SYMPOSIUM KK

Design, Characteristics, and Properties of Cementitious Materials

November 26 – 28, 2001

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* Invited paper

SESSION KK1: MICROSTRUCTURE, HYDRATION AND CHARACTERIZATION I
Chair: David Bonen
Monday Morning, November 26, 2001
Republic A (Sheraton)

8:30 AM OPENING REMARKS

8:45 AM *KK1.1
ARE THERE GEL PORES IN HARDENED CEMENT PASTE?
Sidney Diamond, Purdue Univ, School of Civil Engineering, West Lafayette, IN.

For many years it has been almost universally considered that a substantial portion of the pore space in hardened cement paste consists of gel pores, a special class of ultrafine pores within otherwise solid CSH particles. The history of the gel pore concept is reviewed, and an attempt is made to critically assess some of the limited experimental evidence that pertains to the subject.

9:15 AM KK1.2
AUTOGENOUS SHRINKAGE IN HIGH-PERFORMANCE CEMENT PASTE: AN EVALUATION OF BASIC MECHANISMS.
Pietro Lura, Klaas van Breugel, Technical University Delft, Faculty of Civil Engineering, Delft, THE NETHERLANDS.

High Performance Concretes, characterized by low water-binder ratio and by the addition of silica fume, are particularly sensitive to self-desiccation of the cement paste in the hardening phase, which is a principal cause of autogenous shrinkage. Shrinkage, added to thermal effects, may cause, if external restraint is present, surface and even through cracks, jeopardizing the functionality and durability of a concrete structure. The mechanisms leading to autogenous shrinkage are poorly understood. While there is general agreement about the existence of a relationship between autogenous shrinkage and relative humidity change in the cement paste pores, three different mechanisms are invoked to explain it: change in the surface tension of the solid gel particles, disjoining pressure and hydrostatic tension in capillary water. For each of these approaches, knowledge of the development during hydration of the pore volume and pore size distribution, the state of water in the capillary pores, the relative humidity and the development of the stiffness are needed. In synthesis, one should know the development of the microstructure of cement paste as hydration proceeds. In the present research, an evaluation of different basic mechanisms to explain autogenous shrinkage is presented. The development of the microstructure during cement hydration is simulated with the program HYMOSTRUC. With HYMOSTRUC it is possible to quantify the evolution of the pore structure, the free and adsorbed water, the relative humidity and the stiffness of the hardening cement paste. Calculations of the autogenous deformations according to the different proposed mechanisms, i.e. change in the surface tension, disjoining pressure and capillary tension, are integrated in the model. It is thus possible to compare the different mechanisms and to verify the relative humidity range where each mechanism is prevalent. The results are compared with autogenous shrinkage measurements performed by the authors and with literature data.

9:30 AM KK1.3
STUDIES USING 27Al MAS NMR OF AFm AND AFt PHASES IN HYDRATES OF DIFFERENT CEMENTS AND THE IMPLICATIONS FOR CHLORIDE BINDING.
Roderick Jones, Dundee University, Dept of Civil Engineering; Donald Macphee, Aberdeen Univerity, Dept of Chemistry; Raul Lannegrand, Cementos El Monte, S.A., Departamento de Calidad y Laboratorio; Geoff Hunter and Sandy Chudek, Dundee University, Division of Inorganic Chemistry, School of Life Sciences.

For the engineer the premature ingress of chloride ions into reinforced concrete containing carbon steel is a major problem. It affects important, as well as expensive, infrastructure worldwide and concrete technology researchers have spent considerable efforts over the past 25 years devising more durable concrete. There is broad agreement that blending cements is one way forward but the problem is that the range of blending combinations is enormous. Which is the most effective? One of the most difficult parts of this question to answer is which cement blends provide the most active and reliable binding sites with respect to chlorides. This paper will describe the application of Magic Angle Spinning technique to overcome line broadening problems due to para-magnetics with use of NMR to study the chemical environment of 27Al-bearing phases in Portland cement based concrete. A specific methodology will be described which allows reliable spectra to be measured for combinations of different types of cements and fillers (in this case portland cement, fly ash, slag, silica fume, metakaolin and limestone flour). As well as the study of "molecular structure" of cement matrix the paper will provide data on the time-dependant chemical changes affecting both the hydrates and pore solutions. Finally, the nature of the chloride/hydrate binding phenomena will be described to provide a reasonable robust and fundamental picture of the role different cements can play in the provision of overall concrete durability for a chemical perspective.

10:15 AM KK1.4
A STUDY ON THE HYDRATION BEHAVIOR OF HIGH PERFORMANCE CONCRETE ANALYZED BY SRA.
Ping-Kun Chang, Van Nung Institute of Technology, Dept of Civil Engineering, Chungli, Taiwan, R.O.C.

In this research the Synchrotron Radiation Accelerator (SRA) was applied to analyze the hydration behavior of high performance concrete (HPC) Pastes. The complicated procedures such as making vacunm, drying and sputter coating are unnecessary for tested specimens. In other words, during the research the specimens under absolutely normal situation were studied proceding the whole hydration inspection and evaluating the chemical ingredients. The result shows that this sutdy also indicates that by SRA, could be used for both the qualitative analysis and the quantitative analysis of the crystal structures as Ettringite (AFt), Monosulfoaluminate (AFm) and Ca(OH)2. Therefore, the reasons to cause unstable concrete volume, concrete crack and leak become clearer. The addition of pozzolanic admixture localized industrial waste material such as fly ash in the concrete is beneficial to the durability, safety, workability, economy and ecology of the concrete.

10:30 AM KK1.5
ISOTHERMAL CALORIMETER STUDY ON THE INFLUENCE OF LIMESTONE POWDER ON CEMENT HYDRATION.
Xiangjun Xiong, Klaas van Breugel, Dept of Civil Engr & Geosciences, Technical Univ of Delft, Delft, THE NETHERLANDS.

Limestone powder or crushed limestone has been used in the manufacture of composite cement in France, The Netherlands and many other countries since the 1980s. As early as in 1906, Candlot mentioned that the addition of a very fine limestone powder showed a greater increase of strength than with the addition of slag. From literature study we know that: 1. Limestone powder demonstrates chemical reactivity by accelerating the hydration of C_3A and C_3S rather than a mere "filler effect". 2. Limestone powder has beneficial effect on increasing the early age (< 72 hours) strength and it decreases the water of consistency significantly. In addition, an increase of the limestone powder will increase the chemically bounded water. 3. Limestone powder can accelerate ordinary Portland cement hydration. However, there have been few researches done on the effect of limestone and on the combined effects of limestone, slag and other mineral fillers on the hydration of Portland cement and slag cements. This contribution focuses on the kinetics of the influence of limestone powder on the hydration processes of Portland cement and slag cement in the early ages using isothermal Calorimetry. The temperature of isothermal calorimeter study was 20, 30, 40, and 50°C. The weight percentage of limestone was 15% and 25% and water-solid ration was 0.4 and 0.6. In addition, percentage of chemically bounded water was also measured up to 91 days. Mechanical property of cement paste was also measured at 1 day, 3 days and 7 days. Finally, the influence of limestone content, water cement ratio and slag content on the apparent activation energy for cement mixed with limestone powder was also determined. All these findings and other findings in studies on fly ash, slag, and silica fume were utilized in extending the HYMOSTRUC model developed in Technical University of Delft, which is already quite successful in modeling the hydration processes of Portland cement and microstructure development.

SESSION KK2: MICROSTRUCTURE, HYDRATION AND CHARACTERIZATION II-MODELING AND TRANSPORT
Chair: Paul E. Stutzman
Monday Afternoon, November 26, 2001
Republic A (Sheraton)

1:30 PM *KK2.1
THE COMPUTATIONAL MATERIALS SCIENCE OF CEMENT AND CONCRETE: PAST SUCCESSES, FUTURE CHALLENGES.
Edward Garboczi, NIST, Building Materials Division, Gaithersburg, MD.

This talk will present an overview of current progress in the computational materials science of cement and concrete. Novel techniques that have been developed for handling the complexities of cement and concrete, including how real images and models of cement and aggregates have been fruitfully combined, will be discussed. Future challenges that need to be overcome in order to make further progress will be analyzed.

