

Hydrates-a Novel Concept for Plugging Deep-Sea Severed Pipeline

Proposed Scenario for BP Gulf of Mexico Spill

By

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The disastrous event of British Petroleum (BP) pipeline spill in the Gulf of Mexico on April 20th 2010 has resulted in death, ongoing devastation of gulf environment, thrashing resources and threatening of life and welfare of thousands of gulf residents. Many attempts have been made to stop this spill. Thus far, all attempts have little or no effect. MIK technology of Houston proposes a new novel concept that is worth trying. It is based on sound scientific principals and would cost a small fraction of what has been spent on fabricating those massive containment chambers. Ironically, it is the same concept that caused those containments to fail on May 9th!

What is hydrate?

Hydrate is a term used in chemistry to indicate that a substance contains water. Generally compounds are formed by the union or linkage of water with some other substance. However, the chemical state and molecules assembly of water varies widely between hydrates.

Solid hydrates are compounds which have water in the form of H₂O molecules associated with these compounds. As an example, anhydrous (water free) copper sulfate, CuSO₄ is a gray-white solid. When this chemical is dissolved in water and allowed to crystallize, it produces beautiful translucent blue hydrous solid crystals, which contains water molecules as part of the crystals.

Laboratory analysis reveals that copper sulfate crystal comprises five water molecules, where four molecules are attached to the copper ion in the manner of coordination complexes. The fifth molecule is held to sulfate, presumably by hydrogen bonding. The chemical formula of this crystal is copper sulfate-pentahydrate, CuSO₄ · 5H₂O. Many compounds form one or more hydrate. As an example, lithium chloride, a refrigerant, has 4 hydrates LiCl·H₂O, LiCl·2H₂O, LiCl·3H₂O, and LiCl·5H₂O.

Gas hydrates, also known as clathrate or clathrate hydrates, are crystalline compounds in which an isometric (cubic) H₂O ice lattice of atoms, ions, or molecules are formed by hydrogen-bonded water molecules that interconnect to form polyhedral cage-like structures. Those structures are capable of encapsulating foreign hydrophobic molecules in their cavity. Cages are often built up by pentagonal and hexagonal faces forming different polyhedrons that are impelled by trapped small gas molecules within their cavities.

The lattice of cages is stable at high pressures and low temperatures, providing that these cages contain gas molecules. Conventionally, the gas molecules are considered as guests and the water molecules as hosts. Several gas molecules have the potential to form hydrates such as nitrogen, carbon dioxide, sulfur dioxide, methane, butane, ethylene and many other hydrocarbon gases.

Gas hydrate formation requires availability of five factors; water, gas, high pressure, low temperature and nucleation sites. Stability of hydrates depends on maintaining low temperature, slightly above water freezing point and high pressure of many atmospheres. Deep seabed is an ideal environment for hydrate stability.

Hydrate blockages are major flow problem in offshore and Arctic (permafrost) operations. They can form in subsea transfer lines, high residence time pipelines, gas expansion across valves due to cooling effect, etc. Hydrate formation is also common in hydrocarbon gas transmission lines such as ethane, propane and ethylene that are operating under low temperature environment.

The recent BP failing attempt to place a containment chambers on their severed oil pipe in the Gulf of Mexico is a vivid example of equipment failure due to formation of hydrates. The author of this article had extensive involvement with hydrate blockage of a large ethylene transfer pipeline from salt dome storage to a polyethylene production plant tens of miles away, which resulted not only in plugging the transfer line but also plugging of several unit operations and caused major facility shut down for many days.

The rate of hydrate formation is strongly influenced by gas injection rate and pressure. Hydrate growth is more likely to occur at the interface between gas and water. It is dominated by gas-liquid mass transfer. The driving force is gas concentration at the gas-liquid interface, at the hydrate crystal surface. Gas concentration corresponds to the solubility of gas in water at the prevailing temperature and pressure conditions. The author believes that fresh water allows for higher gas solubility than seawater; therefore, it is recommended for the proposed pipe plugging applications. Salinity has been shown to impact hydrate growth and induction time. Hydrate ceases to form when sodium chloride concentration approaches 14% (Birkedal 2009).

