Methane hydrate formation under controlled pressure in the triaxial apparatus

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ABSTRACT
Laboratory studies on methane gas hydrate bearing soils require a specific testing environment, i.e. where gas temperature and pressure simultaneously meet minimum requirements for hydrate formation. Since the hydrate formation process consumes large amounts of gas volume, the gas supply must continuously feed the specimen during the formation process, while maintaining a constant gas pressure. Large pressure fluctuations occur as the gas is constantly being consumed for the hydrate formation; thus, high-pressure gas cylinders equipped with regulators are not able to maintain steady conditions. In order to overcome this deficiency, a gas system was developed for application to hydrate formation or other conventional triaxial apparatus that have been designed for high-pressure strength testing of soils. The details of the system and formulations for hydrate content determination are presented.

RÉSUMÉ
Les études en laboratoire des sols contenant des hydrates de méthane requièrent des environnements spécifiques de tests: la température et la pression des gaz doivent simultanément satisfaire les exigences minimums de la formation d'hydrates. Comme le processus de formation d'hydrates consomme de larges volumes de gaz, le spécimen doit continuellement être alimenté en gaz pendant la formation d'hydrates tout en maintenant une pression constante. Les bouteilles de gaz de haute pression équipées de régulateurs sont incapables de maintenir des conditions d'équilibre car d'importantes fluctuations de pression se produisent lors de la formation d'hydrates. Afin de surmonter ce problème, un système de gaz a été développé pour la formation d'hydrates et aussi appliqué à d'autres appareils classiques de tests triaxiaux conçus pour les tests de résistance des sols à la haute pression. Les détails de ce système et les équations pour la détermination de la quantité d'hydrates sont présentés.

1 INTRODUCTION

Methane hydrate could be an important future energy resource, if it can be extracted and processed in an environmentally safe way to produce and market the gas. According to some estimates, it can potentially meet global energy needs for the next 1,000 years (Demirbas 2010).

Methane hydrate bearing sediments may undergo instability due to hydrate dissociation and the corresponding pore pressure build up. This, in turn, can cause wellbore failure, loss of platform foundations or, on a large scale, submarine landslides (Carpenter 1981; Field and Barber 1993; Popenoe et al. 1993; Vogt and Jung 2002; Sultan et al. 2004a; Sultan et al. 2004b; Bryn et al. 2005; Kvalstad et al. 2005; Mienert et al. 2005; Crutchley et al. 2007; Nixon and Grozic 2007). Therefore, understanding the geomechanical properties of these sediments and their shear strength characteristics are essential for stability analysis under different environmental conditions.

Different laboratory methods have been developed to form methane hydrates in sediments. The most appropriate, but time-consuming method, that best simulates the natural formation process in deep sediments is the dissolved gas method (Spangenberg et al. 2005; Buffett and Zatsepina 2000). In this method, water saturated with methane gas is circulated through sediment, which is contained within the hydrate stability zone through pressure and temperature control. The hydrate growth rate is limited by the concentration of the gas in water; therefore, the induction time is long, due to the methane's low solubility in water. Hydrate nucleation can be promoted by using surfactants (Zhong and Rogers 2000) or flowing fluid through hydrate granules (Waite et al. 2008).

Another formation method, referred to as partial water saturation, can reduce the nucleation time substantially by flushing pressurized methane gas through partially saturated soil and cooling it into the stability field (Handa and Stupin 1992; Waite et al. 2004). Alternatively, the method can be applied to an initially fully water saturated sample with methane introduced as a bubbling gas through the saturated medium (Winters et al. 2000; 2002). However, an important drawback of the partial water saturation method is that both approaches lead to preferential hydrate formation at contacts and stiffening of the sediment framework, which is a growth habit that

is quite different from the natural process (Ebinuma et al. 2005; Kneafsey et al. 2007; Masui et al. 2005).

Hydrate formation from ice seeding (Stern et al. 1996; Priest et al. 2005) or hydrate premixing (Hyodo et al. 2005) mixes soil grains with ice or methane hydrate granules, respectively. The mixture is then pressurized into the hydrate stability field with methane. Hydrate nucleation is facilitated by the existing ice or hydrate lattice under controlled melting.

Each of the methods for forming hydrate produces different methane growth patterns, resulting in different macro-scale behaviour of seemingly identical sediments, particularly with respect to their mechanical properties (Yun et al. 2007; Lee et al. 2007).

