Hydrate formation and its influence on natural gas pipeline internal corrosion

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PRELIMINARY COMMUNICATION

This study establishes the ability of hydrate formation to initiate internal corrosions along natural gas pipelines. The identified corrosion types, which are cavitations, erosion and corrosions by chemical reactions, are capable to individually or collectively initiate pitting and stress cracking corrosions which are also dangerous to gas pipelines. The impacts of these corrosion types are classified to economics, environmental and human loss with the economic loss as much as US$3 trillion depending on the pipe-length, location, sea depth, wave function, climatic conditions and political situations.
Various predictive measures to minimize hydrate formations are finally recommended.

Key words: natural gas, pipeline, hydrate formation, internal corrosion, economic, environment

1. INTRODUCTION

The global demand and utilization of natural gas and its major component (methane) is in the increase due to its abundant availability coupled with its environmental friendliness compared to other fossil fuels. Its composition varies from field to field and region to region (Table 1). The gas is utilized domestically and industrially. Domestically, it is used for heating buildings and water, cooking, drying, and lighting.[10,33] Home appliances running on natural gas include furnaces, barbecues, fireplace logs, pool and spa heaters, and fire pits. Natural gas air conditioning also exists, though; this is not as popular as the electrical alternative. Industrially, the gas is a major source of electricity generation.[67,73] As an efficient and convenient fuel, the gas is used in developed countries such as Australia, Canada and most European countries in transportation sector to run cars, trucks and heavy duty service vehicles[35,10], while the current research in the aviation industry is targeted at designing aircrafts using natural gas as fuel.[23,24,26] Also, the gas plays a significant role in the power plant technology.[46,59] Natural gas is used in the making of anti-freeze and plastic. Food processing industries essentially use the gas to power up their plants while waste treatment and petroleum refining are also recognised consumers of natural gas. The gas is also useful in the production of petrochemicals.

The gas is globally abundantly available. In 2000, the total world reserve and production of the gas were 150.19 trillion m^3 and 2.4223 trillion m^3 respectively.[75] Russia, with the global highest oil and gas reserves put at 11 billion m^3 (69.1 billion barrel) and 48.14 trillion m^3 respectively (representing 38% of global natural gas reserve) is the major producing nation[24] while United States gas demand for 2003 alone was estimated at 786.32 billion m^3 (27.8 trillion ft^3).[27] Australian conventional gas reserve as at 2006 was 2.43 trillion m^3 (86 trillion ft^3)[14] while gas demand of the EU 15 is projected to be 420-650 bllion m^3 and 610-900 billion m^3 by 2010 and 2020 respectively (Table 2). In 2007, more than 1.02 trillion m^3 of natural gas was transported by interstate pipeline companies in USA on behalf of shippers to the consumers (Railroad Commission of Texas, 2008) while the 2009 national total capacity is about 5.18 billion m^3 (183 billion ft^3) with two-thirds of the lower 48 States almost totally dependent upon the interstate pipeline system for their supplies of natural gas.[18]

Table 1. Natural gas compositions from different gas fields

	Molar composition (%)										
Chemical Composition	Utorogu Nigeria	Kokori Nigeria	Burgan Kuwait	Kirkuk Iraq	Uthmaniyah S. Arabia	Hassi R'mel Algeria	Ekofisk Norway	Kapuni N.Zealand	Uch Pakistan	Lacq France	Groningen Netherland
Methane	90.19	68.42	74.3	56.9	55.5	83.7	83.3	45.6	27.3	69.0	81.3
Ethane	6.94	7.65	14.0	21.2	18.0	6.8	8.5	5.8	0.7	3.0	2.9
Propane	2.09	11.27	5.8	6.0	9.8	2.1	3.4	2.9	0.3	0.9	0.4
Butane	0.775	8.42	2.0	3.7	4.5	0.8	1.5	1.1	0.3	1.0	0.1
C_{5+}	0.012	2.67	0.9	1.6	1.6	0.4	1.0	0.8	-	-	0.1
Nitrogen	-	0.16	2.9	-	0.2	5.8	0.3	-	25.2	1.5	14.31
Hydrogen sulfide	-	-	0.1	3.5	1.5	-	-	-	-	15.3	-
Carbon-dioxide	-	1.02	-	7.1	8.9	0.2	2.0	43.8	46.2	9.3	0.9

Table 2. Summary of some European gas demand scenarios (billion m^3)

	1999	2010	2020
EU 15 [a]	386	500	597
EU 30 [a]	462	642	777
EU 15 [b]	386	420 - 650	533-650
EU 30 [c]		580 - 690	610-900

Sources: [a] OME (2002); [b] IEA (2001); [c] Stern (2001)

Notes:

EU 15 = Austria, France, Belgium, Greece, Germany, Italy, Luxembourg, Netherlands, Portugal, Spain, Ireland, United Kingdom, Denmark, Sweden, Finland.

EU 30 = EU 15 + Turkey, Bulgaria, Greece, Rumania, Czech Republic, Hungary, Poland, Slovakia, Slovenia, Estonia, Latvia, Lithuania, Norway, Switzerland.

Due to its rising global demand, several onshore and offshore inter-state and transboundary natural gas pipeline networks are being constructed with each transporting millions to billions m^3/d with construction cost running into several millions or billions of US dollar (Tables 3 and 4). Nigeria is presently constructing a $550 million pipeline of 617 km offshore pipeline and 57 km onshore pipe-length to transport 11.3 billion m^3/d (399.8 billion ft^3/d) of natural gas to power generators and industrial consumers in Ghana, Benin and Togo for thermal and industrial uses (Figure 1) while Australia is also involved in an on-going Gorgon project of over $50 billion.[59]

1.1 Natural Gas Production and Transportation

Natural gas exists in the reservoir as a non-associated, associated (or solution) or gas-cap gas. The non-associated gas is the one without a contact with oil, the solution gas is the one where the gas dissolves in the oil at the reservoir conditions whereas, the gas cap is the gas overlying the oil phase in the reservoir. Of the three groups, non-associated gas represents 72% of the available global reserves while solution and gas-cap gases are 8.5% and 9.5% respectively.[76] It is located thousands of meters in the ground with the fluid's pressure in the pores of the rocks ranging between 10 MPa/km while in hydrostatic regime (only supporting the weight of the overlying fluid column) to 25 MPa/km in geostatic regime (supporting all or part of the weight of the rock column).[64] The gas molar mass and density at standard temperature and pressure are 19.5 g and 0.862 kg/m^3 respectively while

