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GAS HYDRATES: AN OVERVIEW ON THE NIGER DELTA CONTINENTAL FRONT

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ABSTRACT: *The formation of gas hydrates occurs when gas molecules are trapped in a lattice of water molecules at temperatures above 0°C and pressures above one atmosphere.The Niger Delta occupies the central region of West Africa's Gulf of Guinea. With a land area of some 75,000 km2, it forms the largest delta system in Africa. It continental depth holds a deposit of gas hydrates. The gas hydrate deposit in this region is mostly biogenic, however, small amounts have been found to be thermogenic in nature. The clathrates in this region have 99% methane formation statistics up to the depth which is 1500+ meters below sea level. The hydrates found have been observed to contain sedimented light hydrocarbon alkane gases.These clathrate reserves hold significant amount of energy that is estimated to be more than twice the combined carbon of coal, conventional gas and petroleum reserves and as such holds more commercial and economic value. Gas hydrate can serve as a sustainable energy resource and also as a means of storing and transporting natural gas from one end to the other.This paper presents an overview of gas hydrate in the Niger Delta continental front. It describes the nature of the hydrate formed in the Niger Delta region based on it geological formation. It showcases the huge energy potential of hydrate in the Niger Delta, and how it can posit as a sustainable energy resource to meet the ever-growing energy need of Nigeria and the world at large.*

KEYWORDS: gas hydrates, Niger Delta, continental front

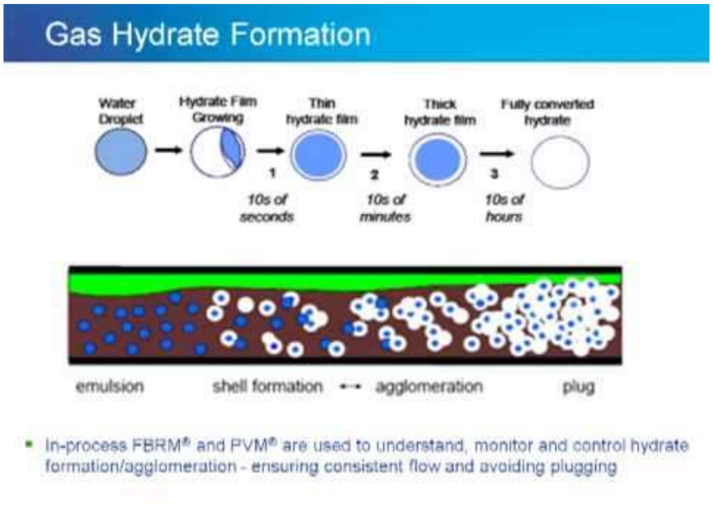
INTRODUCTION

Gas hydrate which is also known as Clathrate hydrates, or gas clathrates, clathrates, hydrates, etc., are crystalline water-based solids physically resembling ice, in which small non-polar molecules (typically gases) or polar molecules with large hydrophobic moieties are trapped inside "cages" of hydrogen bonded, frozen water molecules. In other words, gas hydrates (clathrate hydrates) are clathrate compounds in which the host molecule is water and the guest molecule is typically a gas or liquid. Without the support of the trapped molecules, the lattice structure of hydrate clathrates would collapse into conventional ice crystal structure or liquid water. Most low molecular weight gases, including O_2, H_2, N_2, CO_2, CH_4, H_2S, Ar, Kr, and Xe, as well as some higher hydrocarbons and Freon, will form hydrates at suitable temperatures and pressures. Gas hydrates are not officially chemical compounds, as the sequestered molecules are never bonded to the lattice. The formation and decomposition of clathrate hydrates are first order phase transitions, not chemical reactions. Their detailed formation and decomposition mechanisms on a molecular level are still not well understood. Gas hydrates were first documented in 1810 by Sir Humphry Davy who found that water was a primary component of what was earlier thought to be solidified chlorine.

