport within high performance concrete (HPC) require a precise characterization of the cement paste microstructure. The two-point correlation function is a suitable description of a porous solid microstructure such as cement paste. A unique objective would be to mathematically characterize the porous solid, estimate the formation factor, and then measure the formation factor experimentally. However, due to the chemical nature of cement paste, its microstructure is constantly changing, and the chemical composition of the pore solution can be difficult to know precisely. The method used here is to use a commercial alumina ceramic and a commercial Vycor glass as reference materials for both microstructural characterization and experimental measurement. A scanning electron microscope (SEM - secondary emission) image is used as input to a procedure for determining the two-point correlation function. This information is subsequently used both to reconstruct the microstructure and to determine the microstructural formation factor. The surface area of the reconstructed microstructure is compared to nitrogen sorption isotherm (BET) data, and the formation factor estimate is compared to impedance spectroscopy measurements using specimen saturation solutions at varying concentrations in order to factor out the surface conduction contribution. For porous solids saturated with concentrated electrolytes, an estimate of the formation factor is the most important parameter with which to predict long term performance. Even though the formation factor is measured experimentally using concentrated electrolytes, the formation factor, alone with the self diffusion coefficient, gives the response of the system at infinite dilution. Proper characterization of the ionic diffusion coefficient must consider not only the concentration of that ion, but also the concentration of all other ions present. The "conversion" between the formation factor and the material ionic diffusion coefficient is discussed.

11:15 AM FF4.9

THE INFLUENCE OF ELECTRO-DIFFUSION AND OTHER NON-IDEAL BEHAVIOR ON THE DETERMINATION OF THE IONIC DIFFUSION COEFFICIENT OF RANDOM POROUS MATERIALS. K.A. Snyder, Building Materials Division, NIST, Gaithersburg, MD; J. Marchand, Département de Génie Civil, Université Laval, Sainte-Foy, CANADA.

Determining the diffusion coefficient of saturated porous materials must account for the internal electrical diffusion potential that arises due to the variations in self-diffusion coefficients among the species present. Moreover, the ionic response to this diffusion potential is proportional to the ionic mobility. Not only is the ionic strength of concrete pore solution sufficiently large enough (approximately 0.5 to 1.0 molar) to invalidate the use of the Einstein relation between mobility and diffusivity, D = RT u, the concentration dependence of conductivity differs from that of the diffusion coefficient. These principles have been incorporated into a numerical calculation for the determination of the diffusion coefficient. The program not only accounts for ionic self-diffusion, it also incorporates a number of non-ideal behaviors: activity coefficients are calculated using the Pitzer equations; the diffusion potential is calculated from current conservation; and the concentration dependence of the mobility is calculated from conductivity data. The objective of the calculation is to determine the material formation factor. The computer program uses the formation factor to predict the response from experimental measurements. The estimated formation factor is that which gives a "best fit" to observed experimental data. Use of the program is demonstrated using experimental diffusion data from a commercial alumina ceramic as a model porous material that remains stable over the duration of the test. The insights gained from these measurements have a dramatic impact on the assessment of transport coefficients of cementitious materials. Further, these model materials may be used to study other modes of transport (electrically driven, Darcy flow, etc.) and combinations of modes.

11:30 AM FF4.10

SIMULATING THE CURING OF CONCRETE ON BRIDGE DECKS. <u>Gary S. Wojcik</u> and David R. Fitzjarrald, Atmospheric Sciences Research Center, University at Albany, SUNY, Albany, NY; Joel L. Plawsky, Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY.

