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Research paper

Particle arrangements in clay slurries: The case against the honeycomb structure

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ABSTRACT

The properties of clay slurries (porosity ~0.75) impact a wide range of materials such as commercial clay dispersions and sedimentary deposits. Their material behavior, and in particular the gelation of clay slurries, is thought to be governed by clay particle interactions. In the literature, such interactions are rarely directly probed, but rather inferred from structures observed by cryo-electron microscopy. For example, the honeycomb structure is a widely accepted textbook model that is used to rationalize the observed behavior of clay slurries. Using high-pressure freezing, cryo-electron microscopy, and cryo-synchrotron wide-angle X-ray scattering, this study shows that the honeycomb-structure is an artifact of sample preparation. When samples are high-pressure frozen, individual clay particles and aggregates of particles arrange in a random orientation rather than the closed-cell structure dominated by face-face and face-edge contacts observed in plunge frozen samples. These results substantially contribute to the understanding of the gelation mechanism and particle interactions in colloidal clay slurries, and provide valuable input parameters for meso-scale modeling efforts of clay dispersions and sedimentary deposits to upscale their mechanical properties to the macroscale.

1. Introduction

Several million tons of clay colloidal slurries are used every year in a wide range of industrial applications such as drilling muds, paint fillers, ceramics, and adhesives (Murray, 2000; Harvey and Lagaly, 2006). The rheological properties of these slurries are governed by particle-particle interactions and their resulting gel structure (Luckham and Rossi, 1999). In addition to commercial clay slurries, particle interaction during early stages of deposition, at conditions similar to clay slurries, plays a vital role in the microfabric development of sedimentary deposits, which subsequently affects its physical properties (Bennett et al., 1991). Thus, understanding particle interactions in clay slurries is of great importance to many researchers in different disciplines.

The mechanisms responsible for particle interactions and the development of gel structure in clay slurries have been the topic of much debate with three main competing ideas: a cardhouse structure that favors the formation of edge-edge and face-edge contacts (Goldschmidt, 1926; Lambe, 1953; Van Olphen, 1964; Khandal and Tadros, 1988), a honeycomb structure that postulates the formation of face-face contacts between clay particles (Terzaghi, 1925; Casagrande, 1932; Weiss and Frank, 1961), and the stabilization of the gel structure due to electrostatic repulsion between clay particles (Norrish, 1954; Callaghan and Ottewill, 1974). In an attempt to reveal these mechanisms, researchers utilized plunge freezing to preserve the microstructure of clay slurries, which otherwise collapses upon the removal of water, and reported the presence of a closed-cell honeycomb dominated by face-edge and face-face contacts between clay particles (O'Brien, 1971; Osipov and Sokolov, 1978; Stawinsk et al., 1990; Zbik et al., 2008, 2010; Du et al., 2009, 2010; Morris and Żbik, 2009). This model has gained popularity among several researchers and became a “textbook” model in several fields such as geology (O'Brien and Slatt, 1990, p. 24), geotechnical engineering (Mitchell and Soga, 2005, p. 131), and clay colloid science (Lagaly, 2006, p. 216). However, for optimal structural preservation, biological tissues with thickness > 10 μm (and smaller than 200 μm) are usually prepared by high pressure freezing (HPF) rather than plunge freezing (Moor, 1987; Studer et al., 1989). High-pressure freezing can effectively suppress ice crystallization in hydrated materials up to a thickness of about 200 μm (Studer et al., 1995, 2001, 2008). In contrast,

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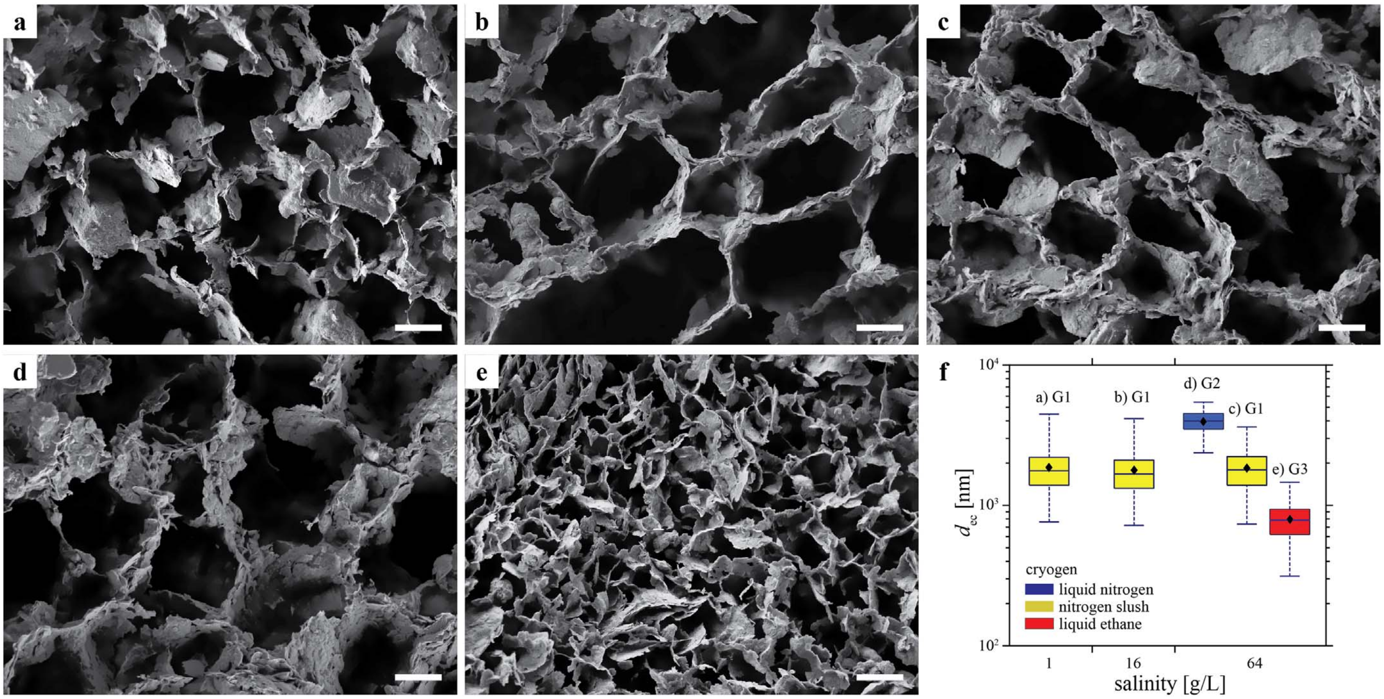

