SYMPOSIUM KK

Design, Characteristics, and Properties of Cementitious Materials

November 26 – 28, 2001

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*Invited paper
OPENING REMARKS

8:45 AM *K01.1
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 C-S-H paste. A 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 K01.2
AUTOGNEOUS SHRINKAGE IN HIGH-PERFORMANCE CEMENT PASTE: AN EVALUATION OF BASIC MECHANISMS.
Pieter Lamm, 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 autogeneous 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 autogeneous shrinkage are poorly understood. While there is general agreement about the existence of a relationship between autogeneous 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 time proceeds. In the present research, an evaluation of different basic mechanisms to explain autogeneous 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 autogeneous 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 autogeneous shrinkage measurements performed by the authors and with literature data.

9:30 AM K01.3
STUDIES USING 27A-MAS NMR OF AFMs AND AFm: PHASES IN HYDRATES OF DIFFERENT CEMENTS AND THE IMPLICATIONS FOR CHLORIDE BINDING.
Roderick Jones, Dundee University, Dept of Civil Engineering; Donald Macphie, Aberdeen University, Dept of Chemistry; Paul Lormeaud, Cementos El Monte, S.A., Departamento de Calidad y Laboratorio; Geoff Hunter and Sandy Chudley, 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 paramagnetics with use of NMR to study the chemical environment of 27A-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 cements and slag. In the case of Portland cement, fly ash, 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-dependent chemical changes affecting both the hydration 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 individual cements can play in the provision of overall concrete durability for a chemical perspective.

SESSION K02: MICROSTRUCTURE, HYDRATION AND CHARACTERIZATION II: MODELING AND TRANSPORT

Chair: Paul E. Suttles
Monday Afternoon, November 26, 2001
Republic A (Sheraton)

1:30 PM *K02.1
THE COMPUTATIONAL MATERIALS SCIENCE OF CEMENT AND CONCRETE Paste 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 concrete phases have been created. Future challenges that need to be overcome in order to make further progress will be analyzed.
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 cement paste material was simulated using the cement hydration model HYMOSTRUC. In this computer-based numerical model, the hydration of cement grains are modeled as gradually growing spheres. A spatial network which is the basis of the microstructure of cement paste material was 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 were recorded. The percolating path of the fluid in three dimensions is traced by using an overlying algorithm. At the same time, a translation factor is determined by finding the normal direction to the line connecting the gravity center of two overlapping pores. From this translation factor, the hydraulic radius and the field 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 of the pore space of the powder. Geometrical results of these algorithms are compared to the numerical results calculated by other microstructural models at various degree of hydration.

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. Taylor's model was used to describe release and sorption of alkalis into the pore water. The binding capacities of cementitious C-S-H and portlanditic C-S-H with respect to sodium and potassium were determined according to binding experiments done by Song and Glaser. 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 Pitzer's method for calculating activity coefficients. The structure is formed with the constant of the growing spheres. Alkaline concentrations are controlled by the ionic strength of approximately 0.1 mol/L. This simulation equation can successfully characterize ionic transport of alkalis in water, parameter-free calculations are compared to published data. To characterize the diffusion transport of arbitrary ion species in concentrations above 0.1 mol/L, a transport equation also account for the dynamic behavior of the ionic species. Here, the dynamic behavior of the ionic species will be characterized by the electronegativity viscosity. A viscosity correction method is used to the existing electro-diffusion equation and parameter-free calculations of the apparent salt diffusivity coefficient in bulk water are compared to data published in journals and handbooks. The results suggest that the viscosity correction extends the accuracy of the electro-diffusion equation to approximately 0.1 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. Moreover, the multiphase viscosity correction suggests a new coupling theory, which may give further insights into the relative contributions of equilibrium and dynamical components of the transport equation.

The set 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 the transport of mixed electrolyte solutions. The benefit of this model is that it can be adapted to different reaction mechanisms, such as precipitation, dissolution, and reaction at solid surfaces. The model can be used to predict the behavior of ionic species in complex systems, such as concrete or mortar, and to optimize the performance of these materials. The model is based on the Fick's law of diffusion, which describes the diffusion of a solute in a fluid, and on the conservation of mass, which describes the balance of mass in a system. The model can be 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 is estimated from the Pitzer equations, with the addition of temperature coefficients for the range 0°C to 250°C.
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 species transport equation together 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. Mapchee, 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 latest advances in soil mechanics 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 fluidizing medium. Existing rheological models do not properly take account of the two phase nature of pastes wherein 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. One advantage of 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 the stress in the paste to relax and then reverse. Some laboratory based results are discussed in terms of the model.

