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RPPR Final Report
as of 28-May-2020

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Begin Performance Period: 01-Apr-2019 **End Performance Period:** 30-Sep-2019
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Major Goals: Clays are among the most abundant earth-forming minerals. They are formed as weathering products of parent rocks in the presence of water and comprise a family of hydrous, aluminum phyllosilicates. Clays are characterized by colloidal size [10?6-10?9 m], anisometric particles with extended specific surface area, and electrical charge imbalance (usually negative) due to isomorphous substitutions of cations in the basal layers. Clays have been used in pottery and brick manufacture for thousands of years. They are widely used in industrial products including ceramics, papermaking, paints, agricultural chemicals, pharmaceuticals and cosmetics [Murray 1991, Murray 1999]. The origin and formation of clays plays a key role in earth science, and is studied extensively in the context of global hydrological processes (earth-atmosphere interactions) and in the functioning of the rhizosphere (and soil microbiome). Engineering properties and rheological behavior of clays are of great importance in applications from the construction industry to waste containment facilities, geoenvironmental remediation, nuclear power and extractive industries (mining and hydrocarbons) [Grambow 2016, Ismadji et al. 2015, Bergaya and Lagaly 2006]. Recent advances in multi-scale modeling, nano-scale characterization of materials, and advanced particle-scale visualization and probing techniques offer new capabilities to understand the complex behavior of clays, and to conceive new applications and products. We identified four distinct communities involved in applied research on clays with surprisingly little interaction among them (based on a review of relevant workshops, conferences and symposiums held during last decade). Our proposal for a two day workshop on this topic was supported by the U.S. Army Research Office in (75034-EV-CF).The event was held on May 2-3, 2019 and brought together a group of renowned researchers from several different fields including the geotechnical engineering, material sciences/engineering, environmental science/engineering and geosciences aiming at:

1. Synthesizing the current state of research (perspectives, approaches, and techniques) for characterizing the mechanical, rheological, and geoenvironmental aspects of clays, including the bottom-up material (atomistic and molecular) modeling, multi-phase and multi-scale behavior, rheological and geomechanical behavior, biogeochemical characterization, colloidal and transport properties.
2. Providing an opportunity for bridging the existing gaps between the diverse research communities to achieve a consistent understanding of common or relevant challenges in scientific and engineering problems on clays and clay systems. This was followed by investigating new opportunities at the intersections between researchers in different fields of expertise.

RPPR Final Report
as of 28-May-2020

Accomplishments: Applications of clay materials depend on a range of specific features including the plasticity, swelling, permeability, aggregation, adsorption/absorption, abrasion, particle shape, and specific surface area. Most distinct properties of clays emerge during hydration of the particle surfaces and their interaction with the aqueous phase. Due to their polydisperse nature, clay soils are conducive to flocculation and aggregation under different environmental conditions. As a result, clays are found in various forms including the well-dispersed suspensions (e.g., as clay slurries), flocculated via favorable colloidal aggregation mechanisms (e.g., as muds), sedimented or consolidated due to gravity-driven mechanisms as well as the externally applied mechanical or chemical loads (e.g., clay deposits), or highly compacted due to complex burial diagenesis (e.g., in clay-shales). Accordingly, we identified and invited scientists from various research areas in the following categories:

• Geotechnical Engineering/Geomechanics this area is concerned with engineering behavior of clay systems (as a geomaterial) for the evaluation of the stability of earth structures (generally based on continuum mechanics approaches). In modern geotechnical engineering applications, drastic thermal, mechanical, hydraulic, and chemical gradients are involved (multi-physical coupled processes). The multi-scale nature of clays and the strong coupling between the microstructure and macroscopic behavior demand an improved understanding of the microscopic material properties.

Our speakers for this area included Dr. Tomasz Hueckel from Duke University, Dr. Kenichi Soga from University of California at Berkeley, Dr. Marcelo Sanchez from Texas A&M, Dr. Ning Lu from Colorado School of Mines, Dr. Gouping Zhang from University of Massachusetts at Amherst, Dr. Tong Qiu from Pennsylvannia State University, Dr. Carlos Santamarina from KAUST, and Dr. Andrew Whittle from MIT.

• Materials Science and Engineering can provide deep understanding of clay properties by incorporating the knowledge of mineralogy, and multiscale characterization and modeling. The insights delivered by recent advances in characterization of the clay systems such as shale formations applied in carbon sequestration and hydraulic fracturing or bentonite barriers in high-level radioactive waste repositories, has highlighted the need for strong interactions between the geotechnical engineering and material science communities.