Table 3. Various interstate pipeline projects, their diameter and length

Project name	Country	Start Point	End Point	Diameter (in.)	Length (km)	Capacity	Cost
	Australia	Ballera	Wallumbilla	16	293		
	Australia	Bayu Undan field	Darwin	24	187	2 250 bbl/d	A$1.5 billion
Eastern Gas Pipeline	Australia	Longford	Sydney	18	312		
	Australia	Darwin	Moomba		3 500	-	
	Australia	Bunbury	Albany		320	-	
	Australia	Darwin	Dunbury		1 530	-	
Tasmania Natural Gas Pipeline (Offshore + onshore)	Australia	Longford, Victoria	Bell Bay, Tasmania	14	734		A$350 million
Gove Lateral	Australia	Moreton Cape York	Weipa	16	670		
PNG-Qweensland Project		Torres Strait (Papua New Guinea)	Gladstone (Australia)		816		
Enbridge Phase 5 (2007)	USA	Black Horse Corners Gate (North Dakota)	Route Segment E North Dakota	42	83.2	30 000 bbl/d	US$78 million
Enbridge Phase 6(2009)	USA	Western End	Minot, n.d.	22 – 24	1050	40 000 bbl/d	US$150 million
Enbridge Phase 6 (2009)	USA	Minot	Clearbrook, Minn.			51 000 bbl/d	
Pathfinder (Proposed)	USA	North Border Pipeline	Moyes, Minnesota and Emerson		440		
Pathfinder Natural Gas (on-going)	USA (2008-2010)	Wamsutter, Wyoming	Markets at Midwest	42	800	2.0 billion ft^3/d	
Bison (On-going)	USA (2008-2010)	Rookies Mountain Area	Markets at Midwest and Chicago	36	1 076.8	Over 610	
Pathfinder	USA	Meeker Colorado	Wamsutter	30	225		
Escravos – Lagos Pipeline System	Nigeria	Escravos Warri	Alagbado Lagos	24	359	2.7 billion ft^3/d	
WAGP	Nigeria	Alagbado Lagos	Badagry Lagos	30	57		
WAGP	Ghana	Takoradi	Effasu	12	80		

Table 4. Various global transboundary natural gas pipeline projects

Project name	From (Start Point)	To (End Point)	Diameter (inches)	Length (km)	Nature	Capacity	Cost USD
PNG-Qweensland Project	Kubutu (Papua New Guinea)	Gladstone (Australia)	16	1 195	Onshore/ Offshore (Gas)		
Keystone XL pipeline (2008)	Alberta Canada	Nebraska USA	36	3 200	Onshore/ Offshore	1.1 million bbl/d	12 billion
WAGP Project	Lagos Nigeria	Takoradi Ghana	Vary with portion	674	Offshore	11.3 billion cmpd	550 million
	Nigeria	Cotonou Benin	20	51	Offshore		
WAGP 2009	Cotonou Benin	Lome & Tema Togo	16	276	Offshore	3.39 billion m^3/d	130 million
WAGP 2009	Tema Togo	Takoradi Ghana	12	233	Offshore	1.7 billion m^3/d	106 million
BTC Pipeline 2004	Baku Azerbaijan	Ceyhan Turkey		1 572	Offshore		3.6 billion
Subsea Gas Pipeline 2004	Sangachal Terminal Azerbaijan	Central Azeri Georgia	28”	186	Offshore		

Fig. 1. Nigeria to Ghana WAGP Project with Laterals at Cotonou, Lome, Tema and Takoradi.
Source: Obanijesu and Macaulay (2009)
Sl. 1. Projekt WAGP (West Africa Gas Pipeline) od Nigerije do Gane s lateralnim odvojcima Cotonou, Lome, Tema and Takoradi
Izvor: Obanijesu i Macaulay (2009.)

(Table 5) shows its thermodynamic properties at normal temperature and pressure.

In addition to methane gas, natural gas from the reservoir contains other hydrocarbons such as ethane, pentane, butane and heavier hydrocarbons in low concentrations. It may also contain water, carbon-dioxide, hydrogen sulphide as well as nitrogen, helium, hydrogen or argon and occasionally, metallic contaminants such as mercury and arsenic. This compressible hydrocarbon is detected in a reservoir by sensors which are geophones for onshore reservoir or hydrophones for offshore based on the analysis of the reflection of elastic waves transmitted by the seismic source gathered on a surface marking the boundary between two layers of different acoustic impedance.

For the onshore located reservoirs, the reflection is generated by the use of explosives. However for offshore reservoirs, air guns are used to discharge compressed air into the water. Alternatively, steam guns or the use of air wave emission by electric discharge into the sea water are used. These will propagate pressure (p) or shear (s) waves which propagate the reflections at different velocities. The reflection of the waves on impedance discontinuities is used to obtain the structural image of the geological layer. The discovered hydrocarbon is then produced using a rotary drilling technique. The well is then completed after acquiring wireline logs to measure the formation's characteristics and fluid in place.

The casing packer and some safety devices (storm choke at downhole or surface-controlled subsurface safety valve near the surface) is then installed before installing the Christmas tree. Finally, pipelines are connected to transport the gas off the field over a long distance to a flowstation for various separation operations as required based on the composition after which

Table 5. Natural gas Thermodynamic properties at normal temp and pressure (293 K, 1 atm)

MW	Density (kg/m^3)	R (Gas constant) (kJ/kg·K)	C_p (kJ/kg·K)	C_v (kJ/kg·K)	$C_p/C_v = \gamma$
19.5	0.8034	0.426	2.345	1.846	1.27

Source: Roymech (2009)

various products are transported through another set of pipeline networks to various end users. Offshore gas wells run from various depths depending on the depth of the water. The waters are generally classified as shallow or deep water. While Sangachal gas terminal pipeline was laid by a pipe-lay barge at 200 m (656 ft) water depth, the depth of the six East Azeri gas well range[5] from 4 000 m (13 123 ft) to 5 300 m (17 388 ft) while the design depth for the Shah Deniz well is 6 285 m (20 620 ft).

1.2 Natural Gas Transportation and Hydrate Formation

Various transportation options of natural gas from off-take include long pipelines transport, Liquefied Natural Gas (LNG), compressed natural gas (CNG) of pressure between 207 and 248 bar (3 000 and 3 600 psi) and methanol.[30] From these options, only long pipelines and LNG are in common use. The unit cost of pipeline option is clearly superior to that of LNG due to the required high cost of refrigeration and liquefaction of boiled-off liquids and the high risk of over-pressurization for LNG. Transportation by methanol and CNG demonstrate unit costs which are similar to pipelines but these are largely theoretical at present.

