

List of oral presentation abstracts

Monday, June 11, 2012

Hydration Kinetics and Materials Characterization

8:30 am – 10:00 am

Location: ECJ 1.202

Moderator: Kyle Riding, Tania Dey

Modeling the effect of calcium sulfates on C₃S hydration: implications for the origin of the optimum sulfate

Luca Valentini, University of Padua, Italy

Jeffrey Bullard, NIST, USA

Gilberto Artioli, University of Padua, Italy

Steven Satterfield, NIST, USA

The addition of calcium sulfate to Portland cement is of fundamental importance, not only for set regulation, but also for the control exerted on strength development. Indeed, compressive strength depends on the amount of calcium sulfate added to the mix and, in a plot strength vs. SO₃ a maximum is commonly observed for intermediate values, ranging from 2% to 8% by weight. In this contribution, we investigate the role of calcium sulfate on the hydration of the silicate fraction, by a numerical and experimental study of the system C₃S + gypsum. In particular, the mechanism of sulfate incorporation within C–S–H is studied numerically for the first time. Both the results of the numerical simulations and those of the in-situ X-ray diffraction and rheological experiments, show enhanced kinetics of C₃S hydration in the presence of calcium sulfate. The possible implications for the optimal amount of gypsum are discussed.

The filler effect: the influence of filler volume and surface area on cementitious reaction rates

Tandre Oey, University of California, Los Angeles, USA

Aditya Kumar, University of California, Los Angeles, USA

Narayanan Neithalath, Arizona State University, USA

Jeffrey Bullard, NIST, USA

Gaurav Sant, University of California, Los Angeles, USA

Finely ground mineral powders have been demonstrated to accelerate cement reaction (hydration) rates. This filler effect has often been attributed to the effects of dilution when the cement content is reduced or to the provision of additional surface area by fine powders. The latter contribution, i.e., the available surface area increase has been speculated to provide additional surface sites for the nucleation of hydration products, which in turn, accelerates reactions. Through extensive experimentation/simulation this work quantitatively deconvolutes the filler effect to describe the influence of surface area and mineral type (i.e., quartz or limestone) on reaction rates. Simulations performed using phase boundary nucleation and growth (BNG) methods reveal that the provision of additional (exposed) surface area, amplifies the nucleation potential (i.e., the number of participating nuclei) which contributes to the acceleration. These indications are in agreement with isothermal calorimetry datasets which provide evidence

for the acceleration in reactions. Overall, the research correlates and unifies the fundamental parameters linked to the filler effect and proposes approaches which can be used to describe, a priori, the influence of filler composition and fineness on the acceleration in overall (hydration) reaction rates.

Modeling and simulation of the cement hydration with different water to cementitious ratio

Yang Park, Stevens Institute of Technology, USA
Jon Belkowitz, Intelligent Concrete, LLC, USA
Frank Fisher, Stevens Institute of Technology, USA
Christopher Samy, Stevens Institute of Technology, USA

This research explores the use of a computer modeling and simulation program to predict the development of strength in the hydrated cement matrix over time. The models and simulations used evaluate the mechanical properties of three different concrete mixtures with the following water-to-cementitious ratios: 0.30, 0.45, and 0.60. The mechanical strength generated from the models and simulations were compared to laboratory specimens made up of a Type I/II Ordinary Portland Cement and a washed alluvial aggregate. The compressive strengths of the various experimental mixtures were determined via a closed-loop hydraulic press during various stages of hydration in-order to ascertain a comparison to the modeling and simulation methods. This analysis illustrates how the water-to-cementitious ratio and water content during cement hydration is related to an increase in porosity and a decrease in compressive strength.

Three-dimensional microstructural analysis of ultra-high performance concretes using neutron imaging

Fei Ren, Oak Ridge National Laboratory, USA
Hassina Bilheux, Oak Ridge National Laboratory, USA
Sophie Voisin, Oak Ridge National Laboratory, USA
Jy-An Wang, Oak Ridge National Laboratory, USA
Michael Lance, Oak Ridge National Laboratory, USA
Beverly DiPaolo, Engineer Research and Development Center, US Army Corps of Engineering

Ultra-high performance concretes (UHPCs) are a family of emerging cementitious materials. Their superior mechanical properties are a result of improvements in the concrete mix design and material processing, along with the addition of reinforcement fibers. By optimizing the water/cement ratio and utilizing ultra-fine pozzolans and superplasticizers, homogeneous and compact microstructures with reduced porosity can be achieved. Neutrons are sensitive to hydrogen absorption and offer great penetration depth. Thus, neutron imaging can provide a nondestructive approach to explore the microstructural features of cementitious materials, especially hydrous phases. This study used the CG-1D beam line of the High Flux Isotope Reactor Facility at Oak Ridge National Laboratory to perform radiographic and tomographic investigations on both UHPC and conventional concrete samples. This presentation will describe the experimental development, present preliminary results, and discuss findings of the research.

Evaluation of nanomechanical properties: an energy-based approach

Kaushal Jha, Florida International University, USA
Nakin Suksawang, Florida International University, USA
Arvind Agarwal, Florida International University, USA

Nanomechanical properties of a material are usually evaluated using a fundamental relation among reduced elastic modulus, initial unloading stiffness and contact area. In the standard Oliver and Pharr method, last two quantities are determined from the unloading portion of the load-displacement curves which may be cumbersome in view of the statistical indentation technique applied to heterogeneous materials. In this presentation, we show that both initial unloading stiffness and contact area (or hardness) could be determined efficiently using energy dissipated and recovered during indentation.

