

SYMPOSIUM GG

Transport Properties and Microstructure of Cement-Based Systems

November 29 – 30, 1999

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* Invited paper

8:30 AM *GG1.1

FRACTAL NUCLEATION 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, although KAMJ theory assumes Euclidean dimensions. The implication that the cement paste has a fractal microstructure is consistent with small angle neutron scattering studies¹. The proposed mechanism of microstructural development is diffusion-limited aggregation (DLA) of the basic 5 nm globules into 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 $d_f > 2$ to $d_f < 2$ has been observed in the hydration of pure tricalcium silicate², but may be obscured in the hydration of the multiphase Portland cement. The transition may be also be associated with the appearance of the denser innerproduct micro structure in the paste. The fractal growth laws lead to an explicit incomplete Gamma functional form for the nucleation and growth kinetics in place of the simpler stretched exponential form of the KAMJ theory.

¹A.J. Allen, R.C. Oberthur, D. Pearson, P. Schofield and C.R. Wilding, *Phil. Mag B* 56 (3) (1987) p. 263.

²S. FitzGerald, D. Neumann, J. Rush and R. Livingston, *Chem. Mater.* 10 (1) (1998) p. 397.

9:00 AM GG1.2

NANOSCALE-TO-MICROSCALE CALCIUM-SILICATE-HYDRATE GEL STRUCTURE AND ITS EFFECTS ON WATER TRANSPORT PROPERTIES. Andrew 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 cementitious microstructures in their natural saturated 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 dominated 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 SANS and SAXS data, and to quantify the C-S-H gel structure as a function of hydration conditions and time. The Porod scattering at relatively 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 formulae 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 cements and concrete, thin coupons 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

MODELLING MICROSTRUCTURAL DEVELOPMENT IN HIGH PERFORMANCE CEMENT-BASED MATERIALS. Dale Bentz, 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 vastly 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 influence of self-desiccation and silica fume addition on 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 state. Further, in the systems with silica fume, 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 equation 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 MICROTOMOGRAPHIC DATA. Eric Landis, Edwin Nagy and Alina Petrell, 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 that 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 isolate and tag each individual void space inside the specimens. We can then use 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 important 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 Environmental SEM is used. A method has been developed to quantify shrinkage microcracking by means of crack mapping. The crack mapping is performed at relative humidity of 90-100% in ESEM, so the internal crack pattern is not overprinted by drying, as would happen 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 (temporary) crack patterns are recorded. Knowledge of the time-evolution of shrinkage microcracks is important for coupled flow-shrinkage-crack growth modeling. Such models can play an important role in assessing the residual strength of concrete that has suffered from the early age shrinkage cracking. An example is the combined lattice gas model and the mechanical lattice 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. Oliver Bonneau^{1,2,3}, Christian Vernet², Micheline Moranville^{1,3}, Pierre-Claude Aitcin¹, ¹CRIB, Université de Sherbrooke, CANADA; ²Direction Scientifique, Bouygues, FRANCE; ³LMT, 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 very dense matrix is achieved by optimizing the granular packing. This compacity 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 logarithm of conductivity $\ln(\sigma)$ and the degree of hydration α , was found as follows:
 $\ln(\sigma) = A_v + B_v \alpha$.

A_v depends on the nature and dosage of mineral and organic components. However, B_v is an invariant characteristic of the granular packing. From 19 different RPC compositions, an average value of B_v 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. At a degree of hydration of 26%, the capillary pore space was discontinuous. This last result is in agreement with the prediction of the NIST microstructural model by Bentz and Garboczi.

11:00 AM *GG1.7

MICROSTRUCTURE AND MINERALOGY OF PORTLAND CEMENT CURED AT 85°C. F.P. Glasser, Chemistry Department, University of Aberdeen, Old Aberdeen, SCOTLAND.

