SYMPOSIUM GG

Transport Properties and Microstructure of Cement-Based Systems

November 29 - 30, 1999

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*Invited paper
SESSION GG1: MICROSTRUCTURE
Chair: Sankar Bhattacharya
Monday Morning, Session 29, 1999
Room 207 (H)

8:30 AM *GG1.1
FRAC TURAL MICROSTRUCTURE AND GROWTH KINETICS MODEL FOR THE HYDRATION OF PORTLAND CEMENT
Richard A. Livingston, Federal Highway Administration, McLean, VA.

The microstructure of hydrated Portland cement results from a nucleation and growth process. Several investigators have modeled this process using conventional Kolmogorov-Avrami-Mehl-Johnson (KAMJ) kinetics. The result is typically an exponent with a non-integer value which very often assumes values for one-dimensional dimensions. The implication that the cement paste has a fractal microstructure is consistent with small angle neutron scattering studies. The proposed mechanism of microstructural development is diffusion limited aggregation (DLA) of the 5 nm globules of the clusters that grow by self-avoiding random walk (SAW) in the pore space between the grains. This yields an intrinsically fractal growth rate with a dimension ~ 2.6. The KAMJ impingement criterion is replaced by percolation when the clusters grow to a critical size. Prior to percolation, the clusters are free to move; after percolation, they are fixed in space. This transforms the growth process to a random walk by the globules on a random lattice, which results in a lower value for the fractal growth dimension ~ 1.5. The transition from d > 2 to d = 2 has been observed in the hydration of pure triclinic silicate, but may be obscured in the hydration of the multiphase Portland cement. The transition may also be associated with the appearance of one of the innerproduct microstructure in the paste. The fractal growth laws lead to an explicit incomplete Gaussian functional form for the nucleation and growth kinetics in place of the simpler stretched exponential form of the KAMJ theory.


9:00 AM *GG1.2
NANO SCALE TO MICRO SCALE CALCIUM SILICATE HYDRATE GEL STRUCTURE AND ITS EFFECTS ON WATER TRANSPORT PROPERTIES J. Allen, NIST, Materials Science and Engineering Lab., Gaithersburg, MD; Richard A. Livingston, FHWA, Turner-Fairbank Research Center, McLean, VA; Jeffrey J. Thomas and Hamlin M. Jennings, Northwestern Univ., Dept. of Civil Engineering, Evanston, IL.

There is increasing interest in the use of small-angle x-ray and neutron scattering (SAXS and SANS) to characterize cementsitious microstructures in their natural hydrated state. The intensity of the scattering, followed as a function of the scattering angle, is a kind of modified Fourier transform of the solid/pore structure over many length-scales (from one nanometer up to a micrometer). The scattering is observed directly by the interface between the calcium-silicate-hydrate (C-S-H) gel and the pore-water. Multi-component fractal models have been developed to interpret SAXS and SANS data, and to quantify the C-S-H gel structure as a function of hydration conditions and time. The period scattering at high scattering angles has also been used to measure the C-S-H gel/pore surface area evolution, directly. The key to obtaining quantitative microstructural parameters from scattering data is accurate composition and density information for the solid C-S-H gel. SANS contrast variation studies exploit the strong H/D neutron scattering isotope effect to determine possible C-S-H formule and densities. These values are governed primarily by the amount of water bound into or associated with each mole of C-S-H, and are thus intimately connected with the water mobility and transport within the cement microstructure. Despite low permeabilities reported for bulk hydrated cement mixes, the permeabilities of cement paste are found to exchange both their pore and bound C-S-H water readily when exposed to D2O. The implications of these studies will be discussed in relation to the water-transport properties through the overall fractal C-S-H gel structure.

9:15 AM *GG1.3
MODELING MICROSTRUCTURAL DEVELOPMENT IN HIGH PERFORMANCE CEMENT-BASED MATERIALS Dale Benz, National Institute of Standards and Technology, Gaithersburg, MD.

In recent years, high performance concretes have been produced with enhanced durability properties, generally due to their largely reduced transport coefficients. This presentation will focus on the special microstructural characteristics of these systems that lead to improved properties. Using three-dimensional computational microstructural models, the independent estimation of the bulking, surface area, porosity, and the microstructure and diffusion coefficients of cement pastes and concretes can be examined. In all cases, the diffusivity is greatly influenced by the water-filled capillary porosity and its percolation at further, in the systems studied, the microstructure is modified at the nanometer scale so that both capillary porosity and silica fume addition rate influence diffusivity. Parametric studies and comparison to available experimental data will be presented. Finally, an algorithm has been developed to predict the chloride ion diffusivity of concrete based on four inputs: water-to-cement ratio, silica fume addition rate, degree of hydration, and volume fraction of aggregates.

10:15 AM *GG1.4
EXAMINATION OF PORE STRUCTURE USING THREE DIMENSIONAL IMAGE ANALYSIS OF MICROTOgraphic DATA Eric Landy, Edwin Nasy and Alan Pettit, University of Maine, Dept. of Civil & Environmental Engineering, Orono, ME.