Laboratory equipment for conducting triaxial strength testing on methane hydrate bearing samples are quite advanced and complicated, due to the various test requirement procedures. Depending on the hydrate formation method, the pore pressure is provided through water or methane gas, in a range up to 30 MPa, which must be applied at a controlled rate. Load application for both confining and pore pressures is crucial to avoiding overconsolidation or premature failure of the sample. Therefore, high-precision systems are used to control the pressure level at all times. When pore pressure is provided through gas, where the gas is continuously being consumed for hydrate formation at the ratio of approximately 164 (gas) to one (hydrate) volume at standard temperature and pressure, the resulting gas pressure drops make maintaining constant pressure conditions more difficult.

This paper describes hydrate formation methodologies, including calculation of hydrate saturation. In addition, a solution for maintaining gas pressure is described. The objective of this paper is to describe the equipment and procedures for these complicated tests; preliminary results are presented in the companion paper by Grozic and Ghiassian (2010).

2   TEST EQUIPMENT

The triaxial system for testing methane hydrate bearing soils is shown schematically in Figure 1. The system is mainly the same as a conventional triaxial apparatus with some added features. These features are described in the following subsections.

2.1   Vacuum Control Valve

Sample preparation for hydrate bearing specimens needed to be revised. Extra flexible membranes are often required to minimize gas diffusion from the specimen into the cell during hydrate formation and also to prevent membrane puncture when testing coarse granular soils (e.g. Ottawa sand) under relatively high confining pressures. This is achieved by using a control valve inside the triaxial cell for vacuum application, as shown by valve V5 in Figure 1. The valve is initially connected only to the top platen during the sample preparation. By closing the valve, vacuum is applied and remains inside

the sample, keeping the sample at a stable condition. Extra membranes can then be placed, and the valve is connected to the pore line and opened at the end, while back pressure line TW3 in Figure 1 is turned off to hold the vacuum. Figure 2 shows the control valve before and after placing extra membranes.

2.2   Pressure Lines

Since hydrate testing requires high-pressure applications for hydrate formation, the apparatus is equipped with a hydraulic system that can provide water pressures up to 20 kPa for both back and cell lines. These pressures can be applied incrementally with any rate set in the software through devices called intensifiers. Any change in the intensifiers' volume can also be recorded and monitored; therefore, drained shear testing can also be run with this system. The intensifiers can provide and maintain the set pressures for any duration.
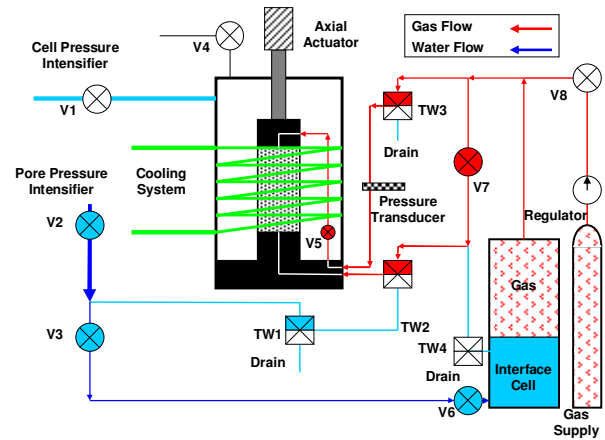

Figure 1. Schematic of triaxial apparatus for testing methane hydrate bearing soil using the partial water saturation method
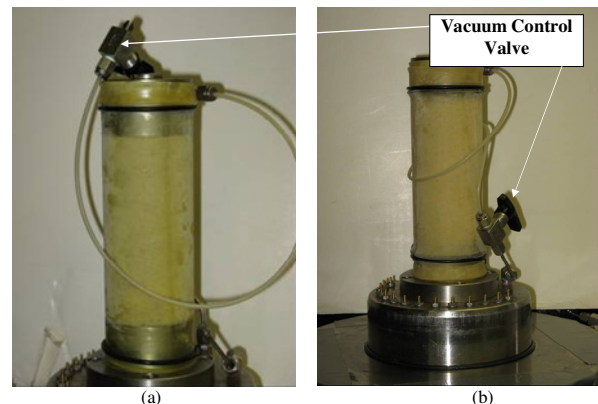

Figure 2. The use of a top-cap valve for holding the vacuum inside the specimen; (a) before placing the extra membranes; and, (b) after placing extra membranes and connecting the valve to the pore line

2.3 Cooling System

Hydrate formation occurs when the gas pressure and temperature meet specific requirements; this condition is called the stability phase or the stability field, as depicted in Figure 3. In laboratory studies, the methane temperature is generally decreased as much as possible yet remaining above zero to avoid water freezing in the system. In the equipment utilized in this study, the cooling tube was made as a coil and placed inside the triaxial cell (Figure 1). By lowering the water temperature inside the cell, the water and percolating gas inside the triaxial specimen are cooled as well. Two thermocouples placed inside the cell near the top and bottom of the specimen can take the temperature measurement at any time. All controls for the temperature and drop rate are done by data acquisition software.

