DISSOCIATION BEHAVIOUR OF CARBON DIOXIDE HYDRATE-BEARING SANDS

L. Wu, University of Calgary, Alberta, Canada
J.L.H. Grozic, University of Calgary, Alberta, Canada

ABSTRACT

Three groups of CO_2 hydrate-bearing sand specimens will be formed using a specialized triaxial test apparatus at different temperature and different pressure to examine pressure and temperature effects on: 1) the formation amount of hydrate in CO_2 hydrate-bearing sands; 2) the amount of pore pressure generated during dissociation; 3) the strength of CO_2 hydrate-bearing sands after dissociation. The anticipated triaxial test data will indicate: 1) the higher the pressure, the higher hydrate content; 2) the lower the temperature, the higher hydrate content; 3) the greater the amount of gas hydrate initially present in the specimen, the greater the reduction of effective stress upon dissociation and, the lower strength; 4) Dissociation of even a small percentage of gas hydrates will cause a dramatic reduction in the soil strength and could lead to failure.

RESUME

Trois groupes de spécimens de sable contenant des hydrates de CO_2 sont formé par l'utilisation d'un appareil triaxial à les températures différentes et les pressions différentes pour examiner les effets de la température et de la pression sur: 1) le montant des hydrates formé dans les sables contenant des hydrates de CO_2; 2) la montant de pression interstitielle produit pendant la dissociation; 3) la résistance des sables contenant des hydrates de CO_2 après la dissociation. Les données d'épreuve triaxial indiquent: 1) quand la pression augmente, le montant des hydrates augmente; 2) quand la température diminue, le montant des hydrates augmente; 3) quand il y a plus d'hydrate de gaz présent dans le specimen au commencement, il y a un réduction plus grande dans la contrainte effective sur la dissociation et il y a une résistance plus basse; 4) la dissociation d'un petit pourcentage des hydrates de gaz vont causé une réduction dramatique sur la résistance du sol et peuvent causé les faillites.

1. INTRODUCTION

Gas hydrates are crystalline compounds that consist of a host water lattice with cavities in which gas or volatile liquid is caged as a guest molecule. Host water molecules, on account of hydrogen bonding, form a three dimensional lattice into whose voids the guest molecules penetrate; the guest molecules interact with the water through van der Waals forces under the conditions of low temperatures and high pressure.

The formation and dissociation of gas hydrate influences the mechanical properties of methane sediments significantly. Water and methane are absorbed from the pore space to form gas hydrate. Replacement of the liquid water by solid gas hydrate will increase the shear strength of the sediments. Meanwhile, the permeability and porosity of the sediments decrease.

Conversely, when gas hydrates dissociate, they release a large volume of water and gas. The effect of transforming solid gas hydrates into a liquid water and free gas will decrease the shear strength of the sediments and the gas bubbles produced will worse the situation. The dissociation result in a pressure increase if the sediments are well sealed or a volume increase if pressure is allowed to dissipate by fluid flow. The associated increases in pore pressure, expansion of sediment volume, and the development of interstitial gas bubbles all have the potential to weaken the sediment (Prior et al. 1984).

Hydrate dissociation due to depressurization or heating, as caused by a decrease in sea level or by hot oil extraction from below the gas hydrate interval, could cause slope instability of sediments along continental margins and drilling accidents (Stern et al. 2000). So it is important to study geo-mechanical properties of the gas hydrate-sediment mixtures. The restrictive thermodynamic conditions are satisfied on many continental slopes and rises around the globe and North Arctices which make it difficult to study in situ therefore laboratory studies are necessary.

The original studies on the properties of hydrate-sediment mixtures used tetrahydrofuran (THF) or other refrigerants Freon 12 and R11 to form hydrate in the soil. More recently researchers have formed hydrates under higher pressure by exposing specimen to free or dissolved gas to simulate in situ hydrate formation conditions. There are four methods to form gas hydrate in the laboratory with various equipments: (1) gas is introduced into seed ice specimens, (2) gas is introduced into the water-saturated sediments, (3) gas is introduced into partially water-saturated sediment, or (4) gas-saturated water is continually feed into the specimen (Winters et al. 2002). Exposing gas directly to specimen below freezing temperature is applicable to simulate permafrost hydrates while exposing gas-saturated water to specimen above freezing temperatures is appropriate to oceanic hydrates (Grozic 2003).