In this study we are exploring concrete microstructure and related durability issues using a high resolution three-dimensional scanning technique called x-ray microtomography. Microtomography is similar in practice to conventional medical CAT-scans, however a synchrotron x-ray source combined with a high-resolution detector allows to achieve a 3D spatial resolution of less than two microns. In previous studies we examined fracture characteristics of small mortar specimens by scanning the same specimens at different degrees of damage inflicted by a small loading frame. In this study we are exploring the microstructural changes brought about by this damage. Specifically we are interested in the changes in pore size distribution, and the addition of new paths to the surface. Using three dimensional image analysis techniques we are able to include and tag each individual void space inside the specimens. We can then extract information about the void spaces to make measurements such as the mean distance from any point in the specimen to a clear path of a certain dimension to the surface. Since our data includes multiple images of the same specimen, we are able to track changes in void properties as damage accumulates.

10:30 AM *GG1.5
TIME EVOLUTION OF SHRINKAGE MICROCRACKING IN YOUNG MORTAR AS OBSERVED WITH ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY Jan Bisschop, Jan van Mier, Delft University of Technology, Dept. of Civil Engineering and Geosciences, Delft, THE NETHERLANDS.

At early ages, drying and autogenous shrinkage may cause microcracking in cement-based materials. Microcracks may influence the transport properties of cement-based materials if they increase permeability; they are of importance from a durability point of view. In concrete and mortar, specimens drying shrinkage results in the development of [micro]cracks perpendicular to the specimen surface and forms typical cell-type cracking patterns. From a durability point of view, the depth of penetration into the specimen and the crack width of this type of shrinkage cracking is particularly important. In concrete and mortar both drying and autogenous shrinkage can result in microcracking due to restraining of aggregate particles. Important parameters of this type of shrinkage are the connectivity of the microcracks with the surface, the interconnectivity of the microcracks, and the crack widths. To determine the actual internal microcrack density and distribution in young mortar Environment SEM is used. A method has been developed to quantify microcrack microstructure by means of crack mapping. The crack mapping is performed at a relative humidity of 80-100% in ESEM, so the internal crack pattern is not overlapped by drying, as would be the case in conventional SEM. In this study the progress of the microcrack pattern in a OPC mortar is followed as a function of drying time. ESEM samples are prepared at certain intervals during drying and the (temporal) crack patterns are recorded. Knowledge of the time-evolution of shrinkage microcracks is important for coupled flow-shrinkage-crack growth modeling. Such models may play an important role in assessing the residual strengt of concrete that has suffered from the early age shrinkage cracking. An example is the combined lattice growth model and the molten-treatment model developed at TU-Delft, which must be tuned through critical comparison of the ensuing crack patterns under drying.

10:45 AM *GG1.6
CHARACTERIZATION OF THE GRANULAR PACKING AND PERCOLATION THRESHOLD OF POWDER REACTIVE CONCRETE Olivier Bonnemaison, Christian Vernet, Micheline Mercenneville, Pierre-Charles Aitcin, C. Ribot, Université de Sherbrooke, CANADA; Direction Scientifique, Bougoux; FRANCE; LMT, ENS de Cachan, FRANCE.

Reactive Powder Concrete, RPC, is a new cement-based material developed through microstructural engineering. RPC is composed of very fine powders, sand, crushed quartz, silica fume, all with particle size between 300 µm to 0.02 µm, and a low water content, W/C<0.2. A high dense matrix is obtained by optimizing the granular packing. This compactness confers to RPC ultra-high strength and durability.
The hydration kinetic of the cementitious matrix was studied using electrical conductivity and isothermal calorimetry. A linear relationship between the conductivity $\Lambda(t)$ and the degree of hydration $\omega$, was found as follows:

$$\Lambda(t) = A + B \times \omega$$

$A$ and $B$ are empirical constants.

Aq depends on the nature and dosage of mineral and organic components. $B$ is an invariant characteristic of the granular packing. From nine different RPC compositions, an average value of $B$ equal to 12.8 was determined with a correlation coefficient of 2.7. The capillary porosity percolation threshold was also deduced from this linear curve of hydration. In other words, the hydration space was discontinuous. This last result is in agreement with the prediction of the NIST microstructural model by Benz and Garboczi.

### SESSION GG2 TRANSPORT I

**Monday Afternoon, November 29, 1999**

### Room 207 (H)

#### 1:30 PM **GG2.1**

**NUMERICAL MODELING OF ION TRANSPORT MECHANISMS IN UNSATURATED CEMENT-BASED MATERIALS.**

Jacques Marchand, Eric Samson, Yannick Malott, Larry University, Dept of Civil Engineering, Quebec City, CANADA, SJO CO Technologies Inc, Quebec City, CANADA.

Over the past few years, the phenomena of ionic transport in unsaturated cement systems have been the subject of a great deal of attention. Most of the work published on the topic have emphasized the intricate nature of the problem and the paramount influence of chemical reactions on the transport mechanisms. Given the importance of the problem, numerous ways of modeling the chemical interaction of ions with the hydrated cement have been proposed. A brief review of these various approaches is presented. Each approach is evaluated on the basis of its ability to account for the influence of parameters such as the pore solution composition, the reversible nature of the reactions, and local moisture variations. Problems related to the implementation of these models in a numerical code are discussed. The influence of ongoing chemical reactions on the material transport properties is also addressed.

