

The American Ceramic Society

2024 Cements Division

14th Advances in Cement-based Materials

Book of Abstracts

June 19-21, 2024

Rolla, MO

Keynote Speaker – Shiho Kawashima

Wednesday, June 19, 2024, 8:30 – 9:15am

Cement Rheology And Processing – why give a CRAP

Abstract: Although cement-based materials are in the plastic state for only a short period of time, its corresponding rheological properties are critically important to enable proper processing and placement so that the final material performs in the way it was intended to. For conventional casting methods, we have been primarily focused on flow properties. However, as 3D concrete printing has emerged as a promising method of construction, we have become more interested in the viscoelastic and elastic properties of cements while still in the fresh state. This talk will highlight some of our recent studies in this area, including understanding the role of different CaCO_3 polymorphs derived from CO_2 mineralization pathways on tailoring structural build-up behavior and capturing the time evolution of viscoelastic parameters (i.e. storage modulus and critical strain) via shear oscillatory strain sweep methods.

Della Roy Lecture – Maria Juenger

Wednesday, June 19, 2024, 4:05 – 5:15pm

The road to sustainable cement

In 1987, the United Nations Brundtland Commission defined sustainability as “meeting the needs of the present without compromising the ability of future generations to meet their own needs.” This definition addresses the importance of continuing to maintain and grow infrastructure in developed and developing regions for quality of life. In 2024, the sustainability of construction, and particularly of cements, has taken on a new urgency as climate goals are becoming more ambitious and formalized. Correspondingly, we are seeing incredible growth in research and development of green cements. In this talk, I'll explore a bit of the history of sustainable cements (including the pioneering work of Della Roy!), putting new cements in their historical and technological context. I'll discuss in more detail the sustainable cements that have been the focus of my research on over the past two decades, namely calcium sulfoaluminate belite cements, alkali-activated materials, and supplementary cementitious materials with an emphasis on synthesis, characterization, and novel applications.

1A: Sustainability and SCMs (Part 1 of 3)

Wednesday, June 19, 2024, 10:25am - 12:25pm

10:25am - Abstract #3306

The mechanical and transport properties of waste limestone filler concrete

Ruben Paul Borg, Faculty for the Built Environment, University of Malta, Msida, Malta and Cyril Lynsdale, Department of Civil and Structural Engineering, University of Sheffield, Sheffield, United Kingdom

Abstract Text:

Significant quantities of waste limestone filler are produced as an industrial by-product in the quarrying of limestone resources for the production of aggregate for civil engineering applications and in the extraction of limestone blocks. Specific streams of waste limestone by-products (Coralline limestone and Globigerina limestone waste) which have been so far discarded have been characterised to assess their suitability as part replacement of cement in concrete when used in powder form. Concrete was produced with different types of waste limestone fillers of varying quality together with an industrial limestone filler, as part replacement of cement. The effect of varying maximum size of limestone filler was also analysed. The mechanical properties and transport mechanisms of the concrete produced with varying types and percentage replacement of limestone filler were analysed in the experimental programme with reference to indirect durability indicators (porosity) and direct durability indicators (Oxygen Permeability, Water Permeability and Chloride penetration methods). The compressive strength of concrete produced with specific limestone filler types demonstrated a comparable performance to the industrial grade filler. In particular 5% and 15% replacement levels led to an improved initial strength of the concrete at 3 and 7 days. The transport properties of concrete with limestone filler replacements up to 5% and in some cases up to 15% led to a comparable and even improved performance with respect to the control. A 35% replacement led to a reduction in compressive strength and also in durability performance. No significant improvements in long term performance in the transport properties including chloride penetration at 90 and 180 days were reported. The research reinforces the potential of limestone filler by-products, which were previously discarded, as part replacement of cement, to reduce the overall embodied energy and carbon footprint whilst transforming waste into a resource.

10:45am - Abstract #3329

Reactivity of amorphous aluminosilicates upcycled from waste cement paste

Diandian Zhao, Joanh M. Williams, Ah-Hyung Alissa Park and Shiho Kawashima, Columbia University

Abstract Text:

A two-step leaching and carbonation process was employed to upcycle waste cement paste into calcium carbonate and an amorphous aluminosilicate residue. The reactivity of the residue material has been explored using model systems to determine its potential hydraulic and pozzolanic reactivity. The residue has been found to possess strong pozzolanic reactivity and improved the compressive strength by 25% at 10 wt% cement replacement level at 3 and 28 days. Time-resolved phase assemblages of cement pastes incorporating the residue material were determined via X-ray diffraction (XRD) and thermogravimetric analysis (TGA). ²⁹Si Nuclear Magnetic Resonance (NMR) was performed to capture the evolution of silicate structures during the leaching and reincorporation process to reveal the mechanisms underlying the high reactivity of aluminosilicates residue.

11:05am - Abstract #3262

Vaterite performance as an SCM extender and binder

Ying Wang, Jesus Gonzalez Pequeno and Craig W Hargis, Product Development, Fortera, San Jose, CA

Abstract Text:

This study investigated the effects of incorporating vaterite as a partial replacement for supplementary cementitious materials (SCMs) in blended cements, aiming to enhance both fresh and hardened properties, including fresh mortar flow, compressive strength, setting time, durability, and hydration kinetics. Results indicated that a vaterite replacement of 5-10% in cement-fly ash blended cement led to a significant enhancement in early-age strength, with a 40% increase observed at 1 day compared to the non-vaterite control. Moreover, the strength superiority persisted throughout the 56-day testing period. Similarly, a 10% vaterite replacement of slag in cement-slag blended cement exhibited a notable increase of approximately 20% in strength at 3 days. In cement-slag-fly ash blended cement systems, a 10% replacement of fly ash with vaterite resulted in substantial strength gains of 30% to 50% within the initial 7 days. Additionally, a noteworthy reduction in the initial setting time by 50-110 minutes was observed, indicating the potential for improved finishing times. Assessment of durability through bulk resistivity measurements revealed enhanced resistance to deleterious effects, suggesting improved long-term performance. Sulfate attack and alkali silica reaction tests corroborated the durability of vaterite-blended cements, demonstrating expansion below specifications. Hydration analysis employing isothermal calorimetry and thermogravimetry illustrated accelerated early-age hydration reactions attributed to vaterite inclusion, contributing to the observed strength enhancements. Furthermore, vaterite's versatility extends to standalone binder applications, where its dissolution-precipitation reaction yields a continuous calcite structure, resulting in rapid strength development. Ultimate strengths exceeding 35 MPa within 48 hours were achieved in cement mortar, with the added advantage of adjustable initial setting times through appropriate admixtures. Integrating vaterite into the building material industry presents a promising avenue for reducing embodied carbon, while achieving the desired engineering properties, such as setting time, early-age strength, and durability.

11:25am - Abstract #3316

Overview of cast stone as a cementitious waste form for simulated and real low activity waste

Jonathan L. Lapeyre, Gary L. Smith, Sarah A. Saslow and Matthew R. Asmussen, Energy & Environment Division, Pacific North West National Laboratory, Richland, WA

Abstract Text:

The safe and effective disposal of low-level waste nuclear waste can utilize several different material science technologies to immobilize constituents of concern such as vitrification, sintering, and, for this presentation, cementitious waste forms. This presentation focuses on Cast Stone; a cementitious binder comprised of blast furnace slag, class F fly ash, and ordinary portland cement that undergoes a hydration reaction like conventional cementitious materials when mixed with liquid low-level nuclear wastes. This present work is a primer on the history and development of Cast Stone, the advantages that cementitious waste forms like Cast Stone bring to the table compared to other immobilization technologies, the challenges associated with varying chemistries found in low-level nuclear wastes, an overview of the hydration reaction-property relationships, how Cast Stone immobilizes radionuclides like technetium-99 and iodine-129, strategies to enhance immobilization such as including engineered additives (e.g., reducing agents or getters) and ensuring durability over the cementitious waste form life cycle. Additionally, discussion on recent work investigating the sensitivity of hydration process with varying dosages of organic chemicals prevalent within waste tanks and how similar or different these behaviors are compared to conventional construction binders is presented.

11:45am - Abstract #3209

Valorization of waste-to-energy ashes in cementitious systems via mineralogical transformations

Vikram Kumar¹, Aniruddha Baral¹, Jeffery Roesler¹ and Nishant Garg², (1)Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, (2)Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Abstract Text:

Waste-to-energy (WTE) ashes are a by-product of waste incineration and a potential supplementary cementitious material. These ashes are enriched in chlorides and heavy metals, which has restricted their use in cementitious systems due to corrosion and leaching risks. To address these limitations, we have developed a novel ash treatment process to transform the chloride speciation in WTE ash to Chlorellestadite ($\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Cl}_2$). This transformation reduces the chloride release from WTE ash in an alkaline pore solution to non-significant levels (<10 mg/l), while simultaneously reducing Pb mobility (<0.5 mg/l). In this work, we evaluate the potential of employing Chlorellestadite-enriched treated WTE ashes in cementitious systems. Our results indicate that the treated WTE ashes alter cement hydration kinetics slightly and do not form any Hydrocalumite ($\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$) – evidence that the chlorides in the form of Chlorellestadite are stable in cementitious systems. These findings demonstrate that chloride enriched WTE ashes after treatment can be a potential cementitious material.

12:05pm - Abstract #3129

Ternary blended cement with off-specification scms

Alexander S. Brand, Civil and environmental engineering, Virginia Tech, Blacksburg, VA

Abstract Text:

Quarries around the world are faced with a wide variety of problems related to by-product and waste material management. To produce crushed aggregate that meets gradation requirements, blasting and crushing operations produce a large amount of excess quarry by-products. Similarly, the decreasing production of fly ash in the U.S. has resulted in a need to consider off-specification fly ashes, even those that do not meet the updated ASTM C618 standard. Therefore, this study aimed to produce a ternary blended cement (i.e., ASTM C595 Type IT) with quarry by-products replacing the limestone powder and with off-specification fly ash as the pozzolan. Through a consideration of three different quarry by-products and three different fly ashes (including one meeting ASTM C618), the combination of quarry by-product with fly ash was optimized for hydration kinetics and mechanical performance. Isothermal calorimetry, pore solution extraction, flow table, compressive strength, and other results will be presented to demonstrate the viability of off-specification SCMs in a ternary blended cement.

1B: Material Characterization

Wednesday, June 19, 2024, 10:25am - 12:25pm

10:25am - Abstract #3221

Phase identification & quantification of anhydrous cements via combined x-ray diffraction and raman imaging

Chirayu Kothari, University of Illinois Urbana Champaign, Urbana, IL and **Nishant Garg**, Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Abstract Text:

In the efforts to reduce the carbon footprint of the construction industry, cements are becoming increasingly complex in terms of mineralogy and physical properties. One of the major challenges in quantifying these complex cements is the accurate identification of phases present in the system, which usually warrants a multi-technique approach. Here, we employ two highly diverse techniques, (1) X-ray Diffraction and (2) Raman Imaging (5mm x 5mm, 250,000 pixels, with 10 μm /pixel resolution), to common samples (ASTM Type I/II OPC and CSA cement). Our results reveal that optimal Raman analysis and optimal XRD analysis were in strong agreement ($R^2 > 0.99$, $\Delta\text{wt.}\% < 5\%$). Finally, by a comprehensive theoretical analysis of $\sim 200,000$ cropped images and experimental validation, we report that smaller areas can be reliably used for OPC phase quantification, significantly shortening the scan time by 2.5 times, from 8 hrs to 3 hrs.

10:45am - Abstract #3219

Novel use of hyphenated TG-IR to quantify degree of hydration in complex cementitious systems

Julia Hylton, Materials Science, Colorado School of Mines, Golden, CO and **Lori Tunstall**, Civil and Environmental Engineering, Colorado School of Mines, Golden, CO

Abstract Text:

Thermogravimetric analysis (TGA) is often used to measure the degree of hydration of cementitious materials. Using several assumptions, the TGA-only method attributes the mass loss of a cementitious sample with the decomposition of either hydration products or carbonates, depending on the temperature range of the decomposition. However, as cementitious systems become increasingly complex with adoption of carbon curing, chemical admixtures, new SCMs, limestone cements, and carbon-rich additives, the assumption that only one product is decomposing in a particular temperature range may no longer be valid. Moreover, it may be prudent to distinguish whether strength contributions are from hydration products or carbonate formation. Using infrared (IR) spectroscopy to analyze the gas evolved from the TGA, specific gases can be identified and, with an accompanying calibration dataset, quantified. This allows for the deconvolution of mixed gases evolving from overlapping decomposition temperatures and more accurate quantification of chemically combined water and CO_2 . This method can reliably quantify decomposition products, even during simultaneous evolution, providing a path to quantify degree of hydration of complex cementitious systems.

11:05am - Abstract #3249

Synchrotron microtomography applied to the study of neutron-induced cracks on irradiated aggregate

Adam Brooks, Oak Ridge National Laboratory, Oak Ridge, TN, **Elena Tajuelo Rodriguez**, Reactor and Nuclear Systems Division, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN, Paula C Bran Anleu, Nuclear Energy and Fuel Cycle Division, Oak Ridge National Laboratory, Oak Ridge, TN, David Arregui Mena, Oak Riddge National Laboratory, Oak Ridge, TN and Mark Rivers, Advanced Photon Source, Argonne National Laboratory, Lemont, IL

Abstract Text:

The prolonged use of the existing nuclear fleet will play an important role in delivering energy needs worldwide in the next decades. Using operating plants longer than anticipated has opened a lot of questions regarding materials integrity and safety, as they will be exposed to high gamma and neutron doses. Concrete is one of the materials requiring further attention, with the concrete biological shield surrounding the reactor pressure vessels being the most irradiation-affected civil structure in a power plant. Most neutron radiation effects are thought to occur on the aggregates and highly depend on their mineralogy. Six Japanese aggregates of varied mineralogical origins; a meta-chert, four felsic sandstones and a limestone, were studied to quantify microcrack patterns induced by four doses of neutron radiation relevant to prolonged operation. The results were compared with those of pristine control samples. The samples were scanned at beam line GeoSoilEnviroCARS (GSECARS) 13 BMD at the Advanced Photon Source (APS) at Argonne National Laboratory. Two tomographies with different resolutions were obtained per sample: A scan covering most of the specimen volume (cylinder of 1cm height and 1cm length) with a pixel size of 5.74 microns, and a scan covering a smaller volume with higher resolution and pixel size of 1.09 microns. The scans were processed using Dragonfly software to develop a 3D reconstruction of the post-irradiation crack structure in which both manual segmentation and built-in Dragonfly modules were employed. These reconstructions were used to qualitatively identify crack orientations and quantify total crack volumes in the aggregates and identify dose effect on each mineralogy. Analyses with higher resolution 2D slices will be performed to identify whether crack propagation occurs across grain boundaries or through grains, when possible and contrast allows, within the acquired resolution.

11:25am - Abstract #3182

High neutron and gamma dose effects on c-s-d

Paula C Bran Anleu¹, Nishant Garg², Joerg C Neuefeind¹, Yann Le Pape³ and Elena Tajuelo Rodriguez³, (1)Nuclear Energy and Fuel Cycle Division, Oak Ridge National Laboratory, Oak Ridge, TN, (2)Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL, (3)Reactor and Nuclear Systems Division, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN

Abstract Text:

The chemical properties of synthetic calcium silicate deuterate (C-S-D) with C/S (Ca/Si) ratios of 0.75, and 1.33 were studied after neutron and gamma irradiation absorbed dose of $1.22E^{19}$ n/cm² ($E > 0.1$ MeV) and 1.02 GGy, respectively, and compared with those of control specimens. Control specimens were stored in different conditions to compare the efficiency of the different current practices for storing control specimens and the effect of temperature during irradiation. The control specimens were exposed to the same temperature history than the irradiated samples; additionally, a set was stored in a desiccator under vacuum, and another set was stored in a moisture and inert gas-controlled glove box at ~11% RH. Thermogravimetric analysis was used to determine the water content, and x-ray diffraction measurements were used to calculate the dimension of the basal spacing. Neutron pair distribution function analysis measurements were taken at NOMAD Spallation Neutron Source at ORNL to investigate the interatomic distances in the structure.

11:45am - Abstract #3142

New insights on surface properties of cementitious materials gathered by inverse gas chromatography (IGC) at infinite and finite dilution conditions

Franco Zunino, Institute for Building Materials, ETH Zurich, Zurich, Switzerland

Abstract Text:

This study introduces a preliminary investigation into characterizing the surface energy properties of clinker phases (C3S and C3A), kaolin, and metakaolin using Inverse Gas Chromatography (IGC). A robust measurement methodology was devised for this purpose. Through an analysis encompassing a range of parameters (including dispersive surface energy, specific polar interaction parameter, acid and base constants, morphology index, nanoroughness, and adsorption energy distribution function), distinctions were observed among powders subjected to different surface treatments. The study reveals a promising correlation between surface properties and the reactivity of the examined materials. Notably, while the increased reactivity of metakaolin compared to raw kaolinite appears to be primarily associated with alterations in local order rather than substantial changes in surface energetics, shifts in the acid/base nature of the surface were also noted based on IGC characterization.

Though further investigations are warranted to comprehensively grasp the potential of IGC in elucidating surface energetics, the outcomes of this study present an encouraging outlook on its contributions to the field of cementitious materials. Specifically, it introduces another avenue for autonomously evaluating surface energy, which could potentially complement estimations derived from molecular dynamics simulations. Nonetheless, a persistent constraint lies in the current inability of IGC theory to determine the polar and hydrogen bonding components of surface energy. Thus, continued refinement of the technique and its theoretical foundations is imperative to fully exploit its capabilities.