2:00 PM KK2.2
THREE DIMENSIONAL MICROSTRUCTURE ANALYSIS OF NUMERICALLY SIMULATED CEMENTITIOUS MATERIALS. Guang Ye, K. van Breugel, A.L.A. Fraaij, Delft Univ of Tech, Faculty of Civil Engr and Geosciences, Delft, THE NETHERLANDS.

In order to predict the transport properties of porous media, such as permeability and conductivity of cementitious materials, a better understanding of the microstructural characteristics, including the geometrical and topological properties, is required. In this contribution, the microstructure of cementitious material is simulated using the cement hydration model HYMOSTRUC. In this computer-based numerical model, the hydrating cement grains are modeled as gradually growing spheres. A spatial network which is the basis of the microstructure is formed with the contact of the growing spheres. This simulated porous medium can be described as a series of sections taken from three orthogonal directions, in which each unit (pixel) is filled either with a solid or a fluid phase (pores). Various algorithms based on a random walk process are utilized to determine the set of connected fluid phase in each section. Local geometrical information such as gravity center's coordinate, perimeter and area of each individual pore are recorded. The percolating path of the fluid in three dimensions is traced by using an overlap algorithm. At the same time, a translation factor is determined by finding the normal direction to the line connecting the gravity center of each two overlapping pores. From this translation factor, the hydraulic radius and throats of the flow channel can be found by comparing the local minimum from three orthogonal directions. Both 3D geometrical information such as internal surface area, volume or characteristic size distribution and Topological space characterization including branch node network and genus of the pores are derived. Calculation results of these algorithms are compared to the numerical results calculated by other microstructural models at various degree of hydration.

2:15 PM KK2.3
COMPUTATION OF ALKALI AND HYDROXYL CONCENTRATIONS IN HYDRATING OPC/SILICA FUME MIXTURES USING CEMHYD3D. R.J. van Eijk and H.J.H. Brouwers, University of Twente, Department of Civil Engineering, University of Twente, Enschede, THE NETHERLANDS.

In this paper the NIST CEMHYD3D model is used for prediction of alkali and hydroxyl pore water concentrations in hydrating OPC and OPC/silica fume mixtures. Degrees of hydration, fractions of C-S-H and (water filled) porosity were computed using CEMHYD3D. Taylors model was used to describe release and sorption of alkalis into the pore water. The binding capacities of cementitious C-S-H and pozzolanic C-S-H with respect to sodium and potassium were determined according to binding experiments done by Song and Glasser. Using this information and using CEMHYD3D, alkali concentrations could be computed as a function of time of hydration. Hydroxyl concentrations were computed as a function of hydration time, considering a small set of relevant solid equilibria, (e.g. the portlandite equilibrium) and Pitzers method for calculating activity coefficients. Results were compared with pore water measurements reported in literature, yielding good agreement.

2:30 PM KK2.4
THE EFFECTS OF CURING ON THE DEVELOPMENT OF CAPILLARY POROSITY IN MORTOR SAMPLES. Nancy Whiting, Minnesota Dept. of Transportation, Office of Materials and Road Research, Maplewood, MN.

Test conditions similar to ASTM C156 Standard Test Method for Water Retention by Concrete Curing Materials were used to examine the effectiveness of five different curing methods. Five sets of mortar samples were cast in 25 cm round by 5 cm deep pans and cured for 28 days under controlled environmental conditions. Each set of mortar samples were subjected to a different curing method: two sets were treated with different concrete curing compounds, a third set was covered with plastic sheeting, a fourth set was cured in a lime bath and the final set of mortar samples were left untreated. The curing environment was controlled by placing samples in a cabinet in which the temperature was held at 37.8 ± 1.1°C, relative humidity was held at 32% ± 2%, and evaporation rate, measured as moisture loss, was held between 2.0 and 3.4 g/h. The loss of hydration water through evaporation was monitored as a percentage of mass loss for all samples for 28 days. Moisture loss test results were compared to the capillary porosity of the mortar samples at 3, 10 and 28 days. The capillary porosity was examined microscopically using fluorescent-dyed epoxy-impregnated thin sections and transmitted ultraviolet light. At 3 days, 10 days and 28 days samples representing each curing method were removed from the pan, cut, polished and placed in ethanol in a covered container. (Ethanol was used to halt the hydration process until thin sections could be prepared.) The development of capillary porosity will be examined and compared to the moisture loss for all curing methods.

3:15 PM *KK2.5
MOLECULAR DYNAMICS MODELING OF WATER-SOLID INTERACTIONS IN CEMENT SYSTEMS. R. James Kirkpatrick, Andrey Kalinichev, Jianwei Wang, Department of Geology and ACBM Center, University of Illinois at Urbana-Champaign, Urbana, IL.

Molecular processes at the interface between pore solution and solid phases control the many of the chemical reactions in cement systems but remain poorly understood. Computational chemistry is an effective tool to study these processes, and we present here results of molecular dynamics modeling of the structural environments and dynamical behavior of water molecules and a variety of cationic and anionic species on and near the surfaces of portlandite, AFm, ettringite, and tobermorite. The results provide significant insight into not just the surface structure but also the effective diffusion coefficients of surface-sorbed species, their surface lifetimes, rotational and translational dynamics, and the controls of the solid structure and composition on the structure of the fluid near the interface. Although the quality of molecular dynamics simulations is highly dependent on the quality of the interatomic potentials used, here this technque is preferable over, e.g., quantum chemical techniques, because it allows simulations of relatively large systems (up to thousands of atoms) over relatively long periods of time (100 - 200 ps).

3:45 PM KK2.6
MODELING DIFFUSIVE TRANSPORT IN CEMENTITIOUS MATERIALS CONTAINING CONCENTRATED ELECTROLYTES. Kenneth A. Snyder, Building and Fire Research Laboratory; Joseph B. Hubbard, Advanced Chemical Systems Laboratory, NIST, Gaithersburg, MD; Jacques Marchand, CRIB, Département de Génie Civil, Université Laval, Sainte-Foy, Quebec, CANADA.

Modeling saturated diffusive transport in cementitious systems requires a thorough characterization of the electrolytic pore solution. In typical cement systems the ionic strength can be 0.5 mol/kg, or more. Under these conditions, a suitable diffusive transport equation must account for the thermodynamics, the ionic interactions, and the bulk electrolyte properties. An electro-diffusion equation based only on the thermodynamics and the coulombic interactions has successfully characterized diffusive transport in porous alumina specimens that were saturated with various electrolytes having ionic strengths of approximately 0.1 mol/kg. This same equation can successfully characterize ionic transport of salts in bulk water; parameter-free calculations are compared to published data. To characterize the diffusive transport of arbitrary ionic species in concentrations above 0.1 mol/L, a transport equation must also account for the dynamic behavior of the ionic species. Here, the dynamic behavior of the ionic species will be characterized by the electrolyte viscosity. A viscosity correction is added to the existing electro-diffusion equation and parameter-free calculations of the apparent salt diffusion coefficient in bulk water are compared to data published in journals and handbooks. The results suggest that the viscous correction extends the accuracy of the electro-diffusion equation to approximately 1.0 mol/L for arbitrary ionic species. The advantage of the electro-diffusion equation is the manner in which the various contributions are expressed separately, in a physically meaningful way, giving insights into the behavior of ionic species. Further, the multiplicative viscous correction suggests a connection to mode coupling theory, which may give further insights into the relative contributions of equilibrium and dynamical components of the transport equation.

4:00 PM KK2.7
THE EFFECT OF TEMPERATURE ON A DIFFUSION-REACTION TRANSPORT EQUATION FOR CEMENTITIOUS SYSTEMS CONTAINING CONCENTRATED ELECTROLYTES. Pierre Henoq, Jean-Michel Lallement, Eric Samson, Jacques Marchand, CRIB, Département de Génie Civil, Université Laval, Sainte-Foy, Quebec, CANADA; Kenneth A. Snyder, Building Materials Division, NIST, Gaithersburg, MD.