Gas Hydrates have been found to occur naturally in large quantities. Around 6.4 trillion (6.4×10^{12}) tonnes of methane is trapped in deposits of methane hydrate on the deep ocean floor. Such deposits can be found on the Norwegian continental shelf in the northern headwall flank of the Storegga Slide. Gas hydrates can also exist as permafrost, as at the Mallik gas hydrate site in the Mackenzie Delta of northwestern Canadian Arctic. These natural gas hydrates are seen as a potentially vast energy resource, but an economical extraction method has so far proven elusive. Hydrocarbon clathrates cause problems for the petroleum industry, because they can form inside gas pipelines, often resulting in obstructions. Deep sea deposition of carbon dioxide hydrate has been proposed as a method to remove this greenhouse gas from the atmosphere and control climate change.Gas hydrates are suspected to occur in large quantities on some outer planets, moons and trans-Neptunian objects, binding gas at fairly high temperatures.

Formation of Gas Hydrates

When gas molecules are trapped in a lattice of water molecules at temperatures above 0°C and pressures above one atmosphere, they can form a stable solid. These solids are gas hydrates. Most gas hydrates are formed from methane (CH4). Methane is the simplest hydrocarbon, and is the primary component of the natural gas that we burn for energy. If hydrate nodule in held and lit with a match, it will burn like a lantern wick. Figure 1 below shows how hydrate is formed.



- In-process FBRM® and PVM® are used to understand, monitor and control hydrate formation/agglomeration - ensuring consistent flow and avoiding plugging

Figure 1: Formation of gas hydrates (Greaver et. al., 2008)

Gas hydrate deposits along ocean margins are estimated to exceed known petroleum reserves by about a factor of three. These hydrate beds leak gases into the water, forming cold seeps on the ocean floor. This hydrocarbon seepage is common on continental margins around the world.

Chemosynthetic communities similar to those found at hydrothermal vents form at cold seeps, using hydrocarbons or hydrogen sulfide for carbon and energy. Seep tube worms, mussels, and clams form two-meter-high bushes over kilometer-sized beds. Most seeps are also characterized by high microbial productivity. Figure 2 below shows some types of gas hydrate deposits.

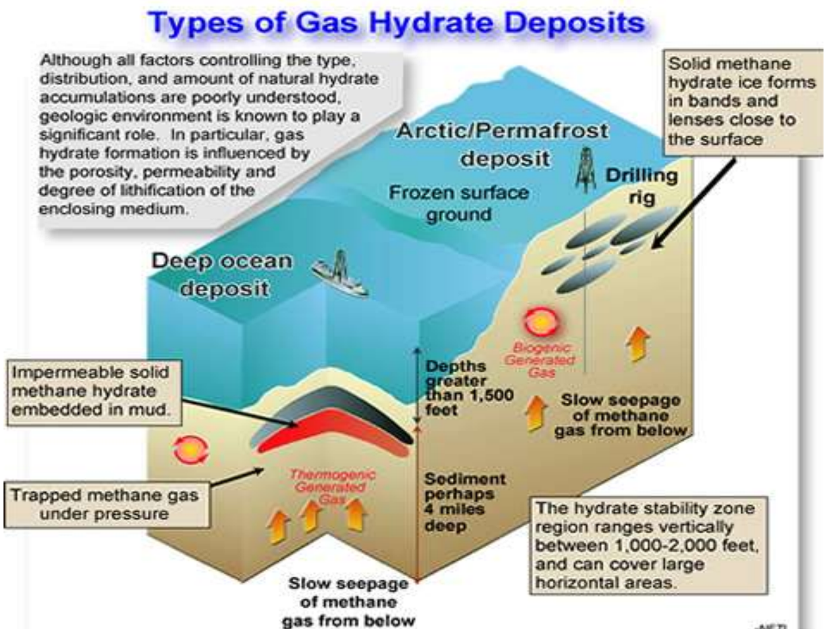


Figure 2: Types of gas hydrate deposits

(https://deepresource.wordpress.com/2013/03/15/more-on-methane-hydrates)

Structure of Gas Hydrate

When water molecules come in contact with gas molecules at low temperature and high pressure, different geometric structures contrary to that of a hexagonal ice are formed. The water molecules serve as host molecules and create cage lattices that can hold gas molecules as guest molecules. These cage-like crystalline structures are less dense than crystalline water structure because of the presence of the gas molecules. The gas hydrate formed is held together by the hydrogen bonds of the water molecules and also stabilized by Vander Waals forces holding the gas and water molecules together. The Vander Waals force is responsible for the stable nature of the gas hydrate and even makes the hydrate more stable than normal ice formed by water. There are different structures of gas hydrate and they are characterized by the shape of their cages. Natural gas composed mainly of methane gas and the complete combustion of methane gas gives water, carbon dioxide, and energy, as shown in the Equation (1.0).