Fig. 1. Cryo-SEM images of plunge-frozen, freeze-fractured GOM-EI clay slurries reveal cellular (honeycomb) micro-fabric. a-c) Slurries prepared at a pore salinity of 1 g/L (a), 16 g/L (b), and 64 g/L (c) were plunge-frozen in nitrogen slush. d, e) Slurries prepared at a salinity of 64 g/L were plunge-frozen in liquid nitrogen (d), and liquid ethane (e). Vitrified pore fluid was removed by freeze-etching (sublimation); pore space therefore appears black. Walls (shades of grey) between the pores are comprised of aggregated clay particles. Scalebars represent 2 μm. f) Boxplot of the equivalent circular cell diameter (d_{ec}) observed in the slurry samples in a-e. The central line in each box represents the median, the black diamond the mean of the data set. Statistical significance was established using a Tukey-Kramer multiple comparison test. The means of groups indicated by different numbers (G1-G3) are significantly different ($p < 10^{-7}$), while groups with the same number are not ($p > 0.05$). See Fig. 3a–e for size distribution histograms of circular cell diameters (d_{ec}).

the thickness of clay slurry samples in virtually all studies was on the order of several millimeters. Therefore, it is likely that water in these samples did not vitrify and that ice crystals formed, altering the clay particle arrangement in the process. We hypothesize that the honeycomb structure is a consequence of this crystallization process and does not represent the clay gel structure. To investigate this possibility, the microstructure of Gulf of Mexico-Eugene Island (GOM-EI) clay slurries prepared using plunge freezing is compared against that prepared by high-pressure freezing.

2. Materials and methods

Unless otherwise specified, all solutions were prepared with ultrapure water (ρ = 18.2 MΩ·cm) produced by a Barnstead Nanopure NanoDiamond UF + UV purification unit (Thermo Scientific, Hanover Park, IL).

2.1. GOM-EI clay slurries

Gulf of Mexico–Eugene Island (GOM-EI) soil has been extensively studied at Massachusetts Institute of Technology (e.g., Fahy, 2014; Casey et al., 2016). It is a high plasticity soil recovered from the Eugene Island block, located approximately 160 km off the coast of Louisiana at a water depth of ~ 77 m. Soil was extracted from drill cores, air dried, and ground to a fine powder with 100% passing the #100 sieve (< 0.15 mm), and homogenized by thoroughly blending the soil. The natural salt content of GOM-EI is 8 g per kg of soil. This is equivalent to a salinity of 80 g/L based on the in situ water content (Adams, 2014). X-ray diffraction (XRD) mineralogy analysis shows that the investigated GOM-EI samples are mainly composed of 46% silt particles (quartz and feldspar), and 54% interlayered illite-smectite particles with an expandability of 70–80% (percentage of smectite layers). Furthermore, hydrometer particle size analysis (ASTM D422) shows that the percentage of particles smaller than 2 μm in these samples is approximately 63%.

Homogenized powders (~300 g) were dispersed in ~350 mL of water, placed in dialysis tubing (Carolina Biology Supply, 1.3125 in, MWCO 12,000–14,000 Da), and dispersed in ~2.5 L water stirring at room temperature. The dialysate was exchanged every 6–12 h for approximately 30 days. De-salting was considered complete when the conductivity of the dialysate became constant at a value of 10–20 μS/cm.

Slurry samples were then prepared by dispersing homogenized, desalted, and air-dried powders (5 g) with artificial sea salt solutions at different salinities (1 g/L, 16 g/L, 64 g/L) and at a water content of 105 wt% (mass of water/mass of solids). Given that the specific gravity of GOM-EI soil is 2.775, as determined in accordance with ASTM D854, the porosity is approximately 0.75. Slurries were then shaken for 10 min using mechanical agitator, and left overnight to fully hydrate at room temperature. The pH of the final clay slurry samples ranged from 7.10 to 7.50.

2.2. Plunge freezing

For plunge freezing, a droplet of clay dispersion was pipetted onto a 3 mm copper planchet (Leica Microsystems, Vienna, thickness = 2–3 mm). The sample was then hand-plunged into a cryogen (ethane, nitrogen slush, or liquid nitrogen) using tweezers, transferred through liquid nitrogen if necessary, and attached to a sample holder under liquid nitrogen. The plunge-frozen sample was then retrieved with a pre-cooled vacuum-cryo-transfer shuttle (VCT, #EM VCT100, Leica Microsystems, Vienna) and transferred to a freeze-fracture system (Leica MED-020 Baltec sputter coater, Leica Microsystems, Vienna), where it was maintained at − 130 °C and a pressure of $\sim 1 \times 10^{-7}$ mbar. The sample was fractured using a cold knife. A layer of surface ice was removed (freeze-etched) by allowing the sample temperature to rise to − 90 °C and holding the temperature at − 90 °C for 5 min before returning the sample to − 130 °C. Finally, the sample