12:05pm - Abstract #3167

The intrinsic mechanical properties and creep of calcium silicate hydrate

Jiaqi Li, Lawrence Livermore National Laboratory, Livermore, CA

Abstract Text:

The intrinsic mechanical properties of calcium silicate hydrate (C-S-H) are of great interest. C-S-H governs the creep of concrete. High pressure X-ray diffraction is a powerful tool to determine the intrinsic mechanical properties of C-S-H and probe the shear behavior of C-S-H under different environments. We investigated the influencing factors (interlayer spacing, cross-linking structure, chemical composition, and temperature) of the bulk modulus of C-S-H and the origin of C-S-H creep. Interlayer sliding lubricated by water is the key reason for C-S-H distortion and concrete creep.

2A: Sustainability and SCMs (Part 2 of 3)

Wednesday, June 19, 2024, 1:40pm - 3:40pm

1:40pm - Abstract #3259

An eco-friendly carbonation method for hydrated cement paste

Xi Chen¹, Xiaodong Wang¹, Maysam Bahmani¹, Monica Amaral¹, Jialai Wang² and Abdulmalik Alawode¹, (1)The University of Alabama, Tuscaloosa, AL, (2)Civil, Construction, and Environmental Engineering, The University of Alabama, Tuscaloosa, AL

Abstract Text:

This study explores a novel carbonation method to convert hydrated cement paste (HCP) derived from end-of-life concrete into a carbon absorbent and new supplementary cementitious material (SCM). Although the carbonation of calcium-rich materials such as HCP can sequester some CO₂, its carbon benefit can be offset by the energy consumed in the accelerated carbonation process. This study adopts an aqueous carbonation method, in which RCF is mixed with water and carbonated through CO₂ bubbling. To accelerate the carbonation process and produce a more reactive carbonation product, a biomolecule, tannic acid (TA), is added to mediate the carbonation process. As a chelating agent for calcium, TA accelerates the carbonation process and drastically increases the CO₂ uptake of the HCP. More importantly, TA can significantly change the morphology and polymorph of the produced CaCO₃ precipitate, producing more metastable CaCO₃. Once added into concrete, metastable CaCO₃ can trigger multiple mechanisms, functioning as a new type of SCM. The carbonated RCF slurry is directly added to the concrete mix without drying. This not only eliminates all energy consumption associated with the drying process but also retains more absorbed CO₂ in the concrete. Experimental results suggest that 80% calcium carbonated at a solid-to-liquid ratio as high as 0.6 with the proposed technology, which is 150% higher than that reached by carbonation without using the admixture. Compared with existing carbonation technologies, the proposed technology enjoys many advantages, including low energy consumption, less water consumption, and much higher CO₂ uptake.

2:00pm - Abstract #3349

High Filler, Low Water (HFLW) Cement-Based Mixtures for Carbon Emissions Reduction

Denise A Silva¹, Rafael Pileggi² and Markus Rebmann², (1)Building Envelope Materials Research/Building and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN, (2)University of São Paulo, São Paulo, Brazil, Brazil

Abstract Text:

Given the advantages that concrete offers, its simplicity of use, worldwide availability, and the pressure to meet housing deficits for the next decades, it does not seem that concrete will be replaced by other technologies in the near future. Hence, it is imperative to deploy technologies that can significantly reduce CO₂ emissions in the near term. A project was conducted at the Oak Ridge National Laboratory to develop high filler, low water (HFLW) concrete mixes to decrease cement content by at least 35% without major impact on mechanical properties or cost of the mixes. Here we describe the methodology used to design the paste fraction of concrete mixes based on materials characterization, rheometry, and using particle packing models. A strong correlation between IPS (Inter-Particle Separation) and the consistency index of the Herschel-Bulkley rheological model guided the formulation of the pastes, together with heat of hydration results that are critical when high doses of polycarboxylate-type of dispersants are applied.

2:20pm - Abstract #3204

Hydration and carbonation behavior of a pure c-s-h – calcite binder

Atolo A Tuinukuafe, Hongkyu Yoon, Melissa Mills, Chven Mitchell and Jessica M Rimsza, Sandia National Laboratories, Albuquerque, NM

Abstract Text:

Pozzolans are commonly used as supplementary cementitious materials with portland cement and can benefit performance while reducing the CO₂ footprint of concrete. Pozzolanic cements without portland cement clinker phases could enable even greater reductions in carbon footprint, but further research is needed on their performance. In this study, an alternative binder comprised of a highly reactive zeolite pozzolan, lime, and varying calcite content was prepared and characterized to evaluate the carbonation behavior of this new binder system. Fundamental insight into hydration kinetics and carbonation mechanisms of hydraulic binders was obtained via analysis of this pure C-S-H and calcite microstructure. X-ray micro-computed tomography (micro-CT) was used to quantify microstructural changes in the binder after carbonation, such as shrinkage or cracking. Crystallographic and thermal analyses measured compositional changes in the binder. The amount of calcite added to the binders influenced the volumetric stability and overall carbonation behavior. These findings support continued development of alternative binders that have comparable features and performance to portland cement, but with lower CO₂ emissions. *SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. SAND2024-03854A.*

2:40pm - Abstract #3206

An ultra-rapid reactivity (UR²) test for real-time quality control of calcined clays

Yujia MIN¹, Hossein Kabir², Chirayu Kothari¹, Muhammad Farjad Iqbal¹ and Nishant Garg², (1)University of Illinois Urbana Champaign, Urbana, IL, (2)Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Abstract Text:

Calcined clay is a sustainable supplementary cementitious material suited for meeting the growing demand of the cement industry and reducing its carbon footprint. However, there is a lack of real-time quality control technology for reactivity assessment during industrial production of calcined clay. This study investigated 47 calcined clay samples (natural and commercial), including kaolinite, montmorillonite, and illite-based clays, and developed a novel reactivity test called UR². When compared to the pozzolanic reactivity measured by the R³ test (ASTM C1897), it was found that the results obtained within 5 min were correlated to the 7d cumulative heat release during R³ testing (R²=0.92). Thus, this UR² method can enable real-time reactivity assessments on the production line and instantaneous adjustments of production conditions. Overall, our study presented a new reactivity test for calcined clays which can be performed within minutes. Our UR² test can facilitate the deployment of calcined clay at commercial scale.

3:00pm - Abstract #3157

On the use of isothermal calorimetry to unveil fly ash reactivity in aqueous environments

Rohan R Bhat¹, Taihao Han², Gaurav Sant³, Narayanan Neithalath⁴ and Aditya Kumar¹, (1)Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO, (2)Materials science and engineering, Missouri University of Science and Technology, Rolla, MO, (3)University of California Los Angeles, CA, (4)Civil Engineering, Arizona State University, Tempe, AZ

Abstract Text:

The *degree of reactivity* of fly ashes can vary significantly due to their varying chemical composition when used as a supplementary cementitious material. This study proposes a novel method to estimate the *degree of reactivity* of fly ashes using the first principles of the Hess's Law coupled with simple isothermal calorimetry observables. In addition to obtaining the *degree of reactivity* of fly ashes, a comprehensive comparison has been made between the proposed method and another method established in literature by Glosser et al. Upon obtaining the *degree of reactivity* of fly ashes, a proxy called *number of constraints* derived from the topological constraint theory was used to represent the *degree of reactivity*. Fly ashes with high value of *number of constraints* presented a low *degree of reactivity*. The *reactivity* of all 13 fly ashes ranged between 10-to-50% at 7 days. Upon comparing the *degree of reactivity* of fly ashes between the proposed method and the method proposed by Glosser et al. an overestimation of $\cong 1.6$ times was observed in Glosser et al. method. This overestimation results due to inappropriate mathematical extrapolations of the cumulative heat and calcium hydroxide consumption along with highly alkali environments and elevated temperatures which do not emulate cement-like environments which results in higher *degree of reactivity* of fly ashes. This study provides a simple method to estimate the *degree of reactivity* of fly ashes to increase their widespread use in the construction industry.

3:20pm - Abstract #3232**Effects of calcium hydroxide and magnesium oxide in alkali-activated metakaolin with low activator concentrations**

Anita Zhang, Civil and Environmental Engineering, Princeton University, Princeton, NJ and Claire E. White, Department of Civil and Environmental Engineering, and the Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ

Abstract Text:

Alkali-activated metakaolin (AAMK), a product of combining calcined kaolinite clay with an alkali activator such as a sodium silicate solution, is a promising type of sustainable alternative cement that emits 40-80% less CO₂ than ordinary Portland cement. Currently, in a standard AAMK mix design, most of its remaining emissions come from the activator, so lowering the alkali concentration of the activator can significantly further reduce AAMK's carbon footprint. Moreover, using a more dilute activator also brings down costs, reduces hazards on construction sites, and minimizes shrinkage cracks. However, the question remains as to what can be added to mix designs with low activator concentrations to minimize both short-term and long-term performance loss without significantly increasing the carbon footprint. In this study, we show that two cation sources, calcium hydroxide (Ca(OH)₂) and magnesium oxide (MgO), may help offset the performance loss associated with lower activator concentrations. The pore size distributions of a standard AAMK mix design and various low-activator-concentration formulations were quantified using both destructive techniques such as nitrogen sorption, mercury intrusion porosimetry, and focused ion beam scanning electron microscopy and non-destructive techniques such as small-angle scattering. The permeability of each mix design was also determined by observing the hydrodynamic relaxation of saturated samples in three-point beam bending tests. Data showed that both cation sources have notable beneficial effects on the low-activator-concentration AAMK system. The mechanism through which they helped was then studied using Fourier transform infrared spectroscopy and isothermal conduction calorimetry. Findings from our work can aid in the design and optimization of future AAMK formulations to achieve both low CO₂ emissions and good performance properties.

2B: Bio-Inspired Cementitious Materials

Wednesday, June 19, 2024, 1:40pm - 3:40pm

1:40pm - Abstract #3318

Biomimetic earth-based cement paste optimised through rapid binding assessment techniques

Samuel J. Armistead¹, Rebecca A. Mikofsky² and Wil V. Srubar III¹, (1)Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, (2)Materials Science and Engineering Program, University of Colorado, Boulder

Abstract Text:

With the shift towards a bio-based economy, there is a great interest in bioinspiration and biomimicry to produce materials with low carbon, energy, and material inputs. Bio-stabilized earthen construction has gained recent attention as a sustainable and circular construction method. Polypeptides, naturally occurring biopolymers, are of particular interest as bio-stabilizers due to the sheer quantity of molecular permutations arising from their twenty amino acid building blocks, yielding an almost limitless possibility of molecular tuning that can facilitate biopolymer-mineral binding. Fully exploring the biophysiochemical space requires the development of high-throughput experimental tools with the ability to decode the composition-structure-function relationships between polypeptides and commonly found earth materials. This presentation will explore preliminary multi-well based experimental results towards achieving this vision, further highlighting the potential of bio-stabilised earth-based materials as a new class of sustainable construction materials.

2:00pm - Abstract #3172

An enzymatic cementitious material

Shuai Wang, Enzymatic,inc, Las Vegas, NV

Abstract Text:

Concrete is the most widely used material in the world and is responsible for 8% of global carbon emissions. It is inherently brittle and requires frequent repair or replacement, which are expensive and generate large volumes of CO₂. Current repair methods by agents such as mortar and epoxies result in structures with reduced strength and resiliency due to material mismatch. Therefore, a self-healing cement paste (concrete's main matrix) is needed to overcome this problem. The leading self-healing mechanism uses bacteria and microbes, which are slow and have limited applications, as well as unknown health effects. Inspired by the highly efficient process of CO₂ transfer in biological cells, this study introduces a method to develop a self-healing mechanism in a cementitious matrix using trace amounts of the enzyme Carbonic Anhydrase (CA). CA catalyzes the reaction between Ca²⁺ ions and atmospheric CO₂ to create calcium carbonate crystals with similar thermomechanical properties as the cementitious matrix. The crystal growth rate using this method is orders of magnitude faster and more efficient than bacterial methods, resulting in shorter healing of large flaws on timescale orders of magnitude. This method can self-heal samples with millimeter-scale flaws within 24 hours and is significantly faster than all current methods that need a minimum of 28 days for strength recovery of microscale cracks. This inexpensive method is biologically safe, actively consumes CO₂, and avoids using unhealthy reagents. It can be an efficient mechanism to repair and strengthen the existing concrete structures.

2:20pm - Abstract #3293

Metakaolin-based geopolymer mixes modified with algal biomass

Cansu Acarturk¹, Brooklyn Lash¹ and Wil V. Sruar III², (1)Civil, Environmental and Architectural Engineering, University of Colorado Boulder, Boulder, CO, (2)Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, Boulder, CO

Abstract Text:

The significant greenhouse gas emissions associated with ordinary portland cement (OPC) production necessitate the exploration of more sustainable concrete binders. One promising approach is the use of alkali-activated metakaolin geopolymers. Obtained by calcining kaolinitic clays, metakaolin offers greater natural abundance and global accessibility compared to other geopolymer binders. Despite its environmental advantages, metakaolin's calcination process still emits carbon dioxide, and its formulation demands a substantial amount of alkaline activators to achieve desired compressive strength. To overcome these challenges, this research explores the incorporation of carbon-negative algal biomass, specifically *Chlorella* algae and algal biochar, into metakaolin geopolymer mixes to enhance sustainability by (1) lowering metakaolin content, thereby (2) reducing the need for alkaline activators, and (3) incorporating a carbon storing material and to improve mechanical properties. In this study, the effects of incorporating varying algal biomass content (1%, 5%, and 10%) of algae or biochar on the fresh and hardened properties of metakaolin mixes were evaluated. Fresh properties were analyzed by measuring setting time and alkali-activation kinetics and hardened properties were evaluated by measuring compressive strength, phase development using X-ray diffraction, and morphological changes visualized using scanning electron microscopy. Replacing metakaolin with algae or biochar generally resulted in a reduction of compressive strength, more so with higher percentages of replacement. However, over a curing period of 28 days, most mixes with replacements exhibited strengths identical to those of the control mix (100% metakaolin). Alkali-activation kinetics indicated that the 1% replacement samples reacted slightly faster than the control, whereas a 10% replacement resulted in a delayed reaction. The findings of this study provide a comprehensive understanding of these novel metakaolin geopolymer mixes and contribute to the development of more sustainable building materials, addressing the environmental concerns associated with traditional cement production.

2:40pm - Abstract #3248

Small doze organic additives augmenting benefit of biochar in concrete

Maysam Bahmani¹, Jialai Wang², Abdulmalik Bamidele Ismail³, Xiaodong Wang¹, **Monica Amaral¹**, Xi Chen¹ and Abdulmalik Alawode¹, (1)The University of Alabama, Tuscaloosa, AL, (2)Civil, Construction, and Environmental Engineering, The University of Alabama, Tuscaloosa, AL, (3)Civil Construction and Environmental Engineering, The University of Alabama, Tuscaloosa, AL

Abstract Text:

This study investigates the synergistic effects of biochar and organic additives—0.2% Tannic Acid, 0.2% Citric Acid, and 0.2% Xylitol—on the compressive strength of cementitious materials. Various concentrations of biochar (1%, 2%, 5%, and 8% by weight of cement) were combined with the mentioned organic additives. To counteract the retarding effect, a pre-hydration technique was employed for half of the cementitious materials.

Results demonstrate that incorporating 8% biochar alongside 0.2% Tannic Acid and 0.2% Xylitol yielded superior performance compared to other combinations. This enhancement is attributed to the chelating ability of these materials, facilitating the formation of stable complexes, thereby improving cement hydration and compressive strength. At 3 and 7 days, the compressive strength showed an approximate 25% improvement compared to control samples devoid of biochar and Xylitol. Moreover, after 28 days, the enhancement reached approximately 30%, indicating sustained strength improvement over time.

This study underscores the potential of biochar and Tannic Acid as effective additives for augmenting the mechanical properties of cementitious materials, particularly in mitigating the retarding effects of certain organic additives. These findings advance the development of sustainable and high-performance construction materials, offering insights into optimizing composite formulations for enhanced strength, durability, and environmental responsibility.

3:00pm - Abstract #3321

Investigating filler and shearing effects on hydration rates of cement-biochar blended pastes

Tung Hoang¹, Julia Hylton² and Lori Tunstall¹, (1)Civil and Environmental Engineering, Colorado School of Mines, Golden, CO, (2)Materials Science, Colorado School of Mines, Golden, CO

Abstract Text:

To reduce the carbon footprint associated with cement production, biochar has been used as partial replacement of the ground clinker. It has been suggested that the biochar acts as a filler, with its high surface area promoting the nucleation of cement hydration products, however this has not been directly evaluated. This research investigates the effects of filler and shearing rate on the biochar-cement pastes using isothermal calorimetry, thermogravimetric analysis, and scanning electron microscopy. Seven types of biochar with a 10% replacement of cement are employed for the experiments. The results reveal that while the biochar's physical factors can accelerate clinker hydration through increased nucleation sites and shearing of anhydrous cement particles, chemical properties of the biochar can reduce the hydration rate.