Broadband dielectric study of early-age concrete mortar containing internal curing materials

Joshua Ojo, Tennessee Technological University, USA
Nan Guo, Tennessee Technological University, USA
Benjamin Mohr, Tennessee Technological University, USA

Broadband Dielectric Spectroscopy is an inexpensive, non-destructive, non-ionizing and low-cost in-situ nano-scale characterization technique has been applied to set of mortars containing selected internal curing materials. Complex dielectric permittivity was measured at frequencies between 300 MHz and 13.5 GHz at 23°C temperatures for seven days. Judging from the shapes of absorption and dispersion curves, it was cleared that the permittivity of each concrete mixture consists of multiple relaxations. The recorded spectra were well described by the combination of both the Cole-Cole and Cole-Davidson spectral functions. Two distinct dielectric absorption peaks were observed and they shift to the lower frequency side according to the age of the concrete. This reflects hydration process and also a consolidation process with growing of C-S-H gel in the concrete as well as heterogeneous of water structures in the mixture.

A procedure of extracting individual spectra from the complicated complex permittivity and determination of relaxation time revealed that reasonable assignment of molecular motion could be given to each spectrum. This is an indication that the amount of water is considered to affect dynamic structure of concrete. The research shows that fast measurements could be done easily for materials having multiple relaxations like concrete.

Degradation of Cementitious Materials

10:45 am – 12:15 pm **Location: ECJ 1.202**

Moderator: TBD Sant, Shahsavari

Nanostructure of high-temperature cured oilwell cements

Jeffrey Thomas, Schlumberger-Doll Research, USA
Andrew Allen, NIST, USA
Simone Musso, Schlumberger-Doll Research, USA
Simon James, Schlumberger Riboud Product Center, France

Oilwell cementing represents a severe challenge for cement, due to the need to ensure the long-term integrity and mechanical properties under extreme conditions, including high temperature (HT) and high pressure. To avoid strength retrogression at temperatures above about 110°C, crystalline silica is added to the cement. This makes the HT hydration process (setting and curing of the cement) more complex, as initially formed hydration products are replaced by more stable phases over time. To study the properties of HT-cured cement, we analyzed specimens cured under a variety of conditions using small-angle neutron scattering and TEM. We observed that, at HT, there is a general coarsening of the nanometer-scale structure of the set cement paste over time, with associated degradation

of the properties. We show that the rate of coarsening depends strongly on the initial curing conditions, providing possible strategies for improving the properties and performance of HT-cured cement.

Nanoscale pore structure analysis of mortars undergoing delayed ettringite formation

Daniel Keaton, Tennessee Technological University, USA
Benjamin Mohr, Tennessee Technological University, USA

This research investigates the nano-scale pore sizes of cementitious mortars subjected to delayed ettringite formation (DEF). DEF is normally found in heat cured concrete, as well as mass concrete, that has been in place for a period of years. It is well known and documented that DEF causes expansion and eventually cracking in concrete. Previous research has found that there are no observable differences in the amount of DEF as seen by environmental scanning electron microscopy (ESEM) on both samples known to have expansion and those known to show little to no expansion. The objectives of this research are: (1) to recognize the pore size(s) responsible for the mass expansions of certain mortars under different curing conditions; (2) to find the effects of curing conditions and initial pore size distributions; and (3) to observe the evolution of the pore size distribution over time.

Chemo-mechanical behavior of carbon nanofiber/cement composites exposed to aggressive environments

Lesia Brown Vanderbilt University, USA
Florence Sanchez, Vanderbilt University, USA

While carbon nanofibers (CNFs) have potential for nano-level reinforcement of cement composites due to their unique chemical and physical properties, efforts to incorporate CNFs into cement-based materials have been hindered by dispersion issues. Much attention has been given to the physical, electrical, and mechanical properties provided by the CNFs, but little attention has been given to the durability of CNF/cement composites subjected to aggressive environments and the possible influence of CNF dispersion. Portland cement pastes with and without CNFs were subjected to decalcification and sulfate attack. Results indicate that the presence of a non-uniform CNF dispersion influenced the chemo-mechanical behavior of the composites, thus impacting the transport and mechanical properties of the composite when exposed to aggressive environments. Microstructural alterations as a function of degradation depth within the composite and CNF dispersion state will be presented. Flexural strengths as a function of exposure duration will also be discussed.

A combined approach of determining physical and chemical ASR parameters and finite element modeling to predict ASR expansive stress in a pure phase system

Kai-Wei Liu, Texas Transportation Institute, Texas A&M University, USA
Anol Mukhopadhyay, Texas Transportation Institute, Texas A&M University, USA
Zach Grasley, Texas, Department of Civil Engineering, A&M University, USA

There is pressing need to develop a rapid and reliable ASR test method and to formulate job specific ASR resistance mixtures. TTI developed a new rapid ASR test method called VEMD which is gradually gaining acceptance by the agencies (ASTM, TxDOT) as a potential rapid ASR test method. In this method, free volume change due to ASR is measured over time and activation energy is determined as a measure of aggregate reactivity. The main approach of this study is to utilize the existing data on activation energy (being generated in the ongoing project) along with newly generated data on physical properties of ASR gel (e.g., gel viscosity) and develop a finite element model to predict ASR expansive stress.

A preliminary study using borosilicate glass balls has been undertaken in order to verify the proposed approach. An experimental program has been designed where borosilicate glass balls is allowed to react with solutions of varying chemistry and measure activation energy by VEMD and the physical properties of the reaction products (e.g., viscosities, density, chemical composition etc.) by AFM and / or nano-indentation. The next step will be (i) developing finite element modeling to predict ASR free expansive stress by incorporating physical properties of gel and activation energy as the main inputs, (ii) casting mortar specimens using the glass balls and measure expansive pressure with and without restraint, (iii) compare the predicted vs. measured free expansive pressure and verify the model - favorable comparison will establish the model, (iv) apply the same approach for one concrete aggregate and estimate the expansion behavior with respect to a typical field condition. Monitoring solution chemistry and microstructures by SEM-EDS are considered as supporting tools.