2. PREVIOUS LABORATORY STUDIES

Little information exists on the geo-mechanical properties of gas hydrate-sediment mixtures. In 1984, Sego et al. formed Freon 12 hydrate-bearing sand in a modified triaxial cell to study the mechanical behaviour of the hydrate-bearing sand. A Freon 12 gas source was applied to the sample mould which was cooled to form hydrate in the sand. The stress strain curves for hydrate-bearing sand demonstrated a remarkable increase in strength and stiffness. The cohesion resulting from the bonging of particles with hydrates was the dominant strength factor. the behaviour of hydrate-bearing sand was similar to the behaviour of frozen sand.

Parameswaran et al. (1988) and Cameron et al. (1989) formed frozen tetrahydrofuran hydrate-bearing sand with a THF.16.5$H_2$0 solution being fed into the sample, then did uniaxial compression tests at -6^0C and -10^0C and strain rates between 10^{-6} and $10^{-3}s^{-1}$.The results showed the hydrate-bearing sand became stronger with decrease in temperature with the same slope of the peak stress-strain rate curves, which were similar to that of the ice-bearing sand; The strain rate dependence of strength for the frozen hydrate-bearing sand was much smaller than that of frozen ice-bearing sand, in the low strain rate region the strength of the frozen hydrate-bearing sand was higher than that of frozen ice-bearing sand whereas in the high strain rate the ice-bearing sand became stronger. Creep tests showed that at -10^0c, ice-bearing sand failed in about 15h under a stress of 7Mpa, whereas hydrate-bearing sand failed after 52.3h under a stress of 12.2Mpa.

Winters et al. (1999) studied sediment properties associated with gas hydrate formation with the Gas Hydrate And Sediment Test Laboratory Instrument (GHASTLI). Methane was percolated up through different type of sediments to form gas hydrate. GHASTLI can simulate natural conditions within the gas-hydrate-stability region with the pressure up to 25Mpa and the temperature from 25^0C to -3^0C.

By measuring acoustic velocity, shear strength and permeability and electrical resistance of the sediment containing natural and laboratory-formed gas hydrate prior to hydrate formation, after hydrate has formed, and after hydrate dissociation, they found the physical properties were significantly altered by the amount of hydrate present in the sediment and by its distribution throughout the specimen, location within pores, and concentration at specific locations (Winters et al. 2002). The dissociation of methane hydrate in GHASTLI produced an excess volume of gas which was related to the test pressure and temperature conditions. Acoustical results indicated that natural-gas hydrates in samples obtained from the Mackenzie Delta existed as part of the sediment frame or as disseminated throughout the pore fluid, but not as cements between grains. Acoustic P-wave velocities increased from 1.7km/s for water- saturated sediment to 4.0km/s after complete hydrate saturation of pores. Plot of the shear stress versus axial strain showed that strength of the sample containing gas hydrate was much higher than the sample without gas hydrate (Winters et al. 2000), the presence of solid hydrate in pore voids caused strength to significantly increased because of dilation during undrained shear resulting in negative pore pressures.

Wright et al. (1999) used the GSC test cell to determine the pressure-temperature phase equilibrium conditions for hydrates in sediments. The test cell can continuously monitor pressure-temperature conditions within the cell and sediment samples with thermistors and pressure transducer. They studied how the grain size and salinity influenced pressure-temperature thresholds for methane hydrate with four samples: quartz-rich sand with pore pressure salinity of 4ppt (parts per thousand), 20ppt and 40ppt, silt sample with a salinity of 31ppt. The test results showed a relatively uniform shift in P-T stability thresholds as pore-water salinity increased, and an additional shift in P-T stability conditions related to grain size influence.

Grozic et al. (2001) formed gas hydrate by exposing a clay specimen to methane saturated water at high pressure and low temperatures using a triaxial apparatus and dissociation was induced by slowly increasing the temperature to investigate the soil response to hydrate dissociation.

The results indicate that the specimen will undergo an increase in pore fluid (water and gas) pressure during dissociation which results in a decrease in effective stress and a loss of shear stress. The laboratory results also showed that as dissociation occurred the specimen swelled during undrained conditions.