$CH_4 + O_2 \Rightarrow CO_2 + H_2O + \text{Energy} \uparrow$ (1.0)

The energy liberated from this process can serve different purposes. This makes natural gas more environmentally friendly than other fossil fuels because more energy is liberated and less CO_2 produced. The pictorial view of the lattice structure of gas hydrate is shown in Figure 3 below. Methane gas is the guest in the middle (Green) while water molecule is the host (Pink). Gas hydrate can be stored or transported at equilibrium conditions with either its saturation temperature or pressure. At the saturation temperature and pressure, hydrates are usually stable. Some factors affect the saturation pressure and temperature of the hydrate. Factors such as cost and weight of material for hydrate storage vessel as well as the environment of the sediments containing the hydrate deposits. Hydrates are usually stable at moderate temperatures and pressures when compared to the conditions required for LNG and CNG.

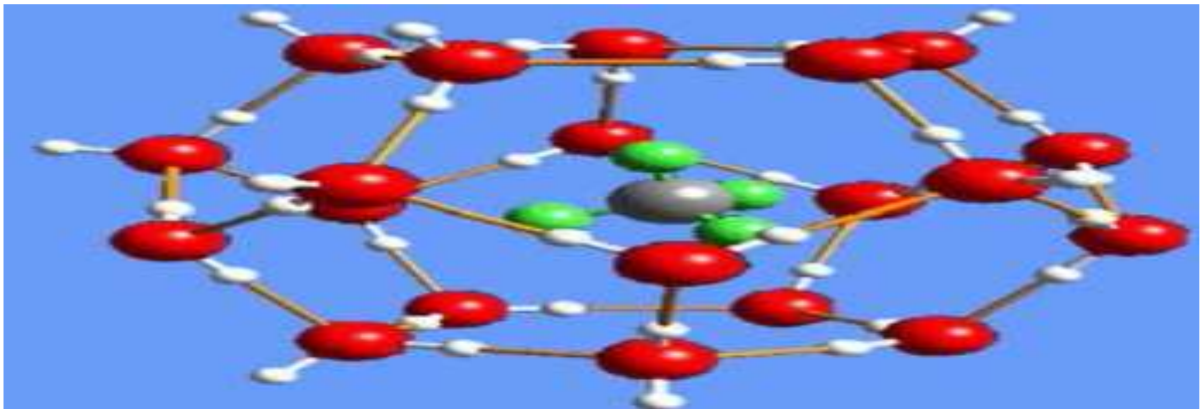


Fig. 3: Cage-Like structure of gas hydrate
(Azeez G. Aregbe, Institute of Oil and Gas Engineering, University of Lagos, Lagos, Nigeria)

Gas hydrates were collected in six-meter piston cores during surface geochemical exploration (SGE) surveys in the deep and ultra-deep-waters of Nigeria during 1991, 1996, and 1998. To date, gas hydrates have been collected in about 21 cores out of the more than 800 core collections on the Nigerian margin. This represents a 2.5% recovery ratio of gas hydrated cores on this margin at sites that are potential conduits for the upward migration of hydrocarbons (i.e., the core locations are sited based on two- and three-dimensional seismic overfaults, mounds, acoustic wipe-outs, etc.). Unlike the Northern Gulf of Mexico where significant percentage of thermogenic hydrates have been retrieved in piston cores, all the gas hydrate collections offshore Nigeria to date are primarily biogenic in nature (methane more than 99% of the hydrocarbon gases; δ13C generally light, −60 to −117%). A few of these gas hydrated sites do contain a mixed thermogenic gas component (ethane to butane gases up to a few hundred ppm of total hydrocarbon gas) but even at these sites the primary gas in the hydrates is methane.