Raw natural gas components such as the low paraffinic homologous (C_1 - i-C_4), combined with the undesired components of the gas such as nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulphide (H_2S) and water vapour[1] to form gas hydrates during the gas transport which eventually plug pipelines. Gas hydrates are ice-shaped, crystal lattice, solid compounds formed by the physical combination of water molecules and certain small molecules in hydrocarbons fluid such as methane, ethane, propane and these undesired components[6] at high pressure and low temperature.[26,15,42] Water is of 90% composition of the hydrate lattice while other components constitute 10%.[1] The solid structure (Figure 2) consists of molecules of the gases of small molecular diameters trapped in the microcavities of a crystal lattice provided by the host water. The solid hydrate may be formed at high pressures and low temperatures (even above the normal melting point of ice) due to the weak Van der Waals forces and the hydrogen bonding properties of water.[31] Specifically, at 1 MPa (145 psi), ethane gas can form gas hydrates at temperatures below 4 °C (39 °F) whereas, at 3 MPa, (435 psi) it can easily form hydrate at temperature below 14 °C (57 °F).[71] Undersea gas transportation pipelines often have such thermodynamically suitable conditions for this formation.[54,43] Formed hydrates can block pipelines, subsea transfer lines and in the event of gas kick during drilling, hydrate can be formed in the wellbore riser, blow-out preventer and choke-lines. The resulted partial or complete plug of inner part of a gas pipeline if not quickly remove develops into high pressure build-up inside the pipe and eventual collapse thus, causing serious risk to the safety of operating personnel and equipment.

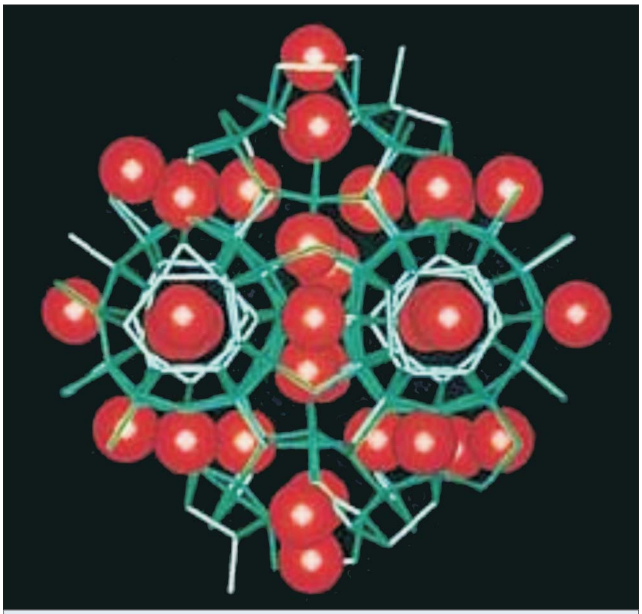

Fig. 2. An image of gas hydrate when formed inside a gas pipeline
Sl. 2. Slika plinskog hidrata formiranog u plinovodu

This collapsed pipeline releases the fluid content into the immediate environment, resulting into various environmental degradation problems. Failure to immediately remove the plug could also bring different difficulties and challenges to drilling and production parameter design, well control and riser design.[17,9]

In terms of cost implication, problems emanating from gas hydrates have been costing the petroleum industry billions of dollars annually and have led to various loss of production time amongst others. Hydrate formation along the natural gas pipeline has been identified as a serious threat to the survival of oil and gas industry. The formation is one of the most challenging aspects in flow assurance studies. This problem costs the industry billions of dollars to mitigate annually with no permanent solution in focus. Annually, a significant operating expense equal to hundreds of millions of US dollars is devoted to hydrate prevention with half spent on inhibition while offshore operations additionally spends approximately US$1 million per mile on insulation of subsea pipelines to prevent hydrates.[32]

All available studies on hydrate formation however have focused mainly on its ability to plug the pipe-length without a consideration of its ability to initiate corrosion, thus, undermining the magnitude of this problem to the industry and hence, the significance of this study. This paper identifies the ability of hydrate formation along the gas pipeline to initiate corrosion, the types of corrosion that could be initiated and the mechanisms, the consequences of the resulted corrosions and the need and means of preventing these corrosions by preventing or properly managing the hydrate from the formation stages to transportation. This work is important as it is able to bridge a knowledge gap by opening a new area of research interest on the implications of hydrate problems on natural gas industry. This new area of research interest is expected to attract more studies which will assist in reducing the havocs of hydrate on the industry.

2. HYDRATE FORMATIONS AS INITIATORS OF NATURAL GAS PIPELINE INTERNAL CORROSIONS

Hydrates can easily influence various types of natural gas pipeline's internal corrosion which is a long-term problem through physical and chemical processes based on the hydrate size, stage and the contact period to wear off the pipe's protection films.[52] H_2S, CO_2 and Cl^- that are components of hydrate are acidic gases which have been established to contribute to internal gas pipeline corrosion rate.[49,51] Methane, the major component of natural gas, as a reducing agent also aids metal corrosion.[80,46] Water is another known corrosive agent.[39]

At each stage of hydrate processes, interaction and reaction take place between the hydrate composition and the pipeline to eventually initiate internal corrosion. Apart from rupturing the pipe like hydrate, corrosion will further lead to gradual degradation of the material and deterioration of the pipe's integrity. Over time (after fixing the formation problem), the pipeline will begin to leak and/or may undergo full bore rupture (FBR).

This, apart from the economic consequences will also generate environmental and political consequences and will lead to complete replacement of the pipe-length at extra production cost.

The resulted corrosion eventually puts the pipe's integrity at risk with a replacement cost of which may be as high as $3 trillion.[20]

2.1 Corrosion Initiation through Physical Process

The corrosion types that could be initiated by physical means include cavitations, erosion, pitting, galvanized and stress cracking corrosions.[52] At different formation stages, the fluid goes from liquid to semi-solid and then to solid states. During each of these stages, a continuous interaction between the hydrate phase and the pipe wall initiate a type of corrosion as explained below.

2.1.1 Cavitation corrosion

At formation stages, the first stage is in a semi-solid state with the hydrate blocks having liquid inside the cavities. At this stage, it can easily break up at high impact with a surface. Cavitations corrosion (Figure 3) is caused by the collapse of bubbles formed at areas of low pressure in the conveyed fluid.[63] The fluid, traveling at a very high speed will experience a drop in pressure at a point of discontinuity in the flow path, especially, at the joints and bends. This will lead to the formation of gas or vapor bubbles (transient voids or vacuum bubbles) in the stream which implode upon hitting the metal surface and produce a shock wave sufficiently strong enough to remove the protective films. Corrosion is then greatly accelerated at this mechanically damaged surface by the reaction between the pipes' 'naked' surface and the acidic content of the fluid.

2.1.2 Erosion corrosion

With time, the hydrates graduate from semi-solid blocks to solidified blocks but will still be travelling in chips. These chips while traveling at high velocity will be bombarding the inner surface of the pipe wall to cause erosion. Erosion is the destruction of a metal by abrasion or attrition caused by the relative motion/flow of liquid or gas (with or without suspended solids in the pipe) against the metal surface. For erosion-corrosion to occur, there must be a constant bombardment of particles on the pipe wall surface.[63] This gradually removes the surface protective film or the metal oxide from the metal surface, thus, exposing the surface to erosion-corrosion (Figure 4) from the fluid properties. Factors such as turbulence, cavitations, impingement or galvanic effects can add to the severity of erosion-corrosion attack which eventually leads the pipeline's rapid failure.