Portland cement has been cured at 85°C in a wet environment for up to 8 years. The cement, mixed to a water: solid ratio of 0.5, was cast into ~200g cylinders and cured at >98% humidity for 30 days at 25°C. Thereafter half the cylinders were cured at 85°C while the remainder continued to cure at ~20°C. At 20°C the proportion of unhydrated clinker decreased, from ~25 - 30% at 30 days to nearly zero after 8 years. But 85°C cure left much clinker unhydrated, despite retention of moisture. The microstructure and mineralogy were much altered by 85°C cure; a relatively non crystalline C-S-H persisted together with siliceous hydrogarnet, portlandite and a hydrocalcite-like phase. AF_t and AF_m , present in 20°C cures, are absent at 85°C. The sulfur is fractionated between C-S-H and hydrogarnet. Extensive microanalytical data are presented. As a consequence of formation of much hydrogarnet, the porosity of the matrix accessible to mercury increases from, ~12% at 20°C to > 20% cure following 85°C.

Some preliminary data are present on the impact of prolonged warm cure on blended cements with slag and fly ash. The implications for performance of cements in warm, humid environments are discussed. Strength and permeability are, as expected, adversely affected by conversion of low-density matrix formers to denser hydrogarnet.

11:30 AM GG1.8

MICROSTRUCTURAL ANALYSIS OF CONCRETE PAVEMENTS WITH EXCELLENT LONG-TERM DURABILITY. Keld A. Jensen, Will Hansen, Elin A. Jensen, Univ of Michigan, Dept of Civil and Environmental Engineering, MI.

The relation between microstructure, chloride permeability and durability was analyzed in 13 different high-performance concrete pavements (11 to 33 years old). All concretes were made from ordinary Portland cements and did not contain any fly-ash. Petrographic analysis showed that the concretes have a wide range in mix characteristics: water-to-cement ratio (0.34-0.69), coarse-to-fine aggregate ratio (0.62-1.81), aggregate type (gravel, limestone, granodiorite), air-content (3.1-9.4 vol.%), and air-void system. The maximum aggregate sizes were larger than those typically found in recent pavements and varied between 25.4 mm (1 in.) to 38.1 (1.5 in.). Macroscopically, these concretes were well-preserved; the aggregates were inert with no apparent alkali-silica-reactions or freeze-thaw cracking in the larger aggregates, and the air-void structure was adequate. However, detailed studies revealed that a few sections did contain secondary ettringite and gels in their pore structure. Some sections also showed water-induced dissolution at their base. Analysis of the chloride permeability, k , showed a systematic decrease in the permeability with increasing compressive strength (32.5 to 75.0 MPa). At 11.43 cm (4.5 inches) below the surface, the relation was: $k=4 \cdot 10^8 \cdot (f'_c)^{-3.39}$ ($R^2=0.70$), where f'_c is the compressive strength. The deep-core chloride permeability was always lower than 2000 coulomb at strengths as low as ~35 MPa. A significantly higher permeability of up to 7030 coulomb was observed at the surface of the concretes where the relation to strength was: $k=3 \cdot 10^9 \cdot (f'_c)^{-3.74}$ ($R^2=0.75$). The increased permeability was probably caused by microcracks and more pronounced for concretes which had been placed in relatively dry regions and a concrete with densely fractured granodiorite aggregates. Mercury porosimetry and detailed thin-section analysis of paste homogeneity, micro-cracking and alkali-silicate reactions are used to further determine the influence of the concrete microstructure on the chloride permeability gradients.

11:45 AM GG1.9

QUANTITATIVE XRD ANALYSIS OF COAL COMBUSTION BY-PRODUCTS BY THE RIETVELD METHOD. Ryan S. Winburn, Dean G. Grier, Gregory J. McCarthy, North Dakota State University, Dept of Chemistry, Fargo, ND.

Quantitative XRD (QXRD) analysis of coal combustion by-products (CCBs) and their hydration products is not straightforward. The

phases in CCBs typically have overlapping peaks, preferred orientation, and varying levels of crystalline order and solid solution. With such materials, the traditional internal standard QXRD method, the Reference Intensity Ratio (RIR) method, has two problems: (1) finding representative standards for determining RIRs, and (2) finding suitable analytical peaks. The Rietveld method, however, is well suited to model each of the problem characteristics. The application of the Rietveld Quantitative X-Ray Diffraction (RQXRD) to CCBs will be illustrated using the National Institute of Standards and Technology Standard Reference Material Fly Ashes, one of which (Class C; SRM 2691) has 11 crystalline phases. The results of the RQXRD analyses will be compared to results obtained previously by the RIR method. RQXRD analyses of other CCBs and their hydration products will also be summarized. This research is supported by the Department of Energy (Grant No. DE-FG22-96PC96207.)

