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Topical Report

**APPROACH TO FORMING HYDRATE BEARING SAMPLES IN FINE-GRAINED
MATERIAL**

**GEOMECHANICAL PERFORMANCE OF
HYDRATE-BEARING SEDIMENTS IN
OFFSHORE ENVIRONMENTS**

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Introduction

Understanding the strength of marine sediments containing gas hydrates is important for seafloor platform and well stability. These sediments contain sands, silts, and clays, and the sediment composition and texture may affect gas hydrate stability. Pore size, salinity, and mineral structure can inhibit or enhance hydrate stability. These effects have been quantified for a number of media, and the change in the equilibrium curve can be described by the temperature difference between the bulk hydrate stability curve and the affected hydrate stability curve. Smaller pores typically inhibit hydrate formation (enhance dissociation) more than large pores, however pore spaces in some minerals may enhance hydrate formation under certain conditions. Salinity is a known inhibitor of hydrate formation. Most minerals studied do not directly affect stability, with the exception of some swelling clays, which under some conditions may enhance stability.

In this report, the sample types to be used in geomechanical tests will be presented, followed by our approach to making hydrates in the porous media. We will present an evaluation of the potential for success of the approach, and a summary of pertinent literature. Based on this evaluation and our experience making hydrate-bearing samples, we believe that we will be able to form hydrate in our samples. In addition to the effects that the medium may have on the samples, heat and mass transfer strongly affect the distribution of hydrate in samples. We intend to pay close attention to these processes in our designs and tests.

Samples to be used in Phase 2 Geomechanical Measurements

The Phase I Topical Report entitled GEOMECHANICAL PERFORMANCE OF HYDRATE-BEARING SEDIMENTS IN OFFSHORE ENVIRONMENTS suggested usage of three sample types:

- a) 100% sand sized particles of average diameter 100 μm
- b) 50% silt-sized particles of average diameter 10 μm and 50% clay-sized of average diameter 1 μm
- c) 100% clay-sized particles of average diameter 1 μm

We intend to use (1) a silica sand that is often used in hydrate experiments (e.g. Kneafsey et al, 2006), (2) silt-size silica flour as silt (used by Santamarina et al. 2004 in studies with THF hydrate), and (3) kaolinite clay for clay (e.g. Uchida et al, 2004). We will attempt to use materials that have grain sizes as suggested in the Phase I Topical Report, however, experiments that have used silt and clay-size particles presented in the literature have typically exceeded the grain sizes suggested above. Silt typically ranges in size from about 4 to about 60 microns, and particles smaller than about 4 microns may be classified as clays. Kaolinite, a non-swelling clay, has been used in hydrate research (Uchida et al., 2004, Klapproth et al., 2006) and has been shown to not enhance hydrate formation. The particles in the kaolinite used by Uchida et al. (2004) averaged about 2.5 to 4 microns in size, and those used by Klapproth et al. (2006) averaged 20 microns in size.

Approach

Samples will be prepared as follows:

- a) The dry mineral components will be mixed until they are visually homogeneous
- b) Water will be added, either directly by pipetting (for sand) (Kneafsey, 2006), by equilibrating the sample in a humidified chamber (expected for samples containing silt or clay) (Uchida et al., 2004), or by stirring in flakes of frost ice (samples containing clay) (Uchida et al., 2004, Klapproth et al., 2006)
- c) The moistened material will be packed into the sleeve
- d) The air will be rapidly evacuated from the sample using a vacuum pump
- e) The sample will be chilled to the appropriate temperature
- f) The sample will be pressurized with methane gas, and the pressure will be monitored. A declining pressure indicates (and verifies) hydrate formation.

Evaluation of Potential for Success

The proposed approach combines techniques that have been deemed successful in the literature, and do not deviate greatly from the technique we have used to make hydrate in porous media in our laboratory. Based on our experience and the experiences of the authors of the supporting literature (below), we believe that we will be able to form hydrate in our samples. None of the cited authors have raised the subject of sample homogeneity, which will be controlled by the packing technique (in terms of porous medium properties), in addition to heat and mass transfer, which strongly affect hydrate distribution. In the current research, we intend to pay careful attention in our experimental setups and procedures to control and characterize the sample heterogeneity.

Supporting Literature

Klapproth et al. (2006) formed methane hydrate in quartz sand, quartz sand with kaolinite, and quartz sand containing montmorillonite clay particles. The water was added by making 10-micron frost particles in a chamber, and 10% to 17% of the frost (by mass) was added to each medium. Hydrate was made at 3°C from the melting ice, and SEM was used to examine the pore structure. Hydrate formed most readily in the samples containing the montmorillonite, which apparently sorbed to the air-water interface prior to hydrate formation. The presence of kaolinite caused more gas to be consumed on hydrate formation, however. Although water and hydrate saturations are not computable from the data shown by the authors, a water saturation of 45% may be deduced if it is assumed that the sand/frost had a porosity of 33% (clays are typically poorly packed without special treatment), and the 17% (by mass) of frost becomes water filling the pore space.

Uchida et al. (2004) investigated the differences in equilibrium between bulk methane hydrate and methane hydrate in silica sand, Berea sandstone, two sizes of glass beads, two kaolinites, and two bentonites. Hydrate formation was impeded where pore spaces

were narrow, yielding stability temperature differences between bulk hydrate and hydrate with bentonite of as much as 8°C. The effects for kaolinite were much smaller (~1.5°C) and were comparable to those for 20-micron glass beads. Bentonite, composed primarily of montmorillonite, swells when wetted by water, allowing hydrate formation between mineral layers. Bentonite was shown to have the ability to enhance hydrate formation under certain conditions.

Uchida et al. (2002) measured the change in dissociation temperature for media (porous glass and silica gel) having small pores (<6 to 100 nm). The largest shift for methane hydrate was -12.3°C for 4 nm pores to -0.5°C for 100 nm pores. Handa and Stupin (1992) measured equilibrium temperature and pressure of methane hydrate in 70A silica gel pores. With this size pore, the equilibrium methane pressure is about 1.72 MPa above that of bulk methane hydrate.

To help explain the difference between the observed and predicted BSR depths at locations on the Cascadia Margin, Lu and Matsumoto (2002) formed and dissociated methane hydrate in nanofossil-rich marine sediments having pore sizes ranging from 40 to 200 nm (average 170 nm) and particle sizes ranging from 1 to 30 (average 10) and 40 to 250 (average 70) microns. Forming hydrate in the porous medium investigated required a lower temperature of 0.4°C and 1.5°C for seawater and pure water respectively than for bulk hydrate.

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