IMPACT OF HYDRATE FORMATION AND DISSOCIATION ON THE STIFFNESS OF A SAND

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ABSTRACT
The exploitation of oil and gas reserves located in deeper waters off our continental margins can lead to the dissociation of gas hydrates commonly found at these locations. Our understanding of gas hydrate formation suggests that the stiffness and strength of the sediment can be significantly enhanced if the hydrate acts like cement, or may be more moderate if the hydrate acts like a mineral grain and supports the sediment frame. Hydrate dissociation, which can occur during the pumping of oil and gas from deeper (and hotter) strata below the hydrate bearing sediments, may therefore lead to a reduction in sediment stiffness, the magnitude of which will depend on the interaction between the hydrate and the sediment, leading to failure of the sediment. In addition, a rise in pore pressure may occur due to the release of gas from the dissociating hydrate, which may also lead to failure of the sediment. Thus hydrate dissociation poses a risk to oil and gas exploitation infrastructure through failure of the sediment, which at the extreme may lead to submarine landslides and tsunamis.

A better understanding of the influence that hydrate formation and dissociation has on sediment stiffness is required to fully assess the risk that drilling activities have in these soils. To that end a series of laboratory tests have been conducted on sand samples during the controlled formation and dissociation of gas hydrates. Measurements carried out during the formation and dissociation of hydrate allowed not only the eventual changes in sediment stiffness to be determined as a function of total hydrate saturation but also the changes in sediment stiffness as a function of the percentage of hydrate during the formation and dissociation process. The results show that sediment stiffness was sensitive to the volume of hydrate dissociated, compared to that which was measured during formation. In addition, factors such as effective stress were also assessed with regard to sediment stiffness.

Keywords: gas hydrates, dissociation, stiffness, resonant column

INTRODUCTION
Increasing global energy demands have led to significant research being conducted to develop alternative energy sources conventional fossil fuels such as oil, natural gas and coal. One area that has gained in interest is the recovery of methane gas from gas hydrates [1, 2]. The reason for such interest is that gas hydrates can store large volumes of methane gas within its structure [3] and are dispersed, on a worldwide scale, in sub-permafrost and deep-water marine sediments [4]. It has been estimated that carbon methane within gas hydrates may be double that of conventional fossil fuels [5]. Recent estimates suggest lower values for the global inventory of gas hydrate
bound methane [6]. However, even these values represent significantly large volume of gas.

Results from a number of drilling sites both in permafrost [7] and deep water marine sediments [8,9,10] have shown that the distribution and morphology of gas hydrates within the sediment is highly dependent on the geology of the soil [11] and is widely dispersed within the sediment column [12]. In a porous media the pore size influences the formation conditions for gas hydrate [13]. In coarse granular sediments where hydrate formation is unimpeded, the hydrate forms readily and can be characterized as pore filling with pore saturations >80% being observed [14, 15]. The small pore sizes inherent in fine grained sediments, which constitute a large proportion of marine sediments, inhibit hydrate formation. Thus methane saturated pore waters can migrate to locations where pore space is larger, such as interlaminar beds of coarser particles sizes or along fractures and faults. This leads to hydrates in fine grained sediments being more localized and heterogeneously distributed with hydrate saturations depending on the distribution of pore sizes, layering and fracture network. In these sediments, saturations values are typically <10% if disseminated in the pore space, but maybe 100% in discrete fractures or segregated layers [16]. Results from CT scans of recovered hydrate bearing cores from a fractured hydrate province, where 10mm thick sections of 200mm long core were analyzed gave pore saturations ranging from 8-60% [17].

The variability in hydrate saturation within fine grained sediments coupled with the technical challenges of extracting the gas from such low permeability sediments is likely to lead to only a small proportion of gas hydrate resource being economically exploitable [18]. This has led to gas hydrate-saturated sands being considered as an economically viable energy resource [19]. The recent Gulf of Mexico Gas Hydrate Joint Industry Project Leg II [20] was undertaken to assess the occurrence of gas hydrates in sand reservoirs but also to validate current technologies and techniques for pre-drill appraisal of gas hydrate concentration. It is anticipated that further research will concentrate on recovery of conventional and pressure cores to further evaluate the resource potential of hydrate bearing sands.