The ultimate goal is to develop job specific ASR resistance mixtures based on this kind of fundamental approach. Adjustment of expansive stress through adjusting mix design will be the basis to develop job-specific ASR resistant field concrete mixtures. The main goal is to develop this approach as a rapid lab test protocol which will be used in the field to ensure successful performance of concrete materials used in highway infrastructures with respect to ASR. No work has been reported yet in this direction.

Life cycle of chromium obtaining the industrial wastes co-incineration process in the cement plant

Suthatip Sinyoung, Mahidol University, Kanchanaburi Campus, Thailand
Puangrat Kajitvichyanukul, Department of Civil Engineering, Naresuan University, Thailand

Normally, Industrial wastes, which are used as alternative fuel or adding material in the cement production process. Several wastes consist of heavy metal such as cobalt, cadmium, lead, zinc, nickel, and chromium. Chromium is one of heavy metals which are present in many industrial wastes. This work aims to investigate the life cycle of chromium which co-burning in the cement production process. The amounts of chromium added in the raw materials, raw meal, clinker, mortar, and finally the leaching processes were studied. Result shows that 89-96 % of chromium still remained in the clinker and approximately 2-9 wt.% of chromium is released to the furnace atmosphere. Chromium dose not incorporated in clinker but also in mortar. However, it indicated that hydration time is not affect on chromium content in mortar mixture. Resulting from the tank test (EA NEN 7375:2004) method under natural condition shows that 57-84% of chromium still remained in mortar and 6-13% of chromium was leached. For acid rain condition, percentage of chromium still remained in mortar lower than natural condition. It is shown that 39-61% of chromium remained in mortar and 26-35% of chromium was leached. Considering, chromium species in leachate, the results showed that both of Cr^{+6} and Cr^{+3} were presented in leachate.

Cohesion, Hybrids, and Composites

2:00 pm – 3:15 pm **Location: ECJ 1.202**

Moderator: Paramita Mondal, Tyler Ley

Behavior of confined water in porous C-S-H

Patrick Bonnaud, MIT Concrete Sustainability Hub, USA
Benoit Coasne, CNRS - Institut Charles Gerhardt Montpellier, France
Roland Pellenq, CNRS CINaM, France; MIT Concrete Sustainability Hub, USA
Krystyn van Vliet, MIT Concrete Sustainability Hub, USA

In the multi-scale porosity inherent to cementitious materials, water may be present in the liquid, solid, and/or gas state depending on the thermodynamic conditions (temperature, pressure, presence of ions). It is thus appreciated that water may play an important role in cement paste damage processes. Here, computational simulations are particularly advantageous because water properties in nanoscale pores are challenging to access experimentally. We have considered how the nature of the water confined within and between C–S–H grains changes with a function of relative humidity at ambient temperature ($T = 300\text{K}$) using semi-Grand Canonical Monte Carlo techniques. To relate the relative humidity (%RH) of the environment with the water content in the cement paste, we calculated adsorption isotherms. When an overall hydrophilic behavior was observed, the intergranular isotherms exhibited discontinuities during the pore filling that can be attributed to surface roughness effects and capillary condensation. Furthermore, to understand the mechanical effects induced by the presence of water in C–S–H pores, we computed virial pressures normal to the pore surface for various %RH and various pore widths. We found that calcium ions are responsible for the overall cohesion in these materials (giving rise to a negative pressure). However, the role of water in reducing or reinforcing this intergranular and intragranular cohesion depended on separation distance between C–S–H grains. The reduced cohesion at separation distances $< 5 \text{ \AA}$... and increased intergranular cohesion at intermediate distances of $5\text{--}10 \text{ \AA}$... were both amplified with increasing %RH. These findings give for the first time an atomistic picture of the confined fluid and its induced pressure effects on the solid structure in the lowest porosities of cement at ambient temperature and 100% RH. It is a first step to understand cement paste damage processes in more extreme conditions as high/low temperatures, high pressures, and/or various ionic concentrations.

Mechanisms of hydrogen bonding between organic polymers and disordered material: case of poly(vinyl) alcohol and calcium-silicate-hydrate

Rouzbeh Shahsavari, Rice University, USA

Hybrid polymer cementitious materials with superior mechanical properties have been recently the focus of increasing interest and applications. This is hypothesized mainly due to the hydrogen bonding between polymers and Calcium-Silicate-Hydrate (C–S–H), the main product of cement hydration. However, understanding the detailed chemical bonding schemes in polymer cementitious materials have received limited attention so far. In this work, molecular dynamics simulation are performed to uncover the complex mechanisms of bonding between Poly(vinyl) Alcohol (PVA) and C–S–H. First, under computational shear loading, a slip-stick motion between PVA and crystalline silicate chains of tobermorite, a crystalline analog of C–S–H, is observed, which indicate a series of simultaneous dual H-bond formation and breakage of PVA over silicate chains. We find the maximum cooperative H-bond strength is achieved with only two mer units of PVA, after which H-bonds strength decreases to an asymptotic level. Next, to predict H-bond strength for different substrate geometries and polymers, we systematically alter the PVA backbone and remove the bridging Silicon tetrahedra in tobermorite. The latter is important to study realistic C–S–H nanostructure. The results show that the defects decrease the H-bond strength and lead to expanded slip-stick motion due to the removal of potential host and donor sites for H-bonds. These findings have important implications on modifying the cohesion, toughness and strength properties of cement hydrate for industrial applications.