3:20pm - Abstract #3294

Photosynthesized CaCO₃ as a raw material for cement clinker production

Danielle N. Beatty, Materials Science and Engineering Program, University of Colorado Boulder, Boulder, CO, Cansu Acarturk, Civil, Environmental and Architectural Engineering, University of Colorado Boulder, Boulder, CO, Matthew H. Fyfe, Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, Boulder, CO and Wil V. Srubar III, Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, Boulder, CO

Abstract Text:

The production of portland cement accounts for 7% of global annual greenhouse gas emissions. Over 60% of these emissions can be attributed to the calcination reaction ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) during cement clinkering. While many sustainable cement chemistries rely on reduced clinker content, most still utilize clinker made using limestone as a raw material, and thus cannot completely avoid calcination emissions. In this work, we target clinker emissions reduction using carbon storing, photosynthetically produced CaCO₃ in place of quarried limestone in cement clinker production. Two sources of photosynthetically produced CaCO₃ with high surface areas (produced by marine macroalgae: 8.26 m²/g and microalgae: 12.22 m²/g) were investigated as main raw materials for clinker production. The elemental composition and mineralogy of each biogenic CaCO₃ source were characterized using inductively coupled mass spectroscopy and X-ray diffraction, respectively. Each source of biogenic CaCO₃ was mixed with reagent grade SiO₂, Al₂O₃, and Fe₂O₃, according to LSF, SR, AR, and Bogue calculations, and heated to synthesize clinker. In situ high temperature X-ray diffraction was used to study the effects of high surface areas of biogenic CaCO₃ on raw mineral reactivity during cement clinkering. Bulk cement clinker was also synthesized at the lab scale. Hydration kinetics and compressive strength were measured and compared to commercially produced OPC Type I/II. Results substantiate that the high purity and high surface areas of photosynthesized CaCO₃ lead to efficient clinker phase formation. Our work shows that photosynthesized CaCO₃ can be used as a carbon-storing limestone source for

producing portland cements that meet ASTM C150, highlighting a nature-based, renewable solution for carbon neutral cement clinker production.

3A: Cement Chemistry (Part 1 of 2)

Thursday, June 20, 2024, 10:10am – 12:10pm

10:10am - Abstract #3216

Raman imaging of static & dynamic systems

Nishant Garg, Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Abstract Text:

Over the last 10 years, the capabilities of Raman imaging have significantly improved, primarily due to hardware and software advancements in the Raman confocal microscopes and spectrometers. In this talk, I will outline recent applications of Raman imaging on both static and dynamic systems. Specifically, Raman imaging allows highly accurate and precise mineral mapping of heterogeneous ingredients of concrete (static systems ranging from aggregates to cement to SCMs) with its ability to detect mineral polymorphs at a high spatial, sub-micron resolution. Accurate quantification of mineralogical compositions is a key advance over bulk elemental compositions, and Raman imaging brings us one step closer to such a technological advance. In addition, various dynamic systems such as cementitious systems subject to carbonation and alkali-silica reaction can be studied via this technique, opening pathways for Raman imaging to serve as a highly complementary tool to electron imaging for complete characterization of concrete.

10:30am - Abstract #3284

Effect of phosphorus and fluorine from phosphogypsum on C₃S and C₃A hydration

Rayara Pinto Costa, Materials engineering, Federal University of Rio Grande do Sul, Porto Alegre, Brazil, Jose S. Andrade Neto, Civil engineering, State University of Santa Catarina, Laguna, Brazil, Paulo R. de Matos, Civil engineering, State University of Santa Catarina, Joinville, Brazil, Maria Juenger, University of Texas at Austin, Austin, TX, Ana Paula Kirchheim, Civil Engineering, Federal University of Rio Grande do Sul, Porto Alegre, Brazil and Carlos P. Bergmann, Materials Engineering, Federal University of Rio Grande do Sul, Porto Alegre, Brazil

Abstract Text:

Phosphogypsum (PG), a byproduct of the fertilizer industry, offers a potential solution as a calcium sulfate source for regulating cement setting. However, this material introduces a soluble source of phosphorus (P³⁻) and fluorine (F⁻) ions into the cement matrix. These elements can delay cement hydration – both of silicate and aluminate phases – and consequently early strength development. Nonetheless, having PG as a substitute for natural gypsum (NG) aligns with the principles of the circular economy which is currently a central topic in the scientific community. Understanding how soluble phosphorus and fluorine affect the hydration of the main mineralogical cement phases is crucial for achieving this objective. Thus, this research explored the impact of phosphorus and fluorine on the hydration kinetics of clinker's main mineralogical phases. For this purpose, the hydration of lab-synthesized pure C₃A and C₃S samples was evaluated through isothermal calorimetry at 22°C for 48 hours. P₂O₅ and F⁻ (coming from analytical grade NaF and Na₂HPO₄, respectively) were incorporated in levels of 0, 0.25, and 1.0 wt%, both alone and combined. In addition, reference systems with PG and NG were assessed. The results indicated that soluble P₂O₅ and F⁻ delayed the hydration of both C₃S and C₃A. Notably, C₃S hydration exhibited a more pronounced delay in the presence of F⁻ compared to P₂O₅ within the first 24 hours. Moreover, the F⁻ and P₂O₅ combination increased the delay in the C₃S reaction compared to those additions alone. Regarding C₃A, soluble P₂O₅ retarded more its hydration than fluorine. However, no significant difference was observed when increasing above 0.25% F⁻ and P₂O₅ dosage during C₃A hydration. Overall, the

phosphorus and fluorine present in PG delayed the reaction of both C_3S and C_3A , the former being undesired in terms of mechanical strength evolution of concrete.

10:50am - Abstract #3241

Calcium hydroxide dissolution kinetics: Rate equation and temperature dependence

Yoonjung Han¹, Natasha Van Dam Levy¹, Mine G. Ucak-Astarlioglu², Jedadiah F Burroughs² and Jeffrey W. Bullard^{1,3}, (1)Zachry Department of Civil and Environmental Engineering, Texas A&M University, College Station, TX, (2)Geotechnical and Structures Laboratory, U.S. Army Engineer Research and Development Center, Vicksburg, MS, (3)Department of Materials Science and Engineering, Texas A&M University, College Station, TX

Abstract Text:

Portlandite ($Ca(OH)_2$) constitutes about 27% of hydrated portland cement paste. It is prominent near aggregates or fiber within the microstructure, often called the interfacial transition zone (ITZ). Portlandite can readily react, either with soluble pozzolans to form a low Ca/Si ratio calcium silicate hydrate (C-S-H), or with dissolve CO_2 to form calcium carbonate ($CaCO_3$). This study investigates the dissolution rate of portlandite as a function of its phase stability index and temperature. We continuously tracked the dissolution rate of portlandite in a mixed flow reactor, using an electrical conductivity probe and correlating the conductivity to dissolved calcium concentration. The data are regressed to a surface normalized rate equation and the activation enthalpy is inferred from the rate's temperature dependence. Results from this work can be used to formulate more accurate computational models of cement hydration, pozzolanic transformations, leaching, and carbonation.

11:10am - Abstract #3257

Effect of gypsum on tricalcium silicate in blended systems: *In situ* atomic pair distribution function study

Hyeonseok Jee, Civil and Environmental Engineering, University of Illinois Urbana-Champaign, Urbana, IL, Chirayu Kothari, University of Illinois Urbana Champaign, Urbana, IL and Nishant Garg, Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Abstract Text:

Despite the various merits of ordinary Portland cement (OPC), its high carbon footprint underscores the need for eco-friendly construction materials. Limestone calcined clay cement (LC^3) has emerged as a promising alternative construction material, comprising OPC, metakaolin, and limestone. Since LC^3 is rich in aluminate from calcium aluminate and metakaolin, it requires higher gypsum content than OPC to control the hydration of aluminate phases. This study delves into the influence of gypsum on the hydration behavior and microstructure of tricalcium silicate (C_3S) in blended systems. Synthetic C_3S , blended with metakaolin and limestone, were examined with and without gypsum using *in situ* synchrotron-based X-ray total scattering and atomic pair distribution function analysis. Additionally, heat evolution was monitored via isothermal calorimetry. The findings shed light on the role of gypsum in the hydration of C_3S within blended systems, contributing to a deeper understanding of LC^3 performance.

11:30am - Abstract #3299

Effect of minor elements and Al/Fe ratios on ferrite formation and hydration

Aniruddha Baral¹, Cecilia Pesce² and Theodore Hanein¹, (1)The University of Sheffield, Sheffield, United Kingdom, (2)The University of Sheffield, United Kingdom

Abstract Text:

Upcycling waste materials into cementitious materials has been a focus of the 21st century to improve resource efficiency, reduce carbon footprint and promote a circular economy. The ferrite phase ($\text{Ca}_2\text{Fe}_2\text{-xAl}_x\text{O}_5$, $x = 0 - 1.4$) is known to preferentially incorporate different minor elements present in the waste materials. However, their effects on ferrite crystal structure and hydration reactivity are not well understood. We synthesized pure ferrite samples with different Al/Fe ratios (0, 0.5, 1, 2) and minor elements (Mn, Ti, Mg, Cr, Zn), and evaluated the effect of minor elements on ferrite formation and its crystal structure using XRD and SEM-EDS techniques. The hydration of the ferrites has been studied *in situ* in pure water and in the presence of excess gypsum and calcium carbonate using synchrotron XRD, TGA, and isothermal calorimetry. The reactivity of the ferrites increased with Al/Fe ratios, and minor elements Mn and Mg.

11:50am - Abstract #3118

Investigating the effects of water activity on the hydration kinetics and thermodynamics of ye'elimite calcium sulfate system

Godwin I Ogbuehi and Monday U Okoronkwo, Chemical & Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO

Abstract Text:

Relative humidity (RH) and water activity (a_H) reductions have been known to suppress the hydration of all anhydrous phases in cement, including ye'elimite ($\text{C}_4\text{A}_3\text{S}$) – the most important clinker phase in calcium sulfoaluminate (CSA) cement. However, the relationship between $\text{C}_4\text{A}_3\text{S}$ hydration kinetics, water activity, and the critical a_H at which the hydration of $\text{C}_4\text{A}_3\text{S}$ is arrested remains unclear. This study employs x-ray diffraction technique, microcalorimetry studies, and thermodynamic analysis to elucidate the influence of water activity on the hydration of ye'elimite-water system [$\text{C}_4\text{A}_3\text{S} + \text{water} = \text{Y}$], and ye'elimite-calcium sulfate-water system [$\text{C}_4\text{A}_3\text{S} + \text{CaSO}_4 + \text{water} = \text{YG}$]. Lowering water activity is accomplished by substituting some of the water in the mixtures with isopropanol (IPA). Experimental findings indicate that as water activity decreases, the rates of all reactions associated with $\text{C}_4\text{A}_3\text{S}$ are proportionately diminished until the reaction is completely brought to a halt at the critical threshold of approximately 90%IPA on a weight basis (%wt IPA). The critical a_H (the threshold where the hydration of $\text{C}_4\text{A}_3\text{S}$ is effectively arrested) and solubility product constant of $\text{C}_4\text{A}_3\text{S}$ estimated from thermodynamic analysis are established as 0.46 and $10^{-25.568}$, respectively. The critical a_H and $K_{\text{C}_4\text{A}_3\text{S}}$ are fundamental data for the numerical modeling of hydration occurring in $\text{C}_4\text{A}_3\text{S}$ -based cementitious systems. Additionally, this research revealed by thermodynamic modeling for the first time, the effects of isopropanol ingress on the precipitation-dissolution of hydrated phase assemblage, and the speciation in the aqueous pore solution.

3B: Microstructure Stabilization

Thursday, June 20, 2024, 10:10am – 12:10pm

10:10am - Abstract #3194

A nature-inspired approach for self-repair in aging concrete structures

Mohammad Irfan Iqbal¹, Geetika Mishra², Parsa Namakiaraghi³, Ethan Yen¹, Hsiao Wei Lee⁴, Christopher M. Sales⁵, Irene Verdú¹, Ahmad Najafi⁵, Mija Hubler⁶ and Yaghoob Farnam², (1)Civil, Architectural and Environmental Engineering, Drexel university, Philadelphia, PA, (2)Civil, Architectural and Environmental Engineering, Drexel University, Philadelphia, PA, (3)Civil, Architectural and Environmental Engineering, Drexel University, Philadelphia, PA, (4)Drexel university, Philadelphia, PA, (5)Drexel University, Philadelphia, PA, (6)Civil Environmental and Architectural Engineering, University of Colorado Boulder, Boulder, CO

Abstract Text:

Self-repair is a natural response to injuries as observed in living organisms. Similarly in concrete self-healing materials can repair corrosion, cracks, scratches, and other alterations independently and autonomously, aiming to recover structural strength and mechanical functionality after sustaining damage. In this study, we have developed a new methodology inspired by nature, involving the creation of artificial vasculature with microchannels inside cementitious composites to enable self-healing capabilities. These microchannels serve multiple purposes within cement composites; (i) establish vascular networks, (ii) facilitate delivery of bio-agents, and (iii) ensure the retention of biological reagents until damage occurs. Our initial investigation confirms the successful delivery of biological reagents through microchannels to damage/crack surfaces. Moreover, we have evaluated the mechanical effects of microchannels considering different aggregate sizes, which suggest that the creation of microchannels leads to controllable mechanical effects on the composites. Additionally, we studied microbially induced calcium carbonate precipitation (MICP) activity using thermogravimetric analysis to assess the transportation of healing agents and the production of self-repairing products, such as calcium carbonate, within crack volumes. Our findings show that microchannels effectively deliver healing agents to the targeted areas, enhancing MICP-based crack healing processes.

10:30am - Abstract #3246

Healing concrete using biotechnology

Christopher Shearer¹, Saurabh Dhiman¹, Clare Fischer¹, Swati Srivastava¹, Heather Luckarift², Rachel Krebs² and Fadime Murdoch², (1)Civil and Environmental Engineering, South Dakota School of Mines and Technology, Rapid City, SD, (2)Battelle

Abstract Text:

Damaged concrete infrastructure can be expensive to remediate as it typically involves removing and replacing large volumes of material. This research seeks to develop repair technologies that can be surface applied and penetrate damaged, cracked concrete. The concrete is then healed through crack filling and strength recovery without the need for demolition and replacement. Four bioeffector technologies were tested for this purpose including cellulose, silk, polyhydroxyalkanoate (PHA), and exopolysaccharide (EPS). These biomaterials serve as a vasculature that fills the crack void. Carbonic anhydrase enzyme is then applied to the vasculature to promote calcite formation over time. Crack filling rates, tensile and compressive strength development, and a suite of materials characterization techniques were used to quantify the effectiveness of each bioeffector in healing the concrete.

10:50am - Abstract #3350

Can self-healing concrete self-destruct? Effects of urea-rich biomineralizing microorganism media on the chemical stability of portland cement paste

Cansu Acarturk¹, **Caitlin Adams**¹ and Wil V. Srubar III², (1)University of Colorado, Boulder, (2)Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder

Abstract Text:

Biological “healing” of cementitious materials has the potential to increase the sustainability, durability, and service life of concrete infrastructure by reducing the impact of crack-induced losses in performance. Microbially-induced calcium carbonate precipitation (MICP), one such “healing” method, leverages biomineralizing capabilities of certain microorganisms to mediate the production of new minerals, thus repairing cracking damage. The most used form of MICP leverages ureolytic microorganisms delivered in a treatment media consisting of urea and often a calcium salt. Despite some notable advances, there is still no fundamental understanding of the physical and chemical limits of this technology, nor of potential urea hydrolysis side reactions in a cementitious environment. This study investigated the effects of treatment media concentration both on MICP yield and on portland cement (OPC) paste properties. *Sporosarcina pasteurii* was selected as a representative ureolytic bacteria for cementitious healing. Aqueous treatment medias consisting of urea, calcium acetate, and yeast extract were prepared in equimolar concentrations as well as in molar excesses of urea and calcium acetate. Deionized water was used as a control treatment. *Ex situ* experiments quantified the potential calcium carbonate production as a function of media concentration using thermogravimetric analysis (TGA). One-centimeter OPC paste cubes (0.5 w/c) were immersed in either *S. pasteurii*-loaded treatment media or abiotic media and re-treated three times weekly until characterization at 7 and 28 days. To elucidate any effects of treatment on OPC paste phases, immersed paste cubes were characterized using X-ray diffraction, scanning electron microscopy, and TGA while the supernatant was characterized *via* inductively coupled plasma-optical emission spectroscopy. These results will provide perspective on the limits and side effects of ureolytic “healing” and will enable optimized media concentration for efficient crack healing in OPC systems.

11:10am - Abstract #3207

Effects of nano-ettringite on the hydration of portland cement

Rupack R Halder and Monday U Okoronkwo, Chemical & Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO

Abstract Text:

Ettringite, a naturally occurring phase in Portland cement (PC), is one of the first hydration products that control the early-age properties of PC-based cement mixtures. A delay in ettringite formation and uncontrolled formation of ettringite can cause deleterious effects in concretes; yet intentional harnessing of this mineral enhances the strength and durability of specific cement-based materials. This study investigates the effects of nano-ettringite seeds on the early-age properties of PC cement paste. Rheology, micro-reaction calorimetry, X-ray powder diffraction, compressive strength analysis, 3D X-ray microcomputed tomography, and scanning electron microscopy were utilized to investigate the nano-ettringite effects. The results reveal that applying nano-sized ettringite accelerates hydration reactions in PC pastes, by catalyzing the precipitation and growth of ettringite, enhancing buildability and early-stage strength. Calorimetry data demonstrate increased rates of hydration reactions. Rheological data further corroborate these findings; indicating the loss of flowability, rate of hardening, and the yield stress growth rate constant all increase with higher ettringite dosage. These results imply that ettringite application accelerates PC hydration reactions, making it a viable accelerator option for use where rapid early strength development is essential. This study not only expands our understanding of ettringite's impact on

cement hydration but also provides insights that can be leveraged to mitigate delayed ettringite formation via nano-seeding.