Gas hydrates have three distinct structural formations. Although all gas hydrates are either biogenic or thermogenic, they are classified into three structures. They are:

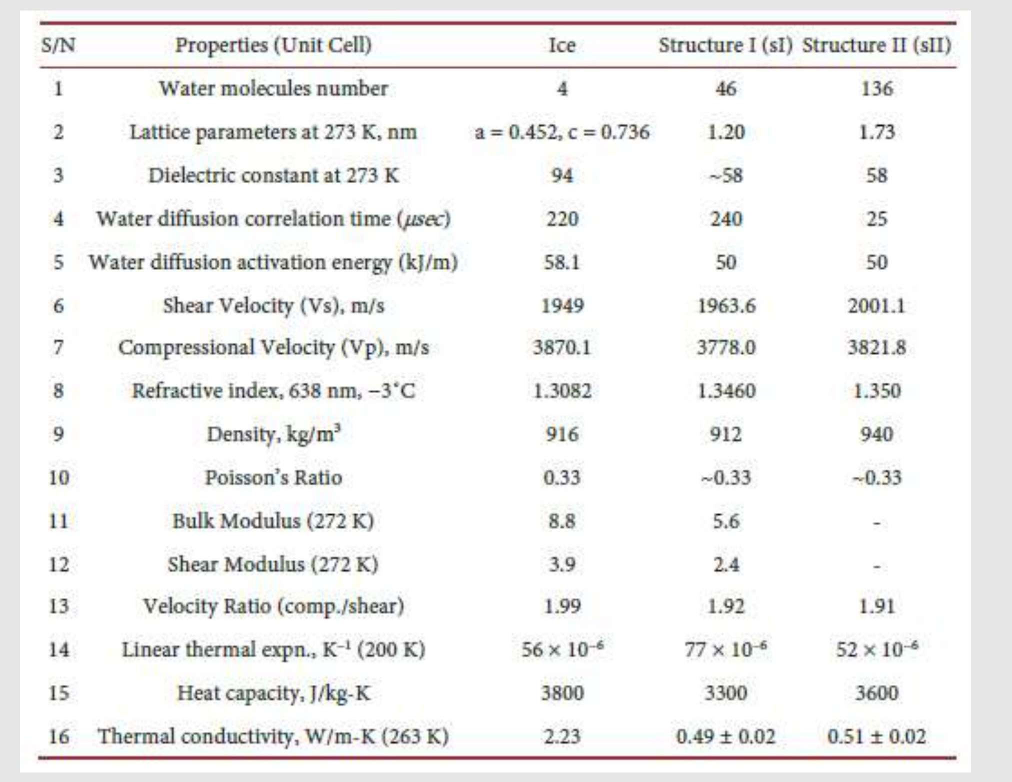
- Structure I (sI)
- Structure II (sII)
- Structure H (sH)

The structure I (sI) hydrates are body-centered cubic structures formed from small gas molecules and are usually found in deep ocean environments. They are formed from two different sizes and shapes of cage; small cages and large cages.

The Structure II (sII) hydrates have diamond lattices within cubic frameworks and are formed when natural gas or oil containing molecules larger than ethane but smaller than pentane. The structure II hydrates are usually found in oil and gas production and processing systems. They are also formed from two different shapes and sizes of cages.

The Structure H (sH) hydrates are the newest structure of gas hydrates discovered and was also found to occur in the Gulf of Mexico. The structure H hydrates have hexagonal framework and also possess cavities large enough to hold molecules as big as naphtha and gasoline.