It is generally accepted that ambient atmospheric conditions influence the state of freshly poured concrete and so may influence concrete's long-term durability. To limit problems such as cracking which may arise during early curing, engineers may benefit from accurate model forecasts of concrete temperature and moisture. Such information would allow them to determine an optimal time to pour. Existing models lack realistic boundary conditions and so cannot properly account for many atmospheric conditions. Also, they often ignore mass transfer, radiation, and mix design. We have developed a simplified modeling system for curing concrete bridge decks which is better suited for the field engineer. To determine proper boundary conditions for the model, we made energy balance estimates of 4 concrete bridge decks from atmospheric and concrete data collected on site over several days after placement. Our analysis suggests that at the bridge's top surface, from which most heat is lost, evaporation, convection, runoff water heat removal, and net radiation must be included explicitly in model boundary conditions since their relative importance to the energy balance changes depending on the ambient conditions. Our model includes a bimolecular (cementitious components & water) heat generation formulation for New York State Department of Transportation's high performance Class HP concrete (cementitious components: 74% cement, 20% flyash, 6% microsilica) which we developed by using calorimetry experiments. We assumed that cement hydration is a pseudo-first order reaction in water concentration (we used excess water) and we determined a temperature dependent, effective hydration rate constant for the Class HP concrete. With this formulation, the model can be easily adjusted for different water/cement ratios, while also being computationally efficient. We use the model to study the sensitivity of curing concrete temperatures to a variety of weather conditions.

11:45 AM <u>FF4.11</u> NUMERICAL STUDY OF THE INFLUENCE OF CEMENT SIZE DISTRIBUTION ON PORE SPACE AND TRANSPORT PROPERTIES DURING HYDRATION. Christian Pignat, Parviz Navi, Swiss Federal Institute of Technology, Laboratory for Building Materials, Lausanne, SWITZERLAND.

The characterization of the porous structure of cementitious materials is of fundamental importance for the understanding of their mechanical and transport properties, and consequently for their durability. The evolution of the microstructure of hardened cement paste and the related development of strength and transport properties, depend strongly on the cement particle size distribution. The use of computer models for simulating the development of the microstructure of cement paste during hydration, gives the possibility to investigate the relation between the particle-size distribution and the microstructure, as well as properties. Based on the continuum representation approach, we have implemented an Integrated Particle Kinetics Model, (IPKM) for three-dimensional simulation of the evolution of tricalcium silicate (C3S) microstructure during hydration. A particular type of spatial tessellation called the additive weighted Vorono diagram is applied to characterize the pore space of the simulated structure. By this method, each pore can be defined by its center and necks (interfaces with other pores). With this kind of characterization of the pore space, the permeability is calculated by solving Poiseuille and dArcy laws, considering the pore space as a network of cylindrical tubes. This method is multiscale since we can consider capillary pore sizes covering several orders of magnitude. The permeability is calculated and the influence of both the particle size distribution and the water-to-cement ratio, at different times, has been studied. Experimental validation of the model is in progress.

SESSION FF5: COMPUTERIZED SYSTEMS AND SHRINKAGE Chair: Jacques Marchand Wednesday Afternoon, November 29, 2000 Room 301 (Hynes)

1:30 PM *FF5.1

BUSINESS-TO-BUSINESS (B2B) e-COMMERCE APPLIED TO CONCRETE AND CONSTRUCTION. Farro F. Radjy, PhD., Digital Site Systems, Pittsburgh, PA.

The tidal wave of information technology (IT) has already engulfed much of Corporate America and has profoundly changed the way businesses operate across industries from manufacturing to construction, and concrete production and delivery. Additionally, during the recent years, e-commerce Web applications have fueled the rapid growth of an ever-increasing variety of business-to-business (B2B) e-hubs, corporate B2Bs, and Internet infrastructure technologies. In the construction industry, as evidenced at the AEC Systems annual June conference, we are witnessing nothing short of a B2B revolution. Within a short space of time over one hundred construction.coms have popped up, funded by estimated venture capital investments exceeding 0.5 bil. The most prominent of these construction B2Bs now have a commanding presence at construction sites, with web portals designed for community project administration, management, and collaboration. Within the same spaces, these construction B2B e-hubs are rapidly developing e-market places for e-procurement of everything from doorknobs to services and construction materials, including concrete. It is estimated that construction B2Bs are managing about 100 billion worth of construction, encompassing tens of thousands of projects and users. Meanwhile, the concrete and construction materials industries have still not transitioned to the B2B stage, and are at best in a state of confusion and self-introspection. A fundamental feature of the Internet-based information economy is the ability to separate products into physical and informational representations, and to use the informational dimensions for networking and collaboration.