The onset of degradation in cementitious systems is largely controlled by both the transport of ionic species through the pore system, and the reaction of ionic species with the minerals within the solid structure. A diffusion-reaction transport equation simultaneously characterizes both the transport and the reaction in a synergistic manner. Previously, a suitable diffusion-reaction transport equation has been demonstrated for cementitious materials containing concentrated electrolytes at ambient laboratory conditions. Concrete in the field, however, is subjected to variations in both relative humidity and temperature; variations in relative humidity have been addressed elsewhere. An existing diffusion-transport equation has been extended to account for the effect of temperature on both the transport and the reaction of the ions. The chemical activity of the ionic species are estimated from Pitzer equations, with the addition of temperature coefficients for the range 0°C to 250°C. These estimates

are then used to determine the appropriate thermodynamic correction to the diffusive transport. In addition, the temperature dependent chemical activity is used to determine the equilibrium species concentrations, given the available minerals, by minimizing the Gibbs free energy. The resulting diffusion-reaction transport equation is unique because it is the first implementation of a temperature-dependent speciation algorithm working in cooperation with transport equation that also accounts for thermodynamic effects. The transport equation has been implemented in a computer program, and results from calculations are compared to laboratory and published data.

4:15 PM KK2.8
UNDERSTANDING THE FLOW OF CEMENT PASTES.
Howard W. Chandler, Department of Engineering, University of Aberdeen, Aberdeen, SCOTLAND; Donald E. Macphee, Department of Chemistry, University of Aberdeen, Aberdeen, SCOTLAND.

This paper presents a new model of the bulk flow of cementitious pastes experiencing small amplitude vibrations important in the placement of concretes. It makes use of the lastest advances in soil mechnics developed in the context of liquefaction during earthquakes to explain not only the reduction in yield stress but also the strain rate dependency of pastes. Chemical factors are incorporated through the permeability of the paste and the viscosity of the fluidising medium. Existing rheological models do not properly take account of the two phase nature of pastes where the skeleton of particles and the fluid matrix can support differing levels of stress. The approach used here is based on an understanding of the way particles in a paste interact and how the stress carried by the fluid phase influences this interaction. Consequently, this model is also uniquely capable of simulating subtle rheological features. These include the lock-up seen when a vibrating poker is moved too quickly, and 'backlash', which occurs when a paste is cyclically stretched and compressed slowly inducing a weakening of the paste and psuedo-elastic behaviour. Some laboratory based results are discussed in terms of the model.

SESSION KK3: CHARACTERIZATION TECHNIQUES
Chair: Donald E. Macphee
Tuesday Morning, November 27, 2001
Republic A (Sheraton)

8:30 AM *KK3.1
CHARACTERIZATION AND MONITORING OF CEMENT-BASED SYSTEMS USING INTRINSIC ELECTRICAL PROPERTY MEASUREMENTS.
W. John McCarter, Malcolm Chrisp, Gerry Starrs, Dept. of Civil and Offshore Engineering, Heriot Watt University, Edinburgh, Scotland, UNITED KINGDOM.

The electrical response of a saturated porous material can be quantified in terms of the fundamental parameters conductance and capacitance. Monitoring these intrinsic electrical parameters as a function of frequency of applied electrical field represents the area of a.c. impedance spectroscopy (IS) and is now a developing technique in the characterization of cementitious systems. The underlying mechanisms responsible for impedance behaviour are directly related to the physical and chemical properties of the material which makes IS a potentially powerful diagnostic method. A number of additional features make this testing methodology of interest: the method is non-destructive and non-invasive; samples need not be restricted to cement pastes as mortars and concretes can also be studied, and continuous monitoring can be carried out under normal ambient pressures and temperatures. The overall aim of this paper is to highlight the application of electrical property measurements as an investigative technique in the study of cementitious systems at the micro- and macro- scale. Both fixed-frequency and spectral measurements are exploited to study cement pastes, mortars and concretes and results will be presented from both laboratory-based investigations and field-monitoring (durability) research programs.

9:00 AM KK3.2
IMPEDANCE SPECTROSCOPY OF CONDUCTIVE FIBER-REINFORCED COMPOSITES.
L.Y. Woo, M.A. Campo, and T.O. Mason, Northwestern Univ, Dept of Materials Science and Engineering, Evanston, IL; E.J. Garboczi, National Institute of Standards and Technology, Building Materials Division, Gaithersburg, MD.

The addition of particles or fibers to cement-based matrices affects not only their mechanical properties (modulus, strength, toughness, etc.), but also on their electrical properties (DC conductivity, AC impedance, etc.). This is especially so when the added particles/fibers are highly conductive with respect to the matrix. The present study addresses the microstructure-electrical property relationships, with special attention to the impedance response, of cement-based composites containing conductive particles or short conductive fibers. In addition to measurements on actual composites (as-fabricated and during deformation/fracture), simulations involving spherical inclusions and single wires in dielectric media (both laboratory and computer simulations) were carried out. A "frequency-switchable coating" model was developed to explain the unique frequency-dependent electrical properties of such composites. The roles of fiber pull-out, fiber/matrix debonding, and fiber properties (aspect ratio, orientation, etc.) were addressed. Ramifications for cement-based composite manufacturing and performance (e.g., damage diagnostics) will also be considered.

9:15 AM KK3.3
NONDESTRUCTIVE CHARACTERIZATION OF JOINTS OF DISSIMILAR CEMENT PASTES BY ELECTRICAL MEASUREMENT.
Sihai Wen, D.D.L. Chung, Composite Materials Research Laboratory, University at Buffalo, The State University of New York, Buffalo, NY.

Cementitious joints are encountered in structures. Joints of dissimilar cementitious materials are particularly problematic, due to the difference in drying shrinkage of the dissimilar materials. Such joints were characterized nondestructively in this work by measuring the DC current-voltage characteristic of the joint. The use of different electrically conducting admixtures, such as steel fibers and carbon fibers, gives electrically dissimilar cement pastes, such as p-type and n-type pastes. Rectifying junctions were attained by using such joints. These junctions can serve as thermocouple junctions, thus allowing the joint to sense temperature.

9:30 AM KK3.4
USING ACOUSTIC EMISSION TO QUANTIFY DAMAGE IN FIBER REINFORCED CEMENT MORTARS RESTRAINED FROM VOLUME CHANGES.
W. Jason Weiss, Byounggeon Kim, Hulya Kayir, Purdue Univ, School of Civil Engineering, West Lafayette, IN.

Portland cement based materials exhibit volume instabilities due to temperature and moisture changes. If these volumetric changes are prevented, tensile stresses may be generated and cracking may occur. One approach that has been suggested to reduce shrinkage cracking is the use of low volumes of fiber reinforcement. This presentation describes the use of acoustic emission to monitor early-age cracking in fiber reinforced mortars. Passive restraint was provided by a steel-testing frame that prevented the length reduction associated with drying. Acoustic sensors placed on the restrained specimens showed a high degree of activity initially due to the development of micro-cracks. Unrestrained specimens also showed similar, albeit slightly lower, acoustic activity during this time period. This may be attributed to surface cracking caused by moisture gradients that cause the surface concrete to shrink much more rapidly than the core concrete. After the first few days, a discrete increase in acoustic activity was observed in the restrained specimens which was followed by the development of a visible crack. The location of this crack was estimated using linear spatial resolution and found to correspond reasonably well with visual observation. It was also found that as the concrete neared the age of visible cracking the acoustic waves generated in the restrained specimen increased in duration and amplitude. Fiber reinforced specimens demonstrated acoustic evidence of cracking at approximately the same time as unreinforced mortars. It should be noted however that cracks in fiber reinforced mortars became visible at a later age which can be attributed to the crack bridging which used the fibers to transmit forces across the crack. These results may explain the apparent discrepancy between researchers that indicate that fibers do not significantly alter free shrinkage, creep, and residual stress development, yet they can significantly influence the age of visible cracking.

10:15 AM KK3.5
BEAM-BENDING METHOD FOR MEASURING PERMEABILITY OF CEMENT AND MORTAR: IV. OSCILLATORY LOADING.
Wilasa Vichit-Vadakan, George W. Scherer, Princeton University, Department of Civil and Environmental Engineering, Princeton, NJ.