**SESSION KK3: CHARACTERIZATION TECHNIQUES**

Chair: Donald E. Mapchee

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 McCarney, 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 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, National Materials Science and Engineering, Boston, MA; 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 the 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 inclusions and single wires in dielectric media (both laboratory and computer simulations) were carried out. A "frequency-switching" 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 SIMILAR CEMENT PASTES BY ELECTRICAL MEASUREMENTS. Shih 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 RESTRICTED FROM VOLUME CHANGES. B. Jason Weis, B. Younghoon Kim, Holyn Kiy, 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 restrained, 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 near 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 become visible at a later age which can be attributed to the crack bridging which used the fibers to transmit force to another crack. These results may explain the apparent discrepancy between researchers that indicate that fibers do not significantly alter 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 MOHR-CRISP OSCILLATORY LOADING. Wilson V. Vakil, 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 incrementally 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 estimate the permeability of the material, 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 with 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, 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 wastes. 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 method involves heating 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. Zygman, Claudio Guerra-Vela, University of Puerto Rico, Dept of Physics and Electronics, Humacao, PR; Fredy R. Zygman, Dept of Physics, Yeshiva University, New York, NY.

With the advent of high performance cementitious 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 radioc frequency standing modes of oscillation along cylindrical samples. An audio-generators-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 transducer. When the resonance is reached, 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 relations we can retain 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 the Young’s modulus of the specimens as a function of the hardening time during the curing process for each sample. For some of our experiments we worked with concrete in use in construction which comes in different types: 3000 psi, 4000 psi and 5000 psi. Our preliminary results show increments of 30% and 20% in the Young and Shear moduli 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 F. Luchowski, Stephanie J. Barnett, Donald E. MacPherson, University of Aberdeen, Department of Chemistry, Aberdeen, SCOTLAND.

Cement and concrete are heterogeneous on a very fine scale: [1 micron] and it is impossible to capture therefore the resolution offered by transmission electron microscopy would make it an ideal tool for the study of these materials. Certainly in the case of cements and other amorphous compounds 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 cements and concretes. Fluidosecrete (in HA) has been shown to be able to accelerate pozzolans 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 crystallization of synthetic C-S-H depends on its homogeneity. Even very sensitive materials such as thiosulfate, currently abstracting much attention because of its role in the thiosulfate form of sulfates, can be studied. Compositional and crystallographic data obtained from ettringite/thiosulfate 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/thiosulfate and the other is a thiosulfate, their compositions overlap extensively, and electron diffraction indicates that both are structurally very similar and more like thiosulfate.

11:15 AM KK3.9
3D MEASUREMENTS OF INTERNAL PORE NETWORK AND THE RELATIONSHIPS TO STANDARD PERMEABILITY TESTS.
Shoe Liu, Eric Lindahl, Afternoon of November 27, 2001, Department of Civil & Environmental Engineering, Orono, ME.

In this study we are exploring concrete microstructure and related durability issues using 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 us to achieve 3D spatial resolution approaching 1 micron. With this experimental technique we are 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 pendant 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, November 27, 2001, Republic A (Sheraton)

1:30 PM KK4.1
THE USE OF MULTICOMPONENT 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. Gili 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 concrete bridge in Borgarfjardarvagur, 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. Determination of concrete in piers from bridges in severe environment is a well-known problem worldwide and Iceland is not 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-cree, one in 1988 and one in 1989. The cover-cree was made with high performance concrete. The selection of the binder for the concrete and the pre-mix design has been described by Gundmundsson and Willevik (2001). Laboratory test show that the use of solid additives generally improves the durability of the concrete mix, chloride permeability, freeze/thaw resistance, sulfate attack. In this research project the durability of the high performance cover-cree will be analysed by means of tests in sensors and samples taken from the structure.