Table 1:



S/N	Properties (Unit Cell)	Ice	Structure I (sI)	Structure II (sII)
1	Water molecules number	4	46	136
2	Lattice parameters at 273 K, nm	a = 0.452, c = 0.736	1.20	1.73
3	Dielectric constant at 273 K	94	~58	58
4	Water diffusion correlation time (μsec)	220	240	25
5	Water diffusion activation energy (kJ/m)	58.1	50	50
6	Shear Velocity (Vs), m/s	1949	1963.6	2001.1
7	Compressional Velocity (Vp), m/s	3870.1	3778.0	3821.8
8	Refractive index, 638 nm, −3°C	1.3082	1.3460	1.350
9	Density, kg/m^3	916	912	940
10	Poisson's Ratio	0.33	~0.33	~0.33
11	Bulk Modulus (272 K)	8.8	5.6	-
12	Shear Modulus (272 K)	3.9	2.4	-
13	Velocity Ratio (comp./shear)	1.99	1.92	1.91
14	Linear thermal expn., K^{-1} (200 K)	56×10^{-6}	77×10^{-6}	52×10^{-6}
15	Heat capacity, J/kg-K	3800	3300	3600
16	Thermal conductivity, W/m-K (263 K)	2.23	0.49 ± 0.02	0.51 ± 0.02

Properties of sI, sII, and sH structures of gas hydrates

Gas Hydrate in the Niger Delta

Nigerian Margin Geological Setting

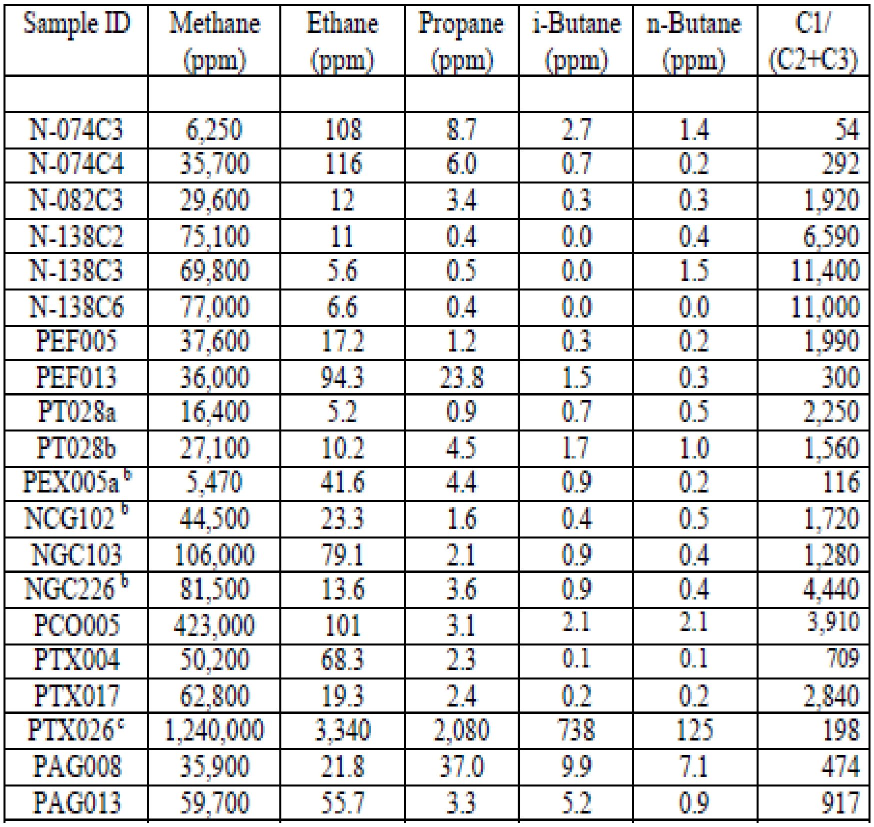
The Niger Delta occupies the central region of West Africa's Gulf of Guinea. With a land area of some 75,000 km^2 it forms the largest delta system in Africa. The delta owes its size to the focus provided by the Benue arm of the Niger Triple Junction for sediment delivery from interior Africa to the Atlantic Ocean. The modern delta began its growth in the late Eocene. Since that time the delta top, as defined by the 200-meter isobath, has prograded south and south-westwards from the Cretaceous shelf-edge hinge line some 300 km across previously deep-water settings. The distal edge of the delta lies some 80 to 170 km further seawards. The continental slope forms the intermediate region and has been the focus of SGE (Surface Geochemical Exploration) cores containing the hydrates reported here.