Our speakers from this area included Dr. Franz Ulm from MIT, Dr. Sujit Datta from Princeton, Dr. Laurent Brochard from ENPC, Dr. Tiziana Vanorio from Stanford, Dr. Leslie Baker from University of Idaho, and Dr. Gaurav Sant from the University of California at Los Angeles.

• Geoenvironmental and Transport aspects of clay particles (or the non-clay particulate systems such as contaminants) with a focus on the influence of geochemistry and mass fluxes in clay systems with environmental implications and health sciences. The strong coupling in terms of physicochemical and adsorption properties makes clays important elements in terrestrial and aquatic environments in various earth surface processes.

Our speakers from this area included Dr. Youjun Deng from Texas A&M, Dr. Satish Mineni from Princeton, and Dr. Michael Holmboe from Umea University.

• Geomorphology and Sediment Transport with disciplines focusing on spatial and temporal evolution of earth surface patterns, including many important natural processes that emerge at the interface of fluid and clay systems. Dealing with natural system, geomorphologists can integrate relevant expertise from the areas of material and environmental sciences as well as geotechnical engineering. Furthermore, the incorporation of expertise from the soft matter physics and colloidal sciences can help for better understanding the natural clay-water systems.

Our speakers from this area included Dr. Paulo Arratia from University of Pennsylvania, Dr. Douglas Jerolmack from University of Pennsylvania, Dr. Ali Seiphoori from MIT, and Dr. Kyle Strom from Virginia Tech.

Each speaker presented their for 20mins (15 min talk + 5 min questions) and included their perspectives on future research challenges and opportunities in clays research. A total of six thematic sessions were designed to accommodate 3-4 talks and each session was followed by a discussion session. Dr. Julia Barzyk, Dr. Michael Bakas, and Dr. Oliver-Denzil Taylor from the U.S. Army Research Office and the USACE Engineer Research and Development Center attended the workshop and briefly provided a general description of related activities at U.S. Army Research Office. Dr. Paramsothy Jayakumar from the U.S. Army RDECOM TARDEC presented his work (via video link) by emphasizing the current challenges and needs related to the geomaterials behavior in the U.S. Army particularly related to interaction of vehicle systems with geomaterials under extreme environmental conditions.

Training Opportunities: Nothing to Report

Results Dissemination: The workshop included 23 invited presentations. Students and researchers were invited to attend the workshop (the audience included 25-30 particpants in this category).
We created a web site for the workshop - which includes presentations from 17 of the lectures:
http://clays.mit.edu

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Other Professional
Participant: Ali Seiphoori
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Summary of the Workshop "Clays: New Perspectives, Challenges & Opportunities"

Ali Seiphoori[1], Andrew J. Whittle[2]

[1]aliseiph@mit.edu [2]ajwhittl@mit.edu

What: A workshop attended by 25 scientists from universities, research laboratories, and federal agencies was held to discuss scientific challenges and opportunities in clays research
When: 2-3 May, 2019
Where: Bush Room (10-105), Cambridge, Massachusetts

Grant source: US Army Research Office, Earth Science Division, Grant No. 75034-EV-CF

1. Motivations

Clays are among the most abundant earth-forming minerals. They are formed as weathering products of parent rocks in the presence of water and comprise a family of hydrous, aluminum phyllosilicates. Clays are characterized by colloidal size [$10^{-6} - 10^{-9}$ m], anisometric particles with extended specific surface area, and electrical charge imbalance (usually negative) due to isomorphous substitutions of cations in the basal layers. Clays have been used in pottery and brick manufacture for thousands of years. They are widely used in industrial products including ceramics, papermaking, paints, agricultural chemicals, pharmaceuticals and cosmetics [Murray 1991, Murray 1999]. The origin and formation of clays plays a key role in earth science, and is studied extensively in the context of global hydrological processes (earth-atmosphere interactions) and in the functioning of the rhizosphere (and soil microbiome). Engineering properties and rheological behavior of clays are of great importance in applications from the construction industry to waste containment facilities, geoenvironmental remediation, nuclear power and extractive industries (mining and hydrocarbons) [Grambow 2016, Ismadji et al. 2015, Bergaya and Lagaly 2006]. Recent advances in multi-scale modeling, nano-scale characterization of materials, and advanced particle-scale visualization and probing techniques offer new capabilities to understand the complex behavior of clays, and to conceive new applications and products. We identified four distinct communities involved in applied research on clays with surprisingly little interaction among them (based on a review of relevant workshops, conferences and symposiums held during last decade). Our proposal for a two-day workshop on this topic was supported by the U.S. Army Research Office (75034-EV-CF). The event was held on May 2-3, 2019 and brought together a group of renowned researchers from several different fields including the geotechnical engineering, material sciences/engineering, environmental science/engineering and geosciences aiming at:

1. Synthesizing the current state of research (perspectives, approaches, and techniques) for characterizing the mechanical, rheological, and geoenvironemntal aspects of clays, including the bottom-up material (atomistic and molecular) modeling, multi-phase and multi-scale behavior, rheological and geomechanical behavior, biogeochemical characterization, colloidal and transport properties.

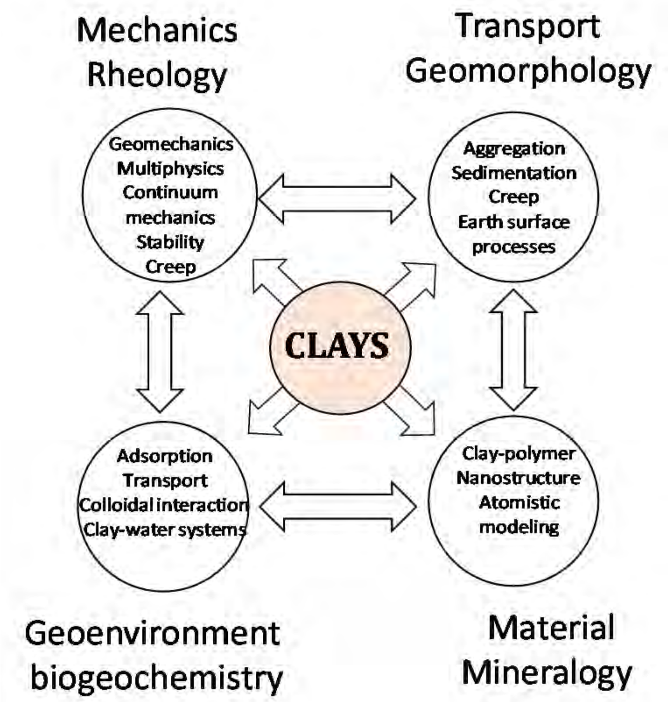

Figure 1. Interconnection between various disciplines involved in applied research on clays, clay minerals and clayey systems.

2. Providing an opportunity for bridging the existing gaps between the diverse research communities to achieve a consistent understanding of common or relevant challenges in scientific and engineering problems on clays and clay systems. This was followed by investigating new opportunities at the intersections between researchers in different fields of expertise (see Figure 1).

2. Identifying the scientific communities

Applications of clay materials depend on a range of specific features including the plasticity, swelling, permeability, aggregation, adsorption/absorption, abrasion, particle shape, and specific surface area. Most distinct properties of clays emerge during hydration of the particle surfaces and their interaction with the aqueous phase. Due to their polydisperse nature, clay soils are conducive to flocculation and aggregation under different environmental conditions. As a result, clays are found in various forms including the well-dispersed suspensions (e.g., as clay slurries), flocculated via favorable colloidal aggregation mechanisms (e.g., as muds), sedimented or consolidated due to gravity driven mechanisms as well as the externally applied mechanical or chemical loads (e.g., clay deposits), or highly compacted due to complex burial diagenesis (e.g., in clay-shales). Accordingly, we identified and invited scientists from various research areas in the following categories:

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DETAILED PROGRAMME | Thursday, May 2, 2019