11:30am - Abstract #3165

Enhancement of hydration and stabilization of cement clinkers using chemically modified TiB₂ nanosheets

Vikash Kumar Singh, Indian Institute of Technology Gandhinagar, Gandhinagar, India

Abstract Text:

Increasing the proportion of dicalcium silicate (C₂S) in Portland cement has proven to be an effective strategy for mitigating the environmental impact of cement production. However, the challenge lies in the relatively insignificant early age strength development of C₂S compared to tricalcium silicate (C₃S). The addition of stabilizing agents during C₂S synthesis has been recognized as a method to enhance its hydration behaviour. A recent focus has emerged on integrating graphene, a pioneering 2D nanomaterial, as a sustainable additive in concrete. Graphene's exceptional mechanical and catalytic properties not only reinforce the composite but also impact the stabilization and hydration behaviour of C₂S. In this study, we explore the potential of a novel class of nanosheets derived from Titanium diboride (TiB₂), a 2D material recently discovered by our research group, as cement additives. Our findings indicate that the inclusion of 3% chemically modified TiB₂ nanosheets results in ~4 times increment in the formation of the β-C₂S polymorph. Isothermal calorimetry analysis of the stabilized C₂S demonstrates heightened peak heat and cumulative heat evolution during early age hydration (24 hours), suggesting that TiB₂-based nanosheets enhance the rate of C₂S hydration. Long-term hydraulic characterization (28 days) further reveals a higher degree of hydration in the nano-modified samples. This unconventional approach, exemplified by TiB₂-derived nanosheets, underscores the promising potential of 2D materials in the development of robust cement additives. The unique properties of TiB₂ nanosheets offer a rich avenue for innovation in enhancing the performance of cementitious materials.

11:50am - Abstract #3199

C-s-h seeds: New insights on pore structure refinement

Faisal Qadri¹, Sudharsan Rathna Kumar¹ and Nishant Garg², (1)Civil and Environmental Engineering, University of Illinois at Urbana Champaign, Champaign, IL, (2)Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, Urbana, IL

Abstract Text:

C-S-H seeds are a new class of commercially available admixtures that serve as nucleation sites for additional hydration products. In the past decade, they have been used to enhance the early strength of concrete. While their impact on strength is well known, relatively little information is available about their influence on microstructure and porosity. In this talk, we will share our latest results on seeded mixtures where the porosity is examined by a combination of helium pycnometry as well as high-resolution confocal laser profilometry. Helium pycnometry reveals a clear reduction in open porosity proportional to the seed dosage. Moreover, laser profilometry reveals a microstructural refinement upon the addition of these C-S-H seeds. Most notably, laser profilometry experiments demonstrated a strong correlation between two critical surface roughness parameters, S_{pc} (peak curvature) and S_{pd} (peak density), and the open porosity of the mixes, suggesting a refinement at the microstructural level. Together, these results provide strong evidence for porosity reduction in the presence of these C-S-H seeds, suggesting potentially enhanced durability.

4A: Computational and Data Science

Thursday, June 20, 2024, 1:25pm – 2:45pm

1:25pm - Abstract #3134

Hierarchical machine learning for the molecular design of nonionic polymers as air-entraining admixtures

Sadegh Tale Masoule, University of Miami, Coral Gables, FL and **Ali Ghahremaninezhad Ph.D**, Civil, Architecture and Environmental Engineering, University of Miami, Coral Gables, FL

Abstract Text:

Traditionally, the design of chemical admixtures for concrete involves experimental modification of the polymer molecular structure in the laboratory, measurement of physico-chemical properties, and incorporating and testing the polymer in concrete. This process is costly, time-consuming and limits the ability to fine-tune the molecular properties that optimize the admixture's performance. In this work, machine learning has been utilized to identify the most influential molecular properties that affect the air-entraining performance of nonionic polymers in concrete. Furthermore, multi-scale relationships are established between the molecular properties of nonionic polymers, the physico-chemical properties of these polymers in cement pore solution, and the air-entrained microstructure in hardened cement paste. To put it concisely, solution properties including interfacial rheology, surface tension and foaming are correlated with molecular hydrophobicity, hydrocarbon length, etc. Subsequently, hardened cement microstructure is obtained through Micro-Computed Tomography and correlated to solution properties through descriptive models. The findings will help explain the underlying mechanisms of air-entraining in cementitious materials, as well as aid in the selection and design of high-throughput admixtures.

1:45pm - Abstract #3186

On the prediction of the mechanical properties of limestone calcined clay cement: A random forest approach tailored to cement chemistry

Bryan K Aylas Paredes SR., Materials Science, Missouri University of Science and Technology, Rolla, MO

Abstract Text:

Limestone calcined clay cement (LC³) is a sustainable alternative to ordinary Portland cement, capable of reducing the binder's carbon footprint by 40% while satisfying all key performance metrics. The inherent compositional heterogeneity in select components of LC³, combined with their convoluted chemical interactions, poses challenges to conventional analytical models when predicting mechanical properties of LC³, many have overlooked the pivotal role of feature selection. Proper feature selection not only refines and simplifies the structure of ML models but also enhances these models' prediction performance and interpretability. This research harnesses the power of the random forest (RF) model to predict the compressive strength of LC³. Three feature reduction methods -Pearson correlation, SHapley Additive exPlanations, and variable importance- are employed to analyze the influence of LC³ components and mixture design on compressive strength. Practical guidelines for utilizing these methods on cementitious materials are elucidated. Through the rigorous screening of insignificant variables from the database, the RF model conserves computational resources while also producing high-fidelity predictions. Additionally, a feature enhancement method is utilized, consolidating numerous input variables into a singular feature while feeding the RF model with richer information, resulting in a substantial improvement in prediction accuracy. Overall, this study provides a novel pathway to apply ML to LC³, emphasizing the need to tailor ML models to cement chemistry rather than employing them generically.

2:05pm - Abstract #3108

Understanding the multiscale dissolution of calcium aluminosilicate glasses

Luis A Ruiz Pestana, Civil, Architectural, and Environmental Engineering, University of Miami, Coral Gables, FL

Abstract Text:

Calcium aluminosilicate (CAS) glasses constitute the primary reactive phases in low-carbon alternatives to Portland cement (PC), the production of which accounts for 6-8% of global anthropogenic carbon emissions. Understanding the complex relationship between the chemical composition and disordered structure of CAS glasses and their dissolution dynamics is a crucial step to identify or develop highly reactive, eco-friendly alternatives to PC. In this presentation, I will introduce a hierarchical multiscale framework we developed to gain insight into the kinetics and mechanisms governing the dissolution of CAS glasses. Our methodology consists of kinetic Monte Carlo (KMC) simulations of the dissolution of realistic CAS glass structures derived from classical molecular dynamics (MD) and conceptualized as undirected graphs. The KMC simulations are informed by free energy barriers to dissolution calculated from ab initio molecular dynamics (AIMD) simulations enhanced with well-tempered metadynamics. I will discuss how this multiscale framework has enabled us to unveil the molecular mechanism that governs the dissociation of Si-O-T bridges,¹ what the general non-trivial effect of heterogeneity is on the dissolution kinetics of disordered solids,² as well as the complex interplay between composition, structure, and dissolution rate in CAS glasses.³

References

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2. Ruiz Pestana, L.; Shantha Raju, S.; Guntoorkar, C.; Suraneni, P. Kinetic Monte Carlo Study on the Role of Heterogeneity in the Dissolution Kinetics of Glasses. *The Journal of Physical Chemistry C*, 2023, 127, 16, 7695–7701.
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2:25pm - Abstract #3215

Sorptivity prediction in seconds: A computer vision approach

Hossein Kabir and Nishant Garg, Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Abstract Text:

The tendency of cementitious systems to absorb and transmit liquid through capillary pores is often characterized by initial sorptivity, which is an important indicator of long-term durability. However, sorptivity measurements, which are based on the continuous mass change of specimens exposed to water, are labor-intensive (up to 6 hours of continuous measurements). In this study, using computer vision, we explain how we may exploit the fundamental surface-wetting characteristics of cementitious systems to estimate their sorptivity in a rapid fashion, i.e., in a matter of few seconds. In a series of 63 unique paste systems of varying w/c ratios (0.4 to 0.8), subject to a range of curing periods (1d to 7d), we establish strong correlations (adjusted $R^2 \geq 0.9$) between the initial sorptivity (~6 hours) and dynamics of drop spreading (contact angle ~0.5 seconds). These results elucidate novel pathways in rapidly estimating the initial sorptivity and durability of a wide variety of hydrated cementitious matrices.

4B: Durability and Service Life Modeling

Thursday, June 20, 2024, 1:25pm – 2:45pm

1:25pm - Abstract #3230

Exploring the potential changes in the morphology and the nanostructures of cement hydrates due to the application of electric field excluding the joule-heating effect

Abdelrahman Hamdan, Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ and **Claire E. White**, Department of Civil and Environmental Engineering, and the Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ

Abstract Text:

The durability of cementitious binders, including hydrated ordinary Portland cement (OPC) and alkali-activated materials (AAMs), is significantly influenced by the permeability of the paste and the chemical stability of the reaction products. Although the durability of the various cement-based materials has been extensively investigated in the literature, little effort has been devoted to increasing the stability of the main binder phases, calcium-silicate-hydrate (C-S-H) gel in hydrated OPC and sodium-alumino-silicate-hydrate (N-A-S-H) gel in low-Ca AAMs, and other reaction products by direct manipulation of these binder phases. This research focuses on exploring the potential effects of an externally applied electric field (E-field) on the crystallinity and morphology of reaction products. To this end, we have cured hydrated OPC, alkali-activated blast furnace slag (AAS), and alkali-activated metakaolin (AAMK) samples in the presence of direct current (DC) and alternating current (AC) generated E-fields (without electrical current flow) for different periods of time. The nano- and micro-structure of the samples have been analyzed using X-ray diffraction, thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM), while the nanoscale morphology of the C-S-H gel, N-A-S-H gel, and other secondary phases has been investigated using atomic force microscopy (AFM). Furthermore, the synergistic effect of doping the cement paste with high-dielectric constant nanoparticles in the presence of E-Field has also been studied. The outcomes of this research may open new opportunities for improving the service life of concrete structures and contribute to ongoing efforts to enhance the sustainability of cement-based materials.

1:45pm - Abstract #3208

Tracking and quantifying the carbonation-front via multi-modal imaging

Sudharsan Rathna Kumar, Civil and Environmental Engineering, University of Illinois at Urbana Champaign, Champaign, IL and **Nishant Garg**, Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Abstract Text:

The carbonation of cementitious systems is of interest due to its potential to permanently store CO₂ via mineralization and to assess carbonation-induced steel corrosion. Several analytical techniques, including the phenolphthalein test and calcite quantification via bulk methods (XRD, TGA), are available for studying carbonation. However, one may overlook fine microstructural changes at the carbonation front because of profile grinding, which is required for these conventional methods. In this study, we explore the use of multi-modal imaging to understand the carbonation front better. We observe a growth of the calcite front and a corresponding depletion of the portlandite front via Raman imaging. Furthermore, via laser profilometry, we analyzed the variation of two roughness parameters: (1) arithmetic mean height (S_a) and (2) core material volume (V_{mc}). S_a and V_{mc} , which are metrics for pore refinement, peak at the carbonation front, complementing other imaging methods. Overall, this research is a step towards using

non-destructive imaging-based techniques to determine the carbonation front, moving towards low-clinker binders that carbonate faster than OPC.

2:05pm - Abstract #3147

Assessing the performance of internal cured concrete using pre-saturated lightweight ceramics manufactured from landfill condition waste coal ash

Yousif Alqenai, Bankole Tejuoso^{2,3}, Sharaniya Visvalingam² and Yaghoob Farnam⁴, (1)Drexel University, Philadelphia, PA, (2)Civil, Architectural, and Environmental Engineering, Drexel University, Philadelphia, PA, (3)Civil, Architectural and Environmental Engineering, Drexel University, Philadelphia, PA

Abstract Text:

This study examines the influence of internal curing technology on highway concrete bridge decks delivered through pre-saturated fine lightweight aggregates (FLWA) manufactured using landfill condition waste coal ash (LC-WCA). Guided by thermodynamic modeling and analytical calculations, LC-WCA was converted into lightweight ceramics referred to as LC-WCA-FLWA. These LC-WCA-based ceramics possess superior buoyancy characteristics, absorption capacity (> 28%), desorption capacity (> 40%), and sufficient compressive strength when compared to traditional FLWA (Stalite-FLWA) available in the market. Following Pennsylvania's bridge deck design criteria, concrete specimens were fabricated with a w/c ratio of 0.42, slump of 6 inches, and air content of 7 %. A comparative assessment was performed for concrete manufactured using LC-WCA-FLWA, Stalite-FLWA, and control concrete samples. The investigation assessed concrete's fresh properties, hardened properties, microstructure, and freeze-thaw durability. Results indicated that concrete manufactured with pre-saturated LC-WCA-FLWA required higher doses of plasticizer, similar air entrainment, and possessed lower fresh density than both Stalite-FLWA and control concrete specimens. Furthermore, LC-WCA-FLWA concrete demonstrated higher compressive strength achieving ~36 MPa after 56 days of curing, with a comparable flexural strength of 7.8 MPa, lower shrinkage by 33.5%, lower absorption rate, and lower freeze-thaw damage when compared to both Stalite-FLWA and control concrete specimens. Higher concentrations of calcium hydroxide (CH) were also found in LC-WCA-FLWA concrete indicating further cement hydration and optimum internal curing. This study's findings conclude that using pre-saturated LC-WCA-FLWA for the internal curing of concrete prompts higher concrete durability and service life performance.

2:25pm - Abstract #3154

Effect of alkali cations in different environments on alkali silica reaction (ASR)

Pengfei Ma, Department of Civil, Architectural, and Environmental Engineering, Missouri University of Science and Technology, Rolla, MO

Abstract Text:

Alkali-silica reaction (ASR) occurs between reactive silica, alkalis (sodium, potassium, and calcium) from cement, and moisture. The resulting ASR products can be expansive by absorbing moisture, thereby inducing deleterious cracks and even pop-outs on concrete structures to compromise the durability. This study investigates the effect of sodium (Na⁺) and potassium (K⁺) respectively on ASR expansion when the alkali cations are dominated in boosting and exposing environments in mortar samples. Experimental results show that the expansion increases with the concentration (<5%) of boosting alkalis irrespective of cation type. Sodium-boosted samples exhibit approximately 3 times more expansion compared to potassium-boosted samples. Observations indicate that ASR products in aggregate veins are amorphous, with EDS analysis revealing these gels are predominantly calcium-free. The atomic ratios of ASR gels are nearly independent of the type and quantity of boosting alkali cations. Aggregate ASR gel exudation occurs in high (≥2.5%) sodium cases and produces potential Na-shlykovite. Crystalline ASR products are rarely present in either Na- or K-boosted samples. However, the deleterious expansion (≥0.1%) was

noted in most of the samples. Regarding the influence of boosting environment with different types of cations, sodium are more effective in ASR expansion while potassium is prone to accelerate the ASR at the early stage. An intriguing observation is reported: in K-boosted samples, a Na-exposing environment inhibits ASR expansion, resulting in zero expansion.

5A: Cement Chemistry (Part 2 of 2)

Thursday, June 20, 2024, 3:10pm – 5:10pm

3:10pm - Abstract #3229

Ionic transport in c-s-h/c(n)-a-s-h/n-a-s-h nanopores: A molecular dynamics study

Weiqliang Chen and Kai Gong, Civil and Environmental Engineering, Rice University, Houston, TX

Abstract Text:

The ionic transport in the nanoscale pores of cementitious binder gels plays a vital role in determining the permeability and durability of cement-based materials. This study leverages force field-based molecular dynamics (MD) simulations to investigate the transport of NaCl and Na₂SO₄ aqueous solutions inside different cement nanopores, which represent the binder gel of three major cementitious systems: (i) Portland cement (calcium-silicate-hydrate (C-S-H)), (ii) alkali-activated cement (AAC) based on high Ca precursor (sodium-containing calcium-aluminium-silicate-hydrate (C-(N)-A-S-H)) and (iii) AAC based on low Ca precursor (sodium-aluminium-silicate-hydrate (N-A-S-H)). The results show that the ionic diffusivity within these nanopores (channel width = 4 nm) generally follows the sequence of C-(N)-A-S-H (Al/Si=0 and Na/Si=0) > N-A-S-H > C-S-H. However, increasing the Al/Si ratio (Na/Al=1) to about 0.1 can significantly reduce the ionic diffusivity in C-(N)-A-S-H gels to be comparable to or even lower than that in the C-S-H gel. These observations are directly linked to the adsorption of Na⁺ ions on the gel surface and the liquid structure at the pore-solution interface, as quantified by the atomic density distribution, radial distribution functions, coordination numbers, hydrogen bond network, and solvation shells. The differences in the liquid structure also explain the varying diffusion coefficients observed for Na⁺, Cl⁻ and SO₄²⁻ ions and the heterogeneity of ionic diffusivity in the C-(N)-A-S-H gels. Finally, the temperature effect on the ionic transport within these nanoconfined gel pores is investigated over 300-360 K, and an Arrhenius dependence is identified. This work deepens our understanding of nanoscale ionic transport behaviors within different binder gels, and the findings have important implications for the design and development of sustainable and durable cement materials.