2:15 PM KK4.3 DURABILITY OF MACROPOROUS PLASTERS TO SOLUBLE SALT DECAY. Antonia Maroulou, Asterios Bakolas, Maria Karagianni, Nikos Pitsakis, 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 masonry and especially of traditional ones. The widely used cementitious plasters are impervious layers, preventing the evaporation of rising damp and causing extended decay of masonry. Macroporous plasters, a modern method to afford 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, resulting by the action of micrometerating 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 the microstructural and mercury porosimetry analysis were used. Their durability to salts decay was examined with sodium sulphate 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. Wen-Ming Hou, W.M. Hou, Van Nang Institute of Technology, Dept of Civil Engineering, Chang-Li, Taiwan, ROC; Ping-Kun Chang, Van Nang Institute of Technology, Dept of Civil Engineering, Chang-Li, Taiwan, ROC.

The synchrotron radiation accelerator (SRA), the porousity survey of mercury intrusion porosimetry (MP), 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. In this study we tested the effect of electrical resistivity and permeability index in this study. The experiment shows that owing to the pozzolanic reaction of slag, it can decrease CH, dwindle the capillary porosity, enhance the densification of concrete, decrease 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 Kriete and Periawarny Arjumand, 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 70°C. The process is complex and is 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 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-five Type I & II Portland cements from across the United States, that represented a statistical survey of range of sulfate, equivalent alkali, CSA 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 Berger, Iwona König, University of Erlangen-Nürnberg, Dept of Inorganic Chemistry, Erlangen, GERMANY, Hans-Bertram Fischer, Jochen Stark, University of Würzburg, F.A. Finger-Institut für Bauwissenscba. Würzburg, GERMANY, C. Rössler, Max-Planck-Institut für Polymerforschung, Mainz, Germany, KNF auf West deutsche Gipswerke, Iphoven, 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 reported. The investigated cement boards consisted of Portland cement CEM I 42,5 and blast furnace cement type CEM III B-N 32,5 and were produced in a modified flow process. For reinforced the cement board incorporated 4% of alkali resistant glass fibres with high ZrO2 content: NEG H-200, tex 32, 14 mm. Oschin A glass, tex 38, 14 µm, A-P size and Oschin A AR, tex 76, 14 µm, A-P 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 alkali resistant glass fibres with high ZrO2 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 interpretation 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 clay with high pozzolanic activity. It was shown by ESEM-technique that in addition of SiO2 the additional SiO2 influences the reactions of the clinker phases and act as filler between clinker grains and the fibres and hence produce a denser core. Moreover the SiO2 exhibits a strong 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 reinforced cement 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

Thursday Evening, November 30, 2001

8:00 PM Exhibition Hall D (Hynes)

KK5.1 CHARACTERIZATION OF ULTRASONIC TECHNIQUES TO STUDY THE FORMATION OF MICROSTRUCTURE IN CEMENTITIOUS MATERIALS AT EARLY AGE. Guang Ye, Klaus van Breugel, A.I.A. Frenaj, 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 setup 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 0.50) and amount of aggregate. The cement hydration model HYMOSTRUC is utilized to simulate the formation of the microstructure. In the HYMOSTRUC model, the hydrated cement grains are simulated as gradually growing spheres. A spatial network, based on the microstructure is formed with the contact of the growing sphere. In this study, the contacts 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 growing cement grains (so called 'bridge volume'). Correlation has been found between the formation of the hydrated and the changes in the 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 H. Zysman, Yeshiva University, New York, NY; Claudio Guerra-Velas, University of Puerto Rico, Humacao, PR.

In the past, we have studied the time evolution of Concrete as a function of the concrete age. The novel technique of mechanical spectroscopy (Mechanical Spectroscopy) is based on the propagation of resonant audio frequency modes of oscillation along the long axis of cylindrical samples. An audio-frequency oscillating (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 vibrations extend 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 pieces 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 composites 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 Els, Zysman, E.Sternberg, J. Mech. Phys. Sol. 34 (1986) 725; PM Naghib, 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**

DEBRUINABILITY AND SERVICE LIFE PREDICTION FOR SULFUR CONCRETE. Amos Rafael Meiklyen, KTH, Royal Institute of Technology Dept of Architecture, Building Engineering, Stockholm, SWEDEN.

Sulfur Concrete (SC) is a thermostatic 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 Concretes (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 15608 part 1 & II. Buildings and constructed assets-Service Life Planning).

SESSION KK6: ALTERNATIVE BINDERS AND UTILIZATION OF WASTE MATERIALS
Chair: Frederik P. Glaser

**Wednesday, 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.

Alkal activation of aluminosilicate materials is an interesting chemical process that allows us to transform glassy structures (partially or totally amorphous) into very compact well-encrusted compositions. 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 matrices for immobiling 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 development, or even on the leaching behavior of the cement-based system, are well known.