Grozic et al. also developed the following equation to predict the effect of hydrate dissociation:

$$-0.13\cdot n\cdot\left(1-S_w\right)+\frac{164.6\cdot n\cdot\left(1-S_w\right)\cdot 1atm\cdot T_{eq}}{298.15K\cdot P_{eq}}=-\frac{\Delta\sigma'}{M(\sigma')}$$

where n is the soil porosity, S_w is the degree of water saturation, $(1-S_w)$ is the degree of saturation of gas hydrates assuming no free gas in the hydrate stability zone, T_{eq} is the equilibrium temperature of gas hydrate in K, P_{eq} is the equilibrium pressure of gas hydrate in atm, $\Delta\sigma'$ is the change in effective stress caused by melting of gas hydrate, and M is the confined compression modulus of soil. The first term represents the difference between the hydrate volume and melted water volume ($1.0m^3$-$0.87m^3$), the second term represents the volume of released gas at equilibrium temperature and pressure and the final term is the volume change of soil.

Figure 1 based on the above equation showed a plot of hydrate content (percentage of voids occupied by hydrates) versus the normalized effective stress. It demonstrates that even 10% gas hydrate exists in the soil voids, complete dissociation could bring about soil failure.

The results also showed that as gas hydrates dissociate due to a temperature increases, water and methane gas are released causing an increase in pore pressure and a decrease in effective stress and that the greater the amount of gas hydrate initially present in the specimen, the greater the reduction of effective stress upon dissociation.

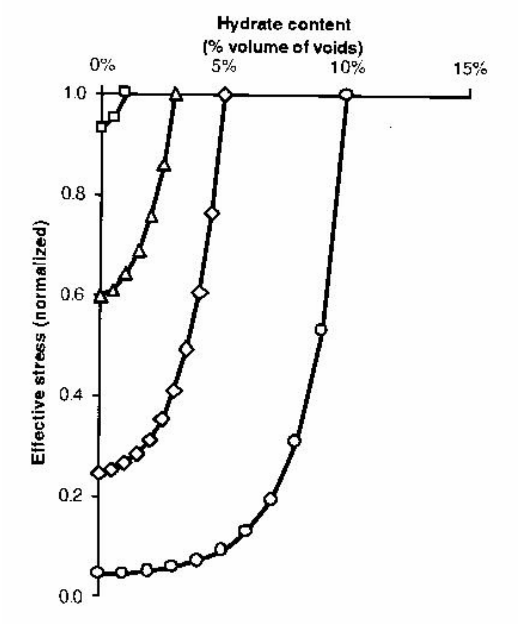

Figure 1. Theoretical stress change with hydrate dissociation (Grozic & Kvalstad 2001)

To date, the authors are unaware of any published research investigating pressure and temperature effects on the geo-mechanical response of soil during gas hydrate formation and dissociation.

3. EXPERIMENT METHODS

3.1 Test Equipment

The specialized triaxial testing apparatus (shown in Figures 2 and 3) consists of an electro-hydraulic testing system, capable of high pressures (up to 20Mpa) and low temperatures (to -30^{0}C). The triaxial testing device is computer controlled which allows input of non-standard stress paths, thus the imposed loading pattern can be varied to simulate different conditions.

Three main types of data are currently measured: 1) shear strength and related engineering properties under triaxial conditions; 2) deformation; and 3) temperature. The equipment can also measure the permeability, acoustic properties (compression and shear wave) and electrical resistance.

Figure 2. Test apparatus

Figure 3. Triaxial cell

3.2 Test Design

Hydrate dissociation produces excess gas which causes pore pressures to increase, resulting in a decrease of effective stress in the sediments and ultimately strength loss.

The amount of pore pressure generated in dissociated hydrate-sediment mixtures depends on several factors: P-T conditions, hydrate cage occupancy, inherent sediment permeability, rate of dissociation, etc. The main objectives of this research program are to examine pressure and temperature effects on: 1) the formation amount of hydrate in c CO_2 hydrate-bearing sands; 2) the amount of pore pressure generated during dissociation; 3) the strength of CO_2 hydrate-bearing sands after dissociation.