#### 2:00 PM **GG2.2**

**MODELING OF CHLORIDE PENETRATION INTO CONCRETE - TRACING FIVE YEARS FIELD EXPOSURE.**

Tao Luping, Lin Olof Nilsen, Chalmers Univ of Tech, Dept of Building Materials, Gothenburg, SWEDEN.

This paper presents the current development of the numerical model ClinCon for predicting chloride penetration into concrete. In the beginning of 1990s, as a part of work in a Swedish national research project, some 40 types of concrete specimens were exposed to sea water at five field stations in the west coast of Sweden for 5 years. The chloride profiles in concrete were measured after exposure of 0.5, 1, 2 and 5 years. These data of chloride profiles together with the transport properties of concrete measured in laboratory are used for modeling of chloride penetration into concrete. In the middle of 1990’s a numerical model for predicting chloride penetration into concrete called ClinCon was developed from our previous work. The model is essentially based on the current knowledge of physical and chemical processes involved in the chloride transport and binding in concrete. In this numerical model most of the factors affecting chloride penetration are considered in a relevant scientific way. The aim is to predict chloride penetration profiles by using those parameters as input data that can be measured independently without relying upon any curve-fitting procedure. With the help of increased knowledge and more available data from the field exposure, the model could be further developed. In the current development, the time-dependence of chloride binding and concentration-dependence of chloride diffusion were taken into account in the modeling. The predicted results are compared with those data measured from the field exposure tracking up to five years. The advantages and limitations of the model are discussed.

#### 2:15 PM **GG2.3**

**FACTORS INFLUENCING THE CHLORIDE DIFFUSION RATE IN CONCRETE STRUCTURES.**

Richard E. Wepner, Virginia Tech, Dept of Civil and Environmental Engineering, Blacksburg, VA.

Chloride ion induced corrosion of reinforced steel in concrete structures is a well known problem. Service life performance in various environmental field exposure conditions are needed to select concrete type and cover depths to minimize service costs. Service life modeling of structures in chloride-laden environments normally include a time-to-initiate corrosion and a time-to-cracking period. The
The concrete properties and materials characteristics of pavements with exceptional long-term performance were investigated from fourteen different pavement projects ranging between 11 and 33 years in age and covering three different climatic regions (wet-freeze, dry-no freeze, and wet-no freeze) in the United States. Field cores were evaluated in the laboratory for their compressive strength and porosity, as well as their water vapor permeability, which is a measure of the rate at which water molecules can pass through the concrete. The permeability is influenced by the concrete type, the environmental conditions, and the concrete microstructure. The results show that the highest permeability levels (between 300 and 3500 perms) were found in the wet-freeze region. Nonetheless, for these good performance pavements, permeability does not appear to be a critical factor.

The microstructure of the concrete was examined using scanning electron microscopy (SEM) and x-ray diffraction (XRD) analysis. The microstructure of the concrete was found to be generallyaccepted limits for air-entrained concrete. The microstructure of these concretes will be discussed.
to ensure that the flux of fresh water outwards is sufficient to prevent the inward diffusion of chlorides.

### 4:45 PM GG2.10

When a saturated rod of cement paste or mortar is bent, a pressure gradient is created in the liquid within the pores. As the liquid flows to eliminate the stress, the force required to sustain a constant deflection. By measuring the kinetics of the force relaxation, it is possible to obtain the permeability of the sample, as well as its elastic modulus and stress relaxation function. We have tested this technique on porous Yvoro (a well-characterized model for rigid porous materials), and on a series of cement pastes and mortars, and have found the results to be very good. With this method we can measure the permeability in a minute timescale, while applying very small stresses on the sample. It is possible to test very young samples, and to follow the change in a given sample over time.

**SESSION GG3: TRANSPORT II**

Chair: Taher El-Kordi

**Tuesday Morning, November 30, 1999**

**Room 207 (H)**

### 8:30 AM GG3.1
**NUMERICAL SIMULATION OF HYDRATION-DRIVEN MOISTURE TRANSPORT IN BULK AND INTERFACE PASTE IN HARDENING CONCRETE.** Klaus van Breugel, Delft University of Technology, Dept., THE NETHERLANDS; Eddie A.B. Koenders, Herrema International, Rotterdam, THE NETHERLANDS.

In real concrete, two types of cement paste can be distinguished, i.e., bulk paste and interface paste. Due to, among other things, the geometrical wall effect the interface paste will generally exhibit a higher porosity than the bulk paste. In this contribution the variation of the water/filler ratio over the "ribbon thickness" is calculated starting from a random distribution of the cement particles between two aggregate surfaces. Starting from a variable water/filler ratio and the associated formation of a microstructure as a function of the type and particle size distribution of the cement, the water/filler ratio and the reaction temperature. For the ribbon paste analysis the ribbon paste is subdivided into slices, each slice having a particular paste composition. In each slice the hydration process starts at the same rate, whereas with progress of the reaction process the rate of reaction between different slices starts to deviate. In the porous water-rich zone the drop of the relative humidity with progress of the hydration process, will be taken into account in the bulk paste. The hydration-caused difference in relative humidity will trigger a moisture transport within the ribbon paste in order to establish thermodynamic equilibrium. It will be explained how the moisture transport is influenced by allowing for a moisture gradient in the case of a pressure difference in the ribbon thickness.