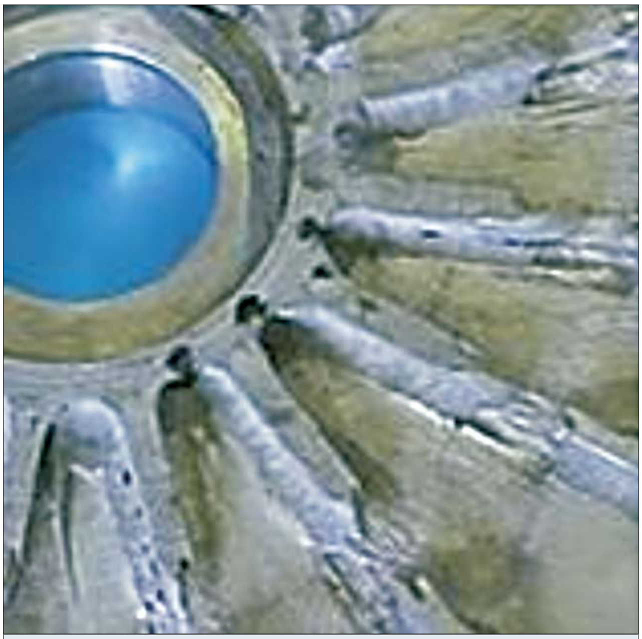

Fig. 3. **Cavitation of a nickel alloy pump impeller blade exposed to a hydrochloric acid medium.** ***Source: CHCMT (2009)***

Sl. 3. Kavitacija lopatice miješala pumpe od slitine nikla izložene klorovodičnoj kiselini *Izvor: CHCMT (2009.)*

Fig. 4. **The "Horseshoe" type erosion-corrosion damage in a copper pipeline.**

Sl. 4. "Potkovičasti" tip erozijsko korozijskog oštećenja u bakarnom cjevovodu

Also at the later stage, the hydrate chips will start agglomerating to form bigger blocks which will require more energy to transport across the surface of the pipe-wall. This movement will induce a relative motion between the pipe-wall and the hydrate block to initiate large scale erosion corrosion.

2.2 Corrosion initiation by chemical/electrochemical processes

Transported natural gas contains CO_2 and/or H_2S gases from the gas constituents; chloride ions (Cl^-) originating from the formation water and sometimes acetic acid (CH_3COOH). These gases go into reaction with the available water during hydrate formation to produce acids that dissociate with time to individually yield corrosive electrolysis products (Equation 1):

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (1)$$
$$CH_3COOH \rightarrow H^+ + CH_3COO^-$$

During the hydrate solidification process, or when the solidified hydrate is melting (during hydrate removal), there will be an interaction between the components of equation (1) and the pipe's inner surface. Since these components are corrosive in nature, corrosion reactions will be promoted over time through electrochemical reactions to yield galvanic and electrolytic corrosions. The corrosion rate will be a function of time, composition of the hydrate, pH and other thermodynamic properties such as temperature, pressure, gas fugacity, e.t.c.[51] Oxidation-reduction (or redox) reaction takes place in electrochemical corrosions with oxidation taking place at anode while reduction takes place at the cathode. However, spontaneous reactions occur in galvanic (voltaic) cells (Figure 5) while non-spontaneous reactions occur in electrolytic cells.

The anode of an electrolytic cell is positive (cathode is negative), therefore, the anode attracts anions from the solution (Equations 2 and 3). However, the anode of a galvanic cell is negatively charged, since the spontaneous oxidation at the anode is the source of the cell's electrons or negative charge. The cathode of a galvanic cell is its positive terminal.

$$\text{Anode: } Fe \rightarrow Fe^{2+} + 2e^- \qquad (2)$$

$$\text{Cathode: } 2H^+ + 2^{e-} \rightarrow H_2 \qquad (3)$$

3. CONSEQUENCES OF THE RESULTING CORROSIONS

Though, hydrate formation has been established to be a problem to the oil and gas industry[62,74], corrosion is of higher consequences because, apart from its abilities to collapse the pipeline system like hydrate[21,47,48], corrosion is bound to deteriorate the integrity of the pipe and cause it to be replaced entirely.[66,2]

Apart from the ability of each of these corrosion types to single-handedly collapse a pipeline, they can also individually or collectively lead to pitting corrosion or stress cracking corrosion (SCC) to partially or totally destroy the system. Generally, the resulting consequences can be broadly classified as economic, environmental and human.

The economic consequences from this accident include the cost of the product lost; public, private and the operator property damage costs and the cleanup/recovery cost.[61] Costs are often considered among the most important categories in ranking the importance of pipeline failures. Two of the six categories included in a 'gravity scale' are related to the cost of production losses and the cost of environmental cleanup.[55]

Though, hydrate prevention costs the gas industry about US$1 million per mile[32] while the pipelines eventual rupture costs the industry an extra cost on welding, product loss and loss of production time. However, corrosion presents a worse scenario. Apart from rupturing the pipe like hydrate, corrosion will lead to gradual degradation of the material and deterioration of the pipe's integrity. Over time (after fixing the formation problem), the pipeline will begin to leak and/or may undergo full bore rupture (FBR) and complete replacement of the pipe-length at extra production cost. Fingerhurt and Westlake (2000) reported that in North America alone (which comprises of USA and Canada alone), the total length of high pressure gas transmission lines is greater than 480 000 km (298 258 miles). Outage cost from a

Fig. 5. Pictures of metals attacked by galvanic corrosion
Sl. 5. Slika metala napadnutog galvanskom korozijom

rupture of such large diameter gas pipeline can be as high as $500 000 to $1 000 000 per day.[20] This loss can be recorded for a rupture from both the hydrate and corrosion. However, in case of corrosion, there will be a need to further cost the assets' capital replacement value. This can be estimated applying the average cost as given by (Parker, 2004)[57] which indicates that each of the 36 in. (91 cm) and 42 in. (106 cm) pipelines has capital replacement cost of about $1 767 710 per mile and $1 977 644 per mile respectively with the cost distributed as material 26%, labor 45%, right of way 22% and misc. 7%. The miscellaneous included the cost on surveying, engineering, supervision, contingencies, allowances, overhead and filing fees. The overall estimate was based on the existing 305 438 km (190 899 miles) of natural gas pipeline in the United States alone. With this estimates, replacement based on corrosion of these pipe-length will cost the gas industries in USA and Canada between $337 - $378 billion and $193 - $216 billion respectively. This estimation excludes other considerations such as location, climatic conditions and political situations as well as specific requirements for offshore productions such as the need for a barge for pipe laying, sea depth, wave function, amongst others. Infact, Fingerhurt and Westlake (2000)[20] put the total replacement cost for the whole North American pipelines at over $3 trillion.