SESSION GG2: TRANSPORT I

Chair: Edward J. Garboczi
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 Maltais, Laval University, Dept of Civil Engineering, Quebec City, CANADA, SIMCO 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 reports published on the topic have clearly 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 paste have been proposed. A brief critical 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 on-going 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. Tang Luping, Lars-Olof Nilsson, Chalmers Univ of Tech, Dept of Building Materials, Gothenburg, SWEDEN.

This paper presents the current development of the numerical model ClinConc for predicting chloride penetration into concrete. In the beginning of 1990's, as a part of work in a Swedish national research project, some 40 types of concrete specimens were exposed to sea water at the field station in the west coast of Sweden. 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 great useful for modeling of chloride penetration into concrete. In the middle of 1990's a numerical model for predicting chloride penetration into concrete called ClinConc 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 ambition 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 tracing 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. Weyers, 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 periods. The

time-to-initiate corrosion is the longest and most critical time period and is typically modeled by Fick's Second Law. Fick's Law includes an ionic diffusion constant. For concrete structures in chloride laden environments, the chloride diffusion constant is influenced by both the concrete type and the environmental exposure conditions. This presentation shall discuss the factors that influence the concrete chloride diffusion constant and provide suggestions for determining chloride diffusion constants for laboratory concrete mixtures and field structures.

3:15 PM GG2.4

THEORETICAL AND PRACTICAL CONSIDERATIONS FOR RAPID CHLORIDE MIGRATION TESTS. James Mackechnie, University of Cape Town, Dept of Civil Engineering, SOUTH AFRICA; Mark Alexander, University of Cape Town, Dept of Civil Engineering, SOUTH AFRICA.

Chloride resistance of concrete is critically important to the durability of reinforced concrete structures exposed to deicing salts or marine conditions. A number of rapid chloride migration tests have been developed to assess the chloride resistance of concrete but these tests have limitations of a theoretical and practical nature. The paper attempts to address how the concrete microstructure needs to be quantified in order to assess chloride resistance in a rational manner. Theoretical issues affecting these rapid chloride migration tests are discussed and their influence is illustrated from the results of a comparative testing programme. Findings from the laboratory testing suggest that rapid chloride migration tests may not be reliable in predicting long-term chloride resistance in service. The influence of longer-term effects on chloride resistance such as continued cementing reactions and chloride binding is also discussed.

3:30 PM GG2.5

CHLORIDE DIFFUSION IN ORDINARY, BLENDED, AND ALKALI-ACTIVATED CEMENT PASTES AND ITS RELATION TO OTHER PROPERTIES. Della M. Roy, Weimin Jiang and M.R. Silsbee, The Pennsylvania State University, Materials Research Laboratory, University Park, PA.

Chloride transport into cementitious materials is critical from the viewpoint of protection of reinforcement. Steady state chloride diffusion studies have been made of pastes of Type I Portland cement, its blends with different proportions of ground granulated blast-furnace slag. Very substantial reduction in diffusion has been found with increased proportion of slag. In addition, alkali activation has been shown to reduce the diffusion by at least a factor of two. Other properties determined include: density, porosity, pore size distribution (H_g), BET (N_2) surface area, shrinkage, compressive and flexural strength, leaching, alkali-aggregate reaction, freezing and thawing resistance. Comparisons are made with results of previous studies and with other blending components.

3:45 PM GG2.6

PHENOMENOLOGICAL MASS BALANCE BASED MODEL OF MIGRATION TESTS IN STATIONARY CONDITIONS. Marta Castellote, Carmen Andrade, Cruz Alonso, Institute of Construction Science Eduardo Torroja, CSIC, Madrid, SPAIN.