Hydrate structures and hydrate formers:

The hydrate lattice structure can take on different forms, the two most common forms are Structure I (sI) and Structure II (sII). Hydrate structures are composed of different combinations of cages type and size, and consequently may be stabilized by different hydrocarbon molecules. The structural feature common to all clathrate hydrates is the pentagonal dodecahedron 5^{12} of water molecules. It has 12 regular pentagonal faces, 20 vertices, and 30 edges. Figure 1 illustrates the basic hydrates structures.

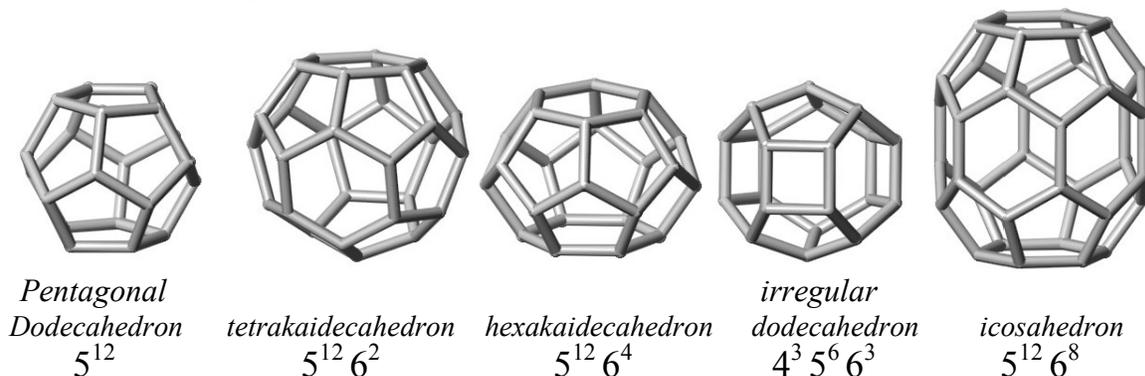


Figure 1: Hydrate Structures and Types

Table 1 describes the different hydrate structures, number of cages (cavities), cage size and water molecules forming each structure.

Hydrate Crystal Structures	I		II		H		
	<u>Small</u>	<u>Large</u>	<u>Small</u>	<u>Large</u>	<u>Small</u>	<u>Medium</u>	<u>Large</u>
Cages (cavity) size	5^{12}	$5^{12} 6^2$	5^{12}	$5^{12} 6^4$	5^{12}	$4^3 5^6 6^3$	$5^{12} 6^8$
Description							
Cages per unit cell	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.94	4.04	5.79
Water molecules per cell	46		136		34		

Table 1: Properties of different hydrate structures. (Derived from Sloan and Koh, 2008)

Type I: Hydrate formers (guests) include: methane, ethane, carbon dioxide, and hydrogen sulfide. Type I hydrates are made up of 8 polyhedral cages; 6 large ones and 2 small.

Type II: Hydrate formers include: propane and isobutane, however, nitrogen which is relatively a small molecule can form a Type II hydrate. Type II hydrates are made up of 24 polyhedral cages; 8 large ones and 16 small. Figure 2 simulates 4 cages methane hydrate of type sII formed of 2 large and 2 small cages.

Type H: Ripmeester et al -1987 have described a new hydrate structure, called structure H (sH), which has three sizes of cavity. Hydrates are formed by larger molecules but only in the presence of a smaller molecule, such as methane. Presence of both the large and small molecules is required. Type H hydrates are made up of six polyhedral cages; 1 large, 3 medium and 2 small. The large molecule occupies the large cage and the small molecule occupies the small and medium cages. Type H formers include: 2-methylbutane, methylcyclopentane, methylcyclohexane, and cyclooctane.