**9:00 AM GG3.3**
**CHANGE IN WATER VAPOR DIFFUSION AND OTHER PROPERTIES IN HARDENED CEMENT PASTE DEPENDING ON RELATIVE HUMIDITY.** Jianchao Ji, NSF Center for Science and Technology of Advanced Cement Based Materials, Northwestern University, Evanston, IL.

Hardened Cement Paste (HCP) is a porous heterogeneous material consisting of dispersed particles like Calcium Silicate Hydrates (CSH) of at least micron to nanometer size forming a porous space on a nanometer scale. Surface forces play a dominant role. Thus adsorbed water molecules decrease the surface free energy. Further capillary condensates can be formed in the pores below bulk conditions acting due to capillary and disjoining forces. All these forces are able to change the structure and properties of HCP depending on the moisture content. One important feature is the transport capability for gases and especially for water vapor. Precise water vapor diffusion measurements were carried out in a closed system at 20°C using an electronic microbalance with continuous weight change monitoring. The thickness of the HCP specimen (θCP, w/H = 0.4) was less than 1 mm and the diameter 20 mm. The relative humidity (RH) were established above saturated salt solutions where the necessary pressure gradient was generated by 10% or less difference of RH between sample holder and the ambient balance device. The diffusion parameters were computed from the linear region and will be shown as functions of their RH mean values. These results are compared to carbonation occurring at atmospheric CO₂ content as well as changes in specific surface area (calculated with the new ESW method) from Nitrogen adsorption of prewetted specimen. Results over the complete RH range will be presented and discussed. This work was carried out at the Institute of Building Physics and Material Science BPM, University of Essen, Germany. The author gratefully appreciates the grant of DFG -German Research Foundation for his stay at ACRM Northwestern University.

### 9:15 AM GG3.4
**EVALUATION OF COMPATIBILITY BETWEEN REPAIR MORTARS AND BUILDING MATERIALS IN HISTORIC STRUCTURES BY THE CONTROL OF THE MICROSTRUCTURE OF CEMENT-BASED SYSTEMS.** Antonis Morougoulis, Asterios Biksos, Panos Mourtouhas, National Technical University of Athens, Dept. of Chemical Engineering, Section of Minerals Science and Engineering, Athens, GREECE.

Longevity of critical structures, like the historic monuments under conservation, are decided by the compatibility of the cement-based systems, which are used as repair mortars and building materials. The compatibility of various repair mortars to the porous building materials is evaluated by their performance in transport and evaporation, in terms of ion/moisture/vapor transport, and is related to their microstructural properties. It is proved that historic mortars could be disturbed by the differential transport behavior of the material components and deteriorated by the subsequently developed tension at the interfaces. The acceptance limits, defined by the original materials, indicate the micromechanical requirements that repair mortars have to fulfill, in order to be compatible and to infer longevity to the material structures. According to these requirements, aerial and hydraulic lime, and lime - cement based systems are prepared, at various mix proportions, water-to-cement ratio, and curing conditions, admixed with pozzolanic and crushed-brick additives and air entraining agents, to produce microstructurally controlled systems. Microstructural parameters during hardening are determined by mercury porosity and transport property analysis. Presently studied, in terms of vapor/moisture permeability, to judge the compatibility of the cement-based systems to the porous building materials of the original structures.

### 9:45 AM GG3.5
**PORE PRESSURE, TEMPERATURE AND MASS LOSS IN HPC AT HIGH TEMPERATURES.** Pierre Kalfin, François Dominique Monneteau, Daniel Quenard, Centre Scientifique et technique du bâtiment, Materials Dept., Grenoble, FRANCE.

HPC are subject to spalling under certain thermal and mechanical conditions. Spalling results from thermal, hydral and mechanical coupled processes. Modeling the spalling phenomenon therefore requires the use of a numerical simulation. The codes predict various fields, among them temperature, pore pressure, water content. The present work aims at providing experimental values of those fields for code validation, as well as at understanding the thermo-hydral process which leads to spalling in a heated piece of concrete. An original device was designed in order to make simultaneous measures of pressure and temperature at various positions in a concrete specimen [380 x 380 x 12 mm] heated on one face up to 800°C. This device was also continuously weighed during the tests, so that the mass loss, resulting mainly from water transport and loss, was recorded. This campaign was carried out in an ordinary concrete (OC) and a high performance concrete (HPC, 90 MPa). As expected, the pressure peaks were much higher than in HPC (48 bars) than in OC (20 bars). In HPC those pressures exceed the saturated vapor pressure. It is demonstrated the thermal expansion of liquid water plays a significant role. The experimental results show clearly that the pressure peaks and the plateau in the temperature curves confirms the hypothesis that the drying front is preceded by a quasi-saturated layer which acts as a moisture clog.