To eventually realise the energy potential, the gas hydrates within the sands needs to be dissociated so that the ice-like structure of the gas hydrates reverts back to its constituent parts of gas and water. This can be achieved by depressurisation of the hydrate-bearing sands, or thermal injection to raise the temperature of the sands [21]. Analytical and numerical studies have been conducted to assess the feasibility of these methods and the implications of hydrate dissociation with regard to well bore stability and production rates [22-24], however in all cases the change in mechanical properties of the sand during dissociation has not been adequately modelled due to a lack of laboratory data on dissociating gas hydrates. This paper therefore reports on a series of formation and dissociation tests conducted on laboratory specimens of synthesised gas hydrate-bearing sands to help provide better physical parameters for use in analytical and numerical models.

**EXPERIMENTAL PROCEDURE**

**Laboratory apparatus**

A Gas Hydrate Resonant Column (GHRC) apparatus developed at the University of Southampton was used to measure changes in the small strain stiffness, and associated attenuation, of the gas-hydrate bearing sand specimens during hydrate dissociation. The GHRC allows torsional and flexural vibration to be applied to the soil specimen, where 10mm thick sections of 200mm long core were analyzed gave pore saturations ranging from 8-60% [17].

The specimen is excited by applying a sinusoidal voltage to the coils that produces a magnetic field which induces motion of the magnets attached to the drive mechanism. An accelerometer attached to the drive mechanism measures the motion of the specimen and drive mechanism as the excitation frequency is altered. The resonant frequency of the system, which coincides with peak output from the accelerometer during the frequency sweep, is used to determine shear modulus of the specimen, $G_{\text{max}}$ (from torsional vibration) Young’s modulus, $E_{\text{flex}}$ during flexural vibrations. Attenuation values can also be derived for both torsional and flexural vibrations although these are not reported in this paper. Detailed description of the apparatus and
the data reduction techniques can be found in [25, 26].

Figure 1: General layout of the GHRC resonant column apparatus.

**Hydrate formation and dissociation**

All specimens were prepared using fine Leighton Buzzard sand (Grade-E), a uniform sub-angular sand with a nominal grain size between 90-150μm (accounting for 85% by weight of the sand). Soil parameters such as specific gravity, minimum and maximum densities and void ratio for this grade of sand can be found in [26].

Gas hydrates within the sand specimens were formed using the ‘excess gas’ method [33]. For this method a known mass of de-aired water is added to a known mass of air-dried sand. Specimens were by tamping the moist sand into a mold in 8 equal layers to form a dense specimen at room temperature (~293 °K). Hydrate saturation of the pore space is calculated from the dimensions of the specimen and the mass of sand and water added to form the specimen.

The specimen is sealed in a butyl membrane with nitrogen gas confining pressure and methane gas pore pressure. Methane gas back pressure was applied to the specimen and raised to 6MPa whilst simultaneously raising cell pressure to maintain an effective stress, $\sigma' = 250kPa$ on the specimen. Once the required pressures are attained the temperature of the specimen of the GHRC was lowered to 293°K to induce hydrate formation.

Resonant column (RC) testing was conducted throughout the formation stage, with full hydrate conversion deemed to have occurred when no appreciable change in specimen stiffness. Full hydrate formation usually occurred within 48 hours. After conducting RC measurements the system temperature was raised to induce hydrate dissociation. RC measurements were conducted throughout the dissociation stage. Figure 2 shows the temperature and pressure path followed by a typical specimen during formation and dissociation (A through D).

![Figure 2: A graph of temperature and pressure regime experienced by a hydrate bearing specimen. The different testing stages and the direction are represented with arrows.](image)

**Resonant Column testing procedure**

Resonant column (RC) tests were conducted using both torsional and flexural vibration. Measurements were conducted at regular intervals during hydrate formation and dissociation stages. In addition RC measurements were conducted after full hydrate formation under isotropic loading in steps of 250 kPa up to $\sigma' = 2000$ kPa, with the unloading steps following the same sequence in reverse. Torsional and flexural resonance frequencies were measured at each loading and unloading step. Each load step was maintained for thirty minutes to allow for any initial consolidation of the specimen to occur (as noted by the axial LVDT) before resonant testing was undertaken.

