DETERMINATION OF SYNTHETIC HYDRATE CONTENT IN SAND SPECIMENS USING DIELECTRICS

Joel T.R. Kliner, University of Calgary, Alberta, Canada
Jocelyn L.H. Grozic, University of Calgary, Alberta, Canada

ABSTRACT: Gas hydrates are solid crystalline compounds (clathrates) that encage gas molecules inside the lattices of hydrogen bonded water molecules within a specific temperature-pressure stability zone. It is imperative that reliable detection and quantification modi operandi are developed, as proposed in this research, to identify hydrate-laden strata and determine economic viability of this potential energy yield. This paper presents the experimental analysis of synthetic refrigerant (R-11) hydrates in 20/30 Ottawa sand using dielectric principles to determine specific hydrate content. Hydrate specimens were constructed via moist tamped Ottawa sand, purged with carbon dioxide (CO_2), saturated with de-aired water, and mixed with a known amount of R-11 to produce precise hydrate contents. The un-hydrated volumetric water content was measured using a Theta Probe by applying the principles of TDR. A negative relationship between hydrate content and the bulk dielectric constant of the specimens depict a consistent response and allow comparison with initial hydrate formation percentages.

RĖSUMĖ: Les hydrates de gaz sont des composés cristallins (clathrates) dans lesquels des molécules de gaz sont piégées dans de la glace sous des conditions spécifiques de température et de pression. Il est impératif qu’un mode opératoire soit dressé pour détecter et quantifier des couches d’hydrates, ainsi que la viabilité économique du leur potentiel énergétique. Cette communication présente une expérience dans la quelle le taux spécifique d’hydrate est déterminé en appliquant des principes diélectriques dans un échantillon de sable (20/30 Ottawa) contenant un réfrigérant synthétique (R-11). Des échantillons ont été construits en compactant du sable par couches humides, puis vidangés par du gaz carbonique pour être éventuellement saturé d’eau et mixé avec une quantité précise de R-11, correspondant à un taux précis d’hydrate. La teneur en eau volumétrique en condition non-hydratée a été mesurée en utilisant une Sonde Théta selon les principes TDR. Une relation « négative » entre la teneur d’hydrate et la constante diélectrique des échantillons permet la comparaison avec les proportions initiales des hydrates à l’état in-situ.

1. INTRODUCTION

As the known conventional oil, gas, and coal reserves are continually depleted at an alarming rate, due to the exponentially rising energy demand on a global basis, gas hydrates are being pushed to the forefront of industrial research initiatives with respect to quantification and extraction. Gas Hydrates are naturally occurring materials known to hold a unique structural complex that encapsulates a variety of gaseous compounds within a water matrix. They have been known to exist since their discovery in 1810 with research first conducted around the 1930’s due to problematic formation of gas hydrates in pipelines. These hydrates also exist naturally within ocean sediments on the continental shelves and embedded in regions of permafrost that harbour acceptable pressure-temperature regimes. The primary focus of consideration on a global scale is the predominance of methane as the host gas within the hydrate lattice. Continual research has expanded into a diverse variety of facets to date, keying in on three chief aspects of naturally occurring hydrates: submarine geohazards, global warming, and an alternate energy source. Recent global estimates have unveiled sizeable gas hydrate deposits distributed across the globe containing ample methane to be considered a significant and viable energy source for the future. Realizing the enormous potential of gas hydrates as an alternate energy source is the ideological cornerstone that underlies the premise of this paper.

The most novel advances in gas hydrate research have been attained through extensive ongoing field and laboratory initiatives/programs geared towards in-situ detection and quantification with relation to fundamental hydrate properties. The distinctive dielectric behavior associated with hydrates is one aspect currently rendering successful laboratory determination of hydrate content with potential for adaptation to in-situ techniques. Time domain reflectometry (TDR), derived from the theory of dielectrics, is a promising method being investigated for analysis and characterization of gas hydrate reserves with respect to hydrate content and spatial distribution. This research focuses on the experimental analysis of synthetic refrigerant (R-11/H_2O) hydrates in Ottawa sand employing time domain reflectometry principles to verify specific hydrate contents. Refrigerant-11 was chosen for ease of formation to create synthetic hydrates at atmospheric pressure and temperatures barely above freezing, closely simulating structure II natural gas hydrates when mixed with water at a volumetric ratio of Water/R-11 = 3.41. Hydrate specimens were constructed via moist tamped 20/30 Ottawa sand, purged with carbon dioxide (CO_2), saturated with de-aired water, and mixed with a known amount of R-11 to produce precise hydrate contents. The main objective of this experimentation is to define a reliable correlation between hydrate content and the dielectric response of the bulk specimens by measuring the un-hydrated volumetric water content using a Theta Probe in comparison with initial hydrate formation percentages. This relationship will provide a stable platform for continued research of similar nature using CO_2 and CH_4 hydrates at much greater formation pressures, as well as the eventual application to natural hydrate deposits in-situ.