**9:00 AM KK6.2**

INFLUENCE OF CONTAMINATED RECYCLED BRICK AGGREGATE ON MATRIX PROPERTIES, STRENGTH AND LEACHING CHARACTERISTICS OF CONCRETE.

F. M. M. Badie, D. D. Haggag, D. P. 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 reuse contaminated masonry. Very little research data is available on the effects of contaminated brick aggregate on concrete strength and durability, or the leaching 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. TG/DTG 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 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 require capacities. The dredged material consists of 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 commodities. A research project at Columbia University has focused on the decontamination of dredged materials that contain 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 to a technically viable, environmentally friendly and economically feasible way. Inert or pozollanic fillers are now widely used in concrete construction. The treatment process presented here is apt to transform treated dredged material into a mineral filler at the same time can 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.
water, and mineral admixtures for preparing a paste which fill into the voids of aggregates to make the resulting concrete having high fluidity and reduced strength. By increasing the packing fraction (PF) of aggregates, the produced concrete could have slump flow of 55±10 cm and compressive strength of 27.5±3.4 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 KKT7.2
STUDY OF THE ROBUSTNESS OF CEMENT/SUPERPLASTICIZER COMBINATIONS IN REACTIVE POWDER CONCRETE.
CONCRETE. Pierre-Claude Aréne, CIBH
Université de Sherbrooke, CANADA.

The robustness of cement/superplasticizer combinations is a new concept recently developed at the Université 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 undersized amount or in unacceptable bleeding, segregation and retardation for an overdose. 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 minimum. Therefore the robustness of cement/superplasticizer combinations is quantified with 3 different admixtures: a copolymer of acrylic ester (CAE), a polynaphthalene sulfonate (PNS) and a polylubemine sulfonate (PMS).

10:30 AM KKT7.3
THE EFFECT OF WASTE OIL-CRACKING CATALYST ON THE COMPRESSIVE STRENGTH OF CEMENT PASTE AND MORTAR.
Jung-Hui Wu, Wei-Lung Wu, Kung-Chung Hsu, National Taiwan Normal Univ. Dep. 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 reduced pastes only slightly. The improvement in the mechanical properties of mortars by the catalyst could be attributed to improved bonds between the cement paste and aggregate. The EPcat in the water/binder (W/B) ratio of 0.3 and the replacement level of EPcat increases, the effect becomes more significant.

10:45 AM KKT7.4
DRIY PRIMING OF SAND/CEMENT MORTARS USING SPOUT-FLUID BED TECHNOLOGY.
Sven Jovanovich, Howard Lifman, Joel L. Plassky, Remscher Polytechnic Institute, Dept. of Chemical Engineering, Troy, NY; Kyle Douglass, Sean Gerozmico, Kenneth Hower, 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. Conventional wet mixing equipment has difficulty dispersing the fine components because electrostatic forces between small particles are very large, it isdifficult to sufficiently 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 pozzolanas. 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 FCP-1500 fluidization and recirculation 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 for the air streams and the air inlet speeds, and the air 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 improved packing of the finest 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 KKT7.5
AN INVESTIGATION OF THE EFFECTS OF AXI STRENGTH ON THE FRACTURE AND FATIGUE BEHAVIOR OF CONCRETE. J. Lou, Princeton University, Department of Mechanical and Aerospace Engineering, Princeton, NJ; K. Blau, A.A. Sozokes, Department of Food, Agricultural and Biological Engineering, Department of Aerospace Engineering, Columbus, OH; W.O. Sozokes, Princeton University, 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 KKT7.6

We have studied the effects of PAA/PEObased 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 electro-acoustic measurement (EAM) technique. Rheological and viscoelastic measurements were carried out on fresh pastes (w/c = 0.35). Our observations provide new insight into the effects of polymer concentration, architecture, and multivalent ion interactions on the stability of dense cement pastes.

SESSION KKS-119: JOINT SESSION CEMENTS IN RADIOACTIVE WASTE IMMobilization
Chair: Kenneth A. Snyder
Wednesday afternoon, November 9, 2001
Republic B (Sheraton)

1:30 PM KKS.1/J16.1
CHARACTERIZATION OF THE BARRIER PERFORMANCE OF CEMENTS. F.P. Glasser, Univ of Aberdeen, Aberdeen, Scotland, UNITED KINGDOM.