3:30pm - Abstract #3222

Reactivity of calcium aluminosilicate glasses

Subhashree Panda, Civil and Architectural Engineering, University of Miami, Coral Gables, FL

Abstract Text:

Cement production contributes 6-8% of global man-made carbon emissions, posing a significant environmental challenge. Addressing this concern, considerable attention has been directed towards supplementary cementitious materials (SCMs), as cement replacements. These low-carbon materials, through long-term chemical reactions in concrete, improve long-term properties. However, a key challenge is the limited availability of these SCMs compared to the growing demand for cement. Additionally, lower early-age strength development in concrete with SCMs is limited due to their slower reactions. To overcome this challenge, the development of "manufactured SCMs" is emerging as a strategic solution. Understanding the composition-structure-reactivity relationships of SCMs at a fundamental level is crucial for optimizing current and future SCMs. However, the high heterogeneity and complex chemistry of existing SCMs make the generation of such knowledge challenging. To overcome the challenge, this study focuses on the reactivity of calcium aluminosilicate (CAS) glasses as a simplified pure phase model system to elucidate fundamental mechanisms underpinning SCM reactivity. By synthesizing multiple CAS glass compositions and employing a suite of experimental techniques coupled with mathematical modeling, we assess their reactivity and reaction kinetics. We show that a very broad range of reactivity, measured using the heat release in a modified R³ test, is possible with CAS glasses.

The heat release increases with CaO content and then decreases as CaO content increases beyond a certain point. While initial heat release is strongly dependent on the CaO, the later-age heat release is more strongly dependent on SiO₂ content. Thus, CaO-rich glasses show rapid reaction kinetics, although SiO₂-rich glasses show sustained reactivity. Glasses with balanced amounts of SiO₂, Al₂O₃, and CaO show the greatest reactivity. The role of reaction kinetics cannot be ignored. Indeed, while many studies have discussed the role of CaO on reactivity, we show that the full picture of reactivity is more complex.

3:50pm - Abstract #3282

Scalable and transportable thermochemical energy storage using cementitious materials

Lakshmi Amulya Nimmagadda, Paul Ginsberg and Arpit Dwivedi, Cache Energy

Abstract Text:

Energy storage based on reversible chemical reactions, termed thermochemical energy storage (TCES), has been proposed since the 1970s. TCES based on calcium oxide and hydroxide, where dehydration of Ca(OH)₂ to CaO (lime) stores energy and the hydration of CaO to Ca(OH)₂ releases the energy, is especially promising. The material is cheap at \$100/ton, has high energy density at ~500 (W·h)/kg, the reaction is highly reversible, and the reaction temperatures of >550 °C can serve ~75% U.S industrial process heat demand. Additionally, the temperatures are high enough to drive efficient heat-to-power conversion cycles for electricity generation. However, commercialization of TCES has been hindered due to several material level challenges. One of the major challenges is the high volumetric change of >150% during charge/discharge process. This leads to lime pulverizing into fine powder which agglomerates and causes mass transfer limitations leading to capacity decay with cycling. In this work we explore various cement-based binders to provide strength and structural stability during high temperature cycling of lime. We demonstrated >1000 cycles with the full capacity retention and no major loss in mechanical strength. The cycling performance was highly sensitive to processing conditions such as water content, curing time and temperature. In summary, the energy storage application requires research and development beyond the conventionally optimized cement properties.

4:10pm - Abstract #3311

Addressing complicated waste chemistries in generation of cementitious waste forms

Suraj A. Rahmon, Gary L. Smith, Sarah A. Saslow and Matthew R. Asmussen, Energy & Environment Division, Pacific North West National Laboratory, Richland, WA

Abstract Text:

The study provided an overview of efforts to develop cementitious waste forms for the immobilization and disposal of chemically complex liquid low-level wastes generated at the Hanford site as a by-product of vitrification. While a significant portion of the legacy waste will be immobilized as glass through vitrification, aqueous waste streams such as liquid effluents from the Hanford Waste Treatment and Immobilization Plant (WTP) and condensate from waste evaporation processes will contain contaminants and radionuclides that must be safely disposed of in accordance with the Department of Energy (DOE) radiological performance objectives outlined in DOE Order 435.1. The Effluent Treatment Facility (ETF) will treat these secondary wastes and generate a concentrated liquid secondary waste (LSW) brines as a byproduct. The ETF is estimated to result in an annual brine production rate of 60,800 gal/yr. The ETF brines produced will require immobilization in a waste form before their eventual disposal at the Hanford Site Integrated Disposal Facility (IDF), for which grout (cementitious) waste forms will be generated. However, the unique chemistry of the ETF brine leads to challenges for effective immobilization such as the elevated concentration of sulfate that can lead to extensive delayed ettringite formation, risking premature damage to grout monolith and significant concentration

of ammonium which combined with the high pH of the grouting processes can shift the speciation equilibrium of aqueous ammonium to release toxic and flammable ammonia gas. This presentation will cover efforts to successfully immobilize this waste stream as a cementitious waste form.

4:30pm - Abstract #3156

Understanding the influence of organic ligands on the formation of magnesium silicate hydrate

Jared Ura, Trinh Thao My Nguyen and Erika La Plante, UC Davis, Davis, CA

Abstract Text:

Magnesium silicate hydrate (MSH) is a potential alternative cementitious binder to ordinary Portland cement, but its utilization is greatly limited by current understandings of structure-property relationships at the nanoscale. Here, we investigate the influence of organic ligands on the formation of MSH to provide a model system for tunable synthesis toward various MSH morphologies. Characterizing solution-grown MSH with increasing concentrations of three organic ligands, our study aims to elucidate the controlled, tunable growth of MSH. Initially, infrared spectroscopy reveals notable shifts and intensification of assumed silicate absorbance peaks, indicating direct interaction between the organic ligands and MSH. Thermogravimetric Analysis (TGA) and X-ray Diffraction (XRD) show that organic ligands influence the decomposition temperatures, content, and crystallinity of MSH phases. These observations are supported by atomic force microscopy (AFM) which visually presents unique precipitate polymorphs for different organic ligands. Overall, this research aims to provide insights into the rational introduction of organic ligands for the controlled growth of MSH in construction applications. The findings of this study can be extended to other magnesium-based cements such as magnesium carbonates.

4:50pm - Abstract #3224

Early-stage dissolution behavior of MgO-clay-based cement.

Yi Xiang, Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA and Juan Pablo Gevaudan, Department of Architectural Engineering, Pennsylvania State University, State College, PA

Abstract Text:

Magnesia-based cement emerges as a promising alternative to traditional OPC due to its lower carbon emissions in manufacturing and its potential for application in nuclear waste disposal, owing to its compatibility with low-pH environments. The dissolution behavior of magnesia-clay-based cement is significantly influenced by pH levels. In this study, citric acid and sodium carbonate admixtures were employed to investigate the early-stage (first 48 hours) dissolution characteristics of MgO-clay-based cement. The phase assemblage of MgO-clay-based cement during the early-stage hydration was examined by utilizing semi-in-situ quantitative X-ray diffraction and solid-state ^{27}Al , ^{29}Si Nuclear Magnetic Resonance spectroscopy. Moreover, time-dependent analyses of suspension samples (comprising Mg, Si, Al, and Ca ions) were conducted to elucidate the mechanism underlying the early-stage dissolution of MgO-clay-based cement with citric acid or sodium carbonate addition. The findings indicate that metakaolin dissolution necessitates dissolved Mg^{2+} species, while citric acid/sodium carbonate addition can disrupt the nucleation/staking process of brucite ($\text{Mg}(\text{OH})_2$) nanosheets through distinct mechanisms.

5B: CO2 Utilization Towards Carbon-Neutral Concrete

Thursday, June 20, 2024, 3:10pm – 5:10pm

3:10pm - Abstract #3334

There is something new under the sun

Anne M Werner, Construction, Southern Illinois University Edwardsville, Edwardsville, IL

Abstract Text:

As in any industry, topics of interest come and go. For portland cement the topic of carbon emissions is not new, but recently concern has become intense. The term “low-carbon concrete” has been popping up just about everywhere. Although the term “low-carbon” refers to the embodied carbon associated with the production of concrete, those who are not familiar with the chemistry of portland cement may assume, when they hear the term, that portland cement concrete contains carbon.

In all the rush to reduce emissions, the incredibly special and unique qualities of portland cement seem to have been forgotten. As many researchers have found over the years, coming up with a similar but better binder replacement has not and is not easy, and in some cases, has been disastrous. From a historical perspective, portland cement is still a relatively new construction material having only been available on an industrial scale for 200 years. During the last 100 years or so of that, researchers have been trying to figure out how to prevent or fix all the problems that have been discovered when using it. Because of the ease of use of portland cement, which is probably one of its best qualities, but also its biggest downfall, anyone can buy a bag at the hardware store use it, and be an expert on the topic.

With what appears to be an 1840's type gold rush going on in the quest for sustainable, green, and “low carbon and carbon neutral” materials and processes, now might be an appropriate time to step back and give a good look at our use of portland cement these last 200 years. Does the good that has come from its use outweigh the bad? What have we learned and how can we apply it to our future?

3:30pm - Abstract #3237

Unveiling bio-molecule-regulated ordinary portland cement as a CO2 sink: A new pathway to decarbonize concrete manufacturing

Xiaodong Wang¹, Jialai Wang², Monica Amaral¹ and Yi Fang³, (1)The University of Alabama, Tuscaloosa, AL, (2)Civil, Construction, and Environmental Engineering, The University of Alabama, Tuscaloosa, AL, (3)College of mechanics and materials, Hohai University, Nanjing, China

Abstract Text:

Ordinary Portland cement (OPC) functions as the main binder in concrete matrix, being the most used construction material globally. Due to its ubiquitous use, OPC's production contributes to approximately 8% of worldwide CO2 emissions. Meanwhile, the substantial volume of concrete deployed annually in construction offers a substantial potential for CO2 absorption via mineral carbonation. However, current methods fall short in sequestering significant amounts of CO2 due to inherent limitations.

This study focusses on amplifying CO2 absorption in concrete by an order of magnitude beyond prevailing technologies while significantly improving the compressive strength of the material. Introducing the Biomolecule-Regulated Carbonation (BioCarb) method, this approach entails transforming cement slurry into a CO2-absorbing substance, with the formation of calcium carbonate regulated by a biomolecule. Test outcomes indicate that this method can sequester at least 15 pounds of CO2 per cubic yard of concrete and augment compressive strength by over 30%, thereby drastically curbing CO2 emissions from concrete production.

3:50pm - Abstract #3320

Carbon neutral concrete with CO₂-sequestering biochar

Julia Hylton, Materials Science, Colorado School of Mines, Golden, CO and **Lori Tunstall**, Civil and Environmental Engineering, Colorado School of Mines, Golden, CO

Abstract Text:

In the last decade, biochar has emerged as a promising partial cement replacement to significantly reduce the carbon footprint associated with concrete. This is because biochar is a carbon negative material, sequestering more than twice its weight in CO₂. The more cement that can be replaced with biochar, the lower embodied carbon the concrete will have; however, most researchers have found that replacing the cement with more than 5 wt% of biochar results in decreased strength, which limits the environmental benefit. In contrast, through a study of 22 distinct biochars, we have found that up to 44 wt% of the cement can be replaced with biochar, resulting in comparable or improved mortar strength and the potential to completely offset the carbon footprint of the cement. Using advanced data processing techniques, we identify three key biochar characteristics that control strength development of biochar-cement mortars: available water sorption capacity, oxygen-to-carbon ratio, and soluble silicon.

4:10pm - Abstract #3203

Use of amines for internal carbonation curing in cementitious materials

Mohammad Sadegh Tale Masoule^{1,2} and **Ali Ghahremaninezhad Ph.D²**, (1)Civil, Architecture and Environmental Engineering, University of Miami, Coral Gables, FL

Abstract Text:

Carbonation curing has emerged as an innovative technology to aid in lowering the carbon food print of the construction materials, which is responsible for a significant share of greenhouse gas emissions. Despite the promising potential of carbon curing, a major drawback remains to be the insufficient depth of carbonation in practical applications. Since the CO₂ provision and curing occurs from the exterior of the material, the densification of the exterior significantly decreases the penetration of CO₂ into the interior of the material. Inspired by internal curing, where water is provided to the interior of the materials to help with hydration, we investigate the use amine solution for internal carbonation curing. Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, X-ray Diffraction, X-ray Microcomputed Tomography were employed to investigate the phase composition and microstructure of the carbonation cured Portland cement pastes. The results indicate an increase in carbonation in the interior of the material when amine solutions are used.

4:30pm - Abstract #3251

Carbon-enriched fly ash characterization and its effect on the hydration of portland-limestone-cement mortars

Erin A Stewartson, Civil, Environmental, and Geodetic Engineering, The Ohio State University, Columbus, OH, Lisa E Burris, Ohio State University and Michelle A Cooper, Department of Transportation, Federal Highway Administration, McLean, VA

Abstract Text:

Supplementary cementitious materials improve concrete durability and sustainability by increasing concrete's service life through the pozzolanic reaction while simultaneously reducing concrete's cement contents. Now, carbon enrichment of coal ash attempts to further concrete sustainability efforts. During

carbon enrichment, coal ash is ground in a pressurized carbon-dioxide environment, thereby initiating calcium carbonate (CaCO_3) precipitation onto the fly ash particle. In large quantities, the presence of CaCO_3 precipitates may have adverse effects on the particle's ability to react with the free lime in the cementitious system to form calcium silicate hydrates, hindering the densification of the concrete microstructure. Moreover, adding carbon-enriched fly ash with slightly soluble CaCO_3 precipitates to a portland limestone cement (PLC) concrete already containing higher limestone content and less clinker may change the rate at which the concrete microstructure develops due to a coupled dilution effect. To better understand the extent, if any, of the potential issues posed, a carbon-enriched coal ash was characterized. Chemical compositions and reactive properties were determined using x-ray fluorescence, quantitative x-ray diffraction (QXRD), the ASTM C1897 R³ Method, isothermal calorimetry, and thermogravimetric analysis. Furthermore, the effect of grinding on the pozzolanic reactivity of the carbon-enriched ash was investigated through particle size analysis and QXRD. Comparable chemical compositions were identified and quantified in the carbon-enriched ash, its uncarbonated counterpart, and another traditional ash. The hypothesized dilution effect from carbon-enriched coal ash was not significant in PLC pastes or mortars. The grinding impact is theorized to have enhanced the reactivity by inducing physical and chemical alterations to the ash.

4:50pm - Abstract #3195

CO₂ uptake in supplementary cementitious materials

Wasiu Olaniyi Alimi^{1,2} and Prannoy Suraneni¹, (1)Civil and Architectural Engineering, University of Miami, Coral Gables, FL, (2)University of Miami, Coral Gables, FL

Abstract Text:

Enforced carbonation, combined with low-carbon technologies is a pathway to achieve carbon neutrality in the concrete industry. Besides its environmental benefits, enforced carbonation has been shown to improve the performance of recycled aggregates and concrete. Relatively little work has focused on the enforced carbonation of supplementary cementitious materials (SCMs). A range of SCMs and fillers with varying compositions and amounts of calcium and magnesium were exposed to high CO₂ environments under different conditions. Powders were characterized before and after CO₂ uptake, and material reactivity was also measured before and after the uptake. Most SCMs, with the exception of steel slags, recycled concrete fines, and recycled cement pastes, showed CO₂ uptake < 8% by mass. Likewise, under these conditions, the reactivity change post-CO₂ uptake was not significant.

6A: Sustainability and SCMs (Part 3 of 3)

Friday, June 21, 2024, 9:40am – 11:40am

9:40am - Abstract #3325

Effect of temperature and CSA dosage on the hydration kinetics and phase assemblage of blended OPC – CSA systems

Olajide Olaniyi Ipindola¹, Rachel E Cook¹, Aron Newman¹ and Mehdi Shokouhian², (1)Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, (2)Civil and Environmental Engineering,, Morgan State University, Baltimore, MD

Abstract Text:

In pursuit of sustainable construction materials, the cement industry faces the dual challenge of reducing its carbon footprint while meeting the growing demands for durable and resilient infrastructure materials. Calcium sulfoaluminate (CSA) cement emerges as an eco-friendly alternative to ordinary Portland cement (OPC). Blended OPC-CSA cement can achieve complementary benefits such as improved dimensional stability; faster setting; rapid hardening; and enhanced mechanical and durability performance. However, the hydration reaction and microstructural development of blended OPC–CSA is not entirely understood. This study aims to elucidate the effect of temperature and CSA dosage on the hydration kinetics and phase assemblage of blended OPC-CSA systems at early ages. Mixtures comprising 0%, 20%, and 40% replacement of OPC with CSA were prepared with a water-to-binder ratio of 0.35 and hydrated at 15°C, 25°C, and 35°C. The hydration kinetics and phase assemblage were studied using isothermal calorimetry; quantitative X-ray diffraction and thermodynamic modeling via Gibbs Energy Minimization software (GEMS), respectively. Increasing the dosage of CSA and temperature was found to influence the reaction rate, shorten the induction period, enhance the heat of hydration, and the hydrated phases quantities formed; generally, the results of the quantitative X-ray diffraction agree with GEMS results. The results of this study provide useful insight into tailoring CSA-based systems for fast setting and high early strength applications.