When a saturated porous material is deformed, pressure gradients are created in the liquid, and the liquid flows within the pores to equilibrate the pressure. This phenomenon can be exploited to measure permeability. When a rod of saturated porous material is instantaneously bent by a fixed amount, the force required to sustain the deflection is measured as a function of time. As the liquid flows to eliminate the gradient, there is a decrease in the force required to sustain a constant deflection. By measuring the kinetics of force relaxation, it is possible to obtain the permeability of the sample, as well as its elastic modulus and stress relaxation function. However, when the permeability is very high, the relaxation can happen too fast for an accurate measurement of the permeability. In this case, a sinusoidal displacement function will yield a phase difference between the applied displacement and the measured load; the permeability can

be extracted by analyzing the frequency dependence of the phase shift. The evolution of permeability from both step displacement experiments and oscillatory displacements will be shown for cement paste of w/c = 0.6 and 0.7.

10:30 AM KK3.6
THERMAL EXPANSION KINETICS: METHOD TO MEASURE PERMEABILITY OF CEMENTITIOUS MATERIALS.
John J. Valenza, II, George W. Scherer, Civil and Environmental Engineering, Princeton Materials Inst, Princeton University, Princeton, NJ.

Permeability of cementitious materials, like concrete, is used to predict freeze-thaw resistance, and suitability for immobilizing hazardous waste. The common laboratory procedure for measuring permeability consists of: preparing a slab, applying pressure to a column of liquid above the slab, and measuring the rate of flow through the slab. This procedure is time-consuming, and introduces error because of leaks and continued hydration. The technique of beam bending does not suffer these inconveniences, and has been successfully applied to materials including porous glass and cement pastes. However, this method is not practical for concrete, because too large a sample is necessary to ensure the sample is representative. Therefore, a method for determining the permeability of concrete is desired. Accordingly, we examine a method of measuring permeability of cementitious materials by observing the thermal dilatation of a saturated body. Unlike beam bending, this method can accommodate large sample sizes. The method is based on the following principle. When the saturated porous material is heated, the liquid will expand much more than the solid. If the permeability of the material is low, liquid flow out of the body will be constrained. As a result, the liquid will expand within the pores contributing to dilatation of the body. When heating is discontinued, the liquid will escape and the body will relax to a dimension dictated by the thermal expansion coefficient of the solid. The kinetics of relaxation of a saturated porous material exposed to an arbitrary thermal cycle is governed by permeability, allowing us to extract this parameter. To ensure feasibility of the thermal expansion method, permeability values for cement paste and mortar obtained by the bending method are compared to corresponding values from the thermal expansion method.

10:45 AM KK3.7
NON-DESTRUCTIVE MEASUREMENTS OF ELASTIC CONSTANTS IN CONCRETE BY MECHANICAL SPECTROSCOPY.
Fredy R. Zypman, Claudio Guerra-Vela, University of Puerto Rico, Dept of Physics and Electronics, Humacao, PR; Fredy R. Zypman, Dept of Physics, Yeshiva University, New York, NY.

With the advent of high performance cementitous materials, it is desirable to have non-destructive characterization techniques. It is also of extreme importance to understand the curing process from a methodological standpoint (even, eventually from a mesoscopic theory). Mechanical Spectroscopy is a non-destructive technique based on the establishment of audio frequency standing modes of oscillation along cylindrical samples. An audio-generator-fed piezoelectric mechanical transducer at one end of the rod excites vibrations in the sample. Off resonance, these vibrations do not propagate away from the piezoelectric neighborhood. When a resonance is reached, the vibration extends all over the bar. A second transducer is placed at the other extreme of the cylinder. To measure the resonant frequency we connect the two piezoelectric transducers to an oscilloscope in the x-y mode and search for simple Lissajous figures. Three types of oscillations are possible: transverse, longitudinal and rotational. By identifying them and using their dispersion relation we can attain indirect measurements of the Young, Shear and Bulk moduli. We have made samples with a variety of fractional content of gravel sand and cement, and measured their corresponding moduli. We found the moduli to be strongly dependent on the ingredient's ratio. We also deduced values of the deformation of the samples as a function of the hardening time during the curing process for each sample. For some of our experiments we worked with ordinary concrete used in construction which comes in three different types: 3000 psi, 3500 psi and 4000 psi. Our preliminary results show increments of 30% and 20% in the Young and Shear modules from the 3000 psi to 4000 psi samples. We will compare our result with theoretical models.

11:00 AM KK3.8
THE ROLE OF TRANSMISSION ELECTRON MICROSCOPY, ANALYSIS AND DIFFRACTION IN THE STUDY OF CEMENT AND CONCRETE.
Eric E. Lachowski, Stephanie J. Barnett, Donald E. Macphee, University of Aberdeen, Department of Chemistry, Aberdeen, SCOTLAND.

Cement and concrete are heterogeneous on a very fine scale (¡ 1 micron) and it would therefore appear that the resolution offered by transmission electron microscopy would make it an ideal tool for the study of these materials. Certainly in the case of clinkers and other anhydrous components much valuable information which cannot otherwise be accessed may readily be obtained. Further, electron diffraction can reveal compositional and structural variations which are not detectable by XRD or microprobe analysis but which may affect the reactivity of clinker minerals. Pleochroite (in HAC) has been shown to be able to accommodate much less silica than was indicated by more traditional methods. Hydration products present particular difficulties due to the risk of beam damage. Nevertheless much valuable information concerning the compositional homogeneity and crystallinity, or lack of it, has been obtained and it has been shown that the crystallisation of synthetic C-S-H depends on its homogeneity. Even very sensitive materials such as thaumasite, currently attracting much attention because of its role in the thaumasite form of sulfate attack, can be studied. Compositional and crystallographic data obtained from from ettringite/thaumasite solid solutions at a sub-micron level show that, apart from the end members which are single phase, two solid solutions co-exist. XRD suggests that one is ettringite-like while the other is thaumasite-like, but their compositions overlap extensively, and electron diffraction indicates that both are structurally very similar and more like thaumasite.

11:15 AM KK3.9
3D MEASUREMENTS OF INTERNAL PORE NETWORK AND THE RELATIONSHIPS TO STANDARD PERMEABILITY TESTS.
Shan Lu, Eric Landis, University of Maine, Department 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 approaching 1 micron. With this experimental technique we were able measure internal capillary pore networks, and their connectivity. Microtomographic scans were made of a conventional concrete mix, and ones containing fly ash, silica fume, and blast furnace slag. In each case the pore networks were evaluated by measuring porosity, pore size distribution, and pore connectivity. In addition, the chloride permeability of each mix was measured using both ponding and electrical standard tests. We identified a microstructural parameter we called "unconnected flow length", measured from the microtomography data, as providing the best correlation with the results of the standard tests.

SESSION KK4: DURABILITY OF CEMENTITIOUS SYSTEMS
Chair: William John McCarter
Tuesday Afternoon, November 27, 2001
Republic A (Sheraton)

1:30 PM *KK4.1
THE USE OF MULTI-COMPONENT CEMENTITIOUS SYSTEMS FOR INCREASING THE SERVICE LIFE OF CONCRETE IN AGGRESSIVE ENVIRONMENTS.
Michael Thomas, University of Toronto, Dept of Civil Engineering, Toronto, Ontario, CANADA.

This paper presents data from a number of experimental studies examining the impact of using multicomponent cementitious materials (i.e. ternary and quaternary cement blends) on the properties of concrete. Blends of Portland cement with two or more supplementary cementing materials such as silica fume, fly ash, slag or metakaolin offer many advantages over plain Portland cement or binary blends. These advantages include reduced permeability, lower diffusivity and enhanced chemical resistance. It can be demonstrated using predictive models that the use of such materials may lead to order of magnitude increases in the service life of concretes exposed to aggressive environments.

2:00 PM KK4.2
DURABILITY OF HIGH PERFORMANCE CONCRETE.
Gisli Gudmundsson, The Icelandic Building Research Institute, Reykjavik, ICELAND.