All the RC tests on the specimens were conducted at low strain levels ($\gamma < 10^{-5}$), which was found to be below the elastic threshold, which is defined as a point when the calculated modulus value ($G$, $E_{flex}$) is independent of applied strain [27].
RESULTS AND DISCUSSION

A number of sand specimens were prepared with different volumes of water within their pore space. These were then subject to controlled formation and dissociation of gas hydrate. During these processes the stiffness of the specimens and attenuation were measured to determine the influence that gas hydrate has on these properties. Table 1 shows the final volume of hydrate for four specimens along with their initial densities, including the eventual porosity of the specimens after the formation of hydrate and the resultant moduli for each specimen. A sand specimen was also subjected to the same stress and temperature regime but without any hydrate within the pore space. This provided base measurements to compare with the hydrate bearing specimens.

Table 1: Material properties of specimen used in the testing.

<table>
<thead>
<tr>
<th>Hydrate saturation (%)</th>
<th>Density (kg/m$^3$)</th>
<th>Porosity after hydrate formation</th>
<th>Shear modulus MPa</th>
<th>Young’s modulus MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1644</td>
<td>0.38</td>
<td>271</td>
<td>630</td>
</tr>
<tr>
<td>5.5</td>
<td>1547</td>
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<td>3970</td>
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<td>5770</td>
</tr>
<tr>
<td>18.1</td>
<td>1605</td>
<td>0.34</td>
<td>4450</td>
<td>7720</td>
</tr>
<tr>
<td>22.5</td>
<td>1585</td>
<td>0.33</td>
<td>4780</td>
<td>8840</td>
</tr>
</tbody>
</table>

1 Calculated from added water
2 Values derived at confining pressure of 500kPa

Formation

Figure 3 shows the change in shear modulus, $G_{\text{max}}$ and Young’s modulus, $E_{\text{flex}}$ for the 4 hydrate bearing sand specimens with time during the formation process. From 0 to ~20 hrs the cell temperature housing the RCA and specimen is reduced from room temperature (~293°K) to 291°K overnight, which is outside of the hydrate stability region for this temperature and pressure. The cell temperature is then further reduced to 274°K to induce hydrate formation. From this second temperature reduction step hydrate formation starts to occur when the specimen temperature is reduced from 281°K to 279°K, which occurs in about 90 mins. Measurements of $G_{\text{max}}$ and $E_{\text{flex}}$ are made throughout the working day, which at the end of was sufficient for ~97% of the eventual increase in $G_{\text{max}}$ and $E_{\text{flex}}$ to have occurred for the 5.5% and 10.1% specimens. For higher hydrate saturations (18.1% and 22.5%) ~75 % of the eventual increase in $G_{\text{max}}$ and $E_{\text{flex}}$ occurs in this time. After ~40 hours no further increase in $G_{\text{max}}$ and $E_{\text{flex}}$ was observed for the 5.5% and 10.1% specimens, whilst for the higher saturations around 98% of the eventual increase in $G_{\text{max}}$ and $E_{\text{flex}}$ was measured. Although not shown in Figure 3 no further increase in $G_{\text{max}}$ and $E_{\text{flex}}$ is evident after 65 hours for any specimen.

Figure 3: Change in shear modulus (a) and Young’s modulus (b) during hydrate formation over time

It can be seen that hydrate formation leads to a large increase in $G_{\text{max}}$ and $E_{\text{flex}}$, which is typically observed for the formation process adopted [26, 28]. Figure 4(a) & (b) shows the change in specimen temperature and shear modulus, and relative change in pore pressure, respectively, with time during hydrate formation for the 11.6% specimen. During the formation process the methane gas pore pressure reduces as the methane is taken up by the hydrate (at the same time cell pressure was reduced to ensure a 250kPa effective stress). It can be seen that the rapid increase in $G_{\text{max}}$ occurs just after a sharp reduction in methane pore pressure. In addition a spike in the specimen
temperature occurs nearly coincident with the rise in $G_{max}$.

![Figure 4](image)

Figure 4: (a) Specimen temperature and calculated change in hydrate volume during formation with time and, (b) Calculated pore pressure (using Peng-Robinson equation) and measured pore pressure with time for the 11.6% specimen.