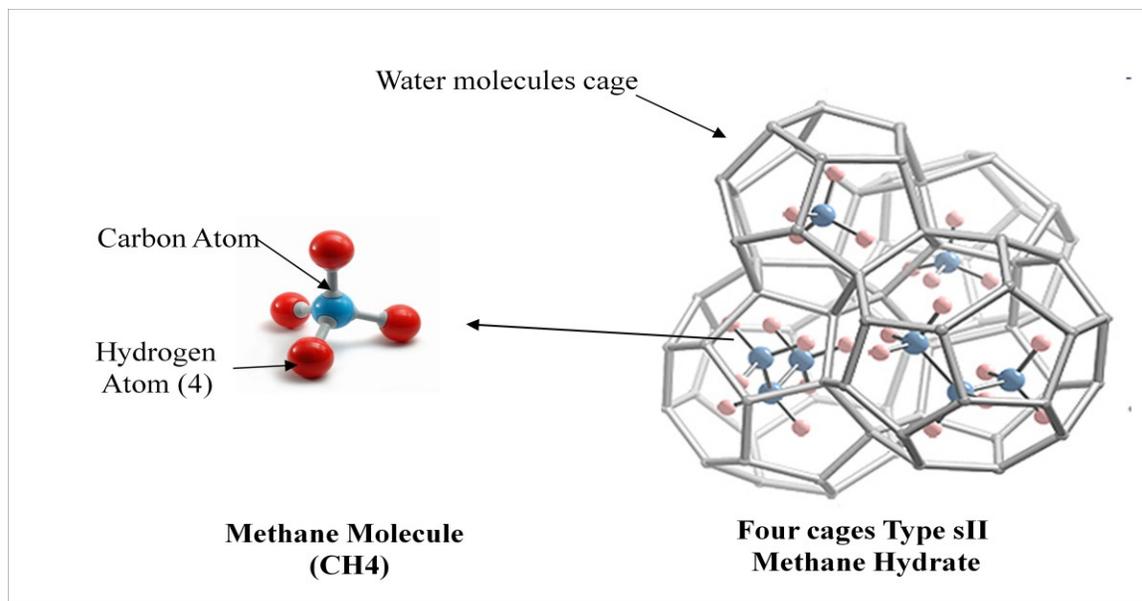


Figure 2: Methane hydrate Type sII (Derived from Janda's Group)

Laboratory experiments (Edmonds et al -1998) indicate that sII hydrate will always be formed first from any gas or gas condensate composition that might occur naturally. Structure H hydrates will only form if there is sufficient water present and if all the sII forming components have been depleted.

Until recently it was assumed that heaviest molecule that resides in the large cavity of sII would be butane. Anything heavier was a non-hydrate former. However, recent investigation (Tohidi, et. al-2009) has identified heavier hydrocarbons, found in oil and gas condensate systems would act as formers. Those hydrocarbons have an effective van der Waals diameter, which would allow them to enter the large cavities of structure sII gas hydrates. It has been proved that several cyclic hydrocarbons will form hydrates with small help gases, such as methane or nitrogen in the small cavities.

Figure 3 is an interesting video entitled “Microsecond Simulations of Spontaneous Methane Hydrate Nucleation and Growth “(Matthew R. Walsh-2009)

http://www.sciencemag.org/content/vol0/issue2009/images/data/1174010/DC1/1174010_movieS2a.mpg

Figure 3: Simulations of Spontaneous Methane Hydrate Nucleation and Growth

Methane (CH₄) hydrate is the dominant natural gas hydrate on earth. One cubic meter of methane hydrate when dissociated can contain 165–180 cubic meter of methane gas. The total amount of methane in gas hydrates is estimated to be very large; about 10¹⁶ cubic meter of methane-carbon is stored in them, or about twice the amount of fossil fuels. Many researchers believe this is a new abundant source of energy. However, others believe that the global warming may destabilize the enormous quantities of methane hydrate in shallow marine slope sediments in massive emission of carbon to the atmosphere.