During the course of a steady-state migration test, three stages can be identified. The first one corresponds to the initial period in which the amount of chlorides that passes to the anolyte is negligible and can be defined as the necessary time for chlorides to penetrate through the concrete disc, saturating it. The second stage is the steady-state period, in which the flux of chloride ions through the specimen is constant, and finally, a third step where the amount of chlorides emerging in the anolyte starts to decrease. In order to understand these phenomena that take place during the test and to obtain a complete picture of the steady state migration system through the transference number values, a phenomenological mass balance based model of the evolution of all ionic species has been developed. This has been done by studying the processes that take place in each of the three zones in which the system can be divided (catholyte, anolyte and concrete disc) and calculating a key parameter comparable to the experimentally obtained one. The selected parameter (pH of the catholyte) is then calculated through a mass balance for each interval between two consecutive samplings. It is important to point out that concerning transference numbers, it is relevant the use of the appropriate one according to a definition previously suggested by the authors. The model can be applied when self-corrodable electrodes are used as anodes in order to avoid the discharge of chlorine gas by oxidation of the chloride ions.

4:00 PM GG2.7

TRANSPORT PROPERTIES OF CONCRETE PAVEMENTS WITH EXCELLENT LONG TERM IN-SERVICE PERFORMANCE. Phil Mohr, Will Hansen, Ivindra Pane, Keld A. Jensen, Elin A. Jensen, The University of Michigan, Ann Arbor, MI.

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 using a variety of test methods including strength, chloride permeability, air-void characteristics, and petrography. The purpose of this study was to determine the relationship between transport properties such as chloride permeability, compressive strength and the concrete microstructure to improving long-term pavement performance and durability in severe environments. Results show that chloride permeability is greatly reduced with increasing compressive strength. Second, very low permeability levels (less than 1000 coulombs) are obtained in higher strength concretes. This is best explained by the role the concrete microstructure has on both properties. As the microstructure develops, the capillary and gel pore structure densifies, and the strength and permeability develop. A trend between permeability and strength levels needed for long-term performance was observed with climatic regions. High permeability (i.e. above 4000 coulombs) and lower strength pavements were found in climates outside the wet-freeze region. Nonetheless, for these good performance pavements, permeability does not appear to be a critical factor. The concretes in the wet freeze region exhibit at worst moderate permeability, and in several cases low to very low permeability. Such pavements can be expected to require much greater protection from deicing salts and freeze-thaw damage. Thus for those pavements to perform well, lower permeability is essential. Petrography and mercury porosimetry were used to evaluate the concrete microstructure. The air-void system was found to be within generally accepted limits for air-entrained concrete. The microstructure of these concretes will be discussed.

4:15 PM GG2.8

IMPEDANCE SPECTROSCOPY OF FIBER-REINFORCED CEMENT-BASED MATERIALS: MODELING AND EXPERIMENTS. J.M. Torrents, Universitat Politècnica de Catalunya, Barcelona, SPAIN; A. Peled, S.P. Shah, T.O. Mason, Northwestern University, Evanston, IL; E.J. Garboczi, National Institute of Standards and Technology, Gaithersburg, MD.

The impedance response of conductive fiber-reinforced cement-based materials was investigated using model systems (conducting needles in aqueous solutions) and pixel-based computer modeling. The results obtained are capable of explaining the behavior of chopped fiber cement composites in terms of general features (dual impedance arcs), fiber aspect ratio, fiber orientation, debonding, pull-out, etc. The dual-arc behavior arises due to thin, resistive, and highly capacitive layers (e.g., oxide film and/or polarization/double layers) that reside on the surfaces of the conducting fibers. These layers are fully insulating at low frequencies (near DC), so that the highly conductive fibers behave as if insulating, i.e., they have negligible effect on the DC resistivity. At intermediate frequencies, however, these layers short out so that the fibers act as highly conductive elements in the microstructure. Spreading resistance effects from the ends of the fibers play an important role in the high frequency behavior. The frequency-switchable coating model has important ramifications for the development of smart concretes. This work was supported by the NSF Science and Technology Center for Advanced Cement-Based Materials.

4:30 PM GG2.9

RELATIONSHIP BETWEEN IONIC DIFFUSIVITY AND FLUID PERMEABILITY IN CONCRETE. Michael Thomas, K. Stonish, Department of Civil Engineering, University of Toronto, Ontario, CANADA.