Corrosion has been established to be responsible for 57% of oil and gas pipeline ruptures in Canada[12] and 31.97% and 18.75% of liquid and gaseous hydrocarbon pipeline accidents in the United States, respectively. A review of the economic effects of corrosion on the U.S. economy alone indicated that corrosion of metals and alloys cost U.S. companies and consumers approximately $300 billion per year with about 1% of it coming from the pipeline industry.[7] The problem of metallic corrosion is one of significant proportions; in economic terms, it has been estimated that approximately 5% of an industrialized nation's income is spent on corrosion, maintenance, or replacement of products lost.[79]

Apart from the cost implication on the industry, pipeline failures cause the fluid to escape to the immediate environment. This may lead to dispersion, explosion, fire, and human death as well as destruction of vegetation in case of onshore pipeline[68] or hydrate formation in water body, dissolution of components, loss of human lives and livestock, climate change as well as flammability amongst others in case of offshore failure.[51]

Also, a pipeline blow-out endangers human life as such accidents have resulted in human deaths in the past. An example is the Piper Alpha disaster in the North Sea of July 6th, 1988 which clearly demonstrated the catastrophic consequence of this type of failure where 165 of the 226 on board died with majority (109) from smoke inhalation. It was further estimated that the energy released during this tragedy was equal to 1/5th of the UK energy consumption for that period.

Fig. 6. **Picture showing human beings burnt to ashes in Nigeria following a fire incidence from a ruptured oil and gas pipeline in 2006**

Sl. 6. Slika prikazuje požar nakon loma cjevovoda nafte i plina u Nigeriji 2006.

Again, pipeline failure of December 26, 2006 in Lagos, Nigeria resulted in over 500 people been burnt to death (Figure 6). The fumes escaping from the fire of such accidents into the air could be carcinogenic as well as having other direct and indirect impacts on human health.

4. PREVENTION AS THE PROPER MANAGEMENT SCHEME

Gas hydrates for a long time have been the most elusive and confounding of hydrocarbon deposits to find and many countries including Japan, U.S.A, India, China and Korea amongst others have put up researches to study the phenomenon. Existing studies include literatures, laboratory works and modelling. It will be a worthwhile investment to intensify research studies in finding out more properties of the formation and means of preventing its occurrence or immediate elimination in the

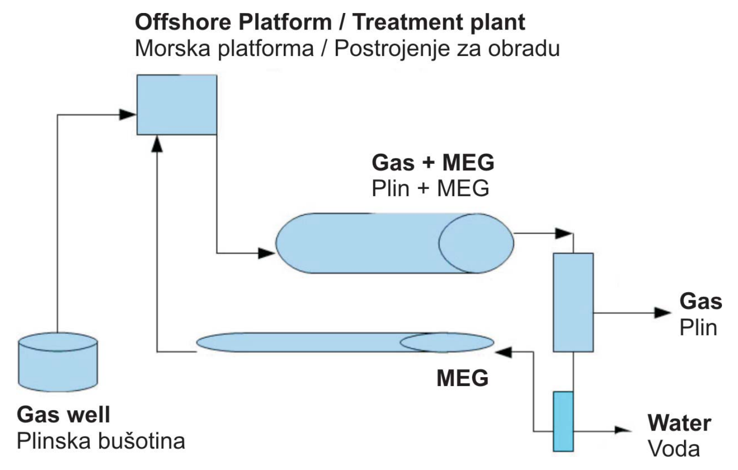

Fig. 7. **Schematic diagram of MEG application as antifreeze in gas industry**

Sl. 7. Shematski prikaz primjene MEG (monoetilen glikola) kao antifriza u industriji plina pipe-length in case of formation as the consequence is always disastrous. Means should be focused on removal of the hydrates located few kilometres away from the shore. Multiphase flow governing equations (including continuity equation and momentum conservation equation), temperature field equations in annulus and drill pipe, and hydrate formation thermodynamics equation should be established based on the characteristics of the operating region.[78]

Although, the industry has designed pipelines to operate outside hydrate forming conditions by either adding inhibitors or by dehydration of the gas/condensate fluids, these techniques are only effective and economical for onshore pipes whereas, the offshore pipelines especially in deep and cold waters are a real challenge.

Different measures are presently being taken by the petroleum industry to prevent hydrates blockages in the pipeline system. These include maintenance of temperature and pressure outside the formation conditions and introduction of antifreeze such as methanol, ethanol, Type-1 antifreeze proteins (AFPs)[16] and Monoethylene glycol (MEG).[40] Figure 7 shows the MEG application technique where the gas is sent from the well to the treatment plant on the platform. MEG is introduces into the gas as antifreeze and it travels with the gas through the pipeline system to change it thermal energy through heat transfer thus preventing it from freezing[34,8], the natural gas is then separated while the MEG is recycled back into the system. Continual introduction of antifreeze is not however cost effective due to the cost of daily rate demand, the handling risk and the impossible total recovery of the fluid from the pipe system during and after the fluid transportation. Also, maintaining both the temperature and pressure outside the formation condition may be too expensive as it requires extra design of insulated or jacketed pipeline system.

Some laboratory investigations have been carried out on the use of inhibitors. This has led to the development of some low dosage hydrate inhibitors (LDHI) as control technology and more cost effective over methanol and glycols.[41,44,71] However, further studies should be carried out to discover and introduce the inhibitors which should delay or prevent hydrates particles from agglomerating in the pipeline system. These inhibitors should be of very low dosage quantity (about 2% weight ratios at most).

Again, major research progresses on hydrate formation have been on the thermodynamic modelling with very little done so far on the kinetics of the process more studies should be focused on this area of research to interest. Nucleation and growth processes should be studied with clear understanding of growth rate and induction time. Of the few studies on kinetics growth, most have been on modelling by measuring the gas consumption rate during hydrate formation in batch agitator reactors. However, studies should be intensified on laboratory investigation to fully appreciate the hydrate formation kinetics. This will enable the study of real-life situation in order to proffer quality solutions.

Furthermore, agitation enhances hydrate formation.[31] There is always an agitation at a start-up condition of any system it is yet to reach a steady-state. Therefore, all cautions should be taken to avoid another shutdown after the flow initiation. This can be achieved by preventing the clathrates from agglomerating through the use of anti-agglomerants. Anti-agglomerants will disperse hydrates into a condensate phase, thus, preventing hydrate plug formation. Some useful studies are going on in this area of research interest to aid this. While Hou et al (2001)[28] used high pressure apparatuses to study the effectiveness of commercially available surfactants and synthesized anti-agglomerants based on their hydrophilic-lipophilic balances, Kelland et al (2006)[37] developed new classes of anti-agglomerants by applying zwitterionic surfactants. They proposed that 3-[*N,N*- dibutyl-*N*-(2-(3-carboxy-pentadecenoyloxy)propy)] ammonio propanoate was a very good anti- agglomerant because it has an encouraging performance at temperatures between 13.4 °C (56.1 °F) and 15.9 °C (60.6 °F). Also, 3-[*N,N*- dibutyl-*N*-(2-hydroxypropyl) ammonio] propanoate was reported to have an excellent synergist for polyvinylcaprolactam KHIs. Other related studies in this area include Kelland et al[37], Kelland et al[38] and Villano and Kelland.[77] It is highly recommended for more studies to be carried out by experts within this area of research interest for more discoveries.