Concrete durability is a critical issue for concrete in aggressive environments. An example of high performance concrete in an aggressive environment is a cover-crete repair in Borgarfjordur Bay, Iceland. A bridge was constructed over the bay in 1976 and 1977. A few years after the bridge was completed, surface scaling was observed in the piers, in some of the piers the scaling was so intense that repair work was needed. Deterioration of concrete in piers from bridges in sea water environment is a well known problem world-wide and Iceland is no exception there. Although, the problem in Iceland is not catastrophic it is a cause of some concern and this research project emerged from this concern. The main goal of this research is to

understand the deterioration process and to produce mix designs able to withstand such an attack. In this project samples made with various types and amounts of solid fillers (silica fume, blast furnace slag, fly ash and rhyolite) were tested in experiments which simulated the aggressive nature of this rather harsh environment. Two piers have been repaired with cover-crete, one in 1998 and one in 1999. The cover-create was made with high performance concrete. The selection of the binder for the concrete and the pre-mix design has been described by Gudmundsson and Wallevik (2001). Laboratory test show that the uses of solid additives generally improves the durability of the concrete (ASR, chloride penetration, freeze/thaw resistance, sulfate attack). In this research project the durability of the high performance cover-crete will be analysed by means of casted in sensors and samples taken from the structure.

2:15 PM KK4.3
DURABILITY OF MACROPOROUS PLASTERS TO SOLUBLE SALT DECAY. Antonia Moropoulou, Asterios Bakolas, Maria Karoglou, Nicolas P. Avdelidis, National Technical University of Athens, Dept of Chemical Engineering, Section of Materials Science and Engineering, Athens, GREECE.

Rising damp accompanied by salt decay is considered among the most deteriorating factors of masonries and especially of traditional ones. The widely used cementitious plasters are impervious layers, preventing the evaporation of rising damp and causing extended decay of masonries. Macroporous plasters, a modern method to affront rising damp, represent the up-to-date evolution in the field of pre-mixed mortars. These plasters, cementitious and non-cementitious, present high porosity values, resorting by the action of air-entraining agents, allowing the masonry to 'breathe' and present high durability to salts decay. In this research work commercial, cementitious and non-cementitious plasters were examined in order to assess their durability to salt decay. For their evaluation of the microstructural characteristics mercury porosimetry was used. Their durability to salts decay was examined with sodium sulfate ageing test. Additionally brick-plaster systems, in attempt to simulate the function of masonry plasters, were examined in the laboratory, using capillary rise tests of salt solution. Infrared thermography was also employed for the monitoring of these tests. From the obtained results it is concluded that plasters with high resistance to soluble salts decay, are the ones with the following characteristics: reinforcement with fibres, interconnectivity of the pore channel, better distribution of pores at the whole range of pore distribution, and large percentage of macropores.

3:00 PM KK4.4
A STUDY ON ANTI-CORROSION EFFECT IN HIGH PERFORMANCE CONCRETE BY THE POZZOLAN REACTION OF SLAG. Wei-Ming Hou, W.M. Hou, Van Nang Institute of Technology, Dept of Civil Engineering, Chung-Li, Taiwan, ROC; Ping-Kun Chang, Van Nang Institute of Technology, Dept of Civil Engineering , Chung-Li, Taiwan, ROC.

The synchrotron radiation accelerator (SRA) ,the porosity survey of mercury intrusion porosimetry(MIP), the crystal analysis of scanning electron microscopy (SEM) was applied to analyzing the pozzolan reaction of slag and anti-corrosion effect in high performance slag concrete is examined by the test of electrical resistivity and permeability index in this study. The experiment shows that owing to the pozzolan reaction of slag, it can decrease CH, dwindle the capillary porosity, increase the density , durability and lower the permeability. Besides, through the electrical resistivity and permeability index, we can verify that adding the effective high performance concrete of slag can strengthen the anti-corrosion effect. KEY WORDS: pozzolan reaction, high performance concrete, synchrotron radiation accelerator, electrical resistivity and permeability index.

3:15 PM KK4.5
INFLUENCE OF CEMENT CHARACTERISTICS ON DELAYED ETTRINGITE FORMATION. Della M. Roy, Barry E. Scheetz, Paul J. Tikalsky, James Rosenberger, Tara Krize and Periaswamy Arjunan, The Pennsylvania State University, University Park, PA.

Delayed ettringite formation is a degradation process that sometimes is identified in concrete that has been exposed to curing at temperatures above 70oC. The process is complex and is still not thoroughly understood, even with intense research interest in the past decade that focused on understanding the process. According to the latest interpretation, any ettringite formed prior to curing at above 70°C is destroyed during the initial heat treatment, and the damage in the concrete structure is associated with the formation or reformation of ettringite during the subsequent service at ambient temperatures. Twenty-one Type I & II portland cements from across the United States, that represented a statistical survey of range of sulfate, equivalent alkali, C3A and fineness, were evaluated for DEF formation following a modified Stark test procedure. The results of these studies will be discussed.

3:30 PM KK4.6
GLASS FIBRE REINFORCED CEMENTS: IMPROVEMENT OF DURABILITY AND VISUALISATION OF DETERIORATION DYNAMICS BY ESEM-TECHNIQUE. Manfred Börger, Inna König, University of Erlangen-Nürnberg, Dept of Inorganic Chemistry, Erlangen, GERMANY; Hans-Betram Fischer, Jochen Stark, University of Weimar, F.A. Finger-Institut für Baustoffkunde, Weimar, GERMANY; Christian Engert, Hans-Ulrich Hummel, Gebr. Knauf Westdeutsche Gipswerke, Iphofen, GERMANY.

The durability of glass fibre reinforced cement boards has been investigated and different attempts of improvement of the long term durability of glass fibres are reportated. The investigated cement boards consisted of Portland cement CEM I 42,5 and blast furnace cement type CEM III IB 32,5 and were produced in a modified flow-on process. For reinforced of the cement cove we incorporated 4% of alkaline resistant glass fibres with high ZrO_2 content: NEG H-200, tex 32, 14 μm. Oschatz AR-glass, tex 38, 14 μm, A PE-size and Oschatz AR, tex 76, 14 μm, APE-size. The results have been compared to reinforcement by E-glass fibres and boards without fibre reinforcement. Reinforcement of both types of cement boards with glass fibres increases the tensile strength and toughness, but these properties deteriorate with time. The deterioration is retarded, but not eliminated, by using alkaline resistant glass fibres with high ZrO_2 content. It is shown by means of ESEM-technique that the glass is attached by the alkaline pore solution which causes changes in the microstructure at the interface between glass and cement paste. Especially growth of CH microcrystals between the filaments of which the fibres are composed alters the mode of fracture and are the dominant cause of deterioration. It could be shown that this kind of interpenetration of CH and glass fibre surface gives rise to some improvement in strength for an intermediate time process. Improvement of the long term durability was achieved by addition of microsilica or trass with high pozzolanic activity. It was shown by ESEM-technique that the additional SiO_2 accelerates the reactions of the clinker phases and act as a filler between clinker grains and the fibres and hence produce a denser core. Moreover the SiO_2 exhibits a stray pozzolanic reaction in the period 7 - 14 days. This reactions binds CH by formation of calciumsilicate phases and avoids the attack of the glass fibre reinforcement by CH formed during cement hydration. The dynamics of incorporated reactions have been visualised in a unique combination of ESEM and X-ray powder diffraction technique.

3:45 PM KK4.7
Transferred to KK4.3

SESSION KK5: POSTER SESSION
Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hynes)

KK5.1
APPLICATION OF ULTRASONIC TECHNIQUES TO STUDY THE FORMATION OF MICROSTRUCTURE IN CEMENTITIOUS MATERIALS AT EARLY AGE. Guang Ye, Klaas van Breugel, A.L.A. Fraaij, Delft University of Technology, Faculty of Civil Engineering and Geosciences, Delft, THE NETHERLANDS.

The development of microstructural formation of cementitious materials at early age becomes essential to forecast their performance in service. Therefore, experimental studies and numerical simulations become increasing important to understand the formation of the microstructure. The characterization of the changes in ultrasonic pulse velocity permits to follow cement hydration and monitor the development of microstructure at early age. In this contribution, an ultrasonic experimental set-up is presented. With this tool, the formation of microstructure in fresh cement paste and concrete was examined. Research parameters include the influence of curing temperature (isothermal curing at 10, 20, 30, and 50°C), water/cement ratio (0.40, 0.45 and 0.55) and amount of aggregate. The cement hydration model HYMOSTRUC is utilized to simulate the formation of the microstructure. In the HYMOSTRUC model, the hydrating cement grains are simulated as gradually growthing sphere. A spatial network, basis of the microstructure is formed with the contact of the growthing sphere. In this study, the concretes are considered as a four-phase system which consists of water, unhydrated cement, hydration products and that part of the hydration product that causes the contact between the hydrating cement grains (so called "bridge volume"). Correlation has been found between the growth of bridge volume calculated from model and the changes in the pulse velocity. It is believed that ultrasonic pulse velocity

measurements can represent a valuable tool to investigate the development of the microstructure at early age.