10:00am - Abstract #3158

Investigating the effect of limestone and gypsum in belite-enriched sulfoaluminate cements at different water to solid ratios

Sai Akshay Ponduru¹, Rohan R Bhat¹, Taihao Han² and Aditya Kumar¹, (1)Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO, (2)Materials science and engineering, Missouri University of Science and Technology, Rolla, MO

Abstract Text:

Belite-enriched calcium sulfoaluminate (CSAB) cement stands out as a highly promising alternative to ordinary Portland cement (OPC). The accelerated hydration of CSAB is facilitated by the presence of limestone (LS), which allows its active participation in forming monocarboaluminate and hemicarboaluminate. Simultaneously, the addition of gypsum contributes to the development of early-age strength via the formation of ettringite. The primary objective of this study is to identify the optimal mixture design by incorporating gypsum and LS to formulate a novel synthetic cement, promoting the sustainability of CSAB cement without compromising the mechanical properties. The study involves replacing CSAB with gypsum and LS at two different liquid-to-solid ratios (l/s) of 0.4 and 0.5. Gypsum replacements are determined to attain the gypsum-to-ye'elinite molar ratio (M) of 2.99, 4.35, and 7.99, while LS replacement ranges from 0% to 30% by mass at 10% increments. The investigation focuses on the hydration kinetics and compressive strength of [CSAB + Gypsum + LS] binders at 3 days. Thermodynamic modeling is employed to analyze the equilibrium phase assemblages of [CSAB +

Gypsum + LS] binders and to obtain the volume fraction of hydrates in the binder. Compressive strength ratios (CSR) are calculated for all pastes at both l/s ratios, revealing that a gypsum-to-ye'elimite ratio of 4.35 at 20% LS replacement is the optimal mixture design. This research aims to reduce the carbon footprint associated with CSAB manufacturing by developing a synthetic cement formulation. This novel synthetic cement formulation reduces the CO₂ emissions by ~ 32% and contributes to the ongoing efforts to enhance sustainability within CSAB cement.

10:20am - Abstract #3169

Assessment of high-volume harvested fly ash blends for use in precast construction

Matthew J Gombeda, Kurt A. Ordillas and Zoe N. Lallas, Department of Civil, Architectural and Environmental Engineering, Illinois Institute of Technology, Chicago, IL

Abstract Text:

Declining supplies of fresh fly ashes in some regions have further driven the importance of using harvested fly ash as a supplementary cementitious material and thus replacement for more energy-intensive ordinary Portland cement (OPC). Higher replacement rates of OPC with fly ash in general has traditionally been limited in precast operations due to stringent early-age strength requirements necessitated by initial prestress and lifting/handling of hardened components – often well within 24 hours after fresh concrete placement. Therefore, a series of mix designs were developed, as part of a larger framework for reassessing high-volume fly ash (HVFA) use in the context of precast construction, to demonstrate the feasibility of using larger fractions of harvested fly ash in concrete formulations suitable for precast fabrication demands. More specifically, a target minimum 24-hour compressive strength of 24.1 MPa (3500 psi) was set, in accordance with conventional precast structural design checks, while increasing the fly ash content to 40% replacement of OPC – at least a 15% increase above the traditional limit of 25%. The effect of using more sustainable Type II cement in contrast to conventional Type III Portland cement (the traditional standard for precast use) – both in conjunction with HVFA use – was also examined. Early-age mechanical properties including compressive strength, modulus of rupture, and modulus of elasticity were evaluated within the aforementioned early-age window. Lastly, corresponding design equations were then reassessed for their applicability with respect to the high-early strength HVFA mixes examined herein.

10:40am - Abstract #3214

Mechanochemical activation of basaltic fines for the production of supplementary cementitious materials

Sofiane Amroun, Luca Galli, Wasiu Olaniyi Alimi and Prannoy Suraneni, Civil and Architectural Engineering, University of Miami, Coral Gables, FL

Abstract Text:

Many mandates require an urgent reduction of the CO₂ emissions associated with cement production. One of the most common ways of reducing these emissions is the partial replacement of cement with supplementary cementitious materials (SCMs). However, typical SCMs, such as fly ash and slag, are reducing in availability and cannot meet the increasing worldwide demand for cement. Thus, manufactured SCMs (also known as engineered SCMs) are critical to ensure sustainable and durable concrete. Basaltic fines are a promising source of SCMs due to their worldwide availability, low cost, and adequate chemistry. However, these materials need to be processed to be used as they are otherwise unreactive. We explore here mechanochemical activation (MCA), where raw materials are exposed to high-energy grinding which alters particle surface structure and chemistry, making them more reactive and thus feasible to use as SCMs. In this project, basaltic fines were characterized before and after MCA

using a variety of techniques. Reactivity was measured using a modified version of the ASTM C1897 R³ test. We show that reactivity increases sharply with increasing grinding time and with increasing ball-to-powder ratio. Partial amorphization of the powders is evident from x-ray diffraction and Fourier-transform infrared spectroscopy. Scanning electron microscopy reveals the formation of rounded particles and agglomeration of particles. Laser diffraction shows a bi-modal particle size distribution with fine and coarse fractions. MCA results are obtained for multiple feedstocks. We show that an increase in reactivity is obtained in all cases, but that the initial reactivity has a strong influence on the increase in reactivity post-activation.

11:00am - Abstract #3305

Characterisation of libyan clays and their potential as supplementary cementitious materials

Ahmed Hamed and **Ruben Paul Borg**, Faculty for the Built Environment, University of Malta, Msida, Malta

Abstract Text:

The use of supplementary cementitious material SCMs such as metakaolin may replace part of the clinker to mitigate CO₂ footprints and to enhance the mechanical properties and durability performance of the concrete. This study focuses on the identification of 9 different clay sources in different regions in Libya, their characterization and potential use in concrete. The different clays were characterized through different techniques; X-Ray Diffraction XRD, Fourier Transform Infrared Spectroscopy FTIR, Differential Thermal Analysis DTA/TG, Scanning Electron Microscopy SEM and Energy Dispersive Spectroscopy EDS. The clays were analysed before and after calcination. On the basis of characterization of the materials, a specific clay (Samnu Clay) was selected for further assessment. The Libyan Metakaolin (LMK) considered was produced by de-hydroxylation of Samnu kaolinite clay at 700°C for 2 h. Three sets of cement mortars with different LMK, weight, replacement levels (0% to 30%), were prepared and tested for their mechanical properties at curing ages of 3, 7, 28, 56 and 90 days. The first set was prepared with a constant water/powder ratio (w/p) of 0.5, the second set with a varying w/p (0.5 - 0.6) and the third set with 0.5 w/p ratio and varying superplasticizer (sp) dosages (1-1.5%). Furthermore, a set of cement paste samples with the same replacement levels and curing time was prepared and tested to determine porosity through vacuum saturation and sorptivity. The results of the study confirmed the potential use of LMK as a SCM, up to 30% replacement of cement, with improvements in the mechanical properties of the materials as well as the durability.

11:20am - Abstract #3168

Quantifying the thixotropic behavior of fresh cement paste infused with wastewater-derived struvite

Ugochukwu Ewuzie, Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO and Monday U Okoronkwo, Chemical & Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO

Abstract Text:

The construction industry faces challenges with waste management, energy consumption, CO₂ emission reduction, and a decline in raw materials, mainly from cement production. Substituting cement with waste materials simultaneously addresses the waste management and CO₂ emission issues confronting the industry in its bid to achieve a near-zero emission target by 2050. Therefore, this study investigates wastewater-derived struvite as a partial replacement for ordinary Portland cement (OPC). Evaluating the thixotropy of struvite/cement mixtures is fundamental for the appropriate design and production of pumped concrete, self-compacting concrete, or 3D-printed concrete. To this end, the thixotropy of

different proportions of struvite/OPC mixes is quantified. We use hysteresis loop areas and flocs' destruction and reconstruction rates to investigate the cement pastes' thixotropic behaviors after different resting periods. The struvite-OPC mix (ST-OPC: 1:9 wt/wt at 0.5 water/binder ratio) shows an initial increase in equilibrium shear stress and hysteresis loop area, which decrease after 20 min resting time, corroborating struvite's high early strength. The result further suggests that hydration, formation, deflocculation, and reconstruction of flocs influence ST-OPC paste's thixotropy mechanism. Moreover, the OPC paste has a faster deflocculation rate than the 10% ST-OPC mixes, which improves after 1 h. Generally, substituting OPC with struvite resulted in a reduced rate and heat of hydration. Based on equilibrium shear stress, hysteresis loop area, incipient structural parameter, hydration heat, and reconstruction and deflocculation rates data, a 10% ST-OPC mix is a promising candidate for mass concrete constructions where improved workability and reduced thermal cracking are required. This research contributes foundational knowledge, facilitating the tailored design of ST-OPC composites for diversified construction applications.

6B: Rheology and Additive Manufacturing

Friday, June 21, 2024, 9:40am – 11:40am

9:40am - Abstract #3307

Size effect of 3D-printed fiber-reinforced concrete considering fiber distribution

Seongho Han, Haodao Li, Yucun Gu and Kamal Khayat, Missouri University of Science and Technology, Rolla, MO

Abstract Text:

Fiber-reinforced concrete (FRC) is used for the 3D printing technology, providing a feasible substitute for conventional reinforced bars for enhancing structural performance. This study investigates the relationship between fiber distribution and extruded filament size in 3D-printed FRC structures. Through a size effect law, it is evaluated how varying filament dimensions impact the dispersion and alignment of fibers within the concrete matrix. Therefore, the size of the filament has an impact on the distribution of fibers within the concrete, thereby influencing mechanical properties such as compressive, flexural, and bonding strengths. The findings provide valuable insights into optimizing the design and fabrication processes of 3D-printed FRC, paving the way for more resilient and efficient construction methodologies in the realm of additive manufacturing.

10:00am - Abstract #3323

Fresh and hardened properties of 3D-printed ultra ductile engineered cementitious composites

Maryam Hojati, Amir Bakhshi and Muhammad Saeed Zafar, University of New Mexico, Albuquerque, NM

Abstract Text:

Engineered Cementitious Composites (ECC) possess remarkable tensile ductility, making them ideal candidates for 3D-printed concrete structures. However, the use of traditional long fibers (12mm) poses challenges in printability and shape retention during 3D printing. This study addresses these obstacles by exploring the design of 3D printable ECC mixes incorporating shorter 8mm fibers. Methylcellulose (MC) was employed as a viscosity-modifying admixture to overcome printability limitations. The addition of 1% MC significantly enhanced fiber dispersion and rheological properties across four ECC mixes, improving dimensional conformity of printed filaments and ensuring successful extrudability and buildability. The research investigated four ECC mixes (S50, FA50, FA40-MK10, FA40-SF10) tailored for mold-casting and extrusion-based printing. These mixes replaced 50% of cement content with various mineral admixtures (slag, fly ash, metakaolin, silica fume) and incorporated PolyVinyl Alcohol (PVA) and Ultra-High Molecular Weight Polyethylene (PE) fibers at 1.5% and 2% volume ratios. Mechanical testing, including compressive, direct tensile, and three-point bending tests, evaluated mix performance. Notably, the S50 mix exhibited superior strength and deflection compared to others, while incorporating 2% PE fibers resulted in significantly higher strain capacities compared to the FA50 mix with similar fiber content. Substituting fly ash with metakaolin improved mechanical performance, whereas silica fume substitution had a negative impact. The research achieved a breakthrough in developing ultra-ductile ECC with 8mm PE fibers, enabling high-quality 3D printing compared to limitations with 12mm fibers. Analysis revealed the critical role of fiber characteristics in reinforcement potential, with ECC specimens achieving remarkable ductility and strength. These findings offer insights for creating sustainable and resilient construction materials.

10:20am - Abstract #3289

Use of lignin-based admixture as water reducer for tailoring the rheological properties of mortars for 3D-printing

Fabian B. Rodriguez¹, Kyle E. O. Foster¹, Xavier Fross¹, Rory Schmidt¹, Anastasia N. Aday¹, Adewale Odukomaiya¹, Michael E. Himmel² and Michael Griffin³, (1)Building Technologies and Science Center, National Renewable Energy Laboratory, Golden, CO, (2)Bioenergy Science and Technology Department, National Renewable Energy Laboratory, Golden, CO, (3)Catalytic Process Development, National Renewable Energy Laboratory, Golden, CO

Abstract Text:

Efforts towards decarbonizing construction materials and industrial processes related to cement and concrete can be aided via multifaceted approaches that target alternative admixtures as well as precision control of fabrication. Chemical admixtures for water reduction have played a crucial role in the development of advanced mortar and concrete mixtures. Newer biomass processing techniques developed for aviation fuel production from corn stover biomass produce a highly reactive lignin byproduct that is suitable for chemical modifications to mimic the properties of commonly used polycarboxylate ethers (PCEs) with a smaller carbon footprint. These lignin-based plasticizers developed at NREL can be used in place of petrochemical-derived superplasticizers to tailor the rheological properties of cement-based systems for applications such as additive manufacturing while reducing the carbon intensity of the concrete mix. Lignosulfonates derived from paper pulping were historically used as water reducers only to be displaced with the rise of PCEs.

The present study examines the use of a NREL produced lignin-based water reducing admixture (WRA), in cement pastes and mortar mixtures for 3D-printing at small- (mm) scale. The experimental program consisted of different formulations of oxidized lignin-based WRAs added in variable dosages to cement pastes with a fixed water-to-cement ratio. The objective is to achieve an appropriate workability, extrudability and buildability of mortar mixtures to produce 3D-printed specimens. The rheological characterization was performed to compare the initial yield stress and viscosity of the different mixtures with lignin-based admixture with respect to conventional PCE superplasticizers. The rheological characterization shows that the proposed material act as an effective water-reducer in cement systems, affecting the yield stress, plastic viscosity, and structuration rate of the mixtures evaluated. On the other hand, the effect on early hydration process of the cement pastes containing lignin-based admixtures is comparable to conventional superplasticizers.

10:40am - Abstract #3330

Synergistic effect of low-carbon cementitious materials on the key performance of 3D printing concrete

Yucun Gu and Kamal Khayat, Missouri University of Science and Technology, Rolla, MO

Abstract Text:

This study aims to investigate the synergistic effects of supplementary cementitious materials (SCMs) and limestone fillers (LF) on the thixotropy, printability, and strength development of 3D printing concrete (3DPC). The studied SCMs/fillers included Class C fly ash, harvested fly ash, Class N calcined clay, and LF with two particle size distributions. Off-line experimental assessment and in-line printable performance evaluation were conducted. The off-line assessment involved evaluating the workability, thixotropy, penetration resistance, and compressive strength of the printed elements. The in-line assessment included conducting a lab-scale 3D printing test using a screw-type printer to evaluate extrudability and quantify the maximum buildable height of the investigated mixtures. By comprehensively analyzing the coupled effect of these SCMs/fillers, the study provides a methodology for designing high volume SCM/filler containing 3DPC with desired extrudability and vertical buildable rate.

11:00am - Abstract #3116

Does it really matter in which order I mix uhpc?

Jedediah F Burroughs, Geotechnical and Structures Laboratory, U.S. Army Engineer Research and Development Center, Vicksburg, MS

Abstract Text:

Ultra-high performance concrete (UHPC) is a unique class of concrete with dramatically improved mechanical properties compared to traditional structural concrete; however, the reduced water content and optimized particle packing using very fine grained materials makes mixing UHPC more challenging. The use of high-range water reducing admixtures and high shear mixers eases some of this burden, but extended mixing times are still necessary to achieve UHPC with adequate workability for placement. Qualitative observations from practitioners have led to improved mixing protocols over time, but a robust quantitative analysis has been lacking. The study presented herein analyzed the various potential mixing sequences for UHPC using rotational rheometry. By tracking the torque necessary to maintain consistent mixing speed over time, a quantitative analysis of mixing energy can be made for each mixing sequence. For the first time, accurate descriptions of time to “break over” can be quantified, indicating the point at which the UHPC transitions from a plastic solid-like phase to a more quasi-liquid-like phase suitable for the incorporation of fiber reinforcement and eventual placement. Findings from studies like this continue to optimize the production of UHPC for more consistent performance.

11:20am - Abstract #3327

Introducing particle shape metric (PSM): A fundamental parameter that encapsulates role of aggregate morphology in enhancing packing and performance

Bayezid Baten, Civil Engineering, University of Illinois Urbana Champaign, Urbana, IL and Nishant Garg, Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Abstract Text:

Current packing models, utilized for enhancing properties of cementitious system, are robust but largely prioritize Particle Size Distributions (PSDs). However, morphology of the aggregate proportion, in a highly packed system such as Ultra-High Performance Concrete (UHPC) plays a role in governing different properties, such as rheology and strength. Here, we image up to 250 unique sand particles from 4 different sands and obtain key shape parameters such as Circularity (C), Roundness (R), and Aspect Ratio (AR). Combining these independent parameters, we introduce a new, fundamental parameter – the Particle Shape Metric ($PSM = C.R/AR$). Interestingly, this PSM has a strong correlation with the Packing Coefficient ($R^2 = 0.98$), obtained independently from helium pycnometry. Most importantly, PSM of the sands seems to have a direct influence on the rheological properties along with compressive strength, and open porosity of a variety of mortar mixtures. These findings highlight the potential role of shape metrics in influencing the granular skeleton of cementitious composites, marking a paradigm shift toward optimizing their workability, strength, and durability.

Poster Session

Wednesday, June 19, 2024, 5:15pm – 7:30pm

Abstract #3187

Increasing the reactivity of abundantly available basalt for sustainable cements: Earth and beyond

Sophia Liron Bergen, Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ and **Claire E. White**, Department of Civil and Environmental Engineering, and the Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ

Basalt is an abundantly available natural resource, but due to its lower reactivity in alkaline environments compared with commonplace supplementary cementitious materials (SCMs), such as calcined clays, it has yet to be extensively explored as a sustainable additive or baseline material for use in concrete. Here, we investigate the viability of increasing the reactivity of basalt via its inter-grinding with an alkali source (such as sodium hydroxide or sodium silicate) to make a “one-part” alkali-activated cement binder. The preliminary findings and characterization of raw materials will be presented, including quantification of amorphous content, mineralogy, calorimetry, and Fourier transform infrared spectroscopy. Moreover, due to the composition and mineralogy similarities between basalt and lunar regolith, this project also explores the development of a “one-part” alkali-activated lunar regolith simulant (LMS-1). NASA's Artemis program is a series of lunar missions designed to return to the moon, and constructing a lunar base is critical to this program. Hence, this research underscores the importance of cross-disciplinary approaches, showcasing the transferability of innovative technologies across seemingly disparate environments, namely Earth and the Moon.