BUSH ROOM, 10-105	
Session 1: Chair: Ali Seiphoori	
08:30	**Welcome Speech** – Andrew Whittle, Ali Seiphoori
09:00	**Ground Vehicle Mobility: US Army Challenges & Progress** - Paramsothy Jayakumar, U.S. Army CCDC Ground Vehicle Systems Center
09:20	**Charged Particles: Challenges in Transforming Particles to Clay Specimens** - Oliver-Denzil S. Taylor, U.S. Army Corps of Engineers
09:40	**Engineering Mechanics of Clay Properties - What You May Feel (and Worry About) and What Not? From Molecules to Fracking** - Franz J. Ulm, Massachusetts Institute of Technology
10:00	**Ferric Clays and Nanoclays: from Mars to the Synthetic Chemistry Laboratory** – Leslie Baker, University of Idaho
10:20	Discussion Session / Coffee Break
Session 2: Chair: Andrew J. Whittle	
10:50	**Desiccation and Drying-Cracking of Clays** – Tomasz Hueckel, Duke University
11:10	**Desiccation Cracking of Shrinkable Granular Media** – Sujit Datta, Princeton University
11:30	**Critical State Soil Mechanics for Clays and Beyond** – Kenichi Soga, University of California at Berkeley
11:50	**Understanding and Modeling Engineering Properties of Clays: New Data at the Macro- and Micro-Scale** – Andrew J. Whittle, Massachusetts Institute of Technology
12:10	Discussion Session / Lunch Break
Session 3: Chair: Paulo Arratia	
13:30	**Soil Sorptive Potential: Unitary Definition of Matric Potential** - Ning Lu, Colorado School of Mines
13:50	**Clays as Barrier Materials** - Marcelo Sanchez, University of Texas A&M
14:10	**A Superhydrophobic Soil as Clay Liners: Preliminary Results and Perspectives** - Guoping Zhang, University of Massachusetts at Amherst
14:30	**Role of Water Adsorption in the Thermo-mechanical Behavior of Clays** - Laurent Brochard, Laboratoire NAVIER, ENPC
14:50	Discussion Session / Coffee Break
Session 4: Chair: Sujit Datta	
15:20	**A Unified Approach for Modeling the Settling of Clay-Sized Particles: from Sedimentation to Consolidation** – Tong Qiu, Pennsylvania State University
15:40	**Sedimentation & Rheology of Clay Suspensions: Sticky & Repulsive** – Paulo E. Arratia, University of Pennsylvania
16:00	**Investigations of the Microstructure of Swelling Clays: Synergy between Experiments and Molecular Modelling** – Michael Holmboe, Umeå University
16:20	**Fine-Grained Sediments - Engineering Implications** – J. Carlos Santamarina, King Abdullah University of Science & Technology
16:40	Discussion Session
17:30	Reception and Dinner at Emma Rogers Room 10-340

DETAILED PROGRAMME | Friday, May 3, 2019

BUSH ROOM, 10-105	
Session 5: Chair: Guoping Zhang	
09:00	**Where Does the Mud Go? Insights into Processes that Impact the Transport and Deposition of Fine Sediment Through the Fluvial to Marine Transition** - Kyle Strom, Virginia Tech
09:20	**Glassy Dynamics of Landscape Evolution** – Douglas J. Jerolmack, University of Pennsylvania
09:40	**Stability of Fluid-Assembled Clay Aggregates: Role of Size Polydispersity** – Ali Seiphoori, Massachusetts Institute of Technology
10:00	**From Ancient Rome to Harsh Environments: The Mechanical Resilience of Cemented Volcanic Ash** - Tiziana Vanorio, Stanford University
10:20	Discussion Session / Coffee Break
Session 6: Chair: Douglas Jerolmack	
10:50	**Understanding the Clay Mineral Formation from Aqueous Solutions** – Satish Myneni, Princeton University
11:10	**Determinative Roles of Mineralogical and Surface Properties of Clay Minerals on its Applications: Examples in Mycotoxin Detoxification** – Youjun Deng, Texas A&M University
11:30	**Isothermal Stimulation of Mineral Dissolution Processes by Acoustic Perturbation** – Gaurav Sant, UCLA
11:50	Workshop Closure

List of invited speakers

Figure 2. Speakers and the thematic sessions in a glance. Detailed information can be found at the event web-page: clays.mit.edu

The multiscale nature of clays and the strong coupling between the microstructure and macroscopic behavior demand an improved understanding of the microscopic material properties.
Our speakers for this area included *Dr. Tomasz Hueckel* from Duke University, *Dr. Kenichi Soga* from University of California at Berkeley, *Dr. Marcelo Sanchez* from Texas A&M, *Dr. Ning Lu* from Colorado School of Mines, Dr. Gouping Zhang from University of Massachusetts at Amherst, *Dr. Tong Qiu* from Pennsylvania State University, *Dr. Carlos Santamarina* from KAUST, and *Dr. Andrew Whittle* from MIT.