KK5.2
CHARACTERIZATION OF PARTICLE-SIZE DISTRIBUTION IN CONCRETE BY MECHANICAL SPECTROSCOPY.
Fredy R. Zypman, Yeshiva University, New York, NY; Claudio Guerra-Vela, University of Puerto Rico, Humacao, PR.

In the past, we have studied the time evolution of Concrete as a function of hardening stage. The non-destructive technique used (Mechanical Spectroscopy) is based on the propagation of resonant audio frequency modes of oscillation along the long axis of cylindrical samples. An audio-generator-fed piezoelectric (at one end of the rod) excites vibrations in the sample. Off resonance, these vibrations do not propagate away from the piezoelectric site. When a resonance is reached, the vibration extends all over the bar. A second piezoelectric is placed at the other extreme of the cylinder. To measure the resonant frequency we connect the two piezos to an oscilloscope in the x-y mode and search for simple Lissajous figures. This parameter provides an indirect measurement of the Young modulus, which was measured twice a day during the 28-day hardening time. Our current goal is to extend this characterization technique to provide information about the components that make up the sample. For this purpose, we have made samples with various contents of gravel, sand and cement, and measured their frequency spectra. By means of Random Matrix Theory, the statistics of these spectra provide information about elemental elastic constants and relative content of the constituents. We will show the experimental results, and compare with theoretical models. The theoretical analysis is based on previous results (RA Eubanks, E Sternberg, J Rational Mech Anal 5 (1956) 735; PM Naghdi, CS Hsu, J Math Mech 10 (1961) 233) in which spherical inclusions were present in an otherwise uniform matrix, to define an effective elastic medium. Work supported by Yeshiva University, NSF and NIH.

KK5.3
DURABILITY AND SERVICE LIFE PREDICTION FOR SULFUR CONCRETE. Amon Raphael Makenya, KTH, Royal Institute of Technology Dept of Architecture, Building Engineering, Stockholm, SWEDEN.

Sulfur Concrete (SC) is a thermoplastic construction material that is recyclable. It is basically composed of mineral aggregates and sulfur as a binder. The material, Sulfur Concrete (SC) is suitable and recommended for applications in hostile environments where other cementitious based materials would normally not resist. The main problem, however, with Sulfur Concrete (SC), is that when exposed to normal temperature cycling, humidity conditions or moisture, it will fail. Modification of the material, sulfur concrete (SC), is therefore necessary during the design phase, in order to meet the desired durability requirements, which are considered as basic in the construction industry. In order to meet these conditions, a systematic theoretical analysis on the Service Life Prediction (SLP) for Sulfur concrete (SC) integrating durability aspects is vital, and it is anticipated that it will qualify the material for industrial application purposes. The applied methodology is basically generic, and this paper refers to the principles of ISO standard (ISO 15686 part I & II-Buildings and constructed assets-Servicve Life Planning).

SESSION KK6: ALTERNATIVE BINDERS AND UTILIZATION OF WASTE MATERIALS
Chair: Frederik P. Glasser
Wednesday Morning, November 28, 2001
Republic A (Sheraton)

8:30 AM *KK6.1
ALKALI-ACTIVATED CEMENTITIOUS MATERIALS: ALTERNATIVE MATRICES FOR THE IMMOBILIZATION OF HAZARDOUS WASTES. A. Palomo, Institute of Eduardo Torroja, Madrid, SPAIN.

Alkali activation of aluminosilicate materials is an interesting chemical process that allows us to transform glassy structures (partially or totally amorphous) into very compact well-cemented composites. On the other hand, waste disposal has become a major concern in most of industrialized countries because of a progressive restricting environmental standards. The potential use of alkali activated fly ashes in form of a matrix to immobilize hazardous elements could simultaneously cover several objectives: Σ To give an application to the exceeding fly ashes (millions of tons are accumulated every year all around the world). Σ To offer alternative cementitious materials for immobilizing toxic and hazardous wastes. Especially in those cases where portland cement matrices are not very effective. A specific research has been conducted in order to prove that the mentioned materials (the alkali activated fly ashes) might really be useful for an efficient stabilization of some particular elements (boron, lead and chromium) which negative effects on the OPC setting, the OPC mechanical strength development, or even on the leaching behavior of the cement-based system, are very well known.

9:00 AM KK6.2
INFLUENCE OF CONTAMINATED RECYCLED BRICK AGGREGATE ON MATRIX PROPERTIES, STRENGTH AND LEACHING CHARACTERISTICS OF CONCRETE.
P.A. Muhammed Basheer, David Hughes, Trevor Elliot and Aidan Hackett, School of Civil Engineering, The Queen's University of Belfast, Northern Ireland, UNITED KINGDOM.

With the re-development of brown field sites and associated demolition of contaminated structures and buildings, there is increasing pressure to re-use contaminated masonry. Very little research data is available on the effects of contaminated brick aggregate on concrete strength and durability, or the likelihood of the contaminants leaching from concrete. The objective of the work presented here was to examine the influence of heavy metals (Cr, Zn, Ni, Pb, Cu) in contaminated brick aggregates on matrix characteristics, compressive strength, water permeability and leaching characteristics of concrete made with the contaminated brick aggregates. The likelihood of the heavy metals leaching from the concrete was investigated using a monolithic leaching test. The results show that the contaminants were encapsulated in the concrete, with release several orders of magnitude lower than the concentrations originally present. It was also found that the presence of heavy metals has a small adverse effect on compressive strength, workability and water permeability. A comparison between concrete subjected to leaching and that kept as a control show that compressive strength is not significantly affected whilst the water permeability of concrete increased as a result of the leaching. TG/DSC has been used to explain this trend, in which it has been found that calcium hydroxide has been leached from the concrete. The change in water permeability after leaching in conjunction with unchanged compressive strength suggests that whilst some hydrated products may have been removed, those contributing most to the strength of concrete remain.

9:15 AM KK6.3
THE USE OF TREATED DREDGED MATERIAL AS FILLER.
Karsten Millrath, Sofiya Kozlova, Christian Meyer, Semyon Shimanovich, Columbia University, Dept of Civil Engineering and Engineering Mechanics, New York, NY.

The proper disposal or beneficiation of dredged material is a major concern to the New York metropolitan area, because dredging is necessary to keep the most important Port on the East Coast operable and economically viable. Facilities to contain the highly contaminated material will their capacities. The dredged material consists to a large extent of clay and silt, with particle size distributions that suggest a use of the treated material as a filler in various applications, such as cement composites. A research project at Columbia University has focused on the decontamination of dredged materials that contains heavy metals and other toxic components. The proposed treatment method not only causes a volume reduction and improvement of various properties, it actually beneficiates it in a technically viable, environmentally friendly and economically feasible way. Inert or pozzolanic fillers are now widely used in concrete construction. The treatment process presented here is apt to transform treated dredged material into a mineral filler and at the same time eases the pressure that port authorities in the U.S. and abroad are exposed to. The proposed method turns a contaminated waste material into a valuable resource.

SESSION KK7: PROCESSING AND PROPERTIES
Chair: Michael D. Thomas
Wednesday Morning, November 28, 2001
Republic A (Sheraton)

10:00 AM KK7.1
A SIMPLE MIX-DESIGN METHOD FOR HIGH PERFORMANCE CONCRETE WITH MEDIUM STRENGTH. Nan Su, National Yunlin Univ of Science and Technology, Dept of Construction Engineering, Yunlin, TAIWAN ROC; Kung-Chung Hsu, National Taiwan Normal Univ, Dept of Chemistry, Taipei, TAIWAN ROC.