Abstract #3234

Elucidating the reaction kinetics and mechanisms in sodium carbonate-activated high-volume blended cement

Samira Hossain and Kai Gong, Civil and Environmental Engineering, Rice University, Houston, TX

Blended cements with high volumes of supplementary cementitious materials (SCMs) offer significant decarbonization potential. However, they often experience significant delays in their early-age reaction kinetics due to the lower reactivity of SCMs, leading to slower strength development. Here, we investigated the impact of sodium carbonate activation on the reaction kinetics and mechanisms of a blended high-volume slag cement (90% slag and 10% Portland cement (PC)) using isothermal conduction calorimetry (ICC), *in-situ* X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analysis. The ICC results showed that 10-20 wt.% Na_2CO_3 solutions significantly accelerated the reaction kinetics occurring in the blended slag-PC system, shifting the main reaction peaks to be comparable to those of pure PC. Furthermore, sodium carbonate activation induced additional peaks preceding the main ICC peak, which are attributed to the formation of intermediate carbonate phases according to XRD and FTIR data. The amount and type of carbonate phase formation (e.g., gaylussite, calcium carbonates and hemicarbonates) are seen to depend on Na_2CO_3 concentration and reaction time. We hypothesize that the formation of these carbonate phases boosted the pH of the pore solution, thereby accelerating slag dissolution and subsequent gel formation in the blended system. Ongoing thermodynamic modeling and molecular dynamic simulations aim to further elucidate the underlying driving force and molecular-level mechanism of this acceleration. This study demonstrates the potential of leveraging sodium carbonate activation to increase slag replacement ratios to 90% (thereby achieving >70% reduction in CO_2 emissions) without delaying the reaction kinetics of high-volume slag blended cement systems.

Abstract #3281

Rheology, 3D printing, and particle interactions of xanthan gum-clay binder for earth concrete.

Yierfan Maierdan, Civil Engineering and Engineering Mechanics, Columbia University, New York City, NY and Shiho Kawashima, Columbia University

This study investigates the potential of xanthan gum (XG) to serve as a biopolymer binder for improving the rheological, mechanical, and 3D printing properties of earth-based concrete, aligning with the pressing need for sustainable, low-carbon construction materials. Experimental results indicate that XG could disperse kaolinite clay particles, which likely arises from the highly negative charges of both kaolinite and XG. Rheological parameters display two trends with increasing XG concentration: initially decreasing yield stress, viscosity, and storage modulus owing to XG's dispersing effect, followed by an increase due to polymer overlapping. The same trend is observed in 3D printing experiments, where the kaolinite clay suspensions exhibited enhanced buildability with increasing XG concentration and eventually achieved a "Printable" state at 5% XG. Additionally, compressive strength was observed to steadily increase with increasing XG content, for instance nearly tenfold with 2.4% XG compared to 0% XG (0.34 MPa to 3.58 MPa). This exploration highlights the pivotal role of XG as a dual-functionality agent, acting as a robust binder and a promising rheology modifier.

Abstract #3212

Impact of calcined clays on rheology and mechanical performance of cementitious systems

Muhammad Farjad Iqbal, University of Illinois Urbana Champaign, Urbana, IL and Nishant Garg, Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Calcined clays have emerged as promising supplementary cementitious materials. However, their high-water demand continues to pose fundamental rheological challenges for practical applications. We investigated the rheology and mechanical performance of 15 calcined clay-OPC paste mixtures. Unary pastes (20% clay content) showed two distinct regions of dynamic yield stress (DYS), i.e., either less than 100 Pa or greater than 250 Pa, with a maximum stress of ~400 Pa. This high workability of the reactive clays was improved by up to 50% using binary mixtures. Despite low flowability, the pastes exhibit shear thinning behavior, and a refined microstructure with increase in clay content. This behavior resulted in approximately 11% strength increase at 28-days, with most mixtures satisfying the ASTM C618 strength activity index criteria by the 7-day mark. Finally, we observed a strong correlation between DHS and the heat at the onset of hydration suggesting that rheology and reaction kinetics are highly interlinked.

Abstract #3130

Probing mechanical properties of carbonation products in reactive MgO cement using high-pressure x-ray diffraction.

Ruoxi Yang and Jiaqi Li, Lawrence Livermore National Laboratory, Livermore, CA

Reactive MgO cement is an emerging binder for CO₂ storage. The phase and corresponding mechanical properties of the carbonation product of the cement remain unclear. Understanding the mechanical properties of its carbonation products is critical to the strength development and materials design for the cementitious systems. High pressure X-ray diffraction is a powerful characterization technique to probe the intrinsic mechanical properties of crystalline phases which may occur in the cementitious system. In this experimental setup, the influences of pores at nano and micro scales on mechanical properties of the phases are precluded. A series of hydrated magnesium carbonates were investigated.

Abstract #3233

Insights on clay calcination via in-situ TEM

Tausif E Elahi, Pablo Romero and Nishant Garg, Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

In order to achieve maximum reactivity for any given calcined clay, it is important to calcine the clay at an optimal temperature for an adequate duration. These parameters, namely time and temperature, can vary depending on the clay mineralogy, physical characteristics, as well as calcination technology. Here, in this study, we report preliminary results on the fundamental changes that occur in individual clay particles upon calcination via in-situ Transmission Electron Microscopy (TEM). We find that observing a statistically sufficient number of particles, subject to heating in a live stage in a TEM, can give insights into the kinetics of the dehydroxylation process. These kinetics of dehydroxylation, sensitive to both time and temperature, subsequently are linked to the reactivity of the clays as measured by the R3 method.

Abstract #3252

Role of crystallinity and al-contents on the decalcification resistance of c-s-h and c-a-s-h

Ishrat Baki Borno¹, Warda Ashraf¹ and Muhammad Intesarul Haque², (1)Civil Engineering, The University of Texas at Arlington, Arlington, TX, (2)HNTB Corporation, Baltimore, MD

Calcium silicate hydrate (C-S-H) and calcium aluminum silicate hydrate (C-A-S-H) are the predominant binding phases in Portland and blended cementitious systems, commonly retaining an amorphous or semi-crystalline structure. The primary objective of this study is to compare how amorphous and crystalline forms of these binding phases are affected by decalcification. Two different decalcifying environments were evaluated – using accelerated carbonation and NH_4NO_3 . Fourier-transform infrared spectroscopy (FTIR) was utilized to observe decalcification during 18 hours of accelerated carbonation (99% CO_2 concentration) using an in-situ setup. The findings indicate that during this period, C-S-H was nearly completely decalcified, as reflected by the decrease in Q^2 silicate species in the network and the formation of silicate species with a higher degree of polymerization (Q^3 and Q^4). Conversely, the crystalline version of these phases, also known as tobermorite, showed minimal impact from decalcification, with only a 10-15% decrease in Q^2 after the same exposure duration. This decalcification observation was corroborated using NH_4NO_3 , yielding similar results. Tobermorite, a significant hydration product present in ancient Roman concrete, is often credited for the remarkable durability of Roman concrete, and this phase is not commonly found in Ordinary Portland Cement (OPC) systems. Optimization of low-carbon alternative binders can facilitate favorable conditions for the crystallization of C-S-H and C-A-S-H, thereby fostering the development of a sustainable and durable cementitious composite.

Abstract #3303

Effect of cellulose nano-fiber gels on the chloride ingress and freeze/thaw properties of cementitious paste

Md Hasibul Hasan Rahat, Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA and Alexander S. Brand, Civil and environmental engineering, Virginia Tech, Blacksburg, VA

Durability challenges posed by freeze/thaw cycles and chloride ingress are significant concerns for concrete materials. This study explored the effects of the inclusion of cellulose nanofiber (CNF) gels on the freeze/thaw and chloride ingress properties of cementitious paste. The specimens were prepared by replacing water in the mixture with three types of CNF gels (CNF-1, CNF-2, and CNF-3), while the control paste specimens (CP) contained water. It was found that specimens containing CNF gels exhibited positive freeze/thaw durability characteristics when compared to specimens without CNF gels. In

compression testing following freeze/thaw cycles, CNF-2 and CNF-3 exhibited the smallest percentage changes in compressive strength (46.1% and 47.1%, respectively), whereas CP exhibited the largest change (71.1%). CNF-2 performs particularly well in freeze/thaw testing, showing the least percentage decrease in the dynamic modulus, ultrasonic pulse velocity, and mass loss. In addition, transmission X-ray microscopy (TXM) was employed to determine diffusion coefficients (D_c), revealing that specimens containing CNF gels exhibited higher resistance to diffusion than those without CNF gels. Across all the sample groups, lower D_c were observed, with CNF-1 and CNF-3 displaying the highest resistance to diffusion, followed by CP and CNF-2. These findings underscore the potential of CNF gels to enhance the overall performance of cementitious matrices against freeze/thaw cycles and chloride ingress.

Acknowledgement

This material is based upon work supported by the Broad Agency Announcement Program and the Cold Regions Research and Engineering Laboratory (ERDC-CRREL) under Contract No. W913E522C0001. The authors would also like to express their gratitude to Dr. Benjamin Hsiao from Stony Brook University for providing the CNF gels used to conduct the study.

Disclaimer

Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Broad Agency Announcement Program and ERDC-CRREL.

Abstract #3152

High temperature and pressure molecular dynamics simulations of sodium-alumino-silicate-hydrate gel

Yangwoo Lee, Civil and Environmental Engineering, Princeton University, Princeton, NJ and Claire E. White, Department of Civil and Environmental Engineering, and the Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ

Geothermal energy, recognized for its potential to mitigate global warming through carbon-neutral solutions, demands durable infrastructure. Well cementing techniques, in particular, must be durable to ensure long-term cost-effectiveness and simultaneously, the cement used must be eco-friendly to minimize the carbon footprint and achieve carbon-neutrality. Low-Ca alkali-activated materials (AAMs) emerge as a promising candidate for this, offering a sustainable alternative to conventional cement with lower environmental impact. This project explores the formation and molecular structure of sodium-alumino-silicate-hydrate (N-A-S-H) gels, a primary component of low-Ca AAMs, under geothermal and ambient conditions. By leveraging molecular dynamics (MD) simulations, we analyze the gelation process of N-A-S-H gels under high temperature and pressure characteristic of geothermal environments. These findings are pivotal for the development of specialized cement formulations tailored for geothermal energy extraction.

Abstract #3253

The synergy between CO₂ and seawater curing of calcium silicate-based cementitious composites

Farzana Mustari Nishat, Ishrat Baki Borno and Warda Ashraf, Civil Engineering, The University of Texas at Arlington, Arlington, TX

This research work evaluated the effects of seawater on CO₂-cured low-lime calcium silicate-based cementitious composite. The combined effect of seawater and carbonation curing was investigated on two types of binders - high blast furnace slag (BFS) containing blended binders and pure β -C₂S. Samples were prepared using freshwater and seawater as mixing water. The samples were exposed to accelerated CO₂ curing immediately after casting. After 7 days of CO₂ curing, the samples were exposed to seawater, and their performance was monitored for up to 90 days. Compressive strength was evaluated as an indicator of the mechanical properties, while thermogravimetric analysis (TGA), Mercury intrusion porosimetry (MIP), and X-ray diffraction (XRD) gave an insight into the microstructural

properties. The results revealed that the use of seawater substantially accelerated the carbonate precipitation rate in these binders at the early stage. The TGA results showed around 30.5% higher CaCO_3 formation in the samples mixed using seawater after 7 days of curing. The seawater sample further showed 20% higher compressive strength compared to the freshwater samples. The enhanced performance of the seawater mixed samples was attributed to the presence of magnesium and sulfates in these samples.

Abstract #3309

Chlorellestadite: A novel carbonatable binder

Mohamed Abdelrahman, University of Illinois, Urbana-Champaign, Champaign, IL, **Vikram Kumar**, Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, Urbana, IL and Nishant Garg, Civil and Environmental Engineering, University of Illinois Urbana Champaign, Urbana, IL

Chlorellestadite ($\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Cl}_2$) is a commonly occurring phase in eco-cement prepared from chloride-rich waste materials such as waste-to-energy (WTE) ashes. CO_2 curing of eco-cement containing chlorellestadite has been observed to develop higher strength. However, the mechanism behind the observed increase in strength upon CO_2 curing of eco-cement remains unclear. In this work, we study the effect of CO_2 curing on chlorellestadite. Our results indicate that chlorellestadite reacts with CO_2 and forms vaterite, calcite, gypsum, amorphous silica, and calcium chlorosilicate ($\text{Ca}_3(\text{SiO}_4)\text{Cl}_2$). As a result of this reaction, we find that upon CO_2 curing, cement paste specimens prepared from 80 percent OPC and 20 percent chlorellestadite develop 7 and 28-day strength similar to specimens prepared with 100 percent OPC. Additionally, the bound chlorides in chlorellestadite become unbound upon CO_2 curing, releasing chloride ions in the pore solution. These findings present new insights that enable using eco-cements containing chlorellestadite as carbonatable binders.

Abstract #3315

An investigation into the suitability of palm kernel shell biochar for use as an alternative fine aggregate in the production of conventional portland cement concretes

Tristan J Pagkalinawan and Alex O Aning, Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA

As an alternative to traditional methods used to dispose of palm kernel shell, along with providing a means to supplement dwindling sand resources, production of biochar and subsequent incorporation in concrete as a fine aggregate were proposed. Palm kernel shell biochar (PKS-BC) was produced, ground, and sieved to achieve a particle size comparable to ASTM C778 Graded Standard Sand. Mortar test cubes were produced using varying compositions of standard sand and biochar replacement followed by curing for 7 and 28 days. Compression testing on mortars with as high as 20 vol% of the total aggregate volume replaced with PKS-BC yielded strengths meeting or exceeding ASTM C90 and ASTM C1329 requirements for comparable materials, while subsequent microstructural analysis suggested good interfacial adhesion between the cement and aggregate phases.

Abstract #3328

Alkali-silica reaction mechanism in lime-pozzolana mortar

Adhora Tahsin¹, **Ishrat Baki Borno**² and **Warda Ashraf**², (1)Department of Civil Engineering, The University of Texas at Arlington, Arlington, TX, (2)Civil Engineering, The University of Texas at Arlington, Arlington, TX

This research investigates the effectiveness of lime-calcined clay binder in addressing alkali-silica reaction (ASR) deterioration. Mortar bars containing two types of reactive aggregates, borosilicate and pumice, were subjected to alkali exposure for up to 2 years. Scanning electron microscopy (SEM) was used to identify the potential mechanisms of reaction product formation. Additionally, the impact of these ASR products on mortar performance was assessed by measuring length expansion and compressive strength. The results showed minimal ASR-induced expansion of only 0.02% in the bar samples. This minimal expansion was attributed to the presence of high alumina content in the ASR product, which promoted silica polymerization and the formation of zeolites like phillipsite and chabazite. These zeolites exhibited a high capacity for alkali uptake, with a (Na+K)/Si ratio of 0.2-0.5, thus reducing the available alkali content for further reaction. A crystalline ASR product, Na-shlykovite, was found to coexist with the zeolites, forming at their core. Furthermore, the use of pumice enhanced the efficiency of ASR mitigation by providing additional alumina and accommodating the reaction products within its internal voids. This prevented shrinkage cracks from propagating into the binder matrix during the conversion of geopolymer gel into zeolites. Replacing borosilicate with pumice also resulted in a 61% higher compressive strength.

Abstract #3146

Toward one-part alkali-activated metakaolin via inter-grinding: Assessing the effects of inter-grinding on reaction kinetics and microstructure

Meddelin Setiawan, Department of Civil and Environmental Engineering, and the Andlinger Center for Energy and Environment, Princeton University, Princeton, NJ and **Claire E. White**, Department of Civil and Environmental Engineering, and the Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ

Various alkali-activated materials (AAM) have been developed to help reduce carbon emissions of the construction industry. However, the commercialization of AAMs has been relatively slow, first due to a lack of widespread awareness of the emissions associated with the cement industry, and second due to the reluctance to work with “two-part” concretes, such as AAMs, that require large amounts of high pH activator solution. Designing AAM starting materials that resemble ordinary Portland cement (OPC), where only water is needed, will potentially accelerate the implementation of this lower-CO₂ cement in engineering applications. Here, we will present preliminary findings on a “one-part” AAM synthesized using abundantly available calcined kaolin clay and solid sodium sources (sodium hydroxide and sodium silicate). The effects of inter-grinding the calcined clay with the different types of sodium sources are assessed using isothermal calorimetry (reaction kinetics), scanning electron microscopy (microstructure), compressive strength testing, and workability. It is anticipated that inter-grinding will aid in the reactivity of the overall system, helping to overcome the known reactivity limitations of current “one-part” AAMs.