Exposing the mysterious nature of concrete viscoelasticity

Zachary Grasley, Texas A&M University, USA

Xiaodan Li, Texas A&M University

Edward Garboczi, NIST, USA

Jeffrey Bullard, NIST, USA

A new constitutive model that couples the evolving microstructure of hydrating portland cement paste and time-dependent deformation has been implemented using a novel numerical routine. Model simulations indicate concrete viscoelasticity may not depend on C–S–H viscoelasticity nearly so much as previously assumed. A new interpretation regarding the source of concrete viscoelasticity is given.

Producing and testing cement paste reinforced with carbon nanofibers

Ardavan Yazdanbakhsh, Texas A&M University, USA
Zachary Grasley, Texas A&M University, USA

This presentation is based on a research program on the incorporation of carbon nanofilaments in cementitious materials started in 2008 at the civil engineering department of Texas A&M University. Some of the important issues when producing and testing hardened cement paste incorporating carbon nanofibers (CNFs) will be discussed and related solutions will be suggested. In addition, some of the test results that demonstrate the benefits of utilizing CNFs in cement paste will be presented.

A new cement-rubber composite material with unique mechanical properties

Simone Musso, Schlumberger-Doll Research, USA
Agathe Robisson, Schlumberger-Doll Research, USA
Jeffrey J. Thomas, Schlumberger-Doll Research, USA
Franz-Josef Ulm, MIT, USA

A new composite material consisting of a nitrile rubber matrix mixed with cement powder has been developed. In contact with water, this composite swells up to 100% while developing significant strength.

This unique response, which is attributed to the hydration of the cement inside the rubber matrix, makes this new material an outstanding candidate for industrial sealing applications.

Mechanical tests and nanoindentation measurements show that the unhydrated cement-rubber composite has elastic modulus, storage modulus, hardness, and ultimate elongation values comparable to those of standard carbon black/rubber composite. Upon hydration and subsequent drying though, a remarkable improvement of physical properties is achieved. This improvement is explained by a threefold mechanism:

- In the first stage, water diffusing through the rubber matrix hydrates the cement particles, causing the composite to swell and stiffen. This was confirmed by thermogravimetric analysis (TGA), X-ray diffraction (XRD), and calorimeter analyses.
- As proved by Fourier transform infrared (FT-IR) analysis, the basic environment ($\text{pH} > 11$) resulting from cement hydration, combined with the elevated temperature, hydrolyses nitrile groups in the rubber, converting them to carboxylate groups ($-\text{COO}^-$).
- The newly formed carboxylate groups bond ionically with counter ions such as Ca^{2+} , creating a network of ionic crosslinks throughout the rubber.

The useful mechanical properties of the hydrated cement-rubber composite are related to the ability of the ionic crosslinks to dissipate more energy than covalent links because they can break and reform indefinitely

Tuesday, June 12, 2012

SCMs: Reactivity and Activation

8:30 am – 10:30 am **Location: ECJ 1.202**

Moderator: Maria Juenger, Mohr

Composite portland cements with fly ash, metakaolin, ground granulated blast furnace slag and geothermal silica waste additions

Cyndy A. Iñiguez-Sanchez, Universidad Autonoma de Nuevo Leon, Mexico

Lauren Gomez-Zamorano, Universidad Autonoma de Nuevo Leon, Mexico

Barbara Lothenbach, EMPA, Switzerland

Nowadays the use of supplementary cementitious materials (SCM) with pozzolanic and hydraulic additions is an important option to decrease the environmental impact effect of cement production, since besides substituting partially the cement; they allow the consumption of industrial wastes that are potentially environmental pollutants. In line with this, the aim of this research was the study of the effect of partially replace cement, using a mixture of four SCM: fly ash (FA), metakaolin (MK), ground granulated blast furnace slag (GGBFS) and geothermal silica waste (GSW). The latter is a by-product of geothermic electric power plants that produce energy by means of steam and brine extraction from underground. The GSW had a nanometric particle size and was incorporated to the systems as an alkaline suspension, which modified the rheology of the pastes, the pH and the content of Ca and Si ions in the pore solution, affecting the final properties of the cements. Compressive strength tests were carried out at curing periods between 1 to 90 days for all the samples. Also, the hydration of supplementary cementitious materials systems was examined by (a) solid phase analyses using X-ray diffraction, thermogravimetry, backscattering electron microscopy and energy disperse X-ray microanalyses, (b) the pore solution analyses by pore pressing and (c) thermodynamic modelling of the hydration processes which is based on the type of cement composition, the dissolution kinetics and the thermodynamic equilibrium of the hydration products. The results indicated that the compressive strength was improved with the incorporation of the SCM, primarily due to their pozzolanic and hydraulic behavior; accelerating the hydration reactions and producing additional C–S–H. With the increase in the temperature, the compressive strength results showed an increase in the early ages and a reduction after 28 days of curing. The effect of the GGBFS in the compressive strength was observed at long hydration periods. The FA and MK also modified the mechanical strength but its effect was lower compared to the GSW. The fine and uniform particle size distribution of the GSW suspension provided a higher specific surface increasing the reaction rate and the formation of new hydration products besides of the calcium hydroxide consumption. The depletion of the CH was corroborated by means of XRD analyses. Furthermore, the blended cements exhibited a very dense microstructure with a diminution in the porosity compared to the neat cement. The hydrates and non hydrate cement phases observed by SEM correlates very well with the findings from X-ray diffraction and thermogravimetric analyses. The modeled hydrated phases development was in agreement with the experimental results.