The relative change in pore pressure is defined as the ratio of pore pressure at any time with the initial starting pressure. Also included in Figure 4(b) is the relative change in pore pressure that would likely occur as a result of change in specimen pressure alone (calculated using the Peng-Robinson equation [29] - Parameters are given in Table 2). It can be seen in Fig 4(b) that from 19hrs ~ 21hrs the calculated change in pore pressure matches the measured value. However, when the specimen temperature falls to around 279°K a sharp reduction in measured pore pressure occurs compared to that which would have been expected to occur due to the drop in temperature. It can also be seen in Fig 4 that the rapid reduction in pore pressure occurs just before a sharp spike in the specimen temperature. It is suggested that this point marks the rapid onset of hydrate formation, with the temperature rise caused by the excess heat generated by the exothermic hydrate formation reaction. The rise in specimen temperature does not give a corresponding rise in pore pressure since methane was consumed at a quicker rate during any potential increase due to temperature.

![Figure 5](image)

Figure 5: Changes in $G_{max}$ with isotropic confining pressure, $\sigma'$.

From the specimen dimensions, measured changes in pore pressure, and temperature, the number of moles of free gas in the pore space during hydrate formation can be calculated using the Peng-Robinson equation. From the measured values it was estimated that around 30% of the total hydrate volume was formed when the temperature spike was observed (~21.5hrs). At this point the value of $G_{max}$ was about double the initial value when no hydrate was formed. After about 23hrs, around 87% of the eventual value of $G_{max}$ was observed corresponding to around 66% of the eventual hydrate volume. Although not shown the changes in $E_{flex}$ follow that for $G_{max}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical temperature of methane (°K)</td>
<td>190.6</td>
</tr>
<tr>
<td>Critical pressure of methane (MPa)</td>
<td>4.656</td>
</tr>
<tr>
<td>Acentric factor of methane</td>
<td>0.0108</td>
</tr>
<tr>
<td>Density of methane hydrate (kg/m³)</td>
<td>917</td>
</tr>
</tbody>
</table>

Table 2: Physical properties of methane and methane hydrate used
Isotropic loading and unloading

Once full hydrate formation had occurred specimens were subjected to isotropic loading and unloading with $G_{\text{max}}$ and $E_{\text{flex}}$ determined for each load step. Figure 5 shows the calculated values of $G_{\text{max}}$ obtained for the specimens highlighted in Table 1. What should be noted about these results is that $G_{\text{max}}$ for the hydrate bearing sands is independent of $\sigma'$, such that normal consolidation processes (increased contact stiffness between sand grains) is prevented by the cementing hydrate (although not shown $E_{\text{flex}}$ shows a similar behavior). This is unsurprising given the large increase in stiffness observed by adding hydrate to the pore space compared to the minor changes in stiffness as a function of effective stress in the non-hydrate bearing specimens.

Dissociation

After the loading and unloading stage, the temperature of each specimen was raised overnight to 278°K (still within the hydrate stability field at 6MPa pore pressure) from the initial temperature of 274°K. The following day the system temperature is set to 285°K to raise the temperature of the specimen and start to induce hydrate dissociation. Throughout the dissociation stage both $G_{\text{max}}$ and $E_{\text{flex}}$ were calculated. Figure 6 shows the changes in $G_{\text{max}}$ and $E_{\text{flex}}$ with time from the start of the dissociation stage. It can be seen that the dissociation process is a reverse of the formation stage in that dissociation leads to a large reduction in both $G_{\text{max}}$ and $E_{\text{flex}}$. In these tests the process of formation followed by dissociation produces no appreciable change in specimen stiffness with the values of $G_{\text{max}}$ and $E_{\text{flex}}$ returning to the pre-hydrate formation values. Considering figures 3 and 6 it can be seen that the dissociation phase appears much quicker than the formation stage. For all dissociation tests the stiffness of the specimen returned to its pre-hydrate formation value within about 4 hrs of the onset of hydrate dissociation, whilst for formation the time for reaching the maximum obtainable stiffness was ~24hrs.

Figure 7 shows the stiffness moduli as a function of time along with the volume of hydrate remaining during the dissociation stage for the 11.6% specimen. It can be seen that small volumes of hydrate dissociation causes a significant reduction in specimen stiffness.

When 2.9% of the hydrate is dissociated a reduction in specimen stiffness of about 25% occurs. When 15% of the hydrate is dissociated (equivalent to a reduction in hydrate saturation of the pore space from approx. 11.6% to 9.3% - ~3hrs after start of stage) the reduction in stiffness is around 80%. Comparing these values with those obtained during hydrate formation, it can be seen that stiffness is much more sensitive to changes in hydrate saturation during dissociation than in formation.