2. SIGNIFICANCE

As global energy demand rises at an enormous rate facilitating ever-increasing depletion of known conventional reserves (Gas, Oil, & Coal) worldwide, today's technological society searches for new means of sustainable energy. Awareness of gas hydrates as a potential alternate energy source is becoming widely accepted and they are commonly recognized as a "frontier" gas resource with future viability. Gas hydrate deposits are distributed predominantly within the first 2,000 meters of the earth's surface storing an abundance of methane worldwide (Kvenvolden 1999). Nearly 99% of all gas hydrate deposits encompass pure methane at a volume of approximately 164 m^3 with respect to standard temperature and pressure conditions per cubic meter of hydrate (Kvenvolden 2000a). This source of methane is highly attractive as a future energy resource because the heat combustion potential realized from 1 m^3 of methane hydrate is 1462.6 Mcal/m^3, substantially greater then the 91.0 Mcal/m^3 released during dissociation (Makogon et al. 1997). However, along with detection and quantification short comings, the ability to recover the encapsulated/hydrated methane as free gas from an unconsolidated mix of sediment and water within a typical hydrate deposit is problematic as low permeability and eminent formation instability deter favorable production schemes (Kvenvolden 1999). Geohazards pose additional constraints on exploitation of gas hydrates resulting from the possible instability of natural submarine slopes and engineered/manmade structures in the vicinity of delicate hydrate bearing strata. The Messoyakha gas field in Western Siberia claims successful natural gas extraction from hydrate deposits, although a great deal of skepticism surrounds this postulation (Collett 1993). The ability to economically recover methane from natural hydrate deposits would not only ensure the longevity of natural gas supplies globally, but also allow many countries to pursue energy independence.

3. GLOBAL SPECIFICS

Gas hydrate deposits are limited to two specific regions in the shallow geosphere worldwide, comprised of excess methane at concentrations well above its water solubility concentration and at a much higher density than free gas, within precise pressure-temperature regimes (Kvenvolden 2000a). Polar regions are know to hold gas hydrates at shallow depths in continental permafrost, usually in conjunction with conventional reserves but some overlap extending into the offshore sediment of the polar continental shelves has been documented (Kvenvolden 2000a; Max and Dillon 2000). The second and most prominent region of gas hydrate significance is located within the shallow sediments under deep water of oceanic outer continental margins, restricted to continental slopes and outer continental margin rises (Kvenvolden 1993). The vast distribution of gas hydrates is spread worldwide with specific deposits surrounding all three major coastlines of Canada as illustrated in Figure 1. The first estimates to quantify the amount of methane stored in natural gas hydrate deposits were made in 1981 by the Potential Gas Committee ranging from 3.1 x 1015 to 7600 x 1015 m3 for marine environments and from 0.014 x 1015 to 34 x 1015 m3 for permafrost regions (Potential Gas Committee 1981). These estimates have since been adjusted conservatively to 21 x 1015 m3 in total at standard conditions (Kvenvolden 1988; MacDonald 1990). For ease of comparison, the quantity of natural gas held in hydrate form globally is in excess of twice all the known conventional reserves with over 98% located in marine sediments (Kvenvolden 1988).