Study of the simultaneous effect of size and type of glass cullet, and curing temperature on the rate of glass reactivity

Mohammadreza Mirzahosseini, Kansas State University, USA

Kyle Riding, Kansas State University, USA

Mixed glass waste is a potential source of supplementary cementitious material (SCM) when crushed finely. Waste glass also serves as an excellent model system which can help guide future studies on SCM hydration. The current study investigates the pozzolanic reactivity of three size ranges of glass cullet – 0 to 25 μm , 25 to 38 μm , and 63 to 75 μm for clear and green glass at three different temperatures – 10°C, 23°C, and 50°C. Chemical shrinkage, isothermal calorimeter, thermogravimetric analysis, and quantitative X-ray diffraction are being used to measure the cement and glass reactions. Glass reactivity is shown to be influenced by the reaction temperature, type and particle size.

Microstructure of cementitious cast stone immobilizing the hanford secondary waste

Chul-Woo Chung, Pacific Northwest National Laboratory, USA
Ashutosh Goel, Pacific Northwest National Laboratory
Nancy Washton, Pacific Northwest National Laboratory
Laura Turo, Pacific Northwest National Laboratory
Joseph Ryan, Pacific Northwest National Laboratory

A solidified cementitious waste form, Cast Stone, was developed to immobilize the radioactive secondary waste from vitrification process in Hanford site. In this work, various analytical techniques, such as helium pycnometry, nitrogen gas adsorption, mercury intrusion porosimetry, X-ray diffraction, nuclear magnetic resonance, and scanning electron microscopy were used to study the effect of secondary waste concentration on microstructural properties of Cast Stone such as porosity, pore size distribution, phase compositions, and compressive strength. It was found that the concentration of secondary waste simulant affected the stability of ettringite and AFm phases. Pore size distribution and skeletal density of Cast Stone specimens were also affected by concentration of secondary waste simulant. The change in reaction kinetics occurred at 2M concentration of secondary waste simulant. However, the compressive strength did not show any changes depending on the concentration of secondary waste simulant.

Preparatory treatments to clay mineral blends for use in concrete systems

Sarah Taylor-Lange, University of Texas at Austin, USA
Kyle Riding, Kansas State University, USA
Maria Juenger, University of Texas at Austin, USA

The goal of this study was to investigate methods to increase the pozzolanic reactivity or early hydration kinetics of impure clay minerals to be used as a supplementary cementitious material (SCM) in concrete. 0.1N HCl solution treatment and the additions of, ZnO prior to the calcination of kaolinite, montmorillonite and illite clays were conducted. The resulting calcined clays were examined using x-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) to investigate the influence of preparatory treatments on the dehydroxylated clay structure. A 15wt% replacement of calcined clay for portland cement was used in investigating hydration per isothermal calorimetry and compressive strength tests. The pozzolanic reactivity was tested using the Chapelle Test (NF P18-513) and XRD scans on SCM-cement pastes at 7 and 28 days. The results demonstrated pre-soaking clay minerals in the acid solution did not influence clay mineral dehydroxylated content and resulted in a decrease in compressive strengths when compared to non-acid treated samples. ZnO additions incrementally increased the heat of hydration and corresponding compressive strengths of the calcined clay-cement systems. The results suggest, using idealized impure clay minerals, that the addition of ZnO to impure clays could facilitate their use as SCM materials for industry.

Mechanical properties and microstructure of clay-based materials prepared with modified yellow river silts

Lei Zhang, Tianjin Institute of Urban Construction, China
Jiu-jun Yang, Tianjin Institute of Urban Construction, China
Jun-Xia Liu, Zhengzhou University, China
Ai-Hua Zhou, Tianjin Institute of Urban Construction, China

The Yellow River silt is a kind of sedimentary soil, which carried by the steam of Yellow River from the loess plateau in China. In this paper, the influence of phosphoric acid on microstructure and surface characteristics of the lower Yellow River silts was analyzed, and modified silts by phosphoric acid was taken as raw materials to prepare clay-based materials with lime(or cement), sand and a few of auxiliary materials. The mechanical properties and microstructure of clay-based material were studied. The results show that: phosphoric acid reacts with calcium carbonate in the particle surface to form fiber-like crystal, which is justified as calcium phosphate. Meanwhile, -OH groups content on the particle surface increased after modification, this plays the effective role of activity of the Yellow River silts, and the best phosphoric acid content is 4% the weight of silts. The 28d compressive strength of phosphoric acid modified clay-based materials with lime reach to 19.3MPa, which is 1.9 times of specimen prepared by un-modified silts. SEM and EDS results reveal that the calcium phosphate and calcium hydroxide wrapped around the sand play a gel role together.

Allowing higher cement replacement by class C fly ashes: a new method

Denise Silva, W.R. Grace, USA
Josephine Cheung, W.R. Grace, USA
Lawrence Roberts, Roberts Consulting Group LLC, USA

It is not uncommon for the concrete producer to limit the replacement of cement by class C fly ash due to the deterioration of the early concrete performance, such as strength and set times. The performance loss is partially attributed to antagonistic and simultaneous chemical reactions that happen in the cement and in the fly ash when in contact with water. In addition, the use of class C fly ash is even banned by some DOTs due to the increased risk deterioration caused by sulfate attack.

This work describes a method developed to achieve performance of concrete with 50% class C fly ash replacement of cement similar to that of a concrete containing 20% class C fly ash replacement. The method involves pre-treating the fly ash in aqueous solution with chemical admixtures for a given period of time. The fly ash treated by this method can either be used as a slurry to prepare concrete or can be added as a powder after being submitted to drying.