Because of this, the B2B revolution has far reaching implications for the concrete industry including its operational, management, and organizational aspects. In this paper, after a review of the B2B fundamentals, and a discussion of the construction.coms, the current developments within the concrete industry are analyzed and future changes are mapped out. In conclusion it is shown that the impending $\mathbf{B2B}$ revolution within the concrete industry will provide an unprecedented opportunity for the distribution of scientific and technological know-how from the centers of research to the industry knowledge workers. However, to take advantage of this opportunity for a paradigm improvement of the industry, the research institutions must also become highly information technology oriented.

2:15 PM FF5.2

A WEB-BASED VIRTUAL CEMENT AND CONCRETE TESTING LABORATORY. Dale P. Bentz, Glenn P. Forney, Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD.

Worldwide, hundreds of thousands of concrete mixtures are prepared each year for the purposes of research, trial batching, and optimization. The goal of the Virtual Cement and Concrete Testing Laboratory (VCCTL) is to provide an Internet-based tool for reducing this number of concrete mixtures and expediting the research and development process via computer modeling. Following careful characterization of the real starting materials, computer models are applied to simulate the hydration and microstructure development of the cementitious binder. During and after hydration, a variety of properties of the model microstructures are assessed and can be compared to experimental data. The system is self-contained, menu-driven, and executable over the Internet. Thus, upgrades and enhancements are seamlessly distributed to the user community. A number of applications of the VCCTL to problems concerning high performance concrete will be presented.

3:00 PM *FF5.3

AUTOGENOUS DEFORMATION AND RH-CHANGE IN PERSPECTIVE. <u>Ole M. Jensen</u> and Per F. Hansen, Aalborg University, Institute of Building Technology and Structural Engineering, DENMARK.

As described in this paper, autogenous deformation and change of the relative humidity (RH-change) have been described and registered for a century. However, only within the last decade these phenomena have received appreciable attention. The reason for this is that autogenous deformation and autogenous RH-change are phenomena of special importance within high-strength (high-performance) concrete technology, and a significant utilization of these concretes did not take place until early 1980s. A characteristic feature of high-strength concrete is a low porosity and a non-connective capillary pore structure of the cement paste. This is encompassed by keeping a low water-cement ratio with the aid of superplasticizers and by adding silica fume to the mixture. From a material point of view these modern concretes generally posess some highly advantageous properties compared to traditional concrete. However, these types of concrete have also proved to present some problematic properties, such as autogenous deformation and RH-change. Micro-cracks due to restrained autogenous shrinkage may connect into a continuous crack pattern and form macro-cracks. Such cracks constitute a serious problem with regard to strength, durability and aesthetics. No contemporary, international review paper exists on autogenous deformation and RH-change. A good overview of research on autogenous deformation carried out in Japan is given in a report from the Japan Concrete Institute. A comprehensive state-of-the-art-report which was published in 1981 by a RILEM commission is outdated. In the present paper a historical overview of autogenous deformation and RH-change is given. In addition, due to the present status of this research field both terminology and measuring techniques are described in detail. Finally, some expectations for the future research in this field are given.

3:30 PM FF5.4

EARLY AGE VOLUME STABILITY OF CEMENT BASED MATERIALS. David Lange, Salah Altoubat, Hak-Chul Shin, Beril Bicer, Nathan Rau, Dept of Civil Engineering, University of Illinois, Urbana, IL.