Coefficients of ionic diffusion and water conductivity have been measured for a broad range of concretes. It is apparent that the coefficient of water conductivity (k) is comparatively more sensitive to concrete quality than the chloride diffusion coefficient (D). For the concretes studied, the value of k varied by almost 5 orders of magnitude whereas D varied by less than 3 orders. This phenomenon can be readily explained on the basis of differences in the pore structure between low-quality and high-performance concrete. However, the changing relationship between D and k has a profound effect on chloride transport due to combined diffusion and convection. For given potentials convective flow is far more dominant in low-quality concrete. In high-performance concrete diffusion may dominate even in the presence of a significant hydraulic pressure gradient. An example is given of a tunnel that passes through saline groundwater and carries fresh water under positive pressure. With high-performance concrete it is quite feasible that the rate of diffusion of chlorides into the tunnel liner is greater than the rate of flux of fresh water out through the liner. One analogy is that of a fish swimming upstream. In such a case, it may be more appropriate although somewhat counter-intuitive to use a concrete of lower quality

to ensure that the flux of fresh water outwards is sufficient to prevent the inward diffusion of chlorides.

4:45 PM GG2.10

BEAM-BENDING METHOD FOR MEASURING PERMEABILITY OF CEMENT AND MORTAR. Wilasa Vichit-Vadakan, George W. Scherer, Princeton Univ, Princeton, NJ.

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 gradient, there is a decrease in 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 Vycor (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 manner of minutes, 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: Tahar El-Korchi
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. Klaas van Breugel, Delft University of Technology, Delft, THE NETHERLANDS; Eddie A.B. Koenders, Heerema 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/binder over the "ribbon thickness" is calculated starting from a random distribution of the cement particles between two aggregate surfaces. Starting from a variable water/binder ratio over the ribbon thickness, the progress of the hydration process and the formation of the microstructure are simulated numerically with the simulation program HYMOSTRUC, developed at the TU Delft. This program simulates the progress of the reaction of cement with water and the associated formation of a microstructure as a function of the type and particle size distribution of the cement, the water/binder 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 less than in the bulk paste. This hydration-caused difference in relative humidity will trigger a moisture transport within the ribbon paste in order to establish thermo-dynamic equilibrium. It will be explained how the moisture transport is modelled, making allowance for the (calculated) difference in pore structure over the ribbon thickness. It is shown how the moisture transport affects the rate of hydration compared to the rate of hydration in plain paste. Results concerning the rate of reaction and the relative humidity changes during hydration are compared with recent measurements published in literature.

8:45 AM GG3.2

PORE PRESSURE, TEMPERATURE AND MASS LOSS IN HPC AT HIGH TEMPERATURES. Pierre Kalifa, François Dominique Menneteau, 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, hydal 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 the build-up of pore pressure in a heated piece of concrete. An original device was designed in order to make simultaneous measurements of pressure and temperature at various positions in a concrete specimen (30x30x12 cm³) heated on one face up to 800°C. The specimen 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 on an ordinary concrete (OC) and a high performance concrete (HPC, 90 MPa). As expected, the pressure peaks were much higher than in HPC (40 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 correlation between 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.

9:00 AM GG3.3

CHANGES IN WATER VAPOR DIFFUSION AND OTHER PROPERTIES IN HARDENED CEMENT PASTE DEPENDING ON RELATIVE HUMIDITY. Jürgen Adolphs, 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 (C-S-H) 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 condensate 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 micro balance with continuous weight change monitoring. The thickness of the HCP specimen (OPC, w/c=0.4) was less than 1 mm and the diameter 20 mm. The relative humidities (RH) were established above saturated salt solutions while 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 areas (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 IBPM, University of Essen, Germany. The author gratefully appreciates the grant of DFG -German Research Foundation for his stay at ACBM 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. Antonia Moropoulou, Asterios Bakolas, Petros Moundoulas, National Technical University of Athens, Dept of Chemical Engineering, Section of Materials Science and Engineering, Athens, GREECE.