2.4 Gas Application

Figure 3 shows that methane hydrate is formed under relatively high pressures and low temperatures. Pressurized methane gas for laboratory applications is supplied in bottles that are under pressures over 2500 psi (17,000 kPa). Regulators are required to control the gas flow and pressure. In triaxial testing on hydrate bearing samples, the pores are filled by gas or gas saturated water or both. It is very important to keep the pore pressure stable for the following reasons:

- Any change in the gas pressure can change the effective confining pressure, which may cause the specimen to fail prematurely or become overconsolidated.
- Any change in the gas pressure can disturb the hydrate formation and may delay or stop the process.

Experiments have shown that precise control of the gas pressure would be impossible by using the gas regulator. This becomes even more crucial when the gas is continuously being consumed for hydrate formation and the system must always maintain a constant pressure. Therefore, a revision was made to the original apparatus, by incorporating the pore pressure intensifier in a procedure called water injection.

As shown in Figure 1, a line was added to the pore pressure intensifier that is controlled by a valve (V3). This line is connected to a chamber called the interface cell, which, in turn, is connected to the gas source. At any time, the water and gas pressures inside the interface cell are in equilibrium. If the gas pressure drops due to the hydrate formation and/or a leak in the system, the water pressure drops accordingly, thereby triggering the pore intensifier to inject more water into the interface cell in order to maintain the set pressure (e.g. 14,000 kPa).

Another advantage is that, as the gas pressure in the supply bottle gradually drops due to the usage, this process can increase the available gas pressure to the required level. For example, if the gas in the bottle is at 7,000 kPa, the gas in the interface cell is at this level at the beginning, but can gradually be increased by injecting

water to the interface cell. This process may require the pore intensifier cell to be refilled several times.

3 HYDRATE FORMATION

Two methods for hydrate formation – partial water saturation and dissolved gas – were examined in this study and are explained in the following subsections.

3.1 Partial Water Saturation Method

As previously mentioned, the description of this method refers to two different approaches. In the first approach (Waite et al. 2004) the soil sample is prepared with predetermined moisture content and compacted to form a partially saturated specimen. The specimen is then pressurized with methane gas and cooled into the stability condition to promote hydrate formation. In the second approach, the sample is initially prepared with full water saturation; and, methane is then introduced as a bubble phase prior to cooling (Winters et al. 2002).

In the experiments performed using the existing apparatus, the first approach would not be possible if the gas were fed directly from the supply bottle. Since the specimen is consolidated prior to the shearing stage, the pore (gas) and cell pressures should be uniformly increased to reach the required pressures (e.g. 15,000 and 14,000 kPa for cell and pore, respectively) without causing any overconsolidation or premature sample failure. This gas pressure environment is not possible to attain, because the gas regulator can not ramp up the pressure under a controlled rate and synchronized with the cell pressure. Manual control of the gas pressure is not feasible either, as any small turn on the regulator valve can abruptly increase the gas pressure to an unintended level. Therefore, this method was not examined, as it can only be applied if a precisely controlled system exists for the gas application, similar to the pore intensifier that can increase the water pressure in a controlled manner.

The second approach uses fully water saturated samples; therefore, it is adaptable to the developed testing system. A triaxial sample can be prepared using a dry pouring method, because the initial moisture content is no longer important. The pore and cell intensifiers can ramp up the pressures under controlled rates, so that the effective confining pressure remains constant at all times.

After the specimen is consolidated to the required effective cell pressure, the high-pressure gas, which is equal to the pore pressure, is applied through the back pressure line (valves TW2 and TW3 in Figure 1). As previously explained, the gas can be continuously maintained at a constant pressure by the injection process. An important point in this method, however, is the adjustment of the required moisture content for hydrate formation. By allowing some predetermined amount of water to drain out from the pore line under the gas pressure (Winters et al. 2002), it is possible to

control the required hydrate content at any level from 0 to 100%.