**10:00 AM GG3.6**

When ice forms at the surface of a porous body, the crystals must first detach from liquid in the body and move to a higher pressure region in the pores before the crystals can penetrate the pores. If freezing is suddenly nucleated at high undercoolings (as is typically the case in laboratory tests), then rapid crystallization causes steep pressure gradients within the pores of the body. Since negative pressure causes the body to contract, the gradient leads to differential shrinking and
stress, and this may be a mechanism for salt scaling. We have devised an experiment to test the magnitude of the resulting stresses: a plate of saturated porous material is covered with a layer of liquid, then cooled below the freezing point; when freezing is nucleated in the pool, the negative pressure created in the pores causes the plate to warp upward. Theoretical analysis indicates that the magnitude of the deformation depends on the temperature at which nucleation occurs, the permeability and rigidity of the plate, and the geometry of the sample. The permeability and modulus of the sample can be measured independently by a beam-bending method. In this paper, the measured definitions are compared to calculated values. The relevance of the stresses to scaling damage is discussed.

9:45 AM GG3.6
INFLUENCE OF MASS TRANSFER PHENOMENA ON THE DEGRADATION OF CEMENT-BASED MATERIALS BY FROST ACTION. Bruno Zehner, Laval University, Dept of Civil Engineering, Quebec City, PQ; ENNS Achan, Dept of Civil Engineering, Cachan, FRANCE; Jacques Jachob, Laval University, Dept of Civil Engineering, Quebec City, CANADA.

A numerical model was developed to investigate the mechanisms of frost action in cement-based materials. The model is derived from thermodynamic and kinetic considerations and divided into two parts. The system of equations of the first part of the model is constructed in such a way to predict temperature-induced phase transitions and the resulting transfers of mass within the material pore structure. All equations are written at the microscopic scale (scale of the material). The second part of the model deals with the generation of local pressures in the liquid and solid phases through the mass transfer and crystal growth. In this part of the model, all phenomena are considered at the pore scale (nanoscopic scale). The model rests on the assumptions that ice behaves as a perfect plastic body and the system of non-linear equations is solved numerically. The influence of various parameters, such as the rate of freezing and the minimum temperature of freezing, on the mechanisms of degradation. The effects of various protective measures, such as air entrainment, are also discussed.

10:30 AM GG3.7
EXPERIMENTAL STUDY RELATING CRACKING TO WATER PERMEABILITY OF CONCRETE UNDER LOAD. Corina Aldea, Masoud Ghandehari, Suresh P. Shah, NSF Center for ACBM, Northwestern University, Evanston, IL; Alan Kurr, NBS, Research Triangle Park, NC.

The goal of the research presented here was to study the relationship between cracking and water permeability of normal strength concrete. The present study is an ongoing extension of previous work relating cracking to concrete permeability performed at ACBM, Northwestern University, and a novel in the crack generation and crack control. 50mm slices were sawn from precast cylinders and used for the tests. The average crack mouth opening displacement (CMOD) of the induced cracks ranged from 0.2 to 3.0 mm. Cracking was characterized by CMOD, crack length and crack area, and water permeability by permeability coefficient and average flow rate. A feedback-controlled edge splitting test method used to generate crack width-controlled cracks. A predefined crack width was used to record the cracking history. Water permeability was evaluated by a low-pressure water permeability test for bonded specimens and CMOD specimens. The experimental results showed that water permeability of cracked material significantly increased with increasing crack width and flow rate was quite repeatable for the same cracking level. Among the considered parameters, crack parameters significantly affect water permeability. Crack parameters are not linearly independent, there is no direct relationship between water flow and crack length, while as comparable relationships exist between either CMOD or crack area and flow characteristics. One parameter, i.e., crack width, is therefore sufficient to characterize the relationship between cracking and water flow. Experimentally measured flow was compared to theoretical models of flow through cracked rocks with parallel walls and a correction factor accounting for the tortuosity of the crack was determined.

10:45 AM *GG3.8
RELATIONSHIP BETWEEN CONDUCTIVITY, DIFFUSION, AND LONG-TERM PERFORMANCE. Neal S. Berk, Anthony Aldykevicz and Marin Hicks, Grace Construction Products, Cambridge, MA.

Chloride induced corrosion of steel in concrete is one of the primary factors in the deterioration of concrete structures exposed to marine or deicing salt environments. Since new structures subjected to chloride exposure are expected to be in service for 50 to 100 years, the ability to predict when a threshold level for corrosion will be reached is critical to designing these structures. Thus, there is a need to be able to have reliable methods to estimate the rate of chloride ingress.

In this paper data are presented that show the effects of water-to-cementitious ratios on the effective diffusion coefficients of chloride. Conductivity measurements using electrochemical impedance spectroscopy and modified ASTM C 1202 (Rapid Chloride) techniques. The data generated show that the effective diffusion coefficients are linearly proportional to conductivity. Furthermore, decreases in conductivity over time relate to decreased effective diffusion coefficients. Finally, a few examples showing how these data can predict corrosion initiation times are given, thus providing the first part of a service life durability model.

11:15 AM GG3.9
THE INTERACTION BETWEEN THE RATE OF CORROSION AND STRESSES IN REINFORCED CONCRETE BEAMS. S.C. Yoon, H.R. Kim, Kojin Wang, Jason Weiss, Suresh P. Shah, NSF Center for ACBM, Northwestern University, Evanston, IL.