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Figure 2 shows the final workshop program. Each speaker presented their work for 20 min (15 min talk + 5 min questions) and included their perspectives on future research challenges and opportunities in clays research. A total of six thematic sessions were designed to accommodate 3-4 talks and each session was followed by a discussion session. *Dr. Julia Barzyk*, *Dr. Michael Bakas*, and *Dr. Oliver-Denzil Taylor* from the U.S. Army

Research Office and the USACE Engineer Research and Development Center attended the workshop and briefly provided a general description of related activities at U.S. Army Research Office. *Dr. Paramsothy Jayakumar* from the U.S. Army RDECOM TARDEC presented his work (via video link) by emphasizing the current challenges and needs related to the geomaterials behavior in the U.S. Army particularly related to interaction of vehicle systems with geomaterials under extreme environmental conditions.

3. Topics Covered

3.1. Multiphysics of Clays

3.1.1. Coupled Thermo-Hydro-(Chemo)-Mechanical Behavior

Clay formations involved in various applications including the radioactive waste storage and shale oil/gas extraction would undergo complex environmental conditions including drastic changes of mechanical, thermal and hydraulic loading. Deep geological disposal is one of the most favorable options for the safe isolation of highly contaminant materials, including the radioactive waste. The multiphysical behavior of clay materials is of central to the performance of such repository systems. Complex Thermo-Hydro-Mechanical and Chemical (THMC) phenomena will take place in the repository near field because of the heating (generated by the radioactive decay of the nuclear waste) and hydration of compacted clay barriers (due to fluid seepage from the surrounding rock) under highly confined conditions. National and international efforts in this area have contributed to improve the understanding of the main THMC phenomena that control the behavior of engineered and natural barriers. However, it is still unclear how some emerging phenomena could affect the final performance of this type of system. *Dr. Sanchez* discussed Some of the relevant challenges to consider including the gas migration and other coupled transport processes through barriers material and discontinuities (such as evolving cracks and contact surfaces between distinct materials); thermo-mechanical considerations in saturated clays, long-term clay-fabric changes; precipitation and formation of minerals in engineered and natural clay barriers; and rheological processes. *Dr. Brochard* highlighted the importance of understanding the relationship between adsorbed and free water in understanding the thermo-mechanical properties observed in clays at the macroscopic scale.

Clay liners with extremely low hydraulic conductivity are widely used as barrier systems in environmental protection and seepage control. However, the major constituents of clay liners are Na-smectites that are prone to rapid degradation in chemically harsh (e.g., highly saline, acidic, or alkaline) environments due to the smectite-chemical interactions or reactions, causing it to be less effective or even lose the desired functionalities. *Dr Zhang* introduced a superhydrophobic hybrid organic-inorganic polymeric (SHOIP) material that can be easily pulverized into an artificial soil with particle sizes of less than 2-20 mm. This superhydrophobic powder is virtually impermeable under low hydraulic head, and it can be a viable alternative to smectite used as impermeable barriers. Moreover, the mixture of smectite clay and SHOIP may possess the advantageous characteristics of both materials. This research highlighted the engineered treatment of the clays surfaces for an improved hydro-chemo-mechanical performance.

3.1.2. Desiccation and Drying

Desiccation cracking is one of the modes of failure of clayey geostructures that has been rarely addressed from the point of view of its multiphase, multiphysics and multiscale complexity. In fact, several elements of drying-cracking process and their coupling are still quite poorly understood. The list of phenomena contributing to drying cracking include: evaporation of surficial pore water, evaporation of capillary and adsorbed clay water, transport of water and vapor through clay pore space, air entry, displacement of water/air interface and its dynamics, evolution of suction, suction resultant force and surface tension force, deformation of the pore space/solid skeleton due to suction/pressure evolution, intergranular force evolution during drying, drying shrinkage, constrained drying shrinkage, effective stress evolution due to constrained shrinkage, effect of air entry on stress distribution and stress concentration due to air entry, onset and development of drying cracking, 1D, 2D and 3D- evolution of drying crack systems, evolution of permeability of drying crack systems. *Dr. Hueckel* described some recent experimental results concerning the aforementioned mechanisms. For small granular assemblies, the main findings include intermittent slow, evaporation rate driven fluid motion, associated with modest pressure gradients, and fast, non-equilibrium driven re-configurations of liquid/-gas interfaces at pore-scale (Haines jumps).