Analytical techniques such as quantitative x-ray diffraction, thermogravimetric analysis, microscopy, analysis of the pore water, and isothermal calorimetry have been used to better understand mortar and concrete performance using pre-treated fly ashes. It is demonstrated that the minimum pre-treatment time to allow performance benefits is determined by an important precipitation of calcium-bearing compounds in the fly ash slurry as indicated by the pore water analysis. XRD studies have indicated that the main crystalline hydration product of the pre-treated class C fly ash is ettringite. With fully reacted calcium aluminates, it is believed that the durability of class C ash-concrete to sulfate attack is improved by this pre-treatment.

Cementitious characteristics of a chemically activated cupola slag

Rosario Jasso-Teran, Cinvestav-IPN Saltillo, Mexico
Jose M Almanza Robles, Cinvestav-IPN Saltillo, Mexico
J Ivan Escalante-Garcia, Cinvestav-IPN Saltillo, Mexico

This investigation explored the cementitious potential of a cupola slag, a byproduct of the iron foundry industry, by means of chemical activation using: Portland cement (substitution of 30, 50 y 70%), calcium hydroxide (15, 30 y 45%), and a mixture of Na₂CO₃/NaOH (4, 8 y 12% Na₂O relative the slag). Initially pastes were prepared using conventional procedures and the compressive strength development was evaluated as a function of time. For the slag-cement, the presence of slag reduced the strength term. Most of the mixtures with the other alkaline agents took more than 24 h to set, however reached good strength. In the second part, a fraction of the slag was submitted to a mechanochemical activation, i.e. ground in the alkaline suspension using most of the water for the paste preparation. In general the mechanochemical activation combined with curing at 60Å°C for 24 h was favorable, the setting time was reduced and the early strengths were enhanced due to the combination of alkaline attack and the reduction of particle size. X-ray diffraction showed that the pseudowollastonite present in the slag did not participate in the reactions and the formation of C-S-H was noted. The microstructures showed matrices of hydration products relatively dense, showing that the mechanochemical activation refined the particle size of the slag and promoted its reactivity. The cupola slag showed great potential as an alternative cementitious material.

Multi Scale Chemistry and Solubility Characterization of Chemical Phases within Fly Ash

Tyler Ley, Oklahoma State University, USA
Qnang Hu, Oklahoma State University, USA
Mohammad Aboustait, Oklahoma State University, USA
Jay Hanan, Oklahoma State University, USA
Jeff Davis, NIST, USA
Robert Winarski, Argonne National Laboratory, USA
Volker Rose, Argonne National Laboratory, USA

This presentation will show the characterization of fly ash from the nano to micro scale lengths by using atomic force microscopy coupled with low voltage scanning electron microscopy, synchrotron and laboratory based X-ray microcomputed tomography coupled with electron microprobe and synchrotron based XRF analysis. The chemical makeup and solubility of the phases within the fly ash are measured and discussed. This work provides fundamental insights into the reactivity of fly ash that have not been previously feasible.

Alternative Binders Based on Calcium Sulfoaluminates and Calcium Carbonates

11:00 am – 12: 30 am **Location: ECJ 1.202**

Moderator: TBD Kurtis, Sanchez

The gypsum effect on CSA cement hydration

Diana Londoño, Universidad Nacional de Colombia, Columbia
Ariel Berrio, Cementos Argos S.A., Columbia
Jorge Iván Tobón, Universidad Nacional de Colombia, Columbia

The Calcium Sulfoaluminate based cement (CSA) has been studied recently by the cement industry, because it has relevant characteristics from a hydraulic and environmental point of view. One of them is the reduced fuel consumption, related to the lower temperature reaction required for this kind of cement production as compared to ordinary Portland cement, another characteristic is the reduced requirement of carbonates as a typical raw material, comparing to Portland cement, plus the reduction in CO₂ coming from combustion. CSA cement has been investigated around the world for over 40 years, and now has attracted the attention of some of the largest cement companies, currently many of these companies have set a goal to produce CSA cement a industrial level but due to the lack information about specific topics of CSA characteristics, research continues to be necessary both at the academic and industrial scenarios.

In this work, eight laboratory-synthesized CSA cements from natural raw materials were made; these were tested for hydration rate, using different levels of sulfate addition, by means of isothermal conduction calorimeter to identify the effect of gypsum. Also each CSA cement were characterized mineralogically and chemically by X-Ray Diffraction and X-Ray Fluorescence respectively, to quantify its main components – yeelimite and belite - that react with the gypsum added.

Porosimetric study of calcium sulfoaluminate cements and its relation to freeze-thaw durability

Kyle DeBruyn, Sauereisen, Inc., USA

The present study examines the porosimetric differences between calcium sulfoaluminate (CSA) cement paste and portland cement paste of water-cement ratios of 0.40, 0.50 and 0.60. Nitrogen sorption and mercury intrusion porosimetry methods are used. The results show that CSA cement paste tends to have a smaller total pore volume and a smaller pore surface area than portland cement pastes of the same water-cement ratio. Further, the results show that the pore structure of CSA cement paste generally has larger median and average diameters than the pore structure of portland cement paste of the same water-cement ratio. The differences can possibly be attributed to the different chemistry of the two cements, where a significant amount of water is used up in the formation of ettringite in the CSA cement during the hydration process, possibly reducing the pore space while the matrix is still relatively soft. A freeze-thaw durability study was also conducted with air-entrained CSA and portland cement concretes with two different types of limestone as coarse aggregate. The results show that CSA cement concrete is able to withstand three times the number of freeze-thaw cycles before failure than portland cement concrete when poor quality aggregate is used. Further, even with good quality aggregate, the CSA cement concrete exhibits 11% less scaling than the portland cement concrete. A hypothesis relating the improved freeze-thaw performance to the porosimetric differences between the two cements is proposed.