The Eocene and younger delta succession is divided into three younger units moving seaward. These are, from the bottom upwards, the Akata Formation, the Agbada Formation and the Benin Formation. The Akata Formation comprises deep marine shales and, as was predicted more than twenty-five years ago, deep-water sands. Shelf to paralic sediments define the Agbada Formation and the uppermost unit, the Benin Formation, consists of primarily non-marine, delta top sands and clays. Delta top loading has been sufficient to mobilize the Akata Formation clays and the entire 10-12 km succession is being actively displaced ocean-wards. The result is a generally clearly defined frontal toe thrust behind which are stacked clay cored diapir belts associated with the lateral translation of the delta slope towards the ocean.

Hydrate Origin and Gas on the Nigerian Margin

The nature of the hydrate gas offshore in Nigeria can be inferred from the examination of headspace gases obtained from the shallow piston cores.

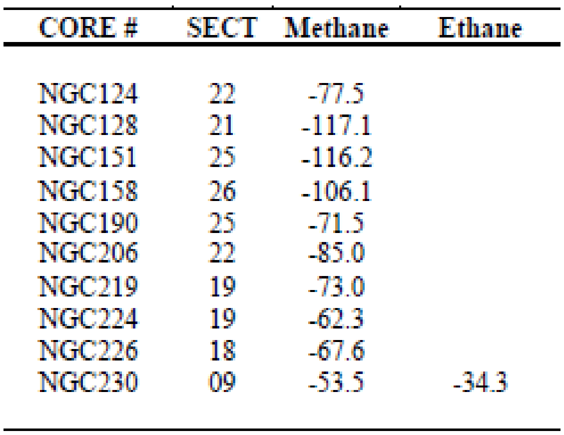
Table 2: *Headspace Gas Concentrations in Gas Hydrated Cores on the Nigerian Continental Slope*



Sample ID	Methane (ppm)	Ethane (ppm)	Propane (ppm)	i-Butane (ppm)	n-Butane (ppm)	C1/ (C2+C3)
N-074C3	6,250	108	8.7	2.7	1.4	54
N-074C4	35,700	116	6.0	0.7	0.2	292
N-082C3	29,600	12	3.4	0.3	0.3	1,920
N-138C2	75,100	11	0.4	0.0	0.4	6,590
N-138C3	69,800	5.6	0.5	0.0	1.5	11,400
N-138C6	77,000	6.6	0.4	0.0	0.0	11,000
PEF005	37,600	17.2	1.2	0.3	0.2	1,990
PEF013	36,000	94.3	23.8	1.5	0.3	300
PT028a	16,400	5.2	0.9	0.7	0.5	2,250
PT028b	27,100	10.2	4.5	1.7	1.0	1,560
PEX005a[b]	5,470	41.6	4.4	0.9	0.2	116
NCG102[b]	44,500	23.3	1.6	0.4	0.5	1,720
NGC103	106,000	79.1	2.1	0.9	0.4	1,280
NGC226[b]	81,500	13.6	3.6	0.9	0.4	4,440
PCO005	423,000	101	3.1	2.1	2.1	3,910
PTX004	50,200	68.3	2.3	0.1	0.1	709
PTX017	62,800	19.3	2.4	0.2	0.2	2,840
PTX026[c]	1,240,000	3,340	2,080	738	125	198
PAG008	35,900	21.8	37.0	9.9	7.1	474
PAG013	59,700	55.7	3.3	5.2	0.9	917

Table 2 above shows the headspace gas concentration in the cores containing the gas hydrates. Unless noted otherwise, the values are the average of three measurements in the bottom half of each core. The C1/(C2+C3) ratios indicate that the molecular compositions are mostly biogenic gas, although small thermogenic components might be present at locations with C1/(C2+C3) ratios less than 1,000. With one exception, methane makes up greater than 99% of the hydrocarbon gases. This is consistent with other headspace gas carbon isotopic ratios from high gas containing cans from these same Nigerian SGE surveys as shown in the table below.