Finally, if properly managed, gas hydrate may be a better transport option for natural gas in long pipelines since the corrosive gases would have been trapped inside the "iced-cubes", thus, reducing the risk of pipeline corrosion. However, there is a need for extensive studies regarding the best means of conveying the hydrates (probably in chip forms) so as to remain fluidized. Also, the possibility of reducing the erosion and cavitations corrosions for this transport option should be seriously studied. Importantly, nitrogen gas which is present in the gas may be problematic hence, the need for studies on this aspect as well. Though, the gas (nitrogen) is scarcely

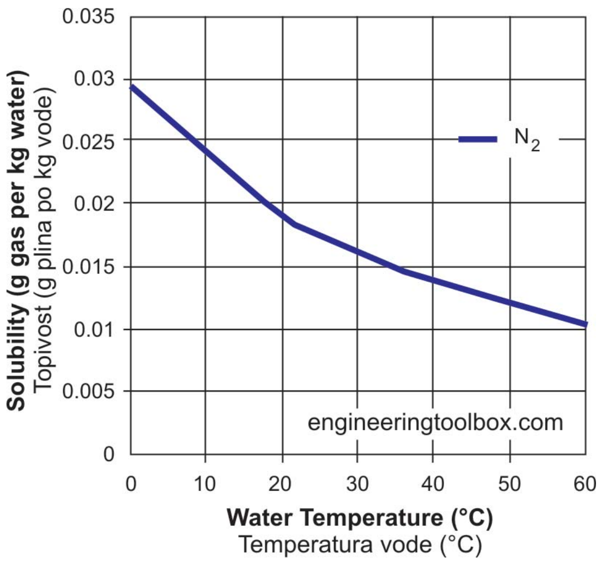

Fig. 8. Solubility of nitrogen (N_2) in water
Source: The Engineering ToolBox (2005)
Sl. 8. Topivost dušika (N_2) u vodi
Izvor: *The Engineering ToolBox (2005)*

soluble in water with its solubility even decreasing with temperature (Figure 8), at the sea temperature of 4 °C (39.2 °F) , the composition of the gas in natural gas may partially or totally dissolve (at about 0.027 g gas/kg water (Figure 8) in the formation water travelling with the natural gas in the pipeline. However, there is a high tendency for the nitrogen gas to be actively involved in the formation of Structure II hydrate[70] hence, comprehensive studies should be carried out on how best to remove nitrogen before this formation.

5. CONCLUSION

Global focus has always been on the removal of hydrate after its formation with so many findings on its properties and ability to rupture a service pipe but not on its ability to initiate corrosion which is a bigger problem to the industry. This paper has been able to establish the relationships between this missing knowledge gaps. The study has been able to predict various types of corrosion that could be initiated during the process, the likely point of initiation and the processes involved.

Economic, environmental and human consequences of the resulting corrosion was mentioned and different hydrate prevention and management options were considered in order to prevent it from resulting into corrosion.

Since all the recommendations have been preventive rather than corrective measures, there is a need for more research activities along this new trend in order to save the industry from higher challenges. This will require the involvement of academics through sponsoring of various research studies in the universities globally.