Volumetric instability is one of the primary causes for early age cracking of concrete payements and structures. Creep and shrinkage of concrete under restrained conditions during the first days after casting have been characterized by experiments that provide data on shrinkage and tensile creep strains, restrained shrinkage stress and the extent of stress relaxation by tensile creep mechanism. Tensile creep of concrete has two major components- basic creep and drying creep (Pickett Effect which reflects the interaction with the surrounding environment). We discuss experiments and analysis that shows that drying creep itself has two components. First, a term associated with

stress-induced shrinkage, and second, a term associated with microcracking due to the non-uniformity of drying. Test results for normal concrete mixes with different w/c are discussed and related to general behavior. Effects of inclusion of steel fibers are explained.

3:45 PM <u>FF5.5</u> EFFECT OF CURING TEMPERATURE AND TYPE OF CEMENT ON EARLY-AGE SHRINKAGE OF HPC'S. Pietro Lura and Klaas van Breugel, Delft University of Technology, Delft, THE NETHERLANDS.

High Performance Concretes, characterized by low water-binder ratio, are particularly sensitive to self-desiccation of the cement paste in the hardening phase, which leads to autogenous shrinkage. Internal restraint in the mixture, due to the presence of the aggregates, may cause microcracking, in the weak interfacial zone. On the other hand, at the scale of the concrete structure, autogenous shrinkage, summed to thermal effects, may cause, if external restraint is present, surface and even through cracks, jeopardizing the durability. The mechanisms leading to autogenous shrinkage are yet poorly understood. Moreover, most of the experimental evidence refers to isothermal tests at room temperature. In the present research, the effects of different isothermal temperatures on early-age shrinkage of HPC mixtures have been investigated. Also the type of cement (Portland cement, blast furnace slag cement and a blend of the two) has been varied, in order to assess its influence on the early-age deformations. In addition, for every concrete mixture and curing temperature, also the self-induced stresses in case of total restraint have been measured. Finally, correlations between the early age deformations and the degree of hydration of the mixtures have also been found.

4:00 PM FF5.6

PREDICTION OF EARLY-AGE CRACKING AND HYGRAL SHRINKAGE CRACKING IN CONCRETE STRUCTURES Erik Schlangen, Ton van Beek, Bianca Baetens, INTRON B.V., Geldermalsen, THE NETHERLANDS.

Durability of concrete structures is strongly related to the microstructure of the concrete including cracks. Cracks are caused by external (mechanical) loading but also by internal processes like self-desiccation, autogeneous shrinkage, thermal and moisture effects. Especially this internal loading is governed by the properties and microstructure of the material. At INTRON a numerical model (HEAT of FEMMASSE) is developed to predict cracks in concrete structures. With this model a combined physical and mechanical analyses can be made of the behaviour in time of materials in a stucture. HEAT incorporates physical models for hydration, maturity development, temperature diffusion, and moisture movement. On the mechanical part the simulation of thermal, hygral and autogeneous shrinkage can be performed. Relaxation and creep combined with cracking, including softening, are integral components of the implemented material behaviour. To analyse the structural behaviour realistic boundary conditions that vary in time can be used, i.e. thermal and hygral boundaries and mechanical restraining. In the paper the background of the model will be explained and practical examples will be given of simulation of structures with High Performance Concrete. Engineering solutions will be explained of various cases in which the model is adopted to prevent cracking in concrete structures caused by different mechanisms.

4:15 PM *FF5.7

DRYING SHRINKAGE PERFORMANCE OF HIGH

PERFORMANCE CONCRETE. Neal Berke, K.A. Rieder, J. Malone, W. Yang, WR Grace & Co., Cambridge, MA.