Concrete structures are deteriorating at an alarming rate. While a substantial body of research exists to describe the corrosion process of pristine concrete systems, this paper describes a recent study in which the corrosion and mechanical response were measured for beams exposed to various loading histories. Specifically, different levels of preloading were applied to generate damage while sustained loading was also used to investigate the interaction between load level and corrosion rate. Results illustrate that loading history can significantly influence the corrosion and mechanical response of reinforced concrete elements. Corrosion in cracked beams much faster than in uncracked beams, presumably due to the cracks which facilitate the ingress of aggressive agents to the surface of reinforcing steel. Specimens with high levels of loading illustrated higher corrosion rates. Corrosion of the beams under sustained loading illustrated a similar load deflection history until the point at which significant corrosion was initiated. After significant corrosion occurred, the crack/corrosion behavior varied in the increase in deflections which ultimately resulted in a creep/corrosion failure of high load level beams. Beams with higher loading levels were observed to have corrosion initiation sooner and undergo larger deflection. These results indicate that corrosion is accelerated in cracked structures and even further accelerated in structures where the load is maintained over a long-term period of time. This suggests the need for models which assess the impact of the loading history in addition to corrosion driving forces, environmental conditions, and material proportions.

11:30 AM GG3.10
FORMATION OF IRON OXIDES AT LOCATIONS DISTANT FROM A CORRODING REINFORCING STEEL BAR. Kalliqua K. Alligzami, Digby D. MacDonald, Center for Advanced Materials, The Pennsylvania State University, University Park, PA.

Iron oxides that form during corrosion of reinforcement in concrete accumulate around the steel bar causing concrete to crack. Iron ions can also be transported in the cement paste and form oxides at locations distant from the steel bar. During this study, iron oxides were observed in the cement paste surrounding coarse aggregates at a distance of 10 to 30 mm away from the corroding reinforcing steel bar. The oxides are located in a zone having a width of 0.5 to 4 mm surrounding the coarse aggregates. Research carried out in the past by various researchers aimed at identifying the properties of the porosity of the cement paste surrounding the coarse aggregates, or the microstructure of the interfacial transition zone around a corroding reinforcing steel bar. However, no studies have been reported yet on iron ions forming in the cement paste surrounding the coarse aggregates at locations distant from a corroding reinforcing steel bar. SEM observations and X-ray diffraction analysis of elemental oxides were made on concrete fractured surfaces in which iron oxides that form in the corroding reinforcing steel bar. The corrosion products cracked due to the burning forces of the corroding embedded reinforcement. The results show the concentration of elements in the cement paste surrounding the aggregates and the change in composition of iron oxidation and corrosion products at the aggregate/cement paste interface.

11:45 AM GG3.11
INFLUENCE OF CORROSION ON BOND STRENGTH IN REINFORCED CONCRETE. Masoud Ghandehari, Michele Zulli, Suresh P. Shah, NSF Center for ACBM, Northwestern University, Evanston, IL.

Constant current corrosion tests were performed on reinforcing bars embedded in concrete cylinders. The influence of the diameter of reinforcing bars and the diameter of cylinders on the extent of corrosion were examined. The relationship between the extent of corrosion and the interfacial bond properties were studied. The applicability of Parshad's law to predict the extent of corrosion was explored. The bulk modulus of the corrosion product was evaluated using fracture mechanics model.
SESSION G4/G6/Q6.1 JOINT SESSION: CEMENT-BASED MATERIALS AND WASTE CONFINEMENT
Chairs: Sarendra P. Shah and Robert W. Smith
Tuesday Afternoon, November 30, 1999
Room 203 (H)

1:30 P.M. *G4.1/Q6.1 SIMULATED MICROSTRUCTURE AND TRANSPORT PROPERTIES OF ULTRA HIGH PERFORMANCE CEMENT-BASED MATERIALS. Micheline Moreville, Lab of Mechanics and Technology, ENS de Cachan, FRANCE; Veronique M flute, Citele Richet, Lab of Materials Studies, French Atomic Energy Commission, Saclay, FRANCE; Jean Michel Trouillet, National School of Roads and Bridges, Marne-La-Vallée, FRANCE.

Ultrahigh-performance cement-based materials expected to be used in nuclear waste containers were submitted to a leaching test, in order to evaluate their long-term durability. Different phases of Portland cement, Portland + silicate fume (10% and 30%), all with a water/cement ratio of 0.2, but two of them heat-treated like Reactive Powder, were attacked by deionised water. SEM observation and quantitative image analysis confirm analytical phases and hydrates, porosity measurements, and calculation of the tritium diffusion coefficient using a diffusion cell, revealed two zones after leaching i.e. a sound zone underneath a degraded zone in which tricalcium and dicalcium silicates were dissolved. As a result of the research work was extended to the properties of the degraded zone, first the microstructure of the sound zone was simulated using the NIST hydration model elaborated by Bentz and Garboczi, searching for the microstructure-property relationships as the capillary pore space connectivity and diffusivity, after having determined the degree of cement hydration and tritium diffusion. Then the cement leaching was simulated and the properties of the modeled microstructure corresponding to the degraded zone were compared to the experimental results. Porosity and tritium diffusion were particularly influential factors of the long-term durability.