Three groups of CO_2 hydrate-bearing sand specimens will be formed. The first group of tests will include CO_2

hydrate-bearing sand specimens formed under a pressure of 3MPa at a temperature of 2^0C, 5^0C, and 8^0C. The formation pressure will then be increased to 5MPa and 10MPa for the second and third test groups respectively. Sample temperatures will be raised to 15^0C for complete dissociation of the CO_2 hydrate prior to strength analysis via shearing.

Physical effects, such as stress and deformation changes of CO_2 hydrate formation and dissociation on the surrounding sand will be measured.

3.3 Testing Procedure

3.3.1 Specimen Preparation

Reconstituted specimens of No.20/30 Ottawa sand were prepared with the moist tamping technique. Carbon dioxide was used because it is non-corrosive, non-flammable and easily dissolved in water which means it can form hydrates at lower pressure and quickly. Mineral oil was used as confining fluid because of the low solubility of carbon dioxide in it. The specimen was enclosed in two rubber membranes and silicone grease and three overlapping strips of thin aluminium foil were placed around the membranes to minimise the passage of gas from the specimen into the confining fluid. The cylindrical specimen was mounted in the triaxial apparatus and then saturated with distilled de-aired water and specimen was consolidated to in situ pressure conditions. Meanwhile, the bottle containing gas and distilled water was pressurized and then rotated until the water was saturated with dissolved carbon dioxide.

3.3.2 Gas Hydrate Formation

The circulation system as shown in Figure 4 was constructed to circulate carbon dioxide saturated water through the specimen until the pore fluid within the specimen has been completely replace by gas saturated water. One bottle (inlet bottle) of gas saturated water was placed about 0.5m above the specimen. The gas saturated water flowed down steel tubing, through the specimen from bottom to top, and to another bottle (outlet bottle) which is about 0.5m below the specimen. The circulation system was driven by a head difference of 1m. A volume of gas saturated water of three times the volume of voids of the specimen passed through the specimen in order to completely replace the pore fluids. All circulation system including the inlet bottle and outlet bottle and specimen all were kept at the same constant pressure.

Following the pore water replacement described above, the specimen was cooled. An external cooling system passed water and antifreeze through the tubing surrounding the specimen. The specimen was chilled, by computer control, to well within the hydrate stability zone and maintained at this temperature. During this time the gas saturated water continued to circulate through the specimen. As the hydrates form, the stresses and deformations within the specimen were monitored closely to determine geo-mechanical response of soil specimen to formation of gas hydrate.