Cementitious reaction via calcium carbonate polymorphic transformation

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Calcium carbonate has three crystalline polymorphs: vaterite, aragonite and calcite, where vaterite being the least and calcite being the most thermodynamically stable polymorph. Previous research has demonstrated that the polymorphic transformation from vaterite to aragonite through a dissolution-reprecipitation process in water exhibits some cementitious properties; however, with low strength. In this study, vaterite was produced by capturing and mineralizing CO₂ from natural gas-generated flue gas in calcium-rich natural brine. For optimum cementitious properties, the vaterite was highly engineered for particle size, surface charge, and surface ion concentration to control its polymorphic transformation to aragonite and the morphology and bridging of the aragonite crystals

formed. As a result, the final cemented material achieved a compressive strength of 4800 psi in paste, and furthermore 5300 psi in mortar and 4300 psi in concrete showcasing the good binding properties with inorganic substances.

Biom mineralization in cement-based materials

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Recently, it has been shown that bacterial induced calcite precipitation may occur in cement paste and results suggest self-healing of surface cracks can be possible. However, it is still unclear whether microbial-induced precipitation can occur within cement-based materials internally. If possible this process can improve durability and mechanical properties of the material and possibly lead to the development of a "bioconcrete" that is prepared with a lower cement content. The objective of this study is to describe the influence of embedded microorganisms on the hydration kinetics and mechanical properties of cement paste. The results showed a significant increase in compressive strength when the microorganisms were added, whereas the initial set of the cement paste was delayed. X-ray diffraction analysis is computed by a semi-quantitative method. Results identified increase in mass percentage of calcite due to addition of microorganisms at early and later ages, which can be correlated with the increase in compressive strength. Calcite precipitation is also observed with ESEM images obtained from 28-day old specimen. Preliminary studies showed that the microorganisms can survive in high pH and further investigation continues on viability of microorganisms in cement paste.

Characterization of biominerals and its effect in improving flexural strength of concrete

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Biom mineralization appears to be promising for healing cracks in concrete to improve durability and reduce maintenance cost. Previous studies showed that *Bacillus pasteurii* when used with suitable nutrient medium could produce calcium carbonate in cracks near the outer surface of concrete and reduce its permeability. However, it is still unclear if mineral precipitation can occur in cracks further away from the outer surface where oxygen supply might be limited. It is also questionable if the calcium carbonate, as a crack-healing material, can bond well with the old cement matrix to promote partial or full recovery of strength which is lost due to cracking. In this study, morphology of bacteria-induced precipitates obtained in cast-in-place notch of mortar beams was compared with the precipitates obtained in flask using the same bacteria and inoculation conditions. X-ray diffraction (XRD) showed that the precipitates were in the forms of vaterite and calcite, and scanning electron microscope (SEM) showed spherical pellets as the predominant morphology. Natural cracks in mortar beams were formed by crack-mouth opening displacement (CMOD) control flexural test and the improvement in flexural strength was observed after treating the cracks with bacteria and nutrient medium.

Thermal Properties of Wollastonite based Inorganic Phosphate Cement (IPC): effect of curing condition

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Wollastonite based Inorganic Phosphate Cement (IPC) was cured in between two aluminium plates for better temperature control, less deformation and shiny look. The curing temperature as well as the curing time were varied

and its effect on the properties of IPC were investigated with the help of ThermoGravimetric Analyzer (TGA), ThermoMechanical Analyzer (TMA), Differential Scanning Calorimetry (DSC) and InfraRed spectroscopy (IR). TGA results showed that mass loss can be minimized by increasing the curing time and decreasing the cure temperature. The second step in TGA curves at 200°C was indicative of Brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) to Monetite (CaHPO_4) transformation accompanied by loss of structural water, which was confirmed by IR. Deformation values recorded from the first heating cycle of TMA results showed a linearly decreasing trend with increase in curing time and was also reduced to some extent due to increase in cure temperature. The values of Coefficient of Thermal Expansion (CTE) were calculated from the slope of the linear curve obtained in the second heating cycle of TMA experiments. The heat of reaction, as obtained from DSC measurements, were also correlated with the curing conditions. This study shows that curing condition can play a vital role in optimizing structure-property-performance relationship in IPC samples.

Geopolymers

1:45 pm – 3:30 pm

Location: ECJ 1.202

Moderator: Jeffrey Chen, Thomas

Impact of mix compositions on geopolymer synthesis

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The alkali activated silico-aluminates is a way to produce high quality cementitious materials (geopolymer binder). Literature research demonstrates that the initial mix compositions such as $\text{Al}_2\text{O}_3/\text{SiO}_2$, alkali concentration, pH values influence the formation and properties of the geopolymer binder. However, these researches usually focus on one certain catalog of silico-aluminate source or a fixed activator; they can not give complete information for a new geopolymer synthesis. Thus, to find the commons of formulation parameters affecting the geopolymer formation, this study researched the materials produced with different silico-aluminates sources: metakaolin and clay, and different activators: silicate potassium, silica fume and potassium hydroxide. The geopolymer binders were identified and evaluated by microstructure observations and compressive strength tests.

Structure of metakaolin geopolymer with calcium hydroxide using XRD and MAS-NMR

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Geopolymers are composed primarily of amorphous aluminosilicates. The geopolymers that were studied for this project were metakaolin based with varying amounts of $\text{Ca}(\text{OH})_2$. Metakaolin geopolymers have been well studied and are composed of only geopolymer gel, an amorphous aluminosilicate with a network structure similar to that found in some zeolites. Typically there is no calcium in metakaolin, but addition of calcium is expected to produce calcium silicate hydrate (C-S-H) as well. Past research has shown that both systems can coexist in the geopolymer, but detection of C-S-H in the presence of geopolymer gel is difficult and little is known about the reaction products, whether C-S-H or aluminosilicate formation is preferred. The objective of this research is to gain confidence in the characterization of C-S-H and aluminosilicate gel as well as to better understand the role calcium has in geopolymer reactions. X-ray diffraction and magic angle spinning nuclear magnetic resonance (MAS-NMR) were used to characterize both the precursor and the geopolymers. XRD was used to monitor the changes in crystalline

and amorphous structures, while both ^{29}Si and ^{27}Al MAS-NMR were used to explore coordination of the silicon and aluminum atoms. Deconvolution of the ^{29}Si MAS-NMR spectra made it possible to detect both reaction products, determine their relative abundance, and observe the effects of increasing calcium content.