The drained water from the specimen is collected in two steps as follows:

- Gas enters from the top, and water is pushed out from the bottom and collected in draining valve TW1 (Figure 1) to a predetermined amount.
- The gas flow direction is reversed; and, gas is allowed to enter from the bottom for a short duration before water, if any, starts coming out from the top. This step is required to make sure that the connecting lines to the specimen are filled only with gas. In addition, it can redistribute the capillary-held water inside the specimen and make the moisture content more uniform.
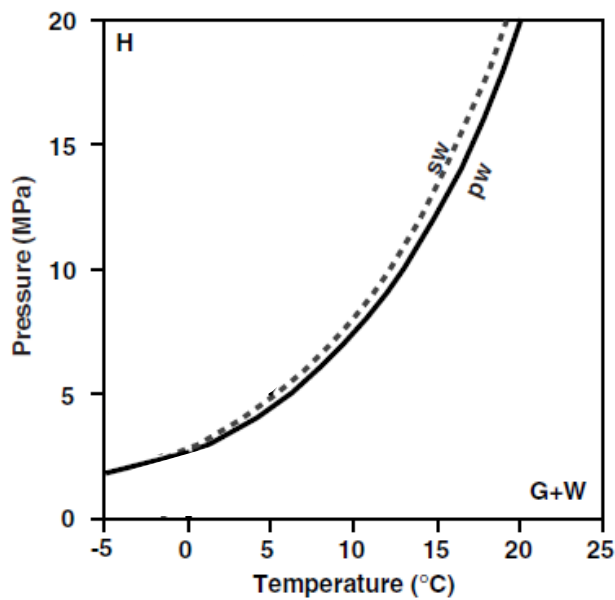

Figure 3. Temperature-pressure phase diagrams for the pure methane / pure water (pw) and pure methane / seawater (sw) systems at high methane concentrations (after Dickens and Quinby-Hunt 1994)

Once adequate water is drained, the valves are set as shown in Figure 1, so that the pressurized methane gas is continuously nourished to the bottom and top of the specimen. The flow direction of gas is shown on the lines in Figure 1.

3.2   Dissolved Gas Method

The low solubility of methane in water limits the applicability of the dissolved gas method for laboratory studies, as the process becomes very lengthy up to 50 days (Spangenberg et al. 2005). This method, however, can better simulate the natural hydrate formation in the field; therefore, it is recommended by researchers (Waite et al. 2009). They state that, because field studies suggest most hydrate occurrences are non-cementing,

laboratory specimens should be formed from the dissolved phase, in the absence of free gas.

The method was utilized using the apparatus, but with a revision in the procedure, as shown in Figure 4. Methane gas saturated water in the interface cell is flushed through the specimen under a very small flow rate. The flow is established by closing valve V7 and opening lines TW2, TW3 and TW4. The flow must be adjusted to a very small rate by the draining valve TW3 to allow enough time for hydrate nucleation of the gas molecules in the circulating fluid. This process continues for a couple of days, during which the temperature is down (e.g. 5°C), until the flow is stopped due to hydrate formation, causing the specimen to become almost impermeable.

The pressure is held constant (e.g. 14,000 kPa) at all points by the injection action of the pore intensifier through valves V2, V3 and V6 (Figure 4). The pore intensifier continuously injects water to compensate for the drained water at valve TW3, as well as the reduced gas pressure due to the gas dissolved into water in the interface cell.
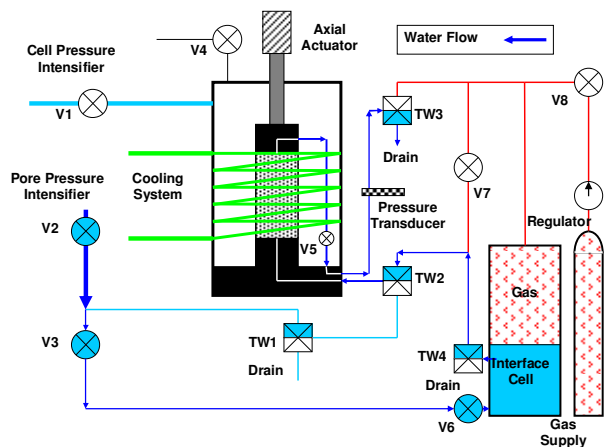

Figure 4. Schematic of triaxial apparatus for testing methane hydrate bearing soils using the dissolved gas method (blue arrows show the water flow direction)

4   HYDRATE CONTENT DETERMINATION

Hydrate content is determined indirectly during the dissociation process, by allowing some volume expansion to the methane gas inside the specimen and using the gas law. The water compressibility is assumed to be negligible. If the first hydration method (i.e. partial saturation method) is used, the formulation is made based on Figures 5 and 6, with the derivations presented in Equations 1 and 2.