Anniversaries are a good time to critically 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 the possibility of corrosion under other types of engineered barrier materials. Research leads to the conclusion that the principal advantage of cements lies in their chemical properties: they are 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 need to address missing or inadequate data is presented. The present show activity affords opportunity to research the next generation of cement barriers and quantify their performance.

2:00 PM KKS.2/J19.2
PRACTICAL MODEL TO EVALUATE DURABILITY OF CEMENT-BASED MATERIALS UNDER LEACHING, COUPLING WITH INTERNATIONAL DATA BASE. Shlomo Kamal, Laboratory...
3:15 PM K8.3/19.3
A SOLID SOLUTION MODEL FOR THE EROSION OF RADIONUCLIDES IN CEMENT: Allen T. Enemark, Chalmers University of Technology, Dept. of Nuclear Chemistry, Goeteborg, 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 the most reactive 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 for other compositions. 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 ions 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.

3:20 PM K8.4/19.4
STABILITY OF HYDROCERAMIC WASTE FORM DURING VHT TESTING: Barry E. Sheets, Michael W. Grutzewicz, Johnson,
Oshkosh, Wisconsin, Materials Research Institute, The Pennsylvania State University, University Park, PA; D. Darrell Seamer, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

The immobilization of INCLE requires cooling the reaction of alkali and an aluminosilicate to form a hydroceramic waste form. This has been carried out for the past ten years by this research team. Subsequent research has demonstrated the rate of formation as well as the ability to be sequenced the hazardous radionuclides and RCRA elements in the calix. Typical hydroceramic formulations were prepared and subjected to testing following the VHT protocol developed at Argonne National Laboratory. This test protocol maintains the test device in an environment of 100% relative humidity at temperatures up to 300°C for varying time intervals. Condensation onto test specimen then initiates surface reactions between water and the waste form at this elevated temperature. The results of the exposure of hydroceramic waste forms compared to EA glass will be discussed.

3:30 PM K9.1
PERFORMANCE OF PORTLAND CEMENT FOLLOWING THERMAL EXCURSIONS: Edgar 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 well 200°C. In order to maintain the integrity of the excavated openings, 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 altered 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-SiO2-H2O system at one bar pressure and 100°C - 200°C revealed differences in kinetics and crystal compositions compared to a 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 presence of Ca(SOH). However, if the cement reacts with mineral aggregate or rock in the new field, scope may exist for permanent and irreversible reduction in pH. Intended for joint session of J3 and K3.

3:45 PM K9.2
LONG-TERM PERFORMANCE OF CEMENTITIOUS MATERIALS AS TECHNICAL BARRIERS FOR NUCLEAR WASTE MANAGEMENT: Thorsten Meyer, Horst-Jürgen Herber, Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Braunschweig, GERMANY. The long-term behavior of cemented fly ash 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 (HA) and brown coal fly ash (BFA), were used in laboratory tests for the investigation of the suitability of the employed leaching experiment was developed in the GRS specifically for the boundary conditions of underground repositories. The experiments were 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 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 Ca2+ whereas Mg2+ is first accumulated in the leachate and then removed due to the formation of new CSH and C-S-H phases. The results of a 10 years leaching experiment with cemented fly ash 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 Mgrich brine will be stable than in NaCl-CaSO4 solution.

4:00 PM K9.3
EFFECT OF MATERIAL PARAMETERS AND ENVIRONMENT ON DURABILITY OF CEMENT-BASED MATERIALS UNDER LEACHING: Silam Kim., Laboratory of Mechanics and Technology, Chalmers, FRANCE; Michele Moreux, Laboratoire de Mechanics and Technology, Chalmers, FRANCE; Bruno Gerard, Laboratory of Mechanics and Technology, Chalmers, FRANCE, Bruno Gerard, Electricité de 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 build an international database with respect to the leaching kinetics. First, the influence of experimental conditions (accelerated or not accelerated test, ancient analogs) is analyzed and discussed. Secondly, the influence of mineral additions and of water-to-cement ratio are considered. Thirdly, the effect of environmental conditions is introduced in terms of waste possible lower and higher pH and different technical conclusions are put forward for consideration to designers and to modelers.

SESSION K9: CEMENTS IN WASTE IMMORLIZATION
Chair: Kenneth A. Snyder, Wednesday, Afternoon, November 28, 2001, Republic A (Sheraton)