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REFERENCES

1. Abdel-Aal, H.K. et al., (2003), "Petroleum and Gas Field Prosessing", Marcel Dekker Inc., New York, USA.
2. Adib, H. et al., (2007), "Evaluation of the Effect of Corrosion Defects on the Structural Integrity of X52 Gas Pipelines Using the SINTAP Procedure and Notch Theory", International Journal of Pressure Vessels and Piping, Vo. 84, Is. 3, pp. 123-131
3. AGL-Protonas Consortium (2006), "PNG - Queensland Gas Pipeline Project - Initial Advise Statement on Ballera Lateral", Document CR 1202_2_v3, Prepared by Enescar Consulting Pty Ltd, East Victoria, Australia, pp 1- 32
4. Al-Adel, S. et al., (2008), "The Effects of Biological and Polymeric Inhibitors on Methane Gas Hydrate Growth Kinetics", Fluid Phase Equilibria, Vol. 267, Is. 1, pp. 92-98
5. Spring (2004), "BP Current Developments: Baku-Tbilisi-Ceyhan Pipeline - BTC Gets Funded", Azerbaijan International, pp 130-132. Accessed on 24th November 2009 at http://azer.com/aiweb/categories/magazine/ai121_folder/121_articles/121_bp.html.
6. Bai, Y. and Bai, Q. (2005), "Hydrates", Subsea Pipelines and Risers, pp. 357-382
7. Battelle. 1996. Economic Effects ofMetallic Corrosion in the United States: A 1995 Update. Battelle Columbus Report to Specialty Steel Industry of North America, USA: Battelle Institute.
8. Bédécarrats, J.P. et al., (2009)'Study of a Phase Change Energy Storage using Spherical Capsules, Part I: Experimental Results', Energy Conversion and Management, Volume 50, Issue 10, October 2009, Pages 2527-2536
9. Botrel, T.et al., (2001), "Offsetting kill and choke lines friction losses, a new method for deep water well control", SPE 67813.
10. Brkić, D. and Tanasković, T.I. (2008), "Systematic Approach to Natural Gas Usage for Domestic Heating in Urban Areas", Energy, Vol. 33, Is. 12, pp. 1738-1753
11. CHCMT (2009), "Erosion and Cavitation Corrosions", Cli Houston Corrosion Material Technology, Texas, USA
12. Cribb, R. (2003), "Danger Below: When Pipelines Go Bad", Canada: Toronto Star. Available from http://www.corrosion-club.com/pipelines.htm (accessed on July 12, 2006).
13. Department of Transportation (DOT). 2005. US Department of Transportation, Office of Pipeline Safety. Available from www.dot.gov (accessed on 24th November, 2009).
14. DRET (2009), "Energy in Australia", Department of Resources, Energy and Tourism, Canbera ACT 2601, Australia Government, pp 1-104
15. Du, Q. et al., (2007), "Mathematical model for natural gas hydrate production by heat injection", Petroleum Exploration and Development, 34(4): 470-473, 487.
16. Du, Y. and Guo, T (1990), "Prediction of Hydrate Formation for Systems Containing Methanol", Chemical Engineering Science, Vol. 45, Is. 4, pp. 893-900.
17. Ebeltoft H. et al., (1997), "Hydrate Control During Deep-water Drilling: Overview and New Drilling Fluids Formulations," paper SPE 38567, presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, October 5-8.
18. Energy Information Administration (2009), "Interstate Natural Gas Pipeline Segment", In "About U.S. Natural Gas Pipelines - Transporting Natural Gas", Accessed online on 17th June, 2009 at http://www.eia.doe.gov/pub/oil_gas/natural_gas/analysis_publications/ngpipeline/interstate.html
19. Felder, R. and Dones, R. (2007), "Evaluation of Ecological Impacts of Synthetic Natural Gas from Wood Used in Current Heating and Car Systems", Biomass and Bioenergy, Vol. 31, Is 6, pp. 403-415
20. Fingerhut, M., and Westlake, H. (2000), "Pipeline fitness-for-purpose certification", Corrosion Prevention & Control March, pp. 3-14. Available from http://www.corrosion-club.com/pipelines.htm (accessed on November 24, 2009).
21. Gbaruko, B.C. et al., (2007), "Gas Hydrates and Clathrates: Flow Assurance, Environmental and Economic Perspectives and the Nigerian Liquified Natural Gas Project", Journal of Petroleum Science and Engineering, Vol. 56, Is. 1-3, pp. 192-198
22. Gazzard, J. (2008a), "Aviation and climate change: Can alternative fuel save the day?", Aviation Environment Federation, London, UK.
23. Gazzard, J. (2008b), "Pros and contrails", Aerospace Testing International, UKIP Media & Events Abinger House, Dorking Surrey, United Kingdom
24. Gelb, B.A. (2006), "Russian Oil and Gas Challenges", Congressional Research Service, Report Order Code RL 33212, Washington, USA, pp. 1-15
25. GreenAir (2009), "The search for alternative aviation fuels: understanding the challenge", Greenair Communications, London, U.K.
26. Hao, Y., Bo, Q. and Chen, Y (2006), "Laboratory investigation of pressure development of natural gas hydrates", Petroleum Exploration and Development, 33(2): 217-220.
27. Hill, Z (2005), "LNG Will Supply More Than 20% of US Gas by 2025", NAFTA Journal, Zagreb, Croatia, Year 56, No 6, pp 220
28. Huo, Z. et al., (2001), "Hydrate Plug Prevention by Anti-agglomeration", Chemical Engineering Science, Vol. 56, Is. 17, pp. 4979-4991
29. IEA (2001), "World Energy Outlook - 2001 Insights, Assessing Today's Supplies to Fuel Tomorrow's Growth", International Energy Agency, October 2001.
30. Imperial Venture Corp (1998), "Natural Gas Utilization Study: Offshore Newfoundland", A Report Prepared for Atlantic Canada Opportunity Agencies and Newfoundland Oceanic Industies Association, pp 1-85
31. Jamaluddin, A.K.M. et al., (1991), "Hydrate Plugging Problems in Undersea Natural Gas Pipelines under Shutdown Conditions", J. Pet. Sci. Eng., 5: 323-335.
32. Jassim, E. and Abdi, M.A. (2008), "A CFD-Based Model to Locate Flow Restriction Induced Hydrate Deposition in Pipelines", Manuscript OTC 19190, Offshore Technology Conference, Houston, Texas, USA, 5-8 May, 2008
33. Joelsson, A. and Gustavsson, L. (2009), "District Heating and Energy Efficiency in Detached Houses of Differing Size and Construction", Applied Energy, Vol. 86, Is. 2, pp. 126-134.
34. Kadnar, R. et al., (2003), "Determination of Inorganic Corrosion Inhibitors in Heat Transfer Systems by Ion Chromatography", Journal of Chromatography A, Vol.997, Is. 1-2, 16 May 2003, pp 285-290.
35. Kamimura, A, et al., (2006), "On the Substitution of Energy Sources: Prospective of the Natural Gas Market Share in the Brazilian Urban Transportation and Dwelling Sectors", Energy Policy, Vol. 34, Is. 18, pp. 3583-3590

36. Kelland, M.A. et al., (2006a), "Studies on some Zwitterionic Surfactants Gas Hydrate Anti-agglomerants", Chemical Engineering Science, Vol. 61, Is. 12, pp. 4048-4059.

37. Kelland, M.A. et al., (2006b), "Studies on some Alkylamide Surfactant Gas Hydrate Anti-agglomerants" Chemical Engineering Science, Vol. 61, Is. 13, pp. 4290-4298.

38. Kelland, M.A.et al., (2009), "Gas Hydrate Anti-agglomerant Properties of Polypropoxylates and some other Demulsifiers", Journal of Petroleum Science and Engineering, Vol. 64, Is. 1-4, pp 1-10.

39. Kritzer, P. (2004), "Corrosion in High-Temperature and Supercritical Water and Aqueous Solutions: A Review", The Journal of Supercritical Fluids, Vol 29, Is. 1-2, pp 1-29.

40. Kontogeorgis, G. M. et al., (2007), "Modelling of Associating Mixtures for Applications in the Oil and Gas and Industries", Fluid Phase Equilibria, Vol. 261, Is. 1-2, pp. 205-211.

41. Lee, J. D. and Englezos, P. (2006), "Unusual Kinetic Inhibitor Effects on Gas Hydrate Formation", Chemical Engineering Science, Vol. 61, Is. 5, pp 1368-1376.

42. Liu, Y. et al., (2007), "Applications of geophysical techniques to gas hydrate prediction", Petroleum Exploration and Development, 34(5): 566-573.

43. Lorenzo, M.D. (2009), "The Hydra Flow Loop: A Tool for Testing the Hydrates Behavior in Gas Pipelines", Commonwealth Scientific and Industrial Research Organization (CSIRO), Australian Resources Research Center Building, Perth, Australia.

44. Luo, Y. T. et al., (2007), "Study on the Kinetics of Hydrate Formation in a Bubble Column", Chemical Engineering Science, Vol. 62, Is 4, pp. 1000-1009.

45. Mahmut, K.A. (2005), "Major Utilization of Natural Gas in Turkey", Energy Exploration and Exploitation, Vol. 23, No. 2, Issue 16, Multi-Science Publishing Co. Ltd, pp. 125-140 (16).

46. McKee. et al., (2007), "Carbon Deposition and the Role of Reducing Agents in Hot-Corrosion Processes", Chemistry and Material Science, 4(8): 1877-1885.

47. Netto, T.A. et al., (2007), "On the Effect of Corrosion Defects on the Collapse Pressure of Pipelines", International Journal of Solids and Structures, Volume 44, Issues 22-23, November 2007, Pages 7597-7614.

48. Netto, T.A. (2009), "On the Effect of Narrow and Long Corrosion Defects on the Collapse Pressure of Pipelines", Applied Ocean Research, In Press, Corrected Proof, Available online 3 August 2009.

49. Norsork Standard (NS) (2005), "CO$_2$ Corrosion Rate Calculation Model", Majorstural, Norway: Norwegian Technological Standards Institute Oscarsgt. 20.