The gas law between stages D and F is written as:

$$\left(\frac{P(V_{gh}+V_{gi})}{T}\right)_D = \left(\frac{P(V_{gh}+V_{gi}+V^*)}{T}\right)_F$$

$$\frac{V_{gh}+V_{gi}}{V_{gh}+V_{gi}+V^*} = \frac{P_F T_D}{P_D T_F} \Rightarrow\Rightarrow \frac{V_{gh}+V_{gi}}{V^*} = \frac{P_F T_D}{P_D T_F - P_F T_D}$$

$$\left.\begin{array}{l} V_v = V_h + V_{gi} \\ V_{gi} = V_v - V_h \\ V_{gh} = 0.13 V_h \end{array}\right\} \Rightarrow\Rightarrow \frac{0.13 V_h + V_v - V_h}{V^*}$$

$$= \frac{P_F T_D}{P_D T_F - P_F T_D} \Rightarrow\Rightarrow \frac{V_v - 0.87 V_h}{V^*} = \frac{P_F T_D}{P_D T_F - P_F T_D}$$

$$\boxed{\begin{array}{l} V_h = \dfrac{V_v(P_D T_F - P_F T_D) - V^* P_F T_D}{0.87(P_D T_F - P_F T_D)} \\[3mm] = \dfrac{V_v}{0.87} - \dfrac{V^* P_F T_D}{0.87(P_D T_F - P_F T_D)} \Rightarrow\Rightarrow S_h(\%) = \dfrac{V_h}{V_v}\times100 \end{array}} \quad [1]$$

where the V_v and V^* values are already known; and, P and T values are obtained from the recorded pressure-temperature (P-T) plot.
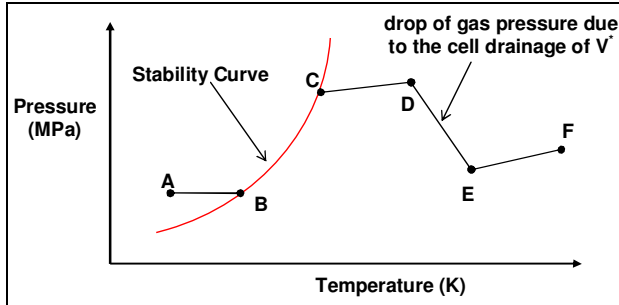

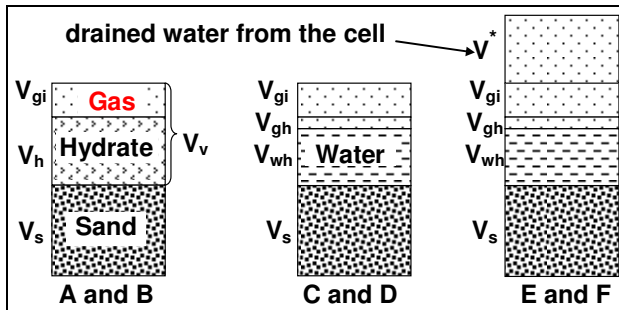Figure 5. Gas pressure variation in the triaxial specimen during dissociation

Figure 6. Volume change of hydrate bearing sand specimen during dissociation in the partial water saturation method, according to Figure 5

The hydrate content can also be estimated from the moisture content of the specimen obtained at the end of test (V_{wf}):

$$V_{wf} = V_{wh} = 0.87 V_h \Rightarrow\Rightarrow V_h = \frac{V_{wf}}{0.87}$$

$$\Rightarrow\Rightarrow S_h(\%) = \frac{V_h}{V_v}\times100 \qquad [2]$$

For the second hydrate formation method (i.e. the dissolved gas method), the hydrate content can be estimated in a similar manner as the first method. The formulation, however, is slightly different because the specimen is fully saturated with the gas solution at the time of hydrate formation as illustrated in Figure 7 and derived in Equations 3 and 4.
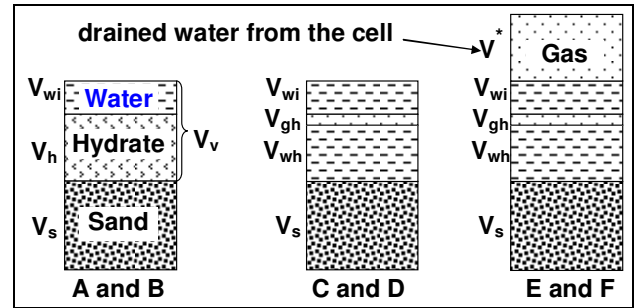