Longevity of critical structures, like the historic monuments under conservation, are depended on the compatibility of the cement-based systems, which are used as repair mortar composites. The compatibility of various repair mortars to the porous building materials is evaluated by their performance in transport and evaporation, in terms of ionic/moisture/vapor transport, and is related to their microstructure. It is proved that historic masonries could be disturbed by the differential transport behavior of the material components and deteriorated by the consequently developed tensions at the interfaces. The acceptability limits, defined by the original materials, indicate the microstructural requirements that repair mortars have to fulfill, in order to be compatible and to infer longevity to the masonry 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 porosimetry and transport phenomena are 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.

9:30 AM GG3.5

PRESSURE GRADIENTS IN CEMENT CAUSED BY SUPERFICIAL FREEZING. Weimin Shen, George W. Scherer, Princeton University, Dept. Civil & Environmental Eng., Princeton, NJ.

When ice forms at the surface of a porous body, the crystals must drain liquid from the body and create a high negative pressure 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 shrinkage 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 pool 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 deflection 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 deflections 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 Zuber, Laval University, Dept of Civil Engineering, Quebec City, CANADA, ENS-Cachan, Dept of Civil Engineering, Cachan, FRANCE; Jacques Marchand, 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 in 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) by 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. The system of non-linear equations is solved numerically. The model was used to study the influence of various parameters, such as the rate of freezing and the minimal 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, Surendra P. Shah, NSF Center for ACBM, Northwestern University, Evanston, IL; Alan Karr, NISS, 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 is 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 50 to 300 microns. Cracking was characterized by CMOD, crack length and crack area, and water permeability by permeability coefficient and average flow rate. A feedback-controlled wedge splitting test was used to generate width-controlled cracks and speckle interferometry was used to record the cracking history. Water permeability was evaluated by a low-pressure water permeability test for loaded specimens at the designed CMOD. The experimental results showed that water permeability of cracked material significantly increased with increasing crack width and flow 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, where 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 CORROSION PERFORMANCE. Neal S. Berke, Anthony Aldykiewicz and Maria 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 exposures are expected to be in service for 50 to 100 years, the ability to predict when chloride threshold levels 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. Comparisons are made to 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, Kejin Wang, Jason Weiss, Surendra Shah, NSF Center for ACBM, Northwestern Univ., 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 assessed 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 is initiated 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 creep/corrosion behavior resulted in increased deformations 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-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. Kalliopi K. Aligizaki, 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 and the porosity of the cement paste surrounding the coarse aggregates, or the microstructure of the interfacial transition zone around a corroded reinforcing steel bar. However, no studies have been reported yet on iron oxides forming in the cement paste surrounding the coarse aggregates at locations distant from a corroding reinforcing steel bar. SEM observations and X-ray dot mapping of the principal elements were made on concrete fractured surfaces in which iron oxides formed away from the corroding reinforcing steel bar. The concrete specimens cracked due to the bursting forces of the corroding embedded reinforcement. The results show the concentration of elements in the cement paste surrounding the aggregates and the change in concentration of iron oxides with distance from the aggregate/cement paste interface.

11:45 AM GG3.11

INFLUENCE OF CORROSION ON BOND STRENGTH IN REINFORCED CONCRETE. Masoud Ghandehari, Michele Zulli, Surendra P. Shah, NSF Center for ACBM, Northwestern Univ., 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. Applicability of Faraday's law to predict the extent of corrosion was explored. The bulk modulus of the corrosion product was evaluated using fracture mechanics model.

SESSION GG4/QQ6: JOINT SESSION:
CEMENT-BASED MATERIALS AND WASTE
CONTAINMENT

Chairs: Surendra P. Shah and Robert W. Smith
Tuesday Afternoon, November 30, 1999
Room 203 (H)

1:30 PM *GG4.1/QQ6.1

SIMULATED MICROSTRUCTURE AND TRANSPORT PROPERTIES OF ULTRA HIGH PERFORMANCE CEMENT BASED MATERIALS. Micheline Moranville, Lab of Mechanics and Technology, ENS of Cachan, FRANCE; Véronique Matte, Cécile Richet, Lab of Materials Studies, French Atomic Energy Commission, Saclay, FRANCE; Jean Michel Torrenti, National School of Roads and Bridges, Marne-la Vallée, FRANCE.