Changes in typical concrete mixture proportions to result in enhanced strength or durability result in what is called high performance concrete. Concretes that are considered to be high performance often have water-to-cementitious ratios (w/cm) well under 0.4, 56 day compressive strengths in excess of 70 MPa, and low permeability to chloride and water (for example, less than 1000 C in the ASTM C $1202\ {\rm rapid}\ {\rm permeability}\ {\rm test}).$ High performance mixtures as defined above have high cementitious contents and lower aggregate contents, which might lead to increased shrinkage. In this paper, we examine the effects of calcium nitrite corrosion inhibitor and a glycol-ether based shrinkage reducing admixture on rheological, mechanical, permeability, and shrinkage properties of concretes with silica fume and fly ash at a w/cm = 0.24. The results show that the combination of inhibitor and shrinkage reducer improved workability and reduced drying shrinkage.

4:45 PM FF5.8

LONG-TERM SHRINKAGE OF HIGH-PERFORMANCE CONCRETE, HPC. <u>Bertil S.M. Persson</u>, Lund Institute of Technology, Lund, SWEDEN.

This article outlines seven-year experimental studies on shrinkage of

HPC with strength up to 170 MPa. Both carbonation, drying and sealed (autogenous) shrinkage were studied. The effect of aggregate type, air-entrainment, mix proportions, silica fume, and water-cement ratio, w/c, on shrinkage was evaluated. Weight losses, strength, hydration and internal relative humidity, RH, were studied in parallel to shrinkage. Depth of carbonation was also studied. The results indicate a substantial ongoing carbonation shrinkage of HPC, which was well correlated to the carbonation depth. Carbonation and carbonation shrinkage was almost eliminated by use of low-w/c concrete and sufficient amount of silica fume in the mix proportions. Drying shrinkage was found to be more or less constant independent of w/c. Sealed shrinkage was increasing at low w/c and clearly dependent on RH (self-desiccation). The amount and type of silica fume affected the size and development of the sealed shrinkage. The study was performed at Lund Institute of Technology, Lund, Sweden, 1993-2000.

SESSION FF6: MECHANICAL PROPERTIES, DURABILITY, AND FIELD PERFORMANCE Chair: Ole Mejlhede Jensen Thursday Morning, November 30, 2000 Room 301 (Hynes)

8:30 AM <u>FF6.1</u>

ENGINEERED CRACK-BRIDGING BY UNBONDED INCLUSIONS IN A CEMENTITEOUS MATRIX. Howard W. Chandler, Donald E. Macphee, Ian J. Merchant and Robin J. Henderson, Departments of Engineering and Chemistry, King's College University of Aberdeen, Aberdeen, Scotland, UNITED KINGDOM.

Cement-based materials are inherently brittle. Conventional toughening of cement materials has involved the use of fibres as crack bridges but their use has not been without practical problems. For example, the introduction of fibres to a cement/mortar mix, even at small fibre volume fractions, can lead to poor fibre dispersion and less than optimum performance. Where glass fibres are used, there is additionally the chemical incompatability of glass and the alkaline cement leading to gel formation and the loss of physical contact between fibre and matrix. The present paper considers an alternative,

fibre-free approach to toughening. In order to minimise its propagation energy, a macrocrack actively seeks out weaknesses in the matrix. These may be interfaces with poorly bonded aggregates, other cracks or porosity. The approach described in this paper aims to deliberately guide the crack towards a series of apparent weakness in the matrix. In practice, these regions contain crack bridging aggregate grains but they appear to the crack as empty pores because they are not bonded to the matrix. As the crack penetrates the interfacial region between the matrix and aggragate grain, some of its energy is dissipated by the limited movement of the matrix on either side of the crack direction as the crack attempts to open. Further crack opening is restricted by the shape of the aggregate which anchors the matrix on its irregular surface. Consequently, crack propagation is impeded or arrested and the matrix is toughened.

Two design approaches are presented. Results showing toughening increases by a factor of up to five are discussed.

8:45 AM <u>FF6.2</u> FIBRE-MATRIX BOND PEOPWETIES IN STEEL FIBRE REINFORCED SELF-COMPACTING CONCRETE. Henrik Stang, Mette Geiker, Technical University of Denmark, DENMARK.