These results suggest that the fundamental mechanics of how the hydrate interacts with the sand and its morphology during the formation and dissociation stages is very different, and is not a
simple reversal in behavior between formation and dissociation. In considering the ‘excess gas’ method, water initially resides at grain contacts due to surface tension. During formation, hydrate growth initiates at the water-gas interface, with hydrate growth continuing inwards into the contact, with the rate of growth of hydrate dependent on the methane gas diffusing through this hydrate rind to the free water at the contacts. Thus for low hydrate saturations the formation process is somewhat quicker than for higher saturation values. At the initial stages of hydrate formation, the hydrate can be idealized as a column between grain contacts which slowly increases in thickness until all the hydrate is formed (fig. 8). Thus during resonance tests, the stiffness of the specimen in the early stages is dependent on the buckling resistance of this hydrate column. The relationship between the volume of hydrate formed at any time and the width of the hydrate column can be estimated by considering the hydrate column as a frustum. When 30% of the eventual hydrate volume is formed the height/thickness ratio of the hydrate rind is ~1/8. Given the relative increase in stiffness obtained, it can be assumed that this hydrate rind is relatively easy to buckle. As more hydrate is formed the thickness of the hydrate column increases along with its buckling resistance. However, even when 80% of the hydrate is formed the thickness of the hydrate is still less than 2/3 its eventual thickness. This may explain why the time taken to increase stiffness from 87% to 100% occurs over many hours.

In contrast, the dissociation process is not dependent on a diffusion process. As the temperature of the specimen is raised and crosses the hydrate stability boundary at the given pressure, shown in Figure 1, then hydrate will start to dissociate. Given the relative scale of the grain contacts and the specimen it can be assumed that all the hydrate at a grain contact will be at the same temperature, and so hydrate dissociation will occur all over the surface area of the hydrate. Therefore, whether the hydrate acts as cement, or restricts particle motion through interlocking, as soon as the hydrate starts to dissociate it will shrink away from the grain contacts. As the strain applied to the specimen during a resonance test is very low ($10^{-6}$), small changes in the volume of hydrate during the initial stages of dissociation lead to large reduction in measured stiffness as shown in Figure 6. Once the cementation and interlocking is removed the hydrate will be
reasonably free to move about in the pore space, and so will have much reduced influence on the stiffness of the specimen. Thus measured stiffness values approach that for the non-hydrate condition when only 15% of the hydrate is dissociated.

CONCLUSIONS

This paper reports on a series of laboratory tests carried out to investigate the behaviour of Leighton Buzzard sand during the controlled formation and dissociation of disseminated methane hydrate with the pore space. Using a special Gas Hydrate Resonant Column (GHRC) apparatus the small strain stiffness of the sand was measured.

Results show that the presence of methane hydrate in the sand using ‘excess gas’ method considerably increase $G_{\text{max}}$ and $E_{\text{flex}}$. The total increase in stiffness for full hydrate formation was up to 20 times that measured when no gas hydrate was in the pore space. The measured stiffness at this stage was independent of the effective confining stress applied to the specimen. During formation, a significant proportion of the hydrate volume was required to generate an appreciable change in sediment stiffness. When 30% of the eventual hydrate volume was formed, only a doubling of specimen stiffness had occurred. It is suggested that this is due to the formation of a hydrate rind that acts like a column, with stiffness changes dependent on the buckling resistance of the column.

Dissociation of gas hydrate causes a reversal in the measured stiffness of the sand, with pre-hydrate formation values being obtained after dissociation. Large reductions in specimen stiffness were measured for very minor changes in hydrate saturation. This is in contrast to that during formation, where a more gradual increase in stiffness was observed. Thus an immediate loss of cementation at the grain contacts seems to occur during dissociation with a 25% reduction in stiffness occurring for only 2.9% of the hydrate being dissociated. The measured stiffness of the specimen returns to its pre-formation values when only 15% of the hydrate is dissociated.

The results show that the change in stiffness during dissociation is non-linear and that quantifying soil strength/stiffness based on hydrate volume remaining would lead to an overestimation of its value. Therefore, the inclusion of this non-linear behaviour will be required to more accurately model the behaviour of hydrate bearing sediments to assess the exploitation of gas hydrates as an energy resource.

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REFERENCES