Figure 1. Canadian Locations of Known and Inferred Gas Hydrate Deposits (Smith 2001)

Biogenic generation of methane resulting from biodegradation of deposited organic matter over time at shallow depths is the primary source of available gas for hydrate formation, especially in marine environments. In contrast, gas hydrates associated with permafrost regions are more commonly supplied by a thermogenic source of methane that requires subsequent migration upward from greater depths at higher temperatures where origination occurs (Rastogi et al. 1999; Max and Dillon 2000). There are four common formational structures that can be encountered in natural hydrate deposits: disseminated crystals, nodules, layers, or massive hydrates (Sloan 1998). The preferable sediment types that harbor gas hydrates as pore-filling constituents are coarse grained sand and sandstones with varying degrees of consolidation, typically unconsolidated or semiconsolidated, providing challenges for production and detriments to stability (Kvenvolden 2000b). Fine-grained soils like clays and mudstone do not preclude hydrate development, however, formation is further inhibited by a few more factors such as permeability, pore size and distribution, bound water, etc (Makogon 1997; Clennel et al. 2000).

4. GAS HYDRATE CHARACTERISTICS

Gas hydrates are solid crystalline compounds comprised of hydrogen-bonded water molecules forming a rigid ice crystal lattice that encapsulates free gas molecules at a denser state, also known scientifically as a clathrate (Max and Dillon 2000; Kvenvolden 2000a). Furthermore, they are nonstoichiometric inclusion compounds consisting of a three-dimensional host lattice comprised of molecular water that encages guest molecules for internal stability. Methane is the predominant gas that forms natural hydrates but there are a variety of other gases with the same ability such as light alkanes of higher density like ethane, propane, isobutene and some non-hydrocarbons (Max and Dillon 2000; Kvenvolden 2000a). Stackelberg discovered two fundamental clathrate structures in the 1950's that are now typically associated with gas hydrate deposits, termed structure I and structure II (Khokhar et al. 2000; Makogon 1997). Structure I hydrates primarily house methane as the preferred guest molecule while larger gas molecules compete for cage occupancy in structure II and H hydrates (Sloan 1998; Makogon 1997; Kvenvolden 2000a). One volume of water can encapsulate up to 207 volumes of methane resulting in 1 m^3 of hydrate containing 164.6 m^3 of methane and 0.9 m^3 of water at standard conditions (Makogon et al. 1997; Kvenvolden 2000a). The representative density for structure I methane hydrate is around 0.91 g/cm^3 but varies according to pressure, temperature, degree of cage occupancy, and methane purity.

5. DIELECTRIC THEORY

Time domain reflectometry (TDR) is a nondestructive experimental technique traditionally used to identify discontinuities in transmission lines and communication cables by monitoring reflections/changes from an electromagnetic step pulse traveling through a line of known length. Application to in-situ and laboratory soil samples has also yielded successful results (Topp et al. 1980) in determination of the unfrozen volumetric water content of soils using coaxial or parallel line configurations to measure the sample's bulk dielectric constant (permittivity) (Topp et al. 1980). The real part of the complex dielectric constant (K') is extremely sensitive to the volumetric water content (θ_v) within a specific frequency range, 1 MHz to 1 GHz, without much dependence on frequency itself (Davis et al. 1977). The complex dielectric constant (K") also has an imaginary part, known as the electrical loss, is essentially negligible in a virtually homogeneous low-loss material. Therefore, the dielectric constant measured by TDR in soil samples is termed the apparent dielectric constant (K_a) as $K_a \approx K'$. The apparent dielectric constant of water ($K_a \approx 80.5$ at 20 °C) dominantly influences the permittivity of the aggregate sample because it significantly greater than air ($K_a = 1$), ice ($K_a \approx 3.15$ to 3.2), or granular soil ($K_a \approx$ 2.0 to 4.0). In 1980 Topp defined the relationship between volumetric water content (θ_v) and the apparent dielectric constant (K_a) as a best-fit third-degree polynomial applicable to a variety of soil types, although calibration to specific soils can be obtained. This correlation is depicted in Figure 2 as the shaded area and expressed mathematically as per Equation 1 (Topp et al.1980).

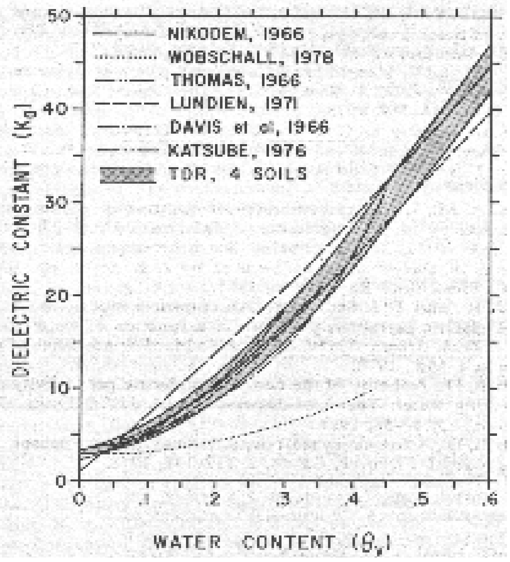

Figure 2. The Dielectric Behavior of Various Soils Using TDR (Topp et al.1980)

$$K_a = 3.03 + 9.3\cdot\theta_v + 146.0\cdot\theta_v^2 - 76.7\cdot\theta_v^3 \qquad [1]$$