Shrinkable, granular materials (i.e., materials composed of hydrated grains that individually shrink when dried) arise in many diverse settings from clays to biological tissues, foods, and coatings. In many cases, these materials crack during drying, critically hindering applications and geoenvironmental conditions. *Dr. Datta* compared results from experiments (with model shrinkable grains), discrete-element simulations, and poroelasticity theory, to show how grain shrinkability dramatically alters crack evolution during drying—in some cases, even causing cracks to spontaneously self-heal. Moreover, he elucidated the physical principles underlying crack formation and evolution, and develop new strategies to control crack evolution and patterning.

3.2. Transport Behavior of Clays

Fine particles constitute 70-90% of the sediment mass transported by rivers to coastal areas where it is deposited as muds in bays, estuaries, marshes, and deltas. Being able to forecast the movement and deposition of this sediment has important implications for society. Part of the complexity in modeling the dynamics of the mud is due to the flocculation whereby mud particles form aggregates, or flocs, which grow or shrink in size and density depending on turbulence levels and other water column properties including the water chemical composition. Clays are plate-shaped charged colloids and exhibit different rheological properties than suspended hard-particles, e.g. thixotropy and shear-banding. Knowing that solutes are common in nature, these observations provide insights for geophysical flows, like particulate gravity currents or the erosion threshold for cohesive river banks. When flocs grow or shrink in size, the rate at which they settle out of the water changes, creating dynamic settling speeds that are difficult to model. Furthermore, estuarine zones and river mouth plumes can be stratified, with positively buoyant freshwater suspensions of mud flowing over clearer saltwater. A presentation in this area by *Dr. Strom* highlighted recent work designed to better understand the vertical flux of muddy cohesive sediment in the fluvial to marine transition, specifically focusing on the response of floc sizes to changing shear and concentration conditions and improvements to simple models of floc size in turbulent flows. *Dr. Aratia's* presentation focused on the colloidal properties of kaolinite clay particles as a model system for a model system for geophysical flows. Sedimentation of kaolinite suspensions in water are performed using various salts to manipulate particle interactions from attractive to repulsive, and sedimentation behavior from hard-sphere to gel-like behavior. Rheological experiments show that the repulsive kaolinite suspensions are Newtonian, while introduction of attractive inter-particle forces leads to non-Newtonian behavior and flow hysteresis. Knowing that phosphate and chloride salts are common in nature, these observations provide insights for geophysical flows, such as particulate gravity currents or the erosion threshold for cohesive river banks. Erodability of clays, like other soils, depends on the ability of aggregates to resist disruptive forces during fluvial or aeolian processes.

The process of drying colloidal suspensions forms aggregates by driving suspended particles together via transient hydrodynamic forces. In the absence of attractive inter-particle forces, however, aggregates are unstable when subject to wetting or fluid shear. *Dr. Seiphoori* and *Dr. Jerolmack* showed that the stability of aggregates formed by evaporation depends on the particle size of their forming aggregates and is independent of the material properties.During evaporation from a polydisperse colloidal suspension, the transient capillary forces condense small particles into capillary bridges which eventually turn into solid structures referred here to as "solid bridges". The submicron/nanoscale particles contribute to stabilizing the entire aggregate by forming solid bridges that bind larger neighboring particles. In the absence of the small particles and their associated solid bridges, the disruptive hydrodynamic forces disintegrate aggregates and easily transport them. We demonstrate that the solid bridges formed after evaporation from polydisperse colloidal systems exhibit a scale invariant (fractal) feature. A consequence of the solid bridging in polydisperse geomaterial systems is the emergence of an effective cohesion which is a key element to predict the onset of sediment transport, the mobility of contaminants, the frictional behavior of hillslope creep, and the collapse of natural deposits upon re-wetting.

Dr. Tong presented a unified approach to model three sequential processes during settling of the clay particles: the initial sedimentation where there is no skeleton (no effective stress), the subsequent self-weight induced consolidation where there is partial development of skeleton (partial effective stress), and the eventual finite-strain consolidation of the skeleton. This unified approach was used to model the settling of an initially uniform suspension of kaolin/bentonite slurries in a column. Significant opportunities and challenges exist in the study of the settling behavior of clay-sized particles in the transition zone between sedimentation and consolidation, where there is only partial development of skeleton.