Abstract #3202

Influence of pH variation on ye'elimite early-age hydration kinetics and microstructure development

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The reactivity of ye'elimite, the principal hydraulic mineral in calcium sulfoaluminate (CSA) cement, is intricately linked to the pH levels within the pore solution. Specifically, variations in pore solution pH directly affect the dissolution-precipitation kinetics of ye'elimite. However, the influence of pH on the kinetics of ye'elimite hydration, especially at the very early stage, remains unclear. This study investigates the impact of pH variation on the early-age hydration properties and microstructure of ye'elimite in cementitious systems. The experimental approach involved the use of dilute nitric acid and dilute sodium hydroxide to modulate the pH levels of ye'elimite paste. X-ray diffraction (XRD) analyses, microcalorimetry studies, and scanning electron microscopy (SEM) were employed to elucidate the resultant changes in mineralogical composition, shedding light on the hydration kinetics and microstructural evolution. Our findings reveal a distinct correlation between pH and ye'elimite reactivity. Lowering the pH through the introduction of dilute nitric acid demonstrated a notable enhancement in ye'elimite reactivity, manifesting in the increased formation of hydration products such as ettringite and monosulfate. In contrast, at elevated pH levels, despite the occurrence of some reactions, a notable portion of ye'elimite remained unreacted. This research contributes valuable insights into the understanding of pH-dependent reactivity in ye'elimite-based cementitious systems. The implications of these findings extend to the optimization of cement formulations, offering opportunities for tailoring early-age properties and microstructure for improved performance in construction materials.

Abstract #3265

Hydrogels as internal curing agents: Interactions with cementitious mixtures from the lab to the field

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Work at Purdue University over the last decade has studied the performance of superabsorbent polymer (SAP) hydrogels used as internal curing agents in cementitious mixtures. This presentation will summarize on-going lab and field scale research efforts to: (1) create a novel SAP composition that refines the cement microstructure through the incorporation of an organic silicate into the hydrogel particle; and (2) compare the performance of SAP-cured concrete in field trials with concrete that is internally cured with a nanosilica-based admixture and externally cured with a curing compound. Lab-scale polymerizations were carried out to synthesize novel hydrogels with nanosilica crosslinks through the incorporation of an organoalkoxysilane monomer, 3-(trimethoxy silyl) propyl methacrylate (TPM), – “TPM-Gels”. The resulting hydrogels were shown to have dynamic swelling and dissolution behavior dependent on their TPM content through gravimetric swelling tests. TPM-Gels and their interactions with cement paste were studied through microscopy and chemical analysis. The shrinkage behavior and mechanical properties of TPM-Gels in mortar was studied in collaboration with researchers at TU Dresden. Calcium silicate hydrate (C-S-H) was precipitated within neat and TPM-functionalized hydrogels through a double diffusion method. The C-S-H chemistry, growth, morphology, and interactions with the hydrogel were studied through small angle X-ray scattering (SAXS), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). Field trials have shown that concrete containing commercially available SAP exhibited enhanced performance attributed to improved hydration due to internal curing, especially compared to mixtures containing nanosilica or treated with a curing compound. Addition of SAP decreased the slab core temperatures by 16%, and decreased the time required to attain peak temperature by 2 hrs. SAP-

containing mixtures also achieved their minimum flexural strength target at 4 days, ahead of the other mixtures, and reached greater compressive strength values at every age, from 7-90 days.

Abstract #3317

Effect of bovine and fish bone as a partial replacement of fine aggregate in mortar mixtures

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Bonemeal, derived from the finely or coarsely ground waste of animal bones, has been used as a natural fertilizer for plants, providing a rich source of calcium and phosphorus. The major chemical phases of bone are hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). Previous literature showed that calcium phosphate, depending on the Ca/P ratio, can undergo pozzolanic reaction in the presence of calcium hydroxide and form hydroxyapatite. Furthermore, addition of synthesized hydroxyapatite in cementitious mixture showed improved mechanical properties. While bone presents itself as a sustainable bio-derived source of hydroxyapatite, limited research has been done to investigate its potential impact when incorporated into cementitious systems. In this study, two sources of bone— i) bovine and ii) fish were used as substitutes for fine aggregate across varying replacement levels (0%, 25%, 50%, 75%, and 100%) within mortar mixtures. All the mortar mixtures were prepared with a water-to-cement ratio of 0.48. Mechanical and microstructural characterizations were used, including setting time, compressive strength, thermogravimetric analysis, X-ray diffraction, and scanning electron microscopy. Preliminary findings show that to achieve an equivalent volume in mortar mixtures, approximately 50% less bone by mass was required compared to conventional fine aggregate due to its lower specific gravity. Furthermore, the addition of bone as fine aggregate decreased the setting time compared to the control mixture (0% bone). Additional data regarding the mineralogy and compressive strength of mixtures without and with bone as a fine aggregate replacement will be discussed. The findings of this study will contribute to a deeper understanding of the challenges and feasibility associated with utilizing bone as an alternative, biobased source of fine aggregate.

Abstract #3171

Permeability of enzymatic concrete

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Water/ion permeability and the resulting corrosion-induced degradation significantly hamper the sustainability of reinforced concrete structures. This study evaluates the durability of recently discovered self-healing cementitious matrices using a ubiquitous Carbonic Anhydrase (CA) enzyme. Here, we propose a novel technique using a custom vacuum-assisted accelerated dye penetration to assess the water permeability of enzymatic cementitious matrices. The results demonstrate that CA-modified samples exhibit substantially reduced dye penetration, indicating high water and chloride transport resistance, with a remarkable 50% reduction compared to the control samples. Notably, the mechanical properties of the cementitious matrix were not compromised, thereby emphasizing the promising potential of CA in extending the service life of concrete structures. Additionally, numerical diffusion simulations were performed to provide insights into the ion penetration mechanisms in mortar and cement paste and to compute their corresponding diffusivities. Complementary analyses, including micro-computed tomography (μ -CT) scanning and Mercury intrusion porosimetry (MIP), offer detailed insights into the mechanism of crystal precipitation induced by CA and the corresponding changes in the pore structure of cementitious matrices to enhance durability. Incorporating enzymes into the cement mix will fill a significant portion of small and dominant pores ($< 100 \mu\text{m}$) with calcite precipitations, thereby considerably reducing the diffusivity of water/ions within the cementitious matrix. This study underscores the significant role of CA in the future of sustainable infrastructure, contributing to reduced CO_2 emissions and cost savings over the lifecycle of concrete structures.

Abstract #3106

Printability of modified cement-based materials and reviewing its mechanical properties at varying layer thickness

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Additive manufacturing or 3D printing allows to obtain accurate geometries across a wide range of applications. It is used in many different fields and now booming in the architecture and construction industry. In the present work, a unique binary mix of cement composed of ordinary Portland cement (OPC) and quick-setting cement (QSC) was mixed with the silica sand aggregate in different proportions for a customized binder jetting 3D printing (BJ3DP) process. Specimens were printed using this blended dry powder with deionized water to find the impact of layer thickness on the properties of the produced specimens. The results show that the properties are influenced by the binary mix proportion and the layer thickness. The investigations highlight significant improvements in mechanical properties by increasing the proportion of Ordinary Portland Cement (OPC) and optimal conditions are identified at a mixed proportion of 35 wt% OPC and 5 wt% QSC. Notable improvements in the mechanical performance are observed as the layer thickness is reduced.

Abstract #3256

Using polymer science to improve concrete printing: Foam gels, microgels, and shampoo

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Admixtures in cementitious mixtures have the ability to contribute their unique material properties to enhance concrete and enable novel processes such as additive manufacturing—a processing method characterized by optimized structures, reduced materials, and rapid construction. Conventional concrete mixtures are typically unprintable without admixture to counter printability, extrudability, or buildability challenges. We sought to investigate three commonly used and mass-produced organic molecules that are not currently used as admixtures in concrete: foam gels, microgels, and shampoo. Foam gels are acrylamide-based polymer networks that provide internal curing benefits and enhance buildability through adsorbing water during early hydration and releasing it slowly over time. Microgels are hydrophilic polymers with the potential to act as a dual admixture: as an internal curing agent and as a viscosity modifying admixture. Shampoo is a micellar-structured surfactant solution that makes the concrete smell nice and promotes hydration. All three systems are hydrophilic and modify viscosity, thus allowing us to make comparisons. Our experimental program focused on determining suitable admixture dosing through the evaluation of printing performance by measures of shape retention, buildability, and extrudability. From these observations, we identified printable dosage regimes, order of mixing, and any additional processing methods unique to each system. Our findings demonstrate the potential of applying these novel materials as admixtures for printed concrete.

Abstract #3173

A self-healing enzymatic construction material

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Concrete is one of the main contributors to global CO₂ emission, and efforts to find an alternative to concrete have not been fully successful. Inspired by the process of CO₂ exchange in biological cells, this paper introduces a novel method to create a negative-emission enzymatic construction material (ECM) with self-healing capabilities. The concept proposed in this paper uses carbonic anhydrase (CA) to catalyze the condensation of CO₂ and water to promote the precipitation of calcium ions in the aqueous solution as calcium carbonate crystals. The resulting ECM has compressive strength and Young's modulus more than twice that of the minimum acceptable for cement mortar and other alternative building

materials. The strengthening mechanism through the growth of mineral bridges that hold the sand particles in the structure of ECM is also modeled and studied. This report provides a new path for development of environmentally friendly construction materials with low cost.

Abstract #3319

3D-printable, sustainable concrete alternative using clay and biopolymer additives

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The building and construction sector contributes 37% of global energy and process CO₂ emissions. Earthen materials offer a low-cost, locally available, sustainable alternative to current building materials which often require high-temperature reactions, intensive mining, and long-distance transportation. In addition to the benefits of earthen materials during construction, they also reduce energy use during building use due to their high thermal mass and potential for recyclability at end of life. However, the broad application of these materials is currently limited due to weak compressive strength, durability concerns, and high labor costs. Biopolymer stabilization and large-scale 3D printing are promising methods to modernize and improve earthen materials. To achieve these goals, we aim to take a rigorous scientific approach to understand the micro-scale effects of biopolymer additives on clay minerals and how those interactions impact the macro-scale properties. Despite the ubiquity of clays as a component of earth, they are highly complex, so their role is not fully understood. In this study, the binding affinity of the two most common clays (i.e., bentonite, kaolinite) with five polysaccharide biopolymers (i.e., guar gum, locust bean gum, methylcellulose, sodium alginate, xanthan gum) was studied through a mineral binding characterization (MBC) procedure employing thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and zeta potential analysis. Locust bean gum exhibited the highest binding potential to both clays across these three test methods. Additionally, preliminary mechanical and rheological testing was performed to investigate the bulk wet and dry state properties to inform printability and applicability in construction. Although the MBC procedure partially explains binding properties, additional experiments are required to fully elucidate the mechanisms between biopolymers and clays towards unlocking the full global potential of 3D-printed earthen building materials.

Abstract #3244

Unlocking concrete's green potential: Integrating supplementary cementitious materials with biomolecule-regulated carbonation for deep decarbonization

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In addressing the pressing need for sustainable practices in the construction industry, this study investigates the combination of the traditional use of supplementary cementitious materials (SCMs) with a novel biomolecule-regulated carbonation (BioCarb) process to significantly reduce the carbon footprint associated with concrete production. Recognizing that relying solely on one method is insufficient to meet sustainability goals, this research aims to bridge this gap by integrating these complementary strategies. The BioCarb method offers a promising avenue for carbon capture and utilization, wherein the cement slurry is converted into a CO₂ absorbent and the formation of calcium carbonate is regulated by a biomolecule. The typical challenge of low early strength associated with the use of SCMs is effectively addressed by the seeding provided during the carbonation process. Moreover, the final mechanical performance is significantly enhanced, with observed improvements of up to 20% in compressive strength. The experimental data suggests that the carbonation process enables the sequestration of at least 15 lbs of CO₂/yd³ of concrete. Additionally, by replacing 20-30% of Ordinary Portland Cement (OPC) with SCMs, a substantial reduction in the carbon footprint of the final concrete mix is achieved. By

harnessing the synergistic benefits of these combined approaches, we can effectively address sustainability challenges and pave the way towards a more resilient and environmentally friendly built environment.

Abstract #3324

Hydration and microstructural evolution of seawater-mixed calcium aluminate cement

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It is well-known that the structural integrity of an ordinary Portland cement (OPC)-based reinforced concrete can become compromised when exposed to salt ions (e.g., Cl⁻) in coastal environments due to corrosion of both the reinforcement and the cement matrix. Calcium aluminate cement (CAC) is a promising alternative to OPC due to its: well-known superior chemical resistivity; and decreased embodied carbon. While “fresh” water-mixed CAC has been historically used for refractory purposes, there is increased research interest in mixtures containing seawater due to potential durability and water conservation benefits. This research seeks to further the understanding of the hydration and phase evolution of seawater-mixed CAC systems via isothermal calorimetry, quantitative X-ray Diffraction, and thermodynamic modeling. Commercially available CAC and a simulated seawater prepared according to ASTM D1141-98 were employed to prepare CAC paste at a water-to-binder ratio of 0.35 in a juxtaposition manner to CAC pastes prepared with deionized water. Hydration kinetics were monitored for 72 hours at different temperatures ranging from 15 °C to 35 °C via isothermal calorimetry, while the phase evolution was studied up to 100 days using quantitative X-ray diffraction. Lastly, thermodynamic modeling was performed via Gibbs energy minimization software to support phase assemblage X-ray diffraction results; quantitative X-ray diffraction and thermodynamic modeling results were in agreement. Overall, this work provides a positive indication of CAC’s potential as an alternative binder to improve the service life and decreased the embodied carbon associate with coastal infrastructure applications.

Abstract #3155

Compressive strength prediction of freeze-thaw damaged concrete using hyperspectral imaging and data-driven methods

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Compressive strength is normally taken as a paramount indicator of concrete under various working environments including freeze-thaw weathering prevalent in cold areas, given its realistic reflection of mechanical performance. The conventional uniaxial compression test method is commonly adopted to measure the strength indicator, which however, needs tedious specimen preparation and cannot preserve structural integrity. A data-driven strength prediction approach based on hyperspectral imaging technology is thus proposed. The hyperspectral data cuboids and other experimental parameters of mix proportion, curing condition, and compressive strength were compiled, based on which, a convolutional neural network model was built, trained, and verified. The evaluative findings demonstrate that the developed model exhibits commendable predictive accuracy, revealing the feasibility of this approach.

Abstract #3345

Insights to the characterisation of alkali-acetate blast furnace slag binders

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This study explored the use of sodium acetate (NaAc) or potassium acetate (KAc) as alternative activators compared to sodium hydroxide (NaOH) or hydroxide (KOH) for producing blast-furnace slag based cements. The acetate-activated slag binders exhibited much slower reaction process compared to the hydroxide-activated binders, consistent with an extended setting time. However, the main crystalline reaction products including calcium aluminosilicate hydrate (C-(A)-S-H) type gels and layered double hydroxides with a hydrotalcite-like structure were detected in all binders after 28 days of curing. Compressive strengths of the acetate-activated slag pastes (~40MPa at 180d) were consistently lower than those of binders produced with hydroxide-based activators (~80MPa at 180d). The structure of C-(A)-S-H types gels formed in acetate-activated slags have similarities to those formed in sodium silicate activated slags, based on ²⁹Si MAS NMR spectra and Ca/Si ratios. This study demonstrates the feasibility of using alkali-acetates as sole alkali-activator for producing slag-based binders.

Abstract #3348

Characterizing CO₂ in cementitious materials with remote fiber optic raman probe

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The urgent need for producing sustainable cementitious materials has led to increased interest in using carbon-negative technology to enhance sustainability. In this regard, measuring the amount of CO₂ is one essential issue. Traditional methods such as Thermal Gravimetric Analysis (TGA), Quantitative X-ray Diffraction (QXRD), Scanning Electron Microscopy (SEM/EDS), and X-ray Fluorescence (XRF) offer valuable insights but often involve destructive testing or require extensive sample preparation. This study introduces the use of a remote fiber optic Raman spectroscopy probe as a non-destructive alternative that enables in situ analysis with minimal sample interference. Raman spectroscopy provides detailed molecular and structural information, allowing for the direct observation of CO₂ incorporation into the cement matrix. This technique is particularly advantageous for its ability to deliver real-time, onsite analysis of cementitious materials under various environmental conditions without the need for sample preparation or removal. By comparing results with those obtained from TGA, QXRD, SEM, and XRF, this study demonstrates that Raman spectroscopy not only validates the findings of these traditional methods but also reveals additional insights into the hydration products and carbonation processes. The deployment of a remote fiber optic probe further enhances the applicability of Raman spectroscopy, making it a superior tool for the comprehensive assessment of CO₂ in cementitious materials.

Abstract # 3351

Biowaste as Sustainable Supplementary Cementitious Materials in Portland Cement Concrete

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The integration of biowaste into concrete production holds promise for mitigating environmental impacts associated with the agricultural and concrete industries, which collectively contribute to over 30% of annual global CO₂ emissions. This study explores the feasibility of two waste materials, eggshell powder and sugarcane bagasse ash (SCBA) to be incorporated into concrete as sustainable supplementary

cementitious materials. Laboratory-scale experiments were conducted to investigate the effect of those waste materials on the hydration of cement and performance of cementitious composites. Results indicate that eggshell powder is a feasible alternative to limestone at 15% replacement level. At higher proportions, the disruption incurred by eggshell membrane becomes significant, delaying hydration and increasing shrinkage. Meanwhile, SCBA has the potential to serve as SCM, with a 5% replacement of sieved SCBA achieving compressive strength comparable to control specimens. Furthermore, comparisons of different processing techniques, including recalcination and sieving, indicate that while recalcination does not significantly enhance pozzolanic properties, sieving improves strength characteristics compared to raw ash. The findings underscore the potential of integrating biowaste into concrete production to create sustainable solutions. This study contributes to the development of more environmentally friendly concrete products, with implications for reducing the environmental footprint and advancing towards a carbon-neutral society. Future efforts will focus on scaling up these innovations for broader application in the marketplace.