Application of TDR to soils requires consideration of the following variables: soil texture, soil structure, soluble salts, water content, temperature, density, and measurement frequency. The soil texture, structure, and density subject minimal to negligible influence on the permittivity of bulk soil samples since the apparent dielectric constant of water is immensely greater than dry soil, masking any possible effects (Topp et al. 1980; Davis et al. 1977). The soluble salt concentration in pore water tends to increase the attenuation of the electromagnetic pulse providing measurement difficulties but does not significantly impact the bulk dielectric constant (Patterson and Smith 1985). Temperature effects must be considered as the dielectric constant of water increases with decreasing temperature, however, the overall permittivity of soil exhibits minimal variation (Topp et al. 1980). The dielectric principles of time domain reflectometry have been utilized to ascertain the degree of pore saturation by gas hydrate. Wright established that the apparent dielectric constant of hydrates is essentially the same as ice, $K_a \approx 3.15$ to 3.2, through TDR experimentation on gas hydrates formed in silica silt. At temperatures above 0 °C it is critical to note that gas hydrate is present within the soil matrix rather than ice. Monitoring the change in the bulk dielectric constant of the sample with respect to a material specific non-hydrate K_a versus θ_v relationship, the amount of gas hydrate can be estimated from the remaining un-hydrated pore water (Wright et al. 2000).

Synthetic hydrates are formed in this research initiative using an H_2O/R-11 mixture at a ratio of 3.41:1. The bulk specimens are comprised of 20/30 Ottawa sand, H_2O, and the inclusion of R-11 as an additional phase liquid prior to hydrate formation. The dominance portrayed upon the apparent dielectric constant of unreacted water in comparison to all other components of the bulk specimen (Table 1), including hydrate formation over time, suggest that Equation 1 will hold true and yield meaningful results. It is also advantageous to employ a reliable dielectric mixing model during specimen calibration and after hydrate formation to accurately determine the theoretical bulk dielectric constant of the specimens under analysis for comparison to the experimentally measured values. The Time-Propagation (TP) model was chosen to best suit this application due to its simplicity and basis on volumetric proportions. The TP model is expressed mathematically in Equation 2 to easily calculate the bulk dielectric constant of an aggregate specimen, consisting of the volume fraction (V_i) and the dielectric constant (K_i) of each component inherent within (Knoll 1996):

Table 1. Breakdown of Dielectric Constants

Component	**K_a**	**Temp.**	**K_a @ 1˚C**
Dry Sand	3 to 6	------	≈5.00
Liquid R-11	2.50	25 ˚C	3.85
Water	78.54	25 ˚C	87.68
Hydrate / Ice	N/A	25 ˚C	3.15 to 3.2

****Assume linear extrapolation to 1˚C from published values**

****Dielectric constant of Ottawa sand included air voids**

$$K_a = [\sum V_i(K_i)^{0.5}]^2 \qquad [2]$$

An ML2x ThetaProbe is used to experimentally obtain the bulk dielectric constant of the test specimens. This device is designed to measure the volumetric soil moisture content (θ_v) by responding to changes in the apparent dielectric constant based on proven transmission line theory using a 100 MHz sinusoidal signal. The ThetaProbe yields a DC output voltage (^{V}) that is converted to the bulk dielectric constant as follows using Equation 3 (Delta-T 1999):

$$\sqrt{K_a} = 1.07 + 6.4 \cdot {}^V - 6.4 \cdot {}^{V^2} + 4.7 \cdot {}^{V^3} \qquad [3]$$