3.3. Sorbtion Potential of Clays

Soil-water interaction in general involves two physical mechanisms: capillarity and adsorption. As such, matric potential or the negative of matric suction should reflect both mechanisms. Adsorption potential of clay minerals is an important feature determine their interaction with organic and inorganic particles in the environment. Modeling the sorption behavior of clay particles is central to various biogeochemical functions of the clay systems. *Dr. Lu* showed that the adsorption can be fully captured in a new concept called soil sorptive potential, leading to a general definition of matric potential. This new definition of matric potential provides thermodynamic ways to bridge the long-standing gap between pore water pressure and soil sorptive potential, and to accurately quantify soil freezing curve (constitutive relationship between soil water content and temperature below 0 ^oC), soil water density (soil water density as a constitutive function of soil water content), and soil water cavitation (soil water phase transition between liquid and vapor).

In terms of geoenvironmental application of clay minerals, *Dr. Deng* shared the findings on the determinative mineralogical and surface properties of smectites, a group of common 2:1 layer silicate minerals, in the detoxification of mycotoxins, the toxic metabolite produced by fungi. He showed that the binding capacity, affinity, selectivity of the smectites before and after modifications for mycotoxins, and the degradation that occurred on smectite surfaces. It was demonstrated that it is possible to achieve the required optimal size and polarity matching between the mycotoxins with the adsorbing surface sites on the smectite at the molecular level and at the nanometer scale. A Smectite exhibits nearly 20% (mass) adsorption capacity for aflatoxin, the most toxic and carcinogenic mycotoxin produced by fungi. It is possible to manipulate the interlayer environment so that the smectite has high selectivity for aflatoxin in a complex biological system. This was achieved by replacing the interlayer cations with different valence and size, reducing the layer charging density by introducing ions into the octahedral structure of smectite, changing the interlayer polarity by including organic nutrients. His studies also suggest the importance of the clay mineral structure-reactivity relationships in its applications. Clay mineral formation in soils and sediments in low temperature environments is highly complex and poorly understood because of the structural intricacies and contrasting Al and Si chemistry in most natural pH conditions. The speciation of Al and Si in aqueous solutions varies significantly: with Al exhibiting octahedral coordination at low pH and tetrahedral coordination at high pH, whereas dissolved Si exhibits tetrahedral coordination (can be different in highly alkaline solutions). However, their interactions on particle surfaces (e.g. Al^{3+} on silica surfaces) can be different from those found in aqueous solution, and these interactions vary with the ion concentration and pH. Adsorption and precipitation of Al-silicate gels is the first step in the formation of clay minerals. These gels are disordered or amorphous, and with time, these phases progressively evolve to the nano-crystalline and crystalline layered silicates. The presence of impurities can interfere with or promote the formation of these phases. *Dr Mineni's* research group has been studying the nature of Al and Si speciation in aqueous solutions, their interactions on particle surfaces, and formation of disordered phases both in the laboratory and in terrestrial and marine environments using X-ray spectroscopy and spectromicroscopy. His lecture included a detailed discussion on the behavior of these systems, and a review of clay precipitation from molecular chemistry perspective in natural and engineered systems.

3.4. Multiscale Testing and Modeling

Advances in multiscale observations of geomaterials including clays microscale particle structures and evaluation of their nanoscale engineering properties have encouraged numerical simulations of the behavior of clays using tools from molecular dynamics. Molecular modelling techniques (electronic or classical DFT, ab initio and classical molecular dynamics and Monte Carlo simulations) have emerged as useful tools to obtain detailed insights into the structure, thermodynamics and dynamics of hydrated clay minerals and other geochemical systems. Recent developments in this area has expanded the types of properties as well as range of both time and spatial scales that can be examined. These computational techniques are particularly powerful when they complement experimental techniques (spectroscopic, wet-chemical, calorimetric, scattering or diffraction techniques). Hence combined experimental and in silico (i.e. computer simulations) investigations are steadily becoming more and more popular. While most prior studies have focused on specific engineering properties such as swelling, *Dr. Whittle* presented a new coarse-graining approach to investigate the formation and properties of mesoscale clay aggregates ($1\mu m$) based on nanoscale interactions between two particles (NaMMT solvated in water). This research highlights the potential of multi-scale modeling to link macroscale engineering properties to the complex micro-structures of clay sediments, residual soils and compacted fills. *Dr. Holmboe* also presented results from molecular dynamics (MD) simulations (using the Gromacs suite of programs) . His work aims to complement experimental data on microstructure and hydration thermodynamics of smectite clay hydration, by predicting the hydration energetics of the Wyoming type (USA) Montmorillonite for a wide range of water contents (up to 60 w% H_2O) and interlayer solutes. Several recent studies have also shown that atomistic simulations in combination with mixed layer modeling of powder XRD reflections, can aid in the interpretation of experimental diffraction data, significantly improving the atomistic understanding of the interlayer solute and water structure. *Dr. Franz Ulm* presented recent advances in characterization of the nanogranular structure of geomaterials including the nanoindentation and advanced nanomechanics experiments combined with molecular simulation results.