2:00 P.M. G4.2/Q6.2 PREDICTION OF THE LONG-TERM RELEASE OF HAZARDOUS SUBSTANCES FROM CEMENT-BASED MATERIALS TO WATER. Ase Andersson, Chalmers Univ, Dept of Building Materials, Göteborg, SWEDEN.

The chemical content in building materials, and the environmental risk these chemicals pose, represent a fairly new field of research. At the same time, customers are demanding more information about these questions, creating a need for guidelines and regulations for the building industry. The environmental risk of a substance can only be decided if the emission behaviour is known. As diffusive emissions, emissions from products, are responsible for severe ecological effects in the water environment, there is an increasing concern being aimed over building materials in contact with water, as possible sources. In this study the leaching of hazardous elements present in concrete additives are discussed. Additives are cement components which are used in cement chemistry to alter the properties of the cement paste in order to improve the performance of the concrete. The aim of the cement chemistry is to determine the efficiency of the leaching tests and discuss whether the tests are capable of delivering confident data to enable the prediction of long-term release of hazardous substances. Concrete with different additives were prepared. The concrete samples were prepared for the leaching tests and air and water leaching were performed. The results were evaluated according to the hydraulic conductivity of the samples. The results showed that the cement content had a significant influence on the leaching of the hazardous substances. The results showed that the cement content had a significant influence on the leaching of the hazardous substances. The results showed that the cement content had a significant influence on the leaching of the hazardous substances. The results showed that the cement content had a significant influence on the leaching of the hazardous substances.

3:30 P.M. G4.6/Q6.6 INFLUENCE OF LIMESTONE ADDITION ON CEMENT LEACHING MECHANISMS IN CEMENT-BASED MATERIALS. Sandrine Constantin, Jacques Marchand, Laval Univ, Dept of Civil Engineering, Quebec City; and J. Benson, NRC Materials Laboratory, Ottawa, CANADA.

In order to investigate the mechanisms of calcium leaching in cementitious based systems (C3S + CaO + C3A + SiO2 + Al2O3), limestone (L = CaO + MgO) was added to the samples. The samples were prepared by mixing and curing in an oven at 50°C for 24 hours, and then leached in distilled water for 24 hours. The results show that the addition of limestone decreases the leaching of calcium, and that the leaching of magnesium and silica is not affected. The results also show that the leaching of calcium is not affected by the substitution of limestone, and that the leaching of magnesium and silica is not affected.

In conclusion, the addition of limestone to cementitious based systems decreases the leaching of calcium, and does not affect the leaching of magnesium and silica.

Cement-based systems are used for radioactive waste storage. In this application, due to a very long service life, we have to consider a calcium leaching of the hardened cement paste by water. Tests have
shown that this phenomenon is driven by diffusivity. This parameter
depends on the microstructure of the cement paste including cracks
that are often present. In this paper we present experimental results
and modeling of the coupling between diffusivity and cracks.

The cracks are created in our samples by means of a compression
test. This is a displacement controlled test that allows us to control
the crack opening. Diffusion tests on samples obtained at three different
compression levels corresponding to three cracked states are then
performed using tritiated water. These tests show diffusivity is
affected by the existence of cracks and the main effect is observed
when there is kerosol flow of the cracks (e.g., in the post-peak regime
of the compression test). Finally we model the diffusion test in a
simple way assuming the cracks are delimited by parallel planes.

With this modeling we can explain the equivalent opening of the cracks which is of
the same order as the opening estimated using strain measurements or
image analysis.

4:00 PM  GG4.8/ QQ6.8
RELEASE OF INTERNAL SEALANTS, ADHESIVES,
WATERPROOFING AND ANTI-CORROSION CHEMICALS INTO
CONCRETE TO REDUCE PERMEABILITY. Carolyn Dry,
University of Illinois, School of Architecture, Champaign, IL.

Various types of hazardous wastes need engineered barriers to prevent
contamination. Concrete is a brittle and porous material which changes
dramatically over its lifetime. In order to design waste barriers using
any type of concrete, the most effective intervention occurs at the
time when it is needed during the life of the material and at the
location undergoing distress. Internally placed encapsulants
containing sealants, adhesives, waterproofing or corrosion chemical
are designed to release these chemicals where and when they are
needed. For example, brittle fibers containing adhesives or sealants
will release the chemicals when the matrix cracks, causing the fiber
to crack and release chemical. The case of corrosion one design allows
the fiber to be corroded, signaling the release of the chemical into the
rebar. Research from over a decade will be presented with special
emphasis on permeability, cracking and corrosion data. Results from
field testing and current work will be presented.

4:15 PM  GG4.9/ QQ6.9
CLAY-BASED GROUTING INTO THE EDZ FOR THE VAULT
SEALING. Yutaka Saida, Tomoko Fujita, JNC, Tokyo, Japan;
Kazuhiko Masumoto, Kajima Corp, Tokyo JAPAN; Neil A.
Glander, AECL, Mississauga, CANADA.