6. EXPERIMENTAL PROCEDURE AND RESULTS

A soil specimen was initially constructed at a loose state within the specific apparatus designed for this experimentation (Figure 3) in order to emulate a favourable environment for hydrate formation. The ThetaProbe was placed in the bottom cap of the apparatus flush with the bottom porous stone and the four metal probe rods extruding above freely. An ample amount of 20/30 Ottawa sand was placed in a mixing bowl and weighed to determine the water requirements for moist tamping method of construction. Distilled water was continually applied to the sand using a spray bottle and thoroughly mixed until 5% by weight had been added. Approximately 400 grams of the prepared sand was carefully placed into the sample cylinder and the top surface smoothed out as shown in Figure 3. The first layer was compacted using a 263 gram drop disc at roughly 10 to 15 mm falling distance repeatedly five times. The second layer was constructed with the same amount of material, leveling the surface prior to compaction, and increasing the number of drops by a factor of two to facilitate a greater compactive effort though both layers. This procedure was repeated once again for the third layer, increasing the original number of drops three fold to ensure thorough compaction. A filter stone was placed on surface of the freshly prepared specimen and then sealed with the top cap. The height of the top cap above the cylinder wall was measured using calipers and compared to the known length of a dummy sample, giving rise to the actual specimen height and its initial volume contained in the apparatus. The average moisture content of the prepared specimen was determined by collecting three samples of the unused sand mixture, weighing, oven dried for 24 hours, and weighing again after drying. The initial volume of voids within the specimen was determined using fundamental soil relations involving the average moisture content and initial volume of the sample.

Figure 3. Specimen Preparation after the first layer is complete

The specimen was now ready to be saturated with de-aired water prior cooling and addition of the R-11 for hydrate formation. Carbon dioxide was cycled upward through the specimen under low pressure at 20 minute intervals via cross-port configuration (bottom left to top right and vice-versa), in conjunction with the top and bottom filter stones, to prevent channeling and effectively replace the air voids with a more water soluble gas. A simple de-airing chamber (Figure 4) was fabricated and connected to a vacuum pump through a liquid nitrogen trap to prevent water vapour from damaging the pump. The de-airing unit was placed at a higher elevation than the specimen apparatus to provide an adequate head difference during saturation. Distilled de-aired water was slowly percolated upwards through the specimen for 45 minutes each direction using the cross-port rational to minimize channeling and sample disturbance as illustrated in Figure 4. A small load was applied to the top of the specimen to compress any air voids that may still exist after the saturation process was complete, ensuring close to 100% saturation achieved. Again the height of the top cap above the cylinder wall was measured and the saturated specimen volume calculated based on the change in height resulting from compression of the air voids. This change in volume is essentially the change in initial void volume prior to saturation. The temperature of the room was recorded and an HH2 Moisture Meter used to take the first millivolt (mV) reading from the ThetaProbe inside the specimen at this stage of the experiment (Table 2).

Figure 4. Specimen CO_2 Cycling and Saturation Procedure

The apparatus was then placed in a cold room at 1 ºC for 24 hours in order to cool and stabilize the specimen temperature at reaction conditions. Another ThetaProbe reading was taken at this point and compared with the first measurement prior to cooling. These values are inputted separately into Equation 3 to determine the experimental bulk dielectric constant of the specimen that is in turn applied to the dielectric mixing model (Equation 2) to fit the data and establish a specific $K_a \approx 8.2$ for Ottawa sand grains since the acceptable range attained from literature includes air voids within the sand. Synthetic refrigerant (R-11) hydrate forms at a precise volumetric ratio of H_2O/R-11 equal to 3.41 under atmospheric pressure at temperatures below 4 ˚C (Mork et al. 2000). The saturated volume of voids was used to determine the amount of R-11 required to form precise hydrate contents. A specific amount of liquid R-11 was squeezed into the specimen, predetermined based on the required hydrate percentage, expelling an equivalent amount of water. The specimen was left for 30 minutes while the R-11 cooled down to the same temperature as the rest of the sample. There is a volumetric expansion associated with the H_2O/R-11 hydrate reaction, thus, the top filter stone was remove and the top cap lifted up a few centimeters to provide an air gap for this expansion. The specimen apparatus was shaken vigorously to provide the mechanical mixing essential to promote hydrate formation and ensure dispersion of R-11 throughout the sample because R-11 is denser then water and tends to settle near the bottom of the specimen over time. This agitation process was repeated every 30 minutes for

2.5 hours, flipping the sample upside-down each hour, then continuing once a day for 2 to 3 days. ThetaProbe readings were taken before and after every mixing interval until no change was noticeable at which time the hydrate reaction was deemed complete. The top cap was compressed flush with the specimen to close any remaining air gap, measuring the final height for volume change due to expansion associated with hydrate formation as illustrated in Figure 5. The experimental results for each theoretical hydrate percentage are displayed in Table 2, including ThetaProbe readings for each specimen at 100% water saturation and after test completion, along with their associated volume calculations.