Dr. Sant presented an unprecedented aqueous dissolution enhancement produced under acoustic perturbation – across a wide range of minerals (i.e., halite, gypsum, calcite, serpentine, fluorite, dolomite, orthoclase, borosilicate, obsidian, and quartz), whose dissolution rates vary by several orders of magnitude – scales with the solute's hardness, and averaged bond energy. This understanding creates new opportunities to exploit and apply acoustic perturbation as a processing pathway of relevance to geological, biological, and engineered material systems.

3.5. Engineering Properties of Clays

Fine-grained sediments form through chemo- and bio-genesis. Clay minerals are a subset of fine-grained sediments. While saturated clays respond to mechanical actions in agreement with principles of effective stress (after Terzaghi), fine-grained sediments also react to chemical and thermal-changes. Concentration-dependent DLVO interactions and pH-dependent surface charges combine to determine fabric formation. Valuable characterization protocols for engineering purposes include measurements of specific surface, plasticity (with different fluids), sedimentation and viscosity. Physical insight gained from index tests and 100 years of field data support the development of the revised soil classification system RSCS proposed by *Dr Santamarina*. High compressibility is a salient characteristic of fine-grained sediments. Asymptotically-correct compaction models are required to address engineering problems that range from enhanced bathymetric interpretation to mud-cake formation and fracking in shales. Due to their compressibility, repetitive loads of all kinds (mechanical, freeze-thaw, and suction) can cause extensive volumetric and shear deformations. Fine-grained sediments can generate high suction under mixed fluid conditions, and trigger a wide range of physical phenomena from altered interfacial phenomena in the presence of nano-particles to Pickering emulsions. High suction favors various forms of localizations, from desiccation fractures (at boundaries and internal) to grain-displacive ice and hydrate formation. Geophysical techniques such as complex permittivity, NMR, X-ray micro-CT, thermal, and shear waves- provide unprecedented information about the evolution of these processes. While bio-activity is limited in small pores, there are multiple examples of bio-inspired processes in fine-grained sediments that can inform new engineering designs. In geotechnical engineering and geomechanics, the central mathematical concepts to explain the mechanical behavior of clays when the water content is within a certain range (i.e. between Liquid Limit and Plastic limit) is established based on the critical state soil mechanics theory and Terzaghi's effective stress theory. *Dr. Santamarina*, *Dr. Whittle*, and *Dr. Soga* presented some of the recent advances in engineering analysis and modeling the clay geomaterials beyond classical soil mechanics by integrating microstructural data, physical modeling and numerical simulations.

4. Final Summary

There are many challenges and opportunities in clay-related applications from nanotechnologies and biotechnologies to geoengineering and geosciences which demand collaborative efforts of engineers and scientists cross various disciplines. Although the above-mentioned scientists addressed various challenges linked to clay systems from their unique perspectives, there were terminologies, perspectives and conceptions developed in isolation with other disciplines. This workshop proved to be an excellent venue for sharing relevant expertise between the involved communities.

The main theme of the workshop was the complexities associated with the prediction of the clays (and geomaterials in general) behavior across the scale as well as scaling up the microscopic models to larger scale problems. In nearly all areas, the need for multiscale testing/modeling and employing high-quality observational data is paramount. Highly controlled and representative experiments, either in the field or in the laboratory, will serve as an effective way to bridge the scale gaps and isolate physical and chemical processes involved in clays systems. Finally, these advances must be matched by improvements in representing the involved processes in clay systems in multiscale numerical models that are able to reproduce and predict the material behavior.

An ambitious prospect from this workshop would be establishing an online platform for sharing news and updates on recent advances, technologies, and perspectives on clay research and providing a multi-disciplinary domain where different communities can interact with each other. To step forward in such direction, we have established a website (clays.mit.edu) to share the outcome of this event and to ideally serve as a channel for future communications. Organizing summer schools to bring together people from all these communities including the soft matter physics, sediment transport, material sciences and geotechnical engineering. Large collaborative projects are excellent venues to involve PIs from various fields to incorporate all disciplines and expertise to approach a problem.

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