Ultra-high 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 pastes of portland cement, portland + silica fume (10% and 30%), all with a water/cement ratio of 0.2, but two of them heat-treated like in Reactive Powder Concrete, were attacked by de-ionised water. SEM observations and quantitative image analysis of cement anhydrous 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 the aim of the research was to determine 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 diffusivity. 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 PM GG4.2/QQ6.2

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 aired over building materials in contact with water, as possible sources. In this study the leaching of hazardous elements present in concrete additives are discussed. The objectives are to analyse the results of present 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 additives were fly ash, slag and accelerating and air entraining admixtures. Substances that were focused upon were metals e.g. copper, chromium, lead, manganese and two active ingredients in admixtures: thiocyanate and tall oil. Two different leaching tests have been carried out, basically adhered to the Dutch standards NEN 7341 (availability test) and NEN 7345 (diffusion test). A selection of the results obtained in the leaching tests are discussed with regard to their correlation to existing models for leaching of cementitious materials, such as diffusional models and models involving a shrinking dissolution front. In addition, several phenomena that will affect the leaching rate are presented. For example, leaching of portlandite causing an increase of porosity and a change of pH, and penetration of CO₂ causing precipitation of CaCO₃, will prevent the emission rate from correlating to Ficks law of diffusion.

2:15 PM GG4.3/QQ6.3

POROSITY AND LEACHABILITY OF CEMENT SOLIDIFIED WASTE-PART I. Tahar El-Korchi, Department of Civil Engineering, Worcester Polytechnic Institute, Worcester, MA; David Gress, Department of Civil Engineering, University of New Hampshire, Durham, NH.

Cement solidification is being used as a stabilization technology for managing of heavy metal wastes prior to land disposal. In this paper, cement solidified waste was leached using synthetic seawater and acid solutions to simulate aggressive environments. The heavy metal wastes included cadmium, lead, chromium, and arsenic. Chemical analysis included heavy metal release, pH and alkalinity. Microstructural analysis on the solidified waste and precipitates

include SEM, EDAX, X-ray diffraction and mercury intrusion porosimetry. The metal leaching results are explained in terms of porosity and microstructural developments during solidification and hydration of the cement and during the dynamic leaching process.

2:30 PM GG4.4/QQ6.4

MODELING THE POROSITY AND LEACHABILITY OF CEMENT SOLIDIFIED WASTE-PART II. Tahar El-Korchi, Department of Civil Engineering, Worcester Polytechnic Institute, Worcester, MA; David Gress, Department of Civil Engineering, University of New Hampshire, Durham, NH.

In this paper, the leaching behavior of cement solidified waste is modeled using diffusion and dissolution models. The models are developed and tested using the heavy metal release data, pH and alkalinity reported in Part I. The heavy metal wastes included cadmium, lead, chromium, and arsenic. Microstructural analysis on the solidified waste and precipitates include SEM, EDAX, X-ray diffraction and mercury intrusion porosimetry. The metal leaching models are explained in terms of porosity, permeability, and pore size distribution. Microstructural developments during solidification and cement hydration and during the dynamic leaching process are incorporated in the leaching models.

3:15 PM GG4.5/QQ6.5

DIMENSIONAL ANALYSIS OF IONIC TRANSPORT MECHANISMS IN CEMENT-BASED MATERIALS.

Rémi Barbarulo, Direction des études et Recherches, Electricité de France, Moret-sur-Loing, FRANCE; Jacques Marchand, Centre de Recherche Interuniversitaire sur le Béton, Université Laval, Sainte-Foy, CANADA.

From an engineering point of view, the mechanisms of ion interaction are quite important. Not only do they play an important role in the development of deleterious chemical reactions but they also affect the transport of ions through the material pore structure. In most recent service-life prediction models, the influence of on-going chemical reactions on the mechanisms of transport is usually taken into account by assuming the existence of a local equilibrium, i.e. that the rate of precipitation (or dissolution) is much faster than the rate of ionic transport. In order to validate this hypothesis, a dimensional analysis of various ionic transport problems currently encountered in civil engineering has been performed. The dimensional analysis allows to compare, on a theoretical basis, the rate of ionic transport to the rate of chemical reaction. This approach has been applied to various cases involving chloride and sulfate ions. The analysis clearly shows that the local equilibrium assumption is verified in most practical cases. The results of this theoretical analysis are compared to experimental results obtained on various cement-based systems.