Hydrate Formation Proposal:

Since the explosion and destruction of BP’s Horizon exploration platform and the consequent collapse and failure of the seabed piping system on April 20, 2010 the company avoids disclosing detail technical causes of failure of this \$650 million installation. Since this disastrous incident is in litigation, it is expected that the company will be tightlipped. Therefore, individuals and entrepreneurs who thrive to seek information and thrill to find answers to help in resolving resolve this catastrophe have to rely mainly on their ability to reconstruct all events, hypothesize failure causes and logically visualize scenario to mitigate problems.

MIK Technology in their attempt to find a solution to plug BP severed pipeline or any other line that have same consequences, is promoting a new novel approach that is environmentally innocuous, risk limited and cost manageable, employing the media available in the theater of operation.

The concept is based on generating gas hydrate in the severed line and allows it to accumulate until it plugs it! How can we do this? The attached drawings shows the primary leak that resulted in the explosion of BP platform and the collapse of the riser pipe between the platform and the blowout preventer (BOP). As well as the proposed containment chamber that has failed on May 9th due to hydrate plugging. The severed pipeline is 21 inches in diameter and about 5000 feet in length, which is the distance between the platform and the BOP.

Referring to Figure 4, MIK Technology concept is based on introducing fresh water at the severed end of the pipeline to form methane hydrate that potentially could plug the leaky line. A 3 inch water pipe will be inserted through the broken line to the first obstruction; valve or line bend.

Based on recent video and photos published by BP in early May 2010, we estimate the flow velocity to be at a rate of 2 feet per second. However, it appears that a relatively large amount

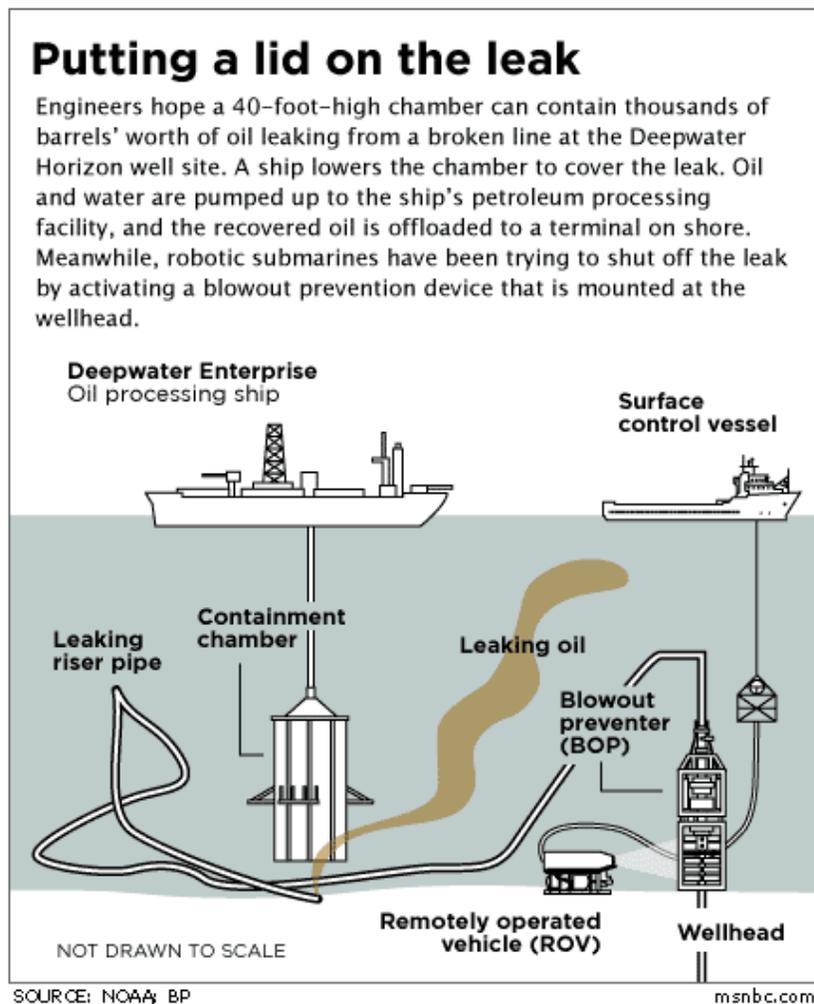


Figure 4: Relative equipment and pipe line

of natural gas is present in the oil that gives the impression of much larger flow and can easily skew estimates. At the seabed, the density of natural gas, mostly in methane form, is just less than 10% of the oil density. As soon as the gas is released from the damaged line, it tends to expand and rise much faster than the accompanying oil. This gives the impression that more oil is being leaked than what is actually happening. We feel the leak could be about 5,000-10,000 barrels per day through the severed end of the pipe.