In Taiwan, high performance concrete with medium strength (HPCMS) is a category of concrete, which has a large market in the area of structural engineering. It is very meaningful to develop good algorithm about the mix proportioning for this category of concrete with low cement content. This paper proposes a new mix-design method for HPCMS. The procedure is determining the contents of aggregates first, and then calculating the contents of cement, mixing

water, and mineral admixtures for preparing a paste which fills into the voids of aggregates to make the resulting concrete having high fluidity and required strength. By adjusting the packing factor (PF) of aggregates, the produced concrete could have slump flow of 55-70 cm and compressive strength of 27.5-34.3 MPa. Results of the investigations on mixes using the proposed method are presented. PF and the amount of superplasticizer are two major factors in determining the workability and compressive strength of HPCMS. Compared to other mix-design methods, this method is simpler, requires less binders, and cost saving.

10:15 AM KK7.2
STUDY OF THE ROBUSTNESS OF CEMENT/SUPER-PLASTICIZER COMBINATIONS IN REACTIVE POWDER CONCRETES. Olivier Bonneau, Pierre-Claude Aitcin, CRIB Universite de Sherbrooke, CANADA.

The robustness of cement/superplasticizer combinations is a new concept recently developed at the Universite de Sherbrooke. This concept is based on the following observation. It is always possible to find a very narrow range of superplasticizer dosage where it is possible to make a concrete with no bleeding and not too much retardation. But, a very slight deviation from this trade-off dosage results either in a rapid slump loss for an underdosage or in unacceptable bleeding, segregation and retardation for an overdosage. Superplasticizers in Reactive Powder Concretes (RPC) are very important to obtain a good workability in such a low water content material (W/C=0.20). An optimum superplasticizer dosage is determined with rheological tools. In this research, variations on rheological behaviour and kinetic hydration are studied as a function of slight variations on the admixture dosage around the maximum. Therefore the robustness of cement/superplasticizer combinations is quantified with 3 different admixtures: a copolymer of acrylic ester (CAE), a polynaphtalene sulfonate (PNS) and a polymelamine sulfonate (PMS).

10:30 AM KK7.3
THE EFFECT OF WASTE OIL-CRACKING CATALYST ON THE COMPRESSIVE STRENGTH OF CEMENT PASTE AND MORTAR. Jung-Hsiu Wu, Wan-Lung Wu, Kung-Chung Hsu, National Taiwan Normal Univ, Dept of Chemistry, Taipei, TAIWAN ROC.

EPcat is the waste catalyst from catalytic crackers of oil companies, consists mainly of silicon oxide and aluminum oxide, and shows pozzolanic properties. In this paper, the compressive strength of cement pastes and mortars containing EPcat were prepared and cured. The water/binder (W/B) ratios were 0.2, 0.25, and 0.3 and the replacement levels of cement by EPcat were 0, 5, 10, and 15 wt%. Proper amount of superplasticizer was added into each mix to ensure similar workability. The results indicate that addition of EPcat would increase the compressive strength of mortars substantially, but increase the compressive strength of the related pastes only slightly. The improvement in the mechanical property of mortars by the catalyst could be attributed to improved bonds between the cement paste and aggregate. As the W/B ratio or the replacement level of EPcat increases, the effect becomes more significant.

10:45 AM KK7.4
DRY PREMIXING OF SAND/CEMENT MORTARS USING SPOUT-FLUID BED TECHNOLOGY. Stevan Jovanovich, Howard Littman, Joel L. Plawsky, Rensselaer Polytechnic Institute, Dept of Chemical Engineering, Troy, NY; Kyle Douglas, Sean Gerolimatos, Kenneth Hover, Cornell University, Dept of Civil and Environmental Engineering, Ithaca, NY.

Controlling the microstructure of cement-based materials depends on how well one can disperse particles in the finest size fraction range. Conventional wet mixing equipment has difficulty dispersing the fine components because electrostatic forces between small particles are very large, it is difficult to efficiently transfer energy from large particles to very small particles, and mixing times are limited. Superplasticizers and water reducers help dispersion, but these additives are limited in their effectiveness because the mixing of concrete or mortar occurs simultaneously with the hydration of cement and other pozzolans. To improve the performance of high concretes, we have been investigating dry premixing the sand and cement in a pneumatic transport line. The goal is to improve the dispersion of the materials, produce a more uniform and durable product, and reduce the consumption of cement. Spout-fluid bed technology, originally developed for the petrochemical industry, has been used to facilitate the mixing process. The equipment consists of a spout-fluid bed feeder and a transport line framed in a custom designed PC-based data acquisition and control system. The desired particle circulation rate and voidage through the transport line are achieved by controlling operating parameters such as the spacing between the inlet jet and the entrance to the transport pipe, the air flow rate through the annulus of the feeder, the air velocity through the pipe, and the pressure at the inlet of the transport line. We report proof-of-concept data that shows how the mixing process works, how mortar properties depend upon the key operating parameters of the transport line, how important retention of the finest cement fraction is to strength development, how we can affect several key properties of fresh and cured mortars via the mixing process, and how the mixing process appears to be more effective as the sand/cement ratio is increased.

11:00 AM KK7.5
AN INVESTIGATION OF THE EFFECTS OF MIX STRENGTH ON THE FRACTURE AND FATIGUE BEHAVIOR OF CONCRETE. J. Lou, Princeton Materials Institute, and the Department of Mechanical and Aerospace Engineering, Princeton, NJ; K. Bhalerao, A.B.O. Soboyejo, Department of Food, Agricultural and Biological Engineering, and the Department of Aerospace Engineering, Columbus, OH; W.O. Soboyejo, Princeton Materials Institute, and the Department of Mechanical and Aerospace Engineering, Princeton, NJ.

This paper examines the effects of mix compressive strength (30, 35 and 40 MPa) on the fracture initiation toughness, resistance-curve behavior and fatigue crack growth behavior of concrete. The fracture initiation toughness and the resistance-curve behavior are shown to increase with increasing mix strength. The observed resistance-curve behavior is then attributed largely to the effects of ligament bridging, which are predicted using small- and large-scale bridging models. The implications of the results are discussed for the design of concrete mixtures with attractive combinations of strength, fracture toughness and fatigue resistance. The underlying fracture and fatigue mechanisms are elucidated via scanning electron microscopy analyses of crack profiles and fracture surfaces.

11:15 AM KK7.6
PAA/PEO COMB POLYMER EFFECTS ON CEMENT PASTE RHEOLOGY. G.H. Kirby, J.A. Lewis, University of Illinois, Dept of Materials Science and Engineering, Urbana, IL; J. Cheung, A. Jeknavorian, X. Zhang, W.R. Grace, Construction Products Division, Cambridge, MA.

We have studied the effects of PAA/PEO-based comb polymers on the flow behavior of Portland cement pastes. These admixtures were synthesized with varying molecular weight of the PAA and PEO-based chains. Their adsorption behavior onto Portland cement was characterized using Total Organic Carbon (TOC) analysis. Their influence on the zeta potential of cement suspensions (w/c = 1) as a function of hydration time was measured by an electroacoustic amplitude (ESA) technique. Both stress viscometry and oscillatory measurements were carried out on fresh pastes (w/c = 0.35). Our observations provide new insight into the effects of adlayer concentration, architecture, and multivalent ion interactions on the stability of dense cement pastes.

SESSION KK8/JJ9: JOINT SESSION
CEMENTS IN RADIOACTIVE WASTE IMMOBILIZATION
Chair: Kenneth A. Snyder
Wednesday Afternoon, November 28, 2001
Republic B (Sheraton)

1:30 PM *KK8.1/JJ9.1
CHARACTERIZATION OF THE BARRIER PERFORMANCE OF CEMENTS. F.P. Glasser, Univ of Aberdeen, Aberdeen, Scotland, UNITED KINGDOM.

Anniversaries are a good time critically to review progress, in this instance, quantifying the barrier performance of cement materials in nuclear waste repositories. Portland cement has intrinsic advantages in this application: persistence in nature, low solubility and ease of fabrication, either in situ or precast. Its disadvantages include inherent brittle properties and possible reactions with other types of engineered barrier materials. Research leads to the conclusion that the principal advantage of cements lies in their chemical properties: they complex and react with waste species forming solubility-limiting solids. Examples are given to show how cements can be tailored to enhance their immobilization potential for specific radionuclides. However, after 25 years it is still not possible to give a comprehensive and quantitative description of reaction sequences and their evolution with time and temperature. A wish list to address missing or inadequate data is presented. The present showdown in activity affords opportunity to research the next generation of chemical barriers and quantify their performance.