3:30 PM GG4.6/QQ6.6

INFLUENCE OF LIMESTONE ADDITION ON CALCIUM LEACHING MECHANISMS IN CEMENT-BASED MATERIALS.

Sandrine Catinaud, Jacques Marchand, Laval Univ, Dept of Civil Engineering, Quebec City, CANADA; Jim. J. Beaudoin, NRC, Materials Laboratory, Ottawa, CANADA.

In order to investigate the mechanisms of calcium leaching in cement-based materials, four different systems (C3S, C3S + C3A + CaSO₄.2H₂O, C3S + C4AF + CaSO₄.2H₂O and cement) were prepared and hydrated. In addition to the mineralogical composition of the system, test variables also included the percentage of calcium carbonate addition (0, 5, 10 and 20%). Sixteen different mixtures were blended and tested. In all cases, the water/solid ratio was fixed at 0.5. After a minimal curing period of 3 months, 1-mm thick samples of each system were cut and immersed in distilled water for a 90-day period. The kinetics of degradation were assessed by thermal and X-ray diffraction analysis after 10, 20, 40 and 90 days of immersion. The influence of calcium leaching on the volumetric stability of the various systems was also followed by length change measurements. Test results clearly indicate that the mechanisms of leaching are directly affected by the mineralogical composition of the system. The phenomenon of leaching also appears to be particularly sensitive to the calcium carbonate content of the mixture. The mechanisms of calcium leaching are discussed from a theoretical point of view. Their implications on the long-term durability of cement-based materials are also discussed.

3:45 PM GG4.7/QQ6.7

COUPLING BETWEEN DIFFUSIVITY AND CRACKS IN

CEMENT BASED SYSTEMS. Claire Tognazzi, LMDC, Toulouse, FRANCE; Jean Michel Torrenti, ENPC, Paris, FRANCE; Jean Pierre Ollivier, Myriam Carcasses, LMDC, Toulouse, FRANCE.

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 unavoidable. 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 localization 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 model we obtain an 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 outflow. 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 encapsulators containing sealants, adhesives, waterproofing or corrosion chemicals 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 chemicals. In the case of corrosion one design allows the fiber to be corroded, signaling the release of the chemical onto 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 Sugita, Tomoo Fujita, JNC, Tokai, Ibaraki, JAPAN; Kazuhiko Masumoto, Kajima Corp, Tokyo JAPAN; Neil A. Chandler, AECL, Manitoba, 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 of long-term stability of the seals. It is anticipated that an excavation damaged zone (EDZ) will exist in the rock immediately adjacent 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 nuclides 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 granitic 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 (TSX). 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 TSX, 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. Masumitsu Toyohara, Masaaki Kaneko, Nuclear Engineering Laboratory, Toshiba Corporation; Fumiyo Matsumura, Norimasa Mitsutsuka, Advanced Energy Design & Engineering Dept., Toshiba Corporation; Yasutoshi Kobayashi and Mitsutaka Imamura, Planning Dept., Japan Nuclear Fuel Limited.

This paper discusses the effects of solution velocity through the cementitious materials on 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 radio-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 radio-elements which have poor sorption on engineering barrier and natural one is current problem. In recent years, the studies reported by PSI, a research institute in Switzerland, showed that the groundwater velocity in cementitious materials was decreased 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 reactions occur under our disposal condition, the migration of the radio-elements with poor sorption will be estimated to decrease. Therefore, their results encouraged us to study on the relation between the solution velocity and formation of secondary hydrates. The column experiments were carried out to measure the amounts of solutions through the cementitious materials filled in a column. Hardened ordinary Portland cement was ground 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⁻ of 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, Donatella Botta, Politecnico di Milano, Dept. of Industrial Chemistry and Chemical Engineering, Milano, ITALY; Isabella Natali Sora, Università di Brescia, INFM and Dept. of Mechanical Engineering, ITALY; Claudio M. Mari, Università di Milano Bicocca, Dept. of Materials Science, ITALY.

Some kinds of hazardous organic pollutants, specifically the aromatic amines, were immobilised by means of a cement-based S/S process. The aromatic amines were pre-sorbed 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 cement 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.