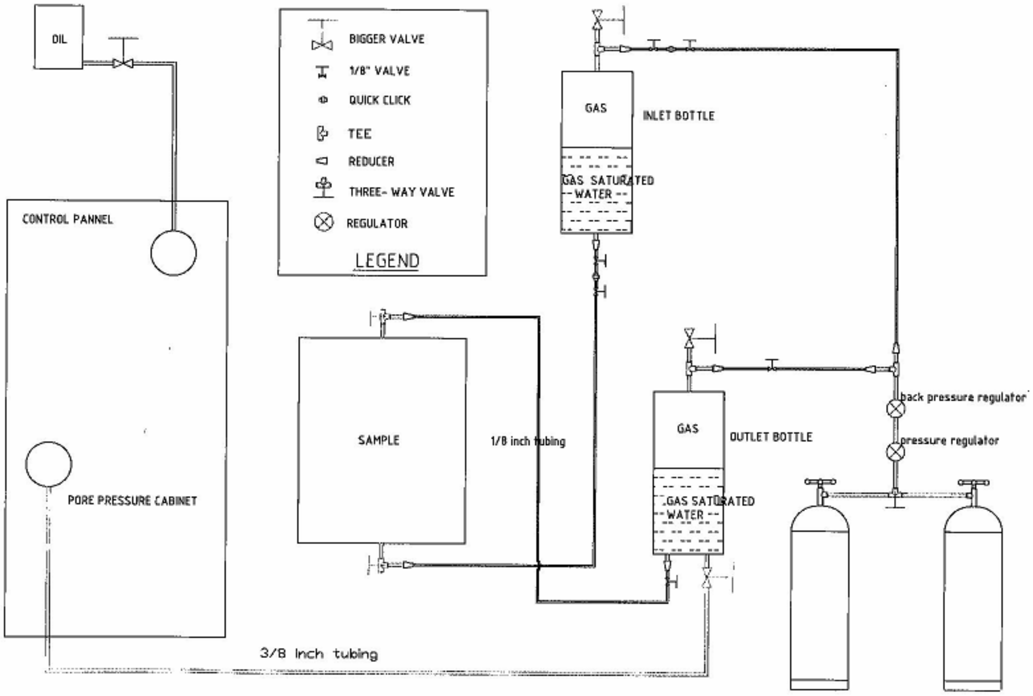

Figure 4. Schematic of the gas circulation system

3.3.3 Hydrate Dissociation

Dissociation can be brought about by either increasing the temperature to simulate heating from a well, or decreasing the pressure to simulate a sea level change or slump, or a combination of pressure and temperature change to simulate production from a hydrate reservoir (Grozic 2003). In this case, the specimens were slowly warmed to 15^0C while maintaining the cell pressure. No drainage was permitted from the specimen and the effective stress and deformation were monitored closely to determine geotechnical response of soil specimen to dissociation of hydrates. Once dissociation was complete, the specimen was sheared by imposing an axial load.

3.3.4 Estimating Gas Hydrate Content

Two concurrent methods were used to obtain measurements of hydrate content. The first one was to measure the change in specimen volume during dissociation. This was achieved by monitoring the cell fluid; as the specimen increased in volume it caused cell fluid to be expelled and when the specimen decreased in volume, additional fluid entered the cell. By knowing the specimen volume changed during undrained dissociation, the volume of hydrate that had been present in the specimen can be calculated from theory.

The second method is as following: after the triaxial testing, the value connecting specimen to the outlet bottle was open, the higher pressure in the specimen expelled water and gas into the outlet bottle. The amount of expelled water and gas were measured. The outlet bottle was designed with a float system and a high pressure, sealed LVDT located inside the bottle. This system allowed the gas to move to the top of the bottle and the gas/water interface to be recorded at all times. By keeping the pressure in the outlet bottle constant using the back pressure intensifier, the volume change device was used to accurately measure any water which was expelled from the outlet bottle. The amount of expelled water and gas was used to back calculate the amount of hydrate that was present in the specimen.

4. RESULTS AND DISCUSSION

At the present time, preliminary laboratory results from the dissociation tests of CO_2 hydrate-bearing sands are not available. However, test results will be presented at the Canadian Geotechnical Conference and published in Wu and Grozic (2004).

It is anticipated that the test results under different temperature and pressure will indicate: 1) the higher the pressure, the higher hydrate content; 2) the lower the temperature, the higher hydrate content; 3) the greater the amount of gas hydrate initially present in the specimen, the greater the reduction of effective stress upon dissociation and, the lower strength; 4) Dissociation of even a small percentage of gas hydrates will cause a dramatic reduction in the soil strength and could lead to failure. However, these hypothesis have yet to be confirmed.

5. ACKNOWLEDGEMENTS

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6. REFRENCE

Buffett, B.A. and Zatsepina, O.Y. 2000. Formation of gas hydrate from dissolved gas in natural porous media. Marine Geology, **164:** 69-77.

Cameron, I. and Handa, Y.P. 1989. Compressive strength and creep behavior of hydrate-consolidated sand. Canadian Geotechnical Journal **27:** 255-258.

Grozic, J.L.H. 2001. Geotechnical aspects of gas hydrate. A report to Jack Clark C-CORE St. John's Newfoundland.

Grozic, J.L.H. and Kvalstad, T.J. 2001. Effect of gas on deepwater marine sediments. Proceedings of the XVth International Conference on Soil Mechanics and Geotechnical Engineering. August 27-31, 2001, Istanbul, Turkey,pp.2289-2294.

Grozic, J.L.H. 2003. A new geotechnical gas hydrates research laboratory. Proceedings of the 56th Canadian Geotechnical Conference, 29 September—1 October, Winnipeg, Manitoba, Vol.1,pp.374-381.

Kayen, R.E. and Lee, H.J. 1991. Pleistocene slope instability of gas hydrate-ladden sediment of the Beaufort Sea margin. Marine Geotech.10, p125-141.