Water could be introduced at a rate of up to 2 gallon per second at a gradually controlled and monitored process. Considering the depth of the operation and the low temperature of the sea bed (estimate is at about 2200 psig and 40 F respectively), the potential of generating hydrate type SI and SII is feasible and could happen in a few hours. The type of hydrates that could be formed is methane hydrate and this based on BP observation that the oil flow contains appreciable amount of natural gas. The rate of hydrate formation is dominated by gas-liquid mass transfer and therefore, proper mixing of water with incoming oil is required.

Based on current research, mixing propane (25%) with natural gas (75%) improve stability of Type sII hydrate. This means that hydrate can be also be formed at relatively lower pressure or slightly higher temperature. Under the current operating pressure and seabed temperature, propane will be in compressed liquid phase that makes it easier to blend with pipeline oil and gas content. Propane has to be introduced in a separate pipe parallel with the water line and discharged from the line preferably at a point ahead of water discharge point to allow for better mixing with oil. Both the water and propane lines could be gradually withdrawn out of the pipe in proportion with the observed reduction of the discharged oil from the severed pipe.

[This concept was presented to BP \(case #319487\) on May 15, 2010 in response to BP call for soliciting ideas on how to mitigate BP Gulf spill.](#)

In fact we believe that by no means this is the total flow of the well and it is assumed that the blow-out preventer (BOP) is still partially engaged in controlling the flow. Otherwise, we could see a jet of oil extend several feet at much greater flow than what is observed. Looking to the half filled cub, we should be thankful that we have a major spill and a not major national calamity, particularly during the coming hurricane season.

Current BP Spill Control Activities

At that time, we were under the impression that this severed riser pipe leak is the only major leak. Figure 5 shows an actual picture of a deflected flanged bonnet on the top of the blowout preventer (BOP) with several twisted piping. Obviously, this could be as a result of the riser pipe collapsing on the seabed and the severe tension that might have been created, causing the deflection of this bonnet. However, the picture reflects one important fact. There are no obvious spills or leaks of any kind at that time!

On 04/29/2010 – 10:50 am PDT, Green Car Congress reported that “BP, in its monitoring of Deepwater Horizon’s blowout preventer (BOP) on the floor of the Gulf of Mexico, has identified a third leak in the riser of the deep underwater well, according to Doug Suttles, chief operating officer for BP Exploration and Production, during a press conference on the incident response held 04/28/2010. US Coast Guard Rear Adm. Mary Landry, the federal on-scene coordinator for

the Deepwater Horizon Response unified command, said that the US National Oceanic and Atmospheric Administration (NOAA) now estimate that as much as 5,000 bpd could be flowing from the riser”.

On May 12, 2010, 8:23 PM, Jonathan Tilove, New Orleans Net LLC, Nola.com, reported about Deepwater Horizon glitches before explosion in Gulf of Mexico that got House panel's attention” The failed blowout preventer on the Deepwater Horizon oil rig had a hydraulic leak and a dead battery in one of its control pods, and testing in the hours before an April 20 explosion revealed that pressure in the well was dangerously out of whack, a House committee investigating the disaster in the Gulf of Mexico said Wednesday”

Then, on May 15, BP published a disturbing video Figure 6, showing the same riser pipe leaving the (BOP) bonnet, but spewing oil profusely. The bottom of the damaged and leaking marine riser sits atop the failed blowout preventer on the floor of the Gulf of Mexico. The main tube of the riser pipe guides the drill pipe into the well, while the other pipes carry hydraulic fluid to operate the blowout preventer. A video of this event can be watched on the following site. (http://www.nola.com/news/gulf-oil-spill/index.ssf/2010/05/new_oil_spill_videos_released.html)

The question now, what has happened before April 29, 2010 and after April 29, 2010? Is this another manmade mishap?