Self compacting concrete, SCC, (i.e. concrete with rheological properties which allows the concrete to be placed in quite complicated form work without any kind of compaction) is a rapidly developing field. Recent experience also seems to indicate that SCC formulations are very compatible with fiber reinforcement. Typically, good homogenization is achieved along with excellent mechanical properties of the hardened material. The present paper addresses the issue of the mechanical properties in tension seen in relation to the structure of the material surrounding the fibers based on a series of experiments in tension and bending with steel fiber reinforced SCC. It is well known that the fiber-matrix bond property is one of the essential properties determining the overall mechanical behavior of fiber reinforced concrete in tension. Given the fiber strength and the fiber geometry, the bond should be high enough the produce significant de-bonding and pull-out resistance during crack opening, however it should not be so high that the fibers break during the de-bonding and pull-out. In the present paper an analysis of bending and uni-axial tension tests is presented which allows for back-calculation of the so-called stress-crack opening relationship which furthermore allows for analysis of the fiber-matrix bond properties. These properties are compared with data for traditional concretes of similar strength and the results are discussed from the view point of the micro-structure of the SCC.

9:00 AM FF6.3

EFFECTIVE MEDIUM THEORY FOR CONCRETE: THEORY.

James G. Berryman, Lawrence Livermore National Laboratory, Livermore, CA; Edward J. Garboczi, National Institute of Standards and Technology, Gaithersburg, MD.

Predicting the properties of concrete using effective medium theory is a difficult problem, because of the three-phase nature of the material: cement paste matrix, aggregates, and interfacial transition zone (ITZ) cement paste. A new method of applying differential effective medium theory to concrete properties, which involves mapping an aggregate grain plus accompanying ITZ into a single effective particle, is presented.

9:15 AM FF6.4

EFFECTIVE MEDIUM THEORY FOR CONCRETE:

APPLICATION. Edward J. Garboczi, National Institute of Standards and Technology, Gaithersburg, MD; James G. Berryman, Lawrence Livermore National Laboratory, Livermore, CA.

The new differential effective medium theory developed for concrete covers linear electric (diffusion), linear elastic, and linear thermal/ moisture expansion/shrinkage problems. The accuracy of this theory is demonstrated by comparison to essentially exact numerical results. The application of this effective medium theory to concrete is discussed

10:00 AM *FF6.5

THOUGHTS ON DURABILITY OF HPC. Jan P. Skalny, Holmes Beach, FL; Jacques Marchand, University of Laval, Quebec, CANADA

Is high-performance concrete the answer to all our durability problems? Is high performance always synonymous with durability? After a brief overview of microstructural features relevant to low water-to-binder-ratio mixtures, the durability of high-performance cement systems will be critically reviewed, with special emphasis on early-age behavior. The resistance of these systems to chemical degradation, reinforcement corrosion, and frost resistance will also be discussed.

10:30 AM *FF6.6

CONCRETES BASED ON SULFOALUMINATE-BELITE CEMENT. Fred P. Glasser and L. Zhang, University of Aberdeen, Old Aberdeen, SCOTLAND.

Water and water migration in conventional concretes results in chemical and physical coupling with their service environment and facilitates adverse reactions. However, it is easy to plasticise and form calcium sulfoaluminate-belite (CA) clinkers such that they undergo internal drying: all water is in chemical combination. As a consequence, the pore structure differs from that associated with traditional cements. C-S-H still has intrinsic gel porosity but lacks a coarse, interconnected pore network. Reduction of coarse porosity is also associated with maximization of ettringite and this maximization of ettringite content also results in high early strengths. Experiments on internal humidity measurements and on water migration are described. The stability of ettringite is reviewed briefly and it is concluded that sulfoaluminate-belite cements should have excellent resistance in a range of sulfate-containing groundwaters. These conclusions are supported by examination of sulfoaluminate concrete pipe exposed to sea water for 14 years.