Figure 5. R-11 Hydrate Specimen at Test Completion

Table 2. Summary of Experimental Results

Sample #	**% Hydrate Formation**		**Volume Measurements (cm^3)**			**ThetaProbe Readings (mV)**		
						100 % Saturated		**Hydrated**
	Theory	**Actual**	**Saturated**	**Hydrated**	**% Expansion**	**23 °C**	**1 °C**	**1 °C**
1	30	36.5	736	746	1.3	952	981	757**
2	50	51.4	738	771	4.4	940	966	614
3	70	71.4	743	826	11.2	945	974	520
4	85	86.0	699	833	19.2	870**	897**	378
5	100	98.9	732	849	16.1	941	969	129

Measurements are flawed!

7. ANALYSIS AND DISCUSSION

The preparation of the specimen and experimentation methods during hydrate formation posed a number of challenges, some of which could be rationalized and others explicitly stated. An arbitrary time of 20 minutes per side using a cross-port configuration was chosen for adequate CO_2 circulation to replace the majority of air in the specimen voids prior to saturation. The specimen was essentially considered saturated after saturation by slow percolation of distilled de-aired H_2O followed with a slight consolidation. A loose soil structure was strived for to promote R-11/H_2O reaction by maximizing the size of the pore spaces and free water contained within thus reducing the potential competition effects of surface tension on the water via individual sand grains. During saturation the specimen was subjected to a small vertical load causing some compression to a denser state and was further disturbed by the vigorous shaking required to thoroughly mix the R-11 uniformly within the specimen at the early stages of hydrate formation. Cementation of the sand grains as hydrate begins to form provides strength to support a looser structure during the remainder of the mixing process, easing the effects of densification and constraints of self weight against volume expansion, especially at the higher hydrate percentages.

Some excess standing water was evident in the specimen immediately after removal of the top filter stone prior to mechanical mixing. Is it assumed that this additional water, drained from the filter stone, offsets both the small leakage during the early turbulent mixing intervals and any possible loss from drying effects over time on the specimen due to the air void induced to accommodate volumetric expansion during hydrate formation. Frequent mixing intervals during the first 2.5 hours minimized the tendency for R-11 to settle toward the bottom portion of the specimen since its density is greater than water, facilitating a more uniform dispersion of hydrates throughout. The experiment was deemed complete once the ThetaProbe yielded no change in its readings over a 24 hour span and the remaining air void, not utilized by hydrate expansion, was compressed to determine the final specimen volume. There was potential for some air voids to remain trapped within the hydrated specimen, especially at the greater R-11 contents due to the rigidity provided by hydrate formation, but this was presumed to be negligible based on predictions from the dielectric mixing model integrating a small volume of air. The lower hydrate percentages did not produce much solid hydrate although some soft gel substance did manifest in patches within the specimen. Obvious hydrate chunks distinctly formed and solidified to a greater extent over time as the R-11 content was increased (Figure 6). The bulk K_a values obtained from the ThetaProbe readings in conjunction with Equation 3 seemed to advocate that the water is bound to the R-11/H_2O hydrate structure well before solidification takes place. It was suspected that over time the hydrate structure continues to solidify to a greater extent. Crude hydrate specimens were prepared at a variety of percentages and left in the cold room for upwards of 2 weeks with periodic shaking to subsequently verify this postulation.