Kayen, R.E. and Lee, H.J. 1993. Slope stability in regions of sea-floor gas hydrate: Beaufort Sea Continental Slope. Submarine Landslides: Selective Studies in the U.S. Exclusive Zone. (ed.) W.C. Schwab, Lee, H.L. and Twichell, D.C.; U.S. Geological Survey Bulletin 2002, pp97-103.

Norwegian Geotechnical Institute (2002). Ormen Lange Slope Stability Assessment. Results of Laboratory Verification Tests; Gas hydrates. NGI report no.1993016-3, dated 1.6.2002.

Parameswaran, V.R., Paradis, M. & Handa, Y.P. 1989. Strength of frozen sand containing tetrahydrofuran hydrate. Canadian Geotechnical Journal **26:** 479-483.

Paull, C.K., III, W.U. and Dillon, W.P. 2000. Potential role of gas hydrate decomposition in generating submarine slope failures. Natural Gas Hydrate in Oceanic and Permafrost Environments. (ed.) M.D.Max. Kluwer Academic Publishers, The Netherlands, pp.149-156.

Prior, D.B. and Coleman, J.M. 1984. Submarine slope instability. Slope Instability. (ed.) Brunsden,D. & Prior, D.B.; John Wiley & Sons Ltd., p419-455.

Sego, D.C. 1982. Laboratory study of gas hydrate formation in fine sand.

Sego, D.C. & Wittebolle, R.J. 1984. Engineering behaviour of a sand containing gas hydrates. Proc. Cold Regions Engineering Speciality Conference, Montreal, pp.589-601.

Sloan, E.D. 1998. Clathrate Hydrates of Natural Gas, 2^{nd} Edition. Marcel Dekker, New York.

Stern, L.A., Kirby, S.H., Durham, W.B., Circone, S. and Waite, W.F. 2000. Laboratory synthesis of pure methane hydrate suitable for measurement of physical properties and decomposition behavior. Natural Gas Hydrate in Oceanic and Permafrost Environments. (ed.) M.D.Max. Kluwer Academic Publishers, The Netherlands, pp.323-348.

Uchida, T., Mikami, J., Masuda, Y. and Satoh, T. 1999. Dissociation properties of natural gas hydrate from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well by X-ray computerized tomography (CT) experiments. Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Well, Mackenzie Delta, Northwest Territories, Canada, (ed.) S.R. Dallimore, T. Uchida, and T.S. Collett; Geological Survey of Canada, Bulletin 544.

Winters, W.J., Pecher, I.A., Booth, J.S., Mason, D.H., Relle, M.K. 1999. Properties of samples containing natural gas hydrate from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, determined using Gas Hydrate And Sediment Test Laboratory Instrument (GHASTLI). Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Well, Mackenzie Delta, Northwest Territories, Canada, (ed.) S.R. Dallimore, T. Uchida, and T.S. Collett; Geological Survey of Canada, Bulletin 544.

Winters, W.J., Dillion, W.P., Pecher, I.A., and Mason, D.H. 2000. GHASTLI—Determining physical properties of sediment containing natural and laboratory formed gas hydrate. Natural Gas Hydrate in Oceanic and Permafrost Environments. (ed.) M.D.Max. Kluwer Academic Publishers, The Netherlands, pp.311-322.

Winters, W.J., Waite, W.F., Mason, D.H., Dillon, W.P. and Pecher, I.A. 2002. Sediment properties associated with gas hydrate formation. Proceedings of the Fourth International Conference on Gas Hydrates. Yakohama, May 19-23, 2002. pp.722-727.

Wright, J.F., Dallimore, S.R., and Nixon, F.M. 1999. Influence of grain size and salinity on pressure-temperature thresholds for methane hydrate stability in JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research-well sediments. Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Well, Mackenzie Delta, Northwest Territories, Canada, (ed.) S.R. Dallimore, T. Uchida, and T.S. Collett; Geological Survey of Canada, Bulletin 544.

Wu, L. and Grozic, J.L.H. 2004. Preliminary results for dissociation tests of carbon-dioxide hydrate-bearing sands. Proceeding of the Canadian Young Geotechnical Engineers and Geoscientists Conference. October 27-30, Quebec city.