Figure 5: BOP before 4/29/2010



Figure 6: BOP after 4/29/2010

On Friday, May 21, 2010, Greg Bluestein with the associated Press reported that BP spokesman Tom Mueller said there was no snag in the preparations, but that the company must get equipment in place and finish tests before the procedure can begin. BP already has three deepwater rigs and other equipment near the blown-out to shoot heavy mud in the BOP to plug the oil well.

A so-called "top kill" has been tried on land but never 5,000 feet underwater, so scientists and engineers have spent the past week preparing and taking measurements to make sure it will stop the oil that has been spewing into the sea for a month. They originally hoped to try it as early as this weekend.

It will be at least Tuesday before engineers can shoot mud into a blown-out well at the bottom of the Gulf of Mexico; BP said Friday in yet another delay in the month long effort to stop the oil

that is now washing into wetlands and onto at least one public beach. Crews will shoot heavy mud into a crippled piece of equipment atop the well, which started spewing after the drilling rig Deepwater Horizon exploded April 20 off the coast of Louisiana, killing 11 workers. Then engineers will direct cement at the well to permanently stop the oil. Figure 7 is a schematic of the blowout preventer and project plan to pump mud.

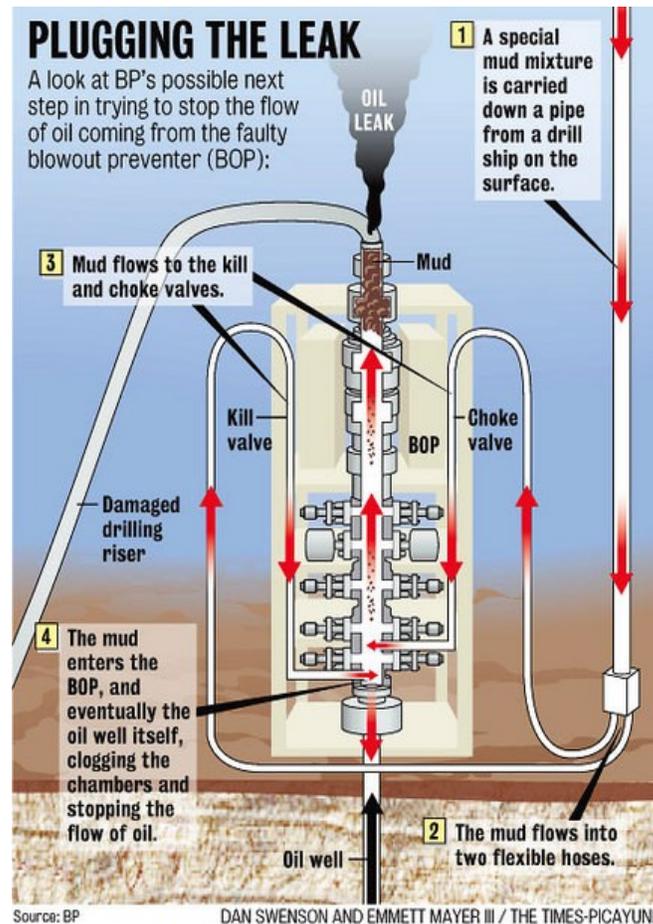


Figure 7: Blowout Preventer and projected Mud Pumping Plan

Conclusion:

We hope that BP has the technical know-how, prudence and wisdom in this trying time to manage their disaster recovery plan. Despite the large spill we are experiencing, it appears that the blow-out preventer (BOP) is still partially restricting the flow. Otherwise we could see much greater flow than what we have observed in the month of May. Instead of this disastrous spill, we might get a national calamity, particularly during the coming hurricane season.

The question now, what will happen if the so-called Mud Top Kill didn't work and we end with a completely failing blowout preventer? We hope that BP doesn't push us to this gloomy destiny.

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