Figure 6. Synthetic R-11/H_2O Hydrate Chunks

The available literature denoted a dielectric constant for 20/30 Ottawa sand within the range of 3 to 6. Results did not agree when a value in this range was used in the dielectric mixing model of Equation 3 after saturation and compared to the bulk dielectric constant of the sample derived from the ThetaProbe reading. A stand-alone test was conducted on dry 20/30 Ottawa sand to determine the bulk K_a and subsequently compared to theoretical value, giving rise to an outcome that falls within the acceptable published range for Ottawa sand. It was deduced that the values of K_a for Ottawa sand were originally obtained from bulk sand samples containing air voids, thus, a similar process of back-calculation was used to determine the approximate value of $K_a \approx 8.2$ for only the sand grains in the bulk specimen under analysis. Both theoretical (Model Fit → Eq. 2) and experimental (ThetaProbe → Eq. 3) bulk dielectric constants were computed for the various hydrate percentages along with the associated volumetric expansion as per Table 3 and Figure 7. A key assumption is that nearly 100% of the R-11 reacted to form hydrates and they were dispersed consistently throughout the specimen. This is supported by back-calculation from the measured bulk K_a to determine the actual hydrate percentage obtained in comparison to the original value expected. It is obvious from the experimental data obtained that there is a distinct relationship between the specimen's bulk dielectric constant and the amount of hydrate contained in the pore spaces. The K_a of the Ottawa sand specimens decreased rapidly as hydrate formation increased and were in reasonable agreement with the predicted values from the dielectric mixing model. However, it is not apparent from these preliminary results whether this relationship is linear or exponential. It is also abundantly clear that a volumetric expansion accompanies synthetic R-11/H_2O hydrate formation, seeming to be proportional in magnitude. These results are only preliminary, thus, further tests are required to achieve consistency in the experimental data, explicitly determine the nature of the K_a versus hydrate content correlation, and establish a reliable constant with respect to density for volume expansion.

Table 3. Comparison of Bulk K_a and Volume Expansion

Hydrate %		Bulk Ka		Δ Volume
Theory	Actual	ThetaProbe	Model Fit	% Expansion
30	36.5	18.37	19.81	1.30
50	51.4	15.66	15.60	4.42
70	71.4	11.08	11.05	11.19
85	86.0	8.00	7.95	19.16**
100	98.9	3.24	5.49	16.05

**Value is inflated due to a denser state after saturation

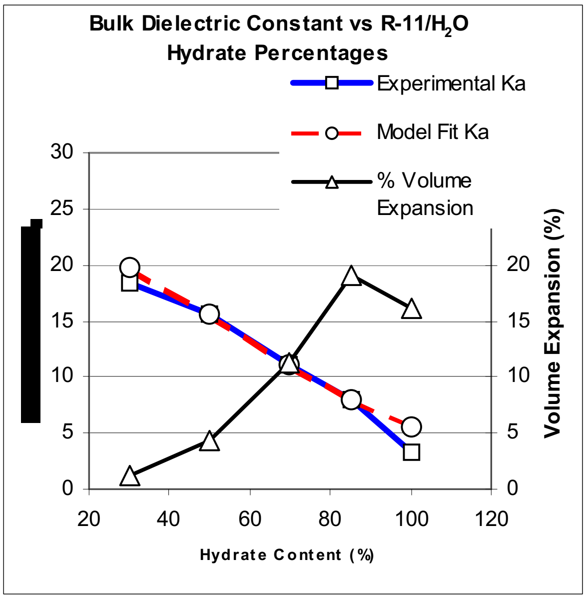

Figure 7. Trends of Bulk K_a and Δ Volume with respect to Synthetic Hydrate Percentage

8. STATEMENT OF OPTIMISM

Fundamentally it has been shown that the theory of dielectrics can be applied to soil specimens and yield successful results as the bulk dielectric constant gives rise to an unmistakable variation with respect to the quantity of hydrate in the pore spaces. The bulk dielectric response exhibits a decreasing trend with greater pore saturation by hydrates, accompanied by a distinct volume expansion. A dielectric mixing model based on volumetrics was employed to produce theoretical values that agreed tolerably to the experimental K_a calculated from the ThetaProbe readings. The results presented within this paper are strictly preliminary with further experimentation ongoing to facilitate confidence and reliability in these findings. Other important variables that need to be addressed as they are expected to play a key role in adapting this method from the laboratory to in-situ conditions are variations in soil type, density, and salinity. It is imperative that reliable detection and quantification modi operandi are developed to identify hydrate-laden strata and determine the amount of natural gas feasibly recoverable as this is the new environmentally friendly energy source of the future.

9. ACKNOWLEDGEMENTS

The author's gratefully acknowledge the financial support provided by the Alberta Ingenuity Fund (AIF) that made this research possible.

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