50. Obanijesu, E.O. (2009), "Modeling the H$_2$S Contribution in Corrosion Rate of Natural Gas Pipeline", Energy Sources Part A: Recovery, Utilization and Environmental Effects, Taylor and Francis Group, U.S.A, Vol. 31, Iss. 4, pp 348-363.

51. Obanijesu, E.O. and Macaulay, S.R.A. (2009), "West African Gas Pipeline (WAGP) Project: Associated Problems and Possible Remedies", E.K Yanful (Ed), Chapter 2, Appropriate Technology for Environmental Protection in the Developing World, Springer Books, Netherlands, pp 101-112.

52. Obanijesu, E.O. et al., (2010), "Hydrate Formation and its Influence on Natural Gas Pipeline Internal Corrosion Rate", SPE-128544-MS, SPE Oil and Gas India Conference and Exhibition (OGIC), Mumbai, January 20-22.

53. OME (2002), "Assessment of Internal and External Gas Supply for the EU, Evaluation of the Supply Costs of New Natural Gas Supply Projects to the EU and an Investigation of Related Financial Requirements and Tools", Executive Report, Observatoire Mediterraneen De L'Energie, Nanterre, France, pp 1-17.

54. Palmer, A.C. and King, R.A. (2008), "Subsea Pipeline Engineering", 2nd Ed., PennWell Corporation, Oklahoma, USA, pp. 1 - 624

55. Papadakis, G.A. et al., (1999), "EU initiative on the control of major accident hazards arising from pipelines", Journal of Loss Prevention in the Process Industries, 12: 85.90.

56. Park, Y.W. et al., (2008), "Fretting Corrosion of Tin-Plated Contacts", Tribology International, Volume 41, Issue 7, pp. 616-628

57. Parker, N.C. (2004), "Using Natural Gas Transmission Pipeline Costs to Estimate Hydrogen Pipelien Costs.", Institute of Transportation Studies, University of California, Davis, Research Report UCD-ITS-RR-04-35, pp 1-85.

58. Pilavachi, P.A. et al., (2009), "Multi-criteria Evaluation of Hydrogen and Natural Gas Fuelled Power Plant Technologies", Applied Thermal Engineering, Vol. 29, Is. 11-12,pp. 2228-2234

59. PPA (2009), "Australia's Major Pipeline System as at 2009", Pipeline Publications Australia, Melbourne, Australia, Accessed at http://pipeliner.com.au/map/map.html on 16th June, 2009

60. Railroad Commission of Texas (2008), "Barnett Shale Information - Updated July 30, 2008", On-line document: http://www.rrc.state.tx.us/barnettshale/index.html

61. Restrepo, C.E. et al., (2009), "Causes, cost consequences, and risk implications of accidents in US hazardous liquid pipeline infrastructure", International Journal of Critical Infrastructure Protection, Vol. 2: 38 - 50

62. Ribeiro, C.P. and Lage, P.L.C (2008), "Modelling of Hydrate Formation Kinetics: State-of-the-Art and Future Directions", Chemical Engineering Science, Vol. 63, Is. 8, pp 2007-2034

63. Roberge, P.R. (2008), "Corrosion Engineering: Principle and Practise", 1st Ed., The McGraw-Hill Companies Inc., New York, pp. 1 - 754

64. Rojey, A. et al., (1997), "Natural Gas: Production, Processing, Transport", Imprimerie Nouvelle, Saint-Jean-de-Braye, France.

65. Roymech (2009), "Properties Of Gases", Accessed on 24th November, 2009 from http://www.roymech.co.uk/Useful_Tables/Matter/Prop_Gas.htm

66. Shipilov, S.A. and May, L.L (2006), "Structural Integrity of Aging Buried Pipelines Having Cathodic Protection", Engineering Failure Analysis, Vol. 13, Is. 7, pp. 1159-1176

67. Shukla, P.R. et al., (2009), "Assessment of Demand for Natural Gas from the Electricity Sector in India", Energy Policy, Vol. 37, Is. 9, pp. 3520-3534

68. Sonibare, J.A. et al., (2005)," Potential Contribution of Volatile Organic Compounds (VOCs) to Nigeria's Airshed by Petroleum Refineries", NAFTA Journal, Croatia, June 2005, Year 56, No 6, pp 231-242.

69. Stern, J. (2001), "Traditionalists Versus the New Economy: Competing Agendas for European Gas Markets to 2020", Briefing Paper-Draft, The Royal Institute of International Affairs - Energy and Environment Programme, London, New Series, No. 26, pp 1-7.

70. Sugahara, K. et al., (2002), "Thermodynamic Stability and Structure of Nitrogen Hydrate Crystal", Journal of Supramolecular Chemistry, Vol. 2, pp 365-368.

71. Talaghat, M.R. et al., (2009), "Experimental and Theoretical Investigation of Simple Gas Hydrate Formation with or without Presence of Kinetic Inhibitors in A Flow Mini-Loop Apparatus", Fluid Phase Equilibria, Vol 279, Is. 1, pp 28-40.

72. The Engineering ToolBox (2005), " Solubility of Gases in Water: Solubility diagrams of gases like Carbon dioxide, Argon, Methane and other gases in water at different temperatures", Accessed at http://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html, on 24th November, 2009.

73. Tourkolias, C. et al., (2009), "Employment Benefits of Electricity Generation: A Comparative Assessment of Lignite and Natural Gas Power Plants in Greece", Energy Policy, In Press, Corrected Proof available online 3 June 2009.

74. Turner, D.J. et al., (2009), "Methane Hydrate Formation and an Inward Growing Shell Model in Water-in-Oil Dispersions", Chemical Engineering Science, Vol. 64, Is. 18, pp. 3996-4004

75. UNCTAD (2009), "Info Comm Market Information in the Commodity Areas", United Nations Conference on Trade and Development, Palais des Nations, Geneva, Switzerland.

76. Valais, M. (1983), "Analyse des Chaines Gas. Etudes, Ressources et Valorisation du Gas. Les Reserves et la Production de Gaz Naturel dans le Monde: Situation et Perspectives", Intern. Rep. Inst. Fr. Petr., No. 31092, p. 31 (fr).

77. Villano, L.D. and Kelland, M.A (2009), "Tetrahydrofuran Hydrate Crystals Growth Inhibition by Hyperbranched Poly(ester amides)s", Chemical Engineering Science, Vol. 64, Is. 13, pp 3197-3200

78. Wang, Z. et al., (2008), "Prediction of gas hydrate formation region in the wellbore of deepwater drilling", Petroleum Exploration and Development, 35 (6): 731 - 735.

79. William, D., and Callister, J. T. 1996. Material Science and Engineering, 4th Edition. Singapore: John Wiley and Sons, Inc.

80. Yan, L. et al., (2002), "High Temperature Corrosion of Gas Blade Material in Methane Gas Combustion Environment with the Injection of SO$_2$/NaCl", Corrosion, NACE International, pp 1-11

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