2:00 PM KK8.2/JJ9.2
PRACTICAL MODEL TO EVALUATE DURABILITY OF CEMENT-BASED MATERIALS UNDER LEACHING, COUPLING WITH INTERNATIONAL DATA BASE. Siham Kamali, Laboratory

of Mechanics and Technology, Cachan, FRANCE; Bruno Gerard, Laboratory of Mechanics and Technology, Cachan, FRANCE, Electricity of France, Moret sur Loing, FRANCE; Micheline Moranville, Laboratory of Mechanics and Technology, Cachan, FRANCE.

The concrete leaching by water damages and reduces the service life of structures like radioactive waste repositories, water pipes and dams. This study develops a practical model to provide decision making in design and diagnosis of concrete structures which may be submitted to leaching. It consists on the prediction of the leaching kinetics according to material and environmental characteristics. The model assumes that the leaching kinetics follows a square root of time. Each parameter is introduced as a weight function. The model is based on international experimental published data dealing with the effect of water-to-binder ratio, silica fume content, aggressive solution pH and temperature. These data are completed by other tests in order to introduce the effect of the cement type (Portland cement, silica fume cement, fly ash cement, blast furnace slag cement) and of the interaction between the cement and water-to-binder ratio. Finally, the model is analysed and applied to practical recommendations.

2:15 PM KK8.3/JJ9.3
A SOLID SOLUTION MODEL FOR SORPTION OF RADIONUCLIDES IN CEMENT. Allan T. Emrén, Chalmers University of Technology, Dept of Nuclear Chemistry, Goteborg, SWEDEN.

Cement consists of a considerable number of phases, the two most important of which are the gel phase and a phase that is almost pure portlandite, calcium hydroxide. Both can be considered as solid solutions. This means that they are able to have a variable chemical composition. This also gives a possibility for the phases to incorporate different elements into their structure. Of these two phases, portlandite is rather compact while the gel phase has a very irregular structure, probably fractal. This suggests that sorption essentially takes place as absorption in the gel phase. Whenever this is correct, the sorption capacity could be expected to be large enough to make the contribution from other mechanisms, e.g. adsorption, negligible. In the present work, a model for multi component solid mixtures has been developed, essentially following the Guggenheim excess free enthalpy approach. Measurement of Kd for one gel composition makes it possible to calculate Kd values during the entire process of cement degradation. The main limitation is that the concentration of the radionuclide has to be low enough for all higher terms in the series expansion to be negligible. The model is mostly valid for elements forming cations and it also requires the sorbed element to form a compound of reasonably low solubility with one of the anions in cement (hydroxide or silicate). This means that it can be used essentially for metals. Kd values from the literature have been used to calculate thermodynamic properties of some solid mixtures.

2:30 PM KK8.4/JJ9.4
STABILITY OF HYDROCERAMIC WASTE FORM DURING VHT TESTING. Barry E. Scheetz, Michal W. Grutzeck, Johnson Olanrewaju, Della M. Roy, Materials Research Institute, The Pennsylvania State University, University Park, PA; D. Darryl Siemer, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

Immobilization of INEEL calcine waste by the reaction of alkali and an aluminosilicate pozzolan to form a hydroceramic waste form has been developed over the past ten years by this research team. Subsequent research has documented the rate of formation as well as the stability of the resulting waste form and its ability to sequester the hazardous radionuclides and RCRA elements contained in the calcine. Typical hydroceramic formulations were prepared and subjected to testing following the VHT protocol developed at Argonne National Laboratory - East. This test protocol maintains the test specimen in an environment of 100% relative humidity at temperatures up to 200°C for varying time intervals. Condensation onto the test specimen then initiates surface reactions between water and the waste form at this elevated temperature. The results of the exposure of hydro-cermanic waste forms contrasted to EA glass will be discussed.

2:45 PM KK8.5/JJ9.5
Abstract Withdrawn.

SESSION KK9: CEMENTS IN WASTE IMMOBILIZATION
Chair: Kenneth A. Snyder
Wednesday Afternoon, November 28, 2001
Republic A (Sheraton)

3:30 PM KK9.1
PERFORMANCE OF PORTLAND CEMENT FOLLOWING THERMAL EXCURSIONS. F.P. Glasser, C. Dickson and S. Y-Hong.

The post-closure scenario at Yucca Mountain predicts a temperature excursion will occur in the excavated drifts used to store spent fuel. Temperatures may attain 200°C. In order to maintain the stability of the excavated opening, concrete liners might be used. Ordinarily, water seeping through concrete will be conditioned to high pH. The question for Yucca Mountain is whether the pH conditioning properties of cement will be affected by the temperature excursion, since water is not expected to enter the drifts until after temperatures peak and again decrease to <100°C. Experiments on phase relations in the CaO-SiO_2-H_2O at one bar pressure and 100°C - 200°C reveal differences in kinetics and crystallisations compared with the same system at self-generated steam pressures. It is predicted that Portland cement, Ca/Si molar ratio >2.5, will retain its pH conditioning ability and remain essentially unchanged by the thermal cycle, mainly because of the persistence of $Ca(OH)_2$. However, if the cement reacts with mineral aggregate or rocks in the near field, scope may exist for permanent and irreversible reduction in pH. Intended for joint session of JJ and KK.

3:45 PM KK9.2
LONG-TERM PERFORMANCE OF CEMENTITIOUS MATERIALS AS TECHNICAL BARRIERS FOR NUCLEAR WASTE MANAGEMENT. Thorsten Meyer, Horst-Jürgen Herbert, Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Braunschweig, GERMANY.

The long-term behavior of cemented fly ashes in high saline brines has been investigated by means of a time accelerating leaching experiment and by the geochemical modeling of the observed reactions. The investigated materials, cemented hard coal fly ash (SFA) and brown coal fly ash (BFA), were mixtures of fly ashes, blast furnace cement, halite and saturated NaCl solution. The leaching fluids were a saturated NaCl-$CaSO_4$ solution as well as an IP21 solution, which is likely to occur in salt and potash mines which are used in Germany as repositories for radioactive and hazardous chemical wastes. The employed leaching experiment was developed in the GRS specifically for the boundary conditions of underground repositories. The experiment was conducted in several steps towards the thermodynamic equilibrium between the leaching fluid and the involved solid phases. The experimentally observed reaction path was modeled using the computer code EQ3/6. In a second step the laboratory scaled and modeled results were compared with results of a full-scale experiment in the Asse salt mine. A good agreement between the experimental data and the modeling results was obtained. The reaction path of all investigated materials in IP21 solution is characterized by a continuous decrease of Mg^{2+} whereas Ca^{2+} is first accumulated in the leachate and then removed due to the formation of new CSH and CSAH phases. The results of a 10 years leaching experiment with cemented fly ashes are in perfect agreement with the reaction path obtained by the time accelerating cascade experiment and the geochemical modeling. Thus we can demonstrate that the employed experimental and modeling tools have proved to be suitable for the evaluation of the long-term stability of cementitious materials in repositories in salt formations. It can be concluded that the cemented materials in Mg-rich brine will less stable than in NaCl-$CaSO_4$ solution.

4:00 PM KK9.3
EFFECT OF MATERIAL PARAMETERS AND ENVIRONMENT ON DURABILITY OF CEMENT-BASED MATERIALS UNDER LEACHING. Siham Kamali, Laboratory of Mechanics and Technology, Cachan, FRANCE; Micheline Moranville, Laboratory of Mechanics and Technology, Cachan, FRANCE; Bruno Gerard, Laboratory of Mechanics and Technology, Cachan, FRANCE, Electricity of France, Moret sur Loing, FRANCE.

The durability of radioactive waste repositories must be evaluated over a long period of time. The leaching of the cement-based materials is one of the main degradation phenomena. The leaching kinetics is closely related to the characteristics of cement-based materials. Numerous authors have already published experimental data. The aim of this paper is to review the available results in order to built an international data bank with respect to the leaching kinetics. First, the influence of experimental techniques (accelerated or not accelerated test, ancient analogues) is analyzed and discussed. Secondly, the influence of mineral additions and of water-to-binder ratio are considered. Thirdly, the effect of environmental conditions is introduced in terms of water pH and temperature. Finally, practical conclusions are put forward for consideration to designers and to modelers.