Figure 7. Volume change of hydrate bearing sand specimen during dissociation in the dissolved gas method

The gas law between stages D and F is written as:

$$\left(\frac{PV_{gh}}{T}\right)_D = \left(\frac{P(V_{gh}+V^*)}{T}\right)_F$$

$$\frac{V_{gh}}{V_{gh}+V^*} = \frac{P_F T_D}{P_D T_F} \Rightarrow\Rightarrow \frac{V_{gh}}{V^*} = \frac{P_F T_D}{P_D T_F - P_F T_D}$$

$$V_{gh} = 0.13 V_h \Rightarrow\Rightarrow \frac{0.13 V_h}{V^*} = \frac{P_F T_D}{P_D T_F - P_F T_D}$$

$$\boxed{V_h = \frac{V^* P_F T_D}{0.13(P_D T_F - P_F T_D)} \Rightarrow\Rightarrow S_h(\%) = \frac{V_h}{V_v}\times100} \quad [3]$$

where the V_v and V^* values are already known; P and T values are obtained from the recorded P-T plot.

The hydrate content can also be estimated from the moisture content of the specimen obtained at the end of test (V_{wf}).

$$V_{wf} = V_{wi} + V_{wh} = (V_v - V_h) + 0.87V_h$$

$$\Rightarrow\Rightarrow V_h = \frac{V_v - V_{wf}}{0.13} \Rightarrow\Rightarrow S_h(\%) = \frac{V_h}{V_v} \times 100 \quad [4]$$

Figure 8 shows a test result during dissociation of a hydrate bearing sample using the partial saturation method, where the gas volume has been increased in two steps of cell drainage (because the pressure had reached the capacity of the transducer). The total volume, V^*, is obtained by adding drained water in two steps. The estimated hydrate content can be calculated based on two points, A and B, as follows.

$$V_h = \frac{V_v}{0.87} - \frac{V^* P_B T_A}{0.87(P_A T_B - P_B T_A)} =$$

$$\frac{152.97}{0.87} - \frac{(89.73 + 28.04) \times 9859 \times 301.9}{0.87(19053 \times 308.5 - 9859 \times 301.9)} =$$

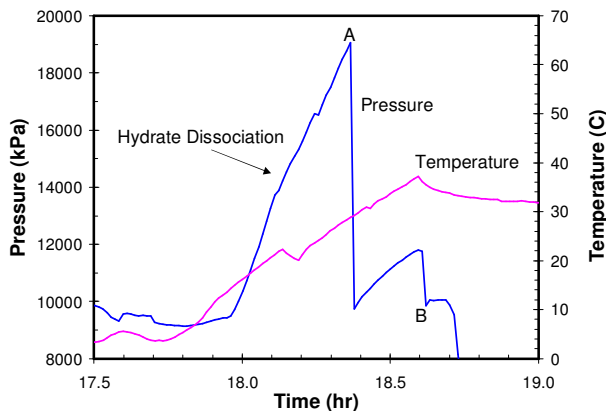$$37.0 \; cm^3 \Rightarrow S_h(\%) = \frac{37}{152.97} \times 100 = 24.2\%$$
$$[5]$$

Figure 8. Pressure buildup during dissociation of a hydrate bearing sand specimen in the dissolved gas method and subsequent pressure drop due to gas expansion

5   CONCLUSIONS

A revision was implemented to the conventional triaxial apparatus for the testing of methane hydrate bearing specimens. The gas pressure can be maintained at the target pressure, by using a cell where water and gas meet at high pressure and a water injection process. Injected water, which is controlled through a pressure intensifier device that is the indispensable part of these high-pressure apparatuses, compensates for the reduced gas pressure due to the hydrate formation.

Both methods of hydrate formation – partial saturation and dissolved gas methods – can be utilized in the proposed test configuration. A method for estimation of hydrate content was suggested that is based on the gas law during the full dissociation of the hydrate. Formulations for hydrate content determination have been derived accordingly and examined for one test example.

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