Table 3: *Carbon Isotope Ratios of Selected Headspace Gases Offshore Nigeria (1998 Program).*



CORE #	SECT	Methane	Ethane
NGC124	22	-77.5	
NGC128	21	-117.1	
NGC151	25	-116.2	
NGC158	26	-106.1	
NGC190	25	-71.5	
NGC206	22	-85.0	
NGC219	19	-73.0	
NGC224	19	-62.3	
NGC226	18	-67.6	
NGC230	09	-53.5	-34.3

Table 3 above lists the carbon isotope values reported as d^{13}_{CPDB} ($^{o}/_{oo}$) measured in alkane gases of concentration greater than 500 ppmV in the headspace of the selected cans from the 1998 program. The data in the table with values more negative (lighter) than -100 $^{o}/_{oo}$ represent cores that contain only biogenic gas. Whereas thermogenic gas is typically represented by d^{13}_{CPDB} of methane from -40 to -50 $^{o}/_{oo}$, values between -50 to -85 $^{o}/_{oo}$ are routinely observed in sediment gases with higher-than-biogenic levels of C2+ alkane gases. We interpret these sites as having some component of thermogenic gas mixed with predominately biogenic gas. This small component of thermogenic gas does not change the basic biogenic nature of the gas hydrated cores. The distribution of the alkane gases obtained from ~230 cores taken in the ultra-deep water (generally >1,500 meters water depth) is shown above. The figure illustrates that 92% of the samples contain sediment light hydrocarbon alkane gases totaling less than 100 ppmV. Concentrations ranging from 1 to 100 ppmV total alkane gases in these marine sediments are considered background, with the predominant hydrocarbon gas being methane in all samples. Table 2 shows that of the remaining 8% (55 total) "above-background" samples, 36 contain alkane gases totaling 100 to 1,000 ppmV and 19 more contain alkane gases totaling more than 1,000 ppmV. Light hydrocarbon concentrations greater than 100 ppmV may be indicating upward migrating thermogenic gas.

Figure 4: Hydrates in the industry today

Applications

Gas hydrate reserves are abundant and can ultimately become a sustainable energy resource in Nigeria and all over the world. These hydrate reserves hold significant amount of energy that is estimated to be more than twice the combined carbon of coal, conventional gas and petroleum reserves. The knowledge gained from the study of properties and formation of hydrates are paramount to the efficient and effective exploration and development of hydrate reserves. Gas hydrate are stored at equilibrium conditions with either its saturation temperature or pressure as the key parameter. The factors that determine the optimum/limiting pressure and temperature are cost and weight of hydrate storage vessel. The stored gas can be used in the future and for peak-shaving applications to obtain a higher price for the natural gas as well as to ensure adequate natural gas supplies during periods of peak usage. Peak-shaving application is storing natural gas when natural gas demand is low, then selling the natural gas during periods of high demand. The possibility of storing and transporting natural gas as either gas hydrate solid or slurry was also considered. The slurry form of transport is usually a better option for distances of approximately 2500 miles or less while the solid form is suitable for distances of roughly 3500 miles or more. Hydrate can serve as a sustainable energy resource and a means of storing and transporting natural gas from one end to the other. This will create an effective and efficient alternative for bulk gas transportation and storage for future use of the gas. Natural gas transportation as LNG is more economical because the shipping costs for gas hydrates are much higher than the shipping costs for LNG and for high transportation distances. The costs for shipping gas hydrates are high because for every ton of natural gas shipped, 6.5 tons of water, which generates no revenue, is also shipped. But for low transportation distances and low production capacities the costs for shipping gas hydrates are lower than the costs for the entire LNG process.

Conclusion

From the study above, gas hydrates have been seen to be abundant in nature in the Niger Delta and the world at large. The Niger Delta continental depth has a large deposit of clathrates which are biogenic and of the alkane group. Methane being the primary gas in the hydrates found in this region. Gas hydrates have not been seen or studied to be energy resources in Nigeria. Due to the abundant nature of these hydrates and its energy level estimated to being more than coal and conventional petroleum combined, gas hydrates could prove to be the next big thing in the energy industry. Apart from the energy giving nature of gas hydrates, its clathrate nature makes it a good mode and method of transporting and storing natural gas.

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