11:00 AM FF6.7

CHARACTERIZATION OF HIGH AND ULTRA HIGH PERFORMANCE CONCRETE: APPLICATION TO THE STUDY OF WATER LEACHING. Charlotte Porteneuve, Héléne Zanni, Laboratoire de Physique et Mécanique des Milieux Hétérogénes, Ecole Supérieure de Physique et Chimie Industrielles, Paris, FRANCE; Christian Vernet, LAFARGE - LCR, Saint Quentin Fallavier FRANCE; Knut O. Kjellsen, NORCEM A.S., Brevik, NORWAY.

The storage of industrial and nuclear waste deep underground requires the use of good water leaching resistant materials. High and Ultra High Performance Concrete (HPC and UHPC) are potential candidates for this purpose. In the present study, we propose to characterize some HPC and UHPC actual formulations by Nuclear Magnetic Resonance (NMR). ²⁹Si NMR enables us to observe the silicates contained in these concrete, more specifically the amount and shape of calcium silicate hydrates. ²⁷ Al NMR allows us to observe the formation of Al containing species. The microporosity is studied through proton magnetization relaxation. The Calcium Silicate Hydrates (C-S-H) appear quite sensitive to some formulation parameters such as the amount and chemical reactivity of silica fume, the type of cement or the water to cement ratio. The C-S-H formed in UHPC present longer and less numerous silicate chains than in HPC. $^{27}\mathrm{Al}$ NMR allows to observe the incorporation of Al into the C-S-H

structure. The porosity features of UHPC observed by proton magnetization relaxation appear to depend on the amount of C-S-H. We also apply these different techniques to the study of the leaching of UHPC and HPC. They were indeed submitted to mineral water leaching in an open system for up to six months, in order to reproduce actual leaching conditions. The evolution of the microstructure is described, evidencing the better potential resistance to leaching of one concrete formulation over another.

11:15 AM FF6.8

CALCULATING LIQUID TRANSPORT INTO HIGH PERFORMANCE CONCRETE DURING WET FREEZE/THAW. Stefan Jacobsen, Norwegian Building Research Institute, Oslo, NORWAY

A model for vapour transport into High Performance Concrete (HPC) during wet freeze/thaw exposure is outlined. This transport gets much higher than absorption above $0^{\circ}{\rm C}.$ The model is based on flow of vapour from the Hardened Cement Paste (HCP) to larger voids in it. The driving force for the transport is lower vapour pressure over ice in the voids than in the saturated HCP. The small quantity of water in the voids is assumed to freeze at 0°C. Steady state flow is assumed since liquid is available at the concrete surface as non-freezeable vapour is flowing from saturated HCP towards ice in the voids of the frozen material. The maximum possible flow into the voids is calculated using Cranks solution for steady-state flow into a hollow sphere. The shell thickness is approximately equal to the mean void spacing factor (L). The flow into a void with mean radius r was then calculated as function of shell thickness (very good air void system; L = 0.1 r, fair; L = r, bad; L = 10 r). Various maximum possible vapour pressure differences between saturated paste and ice at different temperatures were used (-1°C; maximum possible $\Delta P = 550$ Pa, -10°C; maximum $\Delta P = 260$ Pa, -20°C; maximum $\Delta P = 100$ Pa). Realistic r (0,33 mm) and vapour permeabilities k $(10^{-13} \ 10^{-14})$ kg/(m Pa s)) were used. Calculated transport fits well with liquid uptake measured in HPC in wet freeze/thaw laboratory testing. The results also show that there will be less transport into HPC the poorer the air void system. The depth of saturation was 2,5 mm for the particular HPC. Flow was then assumed only into voids near the concrete surface, and with equal total surface area to the exposed concrete surface. Also, service-life calculations of HPC exposed to wet freeze/thaw are shown.

11:30 AM *FF6.9 Abstract Withdrawn.