Correlation between physicochemical and mechanical properties to investigate geopolymer formation

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Geopolymer materials are extensively studied through the world due to their possible use as building materials and their low environmental impact. This class alumino-silicate binder displays an amorphous three-dimensional network and may be synthesized at room temperature by alkaline activation of alumino-silicates raw materials. Previous study has already shown the possibility to obtain a material with a controlled porosity by using various raw materials. This study aims to put in evidence the geopolymerisation phenomenon by in situ infrared spectroscopy. Indeed, the formation of geopolymer network lies in the dissolution of raw materials and in the reorganization of silicon and aluminum tetrahedron obtained from this one. Whatever the material considered the study of the displacement on the infrared band relative of Si-O-M bonds put in evidence the formation of only one polymer network, or of several silicate networks. Three kinds of materials can then be defined, and their repartition could be confirmed by mechanical, morphological and structural study (compressive stress, SEM observations, NMR measurements).

Co-fired fly ash as a precursor for geopolymer production

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The need to reduce CO₂ emissions associated with coal combustion has promoted the development of processes involving the combined combustion of coal with other organic materials, generating a by-product referred to as 'co-fired fly ash'. The chemical composition of co-fired fly ash is comparable to coal fly ash, rendering it a potentially suitable precursor for producing geopolymers (i.e., a less carbon-intensive alternative to ordinary portland cement concrete). However, these ashes differ from standard fly ashes because they contain biomass ash, which has been shown to change phosphate, alkali, magnesium, and reactive silica levels in addition to altering the morphology of the resulting ash product. In this study three ashes—one commercially available coal ash and two co-fired ashes produced by burning coal with wood chips—are activated with alkali silicate and hydroxide solutions, to evaluate the feasibility of using co-fired ash in the production of geopolymer binders. X-ray diffraction shows that using co-fired ash, the formation of zeolitic phases including herschelite ($\text{NaAlSi}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$) and faujasite ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$) is favored within an otherwise X-ray amorphous binder. The extent of gel formation and maturation is assessed by dilatometry and infrared spectroscopy revealing co-fired ash can be more polymerized after alkali-activation compared to coal ash. Determining the fundamental properties of these new materials is necessary before their utilization in low-carbon infrastructure, and in understanding the future of geopolymer

technology as the USA, Europe and other regions move increasingly to biomass co-firing (rather than pure coal) as a fuel source for electricity generation.

Bulk composition and microstructure dependence of effective thermal conductivity of porous inorganic polymer materials

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Experimental results and theoretical models are used to assess the effective thermal conductivity of porous inorganic polymer cements with porosity between 30 and 70 vol.%. It is shown that the bulk chemical composition affects the microstructure (grains size, pores size, spatial arrangement of pores, homogeneity, micro cracks, bleeding channels) with consequently the heat flow behavior through the porous matrix. In particular, introduction of controlled fine pores in a homogeneous matrix of inorganic polymer cements results in an increase of pore volume and improvement of the thermal insulation. The variation of the effective thermal conductivity with the total porosity was found to be consistent with analytical models described by Maxwell-Eucken and Landauer.

Mitigation of early age shrinkage in alkali activated slags through internal curing

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Alkali activated slag (AAS) binders show great promise as environmentally friendly alternatives to binders produced from Ordinary Portland Cement (OPC). The shrinkage behavior of AAS systems, however, is not well understood, and remains a hurdle to widespread adoption. It is well known that internal curing, which uses lightweight aggregate to provide additional water to a system that is beginning to undergo self-desiccation during chemical shrinkage, can effectively mitigate early-age shrinkage in OPC binders and has been investigated here in relation to AAS systems activated by either Na₂CO₃- or waterglass/NaOH solution. Chemical shrinkage measurements were used to determine the amount of additional curing water that needed to be supplied through internal curing. Autogenous- and total shrinkage measurements were used to determine the effects of internal curing on the overall shrinkage of the systems. The results show that it is possible for internal curing to completely mitigate autogenous shrinkage in AAS systems, however, autogenous shrinkage is not always the dominant shrinkage mechanism.

Compressive strength empirical formulation on curing temperature and time of rapid-set high-strength geopolymer for highway repair and rehabilitation

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Geopolymer has the potentials for use as repair cement due to its ability to develop strength rapidly. Experiments shows that compressive strength of fly ash based- and metakaolin based- geopolymer paste increased with curing temperature and time. Samples of geopolymer cubes of 5 cm x 5 cm x 5 cm were prepared by mixing metakaolin or fly ash with sodium silicate solution producing viscous slurry which was then casted in cast iron molds. The slurry in the molds was then cured in a controlled oven with a precision of 2 °C. Curing was performed at room temperature (~27 °C), 40, 50, 60, 90, 100, 120 and 150 °C for 4, 8, 18 and 24 hours. After curing at the specified temperature and time, the geopolymer filled molds were taken out of the oven and left for 10 minutes to cool down before being removed from the mould and tested. Six samples were tested for each combination of curing

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temperature and time. Averaged compressive strength values were plotted against curing time at the specified curing temperature and vice versa.