In the Japanese concept for the disposal of the high-level radioactive
wastes, the potential pathways for radioactive contaminant transport
would be sealed by a combination of tunnel plug, backfilling, and
grouting. The material for these engineered barriers would be
bentonite or a bentonite-based mixture under consideration for
long-term stability of the site. It is anticipated that an excavation
damage zone (EDZ) will exist immediately next to the tunnel, and that this EDZ will have a high hydraulic conductivity
as a consequence of the development of fractures during excavation.
It will be necessary to design the engineered barriers to interrupt the
migration of radionuclides through the EDZ, and one element of the design
will be grouting of the EDZ. Two tests of bentonite grouting for
sealing the EDZ were conducted in the granite rock at Atomic
Energy of Canada Limited’s Underground Research Laboratory. One
test was the trial for the development of grouting procedure and the
evaluation of grouting effectiveness, and the second test was a
demonstration of the grouting around the clay bulkhead of the Tunnel
Sealing Experiment (TSE). In the trial, grout was injected from a
diluted slurry (0.2% bentonite by weight) to a concentrated one
(8.0%) and the injection proportion of 4.0% was the most efficient.

The result of the seepage test around the zone of grouted EDZ showed
that grouting resulted in a reduction of permeability of the EDZ in
the floor of the tunnel. In the TSE, a bentonite-based grout
was injected into the EDZ adjacent to the clay bulkhead using the same
procedure as in the trial. Although the hydraulic pulse test didn’t indicate that the grouting greatly reduced the rock permeability, the
test was useful site-scale demonstration of bentonite grout injection for
the purpose of EDZ sealing around a tunnel bulkhead.

4:30 PM  GG4.10/ QQ6.10
STUDY ON EFFECTS OF HYDRAULIC TRANSPORT OF
GROUNDWATER IN CEMENT. Masahito Toyohara, Masaaki
Kasagi, Nuclear Engineering Laboratory, Toshiba Corporation;
Inoue, Masaharu, Noritsugu Matsuoka, Advanced Energy Design
& Engineering Department, Yawatahama, Japan; Masaaki Imamura, Planning Dept.,
Japan Nuclear Fuel Limited.

This paper discusses the effects of solution velocity through the
cementitious materials and formation of secondary hydrates. These
hydrates are produced by the reaction of hydrates in cement and
chemical compounds in groundwater. In Japan, the ground water
velocity is presumed to be high, and so its decrease in disposal
facilities for radioactive waste is very important in order to reduce the
release of radioactive elements to the environment. Cement is used for the
materials of disposal facilities due to its attractive properties. But
cement structures are not considered to decrease the groundwater
velocity because of the existence of voids or microfractures in it. Thus
the retention of the radioactive elements which have poor sorption on
engineering barrier and natural one is current problem. In recent
years, the state of the art in Switzerland, showed that the groundwater velocity in cementitious materials was
determined by filling the voids and microfractures due to the hydrates
(secondary hydrates) produced by the reaction of cement hydrates and
the compounds in groundwater. If the same reaction occurs under
our disposal condition, the migration of the radioactive elements with poor
sorption will be estimated to decrease. Therefore, our results
encourage us to study on the relation between the solution velocity and
formation of secondary hydrates. The columns experiments were
carried out to measure the amount of solutions through the
cementitious materials filled in a column. Hardened ordinary Portland
cement was grown into particles. After that, they were filled in the column (2cm diameter, 5cm long) and then the column allowed in
nitrogen atmosphere. The solutions were poured into the column and the
amount of solutions passed through the column was measured
periodically. The compounds in solutions were Na2CO3 or Na2SO4,
which were considered to be main ones of groundwater in Japan. Both
these compounds and their concentrations were selected as
parameters. The hydrates formed in the column were also measured
by XRD experiments. The experimental results showed that the
solution flow was terminated by formation of calcite (CaCO3), in the case of 1.8E-2 mol/L CO32- solution. At less than this
concentration, solution flows were decreased and eventually became
constant but were not terminated. From these results, the relation
between formation of secondary hydrates and dissolution of original
ones in materials determined the degree of solution velocity. In the
case of restricted concentration of compositions in groundwater, the
formation of secondary hydrates was expected to decrease
the groundwater velocity in cement structures in disposal facilities.

4:45 PM  GG4.11/ QQ6.11
IS AND XRD STUDY OF CEMENT-BASED MATERIALS
CONTAINING ORGANIC POLLUTANTS. Giovanni Dotelli,
Domenico Bonita, Politecnico di Milano, Italy; Dept. of Industrial Chemistry
and Chemical Engineering, Milano, ITALY; Isabella Natali Sora,
Università di Brescia, INFN and Dept. of Mechanical Engineering,
ITALY; Claudio M. Mai, Università di Milano Bicocca, Dept. of
Materials Science, ITALY.

Some kinds of hazardous organic pollutants, specifically the aromatic
amines, were immobilized by means of a cement-based S/S process.
The aromatic amines were preserved in organophilic clays before
solidification in the cement matrix. Monoliths with different types and
amounts of clays were prepared as well as, for comparison, virgin
clay samples and samples containing clays non wetted with
aromatic amines. The phase composition and the possible structural
alterations in the solid matrix introduced by the presence of the
organic material were studied from XRD data. Moreover the morphology and the size distribution of the various phases were studied
by SEM technique. Impedance spectroscopy (IS) measurements were
performed in order to gain information about the variations of
diffusivity, through the Nernst equation, induced by the presence
of the organic pollutant.

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